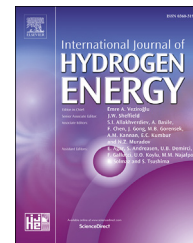




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Photoelectrochemical characteristics of CuO films with different electrodeposition time

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ABSTRACT

This paper explores the effect of electrodeposition time on microstructure, optical, and photoelectrochemical properties of CuO films. CuO films were electrochemically deposited on tin-doped indium oxide (ITO) substrates using a Cu₂O electrodeposition method followed by annealing at 550 °C for 2 h. The electrochemical deposition was carried out at different times (300, 600, 1200, and 1800 s) utilizing a copper sulfate pentahydrate and lactic acid solution. X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM) were used to perform phase and microstructure analysis. Photoluminescence (PL) studies confirmed an increase in emission intensities with increasing deposition time. In addition, a significant change was observed in photoelectrochemical properties of the film by varying the deposition time. The film deposited for 600 s showed a high photocurrent density of -0.55 mA cm^{-2} at -0.5 V . Moreover, a lowest resistance from electrochemical impedance spectroscopy (EIS) was recorded for the films electrochemically deposited for 600 s.

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Introduction

Photoelectrochemical water splitting is an effective way to produce and store hydrogen as a clean energy source and to overcome the energy crisis and environmental hazards such as global warming and acid rain those are associated with the hydrogen production from the sources such as coal and natural gas [1,2]. For this purpose a range of photoelectrode materials has been reported, i.e., Cu₂O, CuO, p-doped Si, CuRhO₂, Cu₂ZnSnS₄, Fe₃O₄ and CuBi₂O₄ [3,4]. Another technique is electrolysis of alkaline water, which has been investigated in depth for the hydrogen evaluation reactions (HER) [5,6]. However, adapting the laboratory practices into industry for the commercial production of hydrogen is still hindered by

several physical and chemical barriers, such as stability and economical feasibility. To address these issues, attempts have been reported to increase the stability of photocathodes in photocatalytic water splitting reactions and utilization of earth-abundant materials (copper based oxides, Fe₂O₃, ZnO, TiO₂, BiVO₄) instead of using expensive and heavy metals such as platinum, iridium, and ruthenium [7,8]. Among these, owing to its narrow band gap (1.21–2.1 eV), CuO is considered as one of the most promising semiconductor material for applications in catalysis, batteries, gas sensing, and photoelectrochemical cells (PECs) [9,10]. The CuO films and powders exhibiting different shapes and sizes have been processed by various synthetic procedures [11–13], such as thermal decomposition of Cu foil, hydrothermal method, sol-gel method, solvothermal method, self-catalytic growth, and

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electrodeposition [14–18], and reference therein. Chiang et al. [19] synthesized CuO nanoparticles utilizing flame spray pyrolysis. The processing parameters such as precursor concentration, gas flow, and temperature were studied in detail. The variation in precursor concentration from 0.5 to 35% w/w resulted in a corresponding increase in particles diameter from 7 ± 2 to 20 ± 11 nm. In addition, the particles grown in the low gas flow showed a significant increase in diameter, which was associated with more retention time in high-temperature zone. Shaislamov et al. [20] developed CuO/ZnO photoelectrode utilizing a two-step synthesis route. The films morphology and PEC performance were studied in depth. In the initial step, CuO nanorods were developed by thermal oxidation of the already electrodeposited CuO films. Next, ZnO nanobranches were grown on the surface of the initially deposited CuO films using a hydrothermal synthesis route. The durability test showed an increase in stability of the electrode up to 90%. Similar studies suggest that microstructure plays an important role in materials' performance. For example, a high hydrogen storage capacity of 220 and 180 mAh/g has been reported for Cu(OH)₂ and CuO nanoribbons [21]. Among these, electrodeposition has been considered as the best technique to develop homogeneous thin films with precise control over film thickness and microstructure. Further, the method is economical due to the use of inexpensive precursor sources and simple experimental setup [14,22,23]. The microstructure of film, grain morphology, and surface topography plays an important role in the photoinduced processes [22,24]. The surface features affect the interaction of light with film surface and consequently, the electron transport mechanism; therefore, it is important to optimize the microstructure-property relationship in these optoelectronic devices. The properties of CuO have been extensively reported; however, no attempt has been reported to investigate the effect of electrodeposition time on the CuO film microstructure and the PEC performance to our best knowledge.

In this paper, we have studied the effect of electrodeposition time on surface morphology of ITO/CuO films and the corresponding effect on the photoelectrochemical properties. For efficient absorption of light, an optimum value of film thickness is required for better PEC performance. The XRD and FESEM were used for the phase and microstructure investigation, respectively. Furthermore, the optical properties and photocatalytic response were studied to investigate the CuO films' electrodeposition time on the photocurrent in water splitting reactions.

Experimental procedure

Copper sulfate pentahydrate (CuSO₄·5H₂O; Aldrich), lactic acid (C₃H₆O₃; Aldrich) and deionized water were used as the starting materials and solvent. The CuO films were deposited on ITO substrates by using a galvanostatic deposition method. Prior to deposition, ITO substrates were washed with a hot detergent solution, acetone, and ethanol for 10 min each. Then, the substrates were dried with a nitrogen blow. The precursor solution was prepared by using a 0.5 M CuSO₄·5H₂O and 1.3 M lactic acid. During the electrodeposition, the

temperature was kept constant at 60 °C, while the pH was maintained around 10–12 by using a 5.0 M NaOH solution. The electrodeposition was carried out for 300, 600, 1200 and 1800 s which corresponds to notation S1, S2, S3, and S4, respectively, by applying a current density of -0.3 mA cm^{-2} . A 50.0 mL of fresh precursor solution was used for each experiment. After deposition, the Cu₂O films were washed with distilled water and subsequently dried in an oven at 60 °C for 24 h. The dried Cu₂O films were annealed at 550 °C for 2 h in air in order to achieve CuO films.

Thin film deposition was carried out using Gamry Instrument (Galvanostatic-potentiostatic; Gamry Interface 1000). Thermo-FTIR spectrometer (Model: smart UR diamond attenuated total reflection (ATR)) was used to determine the phase and the nature of the atomic bond in the films. UV–visible NIR (Model: Cary 7000 Universal Measurement Spectrophotometer (UMS)) was used to study the absorption behavior of the thin films. The surface morphology was investigated by using a FESEM (Model: Zeiss/Supra 55 VP). The phase of CuO films was studied by using X-ray diffraction (XRD, Model: Rigaku Miniflex 600) with a step size of 5° min^{-1} . The PEC characteristics of films were measured by using a CHI analyzer (Model: CHI 660D electrochemical). The scan rate linear sweep voltammetry (LSV) of 5 mV s^{-1} was applied between 0 and -0.5 V range. The EIS measurements were performed in the frequency range of 10^5 Hz and 10^{-3} Hz at open circuit potential and with an amplitude of 5 mV. A 0.5 M Na₂SO₄ solution was used to study the photocatalytic activity of CuO films on water splitting. A solar simulator (Sunlite™ Solar Simulators; M-SLSS) was used to illuminate the samples. The PEC performance was measured in three electrode system using Ag/AgCl (3.0 M KCl solution) as reference electrode, a platinum sheet (2 cm²) as counter electrode and CuO film samples as the working electrode.

Results and discussions

Fig. 1(a) shows XRD profiles for the ITO/CuO films annealed in air at 550 °C for 2 h. The peak profiles were matched to the monoclinic CuO phase (JCPDS card: 048-1548), where the diffraction peaks at $2\theta = 32.48, 35.74, 38.96, 48.75, 53.02$ and 58.64 were indexed to (110), (-111), (111), (-202), (020) and (202) crystal planes, respectively [23,25]. No impurities such as Cu₂O and Cu₃O₄ were observed, which further confirmed that the Cu₂O was converted to CuO on ITO substrates. The relative intensities were observed to increase with increasing deposition time, which might be due to enhanced crystallinity related to the high deposition time [26]. Fig. 1(b) shows FT-IR spectrum of the ITO/CuO films annealed at 550 °C for 2 h. The peaks in the wave number range from 420 to 610 cm^{-1} , which can be resolved in three modes, i.e., Au and Bu modes, and other Bu modes of the CuO. The strong peaks around 597 cm^{-1} and 699 cm^{-1} are the characteristic Cu (II)–O stretching vibration peaks. The peaks around 538 cm^{-1} and 607 cm^{-1} were assigned to Cu–O stretching vibration [14,27]. Similar peaks were observed for all the samples.

Fig. 2 shows PL spectra of the ITO/CuO films annealed at 550 °C for 2 h. So far the origin of luminescence in CuO has not been fully established. The near band edge emission for the

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