

Study of low-temperature Electrodeposition growth of Copper (I) Oxide (Cu₂O) thin films on Indium Tin Oxide (ITO) glass substrate

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1. ABSTRACT

Copper (I) Oxide is well-known as an excellent material used in many photovoltaic applications. Most of the research investigated the fabricating of Cu₂O thin layers on Cu and opaque metal substrates. This will lead to the absorption limitation and the photo response decrement of the fabricated photovoltaic device. Deposition of n-type Cu₂O on a transparent conductive glass substrate is quite a challenge due to its high conductivity and the electrolyte pH, which will lead to poor surface adhering and crystal formation. This study will investigate a procedure of electrodeposition of n-type Cu₂O on ITO glass substrate at low temperature in an acidic medium using the three-electrode method which results in better photo-responsive thin films with good surface adhesion. The current density (J) behavior and the electrolyte pH behavior within the experiment were studied. Then the photo-responsive characteristics, X-ray Diffraction (XRD), and Scanning Electron Microscopy (SEM) characterizations confirmed the proper deposition of Cu₂O thin films on the ITO glass substrate. Importantly, a crystal defect occurring at longer deposition periods was observed using the SEM results analysis.

2. INTRODUCTION

Copper oxide (Cu₂O) is a crucial semiconductor for use in optoelectronic and photovoltaic technologies. Its significance stems from its non-toxic nature and its wide, direct band gap, which ranges from approximately 1.9 to 2.2 eV [1], making it a strong candidate for various technological applications. During the formation of thin Cu₂O films, the copper atoms arrange themselves into a face-centered cubic (fcc) sublattice, while the oxygen atoms form a body-centered cubic (bcc) sublattice [1]. The lattice constant of this structure is 4.2696 Å, with one sublattice shifted by a quarter of the body diagonal. In this configuration, each copper atom is linearly bonded to two neighboring oxygen atoms, while each oxygen atom is surrounded by four copper atoms.

Though Cu₂O is an abundant p-type semiconducting material found in the environment, it can be synthesized as n type semiconductor material using the Cu²⁺ rich acidic

mediums in slightly elevated temperatures using various techniques such as electrochemical deposition [2], thermal oxidation, chemical oxidation, chemical vapor deposition and other methods. The electrochemical deposition expands the fine tune ability of the material's specific characteristics which is very important to soft condensed matter research. This single step deposition process results well deposited firm thin film layers at specific pH levels on transparent conductive glasses, unlike the step thermal oxidation method which produces thin films consisting of pin holes that help the hole layer to leak through the photo-anode layer.

As it is designated a low-cost semiconductor material, Cuprous Oxide (Cu_2O) has been researched for use in low-cost, environmentally friendly material for solar cells and other optoelectronic devices. A previous study by Madusanka attempted to grow Cu_2O thin films on a conducting glass substrate [3]. As a solution for the pin holes that occurred within the Cu_2O deposition on ITO substrate re-proposed and implemented as the three-electrode method single-step acidic electrochemical deposition at below 60°C condition. This paper discusses the electrochemical deposition of the photoanodic semiconductor material Cu_2O and how the deposition time affects the crystal structure of Cu_2O thin film.

3. METHODOLOGY

3.1 Sample Preparation

3.1.1 Cleaning Procedure of ITO

Indium Tin Oxide (ITO) coated glass substrates with surface resistivity ($15\Omega\text{cm}^{-2}$) were cut into $1\text{cm} \times 2\text{cm}$ pieces. ITO glass pieces were cleaned using diluted H_2SO_4 solution and sonicated in an Ultrasonic Wave Sonicator for 30 minutes. Then, the cleaned glasses were washed with Acetone and deionized water and air dried.

3.1.2 Preparation of Electrolyte for Electrodeposition Process

The acidic buffer electrolyte was prepared by dissolving 0.398 g of Cupric Acetate ($\text{Cu}(\text{CH}_3\text{COO})_2$) and 3.85 ml of glacial Acetic acid (CH_3COOH) in 100 ml of deionized water to obtain 0.02M and 0.08M concentrations of Cupric Acetate and Acetic acid, respectively. To adjust the pH to 5.6 in the buffer electrolyte, a 7M NaOH solution was gradually added.

3.1.3 Electrochemical Deposition and Preparation of Cu_2O Electrode

A Keithley 2400 Source Meter Unit (SMU) was used as the voltage source, with Platinum (Pt) wire as the counter electrode connected to the anode and the ITO plate on the cathode. Throughout the electrodeposition process, the electrolyte was heated to $\sim 55^\circ\text{C}$ while continuously stirring using a magnetic stirrer. The area of the ITO plate

dipped in the electrolyte was kept as 1 cm^2 . The electrodeposition was carried for different time periods; 20 min, 30 min, 40 min, 50 min and 60 minutes subjected to a 200 mV potential between the working electrode and the counter electrode with respect to saturated calomel reference electrode ($\text{Cl}^-_{(\text{saturated})}|\text{Hg}_2\text{Cl}_{2(\text{s})}|\text{Hg}_{(\text{l})}|\text{Pt}$). Finally, the Cu_2O deposited ITO glasses were washed with deionized water (to remove extra electrolyte on the surface) and air dried.

3.2 Thin Film Characterization

The pH of the electrolyte was measured at 5-minute time intervals during the electrodeposition process. The current density (J) through the electrolyte was monitored using KEITHLEY 2400 SMU. The crystalline structure and phase of Cu_2O were determined using an X-ray Diffractometer (Rigaku Ultima IV) with $\text{Cu-K}\alpha$ radiation, $\lambda=1.5406 \text{ \AA}$, in the 2θ range of $20 - 80$. The X'pert HighScore Plus Software was used to analyze the XRD data. The photo response of the fabricated thin films was observed by illuminating the ITO/ Cu_2O electrode with a 0.1 W/m^2 white-light source, 0.05M Na_2SO_4 as the electrolyte and Platinum plated glass plate as the counter electrode. Morphological analysis was carried out by Scanning Electron Microscopy (ZEISS EVO LS15) operated at 10.0 kV .

4. RESULTS & DISCUSSION

4.1 XRD Characterization

The 20 minutes electrochemically deposited thin films indicated prominent peaks at 2θ values of 29.14° , 35.98° , 41.89° , 61° , and 73.21° [4] peaks were identified for (110), (111), (200), (220), and (311) planes. The existence of Metallic Cu-crystals were not observed except (220) peak at 73.216° . Beyond 20 minutes of depositions, prominent peaks at 42.92° and 50.027° , were observed with the 73.21° peak which related to (111), (200), and (220) metallic-Cu crystal miller indices [3]. Copper (II) Oxide (CuO) crystals were also not observed in all the depositions. Also, there were no visible peak shifts due to the continued longer periods of electrodeposition.

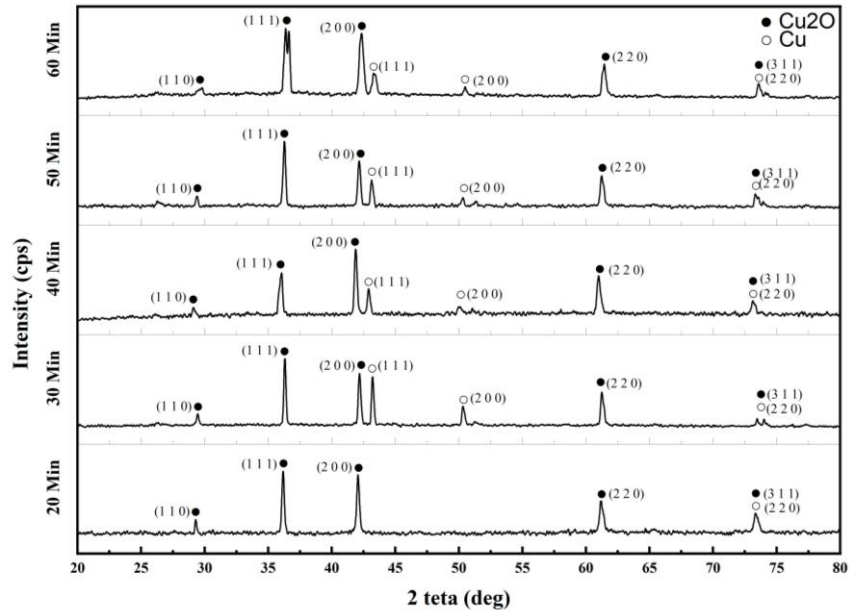


Figure 1: X-ray diffraction (XRD) patterns of Cu₂O thin films of deposition time 20 minutes, 30 minutes, 40 minutes, 50 minutes, and 60 minutes.

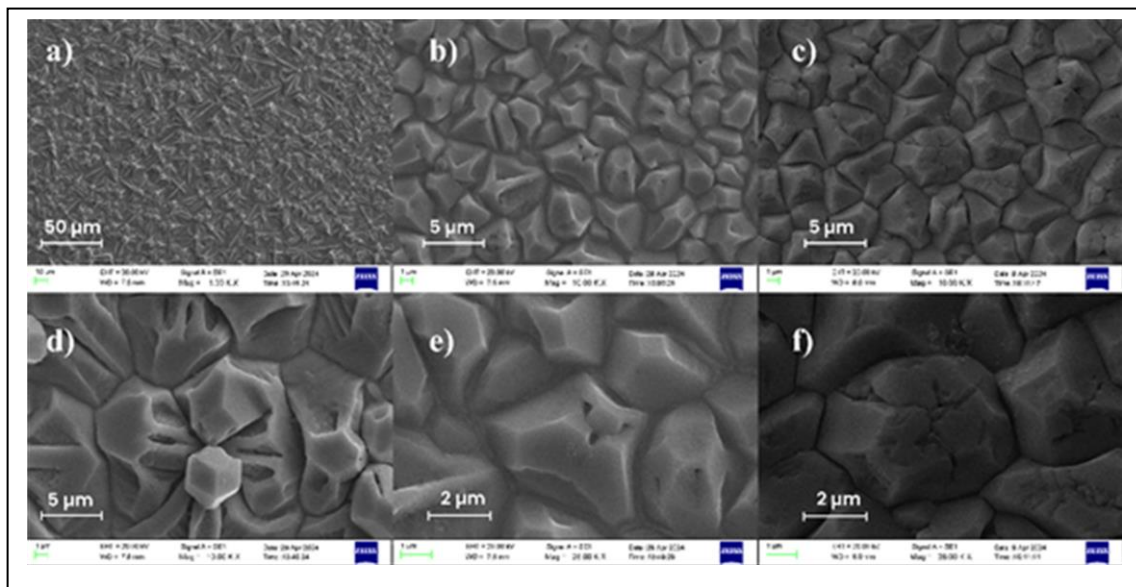


Figure 2: Scanning Electron Microscopic (SEM) images of electrodeposited Cu₂O a) 20 minutes at 1K \times , b) 40 minutes at 10K \times , c) 60 minutes at 10K \times , d) 20 minutes at 10K \times , e) 40 minutes at 25K \times , f) 60 minutes at 25K \times .

4.2 SEM Analysis

By the time of 20 minutes, the ITO glass can be seen fully covered with electrodeposited Cu₂O crystals (Fig 2. a,d)). A typical dendrite-like-crystal growth can be observed in nuclear sites (Fig 2.a). The crystal bodies were formed from four dendritic branches. Each single branch is spread as a dendrite branch and linked together to form crystals. These dendritic crystals develop into truncated/shortened octahedral crystals. The reason for the crystal to be truncated is that the acetate ions in

the buffer solution are preferentially adsorbing $\{1\ 1\ 1\}$ crystal planes slowing down the crystal growth along $\langle 1\ 1\ 1 \rangle$ direction normal to the substrate [5]. The highest number of particles were observed in the 30-35 μm range.

The mean distribution value obtained from the Gaussian curve was 30.154 μm . These crystals prefer lateral growth over increasing thickness/perpendicular growth. This is mainly happening due to the ITO substrates are much more conductive than semiconductive Cu_2O . Therefore, lateral growth is prominent when the crystals grow on ITO substrate.

Then a precursor with 40 minutes of deposition time was analyzed to observe the film formation, crystal growth, and crystal size variations and compare them with previous SEM images. The crystals were much smaller (mean value of 3.906) than the base layer of crystals. These crystal sizes were very similar to the crystal heads observed in base crystals. Cu_2O growth as a $\{1\ 0\ 0\}$ facets truncated octahedral grained structure film with full surface coverage was depicted in the (Fig 2. b)). When upper layers form on the base crystal layers, the nuclei with different orientations will form on the branched Cu_2O base crystal layer. Subsequently, every nucleus grows competitively, resulting in interpenetration and growth inhibition. This results in the formation of irregularly shaped crystalline structures.

When deposition proceeds long period, the (Fig 2. c)) evidence that the crystal grains are grown much perpendicular to the ITO substrate and the space between adjacent crystals got lesser and densely packed. The octahedral crystal structure was observed in both below 40 minutes and above 40 minutes. The most distinguishable observable is that cracks like defects can be seen on the crystals exceeding 40 minutes of deposition time. In magnification of 25K on the defect (Fig 2. f)), explains that they aren't cracks and they resulted because of the dissolving of the Cu_2O to the buffer solution [5],[6]. This is happening due to the deficiency of the Cu^{+2} ions in the electrolyte solution at some point of the deposition. Due to this reason, the dissolving of Cu_2O to Cu^{+2} ions will become dominant. The sudden decrement in photocurrent could be a result of the defect mentioned above.

4.3 Current (I) vs Time Variations Observations of Electrochemical Deposition

The current density vs time graph (Fig. 3) reflects that each deposition time (20 min, 30 min, ect), the starting current was in the range of 1 mAcm^{-2} to 2 mAcm^{-2} and becomes constant after 20-25 minutes at around 20 μAcm^{-2} range. The variation in the above time and current parameters are assumed to be due to small variations in the dipped area of the ITO glass in the electrolyte, variations in the resistivity of the ITO layers and resistance variations at the contacts and the temperature of the electrolyte.

The exponential decrement of the current implies the Heterogeneous Nucleation of Cu_2O on ITO substrate [4]. The resistance between the electrolyte and the ITO substrate

will increase due to the Cu_2O nucleation on ITO, as the surface coverage and growth of the semiconducting Cu_2O islets on ITO, during the first 20 minutes of the electrodeposition. The nucleation density is highly affected by the pH, substrate and temperature of the electrolyte. Therefore, it can be seen that slight changes in those factors can affect the first 20 minutes of current decreasing behavior. [14] After the 20 minutes, the micro-level current region reflects the slow growth of Cu_2O thin film thickness by depositing Cu_2O nanoparticles after the initial nucleation process. The reason for selecting the film deposition times from 20 minutes was that properly deposited firm film could be obtained only after the exponential current decrement ends.

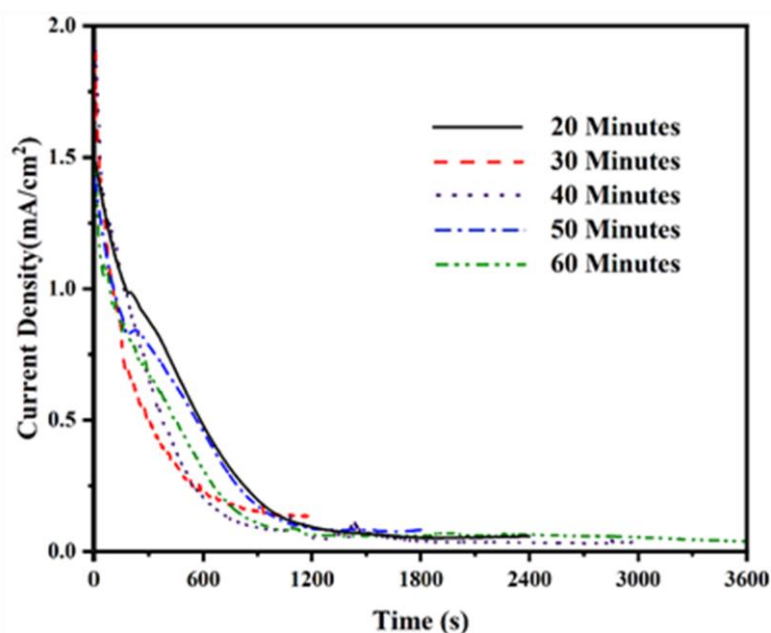


Figure 3: Electrochemical deposition Electrochemical deposition Current (I) vs time (s) for 10-minute time intervals by Source Meter SMU 2400.

4.4 pH vs Time variation Observations of Electrochemical Deposition

As shown in the (Fig. 4) the pH value of the electrolyte remained at a constant value of 5.6 pH from the start till for about 45 minutes (2700 s) of time period. At the end of 1 hour of electrodeposition, it can be seen that the final pH of the electrolyte came down to 5.4 pH from an initial value of 5.6 pH, increasing the acidity of the electrolyte.

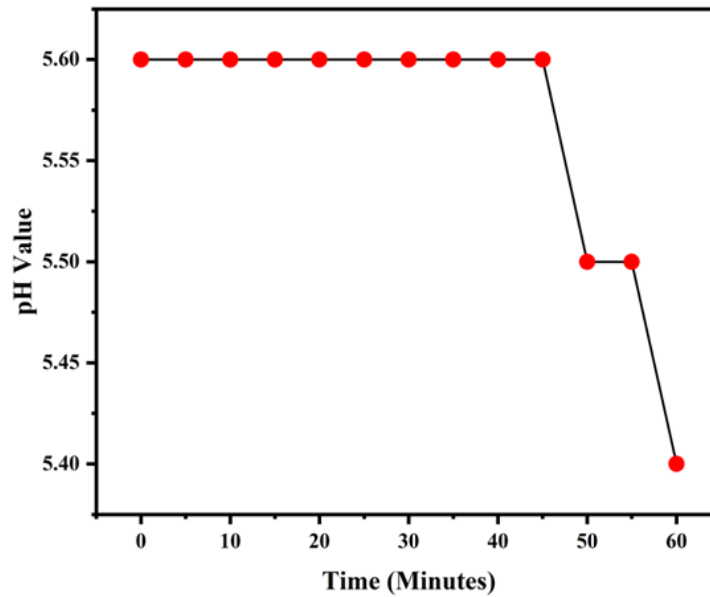
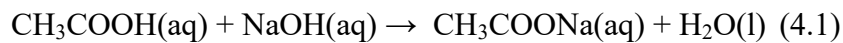


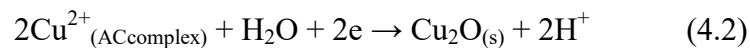
Figure 4: Graph of pH variation vs Time (Minutes) of the $\text{Cu}(\text{CH}_3\text{COO})_2$ electrolyte throughout the Electrodeposition.

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introduction of OH^- and Na^+ ions (in pH adjustment) into the medium generates $\text{Na}(\text{CH}_3\text{COO})$ and H_2O within the electrolyte by reacting with CH_3COOH (Acetic acid). The neutralization of acetic acid leads to pH adjustment (increment) to 5.6 pH [8]. The resulting solution will act as a 5.6 pH buffer solution with a weak acid (CH_3COOH) and its' salt $\text{Na}(\text{CH}_3\text{COO})$.



The electrochemical deposition of the process have been attributed to the electrochemical reduction of $\text{Cu}(\text{II})$ to $\text{Cu}(\text{I})$ with Cu_2O formation (Eq. (4.2)), and electrochemical reduction of $\text{Cu}(\text{II})$ to $\text{Cu}(\text{0})$ (Eq. (4.3)) onto the oxide film, respectively.



As the (Eq. (4.2)) reaction proceeds, the H^+ ion content that is produced in the electrolyte medium increases with time. So, the pH will show a decrease when it comes to longer periods.

4.5 Photo-current Transient Data

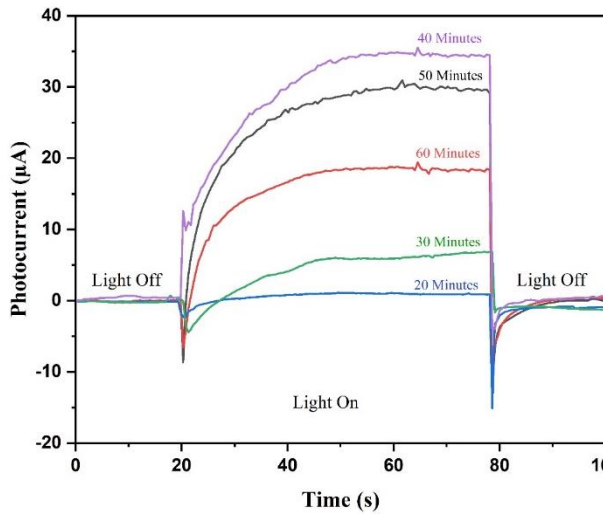


Figure 5: Photo-Current Density vs Time graph for 20, 30, 40, 50, 60 Minutes deposited Cu₂O thin films.

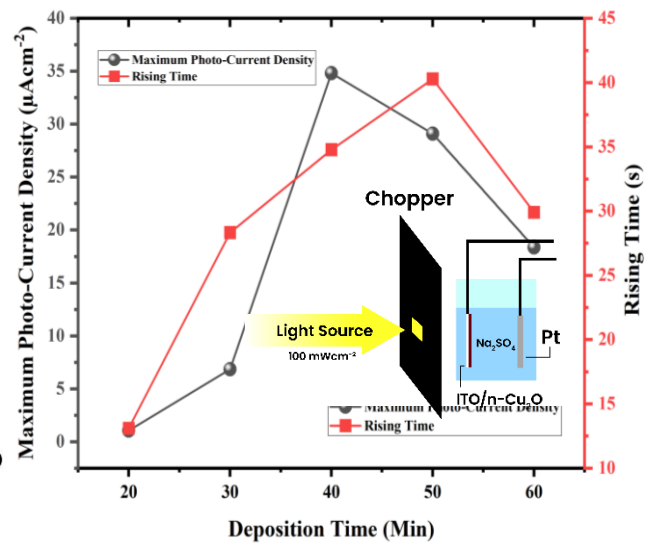


Figure 6: Maximum Photo-Current Density and Rising Time graph for 20, 30, 40, 50, 60 Minutes deposited Cu₂O thin films.

The photo-current transient data is shown in (Fig 5.) Even though, in the growth-time-varying samples, the rising time varies as 13.5s, 28.0s, 34.5s, 40.0s and 29.5s for 20 min, 30 min, 40 min, 50 min, and 60 min of deposition times respectively and the falling edge was found to be similar (< 0.5 s, within the limitations of the instrument). The maximum photo-current generated, and the rising time (shown in Fig 6.) was increased with the film deposition time up to 40 minutes deposited sample. However, it is interesting to note, even though the photo-current decrease for longer deposited sample, the rising time was increased up to the 50 min of deposition. The 50 and 60 minutes of deposition indicated a decreasing trend in photo current. The highest photo-current observed for ITO/Cu₂O/0.5M Na₂SO₄(Electrolyte)/Pt setup was 34.82 μAcm^{-2} for the 40 minutes of deposition period for 100mWcm⁻² intensity.

This decrement in photo-current can be attributed to the film thickness and increase of the trap levels due to the polycrystalline nature of the film. If the deposition layer thickness is considered to be increasing with deposition time, the resistance increment within the deposited material layer will help to recombine the generated electron-hole pairs instantly as they are generated [11],[12]. Suppose the deposition layer is dissolved after some level of thickness, after a specific deposition time due to decrement in the pH after 45 minutes of deposition time will also affect characteristics of the charge transfer process in the thin film, which are occurring from defects on the crystals. In that case, the resulting defects on the thin layer grains can hinder the electron exchange efficiency with the electrolyte [13]. The surface defects will be discussed in the SEM analysis section.

5. CONCLUSION

The low temperature electrodeposition of n-type Cu₂O nanocrystals was performed at different deposition periods while studying current density (J) and pH variation of the electrochemical deposition system. The distinguishable decrement in current density from around 1-2 mAcm⁻² to 20-30 μAcm⁻² reflects the Cu₂O thin layer formation leading to a major resistant increment which is commonly mentioned in studies. The pH variation of the electrochemical bath and photo-current characteristic trends of fabricated thin films indicated a decrement after 40 minutes of deposition. XRD results depict the resulting thin Cu₂O film was CuO-free but consisted of Cu crystals. Scanning Electron Microscope results answered the photo response drop evidencing the dissolving of grown Cu₂O crystals back into the electrolyte solution. As a conclusion, the ideal electrochemical deposition time was recognized as the near below 40 minutes.

6. ACKNOWLEDGMENT

The authors sincerely acknowledge the financial support provided by the University of Sri Jayewardenepura Research Council under the research grant “ASP/01/RE/SCI/2022/37.” Special thanks are extended to M.W.M.V. Wijesekara from the Department of Nano Science Technology, Faculty of Technology, Wayamba University of Sri Lanka, for his assistance in acquiring the XRD spectra. We also express our heartfelt gratitude to the Department of Physics, Open University Sri Lanka (OUSL), Nawala for providing the material characterization facilities.

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