

Photoelectrochemical water oxidation using CuWO₄ – photoanode prepared by Screen Printing Method

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Abstract: We are showing in this study that copper tungstate (CuWO₄) photoanode with band gap 2.3 eV is a good alternative to WO₃ semiconductor for water oxidation under visible light irradiation. We investigated suitable contact layers and co-catalysts to improve photoelectrochemical water oxidation and decrease surface recombination of CuWO₄ prepared by the screen-printing method. A photoanode with CoO_x co-catalyst and Sn contact layer showed 2.5 higher photocurrent response at 1.2 V vs RHE than bare photoanode.

Keywords: CuWO₄, photoanode, Screen-printing method.

1. Introduction

The photoelectrochemical (PEC) water splitting is one of the ways to convert solar energy into the storable chemical form. There are several attracted photocatalysts for preparing photoelectrodes with suitable optical band gap position for oxygen evolution. The requirement for the semiconductor is to be stable in aqueous electrolytes under dark and illumination. Photogenerated electrons and holes should be separated each other. Further requirements are low over-potentials for the redox reaction to obtain high catalytic activity, and to have sufficiently high (visible) light absorption. At this time, the most effective photocatalyst for oxygen evolution is BiVO₄. There are also other low-cost candidates such as α -Fe₂O₃, WO₃, Bi₂WO₆.

In the present study, we have focused on CuWO₄ photoanode with band gap 2.3 eV. This relatively small band gap makes it possible to theoretically prepare photoanode with ca. 9 mA cm⁻² integrated current density. However, there was achieved only 0.3 mA cm⁻² in the present stage.¹ We investigated suitable contact layers and co-catalysts to improve photoelectrochemical water oxidation and decrease surface recombination of CuWO₄ prepared by the screen-printing method.

2. Experimental

CuWO₄ nanoparticles were prepared by the following preparation procedure.² Two mmol of Cu(NO₃)₂ was dissolved in 50 mL polyethylene glycol. Two mM Na₂WO₄ (1mL) aqueous solution was added to the solution, and the mixture was stirred for 3 minutes. Particles were collected by ultracentrifuge with 15000 rpm for 5 minutes and washed five times with ethanol. Green amorphous CuWO₄ was dried under vacuum. A greenish-yellow crystalline powder was formed after calcination at 773 K for 1 hour. CuWO₄ photoanodes were fabricated by a screen-printing method.³ CuWO₄ (0.2 g) was added to the solution consisting of ethanol, ethyl cellulose and α -terpineol with weight ratio 4:8:2:1. The solution was stirred for 30 minutes to obtain ink paste. The ink was pasted on conductive ITO glass substrate by screen-printer (Mitani Micronics). Samples were calcined up to 673 K for 1 hour. Co-catalysts, CoO_x, RuO_x or NiO_x were loaded from Co(NO₃)₂, RuCl₃ or Ni(NO₃)₂ aqueous solution by drop-casting or dipping method. We also investigated the role of metal contact layer between ITO glass substrate and CuWO₄ photocatalyst. Some metals were deposited onto ITO glass substrate by a vacuum evaporation. The samples were characterized using several spectroscopic methods such as XRD, SEM, UV/Vis and XRF to understand properties of photocatalyst and photoelectrode. As-prepared photoelectrodes were tested in a three-electrode photoelectrochemical cell in continuous N₂ flowing under visible light (300 W Xenon, 420 nm < λ < 800

nm), where a Pt wire and Ag/AgCl were used as the counter electrode and the reference electrode, respectively.

3. Results and discussion

XRD patterns showed that annealed CuWO_4 particles have triclinic structure. The average particle size with around 50 nm was observed by SEM. The thickness of a CuWO_4 photoanode thin film deposited on FTO layer was in the range of 1 - 2 μm and not uniform because of large particle size of CuWO_4 . The fast recombination of surface-trapped holes with electrons from the conduction band was reported on CuWO_4 .⁴ CV curves of CuWO_4 showed that cathodic peak can observe at around 0.6 V vs RHE. Such reduction potential resulted in photoinduced surface recombination in the water oxidation on a metal oxide semiconductor. This is an essential limitation to solar water splitting on CuWO_4 electrodes. To improve photoelectrochemical activity and decrease the surface recombination, co-catalysts were loaded on the photoelectrode. Although the kinetics and reaction pathways are still not sufficiently explained, we suggested that the surface of loaded metal-based co-catalysts was preferentially oxidized by photogenerated holes. The loading of CoO_x , NiO_x and RuO_x can enhance the photoelectrochemical activity. Among them, CoO_x loaded sample showed the highest photo-response. The sample loaded suitable amount of CoO_x indicated 2.5 times higher photo-response than bare CuWO_4 photoanode (Fig. 1).

We investigated the optimization of metal contact layer deposited on conductive ITO glass substrate. A contact layer is an important factor for the quality of the electrode-substrate connection, which can enhance charge transfer. We deposited Al, Ni, Cu, Ag and Sn as the metal contact layer on ITO substrate using vacuum evaporation method and compared their photoelectrochemical activity. The photoanode having Sn metal layers with thickness 200 nm showed the highest photocurrent response.

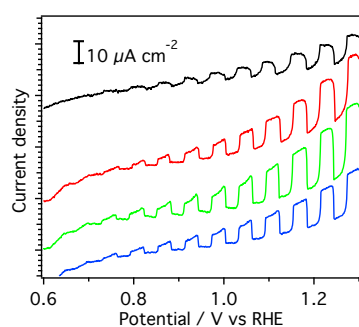


Figure 1. Photocurrent-potential (I-V) curves for PEC water oxidation reaction with different amount of CoO_x loaded on CuWO_4 photoanode (0.25 cm^2) by drop-casting method (0 μL – black line, 2 μL – red line, 4 μL – green line, 6 μL – blue line of 8 mmol $\text{Co}(\text{NO}_3)_2$ (aq.)) in 0.2M borate buffer (pH = 7) under visible light irradiation (300 W Xe lamp, $420 \text{ nm} < \lambda < 800 \text{ nm}$).

4. Conclusions

The best preparation condition of CuWO_4 photoanode using screen-printing method was studied. We found that the highest photocurrent response of CuWO_4 with 200 nm Sn metal contact layer and co-catalyst CoO_x . We still need to investigate preparation and deposition procedure of CuWO_4 to suppress photoinduced surface recombination on the semiconductor and improve quality of photocatalytic layer.

References

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