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Electrochemical Fingerprint of CuS-Hexagonal Chemistry from (Bis(N-1,4-Phenyl-N-(4-Morpholinedithiocarbamato) Copper(II) Complexes) as Photon Absorber in Quantum-Dot/Dye-Sensitised Solar Cells

Mojeed Adedoyin Agoro ^{1,2,*} , Edson Leroy Meyer ^{2,*} , Johannes Zanoxolo Mbese ^{1,*} and Kwabena Manu ³

¹ Department of Chemistry, University of Fort Hare, Private Bag X1314, Alice 5700, South Africa

² Fort Hare Institute of Technology, University of Fort Hare, Private Bag X1314, Alice 5700, South Africa

³ Department of Computer Science, University of Fort Hare, Private Bag X1314, Alice 5700, South Africa; kwabeemanu@gmail.com

* Correspondence: magoro@ufh.ac.za (M.A.A.); emeyer@ufh.ac.za (E.L.M.); jmbese@ufh.ac.za (J.Z.M.); Tel.: +27-781246437 (M.A.A.); +27-792403201 (E.L.M.); +27-728385150 (J.Z.M.)

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Abstract: The main deficit of quantum dot/dye-sensitised solar cells (QDSSCs) remains the absence of a photosensitiser that can absorb the entire visible spectrum and increase electrocatalytic activity by enhancing the conversion efficiency of QDSSCs. This placed great emphasis on the synthesis route adopted for the preparation of the sensitiser. Herein, we report the fabrication of hexagonal copper monosulfide (CuS) nanocrystals, both hexadecylamine (HDA) capped and uncapped, through thermal decomposition by thermogravimetric analysis (TGA) and a single-source precursor route. Morphological, structural, and electrochemical instruments were used to assert the properties of both materials. The CuS/HDA photosensitiser demonstrated an appropriate lifetime and electron transfer, while the electron back reaction of CuS lowered the electron lifetime in the QDSSCs. The higher electrocatalytic activity and interfacial resistance observed from current density-voltage (I–V) results agreed with electrochemical impedance spectroscopy (EIS) results for CuS/HDA. The successful fabrication of hexagonal CuS nanostructures of interesting conversion output suggested that both HDA capped and uncapped nanocrystals could be adopted in photovoltaic cells.

Keywords: single-source precursor; quantum dots; photosensitiser; electrocatalytic; photovoltaic cells

1. Introduction

A main current challenge is the high rate of energy consumption and environmental degradation from the use of fossil fuels. Therefore, it is necessary to search for a new alternative that is not only environmentally friendly, but also a sustainable solution to the energy crisis [1]. Therefore, the need for clean, sustainable, and renewable energy has become a top priority. Various innovations, such as biomass, heat, solar energy, and fuel gas have been adopted for the conversion of energy to electricity [2–5]. In recent times, solar energy has emerged as a popular source of energy. This is because solar energy is clean, sustainable, and abundantly available across many regions of the world. Due to its abundant supply, solar cells, known as photovoltaic cells, are used to directly convert sunlight to electricity through the aid of photochemical and photoelectric effects, i.e., silicon-based cells and quantum-dot/dye-sensitised solar cells (QDSSCs). However, the use of photovoltaic cells remains a

challenge, as they are unable to produce large-scale energy for commercialisation [6,7]. The theoretical efficiency of 44% of QDSSCs as a result of multiple excitons has given them a strong edge over the Shockley–Queisser limit. This multiple-exciton generation accounts for the adoption of quantum dots (QDs), owing to their excellent attributes that include easy fabrication, size dependence, and a tunable band gap.

Due to this quality, QDSSCs are considered promising photovoltaic cells, evidenced by the high levels of research interest in this field [8–15]. This has emphasised the choice of semiconductors that could harvest the entire solar spectrum through their use as QD sensitisers. A major class of semiconductors consists of metal sulfide semiconductor-based photocatalysts that can alter size distribution without changing chemical constituents [16,17]. Copper monosulfide (CuS) has distinguished itself among metal sulfides owing to its different band gap and various morphologies. This makes CuS a hot-spot semiconductor material with great potential in the field of photocatalytic and photovoltaic applications [18–26]. Hexagonal covellite—CuS with a bandgap of ~2 eV and a p-type—enhances absorber abilities to cover the entire solar spectrum [18,19]. Furthermore, CuS absorbs the infrared area through plasmonic absorption emanating from copper valencies due to a high concentration of charge carriers [20,26,27]. Integration of CuS with TiO₂ can enhance photon-absorption properties to visible regions, leading to better conversion efficiency. The major challenge when integrating these elements is the synthesis of QD photosensitisers and deposition on a TiO₂-coated electrode. Deposition of the photosensitiser on the semiconductor electrode occurs via either *ex situ* or *in situ* routes [28,29].

In situ routes are solely electrochemical deposition, successive ionic-layer-adsorption reaction, and chemical-bath deposition, but cannot give accurate size distribution. *Ex situ* routes are direct adsorptions, molecular linker attachment, and electrophoretic deposition, and they separately fabricate the photosensitisers before injecting it with the coated electrode [15]. This study adopted the single-source-precursor route for the synthesis of QD sensitisers through the injection of HDA and oleic acid (OA) to influence their size, morphologies, and structural properties. Direct deposition was used to add the QD sensitisers on the coated electrode by immersing both in a solution for a period of time.

2. Results and Discussion

2.1. X-Ray Diffraction of Metal Sulfide Nanoparticles

The preferred crystal and crystallinity orientation of CuS/HDA and CuS sensitisers was studied through the XRD instrument. Figure 1 shows the diffraction configuration of the sensitisers. The XRD results of CuS/HDA agreed with atomic-force-microscopy (AFM) results, indicating good surface roughness. Crystalline purity and quality were displaced by the strong and sharp diffraction peaks observed in the samples. The observed XRD peaks were indexed by using space group 194: P6₃/mmc, producing the pure hexagonal covellite crystal structure phase of CuS. Additional XRD peaks emanated from the unreacted ions, but impurities were not observed. There were basically high-intensity diffraction peaks for CuS/HDA at 22.2°, 26.1°, 26.4°, 27.4°, 33.2°, 34.6°, 38.6°, 49.2°, 52.3°, 55.9°, 62.4°, 66.2°, 78.9°, and 81.1°. These peaks were related to lattice planes of (101), (102), (103), (008), (110), (108), and (116) (PDF 06-0464) as the hexagonal covellite CuS phase [30]. However, as shown in Figure 2, CuS revealed a nonstoichiometric mixed phase of the covellite as the main phase and could be indexed using JCPDS 06-0464. This indicated space group 194: P6₃/mmc and 62: Pnma, respectively, for CuS. Peak values observed at 2 θ equalled 16.3°, 21.9°, 22.7°, 23.4°, 25.9°, 26°, 30.2°, 32.1°, 35.8°, 39.8°, 41.7°, 43.1°, 46.4°, and 51°. These were related to the (101), (102), (103), (008), (110), (108), and (116) hexagonal CuS crystal [31]. The presence of these lower intensities and minor phases are usually linked to defect chemistry, and the thermodynamics of the solid and thermal gradient. This was caused by internal origins, as described elsewhere [32].

Figure 1. XRD spectra of (a) copper monosulfide (CuS)/HDA and (b) CuS nanoparticles.

Figure 2. SEM images of (a) CuS/HDA and (b) CuS nanoparticles.

2.2. SEM of Metal Sulfide Nanoparticles

SEM morphology for CuS/HDA and CuS is shown in Figure 2. The displayed SEM micrographs corresponded to hexagonal and spherical nanoparticles with agglomeration for both samples, exhibiting a reasonably smooth surface with little microspheres. The shapes displayed in the image implied that CuS had a good crystal structure that provided a more catalytic reduction of the HI-30 electrolyte, and supports previous reports by [33,34].

2.3. Atomic-Force Microscopy of Metal Sulfide Nanoparticles

The surface roughness of two photosensitiser films was evaluated by AFM, providing 3D and 2D images of CuS/HDA and CuS sensitizers (see Figure 3). The CuS/HDA and CuS films exhibited surface roughness in the ranges of 23.9–239 nm and 0.16–1.69 μm , respectively. AFM analysis revealed a smaller percentage for the CuS/HDA film than for the CuS films. The CuS film displayed good size roughness. These promoted electrocatalytic activity with the iodide redox electrolyte [35]. These results connoted that CuS/HDA film charge transfer resistance (R_{ct}) at the TiO_2 /iodide electrolyte interface could be very low. TiO_2 and CuS displaced higher roughness through better contact bonding. Results revealed more electrocatalytic activity for the CuS film on a TiO_2 surface, with good reaction with an HI-30 redox couple iodide electrolyte [36]. The conversion efficiency of the QDSSCs relied majorly on better material surface roughness. The improvement of surface roughness tended to improve the electrocatalytic performance of the system. Therefore, CuS on TiO_2 reduced surface resistivity, which connoted improved short circuit current (J_{sc}) and power-conversion efficiency [37].

Figure 3. Atomic-force-microscopy (AFM) images of: (a) CuS height profile; (b) CuS nanoparticles in 2D; (c) CuS nanoparticles in 3D; (d) CuS/HDA height profile; (e) CuS/HDA nanoparticles in 2D; and (f) CuS/HDA nanoparticles in 3D.

2.4. Cyclic-Voltammetry Results

The cyclic-voltammetry (CV) spectra for CuS/HDA and CuS photosensitisers, as seen in Figure 4, strongly displaced the irreversibility and reversibility attributes of both sensitiser. The shifting of redox peaks strongly exhibited the performance of the CuS/HDA sensitiser. At 50 mV/s, the reduction and oxidation peaks of CuS/HDA sensitiser were shifted in the corresponding directions. This was due to the expansion of the redox peaks by the inability of the materials to complete activation when a current was applied [38,39]. The highest-occupied-molecular-orbital (HOMO) levels and lowest-occupied-molecular-orbital (LUMO) levels were considered the most important developments for photosensitiser regeneration and electron injection. It has been reported that the enhancement of electron transfer is linked to LUMO conductivity bands and closeness. This connotes that there was sufficient mobility force from the LUMO levels to the conduction band of CuS/HDA [40–43]. The almost rectangular CV profile of CuS indicated ideal energy-storage behaviour. However, the presence of redox peaks (oxidation and reduction) observed within the scanned potential range of CuS, implied that the CuS nanostructure has a multilayer composite of higher reversibility and stability [44,45]. The nanostructured CuS photosensitiser could be further optimised to enhance electrical conductivity.

Figure 4. Cyclic-voltammetry (CV) spectra of (a) CuS/HDA and (b) CuS nanoparticles.

2.5. Electrochemical-Impedance Spectroscopy (EIS)

EIS plots (displayed in Figure 5) showed a typical semicircle at the high-frequency region and a straight line at the low-frequency region. EIS results of both CuS/HDA and CuS sensitizers showed similar trends to the obtained results from CV (see Figure 4). Series resistance (R_s) is displayed by the nonzero intercept of the real axis, indicating high frequency while the middle-frequency semicircle was attributed to the R_{ct} at the CE/electrolyte interface. We employed EIS to compare the R_{ct} between the HI-30 electrolyte and the photosensitizers. Both photosensitizers possessed good catalytic activity. The R_{ct} for CuS/HDA was much smaller compared to the R_{ct} of CuS, which connotes that CuS/HDA photosensitizer had excellent charge transfer at the interface of the electrolyte and the photanode. The recombination of electrons in TiO₂ with acceptors in the electrolyte is normally referred to as the electron lifetime. In this study, the electron recombination of CuS/HDA was effectively suppressed [46–50]. This indicated that the CuS/HDA sensitizer displayed a higher level of electrocatalytic activity compared to CuS [51], due to its high specific surface area and strong adhesion to fluorine-doped tin oxide (FTO). This result is in good agreement with the Bode plot (see Figure 6) and I-V (see Figure 7). The semicircle is also a well-established indication of R_{ct} [52–54].

Figure 5. Electrochemical-impedance-spectroscopy (EIS) spectra of CuS and CuS/HDA nanoparticles.

Figure 6. Bode plot spectra of (a) CuS and (b) CuS/HDA nanoparticles.

Figure 7. I–V curve characteristics of (a) CuS and (b) CuS/HDA nanoparticles.

2.6. Bode Plot of Metal Sulfide Nanoparticles

Figure 6 shows the Bode plots of the QDSSCs. The electron lifetimes were obtained from peak angular frequency (f_{max}). Moreover, the lower τ_n in CuS/HDA suggested that electrons had a longer lifetime than those of CuS, and that they were effectively transferred, resulting in higher J_{sc} and energy-conversion efficiency for CuS/HDA. J_{sc} increase resulted in good electrocatalytic activity and electron-transport behaviour. The CuS/HDA on TiO_2 remarkably decreased the recombination of photo-injected electrons with the redox electrolyte compared to CuS photosensitiser. CuS displayed very low electron lifetime as a result of an excess amount of CuS ions, which increased photoanode resistance and recombination for the electrolyte. This accounted for low fill factor (FF), and affected the performance of the CuS photosensitiser [55–60].

2.7. I–V Results

Table 1 and Figure 7 show the photocurrent-voltage I–V summary for cells of CuS/HDA and CuS. They compare I–V analysis on the basis of efficiency (%), open-circuit voltage (V_{oc}), FF, and J_{sc} . Efficiencies of 0.15% for CuS/HDA and 0.01% for CuS were revealed from the measurement. The CuS/HDA photosensitiser showed J_{sc} at 1.78 mA cm^{-2} , FF value at 0.1, and conversion efficiency at 0.15%, which is similar to the report by Kim *et al.*, [61], compared to that of the CuS cell (0.01%). The electrolyte interface suggested that recaptured holes could be the reason for low values in the J_{sc} and FF of CuS compared to those of CuS/HDA [61,62]. It is well known that enhancement in charge transfer at the CE/electrolyte interface reduces recombination rates, internal resistances, and concentration gradients in the electrolyte, resulting in a higher fill factor and J_{sc} [63]. The higher I–V characteristics depicted in CuS/HDA was linked to lower R_{ct} , increased electrocatalytic activity, and relatively higher surface roughness, as displayed in AFM, CV, and EIS [64].

Table 1. I–V characteristics of (a) CuS/HDA and (b) CuS nanoparticles. FF, fill factor.

Dye	Photoanode	Electrolyte	CEs	J_{SC} (mA/cm ²)	V_{OC} (mV)	FF	η (%)
CUS/HDA	TiO ₂	HI-30	Pt	1.78	0.877	0.1	0.15
CUS	TiO ₂	HI-30	Pt	0.64	0.068	0.3	0.01

3. Materials and Methods

3.1. Materials

All material solvents and complexes were purchased from Merck (Johannesburg, South Africa) and used without further purification, while the testing kits were purchased from Solaronix (Aubonne, Switzerland). The complete test kits containing FTO as glass substrate of TiO₂, platinum FTO, HI-30 electrolyte iodide, masks, gaskets, chenodeoxycholic acid (CDC), and hot seal were purchased from Solaronix. Water, OA, methanol, HDA and (*bis*(*N*-1,4-phenyl-*N*-(4-morpholinedithiocarbamate)copper(II) complexes) Merck (Johannesburg, South Africa).

3.2. Synthesis of CuS Nanoparticles with HDA Capping Agent

Nanoparticles were fabricated according to the literature method [65]. Then, 0.20 g (*bis*(*N*-1,4-phenyl-*N*-(4-morpholinedithiocarbamate)copper(II) complexes) was dissolved in 4 mL of OA and injected into 3 g of hot HDA at 360 °C. An initial temperature of 20–30 °C was attained for the mixture. The reaction was stabilised at 360 °C, and the process lasted for 1 h. When the temperature of the mixture dropped to 70 °C, this signified the completion of the process, and about 50 mL methanol was used to remove excess OA and HDA. Centrifugation was used to separate the flocculent precipitate, and redispersed with toluene. Low air pressure was used to remove the solvent, giving rise to the metal sulfides of CuS/HDA nanoparticles.

3.3. Synthesis of CuS Nanoparticles without HDA Capping Agent

Synthesis of CuS nanocrystals was obtained through the high-temperature thermal decomposition of (*bis*(*N*-1,4-phenyl-*N*-(4-morpholinedithiocarbamate)copper(II)) complexes according to [66] using a Perkin Elmer 4000 ThermoGravimetric Analyser. Approximately 25 mg of the complex was loaded into an alumina pan, and weight changes were recorded as a function of temperature for a 10 °C min^{−1} temperature gradient between 30 and 900 °C. A purge gas of flowing nitrogen at a rate of 20 mL min^{−1} was used. At temperatures between 360 and 900 °C, the complex end product was converted into residue, which was expected for the formation of CuS nanocrystals from the residue obtained from the TGA (Perkin Elmer 4000 ThermoGravimetric Analyser, San Jose, CA, USA).

3.4. Solar-Cell Fabrication and Assembly

QDSSCs were prepared with 2 × 2 cm FTO glass plates of platinum. TiO₂ electrodes were purchased from Solaronix with a 6 × 6 mm² active area of TiO₂ screen coated. Dye loading for sensitisation was done using 10 mL of warm water with CuS/HDA and CuS. Coadsorbents were added (coadsorbent/dye), and chenodeoxycholic acid (CDC) was used. The mediating solution was the commercial HI-30 electrolyte solution (Solaronix, Aubonne, Switzerland), with the content of iodide species at 0.05 M. The TiO₂ thin film was soaked into a solution of photosensitisers for 24 h. The two substrates, one coated with TiO₂ loaded with photosensitisers and the other with platinum, were held together using polyethylene and soldering iron. A syringe was used to inject the HI-30 electrolyte (iodide).

Characterisation and solar-cell conversion-efficiency (%) measurements were done using Equations (1)–(4) below. All substitutions were done following Equations (1)–(4).

$$J_{sc} = (I_{sc} \text{ (mA)})/(A \text{ (cm}^2)) \quad (1)$$

$$FF = (V_{max} \times J_{max})/(V_{oc} \times J_{sc}) \quad (2)$$

where FF is fill factor, and V_{oc} is an open circuit voltage; J_{sc} is a short circuit current density.

$$\eta \text{ (%) } = (V_{max} \times J_{max})/P_{in} \quad (3)$$

The above equation was adopted where P_{in} is a light intensity of 100 mW cm^{-2} .

$$\eta \text{ (%) } = (V_{oc} \times J_{sc} \times FF)/P_{in} \times 100\% \quad (4)$$

The final equation for overall conversion efficiency was derived from the following equation.

3.5. Characterisation

Electrochemical studies were carried out using Metrohm 85695 Autolab with Nova 1.10 software. A platinum electrode was adopted as a counter electrode, and TiO_2 as the anode. An HI-30 iodide electrode (Metrohm South Africa (Pty) Ltd) was used as a reference electrode. The CV was performed at scan rates between 0.05 and 0.35 V s^{-1} with an increment of 0.05 V s^{-1} . All experiments were performed at room temperature. EIS was carried out in the frequency range of 100 to 100 mHz . I-V parameters were collected through a Keithley 2401 source meter and a Thorax light power meter (RS Components (SA) South Africa). A Lumixo AM1.5 light simulator was employed, and the lamp was fixed at 50 cm high to avoid illumination outside of the working area. To avoid cell degradation, temperature was kept below 60°C , and light-power density was maintained at 100 mW cm^{-2} (AM1.0). An X-ray diffractometer (Cambridge, CB, United Kingdom) was employed to evaluate the structural pattern of the samples, and the diffraction structure was obtained between 10° and 90° at intervals of 0.05° . The surface roughness of the CuS and CuS/HDA FTO substrates was identified through the use of AFM (JPK NanoWizard II AFM, JPK Instruments, Berlin, Germany) at a scan rate of 0.8 Hz in contact mode. A field emission scanning electron microscope (FE-SEM) Zeiss Auriga SEM (Munich, Germany) outfitted with Smart SEM programming was utilised to study the morphological properties at a quickening voltage of 30 KV .

4. Conclusions

In summary, CuS and CuS/HDA QD photosensitisers were synthesised using single-source-precursor and direct-deposition techniques. The characterisation results confirmed that both samples had hexagonal nanostructures and interesting conversion output by CuS/HDA. Surface roughness improved the electrocatalytic performance of CuS/HDA on TiO_2 by reducing surface resistivity, which implied improved conversion efficiency. The CuS/HDA photosensitiser suggested appropriate lifetime and electron transfer compared to CuS, which demonstrated a lower electron lifetime. Higher electrocatalytic activity and interfacial resistance further cemented the CuS/HDA as a superior photosensitiser.

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