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〈Research Article〉

Cupric oxide thin film as an efficient photocathode for photoelectrochemical water reduction

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Abstract

Preparing various types of thin films of oxide semiconductors is a promising approach to fabricate efficient photoanodes and photocathodes for hydrogen production via photoelectrochemical (PEC) water splitting. In this work, we investigate the feasibility of an efficient photocathode for PEC water reduction of a p-type oxide semiconductor cupric oxide (CuO) thin film prepared via a facile method combined with sputtering Cu metallic film on fluorine-doped thin oxide (FTO) coated glass substrate and subsequent thermal oxidation of the sputtered Cu metallic film in dry air. Characterization of the structural, optical, and PEC properties of the CuO thin film prepared at various Cu sputtering powers reveals that we can obtain an optimum CuO thin film as an efficient PEC photocathode at a Cu sputtering power of 60 W. The photocurrent density and the optimal photocurrent conversion efficiency for the optimum CuO thin film photocathode are found to be −0.3 mA/cm^2 and 0.09% at 0.35 V vs. RHE, respectively. These results provide a promising route to fabricating earth-abundant copper-oxide-based photoelectrode for sunlight-driven hydrogen generation using a facile method.

Keywords : Cupric oxide; Oxide thin film; Photocathode; Photoelectrochemical water reduction; Hydrogen production

1. Introduction

Harvesting sunlight to provide clean chemical fuels such as hydrogen has been considered to be a desired and sustainable method toward satisfying future demands for energy with little destructive environmental impact [1-3]. Several different approaches have been attempted to developing advanced and reliable processes to generate hydrogen from the sunlight-driven water splitting. Among these existent methods [4-6], photoelectrochemical (PEC) water splitting is known to be one of the most promising hydrogen production techniques in a highly-efficient and eco-friendly way. In general, sunlight-driven water splitting process involves two half-cell reactions of the oxygen evolution reaction (OER) or water oxidation and the hydrogen evolution reaction (HER) or water reduction, and thus the process requires the separation of water oxidation and reduction reactions [3]. Therefore, one of the main reasons why PEC cells are widely used as solar-driven water splitting devices is that they spatially separate water oxidation and reduction reactions.

It is well known that the selection and design of the photocatalytic materials

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for the water oxidation and reduction photoelectrodes are crucial in a PEC cell, since the capability of the PEC cell for water splitting is mainly determined by the light absorption and carrier transport in the photoelectrodes [7]. So far, it has been revealed that oxide semiconductors such as titanium dioxide (TiO_2), hematite (Fe_2O_3), zinc oxide (ZnO), cuprous oxide (Cu_2O), and cupric oxide (CuO) exhibit a promising potential as photoelectrodes for hydrogen generation [8-12]. Among them, p-type Cu_2O and CuO have been extensively studied on their potential use as efficient PEC photocathode for water reduction [4-6], since they exhibit several attractive features such as an adequate bandgap in the visible region, a sufficiently low toxicity, a significant earth-abundance, and a simple fabrication method [12]. It has been reported that Cu_2O and CuO have optical band-gaps of 2.1-2.6 eV and 1.3-2.1 eV, respectively [13], which means that CuO has more potential for absorbing a vast majority of the sunlight spectrum. Moreover, CuO is more thermodynamically stable than Cu_2O. It is thus expected that CuO has a promising potential as a photocathodic material for effective PEC water reduction.

In this work, we report on the feasibility as an efficient photocathode for PEC water reduction of CuO thin films prepared via a facile method combined with sputtering Cu metallic films on a fluorine-doped tin oxide (FTO) coated glass substate and subsequent thermal oxidation of the sputtered Cu metallic films in dry air. The PEC water reduction performance of the fabricated ZnO thin film photocathode is found to be dependent on the Cu sputtering power. The optimal CuO thin film photocathode is revealed to exhibit an efficient PEC performance, suggesting that the simply prepared CuO thin film is a promising photocatalytic material for an effective photocathode in a PEC cell system.

2. Experimental Details

CuO thin films were prepared with the use of a Cu nanoparticle layer formed via two consecutive steps [14]. First, Cu metal films were deposited on a glass substrate coated with an fluorine-doped tin oxide (FTO) electrode from a pure Cu metal target by a rf sputtering method in an Ar atmosphere of 5 mTorr during 2 min at various sputtering power of 20-100 W. The substrate temperature was kept at room temperature and the substrate-to-target distance was set to be 12 cm. Second, the as-sputtered Cu films were then thermally oxidized in dry air at 400 ℃ for 1 h by using a rapid thermal annealing system with the initial increasing rate of the annealing temperature being kept at 10 ℃/min.

The crystalline structures of the prepared CuO thin films were characterized by X-ray diffraction (XRD) using Cu Kα radiation along with Raman spectroscopy, and then their microstructures were analyzed by scanning electron microscopy (SEM) along with atomic force microscopy (AFM). The optical properties of the prepared CuO thin films were examined by UV-vis-NIR spectrophotometer. The photocathode was fabricated by securing a Cu wire to the exposed electrically conductive FTO substrate with Ag conducting paint and the substrate was subsequently sealed on all edges with epoxy resin, excepting the active working area. All the PEC measurements for the CuO thin film photocathode were performed in a three-electrode cell with our photocathode as the working electrode, a Pt sheet as counter electrode, and a Ag/AgCl reference electrode with an aqueous 1 mM Na_2SO_4 solution pH-adjusted to 6.6 as the electrolyte. The area of the photocathode exposed to light was 0.5 cm^2. The photoresponse was measured under

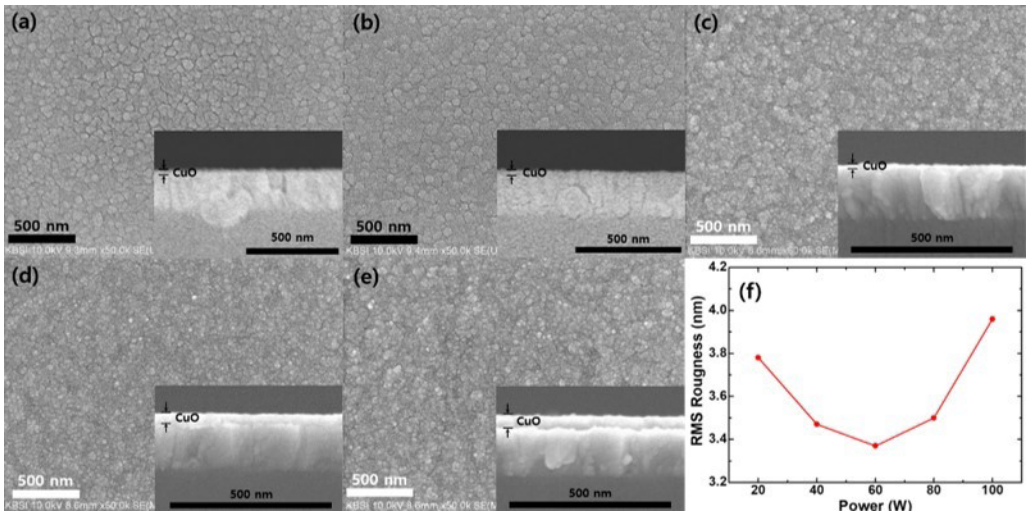

Fig. 1. Typical top-view and cross-sectional SEM images of the CuO thin films prepared on FTO-coated glass substrate for the Cu sputtering power of (a) 20 W, (b) 40 W, (c) 60 W, (d) 80 W and (e) 100 W; (f) represents the variation of the surface roughness with the Cu sputtering power.

a continuous irradiation from a 300 W Xe lamp and the visible light intensity were calibrated to 1 mW/cm^2 for the incidence onto the photocathode, so that the obtained photocurrents can be normalized for the estimation of the photoresponses in the fabricated photocathode samples.

3. Results and Discussion

We present typical SEM images of the CuO thin films prepared on the FTO-coated glass substrate for different Cu sputtering powers of 20, 40, 60, 80, and 100 W in Figure 1(a)-(e). It is clearly seen from these SEM images that the dense CuO thin films with closely packed grains and columnar structure are properly formed for all the sputtering power conditions. The estimated thicknesses of the prepared CuO thin films for the Cu sputtering power of 20, 40, 60, 80 and 100 W are, respectively, 16, 20, 27, 33, and 36 nm. From Figure 1(f), which shows the variation of the estimated surface roughness of the prepared CuO thin films as a function of the Cu sputtering power, the CuO thin film is found to have a minimally rough surface at the Cu sputtering power of 60 W. The observed change in morphology of the prepared CuO thin films for the Cu sputtering power of 20, 40, 60, 80 and 100 W can be attributed to formation of the nanoparticle layer with different size distribution of the Cu nucleation sites corresponding to the Cu sputtering power.

X-ray diffraction (XRD) and Raman spectroscopy were used to verify the formation of the CuO crystalline phase. Figure 2(a) shows typical XRD patterns of

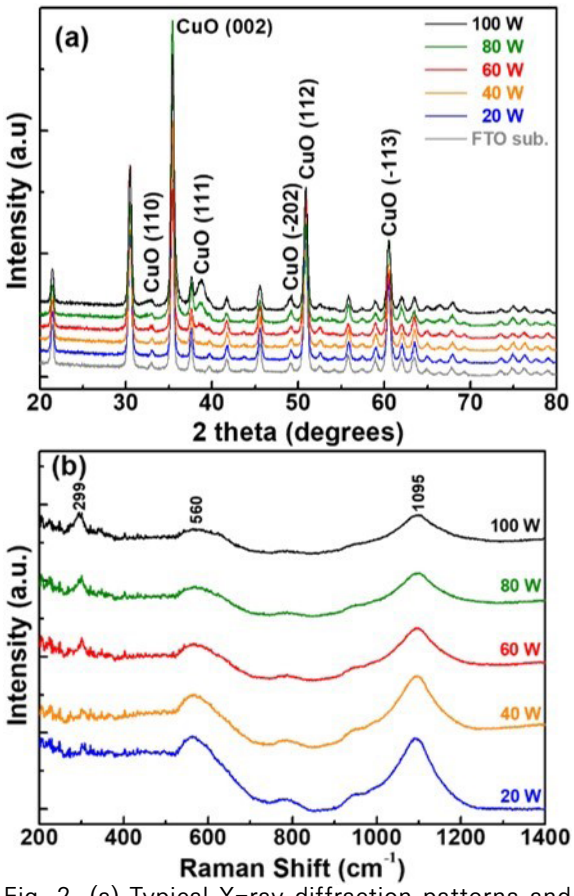

Fig. 2. (a) Typical X-ray diffraction patterns and (b) Raman spectra of the CuO thin films prepared on FTO-coated glass substrate for various Cu sputtering powers.

the CuO thin films prepared on the FTO-coated glass substrate for different Cu sputtering powers of 20, 40, 60, 80 and 100 W. For all the cases, the observed diffraction peaks simply corresponding to the monoclinic tenorite CuO phase (JCPDS card no, 80-1268) were detected and no diffraction peaks of second phases were found in the XRD pattern. And Figure 2(b) shows the Raman spectra of the prepared CuO thin films at room temperature. In these observed spectra, three distinct lines at 300, 560, and 1095 cm^{-1} can be ascribed to the characteristic phonon frequencies of CuO crystalline phase [15]. These observed results obviously indicate the successful preparation of the CuO thin films of the single phase.

Figure 3 shows the UV-vis-NIR absorbance spectra of the CuO thin films prepared on FTO-coated glass substrate for different Cu sputtering powers of 20, 40, 60, 80, and 100 W. It is clearly seen from Figure 3 that the prepared CuO thin films have an absorption edge at about 600 nm due to the optical band gap energy of CuO around 1.5 eV [13]. Also, it is found that the light absorbance of the prepared CuO thin films increases with increasing Cu sputtering power, which is supposed to be related to the decrease of the optical band-gap of the Cu thin film with increasing Cu sputtering power.

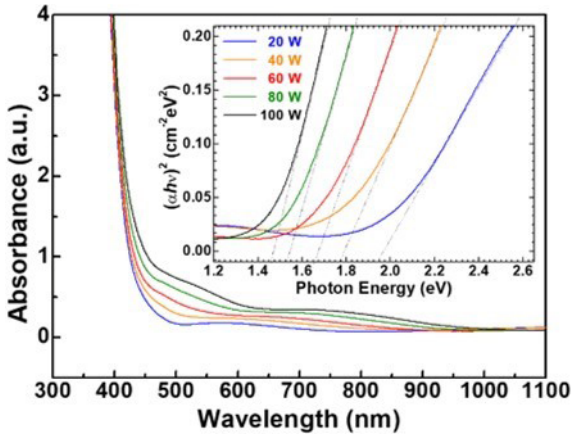

Fig. 3. Optical absorption spectra of the CuO thin films prepared on FTO-coated glass substrates for various Cu sputtering powers. The inset shows the corresponding Tauc plots for the prepared CuO thin films.

In general, Tauc plot, which is obtained from the UV-vis-NIR spectrum, is used to determine the band-gap energy of semiconductor based on the following equation [16]:

$$(ahv)^n = A(hv-E_g)$$

where a is the absorption coefficient which can be obtained from UV-vis-NIR spectrum, hv is the energy of photon, A is a constant, E_g is the optical band-gap energy, and exponent n is dependent on the nature of the optical transition. It is known that n is 2 for direct transition and n is 1/2 for indirect transition [16]. As can be seen in the inset of Figure 3, a straight line is obtained when $(ahv)^2$ is plotted against photon energy (hv), indicating that the absorption is owing to a direct transition for CuO. As expected, the estimated band-gap energy of the prepared CuO thin film is found to decrease notably from 1.91 eV to 1.42 eV as increasing the Cu sputtering power from 20 W to 100 W.

The PEC water oxidation performance of the fabricated CuO thin film photocathode was characterized through the current density-potential (J-V) response curves measured using the linear sweep voltammetry in the dark and under light illumination. Figure 4(a) shows the J-V response curves of the CuO thin film photocathode fabricated for different Cu sputtering powers of 20, 40, 60, 80, and 100 W. From the current density data of the CuO thin film photocathode for Cu sputtering power of 60 W in the dark, the photoelectrode is clearly seen to exhibit quite negligible photocurrent density, which is the case for different Cu sputtering powers. It is clearly seen from Fig. 4(a) that the magnitude of the photocurrent with respect to the cathode potential exhibits a significant increase due to the PEC water reduction with increasing Cu sputtering

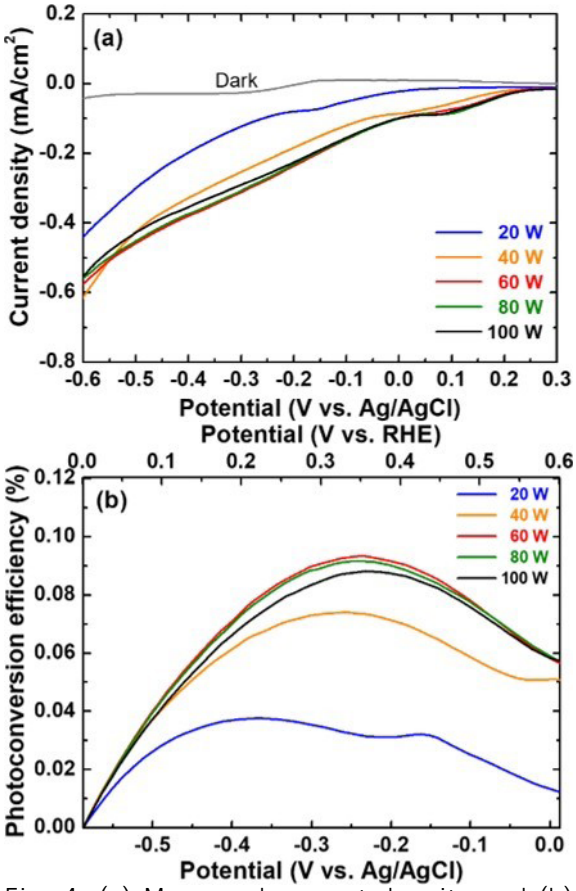

Fig. 4. (a) Measured current density and (b) estimated photocurrent conversion efficiency (PCE) curves of the CuO thin film photocathodes under the applied voltage for various Cu sputtering powers.

power until 60 W while the characteristic of the J-V response curve is hardly sensitive to the Cu sputtering power above 60 W. The observed enhancement of the PEC water reduction performance could be ascribed to the combined effect of the changes in the microstructure and light absorbance of the CuO thin film with respect to the Cu sputtering power.

The photocurrent conversion efficiency (PCE) for photoelectrochemical water reduction of the photocathodes was estimated from our observed J-V characteristic data using the following equation [17]

$$\mathrm{PCE}(\%) = \left[\frac{[J]\times E_{RHE}}{\mathrm{P}_i}\right]\times 100$$

Here, E_{RHE} [V] is the applied external potential vs. a reversible hydrogen electrode (RHE), J [mA/cm^2] is the externally measured current density at E_{RHE}, P_i [mW/cm^2] is the power density of the incident light. The applied potentials were measured vs. Ag/AgCl reference electrode and converted to the RHE scale using the Nernst function [18]

$$E_{\mathrm{RHE}} = E_{\mathrm{Ag/AgCl}} + E^{0}{}_{\mathrm{Ag/AgCl}} + 0.059\ \mathrm{pH}$$

Here, E_{RHE} is the converted potential vs. RHE, $E_{\mathrm{Ag/AgCl}}$ is the external potential measured against the Ag/AgCl reference electrode, $E^{0}{}_{\mathrm{Ag/AgCl}}$ is the standard electrode potential of the calomel reference electrode (0.1976 V vs, RHE at 25 ℃) [7], and pH is the acidity of the solution. Figure 4(b) presents the estimated PEC curves of the CuO thin film photocathodes under an applied potential vs. RHE for various Cu sputtering power. As expected from the observed PEC response characteristics in Figure 4(a), the CuO thin film photocathode for the Cu sputtering power of 60 W is found to exhibit the greatest photocurrent conversion efficiency. Consequently, it is confirmed that the CuO thin film photocathode exhibits the optimal photocurrent conversion efficiency of 0.09% and the corresponding magnitude of the photocurrent density of 0.3 mA/cm^2 at a potential of 0.35 V vs. RHE (that is, around −0.24 V vs. Ag/AgCl). It is noted here that the estimated maximum efficiency of 0.09% for our sputtered CuO thin film is somewhat higher than that of 0.08% at 0.24 V vs. RHE for an electrodeposited CuO thin film [12]. It is also noted that the photocurrent density is not zero but -0.04 mA/cm^2 even at the zero bias (i.e., 0 V vs Ag/AgCl), indicating the possibility of the water splitting with no external bias owing to the photocatalytic effect of the CuO thin film.

The long-term stability of the CuO thin film photocathode was tested by obtaining the photocurrent density-time (J-t) response curve. Figure 5 shows the observed photocurrent response of the

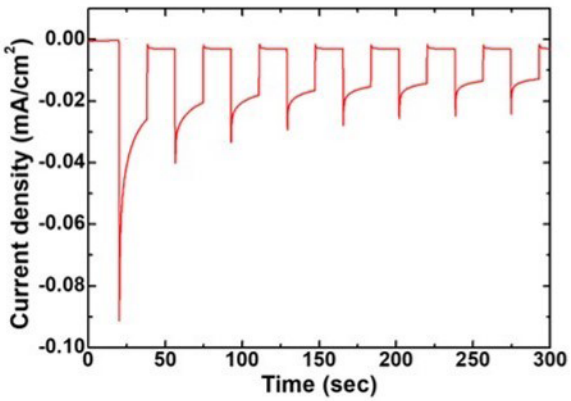

Fig. 5. Photocurrent response of the CuO thin film photocathode at a bias voltage of 0 V vs. Ag/AgCl with light chopped (on/off) for each 20 sec.

CuO thin film photocathode fabricated for the Cu sputtering power of 60 W at a bias voltage of 0 V vs. Ag/AgCl with light chopped (on/off) during each 20 sec. It is seen from Figure 5 that no photocurrent is in the dark. When the light is illuminated, the photocurrent climbs promptly and then gradually reaches a stable state. The observed behavior is associated with the photogenerated electrons under light radiation, the recombination of photogenerated electron-hole pairs, and the balance of generation and recombination of electron-hole pairs [19]. The estimated photocurrent density after 40 sec is found to decrease to about 50% value of the initial photocurrent density, suggesting its long-term stability to be addressed.

4. Conclusion

In summary, the CuO thin film photocathodes fabricated through thermal oxidation of sputtered Cu films in dry air at low temperature exhibited an efficient PEC water reduction performance. From the characterization of the structural, optical, and PEC properties of the CuO thin films prepared for different Cu sputtering powers, it was revealed that we could obtain the optimum CuO thin film as PEC photocathode at a Cu sputtering power of 60 W. The photocurrent density and the optimal photocurrent conversion efficiency obtained on the optimum CuO thin film photocathode were found to be -0.3 mA/cm^2 and 0.09% at 0.35 V vs. RHE, respectively. Our results suggest that the CuO thin film has promising potential as an efficient photocathode for sunlight-driven PEC water splitting.

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