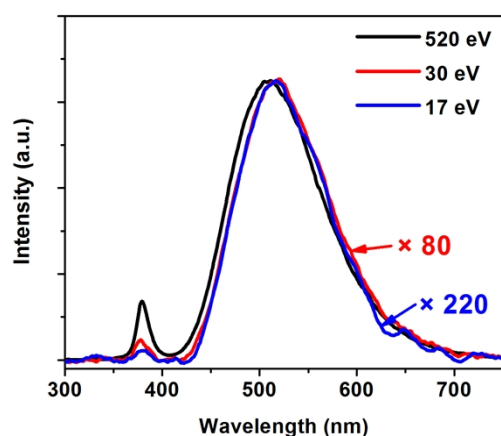


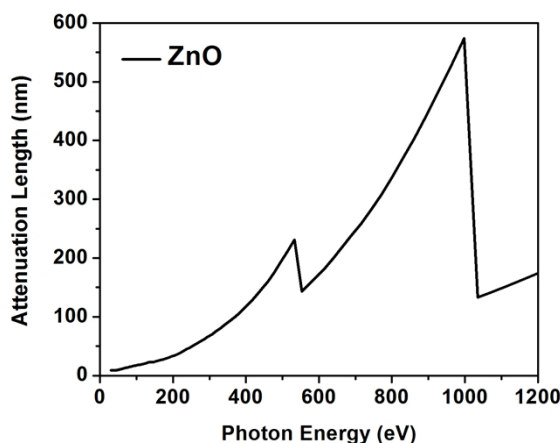
## Supporting Information

### 2D XANES-XEOL Mapping: Observation of Enhanced Band Gap Emission from ZnO Nanowire Arrays

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**Figure S1.** XEOL spectra of ZnO NW arrays with different excitation energies. The spectra with photon energies of 30 and 17 eV were collected at the PGM beamline at Canadian Light Source (CLS). The intensities of the red ( $E_{ex} = 30$  eV) and blue ( $E_{ex} = 17$  eV) curve were magnified 80 and 220 times, respectively.

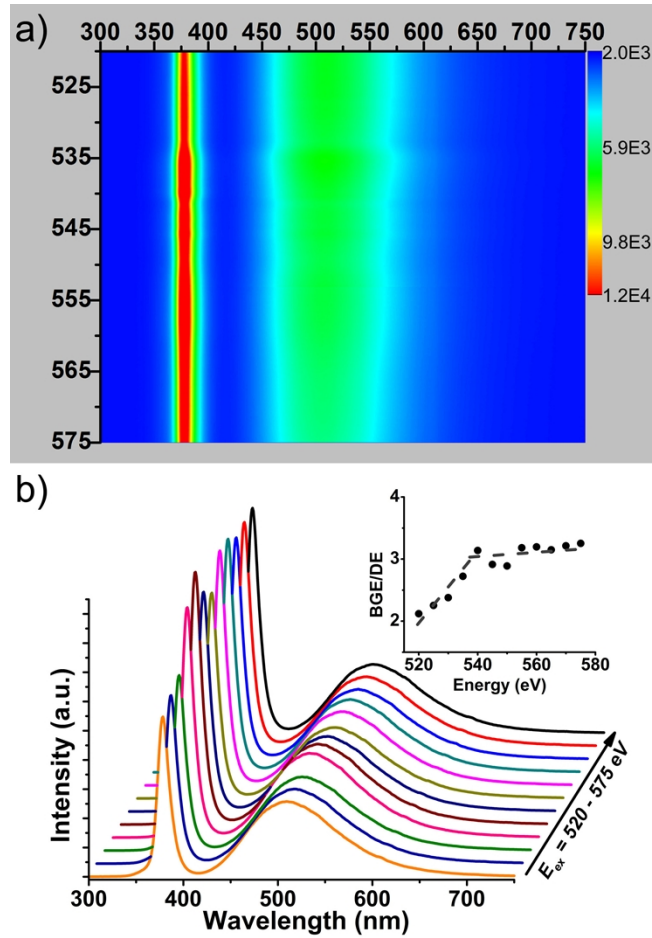


**Figure S2.** X-ray attenuation length vs. photon energy in ZnO. ZnO density =  $5.675$  g/cm<sup>3</sup>, and incident angle = 45 degree ([http://henke.lbl.gov/optical\\_constants/atten2.html](http://henke.lbl.gov/optical_constants/atten2.html)).

Based on our experimental data, the defects are at the near-surface (shallow region) of ZnO NWs. The XEOL spectra of ZnO NW arrays (prior to radiation induced equilibrium) with

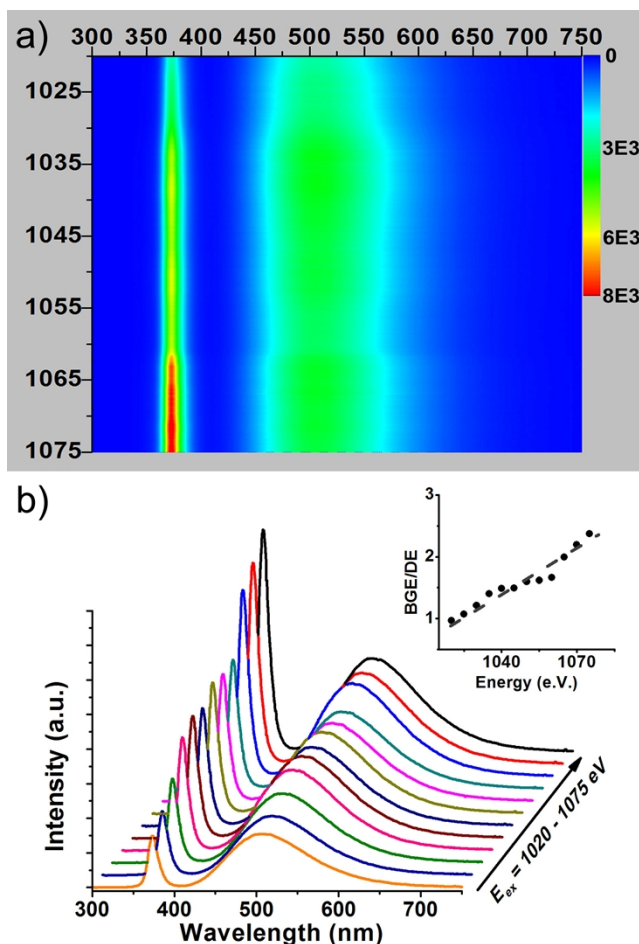
different excitation energies are shown in Figure S1. When the photon energy is turned to 520 eV, X-ray attenuation length is about 220 nm that is larger than the diameter of ZnO NWs. Therefore the luminescence (black curve in Fig. S1) comes from the bulk. When the photon energy is turned to 30 eV, X-ray attenuation length decreases to around 9 nm (see Fig. S2). The luminescence (red curve in Fig. S1) comes from the near surface region of ZnO NWs. Comparing these two XEOL spectra, the intensity ratio between BGE and DE of the red curve (surface signal) is much smaller than that of the black curve (bulk signal). With further decrease of the X-ray energy (e.g.: 17 eV), the intensity ratio of BGE/DE dramatically decreases and the BGE is almost negligible (blue curve in Fig. S1). It indicates that the defects are located at the near surface region of ZnO NWs (if the defects are in the bulk, the intensity ratio of BGE/DE should not change too much when turning the photon energy from 520 to 30 eV (bulk vs. near-surface)). Note that the “near surface region” described here is to be distinguished from the very surface (the first atom layer) of the nanostructure.

A. Janotti and C. G. Van de Walle (Appl. Phys. Lett. 87, 122102(2005)) reported first-principles calculations of ZnO showing that the oxygen vacancy has a deep  $\epsilon(2+/0)$  level at about 1.0 eV below the bottom of conduction band and the luminescence results from hole capture by the neutral vacancy. In our paper, the DE of ZnO NW arrays locates at 509 nm (about 2.4 eV, which agrees with the above calculation) is determined to come from oxygen vacancy. Combined with the XEOL result (see Figure S1), the defect is oxygen vacancy at the near surface region of ZnO NWs.

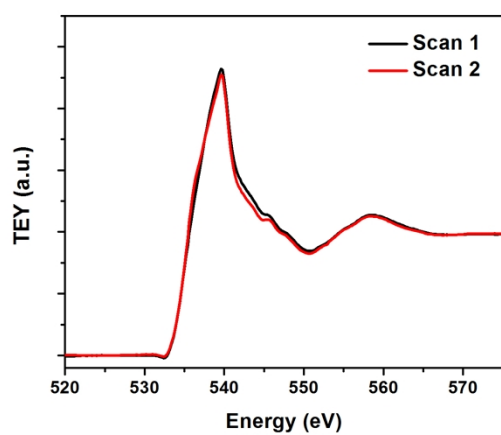


**Figure S3.** a) The second 2D XANES-XEOL map of the ZnO NW arrays with excitations at the O K-edge at the same spot (spot #1) where the first map was measured. The x-axis is the emission wavelength in nm and the y-axis is the excitation energy in eV. The color represents the intensity of XEOL excited across the absorption edge. b) XEOL cuts taken across the O K-edge (horizontal cuts taken in the 2D XANES-XEOL map). The inset shows the intensity ratio of BGE/DE (height) versus excitation energy.

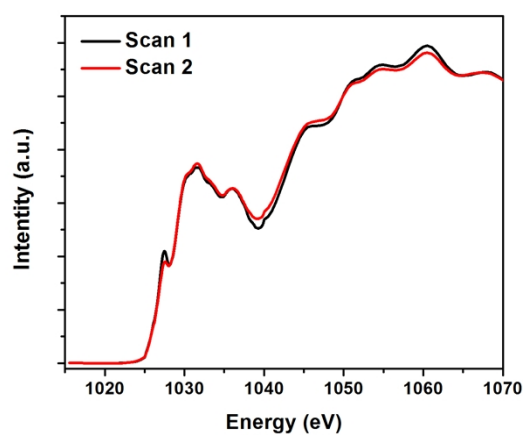
To ensure reproducibility, the O K-edge 2D XANES-XEOL map (see Figure S3) was repeated at the same sample spot (spot #1) where the first 2D XANES-XEOL map (Figure 2) was obtained. Representative XEOL spectra with different excitation energies are shown in Figure S3b. The same phenomenon that BGE increases with photon energy was observed in the second scan. It should be noted that the sharp BGE of the ZnO NW arrays is dominant in all the XEOL spectra that is different from the observation in the first 2D XANES-XEOL map (Figure 2). As shown in the inset of Figure S1b, the intensity ratio  $I_{BGE}/I_{DE}$  shows a gradual increase when the excitation energy increases from 520 to 540 eV and then keeps constant in the range of 540-575 eV. The difference between the first and the second scan indicates that there is an induction period of X-ray exposure for the specimen to reach a steady state.



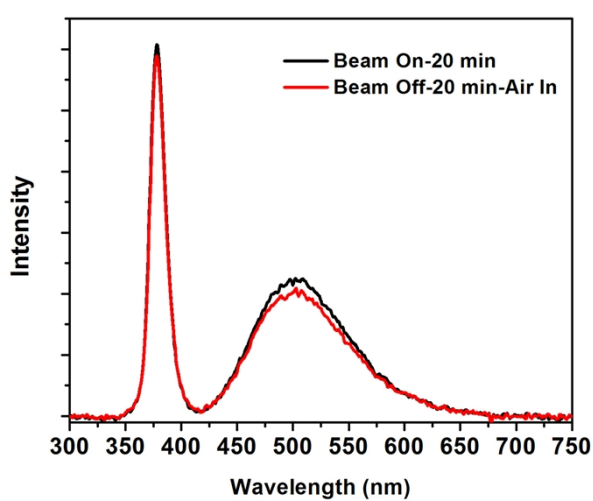
**Figure S4.** a) The second 2D XANES-XEOL map of the ZnO NW arrays with excitations at the Zn L-edge at the same spot (spot #2) where the first map was measured. The x-axis is the emission wavelength in nm and the y-axis is the excitation energy in eV. The color represents the intensity of XEOL excited across the absorption edge. b) XEOL cuts taken across the Zn L-edge (horizontal cuts taken in the 2D XANES-XEOL map). The inset shows the intensity ratio of BGE/DE (height) versus excitation energy.



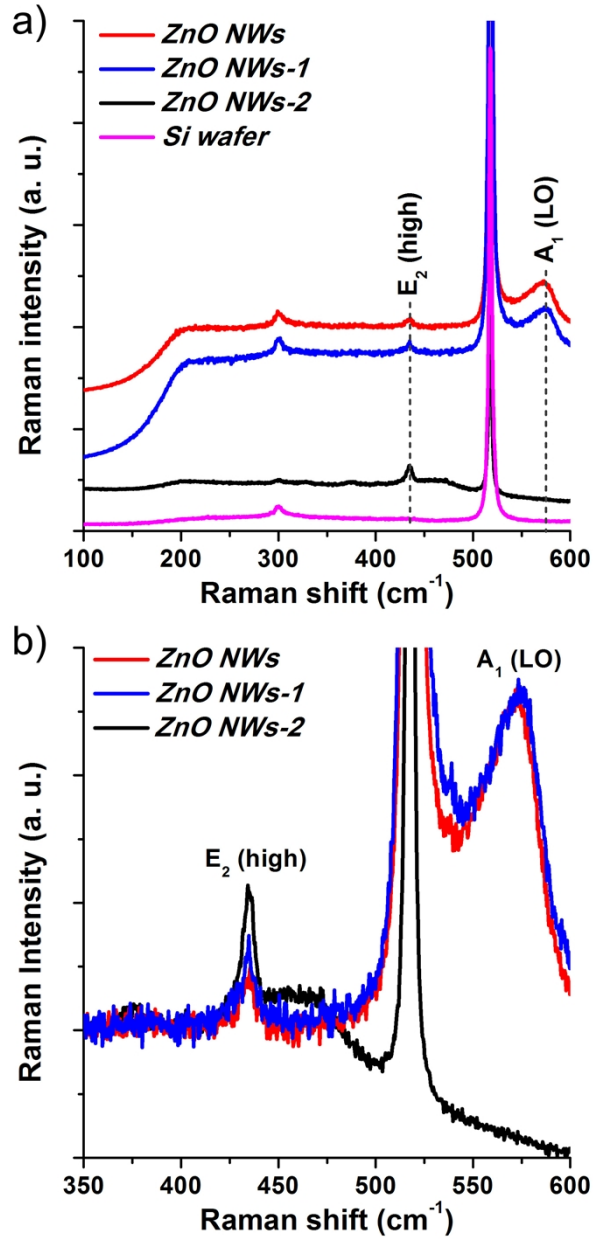
**Figure S5.** TEY spectra in the first and second O K-edge scan at sample spot #1.



**Figure S6.** TEY spectra in the first and second Zn L-edge scan at sample spot #2.



**Figure S7.** XEOL spectra of ZnO NW arrays before and after ventilation (540 eV at sample spot #3).



**Figure S8.** Raman spectra of the ZnO NWs with different intensity ratios of the BGE and DE ( $I_{BGE}/I_{DE}$ : ZnO NWs < ZnO NWs-1 < ZnO NWs-2). ZnO NWs-1 and ZnO NWs-2 were prepared via the same method used to synthesis the ZnO NWs, but with different experiment parameters. b) amplifies the spectral region from 350 to 600 cm<sup>-1</sup> in a).