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1. FINAL TECHNICAL REPORT

Semiconducting metal-oxides have remained of intense research interest owing to their potential for achieving efficient solar-driven photocatalytic reactions in aqueous solutions that occur as a result of their bandgap excitation. The photocatalytic reduction of water or carbon dioxide to generate hydrogen or hydrocarbon fuels, respectively, can be driven on p-type (photocathodic) electrodes with suitable band energies. However, metal-oxide semiconductors are typically difficult to dope as p-type with a high mobility of carriers. Our research is focused on the investigation of new p-type Cu(I)-niobate and Cu(I)-tantalate film electrodes that can be prepared on FTO glass. New high-purity flux syntheses and the full structural determination of several Cu(I)-containing niobates and tantalates have been completed, as well as new investigations of their optical and photoelectrochemical properties and electronic structures via density-functional theory calculations. For example, CuNbO_3 , $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$ and CuNb_3O_8 were prepared in high purity and their structures were characterized by both single-crystal and powder X-ray diffraction techniques. These two classes of Cu(I)-containing compounds exhibit optical bandgap sizes ranging from ~ 1.3 eV to ~ 2.6 eV. Photoelectrochemical measurements of these compounds are currently being performed, and which show strong photon-driven cathodic currents that confirm the p-type semiconductor behavior of CuNbO_3 , CuNb_3O_8 , and $\text{Cu}_5\text{Ta}_{11}\text{O}_{30}$. Incident-photon-to-current efficiencies are measured that approach greater than $\sim 5\%$, with the films exhibiting good resistance to photocorrosion over many hours. Electronic-structure calculations based on density functional theory reveal the visible-light absorption stems from a nearly-direct bandgap transition involving a copper-to-niobium or tantalum (d^{10} to d^0) charge-transfer excitations. Title: "Photoelectrochemistry, Electronic Structure, and Bandgap Sizes of Semiconducting Cu(I)-Niobates and Cu(I)-Tantalates"; Grant number: DE-FG02-07ER15914; Budget period: 9/2010 – 8/2012; Unexpended balance: \$0; Publications resulting from this DOE Support: References 1-15.

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