https://doi.org/10.65646/3rc20dma4w1110

Proceedings of the International Research Conference of the Open University of Sri Lanka (IRC-OUSL 2025)

COMPARATIVE ANALYSIS OF POLYSULFIDE ELECTROLYTE SYSTEMS FOR THE PERFORMANCE ENHANCEMENT IN CdS QUANTUM DOT-SENSITIZED SOLAR CELLS

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This study has focused on improving the performance and stability of TiO_2 /CdS quantum dot sensitized solar cells by investigating two electrolyte optimization methods. One method has focused on solvent effects, and the other method is on redox chemistry optimization. In the first method, this study investigated the impact of the solvent, which consisted of pure methanol, pure deionized water, and a methanol-water mixture (7:3v/v). Among the three solvents, pure methanol produced the highest power output due to its low viscosity and high polarity, this is due to an enhancement in the ion mobility and redox kinetics, However, it seems to have a drawback due to high volatility compromising long-term stability. Although pure water has provided lower efficiency due to its limited ionic conductivity, the methanol-water mixture demonstrated a favorable balance between performance and stability in a specific ratio. Method two has focused on varying the molar concentration of Na_2S. For this purpose, this work tested different concentrations ranges in 0.5 M to 2.5 M to identify the best ratio that illustrates the highest performance of photocurrent and efficiency. The optimal composition (2.5 M Na_2S + 3.5 M S) achieved the highest efficiency, lower charge transfer resistance (Rp), and enhanced Incident Photon-to-Current Efficiency (IPCE) response. However, further increasing of Na_2S to 3M reduced the performance because of the viscosity and side reactions. Overall, combining an optimized redox couple with a stable methanol-water solvent system resulted in a high-performing, reproducible, and practically viable electrolyte formulation. Both of these optimization approaches offer a promising route toward the development of more efficient and stable QDSCs, contributing to their future implementation in solar energy technologies.

Keywords: electrolyte optimization, methanol water solvent system, Na_2S, quantum dot sensitized solar cells

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INTRODUCTION

Quantum dot-sensitized solar cells (QDSCs) have attracted considerable interest due to their low fabrication cost, tunable band gaps, multiple exciton generation capability, and strong light-harvesting properties. A significant advancement over conventional dye-sensitized systems was reported by Chen et al. (2018), who introduced CdS as an effective sensitizer with improved optical and electronic characteristics. CdS offers favorable conduction band alignment with TiO_2 and efficient visible-light absorption, enabling enhanced electron injection and reasonable photostability in TiO_2/CdS-based QDSCs.

Electrolyte composition plays a critical role in determining charge regeneration efficiency, recombination suppression, and long-term redox stability. Wang et al. (2014) demonstrated that cobalt complex-mediated polysulfide electrolytes enhance interfacial charge transfer and reduce recombination losses. Similarly, Choi et al. (2013) reported improved efficiency and stability using ionic liquid-based electrolytes. Redox couple concentration and solvent environment further influence device performance. Excessively high Na_2S concentrations increase electrolyte viscosity, reduce ion mobility, and suppress photocurrent generation (Seo et al., 2013). Moreover, solvent polarity and viscosity significantly affect redox species diffusion and interfacial recombination dynamics (Lan et al., 2016; Xu et al., 2018).

Despite growing interest in electrolyte engineering, comprehensive comparative investigations remain limited. Therefore, this study applies two strategies: solvent variation using methanol, water, and their mixture, and systematic optimization of Na_2S and sulfur ratios in a fixed methanol–water (7:3 v/v) system. Device performance is evaluated through I–V analysis, power output measurements, electrochemical impedance spectroscopy (EIS), and IPCE characterization to identify an optimized electrolyte configuration balancing efficiency and stability.

METHODOLOGY

Preparation of TiO_2 plates

TiO_2 paste was prepared by mixing 0.25 g TiO_2 with 1 ml 0.1 M HNO_3, one drop Triton X-100, and one drop PEG1000, followed by 30 min grinding. The paste was doctor-bladed onto cleaned CTO glass (1.0 × 2.0 cm), ultrasonically washed, dried, and sintered at 450 °C for 45 min.

Deposition of CdS using SLILAR method.

CdS films were deposited on TiO_2 photoanodes via the SILAR method. Electrodes were alternately immersed in $CdCl_2$ and Na_2S for 1 min each, rinsed, and air-dried

per cycle. After ten cycles, films were heated at 80 °C for 30 min to improve adhesion and stability

Preparation of Electrolyte

Two experimental approaches were adopted to examine electrolyte composition effects. Method 1: Electrolytes were prepared according to the compositions in Table 1 and stirred for 3 hours using a magnetic stirrer to ensure dissolution. Stirring time was adjusted when necessary to minimize sulphur precipitation.

Table 1: Electrolytes methanol, water, and a methanol water mixture

Solvent of electrolyte	Na_2S	S	KCl	methanol	water
Methanol	0.1301g	0.283g	0.031	2ml	0
Water	0.1301g	0.283g	0.031	0	2ml
Methanol+ water	0.1301g	0.283g	0.031	1.4ml	0.6ml

Method 2: Table 2 summarizes electrolytes containing Na_2S, sulfur, and KCl in a methanol–water solvent. Na_2S and sulfur concentrations were varied, while KCl concentration and solvent volume were fixed. Excess sulfur ensured saturation, leaving slight undissolved precipitate in each formulation.

Table 02. The preparation details for each electrolyte sample (S1–S9)

Sample of liquid electrolytes	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9
Na_2S (moles)	0.5	1.0	1.5	2.0	2.0	2.5	2.5	3.0	3.0
S (moles)	2	2	2	2	3	2	3.5	2	3.5
KCl (moles)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2

Fabrication of the cell

A counter electrode with a conducting side positioned directly on the CdS coated TiO_2 film and was 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).

Characterization

The fabricated QDSSCs were characterized using a VK-PA-100 PV Power Analyzer to obtain J–V curves and Electrochemical impedance spectroscopy (EIS) was conducted using an AutoLab Nova 2.1 frequency response analyzer to examine

charge transport and recombination. Incident Photon-to-Current Efficiency (IPCE) was measured using a VK-IPCE-10 system to evaluate spectral response and the effectiveness of quantum dots in converting light into photocurrent.

RESULTS AND DISCUSSION

I - V Characteristics of CdS QDSSCs various electrolytes

The I–V characteristics of QDSCs using methanol, water, and a methanol–water mixture as electrolytes are presented in Figure 1.

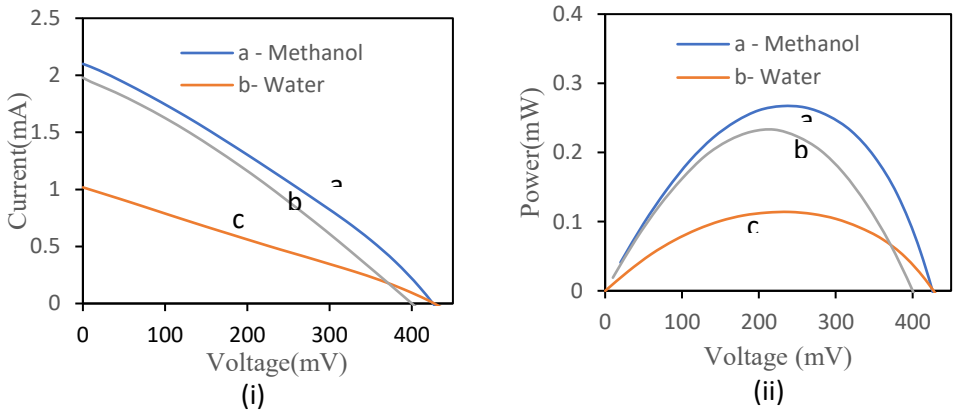

Figure 1: (i) Current–voltage characteristics of TiO_2/CdS with varying electrolytes under illumination at a light intensity of 100 mW/cm². (ii) Voltage-power characteristics of TiO_2/CdS varying electrolytes, under illumination of 100 mW/cm² light intensity.

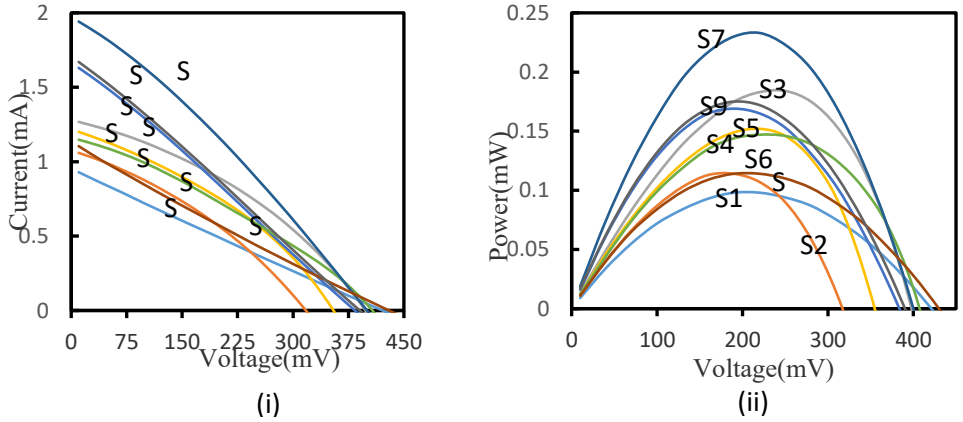

Figure 2: (i) Current–voltage characteristics of TiO_2/CdS with varying electrolytes under illumination at a light intensity of 100 mW/cm². (ii) Voltage-power characteristics of TiO_2/CdS varying electrolytes, under illumination of 100 mW/cm² light intensity.

Figure 1, all devices exhibit similar open-circuit voltages (≈420–430 mV); however, curve profiles differ. Methanol shows a higher fill factor, while water indicates greater resistive and recombination losses. Maximum power outputs were 0.267 mW (methanol), 0.251 mW (mixture), and 0.144 mW (water), though methanol presents practical limitations.

Figure 2 shows that the performance of TiO_2/CdS QDSCs strongly depends on polysulfide electrolyte composition. The electrolyte containing 2.5 M Na_2S and 3.5 M sulfur (S7) achieved the highest photocurrent density (3.942 mA m^{-2}), maximum power (0.233 mW), and efficiency (0.475%), indicating efficient redox cycling and reduced recombination. Lower Na_2S concentrations (S1–S2) limited S^{2-} availability, decreasing current density (1.887–2.151 mA m^{-2}) and efficiency (0.200–0.234%). Sulfur addition improved the S^{2-}/S redox couple, enhanced passivation, and increased fill factor from 0.251 to 0.367, reflecting improved charge extraction.

Electrochemical Impedance Spectroscopy (EIS)

The Nyquist plot shown in Figure 3(i) presents the Nyquist plots of TiO_2/CdS QDSCs with water, methanol, and mixed electrolytes. The water system shows the largest semicircle, indicating high charge transfer resistance. Methanol reduces impedance, while the methanol–water mixture exhibits the smallest semicircle, reflecting optimal redox balance, improved ion mobility, and minimized recombination.

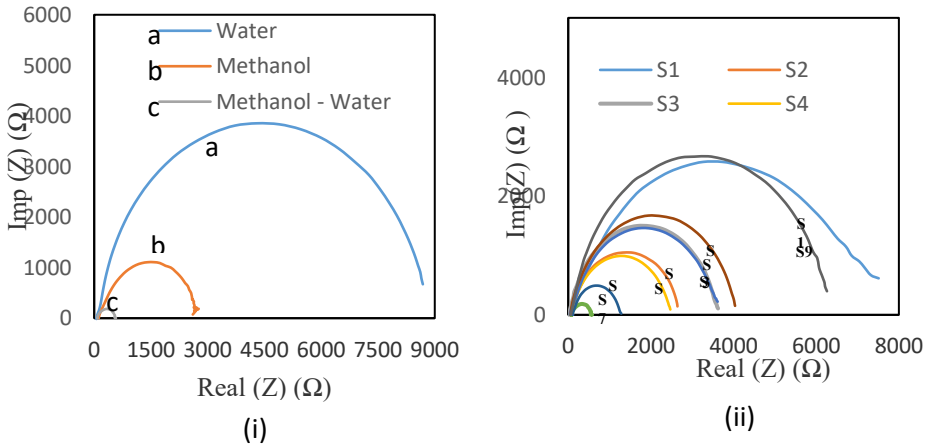

Figure 3 (i) Impedance characteristics of TiO_2/CdS with varying electrolytes (ii) Impedance characteristics of TiO_2/CdS with varying electrolytes. Insertion in figure (i) shows Equivalent circuit

Impedance analysis of Method 2 samples shows minimal variation in series resistance (Rs), indicating limited influence on device performance. Instead, parallel resistance (Rp) dominates recombination and charge transfer behavior. As shown in Figure 3(ii),

S7 exhibits the most favorable characteristics. At low Na_2S concentration (0.5 M, S1), high Rp (7300 kΩ) reflects poor regeneration and dominant recombination (Seo et al., 2013). Moderate concentrations (S2–S4) show similar limitations. S3 (2.0 M Na_2S + 3.5 M S) achieves optimal impedance (Rs = 25.7 Ω; Rp = 3580 kΩ), indicating efficient charge injection and reduced recombination.

Table 3. Parameters of Rs, Rp and CPE in equivalent circuit for different QDSC configuration

	S1	S2	S3	S4	S5	S6	S7	S9
Rs(Ω)	35	41.2	25.7	54.7	39.9	111	82.6	61
Rp(kΩ)	7300	2670	3580	2430	3740	1170	490	6220
CPE	0.778	0.847	0.887	0.867	0.809	0.864	0.811	0.905

Incident Photon-to-Current Efficiency

The IPCE spectra reveal the spectral response of TiO_2/CdS QDSCs with different electrolytes. Pure methanol exhibits the highest peak (~0.048 at 500 nm) due to enhanced ion mobility and improved electron injection (Lee et al., 2013), although volatility limits its stability. The pure water system shows the lowest response, attributed to high viscosity and restricted S^{2-} transport (Lan et al., 2016). The 2.5 M Na_2S + 3.5 M S methanol–water system demonstrates a broader and more stable response, indicating enhanced redox activity and surface passivation (Zhang et al., 2016). This optimized composition improves durability and practical applicability (Xu et al., 2018).

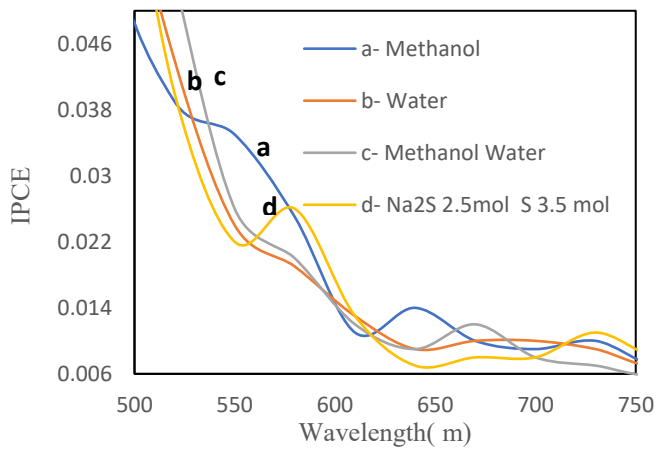

Figure 6. IPCE vs. wavelength for TiO_2/CdS QDSSCs using different electrolyte systems.

CONCLUSIONS

This study investigated two electrolyte strategies: solvent variation (Method 1) and redox tuning (Method 2). In Method 1, pure methanol produced the highest power output (0.267 mW) due to favorable charge transport, but rapid evaporation limits stability. Pure water showed the lowest performance. The methanol–water (7:3) mixture provided balanced behavior, delivering moderate power (0.233 mW), improved stability, and acceptable impedance (Rp ~3740 kΩ).

Method 2, using a methanol–water base with optimized Na_2S and sulphur concentrations, significantly enhanced performance. The 2.5 M Na_2S + 3.5 M S system achieved 0.475% efficiency, 3.942 mA/m² current density, and low charge transfer resistance (Rp ~490 kΩ). Overall, the optimized methanol–water redox system offers superior stability and balanced electrochemical performance for advanced QDSC applications.

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