Electrochemical synthesis and characterization of transparent nanocrystalline Cu_2O films and their conversion to CuO films†

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Transparent nanocrystalline Cu_2O films (E_g = 2.6 eV) were electrodeposited from a dimethyl sulfoxide medium; these films exhibit interesting optical and photoelectrochemical properties, and can be converted to transparent CuO films.

Cuprous oxide (Cu_2O) is a direct band gap semiconductor that exhibits interesting catalytic, electrochemical, electrochromic and photoelectrochemical properties.[1–6] Due to its narrow band gap (E_g = 1.9–2.2 eV), Cu_2O has the potential for use in photovoltaic and photoelectrochemical devices that can efficiently utilize visible light.[7] Additionally, the low cost and environmentally benign nature of copper makes developing cuprous oxide-based devices especially advantageous.

Cu_2O films have traditionally been prepared by the high temperature thermal oxidation of copper metal.[7] However, high temperature processes can limit control over the fine interfacial features of Cu_2O films (*e.g.* surface area, particle size, grain boundaries), which can significantly affect the resulting optical and photoelectrochemical properties. In this context, electrodeposition is an attractive route for the production of Cu_2O films because it is a solution-based procedure carried-out at low temperatures. To date, electrodeposition of Cu_2O has been mainly carried-out using slightly acidic or basic aqueous media.[8,9] A variety of elegant shapes and orientations of Cu_2O crystals have been achieved through these syntheses.

In this study, we report new electrodeposition conditions using a non-aqueous medium, dimethyl sulfoxide (DMSO), to generate *transparent* nanocrystalline Cu_2O films that possess a significantly blue-shifted band gap of 2.6 eV. Transparent films are highly desirable for use in multi-stack photoelectrodes because they can maximize the portion of unabsorbed light transmitted through the film to the underlayer. Using a mild thermal oxidation process, these Cu_2O films can be converted to transparent films of CuO, another important semiconducting material with interesting catalytic, electrochromic and photoelectrochemical properties.[5,10,11] Preliminary characterization of the optical and photoelectrochemical properties of Cu_2O films are discussed in this study.

Cu_2O films were electrodeposited potentiostatically from DMSO solutions containing 0.01 M $Cu(NO_3)_2 \cdot 3H_2O$ as the source of copper ions. The plating medium was saturated with O_2 gas by bubbling before deposition. A conventional three-electrode setup in an undivided cell was used. A glass slide coated with fluorine-doped tin oxide (FTO) and an Ag/AgCl electrode in 4 M KCl were used as the working and reference electrodes, respectively. The counter electrode was prepared by depositing 250 Å of titanium, followed by 500 Å of platinum, onto clean glass slides by sputter coating.

Pure Cu_2O films can be deposited at 60 °C in the potential range $-0.2 \leqslant E \leqslant -0.3$ V against an Ag/AgCl reference electrode. The resulting Cu_2O films are yellow and highly transparent (Fig. 1(a)). At elevated potentials or temperatures, a mixture of Cu_2O and copper metal is deposited. The presence of O_2 in the plating medium increases the potential window for the deposition of pure Cu_2O with no copper contamination; in the absence of oxygen, copper deposition begins at −0.3 V. Additionally, dissolved O_2 in the DMSO also significantly increases the deposition rate of Cu_2O, resulting in rapid deposition of homogeneous Cu_2O films (10 nm min^{-1}). This indicates that O_2 provides oxygen to the Cu^+ ions for the formation of Cu_2O more easily than do H_2O molecules or NO_3^- ions, also present in the plating medium.

Various heating conditions (*e.g.*, annealing temperatures and ramping rates) were investigated for the conversion of Cu_2O to

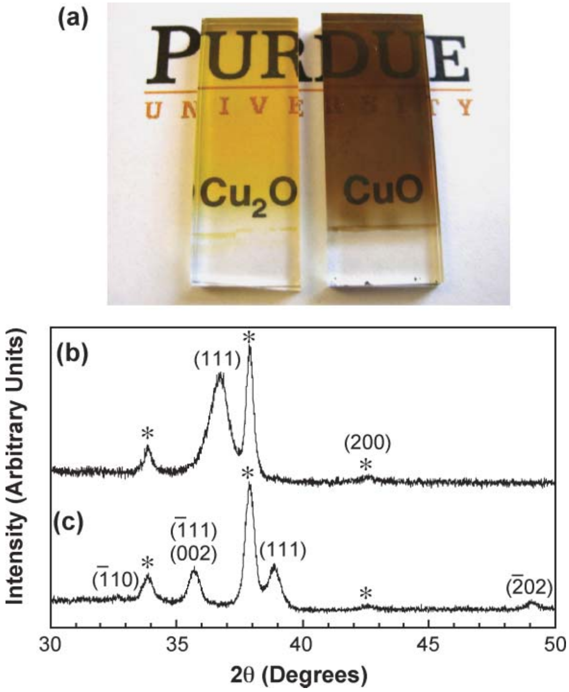

Fig. 1 (a) Photographs of Cu_2O and CuO(ii) films. XRD patterns of (b) Cu_2O and (c) CuO(ii) films. The peaks from the FTO substrate are marked with *s.

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† This paper is dedicated to the memory of Professor Ian P. Rothwell.

CuO. Heating the 300 nm thick Cu_2O films at 300 °C in air for 1 h converts them to pure CuO films, dark brown in color (Fig. 1(a)). A ramping rate slower than 4.5 °C min^{-1} to 300 °C was required in order to maintain the high quality transparency; faster ramping rates resulted in uneven color and transparency. In the following discussion, CuO films, prepared by heating Cu_2O films at 300 °C for 90 min using ramping rates of 9.0, 4.5 and 1.1 °C min^{-1}, will be referred to as CuO(i), CuO(ii) and CuO(iii), respectively.

The X-ray diffraction (XRD) pattern of a Cu_2O film deposited at −0.2 V is shown in Fig. 1(b). The diffraction peaks assigned to Cu_2O are very broad compared to the peaks generated by the FTO substrate, suggesting the presence of nanocrystalline features. The XRD pattern of a CuO(ii) film is shown in Fig. 1(c), confirming the purity of the CuO films. CuO(i) and CuO(iii) show XRD patterns similar to Fig. 1(c), although the CuO(i) film generated slightly sharper Bragg peaks compared to the CuO(ii) film.

Scanning electron microscopy (SEM) images show that, on the micron level, the Cu_2O films possess a relatively flat surface. The films are composed of 100–200 nm-sized granules, which in turn are composed of nanocrystals smaller than 10 nm in size (Fig. 2(a)). Transmission electron micrographs (TEM) of the Cu_2O films confirm the sizes of individual Cu_2O crystals (marked with arrows), approximately 6–10 nm (Fig. 2(b)). SEM images of CuO films (i)–(iii) are shown in Fig. 2(c)–(e). CuO(i) shows evident agglomeration of CuO particles, creating cracks on the surfaces. CuO(ii) and CuO(iii) show relatively mild alteration of the surface morphology.

The nanocrystalline features of the Cu_2O films may cause a significant blue shift in the band gap energy, which may explain the unusual yellow color of the Cu_2O films.[12] (Cu_2O films deposited from aqueous media, using conditions reported in ref. 8 and ref. 9, possess a band gap energy of 1.9–2.2 eV and generally exhibit a purple or deep-red color.) Cu_2O possesses a direct band gap, which is determined by plotting $(\alpha E)^2$ *vs.* E (Fig. 3(a)), where α is the absorption coefficient and E is the energy in electron volts.[13] Extrapolation of the linear portion of the $(\alpha E)^2$ function to the energy axis provides a band gap energy of 2.6 eV, which is significantly blue-shifted from the reported band gap energy of bulk Cu_2O. The band gap of CuO, which is indirect, is determined by plotting $(\alpha E)^{1/2}$ *vs.* E (Fig. 3(b)).[11] The CuO(i) sample displays a band gap of 1.3 eV, while the CuO(ii) and CuO(iii) samples exhibit a slightly blue-shifted band gap energy of 1.4 eV. However, all of these values fall within the range of band gap values observed for bulk CuO ($1.2 \leqslant E_g \leqslant 1.7$ eV); therefore, it is possible that this variation may not be caused by the size effect.

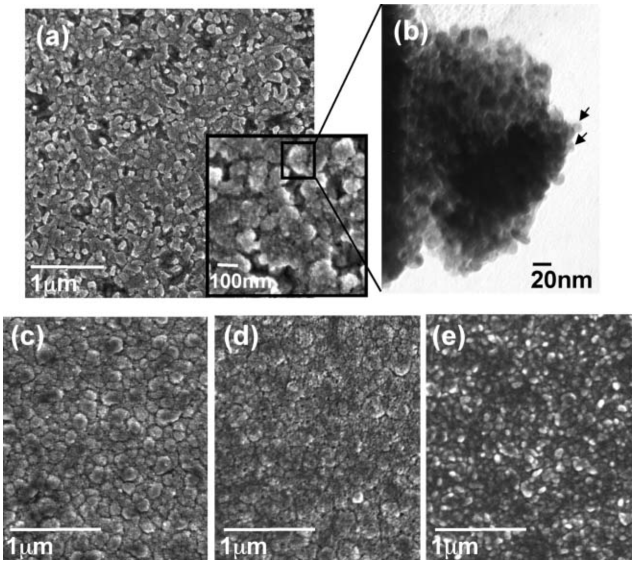

Fig. 2 (a) SEM and (b) TEM images of the Cu_2O film. SEM images of (c) CuO(i), (d) CuO(ii) and (e) CuO(iii) films.

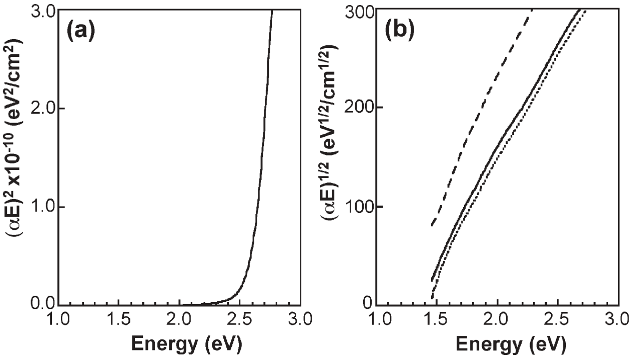

Fig. 3 UV-vis spectra of (a) Cu_2O and (b) CuO films (i) ---, (ii) ...... and (iii) —.

Cu_2O has been investigated as a potential material for the photoelectrolysis of water.[1–3] One of the major limitations of this material is the proximity of its valence band to the oxidation potential of water, leaving little overpotential for the oxidation of water.[2] Therefore, the increased band gap energy observed for our films may allow the photoelectrolysis of water by Cu_2O to become more thermodynamically feasible, if it involves lowering the position of the Cu_2O valence band.

Fig. 4(a) shows a potential–current plot under chopped irradiation with visible light (3.2 W cm^{-2} at the Cu_2O surface) while the potential was swept linearly from 120 to −200 mV using a scan rate of 10 mV s^{-1}. A platinum plate was used as the counter electrode, and the potential was measured against an Ag/AgCl electrode in 4 M KCl. A 0.5 M Na_2SO_4 solution was used as the electrolyte and a 300 W Xe lamp used as the light source, with the UV light being removed by a filter. The Cu_2O electrode had dimensions of 0.9 × 2.0 cm, and the area of the electrode exposed

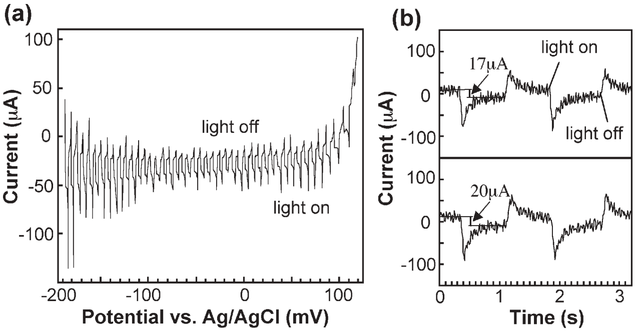

Fig. 4 (a) Current–voltage characteristics for the Cu_2O film under chopped visible irradiation (scan rate, 10 mV s^{-1}). A 0.5 M Na_2SO_4 solution was used as the electrolyte. (b) Comparison of the photocurrent generated by visible light only (top) and by a combination of visible and UV light (bottom) at 100 mV against an Ag/AgCl electrode (equivalent to a zero-bias photocurrent).

to light was 0.24 cm^2. The presence of oxygen in a solution can significantly increase the observed photocurrent *via* the reduction of oxygen, which is more favorable than hydrogen production.[2] Therefore, the electrolyte was purged thoroughly with argon before use.

The Cu_2O films exhibit p-type behavior, generating a cathodic photocurrent. The potential–current plot shows an approximately 17 μA photocurrent at 100 mV, which is the open circuit voltage of the cell in the dark, indicating that the Cu_2O films can generate a significant amount of zero-bias photocurrent under visible light irradiation. The amount of photocurrent gradually increases as the applied potential becomes more negative. Fig. 4(b) compares the photocurrent generated solely by visible light (3.2 W cm^{-2}) with that generated by a combination of visible and UV light (3.4 W cm^{-2}) at a fixed potential of 100 mV against an Ag/AgCl electrode. The steady-state photocurrent generated by only visible light (*ca.* 17 μA) is not considerably lower than that generated by both visible and UV light (*ca.* 20 μA). The transient cathodic and anodic spikes observed when the light is turned on and off, respectively, are most likely due to changes in surface state occupancies and surface charge recombinations.[10,14] We are currently carrying-out more experiments to study these behaviors and to precisely determine the band positions of the Cu_2O films.

In summary, we have demonstrated a facile electrochemical procedure that can produce highly transparent Cu_2O films using a DMSO medium. The resulting films are composed of *ca.* 10 nm-sized nanocrystals and exhibit a band gap energy of 2.6 eV. These films can be thermally converted to CuO films while preserving their transparency. The Cu_2O films show promising photoelectrochemical properties under visible light irradiation that warrant the further investigation of this material for use in solar energy conversion.

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