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The effect of pH and temperature of electrolyte on the morphology and PEC performance of electrodeposited Cu_2O nanostructures

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Abstract

This study examines the influence of electrolyte parameters on the synthesis of Cu_2O semiconductor nanostructures. Cu_2O nanostructures were synthesized using the electrodeposition method for application in photoelectrochemical water splitting. The study focused on investigating the effects of electrolyte pH and temperature during the synthesis process. Cuprous oxide is considered a promising p-type semiconductor due to its excellent light absorption in the solar spectrum window. It is an attractive semiconductor for photoelectrochemical water splitting, given its high theoretical efficiency for this process. Various characterizations including X-ray diffraction (XRD), field emission scanning electron microscopy (SEM), and UV-Visible spectroscopy (UV-Vis) were used to analyze the structural properties of the synthesized Cu_2O. The photoelectrochemical activity of the synthesized samples was evaluated using current-voltage measurements. The results suggest that the optimal electrolyte conditions for Cu_2O synthesis were achieved at pH 13 and electrolyte temperature of 60°C.

Keywords: Cu_2O nanostructures, Photoelectrochemical, Electrolyte parameters, Morphology

1. Introduction

Metal oxide semiconductors are of significant interest due to their unique characteristics, such as abundance in nature, environmental compatibility, and cost-effectiveness. This class of semiconductors finds applications in catalysts, sensors, solar cells, diodes, and transistors [1-4]. In recent years, considerable attention has been directed toward the metal oxide semiconductor Cu_2O in solar cells and photoelectrochemical water splitting processes [5-7]. Cu_2O is a p-type semiconductor with a direct band gap of approximately 2 eV. The theoretical photocurrent calculated for Cu_2O in photo electrochemical water splitting is 14.7 mA/cm^2, corresponding to a solar energy conversion efficiency to hydrogen of about 18% [8-10]. The direct band gap of Cu_2O is particularly advantageous for solar applications because the light absorption process involves the direct transfer of an electron from the valence band to the conduction band without any change in momentum. The conduction and valence bands of Cu_2O encompass the oxidation and reduction potentials of water, satisfying the requirements of water splitting reactions. Moreover, the conduction band of copper oxide is approximately 0.7 V more negative than the reduction potential of water, providing a robust over potential for the hydrogen production reaction [11]. Several methods have been employed to synthesize Cu_2O, including electrodeposition, electrochemical anodization, and thermal oxidation of Cu layers [12-14]. Among these methods, electrodeposition has garnered more attention due to its convenience and the production of Cu_2O samples with the highest photo electrochemical efficiency [15-17].

In this study, our aim was to optimize the synthesis of Cu_2O samples using the electrodeposition method for electrochemical water splitting. Accordingly, various parameters affecting Cu_2O synthesis, such as electrolyte pH and temperature, were investigated to determine the optimal conditions.

2. Experimental

2.1. Materials

All chemicals containing $CuSO_4$, lactic acid, KOH and K_2HPO_4 were prepared from Merck and Sigma-Aldrich companies and used without further purification. All materials had purity above 99%. In all experiments, the temperature was controlled by water bath.

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2.2. synthesize Cu_2O layers on FTO using the electrodeposition method

To synthesize Cu_2O layers on FTO using the electrodeposition method, a three-electrode arrangement was employed. The FTO substrate served as the cathode or working electrode, the platinum electrode as the anode or counter electrode, and the Ag/AgCl electrode as the reference electrode.

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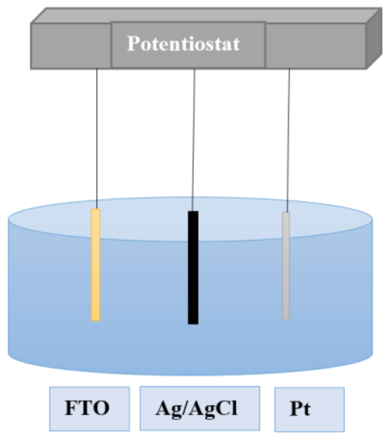

Fig. 1. Schematic diagram of electrodeposition setup of Cu_2O synthesization

A three-electrode system was utilized for the synthesis of Cu_2O samples. In this method, the electrodes are submerged in the electrolyte solution, and the entire setup is placed inside a water bath for temperature control. The application and adjustment of voltage were carried out using a potentiostat device. The electrodeposition setup is illustrated in Fig. 2.

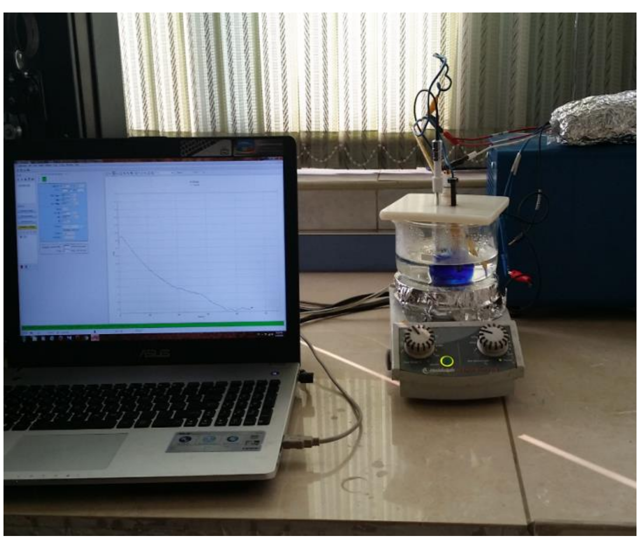

Fig. 2. Fabrication procedure of the Cu_2O nanostructure

The process of Cu_2O formation in the electrolyte solution, comprising $CuSO_4$, lactic acid, K_2HPO_4, and KOH, can be elucidated by the stabilization of Cu^{2+} ions through the formation of complexes with lactate ions ("L") in an alkaline solution. The stabilized Cu^{2+} complexes can then diffuse into the surface of a working electrode, with possible reactions for the cathodic reduction of cupric lactate solution as follows:

$$CuL_2^{2-} + OH^- \rightarrow [CuL_2(OH)]^{3-} \quad (1)$$

$$2CuL_2^{2-} + 2e^- + 2OH^- \rightarrow Cu_2O(s) + 4L^{2-} + H_2 \quad (2)$$

$$2[2CuL_2(OH)]^{3-} + 2e^- \rightarrow Cu_2O(s) + 4L^{2-} + H_2O \quad (3)$$

$$L^{2-} + H_2O \rightarrow HL^- + OH^- \quad (4)$$

In this alkaline solution, the formation of compounds $[CuL_2(OH)]^{3-}$and $[CuL_2{}^{2-}]$ is the most probable (reaction 1). The cupric lactate complexes are reduced to Cu_2O in the diffusion layer. (Reactions 2 and 3) resulting in the separation of L^{2-} ions. [18-19]. Consequently, cupric lactate complexes can be reduced to Cu_2O by a limited reduction of Cu^{2+} to Cu^+ due to the low solubility of monovalent copper in water.

2.3. Characterization

The morphology and structure of Cu_2O samples were investigated using scanning electron microscopy (SEM) and X-ray diffraction analysis (XRD, Xpert, Philips with CuKα radiation) (λ=1.54 A°). The photoelectrochemical properties of the samples were assessed in a three-electrode system using 1M Na_2SO_4 as the electrolyte with a potentiostat device (OrigaMaster). The configuration consisted of an Ag/AgCl reference electrode, a platinum wire as a counter electrode, and the electrodeposited Cu_2O sample as the working electrode. The photo response was studied under the radiation of a 300 W xenon lamp (Oriel) with an intensity of 100 mW/cm^2 (similar to sunlight under AM 1.5). A scan rate of 50 mVs^{-1} was employed for all samples to measure the current-voltage curve.

3. Results and discussion

3.1. XRD analysis

After synthetization of copper oxide samples by three-electrode deposition method, the samples were examined by scanning electron microscope and X-ray diffraction analysis to investigate the structure and morphology. The X-ray diffraction pattern of the synthesized Cu_2O sample is shown in Fig. 3. The characteristic peaks of (111), (200) and (220) at angles of 42.05, 49.05 and 72.6 clearly show the formation of Cu_2O nanostructures on the FTO substrate.

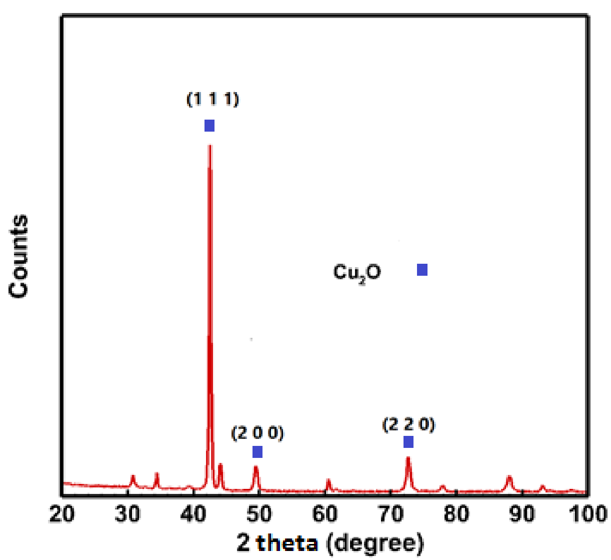

Fig. 3. XRD patterns of the electrodeposited Cu_2O

3.2. SEM study

SEM image of the Cu_2O nanostructures synthesized by electrodeposition method is shown in Fig. 4. The presence of grains with four-sided pyramid shape is clearly visible, which is in agreement with previous reports [20]. The size of the grains formed is about 200 to 600 nm.

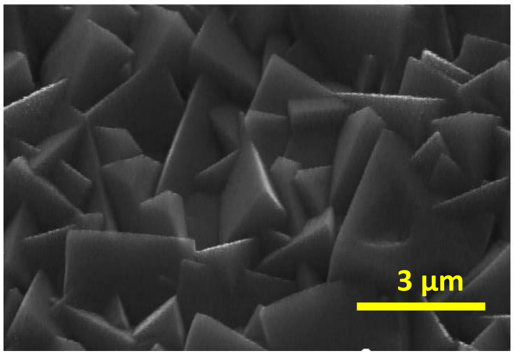

Fig.4. SEM micrographs of Cu_2O layers.

3.3. UV-Vis test

The UV-Vis absorption spectrum of the fabricated Cu_2O sample is shown in Fig. 5. The absorption spectrum shows the photoabsorption range of Cu_2O. The results of the Fig. 5 confirms the high absorption of Cu_2O produced by electrodeposition method in the visible region.

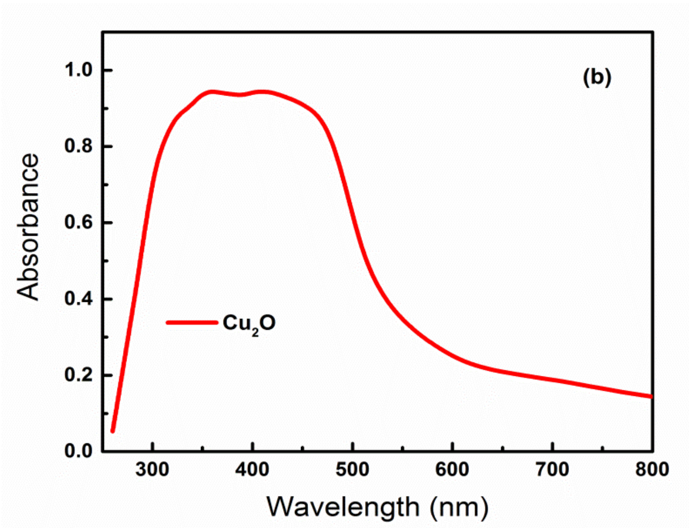

Fig.5. Optical absorption spectrum of electrodeposited Cu_2O nanostructure.

Furthermore, to optimize the efficiency of Cu_2O samples in photoelectrochemical water splitting processes, various factors influencing the synthesis of Cu_2O were investigated, leading to the determination of optimal conditions. A crucial aspect in the electrodeposition process of Cu_2O is how the pH of the electrolyte influences the orientation of the grains on the substrate. According to related literature [19], nanostructures created in an alkaline solution (pH=9) exhibited strong orientation along the (100) plane. Another study reported that Cu_2O grown at pH 12 demonstrated the highest efficiency in photoelectrochemical hydrogen production, as evidenced by the highest photocurrent density [21].

3.4. The effect of pH and FE-SEM study

The impact of electrolyte pH on the grain orientation and morphology of the Cu_2O samples, as well as its influence on the photoelectrochemical characteristics, was examined. Cu_2O nanostructures were synthesized in electrolytes with varying pH levels of 11, 12, and 13, and their morphology and photoelectrochemical characteristics were investigated. The FE-SEM images of the synthesized Cu_2O samples at different electrolyte pH levels are presented in Fig. 6. The FE-SEM images reveal no evidence of the formation of the four-sided pyramid shape in Cu_2O synthesized at pH 11 and 12, with the best structure observed in the sample synthesized using an electrolyte with a pH of 13.

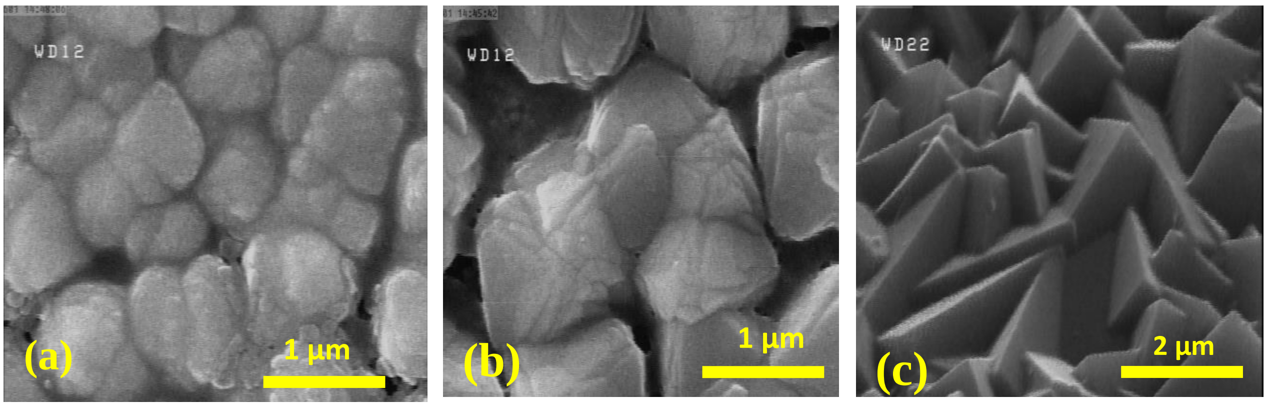

Fig. 6. FE-SEM micrographs of Cu_2O layers electerodeposited at pH electrolyte including (a) 11 (b) 12 (c) 13.

According to the photocurrent results obtained from Fig. 7, the optimal electrolyte pH value for electrodeposited Cu_2O in photoelectrochemical water splitting processes is 13. These samples exhibit the highest photocurrent density compared to other structures.

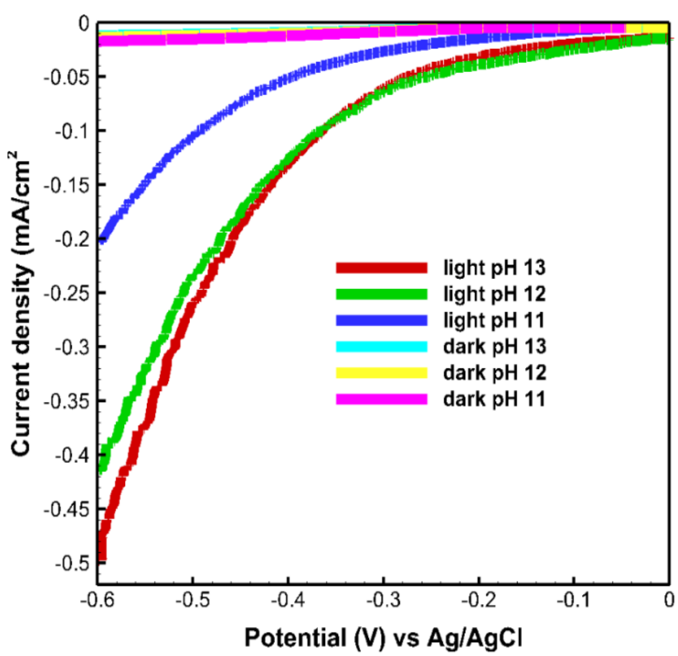

Fig. 7. Current density versus voltage for different Cu_2O layers deposited at different pH of electrolyte

The temperature of the electrolyte affects the shape of the nanostructures and their crystalline properties. Various research reports indicate the suitable temperature range for Cu_2O electrodeposition is between 20°C and 60°C. Experimental findings demonstrate that optimal nanostructures for the photocatalytic application of Cu_2O in water splitting processes can be achieved at the temperature of 60°C.

To examine the impact of electrolyte temperature on the structure and photoelectrochemical characteristics of the electrodeposited Cu_2O samples, this parameter was varied to 20°C, 40°C, and 60°C using a water bath.

Figure 8 presents the top view of the FE-SEM images of the synthesized Cu_2O samples at different electrolyte temperatures of 20°C, 40°C, and 60°C. Fig. 8(a) and 8(b) display the FE-SEM images of Cu_2O nanostructures synthesized at 20°C and 40°C, showing a substantial reduction in the size of granular structures and the absence of grains with four-sided pyramid shapes. Conversely, Figure 8(d) clearly depicts Cu_2O grains with four-sided pyramid shapes observed in the sample synthesized at 60 °C.

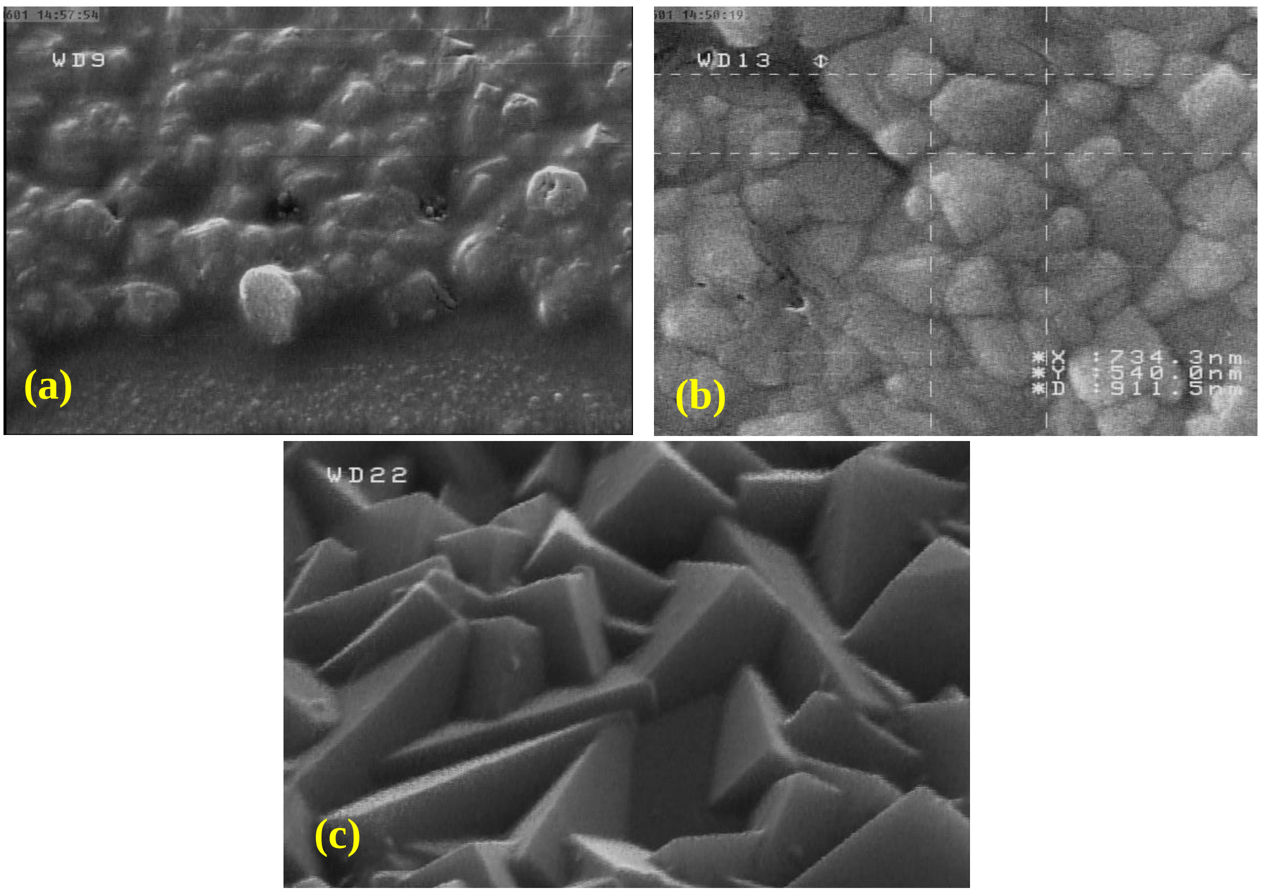

Fig. 8. SEM micrographs of Cu_2O layers deposited at different electrolyte temperatures (a) 20 (b) 40 and (c) 60 ^{0}C.

The results of the photoelectrochemical measurements of the synthesized samples at different temperature conditions are presented in Fig. 9, indicating that the Cu_2O nanostructures synthesized at 60°C exhibit the highest photocurrent density.

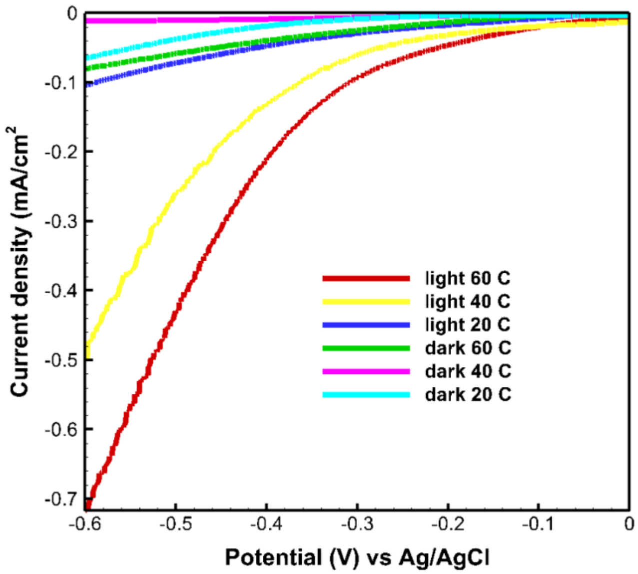

Fig. 9. photocurrent density versus voltage for different Cu_2O layers deposited at different electrolyte temperatures.

4. Conclusion

This study investigated the effect of different electrolyte parameters on the electrodeposition process of Cu_2O nanostructures for use in photoelectrochemical water splitting and obtained the optimal conditions of these parameters. These parameters include electrolyte pH and electrolyte temperature. Through morphology investigation and photoelectrochemical measurements, suitable values of these parameters were determined. Ultimately, the results indicate that the optimum electrolyte conditions for synthesizing Cu_2O are achieved at a pH of 13 and an electrolyte temperature of 60°C.

Conflicts of Interest

The author declares no conflict of interest.

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