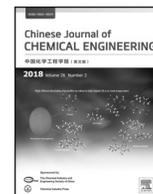




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## Article

Electrodeposition and characterization of Cu<sub>2</sub>O thin films using sodium thiosulfate as an additive for photovoltaic solar cells☆Hassiba Rahal<sup>1,2</sup>, Rafiaa Kihal<sup>1,3</sup>, Abed Mohamed Affoune<sup>1,\*</sup>, Samia Rahal<sup>4</sup><sup>1</sup> Laboratoire d'Analyses Industrielles et Génie des Matériaux, Département de Génie des Procédés, Faculté des Sciences et de la Technologie, Université 8 Mai 1945 Guelma, BP 401, Guelma 24000, Algeria<sup>2</sup> Université 20 Août 1955 Skikda, BP 26, Route El-Hadaiek, 21000, Algeria<sup>3</sup> Université Abbes Laghrour Khenchela, BP 1252, Rue de Batna, Khenchela 40004, Algeria<sup>4</sup> Laboratoire d'Etude des Surfaces et Interfaces de la Matière Solide LESIMS, Département de Physique, Faculté des Sciences, Badji Mokhtar Université, Annaba, Algeria

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## ABSTRACT

Cuprous oxide (Cu<sub>2</sub>O) thin films have been grown by electrodeposition technique onto ITO-coated glass substrates from aqueous copper acetate solutions with addition of sodium thiosulfate at 60 °C. The effects of sodium thiosulfate on the electrochemical deposition of Cu<sub>2</sub>O films were investigated by cyclic voltammetry and chronoamperometry techniques. Deposited films were obtained at −0.58 V vs. SCE and characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and optical, photoelectrochemical and electrical measurements. X-ray diffraction results indicated that the synthesized Cu<sub>2</sub>O films had a pure cubic phase with a marked preferential orientation peak along (200) plane and with lattice constants  $a = b = c = 0.425$  nm. FTIR results confirmed the presence of Cu<sub>2</sub>O films at peak 634 cm<sup>−1</sup>. SEM images of Cu<sub>2</sub>O films showed a better compactness and spherical-shaped composition. Optical properties of Cu<sub>2</sub>O films reveal a high optical transmission (>80%) and high absorption coefficient ( $\alpha > 10^4$  cm<sup>−1</sup>) in visible-light region. The optical energy band gap was found to be 2.103 eV. Photoelectrochemical measurements indicated that Cu<sub>2</sub>O films had n-type semiconductor conduction, which confirmed by Hall Effect measurements. Electrical properties of Cu<sub>2</sub>O films showed a low electrical resistivity of 61.30 Ω · cm<sup>−1</sup>, carrier concentration of  $-4.94 \times 10^{15}$  cm<sup>−3</sup> and mobility of 20.61 cm<sup>2</sup> · V<sup>−1</sup> · s<sup>−1</sup>. The obtained Cu<sub>2</sub>O thin films with suitable properties are promising semiconductor material for fabrication of photovoltaic solar cells.

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## 1. Introduction

The total demand of energy in the world increases with the demographic growth and the development of technology. Among all renewable energy sources, solar energy is extremely useful and promising as an abundant and clean energy source [1]. Photovoltaic conversion is one of the most advanced technologies, which consists in directly transforming solar energy into electric energy using semiconductor knowing that it has attracted attention for many decades. The high production cost of solar energy materials constitutes a serious drawback for the commercialization of photovoltaic cells. Furthermore, toxic substances are involved in the production and processing of most semiconductors, causing environmental problems. Thus, research efforts have been made especially in the last decade in order to develop materials which were able to guarantee

optimal characteristics in terms of environmental compatibility, abundance and photoactivity [2]. Among the various metal oxide materials, cuprous oxide (Cu<sub>2</sub>O) is regarded as a promising material because of its suitable band gap and high absorption coefficient in the visible-light region. In addition with good optical and electrical properties the material has many advantages such as availability and abundance of the starting materials, non-toxic nature and low production cost [3]. Thus it is promising in various applications, including such as gas sensing [4], solar cell application [5], photocatalysis [6], thin film homo-junction solar cells [7], and photoelectrodes for solar water splitting [8,9] and was used as a working electrode in the application of photoelectrochemical solar cell (PESC) [10].

Various synthesis methods are usually used to prepare Cu<sub>2</sub>O thin films, such as sol gel [10], pulsed laser deposition [11], chemical vapor deposition [12], chemical bath deposition [13–15], solvothermal synthesis [16], silar deposition [5,17–19], electron beam evaporation [3] and electrodeposition [4,7–9,20–37]. Besides these methods, electrodeposition provides several advantages over the other methods because of its simplicity, low equipment cost, the possibility of preparing large area

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of thin films and the control of the film thickness [33].  $\text{Cu}_2\text{O}$  films are usually electrodeposited from copper precursor solution, such as copper nitrate [31,9], copper sulfate [8,23–27,30,32,35,37] and copper acetate [4,7,21,22,25,27–29,33–36]. In order to improve the quality of the deposited films such as uniformity, adhesion and crystallinity, it is necessary to add a complexing agent into the electrolytic bath. Many researchers use various complexing agents such as polyvinylpyrrolidone [16], lactic acid [8,20,23,27,38], tartaric acid [38], ethylene diamine tetra acetic acid [20], citric acid [20,26,37], oxalic acid [38], and malic acid [38,39], trisodium citrate [3,13], sodium lactate [30], triethanolamine [3] and sodium thiosulfate [14,15]. Furthermore, sodium thiosulfate shows a promising complexing agent of the deposited  $\text{Cu}_2\text{O}$  because of its non-toxicity and low-cost compared to other complexing agents [3,8,13–16,20,23,26,27,30,38,39]. No work has been published concerning the electrodeposition of  $\text{Cu}_2\text{O}$  using sodium thiosulfate as an additive with copper acetate as precursor.

The aim of this work is devoted to the preparation of  $\text{Cu}_2\text{O}$  thin films onto ITO-coated glass substrates by electrodeposition technique in a solution containing copper acetate with sodium thiosulfate. Cyclic voltammetry and chronoamperometry were utilized to study the electrochemical behavior of electrolyte bath containing copper acetate. The effect of sodium thiosulfate on the electrochemical deposition, structure and morphology of  $\text{Cu}_2\text{O}$  was investigated. Deposited films were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), optical, photoelectrochemical (PEC) and electrical measurements.

## 2. Experimental Details

### 2.1. Reagents

All chemical reagents used in the present work were of analytical grade. Copper acetate monohydrate ( $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$ , 98%, Sigma Aldrich) was used as copper sources. Sodium acetate trihydrate ( $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ , 99%, Sigma Aldrich) and sodium sulfate ( $\text{Na}_2\text{SO}_4$ , 99%, Sigma Aldrich) were used as a supporting electrolyte. However, sodium thiosulfate pentahydrate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , 99.5%, Sigma Aldrich) was used as complexing agent. All aqueous solutions were prepared with distilled water.

### 2.2. Preparation and characterization techniques of $\text{Cu}_2\text{O}$ thin films

Electrodeposition of  $\text{Cu}_2\text{O}$  thin films was carried out using a three electrode electrochemical cell with a platinum (Pt) wire as a counter electrode, indium tin oxide (ITO)-coated glass ( $8\text{--}10 \Omega \cdot \text{square}^{-1}$ , Sigma Aldrich) substrate was used as working electrode. A saturated calomel electrode (SCE) was used in all experiments as a reference electrode. Before the deposition, the substrates were cleaned ultrasonically in acetone and ethanol and then rinsed in distilled water for 7 min [37,40]. Cuprous oxide films were electrodeposited in an aqueous solution of  $0.01 \text{ mol} \cdot \text{L}^{-1} \text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$ ,  $0.1 \text{ mol} \cdot \text{L}^{-1} \text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$  and  $1.2 \text{ mmol} \cdot \text{L}^{-1} \text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  at  $60^\circ\text{C}$ . The pH of solutions was adjusted to 6.2 by  $\text{CH}_3\text{COOH}$  additions. Sodium thiosulfate is used to stabilize  $\text{Cu}^{2+}$  ions in the solution [17–19].

Cyclic voltammetry and chronoamperometry studies were carried out using Princeton Applied Research Model 273 A Potentiostat/Galvanostat, coupled to a personal computer with Power Suite software for data acquisition and potential control. Cuprous oxide films were electrodeposited at  $-0.58 \text{ V}$  for 30 min. Following the deposition, electrodeposited  $\text{Cu}_2\text{O}$  films were dried in air at  $100^\circ\text{C}$ .

The crystalline phase of  $\text{Cu}_2\text{O}$  films was investigated by X-ray diffraction using a Bruker Discover D8 Diffractometer with  $\text{CuK}_\alpha$  radiation ( $\lambda = 0.15406 \text{ nm}$ ). FTIR spectra were recorded on a Shimadzu FTIR-8000 series spectrophotometer. Scanning electron microscopy imaging was performed using a VEGA3 TESCAN scanning electron microscope operating at  $20 \text{ kV}$  accelerating voltage. Optical transmittance of thin

films was measured by a Perkin Elmer Lambda 950 UV–vis–NIR spectrometer. Photoelectrochemical measurements were carried out by cyclic voltammetry technique in a three electrode electrochemical cell using deposited  $\text{Cu}_2\text{O}$  films as a working electrode, platinum wire as a counter electrode and a saturated calomel electrode (SCE) as a reference electrode from an aqueous solution containing  $0.1 \text{ mol} \cdot \text{L}^{-1}$  sodium sulfate ( $\text{Na}_2\text{SO}_4$ ). A tungsten halogen lamp ( $100 \text{ W}$ ) was used to illuminate an active area of  $1 \text{ cm}^2$  of  $\text{Cu}_2\text{O}$  electrode. Electrical properties of deposited  $\text{Cu}_2\text{O}$  films were determined by a HMS 3000 Hall measurement system at room temperature. Ag-paste was used at the corners of films to make four good contacts with probes. Thickness of the films was measured using a Dektak stylus profilometer.

## 3. Results and Discussion

### 3.1. Electrochemical studies

#### 3.1.1. Cyclic voltammetry

We made a comparison of cyclic voltammograms obtained onto ITO substrate of the solution containing  $0.01 \text{ mol} \cdot \text{L}^{-1}$  copper acetate and  $0.1 \text{ mol} \cdot \text{L}^{-1}$  sodium acetate without (Fig. 1(a)) and with  $1.2 \text{ mmol} \cdot \text{L}^{-1}$  sodium thiosulfate (Fig. 1(b)). The potential sweep was ranged from  $0.3$  to  $-1.7 \text{ V}$  with a scan rate of  $50 \text{ mV} \cdot \text{s}^{-1}$ . From Fig. 1(a), we recorded two cathodic peaks.

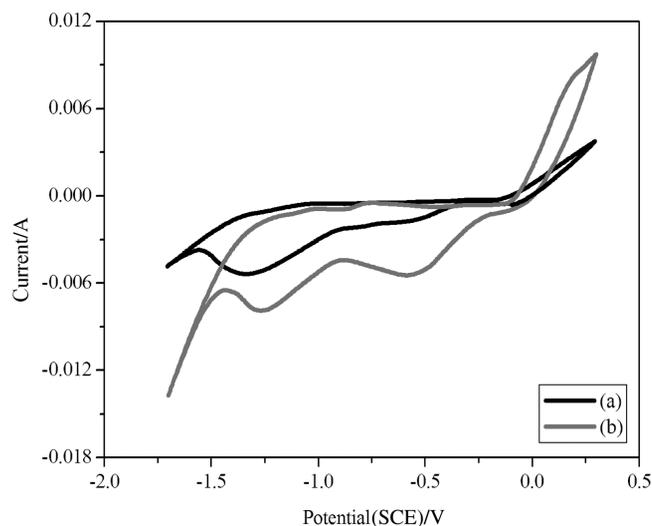


Fig. 1. Cyclic voltammograms of the solution containing  $0.01 \text{ mol} \cdot \text{L}^{-1}$  copper acetate and  $0.1 \text{ mol} \cdot \text{L}^{-1}$  sodium acetate at  $\text{pH} = 6.2$  and  $T = 60^\circ\text{C}$ , without (a) and with  $1.2 \text{ mmol} \cdot \text{L}^{-1}$  sodium thiosulfate (b).

The first cathodic peak at  $-0.56 \text{ V}$ , which attributed to the reduction of  $\text{Cu}^{2+}$  to  $\text{Cu}^+$  where water converted to hydroxide ions molecule. The hydroxide ions react with  $\text{Cu}^+$  in the solution to form  $\text{Cu}_2\text{O}$  on the substrate according to the following reaction [26,27,41,42]:



The second cathodic peak is observed at  $-1.33 \text{ V}$  which can be mainly ascribed to the deposition of metallic copper with release of Hydrogen (Eqs. (3) and (4)).



Similar cathodic peaks are reported in the literature [26,27,33,34,36, 41–44], but the present cathodic peaks are shifted compared with literature.

During reverse scan, an anodic peak is observed at 0.29 V corresponding to the oxidation of metallic copper [26,41], indicating the only formation of  $\text{Cu}_2\text{O}$  on the ITO substrate which is confirmed below by XRD analysis. From Fig. 1(b), we can observe that in the presence of sodium thiosulfate, the cathodic peak currents of the formation of  $\text{Cu}_2\text{O}$  and Cu are much higher which indicates an increase in the deposition rate of  $\text{Cu}_2\text{O}$  and Cu thin films, whereas the oxidation peak current of metallic copper is increased compared to that without sodium thiosulfate (Table 1). This difference can be attributed to a complexation effect of the  $\text{Cu}^{2+}$  ions by the sodium thiosulfate [14,15,17–19], leading to acceleration of the electrochemical reaction kinetics for the formation of  $\text{Cu}_2\text{O}$  films. The cathodic peak current of the formation of  $\text{Cu}_2\text{O}$  with sodium thiosulfate is about  $-5.4$  mA. This value is higher than that of other additives [23,26,32,36].

To study the effect of the scan rate on the reduction of copper Cu (II) ions, we performed a study by cyclic voltammograms at different scan rates ranging from 30 to  $100 \text{ mV}\cdot\text{s}^{-1}$  which are shown in Fig. 2. From this figure, it was noted that the current of anodic and cathodic peaks increases with the increase of scan rates and the cathodic peak potentials have shifted towards negative values. This indicates the presence of a chemically irreversible electrochemical reaction.

Also, the cathodic peak current for the formation of  $\text{Cu}_2\text{O}$  ( $I_{pc}$ ) varied linearly with the square root of scan rate (Fig. 3), suggesting that the electrochemical reaction is diffusion controlled. According to Bard and Faulkner [45], the following equation (Eq. (5)) gives the relationship between the peak potential, the half peak potential and the electron-transfer coefficient for an irreversible electrochemical reaction:

$$|E_{pc} - E_{pc/2}| = 1.857 RT / \alpha' F \quad (5)$$

where  $E_{pc}$  is the cathodic peak potential (V),  $E_{pc/2}$  is the half cathodic peak potential (V),  $\alpha'$  is the electron-transfer coefficient,  $R$  is the gas constant ( $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ),  $T$  is the absolute temperature (K) and  $F$  is the Faraday constant ( $\text{C}\cdot\text{mol}^{-1}$ ). From Fig. 2, we can obtain the half cathodic peak potential ( $E_{pc/2}$ ), the cathodic peak potential ( $E_{pc}$ ), and  $|E_{pc} - E_{pc/2}| = 0.24$  V.  $\alpha'$  can be calculated from Eq. (5) which is estimated to be 0.22.

The diffusion coefficient can be calculated using the Randles–Sevcik relation (Eq. (6)) [46]:

$$I_{pc} = (2.99 \times 10^5) n^{3/2} \alpha'^{1/2} A' CD^{1/2} V^{1/2} (298.15/T)^{1/2} \quad (6)$$

where  $I_{pc}$  is the cathodic peak current (A),  $n$  is the number of electrons exchanged during the redox process,  $A'$  ( $\text{cm}^2$ ) is the active area of the working electrode,  $C$  is the bulk concentration of the electroactive species ( $\text{mol}\cdot\text{cm}^{-3}$ ) (the concentration of the species),  $D'$  is the diffusion coefficient ( $\text{cm}^2\cdot\text{s}^{-1}$ ) and  $V$  is the voltage scan rate ( $\text{V}\cdot\text{s}^{-1}$ ). The diffusion coefficient was calculated to be  $3.61 \times 10^{-4} \text{ cm}^2\cdot\text{s}^{-1}$  at 333 K.

### 3.1.2. Chronoamperometry

Fig. 4 shows the chronoamperometry curve for the deposition of  $\text{Cu}_2\text{O}$  films onto ITO substrate with sodium thiosulfate at  $T = 60$  °C and  $E = -0.58$  V. The current starts with high value, which is assigned to a rapid nucleation growth. The decrease of cathodic current with the

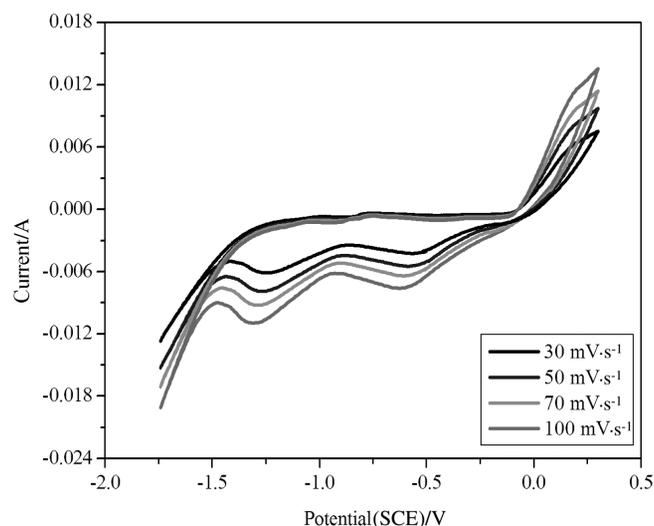


Fig. 2. Cyclic voltammograms of the solution containing  $0.01 \text{ mol}\cdot\text{L}^{-1}$  copper acetate and  $0.1 \text{ mol}\cdot\text{L}^{-1}$  sodium acetate at  $\text{pH} = 6.2$  and  $T = 60$  °C with  $1.2 \text{ mM}$  sodium thiosulfate at various scan rates.

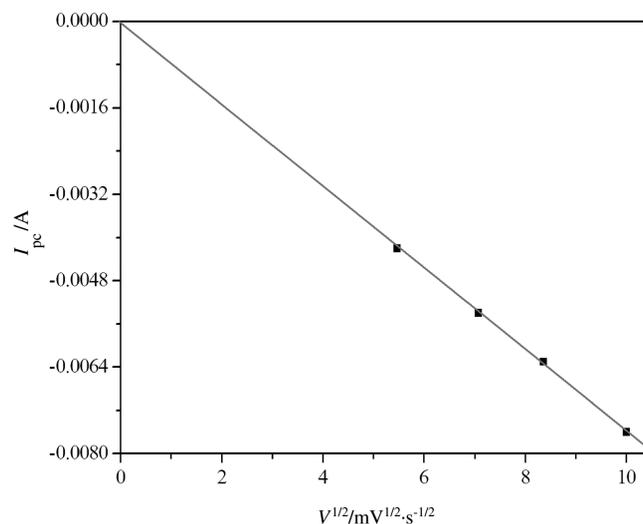


Fig. 3. Plot of  $I_{pc}$  versus  $V^{1/2}$  for the formation of  $\text{Cu}_2\text{O}$  from cyclic voltammograms of Fig. 2.

increase of time is due to the depletion of the metal-ion concentrations close to the electrode surface. The current stabilized at even longer time (1800 s). This confirms that the limited value of the stationary current is related to the formation of cuprous oxide on the surface. A similar behavior was observed for different copper salt solutions with other complexing agents [26].

## 3.2. Characterization of $\text{Cu}_2\text{O}$ thin films

### 3.2.1. XRD analysis

The thickness of the deposited films was measured to be 250 nm. Fig. 5 shows the XRD patterns of  $\text{Cu}_2\text{O}$  films deposited onto ITO

Table 1

Electrochemical parameters obtained from cyclic voltammograms

Samples	First cathodic peak potential/V	First cathodic peak current/A	Second cathodic peak potential/V	Second cathodic peak current/A	Oxidation peak potential/V	Oxidation peak current/A
Without $\text{Na}_2\text{S}_2\text{O}_3$	-0.56	-0.0017	-1.33	-0.0052	+0.29	0.0037
With $\text{Na}_2\text{S}_2\text{O}_3$	-0.58	-0.0054	-1.26	-0.0077	+0.29	0.0097

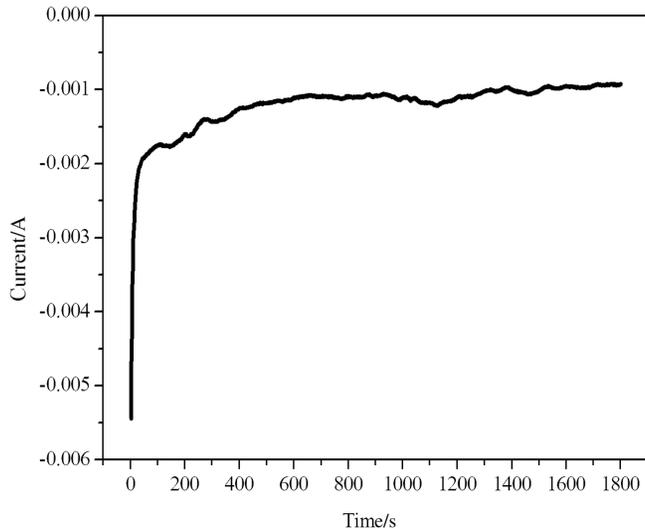


Fig. 4. Chronoamperometry curve for the deposition of Cu<sub>2</sub>O films.

substrates without (Fig. 5(a)) and with sodium thiosulfate (Fig. 5(b)). From this figure, all the diffraction peaks of Cu<sub>2</sub>O thin films correspond to the peaks of cubic phase of standard Cu<sub>2</sub>O (JCPDS 05-0667) [34]. X-ray diffraction patterns show that the intensity of the (200) diffraction peak is higher when compared with the other peaks, indicating preferential orientation along the *c*-axis. It is seen that the film deposited with sodium thiosulfate shows a new (111) diffraction peak of Cu<sub>2</sub>O phase and the intensity of the diffraction peaks is significantly higher than that of the films prepared without sodium thiosulfate. It indicates that the good crystallinity of deposited Cu<sub>2</sub>O films is improved with the addition of sodium thiosulfate.

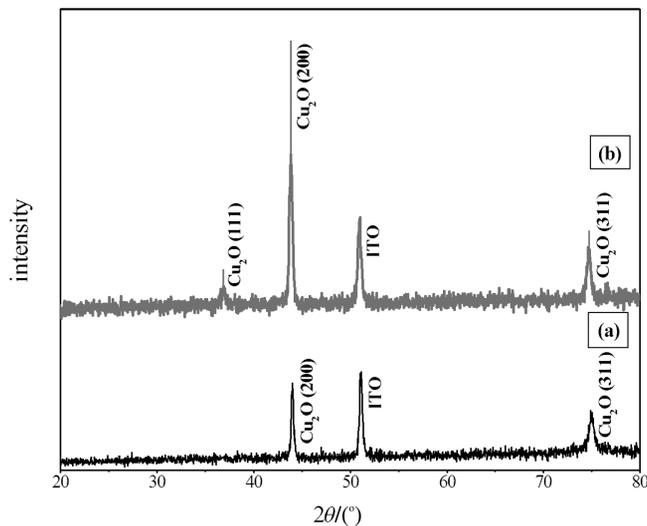


Fig. 5. X-ray diffraction of Cu<sub>2</sub>O films deposited onto ITO substrates, without (a) and with sodium thiosulfate (b).

The calculated value of the lattice constant parameter for the Cu<sub>2</sub>O films ( $a = b = c = 0.425$  nm) was slightly different than that of standard Cu<sub>2</sub>O (JCPDS 05-0667,  $a = b = c = 0.4269$  nm) [47,49].

The crystallite size ( $D$ ) of Cu<sub>2</sub>O thin films was calculated from the major diffraction peaks of the base of (200) using Scherrer's formula (Eq. (7)) [5,13,26]:

$$D = 0.89 \lambda / \beta \cos \theta \quad (7)$$

where  $\lambda$  is the wavelength of the incident beam (0.15406 nm),  $\beta$  is the full width at half maximum and  $\theta$  is Bragg's angle in rad. The average crystallite size of deposited Cu<sub>2</sub>O with sodium thiosulfate is found to be 23.22 nm. This value is greater than that of Cu<sub>2</sub>O films without sodium thiosulfate (22.45 nm).

The comparison of the observed  $d$  values of Cu<sub>2</sub>O films with JCPDS data (05-0667) is shown in Table 2. The value of  $d$ -spacing for Cu<sub>2</sub>O films obtained was slightly different than that of the  $d$ -spacing for standard Cu<sub>2</sub>O [JCPDS 05-0667], suggesting that all the Cu<sub>2</sub>O films exhibited a tensile strain and dislocation density, which is reported by others [5,11].

Table 2  
Comparison of the observed  $d$  values of Cu<sub>2</sub>O films with JCPDS data (05-0667)

$d_{\text{exp}}$ (hkl)/nm	$d_{\text{JCPDS}}$ (hkl)/nm	hkl	Phase
0.24410	0.24650	111	Cubic
0.21251	0.21350	200	Cubic
0.12703	0.12870	311	Cubic

The dislocation density ( $\delta$ ), defined as the length of dislocation lines per unit volume, was evaluated from the formula (Eq. (8)) [5]:

$$\delta = 1/D^2 \quad (8)$$

Strain ( $\epsilon$ ) of the films was calculated by the formula (Eq. (9)) [5]:

$$\epsilon = \beta \cos \theta / 4 \quad (9)$$

The evaluated structural parameters of deposited Cu<sub>2</sub>O with sodium thiosulfate are regrouped in Table 3, which represents the values of full width at half maximum, the crystallite size, the dislocation density ( $\delta$ ) and the strain ( $\epsilon$ ) of the Cu<sub>2</sub>O thin films from the (200) direction.

Table 3  
Structural parameters of Cu<sub>2</sub>O thin films

Plane	Interplanar spacing $d$ /nm	FWHM ( $\beta$ ) $\times 10^{-3}$ /rad	Grain size $D$ /nm	$\delta \times 10^{-15}$ /lines $\cdot \text{m}^{-2}$	$\epsilon \times 10^{-3}$ /lines $^{-2} \cdot \text{m}^{-4}$
(200)	0.21251	5.90	23.22	1.85	1.47

### 3.2.2. FT-IR analysis

The Cu<sub>2</sub>O films deposited with sodium thiosulfate were also examined by FTIR spectroscopy which spectrum is shown in Fig. 6. From this spectrum, the absorption band at  $634 \text{ cm}^{-1}$  is attributed to the stretching vibration of Cu—O in Cu<sub>2</sub>O [47,48]. The observed absorption bands at  $1414.18 \text{ cm}^{-1}$  and  $1566.27 \text{ cm}^{-1}$  are due to the presence of the carboxylate group (COO<sup>-</sup>) and correspond to the symmetric stretching and asymmetric stretching vibrations of the C—O band in the acetate group, respectively [47–50]. We also note the presence of bands at  $3168.265$  to  $3442.608 \text{ cm}^{-1}$  assigned to the stretching vibration of —OH groups of adsorbed water molecules [48,50,51].

### 3.2.3. SEM analysis

The surface morphologies of Cu<sub>2</sub>O films deposited onto ITO substrates obtained without and with sodium thiosulfate are shown in Fig. 7(a) and (b) respectively. The surface morphologies of deposited Cu<sub>2</sub>O films prepared without sodium thiosulfate (Fig. 7(a)) are covered with a single type of small grains. The grains are well defined, spherical shape and an almost similar size (400 nm). In the presence of sodium thiosulfate (Fig. 7(b)), morphology does not change but there is a better compactness with increasing size (650 nm) of the spherical grains. Such

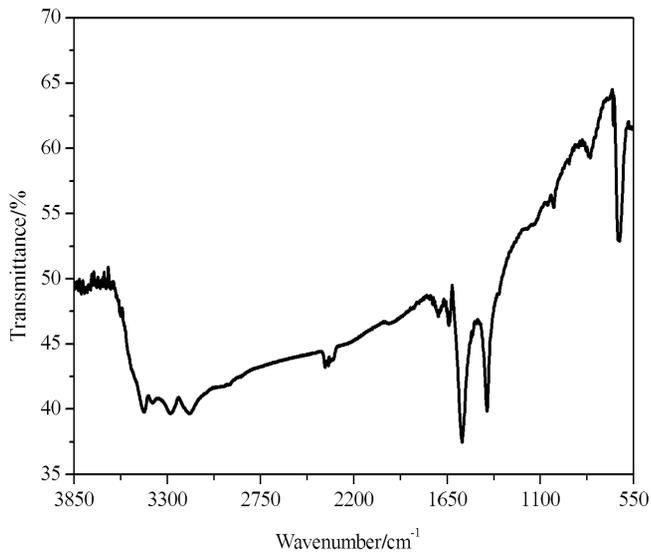


Fig. 6. FTIR spectrum of  $\text{Cu}_2\text{O}$  films.

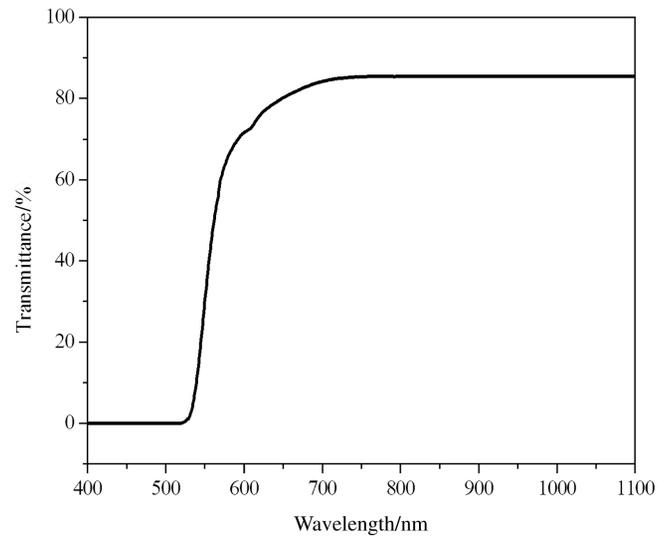


Fig. 8. Transmittance spectrum of  $\text{Cu}_2\text{O}$  films.

type of spherical shape is also observed when  $\text{Cu}_2\text{O}$  thin films deposited onto various substrates by different copper salt solutions [14,32].

### 3.2.4. Optical properties

The optical transmittance spectrum of  $\text{Cu}_2\text{O}$  films deposited onto ITO substrates with sodium thiosulfate from a wavelength range of 400–1100 nm taken at room temperature is shown in Fig. 8. It was shown that the films present a high optical transmission (>80%) in the visible wavelength range, which confirms the good optical quality of the electrodeposited  $\text{Cu}_2\text{O}$  thin films. The absorption coefficient ( $\alpha$ ) was determined in the order of  $>10^4 \text{ cm}^{-1}$ .

The plot of  $(\alpha h\nu)^2$  versus photon energy ( $h\nu$ ) of deposited films was presented in Fig. 9. It has been observed that the plots of  $(\alpha h\nu)^2$  versus ( $h\nu$ ) are linear over a wide range of photon energies indicating the direct type of transitions. The band gap of the films was determined from Tauc's formula which is as follows (Eq. (10)) [22,27,42]:

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (10)$$

where  $\alpha$  is the absorption coefficient,  $h$  is Planck's constant,  $\nu$  is the photon energy,  $A$  is a constant and  $E_g$  is the direct transition band gap. The

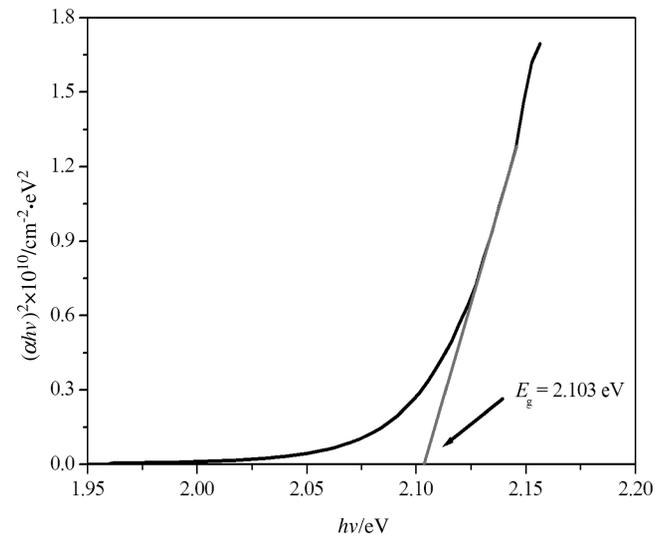


Fig. 9. Plot of  $(\alpha h\nu)^2$  versus  $h\nu$  of  $\text{Cu}_2\text{O}$  films.

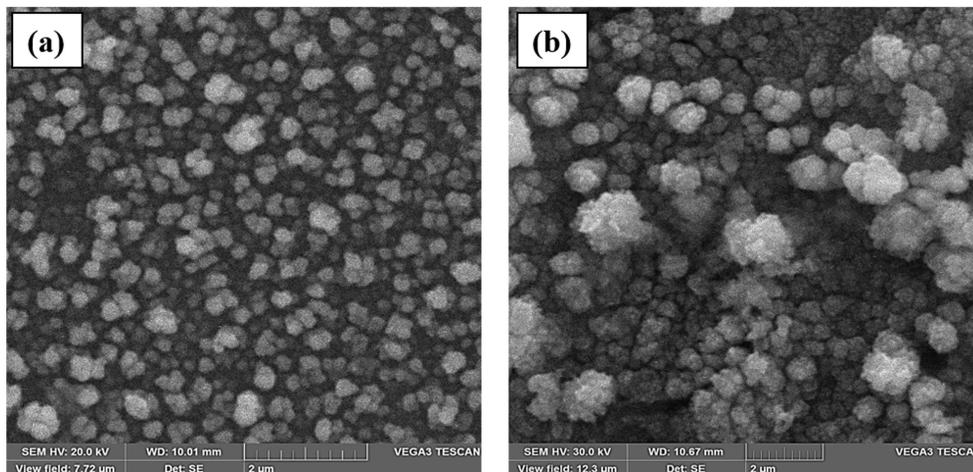


Fig. 7. SEM images of  $\text{Cu}_2\text{O}$  films deposited onto ITO substrates, without sodium thiosulfate (a) and with sodium thiosulfate (b).

optical band gap value was determined by extrapolating the linear portion of the plot of  $(\alpha h\nu)^2$  versus photon energy ( $h\nu$ ), which is illustrated in Fig. 9. The band gap of  $\text{Cu}_2\text{O}$  thin films was estimated to be 2.103 eV, which is in good agreement with the values reported for  $\text{Cu}_2\text{O}$  films by others [28,34]. The obtained energy gap results make  $\text{Cu}_2\text{O}$  film as a promising semiconductor material for fabrication of photovoltaic solar cells.

### 3.2.5. Photoelectrochemical measurements

Fig. 10 shows the photoelectrochemical (PEC) response of cuprous oxide ( $\text{Cu}_2\text{O}$ ) deposited onto ITO substrates with sodium thiosulfate at  $-0.58$  V for the solution containing  $0.1 \text{ mol}\cdot\text{L}^{-1}$  sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), in the dark (a) and under illumination (b). In the dark, there is a negligible anodic photocurrent. However, under illumination of the surface of deposited cuprous oxide, we observe an important anodic photocurrent compared with in the dark indicating the carriers are generated at the  $\text{Cu}_2\text{O}$  film electrode under irradiation [21,52,53]. These observations suggested that the photogenerated charge carrier holes ( $\text{h}^+$ ) can promote oxidation reaction at the semiconductor/electrolyte solution interface. The anodic photocurrent generation represents the typical behavior of the n-type semiconductor of the  $\text{Cu}_2\text{O}$  thin films [21,25,29]. This n-type semiconductor was observed when  $\text{Cu}_2\text{O}$  thin films electrodeposited onto various substrates [4,27–29,33,34,36].

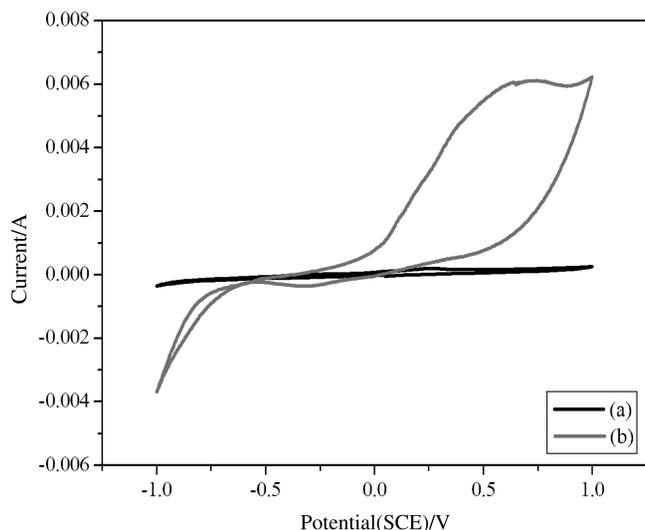


Fig. 10. Photoelectrochemical response of  $\text{Cu}_2\text{O}$  films, in the dark (a) and under illumination (b).

### 3.2.6. Electrical properties

The Hall Effect measurement results showed that the  $\text{Cu}_2\text{O}$  films deposited with sodium thiosulfate have n-type conductivity with a carrier concentration of  $-4.94 \times 10^{15} \text{ cm}^{-3}$ , mobility of  $20.61 \text{ cm}^2\cdot\text{V}^{-1}\text{s}^{-1}$  and low electrical resistivity of  $61.30 \Omega\cdot\text{cm}^{-1}$ . These values are in agreement with the results reported by others [24,35].

## 4. Conclusions

Cuprous oxide ( $\text{Cu}_2\text{O}$ ) thin films have been successfully electrodeposited onto ITO-coated glass substrates from aqueous copper acetate solutions with addition of sodium thiosulfate at  $60^\circ\text{C}$ . We found that the addition of sodium thiosulfate has a strong effect on the electrochemical reaction kinetics, crystallinity and morphology of  $\text{Cu}_2\text{O}$  thin films.  $\text{Cu}_2\text{O}$  thin films were deposited at  $-0.58$  V for 30 min with a

film thickness of about 250 nm. X-ray diffraction analysis revealed that the synthesized  $\text{Cu}_2\text{O}$  thin films have a cubic phase. The crystallite size was estimated to be 23.22 nm. FTIR results confirmed the presence of  $\text{Cu}_2\text{O}$  films at peak  $634 \text{ cm}^{-1}$ . SEM images of  $\text{Cu}_2\text{O}$  films showed a better compactness and consist of spherical shape. Photoelectrochemical measurements of  $\text{Cu}_2\text{O}$  thin films showed that this film behaves as a semiconductor of n-type and presents high photo anodic-generated currents. These films exhibited a high optical transmission ( $>80\%$ ) and high absorption coefficient ( $\alpha > 10^4 \text{ cm}^{-1}$ ) in the visible-light region. The optical energy band gap was found to be 2.103 eV. Hall Effect measurement results confirmed that the  $\text{Cu}_2\text{O}$  thin films have n-type conductivity with a low electrical resistivity of  $61.30 \Omega\cdot\text{cm}^{-1}$ , carrier concentration of  $-4.94 \times 10^{15} \text{ cm}^{-3}$  and mobility of  $20.61 \text{ cm}^2\cdot\text{V}^{-1}\text{s}^{-1}$ . Taken into account of its non-toxicity and low-cost, sodium thiosulfate could be used as a promising complexing agent to prepare  $\text{Cu}_2\text{O}$  thin films with suitable properties for fabrication of photovoltaic solar cells.

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