

## STUDY ON THE PURIFICATION OF CdSe NANOPARTICLES SOLUTION BY REPEATED PRECIPITATION

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*In this work, the qualitative and quantitative of the colloidal trioctylphosphine oxide (TOPO) capped CdSe with 4.0 nm in diameter after several times precipitation from toluene were studied. The fresh solution after the preparation is not pure; there are some excess free ligands in the solution such as TOPO, cadmium acetate, selenium, hexadecylamine (HDA) and tetradecylphosphine acid (TDPA) unbound to the nanoparticles [1] and also impurities from the solvent. The purification process of the fresh solution involves addition of methanol to the fresh solution to drive particle flocculation, followed by centrifugation of the solution. In this process CdSe nanoparticles (NPs) precipitate to the bottom of the centrifuge tube leaving a clear solution (supernatant). The supernatant was removed and toluene was added to the CdSe powders to resuspend the particles in toluene. This procedure is referred as 1x wash. Repetition of the redissolution / reprecipitation process was continued for 2x, 3x, 4x and 5x. Transmission electron microscopy (TEM), was carried to study the quality of the CdSe nanoparticles after several purification process and inductively coupled plasma optical emission spectroscopy (ICP-OES) was used to performed elemental analysis on the ratio of Cd to Se and phosphorous containing ligand bound to the surface.*

**Keywords:** CdSe nanoparticles, repeated precipitation, purification, ligands

### INTRODUCTION

CdSe NPs are one of the group II-VI semiconductor nanoparticle, that has being intensively studied for the ligand chemistry. The CdSe NPs can be prepare with different organic ligand using colloidal synthesis. The organic ligands were used to obtain narrow particle size distribution and to prevent the aggregation of nanoparticles as well as make nanoparticles disperse in aqueous or nonaqueous media depend on the selection of different ligands. Hydrophobic ligands, such as trioctylphosphine (TOP), oleic acid and oleic amine, are common ligands used to suspend nanoparticles in non-polar solvent. Whereas for hydrophilic ligands, such as 3-mercaptopropionic acid, thioglycolic acid and 1-thioglycerol, are ligands used to suspend nanoparticles in polar solvent. However, in many cases these ligands of as-synthesized CdSe NPs are not suitable for their application. For instance, in bioimaging application these excess ions, ligand, and compound are toxic to the target organism [2]. Furthermore in the fabrication of quantum dots solar cell, there is no photocurrent measure if used unpurified CdSe nanoparticles as sensitizer, compare to washed nanoparticle, due to the excess TOP/TOPO on the nanoparticles prevent photocurrent generation at the nanoparticle/TiO<sub>2</sub> interface [3]. In order to remove these excess matters, purification is necessary before the application of nanoparticles. The most common purification technique use to separate nanoparticles from solution is the precipitation-dissolution

technique. For example, to precipitating hydrophobic CdSe NPs, methanol or ethanol was used. Then the nanoparticles were centrifuge to collect the nanoparticles and resuspend them in solvent. Other techniques, such as dialysis, ultra filtration and diafiltration can also be used to purify the as-synthesized nanoparticles, but the problem with the filtration technique is that they rely on the controlled pore size materials which are expensive and suffer from fouling.

In this research we studied the number of purification cycle of CdSe from 1x wash up to 5x wash, to investigate the effect of number of cycle to the quality of the CdSe nanoparticles from the transmission electron micrograph.

### METHODS AND MATERIALS

#### *Synthesis of CdSe*

In the three necked flask, 8.0 g of TOPO, 5.0 g of HDA, and 0.15 g of TDPA were mixed. The mixture was dried and degassed under vacuum at 110 °C for 90 minute with periodical flushing of argon. After 90 minute, TOPSe (trioctylphosphine selenium) was injected into the flask. TOPSe stock solution was prepared in a dry box by dissolving 0.158 g of Se powder in 2.0 ml TOP. Then the temperature was then raised up to 300 °C. A TOPCd (trioctylphosphine cadmium) stock solution prepared in a dry box by adding 0.120 g of cadmium acetate to 3 ml of TOP, was rapidly injected into the mixture at 300 °C under vigorous stirring, resulting in a yellow/orange solution.

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Injection was accompanied by an immediate decrease in temperature to approximately 260 °C. Particle growth from the initially formed nuclei was continued at 260 °C. After 1 minute the flask was removed from the heater and the reaction was quenched in toluene. This cooling in toluene causes much of the excess TOPO to crystallize.

#### Washing procedure

The washing procedure of the CdSe nanoparticles is illustrated in the schematic diagram, Fig.1. In the ratio of 25 ml methanol: 5 ml CdSe solution the nanoparticles were precipitated and isolated by centrifugation (at 5000 rpm for 10 mins). Result in orange pellet at the bottom of the centrifuge tube in a clear solution (supernatant). The clear solution was then decanted, and the resultant orange pellet re-suspend in 5 ml toluene. This was considered as 1x wash. Increasing no. of wash involved further precipitation, centrifugation and re-suspension of the nanoparticles. The prepared QDs have been characterized with UV-vis and photoluminescence spectroscopy enabling calculation of the size and concentration of CdSe nanoparticle solutions using formula developed by Peng *et al.* [4] below:

$$D = (1.6122 \times 10^{-19})\lambda^4 - (2.6575 \times 10^{-6})\lambda^3 + (1.6242 \times 10^{-3})\lambda^2 - (0.4277)\lambda + 41.57 \dots\dots(1)$$

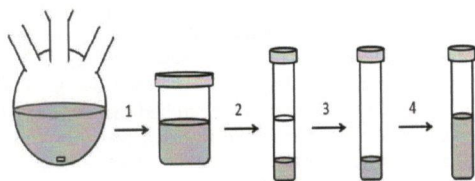


Fig. 1. Schematic of washing procedure. 1) Quenching the CdSe nanoparticles reaction in toluene 2) Precipitate CdSe nanoparticles by adding methanol and centrifuge to separate the nanoparticle and solvent, 3) Decant colourless solution 4) Re-suspend nanoparticles in toluene. Repeat steps 2-4 for every following washing cycles.

#### UV visible spectroscopy

UV visible spectroscopy was performed using Perkin Elmer model Lambda Bio 10 spectrometer, with spectral resolution of 2 nm. Suspensions were placed in quartz cells of pathlength 10 mm. Before each spectrum was measured, a blank or background was recorded using the same solvent as to that of the nanoparticle solution.

#### Photoluminescence spectroscopy

The photoluminescence spectra were measured by placing the CdSe nanoparticles solution into 10 mm quartz cell. For the CdSe nanoparticles the emission was recorded between 350-650 nm with the excitation of 340 nm and integration time of 0.1 seconds.

#### TEM

In this research, TEM was used to gain information about quality of the CdSe NPs after purification and also the distribution of the nanoparticles. Since all the sample was synthesized in colloid solution, a drop of the suspension was placed onto a carbon coated copper TEM grid. The specimens were allowed to dry and after drying the deposit was analysed with JEOL 2010 TEM. The distributions of the particles were analyzed using ImageJ software.

#### ICP-OES

In this research ICP-OES was used to quantitatively analyse the elements in solution after each wash cycle. Samples were prepared by adding about 4.0 μM of CdSe resuspended in toluene from each sample 0x wash through 5x wash into a glass vial. Then 1 ml of 37 % of HCl was added to each vial and the sample allowed to dissolve overnight. Prior to the measurement a further 5 ml of 10% HCl was added. All samples were prepared at room temperature. The instrument was calibrated for Se with the ICP standard solution purchased from TraceSELECT®Ultra Aldrich with phosphoric acid (1000 mg/L P in H<sub>2</sub>O), Se (1000 mg/L Se in 2 % HNO<sub>3</sub>). For Cd 1000 ppm standard solutions were prepared in the laboratory from Cd salts. Results obtain from the measurement were used to determine Cd/Se and Cd/P ratios.

## RESULTS AND DISCUSSIONS

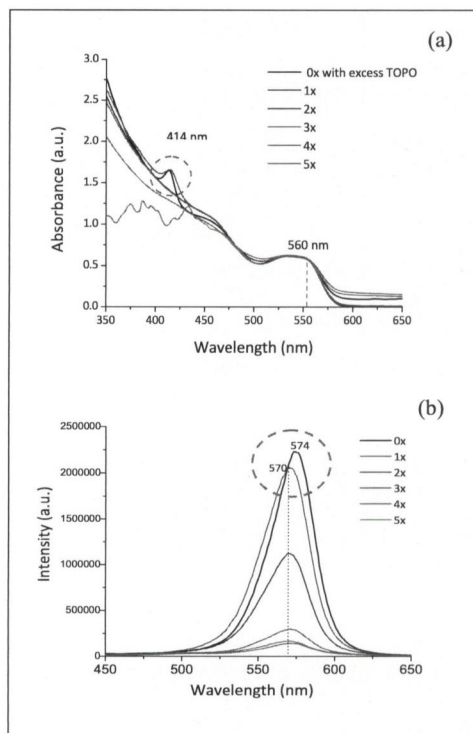
#### Optical Properties of Washed CdSe

Fig.2 presents the absorption and photoluminescence spectra for original, 1x, 2x, 3x, 4x and 5x treated solution. All the samples used for the absorption and photoluminescence measurement were at the same concentration ca.  $6.0 \times 10^{20}$  dots  $\text{cm}^{-3}$  with the particle size of 3.26 nm. In the absorption spectra the peak observed at ca. 560 nm corresponding to absorption at the first exciton does not shift indicating the size of the particles does not change during the washing procedure. It is noticed that 0x and 1x wash exhibited a sharp and narrow absorption peak at 414 nm. This absorption peak has been explained in the literature by invoking "magic sized nanocrystals". The term "magic size" is used to describe extremely stable 'sizes' of nanocrystals that are observed during growth [5] [6]. Such

crystals are believed to have a thermodynamically stable, unique structure which is resistant to growth and exhibits an extremely narrow size distribution [7]. These "magic sized" nanoclusters has been seen at 285 nm and 349 nm by Peng *et al.* at the early stage of nanocrystal growth [5]. El-Sayed *et al.* have also shown that "magic sized nanocrystals" are produce when butylamine is added to a nanocrystal solution [6]. This was attributed to the butylamine etching the nanocrystals until a stable size is obtained. These sharp absorption peaks also appeared in the presence of hexadecylamine but the intensity was reduced greatly in comparison to those observed with butylamine. It is suggested that the energy released by the binding of these ligands is large enough to induce the breaking of the Cd-Se bonds, necessary for reorganization, but not so large as to destroy or dissolve the nanoparticles. After 1x wash the absorption peak for the small nanocrystal disappear. During the washing procedure, the largest nanoparticles in the sample exhibit the greatest attractive van der Waals forces and tend to aggregate before the small particles. The aggregates consisting of the largest nanoparticles are separated by centrifugation and resuspended in solvent. On washing, the smaller nanoparticles remain dispersed in the methanol supernatant and discarded during the purification step. The fluctuations in the absorbance seen at shorter wavelengths for 5x washed particles are believed to be due to the aggregation of the nanoparticles (see Fig.2a). From long term observation, the extensively purified solution (5x wash) CdSe nanoparticles can exhibit a spontaneous precipitation, while the other solutions (1x, 2x, 3x and 4x wash) with similar concentration remain stable for more than 7 days. This shows that after 5x washes of the CdSe nanoparticles large number of ligands has been removed, as reported by Kalyuzhny *et al.* [8].

Fig.2b show the changes observed in photoluminescence spectra on purification of CdSe. As the purification proceeds, the PL maxima peaks shift slightly from 574 nm to 570 nm but no optically active surface traps were introduced, as reported by previous study by Kalyuzhny *et al.*[8].

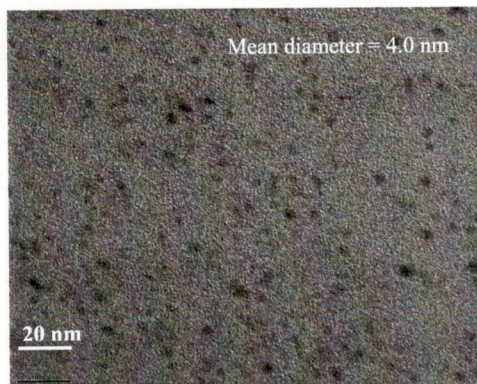
The highest PL intensity is observed for unpurified nanoparticles and significantly decreases with wash cycles. The drop in the intensity after the washing step may have two possible cause (i) ligand loss and replacement by methanol molecules [8] [9] (ii) loss of the smallest nanoparticles during the purification procedure. The losses of the small nanoparticles have being shown in the UV Vis absorption spectra.



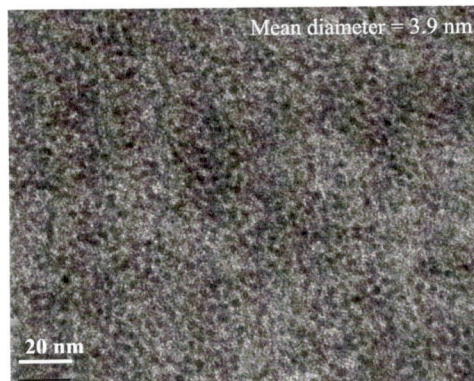
**Fig.2. (a) Absorption and (b) photoluminescence spectra for 1x, 2x, 3x, 4x, 5x and fresh TOPO capped CdSe nanoparticles solution.**

### TEM

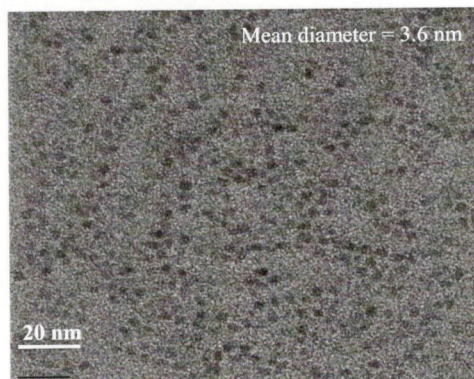
The optical spectra from Fig.2 show the CdSe before and after several purifications showed almost no shift in the PL maxima peak and absorption peak. TEM was also performed on these samples. Fig.3 displays the TEM micrographs of unpurified CdSe and 1x wash through to 5x washes. The TEM images demonstrate obvious changes in the nanoparticles' tendency to aggregate with purifications. Before purification the nanoparticles can be found on the TEM grid well separated by their initial ligand shell (Figure 3a). After removal of the ligand the size of particles does not change substantially with the mean diameter remaining in the range of 3.6 nm to 4.0 nm. The mean diameter of 0x wash is ca. 4.0 nm. After washing 1x, the mean diameter is reduced to 3.6 nm, due to loss of some atoms on the CdSe surface. This is consistent with the shift in the PL peak after the first wash. After 2x, 3x, 4x and 5x wash the mean diameter increases back to 4.0 nm. Their tendency to form aggregates on the TEM grid increases with the number of subsequent purification step (Fig.3 b-f). This aggregation may due the thinner and weaker ligand shell following the washing steps.



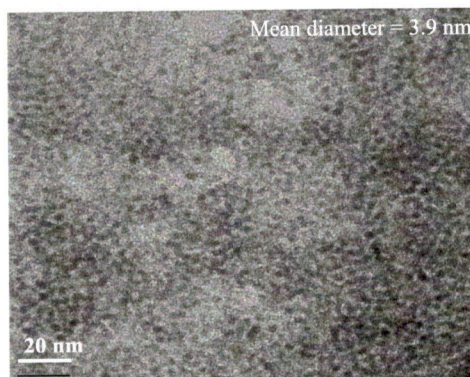
(a) CdSe 0x wash



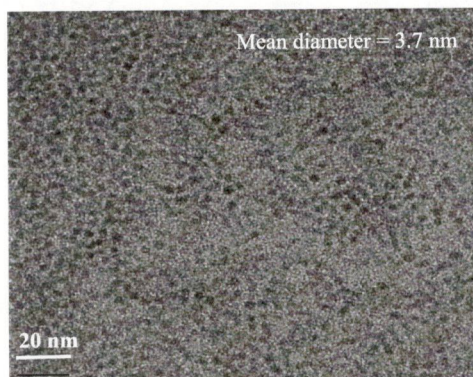
(d) CdSe 3x wash



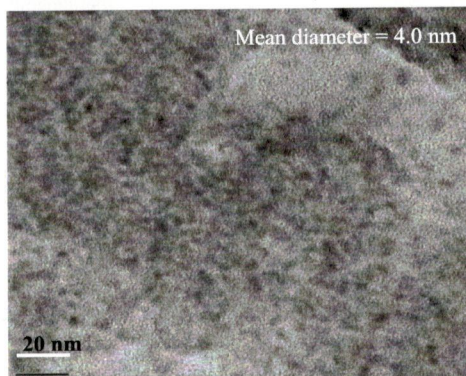
(b) CdSe 1x wash



(e) CdSe 4x wash



(c) CdSe 2x wash



(f) CdSe 5x wash

**Fig. 3** TEM images of TOPO capped CdSe nanoparticles before (a) and after 1x wash (b) 2x wash (c) 3x wash (d) 4x wash (e) 5x wash (f). [Magnification X100K]

**Table 1 Ratios Cd/Se and Cd/P in 2.8nm CdSe quantum dots a measured by ICP.**

No. of wash + particle size	Cd (ppm)	Se (ppm)	P (ppm)	Cd/Se	Cd/P
0x 2.8nm	60	597	6	0.10	10.00
1x 2.8nm	1049	1269	8	0.83	131.13
2x 2.8nm	1418	1655	6	0.86	236.33
3x 2.8nm	1750	1749	10	1.00	175.00
4x 2.8nm	2008	1488	7	1.35	286.86
5x 2.8nm	2614	1654	9	1.58	290.44

**ICP**

In this research inductively couple plasma optical emission spectroscopy (ICP-OES) was used to quantitatively analyse the elements in solution after each wash cycle.

Table 1, shows the value measured from the ICP-OES of Cd/Se and Cd/P. From the literature the elemental ratios of Cd/Se in CdSe nanoparticles range from 1:1 to 6.5:1 [1] [10]. In this work, at the 0x wash or unpurified TOPO capped CdSe show a very low ratio of Cd to Se ~ 0.10, suggesting that Se is in excess. As unwashed TOPO capped CdSe, the excess Se is from unreacted selenium. In the following discussion the data from 0x washes is excluded. The values obtained from the ICP-OES through 1x wash to 5x wash demonstrate that the Cd/Se ratio is increasing as number of wash increase, which indicates that the washing procedures removes Se in preference to Cd.

The ICP-OES measurement of P displayed in Table 1, shows the total amount of P remains stable throughout the washing procedures including the unpurified CdSe solution. A very high amount of P was expected in the unpurified CdSe due to the free unbound TOPO ligands. This may possibly due to the excess TOPO formed a clear layer after addition of HCl. Which potentially leaving only the P present in the ligand bound to the CdSe surface, to be detected in ICP-OES measurements.

**CONCLUSIONS**

The 1x, 2x, 3x and 4x wash CdSe NPs suspensions were stable for extended periods of time, more than one week. Further washing, e.g. 5x, resulted in a suspension that was unstable, the CdSe sedimentation out in approximately 2 days. This suggests the loss of stabilizing agent from the particles surface with excess washing. Sedimentation of CdSe after a few times washes was observed when the washing procedure took place a few months after synthesis of the nanoparticles.

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