Optimization of Precursor Concentration, pH and Cycle Number to Deposit CdS Quantum Dots on TiO₂ Films for Performance Enhancement of QDSSCs

N.F.Ajward and V.P.S. Perera
Department of Physics, The Open University of Sri Lanka, Nawala, Nugegoda
nf2010.ajward@gmail.com

ABSTRACT

Quantum dot solar sensitized cells (QDSSCs) are a promising alternative to traditional silicon cells due to their unique properties. This study investigated optimizing light absorption in QDSSCs by depositing cadmium sulfide (CdS) on titanium dioxide (TiO$_2$) films. They were studied how varying factors like pH, concentration, and coating cycles of the CdS solution impacted the cells. The experiment achieved higher performance in 0.25 M CdS concentration, producing an open-circuit voltage of 451.0 mV and a current density of 3.660 mA cm^{-2}. This research provides valuable insights for developing more efficient and cost-effective QDSSCs.

1 . INTRODUCTION

Quantum dot sensitized solar cells (QDSSCs) have garnered significant attention due to their unique and advantageous properties. Numerous research studies have demonstrated the exceptional properties of QDSSCs, including size-dependent bandgaps with a broad excitation range, remarkable chemical stability, and high molar extinction coefficients. These properties make QDSSCs highly promising candidates for photovoltaic applications. Furthermore, compared to silicon photovoltaic cells, QDSSCs offer the benefits of lower manufacturing costs and simpler fabrication processes.

Cadmium sulfide (CdS) is widely employed as a sensitizer for TiO$_2$ in visible-light-driven applications. TiO$_2$/CdS composites can be synthesized using various techniques, including sol-gel, chemical bath deposition, and electrodeposition [1 – 6]. The architecture of the composite material plays a crucial role in achieving enhanced photo electrochemical properties. Ordered mesoporous TiO$_2$ serves as an effective template for incorporating quantum-confined inorganic semiconductor sensitizers. Due to its larger surface area and multiple scattering properties, mesoporous TiO$_2$ promotes efficient light harvesting and facilitates the transport of reactant molecules through its continuous pore channels [7, 8]

Thin films of titanium dioxide (TiO$_2$) were prepared using the Doctor Blade method, followed by the deposition of cadmium sulfide (CdS) layers using Successive Ionic Layer

Adsorption and Reaction (SILAR) method. The absorption intensity of the films increased with the number of CdS coating cycles, as observed by Yasuhiro Tachibana et al. [10] This is due to the cumulative deposition of CdS material, which enhances light absorption capabilities. According to Muhammad Atif Irshad et al the pH of the Cd^{2+} effects the absorption of Cd^{2+}. [9] In this study, the effects of varying the concentrations of $CdCl_2$ and NaS, as well as the number of coating cycles, and the effect of pH value were investigated.

2. EXPERIMENTAL DETAILS

2.1 Preparation of TiO₂ Plates

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

2.2 Adjustment of pH Values.

Drops of 0.01M NaOH and 0.01M HCl were added to 10 ml samples of various concentration (1M, 0.75M 0.5M and 0.25M) of $CdCl_2$ solution and the pH of each solution was adjusted to 2.5, 3.5, 4.5 and 5.5.

1M concentration: pH 2.5, pH 3.5, pH 4.5, pH 5.5 solutions were prepared to study the effect of pH vales. As well it was repeated same way for concentrations 0.75M, 0.5M and 0.25M same pH values that was considered in 1M solution.

2.3 Preparation of Na₂S and CdCl₂ Solutions in Various Concentration

Table 1: Mass of $CdCl_2$ and Na_2S for Each Concentration

Concentration	1 M	0.75M	0.5M	0.25M
$CdCl_2$	20.13g	15.075g	10.065g	5.0325g
Na_2S	7.804g	5.853g	3.902g	1.951g

CdCl$_2$ and Na$_2$S solutions of above concentrations were prepared dissolving in 100 mL of distilled water according to the mass mentioned in Table 1.

The pH value of each CdCl$_2$ solution was adjusted to 4.5 using 0.01 M NaOH and 0.01M HCl solutions.

2.4 Deposition of CdS Using SLILAR Method.

TiO$_2$-coated films were dipped in each solution of CdCl$_2$ and Na$_2$S for 1 minute each. After each dip, the films were removed, rinsed with distilled water, and dipped again in the same pH solutions with concentrations ranging from 1 M to 0.25 M. This process was repeated from 4 to 25 cycles. Finally, the films were dried on a hot plate at 80°C for 30 minutes.

2.5 Preparation of Electrolyte

2 ml of electrolyte was prepared according to the following table.

Table 02: Mass of CdCl$_2$ and Na$_2$S in Electrolytes

	Number of moles	Weight for 2ml of electrolyte (g)
Na$_2$S	0.5	0.1301 ±0.001
S	2	0.1283±0.001
KCl	0.2	0.0301±0.001

Chemicals were weighed according to the table above, and 1.4 mL of methanol and 0.6 ml of distilled water were used as the solvent. The mixture was stirred with a magnetic stirrer for 3 hours. The stirring time may need to be adjusted to prevent the precipitation of sulfur.

2.6 Fabrication of The Cell

TiO$_2$ films coated onto conductive substrates were subjected to a successive ionic layer adsorption and reaction (SILAR) process for CdS quantum dot deposition. This process involved sequential dipping of the TiO$_2$ film into CdCl$_2$ and Na$_2$S solutions for one minute each, followed by rinsing with deionized water after each dip. The number of dipping cycles was varied to control the thickness and density of the CdS QD layer. After CdS deposition, the films were dried on a hot plate at 80°C for 30 minutes. Subsequently, a counter electrode with a conductive side was placed face-to-face with the CdS-coated TiO$_2$ film and secured with two clamps. The space between the electrodes was then filled with the electrolyte solution, completing the QDSSC assembly.

3. RESULTS AND DISCUSSION.

As observed in Table 3, the highest open-circuit voltage (447.8±0.1 mV) and current density (2.72±0.001 mA cm^{-2}) were achieved at a pH of 4.5, indicating the optimal conditions for efficient charge transport and light absorption. This is consistent with previous reports that highlight the influence of pH on the adsorption of Cd^{2+} and S^{2-} ions onto the TiO_2 surface, which in turn affects the quantum dot size and its subsequent impact on charge recombination kinetics [9]. The quantum size effect plays a crucial role in optimizing charge recombination dynamics in CdS/TiO_2 quantum dot sensitized solar cells. By adjusting the QD size, the energy levels of the QD conduction and valence bands can be precisely controlled, influencing the rate of electron injection from the QD to the TiO_2 and the subsequent recombination process [9,11]. Smaller QDs exhibit a larger band gap, leading to faster electron injection but also with high recombination. Conversely, larger QDs possess a smaller band gap, resulting in slower electron injection but also lower recombination.[9]

Table 03: Open circuit voltage (V_{oc}), current density (J_{sc}), and Fill Factor (FF) at Different pH Values

pH values	5.5	4.5	3.5	2.5	1.5
Sample Number	5	4	2	3	1
V_{oc} (mV)	445.2	447.8	301.3	353.2	275.8
J_{sc} (mA cm^{-2})	2.566	2.72	0.754	0.91	0.374
FF	0.210	0.244	0.386	0.35	0.321

Table 4 highlights the number of dipping cycles that yielded the highest voltage and current density for each tested concentration. This provides a quick reference for identifying the optimal conditions for achieving the best performance.

Table 04: The effects of concentration (0.25 M, 0.5 M, 0.75 M, and 1 M) on the maximum current density, open-circuit voltage, and fill factor across different dipping cycles

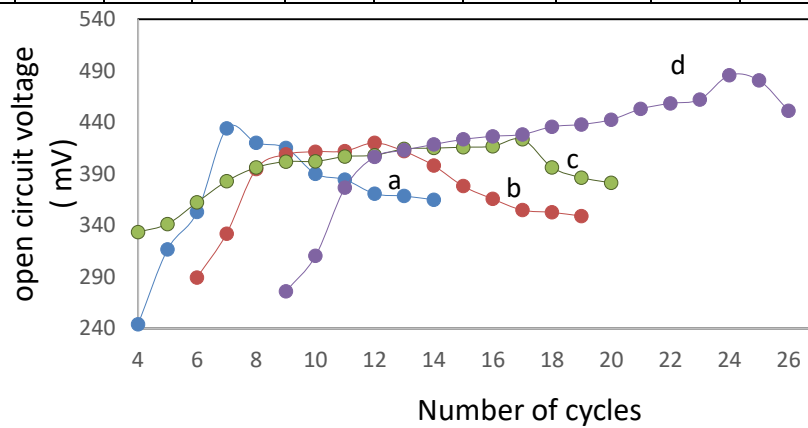| Number of Cycles	0.25 M			0.5 M			0.75 M			1 M		
	Voltage (mV)	Current density (mA cm^{-2})	Fill Factor	Voltage (mV)	Current density (mA/cm^{-2})	Fill Factor	Voltage (mV)	Current density (mA cm^{-2})	Fill Factor	Voltage (mV)	Current density (mA cm^{-2})	Fill Factor
7										410.9	3.239	0.279
12							403.6	2.551	0.272			
17				391.5	2.989	0.261						
24	451.3	3.660	0.256									

Figure 1: Open circuit photo voltage (mV) vs number of cycles of CdS/TiO$_2$ QDSCs made under different concentration of Cd and Sulphur ion concentrations (a) 1M (b) 0.75 M (c) 0.5 M (d) 0.25 M
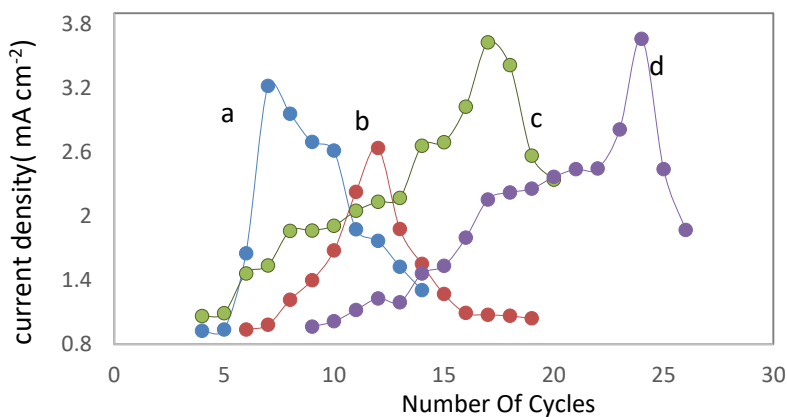

Figure 2: Current density (mAcm^{-2}) vs number of cycles of CdS/TiO$_2$ QDSSC made under different concentration of Cd and Sulpher ion concentrations (a) 1M (b) 0.75 M (c) 0.5M (d) 0.25 M

Figure 01, Table 4 and Figure 02, shows the open circuit voltage and short circuit current of CdS/TiO$_2$ QDSSCs measured using a VK PA 100 power analyzer. The voltage and current increased with increasing cycle number. However, there was a clear optimal value for each concentration that current or voltage was recorded an optimum and further repetition of SILAR cycles lowered the values. Therefore, concentration of the solution and the number of cycles have a significant impact on both the voltage and current. As the concentration of the solution increases, more Cd^{2+} and S^{2-} ions are available for deposition onto the TiO$_2$ substrate, leading to a higher density of QDs. This increased QD loading enhances light absorption and charge transport, resulting in higher photocurrent and open-circuit voltage. But higher rate of agglomeration results large particle growth that led to decrease the efficiency.

 Furthermore, increasing the number of cycles promotes the growth of larger and more uniform QDs, contributing to improved electronic properties and light absorption capabilities. This enhanced QD quality of the cell's performance.

However, that there exists an optimal concentration for each parameter. Excessively increasing either the cycle number or concentration beyond a certain threshold can lead to detrimental effects, such as QD aggregation or electrolyte saturation.
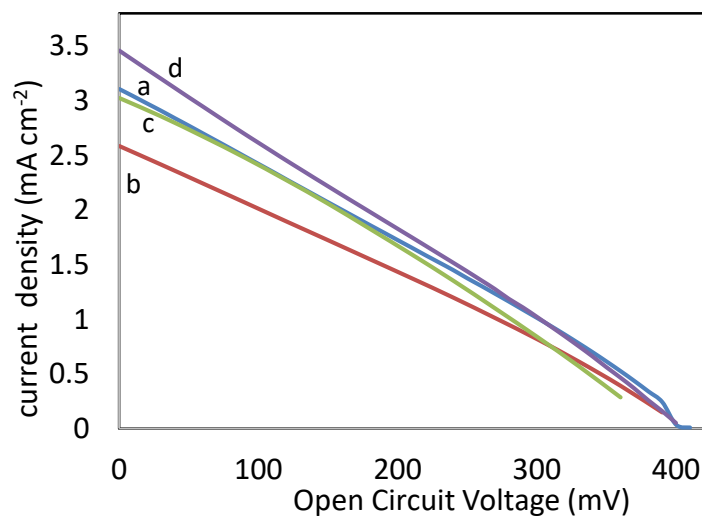

Figure 3: I-V characteristics of CdS/TiO$_2$ QDSCs made under different concentration of Cd and Sulphur ion concentrations (a) 1M (b) 0.75 M (c) 0.5 M (d) 0.25 M

Figure 3, presents the I-V curves for various concentrations (0.25M, 0.5M, 0.75M, and 1M), revealing a concerning low fill factor across all concentrations. As Young Jae Park et al. suggests, several factors can negatively impact the fill factor in QDSSCs: non-radiative recombination (reducing charge carriers available for current generation through pathways like surface defects), incomplete electrode coverage (limiting light absorption and charge generation area), poor electrode contact (impeding charge carrier flow), and slow transport within the QD layer (restricting the extracted current). [12]. Addressing

these potential issues through further investigation is crucial to improving the fill factor and overall performance of the QDSSCs.
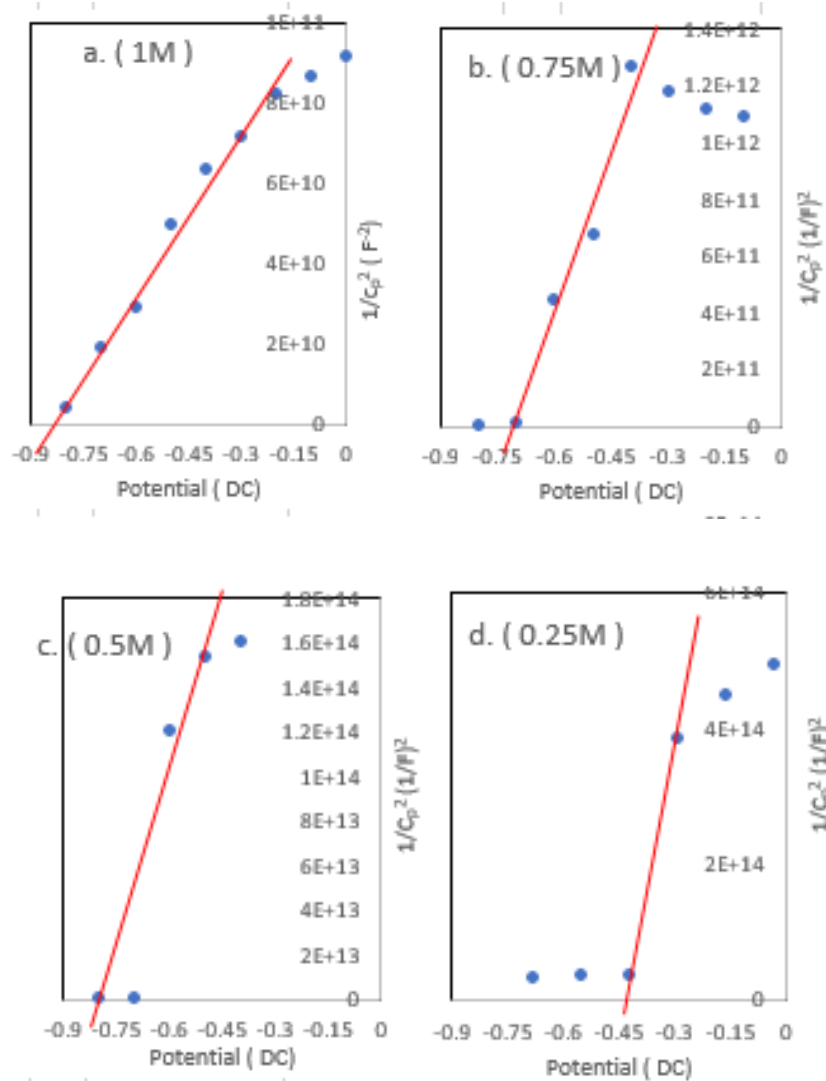

Figure 4: Mott-Schottky measurement of CdS deposited TiO$_2$ films made under different concentration of Cd and Sulphur ion concentrations at the optimum performance (a) 1M (b) 0.75 M (c) 0.5 M (d) 0.25 M

Table 05: Flat band potential of concentrations.

Flat band potentials were measured by the best line for the optimum number of cycles obtained for each concentration 1M,0.75M, 0.5M and 0.25M.

Number of cycles	Concentration	Flat band potential
7	1 M	-0.86 v
12	0.75 M	-0.74 v
17	0.5 M	-0.72 v
24	0.25 M	-0.48 v

Figure 4 and Table 05 presents Mott-Schottky measurements for each dipping cycle, revealing optimal flat-band potential (V_{fb}) values obtained at different precursor concentrations: 1M, 0.75M, 0.5M, and 0.25M. This widely utilized technique provides valuable insights into the electrical behavior of the resulting QD layers, offering crucial information about their doping concentration, built-in potential, and the presence of surface states. These insights are crucial for optimizing the performance of the QDSSCs.[13] Notably, the 0.25M solution exhibited the least-flat V_{fb} curve, suggesting potential challenges in its device behavior that warrant further investigation.

According to the Figure 5, higher J_{SC} and V_{OC} values are observed in the 0.25M which corresponds to the minimum impedance. This decrease in impedance with increasing I_{SC} and V_{OC} is attributed to the contribution of photo generated charge carriers. These charge carriers create a more conductive pathway within the QD layer, reducing the overall impedance. The higher charge carrier density also facilitates more efficient charge transport within the QDs and across the electrode interfaces.

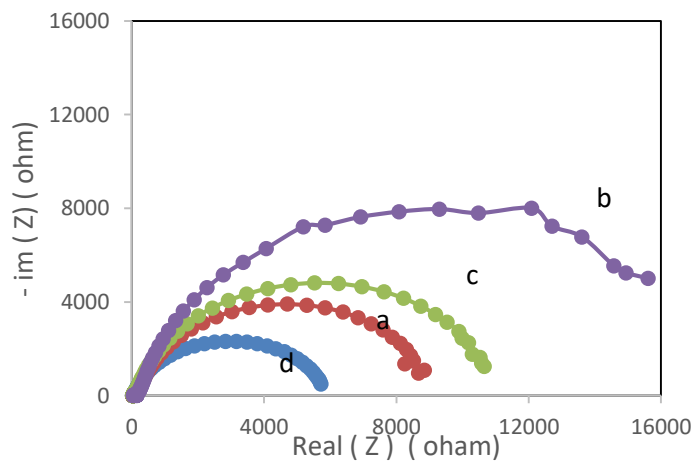The impedance of each cycle in a 1M solution has been considered in figure 05.

Figure 5: Impedance of CdS deposited TiO_2 films made under different concentration of Cd and Sulphur ion concentrations at the optimum performance (a) 1M (b) 0.75 M (c) 0.5 M (d) 0.25 M

This enhanced charge transport further contributes to the reduction in impedance. Additionally, as the charge carrier density increases, the probability of charge recombination decreases. Charge recombination occurs when electrons and holes combine before they can be collected at the electrodes. This reduced recombination further improves the conductivity of the QD layer and lowers the impedance.

4. CONCLUSION

In this study, we investigated the effects of solution pH dipping cycles and concentration on the performance of quantum dot sensitized solar cells (QDSSCs). We found that the

optimal conditions for QDSSC performance are a pH of 4.5 and $CdCl_2$ and Na_2S concentration of 0.25M, with 24 cycles. These conditions lead to the formation of larger and more uniform quantum dots, which improve the light absorption and charge transport properties of the cells. Additionally, these conditions minimize the negative effects of QD aggregation and electrolyte saturation. By optimizing the conditions for QDSC performance, we can achieve higher open-circuit voltage (V_{oc}), current density (J_{sc}), and fill factor (FF), which will lead to more efficient solar cells.

5. REFERENCES

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