Preparation of Cuprous Oxide Photocathode Using Titanium Microfiber Felt as a Three Dimensional Conductive Substrate

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Abstract: Sintered titanium microfiber felt exhibits a three-dimensional porous structure with large surface area. We prepared p-type cuprous oxide (Cu_2O) photoelectrodes using the titanium microfibers as a conductive substrate by a solution-based potentiostatic electrodeposition method. The Cu_2O nanocrystalline thin films deposited on Ti microfibers exhibited enhanced photoelectrochemical properties for reduction of methyl viologen compared to Cu_2O films deposited on two-dimensional substrate such as fluorine-doped tin oxide coated glass sheet and Ti sheet.

Keywords: Photocathode, Photoelectrocatalysis, Copper(I) oxide.

1. Introduction

Photoelectrochemical water splitting to produce hydrogen have been widely studied to convert solar energy to storable and transportable chemical energy. Cu_2O is a candidate for the p-type semiconductor materials for photoelectrochemical water splitting, since the narrow bandgap, ~2.0 eV, is suitable for absorption of visible light in sunlight. The Cu_2O photocathodes are easily prepared on conductive substrates by a solution-based electrodeposition method. Transparent conductive oxide coated glass sheets are usually used as the back contacting substrate. However, the two-dimensional flat sheet may not be an appropriate structure because of the small surface area. In this study, we used three-dimensional titanium microfibers with large surface area for the conductive substrate of the electrodeposited Cu_2O photocathode.

2. Experimental

Sintered Ti microfiber felt was sourced from Nikko Techno (diameter 20 μm, porosity 67%, thickness 0.1 mm).[1] Fluorine doped tin oxide (FTO) coated glass sheet was sourced from AGC Fabritech (< 10 ohms/sq, thickness 1.8 mm). Titanium sheet was sourced from Nilaco (thickness 0.2 mm). Cu_2O films were cathodically deposited on the conductive substrates by potentiostatic mode.[2] The electrodeposition plating bath was an alkaline aqueous solution of copper(II) lactate (0.2 M copper sulfate pentahydrate and 1.5 M lactic acid) with pH of 11, which was adjusted by aqueous sodium hydroxide solutions. The solution was heated to 65°C and magnetically stirred during the cathodic deposition at −0.4 V vs. Ag/AgCl reference electrode. The deposition time was controlled by the electric charge measured with the unit of coulomb (0.5 −3 C/cm^2).

Photoelectrochemical measurement of Cu_2O electrode was carried out in a three-electrode system for reduction of methyl viologen (MV^{2+}) under a continuous flow of oxygen. The electrolyte was 0.5 M sodium sulfate containing 20 mM MV^{2+} dichloride hydrate (pH = 5.3). Photoirradiation was performed using LEDs with center wavelengths of 385 nm (irradiance 40 mW/cm^2) and 470 nm (irradiance 10 mW/cm^2). For cyclic voltammetry, the electrode potential was swept in the range from 0 V to −0.4 V vs. Ag/AgCl. Chronoamperometry was measured at −0.3 V vs. Ag/AgCl.

3. Results and discussion

Figure 1 shows the Cu_2O films coated on Ti microfibers (Cu_2O/Ti-fibers), which was prepared with the electric charge of 0.5 C/cm^2. The part of the deposited Cu_2O appeared orange as shown in the picture. The FE-SEM image shows that the diameter of the individual fibers was approximately 20 μm, and the thickness of the Cu_2O film was ~110 nm. The top view image suggests that the thin film composed of

nanoparticles with a diameter less than 50 nm. The XRD pattern of Cu_2O/Ti-fibers shows the formation of Cu_2O crystallites (PDF#01-071-3645).

The Cu_2O/Ti-fibers electrode exhibited the high cathodic photocurrent in the reduction of MV^{2+} to $MV^{\bullet+}$. The photocurrent density of Cu_2O/Ti-fiber was two times higher than that Cu_2O/FTO-sheet and Cu_2O/Ti-sheet. This suggests that the three-dimensional porous structure of Ti microfibers is a factor improving the photocathode performance. The large surface area resulted in the formation of thin layer of Cu_2O nanocrystallites. In the nanocrystalline thin film, the photoexcited electrons and holes can easily transport to the surface site for reduction of MV^{2+} and the back contact substrate with high conductivity, respectively.

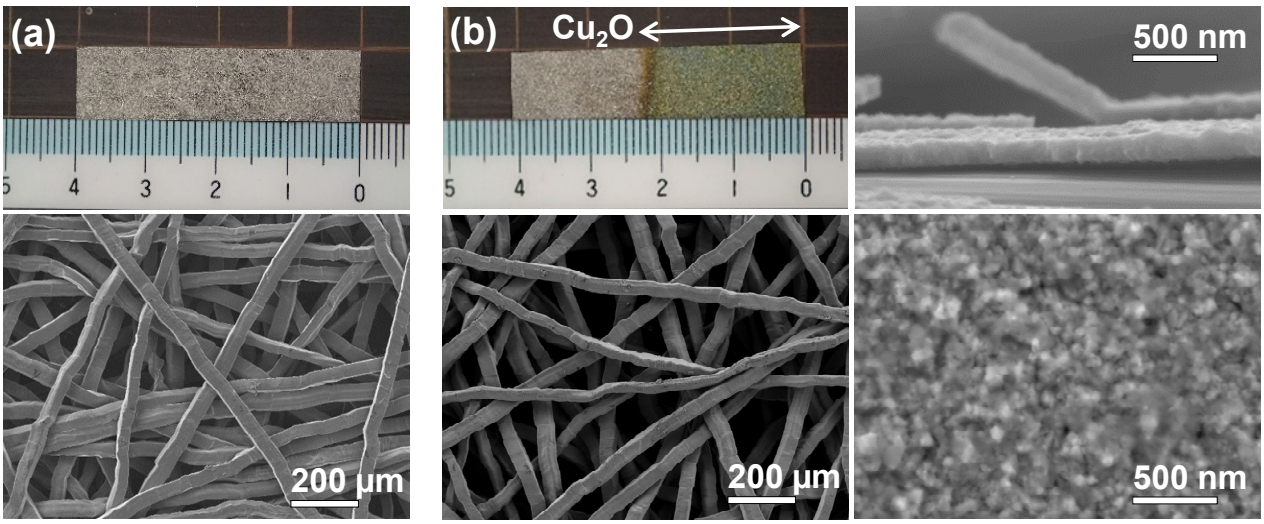

Figure 1. Photographs and FE-SEM images of (a) Ti microfibers and (b) Cu_2O deposited on Ti microfibers.

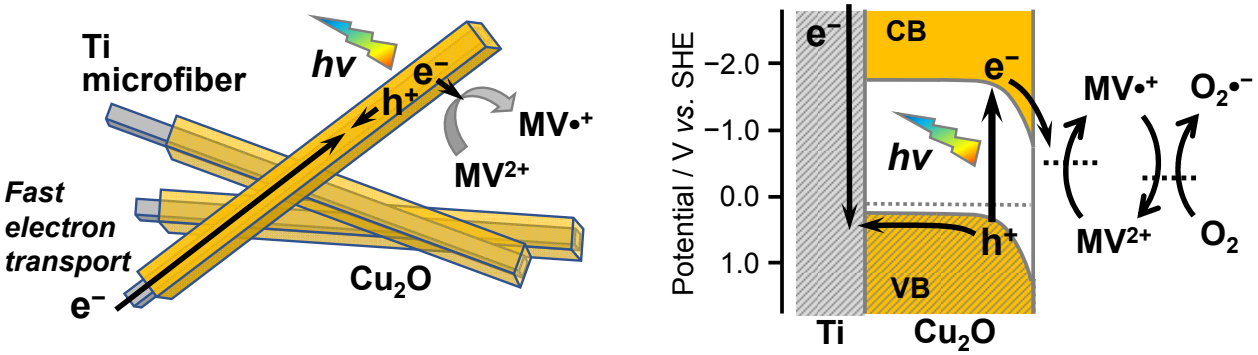

Figure 2. Schematic illustrations of photoelectrochemical reduction of methyl viologen over Cu_2O photocathode.

4. Conclusions

Three dimensional Ti microfibers enhanced the photocathodic property of electrodeposited Cu_2O films owing to the large surface area. The nanocrystalline thin film structure shortens the travel distance of photoexcited electrons and holes to the surface site and the conductive substrate, respectively.

References

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