Impact of CuS counter electrode calcination temperature on quantum dot sensitized solar cell performance

Le Thi Ngoc Tu¹, Ha Thanh Tung²

¹Faculty of Natural Sciences, Dong Thap University, Dong Thap City, Viet Nam ²Faculty of Basic Sciences, Vinh Long University of Technology Education, Vinh Long City, Viet Nam

Article Info	ABSTRACT
Article history: Received Mar 02, 2023	In place of the commercial Pt electrode used in quantum sensitized solar cells, the low-cost CuS cathode is created using electrophoresis. High resolution scanning electron microscopy and X-ray diffraction were used to analyze the structure and morphology of structural cubic samples with diameters ranging from 40 nm to 200 nm. The conversion efficiency of solar cells is significantly impacted by the calcination temperatures of cathodes at 100 °C, 120 °C, 150 °C, and 180 °C under vacuum. The fluorine doped tin oxide (FTO)/CuS cathode electrode reached a maximum efficiency of 3.89% when it was calcined at 120 °C. Compared to other temperature combinations, CuS nanoparticles crystallize at 120 °C, which lowers resistance while increasing electron lifetime.
Revised Apr 20, 2023 Accepted Apr 30, 2023	
Keywords:	
CuS counter electrode Electrochemistry property Structure property	
	This is an open access article under the <u>CC BY-SA</u> license.

Corresponding Author:

Ha Thanh Tung Faculty of Basic Sciences, Vinh Long University of Technology Education 73, Nguyen Hue Road, Sward 2, Vinh Long City, Viet Nam Email: tunght@vlute.edu.vn

1. INTRODUCTION

Inorganic semiconductor quantum dots (QDs), which have an extremely high capacity to synthesize electrons for use in solar cells, have recently gained notoriety as such materials. CdS, CdSe, PbS, PbSe, and InP have all been used in quantum dot sensitized solar cells (QDSSCs) [1], [2]. In comparison to dye molecules, the QDs have a number of advantages, such as the capacity to change the bandgap energy by adjusting the particle size [3], a higher optical absorption coefficient [4], and the capacity to generate a large number of exciton pairs while absorbing photons. QDSSCs now have a lower conversion efficiency than dye-sensitized solar cells (DSSCs) [5]-[9].

Only a portion of the visible spectrum is absorbed by the amazing experiments [9]-[11] because they are all carried out on single QDs of CdS or CdSe. In bulk materials, CdS and CdSe in particular have absorption wavelengths of 550 nm and 705 nm, respectively. Both absorption wavelengths are considerably shorter than the aforementioned values at the scale of the QDs. The performance improvement was rather slight when the binding linker was employed after that. The peak of the absorption spectra must be extended as far into the visible light spectrum as feasible while limiting recombination and dark current in order to increase the performance of QDSSCs. Numerous groups have looked into the possibility of broadening the solar absorption spectrum by combining CdS/CdSe QDs; the yield is significantly larger than QDSSCs employing single QDs [12]-[15].

The counter electrode (CE), which absorbs electrons from the external circuit and the electrolyte through a redox process at the surface of the electrolyte and CE, was the subject of research because it is essential for enhancing the performance of QDSSCs. This research was focused on both the photoanodic electrode and CE.

BY SA

To maximize the electrochemical activity, conductivity, and surface area of CE with the electrolyte, a cathode must thus be very porous [16]. This will speed up, chemically stabilize, and lower the cost of the redox processes with the electrolytes.

For years, researchers have been hunting for CEs to replace the traditional CE Pt that can accomplish the aforementioned capabilities. Metal sulfide materials can replace Pt CEs and fulfill the necessary characteristics, according to research Mo₂S [17], NiS [18], FeS [19], CuS [20]-[22], and Cu₂S [12] are a few examples. Copper sulfide (CuS, Cu2S) is one of the materials in this category and is employed in more investigations than the others due to its band gap energy of 1.1-1.4 eV, strong electrochemical activity, and stability in polysulfide electrolyte [23]-[25]. Copper (brass) thin films with a thickness of a few micrometers are submerged in a sulfide electrolyte solution to create the CEs. This produces either a CuS thin film or a Cu₂S thin film, depending on the period of time, temperature, and surroundings. But if the copper brass is left in the electrolyte for a long time, it will keep deteriorating. Due to the high resistance created by this, the fill factor and open circuit potential are decreased, which lowers the efficiency of QDSSCs [23]-[25].

CuS is one of the materials with the most consistent electrochemical activity. Tachan's group and others have examined and made this electrode, and it has been used in QDSSCs with a high efficiency of 3% [26], demonstrating the material's promise. Nevertheless, CuS has not been investigated using a wide range of manufacturing techniques, nor has it been investigated how the electrochemical characteristics of the electrode and the conversion efficiency of solar cells are affected by the crystallization temperature of CuS film. This is also the rationale for our decision to investigate and create FTO/CuS cathode electrodes for solar cell manufacturing employing electrophoresis at various temperatures.

2. EXPERIMENTAL DETAILS

2.1. Materials

The substrate for the cathode electrode film is a thin sheet of fluorine-doped tin oxide (FTO) conductor with a low resistance of around 7 Ω /cm². These two sizes of commercial TiO₂ paste – at a wavelength of 400 nm as a light reflector and at a wavelength of 20 nm as a transmission layer – are utilized for the anode electrode. A full solar cell is created by joining two electrodes together with Meltonix 1170-25 (surlyn). When we do current and potential density measurements, electrochemical impedance measurements, and employ Na₂S₂O₃.5H₂O and Cu(NO₃)₂ bought from Sigma's firm, Germany, we use colloidal silver as the route of the front and rear of the solar cell. All of the substances listed above are 99.9% pure.

2.2. Fabricated processes

The technique used to create the photoanode electrode is described in the group's earlier article [27]. The commercial conductive glass, FTO (TEC7, Dyesol), was divided into several plates, each measuring 1.2 cm by 2 cm. The FTO plate was then drilled with two tiny holes, each measuring 1 mm in diameter, which were used to inject electrolyte solution. These bases were then processed as shown in Figure 1.

The polysulfide electrolyte solution, which employed in this work, has the oxidation-reduction pair S^2/Sn^2 . It was created by dissolving 1.2 g of Na₂S, 0.064 g of sulfur powder, and 0.149 g of potassium chloride in 10 ml of aqueous solution: methanol at a 7:3 ratio to produce a yellow. Finally, it was stored for preparation of quantum dot – sensitized solar cell.

The successive ionic layer adsorption and reaction (SILAR) technique was used to create this CE. The 4.69 g Cu(NO₃)₂ in 100 ml methanol solution was continuously stirred while the FTO substrate was submerged in it. Then, to generate a thin, black film, it was dipped into a solution of 12 g Na₂S in 100 ml of methanol/DI solvent (volume ratio 1). Finally, it was dried for 5 minutes at 120 °C.

2.3. Characterization

We used a high resolution surface scanning electromagnetic microscope (FESEM, SU820) for samples at different resolutions to analyze Geometric surface analysis of electrodes, Philips X-ray diffraction (XRD) spectroscopy, (PANalytical X'Pert) with CuK radiation to determine the structure of PbS crystals on the FTO film, allowing size calculation particles and lattice parameters, in order to study the properties of the cathode electrode. After putting the battery together, we calculated the current density and potential curves using the Keithley 2400 instrument and the SOLARENA sunshine simulation system, which allowed us to calculate the solar cells' conversion efficiency. Additionally, we use electrochemical impedance spectroscopy to measure and calculate the values of the resistances in the battery, including the resistances across the cathode surface with electrolyte to assess cathode activity. This allows us to better understand the electron transfer processes through the cathode.

3. RESULTS AND DISCUSSION

The CuS counter electrode is seen in high resolution scanning electron microscopy images in Figure 1 at various resolution levels. In general, the film's surface is quite porous, making it ideal for the electrode's electrochemical activity. The porous surface leaves a lot of empty spaces, making it easier for the polysulfide electrolyte system to come into direct contact with the CuS nanoparticles and carry out the electrochemical reaction. The electrolyte system's electron exchange. The CuS nanoparticles were found to range in size from 40 nm to 200 nm, and they were extremely uniformly shaped like square or rectangular blocks. It is shown that the electrophoresis-created film is extremely stable.



Figure 1. FESEM of FTO/CuS film was calcinted at 120 $^{\circ}C$ in vacuum environment with 100 nm, 1 μ m, and 10 μ m resolution

By using electrophoresis to create a strong adhesion layer, the CuS electrode is created. To stop the formation of CuO, the film is crystallized in a vacuum. As a result, we first need to ascertain the structure of CuS in order to use it as electrodes. The CuS electrode's ray diffraction spectrum in a vacuum at 120 °C is shown in Figure 2, together with the CuS film's and the FTO substrate's distinctive diffraction peaks. The lattice planes with the Miller indices (103) and (108) that correspond to the diffraction peaks at locations 43.4° and 48.7° fit well with the standard JCPDS 79-2321 of the face-centered cubic structure. Also, this outcome is entirely compatible with the findings of the research group Varma *et al.* [28], Yang *et al.* [29], and Shyju *et al.* [30]. The CuS face-centered cubic's distinctive peak is the plane (200).

After examining the electrode's structural and morphological characteristics, we join the cathode electrode to the anode using a material that has been assuredly heated to more than 100 °C. Finally, we pump the electrolyte and measure it. The short circuit current density (J_{sc}), open circuit potential (V_{oc}), fill factor, and conversion efficiency of QDSSCs are all determined using current and voltage density curves. Figure 3 depicts the characteristic curves, and Table 1 displays the determined values of the parameter. Figure 3 shows that the electrode heated to 120 °C has the highest current density (18 mA/cm²) and the biggest open circuit potential (0.569 V), resulting in a very high conversion efficiency of 3.89%. The conversion efficiency of this study is greater than that of Zhang *et al.* [31] investigations (1.75%), Tachan and co-workers' studies (3%) [26], and Yang and co-workers' studies (3.91%) [29]. The achieved efficiency is substantially lower, 2.49%, 2.29%, and 1.89%, for the CuS cathode electrode heated at 100 °C, 150 °C, and 180 °C, respectively. Thus, it is clear that a critical factor in the formation of CuS crystals on the FTO substrate is the temperature. This temperature has a significant impact on the electrochemical characteristics of the cathode electrode, which in turn affects the current density in cells and the functionality of QDSSCs.

The kinetics of charge carriers in solar cells and the electrochemical characteristics of cathode electrodes are investigated using electrochemical impedance spectroscopy. After measuring the solar cells and obtaining the experimental electrochemistry impedance spectrum (EIS) from Figure 4, we fit and calculated the resistance values of QDSSCs using the specialized software Autolab, such as: the values for R_{ct1} is shown in Table 1. R_{ct1} is the resistance of excited electrons that are transported via the cathode and cathode surface with polysulfide electrolyte. The EIS of QDSSCs that were created using cathode electrodes heated at various temperatures in a vacuum environment is shown in Figure 4. The cathode heated to 120 °C has the lowest R_{ct1} resistance (11.2 Ω), compared to the cathodes heated to 100 °C (200.1 Ω), 150 °C (79.5 Ω), and 180 °C (699 Ω). Figure 4 illustrates this relationship between semi-circle size and resistance values. This outcome can be explained by the fact that CuS film on FTO crystallized more precisely at 150 °C than it did at other heating temperatures. Moreover, as shown by the XRD data, all films were calcined under vacuum to

prevent Pb from being oxidized to create CuO. Consequently, it can be said that the speed at which electrons travel through the CuS layer and over the surface of PbS with the S^{2}/S_n^{2} electrolyte increases with decreasing R_{ct1} resistance value. The efficiency of the cells for the cathode heated at 120 °C is the highest due to its maximum current density, and this result is entirely compatible with the results of the current and potential curve measurements of QDSSCs. This outcome is also entirely compatible with the findings of Zhang et al. [31], who examined CuS electrode film formation time, and compared it to Pt electrode results [28].





Figure 2. XRD of CuS cathode was heated at 120 °C in vacuum environment for 1 hour



Figure 5 shows the bode spectrum, which was obtained using electrochemical impedance spectroscopy and used to calculate the lifespan of the excited electrons and their capacity for recombination in the PbS film's conduction band. The formula connects this to the minimal frequency, $\tau_{max} = \frac{1}{2\pi f_{min}}$, Table 1 displays the calculation results for electrodes heated for one hour at 100 °C, 120 °C, 150 °C, and 180 °C in a vacuum atmosphere. According to Table 1, when two cathode electrodes are heated to 120 °C, 150 °C, and 1800 °C, respectively, the lifetime of charges is the highest (197 ms and 189 ms), and subsequently it is halved (119.1 ms). Due to the PbS crystals' poor crystallization, the electrode is heated to a temperature of 100 °C for a brief period of time (80.1 ms). The observed current density is larger than that of other electrodes because the longer the lifetime, the less probable it is that the electron would recombine with the hole in the material's valence band. This result is in perfect agreement with the findings of current and potential density (J-V) curve measurements as well as the results of X-ray diffraction (CuS crystals crystallize most ideally at 120 °C).

Table 1. The electrochimical parameters of QDSSCs Fill factor (FF) Efficiency (%) $R_{ct1}(\Omega)$ (mA/cm^2) V_{oc} (V)



Figure 4. EIS of ODSSCs based on different cathodes

Z' (Ohm)

Figure 5. Bode plots of ODSSCs with different cathodes

Frequency (Hz)

4. CONCLUSION

Electrophoresis is used to create a CuS cathode electrode, with the voltage being varied by calcination temperatures. Due to the film's superior performance and reduced cost, it is utilized to replace commercial Pt electrodes. This allowed for the effective fabrication of the CuS nanofilm on the FTO conductive substrate. The resulting film features a face-centered cubic structure, excellent crystallinity (XRD), and rather uniform particle size (FESEM). We note the current density and efficiency performance obtained the greatest of 18 mA/cm² and 3.89% using CuS cathode electrode at 120 °C when compared to other heating temperatures based on the results of measuring current density and potential. Also, this outcome was better than those of other study teams. The electrochemical impedance spectroscopy, or the bode spectrum, is another method used to describe the performance's outcomes. The outcomes shown that the CuS film was calcined at 150 °C for flawless crystallization, resulting in fewer crystal lattice defects, fewer recombination processes by the minimum R_{ct1} resistance (119.1 Ω), and a long lifetime (197 ms).

REFERENCES

- A. Zaban, O. I. Mićić, B. A. Gregg, and A. J. Nozik, "Photosensitization of nanoporous TiO2 electrodes with InP quantum dots," *Langmuir*, vol. 14, no. 12, pp. 3153-3156, 1998, doi: 10.1021/LA9713863.
- [2] P. Yu, K. Zhu, A. G. Norman, S. Ferrere, A. J. Frank, and A. J. Nozik, "Nanocrystalline TiO2 solar cells sensitized with InAs quantum dots," *Journal of Physical Chemistry B*, vol. 110. no. 50, pp. 25451-25454, 2006, doi: 10.1021/jp064817b.
- [3] W. W. Yu, Y. A. Wang, and X. Peng, "Formation and stability of size-, shape-, and structure-controlled CdTe nanocrystals: ligand effects on monomers and nanocrystals," *Chemistry of Materials*, vol. 15, no. 22, pp. 4300-4308, 2003, doi: 10.1021/cm034729t.
- M. C. Beard, "Multiple exciton generation in semiconductor quantum dots," *Journal of Physical Chemistry Letters*, vol. 2, no. 11, pp. 1282-1288, 2011, doi: 10.1021/jz200166y.
- [5] J. Fang, J. Wu, X. Lu, Y. Shen, and Z. Lu, "Sensitization of nanocrystalline TiO2 electrode with quantum sized CdSe and ZnTCPc molecules," *Chemical Physics Letters*, vol. 270, no. 1-2, pp. 145-151, 1997, doi: 10.1016/S0009-2614(97)00333-3.
- [6] W. Lee *et al.*, "Spectral broadening in quantum dots-sensitized photoelectrochemical solar cells based on CdSe and Mg-doped CdSe nanocrystals," vol. 10, no. 11, pp. 1699-1702, 2008, doi: 10.1016/j.elecom.2008.08.025.
- [7] D. Liu and P. V. Kamat, "Photoelectrochemical behavior of thin cadmium selenide and coupled titania/cadmium selenide semiconductor films," *Journal of Physical Chemistry*, vol. 97, no. 41, pp. 10769-10773, 1993, doi: 10.1021/J100143A041.
- [8] L. M. Peter, D. J. Riley, E. J. Tull, and K. G. U. Wijayantha, "Photosensitization of nanocrystalline TiO 2 by self-assembled layers of CdS quantum dots," *Chemical Communications*, no. 10, pp. 1030-1031, 2002, doi: 10.1039/B201661C.
- [9] R. Vogel, K. Pohl, and H. Weller, "Sensitization of highly porous, polycrystalline TiO2 electrodes by quantum sized CdS," *Chemical Physics Letters*, vol. 174, no. 3-4, pp. 241-246, 1990, doi: 10.1016/0009-2614(90)85339-E.
- [10] I. M. -Seró *et al.*, "Factors determining the photovoltaic performance of a CdSe quantum dot sensitized solar cell: the role of the linker molecule and of the counter electrode," *Nanotechnology*, vol. 19, no. 42, 2008, doi: 10.1088/0957-4484/19/42/424007.
- [11] Y. -J. Shen, and Y. -L. Lee, "Assembly of CdS quantum dots onto mesoscopic TiO2 films for quantum dot-sensitized solar cell applications," *Nanotechnology*, vol. 19, no. 4, 2008, doi: 10.1088/0957-4484/19/04/045602.
- [12] Y. -L. Lee and Y. -S. Lo, "Highly efficient quantum-dot-sensitized solar cell based on co-sensitization of CdS/CdSe," Advanced Functional Materials, vol. 19, no. 4, pp. 604-609, 2009, doi: 10.1002/adfm.200800940.
- [13] Q. Zhang et al., "Application of carbon counterelectrode on CdS quantum dot-sensitized solar cells (QDSSCs)," Electrochemistry Communications, vol. 12, no. 2, pp. 327-330, 2010, doi: 10.1016/j.elecom.2009.12.032.
- [14] P. Sudhagar et al., "The performance of coupled (CdS: CdSe) quantum dot-sensitized TiO2 nanofibrous solar cells," *Electrochemistry Communications*, vol. 11, no. 11, pp. 2220-2224, 2009, doi: 10.1016/j.elecom.2009.09.035.
- [15] Z. Yu et al., "Highly efficient quasi-solid-state quantum-dot-sensitized solar cell based on hydrogel electrolytes," Electrochemistry Communications, vol. 12, no. 12, pp. 1776-1779, 2010, doi: 10.1016/j.elecom.2010.10.022.
- [16] S. Wang and J. Tian, "Recent advances in counter electrodes of quantum dot-sensitized solar cells," *RSC Advances*, vol. 6, no. 93, pp. 90082-90099, 2016, doi: 10.1039/C6RA19226B.
- [17] C. K. Kamaja, R. R. Devarapalli, Y. Dave, J. Debgupta, and M. V. Shelke, "Synthesis of novel Cu2S nanohusks as high performance counter electrode for CdS/CdSe sensitized solar cell," *Journal of Power Sources*, vol. 315, pp. 277-283, 2016, doi: 10.1016/j.jpowsour.2016.03.027.
- [18] H. -J. Kim *et al.*, "Highly efficient solution processed nanorice structured NiS counter electrode for quantum dot sensitized solar cells," *Electrochimica Acta*, vol. 127, pp. 427-432, 2014, doi: 10.1016/j.electacta.2014.02.019.
- [19] H. Chen, L. Zhu, H. Liu, and W. Li, "Efficient iron sulfide counter electrode for quantum dots-sensitized solar cells," *Journal of Power Sources*, vol. 245, pp. 406-410, 2014, doi: 10.1016/j.jpowsour.2013.06.004.
- [20] C. J. Raj, K. Prabakar, A. D. Savariraj, and H. -J. Kim, "Surface reinforced platinum counter electrode for quantum dots sensitized solar cells," *Electrochimica Acta*, vol. 103, pp. 231-236, 2013, doi: 10.1016/j.electacta.2013.04.016.
- [21] N. Balis, V. Dracopoulos, K. Bourikas, and P. Lianos, "Quantum dot sensitized solar cells based on an optimized combination of ZnS, CdS and CdSe with CoS and CuS counter electrodes," *Electrochimica Acta*, vol. 91, pp. 246-252, 2013, doi: 10.1016/j.electacta.2013.01.004.
- [22] W. Zheng and S. Zhang, "The effect of CuS counter electrode microtopography on the properties of quantum dot sensitized solar cells," *Inorganic Chemistry Communications*, vol. 122, 2020, doi: 10.1016/j.inoche.2020.108294.
- [23] G. S. Selopal *et al.*, "Highly stable colloidal "giant" quantum dots sensitized solar cells," *Advanced Functional Materials*, vol. 27, no. 30, 2017, doi: 10.1002/adfm.201701468.
- [24] S. Jiao *et al.*, "Band engineering in core/shell ZnTe/CdSe for photovoltage and efficiency enhancement in exciplex quantum dot sensitized solar cells," ACS Nano, vol. 9, no. 1, pp. 908-915, 2015, doi: 10.1021/nn506638n.
- [25] J. -Y. Kim *et al.*, "Highly efficient copper-indium-selenide quantum dot solar cells: suppression of carrier recombination by controlled ZnS overlayers," *ACS Nano*, vol. 9, no. 11, pp. 11286-11295, 2015, doi: 10.1021/acsnano.5b04917.
- [26] Z. Tachan, M. Shalom, I. Hod, S. Rühle, S. Tirosh, and A. Zaban, "PbS as a highly catalytic counter electrode for polysulfidebased quantum dot solar cells," *Journal of Physical Chemistry C*, vol. 115, no. 13, pp. 6162-6166, 2011, doi: 10.1021/jp112010m.

- [27] T. P. Nguyen, T. T. Ha, T. T. Nguyen, N. P. Ho, T. D. Huynh, and Q. V. Lam, "Effect of Cu2+ ions doped on the photovoltaic features of CdSe quantum dot sensitized solar cells," *Electrochimica Acta*, vol. 282, pp. 16-23, 2018, doi: 10.1016/j.electacta.2018.06.046.
- [28] C. V. T. -Varma, S. S. Rao, K. D. Ikkurthi, S. -K. Kim, T. -S. Kang, and H. -J. Kim, "Enhanced photovoltaic performance and morphological control of the PbS counter electrode grown on functionalized self-assembled nanocrystals for quantum-dot sensitized solar cells via cost-effective chemical bath deposition," *Journal of Materials Chemistry C*, vol. 3, no. 39, pp. 10195-10206, 2015, doi: 10.1039/C5TC01988E.
- [29] Y. Yang et al., "Composite counter electrode based on nanoparticulate PbS and carbon black: towards quantum dot-sensitized solar cells with both high efficiency and stability," ACS Applied Materials & Interfaces, vol. 4, no. 11, pp. 6162-6168, 2012, doi: 10.1021/am301787q.
- [30] T. Shyju, S. Anandhi, R. Sivakumar, and R. Gopalakrishnan, "Studies on lead sulfide (PbS) semiconducting thin films deposited from nanoparticles and its NLO application," *International Journal of Nanoscience*, vol. 13, no. 1, 2014, doi: 10.1142/S0219581X1450001X.
- [31] J. B. Zhang, F. Y. Zhao, G. S. Tang, and Y. Lin, "Influence of highly efficient PbS counter electrode on photovoltaic performance of CdSe quantum dots-sensitized solar cells," *Journal of Solid State* Electrochemistry, vol. 17, pp. 2909-2915, 2013, doi: 10.1007/s10008-013-2210-4.

BIOGRAPHIES OF AUTHORS



Le Thi Ngoc Tu **D** S S C received the PhD degree in physics from University of Science, Vietnam National University Ho Chi Minh City, Vietnam, she is working as a lecturer at the Faculty of Natural Sciences Teacher Education, Dong Thap University, Vietnam. Her research interests focus on photoacalyst materials. She can be contacted at email: ltntu@dthu.edu.vn.



Ha Thanh Tung C received the PhD degree in physics from University of Science, Vietnam National University Ho Chi Minh City, Vietnam, he is working as a lecturer at the Faculty of Basic Sciences, Vinh Long University of Technology Education, Vietnam. His research interests focus on developing the patterned substrate with micro- and nano-scale to apply for physical and chemical devices such as solar cells, OLED, photoanode. He can be contacted at email: tunght@vlute.edu.vn.