
Cathodoluminescence and electron microscopy of red quantum dots used for display applications

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Abstract — Cathodoluminescent imaging of the visible light emitted from quantum dots is reported. The shape and uniformity of individual particles is observed in the scanning transmission electron microscope image, and the image of the particles created from their visible light collected simultaneously is shown. Visible light images of the 13 nm sized particles are reported for clusters of particles. The emission spectrum collected from small clusters of quantum dots is also reported.

Keywords — *red quantum dots, quantum dot displays, cathodoluminescence.*

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1 Introduction

Core shell quantum dots (QDs) have a range of applications in the optics industry from displays and lighting to lasers, optical communications, solar cells, and biological markers. The materials studied here are composed of a CdSe core with a shell of ZnCdS that emits red or green light dependent upon the radius of the core material. The materials offer high color gamut and color purity and are manufactured by QD Vision. In 2013, Sony Bravia liquid-crystal display (LCD) televisions, (LCDTV), containing QD Vision's Color IQ optical components were launched onto the international domestic television market with dramatic success, winning prizes in several areas.¹ To enable mass production of this new generation of LCD TVs, it was necessary for QD Vision to mass produce their quantum dots in a tight size and reproducible regime. During SID14, it was also announced that computer monitors manufactured by BOE and TPV will also incorporate these materials. It is recognized that this technology offers one potential way forwards in achieving 100% of the National Television System Committee color space and beyond into the future color standards, for example, Rec. 2020.² The advantage that this offers is in ensuring the longevity of existing investments in money, staff training, and natural resources used in the infrastructure of LCD manufacturing factories whereby only a small change in the manufacturing of the backlighting unit is required. Hence, minimal investment is required to meet the color standards for next generation high-definition televisions.

Figure 1 simulates the impact of using this type of material over existing backlighting technologies, which do not utilize QD color conversion materials (ColorIQ).

Beyond the displays and lighting applications, they also offer a potential step forwards in biological marker applications for use in vacuum environments, although this would require several further procedures to facilitate their use in this application.³ There is also active research into using QDs as conversion materials in solar cells to improve the conversion efficiency.⁴

Brunel University London has recently acquired a new transmission electron microscope (TEM) with a newly available cathodoluminescent detector (Gatan Vulcan), which allows the study of single nanoparticles of phosphors by obtaining cathodoluminescence (CL) spectra and images from individual crystals. One of the questions that phosphor chemists are often asked is how homogeneous is a phosphor sample? This question is not easy to answer as photoluminescence (PL) or CL spectra collected from phosphor samples are the average spectra of the samples making them up. This is true of most samples made either in the laboratory for research or commercial samples prepared by industrial companies. We have demonstrated that it is possible to collect CL spectra from individual nanometer sized particles and began to address the question of homogeneity in such samples with some success.^{5,6} As part of our continuing studies in this important area, we have extended our studies to red quantum dots and report our findings herein.

2 Experimental

A highly concentrated dispersion of the QDs in organic liquid was diluted to an approximate concentration of 22.4 mg/ml. This dilute dispersion of the sample was then dropped onto a holey carbon 300 mesh copper TEM sample grid. The

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FIGURE 1 — Impression of the advantage of using quantum dot color conversion (ColorIQ). Left is with standard backlight, and right is with a quantum dot color converter.

sample was allowed to air dry without further cleaning so as not to damage any surface coating on the particles.

The sample was observed in a JEOL 2100 F TEM. The TEM was operated in scanning mode with a spot size of 0.2 or 1.5 nm. Initial work demonstrated the need to reduce the X-rays in the column generated from the condenser lens aperture, which were found to significantly contribute to disperse excitation of the sample. These X-rays were found to excite the phosphor to emit visible light when the electron beam was not on the sample and a loss of resolution was observed. To reduce this X-ray excitation of the sample, the hard X-ray aperture must be inserted into the column, which reduces the background noise in CL imaging and spectroscopy modes. The TEM was fitted with the Gatan Vulcan CL imaging and spectroscopic detector. This system uses a Czerny–Turner spectrometer with back-illuminated CCD and a grating with 150 lines/mm for collection of CL emission spectra, although a higher resolution grating can be selected when required. A cooled photo-multiplier tube (PMT) is utilized for collection of total light images with the possibility to insert a standard filter into the beam path, for example, by using a band pass filter at the correct wavelength where only the light from the sample is allowed onto the PMT. Light is collected from the sample using a mirror above and below the sample, which allows a solid angle of about 5 sr (nb. nearly half of the sphere). This high solid angle makes light collection highly efficient and makes it possible to collect the light at very low intensity. By collecting the visible light with the Vulcan system simultaneously with the JEOL high angle annular dark field (HAADF) detector, it was possible to observe the visible light that was emitted from the particles. The system is controlled via the Gatan Microscopy Suite, which allowed the simultaneous collection of HAADF and CL images, which are easily overlain after collection using the “colour mix” window. Due to the time taken in familiarization with the imaging system, the spectroscopic analysis has not been fully investigated yet for the QDs. Hence, the CL emission spectrum of the sample was recorded from a small group of QDs while controlling the electron beam in scanning mode using the Jeol Simple Image Viewer (JEOL Ltd., Tokyo, Japan) in area scan mode. Instead of using the PMT for imaging, it is also possible to build an image using spectrum imaging, which will be investigated in the future.

The TEM was operated initially at 200 kV, which yielded excellent high resolution TEM images of the QDs, but no CL emission was observed, even when cooling the sample to $-172\text{ }^{\circ}\text{C}$. Successful observation of CL imaging and spectra in the TEM was achieved using the operating conditions of 100 kV and a sample temperature of $-172\text{ }^{\circ}\text{C}$. It has not been possible to observe any CL emission without liquid nitrogen cooling, and due to sample thermal drift and the potential for vibrations due to boil off and to optimize sample stability, the base temperature of the system was preferred.

For comparison to the CL emission spectra collected in the microscope, photo-luminescent spectra were collected using a Horiba Fluorolog spectrometer.

3 Results

Previous work using lanthanide phosphors^{5,6} in this experimental setup has demonstrated high quality total light images that are comparable to the HAADF scanning transmission electron microscope (STEM) images. CL emission spectra have also been collected over comparable timeframes used for our scanning monochromator system (Bentham Instruments UK LTD, Reading, UK) used for bulk powder sample analysis. Lorentzian fitting of the particle size analysis found that using powder X-ray diffraction line profile analysis shows us that these particles had an average crystallite size of 113 nm and hence an approximate volume of 755499.1 nm^3 . Using particle size values measured directly from Fig. 2, the core is measured to be 4.5 nm and the combined core and shell diameter is 13 nm, hence the volume of the core is shown to be 47.7 nm^3 and a total core and shell volume of 1150 nm^3 is found. This means the QD has a volume of 0.15% of the volume of the previously studied material with the core volume being only 0.0063% of the phosphor. Hence, it was with some trepidation that we should expect similar resolution and image qualities as observed for those lanthanide phosphors.

Figure 3 shows the TEM images of a number of individual nanometer-sized single quantum dots from the material of

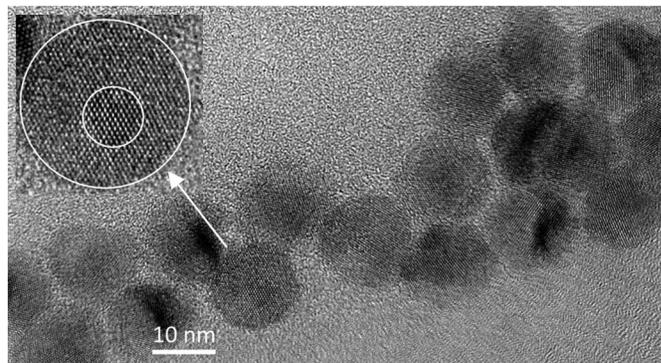


FIGURE 2 — High-resolution transmission electron microscopy image showing the core and shell; the expansion includes circles drawn to emphasize the expected core and shell perimeters.

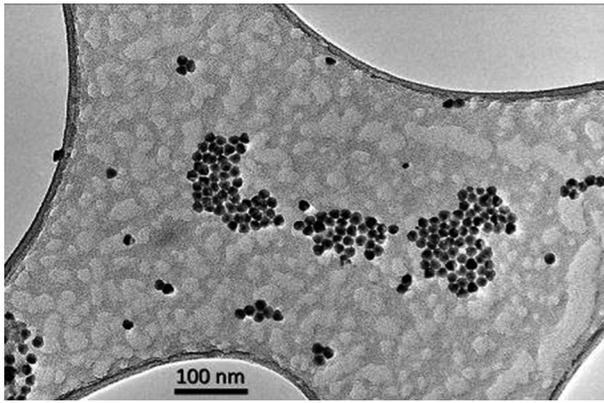


FIGURE 3 — Transmission electron microscope image of red light emitting quantum dots on a holey carbon grid.

which some of the spectra were recorded for the studies presented in this work. The sample is exceptionally well dispersed and dried onto the carbon support as individual particles that are well separated from other particles, along with larger clusters of two particles and upwards. All the quantum dots were approximately of the same size (about 13 nm), although their shapes appeared to vary. However, all were seen to be discrete particles with many appearing to be hexagonal (or some derivative of hexagonal) in shape (Figs 2–4). The observed shapes are in keeping with the known hexagonal structure of the material. Under the magnification used in Fig. 3, the quantum dots have apparently smooth surfaces. Organic residue is observed on the carbon film, which is deposited after the sample dispersion dries. Plasma cleaning was not carried out because of the desire to maintain any surface coating.

In Fig. 4, some organic residue is seen around the quantum dot, which is thought to be due to the residue left from the organic dispersant.

In Fig. 3, the particles are observed at a nominal magnification of $\times 50,000$ because improved stability is observed in the electron beam when recording the CL light image. In this

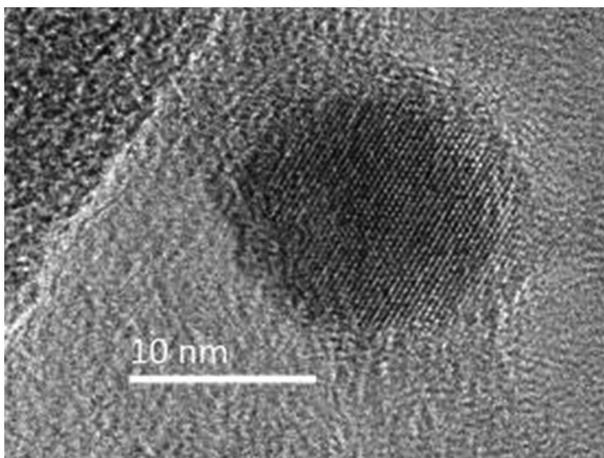


FIGURE 4 — Transmission electron microscope image of an individual red quantum dot.

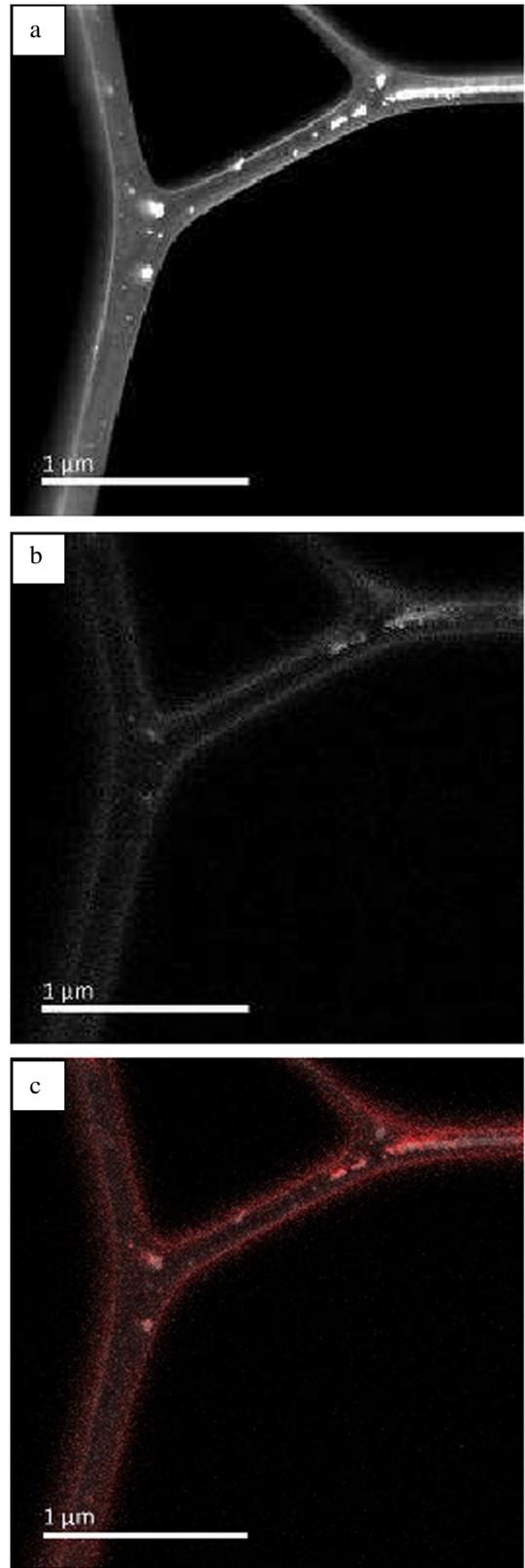


FIGURE 5 — Simultaneous dark field scanning transmission electron microscope image (a) and cathodoluminescence light image (b) and an overlay of the high angle annular dark field and cathodoluminescence images (where the CL image has been colored red) at a nominal magnification of $\times 50,000$.

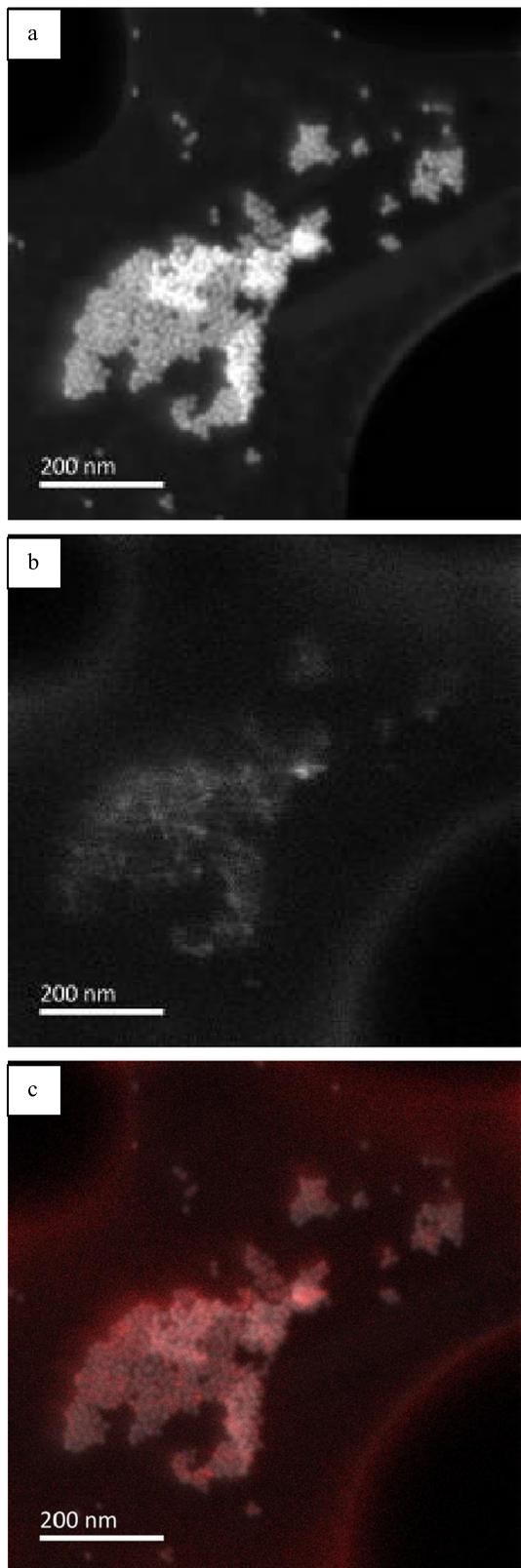


FIGURE 6 — Two sets of simultaneous high angle annular dark field scanning transmission electron microscope images (a), cathodoluminescence image (b), and an overlay of the high angle annular dark field and cathodoluminescence images (where the CL images has been colored red) (c) taken at a nominal magnification of $\times 150,000$ times.

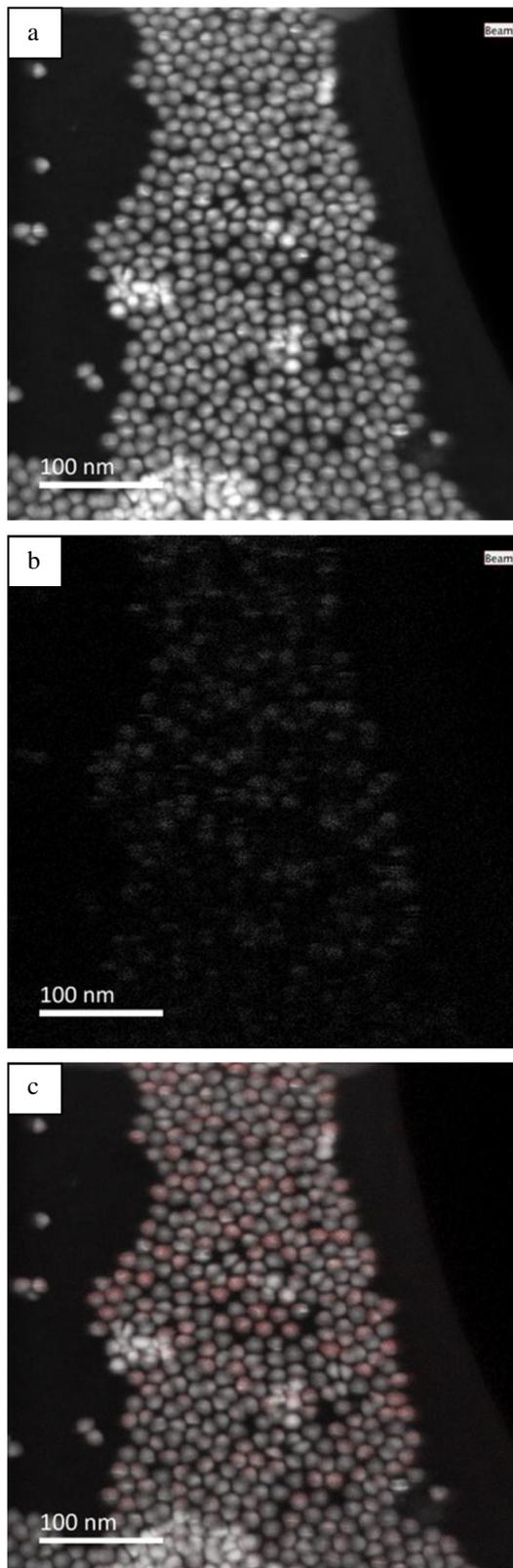


FIGURE 7 — High angle annular dark field scanning transmission electron microscope (a), cathodoluminescence image (b), and an overlay of the high angle annular dark field and cathodoluminescence images (where the CL image has been colored red) (c) taken at a nominal magnification of $\times 300,000$.

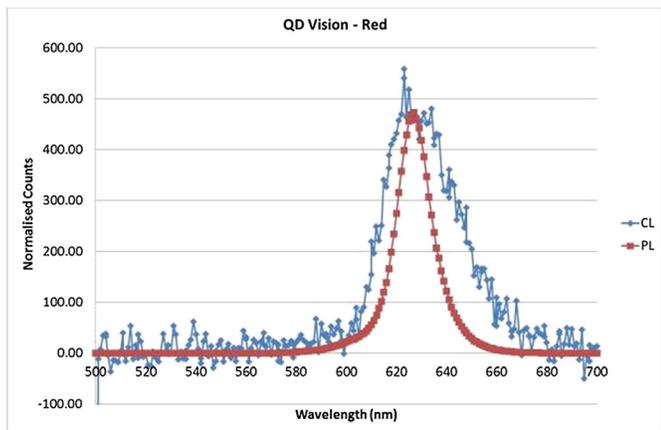


FIGURE 8 — An overlay of the emission spectra of the quantum dot sample. The red line is from the photoluminescent measurement made on the dispersed sample outside of the microscope, and the blue line is from the cathodoluminescent measurement made in the electron microscope.

initial study, a relatively large condenser lens aperture has been used so that the CL emission intensity will be larger at the slight detriment of the STEM resolution. However, small clusters of particles can be observed to emit light.

Figure 5 demonstrates that it has been possible using the current experimental configuration to directly visualize the light emission from the quantum dots. The overlay image shows that the CL images align well with the HAADF image.

In Fig. 6a–c, the QDs are observed at higher magnification; it has become possible to distinguish the light emission that aligns well to individual particles although the resolution does not clearly distinguish these particles.

With well-aligned TEM and STEM modes and using a small condenser lens aperture, improved resolution is possible whereby CL emission from individual QDs is observed as demonstrated in Fig. 7b. Fig. 7a shows a HAADF STEM image at higher resolution, and Fig. 7b shows a CL image of the same area, showing that only some particles are CL emissive and is in agreement with results seen elsewhere.⁷ Of the particles that show the CL emission, light is uniform across the QD, that is, the QD is equally excited across its area, which is in contrast to the findings elsewhere that suggest a thickness effect;⁷ but in some cases, our CL image shows intensity variation in keeping with features seen in the HAADF image, which could possibly be due to thickness. The overlay of Fig. 7a and 7b shows the particles that are giving out CL (the “on” particles). It is noteworthy that in some cases, individual particles are on and all their immediate neighbors are “off”.

In Fig. 8, the sharp red line represents the photoluminescent emission spectrum collected on a “bulk” dispersion of the same material. This has been scaled down such that the λ_{max} values of the two spectra are approximately equal. The blue broader line represents the emission spectrum from about 50 particles as opposed to the PL data that was taken using a dispersion of about 70 mg/ml of particles with a sample path length of 1 cm in a standard cuvette. The broadening of the CL signal is thought to be due to

changes/damage occurring to the sample while the data collection occurs.

4 Conclusions

- Optimal operating conditions for the collection of QD images have been identified; beam at 100 kV, a sample temperature of $-172\text{ }^{\circ}\text{C}$, and a scan rate of $9.5\text{ }\mu\text{s}$ has been found to give excellent CL and HAADF images.
- The shape and uniformity of individual particles can be identified.
- Particles can be identified and the visible light emission can be observed from individual particles.
- The overlays of the HAADF and CL images suggest that only some of the QDs are strongly CL emissive.
- A spatial resolution of 13 nm has been demonstrated for the particles from the CL images.
- Emission spectra can be collected from small clusters of around 50 nanoparticles, and the shape of the particles investigated considered.
- This work represents a significant advance towards reconciling the visible light emission properties of individual QDs and opens up the possibility to combine this analysis with other analytical techniques in the TEM.

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Dr. George Fern was born in Leicestershire, England in 1972. He received his BS degree in 1993 and PhD in 1997 both in Chemistry from the University of Essex. He was a postdoctoral research assistant for 1 year at the University of Hull developing catalysts for green chemistry. In 1998, he joined Greenwich University as a senior demonstrator and also as a research assistant in the Centre for Phosphors and Display Materials and became a senior lecturer in Chemistry. It is here that he started to develop his research interests in studying luminescent materials with a particular emphasis in electron

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Prof. Jack Silver was born in Sunderland, England in 1948. He received his BS degree in 1970 and his PhD in 1973 both from the University of London. After 2 years of postdoctoral work at the University of London, he became a temporary lecturer at the University of Birmingham, and then he was appointed to Inorganic Lectureships at the University of West Indies, Trinidad in 1976 and subsequently at the University of Essex in 1978. He received his DSc from the University of London in 1992 and was appointed to a Readership at the University of Essex in the same year.

In 1996, he was appointed to a full professorship at the University of Greenwich and became head of the Centre for Phosphors and Display Materials. He moved to Brunel University in January 2006 to the post of Executive Director of The Wolfson Centre for Materials Processing, which now also incorporates the Centre for Phosphors and Display Materials (which he still occupies). Since 1 August 2014, he has been the theme leader for Materials Characterisation and Processing in the Institute of Materials and Manufacturing. He was the chairman of the RSC Mössbauer Group from 1996 to 2001. His research interests include fundamental aspects of inorganic chemistry and light emitting materials and the technological applications of phosphors, nanomaterials, nanotechnology, polymers, and polymer processing.



Dr. Seth Coe-Sullivan, PhD, is a co-founder, member of the Board of Directors, and Chief Technology Officer of QD Vision. He received his PhD in Electrical Engineering from the Massachusetts Institute of Technology in May 2005, where his thesis work led to the formation of QD Vision. Seth's technology expertise includes quantum dot materials and devices for solid state lighting and displays, as well as the environmental health and safety implications of quantum dots and nanomaterials. His role as CTO spans technology and intellectual property strategy, technical marketing, fundraising, and

business development for advanced projects. Seth has more than 50 papers, patents, and patents pending in the fields of organic light emitting devices, quantum dots, and environmental health and safety of nanomaterials. He was awarded Technology Review Magazine's TR35 Award in 2006, naming him one of the top 35 innovators under the age of 35. In 2007, BusinessWeek named him one of the top young entrepreneurs under the age of 30, and in 2009, he was a finalist for the Mass Technology Leadership Council's CTO of the year. Under his technology leadership, QD Vision won the Wall Street Journal's Innovation Award in 2009, New England Clean Energy Council's Emerging Company of the Year Award in 2010, and the SEMI Award for North America in 2012. Seth is honored to sit on Brown University's Engineering Advisory Council and the US National Research Council's Committee to develop a research strategy for environmental, health, and safety aspects of engineered nanomaterials. Seth graduated in 1999 from Brown University with an ScB in Electrical Engineering. He then spent a year as a staff engineer at the Boston-based research company Foster-Miller, Inc., in the Emerging Technology division of the Materials Technology Group.