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_2 S. 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_2 S + 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_2 S 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_2 S, Quantum dot sensitized solar cells (QDSCs)

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INTRODUCTION

Quantum dot-sensitized solar cells (QDSCs) have attracted significant attention due to their low fabrication cost, tunable band gaps, multiple exciton generation capability, and strong light-harvesting properties. A major advancement over traditional dye-sensitized solar cells was reported by Chen et al. (2018), who introduced CdS as a sensitizer, offering improved optical and electronic characteristics. CdS provides favorable conduction band alignment with TiO_2 and efficient visible light absorption. Consequently, TiO_2 /CdS-based QDSCs are considered promising due to their efficient electron injection and moderate photostability.

In high-performance solar cells, effective charge regeneration, recombination suppression, and redox stability are essential, and these factors strongly depend on electrolyte composition. Wang et al. (2014) demonstrated that cobalt complex-mediated polysulfide electrolytes enhance charge transfer and reduce recombination. Similarly, Choi et al. (2013) reported that ionic liquid-based electrolytes improve charge transport, resulting in enhanced efficiency and stability. These findings highlight the importance of electrolyte engineering in optimizing QDSC performance.

Redox couple concentration and solvent environment are key parameters influencing device efficiency. Excessively high Na_2 S concentrations increase viscosity and hinder ion mobility, reducing photocurrent and overall performance (Seo et al., 2013). In addition, solvent polarity and viscosity significantly affect redox species diffusion and interfacial recombination dynamics (Lan et al., 2016; Xu et al., 2018).

Despite increasing interest in solvent and redox optimization, comprehensive comparative studies remain limited. This study addresses that gap using two strategies. Method 1 evaluates solvent variation through pure methanol, pure water, and a methanol–water mixture, while maintaining fixed Na_2S, sulfur, and KCl concentrations. Method 2 systematically varies Na_2S and sulfur molar ratios within a fixed methanol–water (7:3 v/v) system to optimize redox activity. Through current–voltage (I–V) analysis, power output comparison, electrochemical impedance spectroscopy (EIS), and IPCE measurements, this work aims to identify an

electrolyte configuration that achieves high photovoltaic performance while maintaining long-term stability suitable for practical applications

METHODOLOGY

Preparation of TiO_2 plates

TiO_2 paste was made by mixing 0.25 g of TiO_2 with 0.1 M HNO_3 (1 ml), Triton X-100 (1 drop), and PEG1000 (1 drop). The mixture was ground for 30 minutes using a mortar and pestle. The paste was then spread by using doctor blade method on the conducting side of the pre-cleaned Conducting Tin Oxide (CTO) glass plates cut to the size of 1.0 cm × 2.0 cm. The cleaning process involved using an ultrasonic bath with detergent and distilled water. Afterward, the TiO_2 coated films were dried on a hot plate and sintered in a furnace at 450 °C for 45 minutes.

Deposition of CdS using SLILAR method.

The Successive Ionic Layer Adsorption and Reaction (SILAR) technique was used to deposit CdS films onto TiO_2 photoanodes. To achieve uniform film deposition, we have used SILAR method. 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. 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.

Preparation of Electrolyte

To investigate the effect of electrolyte composition on the photovoltaic performance of QDSCs, two experimental approaches were adopted.

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

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

Method 2: Table 2 summarizes the electrolyte compositions of Na_2 S, sulfuric, and potassium chloride (KCl) dissolved in the methanol–water mixture. While Na_2 S and S concentrations were varied to evaluate their influence, KCl concentration and solvent volume remained constant. Excess sulfur was added to maintain saturated conditions, leaving slight undissolved precipitate in each sample.

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

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.

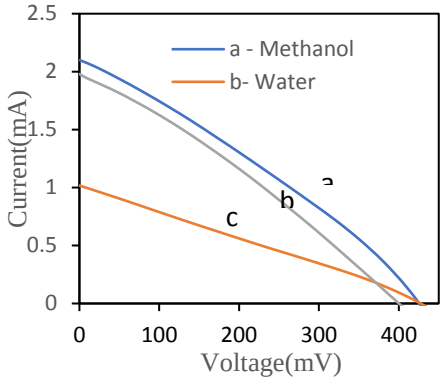
RESULTS AND DISCUSSION

I - V Characteristics of CdS QDSSCs various electrolytes

The current–voltage (I–V) characteristics of QDSCs using methanol, water, and a methanol–water mixture as electrolytic solvents are shown in Figure 1. Although all systems exhibit similar open-circuit voltages (V_oc ≈ 420–430 mV), the curve profiles vary.

As shown in Fig. 1 (i), Methanol yields a higher fill factor, while water shows a more linear declined curve, reflecting higher resistance and recombination losses. Correspondingly, the power–voltage plots confirm

this trend by obtaining the maximum power output of 0.267 mW for pure methanol, 0.251 mW for the methanol–water mixture, and 0.144 mW for only water as per the Fig. 1 (ii). However, pure methanol has practical limitations.



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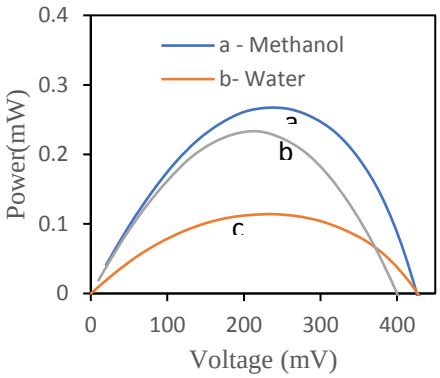
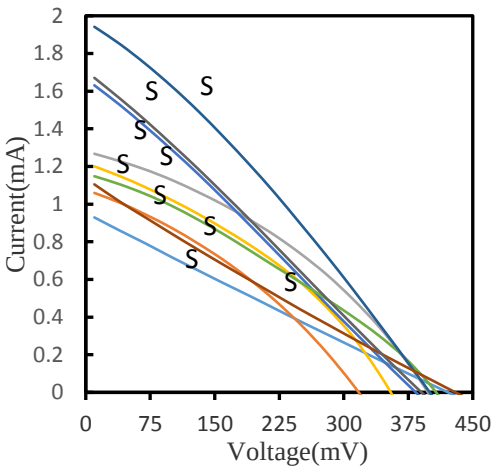


(ii)

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.



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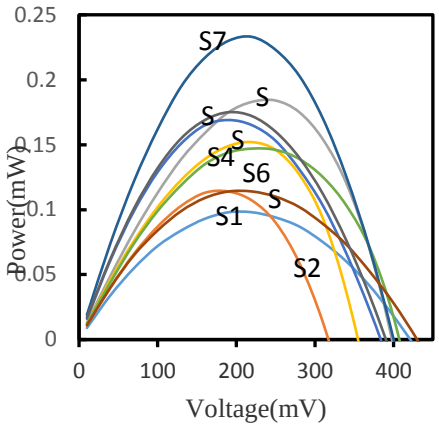


(ii)

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.

According to figure 2, The performance of TiO_2 /CdS quantum dot-sensitized solar cells (QDSCs) is significantly influenced by the composition of the polysulfide electrolyte, acting as a redox mediator and stabilizing agent. The electrolyte containing 2.5 M Na_2 S and 3.5 M elemental sulfur (Sample S7) delivered the highest photocurrent density (3.942 mA m^{-2}), maximum power (0.233 mW), and conversion efficiency (0.475%). These enhancements reflect efficient redox cycling, reduced recombination, and optimal charge regeneration (Xu et al., 2018). In contrast, at low Na_2 S concentrations (e.g., S1 and S2), limited availability of S^{2-} ions hindered effective regeneration of oxidized CdS quantum dots, resulting in reduced current density (1.887–2.151 mA m^{-2}) and lower efficiencies (0.200–0.234%) (Lan et al., 2016). The introduction of elemental sulfur at 3.5 M also contributed to increased power and photocurrent by enhancing the S^{2-} /S redox couple, improving surface passivation, and reducing back-electron transfer (Zhang et al., 2015). Fill factor improved notably from 0.251 in S1 to 0.367 in S3, further indicating reduced series resistance and better charge extraction.

Electrochemical Impedance Spectroscopy (EIS)

The Nyquist plot shown in figure 3 (i) prepared by method 1, compares the impedance response of TiO_2 /CdS QDSCs with electrolytes based on water, methanol, and a methanol + water at optimized composition. The semicircle

diameter corresponds to the charge transfer resistance (Rp), while the intercept on the real axis indicates the series resistance (Rs).

The water-based electrolyte exhibits the largest semicircle, signifying high Rp and poor charge transport due to the high viscosity and low ionic conductivity of water. The methanol-based system significantly reduces the semicircle radius, reflecting improved ion mobility and reduced recombination losses due to methanol's lower viscosity and higher conductivity. However, the smallest semicircle appears in the methanol + water system, indicating the most efficient charge transfer and lowest recombination. This composition benefits from an optimal balance of S^{2-} and polysulfide species, enhancing redox cycling and stabilizing the interface.

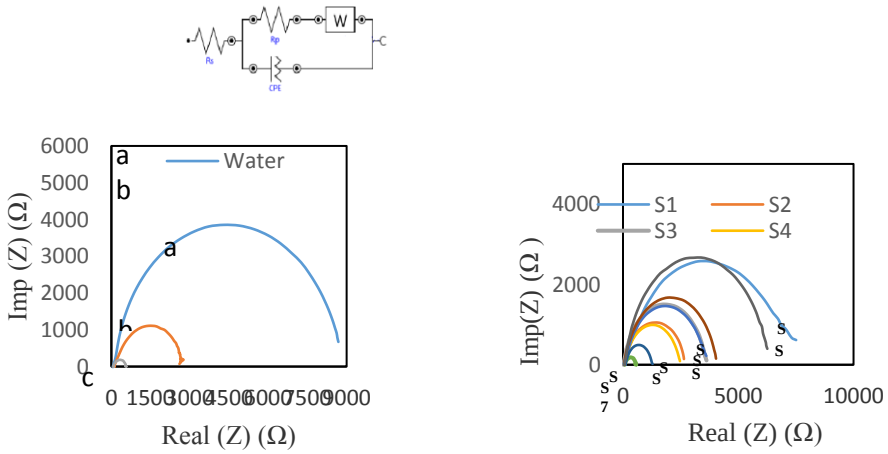


Figure 3 (i) Impedance characteristics of TiO_2 /CdS with varying electrolytes (ii) Impedance characteristics of TiO_2 /CdS with varying electrolytes. Insertion in figure (i) shows Equivalent circuit

In the impedance spectra analysis for the samples prepared by method 2, series resistance (Rs) values showed minimal variation across the samples and did not correlate significantly with performance differences. Therefore, the parallel resistance (Rp), which reflects recombination dynamics and charge transfer resistance, emerges as the more critical parameter for evaluating device efficiency. Based on this, considering figure 3(ii), sample S7 demonstrates the most favorable performance.

At low Na_2S concentration (0.5 M), S1 shows low Rs (35 Ω) and very high Rp (7300 kΩ), indicating limited charge transfer and dominant recombination. Insufficient S^{2-} ions hinder quantum dot regeneration and electron transport. Similar behavior in S2 and S4 (1.0–1.5 M) reflects restricted mobility and increased recombination. S3 (2.0 M Na_2S + 3.5 M

S) shows optimal impedance with lowest Rs (25.7 Ω), moderate Rp (3580 kΩ), and high CPE (0.887), indicating efficient charge injection and limited recombination. S5 also performs well. Higher Na_2 S concentrations increase viscosity, reducing ion mobility and worsening recombination (Seo et al., 2013).

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

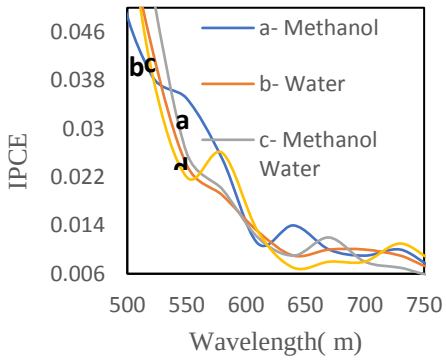
	S1	S2	S3	S4	S5	S6	S7	S9
Rs(Ω)	35	41.2	25.7	54.7	39.9	111	82.6	61
Rp(kΩ)	7300	2670	3580	2430	3740	1170	490	6220
CPE	0.778	0.847	0.887	0.867	0.809	0.864	0.811	0.905

Incident Photon-to-Current Efficiency

The IPCE spectrum reveals the spectral response of TiO_2 /CdS QDSCs under different electrolytes. Pure methanol shows the highest peak (~0.048 at 500 nm) due to improved ion mobility and electron injection (Lee et al., 2013), but suffers from volatility. The methanol– The pure water system exhibited the lowest IPCE response across the visible spectrum, attributed to its higher viscosity and limited capability for S^{2-} ion transport, as discussed by Lan et al. (2016).

The system using 2.5 M Na_2 S + 3.5 M S in a methanol–water medium presented a relatively broad and stable IPCE response. Although the peak intensity was lower than pure methanol, the extended response across a wider wavelength range indicates enhanced redox activity and surface passivation, aligning with the findings of Zhang et al. (2016), who emphasized sulfur enrichment's role in reducing recombination and stabilizing charge separation. This suggests that optimized sulfur-based electrolytes may offer a balance between efficiency and durability, making them a practical choice for real-world QDSC applications. Water mixture provides broader response and improved stability (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 favourable charge transport, but rapid evaporation limits stability. Pure water showed the lowest performance. The methanol–water (7:3) mixture provided balanced behaviour, delivering moderate power (0.233 mW), improved stability, and acceptable impedance (Rp ~3740 kΩ).

Method 2, using a methanol–water base with optimized Na_2 S and sulphur concentrations, significantly enhanced performance. The 2.5 M Na_2 S + 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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