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Title: Micro/nanoscopic Investigation of ZnO towards the Development of Next-generation Separation Platforms

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The overall goal of the project was i) to generate well-defined zinc oxide (ZnO) nano and microstructures in the forms of 2D (thin film), 1D (nanorods, microrods), and 0D (nanoparticles, microparticles) and ii) to examine their crystalline facet-specific chemical reactivity for the design of better separation platforms.

We first established reliable synthetic routes to produce various forms of ZnO materials such as nanorods, nanoparticles, microrods, and microparticles. We have then characterized the as-synthesized (or purified) materials by spectroscopic and imaging tools such as SEM, AFM, pXRD, EDAX, ATR/FTIR, UV-Vis, and Raman. Among the various ZnO forms produced, the NR ensemble samples were further exploited as an active channel in a photodetector device operating not only in the UV but also in the visible wavelength range. The ZnO nanorod (NR)-based devices demonstrated extremely high electrical responses upon light illumination. The outcomes of this endeavor have been reported in ***Nanotech*. 28, 145203, (2017)**. The study outcomes were also filed in a provisional patent application and, subsequently, as a utility patent application.

*D. S. Choi, M. Hansen, E. V. Keuren, and J. Hahm, Highly photoresponsive, ZnO nanorod-based photodetector for operation in the visible spectral range, Nanotechnology, **28**, 145203 (2017); J. Hahm, D. S. Choi, M. Hansen, E. V. Keuren, ZnO Photodetector, U.S. Provisional Patent Application No. 62/426,055 (2017); J. Hahm, D. S. Choi, M. Hansen, E. V. Keuren, ZnO Photodetector, U.S. Utility Patent Application No. PCT/US17/062795 (2018).*

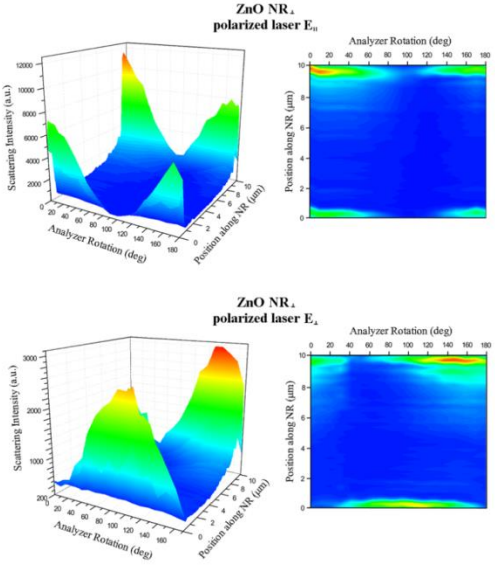

Figure 1. Scattering of a single ZnO NR measured by using two polarization directions of an incoming laser (**E**∥ and **E**⊥) on a NR oriented along the x-axis (ZnO NR⊥**)**. Scattering intensity was measured with respect to the position along the length of the 1D nanomaterial as well as the analyzer angle.

In a parallel endeavor, we also examined the potentially different degrees of chemical reactivity depending on the crystalline facets present within individual ZnO nano- and micro-materials. In addition to the direct imaging methods of AFM and SEM which can provide information on the morphological changes of the crystal surface, an optical scattering-based method capable of providing a subcrystal-level spatial resolution was used to determine position-resolved and crystalline facet-dependent optical and chemical responses from the samples. An example based on elastic scattering is shown in Figure 1 below below whose representative 3D contour and 2D surface plots reveal the typical Mie scattering characteristics measured from individual ZnO NRs. The elastic scattering intensity profile is resolved from the different positions on a single NR.

An inelastic scattering technique of Raman has been increasingly exploited as a noninvasive and sensitive analytical tool to investigate the material properties pertinent to separation and sorption. We have also employed Raman scattering to examine as-grown ZnO nano- and micro-structures as well as those reacted with various sulfur sources in gas and aqueous phases. Firstly, we carefully examined unreacted forms of individual ZnO structures in order to discern any material position-dependent chemical signal differences via the change in intensity and position of ZnO- versus ZnS-related Raman peaks. We determined that this position-dependent signal difference is important for the ZnO NR crystals since their high shape anisotropy (length to width) can lead to unusual Raman scattering behaviors at the two ends of the NRs relative to the main body.

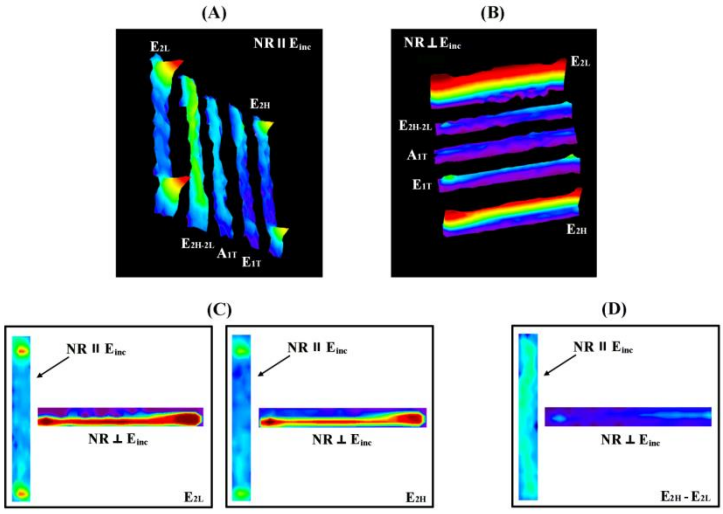

Figure 2. Raman intensity maps of the five ZnO phonon modes identified from a ZnO NR are displayed combinedly for the different light-matter interaction geometries. The data show strongly NR position-dependent Raman scattering profiles for the minor phonon modes per given orientation, whereas the major modes for each orientation display continuous and persistent Raman intensities distributed all along the entire NR length.

In brief, we quantified Raman signals from the five key ZnO phonon modes of E_{2L}, E_{2H-2L}, A_{1T}, E_{1T}, and E_{2H}, and revealed the NR position-dependent Raman scattering characteristics of the phonon modes per given light-matter interaction geometry. We then presented Raman intensity maps and elucidated Raman behaviors that are not only consistent but also incongruous with the predictions from Raman selection rules. In particular, we have identified an intriguing Raman scattering phenomenon from the forbidden modes, distinctively occurring at the two NR ends. Their unexpectedly strong and localized scattering signals at the NR termini were contrasted by the scattering behaviors from the rest of the NR positions agreeing with the selection predictions. Subsequently, by carrying out control measurements on isotropic ZnO MPs, we ascertained that the unique NR position-specific Raman responses observed on ZnO NRs originated from their high shape anisotropy.

Characterizing such position-dependent behaviors will be crucial for the accurate determination and interpretation of the facet reactivity differences measured from sulfur-reacted ZnO crystals. Hence, for the first time, we performed a systematic investigation to understand the Raman outcomes of the highly anisotropic ZnO NRs versus isotropic ZnO NPs/MPs at the individual nanomaterial level. An example of our major findings can be seen from the Raman mapping data presented in Figures 2 and 3 for ZnO NRs and ZnO MPs. Detailed results and discussions on the Raman scattering work can be found in ***Nanoscale*, 9, 8470-8480, (2017)**.

*M. Hansen, J. Truong, T. Xie, and J. Hahm, Spatially distinct Raman scattering characteristics of individual ZnO nanorods under controlled polarization: Intense end scattering from forbidden modes, Nanoscale, **9**, 8470-8480 (2017).*

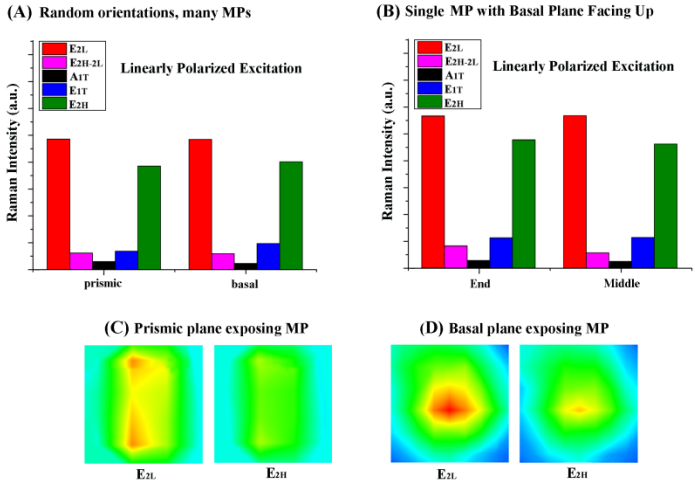

Figure 3. Raman data collected from isotropic ZnO MPs are summarized. The same trend in the Raman mode intensities were observed regardless of the different positions on each facet examined. In all cases, the strongest signals were produced by the E_{2L} and E_{2H} modes.

We have now completed combined measurements on sulfur-reacted samples of ZnO NRs and NPs/MPs. We systematically determined the different chemical reactivities associated with various crystalline facets on the ZnO nanocrystals. Imaging, spectroscopic, scattering, as well as optical measurement techniques were used for this investigation which included SEM, XRD, UV-Vis, ATR/FTIR, PL, and Raman. A manuscript reporting our key findings from the study was submitted over the summer under the title of 'Single Nanomaterial Level Investigation of ZnO Nanorod Sulfidation Reaction via Position Resolved Confocal Raman Spectroscopy' which is currently under review.

M. Hansen, J. Truong, B. Szychowski, T. Xie, M.-C. Daniel, and J. Hahm, Single nanomaterial level investigation of ZnO nanorod sulfidation reaction via position resolved confocal Raman spectroscopy, submitted (2018).