

Raman and Photoluminescence Spectroscopy Detection of NO₂ gas Adsorbed on ZnO Nanowires

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Summary:

NO₂ detection via optical techniques is of significant interest for gaining deeper insight into gas sensing mechanisms. ZnO nanowires represent an excellent model system due to their high surface-to-volume ratio and defect-mediated surface reactivity, which enhance sensitivity to adsorbed species. NO₂ adsorption induces charge transfer processes that modulate oxygen vacancy-related states, leading to measurable changes in both Raman spectra and photoluminescence emissions. The effect of NO₂ adsorption on the ZnO nanowires surface was investigated by Raman spectroscopy, observing an increase in the LO phonon band around 550 cm⁻¹, and related to the PL contribution.

Keywords: spectroscopic detection, Raman, Photoluminescence, ZnO nanowires, nitrogen dioxide

Background, Motivation and Objective

The detection of nitrogen dioxide (NO₂), a toxic and highly reactive pollutant, is crucial for environmental monitoring and industrial safety. Optical sensing approaches based on semiconducting metal oxides have attracted significant attention due to their high sensitivity, fast response, and potential for real-time, non-invasive detection. Moreover, these techniques possibly allow us for a deeper understanding of the interaction of the gas molecules with the material surface and ultimately to the gas sensing mechanisms. Among semiconducting metal oxides, ZnO nanowires (NWs) are known as perfect candidates for their wide band gap (~3.37 eV), large exciton binding energy, and high surface-to-volume ratio, which enhances gas adsorption and surface reactions [1,2]. Upon NO₂ adsorption, charge transfer processes occur at the ZnO surface, leading to modifications in defect states, particularly oxygen vacancies, and changes in both vibrational and electronic properties. Raman spectroscopy is sensitive to lattice disorder and defect-related features, such as the enhancement and broadening of longitudinal optical (LO) phonon modes (~550 cm⁻¹), indicative of oxygen vacancy-related surface defects [3]. Although direct in situ Raman studies on ZnO nanowires under NO₂ are limited, in-situ and operando Raman spectroscopy has been applied to gas sensors [4]. Complementarily, photoluminescence (PL) spectroscopy probes electronic transitions and defect levels, where NO₂ adsorption typically results in modulation of near-band-edge emission and deep-level luminescence associated with intrinsic defects [5]. In our previous work [6], it has been shown that the different PL contributions of ZnO NWs act differently during NO₂ exposure,

giving rise to reversible and irreversible effects. NO₂ adsorption on ZnO nanowires modifies surface charge and defect states, which in turn affects not only electronic recombination but also lattice-related properties probed optically. The observed changes in surface and defect-related emissions imply a coupling between gas-induced charge transfer and polar optical modes, consistent with the sensitivity of ZnO longitudinal optical (LO) phonons to surface electronic conditions. In the present work, we investigated the effect of NO₂ adsorption on the ZnO nanowires surface in the LO phonon band around 550 cm⁻¹, in the Raman spectrum, and related it to the PL contribution.

Experimental Method

ZnO NWs were synthesized by hydrothermal method onto FTO substrate and characterized by scanning electron microscopy (SEM, Fig. 1).

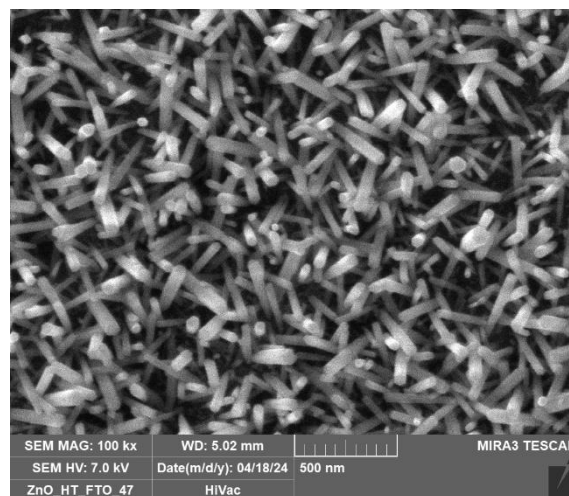


Fig. 1. SEM image at 100 kX magnification of ZnO NWs grown on FTO substrate.

Raman and photoluminescence spectroscopy were carried out on the ZnO NWs sample inside a Linkam stage (HFS600E-PB4), with a Horiba XploRA PLUS system, using a 50x Long Working Distance objective. For Raman spectra, excitation wavelength was 532 nm and grating 1800 l/mm; for PL excitation wavelength was 325 nm and grating 600 l/mm. Dry air and NO₂ gas (5 ppm) were flowed through mass flow controllers in the Linkam stage ($V \approx 33 \text{ cm}^3$) with a rate of 50 sccm. All the experimental measurements were carried out at room temperature.

Results

Before NO₂ gas exposure, ZnO NWs and FTO substrate were characterized by Raman spectroscopy in dry air (RH=0) atmosphere (Fig. 2a). Typical Raman signal from ZnO was observed, with the main wurtzitic phase Raman modes: E_2^{high} (438 cm⁻¹), second order peaks at 200 cm⁻¹ (overtone of the E_2^{low} mode out of detected range) and at $\sim 330 \text{ cm}^{-1}$ due to the combination of $E_2^{\text{high}}-E_2^{\text{low}}$. Linkam stage was then filled with 5 ppm NO₂ gas in dry air at 50 sccm for 30 minutes. In Fig. 2b, the Raman spectrum after NO₂ exposure (red solid line) of ZnO NWs is shown (acquisition time 5 s). An increase in the LO phonon band ($\sim 550 \text{ cm}^{-1}$) was observed. Later, a second spectrum with 60 s acquisition time was collected (not shown here), giving a prolonged laser (532 nm) exposure of the investigated area. The LO band decreased as shown in the second spectrum (red dashed line) of Fig. 2b, obtained with the same parameters (same acquisition time of 5 s). The decreasing of the LO band is interpreted as an effect of NO₂ laser-induced desorption from ZnO NWs surface.

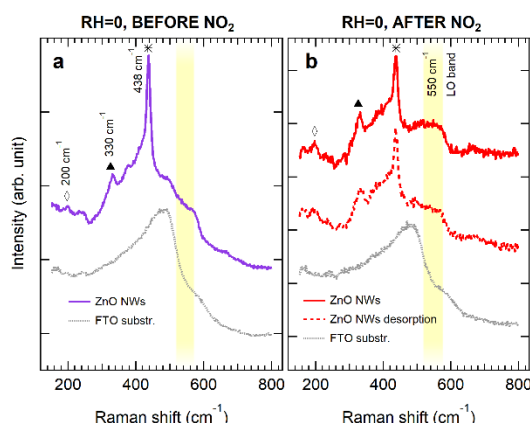


Fig. 2. Raman spectra of ZnO NWs on FTO substrate, (a) before and (b) after 5 ppm NO₂ exposure.

Further investigation is needed to better understand this effect. However, it is already possible to notice how the LO phonon mode variation is strongly related to the adsorbate on the surface. In our previous work [6], a different PL emission at 77 K of the isolated ZnO NWs with different

diameters was observed (Fig. 3), allowing to discriminate “bulk” and surface effects. Three different PL regions were detected: the surface related spectral region around the peak at $\sim 3.35 \text{ eV}$, the donor-acceptor pair (DAP) region centered at $\sim 3.31 \text{ eV}$ and the first order LO phonon replica of DAP (DAP-LO) at lower energy $\sim 3.23 \text{ eV}$. The DAP-LO (signal related to “bulk” ZnO where the optical phonon can propagate) is the only PL region that shows a signal recovery [6] and this is consistent with Raman observation on bundles of ZnO NWs.

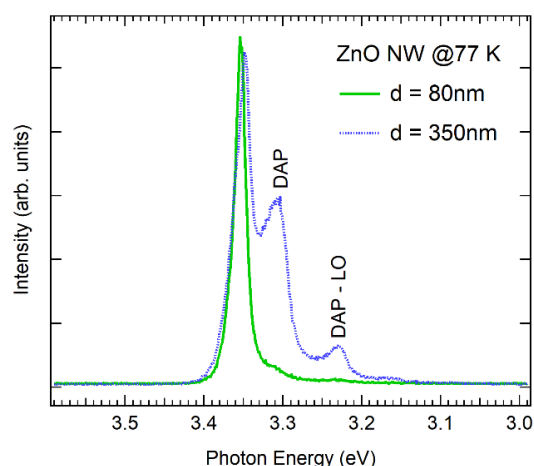


Fig. 3. Photoluminescence emission of two isolated ZnO NWs with different diameters (80 nm, green solid curve and 350 nm, blue dashed curve).

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