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# Spherical Aberration Corrected Z-STEM Characterization of CdSe and CdSe/ZnS Nanocrystals

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## ABSTRACT

Spherical aberration corrected Atomic Number Contrast Scanning Electron Microscopy (Z-STEM) has recently demonstrated an amazing ability to not only obtain sub-angstrom levels of detail but also yield chemical information at that level as well. With an optimal probe size of 0.8 Å, extremely detailed images of CdSe nanocrystals were obtained showing the lattice structure and surface morphology. As an example of the usefulness of this technique, a sample of CdSe nanocrystals prepared using trioctylphosphine oxide (TOPO) as the surfactant was compared to a sample of CdSe prepared using a mixture of TOPO and hexadecylamine (HDA) as the surfactant. The TOPO/HDA nanocrystals exhibit a narrower size distribution and several orders of magnitude greater fluorescence compared to that of the TOPO only nanocrystals. Interestingly, the Z-STEM images show a striking difference in nanocrystal morphology as the result of the addition of HDA to the reaction mixture. This result suggests surface morphology can be tuned through judicious choice of surfactant. A second example of Z-STEM imaging involves the characterization of CdSe/ZnS core/shell nanocrystals. The mass contrast afforded by Z-STEM can easily distinguish between core and shell.

## INTRODUCTION

Semiconductor nanocrystals are of primary interest to several fields of research due to their unique properties. They exhibit quantum confinement effects such as size dependent absorption and emission, which allows for size tunable optical and electronic properties for applications in photovoltaics [1-3], photo-catalysis [4-7], bioassays [3, 8-12] and electronics [13-16]. These unique properties are sensitive to miniscule changes in size and shape requiring a characterization technique with sub-nanometer level of sensitivity and precision. Furthermore, information regarding surface structure would be an enormous asset for the development of nanocrystal-based devices and applications. For example, core/shell nanocrystals systems rely on a surface-passifying layer in order to obtain high fluorescent yields. Surface coverage on the order of a monolayer can significantly impact the fluorescent quantum yield[17-21]. Bulk characterization

techniques such as XRD, absorption and fluorescence measurements only give detail about the ensemble of nanocrystals forming an average, yet incomplete, picture of the nanocrystal sample.

Electron microscopy techniques such as high-resolution transmission electron microscopy (HRTEM) have been the primary technique used to characterize nanocrystal size and shape. HRTEM allows for analyzing individual nanocrystals and obtaining an average size distribution [22, 23]. Unfortunately, it can be very difficult to determine the precise shape and size of the nanocrystal due to nanocrystal movement under the electron beam and poor contrast near the surface of the nanocrystal. Additionally, phase contrast imaging relies on lattice fringes, which arise from the periodic structure of the crystal lattice. This periodicity is broken at the surface and nearby lattice defects complicating image interpretation.

Z-Contrast scanning transmission electron microscopy, however, can provide highly detailed images of the nanocrystal surface, three-dimensional information, and mass contrast simultaneously which can all be directly discerned from the image. Z-STEM uses an incoherent imaging process, which yields images that are directly interpretable to the structure of the object being observed. This technique, combined with a spherical aberration ($C_s$) corrected STEM, high spatially resolved images can be obtained that are able to show subtle details about the shape and faceting of nanocrystals with near sub-angstrom precision.

In this paper we used aberration corrected Z-STEM to image CdSe nanocrystals prepared by two different surfactant mixtures. Striking differences in morphology are observed with an overall improvement in shape when HDA is used. Additionally, we report the first images Z-STEM images of CdSe/ZnS core/shell nanocrystals. The images obtained show in great detail the shape and crystalline nature of the shell and its relative position to the core. The shape anomalies in the shell were attributed to the lattice mismatch between CdSe and ZnS.

## EXPERIMENTAL

The two CdSe samples used for comparison were synthesized using similar techniques to that of Peng et al.[24] and that of Talapin et al who includes HDA into the reaction mixture.[25] For the trioctylphosphine oxide (TOPO) only sample, a reaction solution consisting of (2.5:1.84 by mass solution of dimethyl cadmium (Strem, vacuum distilled), selenium metal (shot, Strem, as received), and tributylphosphine (Strem, as received). A volume of 6 mL of the reaction solution was injected into 12 g of

trioctylphosphine oxide (90%, Aldrich) maintained at 360 ºC. As soon as the solution temperature dropped to 300 ºC, an additional amount (0.5-4ml, depending on the final size desired) of concentrated reaction solution 2.5:1:21 by mass) was added. The nanocrystals were then allowed to grow at 300 ºC. The hexadecylamine (HDA) sample was prepared in a similar fashion with a few modifications. Briefly, 375 mL of dimethyl cadmium with .288 g of selenium powder in 30 mL of tributyl phosphine constitute the reaction solution. The reaction solution is injected into a mixture of 43.2 g of TOPO, 17.85 g of HDA, and .855g dodecyl phosphonic acid (DPA), which is an analogue of a key impurity found in technical grade TOPO, at 300 ºC for crystal nucleation.[26-28] The temperature is then lowered to 265-270 ºC for crystal growth. Growth was monitored for both samples by taking absorption spectra of aliquots removed from the flask until the exciton peak ceased to narrow, at which point the reaction was stopped by removing the heat source.

CdSe/ZnS core/shell nanocrystal samples were obtained through collaboration with Quantum Dot Corp. Synthesis of these core/shells involves placing CdSe nanocrystals in TOPO at 190 ºC and then adding Zn and S precursors such as diethylzinc ($ZnEt_2$) and hexamethyldisilathiane ($(TMS)_2S$). Typically, the reaction is terminated once maximum fluorescence intensity is reached. Specifics for this synthesis have been published elsewhere.[29, 30] [31]

Z-STEM imaging was performed using a VG Microscopes model HB603U STEM operating at 300 kV fitted with a $C_s$ corrector from Nion. The optimal probe size has been measured to be .78 Å with a theoretical limit of .5 Å. The operation and data collection was done using Digital Micrograph running on a Pentium$^{tm}$ 41.7 GhZ personal computer.

## DISCUSSION

A comparison between the TOPO and the HDA/TOPO prepared samples is shown in figures 1a and 1b respectively. In both images, the benefit of the $C_s$ corrector and the small probe size is manifested by the large number of lattice resolved nanocrystals. Since the nanocrystals are free to rotate, obtaining a good lattice-resolved image is dependent on the orientation of the nanocrystal during image capture. As the probe size decreases, the number of lattice resolved nanocrystals increases due to improved ability to image nanocrystals off axis. The small features near the surface that are seen would be very difficult to detect using traditional HRTEM since there is very little material to form a phase contrast image. With single atom sensitivity, Z-STEM can not only image the

nanocrystal lattice, it can also image the amorphous oxide layer on the surface as well as unreacted monomers.

Interestingly, a striking difference between the two images can be seen. Although the size of the nanocrystals differs only by .3 nm on average, their overall shape is markedly

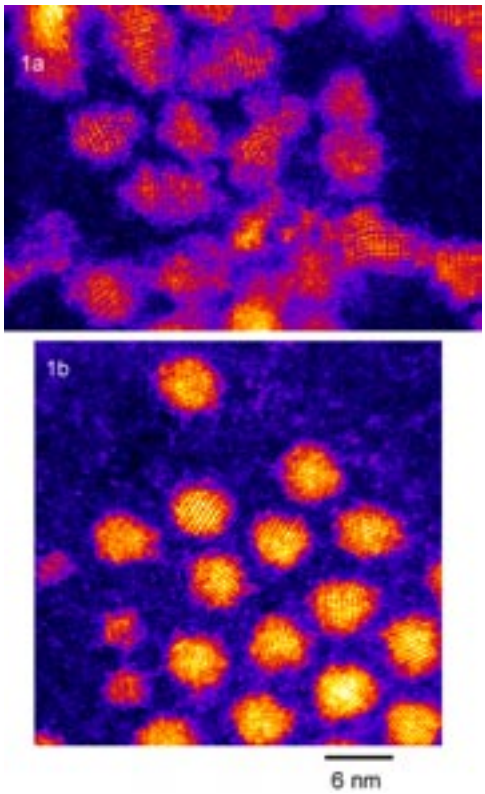


**Figure 1**. Z-STEM Images of CdSe. Images of a sample of TOPO prepared CdSe (1a) and an image of TOPO/HDA prepared CdSe (1b) are shown. The addition of HDA appears to make nanocrystals with more uniform shapes and sizes. The shape differences seen in 1a would be very difficult to see using TEM. The Z-STEM images have been artificially colored.

different. The TOPO prepared CdSe nanocrystals appear to be elongated with some exhibiting an ovoid shape. The inhomogeneous faceting of this sample is likely the result of a preferential growth along this axis. Although, in this image it is difficult to identify which is the Se or the Cd face, other images taken suggest that the Se face caps the end of the nanocrystal with the elongated facets. Additionally, it has been reported previously that CdSe nanocrystals prepared by the TOPO only method are cadmium rich.[32] It is believed the excess Cd found in the TOPO only nanocrystals resides in these elongated facets where there are 2 Se dangling bonds at each Se surface site. In contrast, the nanocrystals prepared by the TOPO/HDA method shown in figure 1b are extremely uniform in size and shape. The nanocrystals seem to be truncated evenly on either side, suggesting a lack of the preferential growth or a more controlled growth as seen in the TOPO sample. Since a majority of the nanocrystals are of the same size and shape, spontaneous 2D-arrays form exhibiting the same hexagonal structure as the nanocrystals.

Figure 2 shows a sample of CdSe/ZnS core/shells with a quantum yield around 34%. In this case, the mass contrast afforded by Z-STEM clearly distinguishes core from shell. The bright center consists of the heavier CdSe core while the less intense coating surrounding it consists of the ZnS shell. Immediately it becomes obvious from the image that the shell does not uniformly grow around the nanocrystal. Also, particles that are not core/shells can also be seen along with excess reactants. These non-fluorescing particles will certainly reduce the quantum yield of the sample. However, improving the shell is also crucial for achieving higher quantum yields. The primary difficulty in coating CdSe with a ZnS shell is the 12% lattice mismatch between the two materials. The effect of this is clearly evident from the image in figure 2b. The ZnS shell is seen growing off of one face of the nanocrystal while the rest of the nanocrystal remains uncoated. What can be deduced from this image is that a single layer of ZnS first attaches to the most reactive face of the nanocrystal, the (001) face. Once a monolayer of ZnS is grown, it is more energetically favorable for the next layer of ZnS to grow on the previous. This leads to a non-uniform shell coating and poor surface passifation.

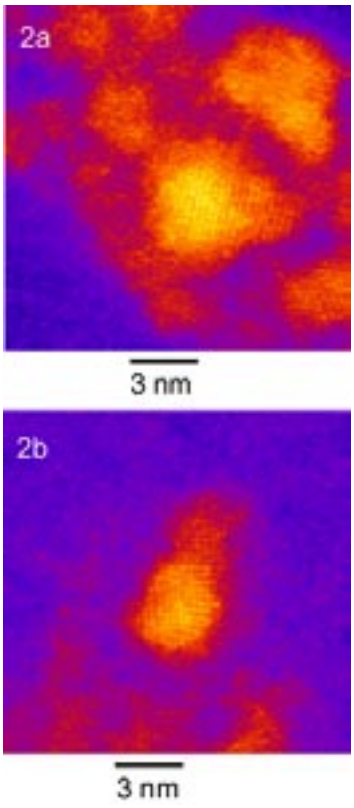


**Figure 2.** First images of CdS/ZnS core/shell nanocrystals. In figure 2a, the bright core can be clearly seen with a less intense shell surrounding it. ZnS particles without cores are also seen. In 2b, the effect of the lattice mismatch is evident, as the shell for this particle has grown only on one face.

## CONCLUSION

This study illustrates spherical aberration corrected Z-STEM as an extremely effective tool for investigating nano-structures. The mass contrast and high spatial resolution leads to simplistic image interpretation and unparalleled structural information. The addition of HDA to the reaction mixture not only narrowed the size distribution as reported elsewhere, but has greatly reduced the amount of shape anomalies compared the traditional TOPO method. The core/shell images show explicitly the affect of the lattice mismatch between CdSe and ZnS has on core/shell growth.

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