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Cu_2O film: production and characterization

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Abstract: The increasing demand for renewable energy solutions has driven research into cost-effective materials for photoelectrochemical hydrogen production. This study presents the synthesis and characterization of Cu_2O thin films obtained via electrodeposition, aiming to optimize their structural, optical, and electronic properties for photocatalytic applications. UV-Vis spectroscopy revealed a direct bandgap of 2.0 eV, confirming the material's suitability for visible light absorption. Grazing Incidence X-ray Diffraction (GIXRD) analysis demonstrated that the films predominantly belong to the cubic crystal system, with a preferential (111) crystalline orientation. On the other hand, X-ray Photoelectron Spectroscopy (XPS), a surface-sensitive technique, indicated the coexistence of Cu_2O and a minor proportion of CuO, likely resulting from surface oxidation. While bulk characterization confirmed that the core material remained Cu_2O, the presence of hydroxides and carbonates in the surface suggests that optimizing deposition conditions or post-treatment processes could enhance stability and phase purity. These findings underscore the potential of Cu_2O films as efficient photocathodes for hydrogen production. Future studies should focus on minimizing surface oxidation and integrating Cu_2O-based electrodes into complete photoelectrochemical cells for sustainable energy applications.

Keywords: Cu_2O Film, Electrodeposition, Semiconductor Film Characterization.

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Filme de Cu_2O: Produção e caracterização

Resumo: A crescente demanda por soluções energéticas renováveis tem impulsionado pesquisas sobre materiais de baixo custo para a produção fotoeletroquímica de hidrogênio. Este estudo apresenta a síntese e caracterização de filmes finos de Cu_2O obtidos via eletrodeposição, visando otimizar suas propriedades estruturais, ópticas e eletrônicas para aplicações fotocatalíticas. A espectroscopia UV-Vis demonstrou que o filme tem um bandgap direto de 2,0 eV, confirmando a adequação do material para a absorção de luz visível. A análise por Difração de Raios X com Incidência Rasante (GIXRD) demonstrou que os filmes pertencem predominantemente ao sistema cristalino cúbico, com uma orientação cristalina preferencial (111). Por outro lado, a Espectroscopia de Fotoelétrons por Raios X (XPS), uma técnica sensível para análise de superfície, indicou a coexistência de Cu_2O e uma pequena proporção de CuO, provavelmente resultante da oxidação superficial. Embora a caracterização em volume tenha confirmado que o material do filme é Cu_2O, a presença de hidróxidos e carbonatos na superfície sugere que a otimização das condições de deposição ou dos processos pós-tratamento poderiam aprimorar a estabilidade e a pureza da fase. Esses achados destacam o potencial dos filmes de Cu_2O como fotocátodos eficientes para a produção de hidrogênio. Estudos futuros devem focar na minimização da oxidação superficial dos fotoeletrodos e na preparação de células fotoeletroquímicas para aplicações em energia sustentável utilizando o fotocátodo de Cu_2O.

Palavras-chave: Filme de Cu_2O, Eletrodeposição, Caracterização de Filmes Semicondutores.

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1. INTRODUCTION

The increasing global energy demand, coupled with the urgent need to mitigate climate change, has driven the search for alternatives to fossil fuels and the reduction of greenhouse gas (GHG) emissions. With this paradigm shift, the study, implementation, and adoption of renewable energy sources that reduce or eliminate GHG emissions, contribute to more sustainable energy matrices, and help achieve net-zero targets have become essential to ensuring a successful energy transition without compromising energy supply for future generations. [1-3].

One of the most promising alternative energy sources is hydrogen gas (H_2), whose combustion in hydrogen fuel cells emits no greenhouse gases (GHG), releasing only energy and water (H_2O) [2]. The generation of green hydrogen through photoelectrolysis, which is still at the research and development (R&D) stage, relies on ambient solar conditions and nanoengineering catalyst techniques [4]. Therefore, understanding the physical characteristics and structure-performance correlations is essential for advancing this field of study.

Photoelectrolysis, a process involving photoelectrochemical reactions that split water molecules into oxygen and hydrogen, is carried out in photoelectrochemical cells (PECs) using a circuit with an anode and a photocathode immersed in an electrolytic solution, which can be alkaline, acidic, or neutral [3-5]. In this setup, the photocathode can be a semiconductor material that acts as a catalyst for the water-splitting reaction. Among the semiconductors suitable for use as photocathodes are those sensitive to sunlight. The desired bandgap should fall within the visible light range, which constitutes the majority of solar light. Additionally, the semiconductor must be cost-effective and abundant on Earth [4,5].

In this context, copper-based materials, such as Cu_2O films, present a promising option, and can be produced in a controlled and cost-effective manner through an electrodeposition [2,6,7]. This technique is particularly attractive for producing high-purity films [8] and is versatile for fabricating optoelectronic and photocatalytic devices [9]. During the electrodeposition of copper (I) oxide, a circuit is set up with a platinum electrode, a reference electrode, and a conductive substrate, all immersed in an electrolytic solution containing copper ions, while an electric current is applied. In this process, nucleation occurs, followed by crystal growth of Cu_2O on the conductive substrate. This growth can be homogeneous, resulting in a uniform film, or heterogeneous, leading to films with roughness and disorganized growth. The film synthesis process can be influenced by factors such as the applied current during electrodeposition, the choice of substrate, the pH of the electrolytic solution, the ion concentration, and the deposition time [2,6,9].

The Cu_2O film is a p-type semiconductor exhibiting a cubic structure and a direct bandgap energy [10]. Upon exposure to visible light with energy exceeding the bandgap, typically at least 2.0 eV, electrons are excited from the valence band to the conduction band, thereby functioning as a catalyst for the water-splitting reaction [6,11].

It has been observed that Cu_2O films with a crystalline orientation along the (111) plane demonstrate improved stability and performance. This enhancement is attributed to the copper atoms protecting the oxygen atoms within the semiconductor's crystal structure from potential degradation, which could be caused by the hydrogen gas (H_2) produced on its surface [2,6,12]. During the electrodeposition, parameters such as temperature, pH, and deposition time were carefully controlled, as they significantly influence morphology [7,11,12]. The applied current density directly affects nucleation, growth rate, grain size, and crystal orientation [11]. The electrolyte with a pH of 12 has been shown to favor the formation of Cu_2O films with a (111) crystalline orientation, which is critical for optimizing photocatalytic performance.

When compared to other photocathode materials, Cu_2O uniquely combines cost-effectiveness, abundance, and environmental safety with properties ideal for photoelectrochemical applications [5,11]. Its direct bandgap of ~2.1 eV is well-suited for visible light absorption, unlike TiO_2 and WO_3, whose larger bandgaps restrict their utility to ultraviolet light [10-12]. Additionally, Cu_2O offers a straightforward and scalable synthesis via electrodeposition, enabling precise control over morphology and preferential (111) crystalline orientation, which enhances stability and catalytic performance. These attributes position Cu_2O as a promising material for advancing efficient and sustainable hydrogen production through photoelectrochemical processes [2,10-12].

The aim of this study was to produce Cu_2O films and characterize their morphological and crystalline structure using SEM/EDS and GIXRD techniques. The bandgap was determined using UV-Vis spectroscopy through the Tauc plot method, while XPS was employed to analyze the surface properties. Cu_2O films were electrodeposited using a standard procedure described earlier, and future work will focus on optimizing them for use in hydrogen production.

2. MATERIALS AND METHODS

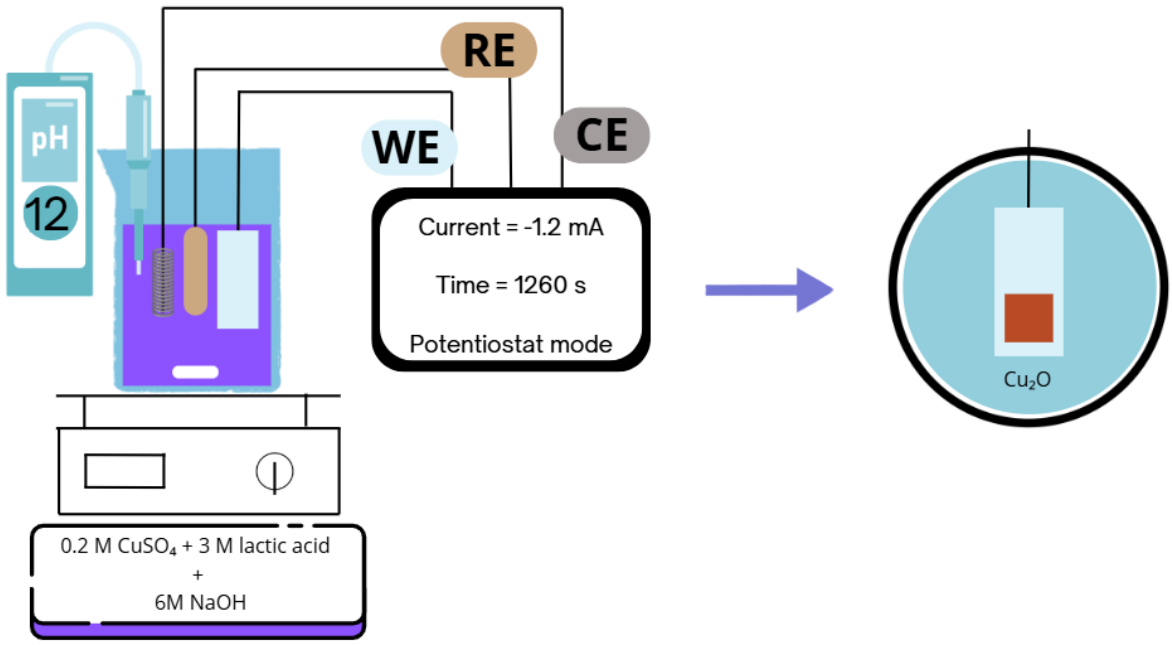
The Cu_2O films were synthesized through electrodeposition method. Following synthesis, their morphology was characterized using SEM, while the elemental composition was assessed by EDS, and the crystalline phases were analyzed by GIXRD. Surface analysis was performed using XPS. To determine the films' absorbance and calculate the bandgap (Eg), UV-Vis spectroscopy was used in conjunction with the Tauc Plot method.

2.1. Cu_2O Film Synthesis by Electrodeposition

The Cu_2O thin films were fabricated in a series of stages. Initially, the FTO substrates were cleaned to remove impurities using an ultrasonic bath in an alkaline soap solution for 20 minutes, followed by rinsing with distilled water. Subsequently, the substrates were subjected to an ultrasonic bath in isopropyl alcohol for 20 minutes and a final bath in acetone, with rinsing in distilled water between each step. After the cleaning process, the substrates were dried in an oven at 30°C.

The Cu_2O films were then deposited via electrodeposition using an electrolytic solution containing 0.2 M $CuSO_4$ and 3 M lactic acid ($C_3H_6O_3$) in distilled water. A 6M NaOH, solution was added to adjust the pH to 12. The electrode system was submerged in the solution, and FTO substrate served as the working electrode, platinum as the counter electrode, and Ag/AgCl (3 M KCl) as the reference electrode. A potentiostat (PGSTAT101, Metrohm) was used to applying a current of -1.2 mA for 1260 seconds. After electrodeposition, the film was rinsed with distilled water and dried at 30°C in an oven.

Figure 1: Illustrative diagram of a three-electrode cell setup



2.2. Cu_2O Film Characterization

The morphology of the films was studied using Scanning Electron Microscopy (SEM) with a Hitachi FlexSEM 1000 instrument, operating at 15 kV, with a focus ranging from 5.6 mm to 5.8 mm, a magnification of 13,000×, and a secondary electron (SE) detector.

The elementar analysis via EDS was realized in a Hitachi S-4000 Plus Scanning Electron Microscopy (SEM) instrument, with EDS accopled, using AztecOne software. The parameters were adjusted to 300 s of time acquisition and spectral resolution of 130 eV.

The crystalline nature of the samples was analyzed by Grazing Incidence X-ray Diffraction (GIXRD) using a Rigaku Ultima IV instrument with a copper tube (Cu-Kα = 1.5418 Å) with an applied voltage of 40 kV and a current of 40 mA. Diffraction patterns were obtained using a fixed angle of 0.1°, 2θ ranging from 25° to 120°, a step size of 0.02°, and a scan speed of 0.53°/min for data acquisition.

To estimate the bandgap energy of the produced films, UV-Vis absorbance measurements were carried out using a Rayleigh – VIS 723G instrument. From the obtained spectrum, the material's absorbance as a function of photon energy was determined. The Tauc Plot method was employed, based on the assumption that the absorption coefficient (α) depends on the photon energy $(h\upsilon)$. The electronic bandgap (E_g) can be determined by plotting $(\alpha\, h\, \upsilon)^n$ against $(h\upsilon)$, where n equals 2 for direct allowed transitions [13]. This relationship is described by the following equation:

$$\alpha\, h\, \upsilon^n \;\propto\; A\,(\,h\upsilon - E_g)$$

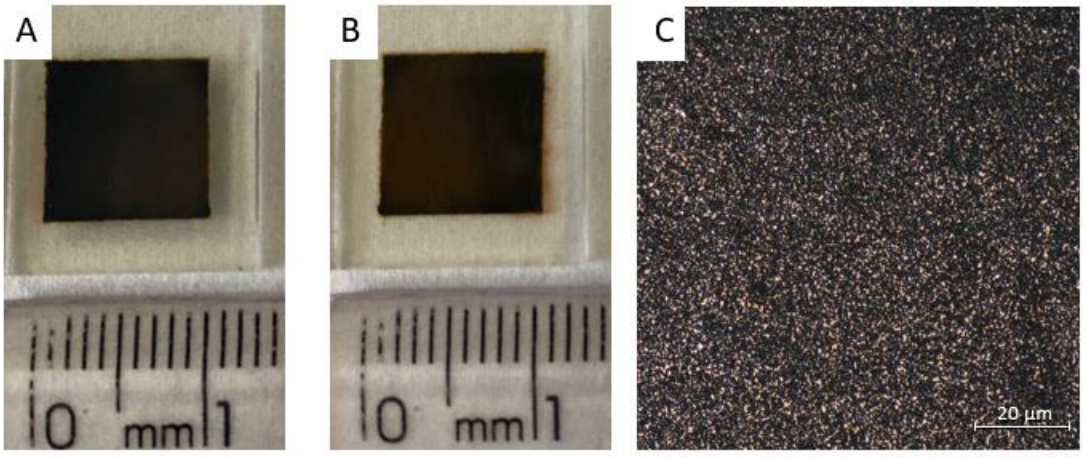
For an ideal crystalline semiconductor, where no excitons are formed, and contributions from phonons or state filling are negligible, the energy at which $\alpha(E)$ becomes zero corresponds to the electronic bandgap (E_g) [13].

X-ray Photoelectron Spectroscopy (XPS) analysis was conducted using a Thermo Scientific Escalab Xi+ system, with data acquisition and processing performed using the Avantage software. The analysis utilized a monochromatic Al Kα source with an excitation energy of 1486.6 eV and a spot size of 650 μm in diameter. Survey scans were acquired with 10 scans at 100 ms using a pass energy of 100 eV. High-resolution scans were performed with 20 scans at 400 ms for Cu2p, 10 scans at 200 ms for O1s, and 10 scans at 200 ms for C1s, all using a pass energy of 20 eV. Charge compensation was applied using the Flood Gun – Charge Comp Standard mode.

3. RESULTS AND DISCUSSIONS

A brown film with slightly orange hues was synthesized, covering an area of 1 cm^2, as shown in figure 2.

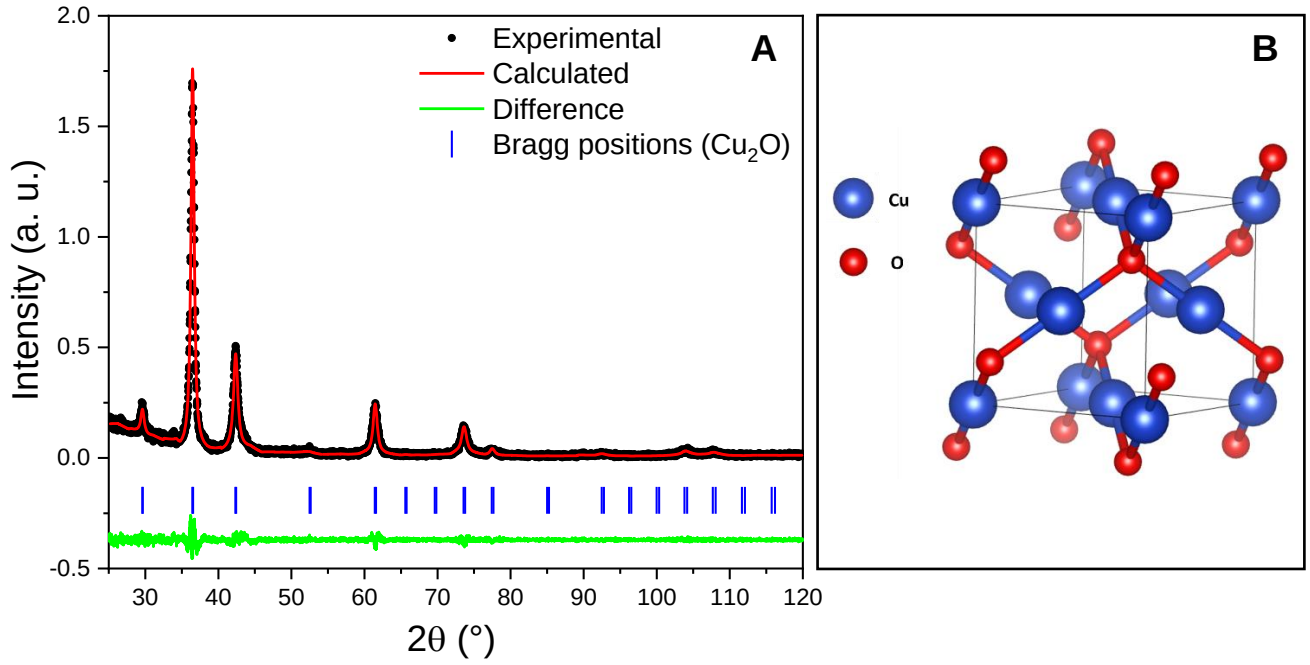
Figure 2: Photographic and microscopic characterization of the synthesized film: (a) front view, (b) back view, and (c) optical micrograph obtained using a Nikon ECLIPSE LV 100ND microscope with a 5× objective.



Grazing incidence X-ray diffraction (GIXRD) analysis confirmed that the crystalline phase formed in the prepared thin film corresponds to Cu_2O. The diffraction peaks at 2θ values of 29.57°, 36.43°, 42.31°, 61.38°, 73.52°, and 77.38° correspond to

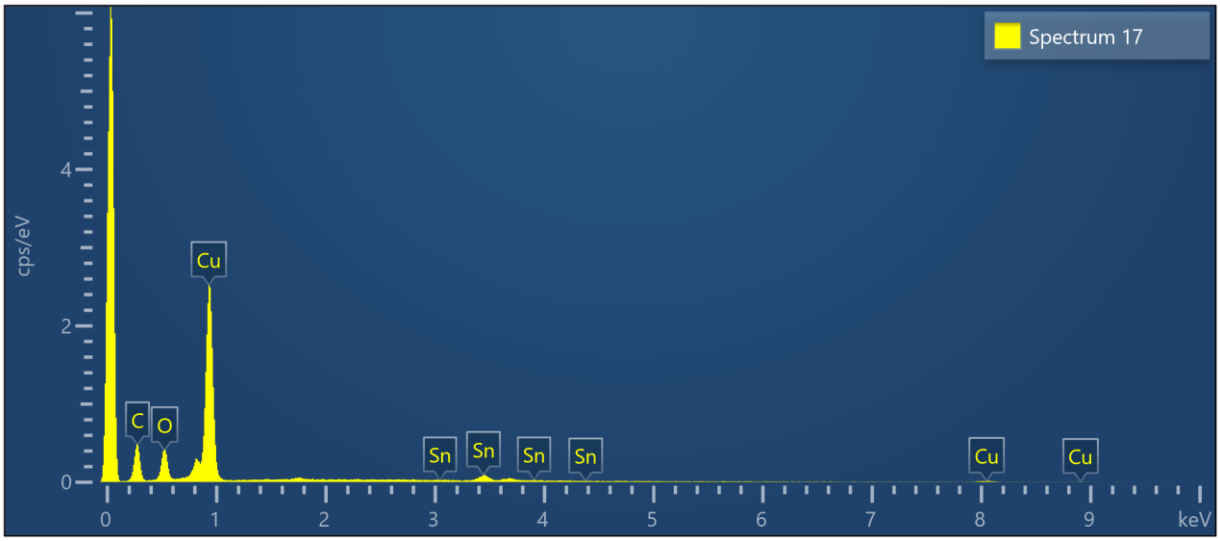
the (110), (111), (200), (220), (311), and (222) Miller planes of Cu_2O, respectively, in agreement with literature reports [14-15] and illustrated in figure 3. Notably, GIXRD primarily probes the bulk material, enabling accurate phase identification in mass fractions above 5%. The electrodeposition process favored a predominant (111) orientation, indicative of preferential growth along this crystallographic direction. This preferential orientation was further corroborated by Rietveld refinement of the X-ray diffraction (XRD) data, which confirmed that the Cu_2O thin film crystallized in a cubic structure with a space group $Pn\bar{3}m$ and lattice parameters a=b=c=4.26658 Å. The refinement also revealed a strong (111) texture, with an estimated fraction of 90%. Microstructural analysis indicated an anisotropic grain distribution, with an average apparent grain size of 11.62 ± 1.162 nm along the dominant growth direction. Additionally, the average maximum strain was determined to be 6.6964 r.m.s, with a standard deviation of 0.0034. The goodness-of-fit parameter (χ^2) for the Rietveld refinement was 1.26, confirming the high reliability of the model.

Figure 3: (a)GIXRD pattern of the Cu_2O film, its Rietveld refinement, (b) the representation of the cubic unit cell structure of the Cu_2O with $Pn\bar{3}m$ symmetry.



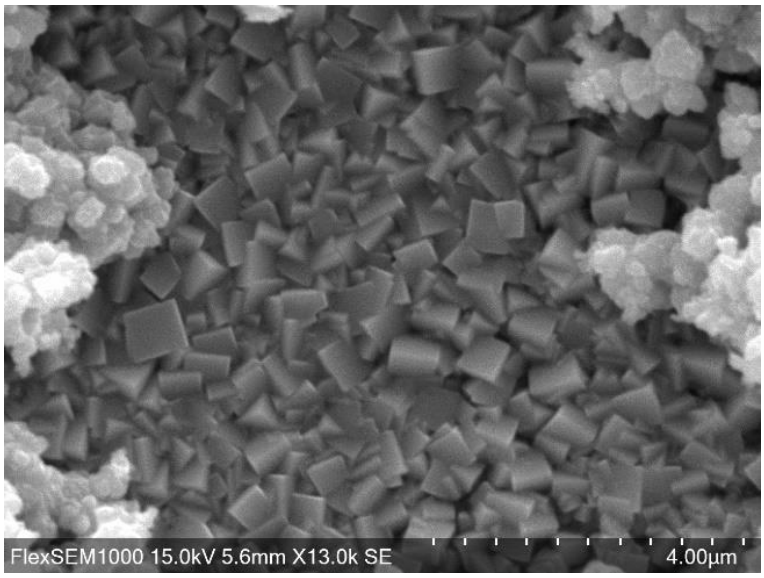
Energy-dispersive X-ray spectroscopy (EDS) confirmed the presence of copper (Cu) and oxygen (O) from the Cu_2O film, along with tin (Sn) and oxygen (O) from the FTO substrate. A detectable carbon (C) signal was also observed, likely resulting from atmospheric adsorption or residual organic species from the electrolyte. The presence of carbon motivated further X-ray photoelectron spectroscopy (XPS) analysis to investigate surface chemical interactions. As illustrated in Figure 4, the EDS spectrum confirms the elemental composition of the sample.

Figure 4: EDS spectrum of the analyzed sample, showing the elemental composition of Cu, O, Sn, and C.



The scanning electron microscopy (SEM) image in Figure 5 reveals that the Cu_2O film exhibits a predominantly homogeneous cubic crystal morphology, with vertices oriented upwards. However, regions of inhomogeneous growth are evident, particularly at the image edges, where larger, irregularly shaped crystals overlay the uniform cubic layer. This variation is likely attributed to the applied current density (-1.2 mA/cm²), which accelerates crystal growth, leading to size disparities in certain regions.

Figure 5: SEM image of the Cu_2O film, showing cubic-shaped crystals in medium to dark gray tones, alongside with brighter regions corresponding to more disordered and inhomogeneous agglomerations



Optical band gap analysis, derived from the Tauc plot (Figure 6), yielded a direct allowed band gap of 2.0 eV, consistent with reported literature values [7,11,12], which range between 2.0 eV and 2.3 eV. This band gap is well-suited for visible light absorption, reinforcing the potential of Cu_2O as an efficient photocatalyst for water splitting applications.

Figure 6: Tauc plot of the Cu_2O film, shown a 2.0 eV of direct allowed bang gap.

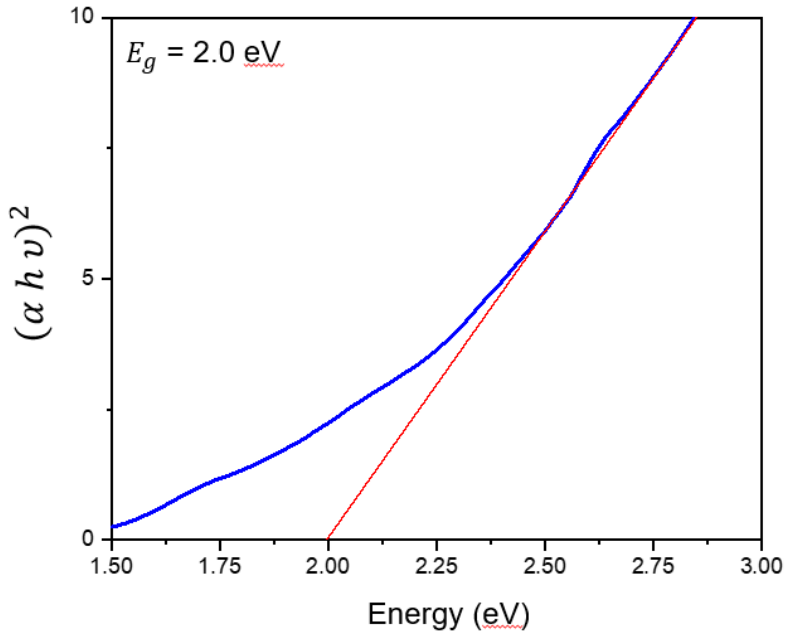
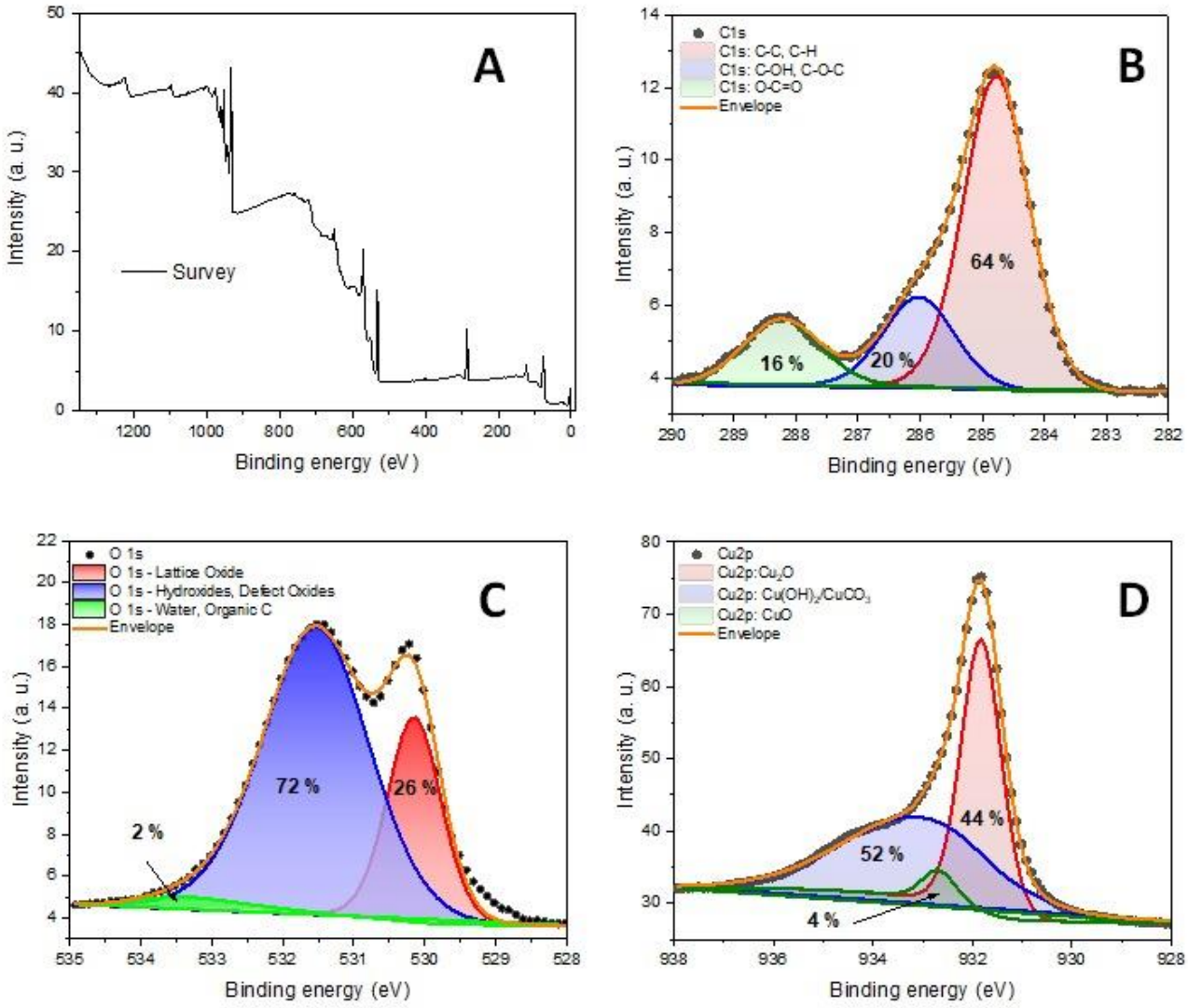


Figure 7 presents the XPS analysis, providing insights into its surface composition and chemical states of the film. The survey spectrum (Figure 7-A) confirms the presence of copper (Cu), oxygen (O), and carbon (C), with the latter likely originating from residual lactic acid in the electrolyte solution or adsorption of atmospheric CO_2. The high-resolution C 1s spectrum (Figure 7-B) indicates contributions from adventitious carbon (C–C, C–H at ~285 eV, 64%), organic residues from the deposition process (C–OH, C–O–C at ~286.5 eV, 20%), and carbonates (O=C=O at ~289 eV, 16%), which may have formed due to the alkaline deposition medium (NaOH, pH 12). The O 1s spectrum (Figure 7-C) further highlights a high concentration of hydroxides and defect oxides (~531.5 eV, 72%) on the film's surface, in addition to Cu_2O (~530 eV, 26%) and minor contributions from water and organic residues (~533.5 eV, 2%). The Cu 2p spectrum (Figure 7-D) reveals that, at the surface, Cu_2O (~932.5 eV, 52%) is accompanied by a significant fraction of CuO (~934.5 eV, 44%), alongside a minor presence of $Cu(OH)_2/CuCO_3$ (~933.5 eV, 4%). The substantial CuO content suggests post-deposition oxidation due to air exposure. The XPS results obtained in this study exhibit a high degree of similarity to previously reported values in the literature, further validating the compositional analysis and surface chemistry of the material [16,17].

Since XPS is a surface-sensitive technique, these findings indicate that while surface oxidation is evident, the bulk material likely remains Cu_2O, as verified by GIXRD. However, surface oxidation could impact film stability and hydrogen production efficiency. Future studies should explore post-deposition treatments to mitigate unwanted surface oxidation while preserving the desired Cu_2O phase.

Figure 7: XPS analysis of the Cu_2O film. (A) Survey spectrum confirming the presence of Cu, O, and C. (B) C 1s spectrum indicating adventitious carbon, organic residues, and carbonate species. (C) O 1s spectrum showing contributions from lattice oxides, hydroxides, and surface defects. (D) Cu 2p spectrum revealing a predominant Cu_2O phase with notable surface oxidation to CuO and minor hydroxide/carbonate contributions.



4. CONCLUSIONS

This study synthesized and characterized Cu_2O thin films via electrodeposition metohds. The films exhibited a predominantly cubic morphology and a cubic structure with preferential (111) crystalline orientation, as confirmed by SEM and GIXRD, respectively.

Optical characterization using UV-Vis spectroscopy and the Tauc plot method determined a direct bandgap of 2.0 eV, consistent with values reported in the literature. These properties position Cu_2O as a promising candidate for photoelectrochemical hydrogen production.

Surface-sensitive XPS analysis identified Cu_2O as the dominant phase, though significant surface oxidation led to CuO formation, potentially affecting film stability and photocatalytic performance. While GIXRD confirmed that the bulk material remained Cu_2O, the detection of hydroxides and carbonates in XPS suggests that further refinement of the deposition or post-treatment processes is necessary to enhance phase purity and long-term stability. To strengthen the practical application of Cu_2O films, particularly in photoelectrochemical cells, improving their stability is crucial. Future work could explore surface modifications, doping, or protective coatings to mitigate surface oxidation and enhance the films' durability while preserving their desirable Cu_2O characteristics.

Future studies should focus on optimizing deposition parameters, exploring post-deposition treatments, and considering strategies to improve the long-term stability of the films to maximize their performance in renewable energy technologies.

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CONFLICT OF INTEREST

All authors declare that they have no conflicts of interest.

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