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## Lead Sulfide Quantum Dot Sensitized Titanium Dioxide Photoanode For Dye Sensitized Solar Cells

.Irshad I.S.<sup>1\*</sup>, Wanninayake W.M.N.M.B.<sup>2</sup>, Bandara T.M.W.J.<sup>3</sup>, Herath A.C.<sup>4</sup>

Department of Physical Sciences, Faculty of Applied Science, Rajarata University of Sri Lanka, <sup>1,3,4</sup> Mihintale,

Sri Lanka, <sup>2</sup>Department of Physics, Faculty of Science, University of Peradeniya, Peradeniya, <sup>2</sup> Sri Lanka.,

Postgraduate institute of Science, University of Peradeniya, Peradeniya, Sri Lanka. <sup>1,2</sup>

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### ABSTRACT

Solar cells are becoming most promising alternative energy source in recent years due to its cleanness, abundance of sun light, low-cost and easy fabrication. Dye sensitized solar cells (DSSCs) have reported higher efficiencies about 12 % however; cell performance degradation due to instability of dye is a problem. Besides the design and synthesis of excellent dyes for DSSCs, another approach to achieve better performance is the use of quantum dots (QDs). In this study, TiO<sub>2</sub> working electrode of the cell was prepared by using doctor blade method and it gave an efficiency of 5.77 % with the iodide/triiodide-based liquid electrolyte with the well-known N719 Dye. In order to replace dye PbS quantum dots are fabricated on the surface of TiO<sub>2</sub> working electrode and it gave poor efficiency with the above mentioned electrolyte. This might be due to the corrosive effects of iodide ions towards the PbS QDs. In order to overcome this problem, polysulfide-based quasi-solid-state or gel polymer electrolyte was introduced to the QDSSC-based system for the 1<sup>st</sup> time. The device consisting the polysulfide-based gel electrolyte which shows the conductivity of  $1.18 \times 10^{-4} \text{ S cm}^{-1}$ , gave an efficiency of 0.03 %. Two methods are employed to fabricate the quantum dots on photo-anode. The first is drop cast method (a new method introduced in this work) and the second method is successive ionic layer adsorption and reaction (SILAR) methods. Device fabricated using the drop casting method gave an efficiency of 0.03%, while SILAR method showed efficiency of 0.01 %. When TiO<sub>2</sub> was sensitized with quantum dots, overall performance of the device was degraded but still the results are confirmed that drop cast method gives a better solar cell performance than conventional SILAR method.

**KEYWORDS:** *Dye sensitized solar cells; quantum dots; lead sulfide, quasi-solid-state, the polysulfide electrolyte,*

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<sup>1\*</sup> Corresponding author: Irshad I.S

## Introduction

Non-renewable energy sources such as fossil fuels, coal and nuclear power will run out within few decades. Fossil fuels have become severely harmful for the environment due to its emission of gases such as sulfur dioxide which causes acid rain and carbon monoxide contributed to greenhouse effect thus increasing global warming and environmental pollution. Above mentioned impacts are pushing us into the adoption of renewable energy.

Energy is derived from natural sources that can be naturally replenished is known as renewable energy and they will exist longer-lasting. To date, the energy transformations into usable forms such as electricity and the high energy consumption are major issues. Energy resources and its conversion cost greatly impact on the global economy and political changes in every aspect. So, there has been a challenge to find out a sustainable, affordable, clean and safe energy conversation techniques. The sun is the earth's primary energy source, which provides us about 10 000 times more energy than our daily consumption [1] and it is the best form of renewable source of energy. Therefore, researchers attempt to convert solar energy into usable form due to its cleanness, abundance and its perpetual nature.

Solar cell is the device which converts solar power into electrical energy in the environmental friendly manner [2]. In 1839 Alexander Edmond Becquerel discovered the photovoltaic effect. Later, in 1954, Bell Laboratories published the first p-n junction solar cell designed with efficiency about 6%. When photons of light impinge on the solar cell, electrons in the valence band of the semiconductor material get excited into the conduction band of the semiconductor thus creating an electric current.

In 2000, solar electric power usage was about 1.5 GW but in 2011 it was grown up to about 67 GW and it shows over 50% of annual growth rate [3]. The maximum theoretical efficiency of single p-n junction solar cell depends on the Shockley-Quiesser (SQ) limit and material which is used [4]. Currently, many emerging technologies are aiming at boosting the efficiency and the reduction of the cost of the solar cells.

## Statement of the Problem

The TiO<sub>2</sub> which is used to fabricate solar cells shows a high photocatalytic effect. And as a result, sensitizer which is attached on to the nanoporous TiO<sub>2</sub> network is prone to degrade rapidly. Another material used in the solar cell is liquid electrolyte. Liquid electrolyte shows some drawbacks such as electrolyte leakage, solvent evaporation and sealing imperfections. Also, electrolyte consists of iodide, which leads to some draw backs of long term usage of the solar cell devices.

## Objective of the Study

In this work, it was attempted to improve the efficiency of solar cell devices by using the PbS quantum dot instead of dye molecules, polysulfide gel polymer electrolytes.

## Review of Literature

Dye-sensitized solar cells (DSSCs) gained great interest among researchers, due to their low production cost and easy fabrication procedures compared to conventional silicon solar cells [5-7]. The TiO<sub>2</sub> shows a high photocatalytic effect and as a result, sensitizer which is attached on to the nanoporous TiO<sub>2</sub> network is prone to degrade rapidly. In order to overcome these problems associated with TiO<sub>2</sub>-based DSSCs, quantum dots (QDs) have been investigated as possible alternative semiconductor materials and sensitizer materials [8]. The quantum dot sensitized cells are theoretically potential to be efficiency of 66% [8]. This is higher than the commercial solar cells that shows Shockley-quiesser limit of 33%. Researches proposed that the two mechanisms of QDs in order to obtain high photocurrent. One is, the absorption of high-energy photons create more than one electron-hole pairs. This is also known as multiple exciton generation (MEG) [9] similar to carrier impact ionization and opposite to Auger relaxation [8]. Another mechanism is intermediate band (IB) absorption [10, 11]. Among these, PbS brought our interest as the sensitizer material. This study focused on synthesizing PbS QDs and applying PbS QDs as a sensitizer on TiO<sub>2</sub> film which Shows relatively higher electron mobility (~250 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) and higher electron-hole separation ability. PbS QD can be synthesized using simple chemical methods. Although the efficiency of QDSSCs is

still low [12], this work was carried out on improving efficiency of quantum dot sensitized solar cell (QDSSCs).

Quasi-solid-state electrolytes show some promising properties such as thermal stability, non-flammability and non-volatility. The use of quasi-solid-state electrolytes instead of liquid electrolytes would help circumvent some drawbacks such as electrolyte leakage, solvent evaporation and sealing imperfections associated with liquid electrolytes. Also, electrolyte consists of iodide, which leads to some drawbacks of long term usage of the solar cell devices. By using polysulfide-based quasi-solid-state dye-sensitized solar cells (QSDSSCs), problems such as corrosiveness toward the platinum counter electrode and competition for visible light absorbing by the iodide/triiodide redox couple can be minimized to a certain extent. In this study, quasi-solid-state dye-sensitized solar cells (QSDSSCs) were fabricated using TiO<sub>2</sub>/PbS QDs composite working electrode, incorporating gel electrolytes consisting of propylene carbonate and ethylene carbonate as plasticizers, polyacrylonitrile as a polymer, sulfur and sodium sulfide to improve the stability of the electrolyte.

## Materials and Methods

Titanium (IV) oxide nanoparticles ( 0.50 g) in 1.00 cm<sup>3</sup> of 0.1 M HNO<sub>3</sub> and 2.00 cm<sup>3</sup> of ethanol were grounded well. The above paste was employed to fabricate working electrode using doctor blade method on pre-cleaned FTO glass. Then, the freshly coated TiO<sub>2</sub> film was sintered at 450 °C for 30 minutes and allowed to cool. Three methods were employed to sensitize this TiO<sub>2</sub> Films with dye and QDs.

1. Sample was immersed in N719 dye solution for 24 hours and then dye coated TiO<sub>2</sub> electrode was taken out and rinsed with ethanol in order to remove loosely bound dye molecules.
2. TiO<sub>2</sub> coated electrode was successively dipped in to 0.1 M Pb(NO<sub>3</sub>)<sub>2</sub> ethanolic solution for 5 minutes and 0.1 M Na<sub>2</sub>S methanolic solutions for 5 minutes ( first SILAR cycle). This electrode was rinsed with alcohol and allowed to dry before the next SILAR cycle.
3. QDs fabricated as suspension of toluene. This solution was used for drop casting methods. Two drops of QD suspension in toluene were added on TiO<sub>2</sub> film. Then the film was air dried till toluene evaporated out.

Then DSSCs were assembled with configuration glass/FTO/dye/TiO<sub>2</sub>/electrolyte/Pt/FTO/glass.

## Results and Discussion

The photocurrent voltage performance of the DSSCs with the iodide/triiodide-based liquid electrolyte was shown in Figure 1. The DSSCs-based on liquid electrolyte gave maximum efficiency of 5.77% with the 15.82 mA cm<sup>-2</sup> of short circuit current density and the 0.630 V of open circuit voltage while showing the 0.58 of fill factor.

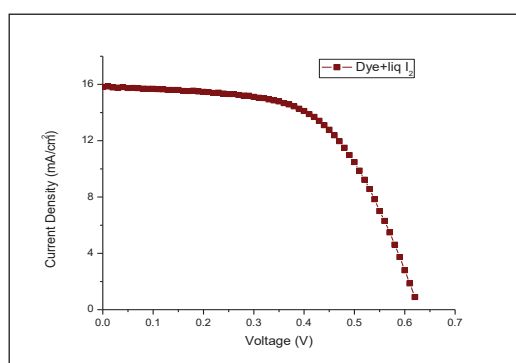


Figure 1 *I V* characteristic curve of DSSCs with liquid iodide electrolyte under 1 sun irradiation. The cell area is 0.25 cm<sup>2</sup>.

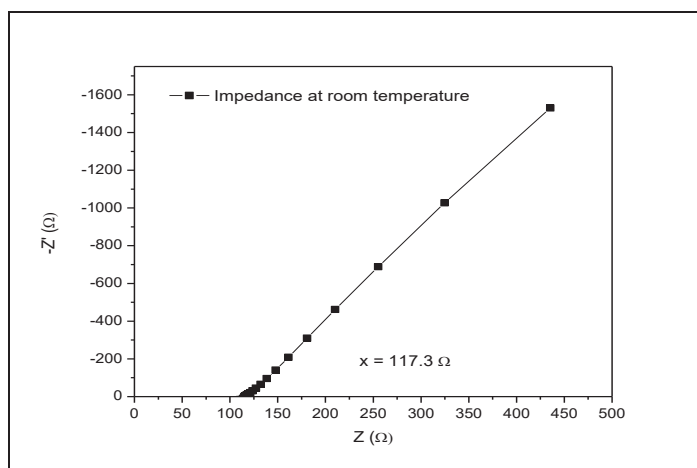


Figure 2 Nyquist plot for the polysulfide electrolyte.

Conductivity of the electrolyte sample was calculated using the equation ( $\sigma = \frac{l}{RA}$ ). Where  $l$  is the thickness of the sample (0.01 cm),  $A$  is the area of conduct between electrolyte and electrode is 0.742 cm<sup>2</sup> the bulk DC resistance ( $R$ ) of the sample can be determined using Nyquist plot where the interaction of the impedance data with the real part of the  $x$ -axis. The room temperature, conductivity ( $\sigma$ ) calculated using this data for this polysulfide electrolyte is  $1.178 \times 10^{-4}$  S cm<sup>-1</sup> this value is in agreement with the reported values in literatures.

The photocurrent voltage performance of the quasi solid state QDSSCs with the gel polysulfide electrolyte was shown in Figure 3 and the corresponding cell performance parameters are tabulated in Table 1.

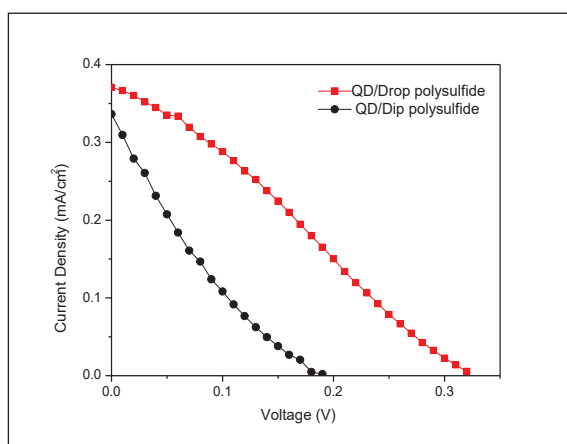


Figure 3 J- $V$  curves for QDSSCs with polysulfide electrolyte for both methods. “Dip” indicates SILAR method and “Drop” indicates the drop casting method.

Table 1 Performance parameters of QDSSCs with polysulfide electrolyte for both methods

	$J_{SC}$ (mA/cm <sup>2</sup> )	$V_{OC}$ (V)	$FF$ (%)	Efficiency ( $\eta$ )/%
QDSSCs drop casting	0.37	0.33	28	0.03
QDSSCs SILAR	0.34	0.19	18	0.01

According to the results, the PbS QDs fabricated with the drop casting method was exhibited an efficiency of 0.03% and 0.33 V of open circuit voltage. This is an improvement while compared to the SILAR cycle method. The photocurrent density shows almost the same value in both methods while showing the nearly

3 times increment of efficiency. Thus, in this work we report solar cell efficacy enhancement with drop cast method compared to the conventional SILAR method. To our knowledge this is known reports on QDDSSCs fabricated using drop cast method used in this study. As expected efficiency of fabricated quasi solid state DSSCs is poor but quasi solid state configuration gives better stability but we could manage to enhance cell efficiency by the novel method introduced in this work.

## Conclusion

Dye-sensitized solar cell fabricated with liquid electrolyte exhibited the efficiency of 5.77% with liquid iodide ion conduction electrolyte. When dye is replaced by PbS quantum dots, the cell performance was degraded but QD-DSSC has some other advantages. QDs fabricated in our laboratory is used to sensitize TiO<sub>2</sub> using drop cast method. The result confirms that drop cast method (that introduced in this work) gives better solar cell performances than the conversational SILAR method.

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