

Investigation of Quantum Dot - Metal Halide Interactions and their

Effects on Optical Properties

Finn Purcell-Milton^{1*}, Maxime Chiffolleau² and Yurii Gun'ko^{1*}

¹ School of Chemistry and CRANN, University of Dublin, Trinity College, Dublin 2, Ireland.

² Département SGM, Institut National Des Sciences Appliquées, Lyon

*Email: Fpurcell@tcd.ie, Igounko@tcd.ie

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1. Synthetic Methods

Materials supplied by Sigma – Aldrich

Acetone (HPLC grade), OA (oleic acid, 90%); ODA (octadecylamine, 97%); ODE (octadecene, $\geq 97\%$); OLY (oleylamine, 70 %); Rhodamine 6G (99 %); Se (99.99 %); TBP (tributylphosphine, 90 %); TDPA (tetradecylphosphonic acid, 97 %); TOP (trioctylphosphine, 90 %); TOPO (trioctylphosphine oxide, 99%); ZnCl_2 (Zinc chloride, 99.999 %; and Zinc powder 95 %

Solvents supplied by Trinity College Solvent Stores

Acetone, chloroform, dichloromethane ethanol, propanol, hexane and toluene

Other suppliers

CdO (99.9998 %, Alfa Aesar); $\text{Cd}(\text{stearate})_2$ (min 90%, Strem Chemicals); HPA (n-hexylphosphonic acid, 97 %, ABCR); ODPA (n-octadecylphosphonic acid, $\geq 97\%$, PCL Synthesis); S (99.999 %, Acros Organics);

(i) Preparation of oleic acid capped CdS Quantum Dots

This work was carried out using a modified method from literature.¹⁻²

Preparation of 0.05 M sulphur stock solution

0.016 g (0.5 mmol) of sulphur was dissolved in 10.0 ml of degassed ODE, produced by heating the solution under argon to 200 °C for 15 minutes.

CdS QD synthesis

0.0128 g (0.997 mmol) of CdO, 0.093 g of OA (0.33 mmol) and 3.9 g of ODE were weighed into a 100 ml 3-neck round-bottom flask equipped with a condenser and thermometer. The solution was heated to 30 °C and degassed for 20 minutes under vacuum. The reaction was then switched to an argon atmosphere and then heated to 300 °C to allow formation of $\text{Cd}(\text{oleate})_2$ which was indicated by a colour change from brown to colourless. Following this 1.0 ml of a 0.05 M solution of sulphur dissolved in ODE was injected. Growth was then allowed to proceed for 10 minutes after which the reaction was removed from the heat source and the CdS QDs were precipitated using degassed ethanol. The QD solution was cleaned using a number of dissolution and precipitation cycles with dry hexane and HPLC grade acetone.

(ii) Preparation of ODPA capped CdSe QDs

This work was carried out using a modified method from literature.³

1.1.1.i Preparation of Se 0.75 M stock solution

0.059 g of Se was mixed with 1.0 ml of TOP under an argon atmosphere and sonicated until the Se become completely dissolved, indicated by a clear transparent solution.

1.1.1.ii Synthesis of CdSe QDs

TOPO (3.0 g), ODPA (0.280 g) and CdO (0.060 g) were added to a 100 ml 3-neck round-bottom flask equipped with a condenser and thermometer. The solution was then heated to 150 °C and degassed under vacuum for 30 minutes. The atmosphere was then changed to argon and the solution was heated to 300 °C and held at this temperature until the solution turned optically clear and colourless, indicating formation of $\text{Cd}(\text{ODPA})_2$. Following this 1.0 ml of TOP was injected into the flask; the solution was then heated to the required temperature. The Se-TOP solution was then injected and immediately the solution was removed from the hot plate and the reaction mixture was allowed to cool. After the solution cooled

to below 150 °C, 20 ml of dried methanol was injected to precipitate the NCs and was left to cool to room temperature. The resulting QD solution was cleaned using a number of dissolution and precipitation cycles with dry toluene and methanol.

(iii) Preparation of oleic acid capped CdSe

This work was carried out using a modified method from literature.⁴

Se-TBP solution preparation

0.1105 g (1.399 mmol) of Se was mixed with and 3.0 ml of TBP under an argon atmosphere and sonicated until the Se become completely dissolved, indicated by a clear transparent solution.

CdSe Synthesis

0.50 g (0.0039 mol) of CdO, 4.0 g of oleic acid and 10.0 g of ODE (octadecene) were weighed into a 100 ml 3-neck round-bottom flask equipped with a condenser and thermometer. Following this, the flask was put under vacuum and degassed for 20 minutes at 30 °C. After this, the flask was switched to argon; the temperature was increased to 260 °C and allowed to stabilize. Time was then allowed for the CdO to convert to Cd (oleate)₂ which was indicated by a colour change from brown to colourless. At this point, the Se-TBP solution was injected. Growth was allowed to proceed for a set amount of time (10 – 220 seconds). The reaction was then removed from the heating mantle and allowed to cool to 200 °C, following by injection of 20 ml of degassed acetone to precipitate the QDs. The resulting QD solution was cleaned using a number of dissolution and precipitation cycles with dry hexane and HPLC grade acetone.

Preparation of ODP A capped CdSe QDs

This work was carried out using a modified method from literature.³

Preparation of Se 0.75 M stock solution

0.059 g of Se was mixed with 1.0 ml of TOP under an argon atmosphere and sonicated until the Se become completely dissolved, indicated by a clear transparent solution.

Synthesis of CdSe QDs

TOPO (3.0 g), ODP A (0.280 g) and CdO (0.060 g) were added to a 100 ml 3-neck round-bottom flask equipped with a condenser and thermometer. The solution was then heated to 150 °C and degassed under vacuum for 30 minutes. The atmospheres was then changed to argon and the solution was heated to 300 °C and held at this temperature until the solution turned optically clear and colourless, indicating formation of Cd(ODP A)₂. Following this 1.0 ml of TOP was injected into the flask; the solution was then heated to the required temperature. The Se-TOP solution was then injected and immediately the solution was removed from the hot plate and the reaction mixture was allowed to cool. After the solution cooled to below 150 °C, 20 ml of dried methanol was injected to precipitate the NCs and was left to cool to room temperature. The resulting QD solution was cleaned using a number of dissolution and precipitation cycles with dry toluene and methanol.

(iv) Preparation of Octadecylamine capped -CdSe QDs

This work was carried out using a modified method from literature.⁵

Preparation of 1.5 M Se stock solution

1.184 g of Se was mixed with 10.0 ml of TOP under an argon atmosphere and sonicated until the Se become completely dissolved, indicated by a clear transparent solution.

Preparation of 0.5 M Cd stock solution

A 0.5 M solution of Cd was created by firstly degassing a solution of 1.285 g of CdO in 10.0 ml of OA and 10.0 ml ODE, which was then switched to an argon atmosphere and heated to 270.0 °C, until a clear solution was created.

SILAR stock solutions of Cd and Se

To grow the CdSe QDs further, we used a solution of 0.2 M Se stock solution and 0.2 M Cd stock solution, diluted using solvents mentioned above.

Synthesis of CdSe QDs

7.50 g of octadecylamine, 2.50 g of TOPO, 20 g of octadecene, and 2.0 ml of 0.5 M Cd-oleate were added to a 100 ml 3-neck round-bottom flask equipped with a condenser and thermometer. This solution was heated to 80.0 °C and degassed under vacuum for 20 minutes. Following this, the solution was switched to an argon atmosphere and heated to 290 °C. After which 1.0 ml of 1.5 M Se-TOP solution was injected and QD growth began. After injection of Se-TOP at 290 °C, the temperature was set at 250 °C for CdSe QD growth for 10 minutes. Following this stock solutions of Se and Cd were slowly injected in cycles to increase the size of QDs, beginning with 0.20 ml of Se, following this 0.40 ml of Cd was injected, then 0.40 ml of Se and finally 0.80 ml of Cd.

After ten minutes, the solution was cooled down to room temperature, and CdSe QDs were precipitation with acetone. The QDs were separated using centrifugation and cleaned using a number of cycle of hexane dissolution and acetone precipitation followed by centrifugation. CdSe core QDs were then re-dispersed in hexane.

(v) Preparation of CdS/CdSe Quantum Dot

This work was carried out using a modified method from literature.^{1, 6}

Preparation of 0.5 M sulphur stock solution

0.016 g of sulphur was dissolved in 10.0 ml of degassed ODE, produced by heating the solution under argon to 200 °C for 15 minutes.

Preparation of 0.4 M Se stock solution

A 0.4 M stock solution was prepared by dissolving 0.063 g of Se in 2 ml of trioctylphosphine using sonication under argon, producing a clear solution.

Preparation of 0.4 M Cd (oleate)₂ stock solution

A 0.4 M solution of Cd was created by firstly degassing 0.5135 g of CdO in 10.0 ml of a 1:1 (v/v) OA: ODE solution which was then switched to an argon atmosphere and heated to 270 °C, until a clear solution was created.

CdS/CdSe QD synthesis

0.0128 g (0.00010 mol) of CdO 0.093 g of OA (0.33 mmol) and 3.9 g of ODE were added to a 100 ml 3-neck round-bottom flask equipped with a condenser and thermometer. The flask was then put under vacuum

and heated to 30 °C, degassing the solution for 20 minutes. The reaction was then switched to an argon atmosphere and then heated to 300 °C to allow formation of Cd (oleate)₂ indicated by the solution becoming clear. Following this 1.0 ml of a 0.05 M solution of sulphur dissolved in ODE was injected (0.016 g of sulphur in 10.0 ml of degassed ODE, produced by heating the solution under argon to 200 °C for 15 minutes). Growth was then allowed to proceed for 10 minutes. After which the vessel was cooled to 215 °C and shell pre-cursor injection began.

Firstly, 0.8 mL of degassed OA was added into the reaction vessel. This was followed by injection of 0.15 ml of a Se stock solution and followed by the addition of an equimolar amount of Cd (oleate)₂ precursor stock solution after a 10 min interval. Following this another ten minutes was allowed for the reaction to take place. This constitutes one cycle of shell deposition. Three more cycles of Se and Cd stock solutions were injected with the same 10 min intervals between each injection, increasing the volume from 0.25 ml, to 0.4 ml to 0.6 ml for each cycle. The reaction was terminated by removing the heating source room and precipitated the QDs with degassed ethanol. The solution was then cleaned using a number of dissolution and precipitation cycles with dry hexane and HPLC grade acetone.

(vi) Preparation of CdSe/CdS Core-Shell Quantum Dots

This work was carried out using a modified method from literature.⁵

Preparation of 0.1 M S stock solution

Sulphur stock solution was prepared by dissolving 0.032 g of sulphur in 10.0 ml of degassed ODE at 180 °C under an argon atmosphere to obtain a 0.1 M sulphur solution.

Preparation of 0.1 M Cd stock solution

A 0.1 M solution of Cd was created by firstly degassing 0.128 g of CdO in 10.0 ml of a 1:1 (v/v) OA: ODE solution, which was then switched to an argon atmosphere and heated to 270 °C, until a clear solution was created.

Synthesis of CdSe/CdS QDs

10 g of oleylamine, 20 g of ODE, and 6.75×10^{-7} mol of octadecylamine capped -CdSe QDs (see section 0) were added to a 100 ml 3-neck round-bottom flask equipped with a condenser and thermometer. The flask was then put under vacuum and heated to 60 °C, degassing the solution for 30 minutes. Following this, the reaction was switched to an argon atmosphere and 0.3 ml of the 0.1 M Cd stock solution was injected. This was heated to 230 °C and allowed to react for 10 minutes. This was followed by injection of 1.25 ml of a S stock solution and followed by the addition of an equimolar amount of Cd(oleate)₂ precursor stock solution after a 10 min interval. Following this another ten minutes was allowed for the reaction to take place. This constitutes one cycle of shell deposition. Two more cycles of shell deposition were carried out with the same 10 min intervals between each injection, increasing the volume to firstly 2.25 ml of S stock solution and 0.45 ml of Cd stock solution and then 3.25 ml of S stock solution and 0.6 ml of Cd stock solution. The reaction was terminated by removing the heating source room and precipitated the QDs with degassed ethanol. The solution was then cleaned using a number of dissolution and precipitation cycles with dry hexane and HPLC grade acetone.

(vii) Preparation of CdSe/CdS Core-Shell Heterostructured Quantum Rods

This work was carried out using a modified method from literature.³

Preparation of 2.5 M S - TOP and CdSe QD stock solution

0.120 g of S was dissolved in 1.5 ml of TOP under argon; the solution was then sonicated, producing a clear transparent solution. To this was added 8×10^{-8} mol of ODPA capped CdSe QDs (see section 0) in TOP solution, which was prepared by mixing a set volume of CdSe QDs in hexane with TOP followed by the use of high vacuum and moderate heat to remove the hexane solvent.

Synthesis of CdSe/CdS core-shell quantum rods

0.057 g of CdO, 3 g TOPO, 0.29 g ODPA and 0.08 g HPA were added to a 3-neck flask with a condenser and thermometer. Initially the mixture was heated to 150 °C under argon, after which the solution was placed under vacuum and degassed for 30 minutes. The flask was then flushed with argon and heated to 300 °C, holding at this temperature until the solution turned optically clear and colourless, indicating formation of the Cd complex. Following this, 1.5 g of TOP was injected into the flask and the solution was heated further to 360 °C. This was then followed by injection of the S-TOP and CdSe QDs stock solution. The QDs are then allowed to grow for 8 minutes after which the heating mantle is removed. After the solution cooled to below 150 °C, 20 ml of degassed methanol was injected to precipitate the QDs and the solution was allowed to cool to room temperature. The QDs were fully separated using centrifugation and then re-dispersed in a minimum volume of dry-toluene. This method of precipitation was repeated twice more to obtain a clean solution of QDs dispersed in toluene.

(viii) Preparation of CdTe/CdSe Type II Core-Shell Quantum Dots

This work was carried out using a modified method from literature.⁷

0.08 M Te Stock solution

0.0127 g (0.995 mmol) of Te, 0.20 ml of TOP (Trioctylphosphine), 0.050 g (0.15 mmol) of ODPA and 1 ml of ODE were added to a sample bottle under a strict argon atmosphere. This was heated to 120 °C and remained at this temperature until the solute became fully dissolved, producing a clear strongly yellow coloured solution, if it became opaque, oxygen contamination has taken place and the solution must be discarded and preparation must be repeated.

0.09 M Se Stock solution

A 0.09 M solution of 0.071 g (0.0009 mol) of Se was added to 1.6 ml of TOP, in 8.4 ml of degassed ODE under argon and sonicated to produce a clear solution.

0.1 M Cd Stock solution

A 0.1 M solution of Cd was created by firstly degassing 0.128 g (0.997 mmol) of CdO in 10.0 ml of solution containing 1.25 ml of OA and 8.75 ml of ODE, which was then switched to an argon atmosphere and heated to 270 °C, until a clear solution was achieved.

Synthesis of CdTe/CdSe Quantum Dots

0.026 g (0.20 mol) of CdO, 0.226 g (0.800 mmol) of OA (oleic acid) and 3 g of ODE was added to a 3-neck flask with a condenser and thermometer. This was degassed 30 °C using vacuum and then heated to 280 °C under argon, and time was then allowed for the Cd to coordinate with the OA, indicated by the solution becoming colourless. This was then followed by injection of the Te stock solution. This is allowed to react for 3 minutes. Following this, the reaction is cooled to 230 °C and shell precursors are added alternatively. This began by injection of 1.0 ml of Se stock solution over one minute, which was then allowed to react for ten minutes, and then followed by 1.0 ml of Cd stock solution, added over a one-minute period, which

was then allowed to react over ten minutes. This process is continued, making alternative injections of shell precursors until all of the stock solutions had been added. The reaction is then cooled, and acetone is added to precipitate the QDs.

(ix) Preparation of CdSe/ZnS Core-Shell Quantum Dots

This work was carried out using a modified method from literature.⁸

0.1 M Zn Stock Solution

0.16276g of ZnO (2 mmol) in 4 ml of oleic acid and 16 ml of ODE at 290 °C under argon atmosphere.

0.1 M S Stock Solution

The sulfur precursor (S-ODE) solution was prepared by dissolving 0.064 g of sulfur in 20 ml of ODE at 190 °C. (changes from straw colour to deep yellow when heated up)

Synthesis of CdSe/ZnS Quantum Dots

Dissolved $5.2 \text{ mol} \times 10^{-7} \text{ mol}$ of CdSe (2.135 nm) QDs in 2.5 ml of hexane were mixed with 5.4 g of ODA, and 27 ml ODE in a 3-neck flask. Firstly, it was degassed at room temperature for 30 minutes to remove hexane, then it was heated to 100 °C and degassed for 20 minutes. The reaction was then heated 140 °C, at which point 2.7 ml of TOP was injected and the reaction was heated to 200 °C and held at this temperature for 30 minutes. Following this 0.9 ml of Zn stock was injected and held at this temperature for 20 minutes. Following this the temperature was dropped to 180 °C and 0.9 ml of S solution. The reaction was then heated to 220 °C and kept at this temperature for 60 minutes, completing growth of one monolayer. If a second layer is desired, the reaction was cooled to 140 °C, at which point 2.7 ml of TOP was added. The reaction was then heated to 180 °C. At this point 1.5 ml of Zn precursor was injected. 10 minutes was allowed to elapse for the reaction to take place. Following this 1.5 ml of S precursor was then injected, followed by 10 minutes of shell growth. This could be repeated multiple times (with larger injections) to grow thicker shells, with a shell of 6 monolayers showing the highest QY (95%)., third injection, need 2.2 ml. The reaction was terminated by allowing the reaction mixture to cool to room temperature. The final product was diluted by hexanes followed by a methanol extraction. The extraction procedure was repeated for three times, and the top hexane layer was stored.

2. Additional Spectroscopic Data

(i) CdSe QD Results

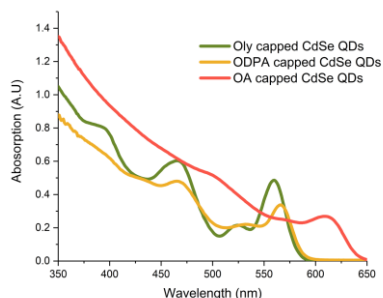


Figure S1. Absorption spectra of CdSe QDs tested, synthesised using three alternative approaches.

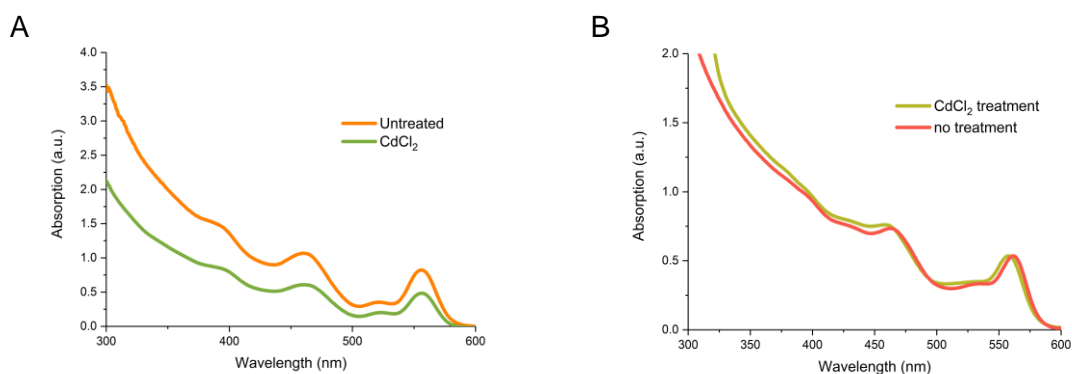


Figure S2. Absorption spectra of octadecylamine capped (A) and octadecylphosphonic acid capped (B) CdSe QDs showing no substantial change due to CdCl_2 treatment relative to untreated samples.

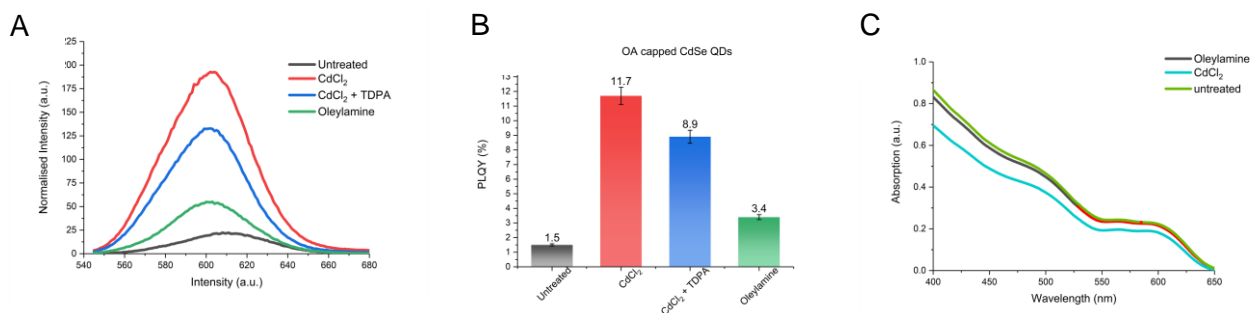


Figure S3. PL spectra (A) of OA capped CdSe QDs 2 treated with a range of solutions with PLQY yields (B) and absorption spectra (C).

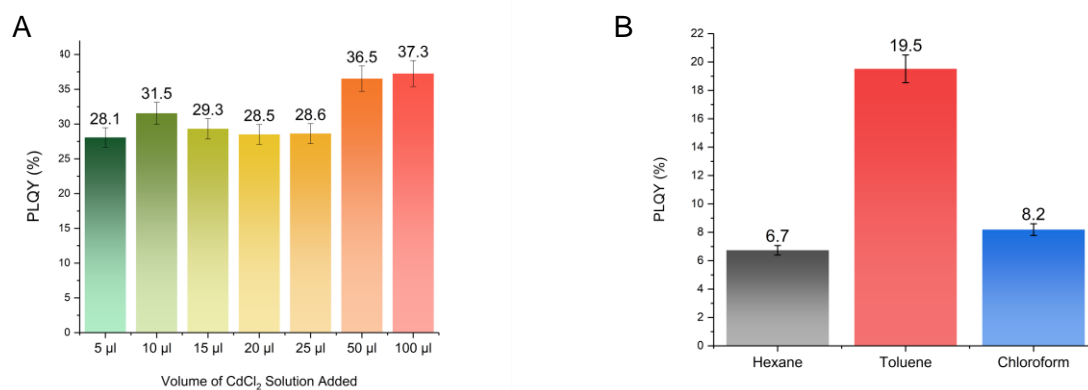


Figure S4. PLQY of CdCl₂ treated octadecylamine capped CdSe QDs dependent upon non-polar solvents or the volume of CdCl₂ solution added.

(ii) CdS QD Results

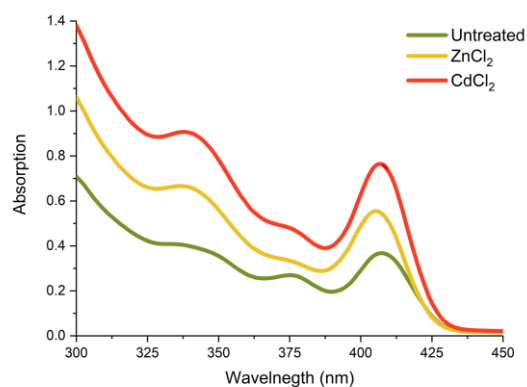


Figure S5. Absorption spectra of CdS QDs tested, also showing no change due to anion treatments

(iii) Core-Shell Quantum Dots Absorption Spectra

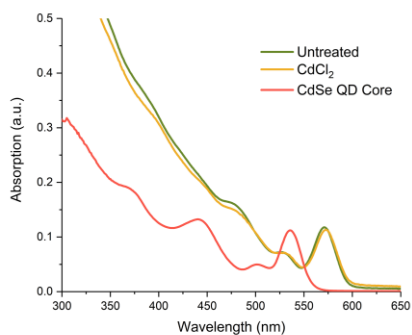


Figure S6. UV-Vis absorption spectra of CdSe/CdS QDs 1

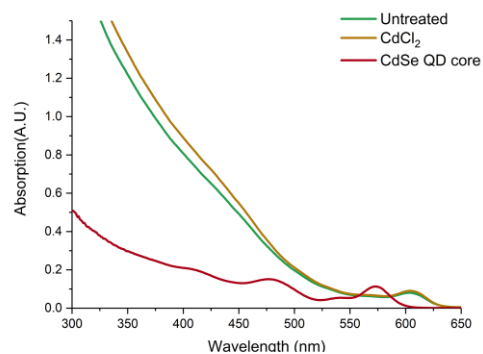


Figure S7. UV-Vis absorption spectra of CdSe/CdS QDs 2

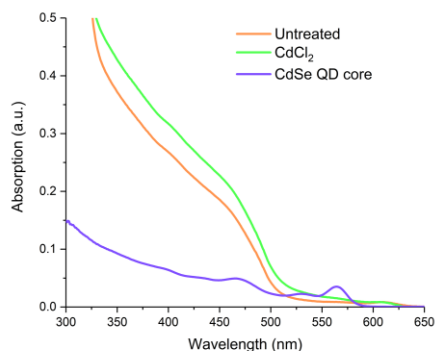


Figure S8. UV-Vis absorption spectra of CdSe/CdS 3 dot in rod sample

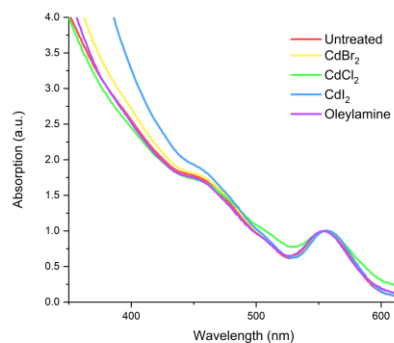


Figure S9. UV-Vis absorption spectra of CdSe/ZnS QDs

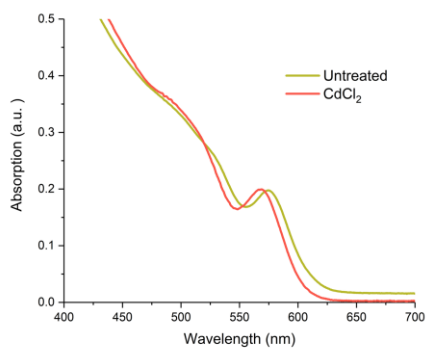


Figure S10. UV-Vis absorption spectra of CdS/CdSe QDs

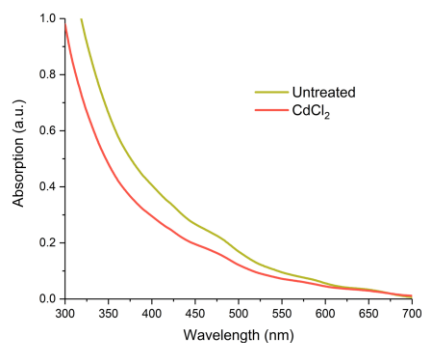


Figure S11. UV-Vis absorption spectra of CdTe/CdSe QDs

(iv) Photoluminescence Lifetime Decay

Equation S1. Amplitude averaging equation used to calculate average lifetimes in Table S1

$$\langle \tau \rangle_a = \frac{\sum a_i \tau_i}{\sum a_i}$$

Table S1. Photoluminescent lifetime measurements of CdSe QDs samples tested

CdSe QD Lifetimes									
Average lifetime	Sample	Treatment applied	T1	Amplitude	T2	Amplitude	T3	Amplitude	χ^2
ns			sec		sec		sec		
1.68E-08	OA CdSe	untreated	1.09E-08	0.4842	2.88E-09	0.17	3.19E-08	0.3458	1.1508
2.43E-08	OA CdSe	CdCl ₂	1.63E-08	0.5435	3.96E-08	0.3821	3.66E-09	0.0744	1.1216
2.86E-08	OA CdSe	oleylamine	1.59E-08	0.4319	4.13E-08	0.504	3.74E-09	0.2471	1.1566
5.13E-09	ODPA CdSe	untreated	1.01E-08	0.0631	4.16E-08	0.05	2.72E-09	0.8869	1.0185
1.11E-08	ODPA CdSe	CdCl ₂	1.62E-08	0.1213	5.86E-08	0.1049	3.87E-09	0.7737	1.1315
1.48E-08	ODPA CdSe	oleylamine	1.44E-08	0.2335	4.93E-08	0.1861	3.82E-09	0.5804	1.0452

Table S2. Photoluminescent lifetime measurements of Core-Shell QD QDs samples tested

Core-Shell QD Lifetimes									
Average lifetime	Sample	Treatment applied	T1	Amplitude	T2	Amplitude	T3	Amplitude	χ^2
sec			sec		sec		sec		
7.51E-09	CdS/CdSe	untreated	6.65E-09	0.2446	2.31E-08	0.2181	1.58E-09	0.5373	1.1738
4.45E-08	CdS/CdSe	CdCl ₂	1.79E-08	0.26	5.96E-08	0.6623	4.43E-09	0.0777	1.1920
2.37E-08	CdS/CdSe	oleylamine	6.88E-09	0.2567	3.43E-08	0.6372	9.48E-10	0.106	1.1797
3.23E-08	CdTe/CdSe	untreated	1.62E-08	0.2425	3.87E-08	0.7311	3.93E-09	0.0264	1.101
3.69E-08	CdTe/CdSe	CdCl ₂	1.84E-08	0.1676	4.12E-08	0.8208	2.86E-09	0.0117	1.0496
3.48E-08	CdTe/CdSe	oleylamine	1.57E-08	0.1762	3.98E-08	0.8031	2.46E-09	0.0207	1.021
1.41E-08	CdSe/CdS 2	untreated	4.49E-09	0.2786	1.40E-08	0.5749	3.24E-08	0.1465	1.3281
1.97E-08	CdSe/CdS 2	CdCl ₂	1.68E-08	0.7121	3.25E-08	0.2287	5.13E-09	0.0592	1.3645
1.86E-08	CdSe/CdS 2	oleylamine	1.63E-08	0.6686	3.13E-08	0.2324	4.93E-09	0.099	1.4024

(v) ZnS QD results

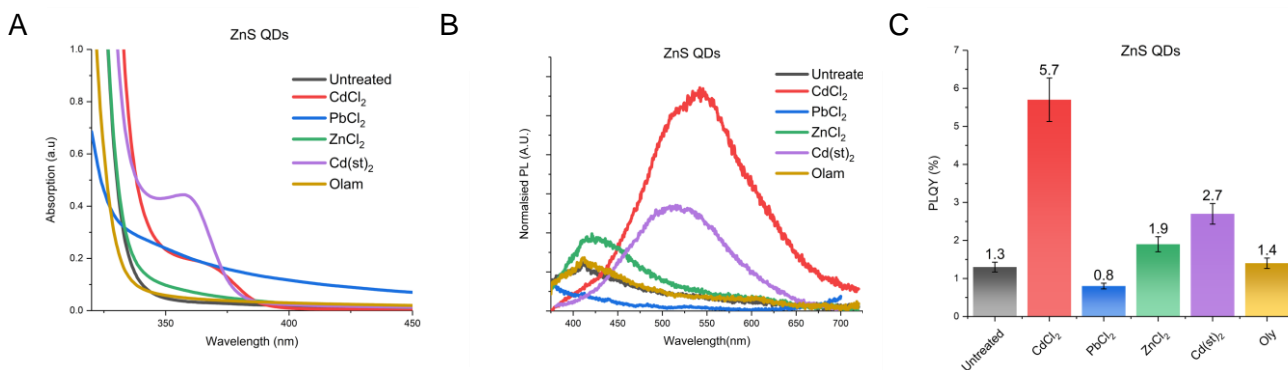


Figure S12. Absorption spectra (A), PL spectra (B) and PLQY yields (C) of ZnS QDs treated with a range of anion solutions.

(vi) Alternative Cation Treatment Results: CdSe QDs

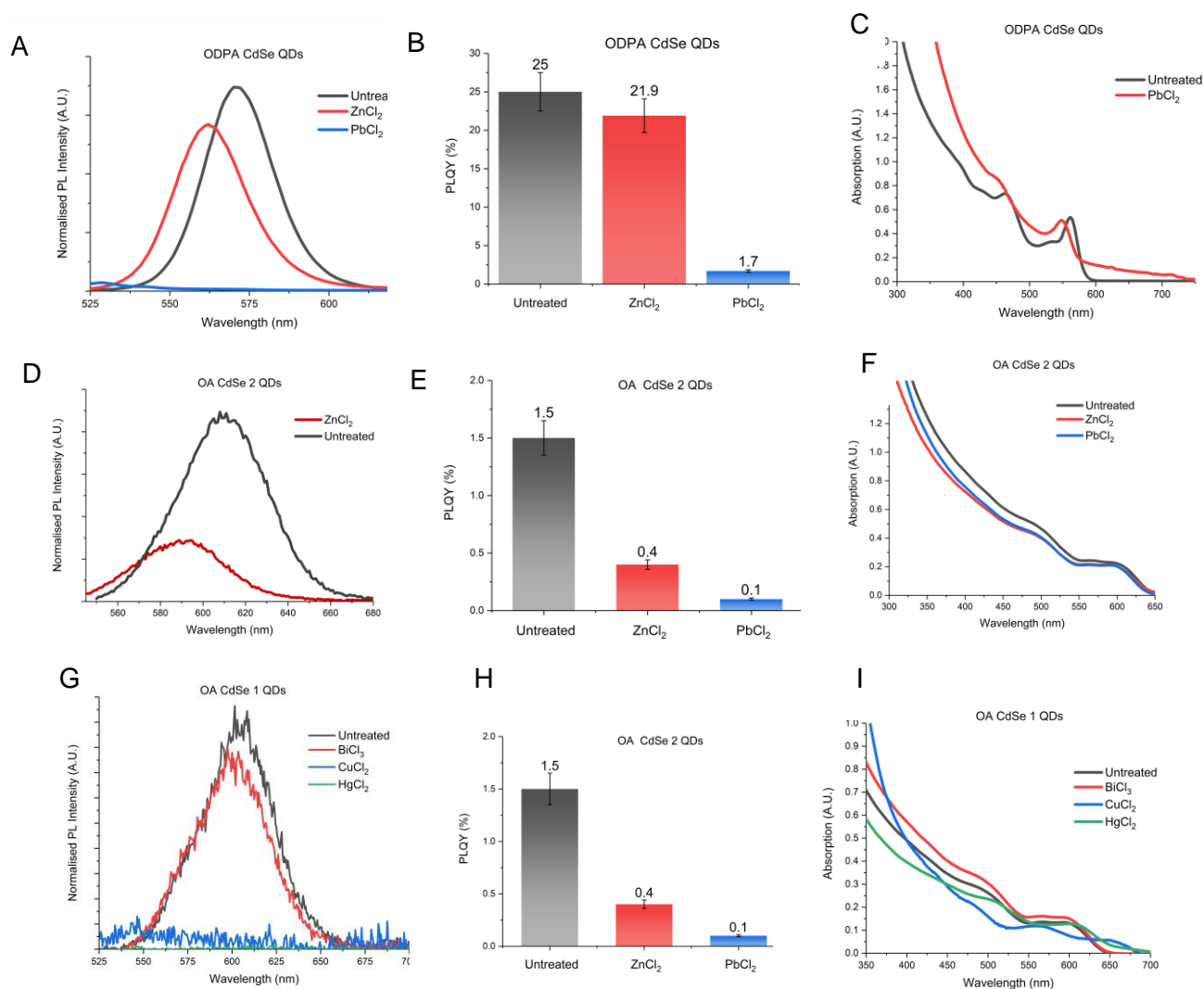


Figure S13. PL spectra and PLQY of OA capped CdSe QDs (A) and (B) and ODPa capped CdSe QDs respectively and treated with a ZnCl₂ and PbCl₂ oleylamine solutions.

(vii) Alternative Cation Treatment Results: Core-Shell QDs

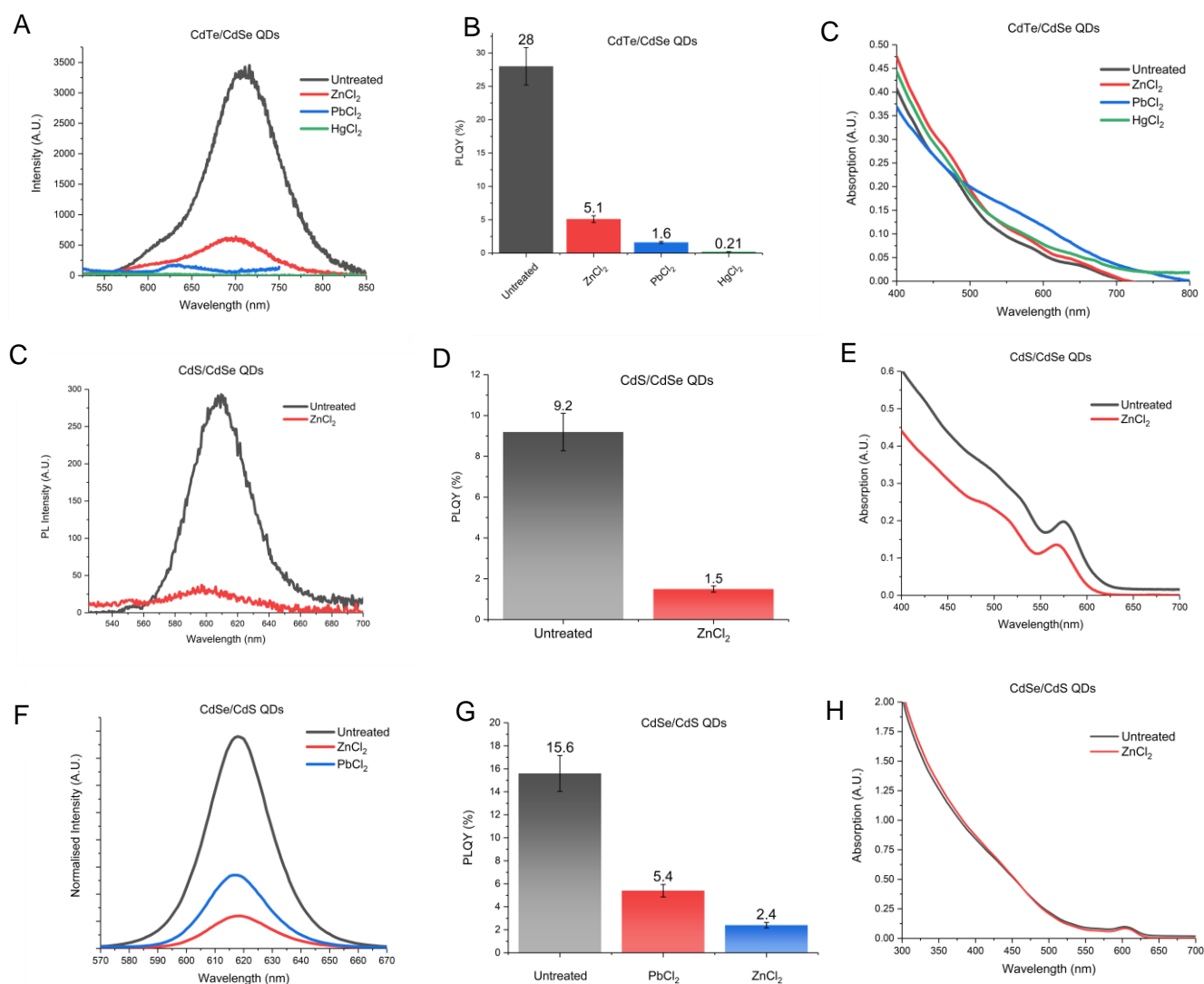


Figure S14. PL spectra and PLQY CdTe/CdSe QDs (A) and (B), CdS/CdSe QDs (C) and (D), CdSe/CdS (E) and (F) respectively and treated with solutions of ZnCl₂, PbCl₂ and HgCl₂ oleylamine solutions.

3. Transmission Electron Microscopy of samples tested

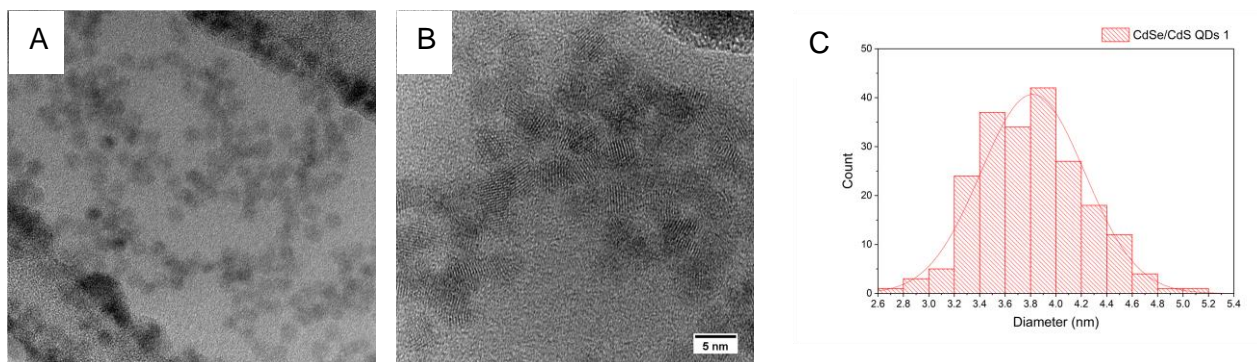


Figure S18. TEM of CdSe/CdS QDs 1, shown in A and B with a histogram of the size distributions in C , giving a diameter of 3.81 ± 0.41 nm

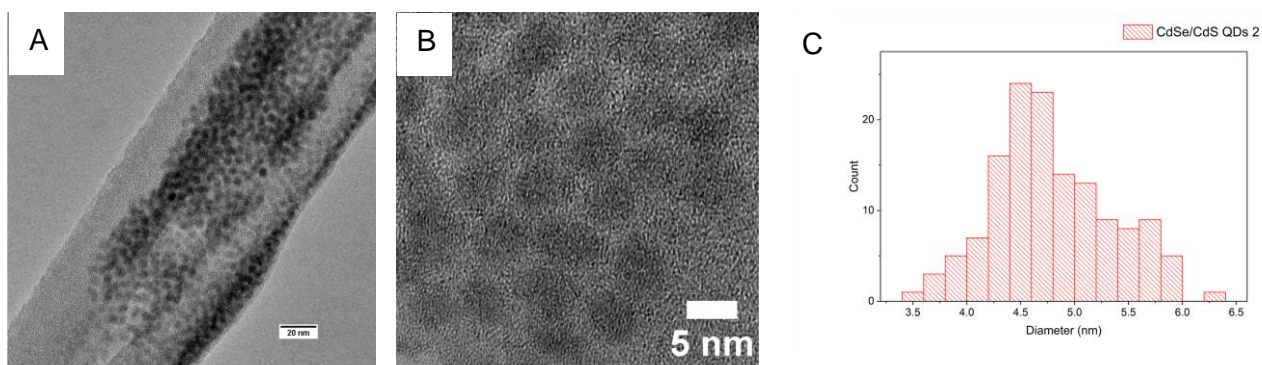


Figure S19. TEM of CdSe/CdS QDs 2 shown in A and B with a histogram of the size distributions in C, giving a diameter of, 4.78 ± 0.55 nm

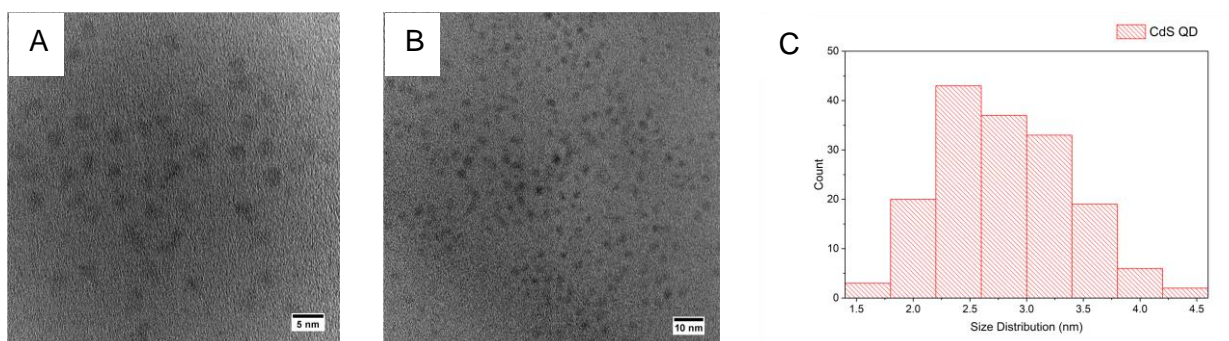


Figure S20. TEM of CdS QDs shown in A and B with a histogram of the size distributions in C , giving a diameter of 2.81 ± 0.57 nm

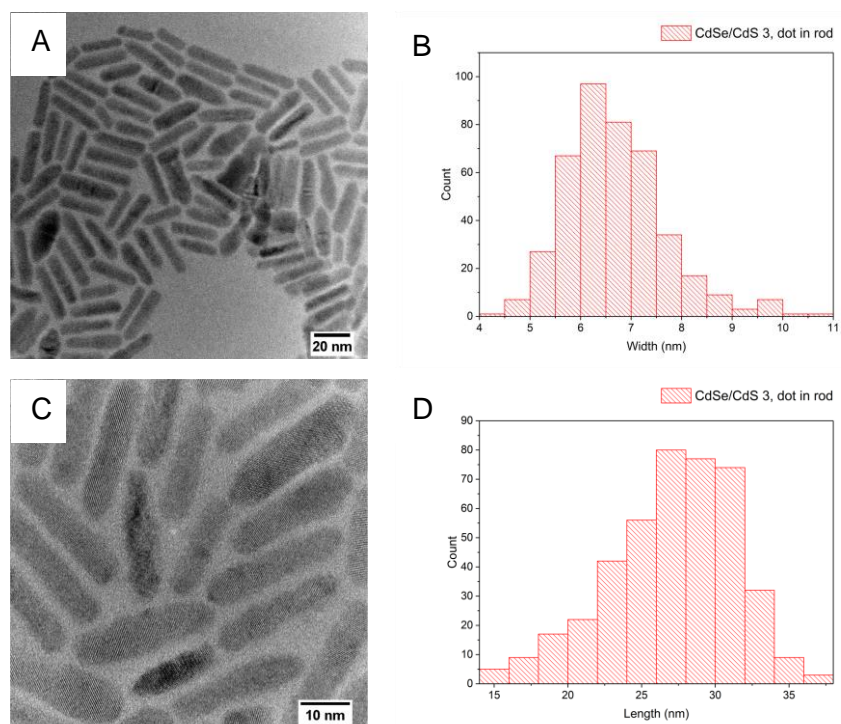


Figure S21. TEM of CdSe/CdS 3, dot in rod, shown in A and C with a histogram of the size distributions in B (width) and D (length), giving a length of 27.13 ± 4.2 and width of 6.61 ± 0.99

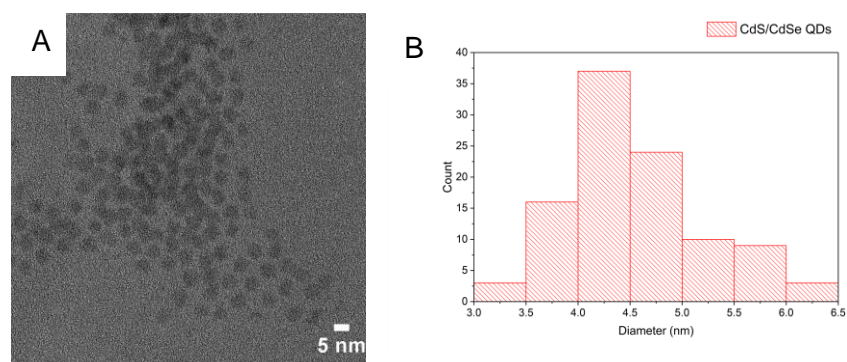


Figure S22. TEM of CdS/CdSe QDs shown in A with a histogram of the size distributions in B, giving a diameter of 4.53 ± 0.66 nm

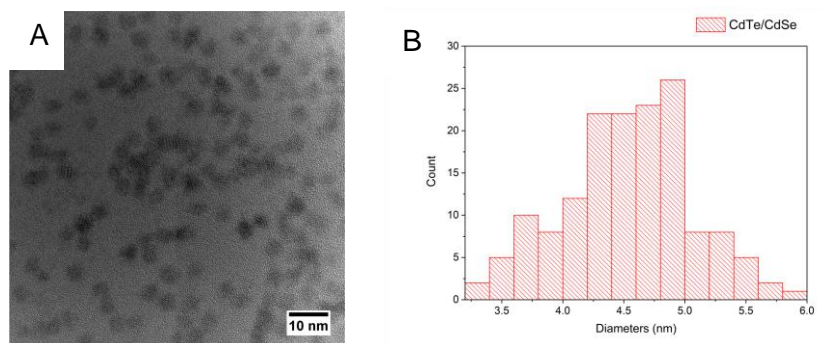


Figure S23. TEM of CdTe/CdSe QDs shown in A with a histogram of the size distributions in B, giving a diameter of 4.5 ± 0.5 nm

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