

# Electron Microscopy of Quantum Dots for Display Applications

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## ABSTRACT

*CdSe/ZnCdS core/shell Quantum dots with high quantum yield (~84%) were used in this experiment. For the first time the red filtered cathodoluminescence images are shown along with their corresponding electron energy loss spectrum map, and high angle annular dark field image of the corresponding particles is shown.*

## 1. INTRODUCTION

Quantum dot displays continue to play a dominant role in the display industry and many manufacturers now use this type of material to meet the colour display requirements for high definition television and computer displays. Since acquiring a Gatan Vulcan system to allow cathodoluminescence (CL) imaging in a new analytical transmission electron microscope (TEM) the group at Brunel University London have begun to use this to analyse various phosphors and quantum confined materials to investigate the potential scientific advancements that can be achieved by gaining combined scanning TEM and CL images. It has now been possible to gain electron energy loss spectra from the areas showing CL.

## 2. EXPERIMENTAL

A red emitting quantum dot dispersion was supplied from QD Vision Inc, prepared by standard batch solution chemistry which is commonplace for this material.<sup>1-3</sup> All electron microscopy measurement were carried out (and CL STEM) at a temperature of around -170°C in a JEOL 2100F analytical TEM operated at 80 kV by dispersing the sample onto holey carbon coated copper grids. STEM was carried out using a Gatan HAADF detector. CL images were collected using a Gatan Vulcan™ system. A red filter (625nm +/- 25nm) was used to select only the QD emission and to reduce background fluorescence whilst collecting CL emission images. A Gatan Electron Energy Loss Spectrometer was used to map the position of the selenium containing dots in relation to the previously recorded CL images.

Visible total ensemble emission spectra were collected using a purpose built phosphor spectrometer from Bentham Instruments Ltd, Reading, UK and a Horiba Fluorolog spectrometer was also used to measure quantum efficiency relative to a 4-(Dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (DCM) solution (Sigma-Aldrich 98% purity, CAS 51325-91-8).

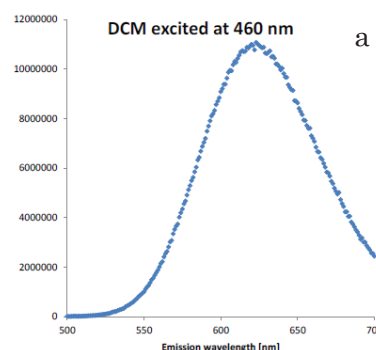
## 3. RESULTS AND DISCUSSION

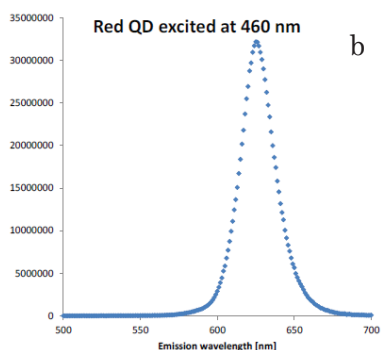
The quantum yield of the highly dilute quantum dots dispersion was measured by comparing to the DCM standard according to the following equation:

$$Q_{unknown} = Q_{ref} \frac{I}{I_{ref}} \frac{OD_{ref}}{OD} \frac{n^2}{n_{ref}^2}$$

### Equation 1 Method for calculating quantum yield of the QD dispersion

Where  $I$  is the integrated emission intensity and  $n$  is the solvent refractive index. Differences in the solvents were corrected for and the photoluminescent (PL) emission spectra recorded are shown in Figure 1 where the very narrow and symmetrical emission of the QD dispersion is seen to be centred at 625nm. The quantum yield for this batch was therefore calculated to be 84% in our measurements.



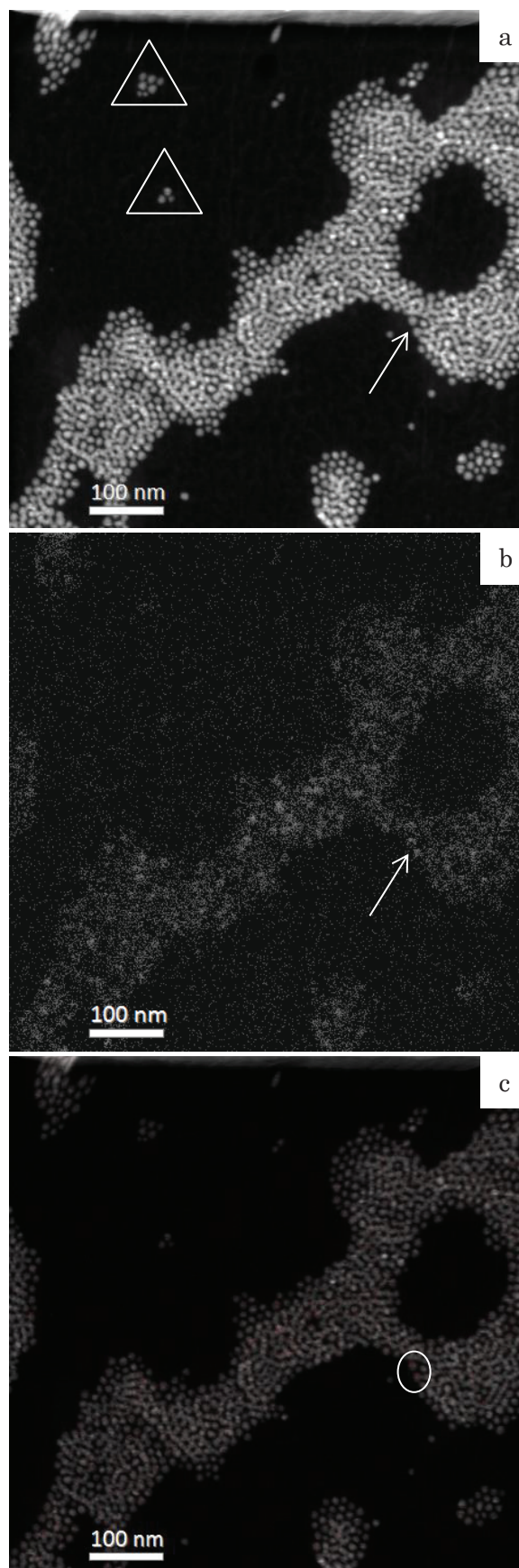


**Fig. 1** Photoluminescent emission spectra recorded at 460nm excitation, a) DCM solution, b) QD dispersion

The PL spectrum of the QDs (figure 1b) shows that nearly all of the light falls within the red filter used for CL measurements with the central wavelength at 625nm and a band pass of 50nm. This will significantly improve the signal to noise when using the Vulcan photomultiplier and ensures that only the visible light emission is used to build the CL image shown in Figure 2.

In Figure 2a the high angle annular dark field (HAADF) image shows the HAADF STEM image of the QD ensemble and figure 2b shows for the first time by us the red light filtered CL image. There is a clear distribution of sizes present, see regions shown inside the triangles. The larger particles show CL activity (e.g. region shown by the arrow in a and b and circled in c) but the smaller particles are not well defined by their CL emission. This is in keeping with our previous findings where we have not been able to show individual green emission from smaller QD samples.

In Figure 3 the HAADF is shown enlarged to see the shape of the 2 particles used for mapping. To ensure accuracy in the results the drift corrector was used to mitigate the slight sample drift observed.



**Fig. 2.** a) HAADF image, b) Red filtered CL image, c) overlay of HAADF and CL images.

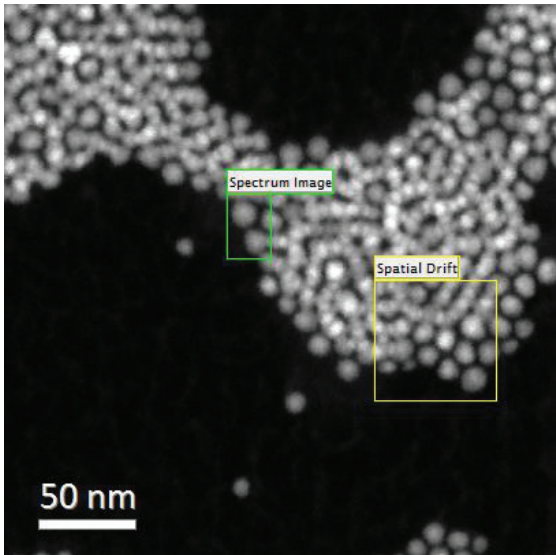


Figure 3 HAADF image showing enlarged area used to map two QD particles showing strong CL emission.

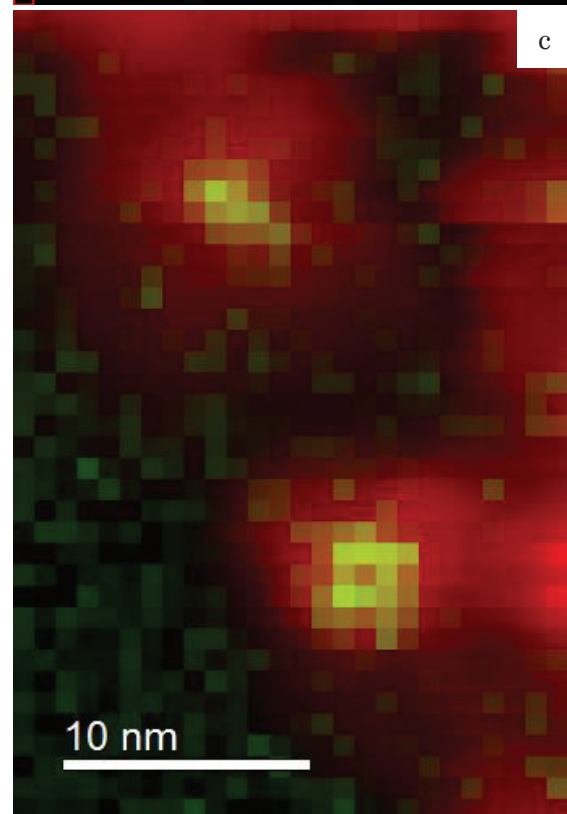
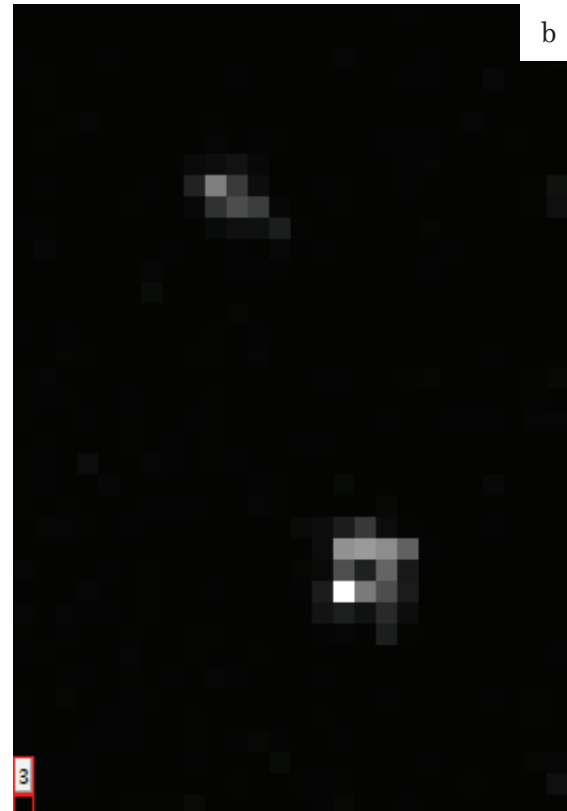
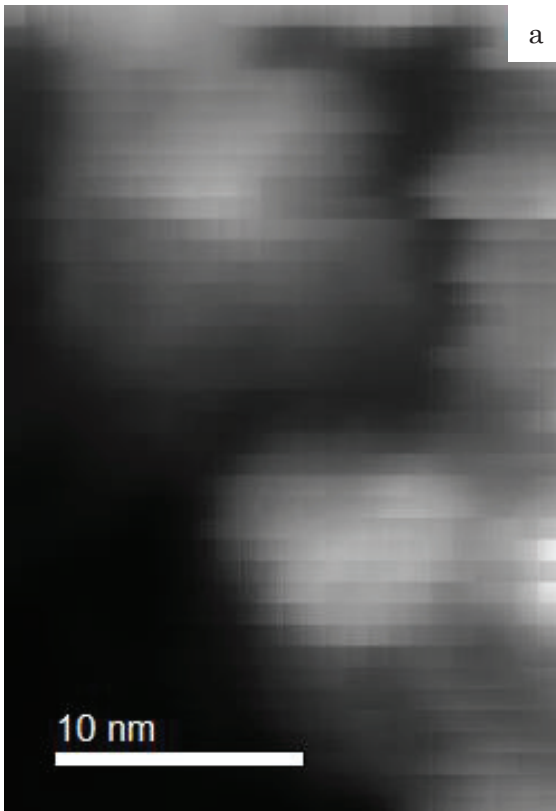


Figure 4 a) HAADF map, b) Processed EELS Se map, c) overlay of a and b where Se is shown in yellow and the HAADF in red colour.

Figure 4 shows the HAADF and Se EELS maps. After standard processing of the EELS signal and overlaying the two images there is very good

correlation between the Se map that shows the Se to be centrally located in both of the QD particles.

#### 4. CONCLUSIONS

A number of findings have been reported herein that are useful for further development of luminescent materials. We have shown that the CL images that are obtained are composed of only the red emission from the QDs. Corresponding EELS maps show the distribution of selenium in the particles and thus we have demonstrated that these techniques can be combined into a powerful technique for studying variations in samples at the particle to particle level when developing synthetic methodology.

#### 5. ACKNOWLEDGEMENTS

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