Supporting information: X-ray total scattering study of magic-size clusters and quantum dots of cadmium sulphide

Lei Tan, Alston J Misquitta, Andrei Sapelkin

School of Physics and Astronomy, Queen Mary University of London, Mile End Road, London, E1 4NS, UK

Le Fang

School of Biological and Chemical Sciences, Queen Mary University of London, Mile End Road, London, E1 4NS, UK

Rory M Wilson

School of Engineering and Materials Science, Queen Mary University of London, Mile End Road, London, E1 4NS, UK

Dean S Keeble Diamond Light Source Ltd, Harwell Science and Innovation Campus, Didcot, OX11 0DE, UK

Baowei Zhang, Tingting Zhu, Frank S Riehle, Shuo Han, Kui Yu Institute of Atomic and Molecular Physics, Sichuan University, Chengdu, 610065, P. R. China

Martin T Dove*

College of Computer Science, Sichuan University, Chengdu 610065, People's Republic of China College of Physical Sciences and Technology, Sichuan University, Chengdu 610065, People's Republic of China and School of Physics and Astronomy, Queen Mary University of London, Mile End Road, London, E1 4NS, UK

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S1. SAMPLE SYNTHESIS AND CHARACTERIZATION

A. Sample synthesis

To prepare the CdS MSC-311 and MSC-322 with phenylacetic acid (PA) ligands, the Cd precursor Cd(OOCCH₂Ph)₂ – Ph being the phenyl group C₆H₅ – was prepared by mixing Cd(OCOOH)₂ (0.60 mmol) and PhCH₂COOH (2.16 mmol) in a temperature at 90 °C. The reaction mixture then heated to 90 °C, to which 1 mL of toluene was added. The Cd precursor was maintained at 60 °C for the preparation of MSC-311, or 90 °C for the preparation of MSC-322¹. A mixture of Bis(trimethylsilyl) sulphide (0.30 mmol), and toluene (1 mL) was then injected into the solution under a nitrogen atmosphere which was held at the injection temperature for about 5 minutes. After the reaction had finished, the mixture was then cooled rapidly in an ice-water bath, resulting in the production of MSCs. For the purification of the CdS MSCs, the as-synthesised reaction solution was centrifuged directly. The precipitate was then washed twice by ethyl acetate (5ml) to remove the unreacted precursors. The precipitate was quickly dried under vacuum.

The synthesis method of CdS MSC-311 and 322 with oleic acid (OA) ligands followed the method of Nevers et al^{2,3}. Breifly, the cadmium precursor Cd oleate was prepared by heating a mixture of CdO (10 mmol) and oleic acid (31.6 mmol) to 160 °C under nitrogen atmosphere. After the mixture formed a tan clear solution, it was then cooled down to 50 °C for the next step which sulphide precursor was injected. The sulphide precursor trin-octylphosphine sulphide (TOPS) was prepared by dissolving sulphur (5 mmol) in tri-noctylphosphine (TOP) (2.0 mL). The sulphide precursor was then injected into Cd oleate solution at 50 $^{\circ}$ C and heated to 140 $^{\circ}$ C. It was then soaked at 140 $^{\circ}$ C for 65 mins. The reaction was quenched with ethyl acetate, resulting in the formation of MSC-322. For the purification of the CdS MSCs, the as-synthesised reaction solution was centrifuged directly and then washed twice by ethyl acetate (10ml). The precipitate was quickly dried under vacuum. The MSC-311 was synthesised by the transformation from MSC-322 to MSC-311^{1,2}. Briefly, 50 mL of ethanol was added to 100 mg of MSC-322 and then stirred at room temperature (in air) for 24 hrs. Over 24 hrs, the waxy-like MSC-322 sample transformed into a fine white powder as it converted into MSC-311. Interestingly we were unable to see the same direct transformation with the MSC with PA ligands.



FIG. S1: Optical absorption spectra of (a)CdS MSC-311, MSC-322 with OA ligands (top left); (b) CdS MSC-311, MSC-322 with PA ligands; (c) RQD-355; (d) RQD-373(middle right) and (e) RQD-439 (bottom). All the data were collected from a solution in which the CdS nanoclusters (ca. 20 mg) dissolved in toluene (3 mL).

B. Sample characterisation

The samples were characterised by ultraviolet visible (UV-vis) absorption as shown in Figure S1. The two CdS MSCs with sharper absorption peaks at 311 nm and 322 nm when compared to the CdS RQDs, which is attributed to the small and exact size of the CdS MSCs.

S2. EXPERIMENTAL PDF ANALYSIS

A. Raw data compare between CdS bulk, RQDs and MSCs

The scattering pattern (raw data) measured for background, bulk CdS, CdS RQD-439, CdS RQD-373, CdS RQD-355 and all the CdS MSCs are shown in Figure S2 and S3.

B. Total scattering function compare between CdSbulk, RQDs and MSCs

The total scattering functions iQ and QiQ measured for bulk CdS, CdS RQD-373 and all the CdS MSCs are shown in Figure S4, S5 and S6.



FIG. S2: The total scattering pattern (raw data) collected in synchrotron x-ray beamline for the (a) background of measurement, (b) the regular quantum dots RQD-373, (c) CdS MSC 311 and 322 with phenylacetic acid ligands, (d)CdS MSC 311 and 322 with oleic acid ligands.



FIG. S3: The total scattering pattern (raw data) collected in silver source x-ray diffractometer for the (a) CdS bulk, (b) the regular quantum dots RQD-439, (c) Che regular quantum dots RQD-355.



FIG. S4: The total scattering data function i(Q) for the (a) bulk phase of CdS, (b) the regular quantum dots RQD-373, (c) CdS MSC-311 (PA), (d)CdS MSC-322 (PA), (e)CdS MSC-311 (OA), (f)CdS MSC-322 (OA). Note the sharp Bragg peaks in the data for the bulk sample, whose positions are reflected in the broader peaks in the scattering functions

of the RQDs and MSCs.



FIG. S5: The total scattering data function Qi(Q) for the (a) bulk phase of CdS, (b) the regular quantum dots RQD-373, (c) CdS MSC-311 (PA), (d)CdS MSC-322 (PA), (e)CdS MSC-311 (OA), (f)CdS MSC-322 (OA).



FIG. S6: The total scattering data function i(Q) for the (a) bulk phase of CdS, (b) the regular quantum dots RQD-439, (c) the regular quantum dots RQD-355. The total scattering function Qi(Q) for the (d) bulk phase of CdS, (e) the regular quantum dots RQD-439, (f) the regular quantum dots RQD-355

C. PDFgui modeling result of CdS bulk and RQDs

We use PDFgui to get the fit results as shown in Figure S9. The procedures we do in PDFgui is as follows. First we collected the standard silicon data in the same condition with the samples, and then we use standard silicon data to extract the two instrument parameters which are Qbroad and Qdamp using PDFgui. We show one standard silicon refinement with PDFgui graph as an example in Figure S7, the R_w value is 0.15. After we get a really good refinement of standard silicon, we extract the two instrument paramters Qbroad and Qdamp value. We then apply these two values in the samples data refinement using PDFgui. The residual function $R_{\rm w}^{4,5}$ is used to quantify the agreement of the calculated PDF from model the PDFgui build to experimental data. We use the wurtzite model and zinc blende model separately to fit the PDF data, and we compare the $R_{\rm w}$ value of both fit in Table S1. We started this simulation using the CdS bulk material, and we didn't get a good fit for wurtzite structure, with a much higher value of $R_{\rm w}$. The zinc blende structure gives superior fits for the bulk structure. However, for the CdS RQD-355, CdS RQD-373 and CdS RQD-439, the fits of wurtzite and zinc blende are comparable, and we can't get a very good fit as shown from the difference curves in Figure S9. The $R_{\rm w}$ values are reported in Table S1. This indicates that CdS RQDs are not a pure phase, they may have mixed phases of wurtzite and zinc blend or contain stacking disorder.

TABLE S1: The refined residual R_w values obtained from PDF analysis assuming the wurtzite and zinc blende structure models with space groups $P6_3mc$ and $F\overline{4}3m$,

	CdS bul	k CdS RQE	0-355 CdS RQD-3	373 CdS RQD-4	39
wurtzite $(R_{\rm w})$	0.58	0.36	0.19	0.36	
zinc blend $(R_{\rm w})$	0.33	0.35	0.21	0.37	

respectively.



FIG. S7: Fitted PDF data (collected in synchrotron x-ray beamline) D(r) for standard silicon (top curve). The experimental data are the black circles and the fitted functions are the continuous red curves.



FIG. S8: Fitted PDF data (collected in silver source x-ray diffractometer) D(r) for the bulk phase (top curve) and nanocluster phases RQD-439 (middle) and RQD-355 (bottom).

PDF data are fitted using (a) the zinc-blende structure model with space group $P6_3mc$ and (b) the wurtizite with space group $F\overline{4}3m$. The experimental data are the black circles and the fitted functions are the continuous red curves.



FIG. S9: Fitted PDF data (collected in synchrotron x-ray beamline) D(r) for the bulk phase (top curve) and nanocluster phases RQD-373 (bottom).PDF data are fitted using (a) the zinc-blende structure model with space group $P6_3mc$ and (b) the wurtizite with space group $F\overline{4}3m$. The experimental data are the black circles and the fitted functions are the continuous red curves.

S3. COMPARISON OF EXPERIMENTAL CDS MSC PDFS WITH CALCU-LATED PDFS OF CAGE STRUCTURES

In this section, we calculated the PDFs of cage structures $((CdS)_{12}, (CdS)_{16}, (CdS)_{18}, (CdS)_{24})$ which predicted using ab inito randoms structure searching⁶. The cage structures we discussed here means the atoms are all tricoordinated and the structure has empty inner core. As shown in Figure S10, S11 and S12, obviously the peak positions and features of these cage structures listed can't be consistent with the experimental PDFs we got for all the four MSCs, which exclude the possibility of being cage of these magic size clusters we synthesised here.

S4. CALCULATED PDFS OF THE SURFACE LIGANDS

In this section, we have computed the weighted PDFs from the OA and PA ligands as shown in Figure S13, the PDFs we talking here is essentially a histogram of interatomic distances scaled by the product of the atomic numbers and broadened by a Gaussian function.



FIG. S10: Comparison of the PDF function D(r) of CdS MSC-311 (OA) with a calculated distribution function (essentially a histogram of interatomic distances scaled by the product of the atomic numbers and broadened by a Gaussian function) with the predicted cage structures (a) (CdS)₁₂, (b) (CdS)₁₆, (c) (CdS)₁₈, and (d) (CdS)₂₄ (bottom right) from our recent study⁶.



FIG. S11: Comparison of the PDF function D(r) of CdS MSC-322 (PA) with a calculated distribution function (essentially a histogram of interatomic distances scaled by the product of the atomic numbers and broadened by a Gaussian function) with the predicted cage structures (a) (CdS)₁₂, (b) (CdS)₁₆, (c) (CdS)₁₈, and (d) (CdS)₂₄ (bottom right) from our recent study⁶.



FIG. S12: Comparison of the PDF function D(r) of CdS MSC-322 (OA) with a calculated distribution function (essentially a histogram of interatomic distances scaled by the product of the atomic numbers and broadened by a Gaussian function) with the predicted cage structures (a) (CdS)₁₂, (b) (CdS)₁₆, (c) (CdS)₁₈, and (d) (CdS)₂₄ (bottom right) from our recent study⁶.



FIG. S13: Calculated distribution function (essentially a histogram of interatomic distances scaled by the product of the atomic numbers and broadened by a Gaussian function) of two different ligands (a) oleic acid and (b) phenylacetic acid. Their peaks mainly focus on the range of 0 to 5 angstrom, compared with oleic acid, the phenylacetic acid affect less in the final PDF of the nanoclusters.

- * Corresponding author: martin.dove@qmul.ac.uk
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