

## Modified copper tungstate photoanodes for efficient solar driven water oxidation

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Photoelectrochemical (PEC) production of hydrogen is a promising technology for generation of hydrogen for uses in the future hydrogen economy. The water oxidation is a challenging process in water splitting reaction as it is a thermodynamically uphill process. In general, water oxidation occurs relatively at large over potentials compared to hydrogen evolution as it involves the transfer of four electrons. It is important to design an efficient water oxidation electrode in order to improve the overall water splitting efficiency. Many metal oxide electrodes have been explored for PEC water oxidation, however they suffer with either with large band gaps or poor charge carrier separation issues. Recently CuWO<sub>4</sub> has received considerable attention due to its low band gap in between 2.2-2.3 eV with theoretical solar-to-hydrogen efficiencies around 13%.<sup>1</sup> Doping of WO<sub>3</sub> with Cu produces CuWO<sub>4</sub> and this in turn shifts the visible light absorption from 2.7 eV to 2.2-2.4 eV.<sup>2</sup> Unlike the parent compound WO<sub>3</sub>, the CuWO<sub>4</sub> exhibits excellent stability in neutral pH solutions under dark and illumination conditions.<sup>3</sup> Though Cu incorporation reduces the band gap, it creates empty 3dx<sup>2</sup>-y<sup>2</sup> orbitals in CuWO<sub>4</sub> which in turn hampers the transport properties of CuWO<sub>4</sub>.<sup>4,5</sup> Therefore it is important to improve the charge carrier transport properties and interfacial charge transfer kinetics of CuWO<sub>4</sub> for subsequent utilization of the same as photoanode and in order to achieve enhance the overall water splitting activity. In the present work we have systematically addressed these issues by modifying the CuWO<sub>4</sub> photoelectrodes.

The porous CuWO<sub>4</sub>/FTO electrodes used in this study were prepared by modifying the electrodeposition method described by Yourey *et al.*<sup>3</sup> The CuWO<sub>4</sub> films were electrodeposited on FTO plates from a 25mL bath composed of 25mM Cu(NO<sub>3</sub>)<sub>2</sub>.nH<sub>2</sub>O, 25mM H<sub>2</sub>W<sub>2</sub>O<sub>11</sub> and 5 wt% sodium dodecyl sulphate (SDS). The acidic peroxotungstate precursor was prepared by adding concentrated 30% H<sub>2</sub>O<sub>2</sub> to an appropriate amount of Na<sub>2</sub>WO<sub>4</sub>.2H<sub>2</sub>O in high purity water. The pH of the resulting solution ranged between 10.5 and 10.8. The acidity of the final deposition solution was adjusted to pH 1.1 by adding 2-3 mL of concentrated HNO<sub>3</sub>. CuWO<sub>4</sub> films were electrodeposited on F-doped SnO<sub>2</sub> coated on transparent glass (FTO; 20-23 Ω/□) after being cleaned by sonication in ethanol and then in acetone for 10 min each. A three-electrode setup with FTO, Pt wire and Ag/AgCl (3M KCl) as working, counter and reference electrodes respectively was used for electrodeposition

Spectral characteristics of electrodes were investigated by placing the photoelectrodes in a single compartment photoelectrochemical cell and the photoresponse was measured using three electrode assembly. A saturated calomel electrode and Pt sheet were employed as reference electrode and counter electrode respectively. Modified CuWO<sub>4</sub> on FTO was

employed as working electrode. Electrical contact was established by contacting the conducting side of the substrate with a copper wire and silver paint. The geometrical area of the modified CuWO<sub>4</sub> on FTO was controlled by applying a thin layer of insulating epoxy to eliminate possible leakage and shorting. A small aperture of unblocked area (typically 1 cm<sup>2</sup> in area) was created in the center of the photoelectrode. All photoelectrochemical measurements were carried out at room temperature. A pyrex glass cell with a volume of ca. 100-120 mL was employed as the test cell for photoelectrochemical measurements. Dynamic polarization measurements with chopped light were done to study photocurrent and dark current generating from the photoelectrodes. Photocurrent spectroscopy was used to determine the band gap and band transition type.

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### References

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