

Probing the core-shell-shell structure of CdSe/CdTe/CdS type II quantum dots for solar cell applications

E A Lewis¹, R C Page², D J Binks³, T J Pennycook^{4,5}, P O'Brien^{1,2}, S J Haigh¹

¹School of Materials, University of Manchester, Manchester, M13 9PL, UK

²School of Chemistry, University of Manchester, Manchester, M13 9PL, UK

³Photon Science Institute & School of Physics and Astronomy, University of Manchester, Manchester, M13 9PL, UK

⁴Department of Materials, Oxford University, Parks Road, Oxford, OX1 3PH, UK

⁵SuperSTEM, STFC Daresbury Laboratories, Warrington, WA4 4AD, UK

Email: sarah.haigh@manchester.ac.uk

Abstract. A greater understanding of multiple exciton generation in heterostructured colloidal quantum dots can be achieved through detailed modelling, and used to optimise their design for solar cell applications. However, such modelling requires an accurate knowledge of the physical structure of the quantum dots. Here we report the use of high angle annular dark field (HAADF) scanning transmission electron microscope (STEM) imaging to study the size and shape of CdSe/CdTe/CdS type II quantum dots at each of the three stages of their synthesis.

1. Introduction

Multiple exciton generation¹ (MEG) is the process, in colloidal quantum dots, where the absorption of a single photon results in the formation of two or more excitons. This phenomena is of great interest for solar cell applications, enabling more efficient use of the solar spectrum and allowing cells to be designed which exceed the Shockley Queisser limit.² Controlling exciton dynamics and interactions by using Type II heterostructures has been suggested as a means of improving the quantum yield of multiple exciton generation and thereby increasing the efficiency of solar cells.³ Changes in the heterostructure of quantum dots affect excitonic interactions, including MEG, in a complex way. Detailed modelling of these processes will enable a greater understanding of MEG in quantum dots to be obtained, and allow the design of optimised heterostructures for enhanced MEG. However, for models to be validated by comparison with experimental results the quantum dot heterostructures must be characterized in detail. This paper reports the use of HAADF STEM imaging to accurately determine the core and shell dimensions of CdSe/CdTe/CdS type II quantum dots.

2. Experimental details

The CdSe/CdTe/CdS quantum dot samples were synthesised using a step-wise route based on the synthesis of CdSe quantum dots reported in reference 4.⁴ The solutions of quantum dots were then cleaned by centrifugation to remove excess capping ligands, before being redispersed in fresh toluene. The resulting quantum dot solutions were drop cast onto holey carbon support grids which were then rinsed with methanol to remove residual solvent.



HAADF STEM imaging was performed using a probe side aberration corrected FEI Titan G2 80-200kV with an X-FEG electron source operated at 200kV (convergence angle of 26mrad and a HAADF inner angle of 52mrad). Image analysis was performed using FEI TIA and Gatan DigitalMicrograph software. STEM imaging and electron energy loss spectroscopy (EELS) was also performed using a Nion UltraSTEM 100 operated at 60kV, equipped with a cold field emission electron source, an aberration corrector capable of neutralising up to fifth order aberrations and an Enfina EEL spectrometer.⁵ EELS compositional analysis revealed the presence of the expected elements (Cd, Se, Te, and S) within the complete nanocrystals. However, the quantum dots were found to be electron beam sensitive at both 60kV and 200kV, shrinking under prolonged imaging. Consequently EELS line scans through individual quantum dots exhibited a poor signal to noise ratio which prevented detection of the core-shell structure via EELS analysis. Instead an alternative approach was employed to quantifying the core-shell-shell dimensions by imaging the dots at each of the three different stages of their sequential growth (CdSe cores, CdSe/CdTe core-shell structures and CdSe/CdTe/CdS core-shell-shell structures).

3. Results and discussion

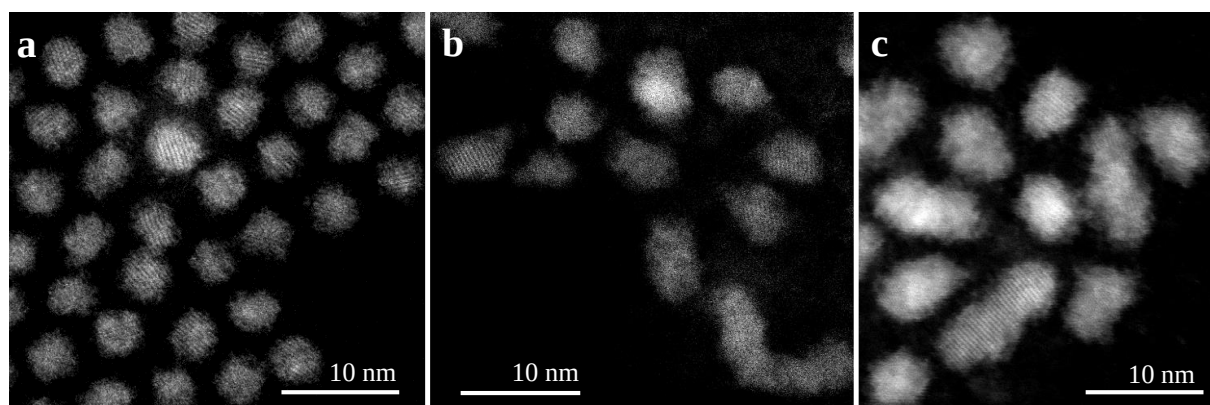


Figure 1. 3 HAADF STEM images from the Titan G2 operated at 200kV showing the sequential growth stages used in the synthesis of the colloidal nanoparticles. (a) CdSe cores (b), CdSe/CdTe core-shell, and (c) CdSe/CdTe/CdS core-shell-shell quantum dots.

Representative HAADF STEM images of the quantum dots at the different stages used in the colloidal synthesis of the CdSe/CdTe/CdS core-shell-shell structures are shown in Figure 1. Atomic resolution lattice fringe information was observable for ~50% of the final CdSe/CdTe/CdS quantum dots imaged in this study. Of these, the majority appeared to be single crystal, with less than 30% containing visible defects in the crystal structure. It was also apparent that the structure at the surfaces of the dots was less crystalline and relatively unstable during exposure to the electron beam, consistent with previous studies.⁶ Lattice separations observable in the images matched those of the zinc blende crystal structure at all stages of growth, in agreement with x-ray diffraction data.

Quantum dot size analysis was performed using the TIA Imaging software to measure 100 particles at each growth stage. Overlapping dots were excluded from the analysis. For each growth step the dot length was estimated as the maximum diameter visible for each dot. This was compared to the width (particle diameter measured in the perpendicular direction) as shown in Figure 2a. The aspect ratio of each dot was calculated from the ratio of the length and width.

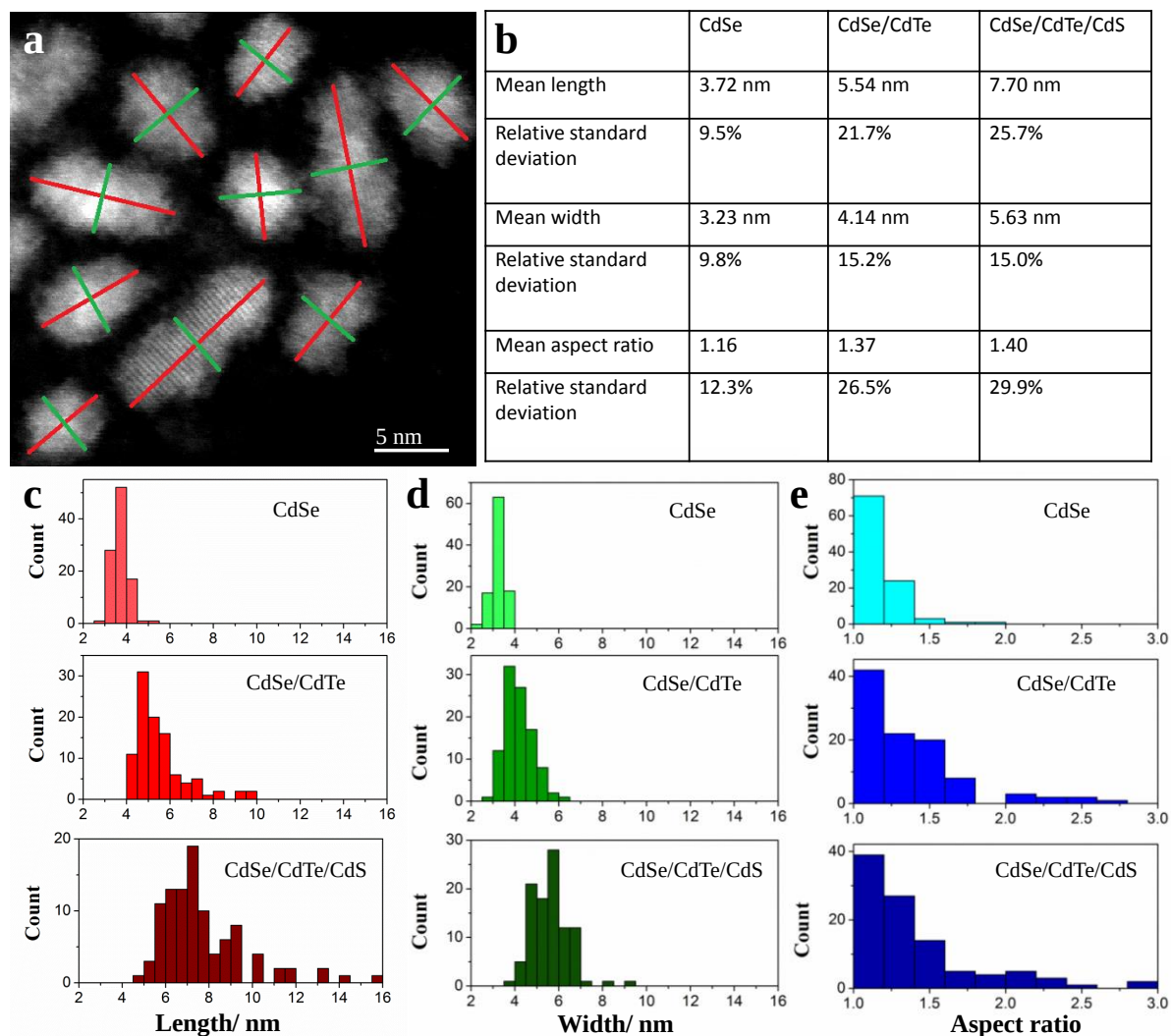


Figure 2. (a) Illustrating the measurement of the individual CdSe/CdTe/CdS quantum dot lengths (red lines) and widths (green lines). (b) Table listing the mean and standard deviations in the lengths, widths and aspect ratios (length/width) measured for 100 dots at each growth stage (CdSe cores, CdSe/CdTe core-shell, and CdSe/CdTe/CdS core-shell-shell). The data used to calculate these values is presented as histograms in (c), (d), and (e).

The mean and standard deviation of the measured dimensions for each stage of growth are shown in Figure 2b. The CdSe seed cores were found to be approximately spherical in shape, with a mean aspect ratio of 1.2. The cores had a mean width of 3.2 nm and narrow size distribution with the standard deviation of both length and width values less than 10%, less than a single Cd-Cd atomic spacing (zinc blende CdSe has a lattice constant of 0.61 nm and a Cd-Cd separation of 0.43 nm). For comparison a standard deviation of less than 5% is typically considered monodisperse.⁷ The uniform nature of the CdSe dots favoured their assembly into periodic 2D rafts as shown in Figure 1a. The uniformity of the population decreases significantly after shell growth such that regular packing arrangements were no longer observed for either the CdSe/CdTe core-shell or the CdSe/CdTe/CdS core-shell-shell structures. As expected, the size increased after the shell growth stage with the CdSe/CdTe and CdSe/CdTe/CdS particles having mean widths of 4.1 nm and 5.6 nm respectively. These measurements are consistent with size estimates obtained using ultraviolet-visible spectroscopy (with band edges of 555 nm, 617 nm, and 637 nm recorded for CdSe, CdSe/CdTe, and

CdSe/CdTe/CdS quantum dots respectively).⁸ The increase in the mean size of the dots is accompanied by a corresponding increase in polydispersity as illustrated by the histograms in Figure 2c-e. The mean aspect ratio of both the CdSe/CdTe and the CdSe/CdTe/CdS is ~ 1.4 . High aspect ratio particles are especially prevalent in the complete core-shell-shell sample, where 11% of particles were found to have having aspect ratios >2 . The increasing polydispersity of the dots at the later growth stages could indicate that monomer addition favours certain crystal facets such that shell growth is not uniform in all directions. An alternative explanation is that dot-dot coalescence plays an important role in the growth process and that elongated dots are a result of two or more cores fusing during the shelling reaction. There is a growing acceptance that the latter mechanism plays an important role in many nanocrystal growth processes, provided in part by in-situ electron microscope imaging.⁹

4. Conclusion

We have measured the size distribution of CdSe/CdTe/CdS core-shell-shell quantum dots at each stage of their growth. Our results show the quantum dots have a mean CdSe core diameter of 3.2 ± 0.3 nm, an inner CdTe shell with a mean thickness of 0.5 ± 0.4 nm and an outer CdS shell with a mean thickness of 0.7 ± 0.5 nm. The initial cores are close to spherical with a mean aspect ratio of ~ 1.2 . At later stages of synthesis the aspect ratio increases to ~ 1.4 , with the complete CdSe/CdTe/CdS dots having the largest shape variation. These results provide essential experimental input for models which will enable a greater understanding of MEG in heterostructured nanocrystals to be gained, allowing optimisation of their design for solar cell applications.

References

- [1] Nozik A J 2008 *Chem. Phys. Lett.* **457** 3-11
- [2] Shockley W, Queisser H J 1961 *J. Appl. Phys.* **32** 510-519
Hanna M C, Nozik A J 2006 *J. Appl. Phys.* **100** 074510
- [3] Binks D J 2011 *Phys. Chem. Chem. Phys.* **13** 12693-12704
- [4] Mohamed J A U, Tonti M B, Al-Salman D, Chemseddine A, Chergui A 2005 *J. Phys. Chem. B* **109** 10533-10537
- [5] Krivanek O L, Corbin G J, Dellby N, Elston B F, Keyse R J, Murfitt M F, Own C S, Szilagyi Z S, Woodruff J W 2008 *Ultramicroscopy* **108** 179-195
- [6] Pennycook T J, McBride J R, Rosenthal S J, Pennycook S J, Pantelides S T 2012 *Nano Lett.* **12** 4415-4415
- [7] Murray C B, Kagan C R, Bawendi M G 2000 *Annu. Rev. Mater. Sci.* **30** 545-610
- [8] Yu W W, Qu L H, Guo W Z, Peng X G 2003 *Chem. Mat.* **15** 2854-2860
Tyrrell E J, Smith J M, 2011 *Phys. Rev. B* **84** 165328
- [9] Liao H G, Cui L K, Whitlam S, Zheng H M 2012 *Science* **336** 1011-1014