Quantum Dots Sensitized Solar Cell: Effect of CdSe Nanoparticles Purification Procedure of QD Sensitized Photoanodes

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Abstract. In this research the effect of purification of CdSe nanoparticles for application in quantum dots sensitized solar cells (QDSSC) photoanodes are studied. The CdSe nanoparticles are attached to the titanium dioxide surface using a linker based approached (CdSe nanoparticles disperse in toluene) and direct mode attachment (CdSe re-disperse in dichloromethane (DCM)). Colloidal CdSe nanoparticles with estimated size of 3.0 nm were synthesized by hot injection method in trioctylphosphine oxide (TOPO) as stabilizing solvent. Prior to the sensitization, the CdSe nanoparticles were purified using a common purification step involving the alternate cycles of precipitation / redispersion in non-polar solvent and polar solvent. With increasing the number of purification, the concentrations of CdSe nanoparticles attached to the titanium dioxide were also increased; from 2.47 x 10^{15} dots/cc for 3x wash CdSe nanoparticles to 3.70 x 10^{15} dots/cc for 4x wash CdSe nanoparticles. Polysulfide electrolyte and Cu_{2}S counterelectrodes were used to assemble a complete QDSSC. The highest efficiency of 0.05% was obtained from 4x wash CdSe nanoparticles; \( V_{oc}=0.2V \), \( J_{sc}=0.34 m\text{A/cm}^2 \) and \( \text{FF}=0.07 \).

1. Introduction

The solar cells with semiconductor nanoparticle have attracted interest in recent years. This generation of solar cells is moving toward for reducing the cost with better efficiency. Furthermore semiconductor nanoparticles have some unique features such as large surface-to-volume ratio, fast charge transport to surface, and controllable morphology, ease for large area processing, and potential for inexpensive fabrication on flexible substrates. Moreover by using nanoparticles one can enhance charge injection into wide band gap semiconductor.

One of the most significant recent advances in photovoltaic was the development of the dye sensitized solar cell (DSSC) or the Gratzel cell. The photoanode in such cells is constituted by a mesoporous TiO_{2} layer sensitized to the visible radiation by an adsorbed dye. Recently, instead of using dyes the sensitization of TiO_{2} mesoporous electrodes can be achieved through modification of the oxide with nanoparticles of semiconducting materials so called quantum dot sensitized solar cell. The use of nanoparticles enables band gap tuning by controlled the size of the nanoparticle size, which allows adjusting the light absorption. There are several methods used to fabricate QDSSC, such as chemical bath deposition (CBD) [1,2] and successive ionic layer adsorption and reaction (SILAR)[3,4]. These two methods give a high coverage of nanoparticles with good anchorage to the
substrate. But there is a limitation of these methods, where it is difficult to control the size of the nanoparticles and a broad size distribution of the deposited nanoparticles is obtained. This problem can be overcome by fabricating the QDSSC using pre-synthesized colloidal quantum dots for which it is much easier to prepare monodispersed samples with the required size[5-7]. Linker based approaches are the most common method used to incorporate these quantum dots into the mesoporous TiO$_2$ electrode. First the TiO$_2$ electrode is coated with bifunctional molecule linker followed by immersion of the electrode in quantum dots solution for long deposition times (24 – 96 hr) in order to achieve high surface coverage. However, linker based approached has been plagued by the instability between quantum dot to linker and linker to substrate interaction, which make this method have low repeatability. An alternative method to attach the QD onto TiO$_2$ mesoporous without using molecular linker termed as direct attachment method has been discover[7]. In this method CdSe nanoparticles capped with TOPO dissolve in dichloromethane (CH$_2$Cl$_2$) and directly absorbed onto TiO$_2$ mesoporous as light harvesting materials for converting light to current in solar cell.

Despite the attachment method, purification of CdSe nanoparticles will also increase the attachment of quantum dots on TiO$_2$ mesoporous films. Parkinson and co-workers have reported that the unwashed TOPO capped CdSe nanoparticles are agglomerated on rutile (110) TiO$_2$ substrate functionalised with 3-mercaptopropionic acid (MPA) [8]. They recommended that the excess free ligands in the CdSe nanoparticles solution such as TOPO, cadmium acetate, selenium, hexadecylamine (HDA) and tetra-decylphosphonic acid (TDPA) absorbed competitively to TiO$_2$ which avoid the attachment of quantum dots to the TiO$_2$ and also promoting the agglomeration of the quantum dots. Riley’s group reported that three washing cycle increased the quantum coverage on the TiO$_2$ and less aggromeration [9]. Whereas, Kamat’s group reported that five washing cycle was optimal to remove excess TOPO and retained some of capping ligands to avoid flocculation in solvent while also allow the quantum dots to interact with MPA on TiO$_2$[10].

In this paper we study two method of attachment, the linker based approaches and the direct attachment method, to link the quantum dots and the TiO$_2$, and study the effect of purification procedure of the quantum dots sensitized photoanodes. We used phosphorous NMR to analyses the present of TOPO in CdSe nanoparticle solution before and after purification. The J-V measurement was performed to measure the efficiency of the complete cell.

2. Experimental Methods
2.1 Synthesis of CdSe nanoparticles.
CdSe nanoparticles were synthesized using hot injection method, both precursors and coordinating solvents were heated together and nanoparticles formed and growth under non-isothermal conditions. Firstly the precursor of TOPSe and TOPCd solutions were prepared in glove box under dry atmosphere (argon). TOPSe was prepared by dissolving selenium (100 mesh with 99.99% trace metals basis, Aldrich) into trioctylphosphine (TOP) (90%, Aldrich). The cadmium stock solution, TOPCd was prepared by dissolving cadmium acetate (99.99% trace metals basis, Aldrich) into TOP. The coordinating solvent is prepared by mixing of trioctylphosphine oxide TOPO (99%, Sigma), hexadecylamine (90%, Aldrich) and tetra-decylphosphonic acid (97%, Aldrich). The mixture were dried, degassed under vacuum and refuxed at 110°C for 1 hour 30 minutes. TOPSe was then injected into the reaction mixture and the temperature increased to 300°C. TOPCd was then rapidly injected under vigorous stirring resulting in the nucleation of CdSe nanoparticles. Once the desired nanoparticle size was reached the reaction was quenched in 40 ml of toluene at room temperature.

2.2 Purification of CdSe nanoparticles solution
Figure 1 illustrated the procedure used to purify CdSe nanoparticles. In the ratio of 40 ml methanol: 40 ml CdSe solution the nanoparticles were precipitated and isolated by centrifugation (at 5000 rpm for 10 minutes). After centrifugation two layers of solution form with the colorless solution on top and the orange powder in the bottom. The colorless solution was poured out and the orange powder redispersed in 40 ml dichloromethane or toluene. This was labeled x1 purification cycle. The remaining
solution was continued for next precipitation cycle, the ratio of 30 ml of CdSe nanoparticles with 30 ml of methanol was used. The same centrifugation was done and the purified nanoparticle is re-dispersed in 30 ml dichloromethane or toluene and labeled x2 purification cycle. This stage was repeated for the desired number of precipitation. For each cycles, the UV-Vis spectroscopy and phosphorous NMR analysis was done to study the effect of precipitating of CdSe nanoparticles.

**Figure 1**: Schematic of precipitation procedure.

2.3 Preparation of CdSe-TiO$_2$ films.
Titanium dioxide (TiO$_2$) paste (Dyesol) was applied to conducting side of the fluorine doped tin oxide (FTO) using a glass rod and quick downward sweeping motions by Doctor Blade technique. Films were subsequently annealed in furnace at 450°C for 30 minutes, in order to remove organic molecules in the paste and to achieve good electrical contact between the TiO$_2$ nanoparticles.

2.4 Molecular Linker Approach.
The annealed FTO/TiO$_2$ films were re-heated to 110°C for 15 minutes to remove any moisture in TiO$_2$ films. The hot FTO/TiO$_2$ films were then directly immersed into acetonitrile (99.5%, Aldrich) solution with 3-mercaptopropionic acid (MPA) (99%, Aldrich) in the ratio of 10:1 for >12 hours. Finally, the TiO$_2$ films were washed with toluene and transferred into a CdSe toluene solution with different number of precipitation. The electrodes were immersed in the solution for >2 days, rinsed with toluene and left to dry in air.

2.5 Direct Absorption with DCM.
The TiO$_2$ films were re-heated to 110°C for 15 minutes to remove any moisture in TiO$_2$ films. The hot films were then directly immersed into CdSe nanoparticles re-dispersed in dichloromethane with different number of precipitation for 2 days.

2.6 QDSSC preparation
In this research we used the Cu$_2$S as counter electrode. The Cu$_2$S counter electrodes were prepare by immersing brass into HCl solution at 70°C for 10 min and later drop a polysulfide on the brass surface for another 10 min. The composition of polysulfide electrolyte was prepared by mixing 1 M Na$_2$S, 1M S, and 0.1M NaOH solution in DI (deionized) water. The solar cells were prepared by assembling of the photoanode and counter electrode using a Scotch tape as a space and with a polysulfide as an electrolyte. For QDSSC, the Cu$_2$S and polysulfide were employed in order to avoid corrosion to the quantum dots [11].

2.7 Characterization
UV-vis absorption spectra of CdSe nanoparticles were recorded with Cary 50 Conc with wavelength range from 190 nm – 1100 nm. Phosphorous Nuclear Magnetic Resonance ($^{31}$P NMR) analysis was performed using Bruker Avance 400 MHz to measure the amount of phosphorus contained in CdSe nanoparticles before and after precipitation. The current density-voltage (J-V) curves for solar
cell characterization were obtained using FRA-equipped PGSTAT 30 from Autolab. The cells were illuminated using a 150 Watt table lamp.

3. Results and Discussions

3.1 Optical Analysis of CdSe nanoparticles

UV-visible spectroscopy was used to monitor the CdSe nanoparticle solution throughout the quantum dots purification. Figure 2 shows the unpurified and purified CdSe nanoparticles from x0 to x4 purification cycle. The number of purifications does not affect the optical properties of nanoparticles. The positions of peak still remain at the same for unpurified CdSe nanoparticle solution throughout the purification which is 560 nm, which give the estimation diameter of ca. 3 nm. The quantum dots diameter was calculated by fitting to the mathematical formula describe by Peng et al. below [12]:

\[
D = (1.6122 \times 10^{-9})\lambda^4 - (2.6575 \times 10^{-6})\lambda^3 + (1.6242 \times 10^{-3})\lambda^2 - (0.4277)\lambda + (41.57)
\]

where \(D\) is the size of a given nanoparticle sample (in nm), \(\lambda\) is the wavelength of the first excitonic absorption peak of the corresponding sample (in nm).

From the calculated diameter, the extinction coefficient per mole of particles, \(\varepsilon\), can be determined by:

\[
\varepsilon = 5857 \times D^{2.65}
\]

From figure 2b, the concentration of CdSe nanoparticles were slightly reduced from x1 purification cycle to x4 purification cycle. For x1 purification cycle and x2 purification cycle, at the higher wavelength (650 – 800 nm) shows a raised baseline which is due scattering effect, compared to third and fourth precipitation. This may be caused by the present of excess impurities such as TOPO, HDA, TOPSe in the CdSe nanoparticles solution. From this we can say that the purification procedure remove the excess TOPO in the CdSe nanoparticles solution.

The concentration in unit dot/cc of the CdSe nanoparticles can be calculated from absorbance by using equation 3:

\[
C = \frac{A \times N_A}{\varepsilon \times L \times 1000}
\]

where \(A\) is the absorbance value at the peak position of the first excitonic absorption peak. \(C\) is the molar concentration (dot/cc) of the nanoparticles. \(L\) is the path length (1 cm) of the radiation beam used for recording the absorption spectrum. \(N_A\) is the Avogadro number.
3.2 Purification of CdSe
Phosphorous NMR spectroscopy is used to identify the phosphorous containing ligands and distinguishing between bound and free ligands in the CdSe nanoparticles solution. The TOPO will form as ligands around CdSe nanoparticles after synthesis. In the phosphorous NMR spectra, if the peak is broadened shows that ligand is bound to the surface. From the result obtained in Figure 3 show that a thin narrow peak, which indicate that ligand are not bound to the surface of CdSe nanoparticles. In this work, TOPO and TOPSe were first measure in order to confirm the peak position for TOPO and TOPSe. The results show that TOPO exist around 49 ppm and TOPSe exist around 37 ppm, similar results were reported by Morris-Cohen e.t al [13]. As can be seen in Figure 3, for unpurified
CdSe nanoparticles solution show the TOPSe peak at 37 ppm and no sign of TOPO exist in the solution. This is because, the as-synthesis CdSe nanoparticles were leave in dark for 3 days in order to allow the unreacted TOPO to solidified and sediment at the bottom of the vial. In this work we only collect the CdSe nanoparticles above the solidified TOPO for the phosphorous spectroscopy analysis. After the x4 purification cycle, the amounts of these two impurities were eliminated from the CdSe nanoparticles solution. Figure 3 indicated that for x4 purification cycle, the presence of TOPSe and TOPO were not detected using phosphorous NMR measurement, which showed that the impurities were removed during precipitating process.

![Figure 3. 31P NMR spectra of TOPO, TOPSe precursor, as-synthesis CdSe and CdSe x4 purification cycle.](image)

3.3 Attachment of CdSe nanoparticle to the TiO2 mesoporous structure

In this work, we have attempt two methods of attachment the quantum dots to TiO2 mesoporous structure, which were linker attachment method (CdSe re-dispersed in toluene) and direct absorption
method (CdSe re-dispersed in dichloromethane). Figure 4 shows the attachment of CdSe nanoparticles onto TiO$_2$ films using direct absorption method and no attachment was observed for molecular linker approach. The absorption of CdSe nanoparticles on TiO$_2$ mesoporous films in toluene was difficult to achieve compared to direct absorption[14]. This is because the CdSe nanoparticles in toluene have better stability where the bonding between particles is much stronger if comparing to CdSe nanoparticles re-dispersed in DCM. As we can see in the inset of figure 4 after x1 and x2 purification, the TiO$_2$ films were yellowish in color, which is the original color of the TiO$_2$ films before sensitized with CdSe nanoparticle. In contrast, for x3 and x4 purification shows areddish color due to the CdSe nanoparticle has attached onto TiO$_2$ film. For x3 purification the CdSe nanoparticles deposited is not uniform as compare to the x4 purification. Besides, x4 purification show a highest coverage of CdSe nanoparticles as compare to x3 purification of CdSe nanoparticle coverage onto TiO$_2$, which show that the surface coverage of CdSe nanoparticles increase when the number of purification increased.

![Figure 4](image)

**Figure 4.** UV-Visible spectrum of deposited CdSe nanoparticles on TiO$_2$ for different number of precipitations. The inset shows photos of CdSe nanoparticles attachment to TiO$_2$ for different precipitations.

UV-vis absorption spectra of attachment of CdSe nanoparticles on TiO$_2$ films from x1 to x 4 purification cycles are represents in figure 4. For x3 and x4 purification cycles solution, the same excitonic peak corresponding to CdSe nanoparticles before the attachment occurs at the same wavelength (560 nm). However, for x1 and x2 purification the peak is not observed due to no or small amount of CdSe nanoparticles that attached to TiO$_2$ film. As mention earlier, the impurities will reduce the performance of nanoparticle during application. This is because some of the TOPO on CdSe nanoparticles will be removed and leaved the Cd$^{2+}$ enriched surface of CdSe nanoparticles. We suggest that this Cd$^{2+}$ enriched surface of CdSe nanoparticles will physisorbed to the negatively charge of OH of TiO$_2$. Increasing the no. of purification will remove more TOPO and leaved more Cd$^{2+}$ side on the surface of CdSe nanoparticle. High Cd$^{2+}$ enriched surface generated, more CdSe nanoparticle will attached to the TiO$_2$. Using equation 1, 2 and 3, the concentration of CdSe nanoparticles on TiO$_2$ film was calculated and shows in Table 1. Concentration for x1 and x2 purification cycle were unable to calculated due to no absorption peak were observe in the UV spectroscopy data in Figure 4b. From the result, by increasing number of purification, the concentration of CdSe nanoparticles on TiO$_2$ film was also increase, which means more CdSe nanoparticles were attached to TiO$_2$ film due to removal of TOPO.
Table 1. The concentration of CdSe nanoparticles sensitized on TiO$_2$ film with different number of purification.

| Number of Purification Cycle | Concentration (dot/cc) |
|-----------------------------|------------------------|
| 3                           | $2.47 \times 10^{15}$  |
| 4                           | $3.70 \times 10^{15}$  |

3.4 J-V measurement of complete solar cell
The current density-voltage ($J-V$) curves was recorded to evaluate the solar energy conversion of full assemble of quantum dots sensitized solar cells. Under illumination of 150 Watt lamp, Figure 5 shows the results of $J-V$ curves for x3 and x4 purification cycles of CdSe nanoparticles. The efficiency ($\eta$) and fill factor ($FF$) of the fabricated solar cell can be calculated using equations below:

$$FF = \frac{P_{\text{max}}}{V_{\text{oc}} \cdot J_{\text{sc}}} \quad (4)$$

$$\eta = \frac{V_{\text{oc}} \cdot J_{\text{sc}} \cdot FF}{P_{\text{inc}}} \times 100\% \quad (5)$$

Where $P_{\text{max}}$ is the maximum power density of the solar cell, $V_{\text{oc}}$ is the open circuit voltage, $J_{\text{sc}}$ is the short circuit current density and $P_{\text{inc}}$ is the incident light power density.

After analyzing the solar cell parameters obtained for different purification cycles reported in figure 5. The open circuit voltage, $V_{\text{oc}}$, short circuit voltage, $J_{\text{sc}}$, fill factor and efficiency of our quantum dot sensitized solar cells for x3 purification cycle are -0.0063 V, 0.0156 mA/cm$^2$, 0.3 and 0.003% respectively and for x4 purification cycle are -0.2 V,3.4mA/cm$^2$, 0.07 and 0.05 % respectively. The efficiency, $\eta$, value increase with number of purification cycle due to the high coverage of CdSe nanoparticles at high purification cycle. This indicated that at high coverage more electrons were transfer to the substrate, which increases the efficiency.

![Figure 5. The J-V curves of the CdSe/TiO$_2$ system for x3 purification cycles and x4 purification cycle.](image-url)
4. Conclusions
To conclude, we have report the effect of purification toward sensitization of CdSe nanoparticles onto TiO$_2$ mesoporous films using direct absorption method. The results show that increasing number of purification will increase the attachment of CdSe nanoparticles onto TiO$_2$ mesoporous structure, which indicated by the greater colouration of TiO$_2$ mesoporous films. This is due to the removal of the free ligands (TOPO and TOPSe) from the CdSe nanoparticles solution after the purification, which is supported by phosphorous NMR result. The devices performance were also observe, obtaining better result for x4 purification cycle. In future we will conduct a more detail characterization of the purified solution and the performance of quantum dots sensitized photoanodes.

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