

## **Efficiency enhancement in solvent free dye-sensitized solar cells by incorporation of PbS quantum dots**

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### **Abstract**

Inexpensive dye-sensitized solar cells (DSSCs) show promise as a viable third-generation solar cell technology. Usually, Ru-based dye molecules are used in DSSCs. A particular dye molecule can only absorb the light photon from a particular wavelength range. The enhancement of Dye-Sensitized Solar Cell (DSSC) performance can be achieved through co-sensitization with additional dyes or quantum dots (QDs). Quantum dots, owing to their diminutive dimensions and quantum confinement phenomena, which are modifiable by altering their size and morphology, manifest distinct electronic and optical characteristics that are particularly pertinent to the optimization of DSSCs. In this study, TiO<sub>2</sub> – based PbS/N719 dye co-sensitized quasi–solid solar cells have been fabricated and characterized. DSSCs comprised with dye and the PbS QDs showed an efficiency of 4.72% with a higher short-circuit current density of 2.30 mA cm<sup>-2</sup> whereas the DSSC fabricated with only Ru N719 dye delivered 4.12% efficiency under the same light condition with 100 mW cm<sup>-2</sup>. The solar cell sensitized solely with N719 dye demonstrates an efficiency of 4.12%. Around 14% enhancement in the efficiency of DSSCs has been achieved due to the incorporation of PbS QDs.

**Keywords:** Co–sensitization, Quantum dots, multiple exciton generation, tunable bandgap, quasi solid electrolyte

### **1. Introduction**

Dye-sensitized solar cells (DSSCs) represent a class of photovoltaic (PV) devices engineered to harness light energy and transform it into electrical energy, employing a photosensitive dye as a pivotal component in the energy conversion process. These remarkable devices were originally pioneered by M. Grätzel and O. Regan in 1991 [1]. The fundamental architecture of a DSSC encompasses a porous layer of titanium dioxide (TiO<sub>2</sub>) nanoparticles that has absorbed the photosensitive dye, situated upon a conductive substrate. An additional essential element includes a platinum-coated counter electrode, along with an appropriate electrolyte solution. The attachment of dye molecules to the semiconductor surface occurs via functional groups present on the dye molecules themselves. Notably, commercially available ruthenium-based dyes like N719 demonstrate superior performance within these DSSCs [2]. Upon exposure to sunlight, the dye-coated TiO<sub>2</sub> layer intercepts photons, initiating the excitation of electrons within the dye molecules. Subsequently, these energized electrons are injected into the TiO<sub>2</sub> layer. Facilitated by an external circuit, these electrons navigate through the conductor, establishing an electrical current in the process. The counter electrode assumes the role of electron collector, ultimately closing the electrical circuit [1-3].

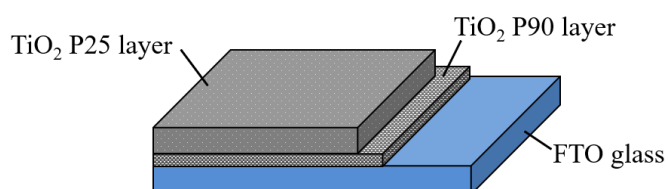
DSSCs have several advantages over traditional silicon solar cells, including lower production costs, greater flexibility, and better performance in low light conditions. However, they also have some disadvantages, including lower efficiency (typically around 10-15%), and a shorter lifespan [1-5]. Despite these drawbacks, DSSCs continue to be an area of active research and development, due to its vital role in the future in the solar energy technology [3-6].

Even though the DSSCs fabricated with liquid electrolytes have shown efficiencies of  $\sim 14\%$ , there exist many problems with the usage of these liquid electrolytes [3,4]. The widespread commercial adoption of these devices faces significant challenges relating to encapsulation and the evaporation of liquid electrolytes. One promising avenue to address these challenges involves substituting the liquid electrolytes with quasi-solid-state alternatives. Nevertheless, it is important to note that the overall efficiencies of quasi-solid-state DSSCs are noticeably lower when compared to their counterparts employing liquid-state electrolytes [3-6]. In these DSSCs, dye molecules capture photons within a specific wavelength range of light [1,2]. Therefore, in order to enhance the efficiency of these DSSCs, the spectral responses of these devices should be widened. This can be done by in cooperating with more than one dye or any other suitable light-absorbing materials and this process is known as co-sensitization. Numerous investigations have been documented concerning co-sensitized dye-sensitized solar cells, as delineated in prior studies [7-10]. In this particular domain, quantum dots (QDs) have garnered substantial interest due to their appealing optical characteristics. These attributes encompass the generation of multiple excitons, tunable bandgap as a consequence of quantum confinement phenomena, and notably high molar extinction coefficients. [10, 11]. Recently, dye/quantum dot co-sensitized liquid electrolyte-based solar cells have been reported with enhanced efficiencies specially based on CdS and CdSe or both together [11-13]. Quantum dots are tiny semiconductor particles that are usually just a few nanometers in size. The most commonly used QDs in solar cells are CdS and CdSe [13]. Very few research investigations have been carried out with the co-sanitization of these QDs in DSSCs with quasi solid-state electrolytes [13,14]. In this study, we investigated the potential utilization of PbS QDs in co-sensitized Dye-Sensitized Solar Cells (DSSC). For the first time, we synthesized and evaluated DSSCs incorporating a co-sensitization scheme involving N719 dye and PbS quantum dots. These solar cells were constructed using a polyethylene oxide-based quasi-solid polymeric electrolyte and subjected to comprehensive characterization.

## 2. Methodology

### 2.1 Fabrication of TiO<sub>2</sub> photoanode

First, Fluorine doped Tin oxide (FTO) glass substrates with 1 cm  $\times$  2 cm size were cleaned with ethanol and dried. In order to prepare a compact TiO<sub>2</sub> layer, a creamy paste was prepared by using TiO<sub>2</sub> P90 nanoparticle with 0.25 g of TiO<sub>2</sub> P90 powder and 1 ml of 0.1 M HNO<sub>3</sub>. Then it was spin coated on the FTO by spin coating process with 3000 rpm for 1 minute. Substrates with TiO<sub>2</sub> films were kept at 450 °C in a furnace about 45 minutes. Then another paste of TiO<sub>2</sub> was prepared using P25 TiO<sub>2</sub> powder of 0.25 g with, 0.02 g of Triton X-100, 0.05 g of Polyethylene glycol (Mw1000), and 1 ml of 0.1 M HNO<sub>3</sub>. This TiO<sub>2</sub> P25 paste was applied on TiO<sub>2</sub> P90 layer by the “doctor blade” method. Then the electrode was sintered at the same conditions and the electrodes were allowed to cool. Figure 1 schematically shows the structure of the fabricated electrode.



**Figure 1:** Schematic diagram showing  $\text{TiO}_2$  photoanode with two different  $\text{TiO}_2$  layers on FTO substrate

## 2.2 Preparation of $\text{TiO}_2/\text{PbS}$ electrodes

$\text{PbS}$  quantum dots were deposited on the above  $\text{TiO}_2$  electrodes using dip-successive ionic layer adsorption and reaction methods (dip-SILAR). 0.1 M  $\text{Pb}(\text{NO}_3)_2$  (aq) was used as the cation source and 0.1 M  $\text{Na}_2\text{S}$  (aq) was used as the anion source. FTO substrates with  $\text{TiO}_2$  films were dipped in the above solutions consecutively. The dipping time was 1 minute for each solution. Photoanodes with  $\text{PbS}$  were dried at 50 °C for 10 minutes and kept in a desiccator for further use. In order to find the suitable size and the amount of the  $\text{PbS}$  quantum dots for efficient DSSCs, several photoanodes were fabricated and tested with several dip-SILAR cycles.

## 2.3 Sensitization with N719 dye

Dye adsorption was carried out on  $\text{TiO}_2/\text{PbS}$  electrodes by dipping in 0.3 mM ethanolic N719 standard dye (Di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium (II)) solution for 12 hours.

## 2.4 Fabrication of quasi-solid state gel polymer electrolyte

At first, iodine (0.0158 g) and 0.1564 g of tetrapropylammonium iodide were completely dissolved in 1.5 ml of acetonitrile by magnetically stirring at room temperature. Then, 0.264 g of Polyethylene Oxide was added little by little while it was magnetically stirred. Stirring was carried out for 12 hours. Finally, a homogeneous quasi-solid electrolyte was obtained.

## 2.5 UV-Visible absorption measurements

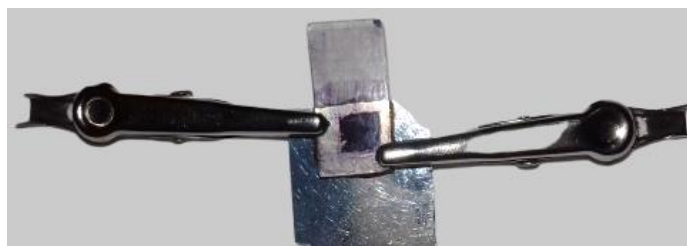
The UV-Visible optical absorption spectra of both the titanium dioxide ( $\text{TiO}_2$ ) electrode and the electrode co-sensitized with lead sulfide ( $\text{PbS}$ ) and N719 dye were investigated using a Shimadzu 2450 spectrophotometer. The spectra were acquired within the wavelength range spanning from 350 to 1100 nanometers (nm).

## 2.6 Energy-dispersive X-ray (EDX) spectrum

The formation of  $\text{PbS}$  quantum dots in the  $\text{TiO}_2$  electrode was confirmed by taking EDX spectrum of  $\text{TiO}_2/\text{PbS}$  electrode by using transmission electron microscope (JEOL JEM-2100).

## 2.7 Electrical characterization

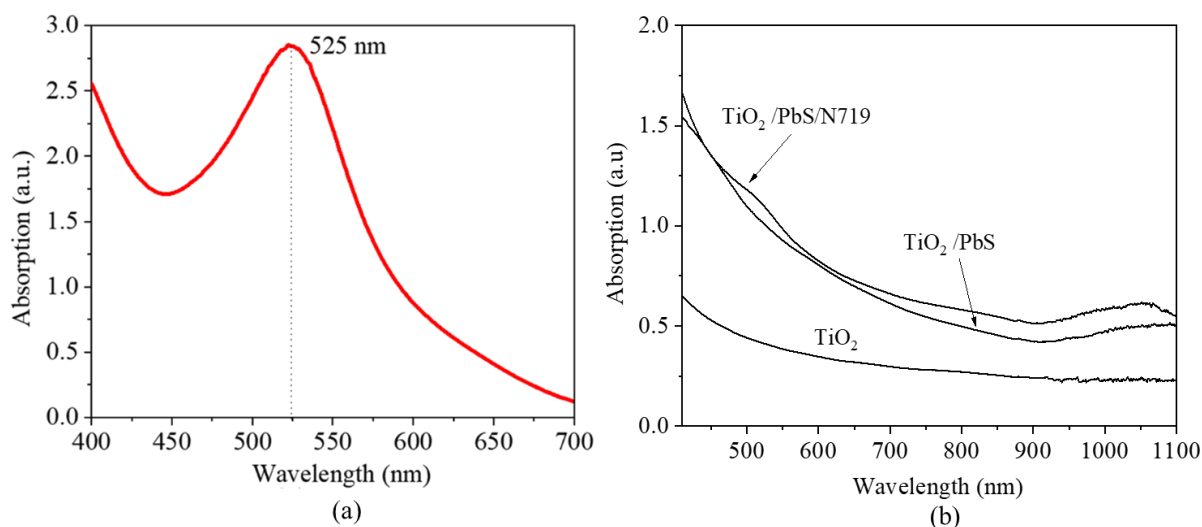
A suitable quantity of gel polymer electrolyte was placed on the active side of the photoanode and sandwiched with a Pt-coated counter electrode. Finally, both electrodes were clamped together using the stainless-steel clips with the cell configuration of  $\text{FTO}/\text{TiO}_2/\text{PbS}/\text{N719}/\text{electrolyte}/\text{Pt}$  as shown in Figure 2. The current density-voltage characteristics of the devices were assessed using a PV power analyzer while exposed to an illumination level equivalent to 1 sun ( $100 \text{ mW cm}^{-2}$ ). The effective area of the solar cell under investigation was determined to be  $0.16 \text{ cm}^2$ .



**Figure 2:** Photograph showing the clamping of electrodes together with steel clips.

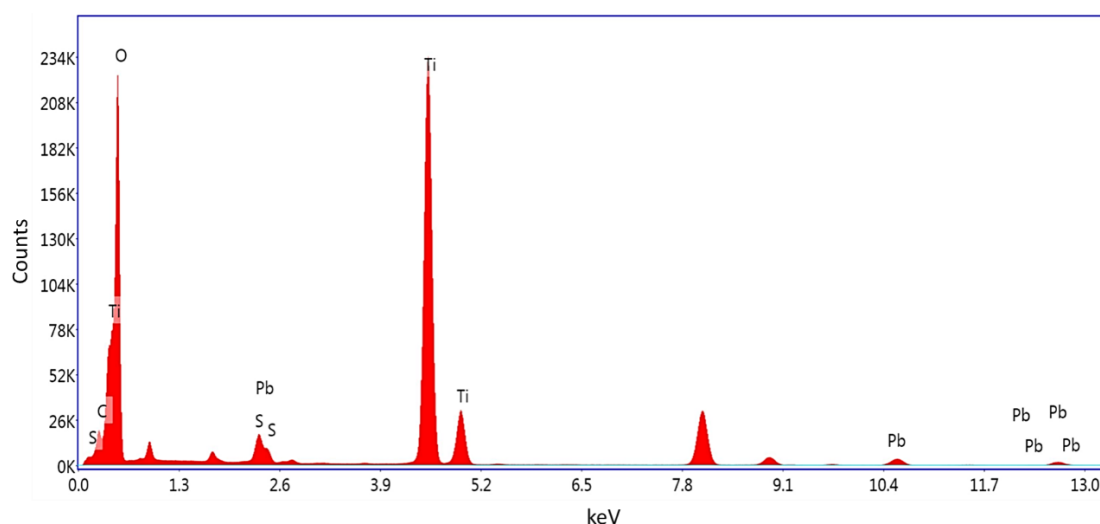
### 3. Results and Discussion

The UV-visible optical absorption spectrum of N719 dye in ethanol is shown in Figure 3 (a) and the characteristic absorption peak around 525 nm can be seen very clearly in the figure. Figure 3(b) shows the absorption of  $\text{TiO}_2/\text{PbS}/\text{N719}$  electrode. There are noticeable prominent peaks within the range of 450 nm to 550 nm, attributed to the absorption of N719 dye. Additionally, a distinct peak at approximately 1050 nm, indicative of the infrared light absorption by PbS quantum dots, is also clearly observable. These observations clearly confirm the light photon absorption in both the visible and IR regions due to the incorporation of both the Ru dye and the PbS QDs respectively.



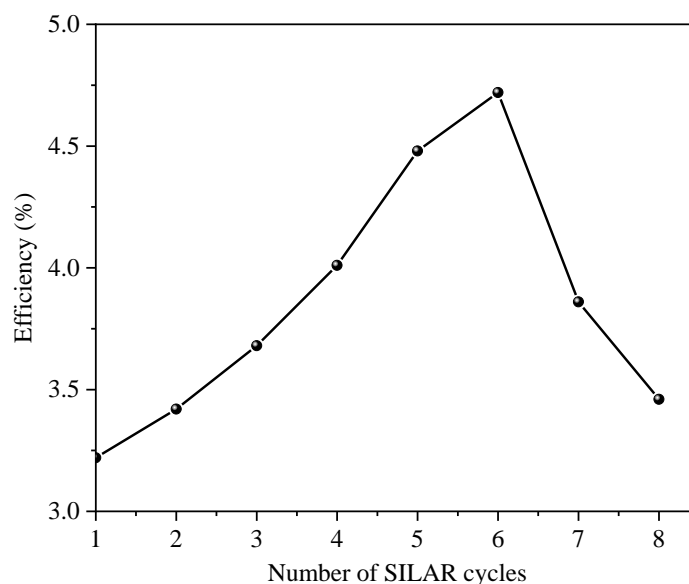
**Figure 3:** Optical absorption spectra of (a) N719 dye in ethanol solution, (b)  $\text{TiO}_2/\text{PbS}/\text{N719}$  dye electrode.

The EDX spectrum obtained on the photoanode with PbS quantum dots is shown in Figure 4. The characteristic peaks are visible in the figure belong to Pb and S further confirming the existence of the PbS in the photoanode.



**Figure 4:** EDX spectrum of  $\text{TiO}_2/\text{PbS}$  photoanode

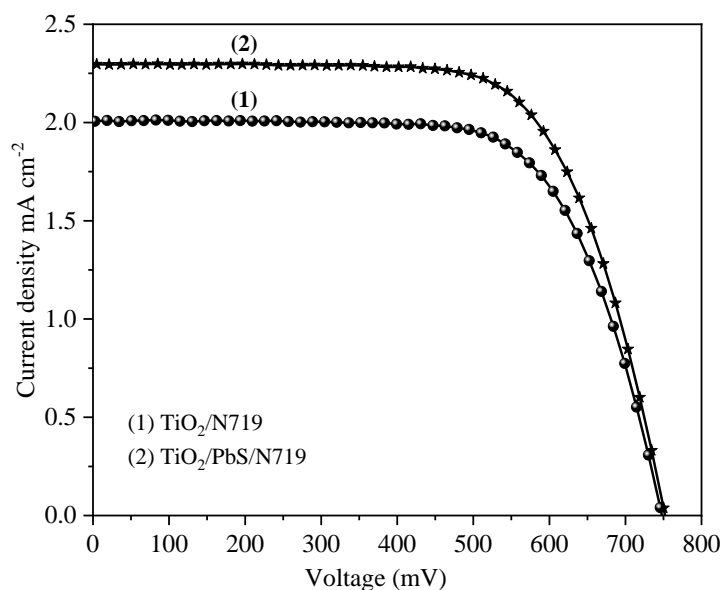
Figure 5 depicts the systematic variation in overall efficiency observed in co-sensitized solar cells fabricated by varying the numbers of Dip-SILAR cycles and under 1-sun illumination conditions, characterized by an incident photon flux of  $100 \text{ mW cm}^{-2}$  and AM 1.5 spectral filtering. As illustrated in the figure, the efficiency of these solar cells exhibits a gradual increase commensurate with the number of SILAR cycles applied, culminating in its maximum at approximately 4.72% efficacy with the utilization of 5 SILAR cycles. However, beyond this critical threshold of 5 SILAR cycles, a decreasing trend in efficiency becomes evident. This declining efficiency can be attributed to two primary factors. First, the escalation in the number of SILAR cycles leads to an increase in the size of the QDs, thereby influencing the average inter distance between PbS QDs and  $\text{TiO}_2$  crystallites. Secondly, the elevated number of SILAR cycles results in the deposition of a greater quantity of quantum dots on the  $\text{TiO}_2$  surface, fostering PbS aggregation and consequently detrimentally affecting the solar cell's performance, as elaborated in references [13-17].



**Figure 5:** Efficiency variation of co-sensitized DSSCs with the number of dip-SILAR cycles in the deposition of PbS quantum dots.

Figure 6 shows the short circuit current-density-voltage characteristics of DSSCs sensitized with only N719 dye and co-sensitized with dye and PbS QDs. As is evident from the figure, the

combination of PbS in the photoanode significantly increased the device's performance. A noteworthy increase in the short-circuit current signifies that PbS effectively enhances the overall efficiency by augmenting light absorption, which in turn promotes the transfer of electrons to the conduction band of TiO<sub>2</sub>. Typical photovoltaic parameters extracted from the Figure 6 are tabulated in Table 1.



**Figure 6:** Current voltage characteristics of DSSCs fabricated (1) without and (2) with PbS under the same illumination

**Table 1:** Current - voltage parameters of the fabricated DSSCs under the intensity of 100 mW cm<sup>-2</sup>

Sensitizers	$J_{SC}$ (mA cm <sup>-2</sup> )	$V_{OC}$ (mV)	$FF$ (%)	Efficiency (%)
N719	2.01	747.2	68.6	4.12
PbS/N719	2.30	751.7	68.2	4.72

As can be seen from Table 1, DSSCs sensitized with both the dye and the PbS QDs showed overall efficiency of 4.72% whereas the devices sensitized with dye alone showed an efficiency of 4.12% efficiency under the same illumination conditions. This enhancement is purely due to the co-sensitization of the DSSc due to the incorporation of PbS QDs.

## Conclusion

Dye-sensitized solar cells (DSSCs) incorporating a combination of PbS and N719 dyes were synthesized, and their properties were examined after fine-tuning the size and quantity of PbS quantum dots immobilized on the TiO<sub>2</sub> electrode. An enhancement of 14.4% in the current density and 14.6% in the efficiency have been achieved due to this co-sensitization of the solar cell by the PbS quantum dots. This study revealed that efficiency enhancement of DSSCs can be obtained using the PbS QDs together with the Ru dye effectively by capturing the light photons in the IR region.

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