Brunel University London

Cathodoluminescence imaging in the electron microscope

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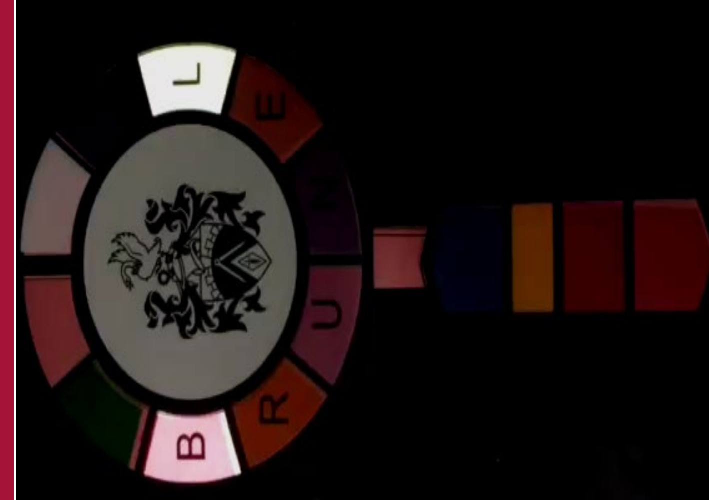


Background and Aim

Cathodoluminescence as an analytical tool in electron microscopy

Examples of SEM CL:

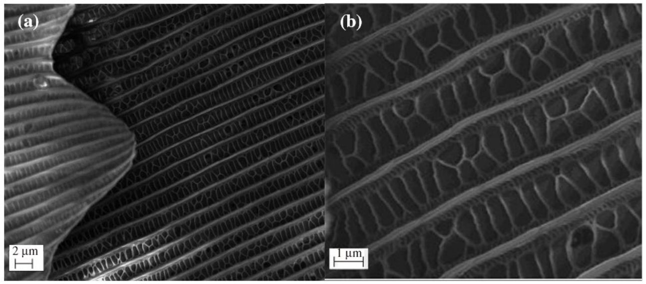
- Butterfly wings
- Gd_2O_2S:Tb
- SEM CL without a CL attachment

Examples of TEM CL:

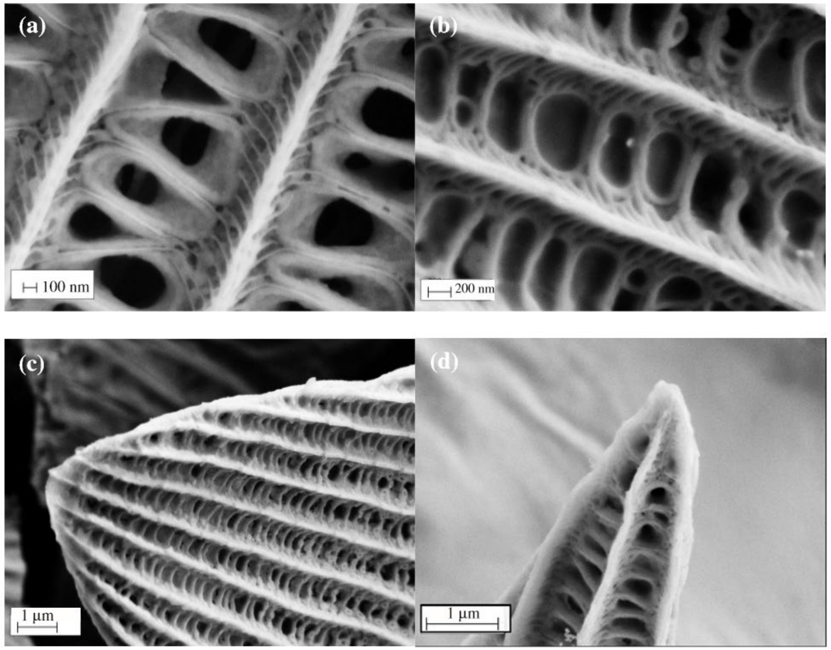
- Mixed Gd_2O_2S:Tb and Y_2O_3:Eu
- CdSe/ZnCdS core shell quantum dots
- CdSe/CdS core shell dot in rods
- Various Y_2O_3 and Y_2O_3 metal(III) doped phosphors
- $REE_2O_2S:Tb^{3+}$ phosphors

Cathodoluminescence imaging and spectroscopy in the FE-SEM

Light-emitting nanocasts formed from bio-templates: FESEM and cathodoluminescent imaging studies of butterfly scale replicas



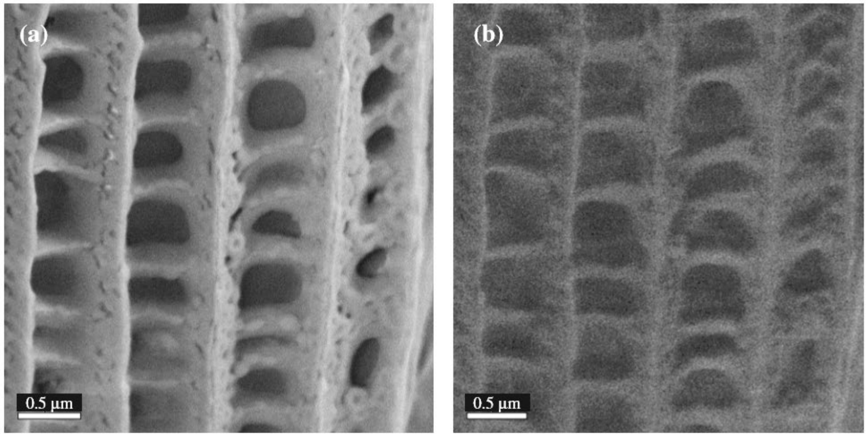
(a) FESEM image of two scale sections of a natural butterfly wing, one showing a dentated scale terminus (scale bar is 2 µm), and (b) a higher magnification study of one of the scale sections shown in (a) having a scale bar of 1 µm.



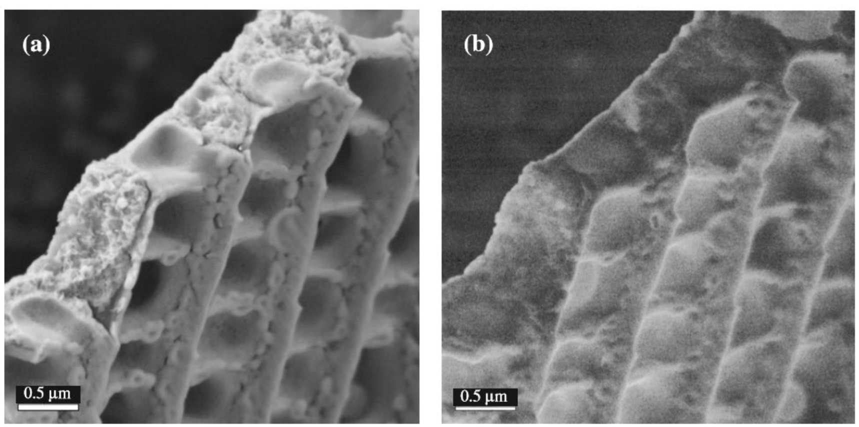
FESEM (Zeiss Supra) studies of butterfly scale casts formed from $Y_2O_3:Eu^{3+}$: (a) detail of scale cast showing the fine replication of structure (scale bar is 100 nm), (b) scale cast with a thicker deposition of $Y_2O_3:Eu^{3+}$ (scale bar is 200 nm), (c) cast section of a dentated scale terminus (scale bar is 1 µm) and (d) cast of a dentated scale tip (scale bar is 1 µm).

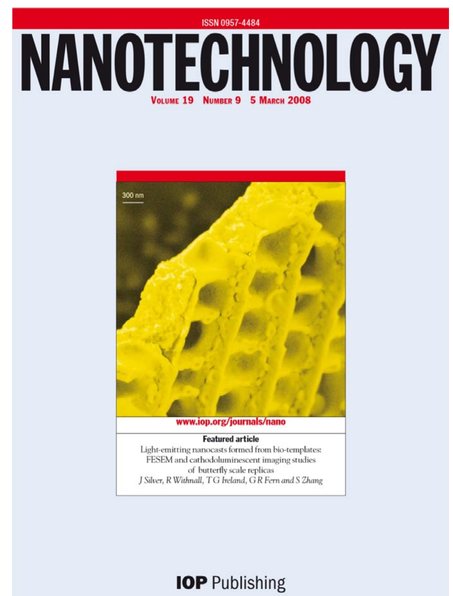
Light-emitting nanocasts formed from bio-templates: FESEM and cathodoluminescent imaging Light-emittingstudies of butterfly scale replicas, J Silver, R. Withnall, T G Ireland, G R Fern and S Zhang, *Nanotechnology* 19 (2008) 095302 (7pp). DOI: 10.1088/0957-4484/19/9/095302

Light-emitting nanocasts formed from bio-templates: FESEM and cathodoluminescent imaging studies of butterfly scale replicas

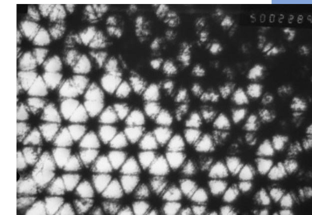


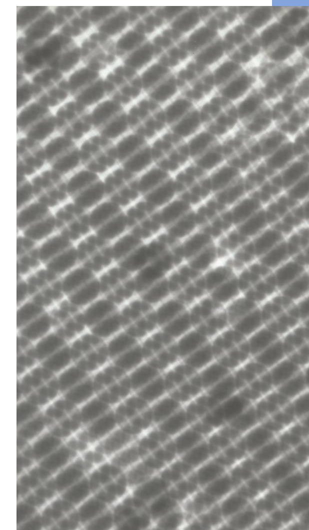
FESEM-CL study of a butterfly scale cast formed from $Y_2O_3:Eu^{3+}$: (a) SEM image and (b) CL image. The scale bar is 0.5 µm in both cases.

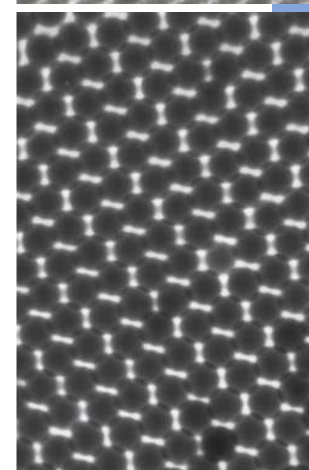




JEOL FESEM AND Gatan-MonoCL







We would like to express gratitude to A Yarwood of JEOL, Welwyn Garden City, UK for providing access to the JEOL FESEM instrument that was fitted with a Gatan CCD detector.

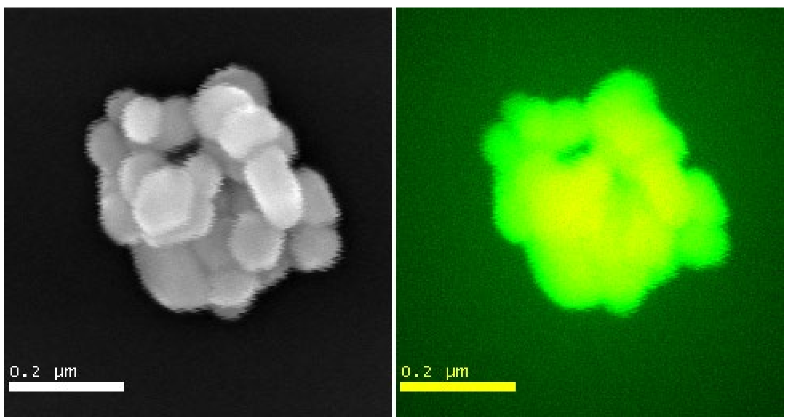
JEOL FESEM and Gatan MonoCL

Gadolinium Oxysulphide (Tb)

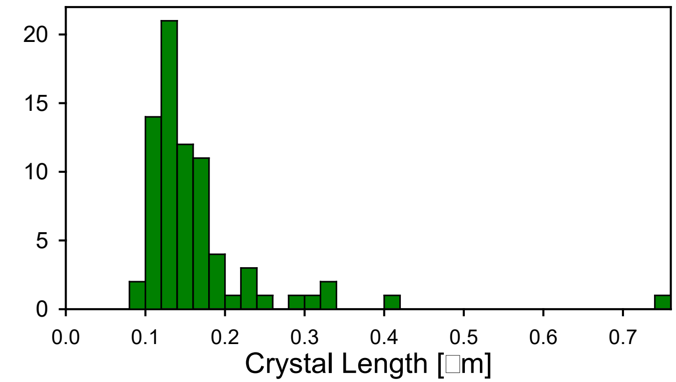
Particle Size: ~130nm

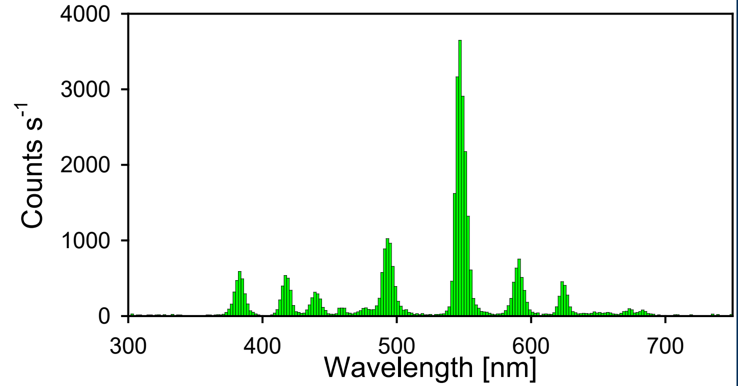
CL spectrum: 545nm (++)

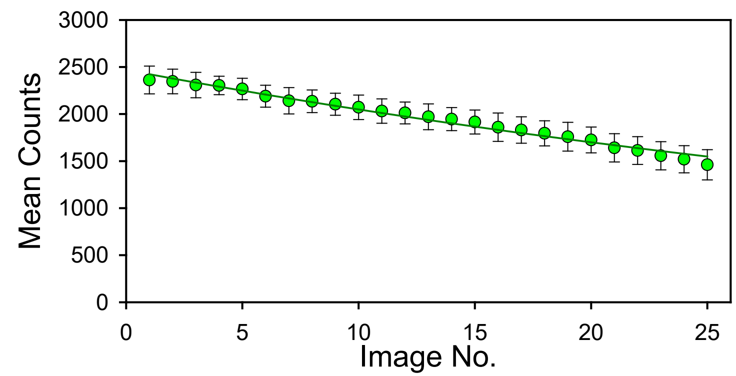
CL stability: high



Overall: In the SEM long collection times are a problem.



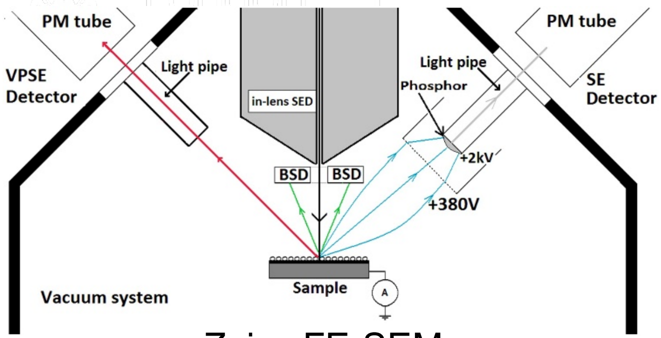




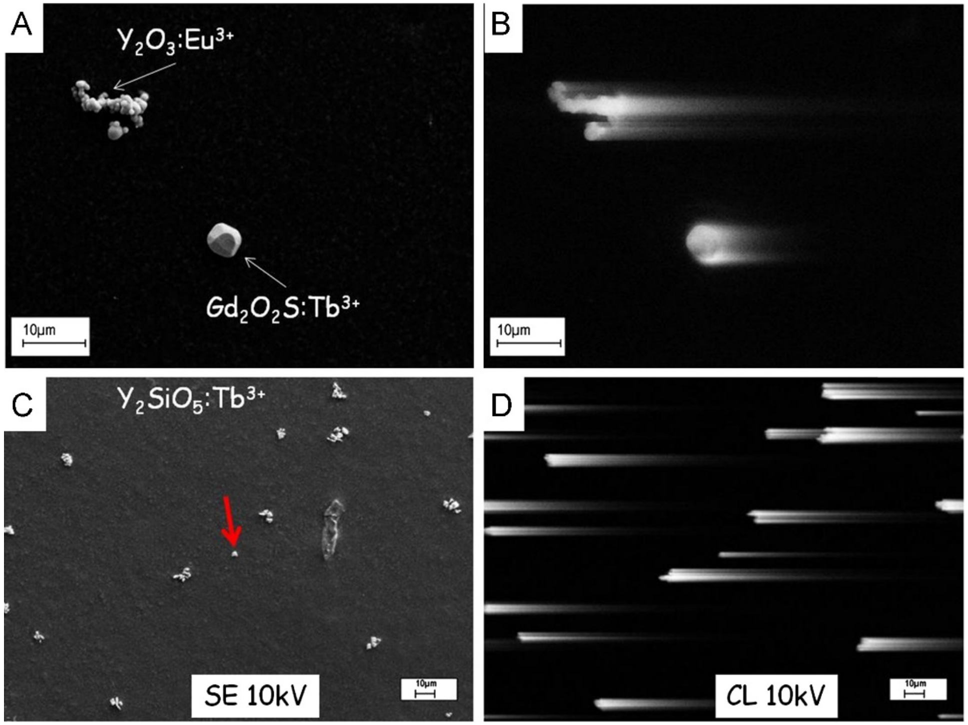
JEOL FESEM AND Gatan-MonoCL

Morrison IEG, Samilian A, Coppo P, Ireland TG, Fern GR, Silver J, Withnall R, O'Toole PJ. [Multicolour correlative imaging using phosphor probes] *Journal of Chemical Biology* 8(4):169-177 Oct 2015.

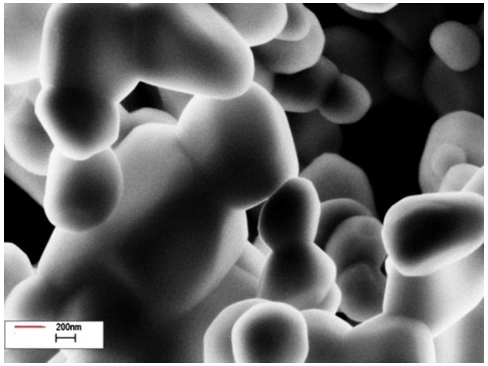
Contrast and decay of cathodoluminescence from phosphor particles in a scanning electron microscope



Zeiss FE-SEM



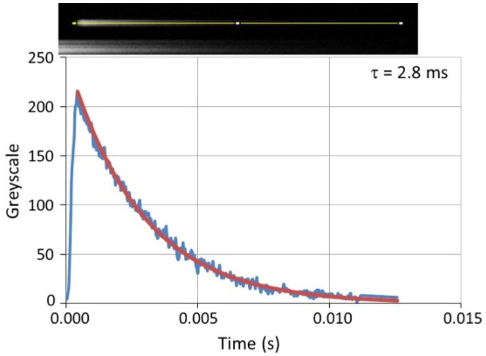
(A) SE-micrograph of a cluster of Y_2O_3:Eu^{3+} particles and a single Gd_2O_2S: Tb^{3+} particle. (B) CL-micrograph of same area as shown in (A). (C) SE-micrograph of Y_2SiO_5:Tb^{3+} particles. (D) CL-micrograph of same area as shown in (C). Primary electron energy 10 keV, scanning rate of 10.1 s/frame.



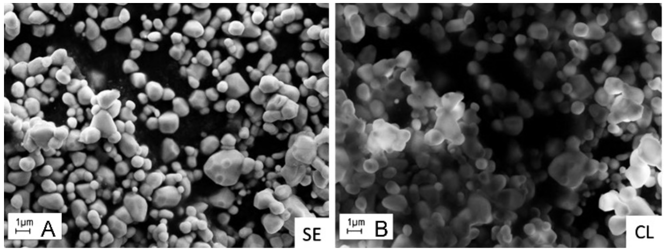
CL-micrograph of ZnO:Zn at 10 keV

Contrast and decay of cathodoluminescence from phosphor particles in a scanning electron microscope, Daniel den Engelsen, Paul G. Harris, Terry G. Ireland, George R. Fern and Jack Silver, *Ultramicroscopy*, 2015, 10.1016/j.ultramic.2015.05.009

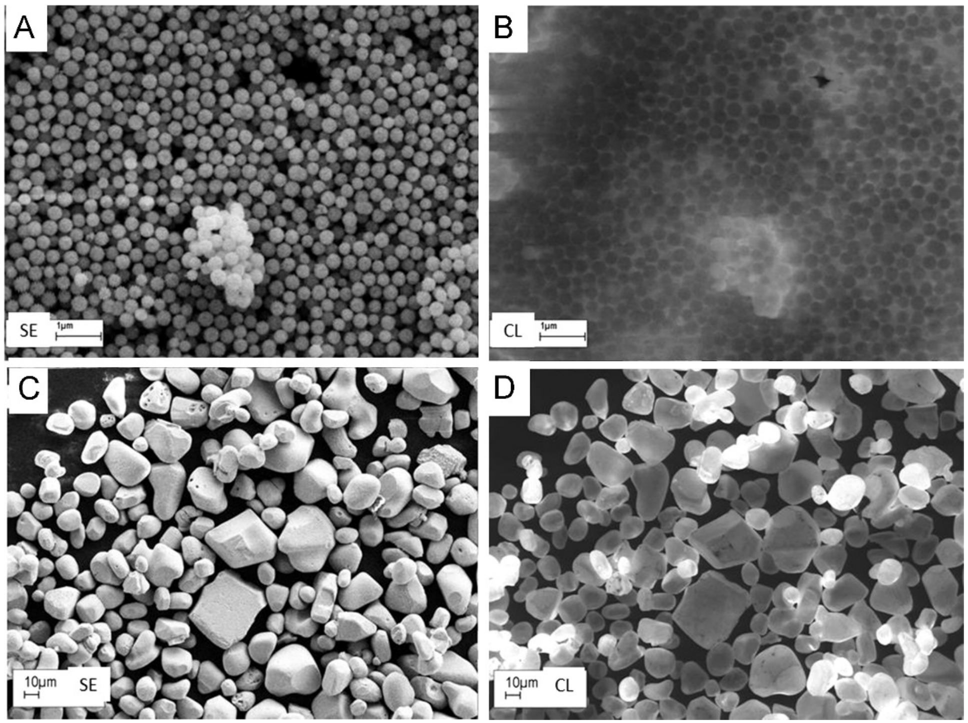
Contrast and decay of cathodoluminescence from phosphor particles in a scanning electron microscope



Grey scale of CL-micrograph (10 keV) versus time for $Y_2SiO_5:Tb^{3+}$ particle. The single particle comet was used to construct the diagram



(A) SE micrograph of ZnO:Zn at 10 kV. (B) CL micrograph of same area of ZnO:Zn at 10 kV ZnO:Zn powder is deposited on carbon substrate.



(A and B) Micrographs of the same area of monosized $Y_2O_3:Eu^{3+}$ at 10 keV on ITO substrate. (C and D) Micrographs of the same area of ZnS:Cu,Cl at 10 keV on C-substrate. (A and C) SE-micrographs, (B and D) CL-micrographs.

Ultramicroscopy, 2015, 10.1016/j.ultramic.2015.05.009

OPTIFED ~2005 Phosphors for screen printed field emission displays

Cathodoluminescence imaging and spectroscopy in the FE-TEM

Microscopy Instrumentation

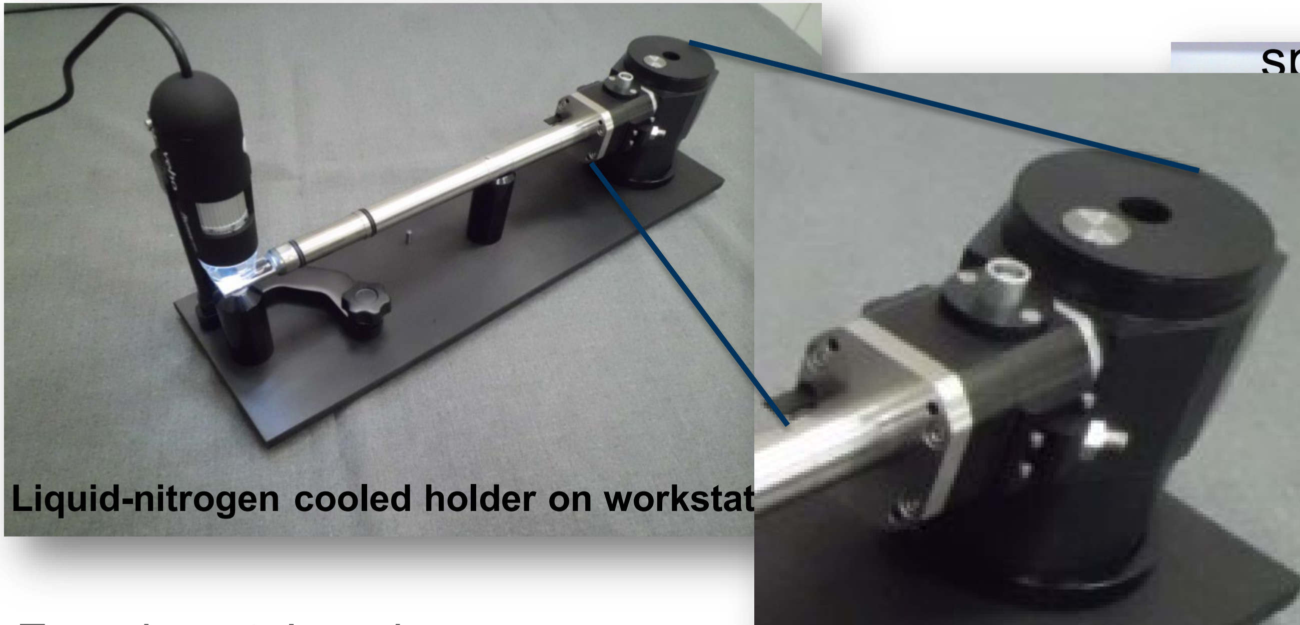
JEOL 2100F Field Emission Transmission Electron Microscope with

Various STEM detectors

Electron Energy Loss Spectrometer (Gatan Quantum EELS)

Cathodoluminescence Spectrometer (Gatan Vulcan)

Cathodoluminescence in the TEM



Liquid-nitrogen cooled holder on workstat

spectrometer and
ntrollers

Footprint: 60 x 80cm

Experimental modes:

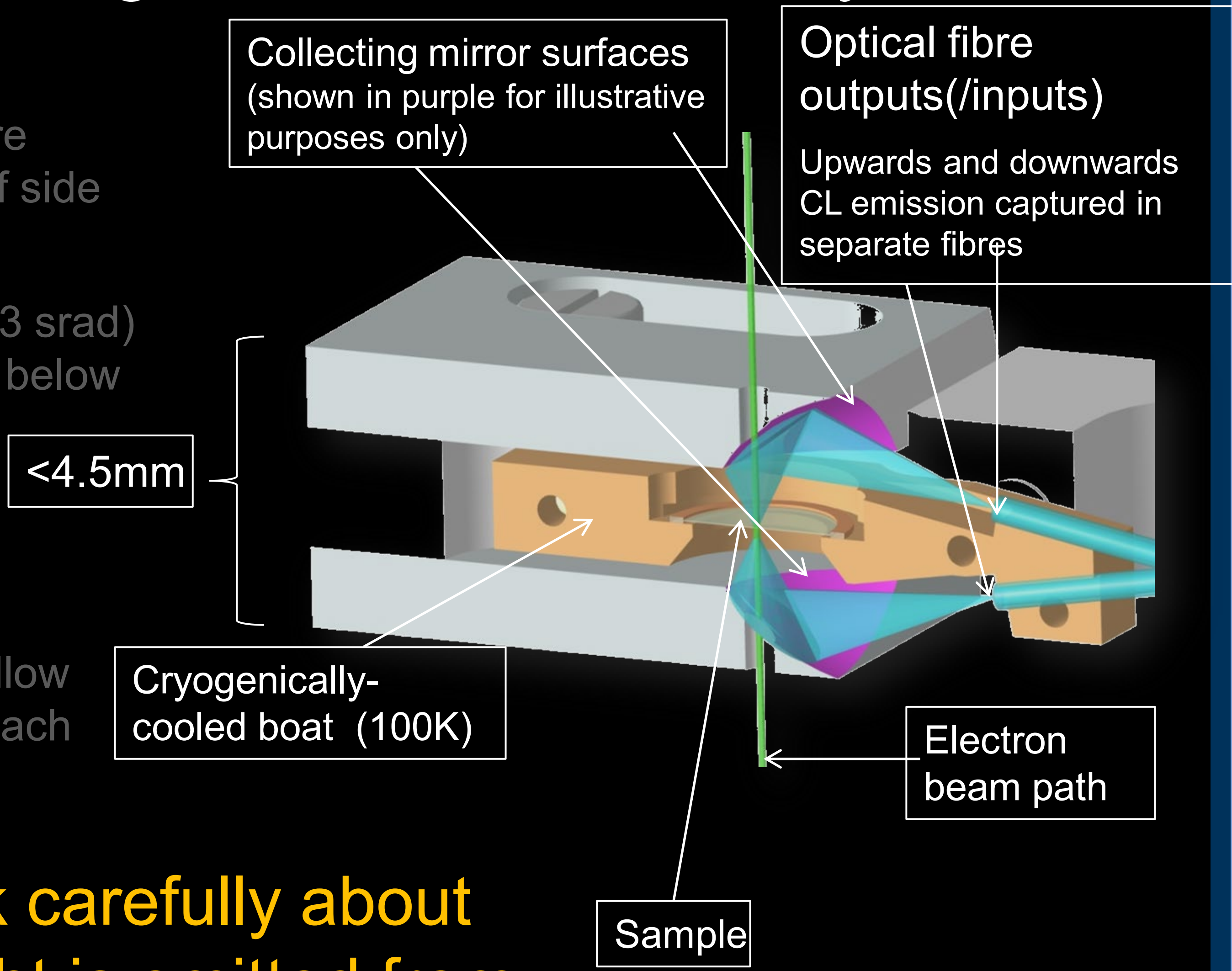
- STEM CL Imaging using cooled-PMT, total light or selected wavelength
- Spectroscopic analysis using Czerny-Turner spectrometer and back-illuminated CCD
- CL Spectrum-imaging
  - Compatible with simultaneous EELS

Hyphenation of Cathodoluminescence in the TEM using the Gatan Vulcan system

Miniature mirrors are integrated into tip of side entry holder

High solid angle (7.3 srad) mirrors above AND below the specimen

Small aperture to allow electron beam to reach specimen



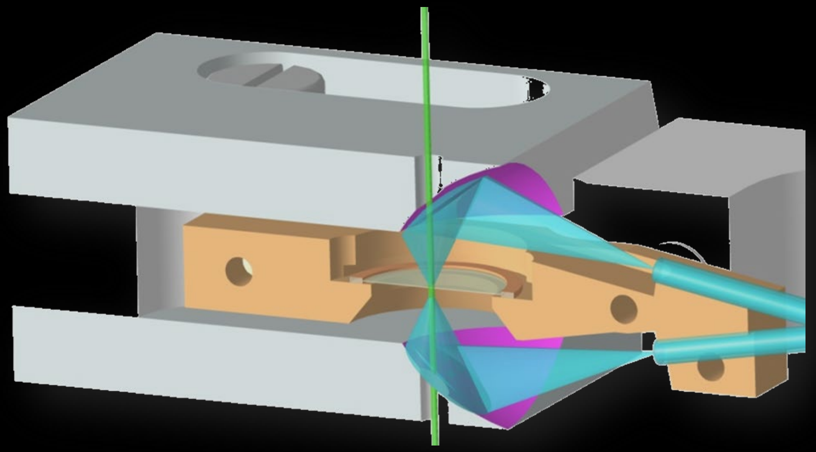
Need to think carefully about where the light is emitted from

Adapted slide from David Stowe - Gatan

Hyphenation of Cathodoluminescence in the TEM using the Gatan Vulcan system

Vulcan also includes optical spectrometer, detectors and software for analysis of CL in the 4.1-1.1eV range (300-1100nm)

Reality, 400+ nm due to optics to about 800nm



Schematic cross section through the Vulcan™ holder showing the specimen region.

Electron beam (green) stimulates the specimen to emit photons (blue) which are focussed by the collection mirrors into optical fibres situated away from the specimen region

Limitations of Brunel's machine:

No possibility to tilt sample

Benefits:

Very sensitive (c.f. bulk time collection)

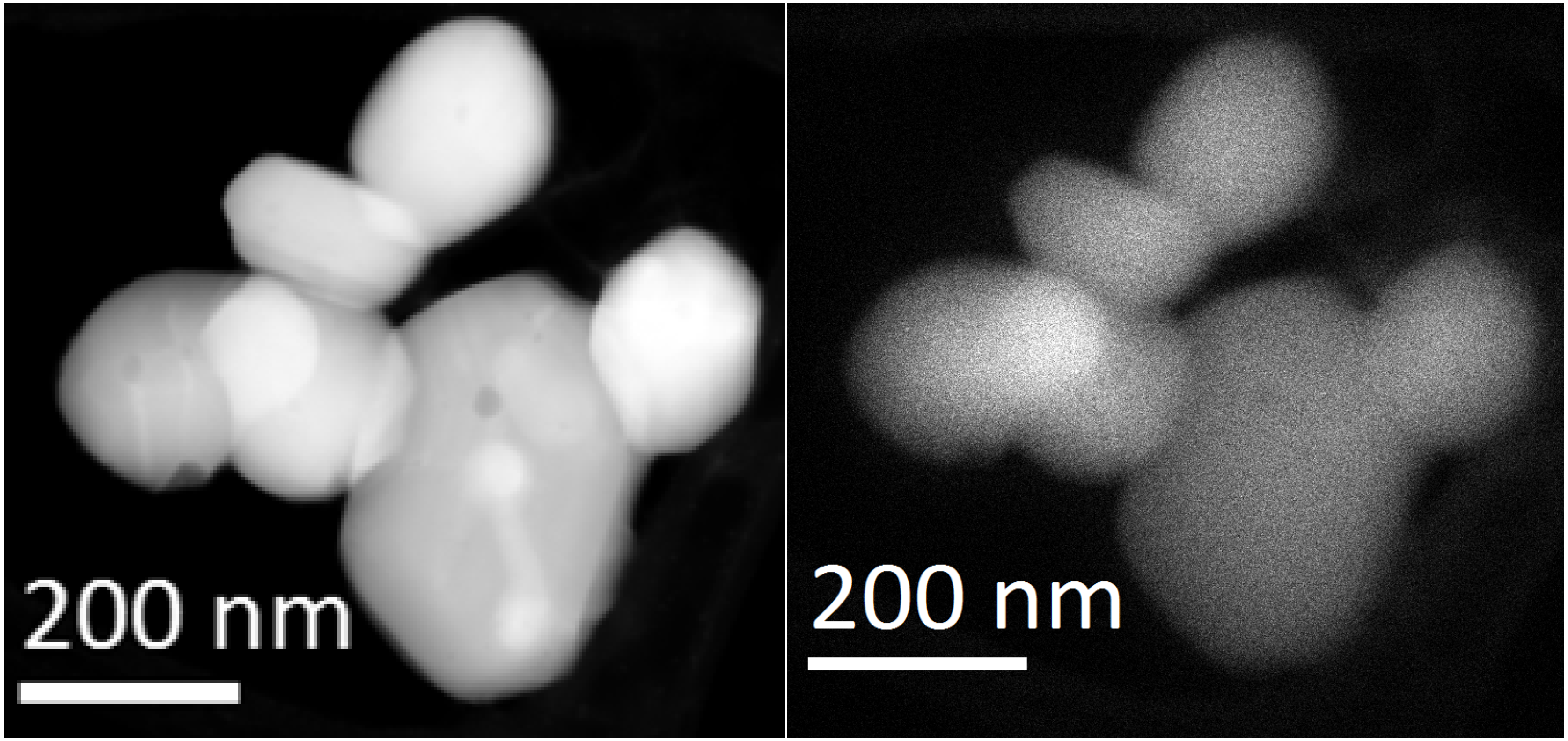
The benefit of using the TEM over the SEM is the much higher beam voltage leading to higher resolution

Adapted slide from David Stowe - Gatan

Imaging of Gd_2O_2S:Tb 5%

(Very bright green emitting phosphor)

Dark Field STEM | **CL Image (Total light)**



Images collected simultaneously

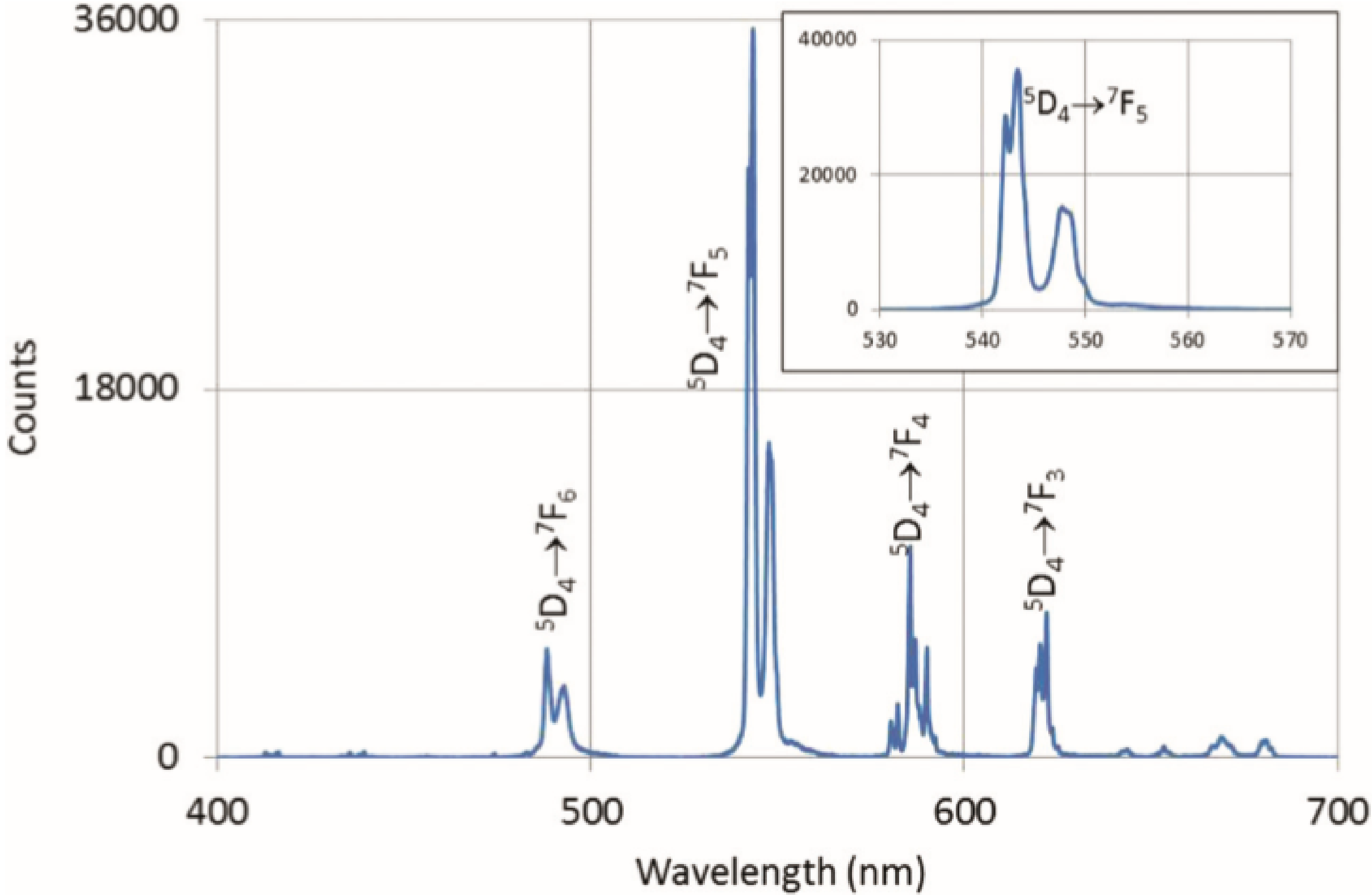
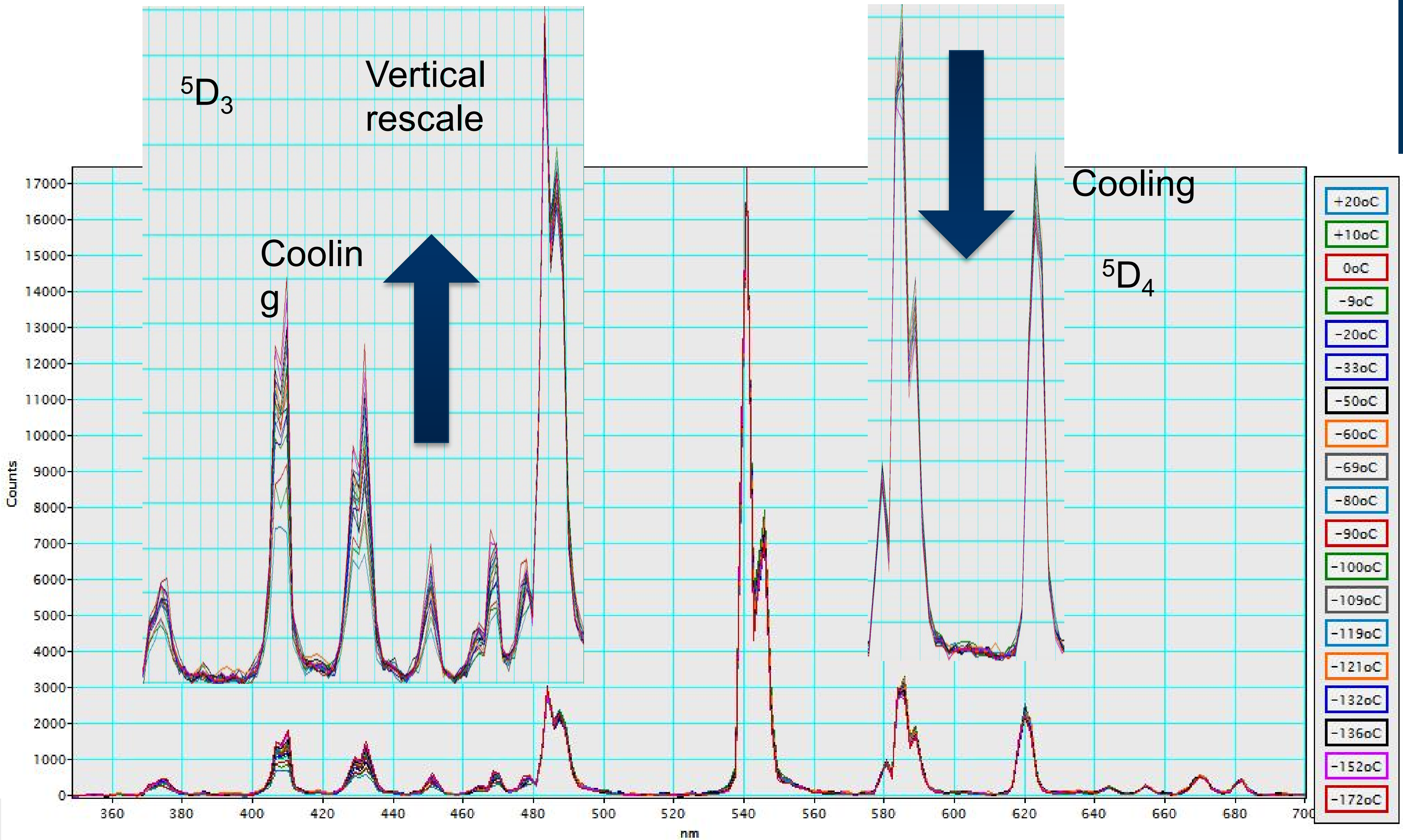


Fig. 9 High resolution CL spectrum of $(Lu_{0.5}Gd_{0.5})_2O_2S$:2%Tb^{3+} recorded at 200 keV and room temperature in the TEM. The insert shows the structure of the Tb^{3+} $^5D_4 \rightarrow ^7F_5$ manifold in more detail.

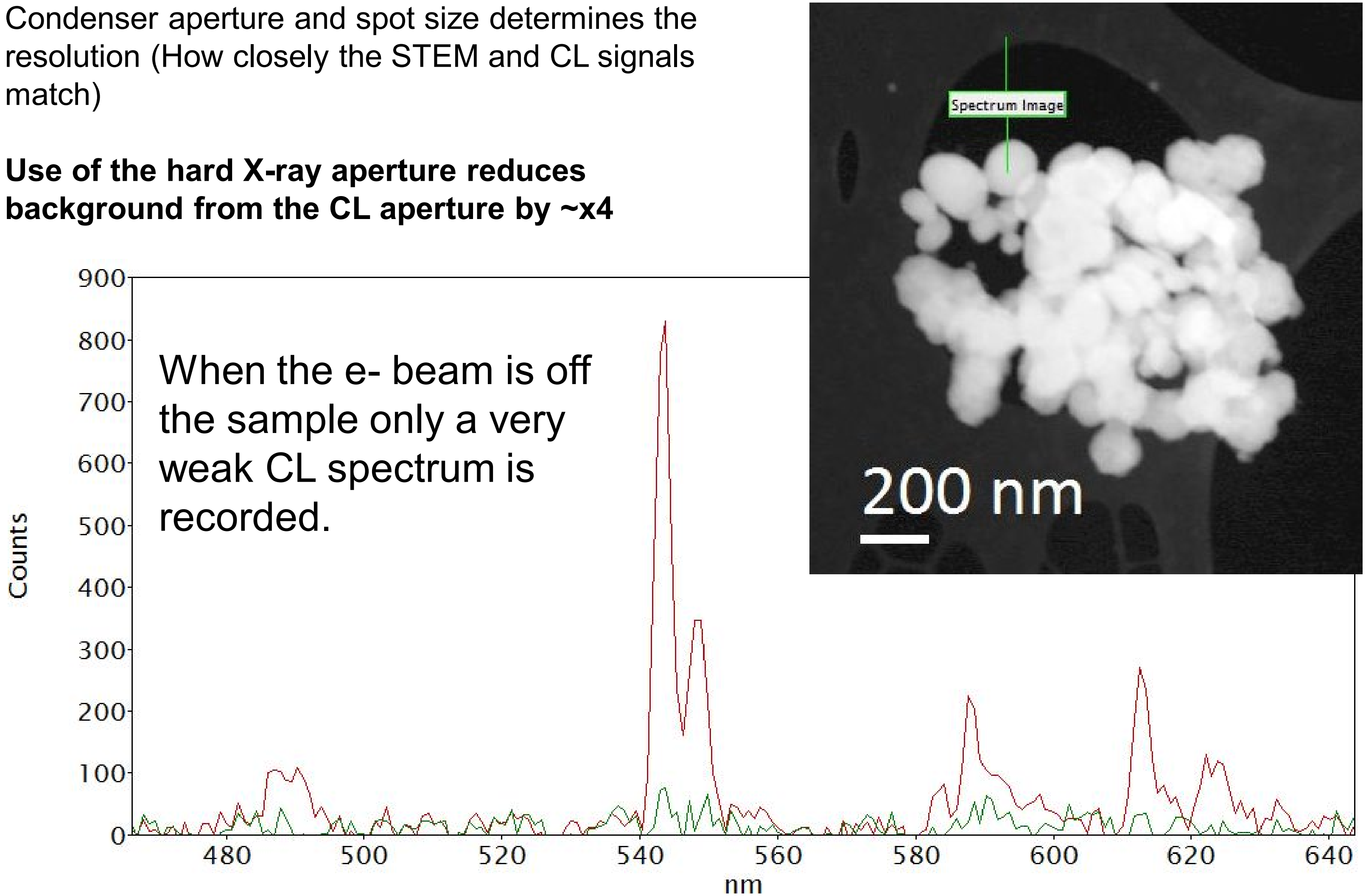
Relative changes of the effect of cooling the sample (normalised at 540nm)



Scan from vacuum to phosphor particle (Gd_2O_2S:Tb)

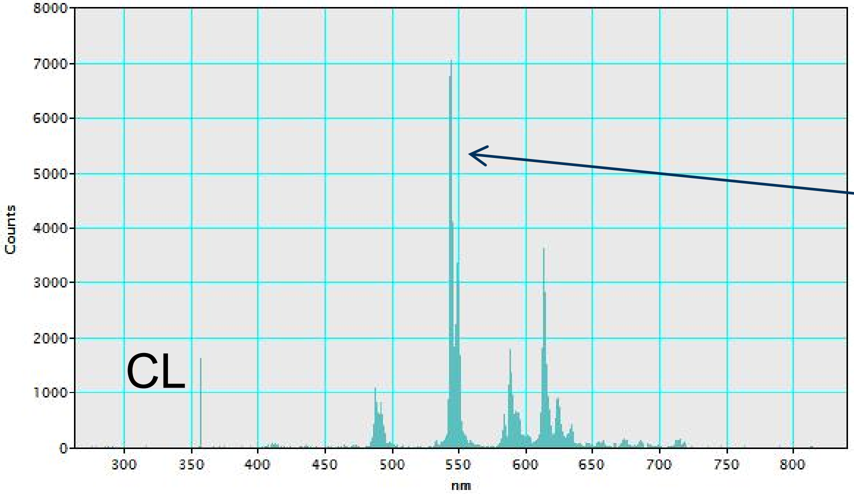
Condenser aperture and spot size determines the resolution (How closely the STEM and CL signals match)

Use of the hard X-ray aperture reduces background from the CL aperture by ~x4

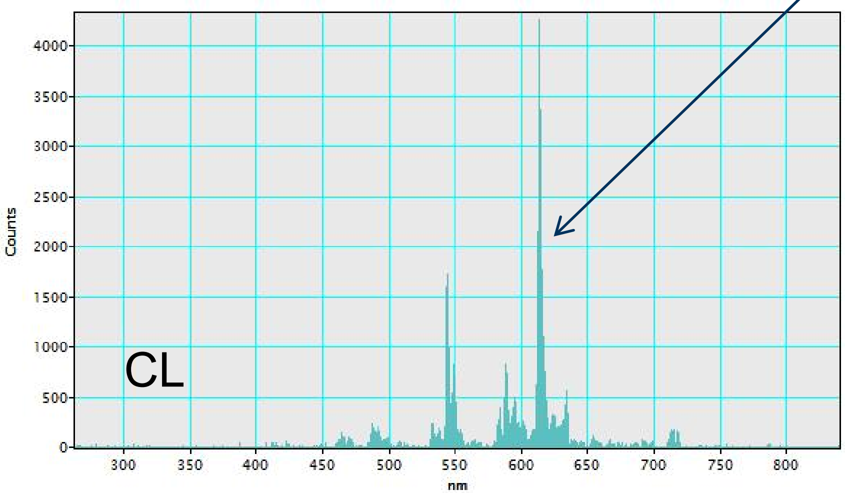


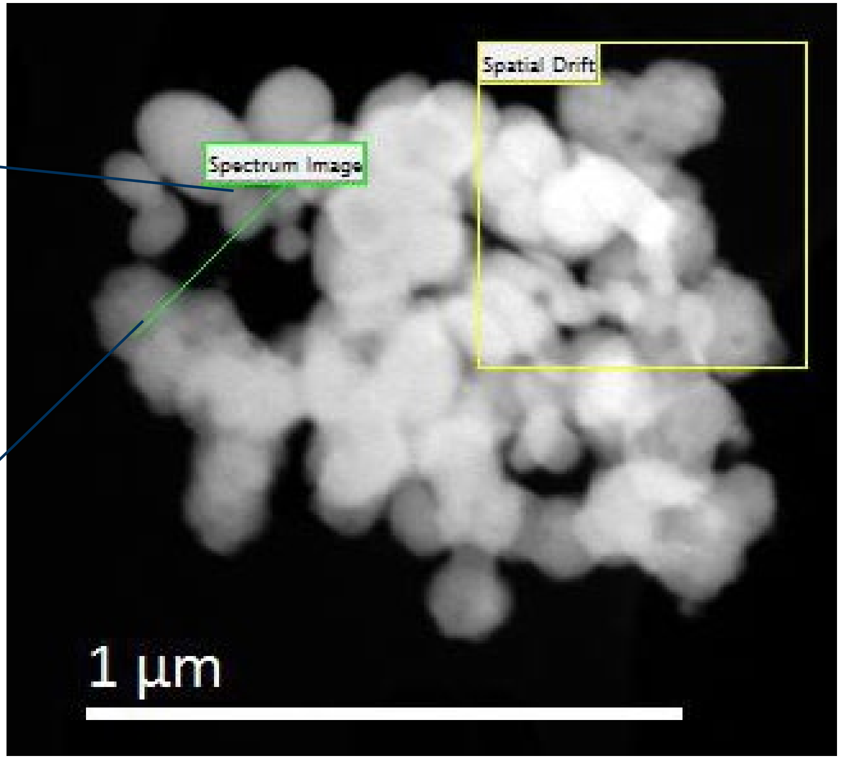
Resolution issues
Particles are separated by 100nm

$Gd_2O_2S:Tb$



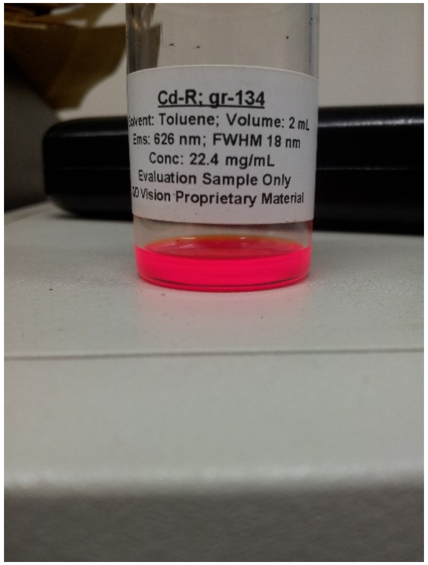
Y_2O_3Eu





However secondary emission causes adjacent particles to emit CL (with thick and high Z samples).

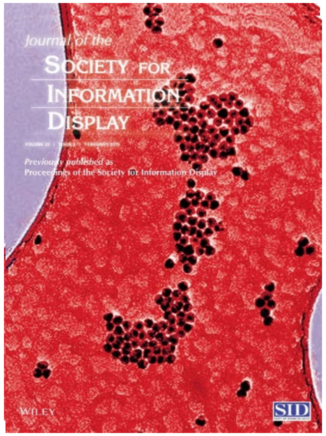
CL imaging from CdSe/ZnCdS core/shell quantum dots to visualise luminescent properties and uniformity



QDV sample

Simulation of a LED TV without (left) and with (right) saturated red (QDV image)

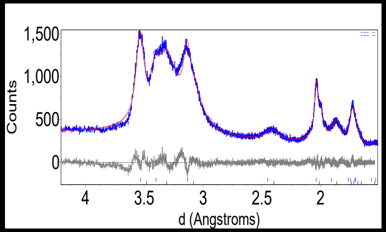
Development of TV backlighting materials suitable for the REC2020 display screen standard.



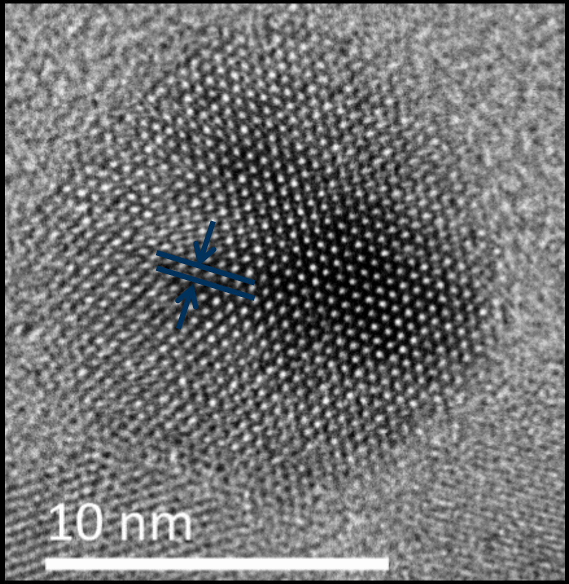
Cathodoluminescence and electron microscopy of red quantum dots used for display applications, Fern, George Robert; Silver, Jack; Coe-Sullivan, Seth, *Journal of the Society for Information Display*, 23(2) 50-55, FEB 2015 DOI: 10.1002/jsid.278

HRTEM from CdSe/ZnCdS core/shell quantum dots

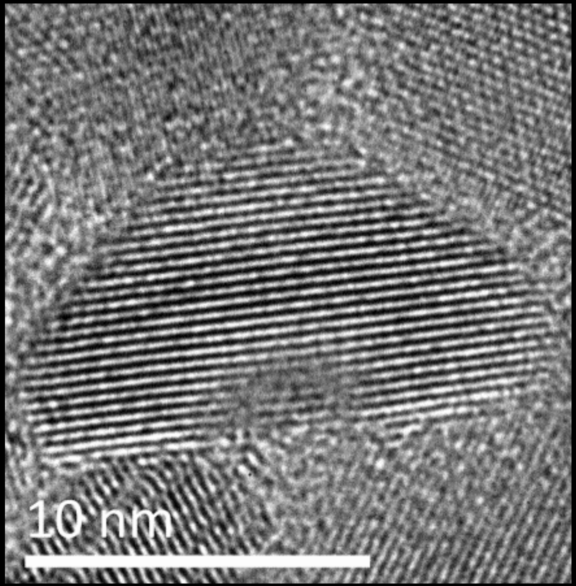
(1 0 0) lattice spacing shown



XRPD of 2 Wurtzite phases (for core and shell)



Showing hexagonal shape looking down the c axis

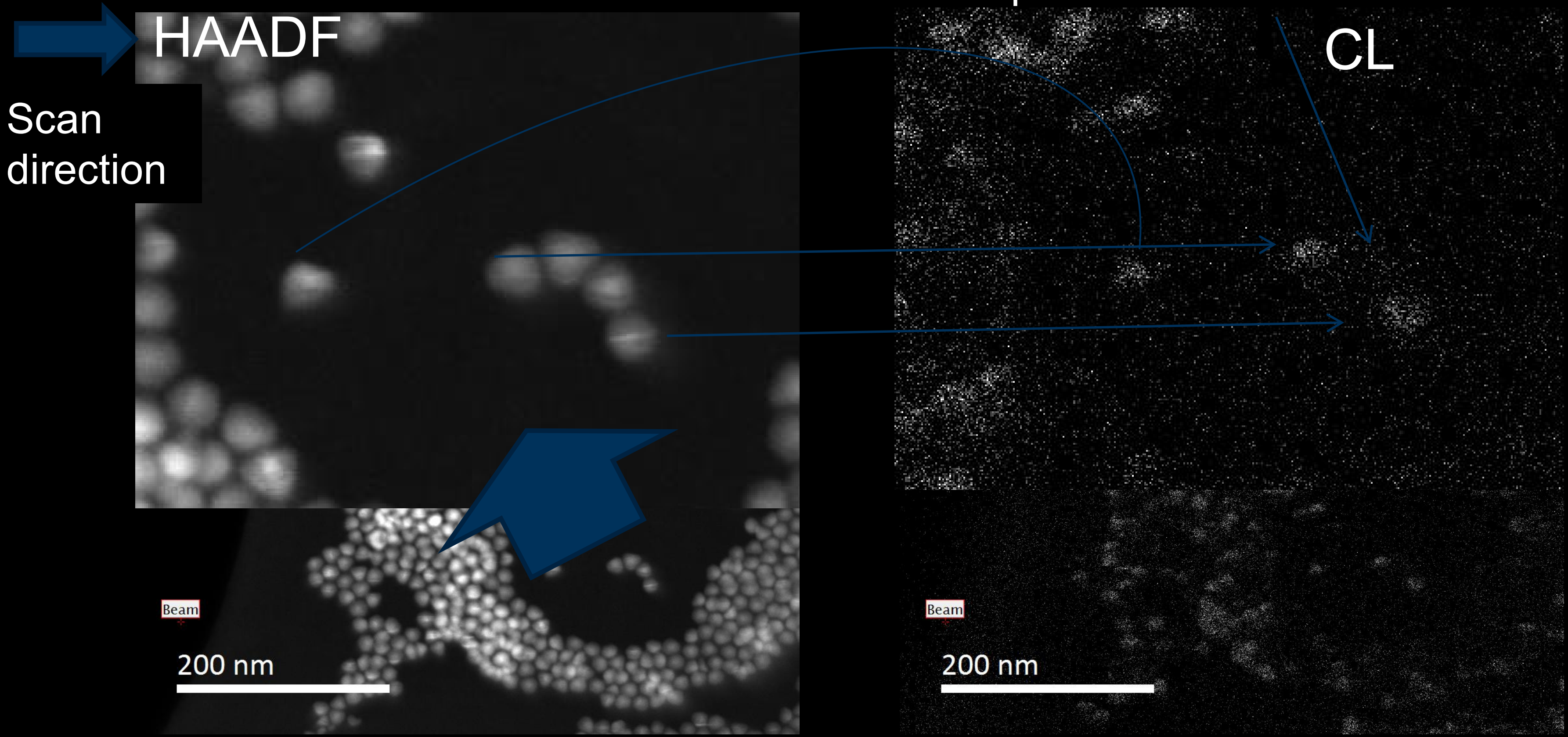


Orthogonal to the c axis

Truncated hexagonal pyramids

It is not possible to know the position of the red emission. Resolution is limited to particle's size. (~13-14 nm)

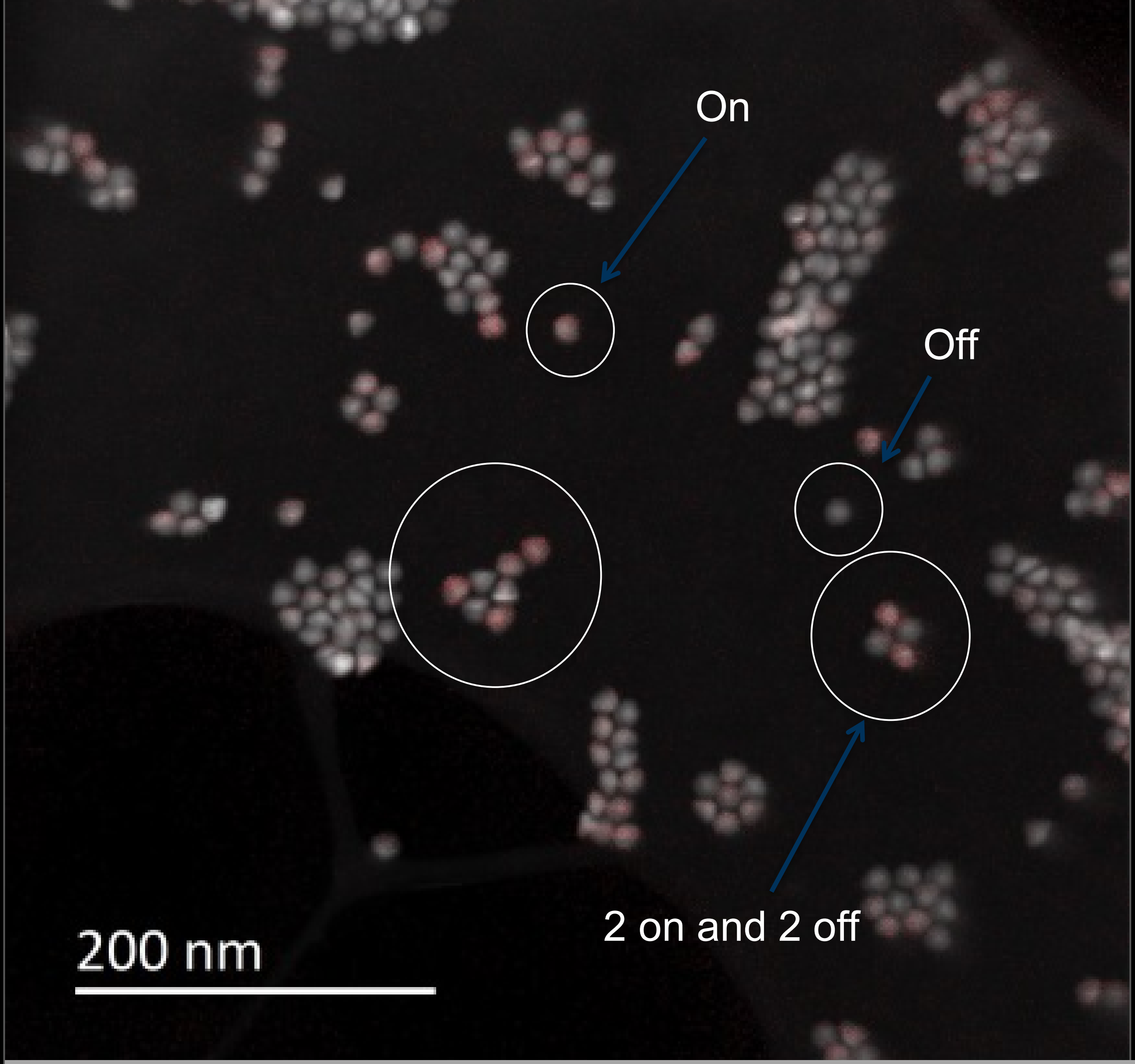
No emission so we must be seeing the true position of emission



Thinness means there is no significant secondary excitation and hence excellent spatial resolution for adjacent particles

Journal of the Society For Information Display, 23(2) 50-55, FEB 2015 DOI: 10.1002/jsid.278

Excellent correlation of the STEM and CL images



Overlay:

Showing a range of particles with some on and some off lying both together and singly.

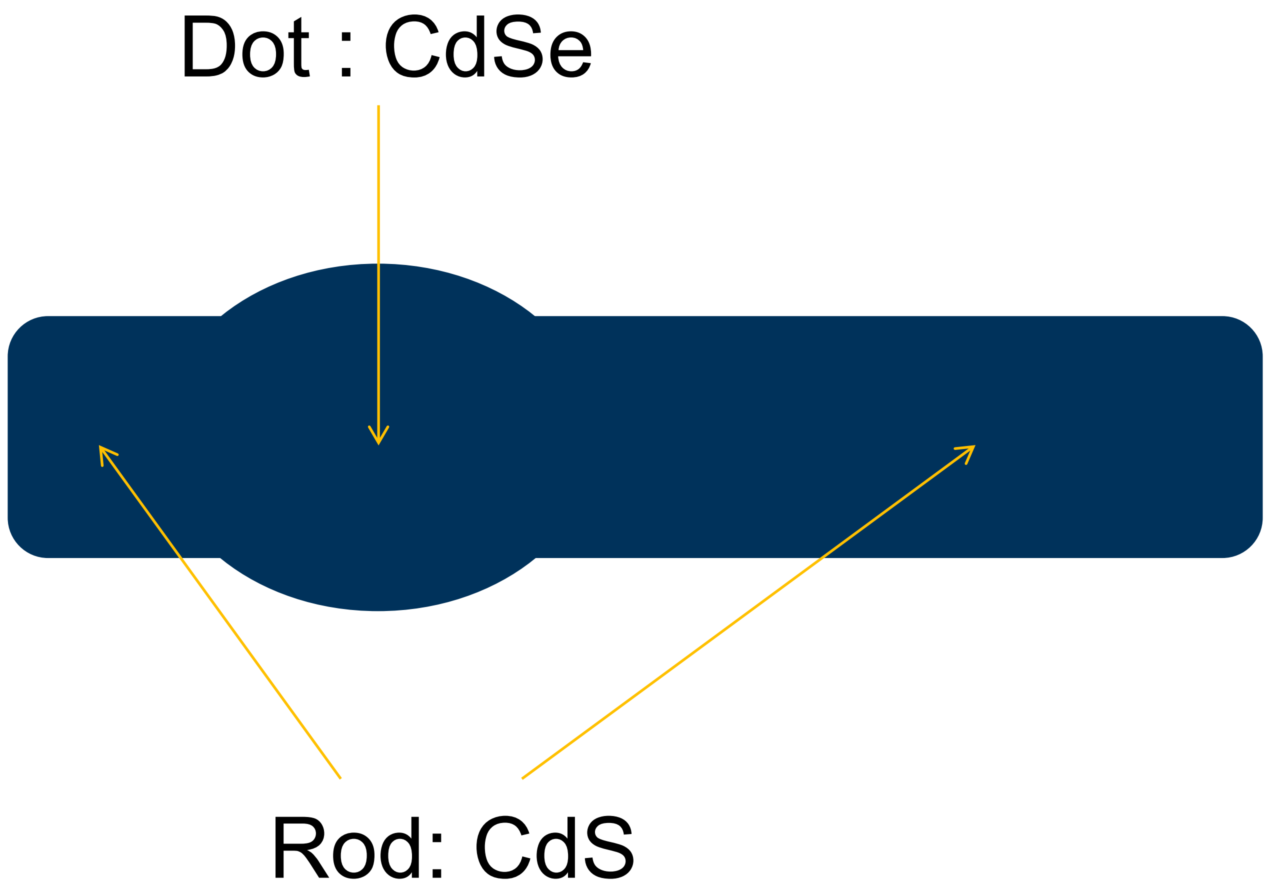
We are able to achieve spatial resolution which is only limited by the size of the QD.

Hence 13 nm resolution with a wavelength of 628 nm

CL imaging from quantum dot in rods

The Material Studied

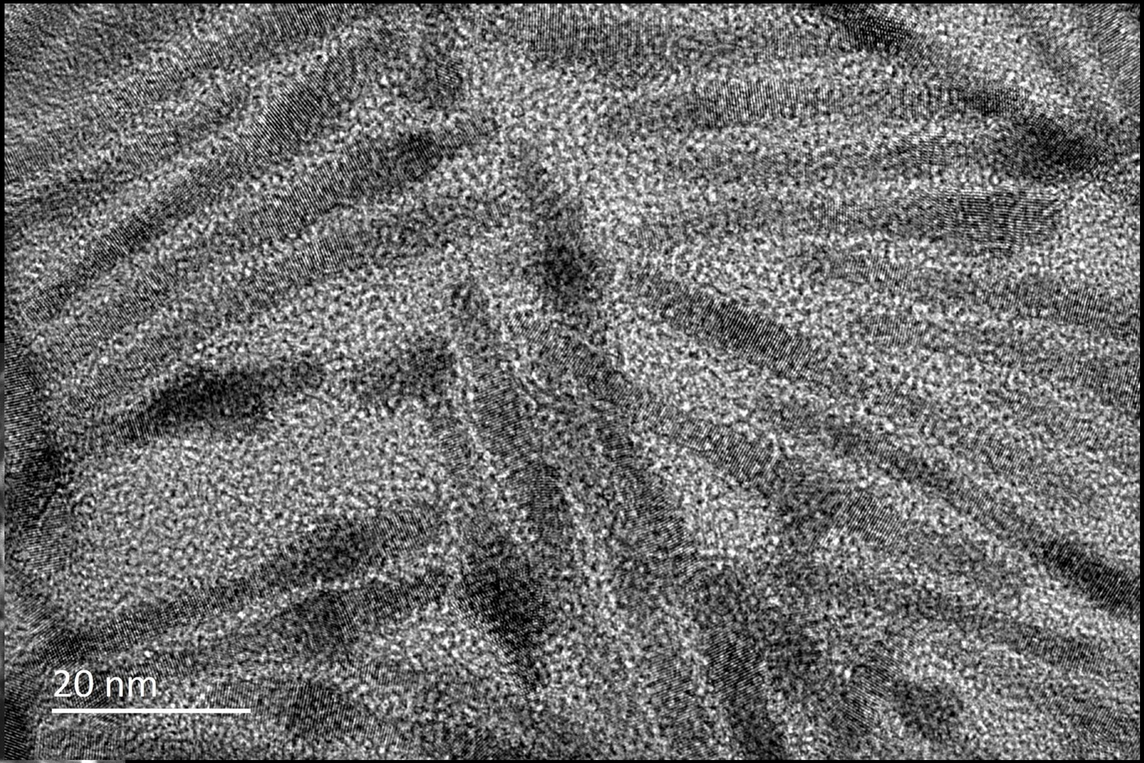
Dot in Rod

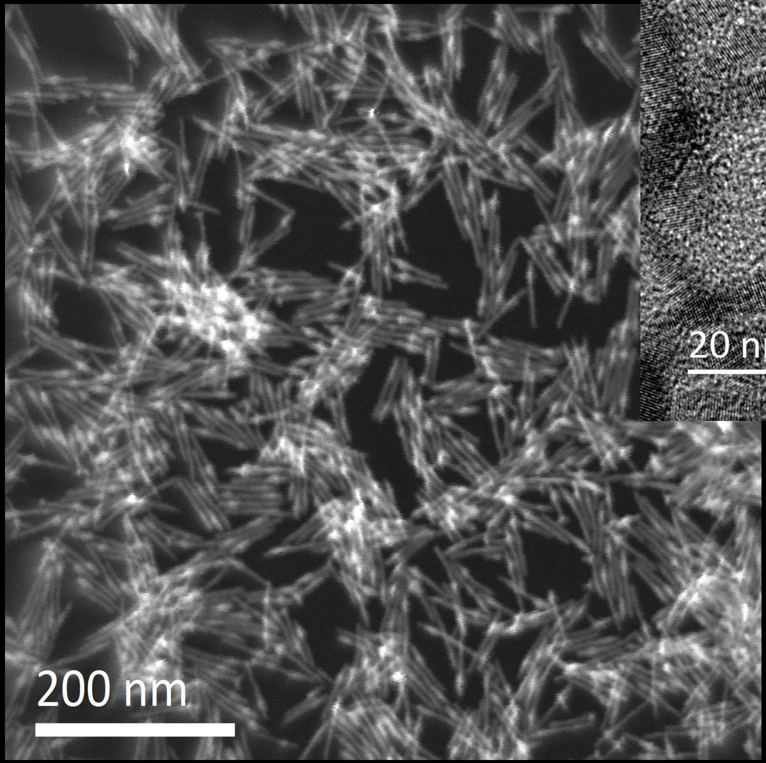


Simultaneous Scanning Transmission Electron Microscopy, Cathodoluminescence Imaging and EELS of Quantum Dot in Rods, George R. Fern*, Jack Silver*, Terry G. Ireland*, Ashley Howkins, Tobias Jochum, Jan S. Niehaus, Frank Schröder-Oeynhausen and Horst Weller. International Displays Workshop, 2015.

CL imaging from quantum dot in rods

- Particle size is ~6 nm wide by 50-60 nm long
- Hence beam interaction volume is small
- Expect minimal scattering

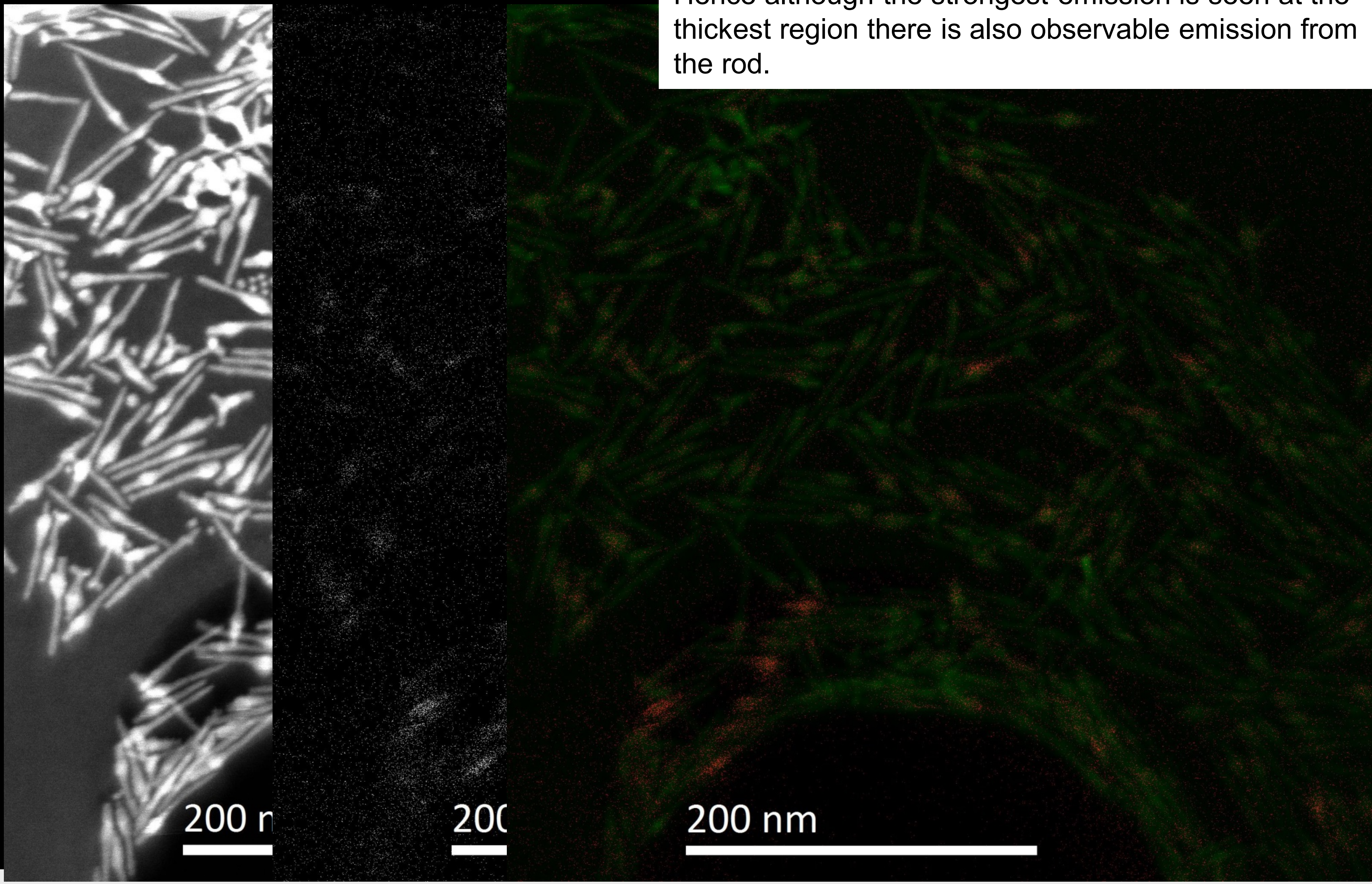




- Rods are separated by a thick organic coating (~1nm)
- Removal of the coating leads to rapid distortion and damage in the electron beam

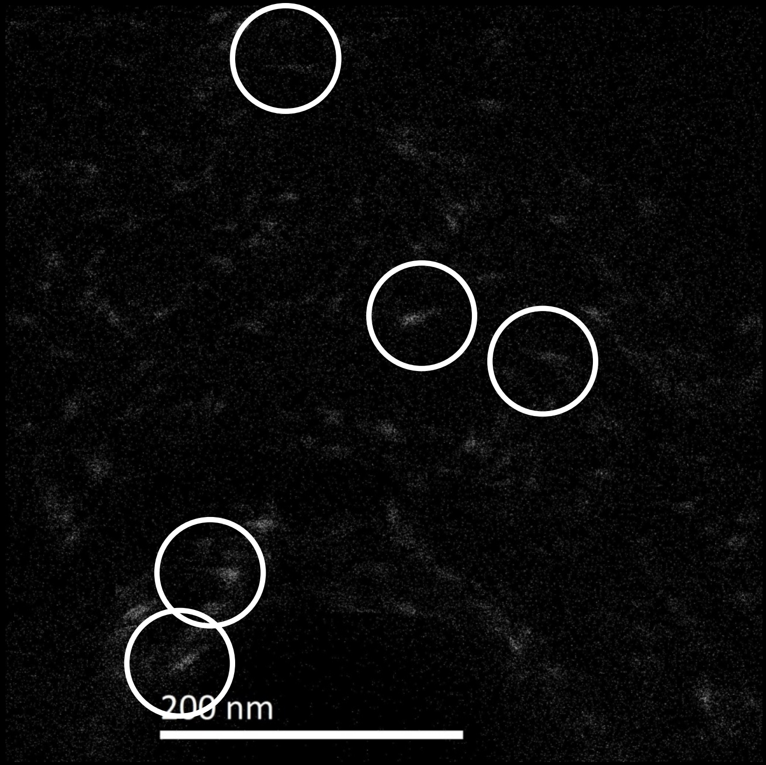
CL and HAADF STEM imaging of fresh DRs

Emission is elongated in CL image. Different to that seen in QDs.
Hence although the strongest emission is seen at the thickest region there is also observable emission from the rod.

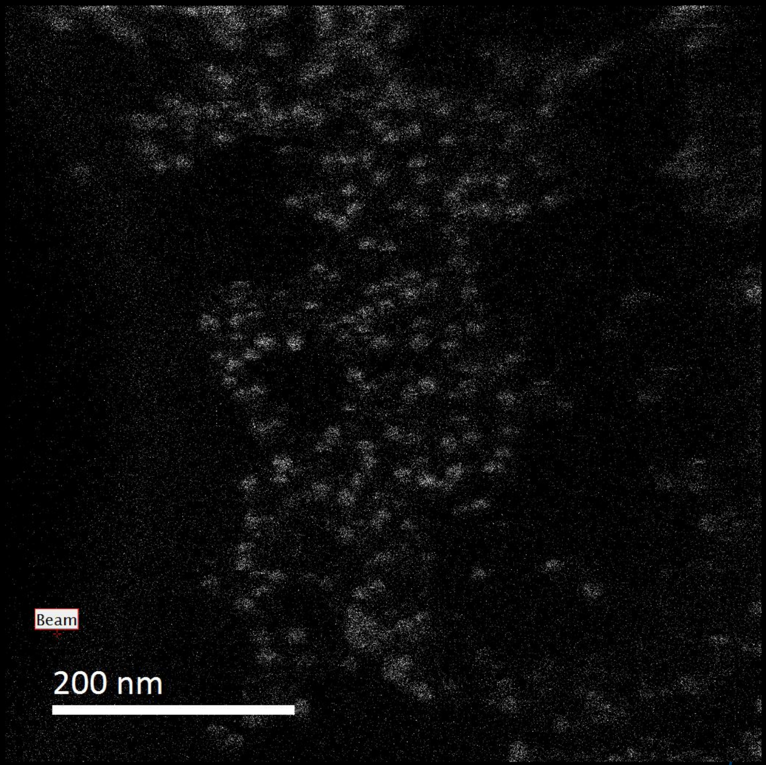


Comparison of DR and QD cathodoluminescence images

Red DR emission



Red QD emission



We observe streaking of the CL emission with some rods but never with the QDs

Hence some rods are able to be excited by the electron beam as it approaches or moves away from the dot in the rod. Conversely some are not.

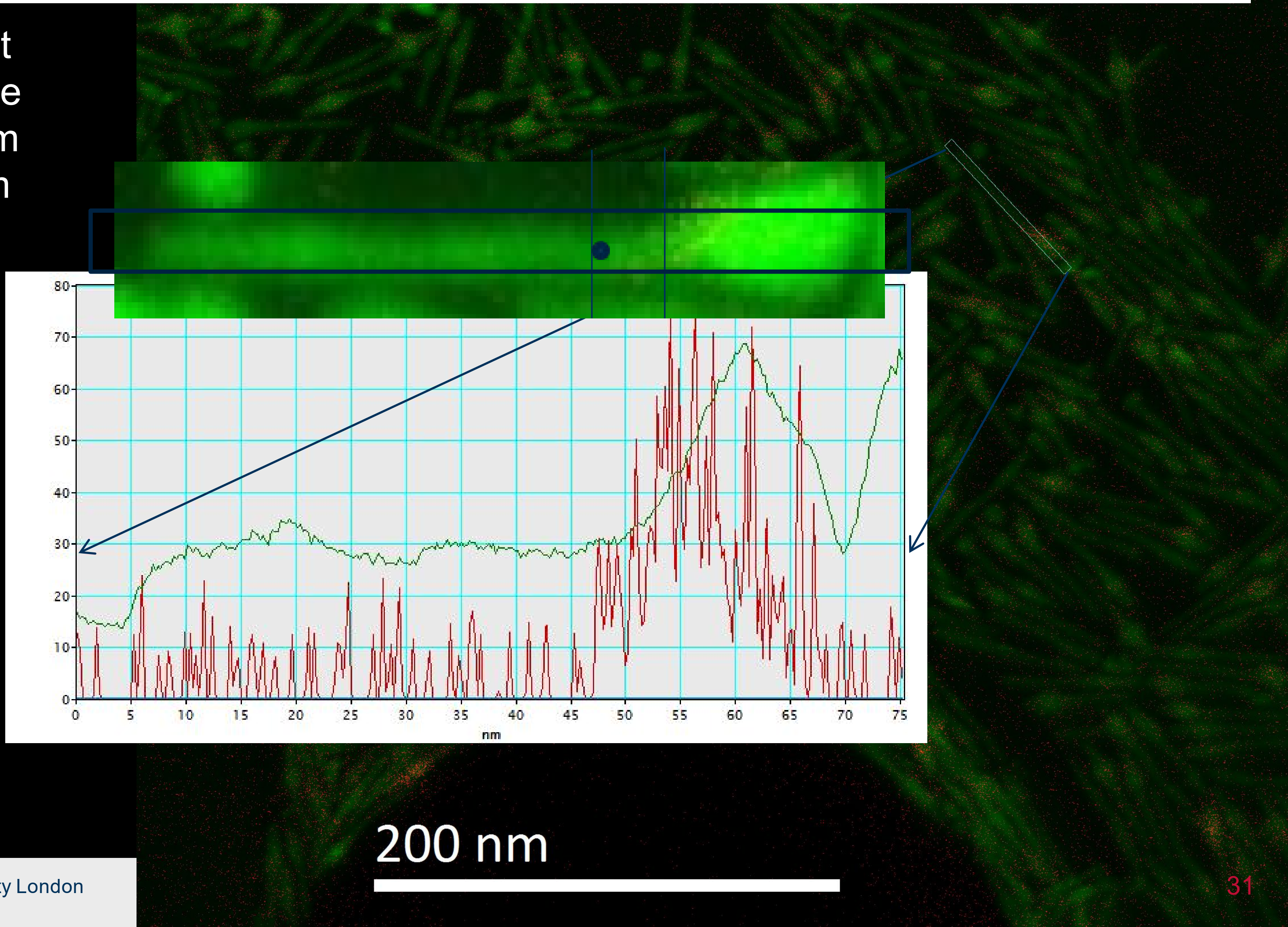
This could be due to many reasons, but we think further investigation could help us to distinguish why some rods are either more stable than others or are able to be excited through the particle.

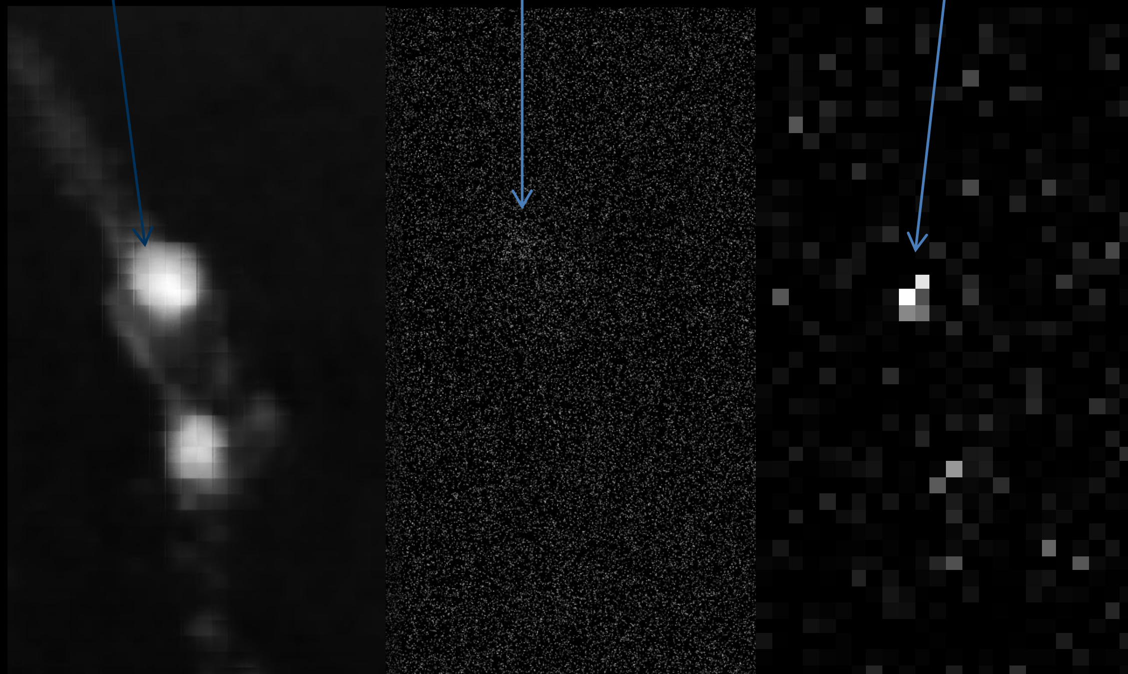
QD emission: Fern, Coe-Sullivan and Silver, SID 2014.

Overlay of CL and HAADF shows the CL emission occurs at the edge of the dot

24 February 2021

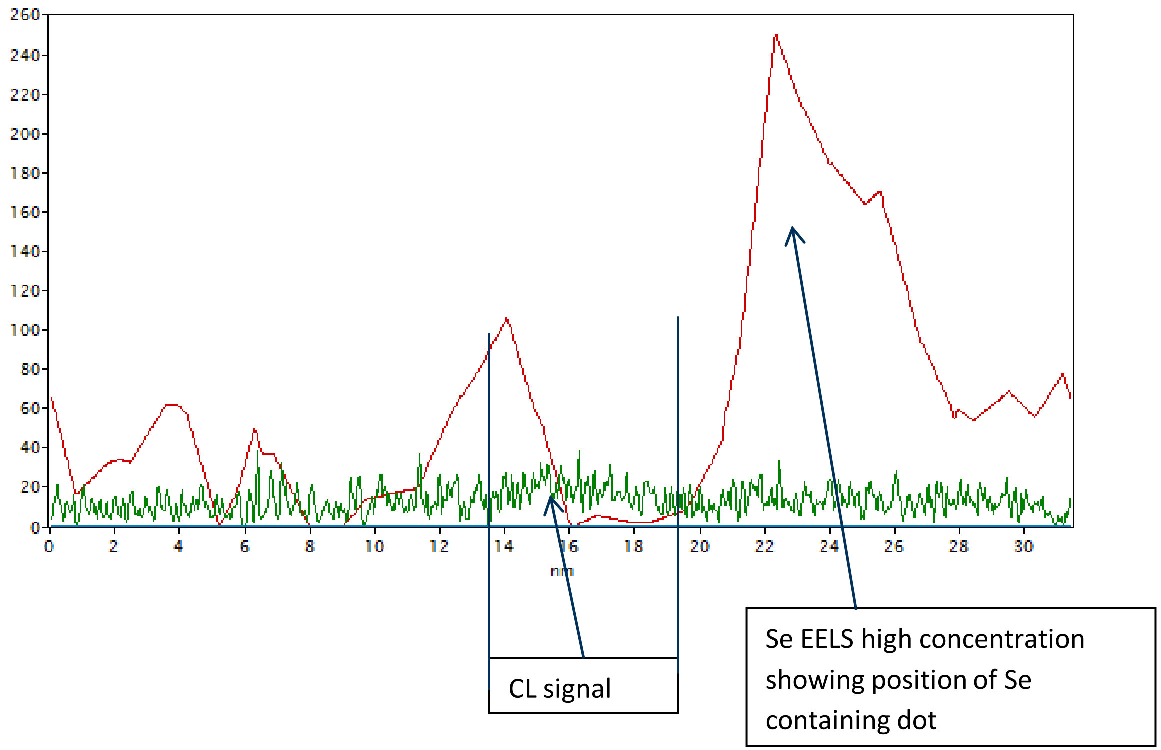
Beam spot size can be varied from 0.2-1.5 nm along with varying aperture





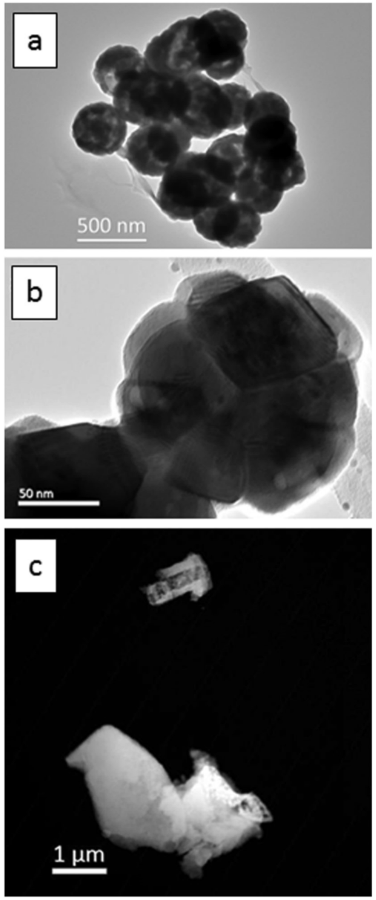
Simultaneous HAADF, CL (625(25)nm bp filter) image and Se EELS

Intensity plot of the overlay of CL and EELS maps. CL signal is 5.2nm in length and about 2nm away from the Se signal.

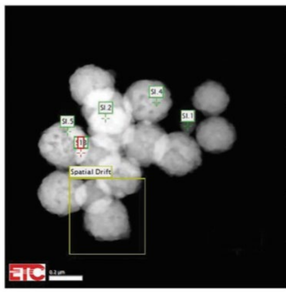


Green is CL signal and red is EELS map

Ultraviolet and blue cathodoluminescence from cubic Y_2O_3 and $Y_2O_3:Eu^{3+}$ generated in a transmission electron microscope

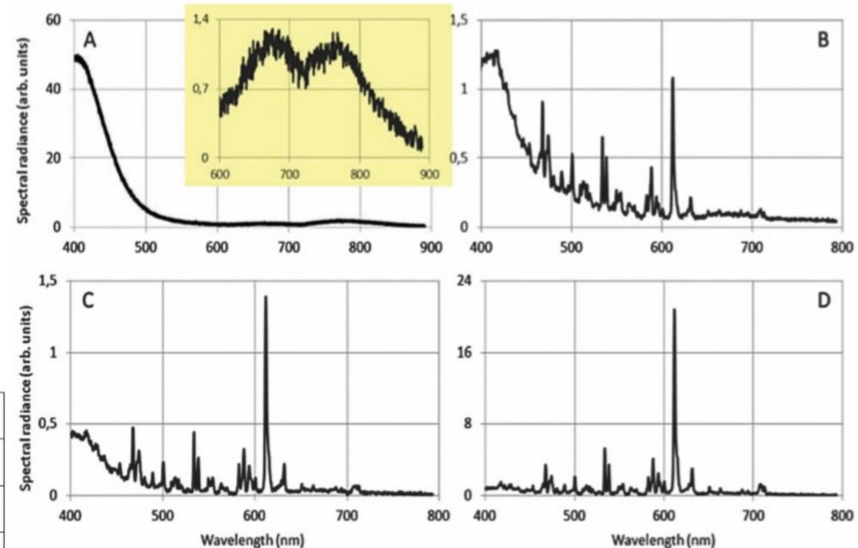


TEM images, (a) and (b), of $Y_2O_3:Eu^{3+}$ particles: (a) urea-precipitated route, (b) higher magnification image of a single particle from (a). (c) HAADF image oxalate-precipitated particles.



Site	SR_{405}	SR_{612}	η
SI-1	0.5	2.6	0.16
SI-2	12.2	10.8	0.53
SI-3	5.3	10.2	0.34
SI-4	3.3	5.6	0.37
SI-5	2.5	8.4	0.23

Quenching factor η at various sites for urea-precipitated $Y_2O_3:Eu^{3+}$ (0.1 mol% Eu^{3+}) at -168°C and 200 keV

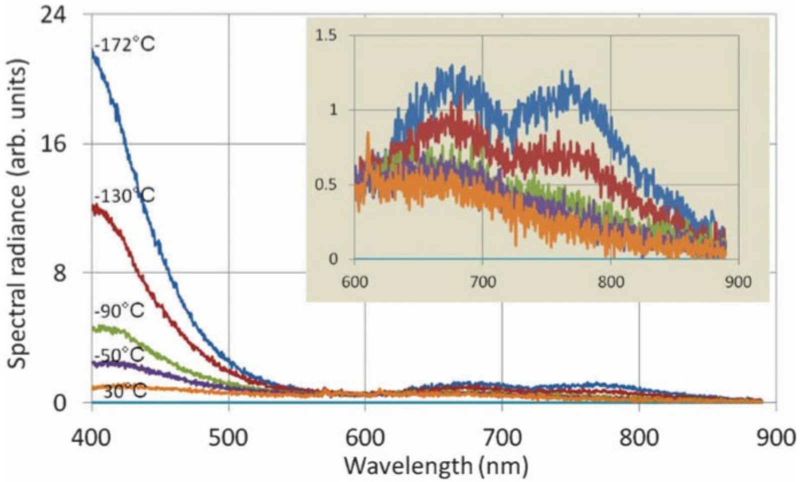


CL spectra of $Y_2O_3:Eu^{3+}$ recorded at -171°C, 200 keV beam voltage and spot size of 1.5 nm. (**A**) non-doped Y_2O_3, inset: spectrum at larger scale between 600 nm and 900 nm; (**B**) 0.1 mol% Eu^{3+}; (**C**) 0.5 mol% Eu^{3+}; (**D**) 1 mol% Eu^{3+}. The sharp lines in the spectrum are $Y_2O_3:Eu^{3+}$ transitions; the strongest is the $^5D_0$ - $^7F_2$ Eu^{3+} transition at 611 nm.

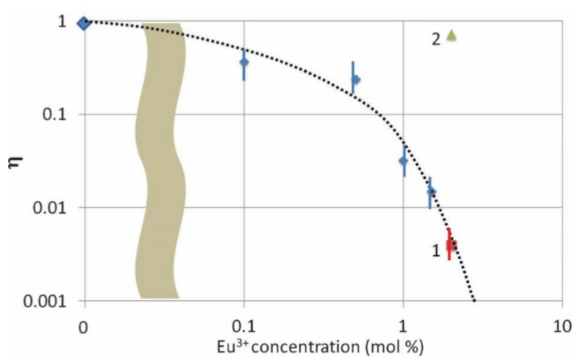
Self trapped exciton (intrinsic) radiation leads to the blue/UV emission observed from the Y_2O_3 lattice under e-beam excitation.

den Engelsen, D.; Fern, G. R.; Ireland, T. G.; et al. *Journal of Materials Chemistry C*, 4(29) 7026-7034, AUG 7 2016.
DOI: 10.1039/c6tc01750a

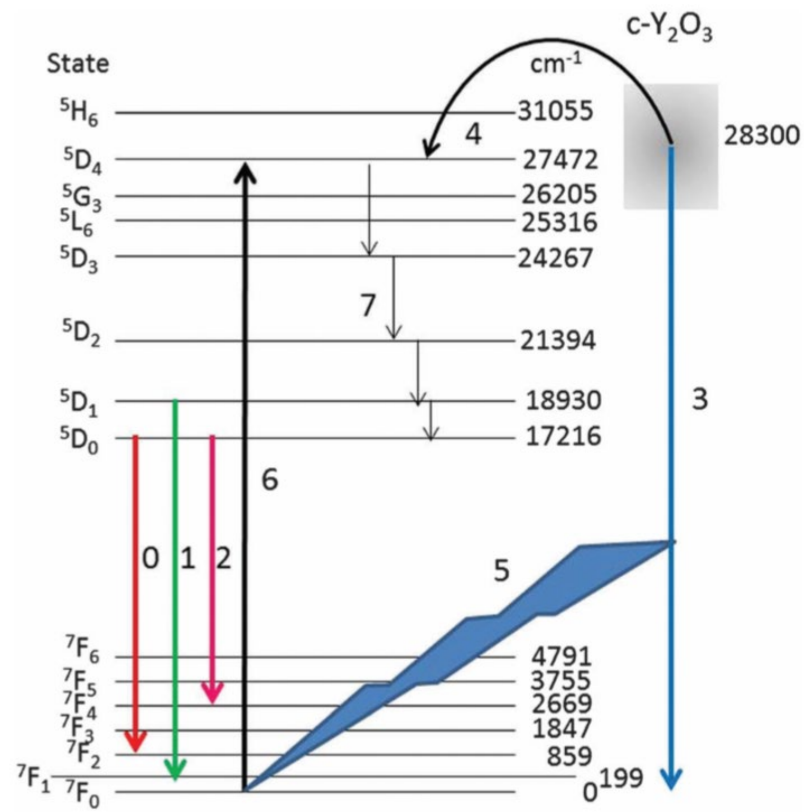
Ultraviolet and blue cathodoluminescence from cubic Y_2O_3 and $Y_2O_3:Eu^{3+}$ generated in a transmission electron microscope



Spectra of undoped Y_2O_3 recorded at 80 keV and various temperatures. The inset shows the spectra between 600 and 900 nm at a different vertical scale.



Quenching factor η as a function of Eu^{3+} concentration in Y_2O_3. (1): oxalate-co-precipitated $Y_2O_3:Eu^{3+}$, (2) SM-oxalate-precipitated $Y_2O_3:Eu^{3+}$. Other points are urea-precipitated.



Energy levels of Eu^{3+} in Y_2O_3. The broad intrinsic luminescence of Y_2O_3 has been represented at 28300 cm^{-1} by arrow (3). The arrows (0), (1) and (2) refer to the $^5D_0$ - $^7F_2$, $^5D_1$ - $^7F_1$ and $^5D_0$ - $^7F_4$ Eu^{3+} transitions respectively, while (4) indicates the radiation-less energy transfer from Y_2O_3 to Eu^{3+}. For arrows (5), (6) this process is more dominant at low temperature because of the much stronger UV luminescence of Y_2O_3 and (7) Eu^{3+} doping quenches this process.

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Conclusions

1. EELS is detected by the primary beam and hence very fast but we need to consider CL differently since this is a secondary process.
2. We have demonstrated that ‘large’ phosphor particles show CL emission from adjacent particles resulting in uncertainty of where the CL signal is produced.
3. Hence ‘large’ particle, phosphors, need to be highly dispersed when collecting Cl spectral information.
4. For quantum dots we can distinguish individual particles by CL imaging. Their thinness reduces secondary processes to a level that is not detected by CL imaging. (In this case the limiting factor is the particle size ~13-14nm due to beam damage).
5. For DRs emission is observed when very close to the quantum dot core or when directly exciting the core. Hence we observe CL emission when the electron beam is about 2nm away from the core as demonstrated by using simultaneous HAADF, CL imaging and EELS.
6. In recent studies we have been able to combine CL imaging or CL spectroscopy with EELS and STEM.
7. High resolution CL emission spectra can be obtained from individual luminescent particles to yield a variety of information about their electronic states / emission spectra.

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