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TIP-BASED ADVANCED CHARACTERIZATIONS OF VAN DER WAALS MATERIALS
FOR ENHANCED FUNCTIONALITY

BY

MD FARHADUL HAQUE

DISSERTATION

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Doctoral Committee:

Associate Professor SungWoo Nam, Chair
Professor Placid Ferreira
Associate Professor Arend van der Zande
Professor Catherine J Murphy

ABSTRACT

Two-dimensional (2D) van der Waals (vdW) materials have unique properties compared to conventional bulk materials. For example, transition metal dichalcogenides (TMDs) show bandgap energy transition from indirect to direct as their thickness is reduced to the monolayer limit. Reducing thickness also yields higher carrier mobility in 2D materials because of the confinement of a 2D surface along out-of-plane direction which results in reduced scattering of charge carriers (e.g., electron-phonon scattering). Enhanced electromechanical actuation has been demonstrated in nanoscale structures of three-dimensional materials compared to their bulk counterparts due to the large “free surface” effect. Probing such emerging properties at the nanoscale and investigating how they are correlated require advanced characterization techniques with atomic-scale precision. Often the spatial resolution of the characterization technique is limited by the resolution of the detection scheme. Therefore, I adopted advanced tip-based characterization technique to probe the unique plasmonic and electromechanical properties of 2D vdW materials at sub-30 nm spatial resolution.

First, I investigated plasmonic resonance tunability of a crumpled graphene using photo-induced force microscopy (PiFM). PiFM is an effective technique for probing light-matter interaction at a sub-20 nm spatial resolution. By applying uniaxial compressive strain, we created crumpled structures of graphene with controlled topographic features (e.g., wavelength, aspect ratio) on a polymeric substrate. I observed a wide tunability of plasmon resonance wavelength (5.77-10.93 μm) which we attributed to both the variation in topography as well as efficient coupling with the incident photon. Our observed plasmon resonance followed a redshift trend with an increase in wavelength and aspect ratio of the crumples, which agrees well with our

established numerical model. Finally, we demonstrated enhanced chemical imaging of a polymethyl methacrylate (PMMA) film aided by the effective plasmon resonance of the underlying crumpled graphene structure. The coupling between PMMA phonon and graphene plasmon showed a two-fold increase in the obtained near-field optical response. Our results suggest widely tunable, plasmonically-enhanced biosensing or spectroscopy in the infrared range.

Next, I studied the electromechanical response driven by converse flexoelectric effect (CFE) of monolayer molybdenum disulfide (MoS_2) and tungsten diselenide (WSe_2) using piezoresponse force microscopy (PFM). PFM is a popular technique for probing electromechanical response at a sub-30 nm spatial resolution. PFM measurements revealed strongly enhanced CFE of the atomically thin MoS_2 and WSe_2 than their bulk counterpart ($\sim 700\%$ enhancement in MoS_2 , $\sim 400\%$ enhancement in WSe_2). The bilayer MoS_2 and WSe_2 exhibited a 50% larger CFE than monolayer samples. Finite element analysis suggested that a puckering deformation during PFM measurement could suppress the CFE of the monolayer structure by $\sim 70\%$. By inducing a built-in in-plane tension to reduce puckering, I observed a $\sim 46\%$ increase in the CFE of monolayer WSe_2 . Our findings can help understanding the fundamentals of flexoelectric behavior in 2D materials.

Finally, I extended my study on electromechanical response on artificially stacked 2D vertical heterostructure. PFM measurement revealed almost five times enhancement in the electromechanical response on a $\text{MoS}_2/\text{WSe}_2$ vertical heterobilayer structure compared to the standalone MoS_2 monolayer. I investigated the underlying mechanism behind the enhancement in light of charge transfer induced built-in dipole and the interlayer coupling strength. The charge transfer was qualitatively estimated by Kelvin probe force microscopy (KPFM). KPFM is a

popular technique to probe surface potential at sub-20 nm spatial resolution. The interlayer coupling strength was estimated from the Raman and photoluminescence spectroscopy. The detailed analysis suggested that both charge transfer and interlayer coupling strength are responsible for the augmented electromechanical response of the heterostructure. The obtained knowledge is beneficial for next generation nanoscale actuator or energy harvesting devices.

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To my family

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CHAPTER 1: ENHANCED FUNCTIONALITIES OF TWO-DIMENSIONAL MATERIALS

1.1 Introduction

Two-dimensional (2D) materials, often termed van der Waals (vdW) materials, possess a wide variety of electronic properties spanning from insulating to superconductivity^[1]. These materials are formed in a layered structure where the layers are adhered via vdW force. Due to the weak vdW forces between the layers, these materials can be exfoliated from their bulk counterpart down to a single layer limit^[2]. The layer-by-layer formation of the vdW materials allows the researchers to investigate the layer dependent electrical, mechanical, or wetting properties^[3–6]. For example, 2D materials exhibit high electron mobility compared to the conventional bulk materials^[7]. The optical band gap of transition metal dichalcogenides (TMDs) undergoes from indirect to direct as the thickness is reduced to the single layer limit^[8,9]. Furthermore, the reduction in thickness reduces electron scattering along the out-of-plane direction of 2D materials, thereby altering the electron mobility^[10]. Due to the atomic-thinness, 2D materials possess extremely low bending stiffness due to weak out-of-plane vdW bonds yet have high in-plane Young's modulus due to strong in-plane covalent bonds^[11]. Such unique features enable advanced functionalities in 2D materials. For example, enhanced electromechanical (EM) response has been reported from deformed monolayer transition metal dichalcogenide (TMD) compared to the flat structure due to the bending induced enhanced EM response (known as flexoelectric effect)^[12]. Apart from the electrical and mechanical properties, 2D vdW materials also exhibit strong light-matter interaction compared to the conventional bulk materials. For example, twisted bilayer graphene can be used as a photonic crystal due to ultra-strong light-matter interaction and periodic variation in optical conductivity^[13]. Exploring such

unique functionalities requires advanced characterization techniques. In this thesis, I have investigated enhanced functionalities of 2D vdW materials by tip-based advanced characterization techniques. In this chapter, I will highlight two advanced functionalities in 2D materials. First, I will discuss strong light-matter interaction (i.e., plasmonic effect) of graphene. Second, I will discuss enhanced electromechanical properties (i.e., flexoelectricity) of nanoscale materials.

1.2 Graphene plasmon

Plasmons are the collective oscillation of electron density or electron gas at the surface of a metal or interface of a metal-dielectric subjected to an external electromagnetic field. The plasmonic oscillation at the material surface or interface creates confined electromagnetic field. This is called surface plasmon polariton (SPP). SPP is a common phenomenon often found in metal surface or semi-metal such as in graphene^[14,15]. Graphene plasmon has three distinct advantages over conventional metal plasmon^[16,17]. First, graphene plasmon has low loss due its exceptionally high electron mobility. Second, graphene has ultra-high light confinement since the plasmonic wavelength can be two orders of magnitude smaller than the incident light. And third, graphene plasmon wavelength can be widely tunable via structural modulation or electrostatic doping. Therefore, graphene plasmon has favorable aspects for applications such as biosensing, light-harvesting, or spectroscopy^[18,19]. Graphene plasmon cannot be directly excited by incident light due to the large momentum mismatch between the plasmon and incident photon. Some popular ways to excite the graphene plasmon are introducing edges via micro/nano patterning, defects, selective doping and spatial modulation of the electric potential.

1.2.1 Graphene plasmon in micro/nano patterned structures

Introducing edges on graphene is an effective way to confine the SPP and induce plasmon resonance^[14–16,20]. The plasmon frequency shifts from terahertz to mid-IR when the graphene structure is reduced to ~ 100 nm scale range. At such small length scale, atomic force microscopy (AFM) coupled with a light illumination set up can be an ideal tool for probing the graphene SPP. In AFM-IR, a metallic AFM tip is used to launch SPPs on graphene, and SPPs are reflected from the graphene edges and create standing waves between the tip and edge. In case of patterned graphene on a carbon terminated surface of 6H-SiC substrate, incident light with a wavelength of $9.7\text{ }\mu\text{m}$ was used to excite graphene plasmon when the graphene structure was reduced to ~ 300 nm^[16]. The near-field image revealed fringe patterns due to the standing wave. The distance between two maxima in the fringe pattern denoted twice the plasmonic wavelength. The plasmon wavelength reported in this study was $1/40^{\text{th}}$ of the wavelength of the incident light, thereby showing strong light confinement of graphene. The study also revealed a strong dependence of the plasmon wavelength on the permittivity of the substrate. By increasing the dielectric constant of the substrate, the plasmon wavelength was reduced. Another report showed that ribbon shaped nanostructures exhibit polarization dependency of graphene plasmon^[20]. Localized plasmon was excited when the incident light was perpendicular to the nanoribbon length. If the light is parallel to the nanoribbon length, light-matter interaction was weakened due to Pauli blocking of the interband transition. The localized plasmon resonance modes were captured by the multiple peaks in the extinction spectra of the nanoribbon structure.

The shape and width of the nanoribbon also play significant roles in capturing localized plasmon resonance^[15]. For graphene nanoribbon with varying ribbon width, near-field images revealed two distinct resonance modes occurred as the width of the nanoribbon was reduced and

converged into a sharp edge. The resonance modes were observed as two bright spots in the near-field image when the plasmon wavelength (~ 200 nm) was larger than the ribbon width. As the incident light was blueshifted, the location of the resonance was moved away from the edge and towards the wider section of the ribbon. Depending on the ribbon width, the reflected plasmonic wave from the edges interacted with each other to form constructive or destructive interference, resulting in a bright or dark spot on the nanoribbon in the near-field image. In another study, an incident polarized laser at 1184 cm^{-1} excitation frequency was directed at graphene nanoribbon on a Al_2O_3 substrate (**Figure 1.1a**)^[14]. When the electric field (E-field) is parallel to the ribbon length, only SPP of graphene are active. The corresponding fringe pattern in the near-field image was symmetric across the ribbon width. When E-field is perpendicular to the ribbon length, surface plasmon resonance (SPR) was activated by the confined area and interacted with the SPP. The corresponding fringes showed asymmetric patterns across the ribbon width. This asymmetry came from the coupling between SPR and SPP excitation. For wider (narrower) ribbon, the left (right) fringe was stronger. This shift from left to right in intensity enhancement was associated with different SPR mode. For wider ribbon, the direction of out-of-plane E-field (E_z) was both downward and upward at both side of the ribbon. On the contrary, E_z on the narrower ribbon was upward on the right edge and downwards on the left edge, thereby inducing different SPR modes.

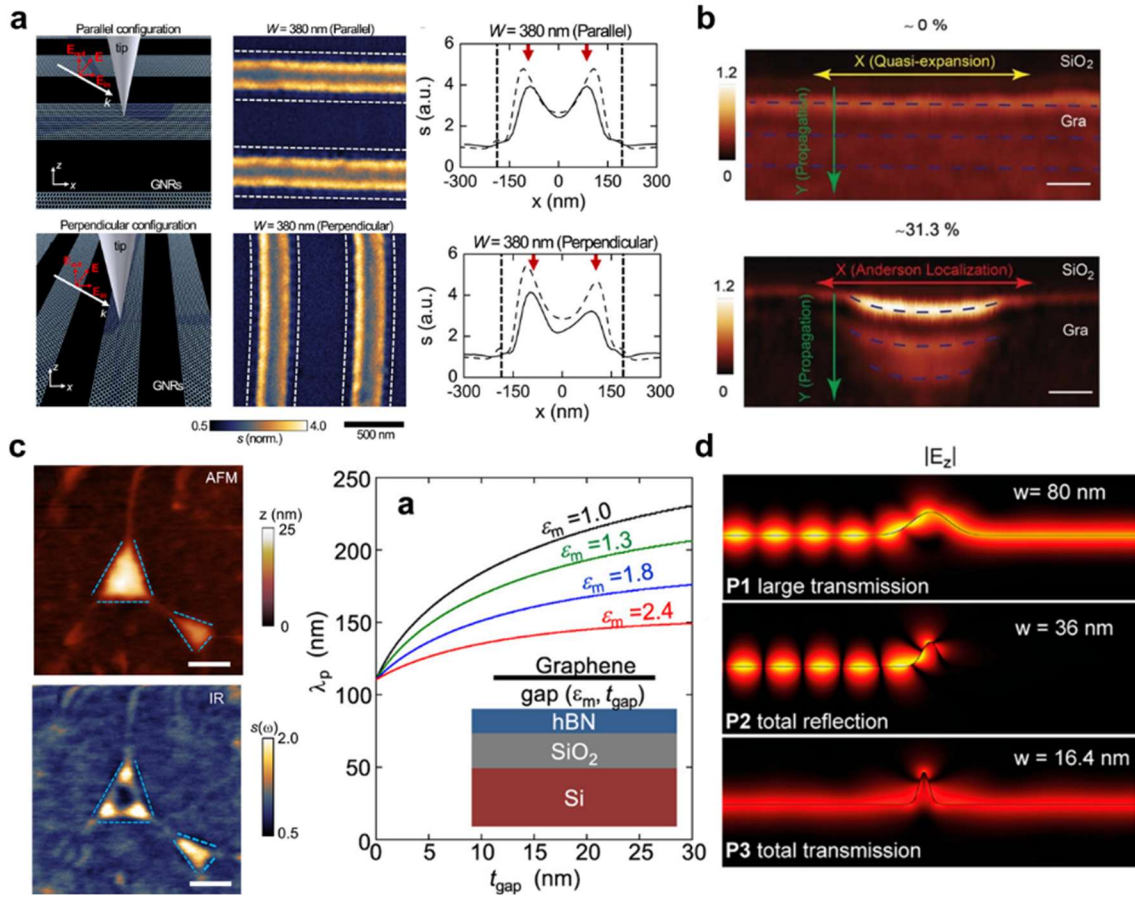


Figure 1.1. Interaction of graphene plasmon with different structural modulation. **a**, AFM-IR images of graphene nanoribbon at two different excitation configuration showing the orientation dependent near-field intensity^{1, [14]}. Schematics of the AFM-IR imaging (left), near-field images (middle) and line profile of the near-field images (right) when electric field of the excitation is parallel (top) and perpendicular (bottom). The ribbon edge and fringe locations are denoted by the dashed line and red arrows on the line profiles. Laser excitation frequency was 1184 cm^{-1} . **b**, Near-field images of pristine or quasi-expansion (top) and highly disordered or Anderson localized (bottom) graphene at 901 cm^{-1} excitation comparing the plasmonic confinement between the two graphene edges^[21]. The blue dashed lines represent the fringe pattern. Scale bar is 300 nm. **c**, AFM topography (top left) and nano-IR image (bottom left) of graphene nanobubble at 910 cm^{-1} excitation showing plasmonic confinement at the bubbled region^{2, [22]}. The boundaries of the nanobubble are shown in blue dashed line in the nano-IR image. Scale bar is 200 nm. Right panel shows the theoretical calculation of plasmon wavelength and dispersion diagram of the graphene nanobubble structure. The bubble area is represented by the gap shown the inset schematics. **d**, Interaction of plasmon wave with a graphene wrinkle with three different widths (W)^{3, [23]}.

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1.2.2 Interaction of graphene plasmon with defects

Graphene plasmon can interact with defects due to an inhomogeneity in the density of states^[21]. An example of such intrinsic defect is Anderson localization which originates from a defect in lattice and causes charge localization due to the disorder of the tensile strain. J. Duan *et al.* reported that whereas the near-field image of a defect-free graphene showed the typical fringe pattern, a relatively highly disordered (Anderson localized) graphene showed finite confinement in the near-field (**Figure 1.1b**). The localization length along the graphene edge for disordered and defect-free graphene were 247.3 nm and infinity, respectively. The localization length was independent to the frequency of incident light. The plasmonic wavelength was unchanged for quasi-expansion case (216.7 nm) and the Anderson localization (220 nm) due to the similarity in doping level of these two cases. The near-field confinement (along the graphene edge) observed on disordered graphene can be explain through the scattering behavior of the plasmon. The scattering behavior of the plasmon was characterized by the factor $k_p l^*$ ($k_p l^*=1$ for ideal scattering and higher value suggests reduced scattering), where k_p and l^* are the wavevector and mean free path of the plasmon, respectively. Defect-free graphene had $k_p l^*=30$, meaning minimal scattering. However, mean free path was much smaller for the disordered graphene (44.1 nm) than the defect-free graphene (200 nm). The $k_p l^*$ for Anderson localization (disordered graphene) was 1.1, meaning strong scattering occurred at the disorder state.

Graphene plasmon can be localized by interacting with defects such as topographic wrinkles, bubbles or blisters^[22–24]. Such defects are originated during transferring 2D vdW materials from one substrate to another. In the case of a bubble on a graphene-hBN heterostructure, plasmonic hotspots were formed near the corners of the blisters (**Figure 1.1c**)^[22]. The hotspots occurred due to the change in dielectric environment at the interface between the

corners bubble and flat graphene region. Since the bubble formation caused a gap between the graphene and the underlying substrate, corresponding dielectric environment was altered compared to the flat graphene on a substrate without a gap. The reduction of the dielectric constant due to the gap formation led the increase in local plasmon wavelength. The upshift in the plasmon wavelength was also maintained with the increase in the gap size. Another study showed that the incident plasmon wave on graphene was reflected or transmitted across a wrinkle or corrugation (**Figure 1.1d**)^[23]. For a smooth corrugation (width $\gg$ height of the corrugation), the scattering of plasmon depended on the dielectric environment. The scattering suggested a blueshift in the reflectance spectral peak as the width of the corrugation was increased. Therefore, the change in the reflectance was attributed to the change in the dielectric environment. However, the nature of scattering was quite different for a sharp corrugation (width $<$ height of the corrugation). If the width of the corrugation is wider than half of the plasmon wavelength, partial reflection occurred with fringe pattern on the incident side of the corrugation. As the corrugation width was further reduced, partial reflection was changed into a total reflection with minimal transmission. Continuing reduction of the corrugation width suggested total transmission in the case of sharp corrugation.

The SPP of graphene can enhance infrared (IR) absorption with the aid of strained bubbles^[24]. In the case of graphene-hBN interface, stronger IR absorption was reported on the bubbled and wrinkled regions. The absorption was dependent to the wavelength (or frequency) of the illumination, *e.g.*, stronger absorption was observed at 1000 cm⁻¹ whereas weaker absorption was reported at 1362 cm⁻¹. The hydrostatic strain and shear strain maps confirmed that the regions under bubbles had higher strain than the surrounding region. The higher strain induced different level of doping into the bubbles which was supported by the Fermi energy

map. The Fermi energy map suggested that the bubbles were doped with energy higher than the Pauli blocking. Since, graphene doped beyond Pauli threshold supports SPP, the origin of enhanced absorption was attributed to the SPP of graphene on the strained bubbles.

1.2.3 Investigating graphene plasmon by selective doping

The plasmon wavelength of graphene can be modulated by selective doping^[25,26]. Terahertz (THz) plasmon in graphene was studied by photocurrent measurement aided by inducing selective carrier concentration^[25]. Graphene was sandwiched between hBN. A narrowly separated pair of gold pad was placed under the sandwich to induce different level of carrier concentration. Then the plasmon was activated by a THz laser in s-SNOM technique. When the tip launched THz plasmon, it bounced back from the graphene edges. The graphene edge was artificially created by applying different bias at the pad to induce opposite level of carrier concentration, thereby creating a sharp pn junction in the graphene between the pads. The incident graphene plasmon interacted with the reflecting plasmon from the edge, thereby creating a local energy dissipation. The dissipated energy heated up the pn junction, induced photoinduced current with oscillation half of plasmon wavelength. The oscillation decreased with increasing incident frequency. The oscillation showed a linear correlation with the incident frequency, thereby indicating acoustic THz plasmon was observed. In another study, selective doping on graphene was obtained by transferring the graphene onto a patterned dielectric-Au ribbon, thereby creating a periodic ridge (conformal graphene) and trench (suspended graphene) structure^[26]. The plasmon wavelength on the ridge and trench area were different due to different doping level (**Figure 1.2a**). As a result, selective plasmon resonance conditions were obtained on the ridge and trench areas. Specifically, plasmon confinement was observed at the ridge area

(supported graphene) with the incident wavenumber of 1380 cm^{-1} (**Figure 1.2a**, left panel). When the incident wavenumber was increased to 1496 cm^{-1} , the plasmon confinement was observed at the trench area (suspended graphene) (**Figure 1.2a**, center panel). When the incident wavenumber was further increased to 1591 cm^{-1} , the plasmon confinement returned to the ridge area (**Figure 1.3a**, right panel).

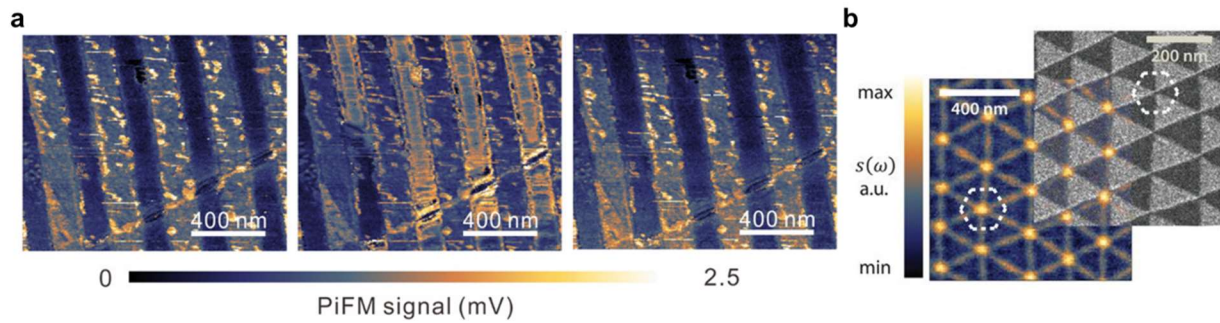


Figure 1.2. Interaction of graphene plasmon with carrier concentration and density of states. **a**, Near-field images of graphene under selective doping by a patterned substrate at 1380 cm^{-1} (left), 1496 cm^{-1} (middle) and 1591 cm^{-1} (right) excitation^{4, [26]}. **b**, Near-field image (left) of a twisted bilayer graphene overlapped with dark field TEM image (right). The dashed hexagon denotes unit cell of the light-matter interaction pattern^{5, [13]}.

1.2.4 interaction of Graphene plasmon with Moiré superlattice

Moiré superlattice offers spatial modulation in the density of states, thereby offering an additional pathway for plasmon interaction^[13,27,28]. Twisted bilayer graphene can act as a photonic crystal, meaning light can travel through a periodic structure with different refractive index^[13]. The near-field image of twisted bilayer graphene revealed a Moiré pattern with stronger near-field signal along the domain walls (**Figure 1.2b**). A perpendicular electric displacement field (perpendicular to the graphene surface) opened up the band gap in the AB or BA domains, thereby enhancing optical conductivity at the domain walls. In another paper, the reflection of SPP from the soliton/domain wall of a bilayer graphene was used to study the tensile or shear

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nature of the soliton walls^[27]. In a twisted bilayer graphene, AB atomic registry can shift towards BA stacking by slight shifting the top layer with respect to the bottom layer, thereby making tensile or shear strain induced 1D soliton like domain wall. The soliton parallel (perpendicular) to the dislocation vector induced shear (tensile) strain at domain wall. The plasmon reflected from the shear or tensile domain wall (due to optical contrast) and corresponding bright features were observed in the near field imaging. This reflection was controlled by electric gating. Three distinct patterns in the near-field images were observed – triangles, L bends and ovals. The shear soliton showed one bright line (triangle and L bend) and the tensile soliton showed two bright lines. The wavelength of graphene plasmon (both edge reflected and soliton reflection SPP) increased with carrier density. Another study reported the interaction of graphene SPP with the Moiré pattern of graphene-hBN heterostructure^[28]. The interface of plain (no Moiré pattern) and Moiré patterned graphene acted as a plasmon reflector with doping dependency. For largest and smallest carrier density, both plain and Moiré patterned graphene showed similar plasmon propagating profile (fringe pattern). In the intermediate doping level, plain graphene showed additional fringes. The optical conductivity linearly varied with fermi level for plain graphene (vs. non-linear for moiré patterned graphene). As doping increases, gapped miniband form in Moiré patterned graphene. The gapped mini band contribution to the optical conductivity was peaked at 0.2 eV Fermi level, then slightly reduced at higher doping.

1.2.5 Tunability of graphene plasmon

One of the biggest advantages of graphene plasmon over conventional metal plasmon is its tunability^[29]. The tunability of graphene plasmon wavelength can be understood via the interaction of graphene plasmon with the modulation in structure and carrier concentration, and

phonon of underlying substrate via hybridization. In this section, the studies on the tunability of graphene plasmon will be reviewed.

The plasmon resonance wavelength can be tuned by modulating the carrier concentration (*i.e.*, doping) or changing the width (W) of nanoribbon structure^[30]. A narrower ribbon width (W) induced higher plasmonic resonance frequency due to 2D plasmon dispersion. The plasmon wave vector (q) is related by $q \sim \pi/W$. Plasmonic dispersion is related to $\sqrt{q}$. Therefore, the plasmonic resonance frequency follows $1/\sqrt{W}$. The plasmon frequency scales with Fermi energy (E_f) by $\sqrt{E_f}$. E_f is proportional to $\sqrt{n}$, where n is the carrier concentration. Therefore, plasmonic frequency is proportional to $n^{1/4}$. Another study showed that the scaling law of plasmon resonance frequencies to the carrier concentration (n) is not only limited to nanoribbon shaped structure but also applies to other microstructure, such as graphene-insulator stacked disks^[31]. In the microdisk study, plasmon resonance frequency was increased with an enhanced intensity in the transmittance spectra due to the strong Coulomb interaction of the graphene layers. However, the plasmon resonant frequency of microdisk with multiple graphene layers showed a $\sqrt{n}$ dependency whereas microdisk with single graphene layer showed the $n^{1/4}$ dependency.

Graphene plasmon exhibits a strong coupling with optical phonon or phonon pertaining to the underlying substrate^[32–34]. Such coupling appears as a dip between the spectral peak in the extinction or transmission spectra, known as plasmon/phonon induced transparency. Such transparency has been reported on a AB stacked bilayer graphene nanoribbon where the Γ -point optical phonon coupled with the graphene plasmon^[32]. Without the presence of graphene plasmon excitation, a symmetric phonon absorption peak was observed at 1580 cm^{-1} . However, the spectral peak became asymmetric with much higher extinction intensity when it was coupled with the graphene plasmon peak. The transparency in the spectra between the broad plasmon

peak and sharp phonon peak was prominent. The transparency window (*i.e.*, the gap between the spectral peaks) became narrower as the graphene plasmon frequency was tuned by the nanoribbon width such that the frequency approached the phonon frequency of AB stacked bilayer graphene (the spectral dip near 1580 cm^{-1} in **Figure 1.3a**). The transparency window was tuned simply by changing the nanoribbon width. A similar observation was reported on a graphene-hBN nanoribbon structure where graphene plasmon coupled with the hBN phonon^[34].

The coupling between graphene plasmon and underlying phonon often exhibits a hybridized surface plasmon-phonon polariton (SPPP)^[33,35]. The most reported SPPP mode is due to the hybridization in graphene-hBN heterostructure^[33]. Upon illumination, the h-BN underwent lattice displacement and exerted a polarization field on the carriers in graphene. Similarly, the polarization field by the graphene carrier interacted with the h-BN lattice. The resulting optical mode exhibits a hybrid mode which inherits features from both plasmon and phonon modes with enhanced intensity in the near-field regime^[35]. Freestanding graphene shows SP2 dispersion where S and P represent the atomic orbitals. Thick hBN exhibits type 2 hyperbolic phonon polariton (HP2) dispersion. When coupled, graphene-hBN formed HP3 dispersion, which is blueshifted than the HP2 dispersion. The HP3 has the hyperbolic response (h-BN phonon-like response) in addition to the gate tunability (graphene plasmon-like response).

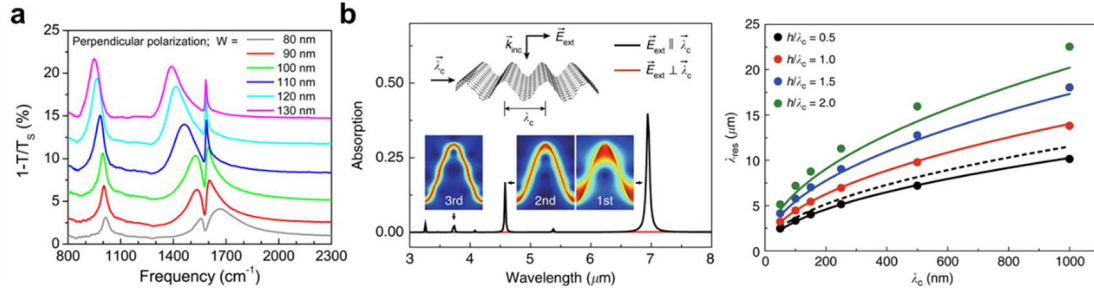


Figure 1.3. Tunability of graphene plasmon. **a**, Reflectance spectra of bilayer graphene ribbon^{6, [32]}. The plasmon-phonon coupling is shown by the spectral dip near 1600 cm⁻¹ which depends on the ribbon width. **b**, Optical absorption spectra of a wrinkled graphene structure for a corrugation pitch (λ_c) of 250 nm and aspect ratio of 1(left)^[36]. E_{ext} denotes the electric field direction of the excitation. Different plasmon resonance modes are shown in the inset. Right panel shows the plasmon resonance wavelength (λ_{res}) dependence on the λ_c and aspect ratio (h/λ_c) where h is the wrinkle height. The solid curves represent λ_{res} calculated from the LC-circuit model and dashed curve represent λ_{res} estimated from conventional analytical model.

Another effective way of tuning the plasmon resonance is introducing wrinkled graphene structure^[36]. Kang *et al.*, reported that the plasmon resonance in a wrinkled graphene is highly dependent on the direction of the incident electric field (E-field). Specifically, if E-field is perpendicular to the wrinkle vector, finite element model predicted no plasmon resonance. However, when E-field is parallel to the wrinkle vector, the model predicted multiple plasmon resonance (**left panel of Figure 1.3b**). The resonance peaks indicated the plasmon confinement on the wrinkled structure. If wrinkle wavelength is fixed, plasmon wavelength redshifts with the higher aspect ratio of the wrinkled (aspect ratio defined as height/wavelength of the wrinkle). Optical absorption and extinction also increased with higher aspect ratio. When aspect ratio was fixed, plasmon wavelength redshifted with higher wrinkle wavelength. Optical absorption and extinction also increased with wrinkle wavelength (right panel of **Figure 1.3b**). The graphene plasmon behavior can be understood by applying theories and models used in an LC circuit, where L and C represented the inductance and capacitance of a non-parallel plate capacitor. The

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sidewall of the graphene wrinkle was modeled as the non-parallel plate capacitors connected in series. The inductance and capacitance represented current and charge induced by the plasmon, respectively. Plasmon wavelength blueshifted with increase in Fermi energy. The plasmon wavelength was found to be more sensitive to wrinkle structure than the change in Fermi energy. Therefore, topography modulation was suggested to be an effective way to modulate the graphene plasmon resonance compared to the doping effect.

1.3 Flexoelectricity: A universal electromechanical response

Flexoelectricity is the polarization of a dielectric material under inhomogeneous strain. Such deformation non-uniformly shifts the atoms, ions or electron densities, thereby inducing polarization. The resulting polarization direction is parallel to the strain gradient direction. For solid ionic materials, strain gradients cause non-uniform displacement of ions. For soft materials or membranes, polarization can be caused by reorientation of irregularly shaped polarized molecules. Unlike piezoelectricity, flexoelectricity can occur in any symmetric system^[37]. As a result, a wider variety of materials can be chosen for electrochemical application based on flexoelectric effect (sensor, actuator, etc.).

Flexoelectricity can be static (from bending) or dynamic (from sound wave), direct, and converse^[38,39]. In the direct flexoelectric effect, a strain gradient induces a homogeneous polarization. Converse flexoelectric response is a linear stress response to a polarization gradient.

In case of centrosymmetric materials under direct flexoelectric effect, induced strain gradient causes (as the crystal symmetry is broken near the surface due to strain gradient) a thin layer at surface to become piezoelectric (as the crystal symmetry is broken near the surface due to strain gradient). For atomically thin materials, this effect is comparable to the bulk

flexoelectric effect and can cause a decrease in permittivity since surface piezoelectricity acts as an external electric field which saturates the polarization^[40].

1.3.1 Flexoelectricity at the nanoscale

Although flexoelectricity is regarded as the universal electromechanical response, it is often neglected due to its low response when compared to piezoelectricity. The required strain gradient to generate significant polarization in a structure often surpasses its mechanical fracture limit. Therefore, flexoelectricity had been underappreciated in the scientific community. The emergence of nanotechnology and nanoscale fabrication over the past several decades has opened new opportunities for exploring flexoelectricity at the nanoscale. In particular, 2D vdW materials are known for their exceptionally low bending rigidity. This low bending rigidity allows application of significant strain gradients without structural failure. Therefore, flexoelectricity has substantial potential at the nanoscale.

Several researchers have previously studied the dependency between curvature and flexoelectric effect in 2D materials. For example, dipole moment density (i.e., polarization) was predicted on a bent graphene sheet via density functional theory (DFT)^[41]. Polarization was found to be reciprocal to the curvature except for low curvature (**Figure 1.4a**). At large radii of curvature, the dipole moment was zero. For very small radius of curvature, the edges met together to form cylindrical shape and the interaction between adjacent atoms became dominant. The constitutive equation for the direct flexoelectric effect is, $p=f(c_1+c_2)$, where p is the polarization, f is the flexoelectric constant, and c_1/c_2 are the principal (Gaussian) curvatures. For graphene systems, $c_2=0$ and $c_1=1/R$, where R is the radius of curvature. The polarization on graphene sheet was explained from an electron redistribution perspective. Graphene has free

electron at p_z orbital. For a 2D graphene sheet, the free electrons were presented as a 2D electron gas (2DEG) over the graphene sheet with thickness, t . Upon bending, the new surface area will be $S_{\text{top}} = S_{\text{graphene sheet}} (1+t/R)$ and $S_{\text{bottom}} = S_{\text{graphene sheet}} (1-t/R)$. Since, $S_{\text{top}} + S_{\text{bottom}} = 2S_{\text{graphene sheet}}$, electron redistribution was local and not across the surface. Another study showed that the flexoelectricity induced dipole in carbon nanotubes (CNTs) increased with the curvature of the bend^[42]. When atomically thin carbon sheet was bent to form CNT, the π orbitals in the concave (inside) region came closer to each other, thereby causing an increased electron repulsion and resulting in a redistribution of the electrons (rehybridization) (**Figure 1.4b**). π orbitals orientation changed from sp^2 to between sp^2 and sp^3 . The rehybridization resulted in electron charge transfer from concave to convex region. Upon bending, the σ bonds became tilted from original plane, the remaining π orbital formed an angle from the axis perpendicular to the original plane, thereby inducing dipole into the structure. Another study reported flexo-induced dipole moment on graphene when bent into a cone shape (**Figure 1.4c**)^[43]. Graphene sheets were bent into different cones and subsequent dipole moments were calculated in three ways: charge redistribution calculation (DFT), linear relation between dipole moments, and pyramidalization angle. Pyramidalization angle is the angle between σ and π orbitals. Dipole moment increased with cone length. For the same cone length, dipole moment reached a maximum at 90° , and zero at both 0 and 180° . With constant surface area, the maximum dipole moment shifts occurred at less than 90° .

Introducing inhomogeneous deformation into thin films is not limited to bending but also extends to other methods such as introducing asymmetric shapes or lattice mismatches^[44–46]. Inhomogeneous strain was introduced into centrosymmetric structures (graphene) by creating holes in the graphene sheet and applying uniform stress^[44]. However, introducing holes into

graphene is challenging. Therefore, another study adopted graphene nitride (g-C₃-N₄) nano sheets which have triangular holes in one phase^[45]. The resultant inhomogeneous strain upon external loading contributed to surface piezoelectricity through flexoelectricity.

Enhanced electromechanical response driven by a combination of piezoelectricity and flexoelectricity has been reported along the domain walls of twisted bilayer graphene^[47]. Although the AA and AB domains are centrosymmetric, the symmetry is broken during a shift from AB to AA, incorporated with strain gradient and symmetry breaking. The piezoresponse was attributed to the broken symmetry while the flexoresposne was attributed to the strain gradient. The out-of-plane (in-plane) polarization was reported to reach its maximum at AA sites and domain walls (domain walls).

There have been a number of studies on flexoelectric effect on non-carbon based materials as well. Introducing lattice mismatch by tuning the fabrication parameter of HoMnO₃ thin films induced significant strain gradients^[46]. HoMnO₃ thin films were deposited on Pt/Al₂O₃ substrates with varying O₂ pressures. The strain gradients and resulting flexoelectric effects were then compared at different O₂ pressures. During deposition, lattice mismatch at the interface caused strain. The strain was relaxed inside the film within tens of nm length scale, thus producing large strain gradients. Low O₂ pressure induced oxygen vacancies into the lattice, thereby helping the relaxation process. As a result, increasing strain gradients were observed for higher O₂ pressures. These strain gradients were found in the order of 10⁵ - 10⁶ m⁻¹. At room temperature, the calculated electric field (5 MVm⁻¹) was smaller than the coercive field (40 MVm⁻¹). However, at elevated temperatures, the electric field became significant compared to the coercive field because the coercive field depleted at high temperatures while the flexoelectric effect remained relatively consistent due to similarity in thermal expansion between the film and

substrate. Another study reported flexoelectric effect in bilayer hBN which was $\sim 10^9$ times higher than monolayer hBN when the structure had a curvature radius of $10 \mu\text{m}$ ^[48]. This significant amplification of the flexoelectric effect in the bilayer system was attributed to the anti-parallel stacking which induced a lattice mismatch (**Figure 1.4d**).

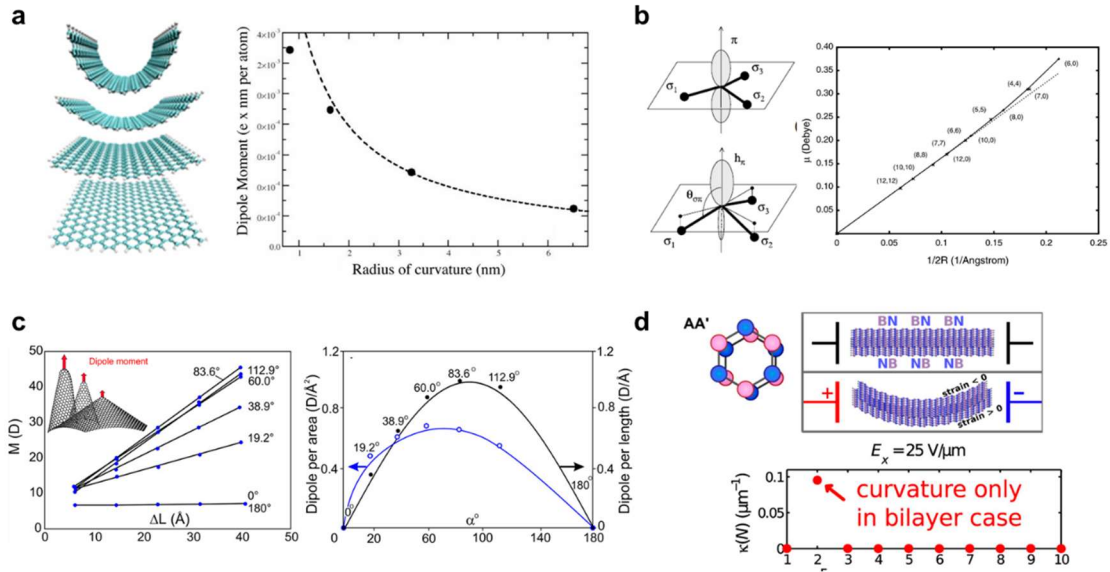


Figure 1.4. Flexoelectricity in ultra-thin material systems. **a**, Schematics of a graphene membrane bent with armchair direction along the circumference (left) and corresponding estimated dipole moment as a function of radius of curvature (right)^{7, [41]}. **b**, Effect of curvature on the dipole of a carbon nanotube system (CNT)^{8, [42]}. Schematics of the symmetric π -orbitals of graphite which are perpendicular to the σ -bond (top left). Schematics of the asymmetric π -orbitals of carbon nanotubes (CNT) which are at a tilt angle to the σ -bond (bottom left). Right panel shows the atomic dipole as a function of CNT curvature. **c**, Dependence of flexoelectric dipole and deformed cone structure of carbon system^{9, [43]}. Correlation between the flexoelectric dipole moment and cone length (left) of nanocone structure. The schematics of the structures are shown in the inset. Correlation between the dipole per area and dipole per length of the cone with the apex angle. **d**, Electrical stimuli induced curvature of antiparallely stacked hBN bilayer^{10, [48]}. Schematic of the antiparallel stacking (top left) and deformation of the hBN bilayer (top right). Bottom panel shows the curvature as a function of number of hBN under electric field of $25 \text{ V}/\mu\text{m}$.

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Among 2D vdW materials, transition metal dichalcogenides (TMD) are of particular interest for harnessing electromechanical response due to their intrinsic piezoelectric properties^[49]. Several studies have explored harnessing the flexoelectric response^[12,50]. The first work on converse flexoelectricity-driven electromechanical response of 2D TMDs investigated MoS₂^[50]. In this work, out-of-plane piezoresponses from flat MoS₂ monolayers were reported, revealed by piezoresponse microscopy (PFM) measurements. The converse piezoelectric coefficients were estimated from the PFM measurements. Because MoS₂ lacks out-of-plane piezoresponse, the origin of the piezoelectric coefficient was attributed to the converse flexoelectric effect. In another study on MoTe₂, PFM measurements revealed enhanced electromechanical responses in bent or deformed regions when compared to flat regions^[12]. The enhancement was attributed to the direct flexoelectric effect which was caused by bending-induced polarization.

1.3.2 Flexoelectricity enabled enhanced functionalities in nanoscale materials

Flexoelectricity can significantly augment electromechanical response. For example, in a study of buckled PZT ribbons, the electromechanical responses were augmented by ~70% by flexoelectricity (**Figure 1.5a**)^[51]. The buckled structures were formed by first patterning PZT ribbons on pre-stretched polymeric substrates. Upon release of the pre-strain, the flat ribbons were transformed into buckled shapes. The strain gradient induced by the bending was estimated to be more than three-fold when the thickness of the ribbon was reduced from 500 nm to 250 nm. The resulting flexoelectricity enhanced the actuation of the ribbon under the application of electric bias.

Moreover, flexoelectricity-induced polarization can be used as a gate to modulate current flow in semiconducting materials. By using an AFM tip as the electrode and means of applying localized indentation on silicon, a polarization of 0.03 Cm^{-2} was obtained from a 10^6 m^{-1} strain gradient^[52]. This polarization modulated the Schottky barrier at the metal-semiconductor interface as well as the carrier transport. The forward current in p-silicon steadily increased as the indentation load was increased up to $7 \text{ }\mu\text{N}$. On the contrary, no reverse current was observed below $7 \text{ }\mu\text{N}$ of indentation load, followed by a significant increase beyond this threshold. The contact barrier at the metal-semiconductor interface decreased with an increase in the indentation load. At the same time, the interface barrier also decreased since the flexoelectric-induced polarization attracted holes at the interface. The combination of the increased load and polarization facilitated the flow of forward current. In the opposite direction, only a strong indentation with a strong polarization reduced the contact barrier low enough to trigger a reverse current.

Furthermore, flexoelectricity-induced polarization, if strong enough, can switch the ferroelectric domains of target materials. Therefore, flexoelectricity can be used for effective domain writing. By applying sliding force with an AFM tip, the ferroelectric domain direction of barium titanate (BTO) was switched from upward to downward (**Figure 1.5b**)^[53]. The minimum force required for domain switching decreased as an externally applied DC bias was increased. Interestingly, the switching phenomena was not observed in the case of static perpendicular load. Simulation results suggest that an unstable ferroelectric domain was generated at the surface under perpendicular load which counteracted the flexo-induced polarization. The sliding force (or strain gradient) -induced ferroelectric domain switching has been additionally reported with other ferroelectric materials such as BiFeO_3 and HfO_2 ^[54,55].

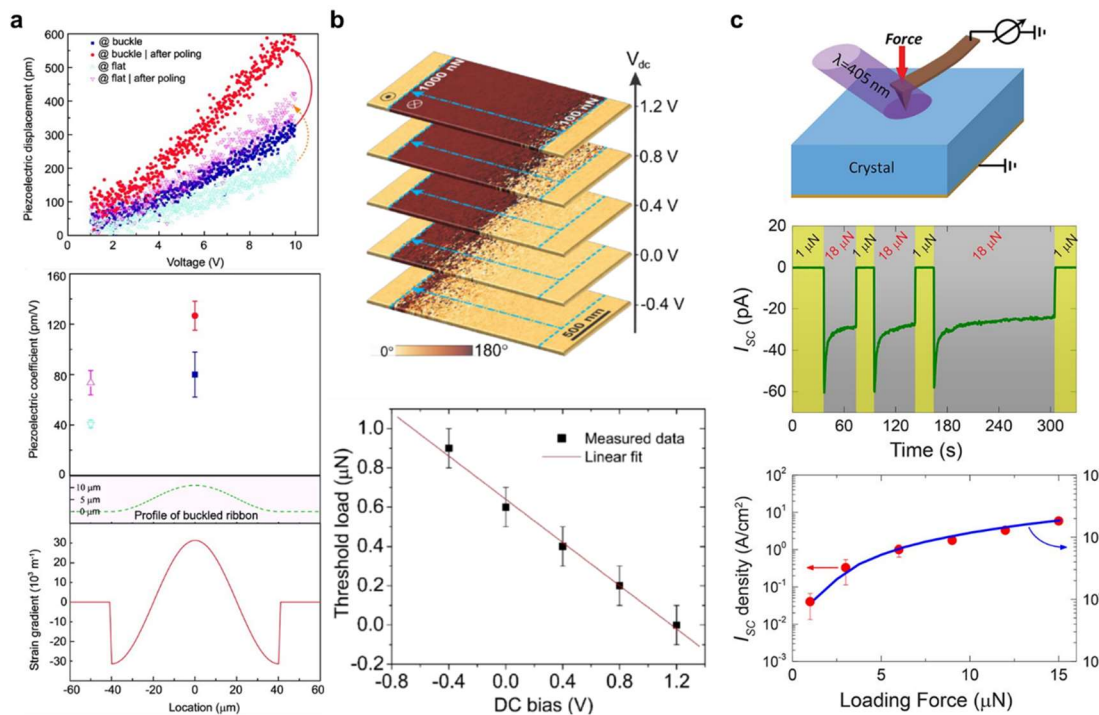


Figure 1.5. Flexoelectricity induced enhanced functionality in thin films. **a**, Flexoelectricity induced enhanced electromechanical response of buckled PZT ribbons^{11,[51]}. The top panel shows the comparison in piezoelectric displacement measured by PFM measurements between buckled and flat PZT structures. The middle panel shows the corresponding piezoelectric coefficients. The bottom panel shows the strain gradient estimated over flat and buckled PZT ribbons. **b**, Flexoelectricity-induced ferroelectric domain switching of barium titanate (BaTiO₃) thin films^{12,[53]}. The top panel shows PFM phase image illustrating the ferroelectric domain switching (shown by the color contrast) under different indent load condition and applied DC biases. The bottom panel shows the trend between the minimum indent load required for domain switching at a given DC bias. **c**, Flexo-photovoltaic effect of SrTiO₃^{13,[56]}. Schematic of the setup is shown in the top panel. The middle panel shows the flexo-induced photocurrent under illumination. The current is generated when the indentation load is increased from 1 μm to 18 μm. The bottom panel shows the photocurrent density as a function of the indentation force.

Finally, light-matter interactions, such as photovoltaics or photocurrents, can also be modulated via flexoelectricity. For example, the direct flexoelectric effect was exploited to extract photovoltaic (PV) effect from single crystal SrTiO₃ (**Figure 1.5c**)^[56]. In this study, an

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AFM tip was used to exert force on the target material, inducing a strain gradient. The flexoelectric PV effect reported in this study was synonymous to the bulk PV effect of ferroelectric materials. This bulk PV effect occurs in ferroelectric non-centrosymmetric materials when incident polarized light causes a short circuit current due to the asymmetric distribution of photoexcited carriers. Strain gradients were found to trigger the same effect in centrosymmetric material such as SrTiO_3 as the indentation created an asymmetric carrier distribution. Another study reported significant enhancement (almost two order of magnitude) in the flexoelectric coefficient for halide perovskite structures under the influence of photoexcitation^[57]. Due to the metal-semiconductor interface, a thin Schottky barrier was formed at the electrode-material interface. The formation of Schottky barrier near the top and bottom electrode induced a relatively more conductive region in the middle. Upon bending, the carriers in the middle region were moved and accumulated near the depletion layer (Schottky barrier region). The photoexcitation increased the carrier density and decreased the depletion width. The increased carrier density compensated for the depleted carriers, thereby increasing the photocurrent. Therefore, flexoelectricity and photoexcitation had synergistic effect on photocurrent augmentation.

1.4 Conclusions

In this chapter, I have reviewed advanced functionalities of 2D materials. The extensive reports on graphene plasmons and electromechanical response on thin film clearly indicate that light-matter interaction and electromechanical response in 2D materials are active research areas. In the next chapter, I will introduce two state-of-the-art characterization techniques that enables investigating these advanced functionalities with ultra-high precision.

CHAPTER 2: TIP-BASED ADVANCED CHARACTERIZATION TECHNIQUES

2.1 Introduction

Atomic force microscopy (AFM) has enabled advanced characterization of materials at sub-50 nm scale. The uniqueness of AFM is the high sensitivity along the out-of-plane direction. In the out-of-plane direction, AFM can detect the force field associated with even a single molecule. In AFM, a cantilever (known as tip) is brought near the surface of interest such that the cantilever can sense the force field associated with the near-surface^[58]. Any inhomogeneity on the surface, such as surface roughness, can perturb the force field which can be detected by the needle-like AFM tip. The perturbation of the force field would induce bending force on the cantilever. The bending of the cantilever is detected by a laser which incidents and reflects from the back of the tip. The reflected laser incidents on a photodiode which senses the motion of the tip. Using the bending force exerted onto the cantilever as feedback, the tool or control system will try to minimize the force variation. A sensor attached to the tip (known as piezo) will try to actuate the cantilever to minimize the force variation. Therefore, the actuation of the cantilever projects the image of the target surface if the tip is allowed to raster along the surface. The spatial resolution of the image depends on the size of the needle at the free end of the tip. Typically, the spatial resolution of an AFM image is limited by the radius of the edge of the needle, often termed as tip radius. Due to the advancement in nanoscale fabrication, 10 nm of tip radius is no exception now-a-days. Therefore, AFM can effectively map the surface within 10-15 nm of spatial resolution. Although, AFM was initially introduced to capture the surface morphology with ultra-high precision, coupling the AFM tool with different external forces such as electrical, magnetic or optical allows us to map various surface phenomena including dielectric constant, ferroelectric domain, magnetic domain, electrostatic, potential, current, light-

matter interactions. In this chapter, I will discuss two advanced tip-based characterization techniques that I implemented to explore the enhanced functionalities of 2D vdW materials.

2.2 Photo-induced force microscopy (PiFM)

Tip-enhanced AFM-IR imaging is a popular technique to collect IR absorption/scattering at sub 20 nm scale, effectively overcoming Abbe diffraction limit. In tip enhanced IR imaging technique, an AFM tip (with conductive coating) is brought closer to a surface^[59]. An IR laser is irradiated at the tip-sample junction, causing a lightning rod effect at the tip, and therefore, near-field material properties can be detected through tip-material interaction. There are several techniques to probe and collect the near-field optical information of the materials. Among them, photo-induced force microscopy (PiFM) is a non-contact mode technique for sensing the light-matter interaction at near-field between the tip and the sample surface (**Figure 2.1a**). Upon IR illumination at the tip-sample interaction, the tip and the sample can be considered as two polarizable materials (**Figure 2.1b**)^[60]. The photo-induced force is the induced dipole force acting between the polarized sample and its mirror image on the tip under the light excitation. Their resulting photo-induced force can be detected by the cantilever deflection. The photo-induced force typically consists of two types of force – scattering force and gradient force. The gradient force results from electric field inhomogeneity, whereas the scattering force results from the momentum transfer between light field and the target materials. The gradient force scales with z^{-4} , where z is the tip-sample distance. The scattering force is mostly dominated by the dissipative part of the tip. Therefore, the scattering force is less sensitive to the spectroscopic properties of the materials. As a result, PiFM technique relies on gradient force and extremely sensitive to tip-sample distance. To effectively decouple the photo-induced force from other tip-

sample interactions, the laser is amplitude-modulated and resulting force is detected at a mechanical frequency away from the resonance of the AFM cantilever. The cantilever is driven at the second eigen mode frequency (f_1) and the laser is modulated such a way that the modulation frequency $f_m = f_1 - f_0$, where f_0 is the first eigenmode frequency of the cantilever. The photo-induced force is collected at f_0 . Such detection technique is more sensitive to the gradient force. Driving the cantilever at the second harmonic frequency allows a narrower tip-sample distance. PiFM appears to be an effective technique to probe and detect optical force at near-field. Using PiFM, light-matter interactions in 2D vdW materials and thin film has been investigated, including graphene plasmons^[26], h-BN phonon polaritons^[61,62], TMDs excitons^[63], nanoscale spectroscopy for chemical footprints^[64,65].

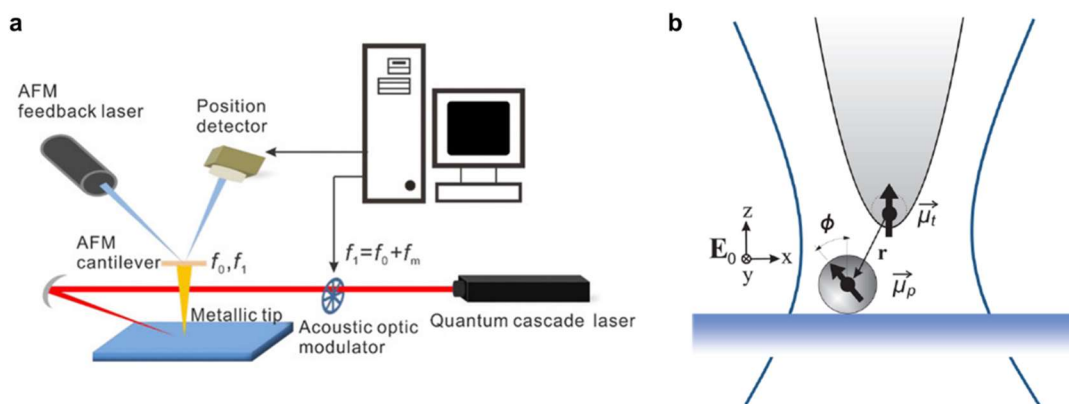


Figure 2.1. Schematics of photo-induced force microscopy (PiFM) technique. **a**, Schematic of the PiFM technique^{14, [26]}. **b**, Schematic of the light-matter interaction (induced dipole-dipole interaction) at the tip-sample interaction area^{15, [60]}. The dipole at the tip (μ_t) and sample (μ_p) induced photo-induced force under light illumination which exerts electric field (E_0) focused at the tip-sample interaction area.

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2.3 Piezoresponse force microscopy (PFM)

Piezoresponse force microscopy (PFM) is a contact mode imaging technique in which a conductive cantilever is brought in contact with the target surface and allowed to raster^[66,67]. An electric bias (AC) is applied during the rastering motion (**Figure 2.2a**). If the target material is piezoelectric, the material will exert an oscillation motion (e.g., expansion-contraction) due to the piezoelectric nature under the influence of the applied electric field (AC bias). The mechanical oscillation (or, piezoresponse) is tracked by the cantilever deflection and suitable lock-ins. The spatial maps of piezoresponse and piezoelectric domain can be obtained via the PFM amplitude and phase images. PFM amplitude image contains the information about the strength of piezoresponse, which is also often termed as piezoelectric coefficient. PFM phase image illustrates the domain direction of the material. If the applied electric field and piezoelectric dipole are in parallel direction, the resulting piezoresponse will cause the material to expand. The resulting phase value will be registered as 0° (**Figure 2.2b**). On the other hand, if the applied electric field and piezo-domain are anti-parallel, the material will contract upon piezoresponse. The corresponding phase image will be registered as 180° .

PFM amplitude signal consists of the convolution between piezoelectric and non-piezoelectric effects (**Figure 2.2c**)^[67]. PFM amplitude is obtained from the first harmonic oscillation of the AFM amplitude and can be shown as,

$$PR = d_{33}V_{ac} + k^{-1}C_z'V_{ac}(V_{dc} - V_{sp}) \quad (2.1)$$

Here, PR is the total amplitude, V_{ac} , V_{dc} and V_{sp} are the AC bias, DC bias (if applied) and surface potential, respectively, and C_z' and k are proportional constant and tip-sample contact

stiffness, respectively. The first term ($d_{33}V_{ac}$) of the right-hand side of Equation (2.1) is the true piezo-/flexo-electric effect, whereas the second term ($k^{-1}C'_zV_{ac}(V_{dc} - V_{sp})$) is the non-piezoelectric effect. The term d_{33} is known as out-of-plane piezoelectric coefficient when the PFM is set to probe the out-of-plane piezoresponse of the target material.

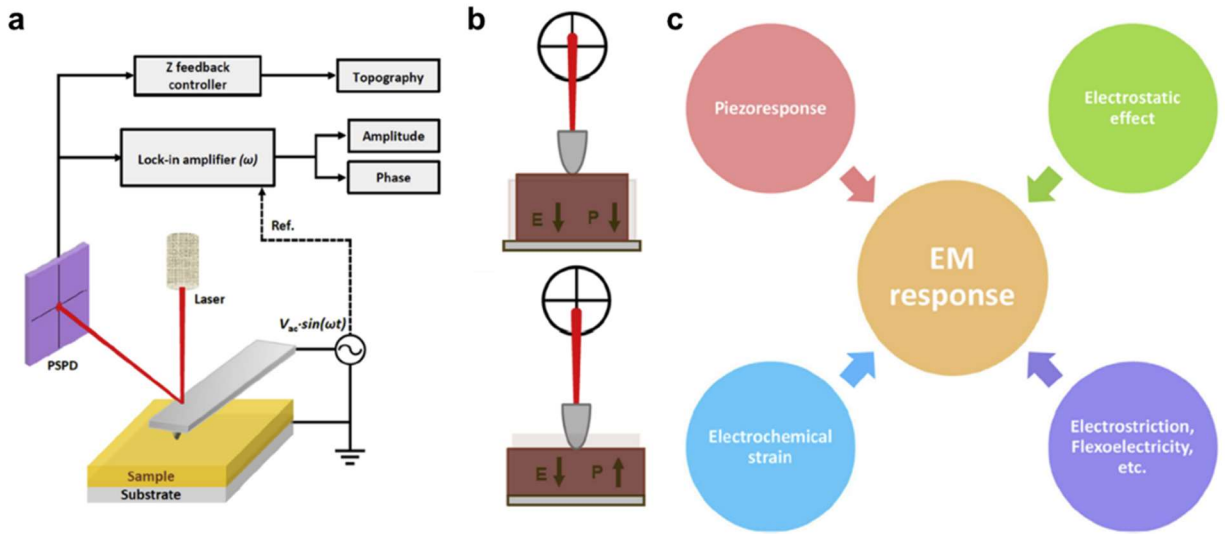


Figure 2.2. Illustration of piezoresponse force microscopy (PFM) technique^{16, [67]}. **a**, Schematics of the experimental setup. **b**, Schematics of the tip-sample interaction and corresponding output of the target sample. **c**, Illustration of different response captured by the PFM technique.

2.3.1 The origins of pseudo-piezoresponse in PFM

There have been several ways to track and minimize the pseudo-piezoresponse or non-piezoresponse captured through PFM^[67–69]. Three most common pseudo-piezoresponse are the electrostatic, electrostriction and electrochemical response. Electrostatic force is induced due to the nature of tip-sample contact in PFM. Since the entire tip is conductive and an electric bias is applied during PFM, the cantilever-sample can act as parallel-plate capacitor. Two types of electrostatic force can be induced – short range and long range. The short-range electrostatic

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force occurs near the tip-sample contact area whereas the long-range electrostatic force occurs between the sample and the long axis of the cantilever. The electrostatic force is proportional to the applied DC bias (if applied) and reciprocal to the tip-sample contact stiffness. Therefore, increasing the tip-sample contact stiffness by using a stiffer cantilever is an effective way of reducing the electrostatic effect. Although using a stiff cantilever reduces electrostatic force, it often results in a rapid tip degradation in contact mode imaging since stiffer cantilever required higher force to measure the piezoresponse compared to the softer cantilever. One way to reduce the electrostatic force without using a very stiff cantilever is to modulate the cantilever at higher eigen mode^[70]. Operating the cantilever at higher eigen mode effectively increases the tip-sample contact stiffness, thereby reducing the electrostatic effect. Another way of reducing electrostatic effect is to combine PFM technique with Kelvin probe force microscopy (KPFM)^[71]. KPFM is another AFM technique for mapping the surface potential (V_{sp}) of the target material. Applying a DC bias equals to the V_{sp} during the PFM measurement would effectively cancel out the non-piezoelectric contribution in Equation 2.1.

Electrostriction force depends on the dielectric nature of the material. Under the influence of DC electric field, the material polarizes due to the dielectric effect. The induced polarization can interact with the applied AC bias and exert pseudo-piezoresponse. Electrostriction maintains a quadratic relation with the applied DC bias. Although sometimes DC bias is applied to augment the contrast in the domain/piezoresponse map, minimizing the magnitude of DC bias reduces the electrostatic and electrostriction effect. Electrochemical response occurs due to the ionic redistribution of the material under electrical stimuli. It is more pronounced in the case of ionically active materials. Although electrochemical response exerts a pseudo-piezoresposne, strong piezoelectric materials exhibit significantly high piezoresponse compared to the

electrochemical response. In case of ionically active materials, electrochemical response microscopy can be implemented to study the movement and redistribution on the target ions.

2.3.2 Estimation of d_{33}

PFM measurements yield the left hand side of the Equation 2.1 which consists of multiple parameters besides d_{33} , as shown in the right side of the equation. Several methods have been practiced in the literatures to accurately estimate d_{33} . Three of such methods will be highlighted in this section.

To accurately identify piezoreponse ($d_{33}V_{ac}$), the $C_z k^{-1}$ and V_{sp} need to be cautiously estimated^[72,73]. The product of C_z and k^{-1} can be measured using PFM spectroscopy. In PFM spectroscopy, a periodic pulsed DC voltage is applied at a pre-defined location. Corresponding amplitude and phase hysteresis loops are obtained during on (with DC voltage) and off (without DC voltage) states. If there is no domain switching during the on state, the differential amplitude hysteresis loop (i.e., the PFM amplitude) becomes a linear function of applied DC voltage. The slope of the linear function is equal to $C_z k^{-1}V_{ac}$. Since V_{ac} is known, $C_z k^{-1}$ can be calculated from the slope. The surface potential (V_{sp}) can be obtained from KPFM measurement as mentioned above. Once $C_z k^{-1}$ and V_{sp} are determined, subtracting the non-piezoelectric effect from total piezoresponse (PR) yields the true piezo-/flexo-response of the system. The only unknown parameter remains in the Equation 2.1 is the d_{33} .

The d_{33} can be estimated from Equation 2.1 via ‘slope’ method (**Figure 2.3a**). Since, piezoresponse (PR) linearly varies with the applied AC bias, obtaining PR as a function of AC bias can be a practical route to estimate d_{33} by avoiding all the rigorous calculations required to estimate the non-piezoresposne described above^[74]. In this case, multiple PFM measurements

can be taken at different AC bias. The PR is calculated from the PFM amplitude images. The correlation can be drawn from the PR vs. AC bias plot. A linear correlation would clearly indicate that the true piezo-effect is the dominant factor of the PR. The slope of the linearly fit PR vs. AC bias plot becomes d_{33} , thereby leaving all the non-piezo components in the Y-intercept of the linear fit.

Another approach to estimate the d_{33} is the ‘vector’ method (**Figure 2.3b**)^[50]. For this method, the scan area should cover the target structure as well as the substrate. In this method, both PFM amplitude and phase information are required to draw a vector diagram of the piezoresponse. The diagram contains two vectors that represent PR of the target structure residing on the substrate and the standalone substrate. Therefore, PR of the target structure becomes the result of vector subtraction of the PR of target structure with substrate and standalone substrate. The d_{33} is then calculated from the newly estimated PR of the structure and the applied AC bias.

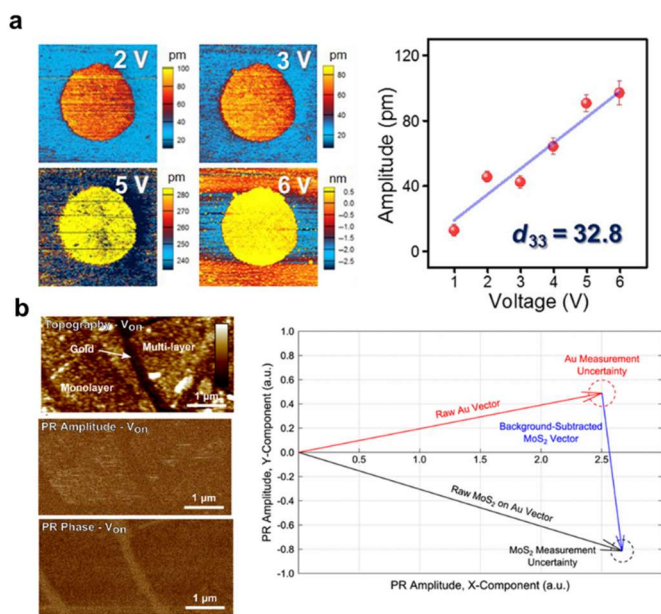


Figure 2.3. Illustration of different methods of estimating piezoelectric coefficient (d_{33}). **a**, Estimation of d_{33} of CdS thin film^[74]. Left and middle panel shows PFM amplitude obtained at different AC bias. Right panel shows the linear correlation between the PFM amplitude and applied AC bias. **b**, Estimation of d_{33} of monolayer MoS₂^{17, [50]}. Left panel shows the topography (top), PFM amplitude (middle) and PFM phase (bottom) of MoS₂. Right panel shows the vector diagram obtained by using the PFM amplitude and PFM phase images shown on the left panel.

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2.4 Conclusions

In this chapter, I have highlighted two advanced tip-based characterization techniques, namely PiFM and PFM. The background of the detection scheme and interpretation of the results have been discussed in detail. PiFM and PFM enable advanced characterization at sub-30 nm spatial resolution. Over the following chapters, I will be adopting these two characterization techniques to probe the light-matter interaction and electromechanical response of 2D vdW materials. Although, other characterization techniques were used to measure the supporting features as required, these two techniques were pivotal in probing the desired properties of the target materials.

CHAPTER 3: TUNABLE PLASMON RESOANCE IN WRINKLED GRAPHENE

3.1 Introduction

Plasmons are light-induced electromagnetic waves of surface charges^[25,75,76] with a wide range of applications in biosensing, light-harvesting, and spectroscopy^[29,30,77–82]. Graphene plasmons, owing to low loss, ultra-high light confinement and tunability via electrical gating, have been actively explored via nano-patterning, selective doping, and defect engineering of graphene (details of graphene plasmon have been discussed in Chapter 1)^[21,26,83]. Besides the nano-pattern structures, plasmonic confinement on semi-infinitely large and continuous graphene occurs when the surface plasmon polaritons are reflected from a surface inhomogeneity^[23]. In this process, unintentional wrinkles or bubbles generated during the sample preparation process are the sources of surface inhomogeneity responsible for the plasmonic reflection^[84,85]. For this reason, generating a well-defined and controllable corrugation on graphene can serve as an alternative solution to support plasmons^[86]. Graphene or other two-dimensional (2D) materials can easily undergo controlled deformation to form wrinkled structure due to the exceptionally low bending rigidity^[87]. Wrinkled graphene structures are ideal platforms for widely tunable plasmonic structures in which the plasmon resonance can be effectively tuned by topographic features such as the pitch (wavelength) and aspect ratio of the wrinkles^[36]. Especially, plasmonic confinement via topographic modulation offers wide range of tunability compared to the conventional electrostatic doping method^[36]. Despite this significant potential, there has not yet been experimental evidence of topography-induced plasmon resonance on semi-infinite atomically thin graphene layers. Since the topographic features on a wrinkled graphene structure can be in sub-100 nm regime, the main challenge in probing plasmonic confinement and spatial

variation of near-field response at such small length scale is due to diffraction limited optics in the detection scheme.

Here, we report experimental studies of tunable plasmonic resonance of wrinkled graphene using photo-induced force microscopy (PiFM) at a sub-20 nm spatial resolution. PiFM is a near-field technique for probing and detecting light-matter interactions at sub-diffraction regime through dipole-dipole interactions between the sample and tip detected via suitable lock-ins (details of PiFM technique have been discussed in Chapter 2)^[59,64]. By applying uniaxial compressive strain, we created nanoscale wrinkled structures of graphene with controlled topography features (e.g., wavelength and, aspect ratio) on a polymeric substrate. We then employed PiFM to examine widely tunable plasmonic resonance wavelength range (5.77-10.93 μm) and its correlation to topography features. Our results showed that the plasmon resonance wavelength was redshifted as both wavelength and aspect ratio of the topography were increased. The PiFM measurements also revealed strong plasmon confinement when the electric field of the incident photon is parallel to the wrinkle vector. Our findings agree well with previously established models as well as the electromagnetic simulation adopted in this study. We further explored plasmon-phonon coupling based on plasmon resonance of our wrinkled graphene where we observed a two-fold increase in the near-field optical response of a polymethyl methacrylate (PMMA) layer on wrinkled graphene due to effective plasmon-phonon coupling.

3.2 Preparation of wrinkled graphene structure

To prepare the wrinkled graphene structure, first we synthesized graphene on a catalytic copper foil via chemical vapor deposition (CVD)^[88]. We then transferred the synthesized graphene from the primary substrate (copper foil) to the polymeric shape memory substrate

(polystyrene or PS) via a wet transfer method^[89]. Finally, we prepared wrinkled graphene structures residing on the PS via mechanical instability (**Figure 3.1a**)^[90]. A controlled uniaxial thermal contraction of the PS resulted in a uniaxial wrinkled graphene structure when PS was heated above its glass transition temperature (120 °C) (**Figure 3.1b**). The structural features (wavelength denoted as λ and aspect ratio denoted as h/λ in **Figure 3.1a**) of the wrinkled patterns can be varied by controlling the amount of thermal shrinkage of the underlying PS (**Figure 3.1c**). The error bars in **Figure 3.1c** indicate the variation in the topographic features for a fixed thermal shrinkage. Such local variation in the topography enabled study of a wider range of topographic features for investigating the effect of topography on plasmon resonance wavelength.

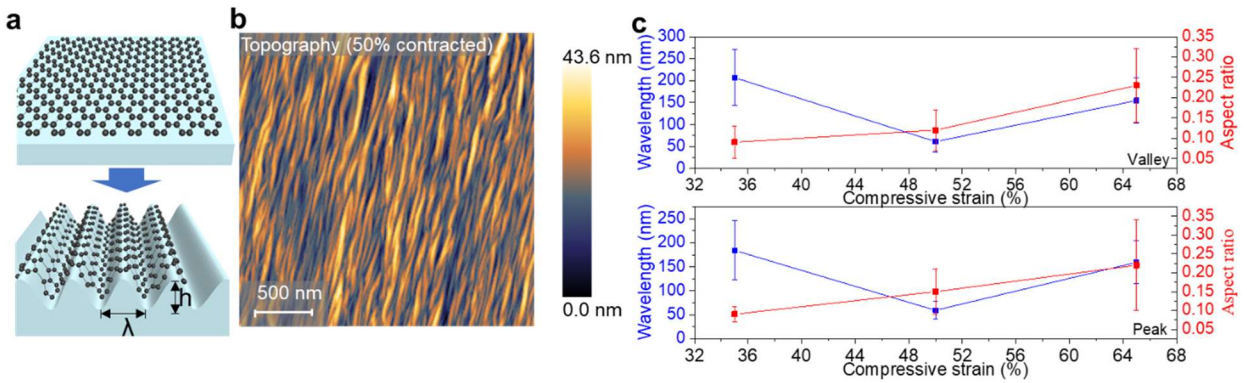


Figure 3.1. Wrinkled graphene on PS. **a**, Schematic drawing of graphene structure before and after thermal contraction of PS. **b**, Topography image of the wrinkled structure obtained by 50% thermal contraction. **c**, Correlation between the topography features (wavelengths and aspect ratio at peaks and valleys) and thermal compressive strain. Error bars denote one standard deviation.

3.3 Observation of plasmonic confinement on wrinkled graphene structure

We used PiFM to characterize the near-field light-matter interactions on the wrinkled graphene structure (**Figure 3.2a**). For efficient light-matter coupling, the electric field of the incident light was set parallel to the wrinkle vector^[36,91,92]. Upon irradiation, photo-induced force

due to the strong electric field confinement were detected at the peak and valley locations of the wrinkled structure (enlarged inset of **Figure 3.2a**). We then positioned the cantilever at specific locations (peak or valley) to measure the photo-induced force infrared (PiF-IR) spectra (**Figure 3.2b**). The resulting spectra showed a distinct peak at 1732 cm^{-1} at a valley location with a wavelength of 70 nm and aspect ratio of 0.11 (inset of **Figure 3.2b**). The corresponding near-field PiFM image at 1732 cm^{-1} showed localized responses of light-matter interaction exclusively at the valleys (**Figure 3.2c**). We attribute the spectral peak at 1732 cm^{-1} and the corresponding spatially localized response to the plasmonic resonance at the valley of the wrinkled graphene structure. To the best of our knowledge, this is the first experimental demonstration of plasmonic resonance on a semi-infinite, wrinkled graphene structure.

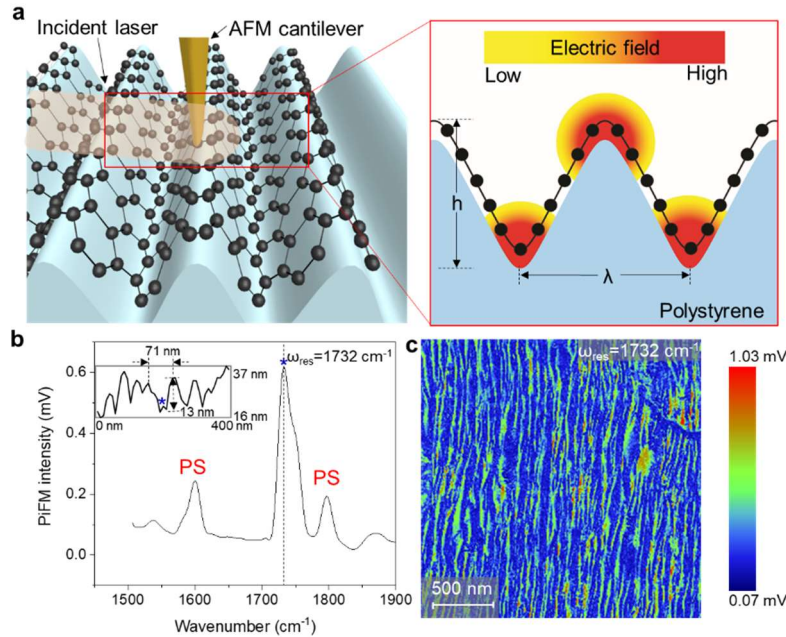


Figure 3.2. PiFM measurements of wrinkled graphene structure. **a**, Schematic illustration of the PiFM measurement. The wrinkled graphene (black spheres) resides on thermally contracted polystyrene (PS) substrate (blue). A zoomed-in view of the tip-sample interaction area is shown in the enlarged inset. Plasmonic confinement due to structural modulation is illustrated at the peak and valley locations. A color bar indicates the electric field strength. The wavelength and height of the wrinkled

structure are denoted as λ and h , respectively. **b**, PiF-IR spectra obtained from PiFM at a valley location. The corresponding line profile of the topography is shown in the inset. The location of the spectral peak and topographical location is denoted by asterisk (*). The spectral footprint of underlying substrate is labelled as “PS”. **c**, Near-field optical response (PiFM image) of the wrinkled graphene structure at the spectral peak of 1732 cm^{-1} shown in (b).

3.4 Correlating topography features with the plasmonic resonance

To further investigate topography-induced plasmon resonance, we conducted nanoscale PiF-IR spectroscopy on multiple locations of the wrinkled graphene structure (**Figure 3.3a-g**). A wide resonance wavelength range ($1260\text{-}1732\text{ cm}^{-1}$ or $5.77\text{-}10.93\text{ }\mu\text{m}$) was observed pertaining to the modulation in topography (top panel of **Figure 3.3**). To investigate the origin of such resonance wavelength variation, we performed near-field optical imaging (PiFM imaging) at the obtained resonance wavelengths (bottom panel of **Figure 3.3**). The near-field images showed spatial modulation in the PiFM intensity for each spectral peak. The spatially confined higher PiFM intensity in the near-field images suggests efficient plasmon confinement at specific locations.

To quantify the topography features responsible for the plasmon resonance, we performed a detailed statistical analysis on each topography and near-field image (**Figure 3.3**). For each resonance wavelength, we identified the plasmon confinement from the near-field images by measuring the localized PiFM signal amplitude. Next, we measured the corresponding topographic features (i.e., wavelength & aspect ratio) from the topography images. To identify the areas under plasmonic resonance in the PiFM images, we set the top 75th percentile of the PiFM intensity magnitude as an estimate for defining the areas under plasmonic resonance. The average wavelength and aspect ratio corresponding to the top 75th percentile of PiFM intensity value was appointed as the topography features related to the plasmon resonance wavelength.

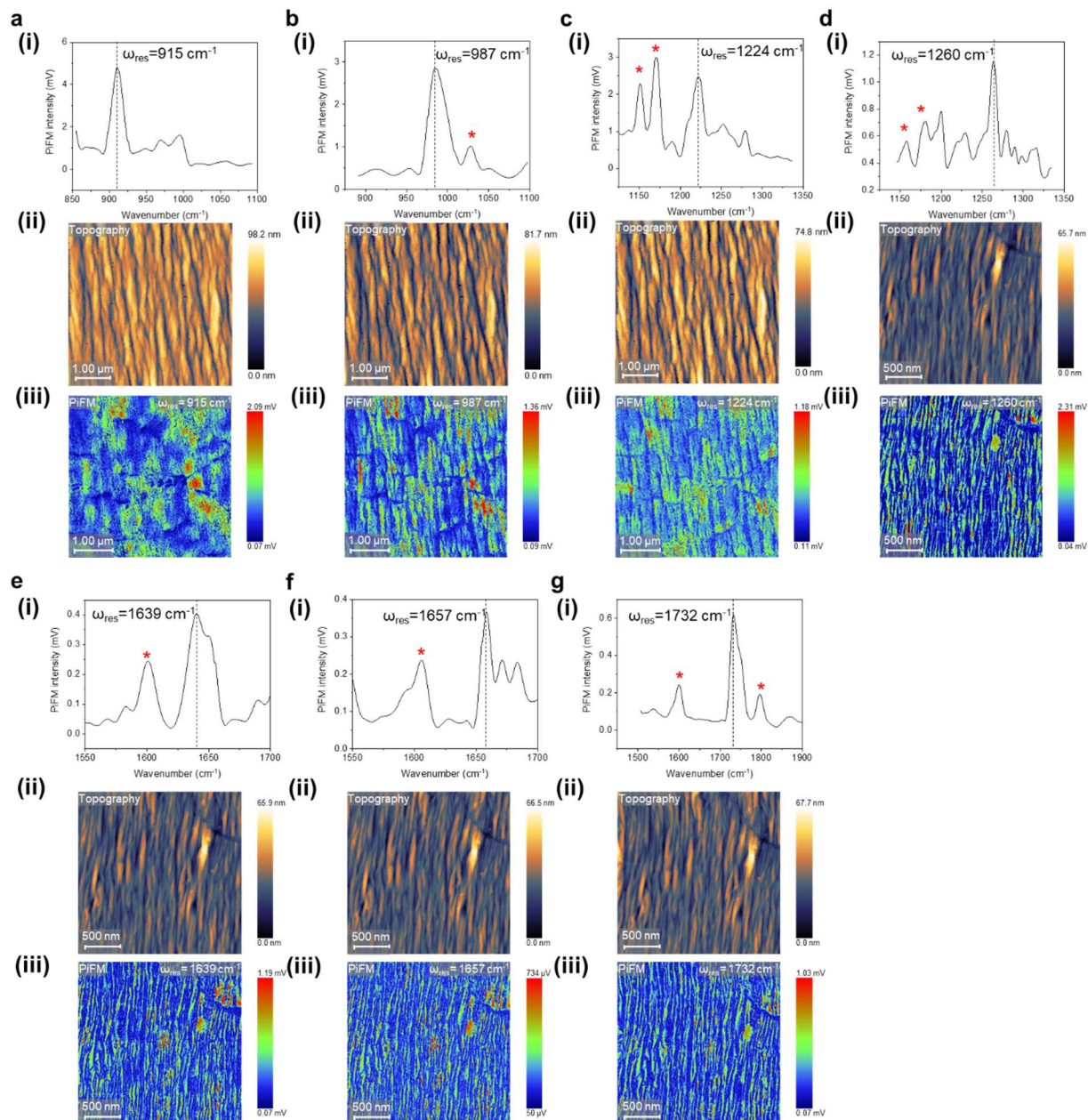


Figure 3.3. Probing plasmonic resonance on wrinkled graphene structure residing on thermally shrunk polystyrene (PS). A total of seven plasmon resonance cases are shown through (a) to (g). PiF-IR spectra obtained on the wrinkled graphene are shown in the top panel (i) of each sub-figure. Some spectra showed additional peaks which present the PS (denoted in red *). The spectral peak corresponding to the plasmonic resonance is denoted by the vertical dashed line. The topography and the near-field images at the plasmonic resonance are shown in the middle (ii) and bottom (iii) panel of each sub-figure, respectively.

3.5 Plasmon resonance wavelength trend with topographic features

To analyze how topography affects plasmon resonance, we investigated the correlation between topographic features and plasmon resonance wavelength (**Figure 3.4**). We observed a redshift in the resonance wavelength (λ_{res}) with an increase in wrinkle wavelength (λ) at both peak and valley locations (**Figure 3.4a, c**). At peak locations, λ_{res} was redshifted by $\sim 3 \mu\text{m}$ from $8 \mu\text{m}$ when λ was increased from 61 nm to 211 nm . The λ_{res} at the valleys underwent $5 \mu\text{m}$ of redshift from $5.77 \mu\text{m}$ when λ was modulated from 50 nm to 240 nm . In contrast, owing to the relatively small change in the aspect ratio in our wrinkle structure, we observed much smaller change in λ_{res} with the aspect ratio (**Figure 3.4b, d**). For example, the AR at peaks and valleys remained at a similar magnitude (0.11) with a small ($20\text{-}30\%$) variation. On the contrary, the wavelengths at peaks and valleys showed approximately 400% modulation ($50\text{-}250 \text{ nm}$).

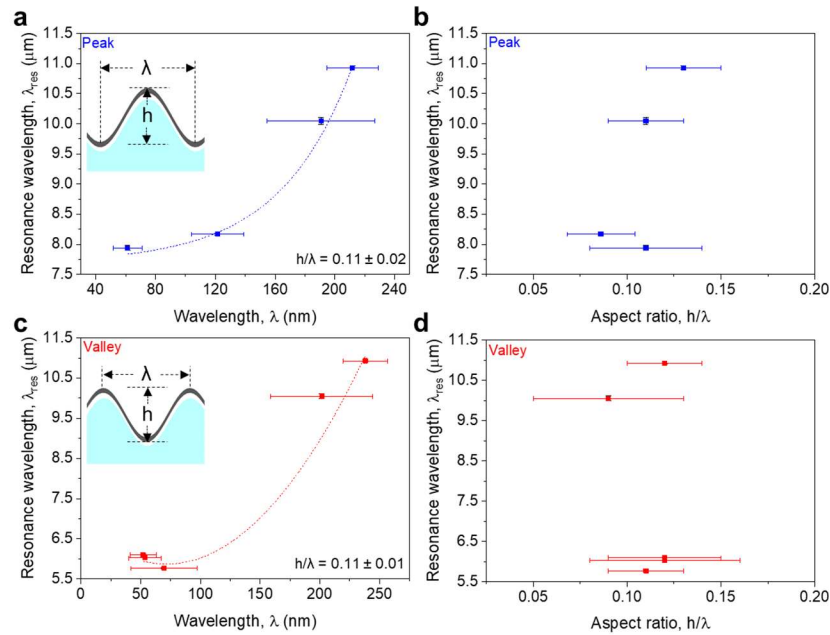


Figure 3.4. Correlation between topography features and plasmonic resonance. **a**, Plasmonic resonance wavelength vs. topographic wavelength at the peak location. The schematic drawing of the topography features is shown in the inset. **b**, Correlation between the plasmonic resonance wavelength and aspect ratio of the topography. **c**, and **d**, Correlation between the plasmonic resonance wavelength and the topographic features (wavelength and aspect ratio) at valley locations similar to (a) and (b), respectively.

Although wrinkle wavelength was the main tuning knob to modulate λ_{res} in **Figure 3.4**, in depth analysis revealed the effect of AR on λ_{res} (**Figure 3.5** and **3.6**). **Figure 3.5** showed a 400 nm redshift in the λ_{res} when we observed a 10% increase in AR and a 28% reduction in λ . We also observed a 2.9 μm redshift in λ_{res} when there was an increase in both λ and AR (79% for λ , 50% for AR, **Figure 3.6a, b**). We observed a similar trend where 1 μm of redshift in λ_{res} was accompanied by a 20% increase in λ and 33% increase in the AR (**Figure 3.6c, d**). These observations suggested that AR also aided in the redshift of λ_{res} along with λ . The redshift trend in λ_{res} with an increase in λ and AR also agrees well with our previous theoretical study^[36].

The effect of λ and AR on λ_{res} becomes clearer for larger AR. Until now, we studied the wrinkled structure on PS which were uniaxially compressed by 50% or 35% (**Figure 3.4, 3.5** and **3.6**). To explore the effect of larger AR on λ_{res} , we prepared wrinkled graphene structures for which the substrate underwent 65% compressive strain and performed PiFM measurements (**Figure 3.7**). The corresponding topography image showed a λ of ~ 150 nm with AR ~ 0.3 . The AR (**Figure 3.7a**) is almost three times higher than the ones shown in **Figure 3.4**. The corresponding plasmonic confinement was obtained at 880 cm^{-1} ($11.36\text{ }\mu\text{m}$) (**Figure 3.7b**). The λ_{res} was $\sim 1.3\text{ }\mu\text{m}$ redshifted than the λ_{res} obtained at a location with only one-third of the AR (red and blue oval in **Figure 3.7c** and **3.7d**). Therefore, we suggested that the increased compressive strain induced a much larger AR which in turn modulated the plasmon resonance.

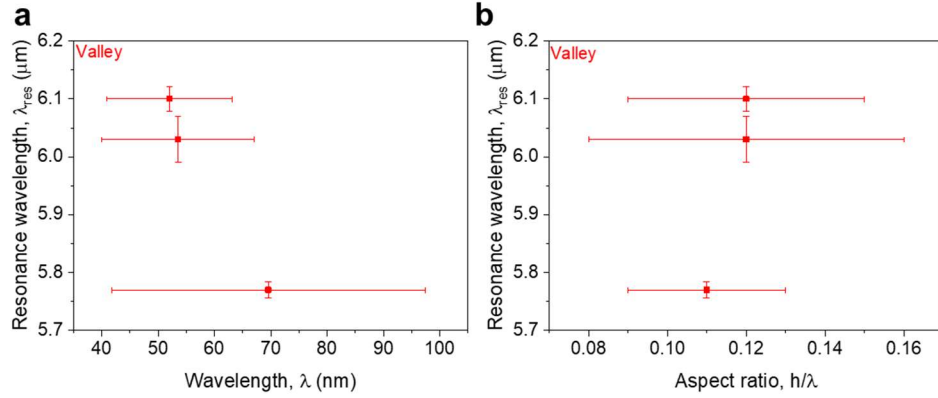


Figure 3.5. Correlation between plasmonic resonance wavelength and the topography features (wavelength & aspect ratio) of wrinkled graphene residing on a 50% contracted PS. a, Correlation between the plasmonic resonance wavelength and wrinkle wavelength. **b,** Correlation between the plasmonic resonance wavelength and aspect ratio.

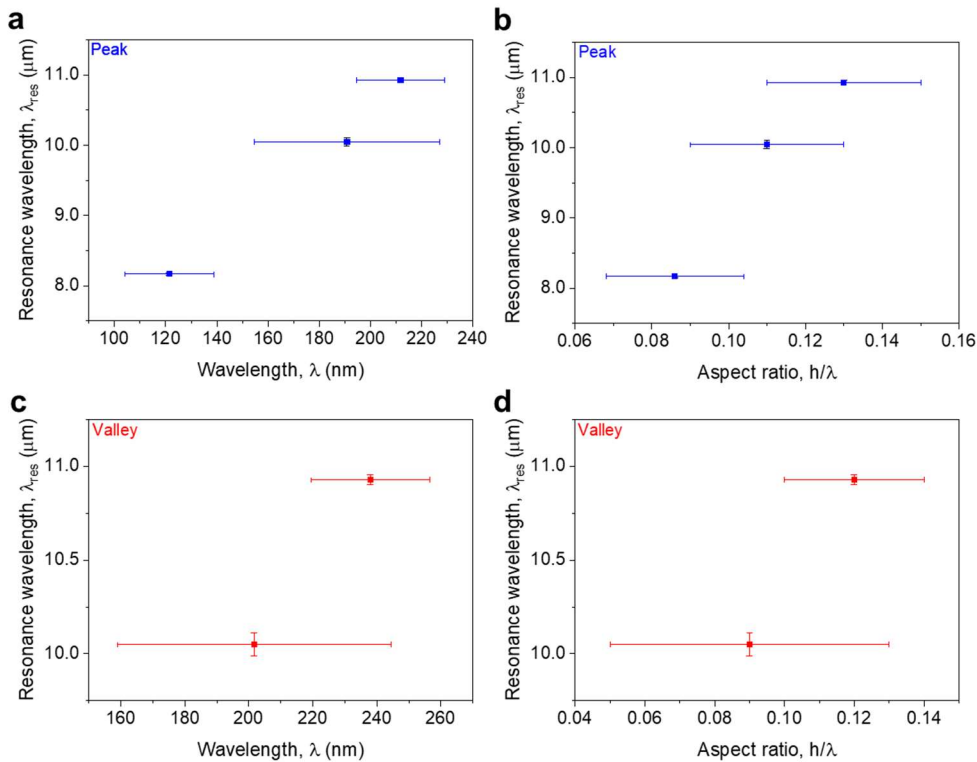


Figure 3.6. Correlation between plasmonic resonance wavelength and the topography features (wavelength & aspect ratio) of wrinkled graphene residing on a 35% contracted PS. a, Correlation between the plasmonic resonance wavelength and wrinkle wavelength at peak locations. **b,** Correlation between the plasmonic resonance wavelength and aspect ratio at peak location. **c,** and **d,** Depiction of the correlation similar to (a) and (b) at the valley locations.

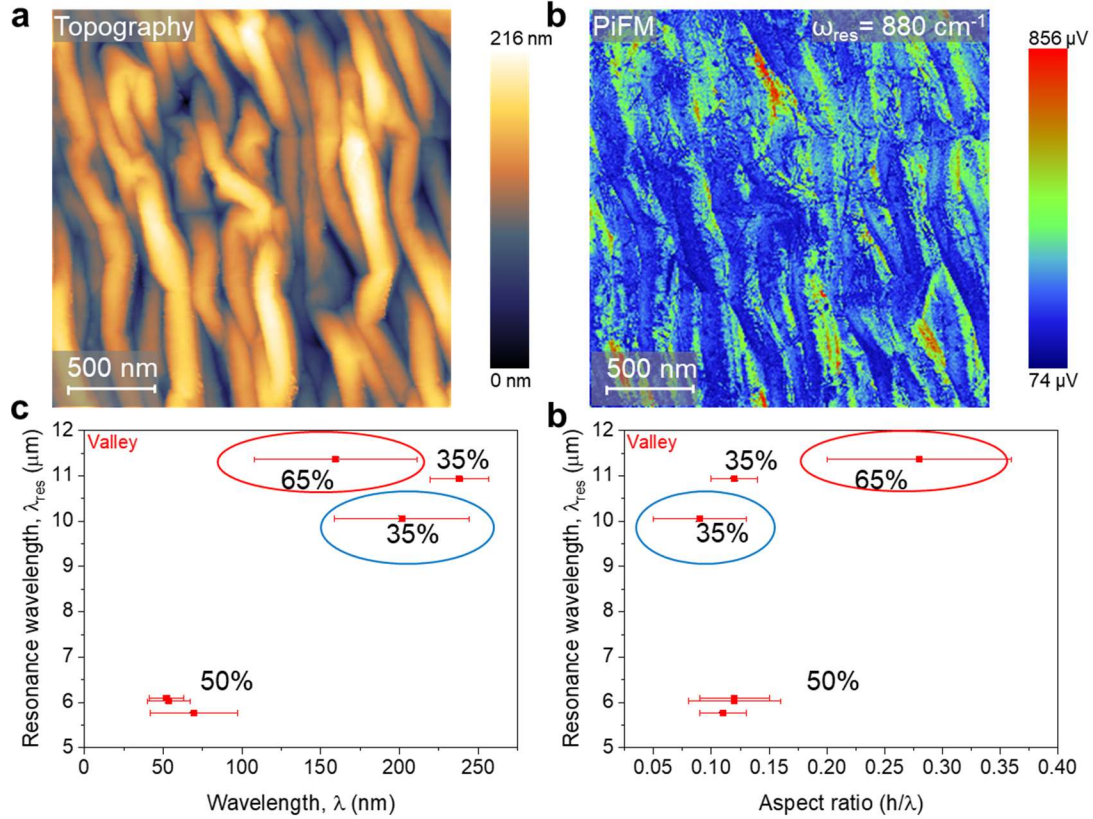


Figure 3.7. Effect of larger aspect ratio on plasmonic resonance. **a**, Topography image of wrinkled graphene residing on a 65% thermally contracted PS. **b**, Near-field image of the area shown in (a) showing plasmonic confinement at 880 cm^{-1} . **c**, Correlation between the plasmonic resonance wavelength and wrinkle wavelength at valley locations. The degree of thermal contraction of the PS for each case is labelled. The λ_{res} comparison between the case of 65% and 35% thermally contracted PS is shown in the ovals. **d**, Correlation between the plasmonic resonance and aspect ratio at valley locations.

3.6 Effect of electric field direction on the resonance wavelength

To study the effects of orientation between the incident photon's electric field direction (E_x) and wrinkle's k -vector, we performed PiFM imaging of the same wrinkled graphene structure at two directions where electric field (E_x) of the incident light was aligned either parallel or perpendicular to the direction of the wrinkle vector (**Figure 3.8**). We defined a term 'Degree of Localization' (DoL) to compare the plasmonic confinement when the direction of electric field (E_x) of the incident light was switched from a parallel to perpendicular orientation with respect to the wrinkle wave vector (**Figure 3.8a** and **3.8b**). From the histogram of the PiFM

intensities obtained from the PiFM images, we identified the PiFM magnitude corresponds to 75th and 25th percentile (denoted by the vertical dashed lines in **Figure 3.8a(iii)** and **3.8b(iii)**). With the help of the PiFM images and histograms, we then calculated the area coverage in the PiFM images for the PiFM magnitudes correspond to 75th and 25th percentile (shown as the blue and orange shades, respectively in **Figure 3.8a(iii)** and **3.8b(iii)**). The DoL was defined as the ratio of the area under the blue and orange region in **Figure 3.8a(iii)** and **3.8b(iii)**. Therefore, an increased DoL indicated stronger confinement in PiFM signal. We found that the DoL for the parallel orientation was twice than that of the perpendicular orientation at the same resonance wavelength. This clearly indicates that the parallel orientation is the preferred direction for efficient plasmonic confinement.

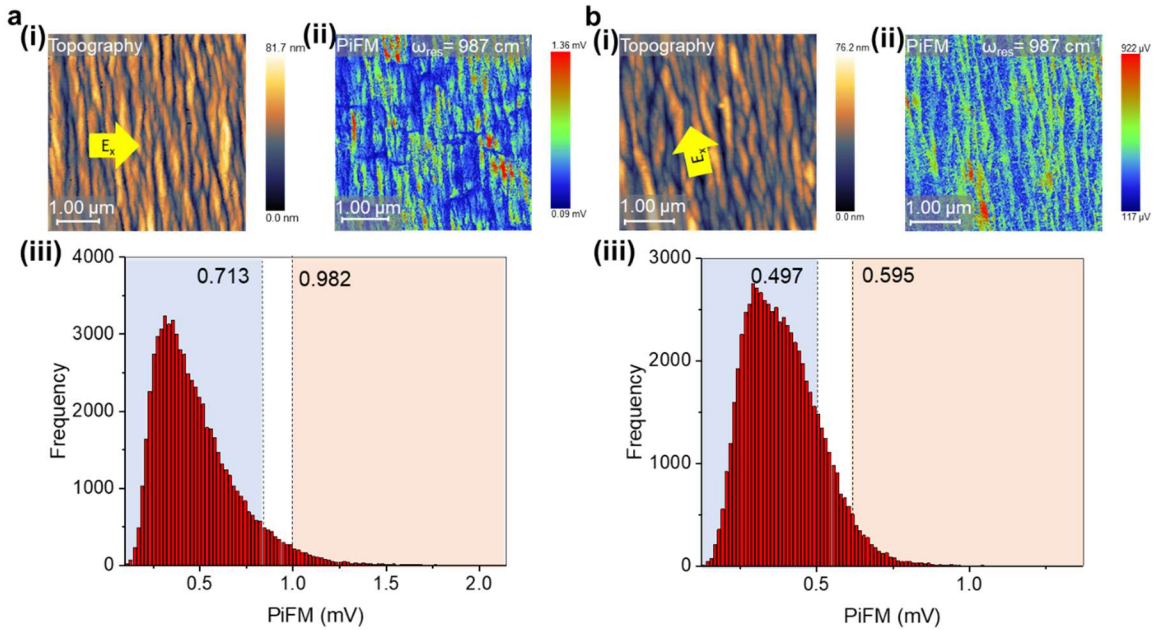


Figure 3.8. Effect of orientation between electric field direction and wrinkle wave vector on the plasmonic confinement. PiFM measurements of wrinkled graphene with electric field (E_x) of the incident photon at parallel (**a**) and perpendicular (**b**) to the wrinkle wave vector. The topography and near-field images of each case are shown in (i) and (ii) of each sub-figure. The histogram of the PiFM intensity distribution for each case is shown in (iii) of each sub-figure. The PiFM magnitude corresponds to 75th and 25th percentile is labelled and marked with the vertical dashed line in the histograms.

3.7 Finite element analysis to estimate plasmon resonance wavelength

To investigate the mechanism behind plasmonic resonance, we performed a finite element analysis to estimate the absorption and near-field distribution of wrinkled graphene structures due to light-matter interaction. The absorption (A), transmittance (T) and reflectance (R) of the graphene were defined as follows,

$$A = 1 - T - R \quad (3.1)$$

$$T = \frac{I_2}{I_0} \quad (3.2)$$

$$R = \frac{I_1}{I_0} \quad (3.3)$$

Here, I_0 , I_1 and I_2 were defined as the incident, reflected, and transmitted intensity upon light-matter interaction of graphene, respectively. The graphene structure was modeled as a cosine function for simplicity. A representative absorption spectrum of a wrinkled structure with λ of 70 nm and AR of 0.11 is shown in **Figure 3.9a**. Our model predicted two distinct peaks in the absorption spectrum, one at 6 μm and the other at 4.45 μm . The absorption peak at 6 μm was at least an order of magnitude larger than the absorption peak at 4.45 μm . The near-field distribution at these two wavelengths suggested that the absorption at 6 μm corresponds to the first plasmonic resonance mode while the 4.45 μm corresponds to the second resonance mode (defined as mode 1 and mode 2 in insets of **Figure 3.9a**, respectively). The mode 1 resonance predicted by our model is in good agreement with the PiF-IR spectrum obtained on a wrinkled graphene with similar topography features (shown in **Figure 3.2b**).

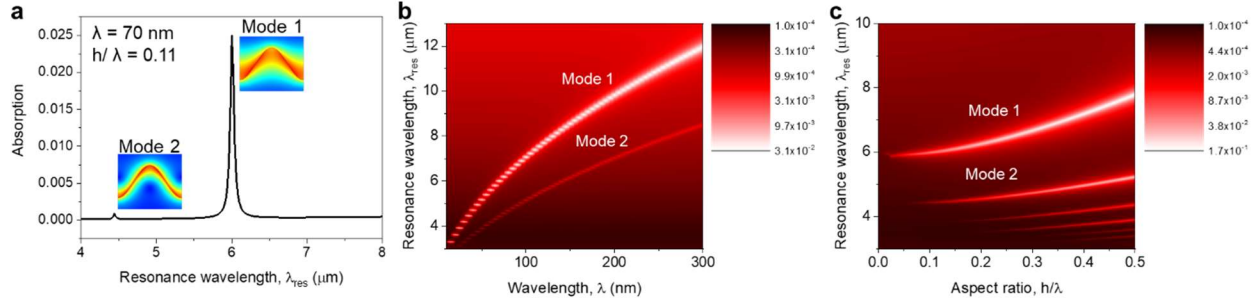


Figure 3.9. Finite element analysis to investigate the correlation between plasmon resonance and topography features. **a**, Absorption spectra of wrinkled graphene at a fixed wavelength (λ) and aspect ratio when the electric field of incident photons is parallel to the wrinkle wave vector. The near-field distribution at the two absorption peaks is shown in the inset. **b**, Correlation between plasmon resonance wavelength and λ for a fixed aspect ratio of 0.1. **c**, Correlation between plasmon resonance wavelength and aspect ratio for a fixed λ at 70 nm.

Once we established our model to predict the plasmonic resonance of wrinkled graphene, we extended our model to predict the relation between λ_{res} and λ as well as λ_{res} and aspect ratio (**Figure 3.9b** and **3.9c**). Our model suggests that λ_{res} follows a red shift trend as λ is increased at a constant AR and vice versa regardless of the modes (**Figure 3.9b** and **3.9c**). However, λ_{res} at mode 1 is larger than the λ_{res} at mode 2 with stronger absorption. For example, the λ_{res} at mode 1 is $\sim 10 \mu\text{m}$ whereas λ_{res} at mode 2 is $\sim 7 \mu\text{m}$ when λ is 200 nm. The λ_{res} at mode 1 is $\sim 6 \mu\text{m}$ whereas λ_{res} at mode 2 is $\sim 4.5 \mu\text{m}$ when AR is 0.1. However, the rate of redshift in λ_{res} is different with respect to the λ and AR. The λ_{res} scales with a cubic polynomial of λ while λ_{res} scales exponentially increasing with AR (**Figure 3.10**). Moreover, **Figure 3.9c** suggests that a higher order of plasmonic resonance would appear as the AR increases.

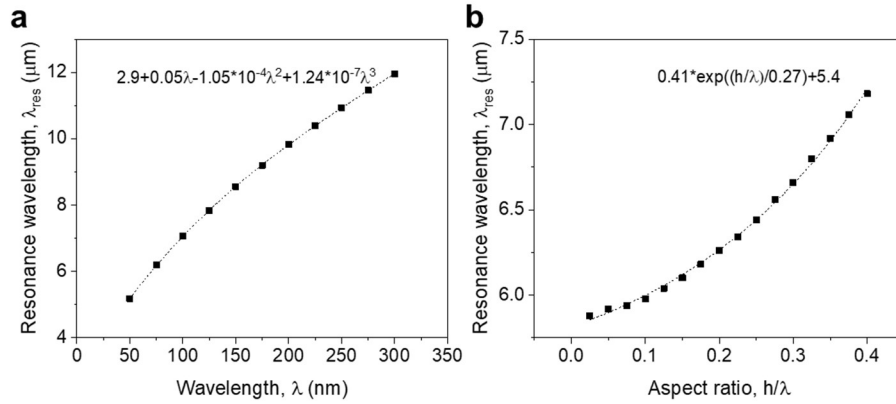


Figure 3.10. Correlation between the mode 1 plasmon resonance wavelength (λ_{res}) and topographic features obtained from Figure 3b and 3c. a, Correlation between λ_{res} and wavelength. b, Correlation between λ_{res} and aspect ratio.

The λ_{res} trend with the topographic features at peak and valley locations predicted by our model at mode 1 is in good agreement with our PiFM measurements (**Figure 3.11**). This clearly indicates that we predominantly observed the first mode of plasmonic resonance with our PiFM measurements. The structures prepared for the current study possessed an AR mostly between 0.08 to 0.13. Since **Figure 3.9c** suggests that only mode 1 and mode 2 can occur for AR below 0.2, we expect that the possibility of observing higher order resonance modes (beyond mode 2) in our PiFM measurements was negligible.

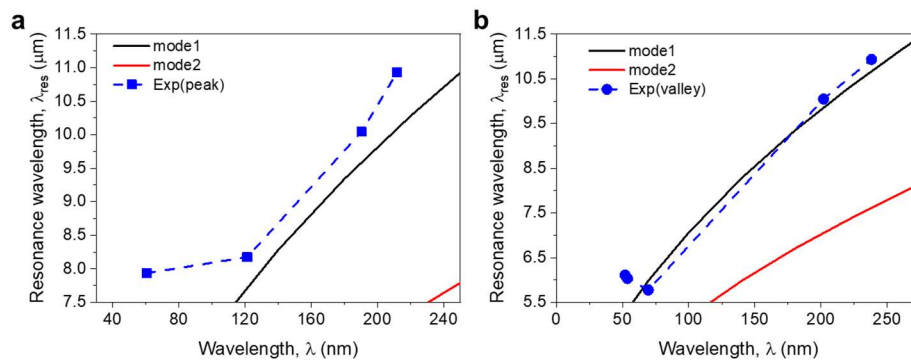


Figure 3.11. Correlation between the finite element analysis (FEA) and the experimental (Exp) measurements of topography induced plasmonic resonance. a, Fitting of PiFM measurements with the FEA model at Fermi energy of 0.34 eV at the peak locations. b, Fitting of PiFM measurements with the model at the same Fermi energy of 0.34 eV at the valley locations.

3.8 Plasmon resonance on wrinkled graphene for enhanced chemical imaging

To study how plasmonic resonance of our wrinkled graphene can be used for enhanced chemical imaging and detection of molecules, we performed PiF-IR and chemical imaging of polymethyl methacrylate (PMMA) with an underlying graphene structure (**Figure 3.12**). The PiF-IR spectroscopy of PMMA with flat graphene underneath showed a peak at 1732 cm^{-1} which corresponds to the vibration of the C=O bond (**Figure 3.12a**). The near-field image of the corresponding structure exhibited homogeneous distribution of the near-field intensity across the PMMA regardless of an existence of graphene (**Figure 3.12c**). The PiF-IR spectra of the PMMA with underneath wrinkled graphene structure showed a spectral peak with a dip at around 1732 cm^{-1} (**Figure 3.12b**). The attenuation at 1732 cm^{-1} is attributed to the plasmon induced transparency which is a signature of coupling between graphene plasmons and PMMA phonons^[93,94]. The PMMA with wrinkled graphene region showed an overall two-fold increase in the PiFM intensity compared to the standalone PMMA region in the corresponding PiFM image (**Figure 3.12d**). The surface roughness of the PMMA was similar when placed on either flat or wrinkled graphene structures (**Figure 3.13**). This result further supports that the enhanced near-field signal was due to phonon-plasmon coupling rather than any topography induced enhancements of the PMMA film itself. The plasmon-phonon coupling and enhanced near-field intensity unequivocally established our wrinkled graphene structure as a promising candidate for efficient detection and enhanced imaging of target molecules.

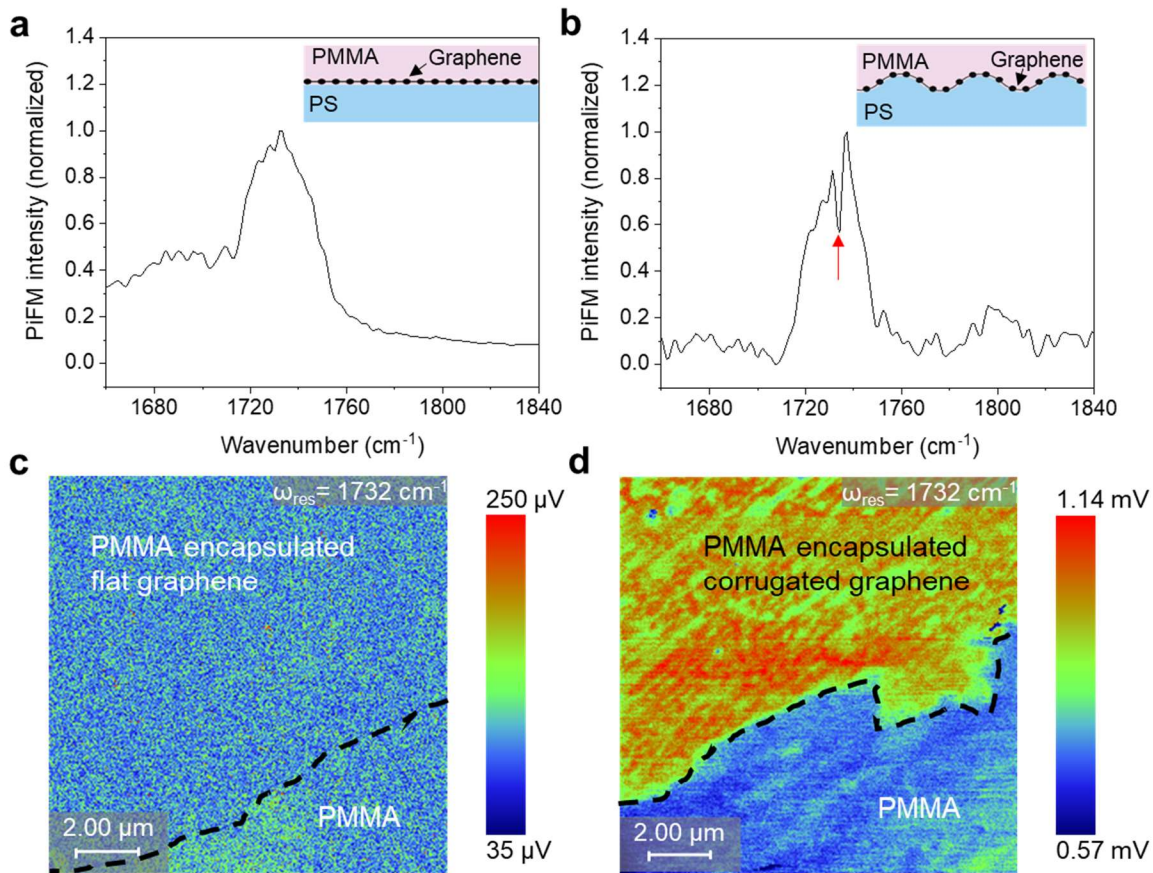


Figure 3.12. Graphene plasmon assisted enhanced chemical imaging of PMMA. **a**, PiF-IR spectra of a PMMA encapsulated flat graphene structure showing a characteristic peak at 1732 cm^{-1} . The schematic drawing of the structure is shown in the inset. **b**, PiF-IR spectra of a PMMA encapsulated wrinkled graphene structure showing optical transparency at 1732 cm^{-1} (denoted with an arrow). **c**, PiFM image at 1732 cm^{-1} for PMMA encapsulated flat graphene. The graphene border is shown as a black dashed line in c and d. **d**, PiFM image at 1732 cm^{-1} for PMMA encapsulated wrinkled graphene.

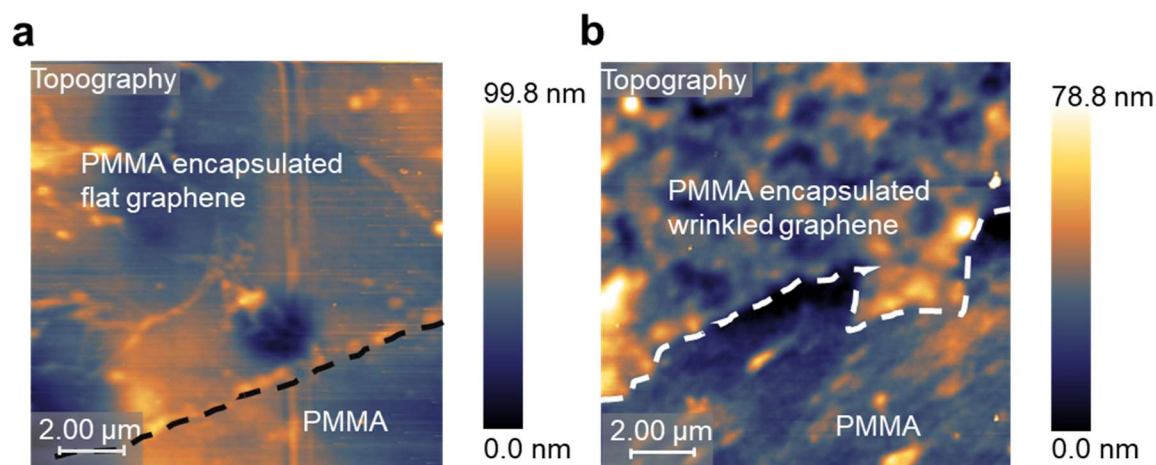


Figure 3.13. Topography of PMMA encapsulated flat graphene (a) and wrinkled graphene (b). The buried graphene edge is shown as dashed lines. The RMS roughness of the PMMA encapsulated graphene area in (a) and (b) is 10.23 nm and 10.81 nm, respectively.

3.9 Conclusions

In conclusion, we demonstrated widely tunable plasmon resonance wavelengths (5.77-10.93 μm) of semi-infinitely large graphene structures driven by controlled topography. Our study proposes a new method for modulating graphene plasmons in addition to the electrostatic doping of nano-patterned graphene. Our experimental observations agreed well with computational electromagnetic simulation, thereby providing an insight into topography-induced plasmonic confinement. Finally, we showed that our proposed structure can be used for enhanced chemical imaging. Owing to the biocompatibility of graphene and wide tunability of the plasmonic resonance via topography engineering, our wrinkled structure can be used to study various chemical/bio-materials via enhanced chemical imaging.

CHAPTER 4: STRONGLY ENHANCED ELECTROMECHANICAL RESPONSE IN ATOMICALLY THIN TRANSITION METAL DICHALCOGENIDES¹⁸

4.1 Introduction

Micro- or nanoscale energy conversion or actuation requires strong electromechanical coupling in the constituent materials^[51,95–99]. Piezoelectricity is the most explored electromechanical response found in materials. However, piezoelectricity occurs only in non-centrosymmetric crystals and therefore, exists in only 20 out of 32 crystal classes^[100]. Flexoelectricity is another form of electromechanical response that exists in all crystal systems^[42,101,102]. In flexoelectricity, materials deform in response to an inhomogeneous polarization such as induced by electric field (E-field) gradient, which is known as converse flexoelectric effect (CFE). The scaling law (E-field gradient $\sim 1/\text{thickness}^2$) has motivated exploring flexoresponse at nanoscale^[54,56]. Furthermore, enhanced electromechanical actuation has been demonstrated in nanoscale structures of three-dimensional materials compared to their bulk counterparts due to large “free surface” effect^[74,103]. Exploiting this free surface could also augment the flexoresponse at the nanoscale.

Two dimensional (2D) transition metal dichalcogenides (TMDs), such as monolayer molybdenum disulfide (MoS_2) and tungsten diselenide (WSe_2), have been extensively explored to harness electromechanical responses^[99,104], owing to their in-plane piezoresponse^[49,105]. However, TMDs do not possess out-of-plane piezoelectricity due to inversion symmetry. Despite this, recent studies have reported CFE enabled out-of-plane electromechanical response (d_{33}) in monolayer TMDs on gold substrate^[106]. Still, the measured d_{33} was smaller than the in-plane piezoresponse, possibly due to strong affinity between the gold substrate and overlaid chalcogen

¹⁸ This work has been published in *Materials Today* in 2021.

atoms^[107]. Furthermore, probing d_{33} of monolayer TMDC on flexible plastic substrates^[108] could expose the in-plane piezoresponse of the TMD to the out-of-plane direction through substrate deformation (e.g., bending). However, the measured response cannot rigorously be attributed to flexoelectricity due to the crosstalk between the in-plane and out-of-plane electromechanical response. Probing converse flexoelectricity without any extraneous effect is critical to study this universal yet underappreciated phenomenon in 2D TMDs.

In this work, we investigated the out-of-plane CFE (d_{33}) of MoS₂ and WSe₂ on silicon (Si) using piezoresponse force microscopy (PFM). First, we compared the CFE with the intrinsic in-plane piezoresponse. Our PFM measurements revealed stronger out-of-plane CFE than the in-plane piezoresponse. Second, we carried out detailed measurements to investigate the layer dependence on CFE. We observed 700% (MoS₂) and 400% (WSe₂) enhancement in CFE as the thickness reduced from bulk to the atomically thin limit. Third, we used a finite element analysis (FEA) to study the potential deformation mechanism dictated the CFE in PFM measurements. Our FEA study suggested that a potential puckering occurred during PFM measurement could attenuate the electric field gradient by an order of magnitude. Finally, we studied the effect of in-plane strain on the CFE. We proposed that in-plane tensile strain could reduce puckering and thereby increasing the CFE by ~46%. We reported CFE of monolayer WSe₂ to be ~8.14 pm/V, the highest electromechanical response reported for any monolayer TMDs.

4.2 Preparation of atomically thin films of transition metal dichalcogenides

The MoS₂ and WSe₂ used in this study were mechanically exfoliated from commercially available bulk crystals (HQ Graphene) on SiO₂/Si substrates, followed by a wet transfer process (**Figure 4.1**). The SiO₂ was used as the sacrificial layer during the wet transfer process.

Polymethyl methacrylate (PMMA) was used as a handling layer. Potassium hydroxide (15 wt%) solution was used at 80 °C to etch away the SiO₂ layer during the wet etching. Once the etching was completed, the material (with PMMA) was transferred on deionized water baths for several iterations to clean up any residual ions from the wet etching process. The material was then transferred onto the target substrate (silicon) followed by PMMA removal by acetone and standard degreasing.

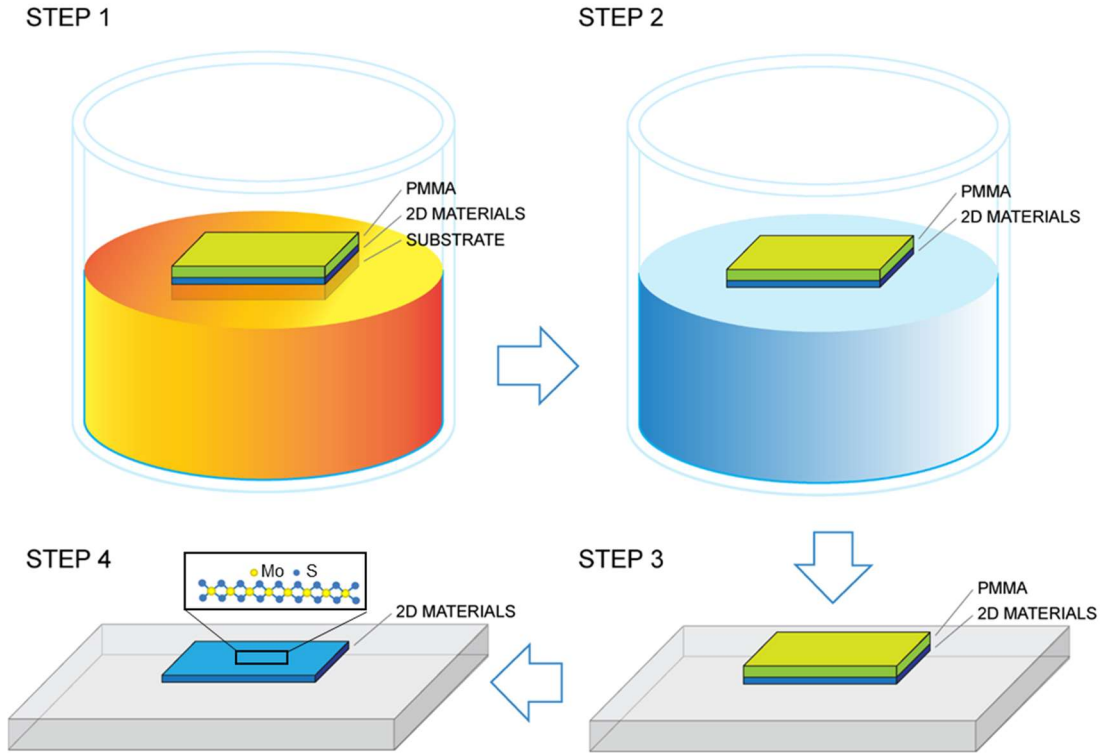


Figure 4.1. Schematic illustration of the sample transfer process used in the study. The 2D material (e.g., MoS₂ or WSe₂), handling layer (polymethyl methacrylate, PMMA) and the primary substrate are transferred in an etchant solution (step 1). Once the primary substrate (i.e., SiO₂/Si wafer) is etched/delaminated from the remaining structure, the structure is transferred to a deionized (DI) water bath for cleaning the residual ions (step 2). The material with PMMA layer is transferred on the final substrate from the DI water bath (step 3). Finally, the PMMA layer is removed with acetone, leaving the 2D material on the final substrate (step 4).

The number of layers was determined by photoluminescence (PL) spectroscopy^[8,109] and tapping mode atomic force microscopy (AFM) (**Figure 4.2**). A 532 nm laser was used in PL

spectroscopy. The monolayer (direct bandgap) and bilayer structures (indirect bandgap) were identified by their respective PL peaks (**Figure 4.2a** and **4.2b**). For thicker (>2 layers) MoS₂ and WSe₂, we relied on AFM imaging to identify the number of layers. The AFM topography images (**Figure 4.2c**) revealed the layer thickness as 0.9 nm and 0.8 nm for MoS₂ and WSe₂, respectively, which were in good agreement with previous results^[110,111].

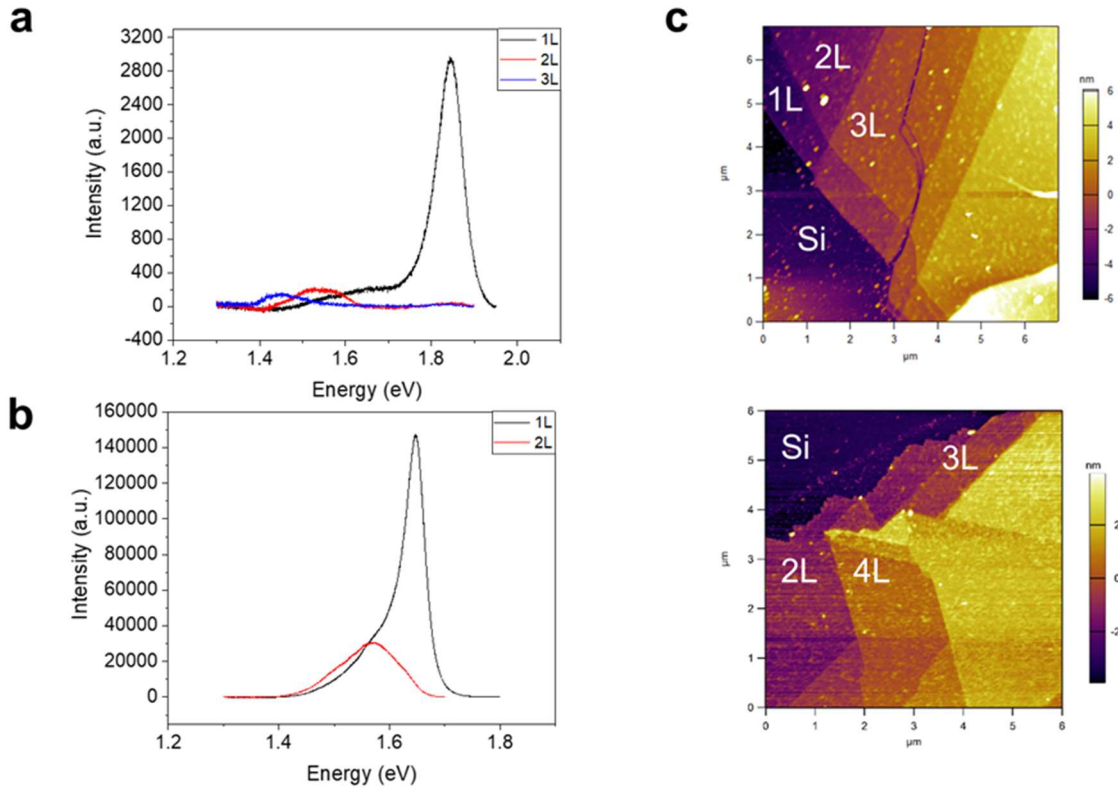


Figure 4.2. Determining the number of layers of MoS₂ and WSe₂. **a, b**, PL spectra of MoS₂ and WSe₂ after transferred onto Si, respectively. **c**, AFM topography images of MoS₂ (top) and WSe₂ (bottom) to identify number of layers.

We also considered the effect of stacking order on the converse flexoelectric effect (CFE) because the variation in stacking order (AA, AB or SP) might induce different electromechanical response^[47]. Since all the samples were prepared by directly exfoliating from the bulk crystal without any manual rotation, we assumed our samples will exhibit the lowest energy stacking

order (AB stacking). We expect that the effect of stacking order on CFE should be minimum in our study.

4.3 Estimating effective out-of-plane electromechanical response (d_{33}) of atomically thin transition metal dichalcogenides

To characterize the converse flexoelectric response of MoS₂ and WSe₂ at a sub-20 nm spatial resolution, we adopted the dual AC resonance tracking piezoresponse force microscopy (DART PFM) technique^[112]. The resonance-enhanced PFM technique adopted in this study enables high signal to noise ratio characterization, which is essential to detect weak electromechanical responses. The details on PFM technique has been discussed in Chapter 2. To recap, during PFM measurement, AC voltage is supplied to the metal coated cantilever (Budget Sensor Multi75E with 3 N/m force constant and platinum coated cantilever was used in this study) which is brought in contact with the sample of interest (**Figure 4.3**). The applied bias rapidly decays away from the atomic force microscope (AFM) tip (inset of **Figure 4.3**), which results in an E-field gradient in concert with substrate serving as a ground electrode (Si as the substrate in this study). As the cantilever rasters along the surface with the oscillating bias applied to it, the sample oscillates due to piezoresponse (or flexoresponse). The oscillation of the sample due to piezoresponse (or flexoresponse) is recorded by the cantilever deflection via a lock-in amplifier. A standard PFM scan yields three images – topography, PFM amplitude and PFM phase. The vertical (lateral) deflection of the cantilever due to the oscillating bias is stored in the case of vertical (lateral) PFM. The amplitude contains information about the strength of the piezoresponse (or flexoresponse) whereas the phase shows the dipole direction. The strength of the piezoresponse (or flexoresponse) is known as the piezoelectric coefficient and estimated

from the linear correlation between the PFM amplitude and applied AC bias. In this study, the effective out-of-plane piezoelectric coefficient is addressed as d_{33} .

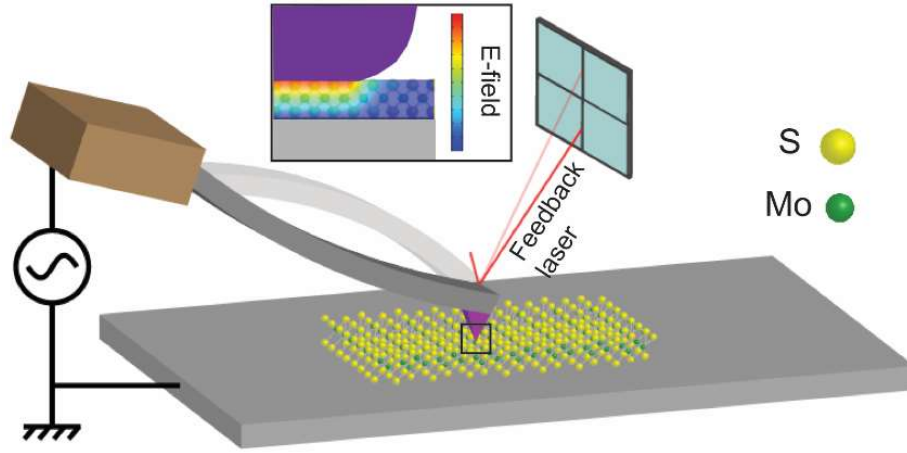


Figure 4.3. Schematic drawing of the PFM measurement technique. The inset corresponds to generated E-field during PFM measurement.

Since TMDs do not possess out-of-plane piezoresponse, we attribute the origin of d_{33} to the CFE after considering all the possible psuedo-piezo effects as described below. The piezoresponse force microscopy (PFM) based measurement may consist of various non-piezoelectric signals due to complex tip-sample dynamics^[67]. There are five possible sources of out-of-plane electromechanical responses – piezoresponse, electrostatic, ion redistribution, electrostriction and flexoelectricity. The electrostatic effect varies linearly with DC bias whereas piezoresponse varies linearly with AC bias. To suppress the electrostatic effect, no additional DC bias was applied during the PFM scans. However, the existence of trapped charges at the surface can still yield a non-zero electrostatic effect. The linear correlation between the PFM amplitude and the applied AC bias rules out the contribution of any electrostatic effect in the estimation of d_{33} . To obtain the d_{33} in this study, the PFM amplitude was obtained as a function of applied AC bias (**Figure 4.4a-c**). To do so, a uniform and homogeneous topography was chosen for the PFM

scan to remove possible coupling between tip-sample contact stiffness (revealed by a change in contact resonance frequency) and electromechanical response^[113]. To maintain stable feedback and homogeneity in topography, the scan size was limited to $<1\ \mu\text{m}$ for most of the cases. Then, AC bias was varied as the cantilever rastered along the surface. In doing so, PFM amplitude was obtained as a function of AC bias after one complete scan. The resultant slope of the linear fit between PFM amplitude and AC bias yielded d_{33} (blue fitted curve, **Figure 4.4d**).

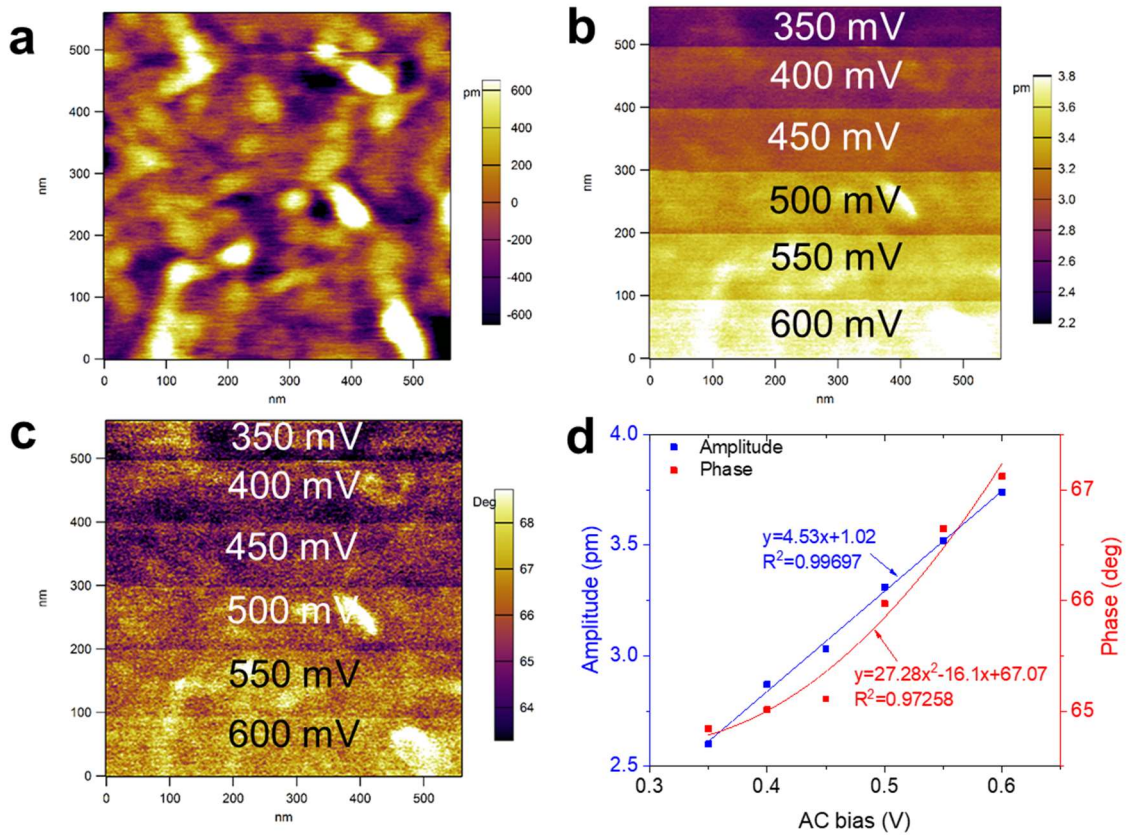


Figure 4.4. An example of PFM scan obtained on bilayer MoS₂. **a,b,c**, Height, PFM amplitude and PFM phase images of bilayer MoS₂, respectively. **d**, The correlation between PFM amplitude (termed as amplitude) and PFM phase (termed as phase) with the applied AC bias with fitted curves and correlation parameters.

It is worthwhile to mention here that we observed a minimal contrast in the phase image (**Figure 4.4c**) as the AC bias was varied during the scans. The phase maintained a quadratic

relation to the applied bias (red fitted curve, **Figure 4.4d**) whereas the amplitude maintained the linear relation (blue fitted curve, **Figure 4.4d**). The phase signal is affected by the interplay among the applied AC bias, forces acting on the cantilever, rate of cantilever deflection, instrumental phase offset and domain direction^[114,115].

The forces on the cantilever and the rate of deflection are inversely proportional to the Q-factor whereas instrumental phase offset depends on the resonance frequency. The Q-factor in our PFM measurement was sufficiently high ($\gg 100$) to suppress the effect of forces and rate of deflection of the cantilever on the phase image. We observed uniform resonance frequency over the scan areas which also cancelled out the possibility of the effect of instrument phase offset on the observed phase contrast. Therefore, the observed contrast in the phase image might be originated from the interplay between the applied AC bias and remnant forces on the cantilever (e.g., electrostatic or electrostriction).

We also considered the effect of ion redistribution and electrostriction on the d_{33} . Ion redistribution is dominant in ionic materials. The materials used in this study possess mainly covalent and van der Waals bonds. Therefore, we expect the effect of ion redistribution would be minimum.

To study the effect of electrostriction, we carried out a control experiment where the effect of electrostriction was expected to be dominant. We performed PFM measurement of MoS₂ and WSe₂ on a SiO₂/Si substrate where the SiO₂ was 300 nm thick (**Figure 4.5**). The correlation of the PFM amplitude of the different regions and the applied bias is shown in **Figure 4.5b**. The PFM amplitude maintained a quadratic correlation with the applied bias for mono- and multilayer WSe₂, monolayer MoS₂ and SiO₂ which is a signature of electrostriction effect.

Because we did not observe such a quadratic relation for the TMDs on Si (**Figure 4.4**), we concluded that the effect of electrostriction was minimum on the estimated d_{33} .

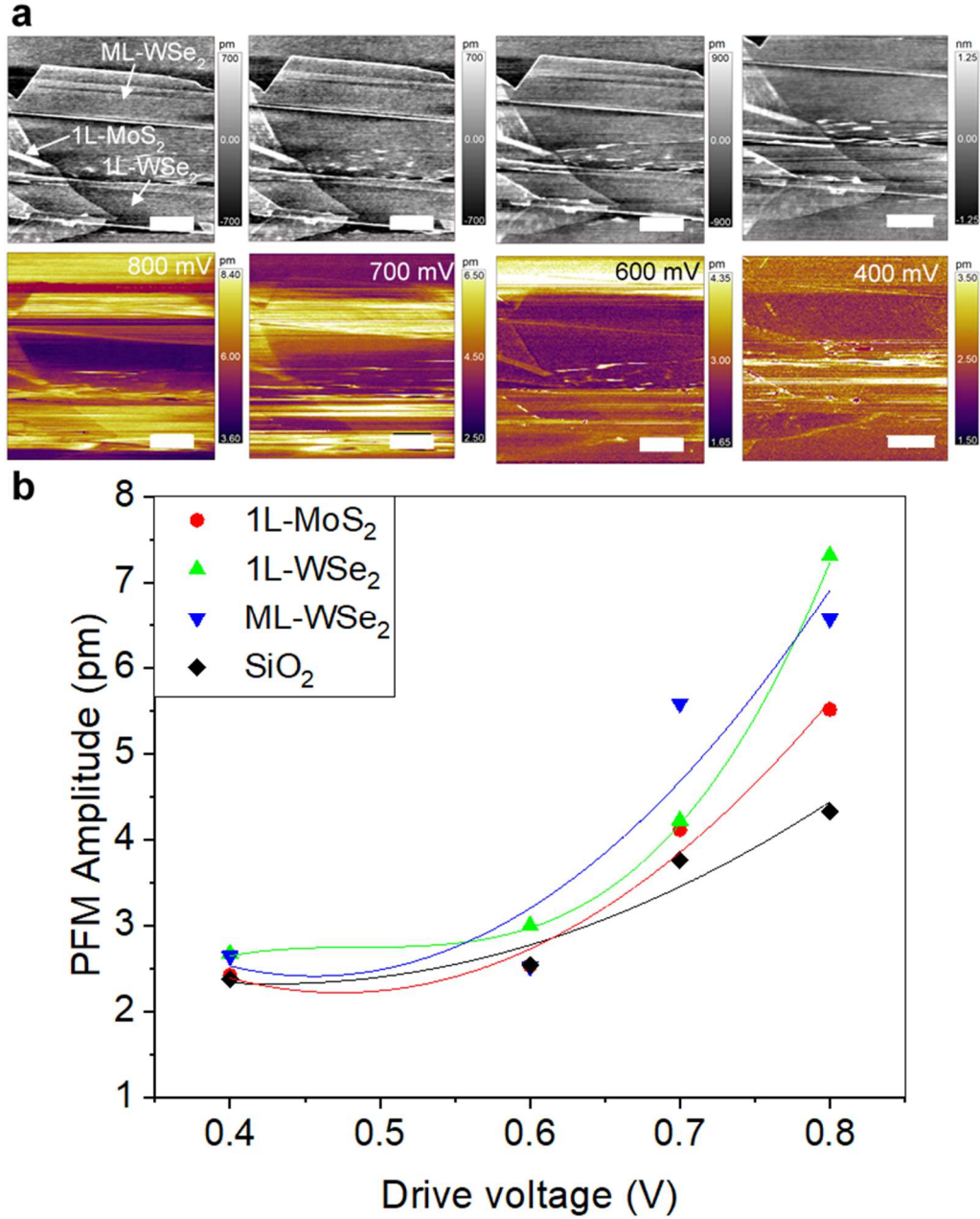


Figure 4.5. PFM scans of MoS₂ and WSe₂ on SiO₂/Si substrate. a, Height (top row) and PFM amplitude (bottom row) of the structure at different drive voltages. Scale bar is 2 μ m. Monolayer and multilayer regions are defined as 1L and ML, respectively. **b,** The correlation between the PFM amplitude and drive voltages of different regions shown in the height image.

To validate our measurement and calculation, we performed PFM on commercially available periodically polled lithium niobate (PPLN). The results are summarized in **Figure 4.6**. The phase image illustrated the characteristic up and down domains with 180° phase difference, whereas the slope of the PFM amplitude vs. AC bias plot yielded d_{33} of the up and down domains. The calculated d_{33} were in close agreement with the literature value^[116]. The asymmetry in d_{33} between the up and down domain can be originated from the trapped charge at the surface^[73]. We note that the inverse optical lever sensitivity (InvOLS) of the cantilever was calibrated before every scan shown in this study.

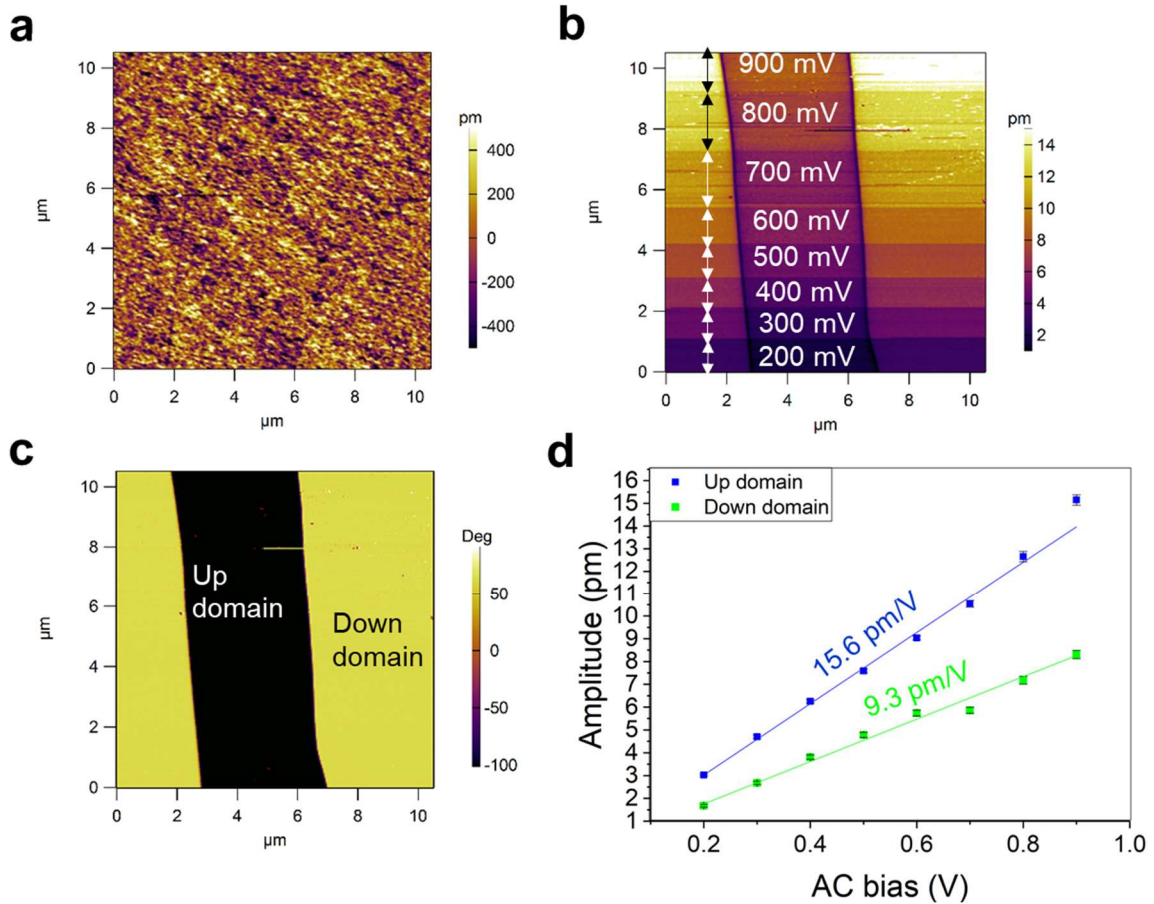


Figure 4.6. Validation of the adopted PFM measurement technique. a, b, c, Height, PFM amplitude and PFM phase images of PPLN, respectively. d, The linear correlation between PFM amplitude and applied bias. The magnitude of the slopes (d_{33}) of the respective domains are shown with the linear fit in (d).

4.4 Comparison between flexoresponse and piezoresponse of atomically thin transition metal dichalcogenides

To decouple flexoelectricity from piezoelectricity, we began our measurement by characterizing bilayer MoS₂ (2L-MoS₂) with in-plane inversion symmetry. The d_{33} of 2L-MoS₂ was 4.92 pm/V (**Figure 4.7**) and is ~500% higher than the previously reported d_{33} of monolayer MoS₂ (1L-MoS₂, ~1 pm/V)^[50]. The substrate (Si) exhibited negligible d_{33} (0.36 pm/V, Figure 1b). We note that our estimated d_{33} is 167% higher than the in-plane piezoresponse (d_{11}) of 1L-MoS₂ (1.84 pm/V)^[49,50]. We attribute the large d_{33} to the optimized substrate selection and measurement technique. Silicon demonstrated reduced interaction which allowed the MoS₂ atoms to more freely stretch towards the out-of-plane direction^[117]. The large d_{33} is also attributed to the high signal to noise ratio enabled by the resonance-enhanced PFM measurement technique adopted in the current study^[112].

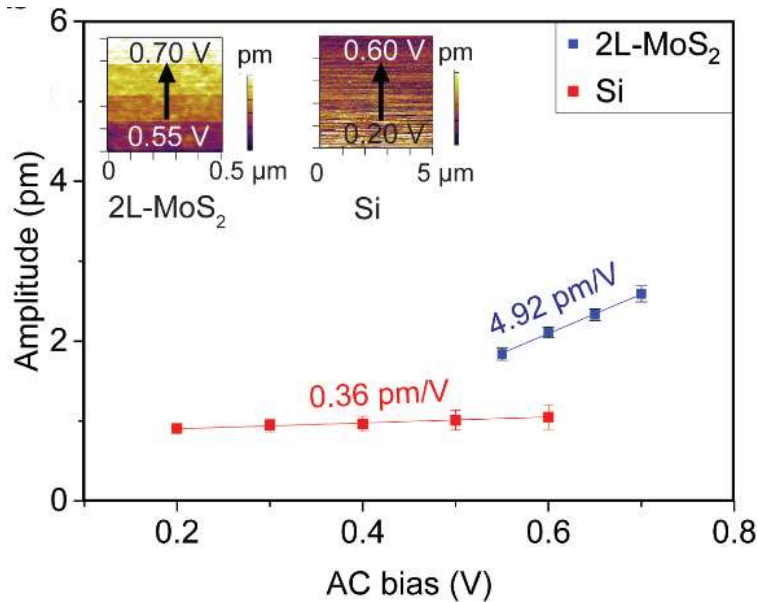


Figure 4.7. Converse flexoelectric effect of bilayer MoS₂. Correlation between the applied AC bias and resulting PFM amplitude on bilayer MoS₂ and Si. PFM amplitude images of MoS₂ and Si under spatially modulated bias are shown in the inset. The error bars denote one standard deviation.

We then estimated the d_{33} of 1L-MoS₂ and 1L-WSe₂ (**Figure 4.8a**). Our d_{33} for 1L-MoS₂ (2.78 pm/V) and 1L-WSe₂ (5.55 pm/V) on Si are significantly larger than the previously reported d_{33} of 1L-MoS₂ (0.94 pm/V) and 1L-WSe₂ (0.43 pm/V) on gold substrate^[106]. Furthermore, the d_{33} of both monolayer MoS₂ and WSe₂ are comparable or higher than the in-plane piezoresponse from previous literature (**Figure 4.8b**)^[50,105]. In the case of 1L-MoS₂, d_{33} exceeded d_{11} (1.84 pm/V) by 50%, whereas 1L-WSe₂ exhibited similar d_{33} compared to the d_{11} (5.1 pm/V). Despite the existence of non-zero d_{11} for 1L-TMDs, we can rule out any crosstalk between d_{11} and d_{33} since the atomically flat Si substrate prevented unwanted exposure of the in-plane to the out-of-plane direction. To the best of our knowledge, this is the first demonstration that the electromechanical response of TMDs induced by the out-of-plane CFE surpasses the conventional in-plane piezoresponse.

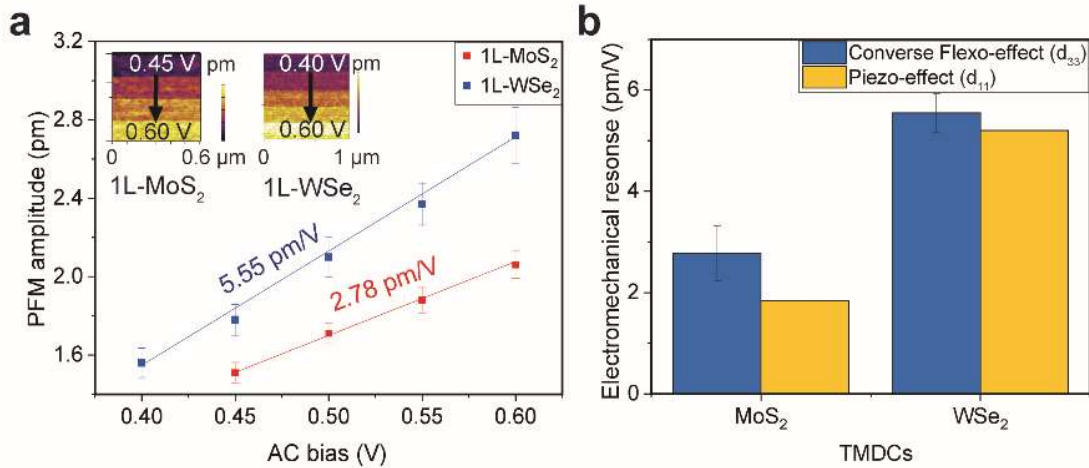


Figure 4.8. d_{33} estimation of monolayer MoS₂ and WSe₂. **a**, PFM responses of monolayer MoS₂ and WSe₂. The corresponding PFM amplitude images are shown in the inset. **b**, Out-of-plane flexoelectric, d_{33} of monolayer MoS₂ and WSe₂ measured in the present study compared to reported values of the in-plane piezoelectric coefficient, d_{11} ^[50,105]. The error bars denote one standard deviation.

To compare the out-of-plane electromechanical response (d_{33}) with the in-plane response under same experimental conditions, we performed lateral PFM measurements on 1L-MoS₂ and

1L-WSe₂ (**Figure 4.9**). The estimated in-plane piezoresponse was 1.54 pm/V (MoS₂) and 3.46 pm/V (WSe₂), which are smaller than the literature values^[50,105]. We note that the difference in substrate interaction might affect the in-plane deformation, resulting in a different in-plane piezoresponse compared to the literature value.

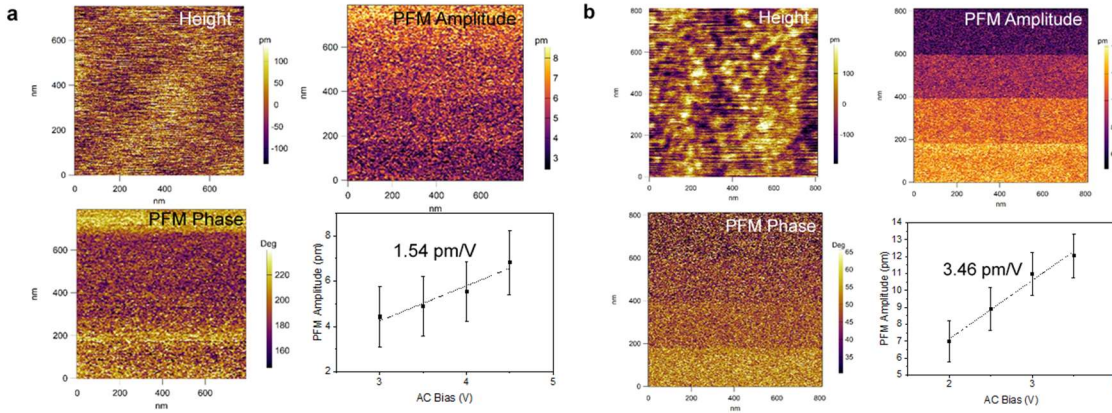


Figure 4.9. Lateral PFM measurement of monolayer TMDs. The PFM measurements and estimation of in-plane piezoresponse of (a) MoS₂ and (b) WSe₂.

4.5 Layer dependence of converse flexoelectric effect (d_{33})

To investigate the effect of the number of TMD layers on CFE, we conducted PFM measurement on atomically thin (1-4 layers) and thick multilayer (>25 layers) MoS₂ and WSe₂ (**Figure 4.10-4.22**). Then, we estimated d_{33} from each PFM scans by linearly fitting the PFM amplitude with the applied AC bias (**Figure 4.23-4.24**). The d_{33} of different layers of MoS₂ and WSe₂ are summarized in **Figure 4.25**. We observed that atomically thin TMDs exhibit larger d_{33} than their bulk counterparts (**Figure 4.25**); ~700% larger in the case of MoS₂ (4.92 pm/V of 2L vs. 0.67 pm/V of >25 layers) and ~400% larger in the case of WSe₂ (8.08 pm/V of 2L vs. 1.9 pm/V of >25 layers). This large enhancement in d_{33} from atomically thin TMDs suggests that increased availability of free surface enhances CFE^[74,103]. The free surface may allow the atomically thin material to ‘stretch’ the atomic bond length compared to the bulk state under E-

field gradient. The evolution in d_{33} as thinning down the materials to the atomically thin limit clearly demonstrates that converse flexoelectricity induced electromechanical response can be enhanced in low dimensional systems.

Furthermore, we carried out a detailed examination of how varying the number of MoS₂ and WSe₂ layers in the atomically thin limit (1-4 layers) influences d_{33} (**Figure 4.25**). For both MoS₂ and WSe₂, we observed a significant increase in d_{33} moving from monolayer to bilayer (2.78 pm/V vs. 4.4 pm/V for MoS₂, 5.55 pm/V vs. 8.08 pm/V for WSe₂). In contrast, comparing d_{33} between 2, 3, and 4 layers of MoS₂ and WSe₂, we observed minimal variation in d_{33} with added layers. This reduction of d_{33} in the monolayer compared to the 2-4 layers contradicts our hypothesis that increased free surface results in enhanced CFE.

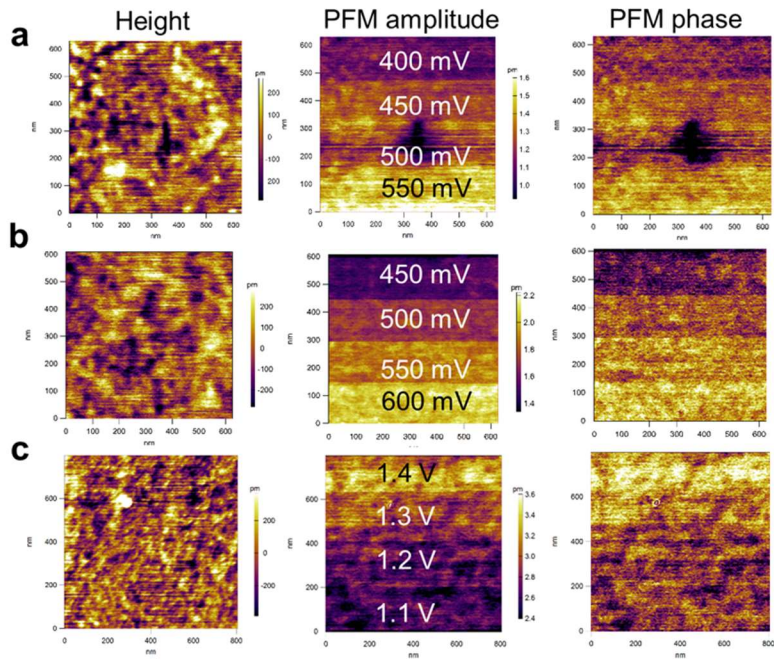


Figure 4.10. PFM measurements on monolayer MoS₂. PFM measurements with height (left), PFM amplitude (middle) and PFM phase (right) images of three set of samples taken 7 days (a), 10 days (b) and 18 days (c) after the wet transfer process.

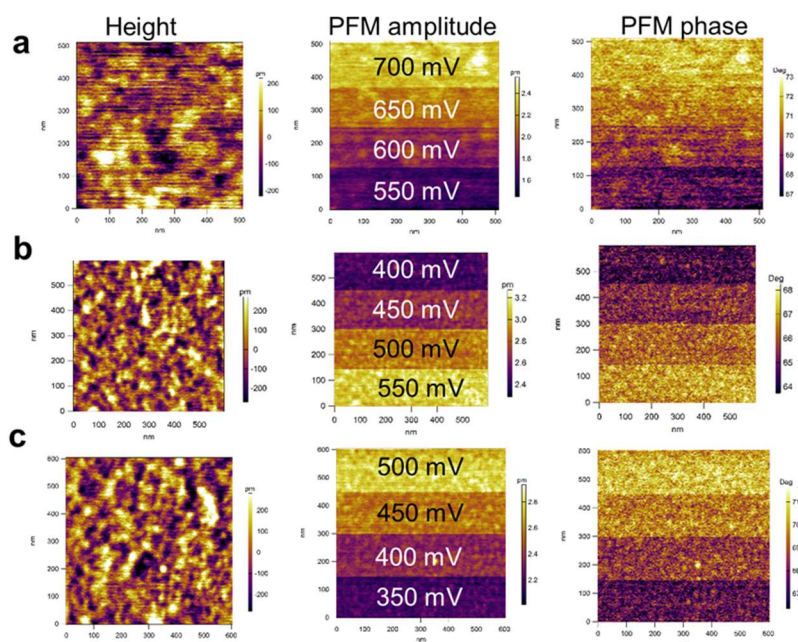


Figure 4.11. PFM measurements on bilayer MoS₂. PFM measurements with height (left), PFM amplitude (middle) and PFM phase (right) images of three set of samples taken 3 days (a), 7 days (b) and 16 days (c) after the wet transfer process.

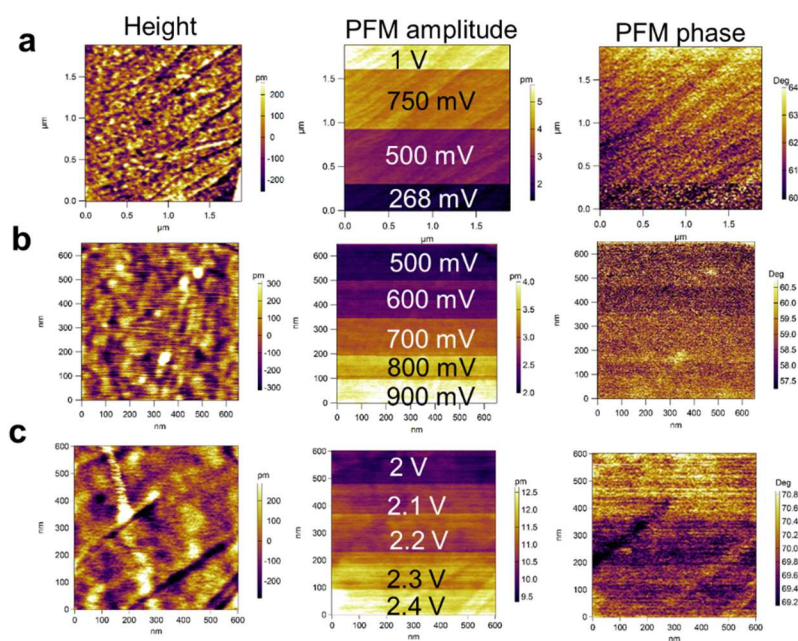


Figure 4.12. PFM measurements on trilayer MoS₂. PFM measurements with height (left), PFM amplitude (middle) and PFM phase (right) images of three set of samples taken 3 days (a), 10 days (b) and 27 days (c) after the wet transfer process.

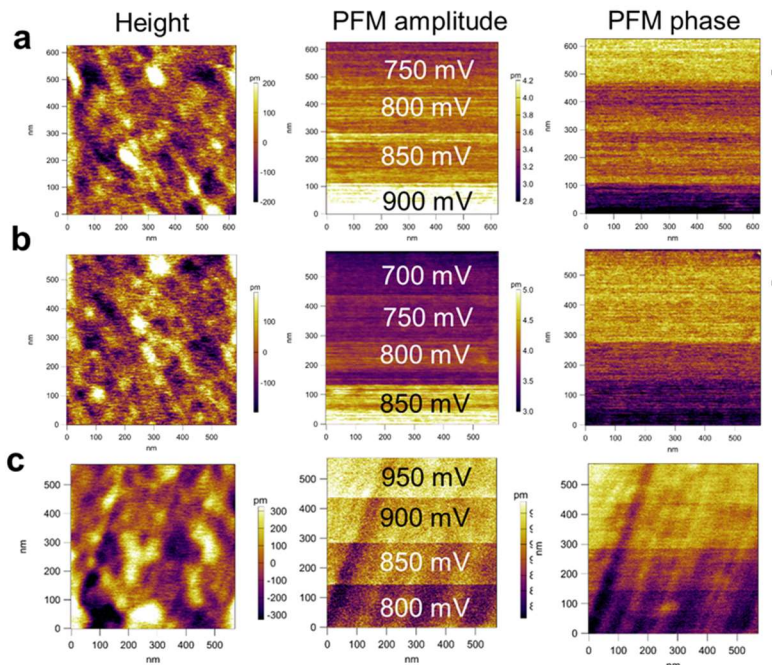


Figure 4.13. PFM measurements on quad layer MoS₂. PFM measurements with height (left), PFM amplitude (middle) and PFM phase (right) images of three set of samples taken 10 days (a), 11 days (b) and 20 days (c) after the wet transfer process.

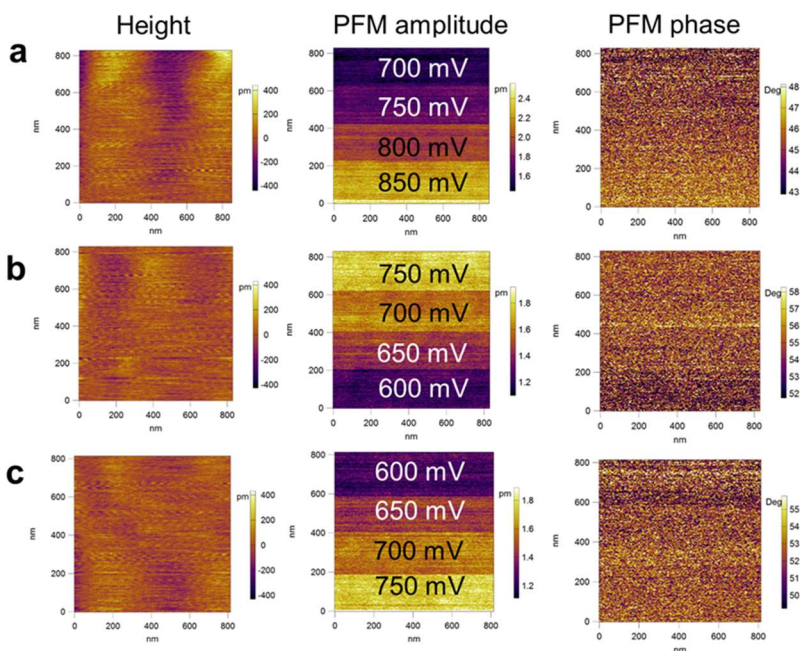


Figure 4.14. PFM measurements on thick multilayer (33L) MoS₂. PFM measurements with height (left), PFM amplitude (middle) and PFM phase (right) images of three set of samples taken 5 days (a), 6 days (b) and 7 days (c) after the wet transfer process.

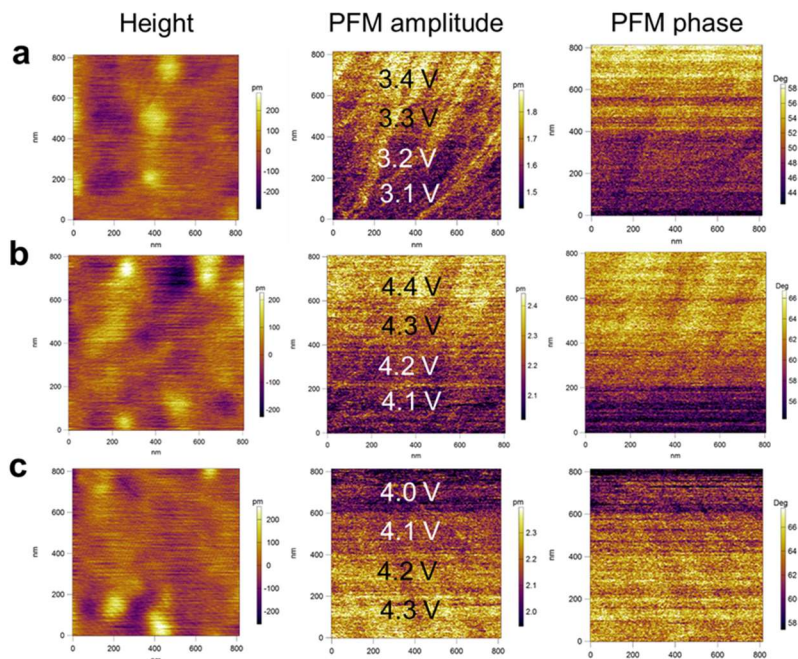


Figure 4.15. PFM measurements on thick multilayer (45L) MoS₂. PFM measurements with height (left), PFM amplitude (middle) and PFM phase (right) images of three set of samples taken 10 days (a), 11 days (b) and 12 days (c) after the wet transfer process.

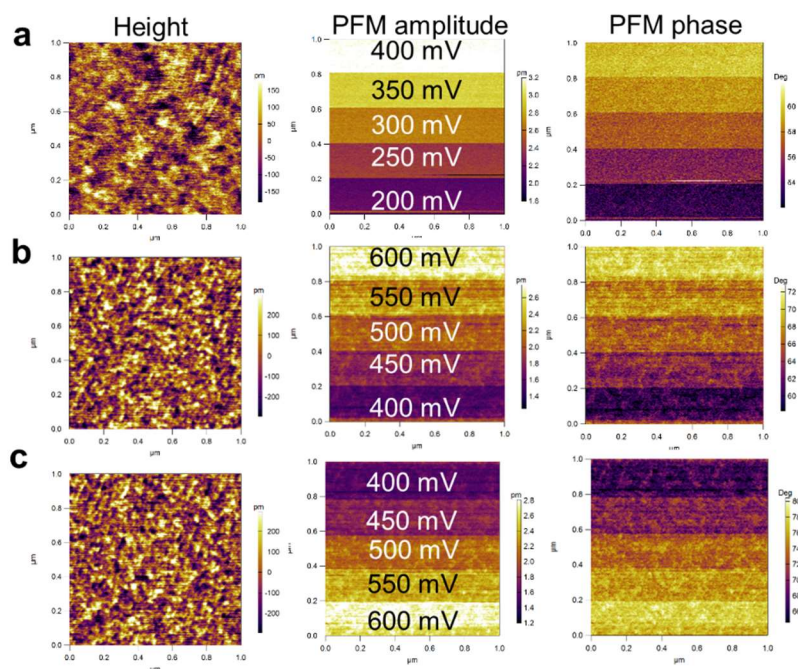


Figure 4.16. PFM measurements on monolayer WSe₂. PFM measurements with height (left), PFM amplitude (middle) and PFM phase (right) images of three set of samples taken 1 days (a), 2 days (b) and 4 days (c) after the wet transfer process.

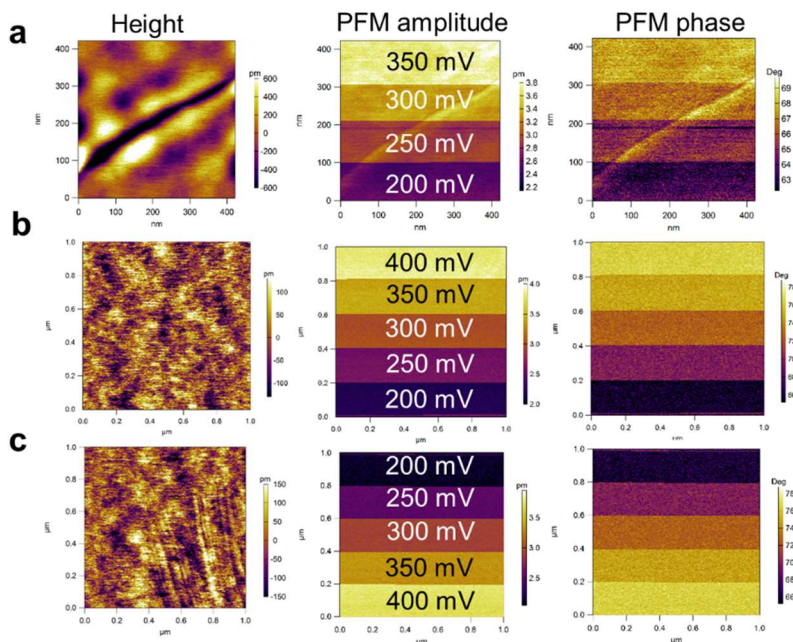


Figure 4.17. PFM measurements on bilayer WSe₂. PFM measurements with height (left), PFM amplitude (middle) and PFM phase (right) images of three set of samples taken 5 days (a), 6 days (b) and 7 days (c) after the wet transfer process. The trench in topography in (a) resulted from a small air trapped bulged region which was pressed down by the AFM cantilever during PFM scanning.

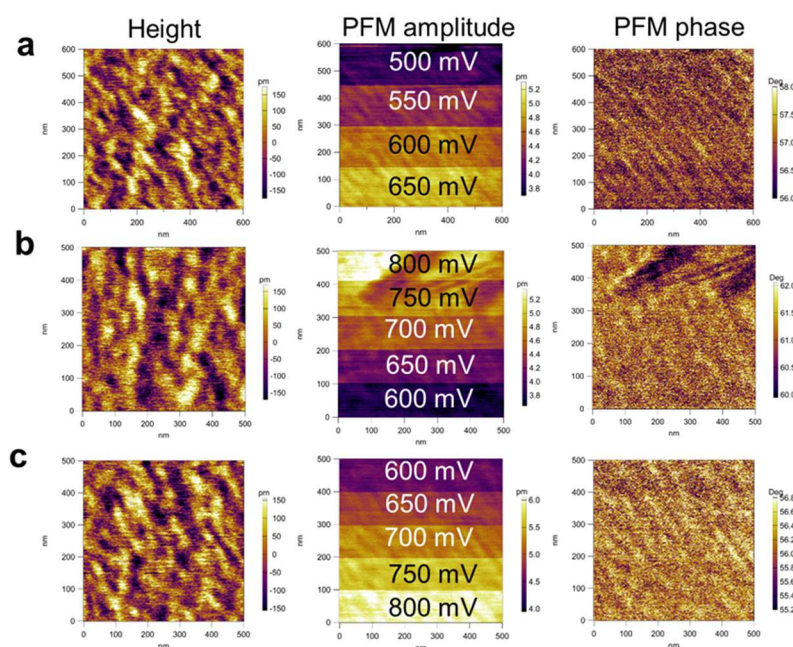


Figure 4.18. PFM measurements on trilayer WSe₂. PFM measurements with height (left), PFM amplitude (middle) and PFM phase (right) images of three set of samples taken 6 days (a), 7 days (b) and 8 days (c) after the wet transfer process.

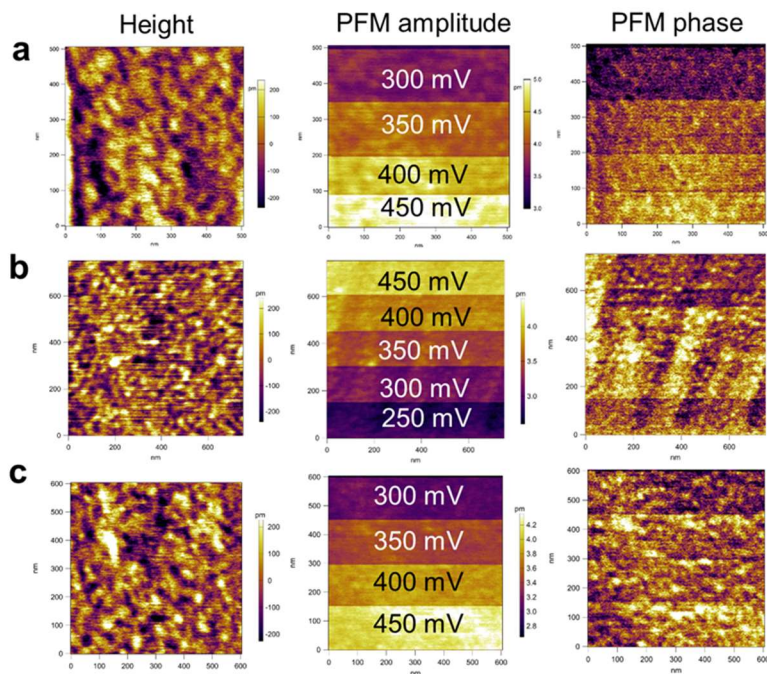


Figure 4.19. PFM measurements on quad layer WSe₂. PFM measurements with height (left), PFM amplitude (middle) and PFM phase (right) images of three set of samples taken 3 days (a), 4 days (b) and 5 days (c) after the wet transfer process.

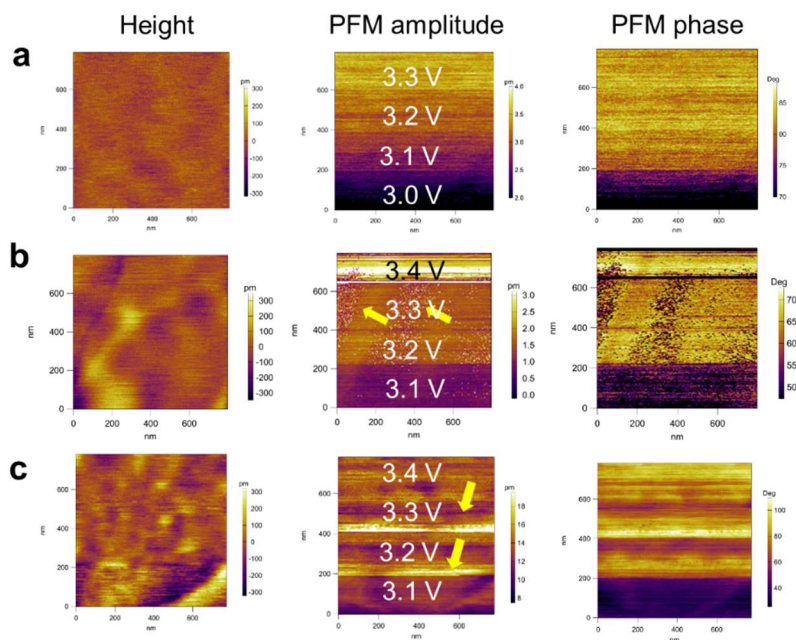


Figure 4.20. PFM measurement on thick multilayer (28L) WSe₂. PFM measurements with height (left), PFM amplitude (middle) and PFM phase (right) images of three set of samples taken 4 days (a), 6 days (b) and 19 days (c) after the wet transfer process. There were some artifacts from frequency lock-in (yellow arrows in amplitude images). These areas were discarded in d_{33} calculation.

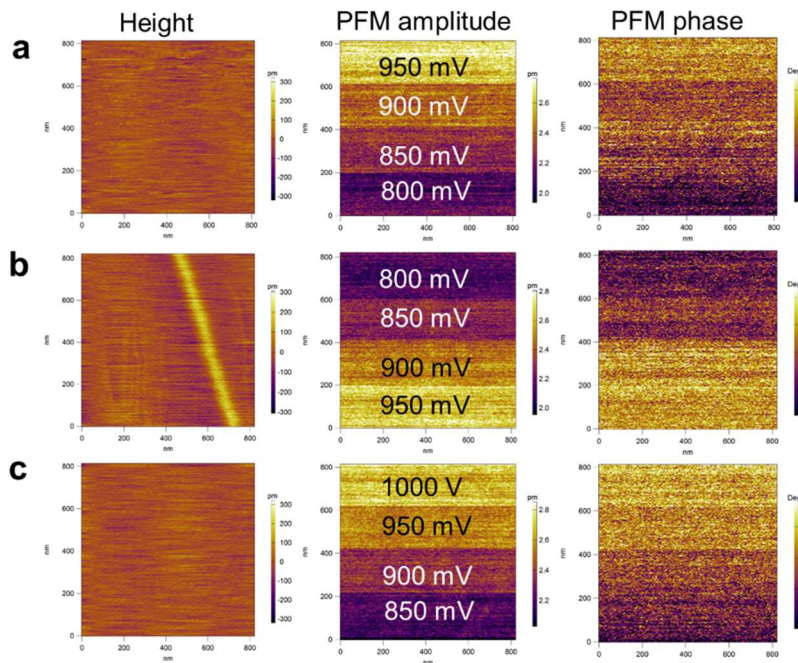


Figure 4.21. PFM measurement on thick multilayer (43L) WSe₂. PFM measurements with height (left), PFM amplitude (middle) and PFM phase (right) images of three set of samples taken 4 days (a), 5 days (b) and 6 days (c) after the wet transfer process.

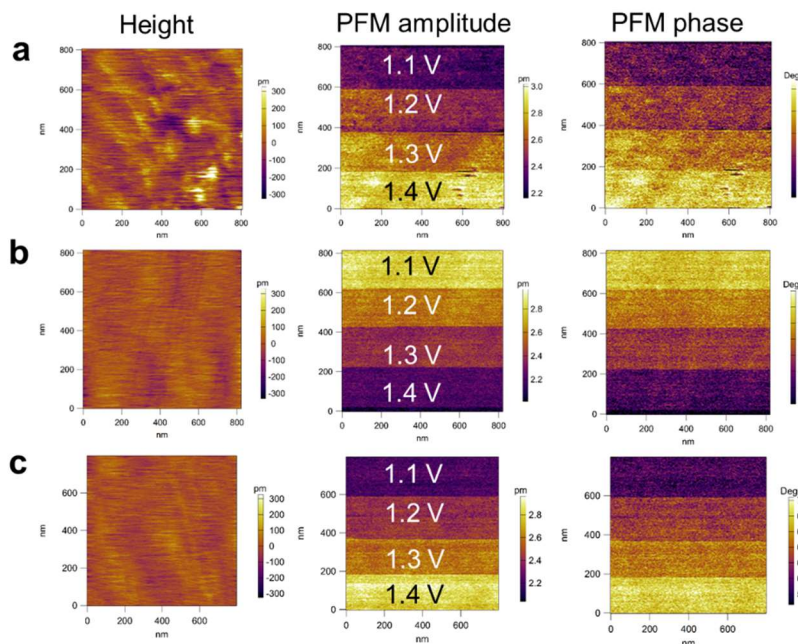


Figure 4.22. PFM measurement on thick multilayer (50L) WSe₂. PFM measurements with height (left), PFM amplitude (middle) and PFM phase (right) images of three set of samples taken 6 days (a), 7 days (b) and 8 days (c) after the wet transfer process.

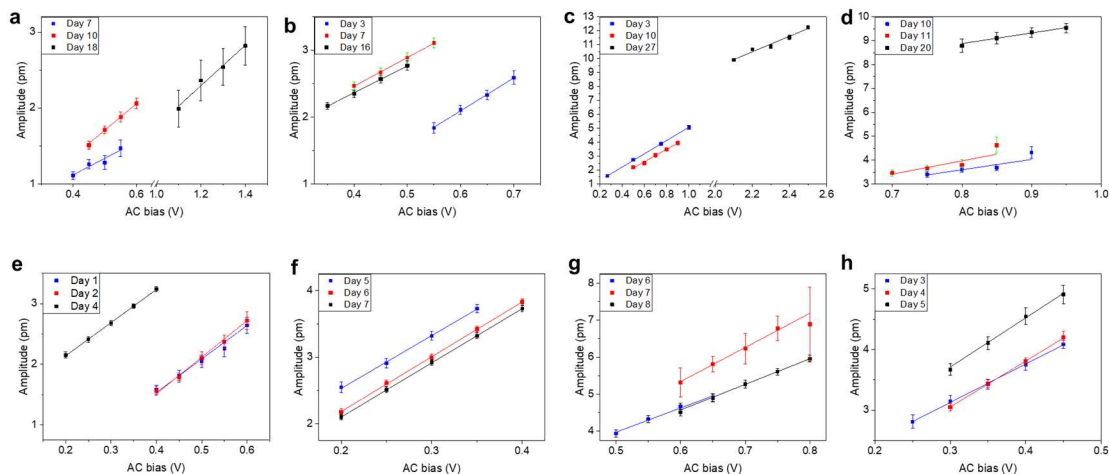


Figure 4.23. Summary of PFM scans of atomically thin MoS₂ and WSe₂. PFM amplitude (termed as amplitude) vs. AC bias plots obtained from the PFM scans shown in Figure 4.10-4.13 for MoS₂ (a) 1L, (b) 2L, (c) 3L, (d) 4L and Figure 4.16-4.19 for WSe₂ (e) 1L, (f) 2L, (g) 3L, (h) 4L. The days in the plot series denote the number of days between sample preparation and PFM scans. Some plots (a-e) showed horizontal or vertical shift possibly due to accumulation of trapped surface charge over time. However, the d_{33} was unaffected by the vertical or horizontal shift of the plots. The error bars denote one standard deviation.

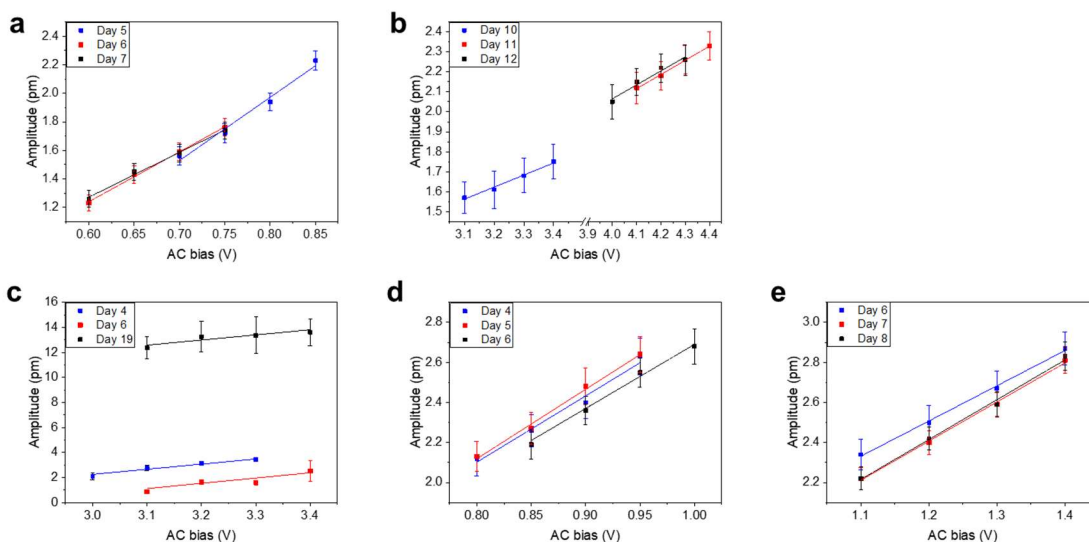


Figure 4.24. Summary of PFM scans of thick multilayer MoS₂ and WSe₂. PFM amplitude (termed as amplitude) vs. AC bias plots obtained from the PFM scans shown in Figure 4.14-4.15 for MoS₂ (a) 33L, (b) 45L and Figure 4.20-4.22 for WSe₂ (c) 28L, (d) 43L, (e) 50L. The days in the plot series denote the number of days between sample preparation and PFM scans. The error bars denote one standard deviation.

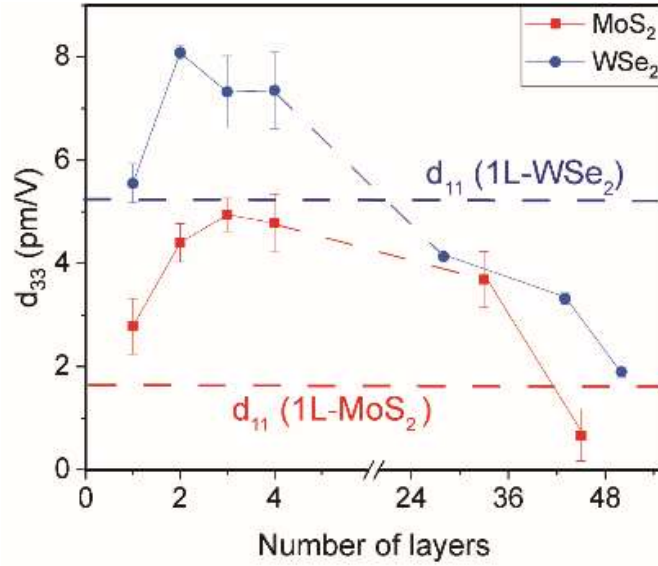


Figure 4.25. d_{33} measurement of different layers of MoS₂ and WSe₂. d_{33} trend with the number of layers of MoS₂ and WSe₂. The literature value of d_{11} of monolayer MoS₂ and WSe₂ are shown as horizontal dotted lines. The error bars denote one standard deviation.

4.6 Deformation mechanism of converse flexoelectric effect

To explain the anomalous reduction in d_{33} of 1L-TMDs, we investigated converse flexoelectricity induced deformation mechanisms. Two potential mechanical effects, bending (**Figure 4.26a**) and puckering (**Figure 4.26b**) induced delamination, can perturb d_{33} . As the likelihood of bending scales inversely with bending stiffness which increases with the number of TMD layers, one would expect higher deformation of thinner TMDs under PFM characterization. In contrast, puckering induced delamination of the TMDs occurs at the leading edge of the AFM tip in contact with TMDs^[118], aided by low bending stiffness, high tip-sample adhesion and high tip-sample friction. Therefore, to fully understand the susceptibility to pucker, one must consider bending stiffness, tip-sample adhesion/stiction and friction.

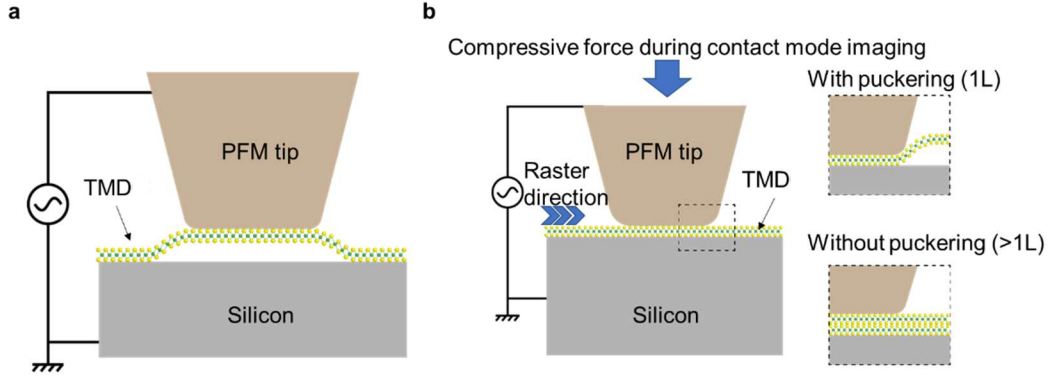


Figure 4.26. Exploring possible deformation mechanisms. Schematic drawings of bending (a) and puckering (b) induced delamination of the material from the substrate.

4.6.1 Bending induced delamination

In the case of delamination, the sample experiences delamination from the substrate during AFM measurement (**Figure 4.26a**) which could result in an enhancement of d_{33} as materials can more readily displace in the out-of-plane direction. Given that delamination requires bending of the material, the likelihood of a material to delaminate can be correlated to bending stiffness. We considered both the continuum plate model (bending stiffness $\sim$ thickness³) and frictionless layer model (bending stiffness $\sim$ thickness)^[119]. The bending stiffness for a continuum plate model is given as,

$$B_{cp} = \frac{Yt^3}{12}(N^3 - N) + B_{ml}N \quad (4.1)$$

The bending stiffness for a frictionless layer model is given as,

$$B_{fl} = B_{ml}N \quad (4.2)$$

In these two equations, Y , t , N , and B_{ml} are the 3D Young's modulus, layer thickness, number of layers, and bending stiffness of a monolayer structure, respectively. Since d_{33} linearly scales with deformation, we studied how d_{33} is correlated with thickness and thickness-cubed

(Figure 4.27a) to gauge the possibility of bending. Figure 4.27a shows that our estimated d_{33} trend does neither correspond to the plate model nor the frictionless layer model, suggesting a different mechanism dictated the d_{33} trend in the atomically thin limit.

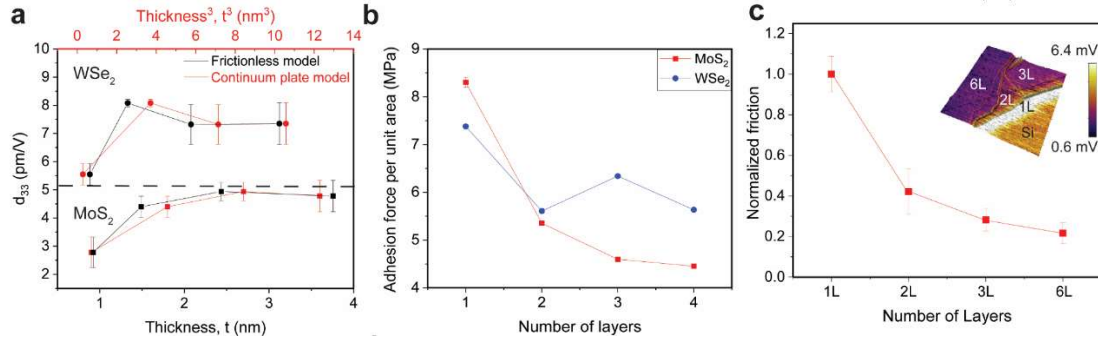


Figure 4.27. Investigation of possible deformation mechanisms in PFM measurement. **a**, d_{33} trend with bending rigidity of the thin films, considering both frictionless layer model and continuum plate model^[119]. MoS₂ and WSe₂ are separated by a horizontal dashed line. **b**, Comparison of tip-sample adhesion force of MoS₂ and WSe₂ samples with different numbers of layers. **c**, Sliding friction between the PFM tip and MoS₂ during PFM measurement as a function of the number of MoS₂ layers. The inset shows the friction force mapped on the topography. All the error bars denote one standard deviation.

4.6.2 Puckering induced delamination

Figure 4.26b illustrates the puckering mechanism. During contact mode AFM imaging, the AFM tip exerts a compressive, sliding force on the material while rastering. This results in puckering at the tip-sample leading edge. As briefly discussed at the beginning of this section, such phenomenon is facilitated by low bending rigidity, high tip-sample adhesion and friction^[118]. We calculated the tip-sample adhesion force by AFM force-curve method (Figure 4.27b). We observed ~35.5% drop in the tip-adhesion force from monolayer to bilayer MoS₂ and ~24% drop for the WSe₂. Compared to the steep drop from monolayer to bilayer, the reduction in tip-sample adhesion was less apparent for 2-4 layers (20% for MoS₂, 13% for WSe₂). The sliding friction between the cantilever and sample was measured by friction force microscopy (Figure 4.27c). The sliding tip-sample friction dropped by 60% on the bilayer structure compared to the

monolayer structure and saturated on the subsequent layers. the significant drop in tip-sample adhesion and friction from monolayer to bilayer structure, followed by a saturation behavior on the next few layers (**Figure 4.27b** and **4.27c**) suggests that puckering induced delamination is most favorable on monolayer structure.

We also considered the susceptibility to slide or pucker of the top layer of a multilayer TMD during contact mode AFM imaging. The puckering of the top layer would change the bending stiffness of the multilayer TMD, thereby making the bending stiffness comparison more challenging. The layered materials (such as TMD) form a weak van der Waals (vdW) adhesion among the layers and to the substrate. Therefore, on a multilayer TMD, the top layer could pucker by delaminating from the remaining structure during PFM imaging. To do so, the top layer must overcome the vdW energy or cleaving energy (energy required for the top layer to delaminate from the structure). However, it has been reported that the vdW energy and cleaving energy of MoS₂ increases with the number of layers^[120]. Therefore, we deduced that it was less probable for the top layer to delaminate from the remaining structure of a bilayer or thicker TMDs.

4.7 Finite element analysis of electric field gradient distribution on transition metal dichalcogenides

To investigate the effect of converse flexoelectricity and puckering on the electromechanical response of the TMDs, we estimated the electric field (E-field) gradient using an electrostatic model in COMSOL Multiphysics. The results are summarized in **Figure 4.28** and **4.29**. **Figure 4.29b** suggests that the midsection of the tip-sample contact area which covers 36% ($= (12/20)^2 \times 100\%$) of the total contact area would experience E-field gradient of $\sim 10^6$ V/m².

The remaining 64% contact area would experience orders of magnitude stronger E-field gradient than $\sim 10^6$ V/m². Such high electric field gradient under the tip is possible due to the “fringe-like” E-field distribution near the cantilever edge and E-field gradient $\sim 1/\text{thickness}^2$ scaling law. Therefore, we reached a conclusion that the major contributor in the d_{33} is the converse flexoelectric effect.

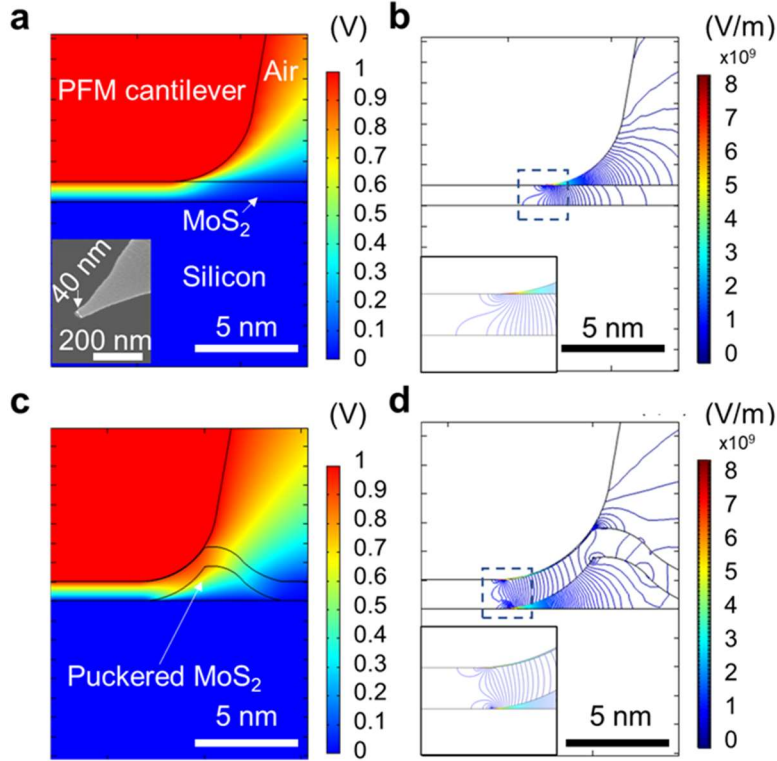


Figure 4.28. Simulated equipotential electric field regions in monolayer MoS₂. Equipotential surface (left) and electric field contour (right) plots for non-puckering (top row; **a,b**) and puckering (bottom row; **c,d**) events. An SEM image of the PFM tip is shown in the inset of (**a**).

To investigate how puckering might affect the converse flexoelectric response, we introduced puckering in the MoS₂ geometry as a small delaminated section (height of <2 nm) at the tip-sample leading edge (**Figure 4.28c**). The simulation results suggested significant distortion in the E-field distribution near the tip-sample edge of the puckered structure (**Figure 4.28d**). Such distortion can lead towards different E-field gradient in the vicinity of the puckered region.

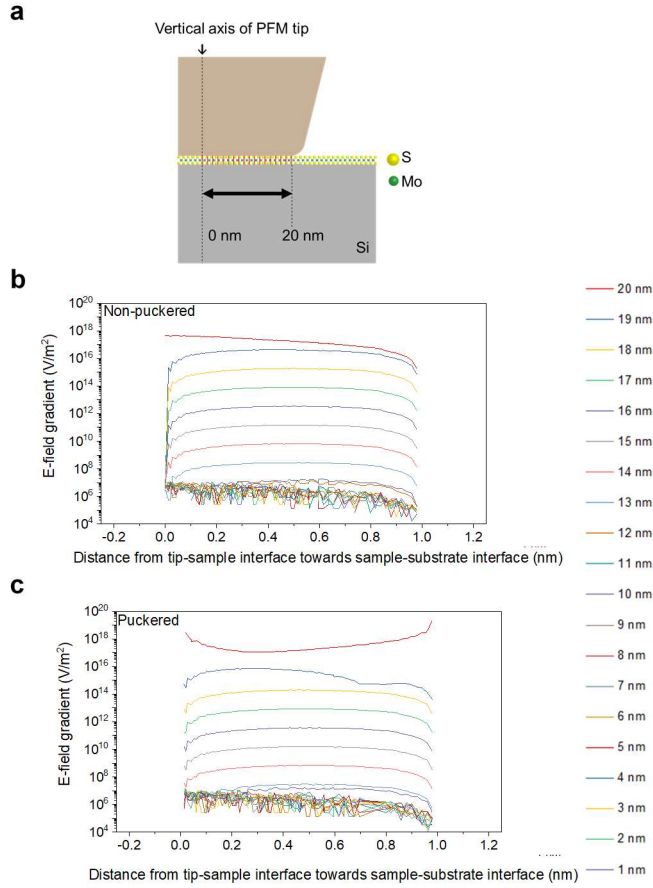


Figure 4.29. Effect of puckering on out-of-plane electric field gradient on monolayer MoS₂. **a**, Schematic drawing of the coordinate system to address the spatial locations at the tip-sample interface. **b**, **c**, Electric field gradient along the MoS₂ thickness at different spatial locations for non-puckered and puckered structure, respectively.

Next, to investigate how the perturbed E-field (due to puckering) affects E-field gradient, we calculated the out-of-plane E-field gradient at different spatial locations at the tip-sample contact plane (schematics shown in **Figure 4.29a**). For both flat and puckered structures, our simulation results showed similar range of out-of-plane E-field distribution near the mid-section of tip-sample contact plane (**Figure 4.29b** and **4.29c**). However, as we moved towards the tip-sample leading edge, the calculation suggested that a flat system would experience stronger E-field gradient than the puckered structure. This clearly suggests that the edge region was the most significant section to contribute to the converse flexoelectric effect. The comparison of the E-field gradient between the flat and puckered structure is summarized in **Figure 4.30**. Our simulation result shows an order of magnitude increase in the E-field gradient near the tip-

sample leading edge when puckering was absent. We estimated that at least 32% ($=0.5 \times (20^2 - 12^2) / 20^2 \times 100\%$) of the contact area (considering puckering at the leading edge) would be affected by the puckering. Therefore, we attribute the reduction of monolayer d_{33} to puckering induced E-field gradient reduction.

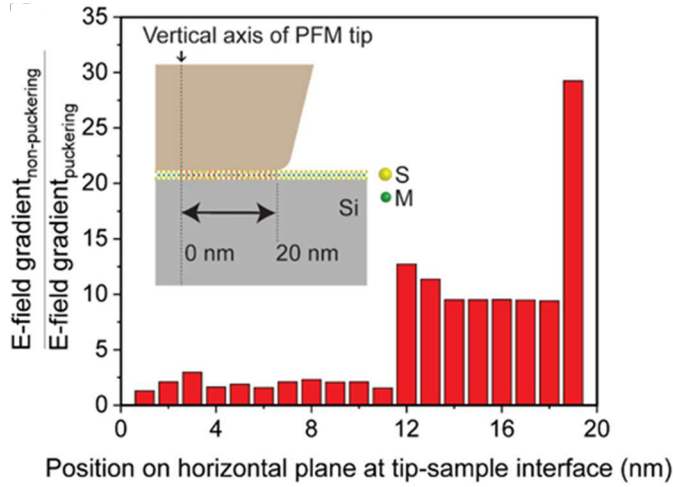


Figure 4.30. Effect of puckering on the out-of-plane electric field (E-field) gradient of monolayer MoS₂. The ratio of E-field gradient of the non-puckered structure to the puckered structure as a function of position under the AFM tip. The center of the AFM tip corresponds to 0 nm.

4.8 Effect of wrinkles/bubbles on PFM measurement

The degree of puckering can be increased by any topographic feature since any unwanted wrinkles/blisters can increase the tip-sample contact area and therefore, increase puckering. The topography of 1L-WSe₂ and 2L-WSe₂ prepared by the wet transfer process show nanoscale wrinkles/blisters and intercalated particles (**Figure 4.31**). We chose the PFM scan areas far away from the wrinkles/particles to avoid any effect from the unintended surface roughness induced by the particles. Furthermore, to avoid such features in microscale, we prepared another set of 1L- and 2L- WSe₂ samples by direct exfoliation on Si. Directly exfoliated WSe₂ showed no wrinkles/blisters (**Figure 4.31**). We then measured the root means square (RMS) surface roughness from the corresponding AFM topography images. For all the cases, the topography of atomically thin TMDs on Si substrate possesses atomically flat surface (~ 1.15 - 1.5 Å, **Figure**

4.32a and **4.32b**) with minimal variation regardless of the number of layers (1-4 layers) and sample preparation techniques (wet transferred vs. directly exfoliated). Furthermore, the roughness levels show little deviation from the Si substrate roughness (~ 1.35 Å). The flatness of the topography suggests that the effect of wrinkles/bubbles/particles to our PFM measurement is minimal.

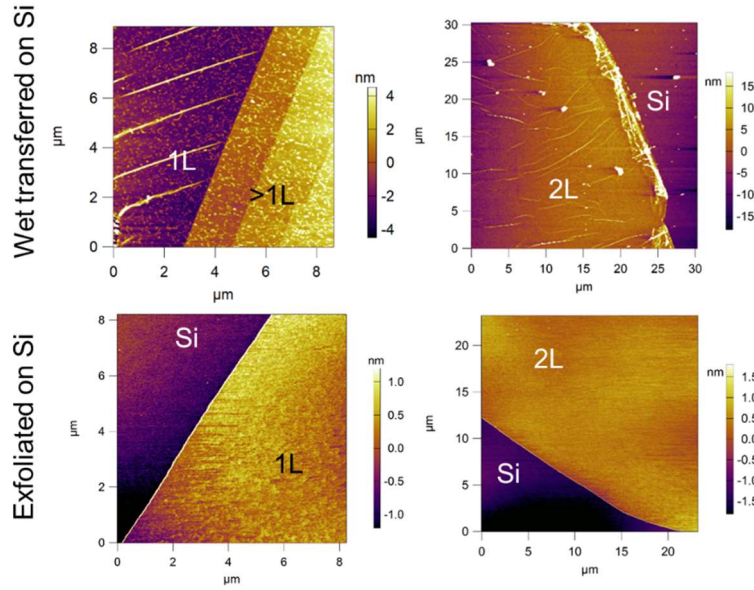


Figure 4.31. Topography comparison between wet transferred and directly exfoliated WSe₂ on Si.

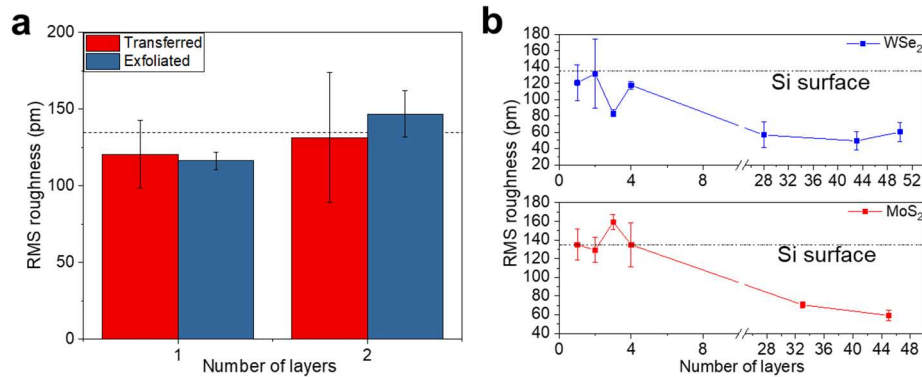


Figure 4.32. Comparison of surface roughness measured from the areas chosen for the PFM scans. a, The roughness from wet transferred (termed as “Transferred”) and directly exfoliated (termed as “Exfoliated”) WSe₂. The surface roughness of the substrate (silicon) is shown as the horizontal dashed line. **b,** The surface roughness of all the TMDs prepared through wet transferred techniques. The error bars denote one standard deviation.

4.9 Effect of strain on d_{33}

Although the wet transferred and directly exfoliated WSe_2 show similar surface roughness, the absence of wrinkles/blisters in directly exfoliated WSe_2 suggests that different levels of strain may exist between wet transferred and directly exfoliated WSe_2 . The difference in strain level was confirmed by photoluminescence (PL) spectroscopy (**Figure 4.33**)^[121,122]. The PL emission peak of directly exfoliated monolayer WSe_2 showed a redshift of ~ 20 meV relative to wet transferred WSe_2 , indicating $\sim 0.4\%$ in-plane tensile strain. The PL peak of directly exfoliated bilayer WSe_2 showed a blue shift of ~ 50 meV with enhanced intensity. Such phenomena indicates indirect to direct band gap transition under an in-plane tension^[122]. Based on the PL peak shift and enhanced intensity, we estimated $\sim 0.75\%$ - 1% in-plane tension on the directly exfoliated bilayer WSe_2 comparing to the wet transferred counterpart.

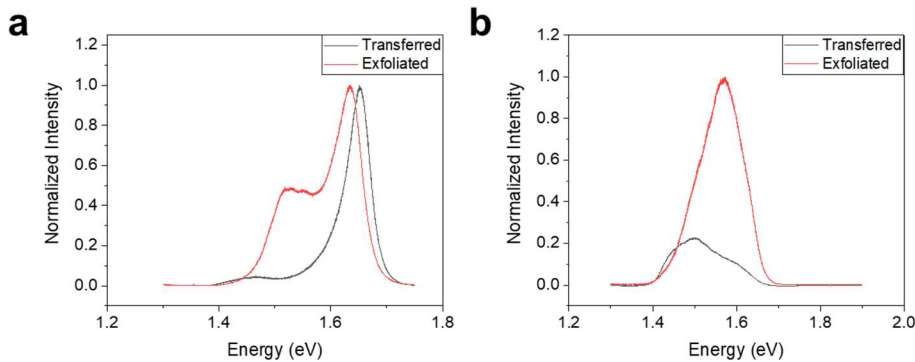


Figure 4.33. PL spectra obtained on wet transferred (termed as “Transferred”) and directly exfoliated (termed as “Exfoliated”) WSe_2 on Si. PL spectra of 1L- WSe_2 (a) and 2L- WSe_2 (b). The additional peak (at ~ 1.53 eV) observed in (a) for directly exfoliated WSe_2 is from nearby bilayer region. 532 nm excitation laser was used.

To investigate how in-plane tension affects d_{33} , we performed PFM scans on directly exfoliated WSe_2 (**Figure 4.34, 4.35**). Then, we estimated d_{33} from the corresponding PFM images (**Figure 4.36**). The d_{33} of directly exfoliated and wet transferred WSe_2 are summarized in Figure . Directly exfoliated 1L- WSe_2 on Si showed a 46% enhancement in d_{33} (8.14 pm/V)

compared to wet transferred 1L-WSe₂ (5.55 pm/V). In contrast, the d_{33} of directly exfoliated 2L-WSe₂ (6.39 pm/V) showed a 21% reduction compared to its wet transferred (8.08 pm/V) counterpart (**Figure 4.37a**). The enhancement in d_{33} of directly exfoliated 1L-WSe₂ suggests that in-plane tension facilitated the reduction in puckering. However, the reduced d_{33} for directly exfoliated 2L-WSe₂ suggests careful balancing of reduced puckering and in-plane tension is necessary to maximize d_{33} . The bilayer structure (wet transferred or directly exfoliated) would experience much less puckering compared to the monolayer structure due to high bending stiffness, reduced tip-sample adhesion (**Figure 4.27b**) and reduced friction (**Figure 4.27c**). Therefore, we hypothesize that both the directly exfoliated and wet transferred 2L-WSe₂ experienced similar degree of minimal puckering. However, the in-plane tension ($\sim 0.75\%$ - 1%) present in directly exfoliated 2L-WSe₂ restricts the out-of-plane deformation, resulting in a reduced d_{33} . Such restricted deformation due to $\sim 0.4\%$ in-plane tension could also be present in directly exfoliated 1L-WSe₂. Nonetheless, the d_{33} of directly exfoliated 1L-WSe₂ yielded the highest CFE (8.14 pm/V) among all the monolayer TMDs studied to date (**Figure 4.37b**). Balancing the anti-puckering and restricted deformation due to in-plane tension might further enhance the d_{33} of monolayer TMDs.

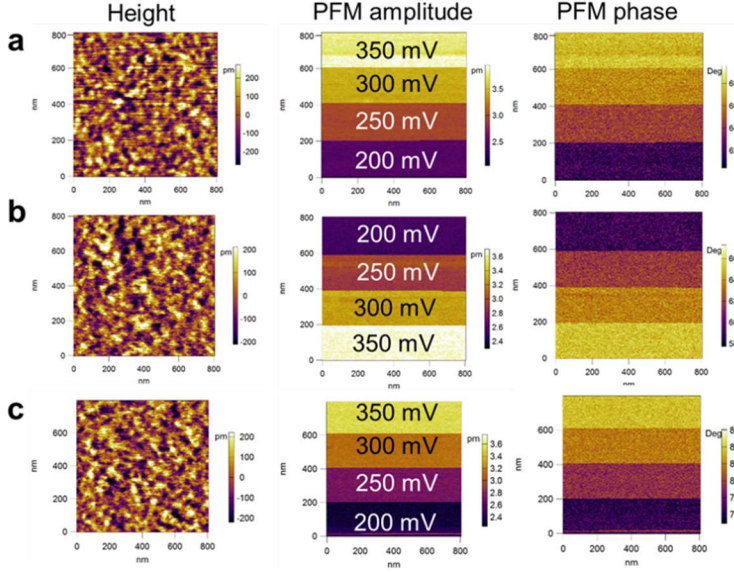


Figure 4.34. PFM measurements on monolayer WSe₂ directly exfoliated on Si. PFM measurements with height (left), PFM amplitude (middle) and PFM phase (right) images of three set of samples taken 3 days (a), 4 days (b) and 5 days (c) after the direct exfoliation.

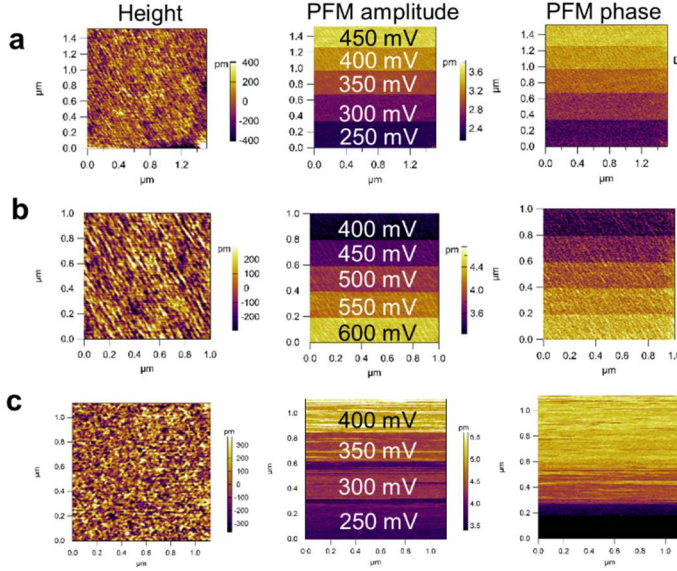


Figure 4.35. PFM measurements on bilayer WSe₂ directly exfoliated on Si. PFM measurements with height (left), PFM amplitude (middle) and PFM phase (right) images of three set of samples taken 2 days (a), 5 days (b) and 7 days (c) after the direct exfoliation.

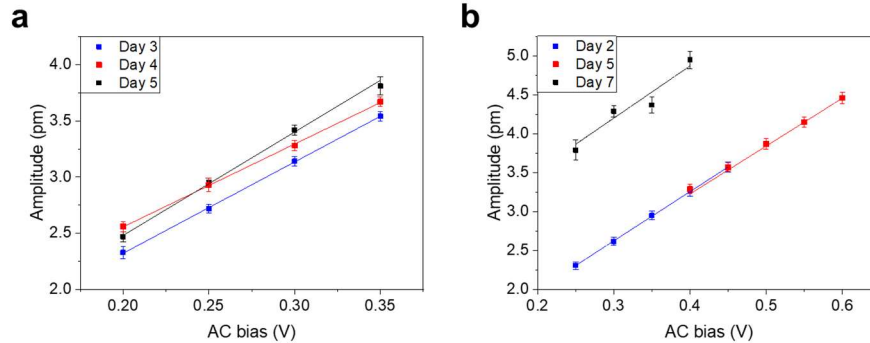
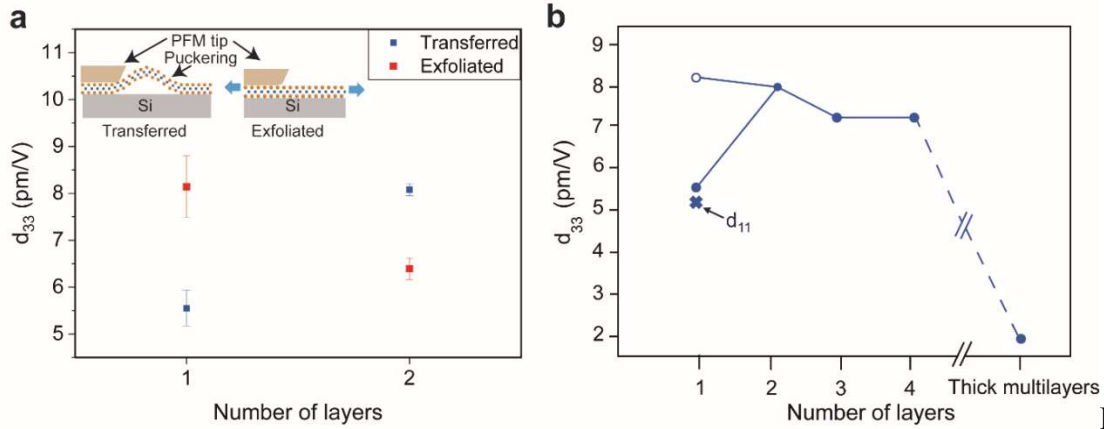


Figure 4.36. Summary of PFM scans of WSe₂ directly exfoliated on Si. a, b, PFM amplitude (termed as amplitude) vs. AC bias plots obtained from the PFM scans shown in Figure 4.34 and 4.35 for 1L-WSe₂ and 2L-WSe₂, respectively. The days in the plot series denote the number of days between sample preparation and PFM scans. The error bars denote one standard deviation.



Figure

4.37. Effect of reduced puckering on d_{33} . **a**, d_{33} measured on wet transferred (denoted as “Transferred”) and directly exfoliated (denoted as “Exfoliated”) WSe₂ on Si. The schematics of the monolayer structures with and without in-plane tension are shown in the inset. The error bars denote one standard deviation. **b**, Comparison of d_{33} measured in this work with the literature value of in-plane piezoelectric coefficient (d_{11}) of WSe₂ monolayer (shown as a cross). The enhanced d_{33} of exfoliated WSe₂ monolayer is shown as a hollowed circle.

4.10 Conclusions

We demonstrated strong CFE (d_{33}) in monolayer MoS₂ and WSe₂ which outperforms their intrinsic in-plane piezoresponse (d_{11}). Furthermore, we showed that the thinning down of MoS₂ and WSe₂ to the atomic layers enhances the CFE relative to their bulk counterpart. We observed reduced d_{33} of monolayer MoS₂ and WSe₂ compared to 2-4 layers which were attributed to increased puckering of monolayer structure which dampens the E-field gradient. By introducing a flatter topography to counter puckering, we observed that 1L-WSe₂ demonstrated a larger out-of-plane deformation relative to puckered samples. This work represents the first demonstration that reducing the thickness of TMDs to the atomic limit enhances the flexoelectric out-of-plane displacement to the point of surpassing the in-plane piezoelectric response. The converse flexoelectricity observed in the atomically thin TMD is comparable to the piezoresponse of commercially available bulk materials and multilayer Janus TMD systems^[116,123], thereby establishing flexoelectricity as an exciting phenomenon for nanoscale

actuation or energy harvesting applications. In addition, given the growing interest in stacking and twisting various TMDs^[124], the control of stacking order and twist angle of multilayer TMDs might allow further modulation of converse flexoelectric effect. We expect that our findings will enable the application of flexoelectric atomically thin materials as next-generation nanoscale energy conversion and actuation systems.

CHAPTER 5: ENHANCED ELECTROMECHANICAL RESPONSE ON MoS₂/WSe₂ VERTICAL HETEROSTRUCTURE

5.1 Introduction

Twisted bilayer structure consisted of similar or dissimilar 2D materials possesses unprecedented phenomena compared to the constituent materials. The interlayer coupling occurred at the twisted bilayer structure stems unique structural effect such as moiré superlattice^[13,27,28,125–128]. The moiré superlattice also results in enhanced piezoresponse due to the breaking of crystal symmetry (piezoresponse) and lattice mismatch induced strain gradient (flexoresponse)^[48]. Among the twisted bilayer structures, the vertical heterostructures (HS) of transition metal dichalcogenides (TMDs) are of particular interest as many of them form type-II band alignment^[129–131], meaning the conduction band minima (CBM) and valence band maxima (VBM) resides on the two different constituent TMD layers of the heterostructure. Such band alignment gives rise to not only unique phenomena such as interlayer exciton, but also emerging phenomena such as photovoltaic, piezo-phototronics, and piezoresponse effects^[132–136]. Among these effects, piezoresponse in vertical TMD HS is of particular interest of the current study. While most of the studies have focused on the piezoresponse based on the atomic registry at the domains and domain walls, there have not been many reports on the collective electromechanical (EM) response of the TMD HS. The type-II band alignment between the constituent TMDs generates charge transfer induced piezoresponse^[137]. The collective EM response can establish TMD HS as a promising candidate in nanoscale actuating, sensing or energy harvesting applications^[104,138]. Despite the potential, there has not been much experimental effort to probe the collective EM response on bilayer TMD HS.

In this study, we investigated the EM response of bilayer MoS₂/WSe₂ vertical HS using piezoresponse force microscopy (PFM). Our PFM measurement revealed five-fold increase in the EM response from the HS region compared to the constituent monolayer TMD. We further studied the effect of interlayer interaction and charge transfer induced dipole on the EM response. Our study suggested a monotonic increase in the EM response with the increase in interlayer interaction strength which we attributed to the strong coupling between the constituent layers. The charge transfer between the constituent layers played a significant role in augmenting the EM response revealed by Kelvin probe force microscopy (KPFM). We observed enhanced EM response in conjunction to the surface potential of the HS region which we attributed to the charge transfer induced dipole. Our studies demonstrate the fundamental principles behind the enhanced EM response of TMD HS and suggest TMD HS as an alternative candidate for designing EM response-based devices.

5.2 Preparation and characterization of the vertical heterostructure

Preparation of MoS₂/WSe₂ vertical HS comprises of two steps – vertical stacking of the HS and choosing the right substrate for PFM measurement. These steps will be discussed here in two subsections.

5.2.1 Vertical stacking of MoS₂/WSe₂ HS

Vertical stacking of the MoS₂/WSe₂ HS consists of two steps – exfoliation of the monolayer TMDs and vertical stacking of the monolayer TMDs. We exfoliated monolayer MoS₂ and WSe₂ on primary substrates (**Figure 5.1a** and **5.1b**). MoS₂ was exfoliated on polydimethylsiloxane (PDMS) whereas WSe₂ was exfoliated on a water soluble polyacrylic acid (PAA) spin-coated on a SiO₂/Si wafer. The existence of the monolayers was confirmed by

photoluminescence (PL) spectroscopy. Once the monolayers were confirmed, the HS was formed by dry transfer technique. MoS₂ on PDMS was brought into contact with the WSe₂ on PAA at 60 °C. The HS was formed by the gentle contact between the monolayer van der Waals (vdW) materials and slow retraction of the PDMS away from the PAA. The vdW attraction between the MoS₂ and WSe₂ aided the MoS₂ to adhere to the WSe₂, thereby forming a vertical HS of MoS₂/WSe₂ on PAA (**Figure 1c**). Finally, the HS was transferred onto a 3 nm Al₂O₃ coated on a conductive Si substrate via wet transfer method (**Figure 1d**). The HS was then annealed at 300 °C for 4 h with 1:4 to H₂:Ar gas flow to drive out any contaminants from the interface. The initial HS formation on PAA was necessary since optical contrast on the final substrate (Al₂O₃ coated Si) was very low, thereby making the alignment of the TMDs during dry transfer extremely challenging. The HS was initially characterized by Raman and PL spectroscopy (**Figure 5.2**). The Raman spectra showed the distinctive spectral peaks pertaining to the E_{12g}¹ (in-plane) and A_{1g} (out-of-plane) modes of WSe₂ (250 cm⁻¹ and 260 cm⁻¹) and MoS₂ (383.1 cm⁻¹ and 407.62 cm⁻¹) (**Figure 5.2a**). The PL spectra showed weaker peak at 1.83 eV corresponds to the MoS₂ optical band gap, compared to the stronger spectral peak at 1.6 eV corresponds to the interlayer exciton emission of MoS₂/WSe₂ HS (**Figure 5.2b**).

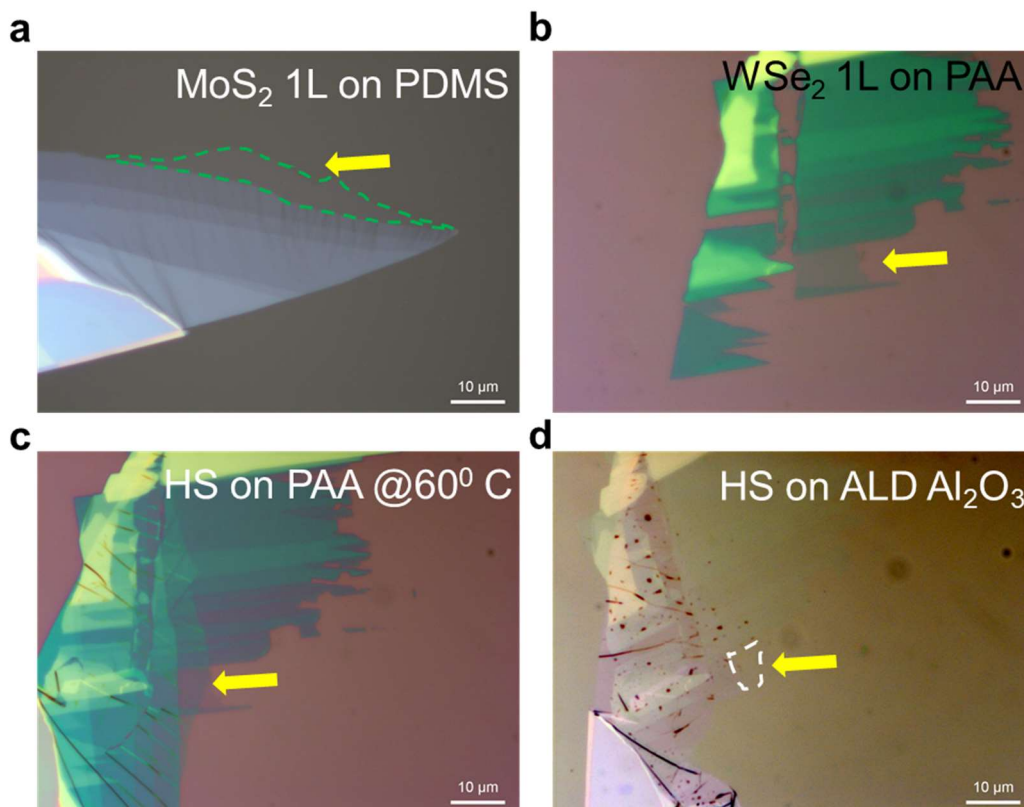


Figure 5.1. Optical images taken at the different steps of heterostructure preparation. **a**, Optical image of the monolayer (1L) MoS₂ exfoliated on PDMS. The monolayer region is denoted with green dashed border. **b**, Optical image of the 1L-WSe₂ exfoliated on the PAA/SiO₂ substrate. The monolayer regions are denoted with yellow arrow in **(a)** and **(b)**. **c**, Optical image of the heterostructure on PAA before wet transfer. **d**, Optical image of the heterostructure on the final structure after wet transfer and annealing. The heterostructure regions are denoted with the yellow arrow and white dashed border.

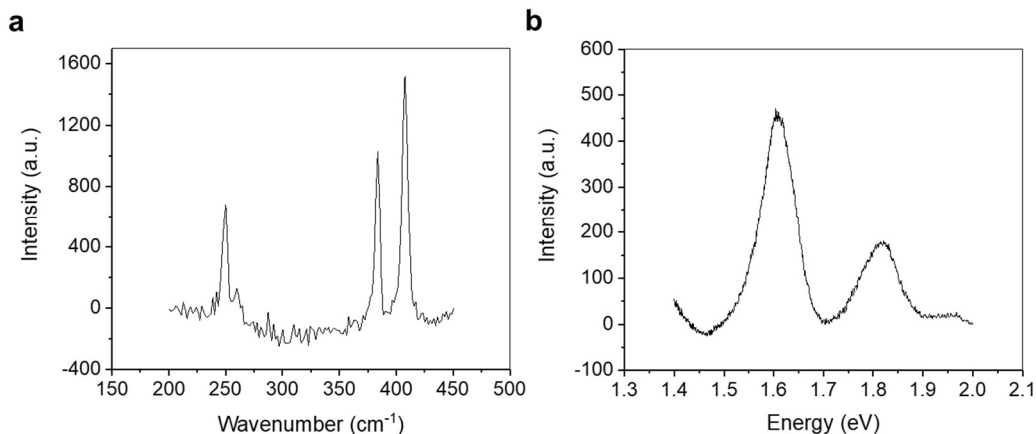


Figure 5.2. Raman (a) and photoluminescence (b) spectroscopy of the MoS₂/WSe₂ heterostructure.

5.2.2 Substrate selection

Choosing a proper substrate is a non-trivial process before probing the heterostructure for EM response because of two reasons. First, the substrate needs to have negligible EM response so that it can minimally perturb the EM response measurements. Second, the substrate should be able to retain the charge transfer induced dipole. To examine the effects of the substrate, we compared the surface potential of EM response of the HS prepared to three different substrates – conductive silicon, 280 nm thick SiO₂ film on Si wafer and 3 nm atomic layer deposited (ALD) Al₂O₃ thin film coated on Si wafer. The surface potential maps were obtained by performing KPFM. The magnitudes of the surface potentials are summarized in **Figure 5.3a**. To minimize the effect of trapped charge from the environment, background (substrate) subtracted surface potential were compared. For example, $\Delta(\text{MoS}_2\text{-WSe}_2)$ in **Figure 5.3a** represents (MoS₂-substrate)-(WSe₂-substrate). We also introduced a parameter, ‘built-in potential’, which is a mathematical difference between MoS₂-WSe₂ and HS-substrate and a qualitative parameter to indicate the charge transfer induced dipole strength. Considering the magnitude of built-in potential, we found that Si exhibited lowest surface potential (<50 mV) among the three substrates. The SiO₂ exhibited the highest surface potential (~750 mV) whereas ALD Al₂O₃ showed intermediate magnitude (~200 mV). The lowest surface potential observed on Si can be explained by the conductive nature of the substrate. The built-in charge in the TMD HS dissipated through the conductive substrate, thereby leaving negligible built-in potential on the HS. Therefore, although Si showed negligible EM response in the previous study (Chapter 4), it cannot be used in this study. The surface potential magnitude on SiO₂ and Al₂O₃ clearly suggested the necessity of having a dielectric layer between the HS and final substrate for

retaining the charge transfer between the TMD layers. Although SiO_2 showed significantly higher surface potential, it is not suitable as a substrate because of strong electrostrictive response (a pseudo EM response) found during PFM measurement (**Figure 4.5**). On the contrary, ALD Al_2O_3 showed negligible EM response (**Figure 5.3b**). Therefore, ALD Al_2O_3 was selected as the substrate for optimized built-in potential with negligible EM response.

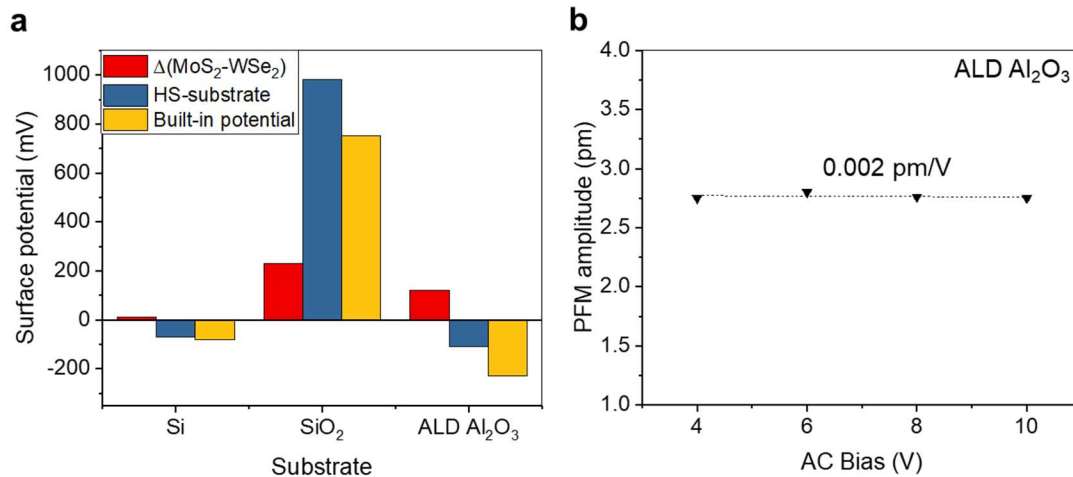


Figure 5.3. Comparison between different substrates for optimizing charge retention and minimizing piezoresponse. **a**, The area average of surface potential at different regions on the heterostructures obtained by KPFM measurement. The red column represents the mathematical difference between the surface potential magnitudes between the standalone MoS_2 and WSe_2 monolayer. The built-in potential on each substrate plotted are obtained by subtracting the blue column (HS-substrate) from the red column ($\Delta(\text{MoS}_2\text{-WSe}_2)$). **b**, PFM amplitude measured on ALD Al_2O_3 at different AC bias. The slope of the linear fit (represented by the dashed line) is calculated as 0.002 pm/V.

5.3 Estimating out-of-plane electromechanical response (d_{33}) of the heterostructure

To better understand the fundamentals behind the proposed concept of collective EM response of the HS, we first set up a hypothesis as illustrated in **Figure 5.4a** and **5.4b**. As mentioned earlier, MoS_2 and WSe_2 forms type-II band alignment when they are vertically stacked. Due to the band alignment, charges will be transferred between the TMD layers (**Figure 5.4a**). Under the assumption of strongly coupled interlayer, the transferred charges will interact

with each other and form a built-in dipole within the HS (the red oval in **Figure 5.4a**). Under externally applied electric bias, the built-in dipole can enhance the induced electric field and therefore, can induce converse piezoelectric effect (deformation under electric stimuli) due to the broken inversion symmetric structure of the HS (**Figure 5.4b**). Such EM response would be absent in the case of monolayer TMDs due to the absence of built-in dipole.

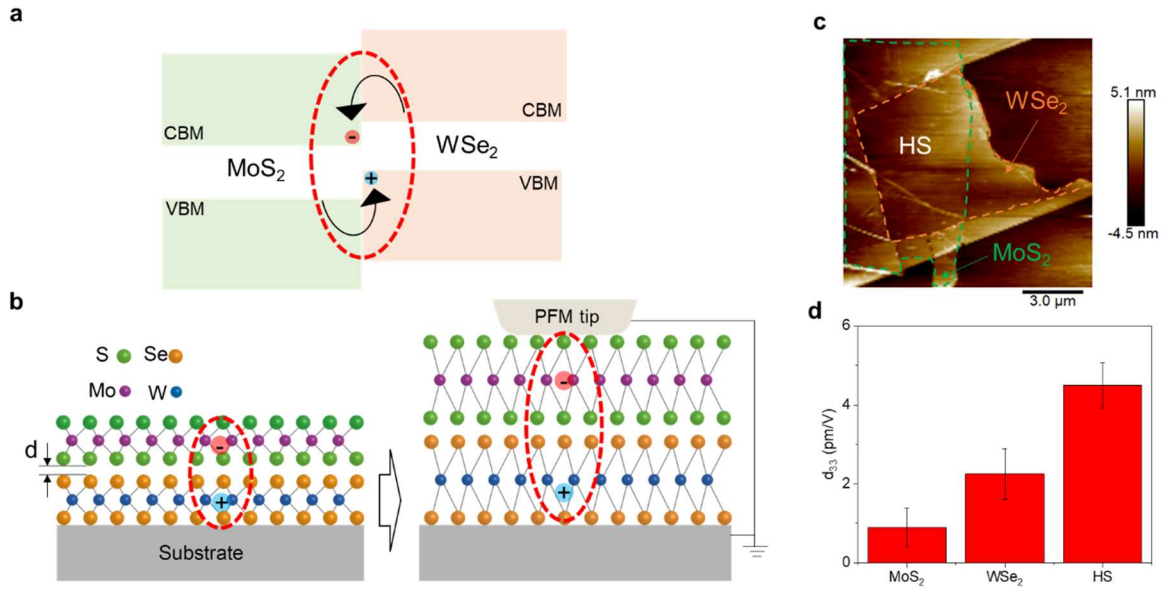


Figure 5.4. The concept and initial measurement of the electromechanical (EM) response on the heterostructure (HS). **a**, Schematic of the type-II band alignment of MoS₂/WSe₂ heterostructure. In case of strongly coupled interlayer, the transferred charge can interact with each other to form a built-in dipole, denoted by the red dashed oval. **b**, Schematic of the strongly coupled HS with built-in dipole (left panel). The right panel shows the EM response of the coupled HS during PFM measurement. **c**, AFM topography image of a representative MoS₂-WSe₂ heterostructure. **d**, Estimated d_{33} of the different region shown in (c) via PFM measurement.

We corroborated our hypothesis by conducting PFM measurement on the MoS₂/WSe₂ heterostructure. The AFM topography revealed no structural damage occurred during the transfer process (**Figure 5.4c**). The standalone monolayer region of MoS₂ and WSe₂ served as reference region for the HS region. We estimated the EM response (d_{33}) of the MoS₂, WSe₂ and the HS region by the ‘vector’ subtraction method discussed in Chapter 2. **Figure 5.4d** shows the d_{33} of

the three regions in the topography image. The d_{33} of HS region was estimated to be 4.5 pm/V, a five-fold increase compared to the MoS₂ region and a two-fold increase compared to the WSe₂ region. The d_{33} on the MoS₂ region was in close agreement with the previously reported literature value using the same substrate^[50]. The origin of EM response on MoS₂ and WSe₂ was attributed to the converse flexoelectric effect (explained in detailed in Chapter 4). However, since electric field gradient scales with $1/\text{thickness}^2$, the converse flexo-effect on the bilayer HS region should be lower compared to the monolayer TMD regions. Therefore, converse flexoelectric effect cannot fully explain the augmented EM response of the HS region. We attribute the EM response of the HS region to the charge transfer induced built-in dipole. The built-in dipole enhanced the electric field (E-field) induced into the HS. The HS has intrinsic piezoelectricity in the out-of-plane direction due to the broken inversion symmetry. Therefore, the enhanced E-field resulted in larger deformation in the HS region.

5.4 Effect of interlayer coupling on the electromechanical response

To investigate the effect of interlayer coupling or interaction on the d_{33} of the HS, we first estimated d_{33} from multiple HS samples (**Figure 5.5**). To characterize the interlayer interaction, we then compared the Raman modes of the HS region from multiple samples^[139]. However, due to the degeneracy between the in-plane (E_{2g}^1) and out-of-plane (A_{1g}) Raman modes of WSe₂, we focused on the E_{2g}^1 and A_{1g} modes of MoS₂ on the HS region. In the following sections, we will first discuss the effect of annealing on the interlayer interaction of the HS. We will then discuss the correlation between the EM response and interlayer interaction of the HS.

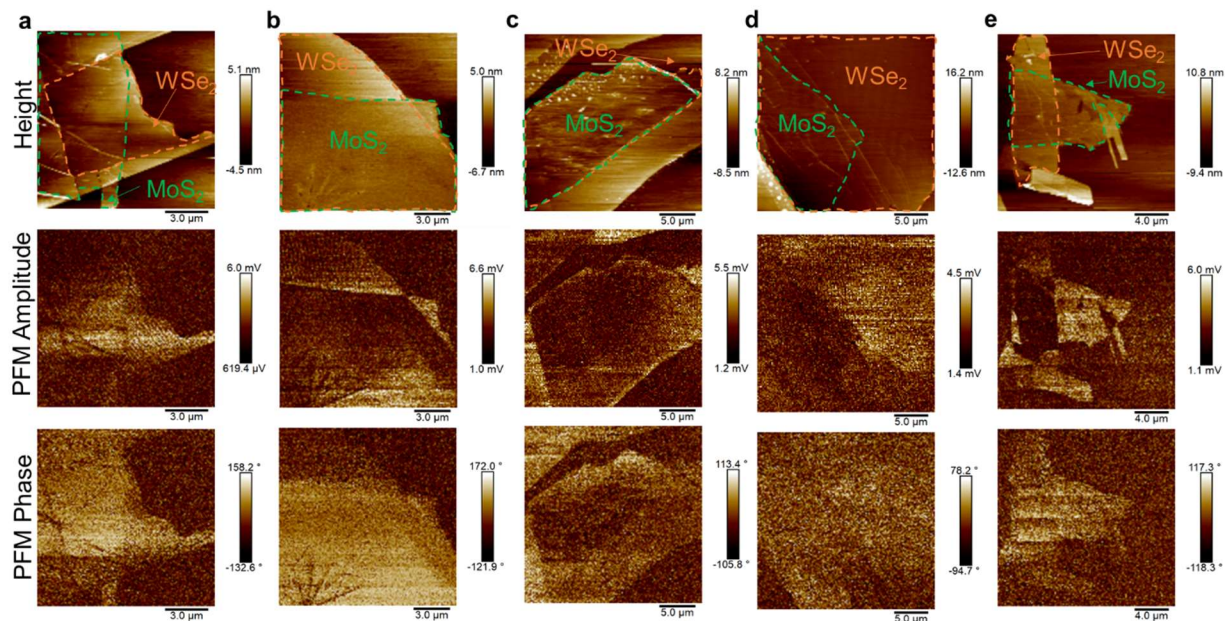


Figure 5.5. PFM measurements on the heterostructures. a, b, c, d, e, PFM images of the five heterostructures that are denoted as HS#1, 2, 3, 4, 5 in this study, respectively. The top, middle and bottom panels represent height, PFM amplitude and PFM phase images, respectively.

5.4.1 Investigation of interlayer interaction of the heterostructure

Figure 5.6 demonstrates the effect of annealing on the Raman modes on the HS regions. The $E_{2g}^1(\text{MoS}_2)$ modes softened upon annealing whereas the $A_{1g}(\text{MoS}_2)$ modes stiffened upon annealing (**Figure 5.6a** and **5.6b**). The resulting mode separation ($A_{1g}(\text{MoS}_2) - E_{2g}^1(\text{MoS}_2)$) showed a positive increase in the magnitude for all the heterostructures (**Figure 5.6c**). The softening and stiffening of E_{2g}^1 and A_{1g} modes, respectively have been reported for multilayer TMDs in the literature due to enhanced dielectric screening^[140]. The increase in mode separation after annealing is a direct indication of stronger interlayer interaction^[136,140,141]. The annealing removed the unwanted residues and contaminants from the interface, thereby reducing the interlayer separation. The reduction in interlayer separation resulted in a stronger interlayer

interaction. Therefore, we concluded that annealing strengthened the interlayer interaction in the vertical HS.

The correlation between the interlayer separation and Raman mode was further investigated with the aid of PL spectroscopy (**Figure 5.7**). As the mode separation of the HS increased, the PL peak on the HS region was shifted from 1.65 eV to 1.6 eV. When the mode separation was lower, the corresponding interlayer interaction was weaker compared to the higher mode separation. In case of weaker interlayer interaction, the constituent TMDs acted as individual layers as opposed to a coupled heterostructure. The resulting PL spectra showed spectral peak at 1.65 eV which correspond to the intralayer exciton emission of monolayer WSe₂. The MoS₂/WSe₂ bilayer structures acted as coupled heterostructures at higher mode separation due to increased interlayer interaction. The resulting PL peak occurred at 1.6 eV, correspond to the interlayer emission peak. Therefore, we established Raman mode separation as an effective parameter to indicate the strength in interlayer interaction of the HS.

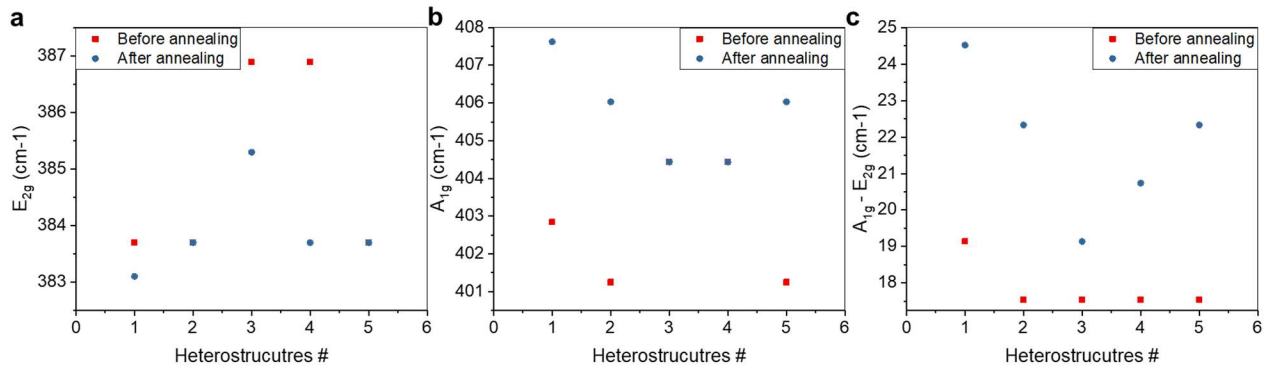


Figure 5.6. Effect of annealing on the MoS₂ Raman modes of the heterostructure. a, Effect of annealing on the in-plane vibrational mode (E_{2g}^1). **b,** Effect of annealing on the out-of-plane vibrational mode (A_{1g}). **c,** Effect of annealing on the Raman mode separation.

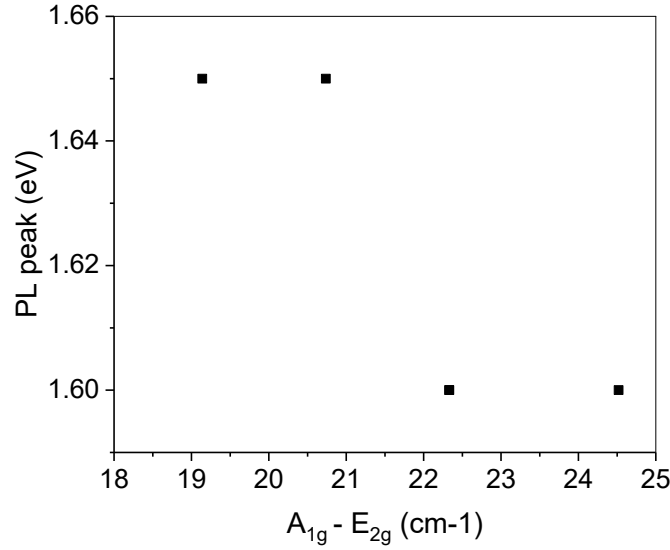


Figure 5.7. Correlation between the photoluminescence (PL) peak and Raman mode separation of the heterostructure.

5.4.2 Correlation between interlayer interaction and d_{33}

To investigate how interlayer interaction dictated d_{33} of the HS, we analyzed the d_{33} in conjunction with the softening (or stiffening) of the Raman modes and the mode separation (**Figure 5.8**). We observed higher d_{33} when the A_{1g} mode was stiffened whereas significantly low d_{33} (<0.4 pm/V) occurred when no stiffening was observed (**Figure 5.8a**). In case of E_{2g}^1 , we observed higher d_{33} when no softening was observed (**Figure 5.8b**). Weaker EM response (low d_{33}) was observed when E_{2g}^1 was softened. The resulting d_{33} trend with mode separation is shown in **Figure 5.8c**. We observed continuous increase in d_{33} as the mode separation was increased. The highest d_{33} occurred at the largest mode separation. Stiffening of A_{1g} is a direct indication of interlayer strengthening whereas softening of E_{2g}^1 indicates presence of in-plane tension^[141,142]. In case of no stiffening in A_{1g} , d_{33} was significantly low since MoS₂/WSe₂ region did not interact as a coupled heterostructure. As the HS region acted as coupled structure indicated by the stiffening of A_{1g} , strong interaction enhanced the EM response resulted in a higher d_{33} . We noted

that despite the stiffening of A_{1g} , one HS showed low d_{33} (~ 0.5 pm/V) in **Figure 8a** which will be discussed in a later section. The heterostructures that did not show stiffening in A_{1g} also experienced in-plane tension compared to the other structures as indicated by the softening of E^1_{2g} mode (**Figure 5.8b**). We attributed the origin of the in-plane tension to the annealing. As the contaminants drove out of the interface, it induced a biaxial in-plane tension to the heterostructure. The in-plane tension can restrict the out-of-plane deformation, thereby resulting in a lower d_{33} (effect of in-plane tension on d_{33} has been discussed in Chapter 4). Nevertheless, the monotonic increase in d_{33} with respect to the mode separation clearly suggested a positive correlation between the interlayer interaction and EM response of the HS region (**Figure 5.8c**). We suggest that reducing the interlayer distance by annealing enhanced the mechanical/interlayer coupling of the HS, thereby resulting in an augmented EM response.

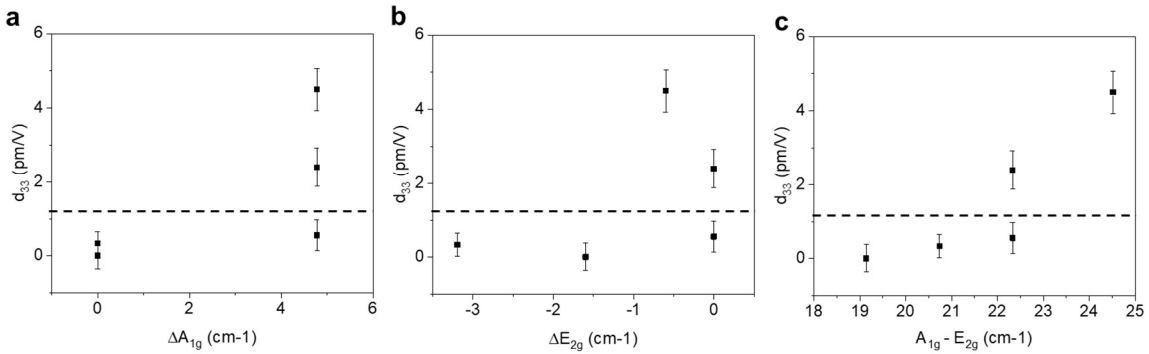


Figure 5.8. Effect of the MoS₂ vibrational modes on the d_{33} of MoS₂/WSe₂ heterostructure. **a**, Correlation between d_{33} and stiffening of the out-of-plane vibrational mode (A_{1g}). **b**, Correlation between d_{33} and the softening of in-plane vibrational mode (E^1_{2g}). **c**, Correlation between d_{33} and the Raman mode separation. For all the cases, the horizontal dashed line indicates the average d_{33} estimated on the monolayer MoS₂. The error bars indicate one standard deviation.

5.5 Effect of charge transfer on the electromechanical response

To study the effect of charge transfer on the EM response of the heterostructure, we conducted KPFM measurement (**Figure 5.9**). The surface potential image showed clear contrast

between the MoS₂, WSe₂ and HS regions, suggesting charge transfer between the constituent monolayer TMDs (**Figure 5.9a** and **5.9b**). The surface potentials are calculated by taking the area average of the focus regions in the surface potential image. The extracted surface potential magnitudes are summarized in **Figure 5.9c**. The built-in potential (indicated by the arrow in **Figure 5.9c**) suggested charge transfer between the MoS₂ and WSe₂ in the heterostructure region and therefore, used as a qualitative parameter to indicate built-in dipole strength. We noted that the surface potential of $\Delta(\text{MoS}_2\text{-WSe}_2)$ varied only by 50 mV across different sample, whereas the surface potential of the HS regions (defined as HS-Substrate) varied by 300 mV, an order of magnitude increase compared to the MoS₂-WSe₂ (**Figure 5.10**). Therefore, we concluded that the surface potential of the HS region was the dominant contributor in built-in potential.

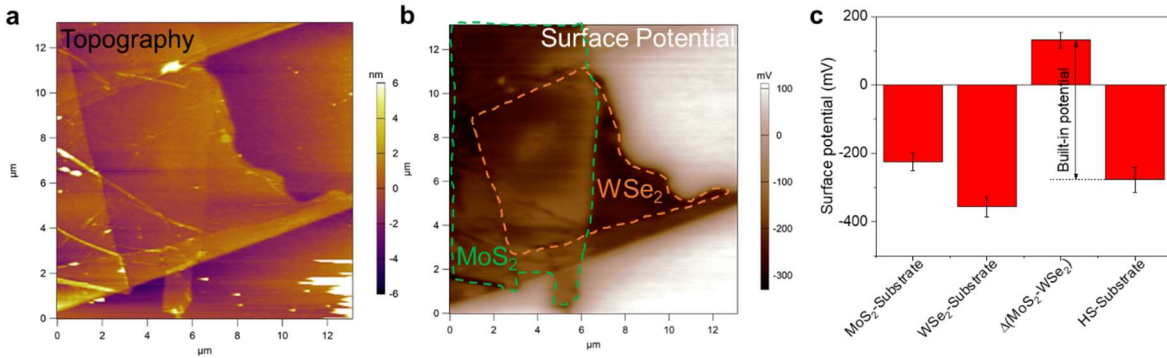


Figure 5.9. Built-in potential in MoS₂/WSe₂ heterostructure revealed by KPFM imaging. **a**, **b**, Representation of the topography and surface potential images of the heterostructure (HS), respectively. The HS is denoted as HS#1 in the study. **c**, The comparison of the surface potential of MoS₂, WSe₂ and heterostructure (HS) regions calculated by the area average of (**b**). The built-in potential in the HS region is shown by the arrow. Error bars indicate one standard deviation.

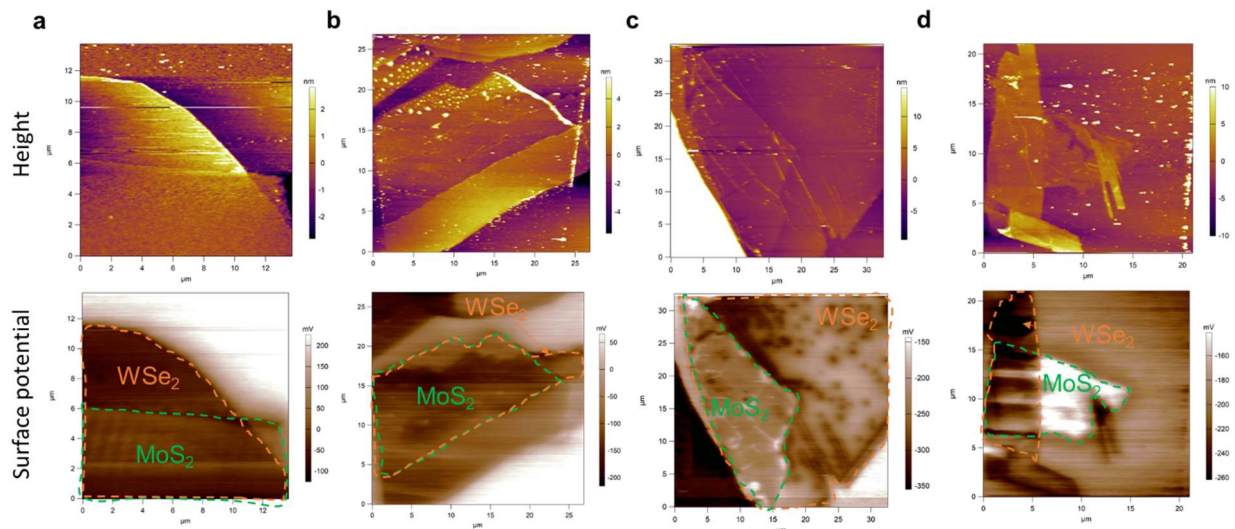


Figure 5.10. KPFM images of four MoS₂/WSe₂ heterostructures. a, b, c, d, The four heterostructure represented as HS#2, 3, 4, 5 in the main text, respectively. The top and bottom panels represent topography and surface potential images, respectively.

We then studied the correlation between d_{33} and surface potential of the HS (**Figure 5.11a**). The d_{33} was highest when the surface potential was highest, followed by a sharp decrease from 4.5 pm/V to 0.01 pm/V as surface potential dropped from ~300 mV to 200 mV (considering the absolute values of the surface potential), then only slightly increased as the surface potential approached zero. We divided the plot into two regions, denoted by the horizontal dashed line which represented the average d_{33} of MoS₂ estimated from different samples. We defined strong response (of d_{33}) region above the dashed line which indicated enhancement in the HS compared to the monolayer MoS₂, whereas region below the line was defined as the weak response. The correlation between the strong (weak) response region with the higher (lower) surface potential is quite distinct for the HS regions only since we didn't observe such correlation on the standalone MoS₂ or WSe₂ region (**Figure 5.11b** and **5.11c**). The d_{33} of MoS₂ (WSe₂) maintained a steady value around 1 pm/V despite the surface potential varying from 50 to mV to -225 mV (-50 mV to -350 mV) (**Figure 5.11b** and **5.11c**). We note that the number of monolayer MoS₂ regions was less than that of WSe₂ because the top MoS₂ was

completely overlapped by the bottom WSe₂ regions for some samples. Therefore, we could not get standalone MoS₂ regions for those samples. Nevertheless, the contrast between the surface potential and d_{33} for the standalone TMDs and HS clearly indicated that the surface potential played a significant role in enhancing the EM response of the HS region. To further highlight the significance of surface potential on the d_{33} , we analyzed the trend between d_{33} and the built-in potential (**Figure 5.12**). The monotonic increase in d_{33} with built-in potential unambiguously established the positive correlation between the charge transfer induced dipole and enhanced EM response of the HS.

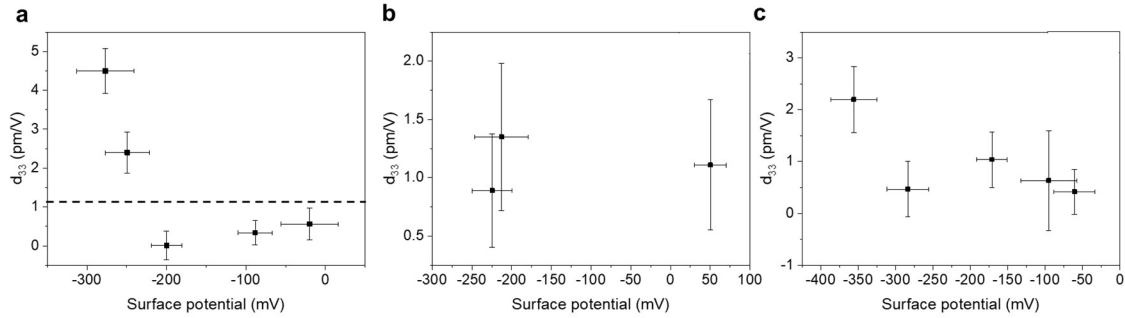


Figure 5.11. Correlation between the d_{33} and surface potential. **a**, d_{33} vs. surface potential plot of the MoS₂/WSe₂ heterostructures. The horizontal dashed line indicates the average d_{33} estimated on the monolayer MoS₂. **b and c**, d_{33} vs surface potential plots for the standalone monolayer MoS₂ and WSe₂ regions, respectively. The error bars indicate one standard deviation.

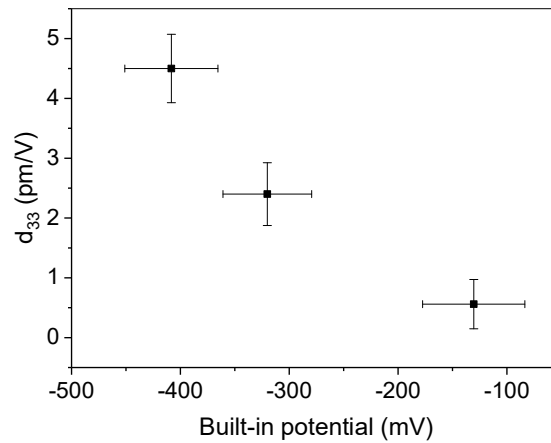


Figure 5.12. Correlation between d_{33} and built-in potential of the heterostructure. The error bars indicate one standard deviation.

We point out a discrepancy briefly mentioned in the previous section where a lower d_{33} (~ 0.56 pm/V) was estimated at a moderately higher Raman mode separation (22.3 cm^{-1}) with no E_{2g}^1 mode softening and stiffening of A_{1g} mode (**Figure 5.8**). After investigating the corresponding surface potential of the same HS, we found that the HS possessed the lowest surface potential and the lowest built-in potential (**Figure 5.11a** and **5.12**). Therefore, we concluded that the poor charge transfer and corresponding weaker dipole strength resulted in a lower d_{33} on that HS.

We also investigated the twist angle dependency on the d_{33} and surface potential of the HS (**Figure 5.13**). The twist angle was estimated from the angle between the straight edges of constituent TMDs^[143]. We observed enhanced d_{33} of the HS when the angle is low ($\sim 11^\circ$) or close to 60° . The d_{33} was below 0.6 pm/V in case of intermediate twist angles. Interestingly, the surface potential also followed a similar trend, i.e., higher potential occurred at low angle and at 60° . We considered the possibility of K-K or K- Γ transition in the HS and its possible effect of charge transfer at low (or 60°) twist angle^[130,144]. However, we observed PL peak at 1.6 eV for all the strongly coupled HS, thereby indicating K- Γ transition irrespective to the twist angle. Previous reports suggested lower interlayer separation at low ($<15^\circ$) and near 60° twist angles of $\text{MoS}_2/\text{WSe}_2$ HS^[130]. Therefore, we suggest that the high surface potential mediated by the strongly coupled HS at low twist angle reinforces the EM response of the HS. As the twist angles deviated from the low angle and 60° , the change in the relative orientation between the constituent TMD layers hindered the charge transfer process, thereby resulting in a reduced surface potential and suppressed d_{33} .

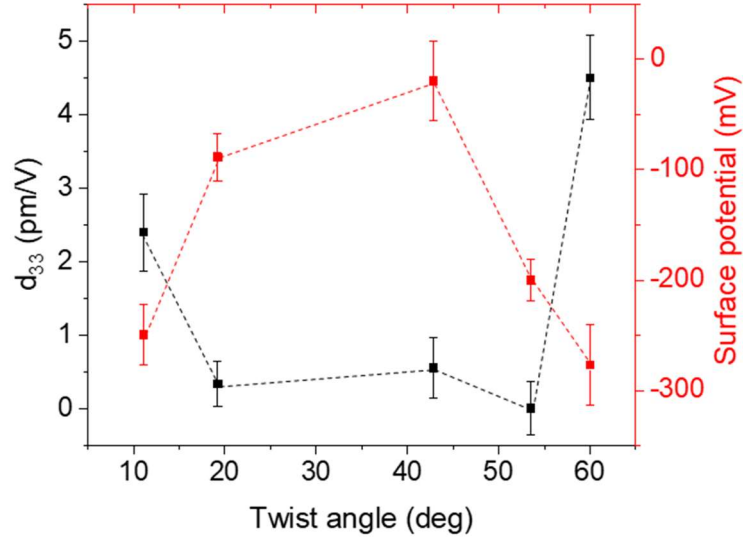


Figure 5.13. Correlation between d_{33} , surface potential with twist angle of the heterostructures. The error bars indicate one standard deviation.

5.6 Conclusions

In conclusion, we demonstrated strongly enhanced EM response of the MoS₂/WSe₂ vertical HS. Our study indicated a maximum of five-fold increase in the EM response compared to the standalone monolayer MoS₂. We conducted detailed analysis to investigate the effect of interlayer interaction and charge transfer on the augmented EM response. Our study indicates that EM response of the HS is affected by both mechanical and electrical coupling where the mechanical and electrical coupling are represented by the interlayer interaction and charge transfer between the TMD layers. We hope that our study would be beneficial for future studies such as the effect of atomic registry on the EM response of vertical HS, tuning the EM response via structural modulation etc. Above all, we believe our knowledge will be used as fundamental building block for the fabrication of next generation devices based on actuation or energy harvesting applications.

CHAPTER 6: CONCLUSIONS

In this dissertation, I have discussed how tip-based characterization techniques have been implemented to investigate the enhanced functionalities of 2D vdW materials. Deformation has allowed us to probe ultra-high light confinement on wrinkled graphene structure. The thinness of the 2D TMDs facilitated the enhanced electromechanical response. And finally, the unique electronic properties of 2D TMD heterostructure enabled enhanced electromechanical responses.

In Chapter 1, I highlighted two exciting functionalities in 2D vdW materials, i.e., plasmonic properties of graphene and flexoelectricity at ultra-thin materials. Some of the breakthrough studies on these two fields have been reviewed to lay out the background knowledge required for this dissertation.

In Chapter 2, I highlighted two advanced tip-based characterization techniques that have been reported to probe the functionalities mentioned in Chapter 1. key aspects of the measurement techniques have been reviewed and a detailed scheme of data interpretation technique have been thoroughly discussed.

In Chapter 3, I have reported the first experimental studies of tunable plasmonic resonance wavelength via control of wrinkled graphene topography. Using photo-induced force microscopy (PiFM), we observed a wide plasmon resonance wavelength tunability (5.77-10.93 μm) when the structural wavelength and aspect ratio of the graphene wrinkle were modulated from 30 to 250 nm and 0.05 to 0.3, respectively. The graphene plasmon resonance redshifted with an increase in wavelength and aspect ratio of the wrinkle, which agrees well with our electromagnetic simulation. Finally, we demonstrated enhanced chemical imaging of an organic thin film aided by plasmon-phonon coupling with the underlying wrinkled graphene structure.

In Chapter 4, I have reported converse flexoresponse of atomically thin TMDs such as molybdenum disulfide (MoS_2) and tungsten diselenide (WSe_2) which exceeds their intrinsic in-plane piezoresponses. Our piezoresponse force microscopy (PFM) measurements revealed strongly enhanced CFE of the atomically thin MoS_2 and WSe_2 than their bulk counterpart ($\sim 700\%$ enhancement in MoS_2 , $\sim 400\%$ enhancement in WSe_2). We observed an anomalous reduction in converse flexoresponse in the monolayer structure attributed to a puckering deformation. By inducing a built-in in-plane tension to reduce puckering, we estimated the CFE of monolayer WSe_2 to be 8.14 pm/V , the highest among the atomically thin TMDs.

In Chapter 5, I have reported enhanced electromechanical response of bilayer $\text{MoS}_2/\text{WSe}_2$ vertical heterostructure (HS). Our study suggested strongly enhanced electromechanical response of the HS, a maximum of five-fold increase compared to the standalone monolayer TMDs. We investigated the effect of interlayer interaction and charge transfer on the augmented electromechanical response. Our study has highlighted the key parameters for the augmented response and suggested TMD HS as a lucrative candidate for ultra-thin electromechanical sensor or actuator based device.

In conclusion, I have investigated the fundamental reasons behind the strong light-matter interaction and enhanced electromechanical response of 2D vdW materials. Our obtained knowledge have laid out the building blocks for designing next generation ultra-thin devices for energy harvesting or sensing applications. Our study on plasmonic resonance on wrinkled graphene structure suggests a widely tunable, plasmonically-enhanced chemical/bio-sensing and spectroscopy platform in the infrared range. The knowledge can open new route for plasmonic device fabrication driven by mechanical instability. Furthermore, the wide tunability of the plasmonic resonance of graphene via wrinkling will allow us to study wider variety of target

molecules in the infrared regime. Combining the tunability with the low loss of graphene plasmon, the crumpled graphene inspired plasmonic device can offer high signal-to-noise ratio in the near-IR to mid-IR range. Therefore, the plasmonic confinement on wrinkled graphene can be a complementary route for plasmonic devices used for surface enhanced characterization techniques (*e.g.*, tip-enhanced Raman scattering). Our study on converse flexoelectricity driven enhanced electromechanical response of atomically thin TMDs enables wider range of materials for harnessing electromechanical response that is not limited to the traditional non-centrosymmetric crystal structures. Furthermore, the flexoelectric effect is insensitive to environmental conditions as long as the device integrity is maintained. Such insensitivity to environment is beneficial for extreme condition (*e.g.*, cryogenic temperature or above Curie temperature) where conventional piezoelectric devices cease to operate. For example, the limited motion of the piezoelectric domain walls at cryogenic temperature hinders the piezoelectric actuation at low temperature. Flexoelectricity based devices demonstrate no such limitation to the temperature. In addition, the ultra-low flexural rigidity of the 2D vdW materials offers wider range of deformation/motion in nanoscale actuation. Therefore, I wish that our knowledge will be critical to next generation micro/nanoactuators, energy harvesters or solid-state fluid handling devices. Finally, our study on electromechanical response of MoS₂/WSe₂ HS provides a critical understanding of interlayer charge transfer and mechanical coupling on out-of-plane electromechanical (EM) response. The systematic investigation on the key factors behind the enhanced EM response allows us to lay out a comprehensive scenario on tuning the EM response. I expect that our results will lay out the platform of nanoscale actuator or energy harvester based on vertically stacked 2D TMD heterostructure.

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