Advancing Photovoltaic Performance in Quantum Dot-Sensitized Solar Cells through Sulfur-Enhanced CdS Quantum Dots and Innovative Material Engineering

N. F. Ajward, J. V. P. Fernando & V. P. S. Perera

Department of physics, The Open University of Sri Lanka

nf2010.ajward@gmail.com

1. ABSTRACT

Quantum Dot-Sensitized Solar Cells (QDSSCs) offer an innovative solution to the global energy crisis, with advantages such as broad visible spectrum absorption, tunable band gaps, and multiple exciton generation (MEG), surpassing efficiency limits. This study investigates the impact of sulfur doping on the photovoltaic performance of Quantum Dot-Sensitized Solar Cells (QDSSCs) using CdS-based quantum dots. Sulfur doping enhances light absorption, charge transport, and overall efficiency of QDSSCs. The research focuses on optimizing sulfur concentrations, with the best performance achieved in sample with 1 mole of sulfur, which exhibited a 7.8% increase in voltage, an 84.5% rise in current density, and a 98.5% efficiency boost compared to the control sample 0 moles. The Incident Photon-to-Current Efficiency (IPCE) spectrum for sample with 1 mole, peaks in the 610–670 nm range, aligning well with the solar spectrum. The results highlight the potential of sulfur-doped QDSSCs as a cost-effective and scalable alternative to traditional solar technologies, offering improved light-to-electricity conversion efficiency and suggesting further optimization for enhanced performance.

Key words: Quantum Dot-Sensitized Solar Cells (QDSSCs), Sulfur Doping, Cadmium Sulfide, SILAR, Photovoltaic Performance

2. INTRODUCTION

Solar cells, as optoelectronic devices, are pivotal in addressing the global energy crisis by converting sunlight into electrical power. Among various solar technologies, sensitized solar cells, such as Dye-Sensitized Solar Cells (DSSCs) and quantum dot-sensitized solar cells (QDSSCs), have emerged as promising alternatives due to their distinctive properties. QDSSCs, in particular, stand out for their broad photo response in the visible spectrum, tunable band gaps determined by the size of Quantum Dots (QDs), and high extinction coefficients, allowing efficient light absorption. Moreover, QDSSCs exhibit Multiple Exciton Generation (MEG), a phenomenon enabling the production of multiple excitons from a single photon, which has the potential to exceed the Shockley-Queasier efficiency limit. [1,2,3,4,5] These attributes, combined with their scalability

and straightforward fabrication processes, make QDSSCs an attractive solution for cost-effective and efficient solar energy conversion.

A fundamental component of QDSSCs is titanium dioxide (TiO_2), which serves as the electron transport layer. TiO_2 facilitates the effective transfer of photogenerated electrons from quantum dots to the external circuit, ensuring efficient charge separation. Its large surface area allows a higher quantum dot loading, enhancing light absorption, while its chemical stability ensures long-term device durability. Ongoing research seeks to optimize the properties of TiO_2 such as crystallinity, morphology, and electronic structure to improve both efficiency and stability, solidifying its role in the advancement of QDSSCs for sustainable energy generation. [6,7]

Quantum dots, including CdS, CdSe, PbS, PbSe, and InAs, are integral to QDSSCs due to their tunable optical and electronic properties. The size-dependent band gap of QDs allows customization for optimal solar spectrum utilization, while their inherent dipole moments and MEG capabilities further enhance device performance. QDs also enable theoretical efficiency limits as high as 44%, far surpassing the 33% limit of traditional thin-film solar cells. Methods like Chemical Bath Deposition (CBD) and Successive Ionic Layer Adsorption and Reaction (SILAR) have proven effective in depositing QDs onto TiO_2 electrodes, promoting strong interfacial bonding and efficient charge transfer. [8,9]

In this study, we explore the potential of TiO_2-based quantum dot-sensitized solar cells (QDSSCs) sensitized with CdS quantum dots. Sulfur was introduced into the Na_2S solution during the preparation of TiO_2/CdS QDSSCs to enhance performance by improving light absorption and charge transport. This study investigates further innovations to optimize QDSSCs for scalable, sustainable energy solutions. The findings underscore the potential of QDSSCs to surpass conventional solar technologies, offering a path to affordable and efficient renewable energy**.**

3. EXPERIMENTAL DETAILS

3.1 Preparation of TiO_2 plates

TiO_2 paste was prepared by mixing 0.25 g of TiO_2 with 1 ml of 0.1 M HNO_3, one drop of Triton X-100, and one drop of PEG1000, followed by grinding the mixture for 30 minutes using a mortar and pestle. The paste was then applied to pre-cleaned conducting tin oxide (CTO) glass plates (1.0 cm × 2.0 cm) using the doctor blade method. The CTO plates were cleaned in an ultrasonic bath with detergent and distilled water to ensure surface purity. After coating, the TiO_2 films were dried on a hot plate and sintered in a furnace at 450 °C for 45 minutes to achieve the desired properties.

3.2 Preparation of Na_2S and $CdCl_2$ solutions in various concentration

The experiment involved accurately measuring 10.065 g of $CdCl_2$ and 3.902 g of Na_2S using an electronic balance with a precision of ±0.001 g. These compounds were dissolved in 100 mL of distilled water to prepare a 0.5 M solution of Cd^{2+} and S^{2-} ions and the pH of the solution was adjusted to the optimal value of 4.5 by adding 0.01 M NaOH and 0.01 M HCl solutions dropwise, with continuous monitoring to achieve the desired pH**.** [10]

3.3 Preparation of Na_2S solution with S

Sulfur (S) was added in various molar concentrations to a 0.5M Na_2S solution, as specified in the table, and the mixture was stirred for up to 1 hour. This prepared solution was then used in the successive ionic layer adsorption and reaction (SILAR) method to coat TiO_2 plates. Table:1

Table 1: Mass (grams) and Moles of Sulfur (S) in Each Sample (S1 to S7)

Sample number	S1	S2	S3	S4	S5	S6	S7
Moles	0.125	0.25	0.5	1	1.5	2	0
Mass(g)±0.001 g	0.0176	0.0352	0.0705	0.1410	0.2115	0.2820	0

3.4 Deposition of CdS using SLILAR method.

The SILAR technique was utilized to deposit CdS films onto TiO_2 photoanodes. Each immersion in $CdCl_2$ and Na_2S solutions was maintained for one minute. Following each immersion, the photoanodes were rinsed with distilled water to eliminate excess reagents and then air-dried. To achieve uniform film deposition, the photoanodes were alternately immersed in the complementary precursor solution (cationic or anionic), followed by another rinsing and drying step. This process was repeated ten times to form a multilayer CdS film. Finally, the coated photoanodes were heated at 80°C on a hot plate for 30 minutes to improve the film's adhesion and stability on the substrate.

3.5 Preparation of Electrolyte

In preparation of 2 ml of electrolyte, 0.130 g of Na_2S, 0.128 g of sulfur, and 0.030 g of KCl were dissolved in a solvent mixture comprising 1.4 ml of methanol and 0.6 ml of distilled water. The solution was stirred for 3 hours using a magnetic stirrer to achieve complete dissolution of the salts. Adjustments to the stirring time may be necessary to prevent sulfur precipitation.

3.6 Fabrication of the cell

A counter electrode with a conductive side positioned directly on the CdS-coated TiO_2 film and held in place using clamps. The space between the electrodes was filled with the prepared electrolyte solution, completing the assembly of the Quantum Dot Sensitized Solar Cell (QDSSC).

3.7 Characterization

The fabricated QDSSCs characterized using a VK-PA-100 PV Power Analyzer to obtain J-V curves, enabling the extraction of critical performance metrics such as Photo Conversion Efficiency (PCE), Photo Current Density (Jsc), Photo Voltage (Voc), and Fill Factor (FF). To ensure reproducibility, at least five devices per batch were tested.

Electrochemical Impedance Spectroscopy (EIS) was employed using a frequency response analyzer (AutoLab Nova 2.1) to study the charge transport and recombination processes within the CdS QDSSCs. Impedance spectra measured over a frequency range of 0.1 Hz to 1 MHz under constant simulated light intensity at room temperature, providing insights into interfacial charge transfer resistance and recombination dynamics. These findings are vital for optimizing the QDSSC performance.

Incident Photon-to-Current Efficiency (IPCE) measurements will assess the light-harvesting efficiency of the QDSSCs across the solar spectrum. The effectiveness of the quantum dots in capturing sunlight and converting it into photocurrent will be evaluated using a VK-IPCE-10 system.

4. RESULTS AND DISCUSSION

4.1 I–V Characteristics of CdS QDSSCs

The figure 1 illustrates the impact of varying sulfur (S) concentrations on the performance of quantum dot-sensitized solar cells (QDSSCs), shown through their current-voltage (I-V) characteristics.

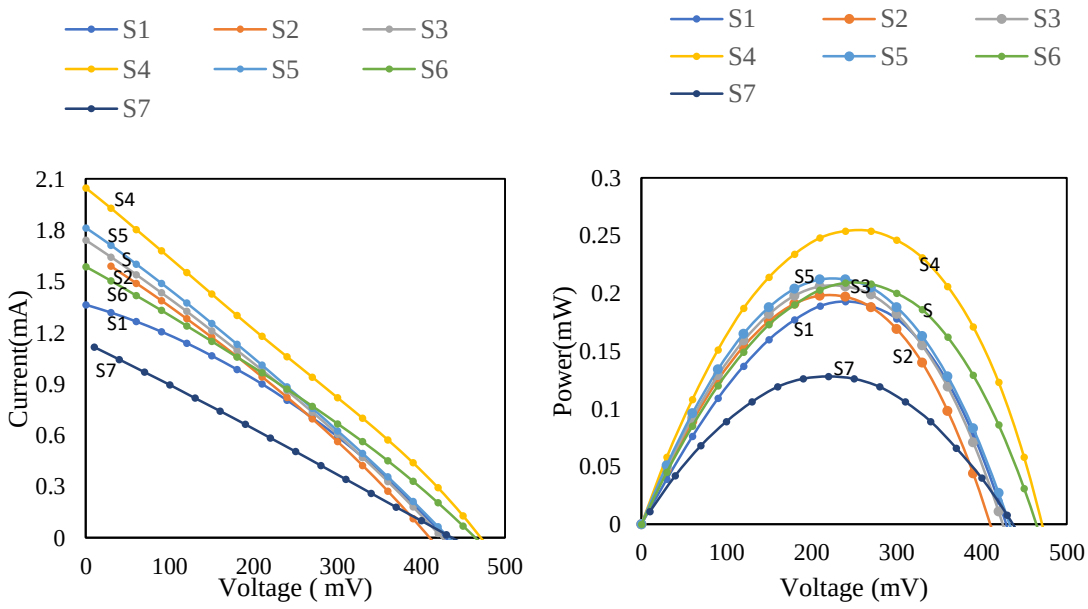


Figure 1: (a) Current-voltage characteristics of TiO_2/CdS varying the sulfur (moles) in Na_2S deposition solution, under illumination of 100 mW/cm² light intensity.

(b) Voltage-power characteristics of TiO_2/CdS varying the sulfur (S) moles in Na_2S solution, under illumination of 100 mW/cm² light intensity.

Significant improvements are observed in sample S4 (1 mole), where voltage increases from 436.7 mV to 470.8 mV (7.8% increase), current density rises from 2.265 mA to 4.176 mA (84.5% increase), and efficiency doubles from 0.262% to 0.519% (98.5% increase), compared to S7 (0 moles). These enhancements are attributed to incorporation of sulfur in improving light absorption and facilitating charge transport. However, beyond the optimal sulfur concentration of 1 mole (e.g., S5 and S6), the performance plateaus or slightly decreases, likely due to excessive sulfur causing aggregation or hindering charge transfer. The lowest current output is observed at 0 moles (S7), highlighting the critical role of sulfur in enhancing QDSSC functionality. It illustrates that sulfur enhances QDSSC efficiency by improving light absorption, charge transfer, and surface passivation. However, an optimal sulfur concentration (1 mole) maximizes efficiency by reducing defects and recombination. At higher concentrations (1.5-2 moles), defects and structural issues may arise, leading to electron trapping and lower efficiency. Overall, the results highlight the importance of precise sulfur tuning, with 1 mole being the optimal concentration for maximum performance.

The power-voltage (P-V) graph compares the performance of QDSSCs with varying sulfur (S) concentrations, highlighting the relationship between power output and voltage. Among the samples, the highest power output is achieved at 1 mole of sulfur (S4), while the lowest is observed at 0 moles of sulfur (S7). The peak power for S4 is significantly higher than S7(98.44%), demonstrating the critical role of sulfur in enhancing the solar cell's performance through improved light absorption, charge transfer, and reduced recombination. In contrast, the S7 sample lacks these advantages, resulting in minimal power generation.

Table 2: Photovoltaic Parameters of CdS Quantum Dot-Sensitized Solar Cells

Sample Number	S1	S2	S3	S4	S5	S6	S7
Sulphur (moles)	0.125	0.25	0.5	1.0	1.5	2	0
Voltage(mV)	428.6	409.9	424.7	470.8	432.9	464.4	436.7
Current Density (mA m^{-2})	2.781	3.434	3.552	4.176	3.701	3.235	2.265
Fill Factor	33.0	28.7	27.9	26.4	27.0	28.3	26.5
Efficiency (%)	0.394	0.404	0.421	0.519	0.433	0.426	0.262
Maximum Power	0.193	0.198	0.206	0.254	0.212	0.209	0.128

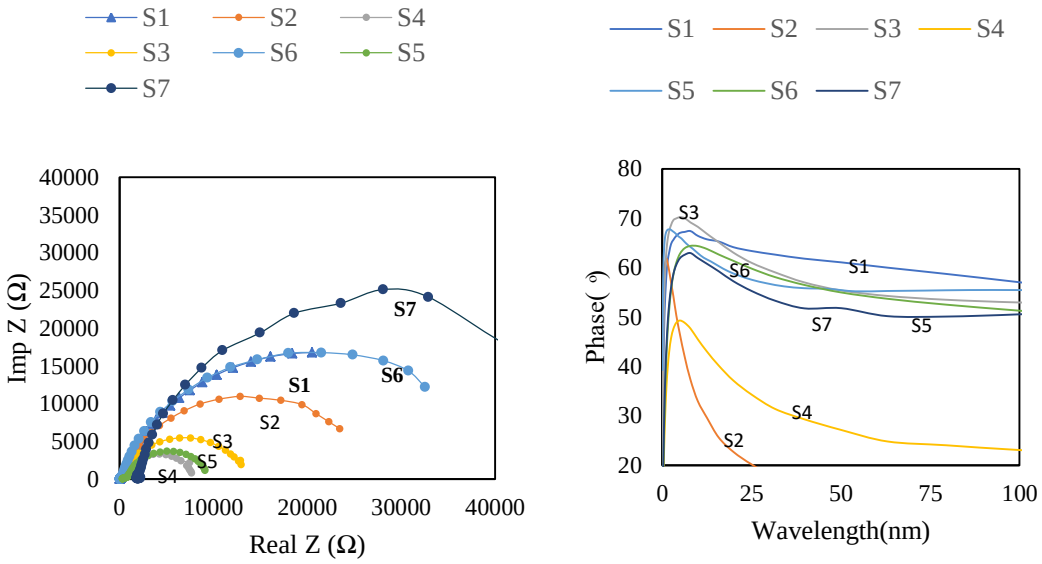
(QDSSCs)

The use of power-voltage plots is essential in QDSSCs as they provide a clear understanding of the cell's efficiency and operating conditions. While current-voltage plots indicate the potential and current capabilities, P-V plots reveal the maximum power point (MPP)—the voltage and current at which the solar cell operates most efficiently. This information is crucial for optimizing the design and tuning the

parameters to maximize energy output, making the P-V graph a critical tool in evaluating and improving QDSSC performance.

4.2 EIS of CdS QDSSCs

Measuring impedance and phase frequency plots is crucial for evaluating the performance and efficiency of QDSSCs. Impedance spectroscopy provides insights into the charge transport and collection processes within the cell, identifying resistive and capacitive components, such as charge transfer resistance and interfacial properties between quantum dots and the electrolyte.



(a) (b)

Figure 2: (a) Impedance spectra characteristics of TiO_2/CdS with varying sulfur (S) moles in Na_2S.

(b) Wavelength and Phase of TiO_2/CdS with varying sulfur (S) moles in Na_2S.

Table 3. Parameters of equivalent circuit for different QDSC configuration

	S1	S2	S3	S4	S5	S6	S7
Rs(Ω)	215	162	71.3	33.4	47.4	349	1.94 kΩ
Rp(kΩ)	108	26.9	8.57	16.4	56.6	16.1	56.2
CPE	0.524	0.866	0.811	0.713	0.745	0.866	0.898
Wavelength(nm)	6.309	1	3.981	5.011	1.584	7.943	7.943
Phase (°)	67.216	61.254	69.962	49.293	67.686	64.401	62.942

The analysis of sulfur-based samples underscores the critical relationship between phase shift, impedance, and current flow in determining electrical performance. Among the samples, S4 (1 mol sulfur) stands out due to its low series resistance (Rs = 33.4 Ω),

moderate parallel resistance (Rp = 16.4 kΩ), and phase shift of 49.273°, which together enable efficient current flow. The constant phase element (CPE = 0.713) for S4 indicates a balanced capacitive and resistive behavior, optimizing impedance. In contrast, S7 (0 mol sulfur) has the highest Rs (1.94 kΩ) despite its high CPE (0.898) and moderate phase shift (62.942°), leading to reduced current flow. Samples such as S1 (0.125 mol sulfur) and S3 (0.5 mol sulfur) exhibit higher Rs values (215 Ω and 71.3 Ω) and significant phase shifts (67.216° and 69.962°, respectively), resulting in greater impedance and reduced conductivity. These findings confirm that reduced series resistance (33.4 Ω) and lower phase shift (49.293°) enhance current flow and charge transport, with sample S4 (1 mole of sulfur) achieving superior efficiency and performance.

4.3 Incident Photon-to-Current Efficiency (IPCE) of QDSSCS

Incident Photon-to-Current Efficiency (IPCE) is a critical metric in Quantum Dot-Sensitized Solar Cells (QDSSCs), as it measures the efficiency of converting incident photons into electrical current at specific wavelengths. By providing a wavelength-dependent performance analysis, IPCE helps identify the quantum dot sizes and materials that optimally absorb light and convert it into electricity, aligning with the solar spectrum.

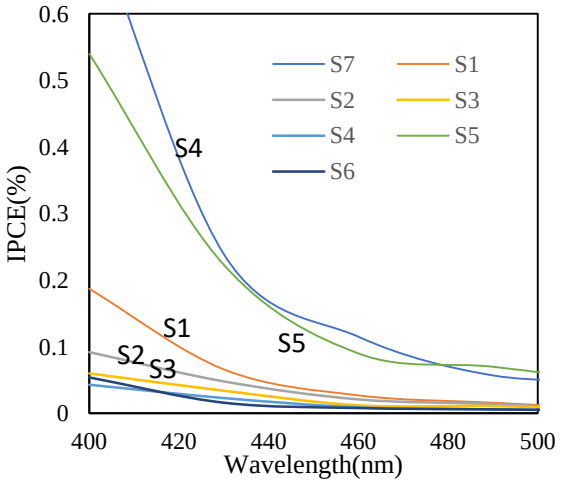
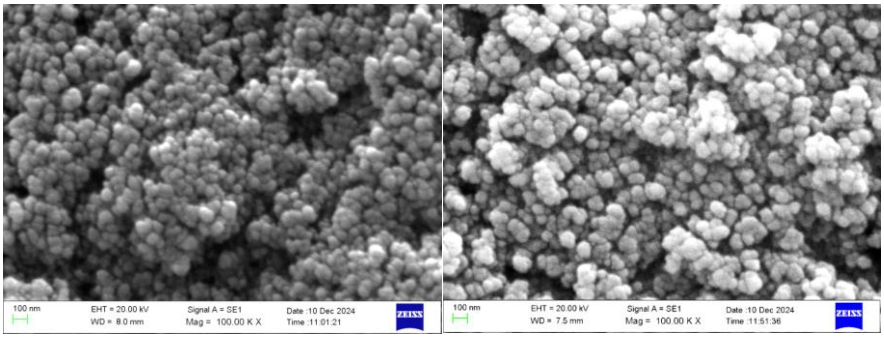


Figure 3: Wavelength-Integrated Photocurrent Efficiency (IPCE) for TiO_2/CdS with varying sulfur (S) moles in Na_2S.

This parameter also reveals inefficiencies such as recombination losses or poor charge transport, guiding the optimization of device components like quantum dots, electrolytes, and electrodes. Moreover, IPCE serves as a benchmark for comparing different QDSSCs, evaluating their performance relative to theoretical limits, and aiding in the design of advanced multi-junction cells. For instance, in analyzing concentrations like S4, a sudden peak in IPCE within the 610–670 nm range highlights its potential for higher efficiency in converting light into electrical current.

4.4 Morphology of TiO_2 and TiO_2/CdS



TiO_2 TiO_2 CdS

Figure 4: SEM images of TiO_2 and TiO_2/CdS

The scanning electron microscopy (SEM) images depict the morphological characteristics of TiO_2 and TiO_2/CdS composite films at a magnification of 100,000×. The left image presents the pristine TiO_2 nanoparticles, exhibiting a highly porous, interconnected nanostructure with relatively uniform particle distribution. In contrast, the right image, corresponding to the TiO_2/CdS composite, reveals noticeable changes in surface morphology due to CdS deposition. The presence of CdS quantum dots appears to increase the overall particle size and surface roughness, suggesting successful sensitization of the TiO_2 framework. This modification is expected to enhance light absorption and electron transport properties, which are critical for photovoltaic applications. The observed morphological changes align with the anticipated improvements in charge separation and reduced recombination rates, contributing to the enhanced performance of quantum dot-sensitized solar cells. [11]

4.5 Maximum Power Point Tracking (MPPT)

MPPT in QDSSCs is a crucial technique for optimizing energy extraction by dynamically identifying and maintaining the maximum power point on the current-voltage (I-V) curve. The maximum power point is the point where the product of current and voltage is maximized, resulting in the highest power output and improved efficiency. This is particularly vital for QDSSCs, as the nonlinear behavior of quantum dots demands precise control to fully exploit their potential for enhanced light absorption and tailored energy conversion. Beyond efficiency optimization, MPPT provides valuable insights into device performance and stability under varying conditions, aiding both research and practical deployment. Furthermore, it facilitates seamless integration with power electronics, ensuring the effective implementation of QDSSC-based energy systems in real-world applications.

As shown in Figure 5, The TiO_2/CdS QDSSC demonstrates an initial efficiency of approximately 0.17%, which stabilizes quickly within the first 2 seconds and remains relatively consistent over a 50-second period, showing only a minor decline. When

observed over a longer period, the efficiency decreases by about 5% within 2 minutes, likely due to thermal effects or charge recombination.

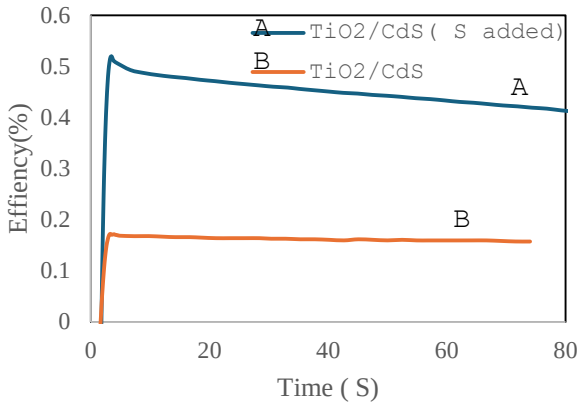


Figure 5: Efficiency-Time Graph for 1 Mole Sulfur Na_2S Solution in TiO_2 / CdS QDSSCs and Efficiency-Time Graph for TiO_2 / CdS QDSSCs

In contrast, the S-doped TiO_2/CdS QDSSC achieves a significantly higher initial efficiency of 0.52027%; however, this efficiency rapidly declines to 0.36943% within just 2 minutes, representing a 29% reduction. This sharp decrease suggests that the S-doped film is prone to rapid degradation, potentially caused by environmental factors or inherent material instability. While S-doping improves the initial efficiency, the TiO_2/CdS cell exhibits better short-term stability. This comparison highlights the need to optimize both efficiency and stability for QDSSCs to enhance their long-term viability in energy applications.

5. CONCLUSION

This study highlights the transformative potential of sulfur doping in quantum dot-sensitized solar cells (QDSSCs), particularly in sample S4, which demonstrates significant performance enhancements. S4 exhibits a 7.8% increase in voltage, an 84.5% rise in current density, and a 98.5% boost in efficiency, with its peak power output being 98.44% higher than the control sample, S7. These improvements are attributed to S4's optimized sulfur concentration, low series resistance (33.4 Ω), moderate parallel resistance (16.4 kΩ), and reduced phase shift (61.254°), ensuring efficient charge transport and current flow. Its constant phase element (CPE = 0.713) reflects balanced capacitive and resistive behavior, further optimizing impedance. A sudden IPCE peak within the 610–670 nm range aligns with the solar spectrum, indicating high light-to-electricity conversion efficiency. However, rapid efficiency degradation (from 0.52027% to 0.36943% within 2 minutes, a 29% decrease) underscores the need for greater stability and durability. Despite this, sulfur-doped QDSSCs present a scalable, cost-effective solution for next-generation solar energy conversion, opening pathways for further research and material optimization.

6. REFERENCES

[1] Panigrahi, S., & Basak, D. (2011). Morphology driven ultraviolet photosensitivity in ZnO–CdS composite. Journal of Colloid and Interface Science, 364(1), 10–17. https://doi.org/10.1016/j.jcis.2011.08.001

[2] Robel, I., Subramanian, V., Kuno, M., & Kamat, P. V. (2006). Quantum Dot Solar Cells. Harvesting Light Energy with CdSe Nanocrystals Molecularly Linked to Mesoscopic TiO2 Films. Journal of the American Chemical Society, 128(7), 2385–2393. https://doi.org/10.1021/ja056494n

[3] Shen, Q., Kobayashi, J., Diguna, L. J., & Toyoda, T. (2008). Effect of ZnS coating on the photovoltaic properties of CdSe quantum dot-sensitized solar cells. Journal of Applied Physics, 103(8). https://doi.org/10.1063/1.2903059

[4] Plass, R., Pelet, S., Krueger, J., Grätzel, M., & Bach, U. (2002). Quantum dot sensitization of organic–inorganic hybrid solar cells. The Journal of Physical Chemistry B, 106(31), 7578–7580. https://doi.org/10.1021/jp020455o

[5] Hanna, M. C., & Nozik, A. J. (2006). Solar conversion efficiency of photovoltaic and photoelectrolysis cells with carrier multiplication absorbers. Journal of Applied Physics, 100(7).

[6] Alharbi F, Mejri IH, Hzez W, Omri K. Ceram Int 2020;46:14972–7. https://doi.org/10.1016/j.ceramint.2020.03.026.

[7] Omri, K., & Alonizan, N. (2018). Effects of ZNO/MN concentration on the micro-structure and optical properties of ZNO/MN–TIO2 nano-composite for applications in Photo-Catalysis. Journal of Inorganic and Organometallic Polymers and Materials, 29(1), 203–212. https://doi.org/10.1007/s10904-018-0979

[8] Zainudeen, U. L., Jaseetharan, T., & Department of Physical Sciences, Faculty of Applied Sciences, South Eastern University of Sri Lanka. (2021). Optimizing the SILAR cycles for PbS/CdS quantum dots co-sensitized solar cells. In Journal of Science-FAS-SEUSL (Vols. 02–02, Issue 01, pp. 25–31).

[9] Yu, X., Lei, B., Kuang, D., & Su, C. (2011). Highly efficient CdTe/CdS quantum dot sensitized solar cells fabricated by a one-step linker assisted chemical bath deposition. Chemical Science, 2(7), 1396. https://doi.org/10.1039/c1sc00144b

[10] Ajward, N. F., & Perera, V. P. S. (2024). Optimization of Precursor Concentration, pH and Cycle Number to Deposit CdS Quantum Dots on TiO2 Films for Performance Enhancement of QDSSCs. In Proceedings of the Technical Sessions (Vol. 40, pp. 54-62).

[11] Li, W., Ding, H., Ji, H., Dai, W., Guo, J., & Du, G. (2018). Photocatalytic degradation of tetracycline hydrochloride via a CdS-TiO2 heterostructure composite under visible light irradiation. Nanomaterials, 8(6), 415.