Use of Ascorbic Acid Linker in Enhancing the Photovoltaic Performance of CdS/TiO2 Quantum Dot Sensitized Solar Cells

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ABSTRACT

This study explores the use of ascorbic acid to enhance the photovoltaic performance of CdS/TiO2 Quantum Dot Sensitized Solar Cells (QDSSCs). Ascorbic acid acts as a mild reducing agent, donating electrons to Ti atoms on the TiO2 film, effectively filling oxygen vacancies known to act as recombination centers for photogenerated charge carriers. By passivating these detrimental sites, ascorbic acid facilitates improved carrier transport and reduces recombination, ultimately boosting photocurrent and overall efficiency. QDSSCs fabricated via the Successive Ionic Layer Adsorption and Reaction (SILAR) method were characterized using I-V measurements, Incident Photon to Current Conversion Efficiency (IPCE), Impedance Spectroscopy (IS), and overall power conversion efficiency. The optimized cell incorporated with ascorbic acid demonstrated a remarkable improvement compared to the control, achieving a short circuit current density (J_{sc}) of 4.863 mA/cm², open circuit voltage (Voc) of 446.1mV, efficiency of 1.368%, fill factor of 24.6%, and maximum power of 0.342mW. Optimization of ascorbic acid absorption time and precursor concentrations resulted an impressive 68.26% enhancement in efficiency (from 0.813% to 1.368%) and increase in maximum power from 0.163 mW to 0.342 mW for 0.64 cm². cell. This study highlights the potential of ascorbic acid as a simple and effective strategy for enhancing the performance of CdS/TiO2 QDSSCs, paving the way for further developments in low-cost and efficient solar cell technologies.

KEYWORDS: *Quantum Dots, Sensitization, Solar Cells, Cadmium Sulfide, Ascorbic Acid.*

1   INTRODUCTION

Quantum dot sensitized solar cells (QDSSCs) have emerged as a promising photovoltaic technology due to their potential to surpass the limitations of traditional silicon solar cells and achieve superior light-to-electricity conversion efficiencies (Im et al, 2011; Chang et al, 2010; Hossain et al, 2012). However, a critical challenge in optimizing QDSSC performance lies in achieving a uniform and dense coverage of the photoanode with light-harvesting materials, such as quantum dots (QDs). There are two main approaches for QD deposition; in-situ growth and post-synthesis assembly (Du Z et al, 2019) In-situ methods, like Chemical Bath Deposition (CBD) and Successive Ionic Layer Adsorption and Reaction (SILAR), involve directly growing QDs onto the photoanode surface. This approach offers high QD coverage but limited control over their size, morphology, and optoelectronic properties. Post-synthesis assembly, on the other hand, offers greater control over QD properties (Du Z et al, 2019). Here, pre-synthesized QDs are tethered to the desired substrate using linker molecules, enabling manipulation of the QD-substrate interface for improved charge transport and device performance (Du Z et al, 2019). Linker-assisted assembly has shown promise for CdSe-sensitized QDSSCs, with various studies exploring different linker molecules like 3-mercaptopropionic acid, thioglycolic acid, and cysteine (Yang J et al, 2014; Aldakov D et al, 2015; Zhang D et al, 2021). However, research on CdS QDSSCs utilizing linker molecules remains limited, despite the potential advantages of CdS, including its broader light absorption spectrum compared to CdSe (Dibbell R S et al, 2009; Qian S et al, 2011; Wei L et al, 2015; Razzaq A et al, 2014; Yu L et al, 2017; Zhang et al, 2018).

This research investigates the potential of Ascorbic Acid (AA) as a novel linker molecule for CdS-sensitized QDSSCs. AA, a readily available and environmentally friendly molecule, has recently been shown to enhance the performance and stability of perovskite solar cells (Xiaobao Xu et al, 2016). Its effectiveness stems from its dual functionality, AA possesses strong antioxidant properties that can potentially retard the oxidation of the CdS during the QD deposition process. This can lead to improved

QD quality, reduced surface defects, and ultimately enhanced device performance. And the other can be consider as interface engineering. AA can interact with both the CdS QDs and the TiO2 photoanode, influencing the QD-TiO2 interface. It is hypothesized that AA can promote favorable surface interactions, facilitating efficient charge transfer between the QDs and the TiO2 substrate. This can potentially suppress charge recombination at the interface, leading to higher photocurrent generation and overall device efficiency.

In this study, we employ the SILAR method for CdS deposition on TiO2 substrates. This technique offers precise control over the thickness and uniformity of the deposited QD layer. We will explore the effectiveness of AA as a linker by systematically varying the AA Dipping Time and Concentration.

The dipping time in the AA solution can influence the extent of linker molecule adsorption on the TiO2 surface. Optimizing the dipping time is crucial for achieving a balanced surface coverage that facilitates efficient charge transfer while minimizing potential blocking effects.

The concentration of $Cd+2$ and $S-2$ precursors in the deposition solution plays a vital role in determining the size, morphology, and optoelectronic properties of the deposited CdS QDs. Optimizing these concentrations will ensure the formation of high-quality QDs with optimal light-harvesting capabilities.

Our previous research has highlighted the importance of pH in influencing the performance of CdS QDSSCs. We will investigate the impact of pH on the effectiveness of AA as a linker and optimize the deposition conditions for achieving the best device performance.

The fabricated QDSSCs will be rigorously characterized using a comprehensive suite of techniques, including Current Density-Voltage (J-V) Measurements, Electrochemical Impedance Spectroscopy (EIS), Incident Photon-to-Current Efficiency (IPCE) Analysis, and Absorption Spectroscopy.

2   EXPERIMENTAL DETAILS

2.1   Preparation of TiO2 plates

TiO2 paste was prepared by mixing 0.25 g of TiO2 with 0.1 M HNO3 (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 the doctor blade method on 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 TiO2-coated films were dried on a hot plate and sintered in a furnace at 450 °C for 45 minutes.

2.2   Ascorbic acid surface-modification

To identify the optimal dipping time, previously prepared TiO2 coated films were fabricated and evaluated following two distinct dipping procedures in a 0.5 M ascorbic acid solution. The solution was prepared by dissolving 1.7613 g of L-ascorbic acid powder in 20 ml of distilled water at room temperature with constant stirring for approximately 5 minutes.

In the first dipping pathway, the films were dipped before CdS layer was deposited on the TiO2 films. The dipping time was varied from 0.5 minutes to 5 minutes for 5-time durations (0.5 min, 1 min, 1.5 min, 2 min, 5 n) to determine the optimal value. This process allowed for the identification of both the optimal dipping time and the optimal concentration of $Cd2+$ and $S2-$ ion solutions described under 3.1. These films are designated as TiO2-AA/CdS

The second pathway involved dipping the films after the CdS coating on the TiO2 substrates using the previously identified optimal concentration of $Cd2+$ and $S2-$ ion solutions and dipping time. This film is designated as TiO2/CdS-AA

2.3   Deposition of CdS using SILAR method.

The masses of $CdCl_2$ and Na2S were measured according to table 1, with an electronic balance accurate to ±0.001 g. Then, 100 ml of distilled water was added to prepare the desired concentrations of Cd^{2+} and S^{2-}.

Table 1. The mass of $CdCl_2$ and Na_2S in each concentration of 100 ml.

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

A Previous study on pH variation (N.F. Ajward et al 2023) has indicated an optimal pH of 4.5. Therefor the pH values were adjusted to 4.5 in all the concentrations (1M, 0.75M,.5M and 0.25M) using 0.01 M NaOH and 0.01 M HCl solutions by adding dropwise while the solution pH was being monitored.

TiO2 coated films underwent a sequential dipping process. They were immersed in varying the concentrations of CdCl2 and Na2S solutions from 1 M to 0.25 M (1M, 0.75M, 0.5M, and 0.25M) for 1 minute each. After each dip, the photoanodes were washed with distilled water, air-dried, re dipped in the opposing precursor solution (anionic following cationic and vice versa), washed again, and finally air-dried. This entire cycle was repeated 10 times using Successive Ionic Layer Adsorption and Reaction (SILAR) method. Then films were finally dried on a hot plate at 80°C for 30 minutes.

2.4 Preparation of Electrolyte

A quantity of 2 ml of electrolyte was prepared using 0.1301 g of Na2S, 0.1283 g of S, and 0.0301 g of KCl. 1.4 ml of methanol and 0.6 ml of distilled water were then added as solvents. The mixture was stirred with a magnetic stirrer for 3 hours. The stirring time may have needed to be adjusted to prevent the precipitation of sulfur.

2.5 Fabrication of the cell

A counter electrode with a conductive side was placed face-to-face with the CdS coated TiO2 film and secured with two clamps. The space between the electrodes was then filled with the electrolyte solution, completing the QDSSC assembly.

2.6 Characterization

The fabricated QDSSCs will undergo rigorous characterization using a VK-PA-100 PV Power Analyzer to measure J-V curves, extracting key performance parameters like Photo Conversion Efficiency (PCE), Photo Current density (Jsc), Photo Voltage (Voc), and Fill Factor (FF), while ensuring reproducibility by testing at least five devices per batch.

To analyze the charge transport and recombination processes within the fabricated CdS QDSSCs, Electrochemical Impedance Spectroscopy (EIS) was employed using a frequency response analyzer (Auto lab Nova 2.1). By measuring the impedance spectra across a frequency range of 0.1 Hz to 1 MHz under constant simulated light intensity at room temperature, valuable insights can be gained into the interfacial charge transfer resistance and recombination dynamics. This information will be crucial for optimizing the device performance of the QDSSCs.

Incident Photon-to-Current Efficiency (IPCE) measurements will be used to evaluate the light-harvesting efficiency of the QDSSCs across the solar spectrum. This information helps us to understand the effectiveness of the QDs in capturing sunlight and converting it into photocurrent which was measured using a VK-IPCE-10 system.

U-V visible absorption spectroscopy was used to characterize the optical properties of the QDs and the overall device. The absorption properties of pure TiO2, ascorbic acid with TiO2, CdS, and ascorbic acid with CdS were characterized spectroscopically.

3   RESULTS AND DISCUSSION

3.1   I–V characteristics of CdS QDSSCs

Table 2 shows the variation of open-circuit voltage and current density across all investigated dipping times (0.5 min, 1 min, 1.5 min, 2 min, 5 min) in AA solution with the concentrations of Cd2+ and S2- ion solution of CdS QDSCs. Furthermore, considering all obtained current densities and voltages, the optimal value was achieved for the 0.5 M concentration with a 1.5-minute ascorbic acid dipping time.

Table 2. The current density and voltage data obtained for different concentrations and AA dipping times.

Cd^{2+} and S^{2-} concentration →	0.25 M			0.50 M			0.75 M			1 M		
AA Immersion time ↓	V_{oc} (mV)	J_{sc} (mAcm^{-2})	η%	V_{oc} (mV)	J_{sc} (mAcm^{-2})	η%	V_{oc} (mV)	J_{sc} (mAcm^{-2})	η%	V_{oc} (mV)	J_{sc} (mAcm^{-2})	η%
0.0 min	386	1.98	0.533	391	2.06	0.813	406	1.83	0.713	379	1.99	0.613
0.5 min	426	2..18	0.586	438	3.95	1.237	397	2.46	0.735	382	2.47	0.815
1.0 min	442	3.29	0.907	440	4.42	1.28	439	3.20	0.887	404	2.07	0.441
1.5 min	448	2.49	0.744	446	**4.86**	**1.368**	450	3.82	1.078	470	3.70	1.098
2.0 min	461	3.21	0.959	395	4.15	1.257	474	3.87	1.174	448	0.02	0.897
5.0 min	445	3.26	0.954	449	4.13	1.221	441	2.02	0.497	414	2.84	0.773

Figure 1 presents the current density-voltage (J-V) characteristics of Quantum Dot Sensitized Solar Cells fabricated by dipping 1.5min in AA solution and without ascorbic acid treatment on the TiO2 photoanode, before and after CdS deposition via SILAR considering the optimum concentration of 0.5M, alongside a reference device without ascorbic acid treatment. This comparison allows us to analyze the impact of ascorbic acid treatment on overall device performance. All the cells have a consistent active area of 0.64 cm².
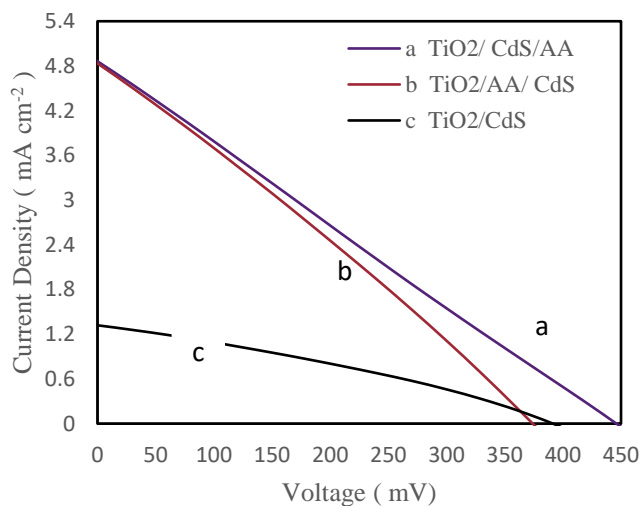

Figure 1. Current density–voltage characteristics of (a) TiO2/CdS-AA (b) TiO2 -AA/CdS (c) TiO2/CdS QDSSCs under the illumination of 100 mW/cm2 light intensity

Table 3 summarizes the crucial parameters extracted from the J-V characteristics, including the short-circuit current density (Jsc), open-circuit voltage (Voc), fill factor (FF), and most importantly, the photovoltaic conversion efficiency (η).

Table 3. Photovoltaic parameters of CdS QDSSCs

	J_{sc} (mA cm^{-2})	V_{oc} (mV)	FF	Efficiency
TiO2/CdS	2.063	391.4	0.315	0.813
TiO2-AA/CdS	4.863	446.1	0.246	1.368
TiO2 /CdS-AA	4.834	374.0	0.270	1.251

The table 3 allows for direct comparison of the impact of ascorbic acid treatment on the performance of the QDSSCs. Notably, the results indicate an increase in both Jsc and Voc for cells where the TiO2 photoanode was treated with ascorbic acid. This enhancement in Voc could be attributed to a rise in the quasi-Fermi level within the TiO2 layer. Ascorbic acid treatment might facilitate a higher density of electrons being injected from the quantum dots, leading to this observed shift in the quasi-Fermi level. The overall effect on cell performance is reflected in the photovoltaic conversion efficiency (η), which is also detailed in Table 01 for QDSSCs fabricated with and without ascorbic acid treatment under various conditions.

The data clearly demonstrated the positive impact of ascorbic acid treatment on device performance. Compared to the reference cell (TiO2/CdS) with an efficiency of 0.813, the inclusion of an ascorbic acid-treated TiO2 layer in the TiO2-AA/CdS configuration resulted in a significant efficiency increase to 1.368. This represents a remarkable improvement of efficiency over 68%.

Interestingly, the order of ascorbic acid treatment seems to have a subtle effect. While both pre-deposition and post-deposition treatments of CdS with ascorbic acid enhanced performance compared to the untreated reference cell, the pre-deposition method yielded slightly better results. It led to a small increase in short-circuit current density from 4.834 mA cm-2 to 4.863 mA cm-2, and a more substantial rise in open-circuit voltage from 374 mV to 446 mV. This ultimately translated into a higher efficiency of 1.368 compared to 1.251 for the post-deposition treatment. While the post-deposition method still offers improvement, the pre-deposition approach appears to be slightly more favorable for optimizing device performance.

3.2   EIS of CdS QDSSCs

Figure 2 presents the Electrochemical Impedance Spectroscopy (EIS) data for QDSSCs highlighting the influence of ascorbic acid treatment. The figure compares the impedance response of cells with and without ascorbic acid treatment, further differentiating between pre-treatment and post-treatment with AA. Interestingly, the data reveals that ascorbic acid does affect impedance. The cell configuration with TiO2-AA/CdS pre-dipped in ascorbic acid exhibits the highest impedance, while the lowest impedance is observed for the device with only ascorbic acid-treated TiO2 (TiO2-AA). These findings suggest that the specific placement of the ascorbic acid treatment layer impacts the interfacial charge transfer processes within the device.
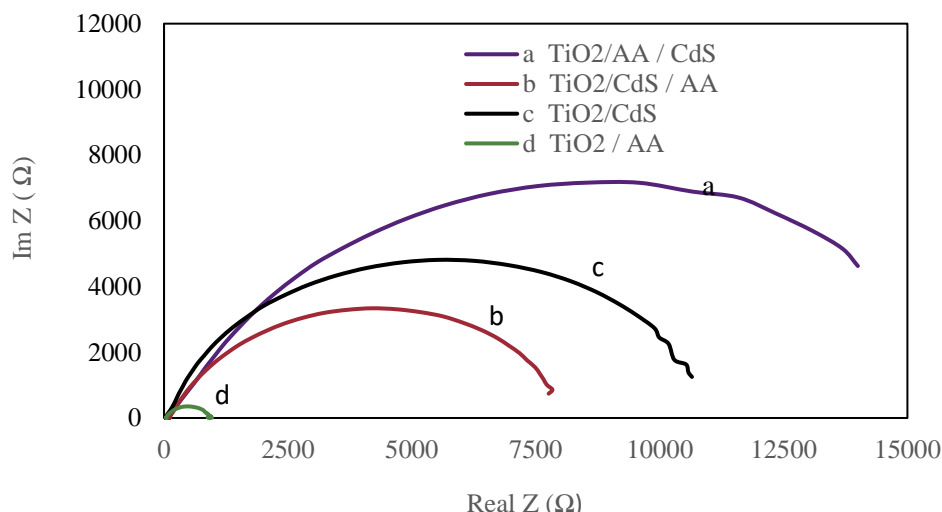
Figure 2. Impedance spectra characteristics of (a) TiO_2 –AA/CdS (b) TiO_2/CdS-AA (c) TiO_2/CdS (d) TiO_2 –AA

Figure 3 depicts the equivalent circuit model employed in this study. This model utilizes fundamental electrical components, including resistors, and capacitors to represent the key electrical characteristics of the actual circuit.
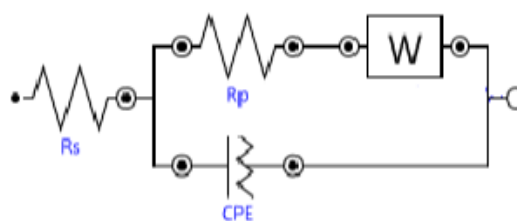

Figure 3. Equivalent circuit

Table 4. Parameters of equivalent circuit for different QDSC configuration

Parameters	TiO_2 /AA	TiO_2 /CdS	TiO_2 /AA/CdS	TiO_2 /CdS /AA
R_S	42.328 Ω	35.05 Ω	65.704 Ω	106.5 Ω
R_P	897.45 Ω	12.651 kΩ	22.49 kΩ	9.007 kΩ
CPE (n)	0.84124	0.82524	0.75527	0.80089

An equivalent circuit model can analyse the electrical behavior of the, revealing key parameters (Table 4). Parallel resistance (Rp) reflects charge transfer ease between materials, impacting photocurrent and photocatalysis efficiency. High Rp hinders charge recombination enhancing achievable current density. Series resistance (Rs) represents the overall resistance the current experiences, leading to energy loss as heat and reduced performance. A high Rs limits the current density by impeding the charge flow and dissipating the energy. (Dr. John T et al, 1990). An equivalent circuit analysis reveals TiO2/AA has the lowest Rp, enhancing recombination and likely causing lower current density. Constant Phase Element (CPE) accounts for non-idealities in the system's capacitance. Notably, a CPE exponent (CPE n) of 1 signifies ideal capacitor behaviour, where capacitance remains constant regardless of QDSC, simplifying the interpretation of charge storage characteristics. (Dr. John T et al, 1990)

3.3   Optical Characterization

Figure 4 presents the absorption spectra of ascorbic acid, CdS, TiO2 and CdS and TiO2 with ascorbic acid treatment. The plot reveals a significant increase in light absorption within the 370-570 nm range for the ascorbic acid-treated samples compared to the untreated bare CdS and TiO2. This enhanced absorption across the visible spectrum suggests that ascorbic acid treatment modifies the electronic properties of TiO2, potentially leading to improved light harvesting capabilities.

Furthermore, the absorption profile of CdS also shows a tendency towards increased absorption with ascorbic acid treatment. A comprehensive understanding of these combined effects on both CdS and TiO2 light absorption is crucial for elucidating the overall impact of the treatment on the device's light-to-current conversion efficiency, which ultimately determines its photovoltaic performance.
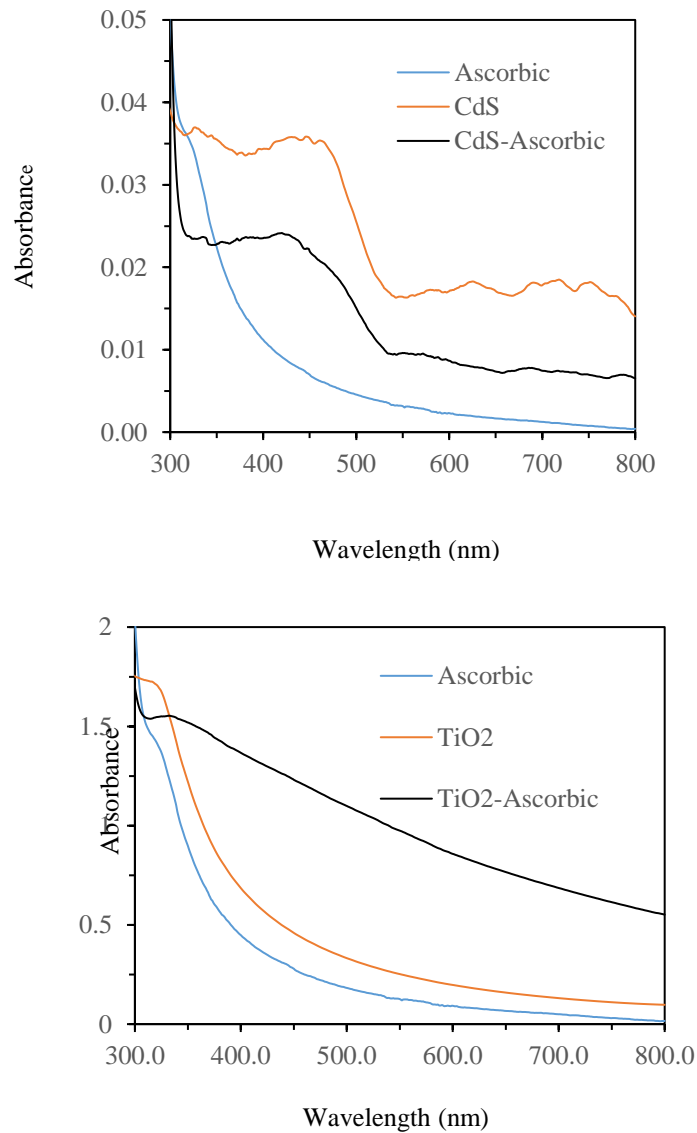

Figure 4. Absorption Spectra of Ascorbic Acid Treated and Untreated CdS/TiO$_2$ Photoanodes

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

The IPCE spectrum offers valuable insight into the light-harvesting efficiency of photovoltaic devices. It depicts the number of electrons generated by the solar cell per incident photon at a specific wavelength (λ), essentially representing the internal quantum efficiency. Figure 5 presents the IPCE spectra of the fabricated CdS QDSSCs, comparing devices with and without ascorbic acid treatment. By analyzing the IPCE response across the wavelength range, we can elucidate the influence of ascorbic acid treatment on the light absorption and current generation processes within the devices. Figure 4. shows that all three materials have a similar trend, with IPCE increasing as the wavelength of light increases. This means that these materials are more efficient at converting longer wavelengths of light into electrical current. The material with the highest IPCE across the measured wavelengths is b-TiO2/CdS/AA.
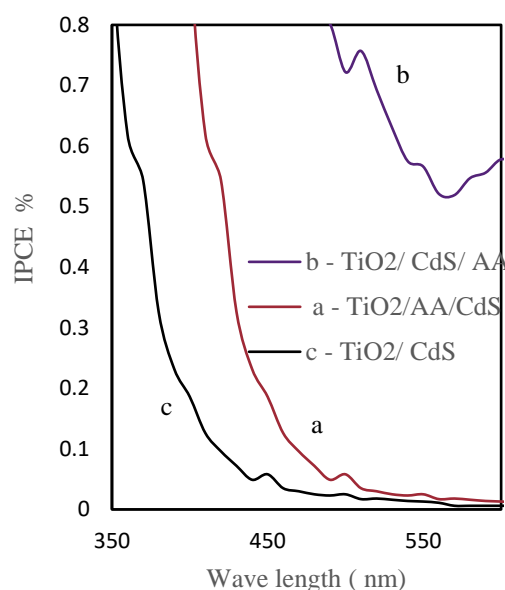

Figure 5. Incident Photon-to-Current Efficiency (IPCE) of CdS Quantum Dot Sensitized Solar Cells (QDSSCs) with configuration (a) TiO_2 -AA/CdS (b) TiO_2/CdS-AA (c) TiO_2/CdS

4 CONLUSION

In conclusion, this work establishes ascorbic acid as a powerful surface modifier for TiO2/CdS photoanodes in QDSSCs. Its absorption spectra revealed a significant increase in light capture (370-570 nm) for treated samples, suggesting potential modification of TiO2's electronic properties. This translated to a remarkable 68% enhancement in overall efficiency compared to untreated devices. Notably, both pre- and post-deposition ascorbic acid treatment increased. the efficiency but pre-treatment yield the highest. These findings highlight the promise of ascorbic acid as a simple and efficient strategy for optimizing light harvesting and boosting QDSSC performance. TiO2/CdS/AA exhibits significantly higher parallel resistance (Rp) compared to other investigated materials. This higher Rp facilitates efficient charge transfer at the electrode interface, leading to a higher achievable photocurrent density reducing charge recombination. The graph shows that all three materials have a similar trend, with IPCE increasing as the wavelength of light increases. This means that these materials are more efficient at converting longer wavelengths of light into electrical current. The material with the highest IPCE across the measured wavelengths is TiO2/CdS/AA. And all materials exhibit increasing IPCE with longer wavelengths, favouring conversion of light into electricity. Among those TiO2/CdS/AA shows the highest light-to-current efficiency across measured wavelengths. Further investigation into its underlying mechanisms and broader applicability is warranted.

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