Electrochemical and Photoelectrochemical Properties of the Copper Hydroxyphosphate Mineral Libethenite

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There has been much interest recently in the discovery of new, non-oxide materials for photoelectrochemical applications. The copper hydroxyphosphate mineral libethenite, $Cu_2(OH)PO_4$ (CHP), which has a Jahn-Teller distorted structure and d^9 electron configuration, has recently been reported to display photocatalytic activity. To better understand the properties of this material, a detailed investigation of the relevant fundamental characteristics such as the flatband potential, conduction type, and band diagram was performed using electrochemical and photoelectrochemical methods on thin films deposited on fluorine-doped tin oxide (FTO) substrates. Density functional theory was used to calculate the band structure, effective mass of electrons and holes, and vacancy formation energies in CHP. CHP was found to be active for electrochemical water oxidation, as confirmed by quantitative O_2 measurements. Possible factors behind the low photocurrents observed in linear scanning voltammetry are discussed. Better understanding of this material may lead to the development of improved catalysts and photocatalysts from natural mineral sources.