ENHANCED PERFORMANCE OF TiO_2 / CdS QUANTUM DOT SOLAR CELL BY INCORPORATING ZnO TO THE PHOTOANODE

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In an effort to improve the efficiency of TiO_2/CdS quantum dot-sensitized solar cells (QDSSCs), ZnO was incorporated into the TiO_2 photoanodes. ZnO serves as an electron transport layer and may help reduce electron-hole recombination by facilitating charge separation and transport. The research explored the photovoltaic performance of the resulting cell, with a focus on varying the mass ratio of TiO_2 and ZnO. Introduction of ZnO at 1:1 ratio to the TiO_2 photoanode significantly enhanced the short-circuit current density (2.059 mA cm^{-2}) and power conversion efficiency (0.642), representing an 81% improvement compared to the TiO_2/CdS cell. The formation of an energy barrier between TiO_2 and CdS by ZnO is supposed to hinder electron backflow and promote efficient charge transport in the photoanode. Additionally, ZnO may also passivate surface states on the TiO2 film, reducing recombination sites for photogenerated charge carriers. Furthermore, EIS studies revealed that the charge transfer resistance between photoanode and electrolyte reduces by incorporating ZnO to the TiO_2 photoanode. The IPCE results indicate that ZnO/TiO_2 ratio significantly influences QDSSC efficiency. ZnO/ TiO_2 1:1 ratio demonstrated optimal performance, especially within the 400-480 nm wavelength range. These findings suggest ZnO holds promise for enhancing TiO_2/CdS QDSSC performance.

Keywords: quantum dots, sensitization, solar cells, Cadmium Sulphide, ZnO

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INTRODUCTION

Quantum dot sensitized solar cells (QDSSCs) have emerged as a highly attractive area of research to develop high-efficiency solar cells. These cells function by utilizing a semiconductor photoanode coated with light-absorbing quantum dots (QDs). (Bang & Kamat, 2009, Fujishima & Honda 1972, Santra & Kamat 2012) Upon absorbing sunlight, QDs generate excitons (electron-hole pairs). The excited electron is then injected into the wide bandgap photoanode (often TiO_2 or ZnO), while the hole is transferred to the electrolyte. (Zhu et al., 2011). This process ultimately leads to generation of electricity QDs possess several advantages over traditional dye sensitizers. Unlike dyes, QDs offer a size-tunable bandgap, allowing efficient absorption across a wider range of the solar spectrum, including the infrared region. Additionally, QDs boast superior stability and resistance to degradation, making them ideal for long-term use. Furthermore, QDs enable multi-layered structures and hold the potential for generating multiple excitons from a single photon, further enhancing light capture and energy conversion. The versatility of QDs extends to their composition, allowing for a vast array of material combinations for optimization.

Several techniques can be employed to deposit QDs onto the photoanode. Among them, successive ionic layer adsorption and reaction (SILAR) stands out for its precise control over QD size and density. This method offers a relatively fast and efficient deposition process, even for multilayer structures. SILAR's ability to precisely control QD growth makes it a powerful tool for tailoring QDSSC performance and paves the way for the development of highly efficient next-generation solar cells. (Toyoda et al., 2003, Tachibana et al., 2008. Barceló et al., 2011)

In most QDSSCs, titanium dioxide (TiO_2) acts as the electron highway, accepting excited electrons from QDs and transporting them to generate electricity. Its stability and well-matched energy levels make it a vital component for efficient solar cell functionality. ZnO, like TiO_2, acts as a QDSSC photoanode, but its wider bandgap might enable higher photovoltages. Scientists have explored various materials to improve TiO_2 solar cells. Different materials such as SiO_2(Jimenez-Villar et al., 2013), Cu_2O (Su et al., 2009), CdS (Hao et al., 2012) and ZnO (Samsuri et al., 2017) have been used in photoanodes to couple with TiO_2 to enhance its performance, where ZnO stands out due to its wide bandgap and strong ability to hold electrons. ZnO can also be formed into many interesting shapes, further enhancing its performance in solar cells. While ZnO itself mostly absorbs UV light, pairing it with CdS, which makes it sensitive to visible light. This TiO_2/ZnO/CdS combination reduces electron loss and enhance efficiently, making it a promising design for solar cell fabrication. Here we have studied about composites made of TiO_2 and ZnO at different composition as photoanode of CdS QDSSCs.

METHODOLOGY

Preparation of TiO_2/ZnO Films

To prepare the paste to cast the films, a mixture of TiO_2 and ZnO was prepared following the weight ratios specified in the table 1.

Table 01: Mass ratios of TiO_2 and ZnO

	TiO_2/ZnO ratio	Mass of TiO_2 (g)	Mass of ZnO (g)
1	1:0	0.25	0
2	3:1	0.187	0.063
3	1:1	0.125	0.125
4	1:3	0.063	0.187
5	0:1	0	0.25

TiO_2/ZnO paste was prepared by combining appropriate amounts of TiO_2 and ZnO powders according to the weight ratios specified in Table 1. The mixture was then ground with 1 ml of 0.1 M HNO_3 solution, 1 drop of Triton X-100, and 1 drop of PEG1000 using a mortar and pestle for 30 minutes to achieve a homogenous past. The paste was then spread by the doctor blade method on pre-cleaned conducting tin oxide (CTO) glass plates cut into a size of 1.0 cm × 2.0 cm. The cleaning process involved washing in 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.

Preparation of Na_2S and $CdCl_2$ solutions.

Mass of 10.065g $CdCl_2$ and 3.902g Na_2S were measured using an electronic balance to an accuracy of ±0.001 g. Then, 100 ml of distilled water was added to prepare 0.5M concentrations of Cd^{2+} and S^{2-} solution. The pH values of the solutions were adjusted to 4.5 using 0.01 M NaOH and 0.01 M HCl adding drop wise while the solution pH was monitored.

Deposition of CdS using SLILAR method

The films underwent a sequential dipping process. They were immersed in 0.5 M $CdCl_2$ and Na_2S solutions for 1 minute each. After each dip, the photoanodes were washed with distilled water, air-dried, dipped again in the other precursor solution (anionic following cationic and vice versa), washed again, and finally air-dried. This process was repeated 10 times using Successive Ionic Layer Adsorption and Reaction (SILAR) method. Then the films were finally dried on a hot plate at 80°C for 30 minutes.

Preparation of Electrolyte

2 ml of electrolyte was prepared dissolving 0.1301 g of Na_2S, 0.1283 g of S and 0.0301 g of KCl in 1.4 ml of methanol and 0.6 ml of distilled water. Concentration of Na_2S, S and KCl in the electrolyte were 0.5 M, 2 M and 0.2 M respectively. The mixture was stirred with a magnetic stirrer for 3 hours. The stirring time may need to be adjusted to prevent the precipitation of sulphur.

Fabrication of the cell

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

Characterization

Fabricated FTO/(TiO_2/ZnO) CdS QDSSCs were characterized using VK-PA-100 PV Power Analyzer to measure J-V curves, extracting key performance parameters like PCE, Jsc, Voc, and 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 (Autolab 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 were 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) measurement was 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 that measured using a VK-IPCE-10 system.

RESULTS AND DISCUSSION.

I–V Characteristics of CdS QDSSCs

Figure 1 shows the current density-voltage (J-V) characteristics of Quantum Dot-Sensitized Solar Cells (QDSSCs) fabricated with TiO_2/ZnO photoanodes prepared using different compositions of TiO_2 and ZnO, as detailed in Table 2.

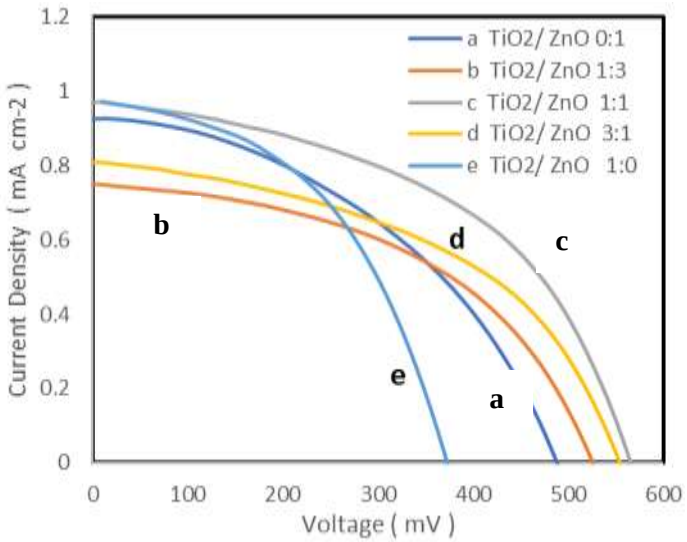

Figure 1: I-V characteristics of CdS QDSSCs with photoanodes of different TiO_2/ZnO compositions under 100 mW cm^{-2} illumination.

Table 02. Photovoltaic parameters of CdS QDSSCs with different compositions of TiO_2/ZnO photo anodes

TiO_2/ZnO ratio by	J_{sc} (mA cm^{-2})	V_{oc} (mV)	FF	Efficiency
1:0	1.87	488.9	43.5%	0.398
3:1	1.531	525.4	48.1%	0.387
1:1	2.059	574.8	54.2%	0.642
1:3	1.645	554.1	47.6%	0.434
0:1	1.975	373.1	48.1%	0.354

According to Figure 1 and Table 2, the composition of photo anode with TiO_2/ZnO of 1:1 ratio by weight achieved the superior performance among the investigated other ratios. This composition exhibited the maximum current density of 2.059 mA/cm² at a voltage of 574.8 mV. Furthermore, it demonstrated the highest fill factor of 54.2% and the greatest efficiency of 0.642%, highlighting its potential for optimized photovoltaic device fabrication.

Moreover, the photovoltaic performance of CdS QDSSCs significantly improved when employing 1:1 ratio of TiO_2 and ZnO by weight in the photo anode compared to devices with solely TiO_2: ZnO 1:1 ratio likely optimizes the morphology and porosity of the photoanode, which need to be further verified enabling superior infiltration of photo generated electrons in the CdS QDs. This enhanced infiltration may create a more efficient pathway for photo generated electrons within the QDs to travel towards the collecting electrode, minimizing recombination losses. Consequently, the 1:1 ratio achieved a significantly higher power conversion efficiency (PCE) of 0.642%, representing an increase of approximately 81.35% compared to devices containing only TiO_2 or ZnO (estimated efficiency around 0.354%). This finding strongly suggests that incorporation of ZnO into TiO_2 photoanode plays a crucial role. The wider bandgap of ZnO compared to CdS likely contributes to this enhancement by potentially acting as a barrier, hindering the recombination of electrons injected from the CdS QDs with holes in the CdS valence band. This suppression of recombination allows for more efficient electron transport and overall improved device performance.

EIS of CdS QDSSCs

Figure 2 represents the Nyquist plots of different TiO_2 /ZnO mass ratios in CdS quantum dot solar cells. These plots unveil the electrical properties of various combinations of ZnO and TiO_2, potentially forming composite electrodes, as analyzed using impedance spectroscopy. Figure 2: Nyquist plots of CdS QDSSCs with different mass ratios of TiO_2 and ZnO

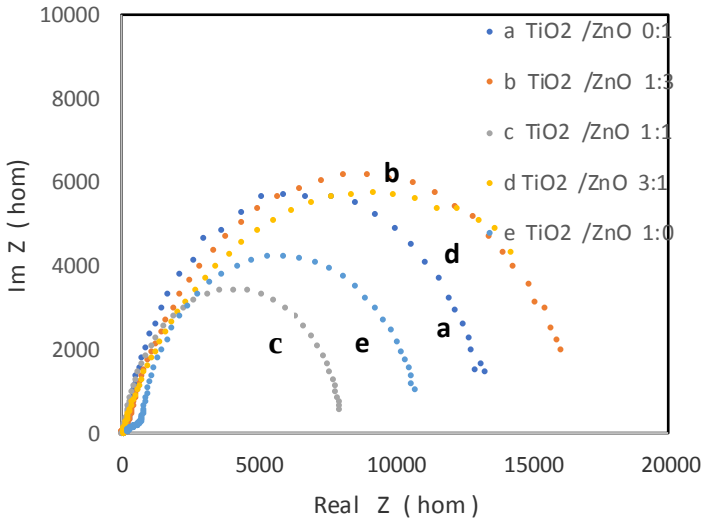

Figure 2: Nyquist plots of CdS QDSSCs with different mass ratios of TiO_2 and ZnO

Figure 3 represents a typical equivalent circuit of a photo anode derived from the Nyquist plots and table 3 shows the relevant values of each composition. Series resistance (R_S) signifies the ease with which charge carriers travel through the photo anode and electrolyte solution, with lower values indicating better conductivity. TiO_2/ZnO with a ratio of 1:1 exhibits the lowest value of 43.9 Ω resulting most efficient charge flow in the photo anode. Conversely, parallel resistance (RP) reflects the resistance encountered during electron transfer at the electrode electrolyte interface. Higher R_P values suggest greater difficulty for charge carriers to move through the interface. Photo anode of TiO_2/ZnO with the composition 1:1 has the lowest value of 8.48 kΩ he constant phase element (CPE) parameter (N) sheds light on the capacitance behaviour of the interface between the electrode and the electrolyte. Values closer to 1 indicate an ideal capacitor-like behaviour. By analysing these parameters across different ZnO: TiO_2 ratios, influence the overall electrical properties of the resulting material.

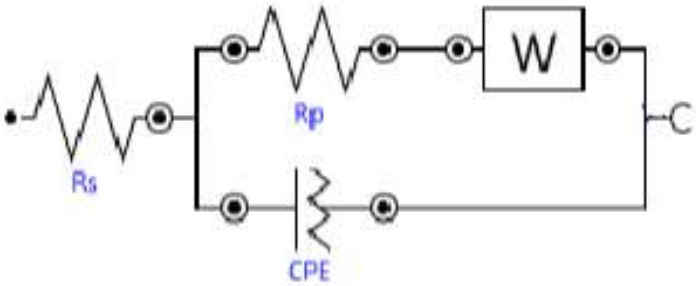

Figure 3. Equivalent circuit

Table 3: Parameters of equivalent circuit for different TiO_2 ZnO mass ratio

TiO_2/ZnO ratio by weight	R_S (R)	R_P (R)	CPE (N)
1:0	301Ω	10.7 kΩ	0.850
3:1	127Ω	16.8 kΩ	0.808
1:1	43.9Ω	8.48 kΩ	0.841
1:3	191Ω	13.3 kΩ	0.899
0:1	57.1Ω	18.1 kΩ	0.722

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

Figure 4 presents the Incident Photon to Current Efficiency (IPCE) spectra of ZnO/TiO_2 quantum dot sensitized solar cells (QDSSCs) for varying TiO_2/ZnO mass ratios. A clear correlation between composition and device performance is observed.

The 1:1 mass ratio of ZnO to TiO_2 demonstrated superior light-harvesting capabilities, as evidenced by its enhanced IPCE values compared to other compositions. This particular ratio exhibited a peak in the 400-480 nm wavelength region, suggesting efficient absorption of light. Furthermore, the corresponding current density measurements confirmed the superior performance of the 1:1 ZnO/TiO_2 QDSSC. The readings indicate that the optimal composition of ZnO and TiO_2 is crucial for achieving high efficiency in QDSSCs.

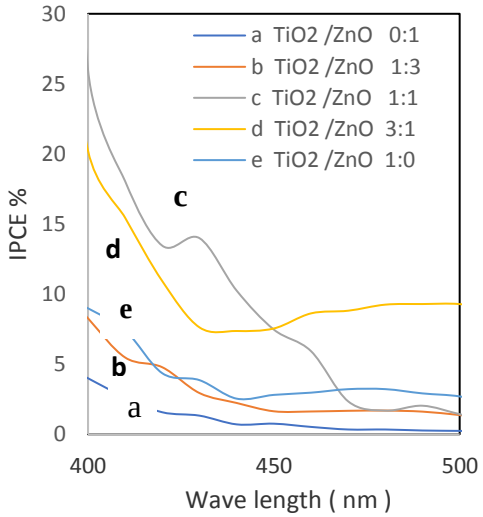

Figure 4: Incident Photon-to-Current Efficiency (IPCE) of CdS Quantum Dot Sensitized Solar Cells (QDSSCs)

CONCLUSION

The incorporation of ZnO to TiO_2 photo anodes significantly influenced the performance of CdS quantum dots photovoltaic devices. Amongst various TiO_2: ZnO mass ratios investigated, 1:1 ratio demonstrated superior power conversion efficiency (PCE). Figure 4 shows that ZnO/TiO_2 ratio significantly affects QDSSC efficiency. The 1:1 ratio excelled, with peak performance at 400-480 nm. Optimal composition is crucial for maximizing light absorption and device efficiency. This composition achieved a remarkable 81.35% enhancement in PCE (0.642%) compared to devices containing only TiO_2 or ZnO (estimated efficiency of 0.354%). Furthermore, the 1:1 ratio exhibited favourable electrical properties. Impedance spectroscopy revealed a lower series resistance (43.9 Ω) and charge transfer resistance in the photo anode and electrode electrolyte interface respectively indicating enhanced charge conductivity within the material. Additionally, Incident Photon-to-Current Efficiency (IPCE) measurements confirmed a significant enhancement for the 1:1 ratio, highlighting the critical role of TiO_2: ZnO composition in optimizing overall cell efficiency.

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