Facile synthesis of Cu₂O nanorods in the presence of NaCl by successive ionic layer adsorption and reaction method and its characterizations

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Cuprous oxide (Cu₂O) nanorods have been deposited on soda-lime glass substrates by the modified successive ionic layer adsorption and reaction technique by varying the concentration of NaCl electrolyte into the precursor complex solution. The structural, electrical and optical properties of synthesized Cu₂O nanorod films have been studied by a variety of characterization tools. Structural analyses by X-ray diffraction confirmed the polycrystalline Cu₂O phase with (111) preferential growth. Raman scattering spectroscopic measurements conducted at room temperature also showed characteristic peaks of the pure Cu₂O phase. The surface resistivity of the Cu₂O nanorod films decreased from 15 142 to 685 Ω.cm with the addition of NaCl from 0 to 4 mmol and then exhibited an opposite trend with further addition of NaCl. The optical bandgap of the synthesized Cu₂O nanorod...
films was observed as 1.88–2.36 eV, while the temperature-dependent activation energies of the Cu$_2$O films were measured as about 0.14–0.21 eV. Scanning electron microscope morphologies demonstrated Cu$_2$O nanorods as well as closely packed spherical grains with the alteration of NaCl concentration. The Cu$_2$O phase of nanorods was found stable up to 230°C corroborating the optical bandgap results of the same. The film fabricanted in presence of 4 mmol of NaCl showed the lowest resistivity and activation energy as well as comparatively uniform nanorod morphology. Our studies demonstrate that the nominal presence of NaCl electrolytes in the precursor solutions has a significant impact on the physical properties of Cu$_2$O nanorod films which could be beneficial in optoelectronic research.

1. Introduction

Cuprous oxide (Cu$_2$O) is a p-type intrinsic semiconductor due to copper vacancies in the crystal lattice with the bandgap of approximately 2.17 eV [1,2] having several promising advantages such as high abundance, low-cost production, visible-light harvesting and non-toxicity. Cu$_2$O has attracted interest as a good candidate material for photocatalysis [3,4] chemo sensing [5,6], electrode materials in lithium-ion batteries [7,8], photovoltaics [9,10] and photoelectrochemical water splitting [4,11].

Still, there are numerous methodological challenges in the research and application of Cu$_2$O including the consistent synthesis of nanostructured Cu$_2$O materials as well as the unavoidable formation of metallic Cu at the p-n heterojunction [12,13]. Moreover, the maximum theoretical limit of the efficiency of single-junction Cu$_2$O is as high as 20% under air mass 1 solar illumination [13], which is far from the achieved results. Recently, Minami et al. [9] fabricated heterojunction solar cells by inserting an n-type zinc-germanium-oxide (Zn$_{1-x}$Ge$_x$O) thin film between an Al-doped ZnO thin film and a p-type Na-doped Cu$_2$O (Cu$_2$O : Na) sheet prepared by thermally oxidized Cu sheets and reported the conversion efficiency of the cell as 8.1% [9]. On the other hand, Ci et al. [14] fabricated Cl-doped n-type Cu$_2$O films by chemical bath deposition by using CuSO$_4$ solution with the addition of CuCl$_2$ as a Cl$^-$ source. Therefore, it looks crucial to study the influence of Na and Cl individually or the electrolytic behaviour of NaCl in a broad spectrum on Cu$_2$O film deposition.

There are various methods to synthesis Cu$_2$O thin films such as atomic layer deposition [15], electrochemical deposition [16–19], metal-organic chemical vapour deposition [20], molecular beam epitaxy [21], successive ionic layer adsorption and reaction (SILAR) [22–24], the direct oxidation of Cu sheets [25], sputtering [26], vapour phase epitaxy [27] and sol–gel technique [28]. However, towards the preparation of nanostructured Cu$_2$O, the electrodeposition of Cu$_2$O thin films allows the greatest control yet [23–26]. To the best of our knowledge, there is no study about the SILAR deposition of Cu$_2$O nanorod films until now. Moreover, chemical bath optimization for epitaxial growth of Cu$_2$O nanorods from surfaces has not yet been reported [29].

SILAR is basically one of the most simple and cost-effective methods since it does not require sophisticated apparatus as required in electrodeposition or other methods. In this study, a modified SILAR method was used to synthesize Cu$_2$O nanostructured thin films. In our prior report, we have shown the modification [22–24] of SILAR by eliminating the rinsing steps during the growth of pure Cu$_2$O thin films and named the method as the modified (m)-SILAR technique. Therefore, we synthesized Cu$_2$O nanorods on SLG substrates by the m-SILAR method in the nominal presence of NaCl into the precursor solution complex. The objective of this work was to study the impact of the NaCl electrolyte concentrations on the growth of Cu$_2$O nanorod films through the investigation of their structural, morphological, optical and electrical properties for photovoltaic applications.

2. Materials

In this work, sodium thiosulfate pentahydrate (Na$_2$S$_2$O$_3$·5H$_2$O; Scharlau: purity approx. 99.0%), copper (II) sulfate pentahydrate (CuSO$_4$·5H$_2$O; Merck Millipore: purity approx. 99.0%), sodium hydroxide (NaOH; Active fine chemicals: purity approx. 98.0%) and sodium chloride (NaCl; Merck Millipore: purity approx. 99%) were collected from the local market and used without further refinement. Soda-lime glass (SLG) microscopy slides (25 × 25 × 1 mm$^3$) were used as substrates to deposit copper oxide thin films.
2.1. Synthesis of copper (I) oxide thin films

Cu$_2$O thin films were deposited on SLG substrates as shown in figure 1 by using the same method described in our previous work [22]. Briefly, the SLG substrates were initially cleaned by detergent to remove loosely attached visible dust particles. Then, the substrates were successively cleaned in an ultrasonic water bath through deionized (DI) water, ethanol, toluene and isopropanol for 15 min in each case. Prior to the film deposition, 10 ml 1 M copper (II) sulfate and 40 ml 1 M sodium thiosulfate solution were added into a 100 ml volumetric flask until the colourless solution of copper-thiosulfate complex appeared. Then, a 2 mmol NaCl electrolyte was added into the same flask and after shaking the remaining portion was filled with DI water. This complex solution was labelled as a cold solution. A 2 M NaOH solution was kept at 70°C (hot solution). After that, the SLG substrate was alternatively immersed in hot and cold solution respectively for 23 s each and had completed one SILAR cycle. This process was repeated for up to 40 immersion cycles. OH$^-$ and Cu$^+$ ions were adsorbed on the substrate respectively when immersed in a hot and cold solution. Consequently, Cu$_2$O thin films were deposited on the substrate owing to the following chemical reactions:

$$\text{Cu(S}_2\text{O}_3)^- \rightarrow \text{Cu}^+ + \text{S}_2\text{O}_3^{2-}$$

and

$$2\text{Cu}^+ + \text{OH}^- \rightarrow \text{Cu}_2\text{O} + \text{H}_2\text{O}.$$ 

After deposition, this as-made sample was washed through DI water to eliminate loosely bound particles and dried naturally in the laboratory ambient. Other samples were prepared in a similar way and stored safely in an air-tight sample box for future characterization purposes. The growth mechanism of Cu$_2$O nanorods are discussed later in the surface morphology section with the support of scanning electron microscope (SEM) micrographs.

2.2. Characterization process

The crystal structure and phase present in the samples were examined through an X-ray diffraction (XRD) spectrometer (Philips PANalytical X’Pert MRD) under $\theta$–$\theta$ coupled mode with CuK$\alpha$ radiation source of wavelength, $\lambda = 0.15406$ nm as well as a sensitive Raman scattering spectrometer (Horiba HR800) where the excitation radiation was 488 nm laser source. SEM (Philips XL30 EEG) was employed to investigate the morphological properties of the samples. An ultraviolet-visible-near-infrared (UV-Vis-NIR) spectrophotometer (Shimadzu UV 2600 ISR Plus) of wavelength, $\lambda = 220$–1400 nm was applied to study the optical response of the deposited samples. A homemade four-point collinear probe coupled with a Keithley SMU2450 was used to measure the surface resistivity of the samples. Temperature-dependent surface resistivity was measured by air annealing the samples from 30°C to 230°C through a homemade two-probe system coupled with a digital multimeter (BK Precision 2704C).
3. Results and discussion

3.1. Crystal structure and phase identification

The crystal structure and phases present in the samples deposited on SLG substrate have been examined through XRD spectroscopy under $\theta$–$2\theta$ coupled mode in the range $30^\circ$–$70^\circ$, and the relevant XRD pattern is illustrated in figure 2a. All the samples exhibited distinguished peaks at $2\theta \approx 36.5^\circ$, $42.5^\circ$ and $61.5^\circ$, respectively, which were assigned to the (111), (200) and (220) plane of pure cubic phase of Cu$_2$O only that matches to the high-quality inorganic crystal structure database (ICSD) of phase pure Cu$_2$O (ICSD PDF no. 180846) [22], and none of the peaks from Cu or CuO phases were present. Figure 2a reveals that all the films were polycrystalline in nature with (111) preferential growth. The intensity of the (111) plane of Cu$_2$O is increased with increasing the concentration of NaCl electrolyte (2–8 mmol) which indicates the improvement of the crystalline quality of the deposited films [23].

The texture coefficient (TC) was assessed to describe the crystallographic nature of the deposited films by using the ratio, $TC(hkl) : I(111)/I(111) + I(200)$, where I(111) and I(200) were the intensity of (111) and (200) planes, respectively [22], and the calculated values are shown in table 1. The average crystallite size (D) was determined by using the Scherrer formula [30], and it was 14.91–16.51 nm. The values of some other structural parameters are listed in table 1. The increasing value of TC, similarly shifting of $2\theta$
values to the higher diffraction angle with respect to the reference $\theta$ value (marked by footnote\footnote{Cu$_2$O powder (purity: 99.99%).} in table 1 and the respective plot is inserted in figure 3\textit{b}, line), signified the improvement of the crystalline quality of the deposited films in presence of a higher concentration of NaCl electrolyte \cite{31}. Variations of crystallite size and TC are shown in figure 3\textit{a}. Although the little amount of NaCl electrolyte (2 mmol) deteriorates the crystalline quality of the film in the case of sample S2 with respect to S0 (zero NaCl), but at higher NaCl concentration, the nano crystallinity of the films was improved which can be seen from figure 3\textit{a}. In this case, sample S8 showed the highest crystallinity among all the samples having the largest crystallite size (16.51 nm) with the minimum dislocation density and micro strain.

To further confirm the phases of the deposited films, the sensitive Raman scattering spectroscopy was also used, and the corresponding Raman spectra is given in figure 2\textit{b}. Raman peaks at 143, 214, 280, 332 and 620 cm\textsuperscript{−1} corresponds to the Cu$_2$O phase only \cite{26,32,33} which perfectly coincided with the demonstrated XRD results and has an alike pattern with ref. \cite{34}. Thus, the addition of an NaCl electrolyte to a cationic precursor solution unaltered the chemical environment of the deposited films while improving nano crystallinity.

### 3.2. Morphological analysis

Figure 4 depicts the SEM micrographs of the samples deposited in presence of an NaCl electrolyte at various concentrations. It is observed that the morphologies are crack-free and very well distributed on the substrate surface. The sample deposited without an NaCl electrolyte revealed pencil-thin nanorod surface morphology with an overgrown cluster in some regions, as also observed in our previous report \cite{23}. When the electrolyte started to be added to the solution, such as 2 mmol of NaCl, the crowded nanorods developed, and with the rise of concentration of NaCl to 4 mmol, the nanorod formation enhanced, having a larger size and shape as distinguished in figure 4\textit{c}. When NaCl electrolyte concentration reached 6 mmol, very rough, tiny and dense spherical grains as well as some overgrown clusters were seen. An overgrown cluster was formed owing to the coalescence of the particles \cite{35}. Further addition of NaCl concentration was culminated at 8 mmol and exhibited distinctively distributed, clear and larger sized spherical grains. Thus, the increasing content of NaCl electrolyte changed surface morphologies from nanorods to spherical grains which have potential influences in electrical and optical properties described in the later sections.

The morphology of the Cu$_2$O nanostructures was sensitive to the concentration of salts added as also reported for CuO \cite{36}. When NaCl concentration was increased gradually, the growth of nanorods also increased but until a limit such as 4 mmol of NaCl addition. These phenomena indicate that NaCl concentration will result in similar morphology of the product and play key roles in controlling the size and shape of the Cu$_2$O nanostructures. Besides the above-mentioned reasons, the steric hindrance effect caused by salt concentration should also influence the micelle aggregates, and these effects together result in the assemblies of the products. Further studies and work are ongoing to additional research of the mechanisms for the fabrication process caused by the new proposed route.

### 3.3. Electrical properties

The electrical resistivities of the samples were measured by using a homemade four-point collinear probe that was reported in our previous work \cite{22}. Measurements were taken at several regions of the sample.
under investigation, and the results are the representative average values of all measurements summarized in table 2. Thickness as well as the type of conductivity of films was measured by a similar technique described in [22].

From table 2, the surface resistivity values were found in between 15,142 and 685 $\Omega \cdot $cm. Thicknesses were used to calculate the surface resistivity of the samples. The average thickness of the film is 1184 nm. The changes in surface resistivity with thicknesses is shown in figure 5a. It is clearly visible that sample S4 showed the maximum thickness with the minimum resistivity among all the samples. With increasing the content of the NaCl electrolyte into the cationic precursor solution, the surface resistivity (S2–S8) is reduced as compared to the sample deposited without NaCl (S0). The resistivity value dropped to 685 $\Omega \cdot $cm in the sample deposited at 4 mmol NaCl electrolyte (S4) which is about 22 times lower than sample S0.

The change of surface resistivity with increasing content of NaCl electrolyte may be explained based on the SEM micrographs observed in figure 4. As the density, size and shape of nanorod were increased with increasing the content of NaCl up to 4 mmol as observed from figure 4a–c, the probability of passing the electrical current through the sample S4 is maximum and consequently the minimum order of surface resistivity (S4, $\rho = 685 \Omega \cdot $cm). Moreover, for the sample deposited at 6 mmol NaCl (S6), the surface was very rough and dense as seen from figure 4d, which may be the cause of a little bit of high resistivity in comparison to sample S4. Furthermore, sample S8 showed lower resistivity than S6 owing to the well-distributed and larger spherical grains, which is also understandable by the look of the micrographs in figure 4d,e.

The type of conductivity was determined by using the hot-probe method [22]. The temperature-dependent surface resistivity ($\rho$) was also measured to determine the activation energy ($E_a$) of the samples. Resistivity value was measured for respective surface temperature of the deposited film in the range between 30°C and 230°C. The $E_a$ values were calculated by using the following Arrhenius equation [7]:

$$\rho = \rho_0 \exp \left(\frac{-E_a}{k_B T}\right)$$  \hspace{1cm} (3.1)
\[ \log \rho = \left( -\frac{E_a}{1000k_B} \right) \left( \frac{1000}{T} \right) + \log \rho_0, \]

(3.2)
where \( \rho \) is the surface resistivity of the films at a specific temperature, \( E_a \) is the activation energy, \( T \) is the temperature in Kelvin, \( r_0 \) is the proportionality constant and \( k_B \) is the Boltzmann constant \((8.617 \times 10^{-5} \text{ eV K}^{-1})\). By plotting \( \log \rho \) versus \( 1000/T \) as shown in figure 5b, the activation energy \( E_a \) is obtained as listed in table 2. Likewise, the surface resistivity, the activation energy followed the same trend, and the values were found to be 0.14–0.21 eV. The measured values were perfectly matched with the reported results [24,37], and in this study, the sample deposited with 4 mmol NaCl electrolyte exhibited the lowest resistivity and activation energy as well as well-distributed nanorods. Hence, the sample S4 has preferentially shown better quality than the other deposited Cu\(_2\)O samples. Also overall, the significant effect of adding NaCl electrolyte in the case of depositing Cu\(_2\)O thin films has been pronounced.

### 3.4. Optical analysis

To assess the optical characteristics of the samples deposited at various NaCl electrolyte concentrations, the diffuse reflectance spectra of the samples has been taken. UV-Vis-NIR ranges of wavelength 220–1400 nm have been passed through the samples from the respective light sources, and the recorded diffuse reflectance spectra are shown in figure 6.

From figure 6a, it is observed that a strong absorption edge occurs at wavelength, \( \lambda \approx 480 \text{ nm} \) which corresponds to the Cu\(_2\)O phase only. No other phase such as CuO is absent which was preliminarily confirmed from both XRD and Raman spectra, those were shown in figure 2a,b. In our study, the diffuse reflectance spectra were mainly taken to eliminate any effect that may come from the SLG substrates. The reflectance was seen about 10–20\%. To investigate the NaCl electrolyte concentration on the optical band gap \( (E_g) \) of the deposited films, a Tauc plot was drawn by using reflectance data in correlation with the Kubelka–Munk function \( F(R_\infty) \) of the following equation [3]:

\[
(hvF(R_\infty))^{1/n} = A(hv - E_g),
\]  

### Figure 5. (a) Variation of surface resistivity with thickness and (b) temperature-dependent activation energy of the samples.
where, $h$ is the Planck’s constant $(6.626 \times 10^{-34} \text{ Js})$, $E_g$ is the optical bandgap, $R_0$ is the diffuse relectance, $A$ is the proportionality constant, $\nu$ is the frequency of the incident photon, $n = 1/2$ for indirect band gap semiconductor and $n = 2$ for direct band gap semiconductor. By plotting $h\nu F(R_0)^2$ versus $h\nu$ (putting $n = 2$ for direct band gap Cu$_2$O semiconductor) and subsequently extrapolated to the $x$-axis, the curves of the following types were found for as-deposited and annealed samples, and the respective $E_g$ values are shown in table 2.

From table 2, it is seen that for as-deposited samples the $E_g$ values were $2.0$–$2.36$ eV [38], whereas it was $1.88$–$2.04$ eV for annealed samples [23]. In the case of as-deposited samples (figure 7a), the $E_g$ value dropped from $2.36$ to $1.96$ eV and then again increased up to $2.24$ eV. The sample deposited at 4 mmol NaCl electrolyte showed the lowest bandgap ($E_g$) among all the samples having the smallest surface resistivity ($685$ $\Omega \cdot \text{cm}$) and activation energy ($0.14$ eV) as well as the well-distributed nanorods that are observed from figure 4c. On the other hand, air annealing lowered the $E_g$ values those observed from table 2 and figure 7b, and the value was approximately $1.95$ eV. The former reports [23,39] and current observed $E_g$ values can conclude that air annealing lowered the band gap but did not change the Cu$_2$O phase into CuO up to annealing at $230^\circ$C (cleared from the inset transmittance absorption spectra shown in figure 6b). Hence, air annealing is beneficial to lower the band gap.

Figure 6. Diffuse reflectance spectra of (a) as-deposited and (b) annealed samples. (The absorption edge is drawn at $\lambda\approx480$ nm by the pink line, and the transmittance data are shown inset of (b) to clarify the phase present in the annealed samples.)
4. Conclusion

In this research, we synthesized Cu$_2$O nanorod films by the variation of concentration of NaCl on top of simple SLG by the modified SILAR technique, and the structural, electrical and optical properties of the nanorod films have been investigated. Structural analysis by XRD and Raman validates the polycrystalline pure Cu$_2$O phase with (111) preferential growth. The SEM micrographs reveal that the deposited films were nanorod structures and closely packed spherical grains, formed with the variation of NaCl concentration. The optical band gap of Cu$_2$O films estimated by UV-VIS-NIR spectroscopy was observed to be in the range of 1.88–2.36 eV and consistent with the reported results in the literature. The resistivity of the Cu$_2$O nanorod films decreased from 15 142 to 685 $\Omega$.cm with the addition of NaCl from 0 to 4 mmol, while the temperature-dependent activation energies of the films were found as about 0.14–0.21 eV. The film optimized in presence of 4 mmol of NaCl demonstrated the lowest resistivity, activation energy and excellent nanorod growth. These results could eventually demand significant attention in the photovoltaic community and research into the development of ecofriendly as well as cost-effective Cu$_2$O nanorod film-based optoelectronics.

Ethics. The work has been started and approved by the Department of Chemistry, Comilla University, Bangladesh and Energy Conversion and Storage Research (ECSR) Section, Industrial Physics Division (IPD), BCSIR Laboratories, Dhaka, Bangladesh as one of the MS thesis research projects done by M. A. Hossain.
Data accessibility. Our data are deposited at Dryad Digital Repository: https://doi.org/10.5061/dryad.37pymcvm4m [40].

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All authors gave final approval for publication and agreed to be held accountable for the work performed therein.

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