EELS and SEM-CL investigations of $ZnFe_2O_4$ nanoparticles and iron-decorated inversion domain boundaries in bulk ZnO.

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Zincoxide (ZnO) is a transparent conducting oxide (TCO) with a direct band gap of 3.3 eV. For improved solar energy conversion in photovoltaics, an intriguing possibility is incorporation of semiconducting nanoparticles in the matrix of a TCO, which could provide functionalization of the photovoltaic top-layer which does not currently contribute actively to absorption. Introduction of high iron concentrations in bulk ZnO enables formation of iron-decorated inversion domain boundaries (IDBs) or spinel $ZnFe_2O_4$ nanoparticles (NPs) in the ZnO bulk [1]. The latter case could provide an appropriate functionalized TCO for photovoltaics, as $ZnFe_2O_4$ is a semiconductor with a bandgap of around 2 eV. Inversion domain boundaries are extended planar defects across which the ZnO C-axis rotates 180 degrees [2].

We have investigated absorption and emission properties of iron-decorated IDBs in ZnO and a nanocomposite with spinel $ZnFe_2O_4$ NPs in a bulk ZnO matrix. Samples were fabricated by ball milling of ZnO and Fe_2O_3 (10 cation percent iron) with subsequent heat treatments. Absorption was measured with electron energy loss spectroscopy (EELS) and diffuse reflectance spectroscopy (DRS). Emission properties were probed with cathodoluminescence (CL). Bulk ZnO and $ZnFe_2O_4$ reference samples were also measured with CL. Structural characterization of the samples was done by (scanning) transmission electron microscopy, energy dispersive x-ray spectrometry and x-ray diffraction.

EELS and DRS revealed an absorption onset around 1.9-2.0 eV in the nanocomposite. CL measurements showed an emission component in the same energy range which was absent in the bulk ZnO reference. Position-dependent measurements in EELS and CL confirmed that the absorption was related to the $ZnFe_2O_4$ NPs. The energy of the transition matches the lowest energy NBE transition of $ZnFe_2O_4$ in previous work by Granone et al [3]. An additional absorption onset at around 2.7-2.8 eV was detected with EELS and two further gaussian emission components were found in the CL spectra.

The sample with iron-decorated IDBs had an absorption onset at 1.9 eV in DRS, with EELS showing an onset at 2.7-2.8 eV. CL measurements revealed a large lateral variation in emission spectra. However, we found that the emission was well fitted by combining Gaussian emission components from the two reference samples. Variation of the relative intensity of the components accounted for the variation in spectral shape. CL results indicate that there may be similarities in emission properties between bulk $ZnFe_2O_4$ and iron-decorated IDBs in ZnO.

EELS spectra and selected CL spectra are shown in Figure 1 and Figure 2 respectively.

[1] K. Haug, "Functionalization of transparent conducting oxides Zinc ferrite spinel in ZnO," UiO, 2019.

[2] O. Köster-Scherger et al., “ZnO with additions of Fe2O3: Microstructure, defects, and Fe solubility,” *J. Am. Ceram. Soc.*, vol. 90, pp. 3984–3991, 2007

[3] L. I. Granone et Al. “Effect of the degree of inversion on the photoelectrochemical activity of spinel ZnFe2O4,” *Catalysts*, vol. 9, pp. 1–13, 2019

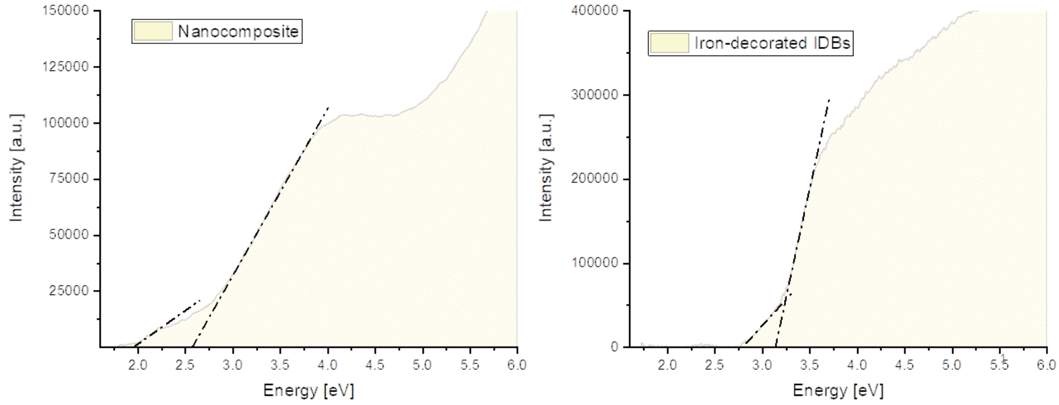

***Figure 1. Left**: EELS spectrum from a single $ZnFe_2O_4$ nanoparticle in bulk ZnO. **Right**: EELS spectrum from the sample containing iron-decorated IDBs.*

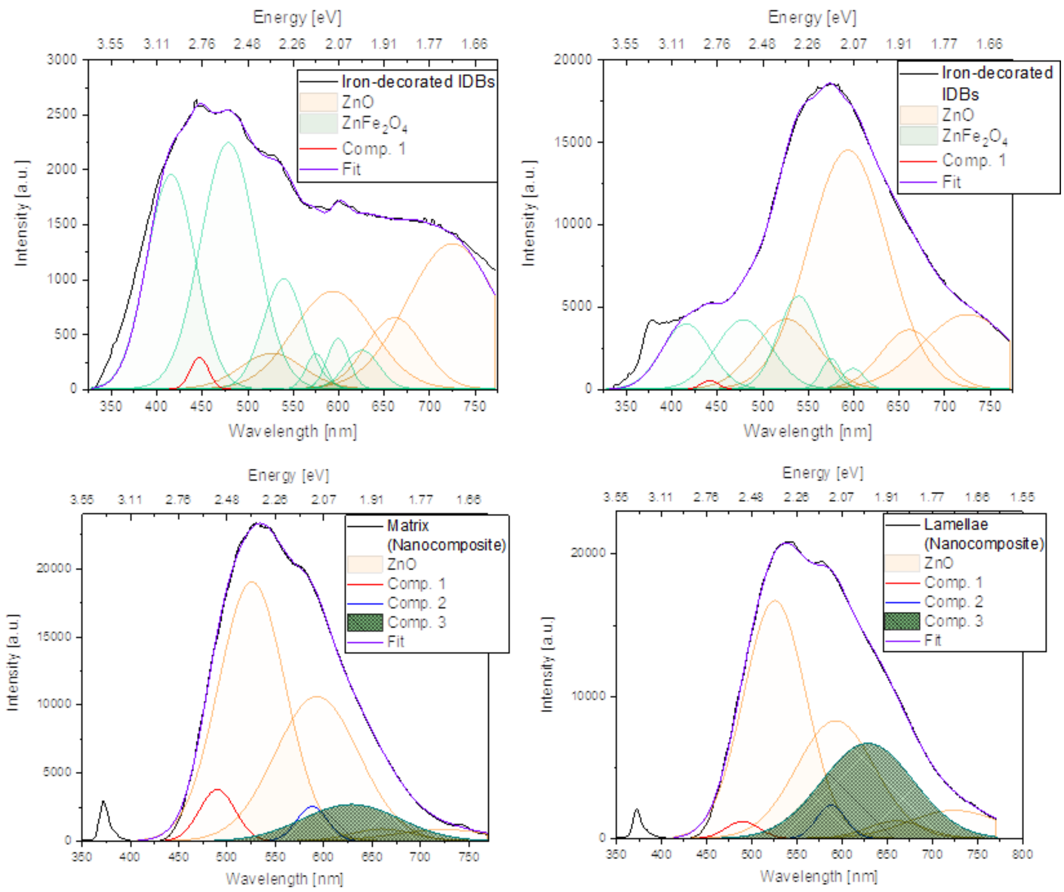

*Figure 2. **Top**: Two CL spectra from the sample containing iron-decorated IDBs with Gaussian curve-fitting. **Bottom left**: CL spectrum from the ZnO matrix of the nanocomposite. **Bottom right** CL spectrum from $ZnFe_2O_4$ nanoparticles in the nanocomposite, showing significant increase in emission around 1.9 eV compared to the spectrum acquired from the matrix. Orange components taken from the ZnO reference and green components taken from the $ZnFe_2O_4$ reference. Component labeling is* not *shared between nanocomposite and IDB samples.*