CHEMICAL AND PHYSICAL EFFECTS OF ULTRASOUND: 
SONOLUMINESCENCE AND MATERIALS

BY

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DISSERTATION

Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry in the Graduate College of the University of Illinois at Urbana-Champaign, 2011

Urbana, Illinois

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ABSTRACT

When a liquid is irradiated with ultrasound, acoustic cavitation (the formation, growth, and implosive collapse of bubbles in liquids irradiated with ultrasound) generally occurs. This is the phenomenon responsible for the driving of chemical reactions (sonochemistry) and the emission of light (sonoluminescence). The implosive collapse of bubbles in liquids results in an enormous concentration of sound energy into compressional heating of the bubble contents. Therefore, extreme chemical and physical conditions are generated during cavitation. The study of multibubble sonoluminescence (MBSL) and single-bubble sonoluminescence (SBSL) in exotic liquids such as sulfuric acid (H₂SO₄) and phosphoric acid (H₃PO₄) leads to useful information regarding the intracavity conditions during bubble collapse. Distinct sonoluminescing bubble populations were observed from the intense orange and blue-white emissions by doping H₂SO₄ and H₃PO₄ with sodium salts, which provides the first experimental evidence for the injected droplet model over the heated-shell model for cavitation. Effective emission temperatures measured based on excited OH• and PO• emission indicate that there is a temperature inhomogeneity during MBSL in 85% H₃PO₄. The formation of a temperature inhomogeneity is due to the existence of different cavitating bubble populations: asymmetric collapsing bubbles contain liquid droplets and spherical collapsing bubbles do not contain liquid droplets. Strong molecular emission from SBSL in 65% H₃PO₄ have been obtained and used as a spectroscopic probe to determine the cavitation temperatures. It is found that the intracavity temperatures are dependent on the applied acoustic pressures and the thermal conductivities of the dissolved noble gases.
The chemical and physical effects of ultrasound can be used for materials synthesis. Highly reactive species, including $\text{HO}_2\cdot$, $\text{H}\cdot$, and $\text{OH}\cdot$ (or $\text{R}\cdot$ after additives react with $\text{OH}\cdot$), are formed during aqueous sonolysis as a consequence of the chemical effects of ultrasound. Reductive species can be applied to synthesis of water-soluble fluorescent silver nanoclusters in the presence of a suitable stabilizer or capping agent. The optical and fluorescent properties of the Ag nanoclusters can be easily controlled by the synthetic conditions such as the sonication time, the stoichiometry of the carboxylate groups to $\text{Ag}^+$, and the polymer molecular weight. The chemical and physical effects of ultrasound can be combined to prepare polymer functionalized graphenes from graphites and a reactive solvent, styrene. The physical effects of ultrasound are used to exfoliate graphites to graphenes while the chemical effects of ultrasound are used to induce the polymerization of styrene which can then functionalize graphene sheets via radical coupling. The prepared polymer functionalized graphenes are highly stable in common organic solvents like THF, CHCl₃, and DMF.

Ultrasonic spray pyrolysis (USP) is used to prepare porous carbon spheres using energetic alkali propiolates as the carbon precursors. In this synthesis, metal salts are generated in situ, introducing porous structures into the carbon spheres. When different alkali salts or their mixtures are used as the precursor, carbon spheres with different morphologies and structures are obtained. The different precursor decomposition pathways are responsible for the observed structural difference. Such prepared carbon materials have high surface area and are thermally stable, making them potentially useful for catalytic supports, adsorbents, or for other applications by integrating other functional materials into their pores.
Acknowledgments

"Life was like a box of chocolates. You never know what you're gonna get."
Indeed, life is filled with all kinds of adventures and experiences impacting people in
many different ways. I feel extremely fortune to have a wonderful group of people that
have accompanied and supported me in the past five years. I would like to thank my
advisor Professor Kenneth S. Suslick, whose support and guidance throughout my
graduate study has been invaluable. I appreciate the freedom that I was given from him to
do the scientific research that seems challenging. I also enjoyed the many helpful and
heuristic discussions with him, through which I learned how to become an independent
researcher and keep working on new scientific areas.

I also would like to thank following committee members for their assistance and
encouragement: Professors Nick G. Glumac, Andrew A. Gewirth, Catherine J. Murphy,
and Benjamin J. McCall.

My work at University of Illinois would not have been possible without the
support and help from many staff members at the Fredrick Seitz Materials Research
Laboratory. Special thanks go to Changhui Lei, Jianguo Wen, Wacek Swiech, Vania
Petrova, Scott MacLaren, Mauro Sardela, Julio Soares, Rich Haasch, Bharat Sankaran,
and Mike Marshall. Their constantly-available assistance and support taught me how to
use many instruments and helped my graduate research a success. I am also deeply
grateful to the staff at the School of Chemical Sciences: Beth Myer, Connie Knight, and
Theresa Struss at the IMP office, and staff members at the SCS machine shop, glass shop,
computer electronics electrical service, and microanalysis laboratory.
I also would like to thank all the past and current Suslick group members for their support and encouragement. In particular, I’d like to thank Dr. Nathan Eddingsaas and Dr. Jin Ho Bang for teaching me how to do sonoluminescence work and set up sonochemical reactions respectively. I also appreciate Dr. Richard Helmich, Dr. Liang Feng, Dr. Hengwei Lin, Dr. Wei Jiang, Dr. Sung H. Lim, Dr. Christopher Musto, Dr. Ming Fang, Dr. Jeremy Weaver, Dr. Maria Fortunato, Dr. Jon Kemling, Scott Dunkle, Howard Kim, Brad Zeiger, John Overcash, Minseok Jang, Katy Filson, Jinrui Guo, Brandon Ito, Jon Askim, Rachel Castleberry, Maryam Sayyah, Tovah Schwartz, Erwin Park, and Nasrin Gahvari for your help and friendship during my graduate life. Outside of the Suslick group, I would like to thank my friends Jianchao Yang, Zidong Wang, Jieqian Zhang, Pulin Wang, Nanshu Lu, Hua Lu, Wenjun Gu, Xiao Li, Yanfeng Zhang, and Jundong Wang. I really enjoy playing all kinds of board games and poker with you. You all made my time in graduate school much better. Thank you all and I hope to be able to keep in touch as I move on to new and exciting opportunities in the future.

At last, I would like to thank my father, my mother, my sister, and other relatives in China for their endless love and support. Thank you for accompanying me through all the highs and lows in my life. Without you, I would not have finished my Ph.D. study. I love you!
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1.1 History and Introduction

When a liquid is irradiated with high intensity ultrasound, high-energy chemical reactions (sonochemistry) occur, often accompanied by the emission of light (sonoluminescence).1-10 Acoustic cavitation, the formation, growth, and implosive collapse of bubbles in liquids irradiated with ultrasound, is the phenomenon responsible for both sonochemistry and sonoluminescence.1, 2, 11, 12 The bubble growth is slow, allowing for accumulation of gas and vapor into the bubble, but the collapse is very fast, with the velocity of the collapsing bubble wall up to 1500 m/s. The implosive collapse of bubbles in liquids results in an enormous concentration of the diffuse energy of sound into compressional heating of the contents of the bubble. This energy concentration process is astounding; the tiny bubble concentrates the vibrational energy by 12 orders of magnitude and generates flashes of light.13 This dramatic energy concentration process leads to intense heating and high pressures with a very short period of time. In a cavitation cloud, the localized hot-spot temperature can be up to 5000 K with pressures of about 1000 atm and heating and cool rates above $10^{10} \text{ K/s}$.14-16 During single-bubble cavitation, the conditions can be even more extreme; temperatures approaching 20000 K, pressures of 4000 atm, and the existence of a plasma during bubble collapse have been experimentally demonstrated.17, 18 The extreme conditions created inside the collapsing bubbles provide a unique means of driving chemical reactions. Although acoustic cavitation can induce chemical and physical conditions nearly beyond imagination, the host liquids are still cold.
The extreme chemical and physical conditions created inside collapsing bubbles during acoustic cavitation have a variety of effects within the liquid medium, which depend on the type of system in which it is generated. Generally, there are three types of system that acoustic cavitation significantly influences: homogeneous liquids, heterogeneous liquid/solid slurries and heterogeneous liquid/liquid mixtures. Figure 1.1

**Figure 1.1.** Summary of some general effects of acoustic cavitation in liquids: (A) acoustic cavitation in a homogeneous liquid, (B) acoustic cavitation at or near a solid surface, (C) acoustic cavitation in a liquid with suspended powders, and (D) acoustic cavitation in a heterogeneous liquid/liquid medium.

lists of some general effects of acoustic cavitation on these systems. In a homogeneous liquid medium two effects occur: (1) the collapsing bubble launches an outward shock
wave which will apply strong shear forces on the substance dissolved in the liquid and cause physical/mechanical effects;\textsuperscript{19-22} (2) extreme temperatures and pressures inside the collapsing bubble will cause the pyrolysis of vapor or solute inside the bubble and induce a variety of chemical effects (sonochemistry). At or near a solid surface the cavitation bubble becomes non-spherical and forms high-speed liquid jets that impinge against the surface.\textsuperscript{23, 24} The liquid jets and associated shock waves cause surface modification, damage, or cleaning. In a liquid with suspended powders, fragmentation and surface erosion usually occur with powders of large dimensions (i.e., diameter is larger or comparable to bubbles). For small particles, high velocity interparticle collision can lead to fusion at the point of impact or composition change via interaction with reaction species formed in the liquid.\textsuperscript{25, 26} In a heterogeneous liquid/liquid system, acoustic cavitation will cause the disruption or mixing of the interface between two liquids and lead to the formation of emulsions.\textsuperscript{27, 28} Sonoluminescence is generally be considered as a consequence of acoustic cavitation in homogeneous liquid media, or a special case of homogeneous sonochemistry.

Cavitation was first noticed in the late 19\textsuperscript{th} century because of its powerful damage to propellers, pumps, and turbine blades, etc. Cavitation was considered as undesirable phenomenon and was poorly understood.\textsuperscript{29} Lord Rayleigh first described a mathematical model of cavitation in 1917 after an investigation of the severe damage to the propellers of a newly built destroyer, the H.M.S. Daring.\textsuperscript{30} He confirmed that the damage to the propellers was caused by the enormous turbulence, heat, and pressure produced by the cavitation bubbles’ collapse against the propeller surface. In 1927, Richards and Loomis reported that cavitation could induce chemical reactions, which was
the first report of chemical effects from ultrasound. In 1934, H. Frenzel and H. Schultes observed luminescence from bubbles formed under ultrasonic transducer in a tank of photographic developer fluid. Marinesco and Trillat also independently observed this light emitting phenomenon in 1933 when they noted fogging of a photographic plate immersed in a water bath irradiated with ultrasound. This phenomenon was later known as multibubble sonoluminescence (MBSL). Since the observation of MBSL, much effort has been devoted to elucidating the underlying mechanisms responsible for this intriguing light-emitting phenomenon. Rich spectral information has been obtained from MBSL in a variety of liquids. In 1970, Temple was able to isolate a single bubble to generate light, but this work was quickly forgotten by the sonoluminescence community. In 1989, a major breakthrough was made by F. Gaitan and L. Crum who were able to trap a single-bubble in an acoustic levitation chamber, and have it stably oscillate with the applied sound field. This was the first report of the generation of stable single-bubble sonoluminescence (SBSL), which allows for a more systematic study of the sound to light conversion process. Indeed, SBSL isolates the complex effects of interactions of neighboring bubbles into one controllable bubble which can be studied under a variety of conditions.

Acoustic cavitation can be quantitatively described in a liquid irradiated with ultrasound with excellent accuracy during the bubble formation, growth, and collapse. It becomes problematic, however, when it comes to describing the final stage of the bubble collapse, and the extreme conditions like light emission and chemical reactions only occur at the final state of catastrophic collapse. Sonoluminescence serves as a diagnostic tool for cavitation (i.e., the light emitted can be used to examine the conditions generated
at the final stage of collapse). Spectra from sonoluminescence usually consist of broad continuum emission extending from the near-IR into the UV. Under certain conditions, atomic and molecular emission lines and bands can be observed and can be used to determine the interior temperatures and pressures inside the collapsing bubbles.\textsuperscript{9, 14-18, 43-47} Variation of the experimental parameters could allow for the comparison of cavitation phenomena under different conditions. Therefore, sonoluminescence leads to a better understanding of the conditions during cavitation and has been an active research field for decades.

1.2 Bubble Dynamics

The radial motion of bubbles in a liquid exposed to ultrasound irradiation can be accurately described by the Rayleigh-Plesset Equation. This equation was originally derived by Rayleigh in 1917 and has been continuously modified to increase its accuracy.\textsuperscript{30, 48-52} A commonly used example of this equation is shown below:

\[
R \dddot{R} + \frac{3}{2} \ddot{R}^2 = \frac{1}{\rho} \left[ \left( P_o + \frac{2 \sigma}{R_o} - P_v \right) \left( \frac{R_o}{R} \right)^{3\gamma} - P_o - P(t) - 4\mu \frac{\dddot{R}}{R} - \frac{2\sigma}{R} \right]
\]

where \( R \) is the bubble radius (\( \dot{R} \) denotes the velocity and \( \dddot{R} \) denotes the acceleration), \( R_o \) is the bubble radius at ambient conditions, \( P_o \) is the ambient liquid pressure, \( P(t) \) is the alternating drive pressure, \( P_v \) is the vapor pressure, \( \rho \) is the liquid density, \( \mu \) is the shear viscosity, \( \sigma \) is the surface tension, and \( \gamma \) is the polytropic ratio. The left hand side of this equation is the inertial characteristics of the bubble interface, while the right hand side of this equation indicates the different pressures acting on the liquid-gas interface. When more factors need to be considered to describe the bubble motion, additional forms of the Rayleigh-Plesset Equation can be used. This mathematical model can accurately describe
and predict the conditions generated inside the bubble upon collapse, however, it fails to follow the equation when the bubble reaches its minimum radius. At the maximum compression, the bubble wall velocity is not a constant and the density of the bubble dramatically increases.\textsuperscript{7, 53, 54}

In practice, the behavior of bubbles in a sound field is often categorized into transient cavitation and stable cavitation.\textsuperscript{11} Stable cavitation typically happens at very low acoustic pressure and a bubble oscillates linearly with the sound field for many acoustic cycles. During transient cavitation, a bubble typically expands to a large size during the rarefaction phase of the sound field. Although the sound field switches from the rarefaction to the compression phase, the bubble continuous to grow against the pressure. At a certain point in the compression phase, the bubble growth stops and starts to collapse nonlinearly. Because the collapsing process is so quick, there is no heat transfer between the bulk liquid and the gas bubble, and the contents of the bubble are heated and excited nearly adiabatically. It is during the transient cavitation that sonoluminescence and sonochemistry occur. The radial motion of bubbles in an acoustic field is very complex and is dependent on many factors: properties and concentration of dissolved gas, applied acoustic pressure, sound frequency, vapor pressure of liquid, viscosity of the liquid, and sometimes under multibubble cavitation, the interaction of neighboring bubbles should also be considered.

To better understand how a bubble oscillates with the applied acoustic field, a real example will be given. The radius of a bubble in water with dissolved 4 torr Xe as a function of time is given is Figure 1.2.\textsuperscript{55} The radius of the bubble at ambient conditions is $R_o (~4.3 \text{ \mu m})$. As the acoustic pressure wave enters the rarefaction phase, the bubble
starts to grow slowly. When the acoustic pressure wave passes the rarefaction phase to compression phase, the bubble still continuously grows due to inertial effect. The growth, however, quickly stops and the bubble reaches its maximum radius ($R_{\text{max}} \sim 38 \, \mu\text{m}$). The time frame for this growth process ($R_o \rightarrow R_{\text{max}}$) is $t_a$ and is about 10 μs. During the compression phase, the bubble begins a rapid and eventually runaway collapse. The velocity of the bubble wall near the final collapse can be several times the sound speed at ambient temperature and pressure. The bubble will bypass the original size ($R_o$) and reaches a minimum radius ($R_{\text{min}} \sim 0.5 \, \mu\text{m}$). The time frame for this collapse process ($R_{\text{max}} \rightarrow R_{\text{min}}$) is $t_b$ and is about 5 μs. It is around $R_{\text{min}}$ that high energy chemical reactions and light emission occur. Because the bubble contents are severely compressed at $R_{\text{min}}$, the bubble starts to rebound for many cycles before it settle down at $R_o$.

The growth, expansion, and collapse process of a bubble under an acoustic field can be repeated from one cycle to another under a finely controlled manner. Single-bubble cavitation shows excellent stability and can oscillate with an applied acoustic field for millions of cycles without fragmentation and destruction. For multibubble cavitation, the situation is more complicated and the majority of the bubbles will undergo one or more acoustic cycles before final collapse, coalescence, and fragmentation.
Figure 1.2. Radius of a Xe bubble as a function of time for one cycle of the sound field. The dotted line represents the experimental data while the black line is the best fit Rayleigh-Plesset equation. Figure adapted from reference 55.

Another interesting phenomenon that differentiates SBSL and MBSL is rectified diffusion. As a bubble expands during the rarefaction phase of the acoustic cycle, the pressure inside the bubble will drop. This pressure decrease causes the vapor molecules and dissolved gas molecules to diffuse into the interior of the bubble through the bubble and bulk liquid interface. At the compression phase, the bubble growth stops and a catastrophic collapse begins. The velocity of the collapsing wall is so quick that the rectified vapor molecules and dissolved molecules do not have sufficient time to transport
to the liquid. These gaseous species therefore are trapped inside the collapsing bubble. Another possible mechanism that contributed to rectified diffusion is known as the shell effect.\textsuperscript{59, 60} The shell effect refers to the existence of a gas concentration gradient near the liquid-bubble interface. The gas diffusion rate is proportional to the gas concentration gradient. As the bubbles undergo collapse, the gradient decreases. The decreasing gradient causes the rate of diffusion of gas away from the bubble wall to decrease. As the bubbles expand, the gradient increases. As a result of the increase, the rate of the diffusion of gas into the bubbles increases. The net effect of the expansion and collapse through shell effect is the accumulation of mass inside the bubbles. This rectified diffusion explains the behavior of bubbles undergoing multibubble cavitation. But it fails to elucidate the reason for stable single-bubble cavitation, which occurs cycle to cycle without mass accumulation (Figure 1.3).\textsuperscript{9, 61}

![Figure 1.3. A calculated stable single-bubble cavitation in an applied acoustic field. The bubble is assumed to be in equilibrium with respect to mass exchange between bubble and bulk liquid. The net flux of mass across the liquid/gas interface is zero after a single cycle. Figure adapted from reference 9.](image)

9
1.3 Multibubble Sonoluminescence

Multi-bubble sonoluminescence is (MBSL) is the light emission from a cloud of cavitating bubbles. MBSL is generated under the same conditions that practical sonochemistry is conducted under. Therefore, MBSL is closely related to sonochemistry and the conclusions derived from MBSL can be applied to sonochemistry. Generally, there are two different experimental setups for generating MBSL. One employs a standing-wave type and the other uses a horn type. Figure 1.4 shows two typical light emitting bubble clouds from ultrasonic transducers under different configurations. In the standing-wave type, the liquid is irradiated by an ultrasonic transducer that is attached to the liquid container. A standing wave is formed by the superposition of the incident wave and the reflected wave. In the horn type, the ultrasonic horn is directly immersed into the liquid and an ultrasonic wave is radiated from the horn tip.

Typical MBSL spectra include a broad continuum extending from the near IR to the near UV with distinct spectral features from atomic and molecular emissions. The exact mechanism for the light emission phenomenon is not yet known, but analysis of the spectral features allows us to gain information on the conditions reached inside the bubble at the time of light emission. MBSL from a large number of liquids has been reported, and spectral features of emitted light are strongly dependent on the choice of liquid.
Figure 1.4. (A) Photograph of sonoluminescence from water saturated with Ar with a standing-wave configuration. (B) Photograph of sonoluminescence from water saturated with Ar doped with luminol (3-aminophthalhydrazide) with a standing-wave configuration. The ultrasound wave was generated from a function generator with frequency of 139 kHz. The output voltage of the function generator was 360 mV_{p-p}, equivalent to ~0.1 W/cm^3. The dimension of the cell is 60×60×79 mm³. (C) Photograph of sonoluminescence from 85% H₃PO₄ saturated with Ar at an applied acoustic power of 24 W/cm². The frequency is 20 kHz and the diameter of the Ti horn is 1 cm. Figure A and B adapted from reference 62.

1.3.1 MBSL from Water

Since the discovery of sonoluminescence, water has been the most studied liquid. MBSL spectra from aqueous solutions generally exhibit weak and broadened OH* emission on top of a continuum emission.^{34-36} If alkali metal salts are added to the solution, the emissions from excited alkali metal atoms are also observed.^{34, 65} An intensive study of aqueous MBSL was conducted by Verrall and Sehgal and later by Didenko. Various effects of external experimental parameters on MBSL in water have
been examined.\textsuperscript{36, 66-68} The effect of temperature on MBSL in water can be seen in Figure 1.5.\textsuperscript{66, 67} It is shown that sonoluminescence diminishes with increased bulk liquid temperature. They also studied the effect of noble gas on the MBSL spectra from water.\textsuperscript{36} They observed that as the dissolved gas changed from He to Xe the excited state OH\textbullet{} at 310 nm gradually disappeared. They concluded that sonoluminescence is a kind of luminescence and the source of the sonoluminescence is not electrical charge or blackbody radiation. The physical conditions that can be achieved inside the imploding bubbles are limited by the polytropic ratio and thermal conductivity of noble gases. The individual bubbles also work as chemical reaction chambers in which water or radicals can decompose and recombine to form a series of chemical substances exhibiting unique spectral features. Depending on the conditions reached inside the collapsing bubbles different excited states lead to the observed changes in MBSL spectra.

\textbf{Figure 1.5.} MBSL spectra from water saturated with Ar at 22 kHz and different temperatures (from top to bottom): 11 °C, 12.5 °C, 26 °C, and 48 °C. Figure adapted from reference 66.
Doping the water with alkali metal salts leads to the formation of excited metal atoms. Figure 1.6 shows photographs of MBSL from water saturated with Ar doped with sodium dodecyl sulfate and luminol respectively. The orange emission in Figure 1.6A is from excited Na atoms. The observation of Na* or other excited metal atoms (e.g., K* and Li*) implied that the conditions inside the bubbles were so extraordinary that metal salts are dissociated and undergo electronic excitation by reactive OH• and H• radicals. In addition to the observed excited metal atoms, the alkali-metal/noble-gas van der Waals molecules can also be detected to the blue of the alkali metal emissions. The existence of alkali-metal/noble gas complexes directly demonstrated that the origin of the metal atom emission is from the highly pressurized gas phase of the collapsing bubbles.

Figure 1.6. (A) Photograph of sonoluminescence from water with 1 mM SDS saturated with Ar. (B) Photograph of sonoluminescence from water saturated with Ar doped with luminol (3-aminophthalhydrazide). The ultrasound wave was generated from a function generator with frequency of 139 kHz in a standing-wave configuration. The output acoustic power of the function generator was ~0.06 W/cm³. The dimension of the cell is 60×60×79 mm³. Figure adapted from reference 62.
1.3.2 MBSL from Organic Liquids

MBSL in aqueous liquids show limited spectral features with low light intensity, which is a direct result of the relatively high vapor pressure of water. The existence of a fairly large number of water molecules inside the collapsing bubbles is not energy efficient; much of the energy concentrated during cavitation is consumed by the bond dissociation and molecular rotations and vibrations. Sonoluminescence and sonochemistry are typically performed in low vapor pressure organic liquids like long-chain alkanes and silicone oil. Figure 1.7A is the MBSL spectrum from dodecane saturated with Ar which consists of a broad continuum with emission bands assigned to $C_2$ ($d^3\Pi_g - a^3\Pi_u$, the Swan lines), the same emission seen in flames. Furthermore, the ultrasonic irradiation of alkanes in the presence of $N_2$ (or NH$_3$ or amines) gives emission from CN* but not from N$_2$* (Figure 1.7B). The emission from CN* but the absence of N$_2$* implied that the origin of molecular emissions is thermal rather than microdischarge. When O$_2$ is present in the system, emission from CO$_2$*, CH•* and OH•* is observed. MBSL spectrum from silicone oil showed the same features as dodecane with additional emission peaks from excited Si atoms.

Ultrasonic irradiation of volatile organometallic compounds (e.g., Fe(CO)$_5$, Cr(CO)$_6$, and Mo(CO)$_6$) in a low-volatility organic liquid produces intense emission light that contains known atomic emission lines. The metal carbonyls are very volatile species and the metal-carbonyl bond is weak. The conditions generated during bubble collapse are sufficient to dissociate the CO ligands from the metal complex and produce excited metal atoms. Figure 1.8 shows the MBSL spectra from metal carbonyl in silicone oil solutions. Intense and well-resolved emission lines corresponding to excited
metal atoms are clearly observed. The intense metal atom emission provides a useful tool to quantify the conditions generated during MBSL.

**Figure 1.7.** (A) MBSL spectrum from dodecane under Ar at 4 °C. (B) MBSL spectra from systems containing nitrogen. a. MBSL from dodecane under 85%/15% Ar/N₂ mixture at 4 °C. b. MBSL from 0.025 M 1,2-diaminoethane in dodecane under Ar at 4 °C. c. MBSL from dodecane 20 min after saturation with NH₃ followed by Ar purge. Ultrasonication is conducted at 20 kHz and ~60 W/cm². Figure adapted from reference 39.
Figure 1.8. MBSL spectra from 0.0025 M metal carbonyl in silicone oil (Dow Corning 200 fluid, molecular weight ≈5000) (solid line) alone with emission from hollow cathode lamp of each metal species (dotted line). (A) Cr(CO)$_6$, (B) Fe(CO)$_5$, (C) Mo(CO)$_6$ and (D) W(CO)$_6$. Figure adapted from reference 77.

1.3.3 MBSL from Inorganic Liquids

MBSL from organic liquids has revealed a number of spectral features which allow for quantitative determination of the conditions inside tiny bubbles. MBSL in organic liquids, however, still suffers from the decomposition of organic molecules into small organic hydrocarbons. The accumulation of small organic compounds (e.g., CH$_4$, C$_2$H$_2$, and H$_2$) will eventually induce bond dissociations, polyatomic rotations and vibrations, which are energy consuming processes. Inorganic liquids like ionic liquids and mineral acids could avoid the decomposition of organic species under ideal conditions.
conditions. Ionic liquids have some unique properties, such as excellent thermal stability, low combustibility, high chemical tolerance, wide liquid regions, and negligible vapor pressure, which make them attractive solvents for sonochemical reactions.\textsuperscript{79, 80} MBSL spectra from a number of different ionic liquids contained emission from excited CH, C\textsubscript{2}, and CN (Figure 1.9).\textsuperscript{63} Head gas analysis shows the formation of a variety of organic decomposition products. The observation of low molecular weight small organic decomposition compounds indicated that the initial decomposition reactions occurred in a liquid phase that either surrounding the bubble or by injection into the bubbles because ionic liquids have negligible vapor pressure. This observation strongly supports the two-site models of sonochemistry but was not able to differentiate them.\textsuperscript{81} Molten salt eutectic (ZnCl\textsubscript{2}/NaCl/KCl) has also been used for MBSL which only exhibits Na* emission lines.\textsuperscript{82}

\textbf{Figure 1.9.} MBSL spectra of (A) 1-methylimidazole, (B) 1-methylimidazole with 1.5\% n-butyl chloride, and (C) BuMeImCl. Sonication was carried out at 20 kHz at 60 W/cm\textsuperscript{2} under Ar. Figure adapted from reference 63.
Liquids that have both low vapor pressure and highly soluble sonolysis products are preferred for MBSL study. Mineral acids like sulfuric acid and phosphoric acid meet such criteria (low vapor pressure plus formation of very soluble H₂S and SO₃ gases) and exhibit bright sonoluminescence (easily observed even in a well-lit room) upon ultrasonic irradiation. Figure 1.10 shows the sonoluminescence spectrum from 95% H₂SO₄ saturated with Ar. The spectrum contains emission from SO (B^3Σ^− – X^3Σ^−), Ar (4p-4s), and a small peak from the emission of oxygen atom (777 nm).

![Figure 1.10. MBSL spectrum from 95 % H₂SO₄ saturated with Ar, sonicated at 20 kHz and 14 Wcm⁻². The spectral features include the emission from excited SO molecules and Ar atoms. Figure adapted from reference 64.](image)

1.3.4 Temperature and Pressure Measurements during MBSL

Ultrasound provides a unique means for converting sound energy to light. The conditions generated during bubble collapse have fascinated researchers for a long time.
The first attempt to measure the temperatures during bubble collapse was via a method termed comparative-rate thermometry.\textsuperscript{81} The basic idea of this approach is to use an Arrhenius relation to determine the reaction temperatures from known specific reaction pathways with known kinetic rate constants and known initial compositions by analyzing sonolysis products. By applying this principle, an effective temperature of $5200 \pm 650$ K inside the gas phase of collapsing bubble was determined. The methyl radical recombination (MMR) method has also been developed for the measurement of temperatures generated during bubble collapse,\textsuperscript{84,85} but this MMR approach is based on unrealistic assumptions, which limits its applications. Effective emission temperatures of 2000–5000 K have been reported from this method.

A number of spectral features have also been revealed from MBSL in a variety of liquids. Those emission lines and bands not only demonstrate that chemical reactions occur during bubble collapse but also can be used to quantify the conditions created inside imploding bubbles. The initially observed C\textsubscript{2} emission was first applied to spectroscopically measure the intracavity temperatures.\textsuperscript{14} High resolution MBSL spectra from silicone oil under Ar have been acquired and analyzed. Synthetic spectra can be generated based on the well-understood theory of diatomic molecular emission. The observed emission from C\textsubscript{2} can be compared to synthetic spectra as a function of rotational and vibrational temperatures. From comparison of experimental spectra with synthetic spectra, an effective cavitation temperature of $\sim5000$ K is determined. Doping water solution with trace amount of organics like benzene also leads to the formation of C\textsubscript{2} emission.\textsuperscript{44,45} An effective emission temperature of 4300 K was obtained. The lower emission temperature determined from water in part is due to the higher vapor pressure of
water (6.6 torr) compared with that of silicone oil (<0.01 torr) (Figure 1.11).\textsuperscript{45} The excellent match between the observed MBSL spectra with synthetic spectra provides definitive proof that sonoluminescence is a thermal process rather than electrical discharge. At the same time, the conclusion derived from the spectroscopic study is very close to the results obtained from comparative-rate thermometry.

![Graph showing emission spectra comparing the intensities of different bands](image)

**Figure 1.11.** Emission spectra comparing the intensities $\Delta \nu=1$ to $\Delta \nu=0$ bands of the $d^3\Pi_g - a^3\Pi_u$ transition (Swan bands) of C\textsubscript{2}. (A) Calculated spectra. (B) Observed MBSL spectrum of 0.01% v/v benzene in water at 278 K under Ar at 20 kHz, with an estimated emission temperature of $4300 \pm 200$ K. Figure adapted from reference 45.

The observed Ar emission during MBSL in concentrated H\textsubscript{2}SO\textsubscript{4} solutions can also be used to measure the emission temperatures. Ar emission has been extensively studied and the energy levels, transition probabilities, statistical weights, and photo energies of excited Ar atoms are well-known.\textsuperscript{86-89} By comparing MBSL Ar spectrum to
synthetic Ar spectra, an emission temperature of 8000 K was obtained (Figure 1.12). The generation of Ar atom emission lines directly proves the existence of a plasma core during bubble collapse. Ar atoms cannot be thermally excited into the $4p$ state (~13 eV above ground state $4s$) at the measured emission temperature of 8000 K. The formation of excited Ar atoms is due to collisional excitation with high energy ions like electrons.

**Figure 1.12.** Spectrum of Ar ($4p$-$4s$ manifold) emission from the MBSL in 95% H$_2$SO$_4$ saturated with Ar compared to the best fit synthetic Ar spectrum. An effective emission temperature of 8000 K is obtained. The synthetic spectra assumed thermal equilibration and a Lorentzian profile with FWHM of 6.4 nm. Figure adapted from reference 64.

Another method to calculate the emission temperatures is based on the relative intensities of atomic emission lines in MBSL spectra. The radiance of a single atomic line can be expressed in equation 1.1:

$$I_{nm} = \frac{hc}{4\pi}\frac{\rho_{n}\lambda_{nm}A_{nm}}{Q\lambda_{nm}}e^{-E_{n}/kT}$$  \hspace{1cm} (1.1)
In equation 1.1, \( h \) is Planck’s constant, \( c \) is the speed of light, \( l \) is the path length of a confining region, \( \rho \) is atom number density, \( g_n \) is the degeneracy of the upper state \( n \), \( Q \) is the partition function or “sum of states”, \( A_{nm} \) is the Einstein transition probability between state \( n \) and \( m \), \( k \) is Boltzmann constant, \( E_n \) is the energy of the upper state \( n \), and \( T \) is the absolute temperature. In order to obtain an accurate temperature measurement, one needs to know the exact value of all the numbers shown in equation 1.1. Fortunately, the relative two-line ratio method eliminates the need to know the path length and atomic number density. The only numbers needed in order to use the relative two-line radiance ratio method is the relative Einstein transition probabilities. The ratio of two emission lines can be derived from equation 1.1 and written as equation 1.2:

\[
\frac{I_1}{I_2} = \frac{g_1 A_{12} \lambda_2}{g_2 A_{21} \lambda_1} \exp[(E_2 - E_1)/kT] \tag{1.2}
\]

The observe emission lines from excited metal atoms produced by sonication of metal carbonyls (e.g., Cr(CO)\(_6\), Fe(CO)\(_5\), and Mo(CO)\(_6\)) in organic liquids were first used to measure the emission temperatures based on the relative two-line radiance ratio method. Figure 1.13 shows the emission lines observed from excited Cr atoms during MBSL in a solution containing Cr(CO)\(_6\) saturated with Ar. By using the relative two-line radiance ratio method and comparing MBSL spectrum with simulated spectra at various temperatures, an effective emission temperature of 4700 K is measured. This approach is applied to measure the emission temperatures based on other excited metal atoms like Fe (\(~5100 \text{ K}\)) and Mo (\(~4800 \text{ K}\)). The emission temperature measured in this way is comparable to that determined from C\(_2\) emission (\(~5000 \text{ K}\)). Using this method, the effect of noble gas on the emission temperature was also determined. The temperature of MBSL increased from 3800 K to 5100 K by switching the gas from He to Xe.\(^{78}\)
The observed excited metal atoms can also be used to estimate the pressures generated during bubble collapse. Under high pressures, the emission lines are known to broaden and shift by predictable amounts. Because of scattering of the emitted light by the bubble cloud, significant experimental broadening can occur. The line broadening is therefore not suitable for estimating the intracavity pressures, but the estimated pressure can be derived from the line shifts of the observed emission lines. Figure 1.14 shows the MBSL Cr* emission lines compared with the spectrum from hollow cathode lamp.\(^\text{16}\)

**Figure 1.13.** (A) Simulation of thermally equilibrated emission from Cr* atoms. The synthetic emission spectra are normalized at 424 nm. (B) MBSL spectrum from a solution of Cr(CO)\(_6\) in silicone oil saturated with Ar compared to a simulated Cr* emission spectrum at 4700 K. Figure adapted from reference 9.
Figure 1.14. MBSL spectrum of 2.5 mM Cr(CO)$_6$ in silicone oil saturated with Ar. Spectrum from hollow cathode lamp (thin lines) is shown for comparison. Background continuum emission has been subtracted for clarity. Figure adapted from reference 16.

By comparing the observed shift from the Cr* lines generated from MBSL in silicone oil containing Cr(CO)$_6$ to ballistic compressor data, it is determined that the pressure inside collapsing bubbles is 300 bar, which is a lower bound for the pressure can be reached during bubble collapse.

1.4 Single-bubble Sonoluminescence

Single-bubble sonoluminescence (SBSL) is the light emission from an isolated, acoustically levitated bubble oscillating around the pressure antinode in a standing sound field. SBSL has been extensively studied because it is believed that much more extreme conditions are generated during single-bubble cavitation than multibubble cavitation. The conditions generated during single-bubble cavitation have been hypothesized to be severe
enough to induce thermal nuclear fusion, with recent controversial reports of neutron production from fusion.\textsuperscript{91-93} The claims of making thermal fusion during acoustic cavitation have been found to be fraudulent and attempts to reproduce the results have been unsuccessful,\textsuperscript{94-96} but researchers remain optimistic about the idea of making fusion reactions possible (i.e., sonofusion) through single-bubble cavitation.

Unlike MBSL, spontaneous cavitation does not occur under the conditions for SBSL. A bubble must be seeded by some triggering mechanisms (e.g., by putting a short current pulse through a metal wire to induce transient boiling, by squeezing air bubbles using a pipette, or by rapid heating through a focused laser beam).\textsuperscript{9} The bubbles will quickly coalesce at the center of the resonator (i.e., pressure antinode) and remain spatially stationary due to the balance between the Bjerknes force (i.e., a translational force applied on the bubble under an acoustic pressure gradient) and buoyancy force. The bubble oscillates radially with the applied sound field.\textsuperscript{97, 98} Using time-correlated single-photon counting, it has been revealed that the pulse width of the light flash ranges from ~35 to 350 ps for a single bubble in water, depending on the type and concentration of gas.\textsuperscript{99, 100} The light flashes in nonvolatile liquids like sulfuric acid and phosphoric acid can reach nanosecond and microsecond durations.\textsuperscript{101, 102}

Water is the most frequently studied liquid for SBSL. Typical SBSL spectra from water include a broad continuum extending from the near IR to the near UV.\textsuperscript{100, 103} The featureless spectra have hindered the pursuit of the mechanisms ultimately responsible for the light emission during SBSL. Recently, rich spectral information has been obtained by switching the liquid from water to mineral acids (e.g., sulfuric acid).\textsuperscript{9, 17, 18, 46, 104, 105}
Analysis of spectral features allows us to gain information on the conditions reached inside the cavitation bubble at the time of light emission.

1.4.1 SBSL from Water

A single, light emitting bubble that oscillates radially with the applied standing sound wave was first achieved in water. Since then the majority of SBSL studies have been performed in water. The typical emission spectrum observed during SBSL from water is a featureless continuum extending from the near IR into the near UV, devoid of any bands or lines. Figure 1.15 shows high-resolution SBSL spectra from water regassed with different noble gases. No distinctive emission bands or lines are observed. The lack of spectral features and high velocity collapse near the bubble collapse led to the speculation that extreme temperatures and pressures are generated during SBSL. The lack of spectral features also poses a problem when trying to quantify the intracavity conditions or elucidate the light emitting mechanism. It is generally thought that the continuum emission is from several possible processes, including radiative plasma processes (e.g., Bremsstrahlung and ion-electron recombination), blackbody emission following Plank’s law, and severe line broadening under extreme temperature and pressure conditions. Because the featureless continuum can occur under many conditions, it is impossible to accurately deduce the mechanism for the light emission process during SBSL.
Emission lines and bands were observed from a very dimly luminescing bubble in water.\textsuperscript{116} It was found that the SBSL spectra from dimly luminescing bubbles contained emission bands from excited OH radicals as well as other lines which could not be identified (Figure 1.16A).\textsuperscript{116} This observation is very important because it directly proves that water molecules are present in the bubble during SBSL and it contributes to the observed emission light. Unlike previous SBSL experiments, the amount of dissolved noble gas in this case is relatively large (150 torr). Instead of rigidly fixed at the pressure antinode of the resonator, the bubble jitters slightly around the pressure antinode as it oscillates with the applied standing sound wave. It was also discovered that the emission spectra are dependent on the dissolved noble gases (Figure 1.16B).\textsuperscript{116} The intensity of the 310 nm peak (due to the excitation of OH•) increases with increased molecular weight of
noble gas. The observed OH emission indicates that chemical reactions (e.g., bond
dissociation and radical recombination) occurred during bubble collapse under SBSL
conditions.

![Figure 1.16.](image)

**Figure 1.16.** (A) SBSL spectra from water regassed with 150 torr Ar under different
acoustic pressures at 25 °C. The acquisition time for the dimmest bubble takes 5 days
while 100 min for the brightest bubble. (B) Dependence of SBSL spectra with dissolved
noble gases at 25 °C with same applied acoustic pressures. Inset: Peak intensities of the
OH• emission at 310 nm vs $\sqrt{\mu}$, the square root of the reduced mass of the noble gas and
OH• radical, for the same integrated light intensity. Figure adapted from reference 116.

### 1.4.2 SBSL from Organic Liquids

Although the majority of SBSL studies are conducted in water, a few attempts
have also been made in nonaqueous liquids.\cite{117,118} For example, spectroscopic studies of
the SBSL generated from various organic liquids like $n$-dodecane and ethanol dissolved
with Xe have been performed.\cite{117} The SBSL spectra obtained from the above organic
liquids show no discernible spectral features, similar to SBSL spectra from water. The
SBSL spectra from the organic liquids are significantly different from the typical MBSL emission spectra observed during the ultrasonic irradiation of organic liquids. MBSL emission spectra from organic liquids always contain emission from the excited states of sonolysis products like \( \text{C}_2 \) and \( \text{CH} \).\(^9,14,37,39\)

Under certain conditions, molecular emissions are observed within SBSL spectra from organic liquids with high heteroatom content (e.g., N, O, S) and low vapor pressure (e.g., \( \text{NC(CH}_2\text{)}_4\text{CN} \), \( \text{(CH}_3\text{)}_2\text{SO} \)).\(^118\) The emission spectra are strongly dependent on the applied acoustic pressure and the bubble dynamics. For example, the SBSL spectra from adiponitrile contained emission from \( \text{CN} \) (\( B^2\Sigma^+ - X^2\Sigma^- \)) at relatively low acoustic pressure.\(^118\) As the acoustic pressure increased, the emission line gradually disappeared and a featureless continuum emission similar to that observed in water emerged. Interestingly, even at relatively low acoustic pressure, the molecular emissions are only observable from a moving sonoluminescing bubble but not from a stationary bubble (Figure 1.17).\(^118\)

![Figure 1.17. SBSL spectra from a stationary and moving bubble in methylformamide at an acoustic pressure of ~1.1 bar. The emission peak at 380 nm arises from \( \text{CN} \) (\( B^2\Sigma - X^2\Sigma^- \)). Figure adapted from reference 118.](image)
1.4.3 SBSL from Sulfuric Acid

In a continuation of the effort to study SBSL in low-volatility liquids, extremely intense SBSL has been discovered from concentrated sulfuric acid (H$_2$SO$_4$). SBSL from 85% H$_2$SO$_4$ was more than 2700 times as bright as from water. The increased light intensity is in part due to the low vapor pressure of 85% H$_2$SO$_4$ (40 mtorr) compared to water (20 torr). In addition to dramatically enhanced light intensity, numerous spectral features including molecular (SO and SO$_2$), ionic (Ar$^+$, Kr$^+$, Xe$^+$, and O$_2$$^+$), and atomic (Ne, Ar, Kr, and Xe) emission bands and lines have been observed. For example, strong Ar emission (13 eV above ground state) can be observed from SBSL in 85% H$_2$SO$_4$ solution regassed with Ar at moderate acoustic pressures (Figure 1.18). This is the first noble gas emission observed since the discovery of sonoluminescence. For an Ar bubble at very low acoustic pressure, the SBSL spectrum consists of not only Ar emission but also more energetic Ar$^+$ (37 eV above ground state) and O$_2$$^+$ ionic emissions (Figure 1.19). In addition, molecular emission (SO) can also observed from the same cavitation event. It is interesting to observe SO and Ar$^+$ emission simultaneously. Ar$^+$ can only be thermally excited at temperatures where SO has already dissociated. The observation of Ar$^+$ and SO means that Ar$^+$ and SO emission are excited at different locations or times inside the collapse bubble or they are generated by a mechanism other than thermal excitation.

A rich set of spectral features (molecular, ionic, and atomic) originated from the liquid and from the dissolved gas has been observed. The intensity of emitted light from concentrated H$_2$SO$_4$ is thousand-fold brighter than that previously observed from any other liquid. Discrete emission lines coupled with bright light enable us to use
spectroscopic methods to quantify the intracavity temperature and pressures in the same manner as mentioned in MBSL.9, 17, 18

1.4.4 Temperature and Pressure Measurements during SBSL

Since the discovery of SBSL, it has been hypothesized that the conditions created during single-bubble cavitation are extreme. The quantification of intracavity conditions during single-bubble cavitation is of great interest both theoretically and experimentally. While effective emission temperatures during multibubble cavitation have been successfully determined by comparative rate thermometry or from excited molecular and atomic emissions, the temperature measurements inside a single collapsing bubble have proven to be much more difficult.

![SBSL spectra from a bubble in 85% H₂SO₄(aq.) regassed with Ar driven at different acoustic pressures (shown above the corresponding spectrum). The neutral Ar atom emission lines in the red and near-IR region of the spectra arise from the 4p – 4s manifold. Figure adapted from reference 17.](image)

Figure 1.18. SBSL spectra from a bubble in 85% H₂SO₄(aq.) regassed with Ar driven at different acoustic pressures (shown above the corresponding spectrum). The neutral Ar atom emission lines in the red and near-IR region of the spectra arise from the 4p – 4s manifold. Figure adapted from reference 17.
Early temperature measurements focused exclusively on continuum emission observed from SBSL in water. Obtaining effective emission temperature from featureless continuum emission spectra depend on the mechanism that generates the continuum. In SBSL, blackbody emission and bremsstrahlung emission are the two most common interpretations of the observed emission spectra.\textsuperscript{106-109, 114, 115} Figure 1.20 shows the SBSL spectra from water at different temperatures and the corresponding best fit blackbody emission spectra.\textsuperscript{108} In this case, blackbody fitting can be used to fit the experimental spectra fairly well. In most water SBSL spectra, however, an obvious peak cannot be observed in the spectral window of interest (200–900 nm).

Bremsstrahlung radiation (i.e., an electromagnetic radiation produced by the deceleration of a charged particle when deflected by another charged particle) has also been used to fit the observed featureless SBSL spectra from water (Figure 1.21).\textsuperscript{106} The emission temperature measured from a Xe bubble is dramatically lower than that from a
He bubble. This conclusion is controversial due to the fact that the thermal conductivity of Xe is much lower than He and a higher intracavity temperature should be achieved in a Xe bubble. A significant difference between the temperatures measured based on blackbody and bremsstrahlung radiation also exists. For a He bubble, blackbody fitting estimates the cavitation temperature is ~8000 K while this number is infinite in a bremsstrahlung fitting! Assumptions based on blackbody and bremsstrahlung radiation are not experimentally valid yet in SBSL. Controversial results obtained during temperature measurements using blackbody and bremsstrahlung radiation drive us to obtain intracavity temperatures from more accurate sources; the discrete emission lines and bands observed during SBSL.

The observation of Ar emission from SBSL in concentrated H$_2$SO$_4$ allows for the definitive determination of effective emission temperatures inside a collapsing bubble without relying on assumptions. The Ar emission spectrum can be calculated based on equation 1.1 and can be used to measure the effective emission temperatures via simple comparison. In this manner, the emission temperature from single-bubble cavitation in H$_2$SO$_4$ regassed with Ar can be determined. Figure 1.22 shows an experimental Ar emission spectrum compared to a best fit synthetic Ar emission spectrum at an emission temperature of 15000 K (assuming thermal equilibrium). If the applied acoustic pressure increases, the Ar emission lines become too broad compared to the underlying continuum emission and temperature measurements are not accurate.
Figure 1.20. SBSL spectra from water regassed with $\text{H}_2$ at (A) 0 °C and (B) 20 °C. Solid lines are best fit blackbody radiation with temperature at 6644 K and 6200 K at 0 °C and 20 °C, respectively. Inset shows spectrum A on a linear scale. Figure adapted from reference 108.

Figure 1.21. SBSL spectra from He (150 torr) and Xe (3 torr) bubbles in water (23 °C) driven at 43 kHz. Thin solid lines are blackbody fits at 8000 K (He) and 20400 K (Xe). Dashed lines are best bremsstrahlung fits 21500 K for Xe and infinite temperature for He. Figure adapted from reference 106.
Temperatures measured from a SBSL Ar bubble in H2SO4 provide definitive proof that a hot plasma is formed during single-bubble cavitation. The measured 15000 K is not hot enough to thermally induce the formation of Xe\(^+\), Kr\(^+\) and Ar\(^+\) in the same system. The most probable route for the formation of excited noble gas ions is via high energy electron impact. The temperature measured from Ar emission does not reflect the core temperature within the collapsing bubble. The plasma formed inside the imploding bubble results in a hot opaque core that is much hotter and denser than the outer region where Ar emission is generated. Therefore, the Ar emission only represents the temperature generated in the shell region surrounding the plasma core and the obtained emission temperature is a lower bound for the temperature reached within the collapsing bubble.

![Figure 1.22. SBSL spectrum from 85% H2SO4 regassed with Ar (blue line) is compare to best fit synthetic Ar emission spectrum at 15000 K (yellow line). Underlying continuum has been subtracted for clarity. Figure adapted from reference 9.](image-url)
Standard tools of plasma diagnostics can be applied to measure densities inside the collapsing bubble and then to obtain the pressure achieved in the spatiotemporal region occupied by the Ar emission. Figure 1.23 compares the SBSL Ar emission profiles and peak positions with Ar emission from a He(Ar) spectral calibration lamp. It is obvious that the SBSL Ar emission lines are severely broadened and red shifted relative to the Ar emission lines from a low pressure environment, indicating that high densities are created during bubble implosion. Several different mechanisms can cause the broadening and shift of observed Ar emission lines and one of them is pressure broadening. If the parameters that contribute to the broadening of the Ar emission lines are known (e.g., instrumental response and Stark effect), proper deconvolution of the line width will leave only the contribution from pressure broadening. Once the contribution from pressure broadening is known, the density within the collapsing bubble can be determined. Application of the van der Waals equation of state with known density and emission temperature leads to an estimated pressure of ~1400 bar. The pressure measured by this spectroscopic method matches well with that determined from a coupling of the measured bubble dynamic and an adiabatic compression model (~1600 bar). As the applied acoustic pressure increases, the Ar emission lines become broadened and indistinguishable from the underlying continuum emission. At this point, both temperature and pressure measurements using spectroscopic methods are not reliable. But the coupled bubble dynamics and adiabatic compression model method still yields an estimated pressure of 4000 bar inside the collapsing bubble. Note that the plasma electron density measured from the collapsing bubble in H₂SO₄ can be controlled over 4 orders of magnitude and exceed 10²¹ cm⁻³—comparable to
that generated by the Lawrence Livermore National Laboratory Nova laser (1.8 kJ in 1 ns at 527 nm) in inertial confinement fusion experiments on a polyethylene target.\textsuperscript{122}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{sbsl_ar_emission_spectra.png}
\caption{Comparison of SBSL Ar emission spectra from 85\% H\textsubscript{2}SO\textsubscript{4} containing 40 torr Ar at an applied acoustic pressure of 3.6 and 4.2 bar respectively and that from a He(Ar) spectral calibration lamp. Underlying continuum has been subtracted for clarity. Figure adapted from reference 18.}
\end{figure}

1.5 Conclusions

Acoustic cavitation is a unique means to drive chemical reactions and convert sound into light. Sonoluminescence provides an opportunity to quantify the conditions generated inside the implosive collapsing bubbles via spectroscopic methods. Discrete emission bands and lines (e.g., relative peak intensities, peak positions, and profiles) observed from electronically excited atoms and molecules have been used to measure the
temperatures and pressures during both MBSL and SBSL. Understanding the extreme intracavity environments during bubble collapse is vital to elucidate the mechanisms at work for light emission. Recent work in exotic liquids like concentrated sulfuric acid provides the first experimental evidence that an optically opaque plasma is formed from collapsing bubbles.

Although sonoluminescence has been rigorously studied for many years, some unanswered questions still remain. What is the ultimate light-emitting mechanism for sonoluminescence? What is the nature of the continuum emission? What is the peak temperature that can be achieved during bubble collapse? How do molecular, atomic, and continuum emission evolve when a bubble starts to collapse? Future work in sonoluminescence is still required with hope to answer the above questions, bring about a better understanding of the cavitation process, and provide more information on how to control the light emitting process.

1.6 References


2.1 Introduction

High intensity ultrasound can induce a variety of chemical and physical consequences and has found many important applications in organic chemistry, materials synthesis, medical diagnostics, disease treatments, and industrial manufacturing processes.\textsuperscript{1-12} In terms of materials synthesis, high intensity ultrasound provides unique reaction conditions that are dramatically different from other conventional synthetic techniques such as photochemistry, wet chemistry, hydrothermal synthesis, flame synthesis.\textsuperscript{2, 4-6} Materials prepared by high intensity ultrasound are not the direct result of an interaction of sound waves with chemical species. Instead, they are produced by the chemical and/or physical effects derived from high intensity ultrasound on molecular species. The velocity of sound in liquids is usually \(~1500\) m/s and ultrasound spans the frequencies of 15 kHz to 10 MHz. The associated sound waves are in the range of 10 to 0.1 cm. Therefore, no direct interaction of sound waves with chemical species occurs in the solutions. The chemical effects of ultrasound primarily derive from acoustic cavitation: the formation, growth, and implosive collapse of bubbles in liquid irradiated with high intensity ultrasound, as illustrated in Figure 2.1.\textsuperscript{5} When a sound wave with sufficient amplitude is propagated through a liquid, the liquid is under dynamic tensile stress and the density changes with alternating expansive and compressive waves. Bubbles will be generated from any preexisting impurities and oscillate with the applied sound field. They can grow to a certain size (usually tens of micrometers) before a
catastrophic collapse begins. The implosive collapse process is nearly adiabatic and results in localized transient hot spots responsible for observed chemical reactions. The conditions created inside the collapsing bubbles during that transient hot spot are extreme: temperatures up to 5000 K, pressures of 1000 atm, and heating and cooling rates $>10^{10}$ K/s. Acoustic cavitation concentrates sound energy into a unique set of conditions that differ from other synthetic approaches, and this synthetic method is called sonochemistry (Figure 2.2).

![Figure 2.1. Schematic illustration of a cavitating bubble oscillating with applied ultrasonic sound field. Figure adapted from reference 5.](image)

The physical effects of high intensity ultrasound, which are usually accompanied by chemical consequences, are frequently used in materials synthesis nowadays.
Cavitation near a liquid-solid interface occurs in a different matter than cavitation in a homogeneous liquid. Near a

**Figure 2.2.** Chemistry, as a consequence of the interaction of matter and energy, changes as a function of time, energy, and pressure. This diagram illustrates the unique domains of chemistry. Figure adapted from reference 13.

solid surface, bubble collapse becomes asymmetric which generates a high-speed jet of liquid directed onto the surface as shown in Figure 2.3.\textsuperscript{13} This accelerating jet, which can reach velocities greater than \(\sim 100\) m/s, absorbs most of the energy. In addition, shock waves generated from collapsing bubbles can be as high as \(10^4\) atmospheres which can easily cause surface damage, fragmentation of brittle materials, and drive particles into high-velocity collisions.\textsuperscript{14-20} A shock wave generated from a laser-induced collapsing
bubble is shown in Figure 2.4. The physical effects of high intensity ultrasound are primarily responsible for: (1) enhanced mass transport due to strong turbulent mixing and acoustic streaming; (2) modification of surfaces by liquid jets and shock waves; (3) fragmentation of brittle materials into small pieces; (4) formation of high-speed interparticle collisions; (5) exfoliation of 3D structured materials into 2D or 1D materials.

![Cavitation Bubble](image)

**Figure 2.3.** Photograph of a cavitation bubble at the surface. A liquid jet is obviously formed during bubble collapse. The width of the bubble is around 1 mm. Photograph courtesy of L. A. Crum.

Materials synthesized by different approaches usually exhibit different chemical, physical, optical, and electrical properties. The unique features obtained from materials prepared by different synthetic routes have been a driving force for the development of new methodologies for materials synthesis. This chapter will give a review of recent progress on applications of chemical and physical effects of high intensity ultrasound for materials synthesis.
Figure 2.4. A spherical shock wave launched from a laser-induced collapsing bubble. Images were acquired at a shutter speed of 20.8 million frames per second, frame size was $1.5 \times 1.8 \text{ mm}^2$, and the exposure time was 5 ns. Figure adapted from reference 16.

2.2 Chemical Effects of Ultrasound for Materials Synthesis

When a liquid is irradiated by high intensity ultrasound, high-energy chemical reactions occur. There are many commercially available apparatus for sonochemical reactions: (1) ultrasonic cleaning baths are easily accessible and inexpensive but have low acoustic intensities ($\sim 1 \text{ W/cm}^2$, $40 \text{ kHz}$); (2) high intensity ultrasonic probes (50~500 W/cm$^2$, 20~40 kHz) are the most powerful, reliable and effective source for laboratory-scale sonochemical synthesis, (3) flow reactors with high ultrasonic intensities (20 kW modular units) are commercially available for large-scale irradiations. Depending on the volatility of solutes in the liquid, the sonochemical reactions can undergo two different pathways as illustrated in Figure 2.5. For materials synthesis involving volatile species (organometallic compounds), free metal atoms generated by bond dissociation due to high temperature and pressure created inside bubbles are injected into liquid phase and nucleated to form large nanoparticles or other structured materials when templates or other reactants are present. For materials synthesis involving nonvolatile chemical
substances (usually metal ions in aqueous solutions, or organic radicals from organic solvents), highly reactive radicals are formed from sonolysis of vapor molecules inside the collapsing bubbles and then they diffuse into the liquid phase to initiate a series of redox reactions to form a variety of materials. Although the formation pathways for materials prepared by sonochemical approach from precursors with different volatility are different, ultimately the origin of chemical reactions involved in the materials synthesis is from the interior of collapsing bubbles.

**Figure 2.5.** Two possible routes involved in materials synthesis as a result of chemical effects of high intensity ultrasound: (1) metal atoms generated from bond cleavage of weak metal carbon bond in organometallic compounds are injected into bulk liquid to form functional materials; (2) chemically active radicals formed during the sonolysis of vapor molecules diffuse into liquid and following chemical reactions induced by these reactive species lead to the formation of a variety of materials.
2.2.1 Materials Prepared from Volatile Precursors

Ultrasonic irradiation of volatile organometallic compounds (e.g., Fe(CO)$_5$ or Cr(CO)$_6$) in a nonvolatile organic liquid (e.g., silicon oil or dodecane) produces intense atomic emission lines from excited metal atoms analogues to flame emission.$^{21-23}$ The hot spot conditions inside collapsing bubbles are sufficient to dissociate metal carbon bonds to generate individual metal atoms. The resulting metal atoms can agglomerate in the liquid phase to form a variety of nanostructured materials. The sonochemical reactions of organometallics have been extensively exploited as a general approach to prepare nanostructured materials, as shown in Figure 2.6.$^4$

![Figure 2.6](image)

**Figure 2.6.** Application of chemical effects of high intensity ultrasound for the synthesis of all kinds of inorganic materials based on volatile organometallic precursors. Figure adapted from reference 4.
Nanostructured metal particles were the first demonstration of the application of chemical effects of high intensity ultrasound for the preparation of nanomaterials. Ultrasonic irradiation of solutions containing volatile organometallic compounds such as Fe(CO)$_5$, Ni(CO)$_4$, and Co(CO)$_3$NO produced porous, coral-like aggregates of amorphous metal nanoparticles (Figure 2.7A). For example, sonication of 1 M Fe(CO)$_6$ in decane at 0 °C under Ar yielded a black powder. Elemental analysis indicated that the material was composed of >96% weight iron, with a small amount of carbon and oxygen present from the solvent and CO ligands. SEM images revealed that the power was an agglomerate of 20 nm iron particles. If organic stabilizers like oleic acid or polyvinyl-pyrrolidone were present in the solvent to trap nanoparticles before aggregation occurs, individual iron nanoparticles were produced in a similar fashion to prepare amorphous iron powder. Such prepared iron nanoparticles had a diameter of ~8 nm and were amorphous as measured by electron diffraction (Figure 2.7B). Magnetic studies indicated that these iron nanoparticles were superparamagnetic. In addition to the monometallic nanoparticles, bimetallic alloy particles were also be prepared in this way. For example, sonication Fe(CO)$_5$ and Co(CO)$_3$NO led to the formation of Fe-Co alloy particles, and the composition was controlled by varying the ratio of the precursors in the solution. Other bimetallic systems like Fe-Ni, Co-Ni, and FePt have also been prepared. Alloy nanoparticles exhibit superior catalytic properties compared to monometallic nanoparticles.
Figure 2.7. (A) Sonochemical synthesized porous, coral-like amorphous iron and (B) sonochemical prepared iron nanoparticles stabilized by oleic acid. Figure adapted from reference 27 and 28.

The metal atoms decomposed from organometallic compounds during sonication are highly reactive and can react with other chemical substance in the solvent to form new compounds. Nanostructured MoS₂ was synthesized by the sonication of Mo(CO)₆ with sulfur in 1,2,3,5-tetramethylbenzene under Ar.³⁶ MoS₂ prepared by the sonochemical method differs from conventional MoS₂ dramatically in morphology (Figure 2.8): conventional MoS₂ was a layered material with platelike morphology, while sonochemical synthesized MoS₂ showed spherical morphology with average diameter of 15 nm. TEM examination revealed that sonochemically prepared MoS₂ contained more
defects and showed much more edges, although both MoS$_2$ had the same interlayer distance of 0.62 ± 0.01 nm.

**Figure 2.8.** SEM images of (A) sonochemically synthesized MoS$_2$ and (B) conventional MoS$_2$. Figure adapted from reference 36.

MoS$_2$ has been frequently used as a hydrodesulfurization catalyst in the petroleum industry to remove sulfur from crude oil before combustion. Sonochemically prepared MoS$_2$ exhibited ~fivefold higher catalytic activity than conventional MoS$_2$ for the hydrodesulfurization of thiophene. The increase in catalytic activity was attributed to the higher surface area and more edges and defects found in sonochemically prepared MoS$_2$. Surprisingly, the catalytic activity of sonochemical prepared MoS$_2$ was comparable to RuS$_2$, one of the best but extremely expensive commercial catalysts available.

Similar to MoS$_2$, Mo$_2$C and W$_2$C are interesting catalysts that showed similar catalytic activity as platinum group metals. However, the synthesis of Mo$_2$C and W$_2$C
remains a challenge because of the refractory nature of metal carbides. In general, metal carbides are synthesized by mixing a metal with carbon at an extremely high temperature. Sonochemistry provides a convenient approach to prepare nanostructured metal carbides that exhibit excellent catalytic activity. Sonication of Mo(CO)$_6$ or W(CO)$_6$ in hexadecane leads to the formation of amorphous metal oxycarbides. Removing oxygen by heating under 1:1 CH$_4$/H$_2$ leads to the formation of Mo$_2$C or W$_2$C. Such prepared metal carbides are porous aggregates of small nanoparticles with surface areas of 130 m$^2$/g and 60 m$^2$/g for Mo$_2$C and W$_2$C, respectively. They exhibit activity and selectivity similar to platinum for dehydrogenation reactions. Meanwhile, these nanostructured metal carbides show superior activity, selectivity, and stability for the hydrodehalogenation of halogenated organic pollutants. Metal nitrides can also be prepared by sonication metal carbonyl compounds under a reductive gas mixture of NH$_3$ and H$_2$. Fe nanoparticles coated on silica gels are also produced by sonication Fe(CO)$_5$ in the presence of silica gels.

When a template is present in the solution, the ultrasonic irradiation of volatile organometallic compounds can deposit metal atoms onto the template to form different structured materials. For examples, ultrasonic irradiation of Mo(CO)$_6$, sulfur, and silica nanoparticles in isodurene under Ar flow led to the formation of MoS$_2$–coated silica nanoparticles. Replacing Ar with air and removing sulfur from the system yielded MoO$_3$–coated silica nanoparticles. After etching of the silica component by HF, hollow structured MoS$_2$ and MoO$_3$ were obtained. Such prepared hollow structured MoS$_2$ had superior catalytic activity toward hydrodesulfurization of thiophene than sonochemically
prepared MoS$_2$ nanoparticles due to the significantly increased edge defects and improved accessibility to both inner and outer surfaces of hollow structures.

Ultrasonic irradiation of Fe(CO)$_5$ in the presence of carbon nanoparticles provided a facile method for the preparation of hollow hematite (Figure 2.9). Carbon nanoparticles were used as a spontaneously removable template through combustion by the heat released from the rapid oxidation of the Fe shell coated outside the carbon nanoparticles upon exposure to air. Porous Co$_3$O$_4$ was produced in a similar fashion but carbon nanotubes were used as the template and Co$_4$(CO)$_{12}$ as the precursor. Co$_3$O$_4$ prepared in this way was found to be an excellent electrode material for lithium-ion batteries.

![Figure 2.9](image)

**Figure 2.9.** (A) TEM image and (B) high-angle annular dark-field (HAADF) STEM image (inset: select area electron diffraction pattern, SAED) of hollow hematite prepared by the sonication of Fe(CO)$_5$ with preexisting carbon nanoparticles as template. Figure adapted from reference 41.
Under suitable conditions, nano-sized catalyst particles can be deposited onto substrates to form supported catalysts. A nanostructured, bifunctional catalyst, Mo$_2$C/ZSM-5, was prepared by the sonication of Mo(CO)$_6$ and HZSM-5 in hexadecane. The free Mo atoms decomposed from Mo(CO)$_6$ by high intensity ultrasound were deposited onto the surface of ZSM-5 support and then they nucleated to form small nanoparticles with diameters of ~2 nm. Such prepared catalyst showed excellent catalytic activity for dehydroaromatization of methane to benzene. Use a similar approach, Co- and Ni-promoted MoS$_2$ supported on alumina were prepared by the high intensity ultrasound irradiation of isodurene slurries containing Co$_2$(CO)$_8$, Mo(CO)$_6$, sulfur, and Al$_2$O$_3$ or Ni-Al$_2$O$_3$ under Ar flow. The sonochemically prepared supported catalysts were active for the hydrodesulfurization of thiophene and dibenzothiophene.

The sonochemical method has also been used to synthesize single-walled carbon nanotubes by the irradiation a solution containing silica powder, ferrocene, and p-xylene (Figure 2.10). In this synthesis, ferrocene was used as the precursor for Fe catalyst, p-xylene was used as carbon precursor, and silica powder was used as the nucleation site for the growth of carbon nanotubes. The extreme conditions created inside the collapsing bubbles provided sufficient energy to decompose ferrocene to form small Fe clusters and pyrolyze p-xylene to carbon atoms and carbon moieties. This approach provides a convenient synthetic route for the preparation of carbon nanotubes under ambient conditions. In addition, no extra purification procedures are needed in this process, which open up the possibility of large-scale synthesis high-purity single-walled carbon nanotubes.
Figure 2.10. (A) Schematic illustration of the preparation process for the formation of single-walled carbon nanotubes on silica powders using sonochemical method. (B) SEM image of carbon nanotube bundles on polycarbonate filter membrane. (C) HRTEM images of single-walled carbon nanotube bundles. Figure adapted from reference 45.

Ultrasonic irradiation of common organic solvents such as CHCl₃, CH₂Cl₂, and CH₃I with HF-etched Si nanowires yielded many different structured hydrocarbon materials (i.e., nanotubes and nano-onions).⁴⁶, ⁴⁷ Nanostructured SiHₓ served as template for the nucleation of carbon species formed from the pyrolysis of organic vapor molecules inside the collapsing bubbles. Another possible mechanism for the formation
of hydrocarbon structures is the accelerated reaction between SiHₓ with organic molecules promoted by ultrasound.

2.2.2 Materials Prepared from Nonvolatile Precursors

Sonochemistry can also be used to prepare materials such as nanostructured noble metals when nonvolatile precursors are present in the solvent (usually water). The sonochemical reduction approach has its own unique features: no reducing chemicals are needed, the reduction rate is generally very fast, and very small nanoclusters can be made in this way when suitable stabilizers are present. The reducing species that ultimately account for the reduction of nonvolatile noble metal ions in the solution are from the sonolysis of water. Specifically, ultrasonic irradiation of water generate highly reactive H• and OH• radicals which are responsible for the redox reaction.48-51 These reactive radicals will further react with organic additives (e.g., 2-propanol and alcohol) in the solution to generate secondary radicals (R•) which can dramatically promote the reduction rate. Overall, the process can be summarized as follow:

\[
\begin{align*}
H_2O & \rightarrow H^\bullet + OH^\bullet \\
H^\bullet + H^\bullet & \rightarrow H_2 \\
H^\bullet + OH^\bullet & \rightarrow H_2O \\
OH^\bullet + OH^\bullet & \rightarrow H_2O_2 \\
RH + OH^\bullet (or H^\bullet) & \rightarrow R^\bullet + H_2O (or H_2) \\
M^{n^+} + nR^\bullet (or H^\bullet) & \rightarrow M^0 \\
mM^0 & \rightarrow M_n (M=\text{noble metal})
\end{align*}
\]
Unlike metallic particles prepared from the sonication of volatile organometallic compounds which are typically amorphous, materials produced from nonvolatile compounds are usually well crystallized.

Nanostructured noble metals (e.g., Au, Ag, Pt, and Pd) have been prepared by a number of synthetic approaches such as controlled chemical reduction, solvothermal synthesis, photochemical reduction, and radiolytic reduction.\textsuperscript{52-56} The sonochemical route is one of the synthetic methods for the preparation of various metallic nanoparticles and has been explored by many research groups.\textsuperscript{57-65} Spherical metal nanoparticles are easy to prepare by ultrasonic irradiation. A systematic study carried out by Grieser \textit{et al.} on the effect of ultrasound on the synthesis of noble metal nanoparticles indicated that the particle size is inversely dependent on alcohol concentration and alkyl chain length.\textsuperscript{59} This observation led to the conclusion that alcohol molecules absorbed on the surface of nuclei can limit the growth of small nanoparticles into large nanoparticles. The other possible mechanism for obtaining small nanoparticles using higher alcohol concentrations is that more secondary radicals can form at higher alcohol concentrations which leads to faster reduction rates which results in smaller and possibly more uniform particles.

When two different metallic ions are present in the solution, bimetallic nanoparticles can be obtained. For example, the sonochemical reduction of an aqueous solution containing both Au(III) and Pd(II) ions led to the formation of bimetallic nanoparticles. Such prepared bimetallic nanoparticles exhibited a core-shell structure with a Pd shell over an Au core (Figure 2.11).\textsuperscript{66, 67} The formation of the core-shell structure is due to the difference in reduction potential between Pd(II) and Au(III) ions.
When Au and Pd nanoparticles are formed simultaneously, excess Au(III) ions will consume Pd nanoparticles via an oxidation reaction to form Au and Pd(II) ions. The Pd(II) ions can be reduced by the reducing radicals again to form Pd which will be oxidized by Au(III) again. This process results in the formation of the core-shell structure via the co-reduction method. A similar approach can be used to prepare Au/Ag core-shell particles by the sonochemical method.\textsuperscript{68}

\textbf{Figure 2.11.} TEM images of sonochemically prepared Au/Pd bimetallic nanoparticles with different molar ratios of Au and Pd precursors: (A) 1:1 and (B) 1:4. Figure adapted from reference 67.
Other than the co-reduction approach, sequential sonochemical reduction can also be used to prepare core-shell structured nanoparticles. Au core and Pd shell nanoparticles have been synthesized by successive reduction of Pd(NO$_3$)$_2$ and HAuCl$_4$ in ethylene glycol via ultrasonic irradiation.$^{69}$ Both Pt and Ru are excellent electrocatalysts for methanol oxidation in direct methanol fuel cells (DMFC). Sonochemical reduction can be applied to synthesize Pt@Ru core-shell nanoparticles via sequential reduction.$^{70, 71}$

The sonochemical method has also been developed to prepare nonspherical nanoparticles in solutions. For example, gold nanorods have been synthesized by the sonochemical reduction of HAuCl$_4$ in the presence of AgNO$_3$, CTAB, and ascorbic acid.$^{72}$ The solution pH influences the aspect ratio of the gold nanorods: as the pH of the solution increases, the average aspect ratio of formed gold nanorods decreases. Ultrasound-induced reduction of HAuCl$_4$ on presynthesized gold seeds using poly(vinylpyrrolidone) (PVP) as a stabilizing polymer leads to the formation of monodispersed gold nanodecahedra (Figure 2.12).$^{73, 74}$ This sonochemical method can significantly increase the yield and reproducibility. Ag nanoplates have also been synthesized by a similar ultrasound-assisted Ostwald ripening process using Ag nanoparticles as seeds.$^{75}$ These platelike nanostructures served as templates to fabricate ringlike metal structures via a simple displacement reaction under ultrasonic irradiation.$^{75}$ Ag nanowires and nanorods have also been prepared by sonication suitable Ag precursors in the solutions.$^{76, 77}$
Polymers or small molecules sometimes can act as structure directing agents as well as stabilizers. Ultrasonic irradiation of HAuCl₄ solution containing α-D-glucose produced gold nanobelts with a width of 30~50 nm and a length of several micrometers (Figure 2.13). A detailed study revealed that gold nanobelts are formed through following 3 steps: (1) formation of gold nanoparticles; (2) aggregation and melting of gold nanoparticles directed by α-D-glucose; (3) further growth along the Au[111] direction and recrystallization finally yield single-crystalline gold nanobelts.
Figure 2.13. (A) SEM image and (B) high-magnification SEM image of sonochemically synthesized gold nanobelts. Conditions for preparing these gold nanobelts are: [HAuCl₄]=50 mg/ml, [α-D-glucose]=0.2 M, sonication time=1 h. Figure adapted from reference 78.

The sonochemical reduction of nonvolatile precursors in solution is not limited to noble metals. For example, trigonal Se nanowires are prepared by the sonication of amorphous Se colloids in alcohol solvents without the presence of templates or
surfactants. Small nanocrystals of trigonal Se can be produced and decorated onto the surface of amorphous Se colloids via localized heating. Trigonal Se can then act as seeds for the growth of Se nanowires through a solid-solution-solid transformation mechanism because amorphous Se has a higher free energy than trigonal Se.

Various metal oxides and metal chalcogenides have been prepared by the sonochemical synthetic method. A typical synthesis of such materials usually involves the sonication of a solution containing a metal salt and an oxygen or chalcogen source (e.g., air for the oxygen, thiorea for S, selenourea for Se, or sometimes, a sulfate or selenate). Reactive species such as radicals (O• or S•) or H₂ can react with metal ions in the solution to form metal oxides or metal chalcogenides. If proper structure directing agents are used, different structured materials (e.g., hollow spheres, nanorods, nanowires, or nanocubes) can be obtained. For example, ultrasonic irradiation of CdCl₂, NaSeSO₃ and ammonia can lead to the formation of hollow CdSe spheres (Figure 2.14). CdCl₂ was hydrolyzed in the basic conditions to form Cd(OH)₂ which acted as an in situ template for the formation of hollow structures. This process can be written as follow:

\[
\begin{align*}
H₂O & \rightarrow H• + OH• \\
2H• + SeSO₃^{2–} & \rightarrow Se^{2–} + 2H^+ + SO₃^{2–} \\
Cd(OH)₂ + Se^{2–} & \rightarrow CdSe + 2OH^- \\
nCdSe & \rightarrow (CdSe)ₙ
\end{align*}
\]

Hetero-structured materials such as core/shell SnO₂/CdS and ZnO/CdS have also been prepared via sonochemical deposition of metal sulfide onto metal oxides.
The sonochemical method can also deposit in situ formed nanoparticles onto preexisting substrates in solution. For example, noble metal nanoparticles generated by the sonochemical reduction method have been deposited onto various substrates (e.g., polystyrene spheres, silica particles, carbon nanotubes, or polymer matrix).\textsuperscript{98-102} Recently, graphene has emerged as a new 2D material with unique electrical, thermal, and mechanical properties. Catalyst assemblies of nanostructured materials with exfoliated, single-layer graphene have great promise for a wide range of applications including sensors, fuel cells, lithium-ion batteries, photocatalysts, and fuel cells. Ultrasonic irradiation of graphene oxide with H\textsubscript{2}AuCl\textsubscript{4} in water produced well-dispersed reduced graphene oxide/Au composites by simultaneous or sequential reduction procedures.\textsuperscript{103}
The mechanism responsible for the formation of reduced graphene oxides and reduction of Au(III) to Au nanoparticles is due to the formation of reactive OH• and H• radicals via sonolysis of water vapor inside collapsing bubbles.

Figure 2.15. TEM images of the reduced graphene oxide/Au composite at low resolution on a holey carbon grid. (A) Sequentially reduced and (B) simultaneous reduced graphene oxide/Au composite by sonochemistry. Figure adapted from reference 103.

The chemical effects of high intensity ultrasound have also been applied to prepare soft materials such as polymers.\textsuperscript{104-109} The majority of polymers are synthesized from monomers that contain reactive groups that can react to form long polymer chains. Acoustic cavitation in liquids can generate high concentrations of radicals which can be used to synthesize polymers in a controllable manner. For example, sonochemically formed OH• and H• radicals have been used to prepare poly(acrylonitrile) in aqueous solutions.\textsuperscript{105} The primary role of ultrasound in the synthesis of polymers is to induce the formation of radicals that are capable of polymerization of vinyl monomers. Radicals can be formed either by the thermal decomposition of pure monomer molecules inside cavitating bubbles or by the decomposition of initiators such as peroxides or azo compounds. Because high temperatures exist inside the collapsing bubbles, monomer
vapor can be pyrolyzed in the bubbles to form insoluble chars in the liquid. Some purification procedures are necessary to obtain high purity and high molecular weight polymers.

High intensity ultrasound can also induce the degradation of high molecular weight polymers.\textsuperscript{110-113} The mechanism of polymer degradation is still not clear: it could be a physical effect due to the shear force applied on polymer chains, or it could be that radicals formed by cavitation process induce the degradation process. The degraded polymer chains, however, can be used to initiate a second polymerization process to prepare block copolymers.\textsuperscript{4, 114} Other soft materials such as protein microspheres have also been prepared by the sonochemical approach.\textsuperscript{115-122} The application of ultrasound for preparation of protein microspheres, which involves both physical and chemical effects of high intensity ultrasound, will be discussed later.

2.3 Physical Effects of Ultrasound for Materials Synthesis

Unlike the chemical effects of high intensity ultrasound, there are no chemical reactions involved when the physical effects of high intensity are applied for materials synthesis. The physical effects of high intensity ultrasound generally arise from the high-speed jets and/or intense shock waves result from bubble collapse. They have been frequently used to prepare emulsions, break down fragile materials, exfoliate layered materials, enhance mass transfer, bulk thermal heating, and the modification of surfaces.

Graphite has a layered, planar structure. The space between each graphene layer can accommodate guest molecules or atoms to form graphite intercalation compounds.\textsuperscript{123} The formation of intercalation compounds is usually a very slow process. Ultrasonic
irradiation, however, can dramatically increase the reaction rate. For example, potassium intercalated compounds (KC$_8$) can be prepared by the sonication of graphite with potassium under an Ar atmosphere in 3 minutes while normal preparatory methods typically require 1~8 hours via a solid state reaction at a high temperature in an inert environment.\textsuperscript{124} H$_2$PtCl$_6$ can also be intercalated into the graphite layers to prepare Pt nanoparticles intercalated in graphite after exposure to H$_2$ gas stream.\textsuperscript{125} The sonication of potassium intercalated graphite in ethanol can generate carbon nanoscrolls. The conversation efficiency is very high, up to \textasciitilde80\%. Ultrasound is essential to form carbon nanoscrolls: very few nanoscrolls can be obtained without sonication.\textsuperscript{126} Carbon nanoscrolls can also be prepared from another graphite intercalated compound, graphite nitrate. The reason for the formation of carbon nanoscrolls is not clear yet, but ultrasound provides the necessary mechanical energy to overcome the van der Waals force between each graphene layer. The individual exfoliated graphene layers can then fold via intralayer interactions to reach a stable structure in the solvent (Figure 2.16).\textsuperscript{126}

![Figure 2.16](image)  

**Figure 2.16.** (A) Schematic illustration of the intercalation and exfoliation process to prepare carbon nanoscrolls. TEM images of (B) a thin layer of graphite sheets in the process of scrolling, (C) an isolated carbon nanoscrolls with open ends, and (D) a bundle of scrolled carbon nanosheets. Figure adapted from reference 126.
Ultrasound has become a formidable tool in the chemical preparation of graphene. In a typical synthesis of graphene oxide, pristine graphite is oxidized by Hammer’s method to form graphite oxide with increased interlayer distance to reduce the van der Waals force.\textsuperscript{127, 128} After mild sonication, single-layered graphene oxides can be produced which then are chemically reduced to form graphenes. A more straightforward method to prepare graphene is the direct liquid-phase exfoliation of graphite by sonication.\textsuperscript{129-134} To obtain high yields of exfoliated graphenes from graphite, the surface energy of the solvent should match the surface energy of graphite with surface tensions of 40–50 mJ/m\textsuperscript{2}. Sonication of graphite in suitable solvents (e.g. N-methyl-pyrrolidone (NMP)) can lead to the formation of single layer and few-layer graphenes. The sonication of graphites in water in the presence of surfactant (e.g., sodium dodecylbenzene sulfate, SDS) can yield graphenes, with concentrations up to 0.1 mg/ml (Figure 2.17).\textsuperscript{130} Ultrasound is also frequently used to detangle single-walled carbon nanotubes which usually form bundles via van der Waals force.

Using a similar approach with suitable solvents, other layered materials like MoSe\textsubscript{2}, MoTe\textsubscript{2}, TaSe\textsubscript{2}, NbSe\textsubscript{2}, NiTe\textsubscript{2}, BN, Bi\textsubscript{2}Te\textsubscript{3}, BN, MoS\textsubscript{2}, and WS\textsubscript{2} can also be exfoliated in the liquid phase to prepare single-layered nanosheets (Figure 2.18).\textsuperscript{135} Therefore, ultrasound can be used as a universal tool to overcome the attractive forces between individual layers to break 3D layer-structured materials down to 2D planer structures.
Figure 2.17. TEM images of graphene sheets exfoliated from graphites in water/surfactant mixture. (A) A monolayer. (B) A bilayer. (C) A trilayer. (D) A disordered multilayer. Figure adapted from reference 130.

Figure 2.18. TEM of individual nanosheets. (A to C) Low-resolution TEM images of flakes of BN, MoS$_2$, and WS$_2$, respectively. (D to F) High-resolution TEM images of BN,
MoS$_2$, and WS$_2$ monolayers. (Insets) Fast Fourier transforms of the images. Figure adapted from reference 135.

The impact of high intensity ultrasound on preexisting particles in a liquid is also an interesting phenomenon. For instance, high intensity ultrasound can drive micro-sized metal particles at high speed to induce local melting at the point of collision (Figure 2.19).$^{19, 20}$ This is another indication of the extreme conditions that can be created in liquid under ultrasonic irradiation. Of course, this can only happen with metals with relatively low melting point like Zn, and Sn. If the melting points of the metals are higher than 3000 K, no melting at the point of impact would occur. Ultrasonic irradiation of Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$ in decane can significantly improve the superconducting properties.$^{136}$ The change in the superconductivity is believed to be due to the enhancement of intergrain coupling which controls the critical magnetic field ($J_c$) that limits the fields that can be formed using Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$ superconductor by ultrasound induced interparticle collisions.
Ultrasound can also be used to promote the diffusion of doping ions into spherical nanoparticles.\textsuperscript{137, 138} For example, high intensity of ultrasound is used to prepare Mg$^{2+}$ doped ZnO nanoparticles with tunable photoluminescence (from yellow to blue, see Figure 2.20).\textsuperscript{137} The quantum yield of these Mg$^{2+}$ doped ZnO nanoparticles is very high; they can reach >60\% under optimal conditions. XRD and HRTEM results indicate that no MgO phase exists in the ZnO nanoparticles. Ultrasonic irradiation of a slurry containing Au colloids and TiO$_2$ particles can lead to the formation of Au nanoparticles intercalated in a mesoporous TiO$_2$ structure which shows enhanced photocatalytic properties.\textsuperscript{138}
The microjets and shock waves produced by high intensity ultrasound near the solid surfaces can also induce a series of physical changes on the surfaces of particles and substrates.\textsuperscript{139} For instance, ultrasonic treatment of fused silica glass in water has been shown to induce erosion on the glass surface (Figure 2.21).\textsuperscript{140} High intensity ultrasound can also induce the erosion of the surfaces of ceramic materials. Figure 2.22 shows the worn surfaces of Al\textsubscript{2}O\textsubscript{3} ceramic and MgO-ZrO\textsubscript{2} ceramic after 360 min exposure to high intensity ultrasound.\textsuperscript{141} The surface of Al\textsubscript{2}O\textsubscript{3} ceramic was dramatically damaged by ultrasonic irradiation while the surface of MgO-ZrO\textsubscript{2} was only partially eroded. It is concluded that the microstructures of ceramic materials play an important role in resistance to the cavitation erosion.
Figure 2.21. Photograph of a fused silica glass eroded by sonication for 180 min at 2 mm from the ultrasonic horn at the acoustic intensity of 49 W/cm². Figure adapted from reference 140.

Figure 2.22. White light interferometer images of the worn surfaces of (A) Al₂O₃ and (B) MgO-ZrO₂ after cavitation erosion in water for 360 min. Figure adapted from reference 141.

The surface of metallic substrates and metallic particles can also be affected by ultrasonic irradiation. The effect of sonication on metal surfaces was first studied on nickel powders.⁴⁴²⁻⁴⁴⁵ After the ultrasonic irradiation of nickel powders, the particle surfaces became smoothed compared to those before ultrasonic treatment. The surface oxide layer was removed by the ultrasonic irradiation and the reactivity of the nickel powder increased by ~100,000 fold.⁴⁴² High intensity ultrasound has also been applied to anticorrosion coatings.⁴⁴⁶ Generally, pure aluminum metal is coated by a 3~7 nm thick natural oxide layer. This layer is not able to protect against corrosion agents and it is not strongly adhered to the subsequent pure metallic layer. The corrosion protection and adhesion properties, however, can be improved via ultrasonic treatment. After ultrasonic
irradiation, the existing oxide layer is removed and a new active oxide layer will form which has been shown to exhibit better resistance to corrosion. Ultrasonic irradiation induced surface modification is caused by the combined effects microjets, shock waves, microstreaming, and microturbulence that arise from physical effects of high intensity ultrasound.

Sol-gel synthesis has been proven to be a versatile technique for the preparation of metal oxides. Ultrasound can accelerate the hydrolysis process and the subsequently obtained metal oxides show better size distribution, higher surface area, and improved phase purity. For example, TiO₂, ZnO, CeO₂, MoO₃, V₂O₅, and In₂O₃ have been prepared by the ultrasonic irradiation of the precursor solutions.¹⁴⁷-¹⁵² TiO₂ nanoparticles prepared by ultrasonic irradiation of precursor solution are more photocatalytically active than commercial TiO₂ nanoparticles. The increase in photocatalytic activity is attributed to the improved crystallinity of TiO₂ by accelerated hydrolysis under sonication. Ultrasound can also induce the formation of unique morphologies during the synthesis of metal oxides in the presence of soft templates. For example, hollow PbWO₄ spindles were prepared from the sonication of a solution of Pb(CH₃COO)₂, NaWO₄, and P123 (EO₂₀PO₇₀EO₂₀, M₄₅=5800) (Figure 2.23).¹⁵³ If ultrasound was not applied to this solution, only solid particles were obtained. It was argued that ultrasound played an important role in the transformation of P123 micelles into hollow micelle aggregates which led to the formation of the hollow spindle structure. The whole process is illustrated in Figure 2.23E.¹⁵³
Figure 2.23. (A) Typical SEM image of the as-prepared PbWO$_4$ sample. (B) SEM image of several broken hollow spindles viewed from different angles. (C) Typical TEM image and (D) SAED pattern of the product. (E) Schematic illustration of the formation of PbWO$_4$ hollow spindles under ultrasonic treatment. Figure adapted from reference 153.

The microbubbles formed by the sonication of an aqueous solution could also act as a template for the formation of hollow spheres.$^{154}$ For instance, ultrasonic irradiation of a solution containing crystalline Pt nanoparticles modified by a thin layer of polymethylmethacrylate (PMMA) led to the formation of hollow 1~2 μm Pt spheres containing 60% amorphous Pt.$^{154}$ The proposed mechanism for the formation of hollow spheres is as follows: Pt catalyzes the decarboxylation of MMA, which results in the
formation of a more hydrophobic Pt surface and the accumulation of Pt nanoparticles at
the surface of cavitation microbubbles, and this ultimately causes the formation of hollow
spheres. The rapid heating and cooling of the cavitation microbubbles induces the
welding of Pt nanoparticles and formation of amorphous Pt. The microbubbles created by
sonication can also be used to prepare polyelectrolyte multilayers via layer-by-layer
assembly. Electrostatic layer-by-layer assembly of polyallylamine (PAH) and
poly(styrene sulfonate) (PSS) was successfully carried out by the ultrasonic irradiation of
a mixture of Span/Tween block copolymers. The polyelectrolyte microcapsules
prepared in this way have a large size distribution and are stable for a minimum of 1
week. Figure 2.24A-B illustrates the preparation process and Figure 2.24C shows the
confocal microscopy image of microcapsules prepared in this way.

The power of the physical effects of high intensity ultrasound is further
exemplified by mechanochemistry, which is a force-induced scission of covalent bonds.
It was demonstrated that the incorporation of mechanically sensitive chemical groups
onto a polymer chain makes it possible to harness the mechanical forces generated by
exposing the polymer solutions to ultrasound. Sonication allows acceleration of the
rearrangement reactions and a bias towards reaction pathways that yield molecules not
obtained from purely thermal or light-induced reactions. As shown in figure 2.25,
when \textit{trans} or \textit{cis} 1,2-disubstituted benzocyclobutene is incorporated into the polymer
chain and undergoes ultrasound triggered electrocyclic ring opening process,
respectively, same products are formed. If the reaction is initiated by light or heat alone,
different products will be obtained. Thus, the mechanical force induced by ultrasound

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Figure 2.24. Schematic illustration on fabrication of hollow gas-filled polyelectrolyte capsules. (A) An aqueous detergent mixture of Tween 80 and Span 60 is used to form gas bubbles through intensive ultrasonication at the air–water interface. (B) Mixing the bubbles with the cationic PAH results in the deposition of the first polyelectrolyte layer. The capsule now has an overall positive charge. These coated bubbles are separated from the unbound polymer by gentle centrifugation to allow binding of anionic PSS in the following step. The deposition procedure is repeated several times until a desired stability is reached. (C) Confocal microscopy image of air-(PAH/PSS)$_6$ microcapsules under bright field mode. Figure adapted from reference 155 and 156.

can alter the shape of the potential energy surfaces so that otherwise forbidden or slow reactions can proceed under mild conditions. Ultrasound offers a way to control the reaction pathways that dramatically differ from those achieved by simply changing chemical or physical parameters. If stress-sensitive and cleavable groups are integrated in the polymer chain, sonication could result in the precise scission of the polymer chains. Some weak covalent bonds like peroxide and azo bonds, strained rings, and weak coordinative bonds (e.g., palladium-phosphorus bond) have been shown to be cleaved by
Figure 2.25. Preparation and reaction of mechanosensitive polymers. Shown are the preparation of link-functionalized polymers 3 and 4 from bifunctional cis-benzocyclobutene units 1 and 3, and the reaction of these polymers with maleimide trap 5 under ultrasound or heat. Figure adapted from reference 157.

Figure 2.26. (A) Ultrasound-induced cleavage of polymer containing a strained dicyano-substituted cyclobutane ring to yield cyanoacrylate-terminated polymers. (B) Control polymer. Figure adapted from reference 158.

Figure 2.26 shows that sonication of polymer containing a strained cleavable ring leads to the formation of reactive cyanoacrylates.
Another intriguing example of the application of the physical effects of high intensity ultrasound is to trigger a gelation process. This sonication-induced gelation phenomenon was first described in a pallado-macrocycles system.\textsuperscript{162} The association-inert dinuclear Pd complex, as shown in Figure 2.27A, is stabilized by intramolecular π-stacking interactions and is shown to instantly gelatinize a variety of organic solvents upon a brief presonication (Figure 2.27B). Ultrasound was then employed as an unexpected but effective stimulus to induce the gelation process via hydrogen bonding, π–π stacking, and/or van der Waals interactions.\textsuperscript{163-168} Ultrasound could also be used to prepare organic crystals.\textsuperscript{169-172} As shown in Figure 2.28, the application of low-intensity ultrasonic irradiation to cocrystals of 2(resorcinol)•2(4,4′-bpe) produces nano- and micrometer-sized cocrystals that are shown to exhibit single-crystal-to-single-crystal reactivity.\textsuperscript{169} Compared to the conventional reprecipitation method, crystals obtained via sonocrystallization have more uniform size and prism morphology with nano- and micro-sized dimensions.

**Figure 2.27.** (A) Molecular structure of dinuclear Pd complexes. (B) anti-1a in acetone at 293 K switching between stable sol state and gel state by a brief presonication for 3 s (0.45 W/cm\(^2\), 40 kHz). Figure adapted from reference 162.
2.4. Chemical and Physical Effects of Ultrasound for Materials Synthesis

Under certain conditions, both the chemical and physical effects of high intensity ultrasound can be applied in materials synthesis. The physical effects of high intensity ultrasound usually have chemical consequences and the chemical effects of high intensity ultrasound are always facilitated by the physical effects. Some examples on the combined application of chemical and physical effects of high intensity ultrasound for materials synthesis will be described in this section.

A notable example of the application both chemical and physical effects of high intensity ultrasound for materials synthesis is the preparation of protein microspheres.\textsuperscript{115-122} Sonication of a protein solution (e.g., serum albumins) led to the formation of microcapsules which contained air or nonaqueous liquid. The mechanism responsible for the formation of protein microspheres involves two acoustic phenomena: emulsification (i.e., physical effects) and cavitation (chemical effects). Ultrasonication creates a
emulsion with proteins in the interface of two liquid phases. However, emulsification is not enough to prepare stable protein microspheres. Chemically produced radicals (e.g., HO$_2$•) via sonolysis of water can induce the cross-linking of the disulfide bonds between protein cysteine residues. Layer-by-layer modification of the surface of protein microspheres with specific peptide ligands can be used for targeted imaging or drug delivery. It is worth mentioning that noncovalently bonded protein microspheres, sodium polyglutamate (SPG) microspheres, were prepared without the involvement of the chemical effects of ultrasound.$^{122}$ Such prepared protein microspheres have been developed as biomedical imaging contrast agents for magnetic resonance imaging (MRI), for optical coherence tomography (OCT), and for sonography (e.g., Albunex, the first FDA approved echo contrast agent).

Hollow inorganic spheres can be produced by the combined effects of high intensity ultrasound. For instance, PbS hollow nanospheres with diameters of 80–250 nm have been fabricated by a surfactant-assisted sonication route from Pb(CH$_3$COO)$_2$, thioacetamide, and sodium dodecylbenzenesulfonate under the irradiation of a 49 kHz ultrasound (Figure 2.29)$^{173}$ These hollow nanospheres consist of PbS nanoparticles with diameters of 12 nm. Under sonication, surfactants accumulate at the surface of micrometer-sized air bubbles. Pb$^{2+}$ ions in the solution are easily attracted by the negatively charged template surface to form hollow Pb$^{2+}$ structures. Then, active H$_2$S formed by reaction between thioacetamide and radicals formed by sonolysis of water will react with Pb$^{2+}$ to form PbS nanoparticles. Compact, hollow PbS nanospheres are finally formed by a mineralization process. Hollow CdSe and MoS$_2$ spheres are also prepared by this approach.
Figure 2.29. (A) TEM and (B) HRTEM images of PbS hollow spheres. Figure adapted from reference 173.

The combination of chemical and physical effects of ultrasound can be applied to prepare organic latex beads in a one-pot fashion.\textsuperscript{174, 175} The physical effects of ultrasound can induce the formation of emulsions that contain the monomers in an aqueous medium. The radicals formed by pyrolysis of water under ultrasound can diffuse into the organic phase to initiate the polymerization process. No additional initiators are required in this approach. In this method, fluorescent or magnetic substances can be incorporated into the latex particles to prepare functional latex beads. For examples, magnetic latex beads with a high content of magnetic nanoparticles have been prepared by ultrasonic irradiation of a mixed solution with magnetite nanoparticles, surfactants, water and monomer.\textsuperscript{175} Short sonication of the above solution results in the formation of a miniemulsion of monomer loaded with magnetite nanoparticles stabilized by surfactants in the water phase. Continuous sonication initiates the polymerization of monomers.

Aligned nanostructured can be achieved upon the application of ultrasound. For example, vertically aligned ZnO nanorods are prepared on various substrates like Zn
sheets, Si wafers, glass, and polycarbonate membranes by sonication a precursor solution containing Zn$^{2+}$ (Figure 2.30).\textsuperscript{176} Ultrasonic irradiation rapidly induces the anisotropic growth of ZnO along the (0001) direction on substrates. The alignment is presumed to be due in part to the relative depletion of Zn$^{2+}$ concentration at the base of the growing rods relative the tops of the rods. This is caused by the physical effects of ultrasound. Chemical effects of ultrasound, for example, the O• radicals formed by sonication of water in air, are also believed to be involved in the formation of ZnO rods. Compared to a conventional hydrothermal process, the growth rate of ZnO is increased by 10 fold, with an average growth rate of $\sim$500 nm/h. This work demonstrates that the combination of the chemical and physical effects of ultrasound can produce aligned nanostructured materials. Such prepared ZnO nanorods have potential applications for solar energy conversion.

\textbf{Figure 2.30.} Tilt-view SEM images of vertically aligned ZnO nanorods produced by ultrasound-induced anisotropic growth long the (0001) direction. (A) Low magnification and (B) magnified view of the oriented ZnO nanorods. Figure adapted from reference \textsuperscript{176}. 

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2.5. Ultrasonic Spray Pyrolysis for Materials Synthesis

Ultrasonic spray pyrolysis (USP) is a synthetic approach that for the preparation of materials with controlled morphologies, structures, and sizes. Unlike the application of chemical effects of high intensity ultrasound for materials synthesis where ultrasound directly induces chemical reactions, ultrasound does not cause chemical reactions. As a matter of fact, the chemical reactions in USP are thermally driven. The role of ultrasound in the USP synthesis of materials is to nebulize a precursor solution into individual droplets that act as microreactors where chemical reactions occur. In USP synthesis, high frequency ultrasound with low intensity (e.g., ~2 MHz) is typically used. In some aspects, USP could be redeemed as the application of physical effects of ultrasound for materials synthesis (i.e., micro-sized droplets that are physically produced by high frequency ultrasound).

The phenomenon of the generation of droplets by high frequency ultrasound was first observed by Wood and Loomis in 1927. In general, nebulization of a liquid by high frequency ultrasound is a result of capillary waves (i.e., waves traveling along the interface between two liquids) or in other words, momentum transfer. The capillary waves created by ultrasonic vibration at the surface of liquid consist of crests and troughs. When the amplitude of the surface capillary waves is sufficiently high, crests of the waves can break off to form individual droplets. Such a phenomenon is shown in Figure 2.31. Many factors influence the size of liquid droplets generated by high frequency ultrasound. In 1962, Lang first correlated the relationship between ultrasonic frequency and average droplet size (Equation 1). The product particle diameter, $D_{\text{particle}}$, can be estimated via equation 2 when the solution concentration is known.
\[ D_{\text{droplet}} = 0.34 \left( \frac{\pi \gamma}{\rho f^2} \right)^{1/3} \]  
(1)

\[ D_{\text{particle}} = \left( \frac{MD_{\text{droplet}}^3 C_s}{1000 \rho} \right)^{1/3} \]  
(2)

In above equations, \( D_{\text{droplet}} \) is average droplet diameter, \( D_{\text{particle}} \) is average particle diameter, \( \rho \) is solution density, \( \gamma \) is surface tension, \( f \) is ultrasonic frequency, \( M \) is molecular weight, and \( C_s \) is solution concentration.

A typical USP apparatus is shown in Figure 2.32. Generally, the USP system consists of an ultrasonic transducer, a container which is separated by a thin membrane from transducer, a furnace, and some bubbler collectors at the outlet of the furnace. The liquid droplets generated by ultrasonic nebulization are carried through a furnace by a gas flow (e.g., Ar, N\(_2\), or sometime reactive gases like O\(_2\) or NH\(_3\)). The final products are collected in the bubblers or other collection apparatus. There are also other types of commercial nebulizers available.\(^{184,185}\)

**Figure 2.31.** Photograph of an ultrasonic fountain generated using 1.7 MHz ultrasound.

Figure adapted from reference 182.
The USP process usually consists of droplet generation, solvent evaporation, solute precipitation, decomposition, thermal reactions (solid-phase or liquid-phase when high melting substances are present), desification, and sometimes pore formation in the presence of templates or release of gaseous products. This is a simple description of the USP reaction process (Figure 2.33). Actual USP process is more complicated and has been discussed in many reviews and books. USP has been widely used in materials synthesis because the apparatus is simple and it can be scaled up for manufacturing. As a materials synthesis tool, USP stands out from other synthetic techniques with the following advantages: continuous production of micro- or nano-sized particles or spheres, high product purity, and facile control over the composition of the final product.

USP has been frequently used to prepare fine powders. A great number of metals, metal alloys, and ceramic materials (e.g., Au, Ag, Pd, Cu, Ni, Co, Au-Ag, and Ag-Pd)}

Figure 2.32. Schematic illustration of a typical USP apparatus. Figure adapted from reference 6.
have been synthesized via USP process. Typically, a metal salt or mixture solution is used as the precursor.

![Schematic Illustration of a Typical USP Process](image)

**Figure 2.33.** A schematic illustration of a typical USP process.

to produce metals or metal alloys particles via thermal decomposition under inert atmosphere (e.g., Ar and N₂). Sometimes, a reductive gas such as H₂ is employed to provide a reducing environment for the preparation of non-precious metal particles. The addition of an alcohol into the precursor solution can create a stronger reducing environment due to the decomposition of alcohol to form CO, H₂, and CH₄ gases.

Metal oxide powders are frequently prepared by USP. Mono-metallic oxides, such as Fe₂O₃, Fe₃O₄, SnO₂, ZnO, TiO₂, V₂O₅, and Co₃O₄, are the most common oxide materials. Other multi-component oxides or binary oxide powders such as NiFe₂O₄, LaCoO₃, SiTiO₃, and Al₂O₃-SiO₂ also have been prepared by USP. To synthesize metal oxide powders, usually water soluble metal nitrates or metal chlorates are used as precursors in an oxygen-rich environment (e.g., air). Essentially all metal oxide powders can be synthesized with appropriate precursors. With a suitable chalcogenide source in the precursor solutions, metal chalcogenides can be fabricated in the same way.

USP can also be used to make thin films. Typically, droplets containing solvent and precursors are delivered to a heated substrate where solvent evaporation and
precursor decomposition occur to form the desired thin films. In some cases, dry spherical powders could be delivered onto a heated substrate where complex decompositions or chemical reactions occur to form desired films. The addition of a small concentration of another element in the precursor solution can lead to the formation of doped thin films. With this approach, a number of metals, metal oxides, metal nitrides, and metal chalcogenides thin films have been prepared.221-228

USP has unique advantages compared to other synthetic techniques and is not limited to make micron-sized powders and thin films. In the past 10 years, USP has emerged as new synthetic approach for the preparation of novel nanostructured materials. The majority of the nanostructured materials prepared via USP require the use of sacrificial templates such as polymers, silica nanoparticles, or metal salts which can be removed by calcination, etching, or washing to form the desired structures or morphologies. Herein, some successful examples of the application of USP to prepare nanostructured materials will be given.

Silica is the most frequently used material that is shown to be able to organize into complex architectures under ultrasonic spray pyrolysis drying. Figure 2.34 shows the SEM images of nanostructured SiO$_2$ spheres prepared by the aerosol spray drying of SiO$_2$ nanoparticle suspensions.229 As the size of SiO$_2$ increases, submicron hierarchical structures are formed. The pyrolysis temperature also affect the morphology of obtained SiO$_2$ spheres: as the pyrolysis temperature was increased, smoother surfaces were observed due to better consolidation of the colloidal particles. Adding lanthanide ions (e.g., Eu$^{3+}$) into the colloidal suspension could lead to the formation of luminescent SiO$_2$ microspheres (or TiO$_2$ microspheres).230, 231 Mixing polystyrene colloids with SiO$_2$
nanoparticles leads to the formation of spherical SiO₂ microspheres with self-organized mesopores (Figure 2.35). 232 In this approach, a mixture of 5 nm SiO₂ nanoparticles and 79 nm polystyrene latex nanoparticles was carried into a two-zone heated reactor (200 °C and 450 °C respectively). In the low temperature zone, the evaporation of the solvent produced a composite of colloidal SiO₂ and polystyrene. Then the polystyrene particles were evaporated to produce the pores into the SiO₂ matrix in the higher temperature zone. In addition, varying the size of polystyrene particles can induce the change of the pore sizes. 233

**Figure 2.34.** SEM images of nanostructured SiO₂ spheres prepared by spray drying at 200 °C of colloidal SiO₂ suspensions with different SiO₂ sizes: (A) 4–6 nm, (B) 10–20 nm, (C) 40–60 nm, and (D) 80–100 nm. All SEM images are magnified by 150 K. Figure adapted from reference 229.
Figure 2.35. SEM images of SiO$_2$ spheres with organized mesopores prepared by ultrasonic spray pyrolysis of colloidal SiO$_2$/polystyrene mixtures. The composition of the precursor mixture is: (A) 10 ml SiO$_2$ with 0.5 ml polystyrene colloids and (B) 10 ml SiO$_2$ with 1.0 ml polystyrene colloids. The size of SiO$_2$ nanoparticles is ~5 nm while the polystyrene colloid is ~79 nm. Figure adapted from reference 232.

In a recent study, tightly packed aggregates with either simple or broken symmetries were produced from SiO$_2$ nanoparticles via the ultrasonic spray pyrolysis method.$^{234}$ Highly ordered porous and hollow nanostructured SiO$_2$ spheres were prepared by the addition of template polystyrene particles and by the control of the zeta potential of the colloids. As shown in Figure 2.36A, aggregates of large SiO$_2$ particles are obtained via ultrasonic spray drying of large SiO$_2$ particles. If small SiO$_2$ nanoparticles are mixed with large polystyrene latex particles, porous or hollow structured SiO$_2$ aggregates will form (Figure 2.36B). Depending on the concentration and zeta potentials, particles within the droplets become organized and the polystyrene latex particles controlling the final structures. After the solvent is evaporated in the low temperature zone, the voids between polystyrene latex particles are filled with small SiO$_2$ nanoparticles (~5 nm). In higher
temperature zone, the polystyrene particles are decomposed to form the final hollow or porous silica aggregates. The architecture of the final products strongly depends on the initial concentration of particles, the particle size, and the surface charges of polystyrene and SiO₂ particles. This example artfully illustrates the application of the aerosol-assisted spray drying technique to prepare colloidal spheres with well-defined structures and symmetries.

Figure 2.36. SEM images and schematic models of large silica aggregates (from 100 nm SiO₂ particles) and mesoporous silica aggregates (from 5 nm SiO₂ particles) produced in the ultrasonic spray drying process. Figure adapted from reference 234.

An alternative approach to prepare porous silica spheres was developed without the use of expensive colloidal polystyrene particles.²³⁵ Figure 2.37A describes the process.²³⁵ Polymerizable organic monomers (e.g., styrene), cross-linker, radical initiator (e.g., AIBN), colloidal SiO₂, and surfactant (e.g., SDS) in aqueous solution was nebulized into the furnace to produce porous, submicron SiO₂ spheres. Co-doped magnetic nanospheres were obtained by adding Co₂(CO)₈ into the precursor solution (Figure 2.37B).
SiO$_2$ nanoparticles can also be used as templates to prepare porous or hollow structured materials. These SiO$_2$ nanoparticles can close-pack in an evaporating droplet and can provide a nanostructured scaffold in situ which can be removed by etching with HF. Figure 2.38 shows SEM and TEM images of porous MoS$_2$ spheres prepared by using SiO$_2$ nanoparticles as templates.$^{236}$ While only spherical solid MoS$_2$ spheres are obtained without the presence of SiO$_2$ nanoparticles during USP process, USP with templating yields SiO$_2$/MoS$_2$ composite from the decomposition of MoS$_2$ precursor mixed with SiO$_2$ nanoparticles. Subsequently, etching with HF leads to the formation of porous MoS$_2$ network. These porous MoS$_2$ spheres are a highly active catalyst for hydrodesulfurization reaction compared to nonporous solid MoS$_2$ particles. Upon doping with cobalt, the porous MoS$_2$ particles exhibit superior catalytic activity compared to RuS$_2$, which is known as the most active catalyst for hydrodesulfurization reaction.
Figure 2.38. Porous MoS$_2$ prepared from ultrasonic spry pyrolysis for catalytic hydrodesulphurization of thiophene. (A) TEM and (B) SEM images of porous MoS$_2$ prepared by USP, (C) hydrodesulphurization activity of thiophene for various catalysts and (D) catalytic selectivity for butenes. Figure adapted from reference 236.

Silica templates have been further utilized to prepare nanostructured metal oxides. When an aqueous solution containing a titanium complex and SiO$_2$ nanoparticles is nebulized and decomposed via the USP process, a titania/silica composite is obtained.$^{237}$ Normally no phase separation will happen in this process and etching of SiO$_2$ leads to the formation of porous TiO$_2$ spheres. In the presence of some transition metal ions in the precursor solution, however, a phase separation occurs with the formation of TiO$_2$ shell outside the SiO$_2$ core.$^{237}$ The exact mechanism to form this phase transition is still unknown. Etching the composites with HF for short time period results in ball-in-ball structure, and full etching leads to the formation of hollow, porous TiO$_2$ microspheres.

Under certain conditions, silica templating method could be used to make nanoparticles instead of creating porous hierarchical structures. For example, ZnS:Ni$^{2+}$ nanoparticles have been synthesized via USP from solutions containing metal nitrates, thiorea, and colloidal silica (Figure 2.39C and 2.39D).$^{238}$ To obtain ZnS:Ni$^{2+}$ nanoparticles, a higher furnace temperature is required (1000 °C). At low temperature
(e.g., 700 °C), only hollow porous ZnS:Ni$^{2+}$ spheres are produced after the silica template is removed (Figure 2.39A and 2.39B). The morphology change is related to rapid crystal growth of ZnS at high temperatures, which causes ZnS nanoparticles larger than silica nanoparticles. Such a structure is not rigid enough after the removal of the silica and the hollow microspheres collapse to form individual nanoparticles. It was found that the photocatalytic activity of the USP prepared nanoparticles for H$_2$ evolution is substantially higher than that of the ZnS:Ni$^{2+}$ powders prepared via a conventional approach (Figure 2.39E). USP is a robust and convenient synthetic approach to prepare photocatalysts and many photocatalysts have been prepared via USP.

**Figure 2.39.** SEM and TEM images of ZnS:Ni$^{2+}$ hollow microspheres (A, B) and nanoparticles (C, D) via silica template approach by ultrasonic spray pyrolysis. (E) Photocatalytic activities under visible light irradiation ($\lambda$>400 nm) of ZnS:Ni$^{2+}$ nanoparticles prepared by USP, as-obtained ZnS:Ni$^{2+}$ powder prepared by traditional co-precipitation, and heat-treated ZnS:Ni$^{2+}$ co-precipitated powder (500 °C, 2 h under Ar flow). Figure adapted from reference 238.
Synthesis of nanoparticles via USP using silica templates still requires the etching step which is time consuming and not safe. Many other attempts have been reported to prepare nanoparticles using USP (e.g., low-pressure spray pyrolysis). But the requirement of a vacuum system and the difficulty in controlling experiment parameters have prevented the application this method for nanoparticle synthesis. In 2001, a novel and rapid approach named salt-assisted aerosol decomposition method was developed to produce nanoparticles with the simple USP apparatus. In this method, metal salts (e.g., KCl, LiCl, and NaCl) or their eutectic mixtures are added into the aqueous precursor solutions to prevent the aggregation of nanoparticles in the droplet. The metal salts also act as hot liquid solvents in the furnace (at a temperature higher than the melting point of the above mentioned metal salts) where nanoparticles can dissolve and precipitate during USP process. In this way, no further aggregation will occur during the densification process and the nanoparticles are well separated. Furthermore, the liquid phase molten salts could also improve mass transport. Due to the enhanced mass transport rate, nanoparticles produced in this salt-assisted aerosol decomposition method are usually much more crystalline than those prepared by normal USP process. These metal salts can be easily washed away leaving only individual nanoparticles behind. A variety of nanoparticles such as NiO, ZnS, ZnO, CdS, Ni, Ag-Pd, CeO₂, LiCoO₂, and (Ba₀.₇₋ₓ,Srx)TiO₃ have been prepared using this salt-assisted USP process. Figure 2.40 shows the TEM images of (Ba₀.₇₋ₓ,Srx)TiO₃, NiO, and ZnS nanoparticles prepared in this salt-assisted aerosol decomposition method. Metal salts can also be used as template instead of as a liquid solvent to prepare porous or hollow architectures.
Figure 2.40. TEM images of some samples prepared in the salt-assisted aerosol decomposition process. (A) (Ba_{1-x}Sr_x)TiO_3, (B) NiO, and (C) ZnS. Figure adapted from reference 242.

Decomposition of metal salts under USP conditions usually leads to the formation of solid metal particles. The addition of some soft template or scaffold into the precursor solution can result in the formation of hollow and porous metal particles. For example, porous hollow silver spheres have been produced using AgNO_3 and glucose as precursors via USP process (Figure 2.41). Glucose is used as a reducing agent to convert Ag\(^+\) to Ag. After the solvent evaporates, glucose and Ag nanoparticles will accumulate at the periphery of the liquid droplets to form Ag nanoparticles-glucose hybrid shells. With increased temperature, the Ag nanoparticles melt to form a Ag skeleton on the surface of glucose. Subsequent washing process removes the glucose and leads to the formation of porous hollow Ag spheres.
Figure 2.41. SEM images of porous hollow silver spheres prepared via USP of aqueous solutions containing glucose (0.1 g/ml) and different concentrations of AgNO₃: (A) and (B) 0.02 g/ml; (C) and (D) 0.06 g/ml. Figure adapted from reference 192.

By rationally selecting organic salts with easy leaving groups (e.g., CO₂, H₂O, HCl, and SO₃), a myriad of porous carbon spheres have been synthesized via USP. In this approach, no additional template is required. Inorganic salts generated from the thermal decomposition of organic salts act as temporary templates in the highly cross-linked carbon network, which are then dissolved during aqueous workup. This one-step process dramatically increases the rate of the formation of porous carbon spheres and does not require expensive templates. Interestingly, depending on the type of alkali salts used, a variety of carbon spheres with different morphologies and structures are obtained (Figure 2.42). Thermal analysis of precursors indicates that the formation of pore
structure is directly related to the melting point and decomposition temperature of the precursors. For example, hollow structures are formed when melting occurs prior to decomposition and the molten salt acts as template to create a hollow structure. Substituted alkali benzoate salts can also be used as carbon precursors to prepare porous carbon spheres, although organic salts are expensive and HCl will be produced during thermal decomposition process. A more cost effective and environmentally benign precursor, sucrose, can be used together with carbonate salts to produce porous carbon spheres.\textsuperscript{249} Carbonate salts such as NaCO\textsubscript{3} or NaHCO\textsubscript{3} act both as base catalysts to promote the decomposition of sucrose and induce porosity by the formation of CO\textsubscript{2} when decomposed. Such prepared carbon materials show interesting hierarchical pore structures consisting of a microporous shell surrounding a macroporous core. Porous carbon spheres prepared by USP can be used as catalyst supports for direct methanol fuel cell and absorbents for environmental pollutants.

\textbf{Figure 2.42.} SEM images of carbon materials prepared by USP of 1.5 M aqueous solutions of alkali metal chloroacetates (CA) and dichloroacetates (DCA). (a) Li-CA; (b) Na-CA; (c) K-CA; (d) Li-DCA; (e) Na-DCA; (f) K-DCA. Figure adapted from reference 247.
In USP synthesis of materials, the final products obtained are usually spherical micro- or nano-sized particles. Recently, by coupling solid-state metathesis reaction with USP, nonspherical single-crystalline Bi$_2$WO$_6$ nanoplates have been achieved. In their synthesis, colloidal BiOCl which is capable of metathesis reaction from the hydrolysis of BiCl$_3$, and Na$_2$WO$_4$ were chosen as precursors. If conventional precursors are used, only spherical polycrystalline particles are obtained. It is believed that the non-transient byproduct and heat produced modified the crystal growth conditions, facilitating the formation of single-crystalline nanoplates. The comparison of Bi$_2$WO$_6$ microspheres with nanoplates are shown in Figure 2.43. There are also few reports of formation of nanowires (e.g., carbon nanowires, Zn nanowires, Co nanowires, and Cd nanowires) from USP process with methanolic precursor solutions, but the exact formation mechanism is still not clear.

**Figure 2.43.** (A) SEM and (B) TEM images, inset ED, of Bi$_2$WO$_6$ microspheres. (C) SEM and (D) TEM images, inset ED, of Bi$_2$WO$_6$ nanoplates. Figure adapted from reference 250.
Despite the fact the USP has been successfully applied to prepare nanoparticles via salt-assisted aerosol decomposition method, the development of new synthetic methods that are able to produce high-quality semiconductors in a continuous and scalable process still remains a challenge. This problem was addressed by using chemical aerosol flow synthesis (CAFS) method developed by Suslick and coworkers.\textsuperscript{253-255} In the CAFS synthesis of quantum dots, organic solutions of high boiling point liquids (e.g., octadecane) containing particle precursors were used instead of using aqueous solutions. A second solvent with a low boiling point was added to the viscous high boiling point liquid to make the solution less viscous and more easily nebulized. As the mist passed through the first heating zone, the low boiling point liquid was evaporated, leaving a concentrated precursor solution in the high boiling point liquid droplet. Then the chemical reactions similar to normal thermal decomposition of organometallic compounds synthesis of quantum dots occurred and high crystalline semiconductor nanoparticles such as CdS, CdSe, and CdTe were produced (Figure 2.44).\textsuperscript{253} The photoluminescent emission property of the obtained quantum dots can be easily tuned by changing the furnace temperature. This synthetic route can also be extended to prepare ternary CdTeSe and CdTeS quantum dots which emit at far-red and near-infrared (NIR) wavelength region. In addition, hollow metallic Al particles were also prepared via CAFS method by reacting trimethylamine aluminum hydride solution droplets with TiCl\textsubscript{4} vapor.\textsuperscript{255} The major difference between USP and CAFS is that in CAFS each liquid droplet acts as a single micro reactor that is capable of synthesis of thousands of nanoparticles while USP each liquid droplet leads to the formation of a single particle.
2.6. Conclusions

In conclusion, the chemical and physical effects of ultrasound (including ultrasonic spray pyrolysis) have been extensively applied in materials synthesis. Ultrasonic irradiation of liquids provides a unique form for the interaction of energy and matter via acoustic cavitation. The extreme temperatures and pressure generated during bubble collapse account for the chemical and physical effects of high intensity ultrasound. Chemical reactions that utilize the chemical effects of high intensity
ultrasound proceed via different mechanisms for volatile or nonvolatile precursors. The physical effects of high intensity sound are now gaining more and more attention in materials synthesis and are able to provide mechanical energy to chemical reactions in solutions. With simple variations of reaction conditions and precursor compositions, a myriad of materials with controlled morphologies, structures, and compositions have been successfully prepared by application of high intensity ultrasound.

In ultrasonic spray pyrolysis, where ultrasound does not directly induce the chemical reactions between precursors in the solution, ultrasound serves to generate micro-sized droplets that contain precursors and act as individual microreactors. USP has been utilized as a synthetic tool to prepare various materials with different morphologies, structures, and compositions. With new chemistry and concepts are incorporated into the USP synthesis of materials, it is expected that USP will be further extended to achieve materials with new morphologies, architectures, and compositions that conventional methods are not able to make.

2.7 References


12. Mason, T. J.; Povey, M. J. W. *Ultrasound in Food Processing*. Thomson Science, New York, **1995**.


46. Sun, X. H.; Li, C. P.; Wong, N. B.; Lee, C. S.; Lee, S. T.; Teo, B. K. Templating Effect of Hydrogen-Passivated Silicon Nanowires in the Production of


CHAPTER 3
METAL ATOM EMISSION AND SPATIAL STUDY IN MULTIBUBBLE SONOLUMINESCENCE

3.1 Introduction

Multibubble sonoluminescence (MBSL), the light emitted during the implosive collapse of clouds of bubbles in liquids irradiated with high-intensity ultrasound, is a consequence of acoustic cavitation: the formation, growth, and implosive collapse of gas bubbles under ultrasonic irradiation.\textsuperscript{1-3} It is a phenomenon that has been known for more than 70 years, dating back to the first report by Marinesco and Trillat, and Frenzel and Schultes in 1933 and 1934, respectively.\textsuperscript{4, 5} We have only recently been able to quantify the intra-cavity conditions created in the gas phase of the collapsing bubble. Our recent investigations with single-bubble sonoluminescence (SBSL) and MBSL in concentrated sulfuric acid\textsubscript{(aq.)} revealed that an optically opaque plasma core was generated in violently collapsing bubbles in both SBSL\textsuperscript{6} and MBSL,\textsuperscript{7} with effective emission temperatures inside the collapsing bubbles approaching 20,000 K.

The origin of the unexpected emission from non-volatile species like alkali metal ions during MBSL, however, remains a central question in the mechanism of acoustic cavitation. It is generally thought that the emission of molecular and atomic species during acoustic cavitation is from the gas phase of the collapsing bubbles, which consists of vapor from the solution. As a matter of fact, emission from excited alkali metal atoms is very common during ultrasonic irradiation of aqueous solutions containing alkali metal salts.\textsuperscript{8, 9} While the emission of excited alkali metal atoms is a widely-observed phenomenon, the mechanism for the formation of the excited metal atoms (originally
from the liquid region) and the site from which these emission lines are generated is still under debate. During MBSL, many bubbles will undergo non-spherical collapse and interact with neighboring bubbles. Liquid droplets, which are usually smaller than a gas bubble containing the nonvolatile species (i.e., alkali metal ions), will be entrained into the gas phase and subsequently pyrolyzed at the final stage of the bubble implosion, leading to the formation of excited radicals from the liquid or vapor molecules. The excited radicals can then initiate redox reactions within the confined space of a bubble and generate atomic emission lines. In addition to the droplet injection route, it has been proposed that a hot liquid shell might exist between the hot gas phase and the cold bulk liquid. The excited metal atoms may be produced through redox reactions between alkali metal ions in the heated shell with radicals generated in the gas phase that have diffused into the interfacial layer.\textsuperscript{10-12} A comparison of these two possible two-site models is shown in Figure 3.1.

**Figure 3.1.** Two possible two-site models proposed to explain the formation of excited nonvolatile species during MBSL. Figure adapted from Xu, H. X. \textit{et al.} Separation of Cavitating Bubble Populations: The Nanodroplet Injection Model. \textit{J. Am. Chem. Soc.} \textbf{2009}, \textit{131}, 6060-6061.
Much effort has been devoted to differentiating the two different explanations for the formation of excited nonvolatile species during acoustic cavitation.\textsuperscript{10, 13, 14} Theoretical calculations by Kamath \textit{et al} indicate that the temperature of the interfacial region between the bulk liquid and the hot gas phase is essentially the same as the bulk liquid. No chemical reactions are expected to occur in this thin interfacial liquid layer.\textsuperscript{13} Matula \textit{et al} also pointed out that the major route to emission from nonvolatile species is by droplet entrainment.\textsuperscript{15} Recently, spectroscopic characterization combined with bubble dynamics studies in SBSL in Na\textsubscript{2}SO\textsubscript{4}-H\textsubscript{2}SO\textsubscript{4} indicates that excited metal atoms are only observable when metal ions are able to enter into the gas phase of the bubble (Figure 3.2).\textsuperscript{16} The observation of excited alkali metal atoms only occurs when bubble motion

\begin{figure}[h]
\centering
\includegraphics{figure32.png}
\caption{SBSL spectra from a moving sonoluminescing bubble in a 74\% H\textsubscript{2}SO\textsubscript{4} solution containing 1.0\% Na\textsubscript{2}SO\textsubscript{4} at different acoustic pressures. Only at high acoustic pressures (i.e., 5.2 bar and 5.4 bar) are we able to observe strong Na* emission at 590 nm. Figure adapted from reference 16.}
\end{figure}
becomes chaotic enough to entrain liquid droplets in the bubble under high acoustic pressures. Direct experimental evidence in favor of one or the other model, however, has been difficult to obtain. The purpose of the work described in this chapter is to further explore how and where excited metal atoms are formed during MBSL.

Early studies of sonoluminescence were exclusively conducted in water, where the MSBL spectra consist of a broad continuum emission with a weak emission band due to the formation of excited OH• radicals. The emission from OH radicals is too weak to be used as a spectroscopic probe to determine intra-cavity conditions. The emission from excited alkali metal atoms under high temperature and high pressure, however, has been extensively studied and the peak positions and spectral profiles are strongly dependent on the conditions under which the excited alkali metal atoms are generated. Thus, attempts to exploit the dependence of line profiles from excited alkali metal atoms on the pressure and temperature of extreme conditions created during MBSL have been performed. The first experimental attempt to measure cavity temperatures and pressures was obtained from studies of the atomic emission derived from excited Na and K atoms produced during acoustic cavitation in aqueous alkali halide solutions. Both sodium and potassium emission lines observed from MBSL spectra are broadened and red shifted relative to the emission from a standard lamp. Figure 3.3 shows the broadened and red-shifted K doublet from MBSL in an Ar saturated KI solution. From the peak positions and profiles of the Na and K emission lines, they calculated an intra-cavity temperature of 3360 ± 330 K and a pressure of 313 ± 50 atm. This approach assumes that the adiabatic compression of the bubbles begins at 285 K and 1 atm. The initial temperature and pressure of the collapsing bubbles are unknown. The method used to
determine the line widths and shifts was erroneous because of line asymmetry and insufficient instrument resolution. Strong light scattering from interacting bubbles was also ignored by their method. The application of excited alkali atomic emissions to determine the temperature and pressure, therefore, remains a challenge.29

In addition to the emission lines from Na and K atoms, satellite bands to the blue of the resonance lines of Na and K have also been observed during ultrasonic irradiation of aqueous solutions containing alkali metal salts (Figure 3.4).27 These satellite bands are from alkali metal and noble gas van der Waals complexes or exciplexes formed when alkali-metal vapor is rapidly compressed under a noble gas atmosphere. The formation of exciplex bands together with the broadening and shift of the atomic emission lines indicates that the alkali metal emission occurs in the gas phase of the collapsing bubbles.16, 27

Figure 3.3. High resolution K doublet observed from MBSL in Ar saturated KI solution. The K lines are broadened and red-shifted compared to a standard lamp. Figure adapted from reference 9.
Figure 3.4. (A) Rb emission spectrum obtained from a 2.0 M RbCl solution saturated with Ar under ultrasonic irradiation. (B) Na emission spectrum obtained from a 2.0 M NaCl solution saturated with Ar under ultrasonic irradiation. Figure adapted from reference 27.

In this chapter, the results from a MBSL study of H₃PO₄ doped with alkali salts together with the effect of alkali salts on the intra-cavity temperatures during MBSL in H₃PO₄ solutions will be discussed. A significant component of this chapter is from the following paper: Xu, H.; Eddingsaas, N. C.; Suslick, K. S. Spatial Separation of Cavitating Bubble Populations: The Nanodroplet Injection Model. J. Am. Chem. Soc. 2009, 131, 6060-6061. Finally, an experimental study of the spatial separation of cavitating bubbles from Na⁺-doped H₂SO₄ and H₃PO₄ to differentiate the two different two-site models will be presented.
3.2 Experimental Methods

The experimental setup is adapted from a previously reported procedure.\textsuperscript{30} Ultrasonic irradiation was performed using a Sonics and Materials VCX 600 Vibra Cell at 20 kHz with a 1 cm diameter Ti horn immersed in 95\% H\textsubscript{2}SO\textsubscript{4} or 85\% H\textsubscript{3}PO\textsubscript{4} in a \textasciitilde{}100 mL quartz round bottom flask after sparging with Ar for a minimum of 2 hours at \textasciitilde{}298 K. The low resolution MBSL measurements were made with a 0.32-m monochromator equipped with a 300 gr/mm grating blazed at 250 nm and fitted with a 1024 X 256 pixel LN\textsubscript{2}-cooled CCD camera. For spatial resolution experiments, a 10 cm black plastic rod drilled with a 1 mm hole down the center was mounted as a collimator to the front entrance of the spectrometer. Instead of using a quartz round bottom flask, a quartz cylindrical cell was used to minimize the light distortion from the glass. The rod was held close to the wall of the cylindrical cell with a 500 \textmu{}m slit between it and the monochromator. High-resolution MBSL spectra were acquired with a 1200 gr/mm grating blazed at 330 nm for OH emission and 1200 gr/mm grating blazed at 750 nm for Na and K emission. The best-fit calculated spectra for simulated OH emission were generated by the LIFBASE program (v 2.0.60).\textsuperscript{31} For simulation of emission temperatures, the underlying continuum has been subtracted to and normalized at the highest intensity. All photographs used in this chapter were taken with a Pentax Super K 100D camera.
3.3 Results and Discussion

When nonvolatile metal ions like Li\(^+\), Na\(^+\), and K\(^+\) are present in an aqueous solution irradiated with high intensity ultrasound, emission from excited metal atoms can be observed. Figure 3.5 shows that after doping with Na\(_3\)PO\(_4\), intense orange emission from electronically excited Na atoms can be observed by the naked eye. Figure 3.6 demonstrates that after doping with different alkali metal salts, strong emission from different excited alkali metal atoms together with OH• and PO• emissions can be observed. From Figure 3.7A we can see that as the concentration of Na\(_3\)PO\(_4\) increases, the relative intensity of Na* emission to the underlying continuum emission increases. The alkali-meta-noble-gas van der Waals exciplexes are also observed, as shown in Figure 3.7B. The observation of a Na•He exciplex suggests that the emitting Na* atoms are formed in the gas phase. The emission lines from excited Na and K atoms are significantly red-shifted and asymmetrically broadened to longer wavelengths compared to the emission lines from a low pressure lamp (Figure 3.8). This observation indicates that alkali metal atoms are emitting from a highly-compressed gas phase environment. The peak positions from helium atmosphere appear to be shifted less to the red relative to the Na emission lines under an argon atmosphere, suggesting that the Na atoms in helium bubbles are emitting from a lower pressure environment than those in argon bubbles (Figure 3.8B). In contrast, the line broadening under a helium atmosphere is much more significant than in an argon atmosphere. The difference in broadening might be due to more collisions between smaller helium atoms with metal atoms in a confined gas phase.
Figure 3.5. (A) Photograph of MBSL from 85% $\text{H}_3\text{PO}_4$ and (B) Photograph of MBSL from 85% $\text{H}_3\text{PO}_4$ with 0.1 M $\text{Na}_3\text{PO}_4$ saturated with He at an acoustic power of 25 W/cm$^2$.

Figure 3.6. MBSL spectra from 85% $\text{H}_3\text{PO}_4$ with (A) 0.1 M $\text{Li}_3\text{PO}_4$, (B) 0.1 M $\text{Na}_3\text{PO}_4$, and (C) $\text{K}_3\text{PO}_4$ saturated with He at an acoustic power of 25 W/cm$^2$. 
Figure 3.7. (A) MBSL spectra from 85% H₃PO₄ doped with different weight percentages of Na₃PO₄ saturated with He at an acoustic power of 25 W/cm². (B) Excited Na emission from 0.2 M Na₃PO₄ in 85% H₃PO₄ together with Na•He exciplex observed during MBSL.

Figure 3.8. (A) High resolution spectra of the K* atom emission lines observed from MBSL in 85% H₃PO₄ with 0.1 M K₃PO₄ saturated with Ar and He respectively and compared to the emission lines from a Na•K hollow cathode lamp. (B) High resolution spectra of the Na* atom emission lines observed from MBSL in 85% H₃PO₄ with 0.1 M Na₃PO₄ saturated with Ar and He respectively and compared to the emission lines from a Na•K hollow cathode lamp. The underlying continuum has been subtracted and spectra are normalized to the maximum peak intensity.
Since we can observe bright light from MBSL in \( \text{H}_3\text{PO}_4 \) and strong OH (\( A^2\Sigma^+ - X^2\Pi \)) emission, we are able to obtain the fine structure of OH (\( A^2\Sigma^+ - X^2\Pi \)) transitions, which can be used as a spectroscopic probe to quantify the intra-cavity temperatures when alkali metal salts are added into the solution.\textsuperscript{32, 33} The effective emission temperatures can be obtained by fitting the experimental spectrum with simulated emission spectra from the LIFBASE program, which is a database and spectral simulation program for diatomic molecules that has been extensively used to determine temperatures from excited diatomic molecules in flames and laser-induced fluorescence.\textsuperscript{31} Although different alkali metal salts are added into the solution, the measured effective emission temperatures are the same for all alkali metal salts. All three salts give an effective emission temperature of 9200 K, as determined from OH emission (Figure 3.9A). The intra-cavity temperature increased 1200 K compared to the measured cavitation temperature from \( \text{H}_3\text{PO}_4 \) without any salts under the same conditions (Figure 3.9B). This phenomenon may be due to colligative properties, which will decrease the vapor pressure. If there is less water vapor inside the bubbles, it is certain that higher cavitation temperatures can be achieved: less energy is consumed by endothermic bond dissociations and polyatomic vibrations and rotations.\textsuperscript{34}

Emission from excited metal atoms can be observed if there are nonvolatile metal ions present in the solution under ultrasonic irradiation.\textsuperscript{8, 9, 16, 35-39} Nonvolatiles can also undergo sonochemical reactions. As mentioned in the introduction, there are two models proposed to explain how nonvolatile species get heated and excited in a collapsing bubble: the shell model and the injected droplet model, as illustrated in Figure 3.1. In the shell model, the metal ions in the liquid phase are reduced and excited in the interfacial
Figure 3.9. (A) Higher resolution spectra of OH ($A^2\Sigma^+ - X^2\Pi$) emission from MBSL in 85% H$_3$PO$_4$ with 0.1 M M$_3$PO$_4$ (M=Li, Na, and K) saturated with helium compared to the best-fit simulation spectrum at 9200 K assuming thermal equilibrium and a Lorentzian profile. (B) Higher resolution spectra of OH ($A^2\Sigma^+ - X^2\Pi$) emission from MBSL in 85% H$_3$PO$_4$ without alkali salts saturated with helium compared to the best-fit simulation spectrum at 9200 K assuming thermal equilibrium and a Lorentzian profile. The underlying continuum has been subtracted; the spectra were normalized at the highest intensity ~309 nm. The discrepancy at 320–340 nm is caused by the strong PO ($B^2\Sigma^+ - X^2\Pi$) emission. Sonication was conducted at 20 kHz and 25 W/cm$^2$ with a titanium horn at 298 K.

region by radicals formed in and diffused from the gas phase. In the injected droplet model, interfacial instabilities due to liquid turbulence, bubble-bubble interactions, capillary surface waves, and microjet formation during bubble collapse will cause the nebulization of nanodroplets of liquid into the hot core of the collapsing bubble.$^{13, 40-43}$ Subsequent pyrolysis and reduction of nonvolatile metal ions leads to the observation of
excited metal atom emission. Unfortunately, there is no direct experimental evidence in favor of one model over the other so far.

As shown in Figure 3.5, we can observe two different bubble clouds from MBSL in Na$_3$PO$_4$-doped H$_3$PO$_4$. This phenomenon is more straightforward from Na$_2$SO$_4$-doped H$_2$SO$_4$ solution. We can clearly observe two spatially separate types of MBSL from 95% H$_2$SO$_4$ with 0.1 M Na$_2$SO$_4$ (Figure 3.10A): (1) blue-white emission near the horn and (2) strong orange emission (from electronically excited Na* atom $D$ lines) farther away. There are three different light emitting regimes upon varying the acoustic intensity from MBSL in 95% H$_2$SO$_4$ as reported previously: filamentous (< 16 W/cm$^2$), bulbous (16~24 W/cm$^2$) and cone shaped (> 24 W/cm$^2$). Addition of Na$_2$SO$_4$ did not alter the shape of bubble cloud, as can be seen from Figure 3.10A. In all three different bubble dynamic regimes, we can clearly see that the orange emission from excited Na* atoms is spatially separated from the blue-white emission. In addition, at lower acoustic intensities with filamentous stage (Figure 3.10A, left), we can see that the orange emission is outside but surrounds the blue-white bubble cloud; at higher intensities, the blue-emission is well separated spatially from the orange emission.

In addition to the visual observation, strong Na* emission at ~590 nm was confirmed from the ultrasonic irradiation of 0.1 M Na$_2$SO$_4$ 95% sulfuric acid solutions (Figure 3.10B). Consistent with previous report, at low acoustic power (~14 W/cm$^2$), Ar emission lines are also observed, which suggests a plasma core formed during bubble collapse. The observed strong Na* emission arises from the well-known $D$ lines ($3p$ to $3s$) (Figure 3.11). In addition to the Na* emission, a relatively weak satellite band to the blue of the Na $D$ lines is also observed and is
Figure 3.10. (A) Photographs (3 s exposure) of MBSL from 95% H$_2$SO$_4$ with 0.1 M Na$_2$SO$_4$ saturated with Ar at 298 K at different acoustic intensities. (B) MBSL spectra from 95% H$_2$SO$_4$ with 0.1 M Na$_2$SO$_4$ saturated with Ar at 298 K at different acoustic intensities. Spectra were normalized at 700 nm and offset for clarity.

attributed to emission from the Na·Ar exciplex. Exciplex emission occurs when Na vapor is rapidly compressed in an Ar atmosphere$^{44}$ and has also previously been observed during MBSL from aqueous alkali halide solutions and recently during SBSL from a Na$_2$SO$_4$ sulfuric acid solution.$^{16}$ Observation of the exciplex emission suggests that the emitting Na* atoms are in the gas phase inside the bubble.
Figure 3.11. MBSL spectrum of Na* D lines (3p to 3s) from the cavitating bubble cloud in 95% H₂SO₄ with 0.1 M Na₂SO₄ compared to spectral resolution of the monochromator for Na emission from a hollow Na•K cathode lamp. The pressure broadening and red-shift explain the apparent orange color (rather than yellow) of the Na* emission.

It is interesting to observe the emission from Na* and Ar* simultaneously because there is a substantial difference in the excitation energies of the populated states of these atoms: the energies of the emitting states of Ar are over 13 eV above the ground state (¹S₀), while the energies of the excited states of Na are only 2.1 eV above the ground state (²S₁/₂). The observation of two emitting species with dramatically different excitation energies indicates that the two emitting species may be formed either at different times during bubble implosion, at different spatial locations within the collapsing bubble, or from different bubbles altogether. In addition, various types of collision-induced reactions like ionization, charge transfer, and recombination are likely to contribute to the observed spectra either directly or indirectly.
Given the substantial spatial resolution seen in Figure 3.10A of two very distinct sonoluminescing bubble clouds, we can measure the MBSL spectrum as a function of position within the bubble cloud. Figure 3.12 shows that at the top of the bubble cloud in the middle acoustic intensity regime, no Na* emission can be detected and the emission is strictly a broad continuum. While at the bottom of the bubble cloud, strong Na* emission is observed and the continuum is diminished tenfold in intensity. This spatial separation is not unique to the H$_2$SO$_4$-Na$_2$SO$_4$ system. We can observe the same phenomenon during MBSL from 0.1 M Na$_3$PO$_4$ in 85% H$_3$PO$_4$ under either Ar or He (see Figure 3.13and 3.14).

![MBSL spectra taken at the top and bottom of the cavitating bubble cloud as shown in Figure 3.11A. Sonication was conducted in 95% H$_2$SO$_4$ with 0.1 M Na$_2$SO$_4$ saturated with Ar at 298 K (19 W/cm$^2$, 20 kHz).](image-url)

**Figure 3.12.** MBSL spectra taken at the top and bottom of the cavitating bubble cloud as shown in Figure 3.11A. Sonication was conducted in 95% H$_2$SO$_4$ with 0.1 M Na$_2$SO$_4$ saturated with Ar at 298 K (19 W/cm$^2$, 20 kHz).
Figure 3.13. (A) Photograph of MBSL from 0.1 M Na₃PO₄ in 85% H₃PO₄ saturated with Ar at room temperature with 24 W/cm² ultrasound at 20 kHz. (B) MBSL spectra taken at the top and bottom of the cavitating bubble cloud from 0.1 M Na₃PO₄ in 85% H₃PO₄ saturated with Ar at room temperature, irradiated with 24 W/cm² ultrasound at 20 kHz.

Figure 3.14. (A) Photograph of MBSL from 0.1 M Na₃PO₄ in 85% H₃PO₄ saturated with He at room temperature with 24 W/cm² ultrasound at 20 kHz. (B) MBSL spectra taken at the top and bottom of the cavitating bubble cloud from 0.1 M Na₃PO₄ in 85% H₃PO₄ saturated with He at room temperature, irradiated with 24 W/cm² ultrasound at 20 kHz.
The distinct spatially separated sonoluminescing bubble populations from the intense orange and blue-white emissions provide the first experimental evidence that favors for the injected droplet model over the heated shell model for the origin of nonvolatiles during cavitation. Because the Na* emission is derived from an initially liquid region (Na* is obviously nonvolatile), if the heated shell model were correct, then a spatial separation of different sonoluminescence emitters ought not to occur. For the heated shell model, emission from nonvolatiles species should always be present whenever conditions are sufficient to give rise to sonoluminescence inside the collapsing bubble: even if interior conditions were so extreme as to lead to complete line broadening of the emission from nonvolatile species, somewhere in the interfacial region there should be a temperature gradient appropriate for Na* emission.

Therefore, excited metal atom emission in MBSL is due to the injection of liquid droplets into the interior of bubbles via capillary wave action, microjetting or bubble coalescence due to the significantly deformed bubble collapse in the cavitation field. Once the droplets containing Na+ enter the hot interior of the bubble, they evaporate and complex redox processes analogous to those in flames generate the Na atom excited states responsible for the MBSL. To further elucidate the difference between two bubble populations, we estimate bubble speed from the streak length of individual bubble emission from photographs with a known shutter speed (Figure 3.15). From the length of the streak, the speeds of bubbles are slowest near the horn due to inter-bubble Bjerknes forces or acoustic stationary waves. The velocity of blue-white emitting bubbles near the horn is estimated to be only ~4 mm/s. The sonoluminescing bubbles further from the horn that are orange in color due to Na* emission are determined to move at ~17 mm/s.
3.4 Conclusions

In conclusion, strong emission from electronically excited alkali metal atoms has been observed from alkali metal doped $\text{H}_3\text{PO}_4$ and $\text{H}_2\text{SO}_4$ solutions under irradiation of high intensity ultrasound. Adding alkali metal salts affects the cavitation temperature that can be achieved during bubble collapse. In addition, a coherent explanation for sonochemistry and sonoluminescence involving nonvolatile species is now beginning to emerge. In a single bubble scenario, only moving single bubbles under high acoustic pressures will undergo sufficient bubble deformation to entrain droplets into the bubble interior and only moving single bubbles give emission from nonvolatile species. In MBFL, there are two distinct bubble populations: (1) bubbles near the horn surface that
are relatively stationary (probably due to inter-bubble Bjerknes forces), whose collapse is highly symmetric, which leads to a hotter core and only continuum emission, and (2) rapidly moving and interacting bubbles in streaming liquid flow outside of the dense clouds, whose collapse is much less symmetric and deformed from which emission from nonvolatiles becomes possible through the mechanism of droplet injection. Subsequent processes that cause the emission from nonvolatile species are analogous to those in flames.

3.5 References


CHAPTER 4
MULTIBUBBLE SONOLUMINESCENCE IN PHOSPHORIC ACID:
MOLECULAR EMISSION AND TEMPERATURE MEASUREMENTS

4.1 Introduction

When a liquid is irradiated with high intensity ultrasound, bubbles form, grow, and implosively collapse: a phenomenon called acoustic cavitation. Acoustic cavitation is the root cause of both chemical reactions (i.e., sonochemistry) and the emission of light (i.e., sonoluminescence, SL).\textsuperscript{1-10} It is generally agreed that both chemical reactions and the emission of light result from the intense compressional heating of gas and vapor inside the collapsing bubbles and the extreme intra-cavity conditions so created (i.e., extraordinarily high temperatures and pressures).\textsuperscript{4} There are two types of sonoluminescence based on the type of cavitation that produces the light: light emission from a cloud of cavitating bubbles (multibubble sonoluminescence, MBSL) and light emission from a single, acoustically levitated bubble oscillating around the pressure antinode in a standing sound field (single-bubble sonoluminescence, SBSL).\textsuperscript{4} MBSL is more closely related to sonochemistry, which has found important synthetic applications in both organic and materials chemistry.\textsuperscript{1-3, 8-10} Quantification of the conditions generated during MBSL can lead to a better understanding of sonochemistry with hopes to apply sonochemistry in a more controlled manner. Previous MBSL studies in aqueous and nonaqueous solution have revealed extreme intra-cavity conditions based on measurements from volatile species created during bubble collapse.\textsuperscript{11-14} Little is known, however, about the conditions of emission derived from nonvolatile species during MBSL, which is directly relevant to the observed sonochemistry of dissolved reactants.
Early studies of MBSL were almost exclusively conducted in water, where the MBSL spectra often consists of a broad continuum extending into the UV and an broadened peak around 310 nm from excited OH radicals (Figure 4.1). Besides spectroscopic analyses, many correlational studies were performed on MBSL; for example, light intensity as a function of external parameters such as bulk liquid temperature, the nature of the gas, the frequency of applied ultrasound, and the power of the applied acoustic field. Sonoluminescence was determined to be dependent on the thermodynamic properties of the intracavity gas and vapor, indicating that compressional heating of the bubble contents limits the light emission and the chemical process should be considered during bubble collapse. MBSL in low vapor pressure liquids like long chain alkanes and silicone oils with volatile organometallic solutes provided rich information about the conditions generated inside the collapsing bubbles. A variety of molecular and atomic emissions have been observed and can be used as spectroscopic thermometers to quantify the conditions generated inside the collapsing bubbles. The Swan bands of C2 were first employed to probe the intra-cavity temperatures during bubble implosion in silicone oil (Figure 4.2). By doping water with organics, the hot spot conditions during multibubble cavitation can be measured to be \( \sim 4300 \) K, which is lower than that observed from silicone oil. The emission temperature difference in silicone oil and water can be explained by the higher vapor pressure of water (6.6 torr) compared to silicone oil (<0.01 torr). Irradiation of solutions of volatile metal carbonyls in \( n \)-alkanes or silicone oil with high intensity ultrasound results in homolytic cleavage of the relatively weak metal-carbon bond, generating excited free metal atoms. Electronic excitation and subsequent radiative relaxation of the metal atoms leads to the observation
of intense and well-resolved metal atom emissions in the MBSL spectra. The intensities of different emission peaks depend on the bubble temperatures. Therefore, the relative ratios of metal atom emission lines can be used to determine the effective emission temperatures during MBSL.\textsuperscript{12, 17} Figure 4.3 shows the emission of a solution of Cr(CO)\textsubscript{6} dissolved in silicone oil saturated with Ar.\textsuperscript{12} With this method, the effective emission temperature was measured to be 4700 ± 300 K. Using the same spectroscopic approach, other metal carbonyls also revealed cavitation temperatures of ∼5000 K: Fe gave 5100 ± 300 K and Mo gave 4800 ± 400 K. MBSL temperatures measured in this way agree well with the emission temperature determined by simulating C\textsubscript{2} bands and kinetic measurements.\textsuperscript{25} Other nonspectroscopic approaches like the methyl radical recombination (MRR) method, which can only measure the temperature at which sonochemistry is taking place (the sonoluminescence region in the bubble can decompose the radicals), have also been developed to measure the temperatures of cavitating bubbles.\textsuperscript{26, 27}

![Figure 4.1](image)

**Figure 4.1.** Multibubble sonoluminescence spectra saturated with (A) Helium and (B) Argon gas at 21 °C. Ultrasonic irradiation was performed at 337 kHz with calorimetrically calibrated acoustic power of 15.5 W. Figure adapted from reference 15.
Figure 4.2. Emission from the $\Delta \nu=+1$ manifold of the $d^3 \Pi_g - a^3 \Pi_u$ transition (Swan band) of $C_2$. Dotted line shows observed sonoluminescence from silicone oil (polydimethylsiloxane, Dow 200 series, 50 centistokes viscosity) under a continuous Ar sparge at 0 °C, vapor pressure ~0.01 torr. Boldface line shows the best-fit synthetic spectrum, with $T_v=T_i=4900$ K. Thin line shows the difference spectrum. The applied ultrasonic power from the horn is ~100 W/cm$^2$. Underlying emission has been subtracted for clarity. Figure adapted from reference 11.

The quantification of intracavity conditions during multibubble cavitation still attracts numerous interest and some unanswered questions still remain. Extensive emission lines and bands have been applied to quantify the intracavity conditions as mentioned above. No prior study, however, has reported simultaneous measurement of temperatures from two or more independent emitting species, which would permit one to
probe the homogeneity of the temperature profile generated in bubble clouds from spatial variance during acoustic cavitation. In addition, the production of low molecular weight sonolysis products (e.g., H2, CH4, and C2H2) proved to be problematic during MBSL in organic liquids.28 These molecules can accumulate inside the collapsing bubbles and limit the maximum temperature that can be achieved. Recently, Ar emission was observed during MBSL in concentrated H2SO4(aq.) and a cavitation temperature of ~8000 K was determined, suggesting a plasma core was formed inside the collapsing bubbles (Figure 4.4).29 In examining the MBSL from aqueous H3PO4 solutions, a liquid similar to H2SO4(aq.), we observe ultra-bright sonoluminescence and find strong molecular emission from both excited OH and PO radicals and have succeeded in using both emission species simultaneously as spectroscopic thermometers to probe the intra-cavity conditions. In this

**Figure 4.3.** (A) Simulated spectra of thermally equilibrated emission from excited Cr atoms. All spectra are normalized to the peak intensity at 424 nm. (B) Comparison of MBSL spectrum from a solution of Cr(CO)6 in silicone oil saturated with Ar gas with simulated Cr emission at 4700 K. The underlying continuum was subtracted for clarity. Figure adapted from reference 13.
chapter, the effects of experimental conditions like vapor pressure, acoustic power and dissolved noble gases on MBSL in H₃PO₄ will be discussed. Furthermore, for the first time, a dramatic temperature inhomogeneity dependent on the location within the bubble cloud is discovered, which is consistent with two distinct kinds of cavitating bubbles: those that collapse symmetrically and those that do not. A significant component of this chapter is from the following paper: Xu, H. X.; Glumac, N. G.; Suslick, K. S. Temperature Inhomogeneity during Multibubble Sonoluminescence. *Angew. Chem. Int. Ed.* 2010, 48, 1079-1082.

![Figure 4.4](image.png)

**Figure 4.4.** Ar (4p – 4s manifold) emission from MBSL in 95 wt % H₂SO₄ saturated with Ar compared to the best fit synthetic spectrum, which yields an effective emission temperature of 8000 K. The synthetic spectra assumed thermal equilibration and a Lorentzian profile. Figure adapted from reference 29.
4.2 Experimental Methods

The experimental apparatus used here is similar to previous reports.\textsuperscript{29, 30} Ultrasonic irradiation was performed using a Sonics and Materials VCX 600 Vibra Cell at 20 kHz with a 1 cm diameter Ti horn immersed in aqueous H\textsubscript{3}PO\textsubscript{4} solutions with different concentrations in a ~100 mL quartz round bottom flask after sparging the thoroughly de-aerated liquid with the desired noble gas (He, Ne, Ar, Kr or Xe) at ~298 K. For concentrations lower than 85\%, the solutions are made by diluting 85\% H\textsubscript{3}PO\textsubscript{4}. The low-resolution MBSL measurements were made with a 0.32-m monochromator equipped with a 300 gr/mm grating blazed at 250 nm and fitted with a 1024 X 256 pixel LN\textsubscript{2}-cooled CCD camera. High-resolution MBSL spectra were acquired with a 1200 gr/mm grating blazed at 330 nm. The best fit calculated spectra for OH emission simulations were generated by the LIFBASE program (v 2.0.60).\textsuperscript{31} For simulation of emission temperatures, the underlying continuum has been subtracted to and normalized at the highest intensity. The emission temperature of PO was determined using a similar approach with a modified LIFBASE program: the emission spectra of the \( \beta \) system of PO were modeled using an identical approach implemented in LIFBASE but using known spectroscopic constants and calculated Franck-Condon factors.\textsuperscript{32, 33}

4.3 Molecular Emission and Temperature Measurements during MBSL

Ultrabright sonoluminescence from 85\% H\textsubscript{3}PO\textsubscript{4} saturated with different noble gases can be observed by the naked eye, even in a well-lit room, as shown in Figure 4.5. MBSL in water and other nonaqueous liquids is very dim and not visible under room light. MBSL from 85\% H\textsubscript{3}PO\textsubscript{4} is much brighter than the light emitted during MBSL in
95% H$_2$SO$_4$. Figure 4.6 shows the photographs from MBSL in water, 85% H$_3$PO$_4$ and 95% H$_2$SO$_4$. The MBSL of water is so weak as to be only barely visible. Because the light from a glowing cloud of sonoluminescing bubbles is diffuse, dynamic, and variable in size and number of cavitating bubbles, it is difficult to make precise comparisons of the total emissivity from one set of conditions to another. A semi-quantitative comparison can be made by examining the average luminosity of the glowing bubble cloud near the horn (using the histogram function in Photoshop CS3) from identical regions of each photograph. The measured luminosities were 1 for water, 58 for sulfuric acid, and 89 for phosphoric acid. Note that the photograph of MBSL in water was taken at a fivefold longer exposure time and more than twice the ultrasonic power; there is no detectable MBSL from water at 17 W/cm$^2$. Thus, the overall emissivities of MBSL are <0.25% for water and 65% for sulfuric acid, relative to phosphoric acid (100%).

Figure 4.7 shows MBSL spectra from different weight percentages of H$_3$PO$_4$ saturated with Ar. The intensity of each spectrum was normalized at 700 nm so that all spectra would fit in one graph, and the spectra were offset for clarity. At relatively low concentrations, (65% and 70%) a prominent peak arising from OH (A$^2\Sigma^+$$-X^2\Pi$) transition centered on 310 nm is observed. As the concentration increases, the intensity of OH emission decreases relative to the continuum emission, and the emission peak gradually broadens out and become indistinguishable from the continuum emission. The excited OH radicals are formed either from the recombination of H and O atoms created during water vapor sonolysis or dissociation of H$_2$O molecules during bubble collapse. At higher concentrations, fewer H$_2$O molecules are present inside the bubbles. Higher intra-cavity
temperatures can therefore be achieved, which leads to dissociation of OH• under elevated cavitation temperatures.

**Figure 4.5.** Photographs of ultrabright sonoluminescence from 85% H₃PO₄ saturated with He, Ne, Ar, Kr, and Xe. Different exposure times were used for each gas to optimize the images: He 20 s, Ne 10 s, Ar 0.5 s, Kr 0.25 s, Xe in dark 0.25 s, and Xe in room light 0.17 s. Sonication was conducted at 20 kHz, 17 W/cm², with a 1 cm² Ti horn directly immersed in the solution at 298 K.

**Figure 4.6.** Photographs of MBSL in (A) water at 40 W/cm², 30 s exposure; (B) 95% sulfuric acid, 17 W/cm², 6 s exposure; (C) 85% phosphoric acid, 17 W/cm², 6 s exposure. All solutions were irradiated at 20 kHz with a 1 cm diameter titanium horn at 298 K, sparged with Ar; for all photographs, the digital camera and sonication apparatus were positioned identically.
The origin of the MBSL from 85% H$_3$PO$_4$ emission also depends on the dissolved noble gases as seen in Figure 4.8. Under He and Ne, the MBSL spectra contain strong molecular emissions from excited OH• ($A^2\Sigma^+-X^2\Pi$) and the PO• β system ($B^2\Sigma^+-X^2\Pi$), with bands at 310 nm and 325 nm respectively.\(^{34}\) Under He, the strong emission from PO• γ system ($A^2\Sigma^+-X^2\Pi$), which is frequently seen in flames containing phosphorus, can also be observed (Figure 4.9). No obvious molecular emission bands can be observed from H$_3$PO$_4$ saturated with Ar, Kr, and Xe, only a broad continuum emission extending into the UV. The broadening of the molecular emission is consistent with expected dissociation of the OH• and PO• radicals at higher cavitation temperatures with heavier inert gases (arising from decreased thermal conductivity).
Figure 4.8. MBSL spectra from 85% H$_3$PO$_4$ sparged with different noble gases (as labeled) and irradiated with ultrasound at 20 kHz and 17 W/cm$^2$ with a titanium horn at 298 K. Spectra were normalized at 700 nm and offset for clarity.

Figure 4.9. The observed emission from PO$^\cdot$ $\gamma$ system (A$^2\Sigma^+$-X$^2\Pi$) during MBSL (17 W/cm$^2$, 20 kHz) in 85% H$_3$PO$_4$ saturated with helium at 298 K.
With bright light from MBSL in H$_3$PO$_4$ and strong OH ($A^2\Sigma^+-X^2\Pi$) emission, we are able to obtain the fine structure of the OH ($A^2\Sigma^+-X^2\Pi$) transitions, which can be used to measure the effective emission temperatures by fitting experimental spectra with simulated emission spectra from the LIFBASE program, which is a database and spectral simulation program for diatomic molecules that has been extensively used to determine temperatures from excited diatomic molecules in flames and laser-induced fluorescence.$^{31}$ For example, by fitting experimental spectra from MBSL in 85% H$_3$PO$_4$ under helium with calculated spectra, an effective emission temperature of 9500 ± 300 K can be obtained (Figure 4.10). This temperature is significantly higher than that measured from water, which is expected because of the dramatic difference in the vapor pressure of water (24 torr) and 85% H$_3$PO$_4$ (2.4 torr): less compressional energy during bubble collapse is consumed by polyatomic vibrations, rotations, and endothermic bond dissociations.$^{28}$

Thanks to the bright and strong OH emission, for the first time, we are able to probe the intracavity temperatures from the most frequently observed emission species during MBSL. MBSL spectra from different weight percentages of H$_3$PO$_4$ can be collected and the emission temperatures can be determined (Figure 4.11) by fitting the experimental spectra with synthetic spectra. As the concentration of H$_3$PO$_4$ increases from 65% to 85%, the measured emission temperature increases from 6600 K to 9500 K. This is consistent with the decrease in vapor pressure inside the collapsing bubbles at higher concentrations. Since strong OH emission can be observed from 65% H$_3$PO$_4$ saturated with different noble gases (Figure 4.12A), the emission temperatures from 65% H$_3$PO$_4$ saturated with different noble gases can also be measured. The observed emission
temperatures range from 6600 K for He up to 9000 K for Kr, consistent with prior MBSL experiments on the effects of noble gases on cavitation temperatures.¹⁷

Figure 4.10. The simulated emission spectra at different temperatures compared to experimental spectrum from MBSL in H₃PO₄ under He, which yields an effective emission temperature of 9500 K. Sonication conducted at 20 kHz and 17 W/cm² with a titanium horn at 298 K. Spectra are normalized at the highest intensity at ~309 nm. The simulated spectra assumed thermal equilibrium and a Lorentzian profile.

As the applied acoustic powers change, there are large and abrupt changes in the bubble cloud dynamics and intensity as shown in Figure 4.13. There are four discrete stages of sonoluminescence emission as the acoustic power increases from low to high: (1) relatively dynamic filamentous emission at 8~17 W/cm², (2) relatively stable bulbous emission at 19~24 W/cm², (3) near horn surface emission at 30~35 W/cm², (4) cone-
Figure 4.11. (A) MBSL spectra from different concentrations of H$_3$PO$_4$ sparged with He. Spectra were normalized at 700 nm and offset for clarity. (B) Higher resolution spectra of OH ($A^2\Sigma^+ - X^2\Pi$) emission compare to the best-fit simulation spectra assuming thermal equilibrium and a Lorentzian profile. Spectra were normalized at the highest intensity at \(\sim 309\) nm. Sonication conducted at 20 kHz and 17 W/cm$^2$ with a titanium horn at 298 K.

![Figure 4.11](image)

Figure 4.12. (A) MBSL spectra from 65% H$_3$PO$_4$ sparged with different noble gases. Spectra were normalized at 700 nm and offset for clarity. (B) Higher resolution spectra of OH ($A^2\Sigma^+ - X^2\Pi$) emission compared to the best-fit simulation spectra assuming thermal equilibrium and a Lorentzian profile. The underlying continuum has been subtracted; the spectra were normalized at the highest intensity at \(\sim 309\) nm. Sonication was conducted at 20 kHz and 17 W/cm$^2$ with a titanium horn at 298 K.

![Figure 4.12](image)
shape emission at 40 W/cm². The same phenomenon was also discovered in MBSL in concentrated H₂SO₄. These are new observations and there are no good explanations so far for the specific origin of these light emitting structures. It cannot be simply explained by the strong interactions between bubbles through Bjerknes forces but should also consider the shielding of bubbles from the sound field by other bubbles in the sonoluminescing bubble cloud. The configurations of transducer and/or the containers used for the solution also influence the formation of bubble clouds. While we can observe abrupt changes in the bubble dynamics from 85% H₃PO₄ saturated with Ar, the broadening of the OH emission peak makes it difficult to answer the question of whether the bubbles are getting hotter or cooler at high acoustic power. When 85% H₃PO₄ is saturated with He gas we can observe strong OH emission even at relatively high acoustic powers, and we can still observe the similar abrupt changes in bubble-cloud dynamics (Figure 4.14). We can therefore use the strong OH emission from 85% H₃PO₄ saturated with He to measure the emission temperatures under different acoustic powers. Figure 4.15 shows the MBSL spectra of OH (A²Σ⁺-X²Π) transitions together with best-fit synthetic spectra. Surprisingly, the measured emission temperature decreases as the applied acoustic power increases. It is generally thought that as the acoustic power increases the bubble size can be larger, which will lead to more violent collapse, thus generating higher intra-cavity temperatures. At least, it is true for the temperatures measured from a single sonoluminescing bubble under different acoustic pressures. But as the bubble becomes larger, more water vapor diffuses into the bubble from the liquid during the bubble expansion phase, which will increase the number of polyatomic
molecules inside collapsing bubbles, thus limiting the maximum attainable temperature.

In addition, with increased acoustic intensity, bubbles might undergo less spherical

![Figure 4.13. Photographs of MBSL from 85% H₃PO₄ saturated with Ar at different acoustic powers as labeled in the photograph (exposure time varies to get best results). Sonication conducted at 20 kHz with a titanium horn at 298 K.](image)

![Figure 4.14. Photographs of MBSL from 85% H₃PO₄ saturated with He at different acoustic powers as labeled in the photograph (exposure time varies to get best results). Sonication conducted at 20 kHz with a titanium horn at 298 K.](image)
collapse (which can result from strong interaction between bubbles, turbulence, and higher bubble density), which will also limit the temperature that can be achieved during bubble implosion. Most importantly, liquid droplets will be injected into the interior of less spherical collapsing bubbles under higher acoustic powers. The evaporation of liquid and dissociation of water vapor molecules will dramatically cool down the intracavity temperatures.

**Figure 4.15.** MBSL spectra from 85% H$_3$PO$_4$ sparged with He at different acoustic powers (black line) with best-fit synthetic spectra (red line). The discrepancy at 320~340 nm is caused by the strong PO (B$^2\Sigma^+-X^2\Pi$) emission. The underlying continuum has been subtracted; the spectra were normalized at the highest intensity at ~309 nm. Sonication conducted at 20 kHz and 17 W/cm$^2$ with a titanium horn at 298 K.

### 4.4 Temperature Inhomogeneity during MBSL

H$_3$PO$_4$ is a strongly hydrogen-bonded liquid; it has a relatively high viscosity and low vapor pressure (~2.4 torr for 85% H$_3$PO$_4$) compared to water. Another unique feature
of H$_3$PO$_4$ is that only water molecules are present in the vapor phase; there are no acid molecules in the vapor over most concentrated H$_3$PO$_4$ even at high temperatures.\textsuperscript{43} Thus, in the gas phase of aqueous solutions of H$_3$PO$_4$, the only volatile component inside bubbles is water molecules; the phosphoric acid molecules can be considered as nonvolatile species (similar to alkali metal ions like Li$^+$, Na$^+$, and K$^+$) during MBSL.

As mentioned previously, the origin of the MBSL from 85\% H$_3$PO$_4$ emission depends on the dissolved inert gas. Under He or Ne, the MBSL spectra show strong molecular emission from OH (A$^2\Sigma^+-X^2\Pi$) and the PO $\beta$ system (B$^2\Sigma^+-X^2\Pi$), with bands at 310 nm and 325 nm respectively. Excited OH radicals are also observed during MBSL in aqueous solutions, but the emission is too weak and too broad to be used for spectroscopic thermometry. In contrast, the MBSL in 85\% H$_3$PO$_4$ under He shows very strong OH and PO emission and excellent resolution of the emission fine structure. With the aid of the OH emission, we have been able to quantify the intracavity conditions during MBSL in H$_3$PO$_4$ solutions upon varying acoustic powers, nature of noble gases, and vapor pressures. The $\beta$ system of PO emission in the 320 to 340 nm wavelength range has been extensively studied. We can use an identical approach applied in LIFBASE to calculate PO emission spectra using known spectroscopic constants and calculated Franck-Condon factors.\textsuperscript{32, 33} The emission from excited PO radicals can also be used as a spectroscopic thermometer to probe the intracavity temperatures generated during MBSL containing PO emission. As shown in Figure 4.16A, we can see that the PO emission decreases rapidly below 320 nm and hence does not affect the accuracy of the measurement of OH emission. This permits us to use spectroscopic methods to measure emission temperatures from two independent emission species. Because the OH
emission tail at ~330 nm overlaps the PO emission band, we subtract the best-fit synthetic OH emission spectrum from the observed MBSL spectrum to obtain an accurate PO emission spectrum. By fitting the PO emission spectra (Figure 4.16C), the emission temperature of PO is determined to be 4000 ± 400 K, which is substantially lower than that measured from OH emission (9500 ± 300 K). Similar results are also observed at higher acoustic intensity. The difference in measured temperatures as a function of acoustic intensity might reflect minor differences in the relative number of bubbles in two populations or less spherical collapse as discussed in the previous section.

Figure 4.16. (A) Spectrum of OH ($A^2\Sigma^+ - X^2\Pi$) emission and PO ($B^2\Sigma^+ - X^2\Pi$) emission from MBSL in 85% H$_3$PO$_4$ saturated with He and irradiated with ultrasound compared to the best fit calculated spectra (red: calculated OH emission spectrum at 9500 K; blue: calculated PO emission spectrum at 4000 K). (B) Observed MBSL OH emission spectrum compared to calculate spectra at different temperatures. (C) Observed MBSL PO emission spectrum compared to calculated PO emission spectra at different temperatures. Sonication was conducted at 20 kHz and 17 W/cm$^2$ with a Ti horn directly immersed in the solution at 298 K. The synthetic spectra assumed thermal equilibrium and a Lorentzian profile. The underlying continuum has been subtracted and spectra are normalized to the maximum intensity peak at ~309 nm.
Figure 4.17. (A) Spectrum of OH \( (A^2\Sigma^+-X^2\Pi) \) emission and PO \( (B^2\Sigma^+-X^2\Pi) \) emission from MBSL in 85% \( \text{H}_3\text{PO}_4 \) saturated with He and irradiated with ultrasound compared to the best fit calculated spectra (red: calculated OH emission spectrum at 8000 K; blue: calculated PO emission spectrum at 5000 K). (B) Observed MBSL OH emission spectrum compared to calculated spectra at different temperatures. (C) Observed MBSL PO emission spectrum compared to calculated PO emission spectra at different temperatures. Sonication was conducted at 20 kHz and 25 W/cm\(^2\) with a Ti horn directly immersed in the solution at 298 K. The synthetic spectra assumed thermal equilibrium and a Lorentzian profile. The underlying continuum has been subtracted and spectra are normalized to the maximum intensity peak at \( \sim \)309 nm.

It is very interesting to observe two dramatically different emission temperatures from two simultaneously emitted spectroscopic thermometers. The different MBSL temperatures from the two simultaneously-observed, independent molecular species look paradoxical because both OH and PO emissions are from the same cavitation event. The observed temperature inhomogeneity, however, can be explained by the two different cavitating bubble populations, as recently observed during MBSL in \( \text{H}_2\text{SO}_4 \) and \( \text{H}_3\text{PO}_4 \) solutions doped with nonvolatile alkali salts.\(^{30, 44, 45} \) The two distinct cavitating bubble populations in \( \text{H}_3\text{PO}_4 \) can be categorized into: (1) relatively stationary bubbles whose
collapse is highly symmetric and spherical and (2) relatively rapidly moving bubbles whose collapse is much less spherical and involved injection of micro- or nano-sized liquid droplets into the gas phase of the collapsing bubbles. The OH emission comes dominantly from the relatively stationary cavitating bubbles with spherical collapse. In contrast, the PO radical, which is decomposed from H$_3$PO$_4$ molecules, is analogous to the emission of alkali metal atoms in aqueous solution and represents the conditions present in cavitating bubbles with less spherical collapse.

This interpretation can be confirmed by the observation of spatial separation of the cavitating bubble populations during MBSL. As shown in Figure 4.18, there are two distinctly different bubble populations: OH emission appears both at the top and bottom of the cavitating bubble cloud, whereas PO emission is only observable at the bottom of the cloud. The emission of PO radicals comes from H$_3$PO$_4$ molecules and involves injection of liquid droplets into the interior of bubbles via capillary wave action, microjetting or bubble coalescence due to significant deformation during bubble collapse in the dense cloud of cavitating bubbles, as depicted in Figure 4.18B.$^{30,46-49}$ After the liquid droplets are injected into the interior gas phase of the collapsing bubble, a process analogous to the flames begins (e.g., solvent evaporates and decomposition of H$_3$PO$_4$ molecules), which leads to the formation of excited PO radicals. Because both the evaporation of the liquid droplet and endothermic decomposition of H$_3$PO$_4$ and H$_2$O molecules consume a large amount of cavitation energy, liquid droplets can significantly cool intracavity temperatures inside the cavitating bubbles. Thus the measured PO emission temperature represents the hot spot conditions generated inside nonsymmetrically collapsing bubbles that contain liquid droplets, while the measured OH
emission temperature dominantly represents the more symmetric collapsing bubbles and is much higher than that determined from PO emission. It is likely that the spatial separation of the two bubble populations is caused by the pressure gradient propagated from the ultrasonic horn. Such separation might not be observable in a more uniform ultrasonic field. The observed temperature inhomogeneity can also be observed from other H₃PO₄ solutions. As shown in Figure 4.19, we can also observe two different emission temperatures from 80% H₃PO₄ based on OH emission and PO emission respectively. Due to the higher vapor pressure of 80% H₃PO₄, the observed emission temperatures are much lower than these observed in 85% H₃PO₄.

![Figure 4.18](image)

**Figure 4.18.** (A) MBSL spectra taken at the top and bottom of the cavitating bubble cloud from 85% H₃PO₄ saturated with He. Sonication conducted at 20 kHz, 25 W/cm², with 1 cm² Ti horn directly immersed in the solution at 298 K. (B) A schematic illustration of the non-symmetric collapse of a bubble that involves injections of liquid droplets into the interior of the collapsing bubble.
**Figure 4.19.** (A) Spectrum of OH ($A^2\Sigma^+ - X^2\Pi$) emission and PO ($B^2\Sigma^+ - X^2\Pi$) emission from MBSL in 80% $\text{H}_3\text{PO}_4$ saturated with He and irradiated with ultrasound compared to the best fit calculated spectra (red: calculated OH emission spectrum at 7400 K; blue: calculated PO emission spectrum at 3000 K). (B) Observed MBSL OH emission spectrum compared to calculate spectra at different temperatures. (C) Observed MBSL PO emission spectrum compared to calculated PO emission spectra at different temperatures. Sonication was conducted at 20 kHz and 17 W/cm$^2$ with a Ti horn directly immersed in the solution at 298 K. The synthetic spectra assumed thermal equilibrium and a Lorentzian profile. The underlying continuum has been subtracted and spectra are normalized to the maximum intensity peak at $\sim$309 nm.

The dissociation energy of diatomic molecules provides an upper limit on the maximum temperature that can be measured via spectroscopic method: at a sufficiently high temperature, the emitting diatomic molecules would dissociate into atoms.$^{25, 50}$ The dissociation energies of OH and PO are 428 kJ/mol and 595 kJ/mol, respectively.$^{51}$ In flame spectroscopy, the temperature measured from OH emission can be up to 10000 K. Since the bond energy of PO radicals is larger than OH radicals, excited PO radicals dissociate at temperatures higher than 10000 K.$^{50}$ In addition, excited PO radicals are frequently observed from very high temperature arcs, flames, and discharges containing
trace amounts of phosphorus. Thus, both OH and PO radicals will persist even under the extreme intracavity conditions that we observe and the emission temperatures measured from them are valid.

4.5 Conclusions

It has been demonstrated that MBSL in H₃PO₄ provides rich molecular emission features and spectroscopic methods have become a formidable method of quantifying the intracavity conditions temperatures created during multibubble cavitation.⁴, ¹¹-¹⁴, ²⁹, ⁴² The effects of various experimental parameters (e.g., acoustic power, vapor pressure of solution, and noble gases) have been well examined and lead to controllable MBSL. Two independent molecular thermometers (OH and PO molecular emission) inside a cavitating cloud of bubbles during MBSL have been applied to quantify the temperature profile in a cavitating bubble cloud. Two distinct cavitating bubble populations are found during MBSL in H₃PO₄. Spatial separation is observed in MBSL emission spectra from (1) bubbles near the acoustic horn whose collapse is highly symmetric and (2) rapidly moving bubbles whose collapse is much less symmetric and involves injection of liquid droplets into the interior of the collapsing bubbles. The spectroscopic temperatures from OH emission come dominantly from very hot bubbles (~9500 K) that collapse near the ultrasonic horn whereas the PO emission comes from colder (~4000 K) bubbles that collapse from deformed bubbles associated with injection of liquid droplets far from the horn.
4.6 References


CHAPTER 5
MOLECULAR EMISSION AND TEMPERATURE MEASUREMENTS FROM SINGLE-BUBBLE SONOLUMINESCENCE IN PHOSPHORIC ACID

5.1 Introduction

Single-bubble sonoluminescence (SBSL), light emission from an isolated nonlinearly oscillating bubble in a standing acoustic field, is a phenomenon that arises from acoustic cavitation: the formation, growth, and implosive collapse of a gas bubble in a liquid.\textsuperscript{1-4} Although SBSL has been extensively studied for nearly 20 years, little definitive experimental information regarding the light emitting process is known. Light emission from SBSL usually reveals little about the physical conditions and chemical processes during bubble collapse because the typical SBSL spectrum is featureless. Since the first report of SBSL, the majority of SBSL studies have been conducted in partially degassed purified water. In fact, SBSL from pure water (Figure 5.1), the liquid used most often for SBSL experiments, displays a continuum whose intensity increases smoothly from the near-IR into the near-UV devoid of any lines or bands.\textsuperscript{5, 6} Later work with enhanced spectral resolution (1 nm FWHM vs. 10 nm FWHM) confirmed that SBSL spectra from water were featureless within the parameter space explored.\textsuperscript{7} The featureless continuum spectra has been interpreted as arising from a variety of possible processes, including blackbody radiation following the Planck’s law, radiative plasma processes (e.g., Bremsstrahlung and ion-electron recombination), and severe line broadening under extreme high temperature and pressure environments.\textsuperscript{8-18} Because all of the above processes generate a featureless emission continuum, determination and differentiation of
the specific mechanisms responsible for SBSL from water has proven difficult and been the subject of much debate.

**Figure 5.1.** SBSL spectra from water with different noble gases or mixtures of noble gases and N\textsubscript{2}. The water was partially regassed with 150 torr gases. Spectra were taken with a driven frequency of 33 kHz at 24 °C. Figure adapted from reference 5.

It is desirable to observe lines and bands within SBSL spectra to elucidate the process at work during bubble implosion. The first molecular emission was observed from a single freely oscillating bubble in aprotic organic liquids like adiponitrile (NC(CH\textsubscript{2})\textsubscript{4}CN) and dimethylsulfoxide ((CH\textsubscript{3})\textsubscript{2}SO) with low vapor pressure and high heteroatom content.\textsuperscript{19} An increase in SBSL radiant power over that typically observed from water was found in some of the liquids studied. At relatively low acoustic pressure,
the SBSL spectra from adiponitrile contained emission from CN (B^2Σ – X^2Σ) (Figure 5.2). As the acoustic pressure increased, the emission line disappeared and a featureless continuum similar to that observed in water remained (Figure 5.2). Interestingly, the molecular emission was only observable from a moving sonoluminescing bubble. Stationary bubbles only yielded featureless spectra (Figure 5.3). In addition, SBSL spectra of dimethylsulfoxide and adiponitrile at high acoustic pressures were quite flat across the entire bandwidth studied indicating that blackbody radiation was not responsible for the observed emission. Other than CN emission, emission from excited OH radicals was discovered in very dimly sonoluminescing bubbles (5 days were needed to acquire a spectrum for the dimmest bubble). In order to acquire SBSL spectra with OH emission from a very dimly luminescing bubble, a relatively large amount of noble gas (e.g., 150 torr Ar) was required. The presence of 150 torr noble gas in the bubble caused the bubble to jitter and move about the pressure antinode. The spatial movement of the bubble might lead to microdroplet injection into the interior of the gas bubble. Evaporation of water microdroplets followed by pyrolysis of water molecules resulted in the dissociation and formation of excitation OH radicals. This conclusion is the same as that observed from SBSL from moving bubbles in aprotic organic liquids. The difference between a moving bubble and stationary bubble lies in the sphericity and severity of the bubble collapse and the effect this has on the bubble content. The observation of molecular emission from SBSL is exciting. It demonstrates that chemical reactions exist during SBSL and sonolysis products contribute to the emission lines and bands. The low signal to noise ratio and dim light observed, however, limited the utility of the SBSL spectra for quantitative analysis. It is still a challenge, therefore, to derive the effective
Figure 5.2. (A) Moving SBSL spectra from adiponitrile as a function of acoustic pressure. Acoustic pressure increases from bottom to top, from 1.7 bar to 1.9 bar. The emission peak at 380 nm arises from CN ($B^2\Sigma - X^2\Sigma$). (B) SBSL spectra from a stationary and moving bubble in methylformamide at an acoustic pressure of ~1.1 bar. Figure adapted from reference 19.

Figure 5.3. SBSL spectra from pure water regassed with 150 torr Ar under different acoustic pressures at 25 °C. The acquisition time for the dimmest bubble was 5 days while for the brightest bubble was 100 min. Figure adapted from reference 20.
temperatures and pressures or to describe process during bubble collapse and the mechanisms ultimately responsible for the light emission.

Aprotic organic liquids with low vapor pressure still suffer from the decomposition of organic vapor inside the cavitating bubbles, which lowers the efficacy of cavitation and limits the final effective temperatures that can be achieved. Concentrated aqueous H$_2$SO$_4$ solutions also have low vapor pressure (e.g., 40 mtorr for 85\% H$_2$SO$_4$ at 25 °C) but their sonolysis products (e.g., SO$_x$, H$_2$S, and elemental sulfur) are either highly soluble or are solids.$^{21}$ In addition, concentrated aqueous H$_2$SO$_4$ solutions are essentially transparent within the spectral window of interest (200 to 900 nm). This feature allows for direct comparison of the spectra to water SBSL spectra, which contain all spectral features in the range 200 to 800 nm. Water is also transparent in the bandwidth of interest. The above mentioned unique properties of aqueous sulfuric acid (H$_2$SO$_4$) solutions make it an ideal candidate for spectroscopic studies of SBSL. Indeed, SBSL in 85\% H$_2$SO$_4$ demonstrates a dramatic increase in SBSL intensity ($10^3$ higher than the brightest bubble in water, see Figure 5.4) and provides a variety of atomic, ionic, and molecular emission lines (Figure 5.5).$^{22-26}$ Most importantly, intense emission with resolvable spectra allows for the spectroscopic determination of emission temperatures. The emission temperature from a single bubble in H$_2$SO$_4$ can be obtained by comparing to calculated emission temperatures (Figure 5.6).$^{22}$ It is demonstrated that the SBSL temperatures strongly depend on the properties of the gas and vapor comprising the bubble and the applied acoustic pressures.
Figure 5.4. (A) SBSL spectra from 85% H$_2$SO$_4$ and pure water regassed with Xe and Ar (solid lines). The noble gas content, acoustic pressure and frequency are adjusted to get the brightest SBSL emission. Dashed lines show blackbody fits to obtained spectra. Figure adapted from reference 22.

Figure 5.5. (A) SBSL spectrum from 85% H$_2$SO$_4$ with 50 torr Ar and acoustic pressure of 2.2 bar. Spectral features include emission from Ar, Ar$^+$, O$_2^+$, and SO. (B) Enlarged region of the SBSL from 410 to 510 nm as shown in (A). Figure adapted from reference 23.
The success of SBSL in H$_2$SO$_4$ suggests that the study of similar liquids like phosphoric acid (H$_3$PO$_4$) may also be fruitful. In this chapter, the study of SBSL from phosphoric acid (H$_3$PO$_4$) and measurement of emission temperatures from strong OH emission lines will be discussed. H$_3$PO$_4$ is a strongly hydrogen-bonded liquid with a relatively high viscosity and low vapor pressure (2.4 torr for 85% H$_3$PO$_4$ vs. 23 torr for H$_2$O at 300 K). An interesting property of aqueous H$_3$PO$_4$ is that only water molecules exist in the vapor phase; due to strong hydrogen bonding the acid molecules themselves have no significant presence in the vapor phase even at high temperatures. In addition, pyrolysis of H$_3$PO$_4$ only leads to dehydration forming polyphosphoric acids, so the exclusive volatile decomposition product of H$_3$PO$_4$ is H$_2$O. It is desirable to observe spectral features arising from molecular OH emission in SBSL spectra that could be used
to assign effective temperature as well as some insight into the light emitting process. A significant component of this chapter is from the following paper: Xu, H. X.; Suslick, K. S. Molecular Emission and Temperature Measurements from Single-Bubble Sonoluminescence. *Phys. Rev. Lett.* **2010**, *104*, 244301.

5.2 Experimental Methods

Solutions were prepared by diluting 85% H$_3$PO$_4$ as purchased with purified water (18 MΩ·cm) to 65% and completely degassed via 3 cycles of freeze-pump-thaw. Solutions were then regassed in a closed system with 50 torr of monatomic gases (He, Ne, Ar, Kr, and Xe from Matheson Tri-Gas, research purity) with vigorous stirring at 25 °C for 1 h. All spectra have been corrected for absorption by the solution and the quartz round bottom flask as well as the optical response of the system against NIST traceable standard lamps. For simulation of emission temperatures, the underlying continuum has been subtracted to and normalized at the highest intensity. The simulation spectra are generated from LIFBASE (v 2.0.60). All pictures are taken with a Nikon D90 digital camera with a Nikon 60mm f/2.8G ED AF-S Micro-Nikkor Lens.

5.3 Results and Discussion

H$_3$PO$_4$ has a much lower vapor pressure than water; therefore, the collapse of a single bubble is much more efficient in H$_3$PO$_4$: less energy is consumed by endothermic bond dissociations of vapor molecules inside the collapsing bubble. The sonoluminescing bubble observed from SBSL in H$_3$PO$_4$ is exceptionally bright (Figure 5.7). More importantly, we are able to easily observe SBSL spectra from 65% H$_3$PO$_4$
dominated by strong molecular emission from excited OH radicals. This observation is unusual because only very weak emission from excited OH radicals has been reported from MBSL in water and from SBSL in weakly driven, dimly

Figure 5.7. Photograph of a rapidly moving sonoluminescing bubble trapped at the velocity node of a spherical quartz resonator. The driving piezoceramics are mounted at the both sides of the quartz cell and the microphone is attached to the bottom of the cell. This apparatus is rigidly clamped at the narrow neck of the quartz cell buffered with a thin layer of epoxy resin.

sonoluminescing bubbles in water or dilute H$_2$SO$_4$.$^{20, 30, 31}$ The exceptionally high intensity of the emission in H$_3$PO$_4$ permits us to obtain the fine structure of OH A$^2\Sigma^+$–X$^2\Pi$ rovibronic transitions,$^{32}$ and the experimental spectra obtained can be fit well with synthetic spectra to determine the effective emission temperatures during single-bubble cavitation.
The single cavitating bubble in H₃PO₄ is moving within a small volume at the center of the quartz resonator. This phenomenon is similar to the single bubbles generated in polar aprotic organic liquids and H₂SO₄.¹⁹,²₂,²⁵ As shown in Figure 5.8, the bubble is moving around in a confined space (~20 mm³) with no predictable route. The translational movement of the bubble varies with the applied acoustic pressures: as the acoustic pressure is increased, the bubble motion becomes more rapid primarily near the center of the resonator cell while maintaining its bright sonoluminescence. If the applied acoustic pressure is too high, the bubble cannot maintain the position at the velocity node and is forced to move away from the center of the resonator.

**Figure 5.8.** Photographs of a moving sonoluminescing bubble in 65% H₃PO₄ regassed with 50 torr Ar at an acoustic pressure of 3.1 bar as measured from hydrophone. The exposure time is shown in each photograph.

The observed bright light emitted from the rapidly moving bubble allows us to acquire the spectra in minutes compared to the observed OH emission from dim bubbles which required days! Figure 5.9A shows SBSL spectra obtained from 65% H₃PO₄ under different acoustic pressures (Pₐ). The spectra contain strong molecular emission from excited OH radicals at 310 nm and an underlying continuum, the radiant power of which
increases from the near-IR to mid-UV. This observation indicated that chemical processes must be considered in the discussion of the light-emitting mechanism during single-bubble cavitation in order to explain the formation of excited OH radicals. Excited OH radicals are formed either from the recombination of H and O atoms created during water vapor sonolysis or from the initial dissociation of H₂O molecules. As the acoustic driving pressure is increased, the intensity of OH emission decreases relative to the continuum emission, perhaps due to increasing dissociation of the OH radicals under more extreme bubble conditions (i.e., higher bubble temperatures).

There are many unknowns during single-bubble cavitation; the quantification of intracavity conditions during single-bubble cavitation is both theoretically and experimentally important. While the effective temperatures of multibubble cavitation have been previously determined (e.g., by comparative rate thermometry or MBSL from excited molecules or metal atoms), temperature measurements from SBSL has proved much more difficult, given that SBSL spectra are usually featureless continua. Previous experimental studies of SBSL temperature generally assume that the continuum is due to blackbody emission, an assumption that remains controversial. Although there have been a few reported observations of molecular emission during single-bubble cavitation, these spectra were too weak for quantitative analysis. The OH emission that we now observe in 65% H₃PO₄, however, is extremely bright and permits us to obtain the fine structure of the OH A²Σ⁺-X²Π rovibronic transition. We are thus able to determine SBSL temperatures from molecular emission by fitting the experimental spectra to calculated spectra under different temperatures generated from known parameters. LIFBASE, a database and spectral simulation program for diatomic
molecules, which has been extensively applied to temperature determinations of excited molecular emission from flames and laser induced fluorescence, was used to generate synthetic spectra.\textsuperscript{28}

In the OH spectrum taken at an acoustic pressure of 2.4 bar (Figure 5.9B), for example, the OH emission spectrum can be very accurately simulated by a fully thermalized ($T_{\text{rot}}=T_{\text{vib}}$) emission at 8300 ± 200 K. OH emission temperatures generated during SBSL from 65\% H$_3$PO$_4$ were observed to increase with increasing acoustic pressure: 6,200 K at 1.9 bar, 7,000 K at 2.1 bar, 8,300 K at 2.4 bar, 9,000 K at 2.7 bar, and 9,500 K at 3.1 bar. As the applied acoustic pressure increases, the bubble undergoes a more violent collapse, which generates more extreme bubble conditions like increased effective emission temperature inside the collapsing bubble. These experimentally determined temperatures from 65\% H$_3$PO$_4$ are consistent with theoretically predicted SBSL temperatures in water using a model that accounts for the endothermic decomposition of the water vapor trapped during bubble expansion.\textsuperscript{39-41} At higher acoustic pressures (>3.1 bar), accurate acquisition of SBSL spectra becomes difficult because the bubble motion becomes more extreme and is no longer confined to a small space and the bubble is forced away from the center of the resonator.

We have also fit the slope of the continuum to an effective blackbody temperature,\textsuperscript{8, 10} which, surprisingly, is ~11,000 K for each acoustic pressure (Figure 5.10). The meaning and accuracy of such a parameter, however, is open to question. First of all, it is still under debate whether the continuum is true blackbody emission,\textsuperscript{9, 11, 13} and second, the fit of the continuum region is limited to only a 200 nm range (i.e., between
400 and 600 nm, due to strong OH emission in the near UV and noble gas atom emission in the red) and is therefore of limited accuracy.

**Figure 5.9.** (A) SBSL spectra from 65% H$_3$PO$_4$ regassed with 50 torr Ar at different acoustic pressures ($P_a$). All spectra were collected from the same rapidly moving bubble driven at different $P_a$, as labeled above the corresponding spectra. The peak around 310 nm is from OH ($A^2\Sigma^+\rightarrow X^2\Pi$) emission. Spectra were acquired with a 300 grooves/mm grating blazed at 250 nm. (B) Higher resolution SBSL spectra of OH ($A^2\Sigma^+\rightarrow X^2\Pi$) emission from the same bubble driven at different acoustic pressures compared to best-fit synthetic spectra. The underlying continuum has been subtracted; spectra are normalized to the highest intensity at ~309 nm. Spectra were acquired with a 1200 grooves/mm grating blazed at 330 nm.
Figure 5.10. SBSL spectra from 65% H₃PO₄ at different acoustic pressures ($P_a$) with simulated blackbody fit (dashed lines). Temperatures of blackbody fits are shown next to their corresponding plot.

It is generally accepted that the bubble content is a key parameter in controlling the intracavity conditions generated during bubble implosion,

so we have examined the SBSL spectra from 65% H₃PO₄ regassed with different noble gases. SBSL spectra from 65% H₃PO₄ regassed with 50 torr of different noble gases at an acoustic pressure of 2.4 bar are shown in Figure 5.11. The intensity of the SBSL depends dramatically on bubble content (i.e., the dissolved noble gas in the bubble) (Figure 5.11A) and increases roughly a hundred-fold from He to Ne to Ar to Kr to Xe. In all cases, an emission peak around 310 nm corresponding to molecular emission of neutral OH radicals is observed and broadens substantially as we progress from He to Xe. These results are consistent with
prior MBSL experiments: the intensity and temperature of sonoluminescence increases from He to Xe.\textsuperscript{42}

It is generally accepted that the initial stage of bubble collapse is slow and isothermal, during which the energy deposited in the bubble interior is readily transferred to the surrounding liquid via thermal conduction. As the speed of bubble collapse increases the interior of bubble undergoes compressional heating and becomes increasingly adiabatic due to the rapidity of the bubble collapse. The extent of adiabaticity will depend on the thermal conductivity of the gas/vapor mixture within the bubble. If the thermal conductivity of the gas within the bubble is high, increased thermal transport from the heated gas to the cold surrounding liquid will lead to much colder bubble temperatures.\textsuperscript{42} As a matter of fact, theoretical calculations using combined hydrodynamic and chemical kinetic modeling indicate that the higher thermal conductivity of the lighter noble gases leads to cooler SBSL temperatures.\textsuperscript{43-45} By varying the composition of Ar and Ne mixtures, Flannigan and Suslick were able to determine the effect of thermal conductivity during single-bubble cavitation based on the Ar emission temperature;\textsuperscript{22} this method, however, neglects the possibility that different noble gas molecules in the bubble might segregate spatially during bubble collapse.\textsuperscript{46, 47} Because we are able to observe strong OH emission from SBSL in phosphoric acid, we were able to experimentally determine the effect of noble gases directly on sonoluminescence temperatures during single-bubble cavitation. As shown in Figure 5.11B, the emission temperature of SBSL increases as the thermal conductivity of the gas within the bubble decreases. The observed emission temperatures range from 6000 K for He up to 9600 K for Kr, consistent with the published simulations. The effective emission temperatures
from collapsing bubbles increase with decreased thermal conductivity of different noble gases. The emission temperatures with thermal conductivity of different noble gases are summarized in Table 5.1.

![Figure 5.11](image)

**Figure 5.11.** (A) SBSL spectra from 65% H₃PO₄ with 50 torr of different noble gases at an applied acoustic pressure of 2.4 bar. (B) Higher resolution SBSL spectra of OH (A²Σ⁺−X²Π) emission from the same bubble driven at \( P_a = 2.4 \) bar compared to best-fit synthetic spectra. The calculated temperatures were obtained by fitting experimental SBSL spectra with synthetic spectra using the LIFBASE program. The simulation for SBSL spectra from Xe gas filled bubbles cannot proceed because the OH emission peak is severely broadened under extreme intra-cavity conditions.

**Table 5.1.** List of effective emission temperatures observed from SBSL in 65% H₃PO₄ with different noble gases and thermal conductivity of different noble gases at 300 K.⁴⁸

<table>
<thead>
<tr>
<th>Gas</th>
<th>He</th>
<th>Ne</th>
<th>Ar</th>
<th>Kr</th>
<th>Xe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>6000 K</td>
<td>7200 K</td>
<td>8300 K</td>
<td>9600 K</td>
<td>&gt;10000 K</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>156.7 mW/m•K</td>
<td>49.8 mW/m•K</td>
<td>17.9 mW/m•K</td>
<td>9.5 mW/m•K</td>
<td>5.5 mW/m•K</td>
</tr>
</tbody>
</table>
SBSL in liquids other than water (including both low-volatility organic liquids and concentrated sulfuric acid) has led to valuable insights on the conditions created in the gas phase of the collapsing bubble. Comparing these studies in phosphoric acid with our recent work in sulfuric acid, we find that the emission temperature in 85% H\textsubscript{2}SO\textsubscript{4} (simulated based on excited atomic Ar emission) is much hotter and can approach 20,000 K.\textsuperscript{22} Note all the temperatures measured here are effective temperatures rather than peak temperatures. In addition, a hot, optically opaque plasma core was also experimentally observed from SBSL in H\textsubscript{2}SO\textsubscript{4}. In contrast, we do not observe atomic emission from noble gases in the SBSL from 65% H\textsubscript{3}PO\textsubscript{4}.\textsuperscript{22, 23} We suggest that this difference is due (at least in part) to the relatively high vapor pressure of water in 65% H\textsubscript{3}PO\textsubscript{4} compared to that of 85% H\textsubscript{2}SO\textsubscript{4} (8.7 torr vs. 40 mtorr; a bubble in H\textsubscript{3}PO\textsubscript{4} contains 200-fold more water molecules than that in H\textsubscript{2}SO\textsubscript{4}!): more of energy of cavitation is consumed by endothermic bond dissociations of the water molecules (leading to the formation of hydrogen and oxygen atoms, and OH, etc.). Thus, the water vapor trapped inside a cavitating bubble is a major temperature-limiting factor and the content of polyatomic molecules inside the collapsing bubble determines the intra-cavity conditions that a bubble can achieve.\textsuperscript{41, 49, 50} Therefore, collapsing bubbles are considerably cooler in 65% H\textsubscript{3}PO\textsubscript{4} than in 85% H\textsubscript{2}SO\textsubscript{4}.

Since both MBSL and SBSL exhibit strong molecular emission, we can also compare MBSL to SBSL spectra from phosphoric acid: in both systems, strong molecular emission is observed from OH with comparable effective emission temperatures, but PO emission can only be observed in MBSL.\textsuperscript{51} In both the SBSL and MBSL of phosphoric acid, excited OH radicals are produced during collapse from the water vapor inside the
bubble. This different phenomenon is caused by the difference in the shape of collapsing bubbles during SBSL and MBSL. The collapse of single bubbles is expected to be highly symmetric, whereas bubble collapse in a cloud of cavitating bubbles gives rise to more asymmetric collapse; this greater asymmetry in MBSL explains the observation of PO emission, which must arise from the liquid phase by the introduction of nanodroplets into the hot core of the collapsing bubble and then followed by evaporation of solvent and decomposition of molecules inside the bubbles.\textsuperscript{51, 52}

5.4 Conclusions

In conclusion, strong molecular emission was discovered from SBSL in phosphoric acid. The observation of intense OH emission from a bright, rapidly moving bubble enables us to acquire fine structures of the OH A^2Σ^+-X^2Π rovibronic transition. The rovibronic emission of excited-state OH radicals can be used as a direct spectroscopic probe of the emission temperature inside the collapsing bubble by fitting the OH emission spectra to calculated spectra. The effective emission temperatures measured from phosphoric acid increase with increased applied acoustic pressure and also increase with decreasing thermal conductivity of the noble gases inside the bubble. The observed emission temperatures from SBSL in phosphoric acid are limited by the water vapor molecules trapped inside the collapsing bubble and are comparable to the emission temperatures measured from MBSL in phosphoric acid.
5.5 References


CHAPTER 6
SONOCHEMICAL SYNTHESIS OF HIGHLY FLUORESCENT SILVER NANOCLUSTERS

6.1 Introduction

Noble metal nanoparticles have unique size- and shape-dependent optical, electrical, catalytic, magnetic, and chemical properties.\textsuperscript{1-5} They have been the subject of intense research in the past decade. Even smaller than nanoparticles, noble metal nanoclusters consist of several to ~100 metal atoms and possess sizes comparable to the Fermi wavelength of electrons (i.e., the de Broglie wavelength of the electrons at the Fermi level: \(\sim 0.5\) nm for Ag and Au). Such nanoclusters have received increasing attention in recent years because their optical, electrical and chemical properties are significantly different than their larger cousins, i.e., noble metal nanoparticles.\textsuperscript{6-9} Metal nanoclusters exhibit molecule-like properties like discrete electronic transitions and strong fluorescence upon photoexcitation in the UV-visible range (Figure 6.1).\textsuperscript{10-14} Ag nanoclusters are especially fluorescent and have been shown to be excellent fluorophores for a wide range of applications including chemical sensing, bioimaging, and single-molecule studies.\textsuperscript{15-23} Gas-phase and low-temperature matrix-isolated Ag nanoclusters were the first observed to exhibit fluorescence.\textsuperscript{24} Chemiluminescence induced by the formation of excited \(\text{Ag}_2^+\) and \(\text{Ag}_3^+\) clusters during Ag condensation with Ar has also been reported.\textsuperscript{25} Inorganic glasses and zeolites were also used to immobilize Ag nanoclusters which show excellent photostability under UV irradiation.\textsuperscript{26-30} Ag nanoclusters synthesized in these conditions are, however, not amendable to real world applications.
Figure 6.1. Size-dependent properties of metals. Bulk metal and metal nanoparticles have a continuous band of energy levels, but metal nanoclusters with their limited number of metal atoms have discrete energy levels. Metal nanoclusters can interact with light via electronic transitions between different energy levels, leading to intense light emission and absorption. Figure adapted from reference 14.

To explore potential applications of Ag nanoclusters, synthesis of individual Ag nanoclusters that are stable and soluble in aqueous solutions are essential. The synthesis of Ag nanoclusters in aqueous solutions, however, is difficult because Ag nanoclusters would strongly interact with each other and tend to aggregate: Ag nanoclusters will grow continuously, forming larger nanoparticles and reducing their surface energy, until their growth is stopped by pre-formed templates or capping agents. A number of organic scaffolds like DNA, polymers, dendrimers, polymer capsules, polymer microgels, and
multiarm star polymers have been used as protecting and stabilizing agents to prepare fluorescent Ag nanoclusters in aqueous solutions. Water-soluble highly fluorescent Ag nanoclusters have been prepared from the radiolytic, chemical, or photochemical reduction of silver salts in aqueous solutions containing the above mentioned capping agents. Sonochemistry has been widely used in materials synthesis and a variety of materials have been prepared via sonochemical method. The chemical effects of high intensity ultrasound derive primarily from acoustic cavitation: the formation, growth and implosive collapse of bubbles in a liquid irradiated with ultrasound. Localized hot spots with temperatures of ~5000 K and pressures of hundreds of bars can be generated during ultrasonic irradiation of water. As a consequence, highly reactive species, including HO₂⁻, H•, OH•, and perhaps eaq⁻, are formed during sonication of aqueous solution, similar to the effects of γ-ray or deep-UV irradiation of aqueous solutions. While sonochemical method has been used to prepare many different noble metal nanoparticles in aqueous or alcohol solutions, to the best of our knowledge, there is no prior report of the synthesis of ultra-small metal nanoclusters using a sonochemical method. This chapter will describe a sonochemical synthesis of water-soluble fluorescent Ag nanoclusters using a common polyelectrolyte, polymethylacrylic acid (PMAA), as the capping agent to stabilize and protect the Ag nanoclusters in the solution. A significant component of this chapter is from the following paper: Xu, H. X.; Suslick, K. S. Sonochemical Synthesis of Highly Fluorescent Ag Nanoclusters. *ACS Nano* **2010**, *4*, 3209-3214.
6.2 Experimental Methods

6.2.1 Synthesis of Ag Nanoclusters

The polymers used in this work and AgNO₃ were purchased from Sigma-Aldrich and used as received. Water-soluble fluorescent Ag nanoclusters were prepared as follows: 30 ml PMAA-Ag⁺ solutions with different RCO₂⁻/Ag⁺ ratios were prepared using 5 ml AgNO₃ solution containing 45 mg AgNO₃ mixed with 25 ml PMAA solutions of different concentrations. The solution was adjusted to pH 4.5 with either 0.1 M HNO₃(aq) or NaOH(aq). The mixture was then transferred to a sealed vessel and sparged with Ar for 2 h at 20 °C. Sonication time was varied from 10 to 180 min under Ar flow with an ultrasonic horn (Sonics & Materials, model VCX-750, 1 cm² Ti horn at 20 kHz and 25 W/cm²).

6.2.2 Characterization of Ag Nanoclusters

UV-Vis absorption and fluorescence spectra were obtained using a HITACHI 3300 double monochromator UV-Vis spectrophotometer and a Jobin Yvon Horiba FluoroMax-3 spectrofluorometer, respectively. Fresh solutions (with an absorption at 510 nm of 0.1) were transferred into quartz cuvettes and their spectra recorded. The quantum yield of fluorescent Ag nanoclusters was determined by measuring the integrated fluorescence intensities of the Ag nanoclusters compared to a reference solution (i.e., the quantum yield of Rhodamine B in ethanol at 510 nm is 0.756) using 510 nm excitation. TEM images were taken with a JEOL 2100 Microscope with an accelerating voltage of 200 kV. Dark-field TEM images were acquired with a JOEL 2010 field emission Scanning Transmission Electron Microscope (STEM). Samples were prepared by placing
a drop of solution onto copper grids with ultrathin carbon film and dried at room temperature.

6.3 Results and Discussion

Similar to other approaches, sonochemical reduction of Ag⁺ still requires the use of a template or capping-agent to prevent the aggregation of Ag nanoclusters in the solution to form large Ag nanoparticles. PMAA has been shown to be a versatile template for preparing Ag nanoclusters under UV irradiation. The carboxylic acid groups have a strong affinity for silver ions and silver surfaces which can provide stability for Ag nanoclusters. Once the Ag nanoclusters are capped by the carboxylic acid group, the growth of nanoclusters to large nanoparticles in the solution can be stopped. In addition, PMAA also serves as OH• radical scavengers during the ultrasonic irradiation to prevent oxidation of small silver clusters by OH• to form silver oxide. Meanwhile, the secondary radicals (R•) formed from reaction of PMAA with OH• exhibit strong reducing power and can produce Ag atoms associated with the polymer chains. Strong fluorescence appears from the aqueous AgNO₃ solution with dissolved PMAA under ultrasonic irradiation.

The preparation of fluorescent Ag nanoclusters starts with a freshly prepared solution of AgNO₃ mixed with an aqueous PMAA (Mₜₕ = 9500, sodium salt) solution. The molar ratio of carboxylate groups (from the methacrylic acid units) to Ag⁺ was set to be 1:1. The pH value of the resulting solution was adjusted to 4.5 by HNO₃(aq.) or NaOH(aq.) to form a compacted coil conformation of PMAA in the solution, which has been claimed to favor the formation of Ag nanoclusters. The solution was sparged with
Ar for 2 h and then subjected to sonication for various time intervals. A schematic illustration of fluorescent Ag nanoclusters synthesis process is given in Figure 6.2.

Figure 6.2. Schematic illustration of sonochemical synthesis of fluorescent Ag nanoclusters.

Upon sonication, the initially colorless solution gradually turns pink (90 min) and then dark red (180 min) (Figure 6.3A). As expected, the resulting Ag nanoclusters are highly fluorescent (Figure 6.3B). From the transmission electron microscopy (TEM) images, we can see that the sonochemically prepared Ag nanoclusters are less than 2 nm in diameter (Figure 6.4). These ultra-small Ag nanoclusters are more clearly visible with a high angle annular dark field (HAADF) STEM image (Figure 6.5).
Figure 6.3. (A) UV-vis spectra and (B) fluorescence emission spectra of the solution containing PMMA and AgNO₃ after increasing length of sonication time; the excitation spectrum shown in (B) corresponds to the 90 min sample with an emission wavelength of 610 nm. Inset in (B) shows the solution of Ag nanoclusters illuminated by a UV lamp with 365 nm excitation.

Figure 6.4. TEM images of as-prepared Ag nanoclusters from different length of sonication: (A) 60 min, (B) 90 min (inset shows a single magnified Ag nanocluster), and (C) 180 min.
Figure 6.5. A HAADF STEM image of Ag nanoclusters prepared from a sonication length of 60 min.

It is interesting to observe the evolution of absorption and fluorescence of the sonochemically prepared Ag nanoclusters with changes in sonication time (Figure 6.3). No absorption peaks in the range 300–800 nm are observed before sonication. After 10 min sonication, a peak around 440 nm appears and further sonication results in the increase of the intensity of this peak. As sonication continues, a shoulder at 520 nm grows, the peak at 440 nm gradually disappears, the 520 nm peak gradually blue-shifts to 490 nm, and, finally, a new absorption peak around 390 nm begins to emerge after sonicating for 180 min. This trend has also been reported in UV-irradiated formation of Ag nanoclusters in polymer microgels. Absorbance in the region from 440 to 520 nm has been observed previously and ascribed to the formation of Ag nanoclusters clusters, with shorter wavelength corresponding to smaller nanoclusters. The peak at 390 nm is the
A distinctive feature of our Ag nanoclusters is their strong fluorescence, which is not observed for large Ag nanoparticles. An intense fluorescence emission band around 610 nm is observed upon excitation at 510 nm (Figure 6.3B). The emission intensity increases when the sonication time reached 90 min and prolonged sonication (after 90 min) led to the gradual decrease of the fluorescence intensity due to the formation of large non-fluorescent Ag nanoparticles. The formation of large non-fluorescent Ag nanoparticles has been confirmed in the absorption spectra plasmon band at 390 nm and by direct observation of large nanoparticles (Figure 6.4C). The corresponding fluorescence excitation spectrum at 90 min was recorded, which exhibited a peak at 510 nm and a weak shoulder around 400–440 nm (Figure 6.3B). The observation of two peaks in the excitation spectrum indicates that Ag nanoclusters of different sizes contribute to the emission at 610 nm. The quantum yield of sonochemically prepared Ag nanoclusters is substantial, ~11%, calculated by use of Rhodamine B in ethanol as a reference. Furthermore, such prepared Ag nanoclusters are stable in air; essentially no change in fluorescence intensity was observed even after 1 month storage in the dark.

Interestingly, the sonochemically prepared Ag nanoclusters can be excited by a wide range of excitation wavelength. Strong fluorescence can be observed upon excitation between 450 nm and 570 nm with the maximum emission observed at the excitation wavelength of 510 nm (Figure 6.6). The emission maximum was found to shift to longer wavelengths with increasing excitation wavelengths, which confirms that sonochemical synthesized Ag nanoclusters contain different sized Ag nanoclusters with
different numbers of Ag atoms.\textsuperscript{36,58} Note that essentially all Ag nanoclusters prepared to date by any synthetic method show a similar phenomenon, i.e., the emission maximum shifts as the excitation wavelength varies. There is a strong relationship between the size of Ag nanoclusters and their emission properties.\textsuperscript{7} The ability to control nanocluster distribution to a single nanocluster size has not yet been achieved and remains a challenge.

Figure 6.6. Fluorescence emission spectra of Ag nanoclusters sonochemically synthesized from a sonication time of 90 min excited by different wavelengths.

Interestingly, the stoichiometry of the carboxylate groups (RCO$_2^\text{-}$) to Ag$^+$ also plays an important role in the preparation of water-soluble fluorescent Ag nanoclusters. Figure 6.7 shows the absorption and emission spectra of sonochemically prepared Ag nanoclusters with different RCO$_2^\text{-}$/Ag$^+$ ratios with same sonication time and Ag$^+$ concentration. It is obvious that excess carboxylate groups (RCO$_2^\text{-}$/Ag$^+$ = 4/1 or 2/1) leads to the formation of smaller Ag nanoclusters with an absorption peak around 440
nm, while fewer carboxylate groups ($\text{RCO}_2^-/\text{Ag}^+ = 1/4$ or $1/8$) yields larger Ag nanoclusters with an absorption peak around 520 nm. Both kinds of Ag nanoclusters are formed when the $\text{RCO}_2^-/\text{Ag}^+$ ratio is in the middle region ($\text{RCO}_2^-/\text{Ag}^+ = 1/1$ or $1/2$). For solutions sonicated for 60 min, the color is yellow with excess carboxylate groups and pink with a lower $\text{RCO}_2^-/\text{Ag}^+$ ratio. In contrast to a prior photochemical preparation, when the $\text{RCO}_2^-/\text{Ag}^+$ ratios are changed, we cannot observe obvious shift in the emission maximum; likewise, in Figure 6.3B, the emission peak does not shift as a function of nanocluster size distribution. The change in absorbance wavelength, but not in fluorescence emission lead us to conclude that there is one dominant fluorescing nanocluster, regardless of the change in the overall nanocluster distribution, which does affect the absorbance spectra. The fluorescence intensity increases as the ratio of $\text{RCO}_2^-/\text{Ag}^+$ decreases with a maximum at $\text{RCO}_2^-/\text{Ag}^+ = 1/2$. If the carboxylate groups are further decreased, a decrease in total fluorescence intensity can be observed. This is possibly caused by the agglomeration of Ag nanoclusters due to the insufficient carboxylate groups present in the solution to stabilize freshly synthesized nanoclusters.

The structure and configuration of the polymer in the solution also affect the formation of Ag nanoclusters. PMAA with different molecular weights ($M_w = 4500, 15000$ and $100000$) can be used to prepare fluorescent Ag nanoclusters. The fluorescence intensity, however, decreases as the molecular weight increases even for the same length of sonication (Figure 6.8). It is likely that this is because of slower diffusion of reactive species produced by sonolysis into the interior of the longer chain length polymers. With shorter polymer chains, Ag$^+$ can be easily reduced and more fluorescent Ag nanoclusters can be produced with the same duration of sonication time. Other commercially available
polymers were also tested in our sonochemical synthesis of Ag nanoclusters. PAA and poly(acrylic acid-co-maleic acid) also led to the formation of water-soluble fluorescent Ag nanoclusters because they also contain carboxylic acid groups. To our surprise, polymers containing other functional groups that also have a high coordination affinity for Ag⁺ (e.g., polyvinylpyrrolidone, polyvinyl alcohol, polyethylenimine, and poly-N-isopropylacrylamide) did not lead to the formation of fluorescent Ag nanoclusters (Figure 6.9); with those polymers, only large, non-fluorescent Ag nanoparticles (Figure 6.10) with a characteristic surface plasmon absorption band around 400 nm were obtained.

**Figure 6.7.** (A) Absorbance spectra and (B) fluorescence emission spectra of sonochemically prepared Ag nanoclusters (60 min) from samples with different ratios of polymethylacrylic acid carboxylate groups to Ag⁺, as labelled in the figures. The excitation spectra are identical to that of Figure 6.2B.
Figure 6.8. Fluorescence emission spectra of sonochemically prepared fluorescent Ag nanoclusters with different molecular weights of PMMA (RCO2⁻/Ag⁺ = 1/1, 60 min sonication).

Figure 6.9. Photograph of solutions contain AgNO₃ and different polymers after 60 min sonication under the excitation of a UV lamp (365 nm). Polymers as shown in the picture are: PVP: poly(vinylpyrrolidone), PVA: poly(vinyl alcohol), PMAA: poly(methacrylic acid), PAA: poly(acrylic acid), PEI: poly(ethylenimine).
6.4 Conclusions

In conclusion, a convenient sonochemical method has been developed for the synthesis of water-soluble fluorescent Ag nanoclusters using a simple, inexpensive and commercially-available polyelectrolyte, PMAA, as a stabilizing agent. Such prepared Ag nanoclusters are very stable under ambient conditions. The chemical and physical properties of Ag nanoclusters can be easily controlled by varying the synthetic conditions. It can be surmised that the stability and excellent fluorescent properties of these sonochemically prepared Ag nanoclusters are likely to find potential applications in bioimaging, chemical- and bio-sensing, single molecule studies, and, possibly, catalysis. In addition, other noble metal nanoclusters like Au and Pt could also be prepared via this sonochemical approach.

Figure 6.10. UV-vis spectrum of the solution containing PEI and AgNO₃ after a sonication time of 60 min.
6.5 References


38. Diez, I.; Pusa, M.; Kulmala, S.; Jiang, H.; Walther, A.; Goldmann, A. S.; Muller, A. H. E.; Ikkala, O.; Ras, R. H. A. Color Tunability and


CHAPTER 7
SONOCHEMICAL PREPARATION OF POLYMER FUNCTIONALIZED GRAPHENES

7.1 Introduction

Graphene is an atomically thick, two-dimensional (2D) sheet composed of $sp^2$ hybridized carbon atoms arranged in a honeycomb lattice. Its extended honeycomb carbon network is the basic building block of other important graphitic carbon allotropes with different dimensionality. It can be wrapped to form 0D fullerenes (buckyballs), rolled to form 1D carbon nanotubes, or stacked to form 3D graphites (Figure 7.1). A single-layer graphene was first experimentally obtained in 2004 by Geim et al. at Manchester University by mechanically peeling off graphene sheets from bulk graphite crystals. Since then, graphene has received enormous attention in the fields of microelectronics and composite materials when incorporated appropriately, graphenes can dramatically enhance the electrical, physical, mechanical, and barrier properties of polymer composites at extremely low loadings. For example, functionalized graphene sheets (FGS), single-walled carbon nanotubes (SWNTs), and expanded graphites (EG) were incorporated into poly(methyl methacrylate) (PMMA) thin films to compare the thermomechanical properties. FGS reinforced composites show the best performance (Figure 7.2). This is attributed to the nanoscale surface roughness of graphene sheets which induces an enhanced mechanical interlocking with the polymer chains. The properties of graphene/polymer composites also depend on how well the graphenes can be dispersed into the host polymers. Substantial efforts are now being
made to modify graphene surfaces to improve their processability and their performance as composites.\textsuperscript{17-29}

\textbf{Figure 7.1.} Graphene is a 2D building material for carbon materials of all other dimensionalities. It can be wrapped into 0D fullerenes, rolled into 1D carbon nanotubes, or stacked into 3D graphites. Figure adapted from reference 1.

\textbf{Figure 7.2.} (A) A comparison of thermomechanical property improvements for 1 wt % FGS-PMMA with SWNT-PMMA and EG-PMMA composites. (B) SEM images of EG-PMMA and (C) FGS-PMMA obtained under 3 kV accelerating voltage. Figure adapted from reference 9.
Currently, chemical modification or functionalization of graphene is based on graphenes from pre-prepared graphene oxide. Figure 7.3 shows the general chemical modification process to graft organic molecules onto the surfaces of graphene oxides. The hydroxyl, carboxyl, epoxide, and similar functional groups on the surface of graphene oxides offer an opportunity to functionalize graphene oxides with other molecules. However, the production of graphenes from graphene oxide is a multi-step process involving strong oxidizing and reducing agents. In addition, such prepared graphenes often contain a large amount of defects even after reduction compared to graphenes obtained from other methods. An alternative approach to prepare graphenes is direct exfoliation of natural graphite flakes via sonication in organic solvents, surfactant/water solutions, or ionic liquids. Figure 7.4 shows some typical TEM images of graphene sheets obtained via exfoliation of graphite in surfactant solutions. Both the exfoliation of graphite in liquid phase approach and the chemical oxidation of graphite method rely on the physical effects of ultrasound to break the 3D graphite structure down to a 2D graphene structure.

Figure 7.3. Schematic illustration of the formation of amino bonds between graphene oxides and amine terminated organic molecules. Figure adapted from reference 15.
Figure 7.4. TEM images of graphene sheets obtained by the sonication of graphites in a surfactant solution. (A) A monolayer graphene sheet. (B) A bilayer graphene sheet. (C) A trilayer graphene sheet. (D) A disordered multilayer graphene sheet. (E) A very large flake. Inset: A closeup of an edge of a very large flake showing a small multilayer graphene flake protruding. (F) A monolayer from a sample prepared by sediment recycling. Figure adapted from reference 35.
Ultrasound has found important applications in a diverse range of materials and chemical syntheses.\textsuperscript{40, 41} Both the physical and chemical effects of ultrasound arise from acoustic cavitation: the formation, growth and collapse of bubbles in liquids irradiated with high intensity ultrasound.\textsuperscript{40-42} Localized hot spots with \(~5000~K\) and pressures of hundreds of bars are formed during bubble collapse within liquids irradiated with high intensity ultrasound; these hot spots generate highly reactive species including radicals from sonolysis of solvent vapor.\textsuperscript{43} The chemical effects of high intensity ultrasound which is usually accompanied the mechanical and physical effects of ultrasound, however, have been not been previously utilized in graphene synthesis.

If a reactive medium is chosen as the solvent, the combined mechanochemical effects of high intensity ultrasound can, in a single step, readily induce exfoliation of graphite to produce functionalized graphenes. To obtain high yields of exfoliated graphenes from graphite, the surface energy of the solvent should match the surface energy of graphite, and the optimal solvents therefore have surface tensions of \(\sim 40\) to \(50\) mJ m\(^{-2}\).\textsuperscript{34} In addition, the solvent must also be able to undergo sonochemical reactions during the sonication process to produce radical functionalization of the graphene sheet. Styrene meets these dual criteria, having an appropriate surface tension (\(\sim 35\) dynes/cm at \(0\) °C) and reactive vinyl groups capable of polymerization.\textsuperscript{44} In this chapter, the application of chemical and physical effects of high intensity ultrasound to prepare polymer functionalized graphenes via the sonication of graphites in styrene will be described. A significant component of this chapter is from the following paper: Xu, H. X.; Suslick, K. S. Sonochemical Preparation of Polymer Functionalized Graphenes. J. Am. Chem. Soc. 2011, 133, doi: 10.1021/ja200883z.
7.2 Experimental Methods

The preparation starts with natural graphite flakes (10 mg, Aldrich) in freshly distilled styrene (15 ml, Aldrich), which is then sonicated with high intensity ultrasound using a Sonic & Materials model VCX-750, 1 cm$^2$ Ti horn at 20 kHz and 50 W/cm$^2$ at 0 °C for 2 h under Ar flow. This setup is shown in Figure 7.5. The resulting mixture was then subjected to low speed centrifugation at 1000 rpm for 5 min. The black supernatant was then vacuum-filtered through a 0.22 μm PVDF membrane and washed with tetrahydrofuran (THF). The collected black solids were redispersed in THF and then filtered and washed with excess THF again. This dispersion-filtration-washing cycle was repeated at least three times to remove any residual styrene or polystyrene. The black solid is redispersed in THF and subjected to three more cycles of centrifugation (1000 rpm, 3 min) again to remove large multi-layer graphenes.

Figure 7.5. Experimental setup of the one-step mechanochemical process for exfoliation of graphites and sonochemical functionalization of graphenes.
TEM images were taken with a JEOL 2100 transmission electron microscope with an accelerating voltage of 200 kV. SEM images were taken using a Hitachi S4800 field-emission scanning electron microscope with an accelerating voltage of 10 kV unless otherwise specified. Atomic force microscopy (AFM) images were obtained using a tapping mode from an Asylum Research MFP-3D AFM. Thermal gravimetric analysis (TGA) was conducted on TA Instruments Q600-SDT Simultaneous DSC-TGA, with a heating rate of 10 °C/min under N₂. FT-IR spectra were recorded on a Thermo-Nicolet Nexus 670 spectrometer. X-ray powder diffraction patterns were collected using Cu Kα radiation (λ = 1.5418Å) with a Seimens -Bruker D5000 instrument operating at 40 kV and 30 mA. UV-vis spectra were recorded on Cary 50 UV-vis spectrophotometer. Raman spectra were obtained directly from a thin film of graphene sample deposited onto a Si wafer excited with a 532 nm laser. ¹H NMR spectra were recorded on a Varian Ul400 MHz spectrometer. Gel permeation chromatography (GPC) experiments were performed on a system equipped with an isocratic pump (Model 1100, Agilent Technology, Santa Clara, CA), a DAWN HELEOS 18-angle laser light scattering detector (also known as multi-angle laser light scattering (MALLS) detector, Wyatt Technology, Santa Barbara, CA) and an Optilab rEX refractive index detector (Wyatt Technology, Santa Barbara, CA). XPS spectra were collected with a Kratos Axis ULTRA system.

### 7.3 Results and Discussion

Polystyrene functionalized graphenes were prepared by irradiating natural graphite flakes in freshly distilled styrene (15 ml) with high intensity ultrasound (Figure 7.5). Typical yields of the functionalized graphenes are ~10% based on the initial
graphite used in this small-scale sonochemical synthesis. These polymer functionalized graphenes are very stable, can be easily dispersed into different common organic solvents (~ 2 mg/ml in dimethylformamide, and similarly soluble in THF, toluene and chloroform), and are still soluble in the solvents even after 6 months (Figure 7.6 and Figure 7.7).

![Image of graphene sample in THF after 6 months at room temperature, showing no precipitation. The Tyndall effect (i.e., light scattering) is observed here using a green laser pointer through the graphene solution.](image1)

**Figure 7.6.** Photograph of a graphene sample in THF after 6 months at room temperature, showing no precipitation. The Tyndall effect (i.e., light scattering) is observed here using a green laser pointer through the graphene solution.

![Image of graphene samples suspended in different organic solvents after one week: (A) THF, (B) chloroform, (C) toluene, (D) DMF and (E) more concentrated graphenes in DMF (~ 2 mg/mL). No precipitation is seen.](image2)

**Figure 7.7.** Photograph of graphene samples suspended in different organic solvents after one week: (A) THF, (B) chloroform, (C) toluene, (D) DMF and (E) more concentrated graphenes in DMF (~ 2 mg/mL). No precipitation is seen.
The black graphene colloid solution was investigated by transmission electron microscopy (TEM). TEM samples were prepared by placing a few drops of the solution onto copper grids with an ultrathin holey carbon film. Figure 7.8A and 7.8B show the TEM images of a single-layer and trilayer graphene respectively. The formation of single- and few-layer graphenes was further confirmed by selected area electron diffraction (SAED) (Figure 7.8 insets). The Figure 7.8A inset shows the SAED pattern of the graphene sample, and the {1100} spots appear to be more intense than the {2110} spots which is the fingerprint of single-layer graphenes.\textsuperscript{34, 45} For comparison, in the Figure 7.8B inset, the {2110} spots are more intense than the {1100} spots which is characteristic of multilayer graphenes.\textsuperscript{34, 45} The relative intensity of the {1100} and {2110} spots observed from the single-layer and few-layer graphenes is shown in Figure 7.9. At the same time, folded and disordered graphenes were also observed under TEM (Figure 7.10). Furthermore, TEM analysis of the graphenes revealed that ~80% of the exfoliated graphenes are less than 5 layers, as determined by measuring the distinguishable edges of the exfoliated graphenes (Figure 7.11).\textsuperscript{34, 35, 38}

**Figure 7.8.** TEM images of (A) single-layer graphene and (B) tri-layer graphene with SAED insets confirming single-layer and few-layer graphenes, respectively. Lacey carbon serves as the support.
Figure 7.9. (A) Selected area diffraction electron diffraction pattern and diffraction intensity of a single-layer graphene as shown in Figure 7.8A. (B) Selected area electron diffraction pattern and diffraction intensity of a few-layer graphene as shown in Figure 7.8B.

Figure 7.10. (A and B) Folded and wrinkled single-layer graphene and (C) disordered few-layer graphene observed under TEM.
Atomic force microscopy (AFM) has been frequently employed to measure the thickness of a single layer graphene sheet and was also used here to examine the thickness of these polystyrene-functionalized graphenes. Figure 7.12 shows a graphene sheet with thickness varies from 1.0 to 1.4 nm according to cross-sectional analysis, which is slightly higher than the reported apparent thickness of a single-layer graphene.\textsuperscript{5, 46} This apparent height difference is probably caused by absorbed polystyrene chains on the surface of the graphene. In addition to the thickness difference, the presence of functionalized polymer chains is further supported by the roughened graphene surface. The absorbed polymer chains on the surface of graphene will result in surface roughness because the functionalization sites via radical coupling on the surface of graphene are randomly distributed on the surface.\textsuperscript{47} In contrast, unmodified graphenes always show a smooth and flat surface.\textsuperscript{20} Few-layer graphenes were also observed under AFM characterization (Figure 7.13).
Figure 7.12. (A) AFM image of a functionalized single-layer graphene on Si wafer. (B) Line scan profile along path indicated in (A).

Figure 7.13. AFM image and corresponding height profile of few-layer graphene on Si wafer.

The presence of polystyrene on the surface of graphene was confirmed by the surface characterization techniques. The FTIR spectrum of functionalized graphenes shown in Figure 7.14A shows characteristic absorbance of polystyrene even after exhaustive washing: peaks at 3024, 1602, 1492 cm⁻¹ and combination bands in the range
of 2000 to 1700 cm\(^{-1}\) correspond to the phenyl group, the peaks at 2922 and 2850 cm\(^{-1}\) correspond to the methylene and methenyl groups, and the peaks at 1028 cm\(^{-1}\) correspond to the C-Ph groups.\(^{48}\) The FTIR spectrum of graphite or non-functionalized graphenes does not contain any of those absorbance peaks. This suggests the presence of polystyrene in the functionalized graphenes. In addition, polystyrene standards, sonochemically synthesized polystyrene and polystyrene functionalized graphenes show similar \(^1\)H NMR spectra (Figure 7.15). This further supports the presence of polystyrene on graphenes. Thermal gravimetric analysis (TGA) was used to determine the content of polystyrene in the functionalized graphenes. By comparing the weight loss of functionalized graphenes to graphite, the content of polymer is measured to be about 18 wt % (Figure 7.14B). The molecular weight of polystyrene on the surface of graphene is difficult to measure due to the covalent bonding between polystyrene and graphene. But we can estimate the number average molecular weight (upper limit) from polystyrenes polymerized by sonication of styrene alone at the same conditions which was determined to be \(1.5 \times 10^5\) with a polydispersity index of 2.1 (Figure 7.16).

![Absorbance vs. Wavenumber and Relative Mass vs. Temperature](image)

**Figure 7.14.** (A) FTIR spectra in KBr pellet and (B) TGA of graphite (black line) and polymer functionalized graphene (red line) with a heating rate of 10 °C/min under N\(_2\).
Figure 7.15. $^1$H NMR spectra of (A) polystyrene grafted graphene (B) sonochemically synthesized graphene and (C) polystyrene standard from Aldrich.

Figure 7.16. Gel permeation chromatography (GPC) trace of sonochemically synthesized polystyrene.

Of course, any surface modification of graphene must partially destroy the $sp^2$ hybridization of graphene. In order to probe its overall structural integrity, we have examined the Raman, XPS, and UV-vis spectroscopy of our functionalized graphene. Figure 7.17A shows the Raman spectra of graphite and functionalized graphene. The D band is obvious in polymer functionalized graphene compared to graphite, which
indicates the formation of $sp^3$ hybridized carbon on the graphene surface due to covalent bonding of polystyryl chains to graphene. The G band of polystyrene functionalized graphene shifts to a position slightly higher (~4 cm$^{-1}$) than graphite, while the 2D band of polymer functionalized graphene shifts to a lower position (~8 cm$^{-1}$) together with an intensity increase compared to graphite. This further supports that graphite is exfoliated to single- or few-layer graphenes. The intensity ratio of the $I_D/I_G$ for the polymer functionalized graphene is ~0.78 which is much lower than that of graphene oxide and chemically reduced graphenes. This indicates that the surface of polymer functionalized graphenes is not extensively destroyed. XPS spectra (Figure 7.17B and C) of graphite and polystyrene functionalized graphene show a single peak around 284.5 eV, which is associated with graphitic carbon. No additional signals from C-O or C=O groups are observed which demonstrates that the graphenes are not oxidized; recall that the sonication was carried out under Ar. The structural integrity of graphene is further supported by UV-vis spectroscopy (Figure 7.18). The UV-vis spectrum of polystyrene functionalized graphene in tetrahydrofuran shows a strong absorption peak around 275 nm, which is comparable to reduced graphene oxide after the conjugated graphitic structure has been restored by chemical reduction. This demonstrates that the structure of graphene in the polystyrene modified form has not been extensively modified compared to reduced graphene oxide.
Figure 7.17. (A) Raman spectra of graphite (black line) and polystyrene functionalized graphene (red line). (B) XPS spectra of graphite and (C) polystyrene functionalized graphene.

Figure 7.18. UV-vis spectra of polystyrene functionalized graphene (red line) and sonochemically synthesized polystyrene in THF (black line).
The results of the mechanical/physical effects of ultrasound on graphite are clearly seen in the SEM images (Figure 7.19) of graphite flakes before and after sonication, which show that graphite flakes become smaller and thinner after ultrasonic irradiation. We can even observe a wrinkled graphene absorbed on the surface of Si wafer at low accelerating voltage. From XRD spectra (Figure 7.20), we can see a rhombohedral phase emerges after sonication of graphite flakes in styrene. This new phase is a thermodynamically unstable allotropic form of graphite that arises from the formation of ABCABC stacking of graphene layers instead of normal ABAB stacking sequence (hexagonal). The deformation and exfoliation of graphite are caused by the mechanical shockwaves and shear forces created by the collapse of cavitating bubbles that form during irradiation of ultrasound in liquid. As shown in Figures 7.19 and 7.20, the graphite after sonication indeed has become thinner and the lateral sizes of the pieces become smaller; as a consequence, the intensity of the (002) peak decreases and the FWHM of the (002) peak increases as a result of Scherrer broadening.

The chemical reactivity of the solvent is a key parameter in the sonochemical preparation of functionalized graphenes. We tested a variety of other solvents, including toluene, ethylbenzene, 1-dodecene, and 4-vinylpyridine to prepare functionalized graphenes. Only the easily polymerizable reactants containing vinyl groups, styrene and 4-vinylpyridine, lead to stable functionalized graphenes (Figures 7.21, 7.22, and 7.23). The characterization of poly(4-vinylpyridine) functionalized graphene is presented in Figures 7.24 and 7.25; FTIR demonstrates that the surface of graphenes are grafted by poly(4-vinylpyridine) and the TGA shows that the content of the polymer is ~20 wt %.
Figure 7.19. (A) and (B) SEM images of graphite flakes before sonication. (C) SEM image of graphite after sonication recovered as a precipitate after centrifugation. (D) SEM image of a single-layer graphene with a wrinkled morphology (accelerating voltage is 2 kV).

Figure 7.20. XRD spectra of (A) pristine graphite flakes (as shown in the SEM of Figure 19A and B) and (B) graphite after sonication recovered as a precipitate after centrifugation (as shown in the SEM of Figure 7.19C). After sonication, the graphite indeed has become thinner and the lateral sizes of the pieces become smaller; as a consequence, the intensity of the (002) peak decreased from ~10300 to ~6300 counts and the FWHM of the (002) peak increased from 0.25° to 0.34°.
Figure 7.21. Control experiments with non-polymerizable solvents. Photograph (taken after 1 day) of graphene samples after sonication in different organic solvents: (A) toluene, (B) ethylbenzene, (C) 1-dodecene, and (D) styrene. Stable suspensions are only formed by sonochemical functionalization with styrene.

Figure 7.22. Effect of styrene concentration on functionalization of graphene. Photograph of graphene samples after sonication in: (A) 1 M styrene in 1-dodecane, and (B) styrene after ~24 hours. Sonication in pure styrene is much more effective in producing a permanent suspension.
Figure 7.23. Photograph of poly(4-vinylpyridine) functionalized graphene sample suspended in DMF. Image was taken after one week.

Figure 7.24. (A) A single-layer graphene, (B) a partially folded single-layer graphene and (C) a few-layer graphene observed under TEM from sonication of graphites in 4-vinylpyridine.
Our sonochemical approach is a mechanochemical combination of the mechanical exfoliation of graphite using ultrasound combined with the chemical functionalization of graphenes from sonochemical reactions of the solvent; both of these processes occur at the same time during the sonication. The surface tension of styrene is an excellent match to the surface energy requirements of graphenes; combined with the mechanical forces (from both shear and shockwave) created by the implosive collapse of cavitating bubbles, the breakage and exfoliation of graphite flakes into single- or few-layer graphenes occurs. Radicals formed during sonication of solvent can polymerize the solvent and then couple to the graphene surface to form the polymer functionalized graphenes that we obtain. Alternatively, the surface of graphite may first be functionalized by the radicals followed by exfoliation and further functionalized of the newly exposed graphene face.

**Figure 7.25.** (A) FTIR spectrum of poly(4-vinylpyridine) functionalized graphene in KBr pellet. (B) TGA of poly(4-vinylpyridine) functionalized graphene (under Nitrogen, heating rate at 10 °C/min).
7.4 Conclusions

In summary, a convenient single-step sonochemical approach for the preparation of polymer functionalized graphenes from bulk graphite has been demonstrated using a reactive solvent with appropriate surface tension. The styrene used here serves both as a good solvent for exfoliation of graphite and monomer for formation of reactive polymeric radicals which can react with $sp^2$ hybridized carbon of graphene. The graphitic structure of polymer functionalized graphenes has not been extensively affected. Such functionalized graphenes have good stability and solubility in common organic solvents and have great potential for graphene-based composite materials.

7.5 References


CHAPTER 8

ENGINEERING POROUS CARBON SPHERES FROM ENERGETIC CARBON PRECURSORS VIA ULTRASONIC SPRAY PYROLYSIS

8.1 Introduction

Porous carbon materials have unique physicochemical properties and are now extensively used in gas storage and separation, water treatment, catalysis, and electrode materials for fuel cells, capacitors, and batteries.1-23 Most porous carbons are prepared by carbonization of raw natural materials such as wood, coal, nutshells, etc.1, 24-29 During the carbonization process, most of the oxygen and hydrogen are eliminated via the formation of volatile gaseous products, and the residual carbon atoms form porous structures based on the initial biomass microstructure. The pore structure of carbons prepared in this way can be enhanced by “activation” using either physical or chemical treatments. “Chemical” activation processes usually use chemicals which prevent tar formation and subsequent pore fracture during the carbonization process (e.g., KOH, Na₂CO₃, ZnCl₂, and H₃PO₄). “Physical” activation processes usually use high temperatures (~ 700-1100 °C) with a weakly oxidizing gas (e.g., H₂O or CO₂) to remove active carbon atoms to open and form pores.

Ancient Egyptians and Hindus made porous carbon materials from wood and used them for filtering water and for medical purposes.1 New methods in making porous carbons via carbonization of other carbon precursors such as block copolymers, sugars, or resorcinol-formaldehyde resin aerogels have also been developed.30-35 One of the most recent approaches in synthesizing porous carbon materials is templating because it provides a route to fabricate uniform and predetermined size or structure of carbon
materials. A variety of templates such as porous silicas, metal-organic frameworks, and zeolites have been used for porous carbon synthesis (Figure 8.1). The templating method was first used by Knox and coworkers to prepare porous carbons from a phenol-hexamidine mixture within the pores of a silica gel. The self-assembled structures from block copolymers and surfactants have also been utilized in porous carbon syntheses.
Figure 8.2 shows the SEM images of porous carbon films obtained using Pluronic surfactant F127 (PEO-PPO-PEO) as a template and resorcinol-formaldehyde as the carbon source.46 As the carbonization temperature increases from 400 °C to 800 °C, the surface area and the content of carbon in the porous films dramatically increase.

Aerosol methods, a facile and continuous route to prepare functional materials, have also been developed to prepare porous carbon spheres.48 Ordered mesoporous carbons were prepared using amphiphilic triblock copolymers (e.g., P123) as a soft template and soluble slightly crosslinked phenol resols as the carbon source. The porous structure was formed by self-assembly of the template and precursor during the evaporation process within the aerosol droplets. An additional carbonization process, however, is required to remove the template and obtain a rigid porous carbon structure. Silica colloids were also employed in the aerosol synthesis of porous carbon materials, where the template was removed after carbonization by dissolving in HF.49, 50

**Figure 8.2.** FE-SEM images of carbonized COU-1 using PEO-PPO-PEO (Pluronic surfactant, F127) as template. The carbonization temperatures were: (A) and (B) 400 °C, (C) and (D) 600 °C, and (E) and (F) 800 °C. Figure adapted from reference 46.
A continuous, one-step, and template-free approach to prepare porous carbon spheres with organic salts (e.g., alkali chloroacetates, alkali dichloroacetates, and substituted alkali benzoates) and sucrose with easily dissociated leaving groups (e.g., CO₂, H₂O, and HCl) as carbon precursors via ultrasonic spray pyrolysis (USP) have been developed in the Suslick group. The morphology and structure strongly depend on the types of alkali halocarboxylates used. The inorganic salts formed in situ during the decomposition process act as temporary templates for the evolution of pore structures. For example, the USP products of an aqueous solution of alkali metal chloroacetates are macroporous hollow carbon spheres, whereas the pyrolysis of a lithium dichloroacetate leads to the formation of mesoporous carbon spheres. Thermal analysis of the precursors revealed that the formation of pore structure is closely related to the relative order of melting and decomposition of precursors. Such prepared porous carbon spheres can be used as catalyst supports for direct methanol fuel cells and absorbents for environmental pollutants.

In a typical USP synthesis, individual liquid droplets acting as microreactors pass through a hot furnace by carrier gas, and subsequent solvent evaporation, solute and/or precursor decomposition, and product densification occur. Figure 8.4 shows a typical USP apparatus and a simplified USP process. USP has been widely used in industry for fine powder production and thin film deposition because this process is simple and can be easily scaled up for mass production. In addition, the facile control over the chemical and physical composition in the USP method makes USP particularly useful in the preparation of composite or multicomponent materials.
Figure 8.3. SEM images of USP porous carbon spheres prepared from various precursors: (A) lithium chloroacetate, (B) sodium chloroacetate, (C) potassium chloroacetate, (D) lithium dichloroacetate, (E) sodium dichloroacetate, and (F) potassium dichloroacetate. Figure adapted from reference 51.

Figure 8.4. Schematic illustration of (A) typical USP apparatus and (B) a simplified USP process. Figure adapted from reference 57.
In this chapter, porous carbon spheres with relatively high surface area prepared from energetic carbon precursors, alkali propiolates (i.e., \( \text{CH}≡\text{C-COOM}, \text{M= Li, Na, and K} \)), via ultrasonic spray pyrolysis will be discussed. Because most porous carbon materials are amorphous and require high temperature carbonization, the control over structure and morphology of porous carbons is significantly limited and remains a challenge compared to nanostructured metal and metal oxides and silica-based materials whose structures and morphologies are easy to tailor via colloidal synthesis. The architectures of porous carbon spheres presented here, however, can be easily controlled by adjusting different compositions of alkali salts. Some unprecedented carbon structures, in addition to general hierarchical porous carbons like Janus, jellyfish, yolk-shell, and bowl-like porous carbon spheres, can be prepared by pyrolysis of mixtures of different alkali propiolates.

8.2 Experimental Methods

The experimental setup used in this work is same as the USP apparatus shown in Figure 8.4A.\(^{57}\) The operating frequency of the water nebulizer is 1.65 MHz. The furnace was preheated to the desired temperature (700 °C, unless otherwise noted). Argon was used as the carrier gas at a flow rate of 1 L/min. The carrier gas was flowed through the system for at least 30 min to purge the system prior to the addition of the precursor solution. The black powders obtained by trapping in aqueous bubblers were then washed and centrifuged with deionized water at least 5 times to remove any salt formed during synthesis. The final products were dried overnight in a vacuum oven at 60 °C.
Propiolic acid (95%), lithium hydroxide monohydrate (99.995%), sodium hydroxide (99.99%), and potassium hydroxide (99.99%) were purchased from Sigma-Aldrich and used as received. The precursor solutions were prepared by first dissolving the appropriate amount of acid in water and then adding a stoichiometric amount of an alkali hydroxide solution (e.g., LiOH, NaOH, and KOH). Suspensions were sonicated for 5 min and then stirred for 1 hour to achieve homogeneous solutions. All solutions were prepared at room temperature.

TEM images were taken with a JEOL 2100 transmission electron microscope with an accelerating voltage of 200 kV. SEM images were taken using a Hitachi S4800 field-emission scanning electron microscope with an accelerating voltage of 10 kV. Samples for SEM images were prepared by placing a droplet of ethanol solutions of porous carbon spheres on a Si wafer and drying at room temperature. Focused ion beam (FIB) images were obtained on a FEI Dual Beam 235 FIB. Typical operating conditions were 15 kV and 50 pA. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) was conducted on a TA Instruments Q600-SDT Simultaneous DSC-TGA, with a heating rate of 10 °C/min under Ar. FT-IR spectra were recorded on a Thermo-Nicolet Nexus 670 spectrometer. X-ray powder diffractograms were collected using Cu Kα radiation (λ=1.5418 Å) with a Siemens-Bruker D5000 instrument operating at 40 kV and 30 mA. Raman spectra were obtained directly from a thin film of graphene sample deposited onto a Si wafer excited with a 532 nm laser. Solid state $^{13}$C NMR spectra were recorded on a Varian Unity Inova 300 spectrometer. N$_2$ isotherms and surface area measurements from 3-point BET method analyses were performed on a Quantachrome Instruments Nova 2200e Surface Area and Pore Analyzer. Carbon
samples were degassed under vacuum at 130 °C for 12 hours before analysis. Bulk elemental analysis for CHN and ICP-MS were performed by the UIUC School of Chemical Sciences Microanalysis Laboratory using an Exeter Analytical, Inc. Model CE-440 CHN analyzer and a Perkin-Elmer-Sciex Elan DRCe respectively.

8.3 Results and Discussion

Metal propiolates, which are a class of energetic materials (i.e., the \( \equiv C \) bond contains \(~490 \text{ kJ/mol}\) more energy than the \( \text{C}–\text{C} \) bond), contain facile leaving groups (e.g., \( \text{CO}, \text{CO}_2, \) and \( \text{C}_2\text{H}_2 \)) and produce inorganic salts during decarbonylation or decarboxylation process.\(^{59}\) The decomposition process can be qualitatively described as:

\[
\text{CH}≡\text{CCOOM} \rightarrow \text{M}_2\text{CO}_3 + \text{CO} + \text{CO}_2 + \text{C}_2\text{H}_2 + \text{C} \quad (\text{M} = \text{Li, Na, and K})
\]

Propiolates can polymerize to poly(propiolate) salts when exposed to heat or X- or \( \gamma \)-ray irradiation.\(^{60}\) Voluminous and fragile residues are rapidly produced during thermal decomposition. When mixed with strong oxidants, they can become explosive. Another intriguing feature of metal propiolates is different metal propiolates exhibit different thermal decomposition behaviors. For example, \( \text{Co} (\text{CH}≡\text{CCOO})_2 \) and \( \text{Ni}(\text{CH}≡\text{CCOO})_2 \) will explode upon heating.\(^{59}\) Coupling reactions between two salts occurs in all propiolate salts under a confined state. But the \( \text{Rb}^+, \text{Zn}^{2+}, \) and \( \text{Co}^{2+} \) salts also show coupling reactions in the unconfined state.\(^{59}\) These unique properties of alkali propiolates make them interesting carbon precursors for USP preparation of porous carbon spheres.

Porous carbon spheres were produced using USP of 1 M solutions of \( \text{CH}≡\text{CCOOLi}, \text{CH}≡\text{CCOONa}, \) and \( \text{CH}≡\text{CCOOK} \) as carbon precursors. The structure of the porous carbon spheres produced in this way varies with the choice of the alkali salt.
Droplets containing CH≡CCOOLi yield porous carbon spheres with a thin carbon shell. When CH≡CCOONa is used as precursor, hollow carbon spheres with porous shells are produced. Carbon spheres decomposed from CH≡CCOOK exhibit the similar structure to those decomposed from CH≡CCOOLi but with larger inner pores. SEM images of the porous carbons before washing demonstrate that the inorganic salt byproducts are washed off the surfaces and pores (Figure 8.7). The formation of inorganic salts was confirmed by XRD (Figure 8.8). These salts can be washed off leaving only porous carbon spheres.

**Figure 8.5.** SEM and TEM images of porous carbon spheres prepared by USP of (A and D) 1 M CH≡COOLi, (B and E) 1 M CH≡CCOONa, and (C and F) 1 M CH≡CCOOK.
Figure 8.6. Low magnification SEM images of porous carbon spheres prepared by USP of (A) 1 M CH≡CIGO\(_2\)Li, (B) 1 M CH≡CCOONa, and (C) 1 M CH≡CCOOK.

Figure 8.7. SEM images of porous carbon spheres prepared by USP of (A) 1 M CH≡CCOOLi, (B) 1 M CH≡CCOONa, and (C) 1 M CH≡CCOOK before washing.

Figure 8.8. XRD patterns of porous carbons from (A) CH≡CCOOLi, (B) CH≡CCOONa, and (C) CH≡CCOOK collected at the end of furnace before washing (black). Peaks correspond to the anticipated alkali carbonates (red).
Porous carbon spheres prepared from different alkali salts exhibit similar type-IV isotherms (Figure 8.9). The surface area of porous carbon spheres from different alkali salts increases from 127 m$^2$/g for carbons from CH≡CCOOLi to 591 m$^2$/g and 786 m$^2$/g for carbons from CH≡CCOONa and CH≡CCOOK, respectively. The higher surface area attained in porous carbon spheres from K salts is due to the formation of micropores in the carbon shell as revealed by the N$_2$-isotherm. Pore size distribution measurements reveal that the majority of the pores are <10 nm in diameter (Figure 8.10). TEM confirms that micropores are formed and contribute to the substantially high surface of the internally macroporous carbon spheres (Figure 8.11).

![N2 Isotherms](image)

**Figure 8.9.** N$_2$ isotherms of porous carbon spheres prepared from CH≡CCOOLi, CH≡CCOONa, and CH≡CCOOK via USP.
Figure 8.10. Pore size distribution of porous carbon spheres prepared from (A) 1 M CH≡CCOOLi, (B) 1 M CH≡CCOONa, and (C) 1 M CH≡CCOOK.

Figure 8.11. High magnification TEM image of a carbon sphere prepared by USP of 1 M CH≡CCOOK.

It is interesting that such varied morphologies can be obtained by the choice of different alkali propiolates. This phenomenon is caused by the different thermal decomposition behaviors of precursors, which were determined by simultaneous TGA and DSC (Figure 8.12). For CH≡CCOOK, no melting occurs before the decomposition at 192 °C. The porous carbon network is produced through solid-state reactions. The
diffusion of precursor in the carbon network is limited and large pores are produced upon rapid thermal decomposition. The micropores are formed due to the releasing of gaseous products like CO₂, CO, and C₂H₂ (~13 %) during decarboxylation and decarbonylation process at higher temperatures.⁵⁹

In contrast, for CH≡CCOONa, a melting peak is observed before decomposition starts at 210 °C. The molten salt as produced acts like a template for the formation of a carbon shell, which leads to hollow-structured carbon spheres.⁵¹ The large pores and micropores in the carbon shell are formed by the resulting molten Na₂CO₃ and the slow release of CO₂, CO, and C₂H₂ (~22 %) at higher temperature, respectively.

Melting also occurs before the decomposition of CH≡CCOOLi at 222 °C. The dramatic mass loss (~70 %) during the decomposition of CH≡CCOOLi indicates that this is a very quick thermal transport process. Thus, the decomposition of the molten salt occurs rapidly starting from the surface and immediately transports to the inner core. After thermal decomposition starts, porous carbon structure is produced and the droplet is no longer a liquid phase. Therefore, the melting salt cannot act as a template for the formation of hollow structures but instead leads to the formation of porous spheres with Li₂CO₃ (e.g., decomposed from CH≡CCOOLi) as a temporary template for pore formation. The much smaller amount of released gaseous products (~7 %) at higher temperature explains the lower surface area of porous carbon spheres produced by the decomposition of CH≡CCOOLi compared to porous carbon spheres produced from Na and Li propiolates.

As a control, bulk thermal decomposition of the precursors was also examined and compared to the USP products. Inflated and porous carbon foams are formed during
TGA (Figure 8.13). The spongelike carbon foam is very fragile. The microstructure of the carbon foam is similar to the observed porous carbon spheres with larger dimensions (Figure 8.14) but the USP method is necessary for the formation of spherical morphology. The isolated aerosol droplets generated by the ultrasonic nebulization act like microreactors inside the hot furnace and confine the decomposition process within the microspheres.

**Figure 8.12.** TGA (black) and DSC (blue) curves for (A) CH≡CCOOLi, (B) CH≡CCOONa, and (C) CH≡CCOOK under Ar atmosphere with 10 °C/min heating rate.

**Figure 8.13.** Photographs of voluminous and fragile carbon foams (A) CH≡CCOONa and (B) CH≡CCOOK formed during TGA compared to their original salts.
Figure 8.14. SEM images of thermally decomposed precursors: (A) CH≡CCOONa and (B) CH≡CCOOK.

The size and structure of the porous carbon spheres are also influenced by precursor concentrations. The average size of carbon spheres decreases from ~1 μm to ~200 nm when the CH≡CCOOK solution decreases from 1 M to 0.01 M (Figure 8.15). The size of loose carbon networks is ~100 nm when the precursor concentration is 0.001 M. This is consistent with the Lang equation (Eq. 1).61 When the solution concentration and properties of the generated products are known, the diameter of the obtained carbon spheres can be approximately predicted (Eq. 2).

\[
D_{\text{droplet}} = 0.34 \left( \frac{8\pi \gamma \rho f^2}{\rho_f^2} \right)^{1/3} \quad (1)
\]

\[
D_{\text{particle}} = \left( \frac{MD_{\text{droplet}}^3 C_s}{100\rho} \right)^{1/3} \quad (2)
\]

\(D_{\text{droplet}}\) is average droplet diameter, \(D_{\text{particle}}\) is average particle diameter, \(\rho\) is solution density, \(\gamma\) is surface tension, \(f\) is ultrasonic frequency, \(M\) is molecular weight, and \(C_s\) is solution concentration. The structure also changes when the precursor concentration
decreases. Hollow carbon spheres are produced when the CH≡CCOOK solution concentration changes from 1 M to 0.01 M, but only loose carbon networks, not carbon spheres, are obtained when the concentration is lowered to 0.001 M. The effect of temperature on the morphology was also studied (Figure 8.16). When the temperature was reduced to 500 °C, no solid materials were produced. The bubblers contained a brown liquid, indicating incomplete pyrolysis of the precursor. No dramatic morphology changes are observed when the temperature varies between ~600–800 °C.

![TEM images of porous carbon spheres](image1)

**Figure 8.15.** TEM images of porous carbon spheres prepared from different concentrations of CH≡CCOOK: (A) 1 M, (B) 0.01 M, and (C) 0.001 M.

![SEM images of porous carbon spheres](image2)

**Figure 8.16.** SEM images of porous carbon spheres prepared from USP of 1 M CH≡CCOOK solutions at different temperatures: (A) 500 °C, (B) 600 °C, (C) 700 °C, and (D) 800 °C.
Interestingly, dramatically different structures and morphologies emerge if mixed alkali salts are used as precursors. Figure 8.17 shows representative SEM and TEM images of porous carbon spheres produced from USP of mixed CH≡CCOOLi/CH≡CCOONa solutions. When 0.25 M CH≡CCOO Li and 0.75 M CH≡CCOONa are mixed and used as precursor, Janus carbon spheres with different pore sizes on each hemisphere are obtained (Figure 8.17A, 8.17C, and Figure 8.18A). Jellyfish-like carbon spheres can be produced if the concentration of CH≡CCOO Li is increased (i.e., a mixed solution of 0.75 M CH≡CCOO Li and 0.25 M CH≡CCOONa) (Figure 8.17B, 8.17D, and Figure 8.18B). SEM images of carbon spheres before washing show that the pores were occupied by salts formed from the decomposition of organic ligand (Figure 8.19). N2-sorption measurements show display type-IV isotherms (Figure 8.20). The surface area of carbon spheres decrease from 488 m²/g to 365 m²/g when the concentration of CH≡CCOO Li increases in the mixed solutions. The majority of the pores formed in these carbon spheres are <10 nm (Figure 8.21).
Figure 8.17. SEM and TEM images of porous carbon spheres prepared by USP of (A and C) 0.25 M \( \text{HCOOLi} \) and 0.75 M \( \text{CH≡CCOONa} \), and (B and D) 0.75 M \( \text{CH≡CCOOLi} \) and 0.25 M \( \text{CH≡CCOONa} \).
Figure 8.18. Low magnification SEM images of porous carbon spheres prepared by USP of (A) 0.25 M CH≡CCOOLi and 0.75 M CH≡CCOONa and (B) 0.75 M CH≡CCOOLi and 0.25 M CH≡CCOONa.

Figure 8.19. SEM image of carbon spheres prepared by USP of (A) 0.25 M CH≡CCOOLi and 0.75 M CH≡CCOONa and (B) 0.75 M CH≡CCOOLi and 0.25 M CH≡CCOONa before washing. The SEM and TEM images of corresponding carbon spheres are shown in Figure 8.17.
Figure 8.20. $N_2$ isotherm of porous carbon spheres prepared from mixtures of CH≡CCOOLi and CH≡CCOONa via USP. SEM and TEM images are shown in Figure 8.16.

Figure 8.21. Pore size distribution of porous carbon spheres prepared from (A) 0.25 M CH≡CCOOLi and 0.75 M CH≡CCOONa and (B) 0.75 M CH≡CCOOLi and 0.25 M CH≡CCOONa. SEM and TEM images are shown in Figure 8.17.
When a solution of 0.25 M CH≡CCOOLi and 0.75 M CH≡CCOOK is used as precursor, bowl-like carbon spheres with obvious crack on the edges are obtained (Figure 8.22). Interestingly, for essentially every carbon bowl there is a smaller bowl trapped in the relatively larger outer bowl. We also observed very few carbon spheres with fractured, broken, or collapsed outer shells (Figure 8.23). This observation together with crack on the edge of the carbon spheres indicates that the double-bowl like carbon spheres are formed from the fracture of double-shell carbon spheres (Figure 8.23C). The formation of this carbon structure is schematically illustrated in Figure 8.24. Carbon spheres collected at the end of the furnace tube before washing exhibit intact spherical morphology (Figure 8.25), which further proves that the bowl-like morphology is from the fracture of intact spherical double-shell carbon spheres in bubblers or in the workup process. Interestingly, slow evaporation of a diluted ethanol solution containing bowl-like carbon spheres can induce the self-assembly of them to form a thin film with strict orientation on a silicon wafer (Figure 8.26). The surface area of double-bowl like carbon spheres is measured to be 550 m²/g. The N₂-sorption measurement of these porous carbon spheres displays a type-IV isotherm (Figure 8.27A). BJH pore size distribution indicates that the majority of the pores are <10 nm (Figure 8.27B). Varying the ratio of the CH≡CCOOLi and CH≡CCOOK leads to the formation of similar bowl-like morphologies. For example, crumpled bowl-like carbons are produced from USP of a precursor solution with equal concentration of CH≡CCOOLi and CH≡CCOOK (Figure 8.28).
Figure 8.22. (A) SEM and (B) TEM images of porous carbon spheres prepared by USP of 0.25 M CH≡CCOOLi and 0.75 M CH≡CCOOK. (C) Low magnification SEM images of above porous carbon spheres.

Figure 8.23. (A) SEM image of a broken carbon sphere. (B) SEM image of a carbon sphere with broken outer shell capped an inner sphere. (C) TEM image of a double-shell carbon sphere. (D) SEM and (E) TEM image of collapsed double-shell carbon sphere. The carbon precursor for above carbon spheres is 0.25 M CH≡CCOOLi and 0.75 M CH≡CCOOK.

Figure 8.24. Schematic illustration of the formation of double shelled carbon bowl structure.
Figure 8.25. SEM image of carbon spheres prepared by USP of 0.25 M $\text{C}_2\text{H}_3\text{COOLi}$ and 0.75 M CH≡CCOOK before washing.

Figure 8.26. (A) SEM image of self-assembled bowl-like carbon spheres on a silicon wafer via solvent evaporation process. (B) SEM image of bowl-like carbon spheres accumulated randomly without orientation.
Figure 8.27. (A) N\textsubscript{2} isotherm and (B) pore size distribution of porous carbon spheres prepared from mixtures of CH≡CCOOLi and CH≡CCOOK. SEM and TEM images are shown in Figure 8.20.

Figure 8.28. Crumpled carbon bowl-like carbon spheres observed from 0.5 M CH≡CCOOLi and 0.5 M CH≡CCOOK.

Carbon spheres with yolk/shell or rattle-type structure are produced when a solution of 0.25 M CH≡CCOONa and 0.75 M CH≡CCOOK is used as a precursor (Figure 8.29). The preparation of yolk/shell structures typically requires the formation of
core/shell structure followed by the generation of void through the Kirkendall effect (i.e., the movement of boundary layer as a consequence of the difference in diffusion rates of different atoms) or Ostwald ripening processes (i.e., small crystals or sol particles dissolve, and redeposit onto larger crystals or sol particles over time).\textsuperscript{62-65} The templating approach was also developed to prepare yolk/shell structure with silica as the permeable shell which grows on the micelles containing smaller particles prepared from self-assembly of surfactants.\textsuperscript{66, 67} Our preparation of yolk/shell structured carbon spheres, however, is a one-step process without the use of additional templates. The surface area of such prepared yolk/shell structure is highest among all the carbon spheres and is measured to be 850 m\textsuperscript{2}/g. N\textsubscript{2}-sorption measurement of above porous carbon spheres exhibit type-IV isotherm and BJH pore size distribution indicates that the majority of the pores are <10 nm (Figure 8.30).

\textbf{Figure 8.29.} (A) SEM, (B) TEM, and (C) FIB images of porous carbon spheres prepared by USP of 0.25 M CH≡CCOONa and 0.75 M CH≡CCOOK. (C) Low magnification SEM images of above porous carbon spheres.
Figure 8.30. (A) N\textsubscript{2} isotherm and (B) pore size distribution of porous carbon spheres prepared from mixtures of CH≡CCOONa and CH≡CCOOK. SEM and TEM images are shown in Figure 8.29.

When CH≡CCOOLi, CH≡CCOONa, and CH≡CCOOK are mixed at a ratio of 1:1:1, hollow carbon spheres can be obtained (Figure 8.31). The N\textsubscript{2}-sorption measurement of these porous carbon spheres exhibits a type-IV isotherm (Figure 8.32A) and a surface area of 433 m\textsuperscript{2}/g. BJH pore size distribution indicates the majority of the pores are between 3~10 nm (Figure 8.32B).

Figure 8.31. (A) SEM and (B) TEM images of porous carbon spheres prepared by USP of 0.33 M CH≡CCOOLi, 0.33 M CH≡CCOONa, and 0.33 M CH≡CCOOK. (C) Low magnification SEM images of above porous carbon spheres.

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Figure 8.32. (A) N₂ isotherm and (B) pore size distribution of porous carbon spheres prepared from mixtures of CH≡CCOOLi, CH≡CCOONa, and CH≡CCOOK. SEM and TEM images are shown in Figure 8.31.

The mechanism for the formation of such dramatically different morphologies observed from pyrolysis of mixed alkali propiolates is difficult to explain due to the complex thermal decomposition behaviors of precursors, but it is certain that this phenomenon is caused by the interaction of melt formation by the salts and the complex decomposition pathways of mixed alkali propiolates. Here speculative explanations for the formation of unique carbon morphologies are presented. Mixed CH≡CCOOLi/CH≡CCOONa shows a single sharp decomposition peak at 202 °C (Figure 8.33A) which is lower than that of the individual alkali propiolates. No melting is observed when the two salts are mixed, although melting occurs before the thermal decomposition of Li or Na propiolate alone. It is likely that eutectic-like salts are formed after the evaporation of water, and a phase separation occurs, which yields Janus carbon spheres. Mixed CH≡CCOOLi/CH≡CCOOK also shows a single sharp decomposition
peak at 172 °C (Figure 8.33B) which is much lower than the melting point of the corresponding individual salts (e.g., \(\text{CH≡CCOOLi}\) decomposes at 222 °C and \(\text{CH≡CCOOK}\) decomposes at 192 °C). There are two exothermic peaks observed on the DSC curve indicating two decomposition events occur: decomposition of the eutectic salt at a lower temperature and decomposition of \(\text{CH≡CCOOK}\) at the higher temperature. Because melting cannot be observed before decomposition starts, the decomposition process undergoes a solid state. The thermal decomposition of two different salts leads to the formation of a double-shell structure. \(\text{CH≡CCOONa/CH≡CCOOK}\) mixtures which produce yolk/shell structures also shows two decomposition peaks on the DSC curve (Figure 8.33C): decomposition of the eutectic salt at a lower temperature and decomposition of the K salt at a higher temperature which leads to the formation of a yolk/shell structure. No melting occurs before the decomposition of two salts together.

When all of the three alkali salts are mixed, only one decomposition peak occurs after melting (Figure 8.33D). The melting temperature is lower than each individual alkali propiolate. The hollow structure is formed due to the templating effect of the molten eutectic salt. The pores observed in each carbon sphere are caused by the inorganic salts generated during precursor decomposition. The black solids collected before washing show comparatively nonporous solid whose pores are presumably clogged by salt; upon washing, the salts dissolves and the porous structure revealed.

Similar to the decomposition of individual alkali propiolates, the thermal decomposition of mixed alkali propiolates generates alkali carbonates as confirmed by XRD (Figure 8.34). This method provides a convenient approach for the preparation of porous carbon spheres. Unlike many of the other techniques being developed elsewhere,
no tedious and expensive templating methods are required in this approach. Instead, the inorganic salts formed in situ during precursor decomposition act as temporary templates and can be easily washed out during workup.

**Figure 8.33.** TGA (black) and DSC (blue) curves for (A) 0.25 M CH$\equiv$CCOOLi and 0.75 M CH$\equiv$CCOONa, (B) 0.25 M CH$\equiv$CCOOLi and 0.75 M CH$\equiv$CCOOK, (C) 0.25 CH$\equiv$CCOONa and 0.75 M CH$\equiv$CCOOK, and (D) 0.33 M CH$\equiv$CCOOLi, 0.33 M CH$\equiv$CCOONa, and 0.33 M CH$\equiv$CCOOK under Ar atmosphere with 10 °C/min heating rate.
Figure 8.34. XRD patterns of porous carbons from (A) 0.25 M CH≡CCOOLi and 0.75 M CH≡CCOONa, (B) 0.25 M CH≡CCOOLi and 0.75 M CH≡CCOOK, (C) 0.25 M CH≡CCOONa and 0.75 M CH≡CCOOK, and (D) 0.33 M CH≡CCOOLi, 0.33 M CH≡CCOONa, and 0.33 M CH≡CCOOK collected at the end of furnace before washing (black). Peaks correspond to the anticipated alkali carbonates.

Porous carbon spheres produced in this approach are amorphous and contain functional groups. Powder XRD shows these porous carbon spheres to be amorphous both before and after annealing at 800 °C under Ar atmosphere (Figure 8.35). Bulk elemental analysis reveals that such prepared carbon spheres contain 75–87 wt % C, 1–2 wt% H and 10–26 wt % O (by difference) before annealing. Solid state MAS $^{13}$C NMR spectra of porous carbon spheres show characteristic resonance peak at $\sim$130 ppm.
corresponding to polyaromatic carbon in amorphous C:H materials (Figure 8.36). Two small resonance peaks around 60 ppm and 195 ppm are assigned to acetylenic groups and carboxylic or ketonic groups, respectively.

This observation is consistent with the results from infrared spectroscopy study (Figure 8.37). The absorption at 3450 cm\(^{-1}\) corresponds to the \(\nu(O-H)\) stretch from hydroxyl groups. The weak absorption at 3150 cm\(^{-1}\) is from aromatic C-H. There is an absorption at 1630 cm\(^{-1}\) from \(\nu(C=C)\) and an absorption from 1380 cm\(^{-1}\) from anti-symmetric carboxylic acid vibrations. Raman spectra of such porous carbon spheres contain two broad peaks at \(~1360\text{ cm}^{-1}\) and \(~1600\text{ cm}^{-1}\) which are consistent with defect (D) and graphitic bands (G) (Figure 8.38). The D band is the disordered peak characteristic of \(sp^3\) bonded amorphous carbon while the G band is characteristic of well-ordered, crystalline \(sp^2\) bonded carbon. The ratio of D and G bands can be taken as a measurement of the relative crystallinity of a carbon material.\(^{68, 69}\) Raman analysis of the D:G ratio for porous carbon spheres synthesized by USP of different alkali propiolates indicates that there is no dramatic difference between porous carbon spheres prepared from different alkali precursors.

In addition, acetylenedicarboxylic acid, which is dicarboxylic acid form of the propiolic acid, can also be used as the carbon precursor for preparation of porous carbon spheres. The SEM and TEM images of porous carbon spheres produced from pyrolysis of alkali salts of acetylenedicarboxylic acid are shown in Figure 8.39. The morphologies of the porous carbon spheres prepared from above alkali salts are the same as the carbon spheres prepared from the corresponding alkali propiolates.
Figure 8.35. XRD spectra of porous carbon spheres prepared from USP of 1 M HC≡CCOOK before and after heat treatment at 800 °C under Ar for 12 hours.

Figure 8.36. MAS $^{13}$C NMR spectrum of porous carbon spheres prepared from USP of 1 M HC≡CCOOK.
Figure 8.37. FTIR spectra of porous carbon spheres obtained from USP of (1) HC≡CCOONa, (2) HC≡CCOOLi, (3) HC≡CCOOK, and (4) 0.25 M CH≡C-COOLi and 0.75 M CH≡C-COONa.

Figure 8.38. Raman spectra of porous carbon spheres obtained from USP of (1) HC≡CCOONa, (2) HC≡CCOOLi, (3) HC≡CCOOK, (4) 0.25 M CH≡C-COOLi and 0.75 M CH≡C-COONa, (5) 0.25 M CH≡C-COONa and 0.75 M CH≡C-COOK, and (6) 0.25 M CH≡C-COOLi and 0.75 M CH≡C-COOK.
Figure 8.39. SEM and TEM images of porous carbon spheres prepared by USP of (A and D) 1 M LiOOC≡COOLi, (B and E) 1 M NaOOC≡COONa, and (C and F) 1 M KOOCC≡COOK.

8.4 Conclusions

A convenient synthetic approach to prepare porous carbon spheres with unique and unprecedented morphologies has been demonstrated using energetic carbon precursors via ultrasonic spray pyrolysis. The unique decomposition behaviors of alkali propiolates and their mixtures lead to dramatically different carbon structures and morphologies. Engineering the porous carbon spheres can be achieved through controlling the compositions of the alkali propiolates without using templates. The high surface areas and unique porous structures suggest that they could be used as adsorbents,
catalyst supports, or for other applications by integrating other functional materials into their pores.

8.5 References


AUTHOR’S BIOGRAPHY

Hangxun Xu was born in Zhejiang, China, in 1983. He obtained his B.S. degree in polymer chemistry from the University of Science and Technology of China (USTC) in 2006. His work at USTC included the polymer functionalization of carbon nanotubes via $\gamma$–ray irradiation, structural fixation of vesicles and wormlike micelles via polymerization, and incorporation of noble metal nanoparticles inside unimolecular micelles with controlled spatial distribution. He was awarded the best B.S. thesis award from the university. He was also the recipient of the prestigious 25th Guo Moruo Scholarship which is the highest honor for undergraduate students at USTC.

After earning his B. S. degree in 2006, he came to the United States and started his Ph.D. study in Materials Chemistry working under the supervision of Professor Kenneth S. Suslick at the University of Illinois at Urbana-Champaign. In the Suslick research lab, his research primarily focuses on the light emission and materials synthesis based on the chemical and physical effects of ultrasound. His achievements include: experimentally validated injected-droplet model for the excitation of nonvolatile species during acoustic cavitation, applied molecular emissions to measure emission temperatures during sonoluminescence, synthesized water-soluble fluorescent silver nanoclusters via sonochemical method, fabricated polymer functionalized graphenes using mechanochemical approach, and prepared porous carbon spheres from energetic carbon precursor via ultrasonic spray pyrolysis. For his academic performance, he was awarded the graduate college fellowship and the 2010 Chinese Government Award for Outstanding Self-Financed Students Abroad.