

Investigating the Origin of Luminescence in Zinc Oxide Nanostructures With STEM-Cathodoluminescence

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ZnO nanostructures display luminescence in the UV and across the visible spectrum, and show promise as future nanoscale electronic, optoelectronic, and sensing devices [1]. The visible luminescence arises from surface or bulk states at energies inside the ZnO bandgap, however, a fundamental understanding of the luminescent sources is still lacking. The assignment of particular defects to different visible emission peaks is a highly controversial and active area of current research [1,2]. Here, we perform the first spatially resolved scanning transmission electron microscopy cathodoluminescence (STEM-CL) measurements on ZnO nanostructures, and show the emergence of CL spectral peaks associated with morphological changes in ZnO nanorods. Further studies using parallel techniques in the TEM sensitive to intrinsic and extrinsic defects (e.g. HRTEM, atomic resolution HAADF-STEM, EELS, and EDS) will likely conclusively reveal the origin of emission in ZnO and other technologically relevant, luminescent nanostructures.

Unlike photoluminescence, cathodoluminescence can probe the emission properties of individual nanostructures since the electron beam can be condensed to nanometer scale. SEM-CL has been used to study defect emission in individual ZnO structures previously, with studies showing, for example, green emission associated with Zn vacancies [2] and a blueshift in the near-band-edge emission with decreasing particle size[3]. However, SEM cannot resolve atomic features to correlate with emission changes, as SEM resolution is limited to a few nanometers. Cathodoluminescence measurements done in the TEM have this unique capability.

Here, we use a Gatan Vulcan STEM-CL system to measure changes in cathodoluminescence spectra within individual ZnO nanostructures. Figure 1 shows STEM images and a CL spectrum image acquired across an 800 nm long ZnO nanorod. The spectrum image contains 100 individual spectra, each acquired as the electron beam rasters over an area 8 nm long × the width of the nanorod (50 nm). The emission onset at 375 nm is consistent with the near-band-edge in ZnO [1]. Comparison of the CL spectrum image and the STEM images of the same rod illustrates the dramatic changes in visible emission with morphological changes in the nanorod.

The most obvious spectral feature in Figure 1d is the orange emission at ~600 nm. Previously, orange emission has been attributed to surface dislocations, oxygen interstitials, and zinc vacancies; a definitive source remains elusive [1]. Comparing Figures 1c-d it is evident the orange emission is coincident with an increase in HAADF signal. Figure 2 illustrates this more clearly; the amplitude of Gaussians fit to the UV near-band-edge and orange deep-level emissions are plotted as a function of distance along the rod. Other CL spectral peaks also correlate with structural features in the nanorod. There is strong blue emission centered at ~450 nm associated with the tip of the nanorod. There is weak, broad emission centered at ~435 nm in the region with the strong emission at 600 nm. Finally there is weak, but sharp, violet emission at 400 nm, associated with strain in lower portion of the rod, visible in the ADF STEM

image (Figure 1b). Correlating these spectral peaks and morphological changes with further defect investigations promises to reveal the origin of visible luminescence in ZnO nanostructures [4].

References:

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 [3] CW Chen *et al*, *Applied Physics Letters* **88** (2006), p. 241905.
 [4] The authors acknowledge funding from EPSRC grant number EP/K035274/1, and Brunel University and the Experimental Techniques Centre for funding and making available the STEM-CL system, respectively.

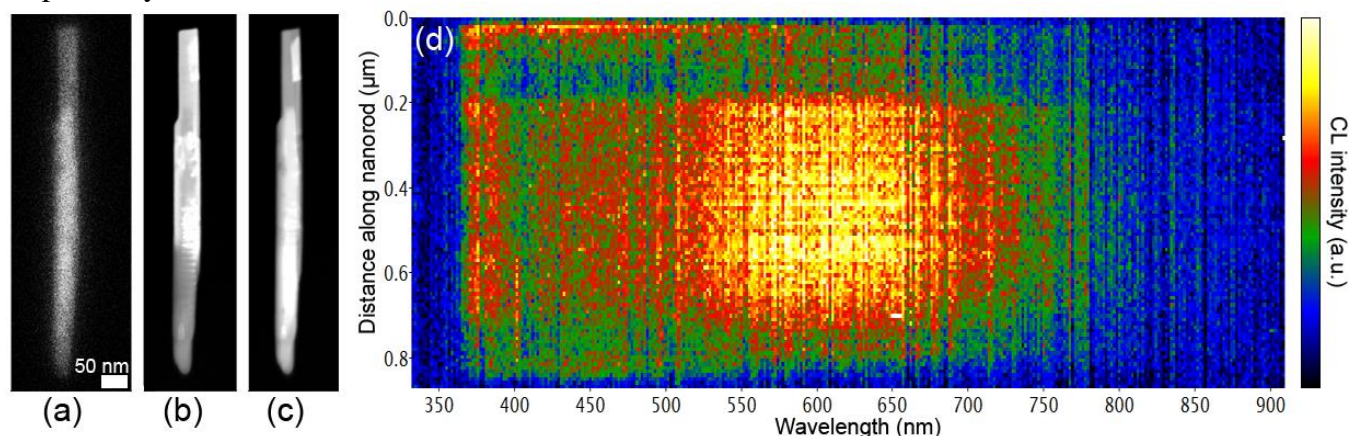


Figure 1. STEM images and CL spectrum image acquired along the length of a ZnO nanorod. Simultaneously acquired (a) panchromatic CL, (b) ADF, and (c) HAADF images. (d) CL spectrum image of the ZnO nanorod pictured in (a)-(c).

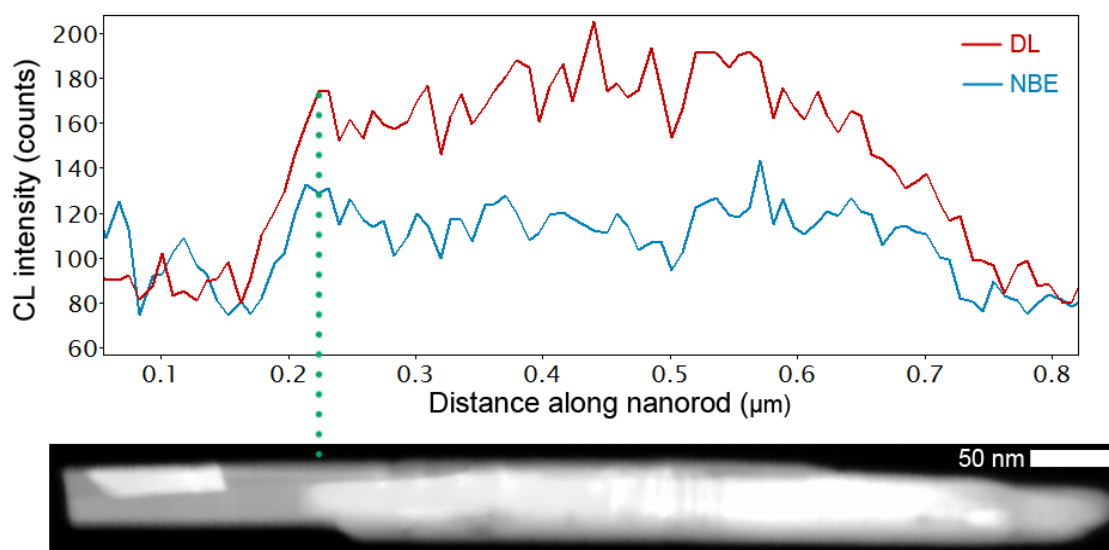


Figure 2. Increase in deep-level (DL) emission intensity relative to the near-band-edge (NBE) intensity associated with morphological changes in the ZnO nanorod. (top) Plot of emission intensity vs. distance along the nanorod for the NBE and DL peaks. (bottom) HAADF image of the nanorod. The green dotted line is added as an aid to the reader to show that the increase in the DL emission is coincident with an increase in HAADF signal.