



# Phosphine-Free Heat up Synthesis of CdSe Nanocrystals for Quantum-dot-sensitized Solar Cells

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**Abstract:** We demonstrate a low cost, phosphine-free route to synthesize CdSe quantum dots (QDs) by heating the mixed precursors of Se and Cd up to 260 °C. The as-synthesized CdSe QDs are characterized by using UV-visible absorption spectroscopy, high resolution transmission electron microscopy, X-ray diffractometry, and EDX analyses. The CdSe QD-sensitized TiO<sub>2</sub> films of solar cells has been fabricated by decoration of CdSe QDs on TiO<sub>2</sub> films deposited on FTO/glass substrate, which exhibits fill factor and photo-conversion efficiency 42.26 % and 0.95 %, respectively.

**Keywords:** CdSe quantum dots, Heat up, Phosphine-Free, Dodecanethiol, Solar cells

## I. INTRODUCTION

Colloidal semiconductor quantum dots (QDs) have great fundamental and technical importance due to their size tunable and light harvesting properties [1]. By recombination control using inorganic ZnS/SiO<sub>2</sub> double layer treatment onto the QD-sensitized photoanode, photo-conversion efficiency ( $\eta$ ) of quantum dot solar cells (QDSCs) can be boosted beyond 8% [2]. In past years, QDSCs chalcogenide semiconductors such as CdSe [3], CdTe [4], and PbS [5] have been engaged as sensitizers due to the size tunable band energy and the generation of multiple electron pairs with one single photon [6].

In recent years, both heat up and phosphine free procedure for nanocrystals (NCs) synthesis created great interest for low cost, less toxic and high power conversion efficiency [7-9]. A major challenge for the synthesis of phosphine free QDs is to achieve homogeneous distribution of the elements within the QDs. CdSe is one of the most popular NCs showing full range optoelectronic properties by varying their shape and size. However, the majority of the synthesis of CdSe NCs relies on the use of trioctylphosphine (TOP) based precursors namely TOP-Se, which are toxic in nature [10]. Consequently, alternative approaches of phosphine-free routes, including direct dissolving Se powder with high-boiling-point solvents such as octadecene (ODE) [11,12], oleylamine (OLA) [13], olive oil, and non-coordinating solvent paraffin [14], have been explored in photovoltaic application.

Herein, we present an alternative phosphine-free heat up route for the synthesis of CdSe QDs (Scheme 1). In this method, reduction of elemental Se with ODE in the presence of dodecanthiol (DT) generated Se-ODE precursor in situ. The Se precursor was found to be highly reactive, and suitable for the synthesis of CdSe NCs. We succeed to synthesize ~9.8 nm size of CdSe NCs at 260 °C for 5 min. To achieve the widespread use of QD-based solar cells, TiO<sub>2</sub> film deposited on FTO/glass substrate was decorated by CdSe QDs and the photovoltaic properties were investigated.

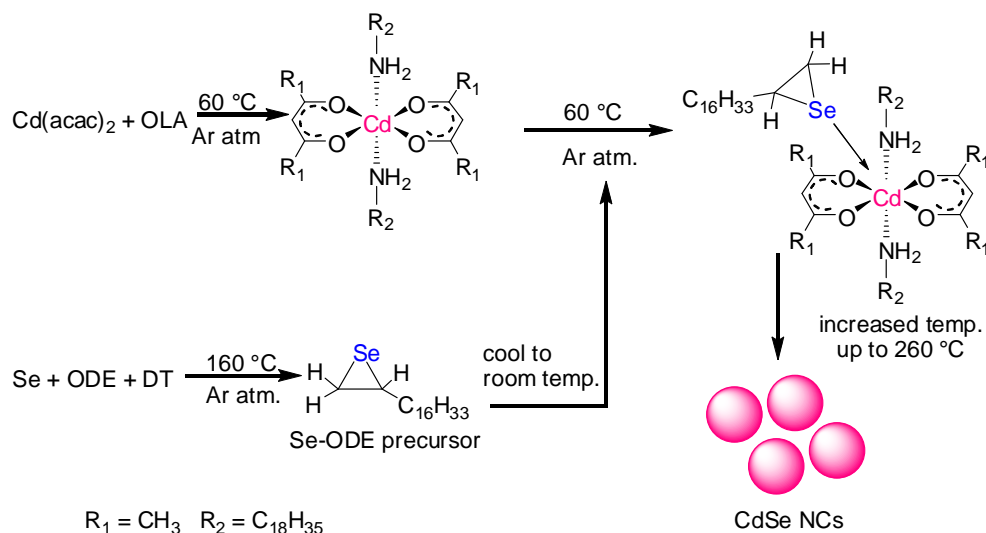
## II. EXPERIMENTAL

### MATERIALS

Cadmium acetylacetonate [Cd(acac)<sub>2</sub>, 98%], 3-Mercaptopropionic acid (3-MPA), Trioctylphosphine (TOP 90%), Oleic acid (OA, 95.0%), 1-octadecene (ODE, 90%), oleylamine (OLA, 70%), titanium diisopropoxide bis(acetylacetonate), mesoporous anatase P25 TiO<sub>2</sub> paste, plutonic acid (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O), and TiCl<sub>4</sub> were purchased from Sigma Aldrich. Fluorine doped tin oxide (FTO) was obtained from Nippon Sheet glass, Japan. Selenium metal powder (Se, 99.5%), Na<sub>2</sub>S, S powder and KCl were purchased from Sinopharm Chemical Reagent Co. Ltd. Acetone (99.9 %), toluene (99.9 %), hexane, (99.9 %), and ethanol (90 %) were obtained from Fisher Scientific. All chemicals and solvents were used directly without further purification.

### SYNTHESIS OF CdSe QDs

CdSe QDs were prepared via a modified reported procedure [13,15]. Typically, Se precursor was first prepared in a three necked flask containing 1 mmol Se powder, 5 mL ODE and 3.6 mL DT. This mixture was put under vacuum for 30 min and then maintained at 160 °C for 2 h, followed by cooling the resulting light yellow solution to room temperature. A mixture of 1 mmol Cd(acac)<sub>2</sub> and 3 mL OLA in another flask was stirred at 60 °C under vacuum for 30 min until the solution became clear light yellow. The as-prepared Se precursor



Scheme 1. Sketch of the mechanism on phosphine-free heat up synthesis of CdSe QDs.

solution was then added to the Cd precursor solution under Ar flow, followed by increasing the temperature to 260 °C with a slope of 5 °C/min, and keeping the reaction at 260 °C for 5 min. After that, the flask was rapidly cooled to room temperature, and the as-synthesized CdSe QDs were washed three times by precipitation with ethanol and re-dispersed in chloroform for further analysis and fabrication of solar cells.

## SENSITIZATION OF TiO<sub>2</sub> FILM AND FABRICATION OF SOLAR CELLS

The F-doped SnO<sub>2</sub>-coated substrate (FTO/glass, 2.5 mm thickness) were used as conductive substrates to prepare TiO<sub>2</sub> photoanode. Anatase P25 TiO<sub>2</sub> film were pasted on cleaned FTO glass by screen printing method followed by previously reported thermal sintering procedure (150 °C for 10 min, 325 °C for 15 min, 375 °C for 5 min, 450 °C for 7 min and 500 °C for 5 min) [16]. Before the paste of TiO<sub>2</sub> on FTO glass, a blocking layer of titanium diisopropoxide bis(acetylacetonate) prepared in 75% isopropanol was deposited by spray pyrolysis (one round spray was done in every 10 second, for 2 minute (approx. 12 rounds) at 450 °C). The as-sintered TiO<sub>2</sub> photoanode were then immersed into 1 M 3-MPA solution (in acetonitrile) for 4 h, and rinsed thoroughly with acetonitrile and chloroform. The MPA-modified TiO<sub>2</sub> film was transferred into the CdSe NCs/chloroform solution for 24 h to ensure saturated sensitization of QDs onto the TiO<sub>2</sub> electrode. The Pt counter electrode was prepared by thermal decomposition of Pt precursor at 450 °C for 15 min [1]. The CdSe QD-sensitized TiO<sub>2</sub> electrode and Pt-coated FTO was sandwiched by using 25 μm thick Surlyn gaskets followed by pre-drilled backfilling holes at counter electrodes by polysulfide electrolyte (2.0 M Na<sub>2</sub>S, 2.0 M S, and 2.0 M KCl) [1,17]. A small glass holes was covered by Surlyn film and cells were connected with wires for further photocurrent efficiency test.

## MORPHOLOGICAL, OPTICAL AND PHOTO-ELECTROCHEMICAL MEASUREMENT

The absorption spectra of CdSe QDs were recorded on a UV-vis spectrophotometer (UV1601PC, Shimadzu, Japan) in the wavelength range of 300-600 nm. The powder X-ray diffraction (XRD) patterns were collected using a D8 Advance X'Pert ProX-ray diffractometer. High resolution transmission electron microscopic (HR-TEM) analysis was taken by a JEM 2100F microscope operated at 200 kV. Energy dispersed X-ray spectra (EDX) were obtained using the same microscope to determine the composition of the as-synthesized QDs. The solar cells, 0.16 cm<sup>2</sup> active illuminated area, were tested using Newport Oriol I-V station (PVIV-412V) solar simulators using an AM1.5 G spectrum at a light intensity of 100 mW cm<sup>-2</sup>, and calibrated using Si photodiode as reference.

## III. RESULTS AND DISCUSSION

### MORPHOLOGICAL AND OPTICAL ANALYSIS

The HRTEM images show that the as-synthesized CdSe QDs are well-developed single crystals with the interplanar distances of 0.349 nm, which is in agreement with (002) crystallographic facet of hexagonal CdSe (Fig.1a-b). We notices that NCs with lattice distance of 0.328 nm, which is consistent with the (101) crystallographic facet of CdSe, were also formed at 60 °C for 24 h (Fig. 1d-e). The average diameter of 60 °C and 260 °C NCs was estimated to be around ~7.6 nm and ~9.8 nm, respectively. The fast fourier transforms (FFTs) pattern of a single NCs also confirm the (002) and (101) directions at both 260 °C and 60 °C samples (Fig. 1c,f). The well-determined lattice images indicate the highly ordered crystalline structure.

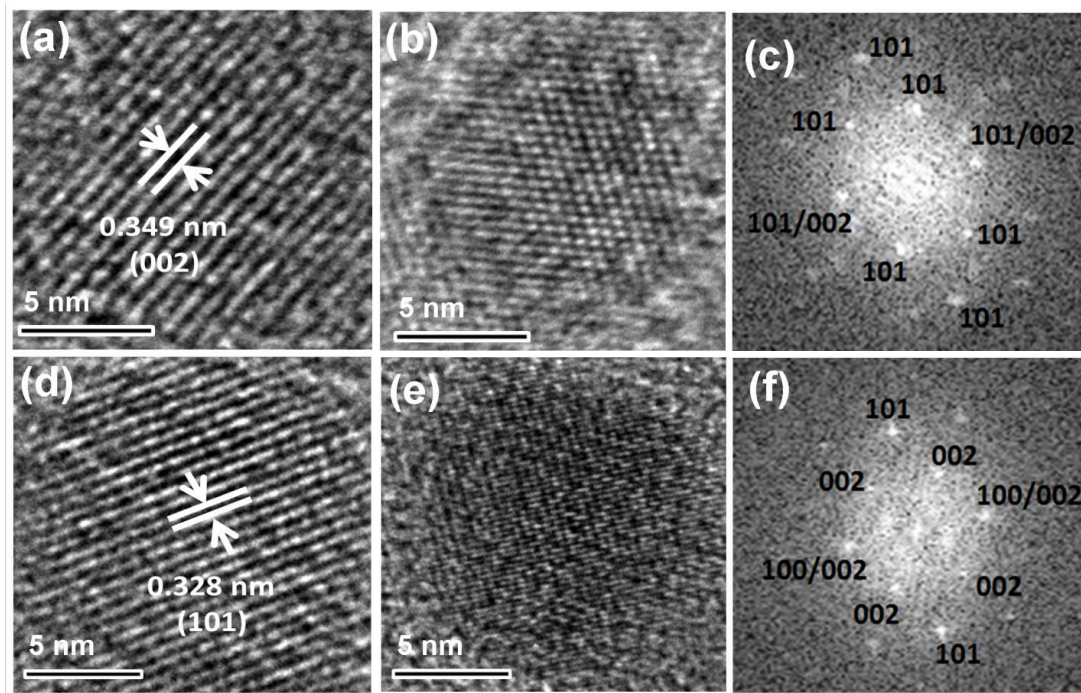


Fig. 1. HR-TEM images (a-b, d-e) and FFT patterns (c,f) of the as-synthesized CdSe QDs collected at 260 °C for 5 min (a-c) and at 60 °C for 24 h (d-f), respectively.

Fig.2 demonstrates the evolution of optical absorbance of aliquots of NCs collected at different temperatures during the heating up. With injection of Se-ODE-DT precursor into the Cd-OLA precursor at 60 °C, a broad peak (436 nm) was observed at 140°C and it is red shifted up to 447 nm over the increasing course temperature at 260 °C. The red shift of absorbance edge with increasing reaction temperature indicates the increasing particle size of the CdSe NCs.

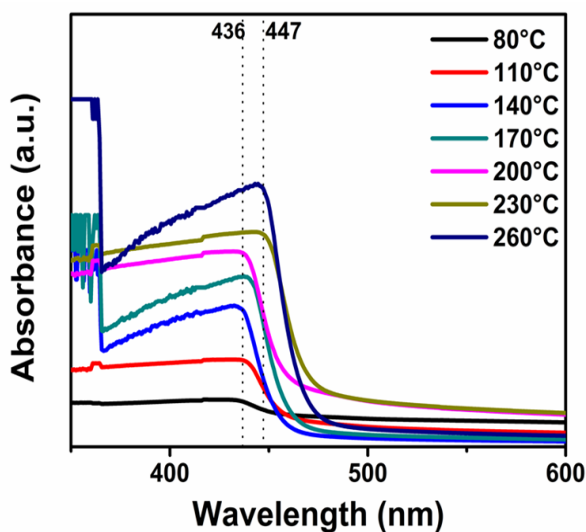


Fig. 2. The evolution of UV-vis absorption spectra of the aliquots of CdSe NCs collected at different temperatures during the heating up.

#### PHASE AND COMPOSITION ANALYSIS

The XRD pattern of the as-prepared sample indicates the formation of hexagonal CdSe (Fig. 3a). The diffraction peaks at 25.39°, 41.99° and 50.69° could be assigned to the (002), (110) and (201) reflections of hexagonal structure of CdSe (JCPDS No. 01-077-2307). The EDX elemental analysis reveals that the Cd:Se ratio is around 1:1 (see Fig. 3b), which is in agreement with the phase analysis from XRD pattern.

#### SOLAR CELL PERFORMANCE

The photocurrent density-voltage (*J-V*) curves of the QDSCs fabricated by the CdSe sensitized 3-MPA-capped-TiO<sub>2</sub> photoelectrodes were measured under AM1.5G at 100 mW/cm<sup>2</sup> illumination intensity (Fig. 4). The value of open circuit voltage (*V*<sub>OC</sub>) and short circuit current (*J*<sub>SC</sub>) of 0.674 V and 3.35 mA/cm<sup>2</sup>, respectively, were observed in one sun solar simulators adjusted by calibrated Si photodiode as reference. The photo-to-current conversion efficiency ( $\eta$ ) of 0.93 % and fill factors (FF) 42.26 % are achieved. The solar cell performance measurement confirmed good photo activity of CdSe QDs synthesized at 260 °C by phosphine-free heat up procedure.

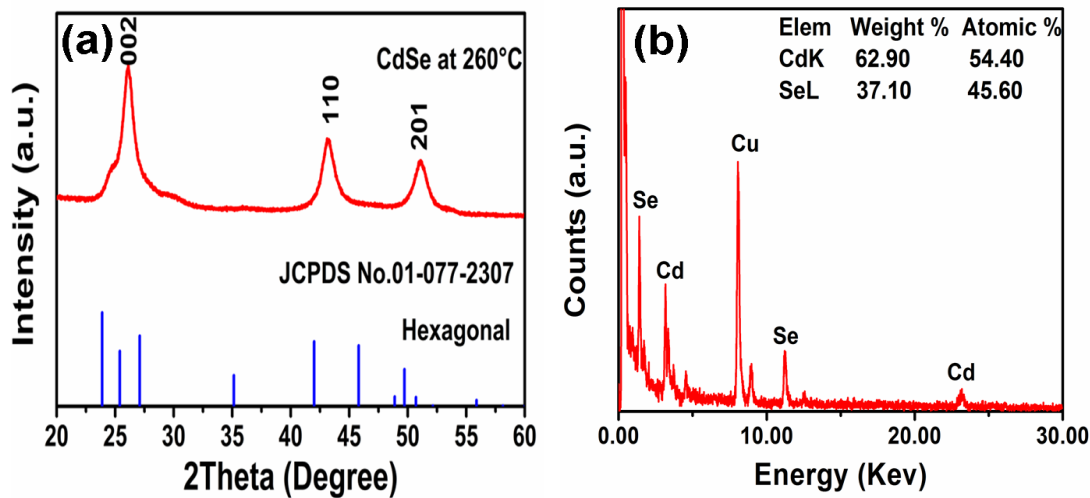


Fig. 3. (a) The XRD patterns correspond to hexagonal CdSe QDs. EDS spectra of CdSe, synthesized at 260 °C (b). Note: The strong peak of Cu is belongs to sample holder of Cu for EDS analysis of 3b.

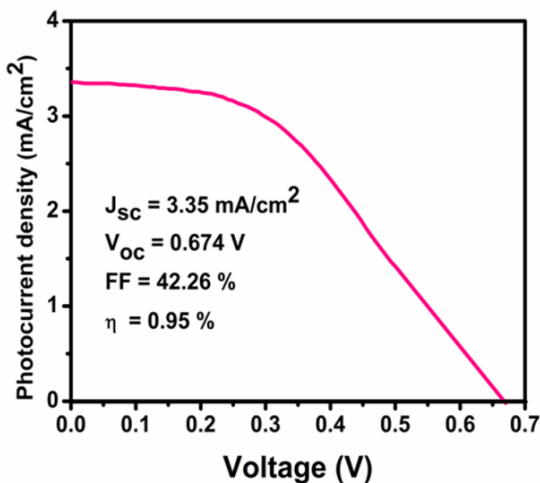


Fig. 4. *J-V* curve of CdSe QD-sensitized solar cells under 100 mW/cm<sup>2</sup> simulated sunlight.

#### IV. CONCLUSION

In summary, we have successfully synthesized high quality CdSe QDs by using phosphine-free heat up procedure. Our XRD and EDS results confirm the formation of hexagonal CdSe NCs. The efficiency and fill factors of the solar cells fabricated by using the as-synthesized CdSe NCs are recorded to be 0.93 % and 42.26 %, respectively.

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