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Electrochemical synthesis of p-type copper oxides

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Copper oxide is a narrow band gap, low cost, nontoxic, photoactive metal oxide and can be considered as the best candidate for photo-electrochemical applications. Thin films of p-type copper oxide are prepared by cyclic voltammetric technique. The electrochemical method is a cost effective low temperature technique for the preparation of functional thin films. Tools like, GIXRD, Raman Spectroscopy, UV-Vis Spectroscopy, PL, SEM and EIS analysis are done to study the structure, phase, optical, morphological and electrochemical behavior of the copper oxide thin film. The effect of deposition conditions on the electrical and optical properties of the thin films are analyzed in detail.

Keywords: cyclic voltammetry, electrochemical impedance analysis.

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1. Introduction

Copper oxide is a low cost, non-toxic, narrow band gap metal oxide [1]. Oxides of copper crystallize mainly in two forms, cuprous oxide (Cu_2O) and cupric oxide (CuO) [1, 2]. Cuprous oxide is a direct bandgap [1] and cupric oxide is an indirect band gap [1] metal oxide. These metal oxides exhibit interesting properties suitable for catalytic [3], electrochromic [4], electrochemical [4], photoelectrochemical [5] and photovoltaic applications [4]. Due to the narrow band gap (Cu_2O – 1.9–2.2 eV and for CuO is 1.2–1.7 eV) it has high potential in photovoltaic and photoelectrochemical applications. Commonly, copper oxide films have been synthesized by the high temperature thermal oxidation of copper metal [6] that limits the control over the interfacial features like surface area, particle size, and grain boundaries etc, which affect the optical and electrochemical properties. Hence, the present study focus on electrodeposition method [7] which is an attractive method for thin film synthesis under low temperature conditions. The efficiency of electronic and charge transfer mechanism between the nanoparticles or the nanoparticles and the adjacent layer depends highly on the shape and size of the particles participating in the process. This highlights the significance of deposition of size and shape controlled nanostructures by electrochemical deposition.

2. Experimental method

Electrodeposition of copper oxide is done using three electrode system, where cleaned FTO is used as the working electrode, platinum wire as counter electrode and Ag/AgCl as reference electrode. The Cu_2O is deposited on the FTO substrate under neutral pH the potential is swept between 0 V to -0.8 V from the solution containing 5 mM $CuSO_4$ and 50 mM KNO_3 and repeat the cycles three times to get a yellow colored film. The CuO is deposited from solution containing 5 mM $CuSO_4$ and 50 mM KNO_3 under acidic (2.5 mM H_2SO_4) pH the potential is swept between 0 V to -0.8 V and repeat the cycles three times to obtain a black colored film. Fig. 1 shows the photographs of the obtained yellow and black films of copper oxides.

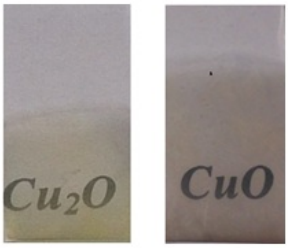

FIG. 1. Photographs of Cu_2O and CuO films

3. Result and discussion

3.1. Cyclic voltammetry

Figure 2 depicts the cyclic voltammogram for the electrodeposition of both Cu_2O and CuO. Cu_2O formed under neutral pH. In Fig. 2(a), the peak at -0.21 V shows the film formation and there are two peaks at Fig. 2(b) shows the conversion of Cu^{2+} ion from Cu^{+}ion i.e, the formation of CuO. The Cu^{2+} ion accepts an electron from the electrode and becomes a Cu^{+} ion to attain a stable electronic configuration. The positive nature of the metal ion helps, forming weak Van der Waals interactions with the non-bonded electrons of oxygen atom of the water and the adsorbed Cu-H_2O complex on FTO substrate is neutralized by releasing H^{+} ion, which resulted in the deposition of Cu_2O. An increase in cathodic current is found near a cathodic potential of -0.21 V, indicating the deposition of Cu_2O film. When the cycle is repeated, the deposition current diminishes with an increase in film coverage on the substrate, since Cu_2O is less conducting than FTO. But at acidic pH, the H^{+} ion from H_3O^{+} ion complex reduced by accepting electron from Cu^{+} ion, leads to the formation of Cu^{2+} ion which is the then converted into CuO.

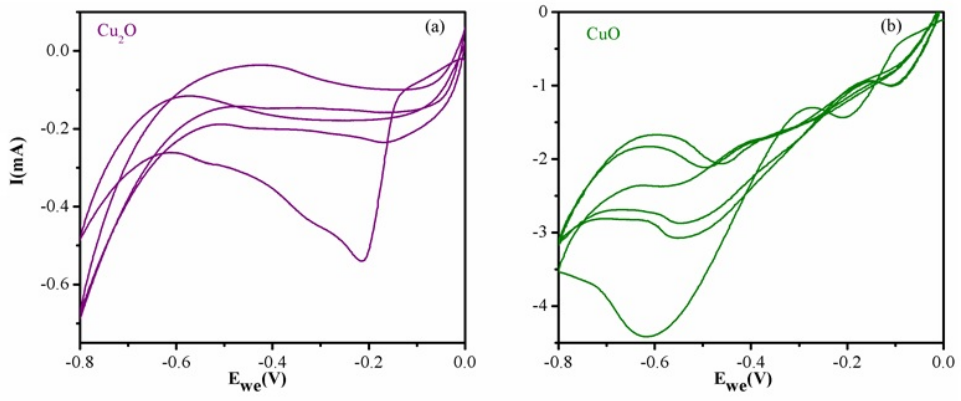

FIG. 2. Cyclic voltammogram of electrodeposition of (a) Cu_2O and (b) CuO

3.2. Structural analysis

The crystallinity of the deposited films was analyzed using a grazing angle X-ray diffraction (GIXRD). Fig. 3 depicts the XRD spectra of the deposited films and is compared with standard JCPDS files 78-2076, 80-1917, which correspond to cubic and monoclinic crystal structures respectively for cuprous and cupric oxide of space groups Pn3m and C1c1. In cubic Cu_2O, the copper atoms are at fcc sub lattices and oxygen atoms are at bcc sub lattices [8]. In the case of monoclinic CuO, the copper atom is coordinated by four oxygen atoms in an approximately square planar configuration and the oxygen is coordinated to four copper atoms at the corners of a distorted tetrahedron [9].

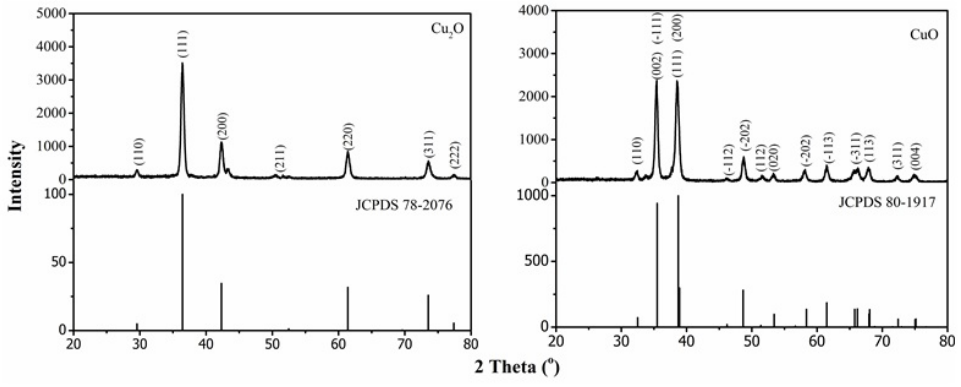

FIG. 3. XRD spectra of Cu_2O and CuO films compared with standard JCPDS

3.3. Morphology

The morphology of the film obtained from SEM analysis. Fig. 4 depicts the average size of Cu_2O is 75 nm and that of CuO is 93 nm. The morphology of Cu_2O is square in shape, while that of CuO is spherical shape.

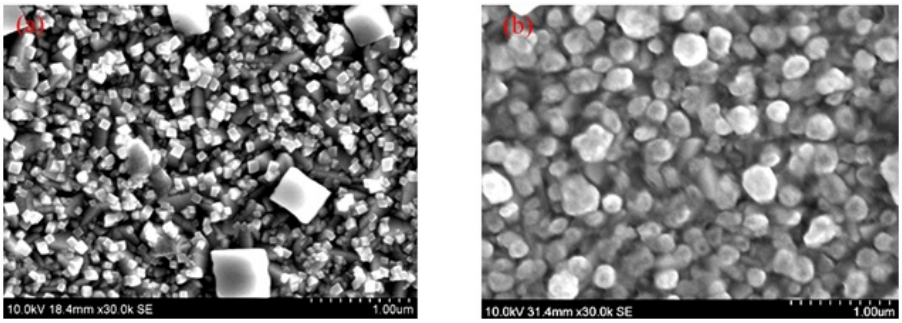

FIG. 4. SEM image of Cu_2O and CuO films

3.4. Optical properties

Optical properties of the films were analyzed by using UV-Visible spectroscopy. The absorption spectra and Tauc plots for Cu_2O and CuO are shown in Fig. 5. The band gap is estimated from the Tauc plot and the obtained values are 2.43 eV and 1.73 eV respectively for Cu_2O and CuO. The PL spectra give idea about the defect state. Fig. 6 depicts three peaks in the PL spectra corresponding to band edge emission, oxygen ion vacancy and copper ion vacancy [10]. The band edge emission is slightly red shifted (562 nm) in the case of cupric oxide than cuprous oxide (527 nm). All the defect emissions are also red shifted. The p-type nature of the films is due to the presence of copper ion vacancies.

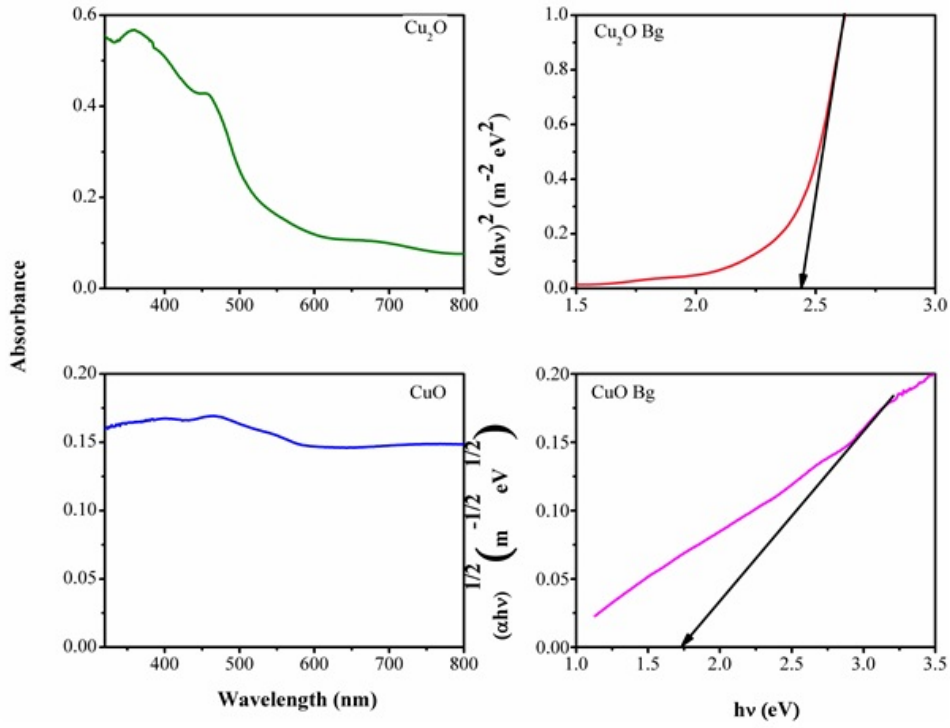

FIG. 5. UV-Visible spectra and Tauc plot of Cu_2O and CuO films

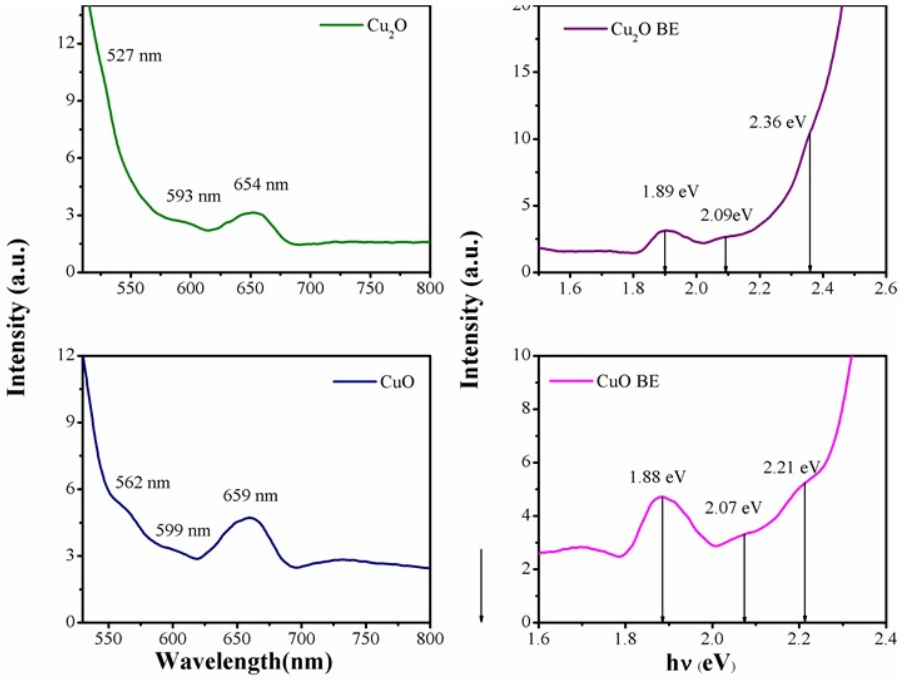

FIG. 6. PL spectra of Cu_2O and CuO films

3.5. Electrical properties

The electronic properties of the films are studied using hall measurement system. From this measurement both Cu_2O and CuO are p-type semiconductors with conductivity of 4.71×10^2 Scm^{-1} and 4.12×10^3 Scm^{-1} respectively. Fig. 7. depicts the Nyquist plots obtained from electrochemical impedance (EIS) analysis of copper oxides, which measure the interfacial resistance between the electrode and electrolyte in the dark and light condition. This analysis confirms the photo activity of copper oxide. Cu_2O is more photoactive than CuO.

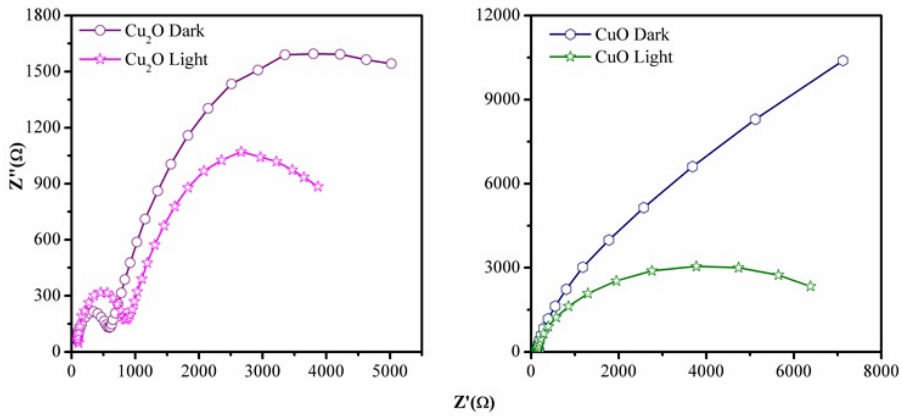

FIG. 7. Nyquist plots of electrodeposited Cu_2O and CuO films

The efficiency of the cell was obtained from chronoamperometric analysis in 0.1 M Na_2SO_4 electrolyte by using three electrode system where deposited film was a working electrode, Pt wire was a working electrode and Ag/AgCl was the reference electrode. The efficiency is calculated from equation 1, where η is the efficiency of the cell, I is the steady current density obtained from I-t curves (shown in Fig. 8), V is the applied potential -0.2 V and J_{Light} is the irradiance intensity of 100 mW/cm^2. The efficiencies obtained for Cu_2O and CuO were 0.5 % and 0.2 % respectively.

$$\eta = \frac{I(1.23 - V)}{J_{Light} \cdot 100}. \tag{1}$$

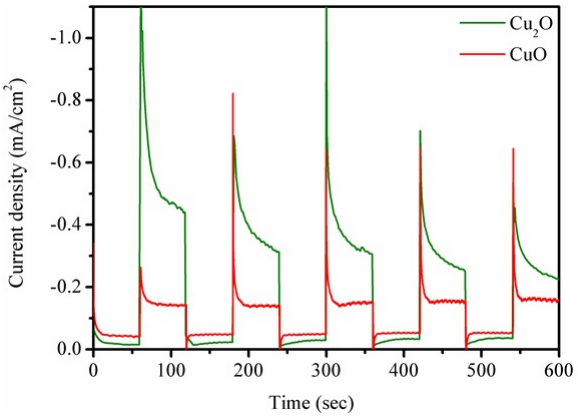

FIG. 8. Chronoamperometric spectra of electrodeposited Cu_2O and CuO films

4. Conclusion

Cyclic voltammetric deposition techniques were utilized to synthesize p-type copper oxides at potentials ranging from 0 V to −0.8 V at a scan rate of 20 mV/s. Cu_2O is formed under neutral pH and CuO is formed at lower pH values. The band gaps of both copper oxides are narrow ie; 2.43 eV and 1.73 eV for Cu_2O and CuO respectively. The p-type nature is confirmed from Hall measurement system. Both are p-type copper oxides. The electrochemical impedance analysis shows that the cuprous oxide thin films are more photoactive than cupric oxide, which was confirmed through chronoamperometric analysis. The efficiencies of Cu_2O and CuO were 0.5 % and 0.2 % respectively.

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