

THE ROLE OF LATTICE DEFECTS ON THE ELECTRON DYNAMICS AND PHOTOCHEMISTRY OF CuFeO₂ DELAFOSSITE

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Metal oxides are stable, earth abundant semiconductors for the photochemical conversion of sunlight into chemical energy. Delafossite CuFeO₂ is a promising material for photochemical energy conversion due to its small band gap (1.5 eV) and p-type conductivity. CuFeO₂ has also shown promise for catalyzing both the hydrogen evolution and CO₂ reduction reactions. Despite significant work in this area, important questions remain regarding the complex defect chemistry in copper-iron oxides and the effect of various defects on the carrier lifetime and photoelectrochemical efficiency. Of the various defects possible, here we investigate the role of type II heterojunction structures with interfaces of CuO and CuFeO₂, Cu vacancies, and O interstitials on the photocarrier dynamics of this material. To elucidate the effects of carrier lifetimes on the photochemical efficiency of mixed phase CuFeO₂, we probe the photocarrier dynamics using optical transient absorption spectroscopy. First, we consider the role of grain boundaries between CuO and CuFeO₂ in mixed phase systems, which have been hypothesized to facilitate charge separation across this type II heterostructure. Transient absorption measurements suggest that photoexcited electrons in the most active materials reside on Fe 3d conduction band states, and we do not observe evidence for electron transfer to CuO, which indicates interfacial charge transfer from CuFeO₂ to CuO is not responsible for enhanced carrier lifetimes in the catalysts studied here. We find that Cu vacancies appear to improve the efficiency of CuFeO₂ due to fast charge separation as holes thermalize from O 2p to Cu 3d valence band states. This is confirmed by DFT calculations demonstrating a lowering of the Cu 3d band center with the introduction of Cu vacancies. In contrast, DFT calculations show that the valence band maximum of CuFeO₂ changes from Cu 3d to O 2p states with the introduction of interstitial O atoms which tends to inhibit charge separation. Based on our results as well as DFT calculations, we conclude that Cu vacancies are primarily responsible for charge separation in this material.