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On the Resonance Raman excitation of Zinc Oxide nanoparticles

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Our project aims to develop novel nanosubstrates for Surface-enhanced Raman scattering (SERS) and Surface-enhanced fluorescence (SEF) based on zinc-oxide nanoparticles

INTRODUCTION

ZnO NPs have been extensively used in the industry and investigated in various application fields such as electronics, optoelectronics, biomedicine, agriculture, food and cosmetics. We synthesized a series of ZnO NPs of different morphologies (spherical, polyhedral, flowers) and diameters [1]. The NPs were analysed using Raman spectroscopy under non-resonant 532 nm and near-resonant 442 nm excitation. In ambient conditions, ZnO exists in the hexagonal wurtzite structure, showing 6 Raman-active bands - the unipolar E_2 mode, consisting of E_2^{low} and E_2^{high} components and the polar A_1 and E1 modes, both separated into longitudinal (LO) and transversal (TO) components (Fig. 1).

ANALYSIS

Renishaw InVia confocal microscope; 442 and 532 nm lasers;
ZnO NPs prepared by drop-coating method: dry nanoparticles were mixed with distilled H_2O and deposited on CaF_2 or quartz plates. Measurements with 100x objective upon water evaporation.
Band shapes analysed by fitting with Gaussian profiles.

REPORTED OBSERVATIONS

Studies usually report the increase of the A_1(LO) mode intensity (570 - 585 cm^{-1}) and its overtones up to four times, as well as of the photoluminescence emission observed in the visible range (~ 470 nm) [2] (Fig. 2).

OUR OBSERVATIONS

- E_2^{high} band position depends on the ZnO NPs morphology (spherical NPs 440 cm^{-1}, flower-like shapes 449 cm^{-1});
- High g=1.96 EPR signal (not shown here) and low green emission – lowest E_2^{high} position, while ZnO NPs showing negligible g=1.96 EPR signal presented blue shifts;
- Immense widening (4-5 fold) and several wavenumbers shift of the non-polarizable E_2^{high} band [3] for the 442 nm excitation (Fig. 2).

DISCUSSION

While the increase of the LO bands are commonly explained by Raman scattering by considering the dominant electron-phonon interactions (macroscopic electric field generated in the primitive cell by the relative displacement of oppositely charged atoms) at resonance excitation, considerably less is known about the vibrations giving rise to the E_2(high) band.

OUTLOOK

The UV-Vis absorption spectra of our samples (Fig. 3) indicate that our observation is wavelength-dependent rather than a resonance effect. Nevertheless, E_2(high) widening was not reported before and provides a gateway to further investigations.

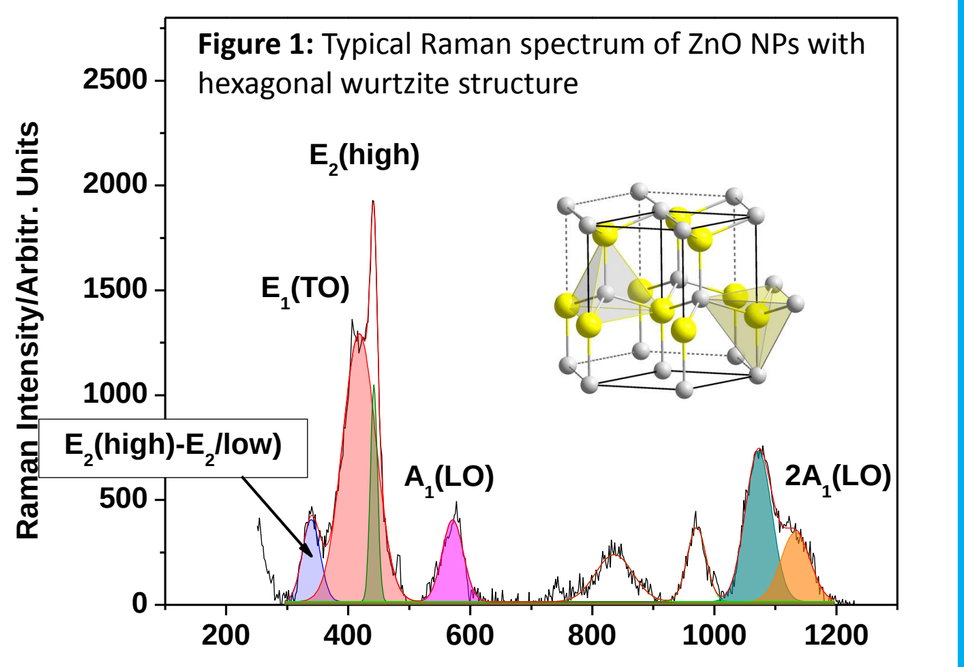


Figure 1: Typical Raman spectrum of ZnO NPs with hexagonal wurtzite structure

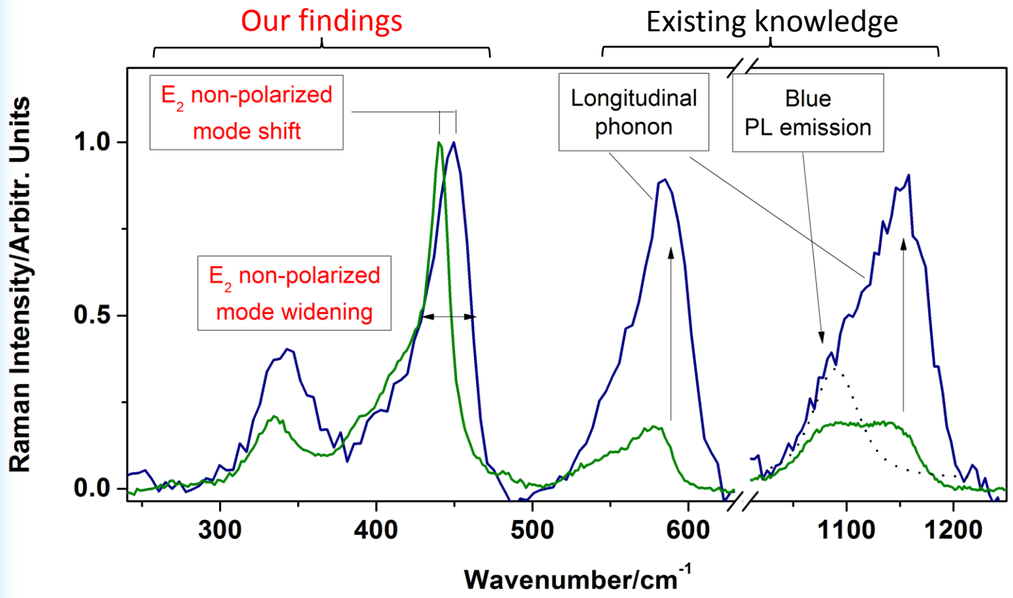


Figure 2: Comparative analysis of representative Raman spectra obtained from ZnO NP (d = 7.9 nm) recorded with non-resonant 532 nm (green spectrum) and near-resonant 442 nm (blue spectrum) excitation

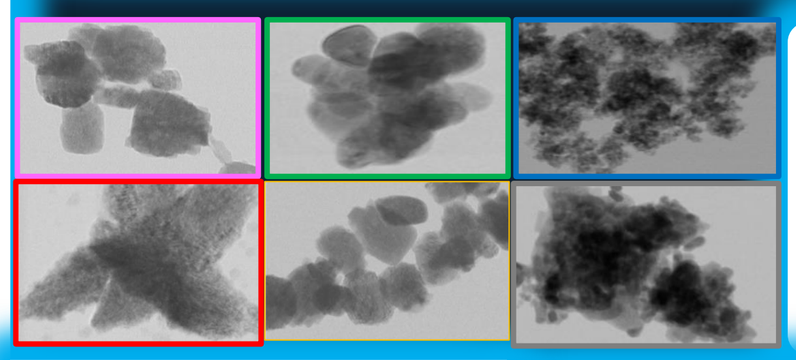
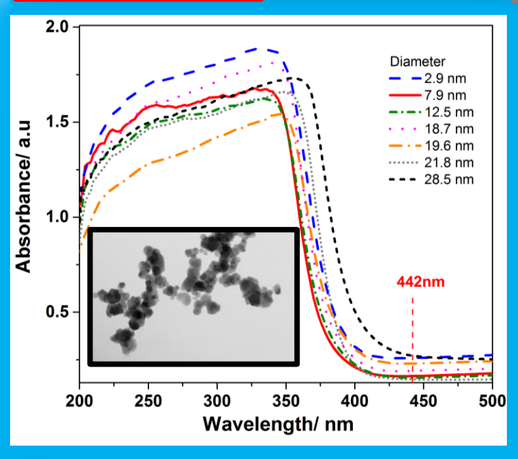
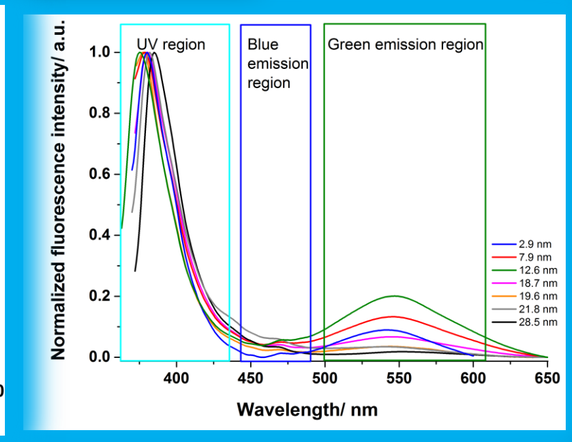


Figure 3: UV/Vis absorption (left) and fluorescence emission (right) spectra of the investigated ZnO NPs, with SEM images (color-coded)





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