Synthesis and Characterization of Aqueous Lead Selenide Quantum Dots for Solar Cell Application

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Abstract. High quality, colloidal lead selenide (PbSe) nanoparticles possessing cube shaped morphology have been successfully synthesized by organometallic synthesis method, using oleic acid (OA) as capping agent. The use of non-coordinating solvent, 1-Octadecene (ODE), during the synthesis results in good quality nanocrystals. Morphology analysis by transmission electron microscopy reveals that cube-shaped nanocrystals with a size range of 10 nm have been produced during the synthesis. The absorption and PL spectra analysis showed an emission peak at 675 nm when excited to a wavelength of 610 nm, further confirmed the formation of PbSe nanocrystals. The surface modification of this colloidal quantum dots was then carried out using L-cysteine ligand, to make them water soluble, for solar cell application. The J-V characteristics study of this PbSe quantum dots solar cell (PbSe QDSC) showed a little power conversion efficiency which intern it shows significant advance toward effective utilization of PbSe nanocrystals sensitized in solar cells.

1. Introduction
The growing world energy demands, limited fossil fuel resources etc. are encouraging the search for feasible renewable energy sources. Among the opportunities, energy conversion from sun is of great inference because it is globally accessible. Photovoltaic conversion is taking place in solar cells. In a solar cell, the light absorbing material absorbs photon and generate electron and hole charge carriers or excitons [1-3]. In semiconductor solar cells of inorganic in nature, exhibiting efficiency maximum up to ~31%. However, their wide application is hindered by their high fabrication equipment cost. Quantum dots (QDs) sensitized solar cells are emerging third generation thin film photovoltaic technology. In recent years, quantum dots based solar cells have been the subject of broad research as favourable substitute to existing Si based solar cells and dye sensitized solar cells (DSSC) [4]. Quantum dots are semiconductor nanostructure that limits the motion of excitons in all three possible spatial directions with dimensions 1-10 nm. Intonation of band energies through size control open new ways to regulate photo response and photo conversion efficiency.

In recent years, many research work on Quantum Dots Sensitized Solar Cells (QDSSCs) on QD-sensitized have been reported, with Cadmium selenide (CdSe) [5], Cadmium sulfide (CdS) [6] etc.
which could change the device performance considerably. Some work has been already reported for the quantum dots sensitized solar cells with lead selenide (PbSe) nanocrystals [7]. PbSe QDs are optically active and are widely used as a good sensitizer in solar cells. [8]. Here, nanosized lead selenide particles possessing cube shaped morphology have been successfully synthesized by already known organometallic synthesis method [9]. PbSe QDs posses high quantum confinement energy greater than 0.5eV. This corresponds to band gap energy greater than of 0.8eV. This high degree of quantum confinement effect should enhance the charge carrier transport. [10]. PbSe QDs revealed greater photocurrent due to multiple exciton generation.

Here we synthesized PbSe quantum dots by organometallic synthesis using oleic acid (OA) as the capping agent and 1-Octadecene (ODE) as the solvent. Using this PbSe quantum dots, the device FTO/TiO2/PbSe was fabricated and its photovoltaic parameters were studied.

2. Experimental sections

2.1. Materials and chemicals used
The chemicals used in this work were, Lead Oxide (PbO), selenium powder (Se), trioctylphosphine (TOP), oleic acid (OA) and 1-octadecene (ODE), acetone, methanol, toluene, L-cysteine, PBS buffer solution (Sigma-Aldrich). All chemicals were used without further purification. FTO glass slides, TiO2 nanopowder (Degussa P25), Chloroplatinic acid, Acetonitrile, 1-butyl 3-methyl imidazolium iodide, LiI, Guanidium thiocyanate, Iodine, 4-tert butyl pyridine are also used.

2.2. Synthesis of OA capped PbSe QDs
PbSe quantum dots were synthesized by already known organometallic synthesis procedure [8]. The procedure was divided into different steps. (i) PbO (0.80 mmol, 0.179 g) and OA (2 mmol, 0.6 mL) were mixed with 3.1 mL 1-octadecene (ODE) in a 50 mL three-necked RB flask, equipped with a condenser. (ii) The mixture was then heated to 170 °C under inert condition until the solution becomes clear. (iii) A solution of Se (1.6 mmol, 0.126 g) dissolved in 2 mL (4 mmol) trioctylphosphine (TOP) was swiftly injected into the heated solution. The formation of quantum dots was indicated by the color change to dark brown solution. The reaction mixture was cooled to 150°C. (iv) The reaction temperature was maintained at 150°C for 15 minutes to allow the complete growth of PbSe nanocrystals (PbSe NCs).

2.3. Purification of QDs
The sample was taken from the RB flask and suspended in 10 mL toluene. The yield of QDs is ~90% and the concentration of QDs solution is 0.0072 mM. The sample then washed with acetone followed by methanol by centrifugation and redispersed in toluene. To maintain inert condition, nitrogen was passed synthesized QDs. For the conformation and analysis of QDs, photoluminescence spectra (PL), absorption spectra, and TEM images were taken.

2.4. Surface Modification of PbSe QDs with L-Cysteine Ligand
For making the QDs water soluble, L-Cysteine ligand was attached to the surface of QDs. For this, 200 mg of L-cysteine ligand was dissolved along with 5 ml PBS buffer in 10 mL RB flask. The solution was stirred for 6-7 hours by adding 5 mL QDs solution. After complete mixing two separate layers (upper organic layer and lower aqueous layer) are seen in the reaction pot, indicated that the quantum dots were transferred to aqueous phase from organic phase. The upper organic layer was separated by filtration. The acetone was added to the aqueous layer for the precipitation of QDs and then centrifuged at 3000 rpm for 10 min. The precipitated QDs was dissolved in PBS buffer (with pH=7.4) until a clear solution was obtained. To prevent the dimerization of sulphur, 0.5 mL, 14 M mercaptoethanol was added to the QDs solution. The QDs aqueous solution thus obtained was as such used to make PbSe QDs solar cell.
2.5. Fabrication of FTO/TiO$_2$/PbSe solar cell

FTO glass slides were washed using detergent, distilled water and acetone respectively and masked it with dimensions 1.5 cm×1.5 cm. TiO$_2$ Nanopowder was crushed for three to hours continuously, then mixed it with distilled water and sonicated for 15 minutes. Now the paste of TiO$_2$, added with a few drops of triton X-100 and coated onto FTO glass slides by means of Doctor-blade technique and kept it over-night for air-drying. The slide is then placed in oven at 80°C for 1 hour and for 30 minutes at 450°C in muffle furnace. After cooling, the sample, water soluble PbSe QDs were spin-coated onto the photoanode.

Counter electrode was prepared using chloroplatinic acid which was spin-coated onto FTO glass slides. After air drying it was kept at 80°C for 1 hour and allowed to cool, then placed it in Muffle furnace at 150°C for 30 minutes.

LiI electrolyte was prepared as follows. 25ml of acetonitrile was taken in a beaker. Then, 4mg of 1 butyl 3 methyl imidazolium iodide, 0.35g of Li, 0.35g of Guanidium thiocyanate, 0.35g of Iodine (I$_2$) and 1.7g of 4-tert butyl pyridine were added into the beaker, by continuous stirring until it dissolves. Then the solution was sonicated for 15 min. Solar cell was assembled and J-V characteristics were taken using Keithely I-V meter 2420A with light input power 100mW/cm$^2$. Dark current was measured to confirm diode characteristics.

Characterization Techniques: Absorption and PL spectra of the synthesized using UV-Visible spectrometer. HRTEM images were taken in a carbon coated copper grid using Transmission Electron microscope.

3. Results and Discussion

With the help of organometallic synthesis procedure, the OA-capped PbSe quantum dots were successfully synthesized. Here we used PbO and Se powder as lead and selenium precursors respectively. The purpose of solvent ODE is to prevent any other chemical changes after the formation of Quantum dots (QDs). It also helps to produce good quality nanocrystals. In this synthesis, OA acts as a capping agent, which makes uniform solution of QDs in organic solvent. It also provides uniform heat to the reaction mixture, since the boiling point of OA is 360°C. At 170°C during the synthesis, PbO reacted with OA to form lead oleate (Pb(oleate)$_2$). At this temperature the injection of TOP/Se solution into the hot Pb precursor caused the nucleation and growth of QDs. Here we kept the reaction temperature at 150°C for 15 minutes to complete the reaction. The colloidal PbSe QDs was transferred
to aqueous solution using L- Cysteine ligand and PBS buffer. L-Cysteine replaces the weak OA ligand from QDs and makes them soluble in water. The addition of mercaptoethanol to aqueous QDs solution helps to prevent the dimerization of sulphur atoms in Cysteine ligand, which affects the stability of QDs solution. The assembled solar cell showed an efficiency of 0.0014%.

3.1. UV-Visible Absorption and PL Spectra Analysis of PbSe QDs
The absorption spectra of synthesised PbSe nanocrystals show a broad absorption in the region 500-700 nm. It is shown in Figure 2(a). The absorption maxima 610 nm corresponds to an energy gap of 1.99 eV. The peak of photoluminescence (PL) spectra is obtained at 675 nm, which corresponds to a large Stokes shift. It is shown in Figure 2(b).

![Figure 2. Absorption Spectra (a) and (b) PL spectra of OA-capped PbSe quantum dots.](image)

3.2. Size and Shape Evolution of OA Capped PbSe QDs Using TEM Analysis
Figure 3 display the TEM micrographs of cube-shaped PbSe NCs synthesized at 150°C for 15 min using OA as capping agent, with a ratio of Pb/Se/OA/TOP = 1:2:2.5:2.7. Figure 3(a) and 3(b) are the low resolution TEM micrograph of PbSe QDs, taken at a scale of 100 nm and 50 nm respectively. From the TEM micrograph, it is evident that QDs are uniform in nature and are unaggregated in the entire film. The TEM micrograph clearly shows that the OA capped PbSe QDs have cube-shaped morphology and the average size of the PbSe QDs is 10 nm and are in uniform size distribution.

Figure 3(c) and 3(d) are the HRTEM micrographs of OA capped PbSe QDs taken at a scale of 5 nm. The HRTEM images confirm the existence of lattice planes which also confirm high crystallinity of NCs. The HRTEM micrographs also confirm the cube-shaped morphology and unagglomeration of nanoparticles. The average size of synthesized OA-capped PbSe is of 10 nm which was smaller than the Bohr radius 46 nm of bulk PbSe. TEM micrograph, clearly shows that the average size of the OA capped PbSe nanoparticles is smaller than the Exciton-Bohr radius of bulk PbSe.

3.3. J-V Characteristics of the device
Figure 4(a) represents the dark current characteristics which resembles the forward characteristics of a diode. Figure 4(b) represents J-V characteristics of quantum dot sensitized solar cell. $J_{sc}$, the short circuit current density of our solar cell was 20µA/cm² and $V_{oc}$, the open circuit voltage was 0.35V. Maximum current density and voltage, $J_{max}$ and $V_{max}$ were fixed from the rectangle drawn in J-V characteristics. With the above values we calculated Fill factor, by the equation, $FF= (J_{max}.V_{max})/ (J_{sc}.V_{oc})$, which was found to be 20% for our device. Efficiency of the fabricated device was calculated from the relation $\eta= (FF.J_{sc}.V_{oc})/ (\text{Input Power})$. Efficiency of our device was found to be 0.0014%.
Figure 3. (a-b) TEM images of OA capped PbSe cube-shaped Quantum dots. Figure 3. (c-d) HRTEM images of OA capped PbSe quantum dots, showing crystal planes.

Figure 4. (a) Dark current characteristics and (b) J-V characteristics of PbSe quantum dots sensitized solar cell.

4. Conclusion
We successfully synthesized OA-capped PbSe cube shaped nanocrystals by organometallic synthesis method. From the UV-Visible absorption and PL spectra analysis it was found that the synthesized nanocrystals showed absorption and emission in the visible region (400-700 nm). TEM analysis
confirmed that the synthesized nanocrystals possessed cube shaped morphology with particle size in the order of 10 nm and it was mono dispersed in nature. In order to assemble QDs sensitized solar cell, we modified the surface of quantum dots with L-cysteine ligand in PBS buffer solution. The use of L-cysteine makes the quantum dots water soluble. The photovoltaic parameters of the fabricated solar cell were studied and it was found that the power conversion efficiency of the device is very low.

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