PROBING THE PHYSICAL AND CHEMICAL PROPERTIES OF ZINC OXIDE NANORODS USING CONFOCAL RAMAN SPECTROSCOPY

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By

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ABSTRACT

Zinc Oxide (ZnO) is a known waveguiding material whose bulk properties have widely been studied using Raman spectroscopy. Confining the material to the nanometer size domain affects the light-matter interaction of the material, leading to many interesting and useful phenomena which make ZnO nanomaterials promising candidates for development of nanometer sized probes for a variety of spectroscopic techniques. Raman spectroscopy is a powerful vibrational spectroscopic tool which can provide both concentration and structural data for a variety of molecules and is especially useful in biological matrices where water interference is problematic for other vibrational techniques. In developing ZnO nanorods (NRs) as miniature Raman probes, it is paramount to understand how the physical and chemical properties of this material are affected by nanometer size constraints to fully exploit their potential as substrates.

Spatially resolved Raman spectroscopy was used to probe the unique light-matter and chemical properties of ZnO NRs. The position-resolved Raman scattering revealed behaviors both consistent and inconsistent with selection rules. More specifically, I observed the appearance of geometrically forbidden modes exclusively at the ends of the NRs. This was accompanied by an increase in the intensity of the allowed modes at the ends of the NRs. Building on these findings, ZnO NRs were reacted with hydrogen sulfide (H₂S) in order to understand facet specific reactivity of the ZnO NRs. I demonstrated that the end facets of the NRs are more reactive than the side
facets towards sulfidation, owing to their chemically unique surface. Finally, I demonstrate that
the inclusion of copper into the ZnO crystal lattice alters the Raman properties of the ZnO NRs in
two different ways. First, incorporation of Cu in the crystal lattice leads to a shift in the $E_{2\Gamma}$ mode
and secondly, the copper leads to symmetry breaking allowing for the appearance of non-Raman
active peaks. These insights should prove to be an important base of knowledge for further
development of ZnO NR probes.
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Chapter 1. Introduction

1.1. Optical Properties of Zinc Oxide Nanorods

Zinc Oxide nanorods (ZnO NRs) are an emerging important tool used for many optical and electronic applications, including waveguiding, lasing and light generation, bio detection, and photovoltaics owing to their unique chemical and physical properties. These same properties make them ideal candidates for use as miniature sized probes which can be used to deliver and collect light to and from areas much smaller than traditional techniques. The material properties of ZnO which make it an ideal substrate for this task are its wide band gap (~3.3 eV), large refractive index (~2.2 in the visible region), ability to enhance optical signals, and facile defect free synthesis.

1.1.1. Zinc Oxide Bandgap

The large band gap assures that there is no fluorescence in the visible range, since excitation and emission happen in the UV regime (355 and 388 nm for excitation and emission, respectively). Additionally, this material can be used as a light generating source. If the NR is supplied with enough excitation light, stimulated bandgap emission is possible resulting in lasing from the NR. Interestingly, because of the small diameters of the ZnO NRs, they can be used as a sub-diffraction limit source capable of delivering light in smaller volumes than traditional methods.

The facile synthesis means that optical quality NRs with well-defined size, shape, and in any array of patterns suitable for analytical substrates can be made. Defect free ZnO NRs are extremely important as they ensure that there is no visible light fluorescence to interfere with measurements, since defect emission of ZnO materials appears between 500-600 nm.
Being able to precisely control the physical dimensions of the ZnO NRs means that their lengths and widths can be tuned for specific uses. For waveguiding this is extremely important, the widths of the NRs can be controlled to maximize the waveguiding modes overlap with the excitation source to maximize efficiency.\textsuperscript{10, 27} As has been previously shown, the aspect ratio is important when directing light to the ends of the NRs, with the effect increasing with the increasing aspect ratio.\textsuperscript{34} This makes it possible to fabricate nanoprobes or arrays of nanoprobes to fit a variety of applications.

1.1.2. Zinc Oxide Refractive Index

The high refractive index makes this material an ideal substrate for visible light wave guiding. By reducing the dimensions of the material to nanometer size, the high refractive index allows this material to trap and guide light that is larger than the diameter of the material, a phenomenon known as subwavelength waveguiding. Figure 1 shows a ZnO NR with a width less than 350 nm illuminated with three different wavelengths of light, 405 nm (B), 532 nm (C) and 785 nm (D).
For each of the two smaller wavelengths, the light is clearly being guided to the end of the NR, while for the 758 nm light, the light is not being efficiently guided hence no light is observed at the far end of the rod. This also highlights an important aspect of the sub wavelength guiding, the interplay between the refractive index and the width of the material.$^{10, 27}$ The physically important part to waveguiding is the refractive index (RI), the high RI is what enables the material to trap light into the material’s waveguide modes, and it also dictates the minimum and maximum physical dimensions for waveguiding.$^{10, 27, 29}$ From Figure 1, it is apparent that 785 nm light is too long to be captured efficiently by the waveguiding modes of ZnO at this width of material, hence it is not guided well towards the opposite end. Since I will be focusing on ZnO NRs in this dissertation, the small diameter of the material compared to the wavelength of light means that the majority of the electromagnetic energy of the guided light should be carried outside of the NR. This creates an electromagnetic field around the NR which can extend several tens to over a

Figure 1: Waveguiding light through a zinc oxide nanorod. (A) ZnO NR without illumination, (B) illuminated with 405 nm laser, (C) illuminated with 532 nm laser, and (D) illuminated with 785 nm laser. The red arrows designate where the laser is being focused on the NR and the white arrow indicates where the guided light is being emitted. (B) and (C) clearly show the light being guided to the far end of the NR, while no light appears to be guided in (C).
hundred nanometers beyond the material.\textsuperscript{10, 29} This evanescent field can be used to excite only molecules very close to the surface reducing interference from the surrounding medium.\textsuperscript{10, 16-17, 27, 29, 34} Fine tuning the width of the material for a given wavelength and refractive index, the penetration of the evanescent field into the surrounding medium can be adjusted.\textsuperscript{27} This is illustrated in Figure 2. Figure 2A demonstrates calculations for the fraction of guided light ($\lambda = 532$ nm) for different waveguide modes and materials with different refractive indices, the solid line is for a material with the same refractive index of ZnO. Apparent from this figure is that there are widths where a maximum amount of waveguiding occurs for each of the different modes. The maximum intensity of the guided light occurs at the intersection of the RI with the ideal width of the given material.\textsuperscript{25} More importantly, Figures 2B and 2C, demonstrate where the guided light is carried through the material. These calculations were done using 761 nm light. In Figure 2B, a rod of 400 nm (red) carries most of the guided light along the surface allowing the evanescent wave to penetrate deeply into the surrounding medium. When the diameter increases to 1000 nm (black), most of the guided light is carried through the core of the material and very little is penetrates to the surroundings.\textsuperscript{10} Figure 2C is a 3-D map of this effect.
Finally, ZnO NRs have been shown to enhance optical signals due to both their inherent optical properties and their unique shape anisotropy. These enhancements have been shown using surface attached fluorophores and result in fluorescence intensities well above other substrates with intensities higher than predicted from the increased surface to volume ratio by reducing its dimensions to the nano size regime. This enhancement has been largely attributed to the intense electromagnetic field that runs along the outside of the material brought about by

Figure 2: Width dependence of guided light. (A) shows both the diameter dependence of guided mode light intensity for materials with different refractive indices for 532 nm light. Each material has a different width which corresponds to the maximum intensity of guided light for each activated mode. This figure is used without permission from Ref. 25. (B) and (C) show the penetration of the evanescent field as a function of diameter of material for ZnO and 761 nm light. When the NR is sufficiently small (400 nm, red) as in (B) and the leftmost figure in (C), most of the light is guided along the surface of the NR, allowing for a maximum penetration of the evanescent field into the surrounding medium. With the diameter is increased to 1000 nm (B, black line) and the right-most figure in (C), most of the light is carried through the core of the material, leading to little or no extension of the evanescent wave into the surrounding. The figures in (B) and (C) were used from Ref. 8 without permission.

1.1.3. Optical Enhancement of Zinc Oxide

Finally, ZnO NRs have been shown to enhance optical signals due to both their inherent
subwavelength wave guiding.\textsuperscript{16} In addition to the increased fluorescent signal, the total time to photobleaching of the fluorophore was increased for those fluorophores excited by this evanescent field.\textsuperscript{16} Their reduced dimensions and high aspect ratio also lead to a unique optical phenomenon termed FINE, or fluorescence intensification on NR ends, in which the ends of the ZnO NRs exhibited a markedly increased fluorescence from the surface bound fluorophores compared with the fluorescence from the main body.\textsuperscript{34, 36} This phenomenon has also been displayed for elastic light scattering in ZnO and other semiconductor metal oxides.\textsuperscript{37}

\subsection{1.1.4. Zinc Oxide Nanorods as Probes for Raman Spectroscopy}

All of the above properties make ZnO an ideal material for nano-based probes and biological assays which has been demonstrated numerous times as a platform for fluorescence detection.\textsuperscript{16-18, 34, 36} The main drawback of fluorescence-based assays, however, is that they lack any chemical information and simply provide concentration-based sensing. Raman spectroscopy, on the other hand, is an ideal spectroscopic method for biological and other chemical sensing since it can provide both chemical information that is intrinsic to the analyte and concentration data.\textsuperscript{27, 38-41} Additionally, many of the aspects which make ZnO such an ideal platform for fluorescence spectroscopy also make them ideal as a Raman spectroscopy nanoprobe or array substrate material. ZnO is free from interference in the regions of interest in chemical sensing (1100-3000 cm\textsuperscript{-1}) since all its most intense first order Raman peaks occur between 100 cm\textsuperscript{-1} to 1154 cm\textsuperscript{-1}.\textsuperscript{1} Raman spectroscopy, like many biological fluorescence assays, relies on a visible light signal for inciting a response, and the most common wavelengths for Raman excitation are insufficient to excite bandgap emission. However, exciting bandgap emission lasing could have potential to serve as a subwavelength source for Raman excitation.\textsuperscript{31} As long as there is no damage or induced
fluorescence in the analyte, the lower wavelength laser should provide a suitable excitation source since Raman intensity is based on a $\nu^4$ relationship. Having ZnO NRs of optical quality means there will also be no interference from excitation in the visible range which could overwhelm any Raman signal. Since Raman shifts are relative to the excitation source of light, Raman scattered light will also be well within the regime for subwavelength waveguiding. This would allow for both the delivery of excitation illumination to the analyte area and collection of the Raman signal while shuttling it to the collection area, meaning that Raman signals could be collected offset from the excitation source. This has been demonstrated previously using bulk ZnO layers in a technique known as waveguiding Raman spectroscopy. Finally, ZnO NRs should be able to provide enhancement to the Raman signal. In waveguiding Raman spectroscopy, a significant enhancement in the Raman signal due to waveguiding is achieved due to both area and radiance enhancement effects. The area enhancement is particularly potent as Raman is collected from a larger area of the waveguide than the illumination/collection area from traditional confocal Raman. For suitably small waveguides, such as ZnO NRs, the Raman signal collected should be from all molecules on the NR surface due to excitation by the evanescent field. Furthermore, signal collection from the ends of the NR should provide additional enhancement. Both of these phenomena have been recently observed in literature for ZnO nanobelts and NRs, respectively, however, these papers only provided a cursory observation of these phenomena, and up to this point, no in depth analysis of these phenomena have been conducted. In fact, most of what is known about the Raman of ZnO and ZnO as a waveguiding substrate for Raman enhancements have been conducted primarily on bulk materials. Those few studies which have looked at the Raman spectroscopy of nano ZnO (belts or rods) have done so from a bulk materials perspective.
and have failed to take into account effects of the reduced dimensionality or the high shape anisotropy of the material.44-46 This leaves a gap to thoroughly understanding how the chemical and physical properties of ZnO NRs can be exploited to create an ideal nanoprobe substrate for Raman spectroscopy. This is the main concern of this thesis. In the following pages, I will systematically look at the fundamental physical and chemical properties of ZnO NRs, accounting for the differences seen due to their reduced dimensionality and high aspect ratios, I will demonstrate many of the advantages that make ZnO NRs an ideal platform for fluorescence sensing also translate to Raman spectroscopy, and show why it is important to account for material properties arising from the reduced dimensionality in the nano-regime.

1.2. Introduction to Raman Spectroscopy

Before continuing with the rest of this dissertation, I feel it is important to give some basic background information on Raman spectroscopy for crystalline solids, specifically focusing on the effects when looking at a single crystal. Additionally, I will briefly discuss applications of waveguides for Raman spectroscopy as well as Raman enhancement, focusing specifically on dielectric signal enhancement, in order to further stress the importance of developing ZnO NRs as nanoprobe substrates for Raman Spectroscopy.

1.2.1. Raman Spectroscopy of Crystalline Solids

Raman spectroscopy is a form of inelastic scattering that arises when an incident photon interacts with a sample imparting some of its momentum into the sample in the form of molecular vibrations.47 Unlike in liquids or single molecule Raman, the atoms in the crystalline solid are sufficiently close together that the excited atoms pull and push on their nearest neighbors, a behavior that propagates through the entire crystal lattice, creating a pressure wave known as a
phonon. The incident excitation can interact with a solid to either create or destroy a phonon.\textsuperscript{47-48}

If the molecule exists in the v=1 vibration state, there already exists a phonon with frequency, $v_m$. When the incident photon interacts with this molecule, promoting the electron to the virtual excited state, and upon relaxation back to the v=0 ground state, the emitted photon will have absorbed the energy of the phonon, destroying it, resulting in a higher frequency that is the sum of the incident and phonon frequencies ($v_0 + v_m$). This phenomenon is known as anti-Stokes scattering. Alternatively, when the incident photon reacts with a molecule in the v=0 state exciting an electron to the virtual excited state which then relaxes to the v=1 ground state, a phonon is created with the frequency of $v_m$. The scattered photon is emitted at a frequency minus that of the phonon frequency ($v_0 - v_m$). This process is known as Stokes scattering. This is outlined in Equation 1.\textsuperscript{49}

$$P = \alpha_0 E_0 \cos 2\pi v_0 t + \frac{1}{2} \left( \frac{\partial \alpha}{\partial q} \right)_0 q_0 E_0 [\cos 2\pi (v_0 + v_m) t + \cos 2\pi (v_0 - v_m) t]$$ (1)

In Equation 1, $P$ is the induced dipole moment, $\alpha_0$ is the polarizability, $E_0$ is the vibrational amplitude of the laser, $v_0$ is the frequency of the laser, $q_0$ is the vibrational amplitude of the molecule, $v_m$ is the frequency of the molecular vibration, and $t$ is time. The leftmost term (prior to the first plus sign) is independent of any phonon frequency and represents Rayleigh scattering, or elastic scattering. The two parts of the second term correspond to Stokes ($v_0 - v_m$) and anti-Stokes ($v_0 + v_m$) scattering. Figure 3 gives a pictorial representation of this phenomenon using an energy level diagram. In the figure, as the incident light interacts with the molecule, an electron is promoted to a virtual excited state and one of three outcomes is possible. If the electron relaxes down to the same state with no energy change, then the photon is elastically scattered (Figure 3B). If the electron occupies the v=1 vibrational state prior to promotion to the virtual excited state,
when the electron relaxes to the \( v=0 \) vibrational state, the phonon energy is added to the scattered photon leading to anti-Stokes scattering (Figure 3A). In the last case, Figure 3C, the electron is in the \( v=0 \) ground state, then is excited by a photon to the virtual state, after which is relaxes down to the \( v=1 \) where the scattered photon has a lower energy from the energy lost due to the creation of a phonon. This is Stokes scattering and is the normal condition under which Raman scattering is measured. In both Stokes and anti-Stokes scattering, the change in energy is the same, only varying in the sign \((\pm)\) of the phonon interaction. This leads to a symmetrical Raman spectrum about the zero (laser) wavelength.\(^{47}\) However, because in the ground state the \( v=0 \) state is much more populated than the \( v=1 \) state, the Stokes scattering component will have a much higher intensity than the anti-Stokes component.\(^{47}\) Stokes scattering will be used exclusively throughout this dissertation.

The positions of the Raman peaks can be determined according to Equation 2.\(^{49}\)
\[ \tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}} \]  

Where \( \tilde{\nu} \) is the vibrational frequency, \( K \) is the force constant of the bond, and \( \mu \) is the reduced mass. These changes in frequency of Raman peaks can be caused by a change in the reduced mass, the force constant, or a combination of both. In Chapter 4 this effect will be apparent when studying copper doping of ZnO NRs. Doping ZnO with copper causes a shift in the \( \text{E}_{2\text{H}} \) Raman mode associated with the ZnO wurtzite crystal, causing it to move to lower energies as more doping is present. This shift in frequency is most likely caused by a change in the force constant of the chemical bond when copper is substituted for zinc and unlikely due to a change in the reduced mass, since zinc and copper have molecular masses that only vary slightly, 65.38 amu and 63.546 amu, respectively.

1.2.2. Symmetry and Raman Active Modes

As shown in Equation 1, when light interacts with a molecule, a dipole moment is created leading to a polarization of the molecular bond. For a molecular vibration to be Raman active, its polarizability needs to change with the changing displacement of the atoms. This is given in Equation 1 by the \( (\partial \alpha/\partial q) \) term and must meet the condition in Equation 3.

\[ (\frac{\partial \alpha}{\partial q}) \neq 0 \]
However, since these Raman modes will only be excited when specific geometric conditions are met between the beam polarization, the wavevector, and the molecule, it is important to understand a little about the symmetry of the molecules. Symmetry is of particular importance for the work in this dissertation since I will be focusing on single crystalline ZnO which will have one geometric orientation with respect to the polarization of the incident light for each given measurement. Furthermore, since I will almost exclusively be dealing with wurtzite ZnO, I will focus the discussion on the symmetry elements for only this crystal type. Wurtzite is a crystal with six-fold

**Figure 4: Vibrational modes for the C$_{6}$v symmetry group.** (A) All the vibrational modes of the C$_{6}$v symmetry group are illustrated. There are six total vibrational modes for this group, however only four are Raman active (those outlined in the blue box) and of those four, two are both Raman and IR active (those outlined in the red box). (B) The Raman tensors for the Raman active modes of the C$_{6}$v symmetry group$^{1-2}$. The tensors give the light-matter geometries under which each of the vibrational modes will be Raman active. The tensors for the modes which are both Raman and IR have the direction of the phonon polarization indicated following the mode identity. (C) A crystal packing diagram showing the crystal structure of wurtzite crystal. The atoms making up the Raman vibrational modes are highlighted in red.
symmetry belonging to the $C_{6v}^4$ point group (or P6$_3$mc space group). Important for the discussion on symmetry is the point group $C_{6v}$ which gives the vibrational modes for the wurtzite crystal. According to the character table for the $C_{6v}$ group, ZnO has 6 molecular vibrations consisting of $A_1$, $E_1$, two $E_2$ ($E_{2H}$ and $E_{2L}$), and two $B_1$ ($B_{1H}$ and $B_{1L}$) modes, and these are shown in Figure 4A. Of these modes, the $E_2$ modes are Raman only active while the $A_1$ and $E_1$ modes are both Raman and IR active. The $B_1$ modes are neither Raman nor IR active. The Raman tensors for wurtzite Raman are given in Figure 4B, and represent the specific geometries where Equation 3 is non-zero for each mode. The $B_1$ symmetry has no tensor since under all orientations $\partial \alpha / \partial q = 0$. I have added x, y, z coordinates in red above the $A_1$ tensor to make the matrices a little easier to follow. In describing the tensors, it will be good to first introduce Porto polarization notation for Raman spectroscopy. This notation takes on the form of $k_i(E_s)k_s$, where the two letters outside of the parenthesis indicate the direction from which the incident light propagates ($k_i$) and the direction the scattered light is collected from ($k_s$). For all experiments in this thesis, a backscattering geometry will be used to take Raman measurements, as such the propagation and collection of light will be assigned to the positive x direction for the excitation source ($x$), and the negative x ($\bar{x}$) for the collected light, such that all orientations will take on the form $x(E_iE_s)\bar{x}$. Additionally, the z-direction will be assigned to the c-axis of the ZnO NR, such that when light is polarized in the z-direction it will be parallel to the c-axis. For example, looking at the $A_1$ Raman tensor the terms in which $\partial \alpha / \partial q \neq 0$ are $\alpha_{xx}$, $\alpha_{yy}$, and $\alpha_{zz}$. When illuminated, a ZnO NR with the polarization of the laser and scattered light parallel to the z-axis ($\bar{x}(zz)x$), only the $A_1$ mode will be present in the spectrum since it is the only mode with a non-zero term with this polarization. However, when illuminated with laser and scattering polarization are perpendicular to the z-axis
both the $A_1$ and $E_2$ modes should be present since they are both non-zero in this polarization/orientation. Extensive studies have been carried out to assign the observed Raman peaks for ZnO to the correct Raman modes.\textsuperscript{1, 51} Figure 5 is taken from Porto’s work assigning the

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure5.png}
\caption{Raman Spectrum of zinc oxide for each light-matter geometric orientation in right angle Raman scattering. Figure showing all the Raman peaks for wurtzite ZnO. The $A_1$(TO) peak is visible unaltered in (B) where it is geometrically allowed. The $E_{2H}$ and $E_{2L}$ peaks are visible in (A) and (E). The $E_1$(LO) peak is seen unaltered in (D) and (F). In (A) and (E) there is mixing between the $A_1$(TO) and the $E_1$(TO) resulting in a peak with a center between the two values for the unadulterated peaks. The $E_1$(LO) peak is present in (C) and (F). The $A_1$(LO) peak is not shown as it is not allowed in any of the orientations for right angle scattered Raman spectroscopy. Figure used from Ref. 40 without permission.}
\end{figure}
modes to ZnO and has been included here to demonstrate the necessity of polarization control for studying the Raman modes of ZnO.¹

1.2.3. Second Order Raman Modes

Second order Raman modes also display symmetry tensors, but because they are combinations of multiple first order peaks, the light-matter geometries which determine when they are allowed or forbidden are much more complicated. Second order peaks are mostly absent from the Raman spectra for ZnO and making identification of the E2H-2L mode easy. However, ZnS has a higher deformation potential than ZnO, which results in the appearance of multiple second order peaks in the spectrum of ZnS.⁵² Many of these second order peaks overlap in the same spectral region resulting broad peaks which are a combination of these modes. For this reason, in Chapter 3, I make no attempt to identify the second order peaks present for ZnS and instead present a table with likely second order peaks which construct the spectra I observe. Additionally, it is important to point out that second order peaks are generally much broader than first order peaks, resulting from a larger density of states.⁴⁷ These broad peaks will be evident when looking at the spectrum of ZnS in Chapter 3.

1.2.4. Polar Modes of C₆ᵥ Symmetry Group

The unique characteristics of the modes which are both Raman and IR active will be discussed next. The two modes of the C₆ᵥ symmetry that are both Raman and IR active are the A₁ and E₁ modes (outlined in the red box in Figure 4). Unlike the Raman only active modes which experience only very localized, short range electromagnetic fields on the vibrations, those that are both Raman and IR active feel both long and short range forces.¹,⁴⁸ The influence of the long and short range forces leads to a condition in which the photon and phonon can couple into each other
creating a polariton. A polariton is a polarized vibrational mode with longitudinal (parallel to the c-axis) and traverse (perpendicular to the c-axis) components. These polarized modes can lead to interesting effects such as loss of degeneracy, shifting frequencies, and vibrational mode mixing. Each of these is seen for the A\textsubscript{1} and E\textsubscript{1} modes of ZnO. From the character tables the A\textsubscript{1} and E\textsubscript{1} modes should be singly degenerate, however, because these modes are polarized in the C\textsubscript{6v} symmetry, they split into doubly degenerate modes with both a longitudinal optical (LO) and transverse optical (TO) mode associated with each. The TO modes for the A\textsubscript{1} and E\textsubscript{1} peaks appear at 380 and 407 cm\textsuperscript{-1}, while the LO modes appear at 574 and 583 cm\textsuperscript{-1}, respectively. Additionally, under certain geometries, the modes of the A\textsubscript{1} and E\textsubscript{1} peaks can mix, leading to peak frequencies shifted to be between the two pure modes. This is demonstrated in Figure 4C, where E\textsubscript{1} (TO) and (LO) peaks have shifted from their expected values to lower values moving towards the wavelength shifts of the A\textsubscript{1} modes.

1.2.5. Waveguiding Raman Spectroscopy

Waveguiding Raman Spectroscopy is a Raman technique in which a waveguide is employed to provide a signal enhancement which allows for the measurement of analytes at much lower concentrations than traditional or confocal Raman can afford. This technique has been demonstrated to be capable of detecting concentrations of surface bound analytes down to picomolar concentrations. This enhancement in actuality is due to a combination of multiple enhancement effects, the two main effects being radiative and area enhancements. Radiative enhancement is due to the high electromagnetic field at the surface of the waveguide caused by its evanescent field. However, the more prominent enhancement is actually caused by the area enhancement effect. Area enhancement is caused by the propagation of the excitation
source through the length waveguide, allowing it to excite all molecules on the surface. This effect scales linearly with length, and due to very small losses, < 2dB/ cm of waveguide, this effect can be maximized by increasing the length of the waveguide to many centimeters. Combined, these two effects have been shown to have a theoretical enhancement of up to four orders of magnitude over confocal Raman spectroscopy for low index of refraction materials. This enhancement can be further increased to six orders of magnitude higher for high refractive index materials, ZnO belongs to this class of waveguide material. However, these high theoretical enhancement factors are seen for slot waveguide materials as opposed to strip waveguides. Slot waveguides and strip waveguides differ in that a strip waveguide is a single piece of material with a width tuned to the specific wavelength of light being guided, whereas a slot waveguide is a strip waveguide with a small gap that runs down the length of the center of the waveguide. The greater enhancement for slot waveguides is due to the coupling of the electromagnetic fields from each of the two strips surrounding the small slot. Single ZnO NRs would fall under the category of strip waveguides, and as such, such high enhancement factors should not be expected from them. However, arrays of closely packed, aligned ZnO NRs with finely tuned separation distances may be able to achieve these high enhancements due to electromagnetic coupling between adjacent NRs similar to how the slot waveguides work.

1.3. Dissertation Outline

This dissertation is focused on the development of ZnO NRs and ZnO NR arrays as nanoprob es for Raman spectroscopy, and more specifically, understanding the fundamental properties of ZnO NRs and how their physical and chemical properties can be exploited for their future development for this purpose. In Chapter 2, I will set the groundwork for understanding
how the Raman spectrum of this material is affected by the nano size effect coupled with their high shape anisotropy. Understanding these effects will allow us to better understand the unique light-matter interactions of the materials, as well understanding how these interesting properties can be exploited. Using position resolved Raman spectroscopy with polarization control, I will demonstrate a unique phenomenon in which there is a signal enhancement from allowed modes and the appearance of forbidden Raman modes at the ends of the NRs.

The third chapter will focus on understanding the chemical properties of ZnO, specifically focusing on facet specific reactivity by monitoring the reaction of ZnO with hydrogen sulfide (H$_2$S) using Raman spectroscopy. ZnO is a widely used as a hydrogen sulfide scrubber used to remove the gas from syngas production$^{56-59}$ and from agricultural sources where it is a byproduct of raising cattle.$^{60-61}$ Furthermore, ZnO H$_2$S scrubbers are capable of being regenerated by treating the ZnS under high pressures of oxygen. This regeneration, however, is highly dependent on ZnO retaining its structural integrity upon conversion to ZnS.$^{56,58-59}$ Currently, much research has been devoted to determining the optimal morphology for maximizing both the reactivity and the stability of ZnO during ZnS conversion. Finally, the ZnO to ZnS reaction is important in many optoelectronic applications including photocatalysis$^{62-65}$ and optoelectronics.$^{66-67}$ Facet specific reactivity will be important to both understand the stability and the reactivity of the materials and identify important responses when developing these as chemical sensors. I will demonstrate that the end facets of the ZnO NRs are highly susceptible to sulfidation, while the side facets are more stable. This leads to a faster reaction process at the ends of the NRs and a much slower Kirkendall effect happening along the sides.
The fourth chapter will look at how doping or altering the structure and chemical properties in minor ways affects the Raman properties of ZnO. This will provide a nice complement to the structural and chemical properties studied in Chapters 2 and 3. Observed changes in Chapter 4 will be markedly different than those in Chapter 3. In Chapter 3, the Raman of ZnO is unchanged throughout the reaction process due mainly to the compartmentalized way in which the sulfidation reaction occurs, resulting in two chemically distinct layers of ZnO and ZnS. Contrast this in the scenario where doping occurs, with pockets of copper interspersed in the ZnO crystal, and it is apparent why peak shifts and symmetry breaking occurs in this case versus when ZnO is reacted with H2S.

I will conclude this dissertation by reiterating my conclusions and providing some insight into on-going, yet incomplete work that I am currently undertaking, and provide some brief words on the future outlook for understanding the physical and chemical properties of ZnO NRs in developing them as nanoprobes for Raman spectroscopy.

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Chapter 2. Spatially Distinct Raman Scattering Characteristics of Individual ZnO Nanorods Under Controlled Polarization

2.1. Introduction

Nanoscale zinc oxide (ZnO) materials exhibit useful optical properties which have facilitated their applications in photoconduction, waveguiding, light collection, light emission, lasing, optical routing, and biosensing.\textsuperscript{1-5} In particular, one-dimensional (1D) ZnO materials in the form of nanowires (NWs) and nanorods (NRs) have been proven effective in previous studies for optical applications geared towards operation in a highly miniaturized format.\textsuperscript{2, 5-7} Recent endeavors in ZnO NR-based elastic/inelastic scattering,\textsuperscript{8-10} active/passive light guiding\textsuperscript{2, 5, 7, 11-17} and lasing\textsuperscript{5-6, 18-21} have utilized the employment of single NRs instead of their bulk counterparts or NR ensembles. Central to such functional use of 1D ZnO NRs is the precise understanding of the light–matter interaction between individual ZnO NRs and incident (excitation) as well as the scattered (emitted/guided) light. The light–matter interaction characteristics have been carefully scrutinized in the past\textsuperscript{9} for the elastic scattering behaviors of ZnO NRs as well as for the subwavelength waveguiding of fluorescence signals coupled into ZnO NRs from nearby fluorophores.\textsuperscript{13-15, 22} In both of these cases, the high shape anisotropy inherent to 1D ZnO NRs was shown to have significant effects on the magnitude and direction of the optical signals measured from discrete ZnO NRs, demonstrating the importance of the light–matter interaction geometry not only for the effective manipulation of incident light but also for the optical outcomes of NR-originated and NR-guided signals. However, very few studies are currently available for systematic light–matter examinations pertinent to Raman scattering of individual ZnO NRs.
Raman scattering has been employed for identifying the chemical composition, defect state, lattice dynamics, and phonon confinement of various materials. More recently, Raman spectroscopy has been demonstrated as a convenient and nondestructive analytical tool for obtaining information on ZnO nanostructures such as the growth direction, morphology, structure, crystalline lattice order, and self-assembly process. For example, a shift in $E_2$ high peak from the bulk ZnO value of 437–439 cm$^{-1}$ can be an indication of internal stress present in the crystalline lattice of ZnO. The intensities of $A_1$ transverse optical and $E_2$ high modes can be linked to provide information on the ZnO NR diameter. However, the characteristic Raman spectra of ZnO nanomaterials can be strongly governed by the aforementioned light–matter interaction geometry, especially for ZnO NRs with high shape anisotropy. Therefore, elucidation of the exact nature and consequence of the light–matter interaction related to Raman scattering phenomenon of individual ZnO NRs is important in accurately and meaningfully relating the Raman measurement outcomes in peak intensities and shifts to the nanomaterial characteristics. To date, only few studies have examined polarization-resolved Raman scattering behaviors of individual ZnO NRs. There still exits a lack of systematic studies on the effects of light polarization and shape anisotropy on the Raman scattering behavior of single ZnO NRs, particularly related to spatially resolved Raman scattering characteristics along individual NRs.

In this paper, we unambiguously determine the precise effects of incident/scattered light polarization on key Raman active modes of ZnO NRs. We ascertain the varying degrees of Raman responses of specific Raman modes and their variations as a function of the position on the NRs. In addition to the dominant Raman scattering modes of wurtzite ZnO for given light–matter interaction geometry as dictated by Raman selection rules; we identify very intriguing, highly localized scattering behaviors from the forbidden modes. The Raman scattering signals corresponding to the forbidden
modes are absent along the main body of the NRs while the two ends of the NRs display strikingly strong signals. By comparing the spatially resolved, polarization-controlled Raman scattering profiles of the NRs with those of MPs, we explicitly demonstrate that the origin of the uniquely observed Raman behaviors at the NR ends is attributed to the high shape anisotropy of the nanomaterial.

2.2. Experimental Details

ZnO NRs and MPs were synthesized in a home-built, chemical vapor deposition reactor, similar to the previously described procedures.\textsuperscript{19,31-34} Using 20 nm Au colloids (Ted Pella, Inc.; Redding, CA.) as catalysts, subsequent ZnO growths were carried out on a Si growth substrate (Silicon Quest International Inc., San Jose, CA). The source materials obtained from Alfa Aesar Inc., 0.45 grams of a 2:1 mixture of graphite (99%) to zinc oxide powders (99.999%), were placed in a quartz boat at the center of a horizontal resistance furnace and a target boat containing the catalyst-deposited Si substrate was placed at approximately 15 cm downstream. The furnace was then heated to 850–950 °C for 15–35 min at a ramp up/ramp down rate of 15 °C min\textsuperscript{−1} under a constant Ar flow of 100 standard cubic centimeters per minute. As-synthesized ZnO NRs were sonicated off from the growth substrate and dispersed in ethanol. A drop-wise deposition of the ZnO NRs in ethanol onto a clean Si wafer led to NRs lying flat on the Si surface. ZnO MPs were used as-prepared directly after their growth. For morphological characterization of the ZnO NRs and MPs, the samples were imaged using a FEI/Philips XL 20 scanning electron microscope (SEM) operating at 20 kV.

Raman spectra were collected using a LabRAM HR Evolution Raman confocal microscope (Horiba Instruments Inc., Sunnyvale, CA) with a 100× objective lens of a numerical aperture value of 0.9 (Olympus Corp., Waltham, MA). A linearly polarized 532 nm laser with a power setting of 25 mW was used to illuminate individual ZnO NRs (MPs) as a function of position along the NR (MP) on a
computer-controlled motorized XY stage. For 2D mapping of Raman signals, the DuoScan option of fast mapping was employed under which the laser was scanned over individual NRs held at fixed positions on the sample stage. In a typical Raman mapping run, the laser beam of approximately 1 μm in diameter was rastered over a ZnO NR area of interest in steps ranging 550–750 nm and 270–440 nm along the long and short axis of the NR, respectively. Subsequently, the position-resolved Raman data from individual ZnO NRs and MPs of different orientations were collected in the scan range of 50–500 cm\(^{-1}\) using a 1800 lines per mm grating and a charge-coupled-device (CCD) detector. For direction-controlled collection of Raman scattered signals from the samples, a second polarizer referred to as an analyzer was placed prior to the spectrophotometer and detector. For producing unpolarized measurement conditions, a scrambler, a \(\lambda/4\) waveplate, was inserted in the beam path in the absence of the analyzer.

2.3. Results and Discussion

A schematic representation of the measurement setup to examine the Raman scattering behaviors of individual ZnO NRs as a function of incident/scattered light polarization and position along the NR is given in Fig. 6A. The illumination source is a 532 nm diode-pumped solid state laser that is linearly polarized with the polarization ratio greater than 100:1 in the \(z\)-direction, as designated by the blue double arrow and labelled as \(E_{\text{inc}}\) in Fig. 6A. The light entering through the objective lens of the confocal microscope illuminates the ZnO NR sample from above (\(x\)-direction). The scattered light is then collected in a backscattering configuration where it passes through to the spectrograph. For the experiments conducted under an unpolarized setting, a \(\lambda/4\) plate (designated as scrambler in Fig. 6A) can be inserted between the illumination source and the pinhole. Likewise, for experiments requiring control over the polarization state of the scattered light, an analyzer can be placed prior to the
spectrograph. In lieu of altering the polarization of the laser in these experiments, we measured two sample conformations the ZnO NRs, vertical and horizontal. This detection configuration ensures that
no potential variations in the polarization-dependent optical constants associated with different optical components in the setup will affect the measurement outcomes. Vertical NRs correspond to NRs
oriented with their long axis ($c$-axis) parallel to the direction of polarization (NR$\parallel E_{\text{inc}}$), whereas horizontal NRs have their long axis oriented perpendicular to the incident polarization (NR$\perp E_{\text{inc}}$). The three-axis diagram shown next to the sample plane in Fig. 6A displays the crystalline facet directions of a vertically placed ZnO NR with respect to the laboratory coordinates of $x$, $y$, and $z$. NR position-specific Raman scattering signals can be obtained by focusing the laser beam of approximately 1 μm in diameter on different NR locations. For NR spectra presented with no specific indication of the laser beam position on the NRs, the illumination was centered on the middle part of the NRs, as the schematic depicts in Fig. 6A.

Fig. 6B shows representative SEM images of wurzite-type ZnO NRs used in this experiment. The exterior surfaces of wurzite ZnO NRs show two main crystalline facets; the basal facet (the hexagonal planes found at the two NR ends) and the prismic facet (the rectangular planes found along the NR main body). The SEM images also show that the NR crystalline facets are catalyst particle-free after undergoing the steps to re-disperse ZnO NRs onto a clean Si substrate after their synthesis. The NRs examined in this study exhibit aspect ratios in width:length of 1:15–1:75, typically ranging from a few hundred nanometers in width and several to ten of micrometers in length. In contrast, the images in Fig. 6C are typical SEM images of the ZnO MPs which were used as a control to study the effect of the nanomaterial's shape anisotropy on Raman scattering. The hexagonal (basal) and rectangular (prismic) facets are also clearly seen in the SEM images of the ZnO MPs, typically exhibiting an aspect ratio of $\sim$1:1.

Wurtzite ZnO, belonging to the space group of $C_{4v}^6$, has the optical modes of $\Gamma_{\text{opt}} = A_1 + 2B_1 + E_1 + 2E_2$ at the $\Gamma$ point of the Brillouin zone according to group theory.\textsuperscript{23, 35-37} $A_1$ and $E_1$ are Raman active whose polar modes split into different frequencies for the transverse-optical (TO) and
longitudinal-optical (LO) modes. The nonpolar E\textsubscript{2} mode is also Raman-active and its symmetry allows two frequencies of high and low E\textsubscript{2}, \textit{i.e.} E\textsubscript{2H} and E\textsubscript{2L}, respectively. The E\textsubscript{2H} mode is associated with oxygen atoms whereas E\textsubscript{2L} is related to Zn atoms. B\textsubscript{1} is Raman-silent.

Fig. 7A shows a typical Raman spectrum taken from single ZnO NRs in the scan range of 75–500 cm\textsuperscript{-1}. The five peaks of interests (labelled i–v) appear at 98, 331, 378, 413, and 437 cm\textsuperscript{-1} for the NRs and they correspond to the E\textsubscript{2L}, E\textsubscript{2H-2L}, A\textsubscript{1T}, E\textsubscript{1T}, and E\textsubscript{2H} mode, respectively. The Raman spectra taken from dense ZnO NRs as-synthesized on the Si growth wafer are provided in Appendix A, Fig. S1(A). Unlike all five modes resolved in the Raman spectra of individual NRs in Fig. 7(A), the Raman spectrum of as-synthesized NR samples showed E\textsubscript{2L}, E\textsubscript{2H-2L}, E\textsubscript{1T}, and E\textsubscript{2H} peaks but not A\textsubscript{1T}, similar to the previously reported es of ZnO thin films.\textsuperscript{38-39} According to Raman selection rules, the five peaks of individual ZnO NRs will tend to emerge or disappear depending on the orientation of the NR with respect to the polarization of the incident light (E\textsubscript{inc}) and that of the scattered light (E\textsubscript{sca}). We first focus on measurement conditions in the absence of the analyzer and reserve our discussion for cross-polarized conditions for later in this paper.
Figure 7: Representative Raman Spectra of zinc oxide nanorods not controlling for laser polarization nor rod orientation. Raman spectra were collected from ZnO NRs using a linearly polarized laser. All scattered signals from the NRs were collected regardless of their polarization states. (A) A typical Raman spectrum taken from a ZnO NR is shown in the fingerprint wavenumber region of 75–500 cm\(^{-1}\). The peaks of focus in this study correspond to the (i) \(E_{2\text{L}}\) mode at 98 cm\(^{-1}\), (ii) \(E_{2\text{H}}-E_{2\text{L}}\) mode at 331 cm\(^{-1}\), (iii) \(A_{1\text{T}}\) mode at 378 cm\(^{-1}\), (iv) \(E_{1\text{T}}\) mode at 413 cm\(^{-1}\), and (v) \(E_{2\text{H}}\) mode at 437 cm\(^{-1}\). (B) Polarization-dependent Raman scattering behaviors of ZnO NRs were examined from a large number of individual ZnO NRs while sampling random positions on the NRs. Averaged intensities at the five peaks were normalized with respect to the highest intensity mode and subsequently graphed for the two different NR orientations, parallel and perpendicular to the incident polarization. When ZnO NRs were in parallel direction to the laser polarization, the prominent Raman intensities collected were the \(E_{2\text{H}}-E_{2\text{L}}\) and \(A_{1\text{T}}\) modes. The \(E_{2\text{L}}\) and \(E_{2\text{H}}\) peaks were largely suppressed. On the contrary, ZnO NRs oriented perpendicular to the laser polarization yielded extremely strong Raman intensities from the \(E_{2\text{L}}\) and \(E_{2\text{H}}\) modes relative to the other modes. The \(E_{1\text{T}}\) mode was weak under both orientations.
Fig. 7B shows the scattering intensity of each of the 5 peaks discussed above for both the NR\text{\text{E}}_{\text{inc}} and NR\perp\text{E}_{\text{inc}} es averaged from 30 ZnO NRs. Raman scattering profiles from arbitrary positions on the NRs were examined in this analysis, sampling 30 spots and 67 spots from the NR\text{\text{E}}_{\text{inc}} and the NR\perp\text{E}_{\text{inc}} configuration, respectively. The apparent differences in the dominant Raman modes for the two cases are clearly seen when comparing the average Raman intensities taken from the five peaks. For the NR\text{\text{E}}_{\text{inc}} orientation, the relative intensity ratios of the five peaks are 0.3:1:0.85:0.06:0.14 (E_{2L}: E_{2H-2L}:A_{1T}:E_{1T}:E_{2H}). Therefore, for the vertically positioned ZnO NRs, the E_{2H-2L} and A_{1T} peaks are the predominant features and the remaining peaks are much weaker in intensity. For the NR\perp\text{E}_{\text{inc}} orientation, the relative Raman intensities between the five peaks change to 1:0.1:0.05:0.17:0.85 (E_{2L}:E_{2H-2L}:A_{1T}:E_{1T}:E_{2H}). Hence, the predominant features for the horizontal ZnO NRs are the E_{2L} and E_{2H} peaks, while the remaining three peaks are weak. The relative intensity contribution from the E_{1T} mode is small in both cases.

Under the measurement condition involving polarization control over the incident light only (i.e. with no analyzer) in a backscattering geometry, the Raman selection rules suggest particular sets of Raman processes for the five peaks under investigation.\textsuperscript{29-30, 37} They are detailed in Table 1 for the vertically and horizontally oriented ZnO NRs when all polarization states of the scattered light are collected.
Table 1: Raman modes allowed for the vertically and horizontally placed zinc oxide nanorods under the backscattering configuration with the polarization control of the incident light.

<table>
<thead>
<tr>
<th>NR orientation</th>
<th>Frequency (cm(^{-1}))</th>
<th>Process</th>
<th>Observation geometry using the Porto notation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vertical NRs</td>
<td>378</td>
<td>A(_{1T})</td>
<td>(x(zz)\bar{x})</td>
</tr>
<tr>
<td></td>
<td>413</td>
<td>E(_{1T})</td>
<td>(x(zy)\bar{x})</td>
</tr>
<tr>
<td></td>
<td>331</td>
<td>E(<em>{2H})–E(</em>{2L})</td>
<td>(x(zz)\bar{x})</td>
</tr>
<tr>
<td></td>
<td>378</td>
<td>A(_{1T})</td>
<td>(x(yy)\bar{x})</td>
</tr>
<tr>
<td>Horizontal NRs</td>
<td>413</td>
<td>E(_{1T})</td>
<td>(x(yz)\bar{x})</td>
</tr>
<tr>
<td></td>
<td>437</td>
<td>E(_{2H})</td>
<td>(x(yy)\bar{x})</td>
</tr>
<tr>
<td></td>
<td>98</td>
<td>E(_{2L})</td>
<td>(x(yy)\bar{x})</td>
</tr>
</tbody>
</table>

We subsequently compared the Raman intensities of the allowed modes for each light–matter interaction geometry. The A\(_{1T}\) peak at 378 cm\(^{-1}\), allowed both for NR\|E\(_{inc}\) and NR\(\perp\)E\(_{inc}\) according to Table 1, was present for both vertical and horizontal es in Fig. 7B where its intensity was strong (extremely weak) for vertical (horizontal) ZnO NRs. The signals corresponding to the E\(_{2L}\) (98 cm\(^{-1}\)) and E\(_{2H}\) (437 cm\(^{-1}\)) modes, allowed only for NR\(\perp\)E\(_{inc}\) in Table 1, appeared weak for the vertical ZnO NRs in Fig. 7B, whereas they were the dominant intensity peaks for the horizontal NRs. Therefore, upon analyzing Raman data taken from arbitrarily chosen NR positions averaged over many ZnO NRs, our experimental observations agree well with the Raman selection rules for the predicted allowed modes and concur with the previously reported trend of dominant A\(_{1}\) with weak E\(_{2}\) signals under NR\|E\(_{inc}\) as supposed to the very strong E\(_{2}\) with minor A\(_{1}\) intensities under NR\(\perp\)E\(_{inc}\). Between the two light–matter interaction geometry, the Raman intensity ratio of A\(_{1T}\) between the es of NR\|E\(_{inc}\) and NR\(\perp\)E\(_{inc}\) is \(\sim 1:3\). The intensities of the E\(_{2L}\) and E\(_{2H}\) peaks between NR\|E\(_{inc}\) and NR\(\perp\)E\(_{inc}\) are \(\sim 21:1\) and 36:1, respectively. The large difference and, hence, the high sensitivity to the incoming polarization
shown for the E\textsubscript{2} symmetry relative to A\textsubscript{1} is likely because E\textsubscript{2} is allowed only for NR⊥E\textsubscript{inc}, unlike A\textsubscript{1} permitted for the parallel and perpendicular geometries. In addition, we clearly observe the E\textsubscript{2H}–E\textsubscript{2L} peak at 331 cm\textsuperscript{-1} which is associated with a 2\textsuperscript{nd} order multiphonon scattering. The much more pronounced E\textsubscript{2H}–E\textsubscript{2L} signal for the vertical than horizontal NRs is also in agreement with previously reported results.\textsuperscript{37}

In order to understand the exact consequence of light interaction as a function of light polarization state and position along the NR, the data summarized in Fig. 8 display the incident polarization-specific Raman scattering outcomes measured from the middle position of a single ZnO NR. Fig. 8(A) and (B) show the effect of using linearly polarized \textit{versus} unpolarized light as an illumination source when probing the same ZnO NR oriented either vertically or horizontally. The polarized scattering results from the NR\|E\textsubscript{inc} and NR⊥E\textsubscript{inc} es are then combinedly shown in Fig. 8A for comparison. Similar to what was observed in the NR- and position-averaged spectra in Fig. 7B, the single NR yielded the same predominant E\textsubscript{2H} and E\textsubscript{2L} peaks under NR⊥E\textsubscript{inc} while the A\textsubscript{1T} and E\textsubscript{2H}–E\textsubscript{2L} peaks were the strongest in the NR\|E\textsubscript{inc} orientation. The relative intensity ratios of the E\textsubscript{2L}:E\textsubscript{2H}:E\textsubscript{2L}:A\textsubscript{1T} :E\textsubscript{1T}:E\textsubscript{2H} peaks under NR\|E\textsubscript{inc} and NR⊥E\textsubscript{inc} were also similar to the values discussed for Fig. 7.
Figure 8: Raman scattering behaviors of single zinc oxide nanorods. The nanorods were systematically investigated by examining the effect of polarized versus unpolarized light on the scattering profiles of the same ZnO NR while varying its orientation. The incident beam was centered in the middle of the NR and all scattering signals were collected regardless of the polarization state of the scattered light. Normalized Raman intensities with respect to the highest intensity peak are then plotted for the five phonon modes. (A) The bar graphs show the principal modes as well as the relative intensity ratios between the five peaks for both the NR∥E_{inc} versus NR⊥E_{inc} orientations. For each NR orientation, polarization-dependent Raman spectra resulted in consistent trends in the intensity ratios between the five modes as discussed in Fig. 7. (B) When unpolarized light was used instead for illumination on the same NR placed either vertically or horizontally, the dominant peaks remained the same as E_{2L} and E_{2H}, regardless of the NR placement.
The effect of unpolarized incident light on the Raman spectra of the same ZnO NR in Fig. 3A is displayed in Fig. 8B. The scattering intensity differences of the five peaks between the NR∥E_{inc} and NR⊥E_{inc} es have significantly reduced under the unpolarized illumination relative to the linearly polarized e. The E_{2L} and E_{2H} peaks appeared strong even for the vertical orientation under unpolarized light, which was not the e under the polarized light. This indicates that the relative contributions from the minor modes in the vertical versus horizontal orientations (E_{2L} and E_{2H},versus E_{2H–E_{2L}} and A_{1T}, respectively) have increased greatly under the unpolarized illumination. At the same time, the signal contributions from E_{1T}, which produced relatively minor peaks in both orientations under the linearly polarized light, have also risen considerably under no polarization.

The reported NR Raman behaviors in this paper are not related to potential heating or mechanical damage at the NR ends induced by the focused laser. The laser output power of 25 mW used in our experiments is comparable to the typical Raman measurement conditions, often involving a power setting up to 500 mW. Also, in subwavelength waveguiding, UV lasing, and UV photoluminescence studies, ZnO NRs are known to be stable even after prolonged exposure to a short pulsed, high power laser that can reach a peak power well above 10^5 W.\textsuperscript{7,12,16,20,24}

Subsequently, Raman intensity maps of single ZnO NRs were collected by rastering the incident beam over the same NRs placed in both the NR∥E_{inc} and NR⊥E_{inc} orientations. Fig. 9 summarizes the rastering Raman results of the same ZnO NR discussed in Fig. 8. The spatially resolved, Raman heat maps consist of all scattered signals regardless of their polarization states. Raman maps for each of the five phonon modes of the ZnO NR were then generated. The 3D contour plots in Fig. 9A and B show the resulting intensities for the ZnO NR oriented parallel and perpendicular to the incident polarization, respectively. The 3D slices are displayed in color gradients ranging from red (high intensity) to blue
(low). Each slice in the series of Raman maps presented in Fig. 9A and B represents the scattering signals associated with the $E_{2L}$, $E_{2H-2L}$, $A_{1T}$, $E_{1T}$, and $E_{2H}$ mode as indicated next to each map. When inspecting the slices corresponding to the major modes of $E_{2H-2L}$ and $A_{1T}$ in Fig. 9A, their scattering intensities were present continuously along the entirety of the NR. This trend can be seen by the green and sky-blue region in the $E_{2H-2L}$ and $A_{1T}$ slice, respectively, spanning the whole length of the NR. A similar effect is seen in Fig. 9B for the same NR in the horizontal orientation for its major modes. Raman signals from the $E_{2H}$ and $E_{2L}$ were continuously observed along the entire length of the NR, as displayed in the topmost and bottommost slices in Fig. 9B.
Figure 9: Raman intensity maps of the five zinc oxide phonon modes are displayed combinedly for the different light–matter interaction geometries. The data show strongly NR position-dependent Raman scattering profiles for the minor modes per given orientation, whereas the major modes for each orientation display continuous and persistent Raman intensities distributed all along the entire NR length. (A and B) 3D contour profiles of the Raman intensities were mapped for the five peaks under (A) NR\(\parallel\)E\text{inc}\) and (B) NR\(\perp\)E\text{inc}. The NR end-related scattering behaviors of the minor modes can be seen from the E\text{2L} and E\text{2H} slices in (A) and from the E\text{2H}–E\text{2L} and A\text{1T} slices in (B). (C and D) For clarity, the 2D surface maps for the same ZnO phonon modes taken under the two light–matter interaction geometries are displayed side by side. The Raman maps for the E\text{2L} and E\text{2H} modes in (C) clearly display discrete (continuous) scattering intensities at the two ends (all along the NR) when the NR is oriented parallel (perpendicular) to the laser polarization. The opposite trend is observed in (D) for the E\text{2H}–E\text{2L} mode. The NR ends tend to produce higher scattering than other positions on the NR for E\text{2H}–E\text{2L} under NR\(\perp\)E\text{inc}, whereas NR\(\parallel\)E\text{inc} leads to continuous Raman signals along all positions on the NR.

In ensuing examination of the minor modes for each orientation, their scattering intensities were largely absent from the NR main body but appeared as highly enhanced and spatially localized signals.
at the two ends of the NR. For the NR\(\perp\)E\(_{\text{inc}}\) geometry in Fig. 9A, the signals from the \(E_{2H}\) and \(E_{2L}\) modes were suppressed along the NR main body as expected. Yet, the Raman maps for these two minor modes clearly resolve the highly intense scattering at the two NR ends. This phenomenon can be further evidenced by the NR position-specific Raman scattering data presented additionally in Appendix A, Fig. S1(B). The two spectra obtained from a vertically oriented ZnO NR (NR\(\perp\)E\(_{\text{inc}}\)) clearly show that, in addition to the dominant modes of \(E_{2H-2L}\) and \(A_{1T}\) peaks in both the NR end and middle spectra, the forbidden modes of \(E_{2L}\) and \(E_{2H}\) peaks were detected in the NR end spectrum. In contrast, the Raman spectrum of the NR middle position of the same ZnO NR did not show any scattering from these forbidden modes. Similarly, this unusual NR end behavior was also observed from the NR\(\perp\)E\(_{\text{inc}}\) orientation. In this case, the modes of \(E_{2H-2L}\) and \(E_{1T}\) with negligible scattering along the NR main body yielded noticeably high scattering intensities at the NR ends.

This intriguing Raman scattering phenomenon at NR ends can be seen more clearly in the 2D intensity profiles in Fig. 9C and D. In these heat maps, the 2D projected views of the mapped Raman data for the \(E_{2H}\), \(E_{2L}\), and \(E_{2H-2L}\) modes are presented side by side, comparing the different scattering behaviors from the same mode under the NR\(\parallel\)E\(_{\text{inc}}\) versus NR\(\perp\)E\(_{\text{inc}}\) orientations. For the same phonon mode, the continuous scattering profile along the NR, when the modes are allowed, switches to intense, NR end-confined scattering profile when the light interaction geometry changes such that these modes become forbidden. Data in Fig. 9C and D show the scattering profile of highly intense NR end and largely suppressed main body from the \(E_{2H}\) and \(E_{2L}\) modes under NR\(\parallel\)E\(_{\text{inc}}\) and from the \(E_{2H-2L}\) mode under NR\(\perp\)E\(_{\text{inc}}\). The 2D heat maps also show that, when the NR orientation with respect to the incident light is such that the given mode becomes a dominant transition, the corresponding Raman signal is continuously present along the length of the NR. This corresponds to the NR\(\perp\)E\(_{\text{inc}}\) geometry for \(E_{2H}\) and
E_{2L} and to the NR\textit{E}_{\text{inc}} geometry for E_{2H-2L}. In brief, our observations indicate the NR end-exclusive Raman scattering effect occurs for the minor modes per given light–matter interaction geometry. Major phonon modes exhibit NR position-independent scattering whose signal presence followed the predictions from the Raman selection rules. In contrast, minor modes produce the unexpected, NR end-related, Raman scattering characteristics. Possible origins of the NR end-related abnormalities will be discussed later, following the measurement outcomes of cross polarizer configurations.

We continued to investigate the Raman scattering behavior of individual ZnO NRs by additionally controlling the polarization state of the scattered signal (E_{\text{sca}}) and subsequently examining agreements and deviations from the Raman selection rules. We accomplished this by placing an analyzer prior to the detector and altering its angle from 0 to 90 degrees (°), while probing the middle position of the ZnO NRs. As the analyzer angle is changed from 0° and 90°, the cross polarization setting changes from $E_{\text{inc}}\parallel E_{\text{sca}}$ to $E_{\text{inc}}\perp E_{\text{sca}}$. These cross-polarized Raman scattering data were systematically collected for the NR orientation of NR\textit{E}_{\text{inc}} well as for NR\textit{E}_{\text{inc}} and changes in Raman intensities associated with the dominant phonon modes per light interaction setting were inspected. In addition, $E_{1T}$ was included in the evaluation since the Raman selection rules suggest $E_{1T}$ as the only allowed mode when the polarization state of $E_{\text{sca}}$ is perpendicular to that of $E_{\text{inc}}$. Fig. 10A displays the different tendencies observed for the polarization states of the scattered signals corresponding to the two dominant ($A_{1T}$ and $E_{2H-2L}$) and $E_{1T}$ modes measured under NR\textit{E}_{\text{inc}}. In both the scatter plot and the bar graph for $E_{1T}$ in Fig. 10A, it can be seen that $E_{1T}$ exhibits a very steep rise in intensity when the analyzer rotation becomes close to $E_{\text{inc}}\perp E_{\text{sca}}$. The Raman intensities belonging to the $A_{1T}$ and $E_{2H-2L}$ peaks either decrease or only show a slight increase for $E_{\text{inc}}\perp E_{\text{sca}}$. Fig. 10B displays the scattering intensity of the two dominant ($E_{2H}$ and $E_{2L}$) as well as the $E_{1T}$ modes under NR\textit{E}_{\text{inc}} for the same NR. Similar to the
NR\textsubscript{inc} e, the E\textsubscript{1T} intensity showed a considerable increase as the analyzer angle changed to the E\textsubscript{inc}⊥E\textsubscript{sca} condition whereas the intensities from the E\textsubscript{2H} and E\textsubscript{2L} modes decreased as the analyzer rotation was changed towards E\textsubscript{inc}⊥E\textsubscript{sca}.

Figure 10: The Raman scattering behaviors of the E\textsubscript{1T} mode as well as the major modes for given light–matter interaction geometry were examined from the same zinc oxide nanorod while varying the analyzer rotation under the vertical and horizontal nanorod orientations. The linearly polarized laser was centered at the middle of the NR and the scattered Raman signals were probed in a cross polarized setting for different polarization states, ranging from 0° (E\textsubscript{inc}‖E\textsubscript{sca}) to 90 deg (E\textsubscript{inc}⊥E\textsubscript{sca}). (A) Under NR\textsubscript{inc} e, the E\textsubscript{1T} intensities became highly pronounced relative to the major peaks of E\textsubscript{2H}–E\textsubscript{2L} and A\textsubscript{1T} as the cross-polarization condition was changed towards E\textsubscript{inc}⊥E\textsubscript{sca}. (B) The intensity of the E\textsubscript{1T} mode also increased for the NR⊥E\textsubscript{inc} e when the E\textsubscript{inc}⊥E\textsubscript{sca} setting was reached. The signals from the major peaks of E\textsubscript{2L} and E\textsubscript{2H} tended to decrease as E\textsubscript{inc} became perpendicular to E\textsubscript{sca}.

According to the selection rules in Table 1, the allowed Raman mode for wurzite ZnO NRs probed in the \(x(z)\) or \(x(y)\) configuration is the E\textsubscript{1T} mode, and under these configurations, other
modes become forbidden. Hence, our observation of higher E₁T intensities with increasing analyzer rotation towards E_{inc}⊥E_{sca} is consistent with what is predicted for NRIE_{inc} and NRLE_{inc}. Yet, forbidden modes such as the A₁ and E₂ modes were also observed with weak intensities. The nonvanishing peaks of forbidden modes in the ZnO NR spectra may be attributed to potential deviations in the NR placement with respect to the light polarization. In ZnO, the transverse optical (TO)-longitudinal optical (LO) splitting is much larger (hundreds of cm⁻¹) than the A₁–E₁ splitting (tens of cm⁻¹). Mixing of A₁ and E₁ modes can occur if the phonon propagation direction is not perfectly in parallel or perpendicular to the crystal axis.⁴⁰ Therefore, slight errors in the ZnO NR alignment with respect to the polarization direction may be enough to produce this intermediate phonon propagation situation, resulting in the weak presence of the forbidden modes.

However, this does not explain the unique findings pertaining to the NR end-confined abnormalities detailed earlier. The unusual phenomena summarized in Fig. 9 differ from what were reported in previous works for explaining the non-vanishing forbidden modes.²⁹-³⁰ In those studies, the weak to moderate signals of forbidden Raman bands were generally attributed to the defects such as O or Zn vacancy in the ZnO crystalline lattice as well as to the physical disorder in ZnO. Examples of the latter include non-uniform crystal growth along the c-axis and small grains found on the surface of ZnO nanostructures. ZnO nanostructures in these previous studies were synthesized via hydrothermal methods and the presence of chemical and physical defects were confirmed by photoluminescence and electron microscopy.²⁹-³⁰ However, ZnO NRs in this work were synthesized via a gas phase approach which has shown to yield highly crystalline and atomic defect-free NR crystals.⁴¹-⁴² The X-ray diffraction data and additional luminescence data of the ZnO NRs used in this study are provided in Appendix A, Fig. S2. The data clearly demonstrate that the ZnO NRs are optical quality materials.
whose luminescence image and spectra, taken by using both the below- and above-bandgap excitation, showed no visible emissions characteristic of atomic defects. Only an intense UV photoluminescence peak associated with the ZnO bandgap appeared at 388 nm when the NRs were excited with 337 nm light.

Therefore, the same explanation for non-vanishing forbidden modes described in previous works do not apply to the polarization- and position-dependent Raman outcomes of ZnO NRs discussed here. In addition, we reveal that only forbidden modes produce the high scattering signals localized at the two NR ends. Their signals on the NR main body, on the contrary, follows the general behavior of the forbidden modes as reported previously. Hence, our finding signifies that the Raman scattering behaviors from individual ZnO NRs become highly position-dependent when the forbidden modes of ZnO are evaluated and should be interpreted accordingly as a function of the position along the NR.

From the electromagnetic enhancement point of view, a greater $E_{inc}$ field can be assumed at the NR termini relative to the main body similar to the lightning rod effect seen in surface enhanced or tip enhanced Raman scattering. More recently, similar Raman enhancement effects were reported for other systems beyond the commonly known, noble metals of Au and Ag. Metal oxide nanomaterials such as iron oxide and vanadium oxide were exploited in nonplasmon-based, Raman enhancement. These studies also indicated that the metal oxide-based enhanced Raman scattering can be applicable to a variety of systems such as TiO$_2$, WO$_3$, and ZnO. Hence, higher Raman scattering observed at the ZnO NR ends in this study could be considered to arise potentially from this enhanced $E_{inc}$ field. Yet, this consideration cannot still account for the fact that not all Raman modes were equally affected under the same $E_{inc}$ condition. In fact, a much more significant increase in Raman intensities were detected at the NR ends for the minor modes, but no distinct increase in scattering intensities were noted for the
major phonon modes. And this trend persisted regardless of the light–matter interaction geometry. These results indicate that the origin of the unusual Raman behaviors associated with individual ZnO NRs lie elsewhere.

Although not specifically pertaining to Raman transitions, we have previously observed unusual optical phenomena similarly occurring at the end positions of individual ZnO NRs. For example, the elastic scattering behaviors of single ZnO NRs under certain light–matter interaction geometry led to intense signals only at the two NR ends. In another instance, fluorescence signals emitted from biomolecules such as proteins and DNA exhibited much greater intensities at the two ends of ZnO NRs relative to those from the NR main body. Factors such as shape anisotropy, crystalline quality, and light–matter interaction orientation were crucial in controlling the NR position-dependent elastic scattering signals in the former e. For the latter, factors such as fluorophore spectroscopic characteristic, NR dimension, and shape anisotropy were important in enhancing the degree of fluorescence intensification at the NR ends whose process was based on the NR's subwavelength guiding and surface evanescent wave propagation of visible light. Specifically, the high shape anisotropy inherent to ZnO NRs played an important role in both circumstances. We hypothesize that, similarly for Raman, the high shape anisotropy of 1D ZnO nanomaterials may cause the NR position-dependent abnormalities in Raman scattering.

To further evaluate this potential influence of the high shape anisotropy of the ZnO NRs, we performed control Raman measurements on isotropic ZnO MPs, exhibiting an average aspect ratio of approximately 1:1 (width:length). Fig. 11 shows the summary of the Raman data obtained from these control experiments. Upon synthesis, ZnO MPs are found to expose two different crystalline planes as shown in Fig. 6(C), the hexagonal basal plane and the rectangular prismatic plane facing up. 40 and 24
ZnO MPs of random orientations, exposing their basal and prismic planes, respectively, were examined in the control experiments. We observed the same Raman intensity trend from the five peaks consistently on all ZnO MPs examined, showing the $E_{2H}$ and $E_{2L}$ modes as the predominant transitions regardless of the crystal planes, as shown in Fig. 11A. We then acquired position-resolved Raman spectra on the ZnO MPs. Fig. 11B shows subsequent Raman data taken from both the middle and edge areas of a single ZnO MP exposing its basal plane. From the intensity comparison between the five Raman modes, it is evident that there is no discernable difference in signals measured in the middle versus at the edge of the MP, both showing $E_{2H}$ and $E_{2L}$ peaks as the dominant ones. In addition, Raman intensities from individual ZnO MPs were mapped by rastering the beam across the MPs. Fig. 11C and D display representative raster results for the dominant, $E_{2H}$ and $E_{2L}$, Raman modes after mapping individual ZnO MPs exposing the prismic and basal plane, respectively. In both es, Raman signals for the $E_{2H}$ and $E_{2L}$ modes were strongest in the middle of the MPs and their intensities decreased near the MP edges. The stronger intensity of the Raman signals at the center of the MPs is due to this position maximal overlap of the incident beam with the MP mass. As the incident beam was placed closer to the edges, Raman intensity gradually decreased since the effective illumination area on the ZnO MPs relative to the Si substrate reduced at the particle boundaries. Regardless, the mapped Raman data in Fig. 11C and D reveal that the position-dependent scattering effect tends to decrease as the ZnO becomes isotropic in shape. The scattering profiles from the isotropic MPs in Fig. 11 are contrary to the Raman scattering characteristics identified from the highly anisotropic ZnO NRs. As discussed earlier for the NRs, Raman signals were generally higher at the NR ends than the NR middle (i.e. main body). In particular, even forbidden modes could yield very intense, spatially confined scattering signals at the NR ends.
Figure 11: Raman data collected from isotropic zinc oxide microparticles are summarized. 
(A) The five phonon modes were compared for their intensities measured on the prismatic versus basal facets of ZnO MPs using a linearly polarized incident light and no analyzer. Regardless of the crystalline facets and their orientations with respect to the incident polarization, the $E_{2L}$ and $E_{2H}$ modes exhibited dominant intensities. (B) 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. (C and D) Raman intensity maps of the two dominant of $E_{2L}$ and $E_{2H}$ modes are displayed for a ZnO MP presenting a prismatic facet in (C) and a basal facet in (D). In both panels, Raman signals were stronger at the center and weaker at the edge due to better overlap of the incident beam with the MP at the center which decreases as it moves towards the edge of the MP.

The ZnO NR and MP results combinedly demonstrate that the high shape anisotropy of the 1D nanomaterials plays a critical role in the unique, NR position-sensitive, Raman scattering characteristics of single ZnO NRs. The key significance of our study is that ZnO NR-position specific scattering behaviors were thoroughly examined for all five fingerprint Raman modes, which subsequently resulted
in the identification of unique NR end behaviors depending on the light–matter interaction geometry. By validating with a large number of NRs, various NR positions, and five different phonon modes, our results systematically show that Raman behaviors of the NR ends are indeed drastically different than those of the NR main body. Hence, it is not always suitable to assume that the scattering intensities of allowed or forbidden modes are uniformly and equally present on all positions of highly isotropic nanomaterials such as ZnO NRs and, hence, any generalization of the Raman behaviors from NR position-averaged data should be done in caution. Our findings in this study may promote novel applications of polarized Raman scattering whose optical outputs can be selectively modulated along the various positions on individual ZnO NRs. The position-resolved understanding of the polarized Raman responses from individual ZnO NRs provided in this work may also facilitate the accurate correlation of Raman scattering data with the NR properties pertinent to their optical and optoelectronic applications.

2.4. Conclusion

We have elucidated polarization-controlled Raman scattering behaviors of wurtzite ZnO NRs and MPs by explicitly determining their spatially distinct scattering profiles from individual nanomaterials. We have examined the five fingerprint Raman modes of ZnO NRs (E\textsubscript{2L}, E\textsubscript{2H}-2L, A\textsubscript{1T}, E\textsubscript{1T}, E\textsubscript{2H}) and identified polarization-specific, major and minor modes. We have subsequently ascertained polarization-specific behaviors of each phonon mode as a function of the position on the NR, consistent and incongruous with the Raman selection rules. In particular, we have reported a unique position-sensitive Raman scattering effect observed only from the NR ends which is related to the highly intense, NR end-localized scattering signals exhibited by the minor modes for given light–matter interaction geometry. By systematically comparing scattering features of individual ZnO NRs to the
profiles of individual MPs, we have shown that the polarization- and position-dependent Raman characteristics of ZnO NRs are absent in Raman profiles from the isotropic MPs. Consequently, we confirmed that the very strong, NR end-localized Raman scattering from the minor modes in ZnO NRs originates from the large shape anisotropy inherent to the NRs.

2.5. References


Chapter 3. Single Nanomaterial Level Investigation of Zinc Oxide Nanorod Sulfidation Reactions via Position Resolved Confocal Raman Spectroscopy

3.1. Introduction

The conversion of zinc oxide (ZnO) to zinc sulfide (ZnS) is an important process in many technological and industrial applications such as optoelectronics, photocatalysis, gas sorption, and gas removal.\textsuperscript{1-11} For developing technologically useful materials, the conversion reaction has been exploited to synthesize one of the important wide-bandgap semiconductors of ZnS from a pre-made template of ZnO via reaction with hydrogen sulfide (H\textsubscript{2}S)-generating reagents such as thioacetamide (TAA), sodium sulfide (Na\textsubscript{2}S), and ammonium polysulfide ((NH\textsubscript{4})\textsubscript{2}S\textsubscript{x}).\textsuperscript{5-6,8-9,12-17} In industrial and agricultural processes, the important uses of this conversion reaction involve ZnO-based sorbents for removing H\textsubscript{2}S in syngas production\textsuperscript{2,4,7,10-11} and controlling the release of biogas-derived H\textsubscript{2}S to the atmosphere.\textsuperscript{1,3}

In particular, due to the enhanced sensing and catalytic functionalities that can be enabled by ZnS materials with reduced dimensionality,\textsuperscript{5} nanoscale forms of ZnO have been extensively utilized as sacrificial templates for conversion to ZnS nanostructures. For example, different nanoscale ZnO structures have been identified as S-scrubbers,\textsuperscript{1,3,18-19} even leading to commercially available, ZnO nanomaterial-based, S-sorbent products.\textsuperscript{20-21} The use of nanosized ZnO in these applications has shown great promise as the inherently large surface-to-volume ratio of the nanomaterials offers higher conversion to ZnS than micron or bulk scale ZnO.\textsuperscript{5} However, there is still a lack of fundamentally driven guiding principles for selecting one type of nanomaterial over the others for ZnO sulfidation, and the majority of current approaches to study the conversion of ZnO to ZnS rely on ensemble-averaged, macroscopic scale characterization methods or reactor-scale product testing. Sulfidation reaction of
ZnO nanomaterials, therefore, has to be examined more systematically, especially at the individual nanomaterial level.

Different reactivities of ZnO materials towards sulfidation have been reported, but with mixed outcomes. When ZnO sulfidation was carried out with (NH₄)₂Sₓ, it was found that the (0001) surface was the least reactive to sulfidation with the (000–1) and (10–10) surfaces reacting similarly better. No appreciable morphological changes of ZnO were observed in this case. In another study of a ZnO reaction assisted by (NH₄)₂SₓOᵧ and Na₂S, a significant change in ZnO structure was obtained after sulfidation. Another set of studies involving the starting material ZnO or ZnTiO and the sulfidation agent TAA or H₂S gas at elevated temperatures reported that the (0001) surface was the most reactive towards sulfidation. In these studies, considerable deformation of the starting ZnO material was detected. Comparatively, very few studies exist that elucidate the sulfidation reaction taking place on individual ZnO nanomaterials. Distinct from many past efforts using large-scale, ensemble-averaged evaluation of ZnO sulfidation reaction, a chemically sensitive measurement approach capable of examining individual ZnO nanostructures and quantitatively providing information on crystal facet-specific sulfidation reaction will be highly beneficial in this regard.

Raman spectroscopy represents a powerful tool for probing chemical and structural changes of nanomaterials. Unlike electron microscopy (EM)-based techniques, Raman scattering can detect composition- and structure-associated material changes in various surrounding media. Despite this, the utility of Raman scattering for discerning facet-dependent chemical reactivities from discrete ZnO nanostructures has not yet been demonstrated.
In this work, we demonstrate that spatially resolved confocal Raman spectroscopy can be exploited to unambiguously reveal the different facet-dependent reactivities in the sulfidation of ZnO nanorods (NRs). ZnO NRs were selected for study due to the wealth of knowledge available, allowing for the facile synthesis of well-defined and defect-free single crystals using chemical vapor deposition (CVD). Individual ZnO NRs produced with high optical quality and well-defined crystalline structures can provide an ideal scaffold to elucidate ZnO facet-dependent reactivity differences towards sulfidation. We quantitatively determine NR facet-dependent sulfidation reactivities by resolving newly appearing ZnS Raman peaks measured from different NR positions on the same ZnO NRs and subsequently comparing the intensities of various ZnS phonon peaks from different facets. The Raman results are further supported by electron microscopy and fluorescence emission data obtained from the same NRs. Our efforts in this work can provide a single crystal level understanding of the facet-dependent S reactivity of ZnO NRs whose insight, in turn, may lead to fundamentally guided, nanomaterial design principles important for the aforementioned applications. Together with the fact that ZnO nanomaterials can be made in a variety of shapes and crystal structures, our endeavors in this work can be broadly beneficial to meet the ever-increasing demand for ZnO-derived nanomaterials in the adsorption, removal, conversion, and separation of H$_2$S.

3.2. Experimental Methods

The synthesis of ZnO NRs was performed via CVD in a customized horizontal tube furnace. The feedstock source, a 2:1 by weight mixture of ZnO (99.999% purity) and graphite (99.99% purity) powders obtained from Alfa Aesar Inc. (Haverhill, MA), was placed in a source quartz boat and positioned on top of a heating element located at the center of the tube furnace. A target quartz boat containing the growth substrate, a 1 × 1 cm$^2$ Si wafer received from Silicon Quest, Inc. (San Jose, CA),
was placed 15.6 cm away from the source boat, downstream from the Ar carrier gas flow. The Si wafer was pretreated with 20 μL of a growth catalyst, 20 nm Au colloid from Ted Pella, Inc. (Redding, CA), for 5 min. Subsequent thermal reduction of the feedstock source was achieved by heating the furnace to 950 °C for 20 min to 1 h at a ramp-up/ramp-down rate of 15 °C min\(^{-1}\) under a constant Ar gas flow of 100 standard cubic centimeters per minute.

The conversion of ZnO NRs to ZnS was carried out using thioacetamide (TAA), obtained from Sigma Aldrich Corp. (St Louis, MO), dissolved in deionized water (DI) to a desired concentration of 0.002 to 0.2 M. Either densely grown ZnO NRs (referred to as the dense NR plate method) or dispersed ZnO NRs (the dispersed NR reaction method) on a Si substrate were reacted by submerging the plate in 1 mL of TAA solution in a sealed tube. The sample was left to react at 90 °C for 24 h, after which it was rinsed with DI and subsequently dried under nitrogen. For attaining the different degrees of sulfidization reaction described in this paper, the concentration of TAA was adjusted while keeping the reaction time as 24 h. NR reactions with 0.002 M, 0.02 M, and 0.2 M of TAA yielded mildly, moderately, and highly sulfidated NRs, respectively. Regardless of the NR preparation protocol used, our measurements were focused on collecting data from individual NRs. To achieve this, in the dense NR plate method, the densely grown mat of ZnO NRs on the growth substrate was first reacted with TAA. Subsequently, the TAA-reacted NRs were sonicated off from the original plate and redispersed onto a clean Si substrate for subsequent NR characterization. In the dispersed NR method, the NRs were initially sonicated from the growth substrate containing dense ZnO NRs and dispersed in ethanol. Reconstituted ZnO NRs were then deposited onto a clean, gridded Si plate via drop-casting to track the same NRs during repeated measurements. All the presented data showing the changes before and after TAA reaction by tracking the same NRs were obtained from the dispersed NR reaction method.
The morphological structures of the unreacted and S-reacted ZnO NRs were characterized using a field emission scanning electron microscope (FESEM), FEI Nova NanoSEM 450 (FEI Company, Hillsboro, OR), operated at 20 keV. Scanning tunneling electron microscopy (STEM) images and energy-dispersive X-ray spectroscopy (EDX) data were also acquired on the same instrument using a STEM and EDX detector, respectively, operating with a voltage of 30 keV. EDX data were then analyzed using AZtecTEM software from Oxford Instruments (Concord, MA). For STEM and EDX, TAA reacted NR samples were first prepared by the dense NR plate method described above. 5 μL of the reacted NRs, resuspended in ethanol via sonication, was then deposited onto a TEM grid of a pure C film on 200-mesh Au (Electron Microscopy Sciences, Hatfield, PA). For all optical measurements, a Zeiss Axio Imager A2M (Carl Zeiss, Inc., Thornwood, NY) microscope equipped with an AxioCAM HRm digital camera was employed. Reflected bright/dark-field (BF/DF) illumination and unpolarized fluorescence excitation were produced using a 12 V per 100 W halogen lamp and a 120 W mercury vapor lamp (X-Cite 120Q), respectively. The wavelength range used for the fluorescence measurements was 450–490 nm for excitation and 510–540 nm for collection. BF, DF, and fluorescence images were acquired with EC Epiplan-NEOFLUAR 50× (numerical aperture, NA = 0.8) and 100× magnification (NA = 0.9) objective lenses using 2 s exposure. X-ray diffraction (XRD) measurements were made using a Rigaku Ultima IV X-ray diffractometer (The Woodlands, TX), operated with an accelerating voltage of 40 kV under Cu Kα radiation (1.542 Å) that was scanned in the range of 2θ = 20–55° at a rate of 1° min⁻¹.

Raman scattering data were collected using a LabRAM HR Evolution confocal Raman microscope (Horiba Instruments Inc., Sunnyvale, CA). The scattering data were obtained through a 100× magnification, long working distance, objective lens of NA = 0.8 (Olympus Corp., Waltham, MA) using
a 100 mW 532 nm laser or, alternatively, a 40 mW 405 nm laser, which was focused on an approximate beam size of 1 μm. The polarization of the incident laser ($E_{\text{inc}}$) was kept perpendicular to the NR long axis ($c$-axis), i.e. $\text{NR} \perp E_{\text{inc}}$, for all Raman data of the individual NRs reported in the paper. Raman scattering signals were then collected using an 1800 line per mm grating and a charge-coupled-device (CCD) detector. The scan range used was 50–500 cm$^{-1}$ and 125–500 cm$^{-1}$ for the 532 nm and 405 nm lasers, respectively. The stated frequency window was chosen to examine the characteristic Raman fingerprint regions for the materials of ZnO and ZnS, while considering the filter specifications used in our experimental setup for the two excitation lasers.

3.3. Results and Discussion

We first acquired ensemble-averaged data collectively from many ZnO NRs. Fig. 12 displays the Raman, fluorescence, and XRD data obtained from the different TAA reaction stages of densely grown ZnO NRs on a Si growth plate, from unreacted, to mildly reacted, and to extremely reacted stages in Fig. 12(A), (B), and (C), respectively. The image inserted above the Raman spectrum in Fig. 12(A) displays a BF view of a densely grown mat of ZnO NRs on Si. The typical Raman spectrum of unreacted ZnO NRs as-grown on Si is provided in Fig. 12(A). The Raman peaks at 98, 331, 378, 413, and 437 cm$^{-1}$ correspond to the $E_{2L}$, $2^\text{nd}$ order $E_{2H}–E_{2L}$, $A_{1T}$, $E_{1T}$, and $E_{2H}$ phonon modes, respectively. These peaks are the characteristic Raman modes associated with ZnO exhibiting a wurtzite crystal structure of the $C_{6v}^4$ space group.$^{29,30}$ This symmetry group has six $1^\text{st}$ order optical modes ($\Gamma_{\text{opt}} = A_1 + 2B_1 + E_1 + 2E_2$ at the $\Gamma$ point of the Brillouin zone (BZ)), consisting of $A_1$, $B_{1L}$, $B_{1H}$, $E_1$, $E_{2L}$, and $E_{2H}$. Of these, all but the two $B_1$ modes are Raman active. With further reaction of the ZnO NRs with TAA, new Raman peaks emerged that were consistent with the presence of ZnS. The Raman spectrum in Fig. 12(B) from the moderately reacted ZnO NRs now displays peaks from both ZnO and ZnS. The new peaks at 150,
261, and 349 cm$^{-1}$ belong to ZnS. The broad shallow peak centered at 150 cm$^{-1}$ is associated with multiple 2nd order Raman modes such as 2TA$_{L}$, [TO$_{u}$-LA]$_{Σ}$, [LO-LA]$_{Σ}$, and 2TA$_{X}$.

Another broad peak spanning the frequency of 240 to 285 cm$^{-1}$ stems from both the 1st order (three weak phonon modes of A$_{1T}$, E$_{1T}$, and E$_{2H}$) and 2nd order (contributions from acoustic overtones such as [2TA$_{u}$]$_{Σ}$, [LA + TA$_{l}$]$_{W}$, and [LO-TA$_{u}$]$_{X}$) ZnS peaks.

T, L, A, and O stand for the transverse, longitudinal, acoustic, and optic modes. The subscripts u and l indicate the upper and lower branches of the mode, respectively, whereas those of Σ, W, and X denote the different symmetry points in BZ. The peak appearing at 349 cm$^{-1}$ is a contribution from the co-located, 1st order A$_{1L}$/E$_{1L}$ modes. The spectrum in Fig. 12(B) also shows an additional ZnS peak in the frequency region of 275–283 cm$^{-1}$ that matches the predicted Raman shift region of the weak ZnS phonon modes of A$_{1T}$, E$_{1T}$, and E$_{2H}$. However, due to the close proximity and weak signal of these phonon modes, we cannot distinguish the exact peak location for each mode. As such, we report them as a range indicating a combined peak contribution from all three modes. At the same time, ZnO signals are also present in the Raman spectra of the moderately reacted NR ensemble sample. The E$_{2L}$ and E$_{2H}$ modes of ZnO still remained pronounced. The minor ZnO modes of E$_{2H}$–E$_{2L}$ and A$_{1T}$/E$_{1T}$ under this light interaction geometry were still identifiable. The peak near 334 cm$^{-1}$ is a combined contribution from the surface optic (SO) mode of ZnS.

Lastly, the Raman spectrum of the fully reacted NRs is shown in Fig. 12(C). The NRs underwent near complete sulfidation which can be seen by the negligible presence of ZnO-related Raman peaks. Rather, in the extremely reacted NRs, ZnS signals were prominently observed, particularly from the higher order peaks at 150 cm$^{-1}$ and 261 cm$^{-1}$. In addition, another dominant ZnS peak appeared at 349 cm$^{-1}$, which is due to the combined contributions from A$_{1L}$ and E$_{1L}$ modes of ZnS. Table 2 summarizes these different phonon modes that were resolved in our Raman measurements of the unreacted and S-reacted ZnO NRs.
Figure 12: Raman scattering, fluorescence, and X-ray diffraction data of a dense mat of zinc oxide nanorod ensemble samples taken after varying the degree of the thioacetamide reaction. (A through C) Raman scattering spectra and fluorescence emission panels were obtained from (A) unreacted, (B) moderately reacted, and (C) extremely reacted ZnO NR ensemble samples. An exemplar BF panel of a dense mat of as-synthesized ZnO NR ensemble is inserted in (A). Raman scattering measurements were carried out with 532 nm incident light. Fluorescence data of the samples were collected using $\lambda_{\text{excitation}} = 450-490$ nm and $\lambda_{\text{collection}} = 510-540$ nm. (A) Raman scattering profiles of the pristine ZnO NRs show the characteristic ZnO phonon peaks of E2L, E2H–E2L, A1T, E1T and E2H, as annotated in the spectrum. No fluorescence emission was seen from these pristine ZnO NR ensembles. (B) When moderately reacted with TAA, the Raman scattering spectrum of the ZnO NR ensemble sample exhibits peaks associated with both ZnO and ZnS. Pertinent ZnO and ZnS phonon modes are annotated next to each peak in the spectra. Considerable green fluorescence was emitted from the moderately reacted sample. (C) When the ZnO NR ensemble sample was reacted to near completion, ZnS peaks dominated the Raman spectrum with negligible peak presence of ZnO. The extremely reacted sample showed intense green fluorescence. (D through F) XRD patterns of (D) unreacted, (E) moderately reacted, and (F) extremely reacted ZnO NR ensemble samples. (D) Diffraction peaks belonging to pure ZnO NRs are annotated in the XRD spectra. (E) A new peak at $\sim29^\circ$ belonging to ZnS appeared after a moderate TAA reaction. All characteristic ZnO diffraction peaks are still largely retained in the XRD spectra, one of which shares the same peak location as ZnS, as assigned in the spectra. (F) The ZnS-associated diffraction peaks grew stronger in intensity in the extremely reacted sample.
Table 2: Measured frequencies of the first and second order Raman peaks pertinent to sulfidation of zinc oxide. ZnS Raman modes corresponding to the crystal phases of hexagonal wurtzite and cubic zinc blend are indicated as (h) and (c), respectively. The two lowest frequency peaks marked with "*" were observed only under 532 nm excitation due to our instrument setup allowing frequency detection greater than 125 cm$^{-1}$ with 405 nm excitation.

<table>
<thead>
<tr>
<th>Peak location (cm$^{-1}$)</th>
<th>Phonon mode assignment</th>
<th>Peak feature</th>
<th>ZnO or ZnS</th>
</tr>
</thead>
<tbody>
<tr>
<td>70*</td>
<td>$E_{2L}(h)$</td>
<td>Medium</td>
<td>ZnS</td>
</tr>
<tr>
<td>98*</td>
<td>$E_{2L}$</td>
<td>Intense under NR(\perp E_{\text{inc}})</td>
<td>ZnS</td>
</tr>
<tr>
<td>150</td>
<td>2$^{\text{nd}}$ order multiple optic and acoustic overtones</td>
<td>Broad, spanning 130–180 cm$^{-1}$</td>
<td>ZnO</td>
</tr>
<tr>
<td>261</td>
<td>2$^{\text{nd}}$ order multiple optic and acoustic overtones</td>
<td>Broad, spanning 240–270 cm$^{-1}$</td>
<td>ZnS</td>
</tr>
<tr>
<td>275–283</td>
<td>$E_{1T}(h)$, $A_{1T}(h)$, $T_{2T}(c)$ $E_{2H}(h)$</td>
<td>Weak</td>
<td>ZnS</td>
</tr>
<tr>
<td>331</td>
<td>2$^{\text{nd}}$ order $E_{2H}$–$E_{2L}$</td>
<td>Weak</td>
<td>ZnO</td>
</tr>
<tr>
<td>334</td>
<td>SO(h,c)</td>
<td>Weak</td>
<td>ZnS</td>
</tr>
<tr>
<td>340–360</td>
<td>$E_{1L}(h)$, $A_{1L}(h)$, $T_{2L}(c)$</td>
<td>Medium to strong</td>
<td>ZnS</td>
</tr>
<tr>
<td>378</td>
<td>$A_{1T}$</td>
<td>Weak under NR(\perp E_{\text{inc}})</td>
<td>ZnO</td>
</tr>
<tr>
<td>413</td>
<td>$E_{1T}$</td>
<td>Weak under NR(\perp E_{\text{inc}})</td>
<td>ZnO</td>
</tr>
<tr>
<td>437</td>
<td>$E_{2H}$</td>
<td>Intense under NR(\perp E_{\text{inc}})</td>
<td>ZnO</td>
</tr>
</tbody>
</table>

The image panel to the right of each Raman spectrum in Fig. 12(A through C) displays the corresponding fluorescence emission data of the NR ensemble sample. The fluorescence panel of the as-synthesized ZnO NRs in Fig. 12(A) is completely dark. This is as expected from high purity ZnO NRs grown using CVD,$^{24-25,36}$ which show negligible chemical and crystalline defects. In contrast, ZnO NRs after TAA reaction in Fig. 12(B) and (C) display considerable green emission. The green fluorescence stems from sulfidation-caused atomic and structural defects that started developing in the original ZnO NR crystal. Similar defect-originated luminescence in the visible range has been well documented from ZnO and is known to be associated with atomic point defects in the material such as interstitial and vacancy sites.$^{37-39}$ As the reaction proceeded towards near completion, the intensity of the green fluorescence also increased, as evidenced by comparing the fluorescence panels shown in Fig.
12(B) and (C). Corroborating the trend in ZnS-associated Raman signals in the Raman spectra in Fig. 12, the higher fluorescence emission found in Fig. 12(C) relative to that of Fig. 12(B) indicates that fluorescence intensity is correlated to the level of NR sulfidation.

Fig. 12(D) through (E) display the XRD data for both the unreacted, moderately reacted, and extremely reacted ZnO NR ensemble samples. The diffraction peaks of the as-grown, dense mat of ZnO NRs on Si are presented in the XRD spectrum in Fig. 12(D). Characteristic wurtzite ZnO (JCPDS PDF card no. 36-1451) peaks of (10−10), (0002), (10−11), and (10−12) appear at approximately 2θ = 31.8°, 34.5°, 36.5°, and 47.5°, respectively. Fig. 12(E) displays the XRD pattern of the NR ensemble sample after a moderate reaction with TAA. The XRD spectrum after TAA reaction exhibits a new small peak at approximately 28.5°, corresponding to ZnS (JCPDS PDF card no. 36-1450). In addition, the (11−20) peak of ZnS at 47.5° appears at the same positions as (10−12) of ZnO, as indicated in Fig. 12(E). As the reaction was proceeded to near completion, the two ZnS-associated diffraction peaks of (10−10) and (11−20) at 28.5° and 47.5°, respectively, increased their intensities substantially relative to the ZnO diffraction peaks, as shown in Fig. 12(F).

We continued the structural and chemical investigation of ZnO NRs while focusing on individual NRs instead of their ensembles. Fig. 13(A) shows an illustration of collecting spatially resolved Raman scattering signals along different positions on single NRs. The excitation polarization was held perpendicular to the long axis (c-axis) of the NR, whose light–matter interaction geometry is known to provide the greatest sensitivity from ZnO NRs with the intense and dominant E\textsubscript{2L} and E\textsubscript{2H} signals.\textsuperscript{40-41} Although much lower in intensity under this light–matter interaction orientation, additional ZnO phonon modes such as E\textsubscript{1T}, A\textsubscript{1T}, and the 2\textsuperscript{nd} order E\textsubscript{2H}–E\textsubscript{2L} are also expected to be present according to the selection rule. The molecular origins of the vibrations associated with the allowed ZnO Raman modes are schematically depicted using a ball-and-stick model in Fig. 13(A). Fig. 13(B) displays a SEM image of a single, unreacted ZnO NR as well as its spatially resolved Raman spectra collected using a 532 nm laser. Raman measurements were performed from two distinctive positions of the NR middle (blue) and end (red) to ascertain the reactivity differences associated with the side (prismic) and end (basal) facets of a ZnO NR, respectively. Both the SEM micrograph and the Raman spectra
presented in Fig. 13(B) are typical of pristine, individual ZnO NRs before TAA reaction. The two end facets of wurtzite ZnO NR crystals consist of purely Zn-containing (0001) and O-containing (000−1) planes in contrast to the six side facets of the {10−10} planes on the NR main body that have an equal surface density of Zn and O atoms due to the alternating Zn and O layers in the crystal. The SEM micrograph of the unreacted ZnO NR in Fig. 13(B) shows that the NR indeed exhibits clean and smooth hexagonal facets at the two ends and rectangular facets on the six sides of the wurtzite crystal. The corresponding Raman scans in Fig. 13(B) display the two dominant ZnO phonon modes of $E_{2L}$ and $E_{2H}$ from both NR middle and end locations. The spectra also show other allowed modes of $E_{1T}$, $A_{1T}$, and $E_{2H}$–$E_{2L}$, as discussed above.
Figure 13: Experimental setup for the Raman scattering measurements along with an exemplary zinc oxide nanorod showing the expected zinc oxide Raman spectrum. (A) Schematic illustration depicting the position-resolved Raman scattering measurements focusing on individual ZnO NRs using a linearly polarized laser ($E_{\text{inc}}$) with its excitation polarization oriented perpendicular to the NR long axis, i.e. c-axis. All allowed Raman active modes expected from a wurtzite ZnO crystal are depicted using a ball-and-stick model, displaying the different vibrations associated with the Zn and O atoms for each phonon mode. (B) Typical SEM panel and Raman spectra obtained from unreacted, individual ZnO NRs are displayed. The grey scale SEM image shows the basal and prismatic facets of a wurtzite ZnO NR crystal where the NR region marked with an asterisk is also provided as a zoomed-in SEM inset. The BF panel represents the typical optical image of pristine ZnO NRs viewed under the confocal Raman microscope to focus the laser beam on a specific point along the NR long axis such as the middle or end position. The blue and red Raman spectra correspond to the scattering signals measured at the middle and end positions, respectively, of the ZnO NR shown in the SEM panel. 532 nm incident light was used for Raman scattering collected at the Raman shift window of 70–500 cm$^{-1}$. ZnO Raman peaks corresponding to the $E_{2L}$ (98 cm$^{-1}$), $E_{2H}–E_{2L}$ (331 cm$^{-1}$), $A_{1T}$ (378 cm$^{-1}$), $E_{1T}$ (413 cm$^{-1}$) and $E_{2H}$ (437 cm$^{-1}$) modes were detected in both spectra which, under this light–matter interaction geometry of NR$\perp E_{\text{inc}}$, show the two $E_{2}$ peaks ($E_{2L}$ and $E_{2H}$) as the dominant ZnO phonon modes.
We then investigated the effect of TAA reaction on single ZnO NRs prepared by the ‘dense NR plate’ method where the as-synthesized ZnO NRs were first reacted with TAA on the Si growth substrates. Subsequently, the TAA-reacted ZnO NRs were sonicated off and redeposited onto a clean Si plate for the ensuing optical, fluorescence, SEM, and Raman measurements of single NRs. As the NR data in Fig. 14 through 16 were created this way, the reactivities on the two NR ends were not identical to each other. Only one end of the NRs was freely exposed to the TAA solution whereas the other end was anchored to the underlying growth plate and partially buried by the neighboring NRs. Despite this, a general trend in S reactivity was observed between the NR middle and end positions.
Figure 14: A representative set of correlated scanning electron microscopy, fluorescence emission, and Raman scattering data from mildly sulfidated zinc oxide nanorods. (A) The SEM panel of a ZnO NR after a mild reaction clearly displays small NPs of ~35 nm diameter decorating the outer surface of the still largely intact NR. In contrast to the complete absence of fluorescence seen in unreacted ZnO NRs, green fluorescence was noticeable at all the positions of the mildly reacted NR. (B) Raman spectra taken at the middle (blue) and end (red) positions of the NR discussed in (A) are presented. The incident laser used was 532 nm in wavelength with its polarization perpendicular to the NR c-axis. The exact NR positions from which the presented spectra were obtained are indicated in the SEM image. A zoomed-in SEM view of the NR region marked with an asterisk is also shown. Overall, the Raman scattering data from both NR positions indicated that the NR with the strong E$_{2L}$ and E$_{2H}$ ZnO peaks is still largely made up of ZnO. At the same time, the presence of ZnS in the NR was confirmed with a small peak newly appearing at 70 cm$^{-1}$ that corresponds to the E$_{2L}$ mode of ZnS. (C) STEM/EDX data of a ZnO NR after a mild sulfidization reaction. The grey scale panel corresponds to the STEM viewgraph of the NR whose chemical compositions and their spatial distributions were subsequently assessed by EDX measurements performed on the NR. The green, blue, and yellow channels display EDX maps of the NR corresponding to the atomic elements Zn, O, and S, respectively.
A representative set of BF, SEM, fluorescence, and Raman data was obtained from single ZnO NRs that underwent a mild sulfidation reaction with TAA, as shown in Fig. 14. The SEM panel in Fig. 14(A) reveals that the sulfidation reaction resulted in the formation of small nodules decorating the surface of a NR. The inset marked with an asterisk in Fig. 14(B) further shows a zoomed-in SEM view of these nanoparticles (NPs) of ~35 nm diameter produced on the mildly reacted ZnO NR. Similar ZnS particles have previously been reported to form outside ZnO voids via the Kirkendall effect.\(^{12,15,22}\) The fluorescence panel in Fig. 14(A) shows green emission present continuously at all positions along the length of the NR. NR position-resolved Raman spectroscopy was subsequently performed under 532 nm excitation. Fig. 14(B) displays the resulting Raman spectra. The exact positions on the NR from which the Raman spectra were obtained are marked using the SEM viewgraph of the NR. In both the Raman spectra acquired from the middle (blue) and end (red) positions, the dominant signals were the \(E_{2L}\) and \(E_{2H}\) modes of ZnO. In addition to the ZnO peaks, a small hump at around 70 cm\(^{-1}\) newly appeared in both Raman spectra after a mild TAA reaction. The peak is due to the \(E_{2L}\) mode of ZnS formed via the chemical conversion of ZnO to ZnS, as shown below.\(^{15}\) \(\text{H}_2\text{S}\) released after the hydrolysis reaction of TAA further reacts with ZnO NRs and converts ZnO to ZnS, an energetically favored process with \(-87.9\) kJ mol\(^{-1}\) at 90 °C.

\[
\begin{align*}
\text{CH}_3\text{CSNH}_2 (\text{TAA}) + \text{H}_2\text{O} & \rightarrow \text{CH}_3\text{CONH}_2 + \text{H}_2\text{S} \\
\text{CH}_3\text{CSNH}_2 + 2\text{H}_2\text{O} & \rightarrow \text{CH}_3\text{COOH} + \text{NH}_3 + \text{H}_2\text{S} \quad \text{(or CH}_3\text{COONH}_4 + \text{H}_2\text{S)} \\
\text{ZnO (s)} + \text{H}_2\text{S (aq)} & \rightarrow \text{ZnS (s)} + \text{H}_2\text{O (l)}
\end{align*}
\]

Fig. 14(C) displays typical STEM and EDX data collected from NRs after sulfidation. The EDX spectrum of a NR shown in the STEM panel in Fig. 14(C) is presented along with the EDX images that contain the elemental mapping results for Zn, O, and S. These results agree with the Raman outcomes and confirm the presence of the three atomic elements on the NR after undergoing the sulfidation reaction shown above. Furthermore, the EDX maps of the NR qualitatively show the spatial distribution of Zn, O, and S in the NR. O is found in the NR interior, showing a weaker presence in the NR exterior. In contrast, S, along with Zn, is found in both the interior and the exterior of the NR where more S is
positioned near the exterior. The distribution of Zn, O, and S in a sulfidated NR can be more clearly seen in the overlapped channels of EDX chemical maps provided in Appendix B, Fig. S1.

A representative data set obtained from moderately reacted ZnO NRs is displayed in Fig. 15. The morphology of a moderately reacted NR revealed by SEM in Fig. 15(A) confirms that the ZnO NR was subject to more substantial reaction around the NR side and end facets. The speckled ZnS NPs on the NR surface seemed to have coalesced into a near complete shell, separated entirely from the core by a layer of void region in some parts and into small cavities in other parts of the NR. Such shell and void structures of the NR can be seen more clearly in the zoomed-in SEM panel in Fig. 15(B) for the NR examined with BF, SEM, fluorescence, and Raman spectroscopy as well as in the high magnification SEM data in Fig. 15(C) acquired from similarly reacted NRs. Additional structural changes were observed all along the NR length where local dissolution of the NR seemed to have occurred. The NR side and end facets were no longer clean and smooth. The crystal in Fig. 15(A) now appears tapered on the left end while the facets on the side and the right end have an uneven, gnawed morphology. The fluorescence emission panel in Fig. 15(A) shows that the fluorescence intensity is overall higher for the moderately reacted NR relative to the case of Fig. 14(A). As discussed before, the fluorescence intensity profile along the NR seemed to be consistent with the level of sulfidation-induced NR morphological change observed by SEM. The left end of the NR showing the higher fluorescence emission belongs to the more disrupted NR end with greater degradation and loss of its original facet structure in the SEM panel. The Raman spectra of the moderately reacted ZnO NR provided in Fig. 15(B) resolve the scattering signals from the NR middle (blue) and end (red) positions as marked in the SEM image. The ZnS $E_{2L}$ peak at 70 cm$^{-1}$ is more pronounced than the case of Fig. 14(B). Furthermore, additional characteristic peaks of ZnS are now present such as the ones centered at 283 cm$^{-1}$ and 349 cm$^{-1}$ due to the combined contributions from multiple $1^{st}$ order phonon modes as specified in Table 2. In addition, broad peaks are observed at 150 cm$^{-1}$ and 261 cm$^{-1}$ which belong to the $2^{nd}$ order ZnS Raman modes as discussed earlier. Rather shallow and broad peaks located at 320–400 cm$^{-1}$ are due to the combined contributions of ZnS and ZnO where the $2^{nd}$ order ZnS peaks emerge together with the signals from the $E_{2H}$–$E_{2L}$, $A_{1T}$, and $E_{1T}$ modes of ZnO, as annotated in the spectra. At the same time, the once dominant
$E_{2L}$ and $E_{2H}$ peaks of ZnO are still quite noticeable, but their relative intensities compared to those of the ZnS $E_{2L}$ and $E_{2H}$ peaks now have been significantly diminished both in the middle and end spectra.
Figure 15: A representative set of correlated bright field, scanning electron microscopy, fluorescence emission, and Raman scattering data from moderately sulfidated zinc oxide nanorods. (A) The SEM panel of a moderately reacted ZnO NR reveals a shell-like structure that is separated from the NR core by a thin void layer formed just beneath the NR surface. Strong fluorescence emission was observed at all the positions of the NR. (B) Raman scattering data of the moderately reacted NR are presented as two spectra, corresponding to the signals collected from the middle (blue) and end (red) positions of the NR. An excitation wavelength of 532 nm was used with its polarization perpendicular to the NR c-axis. Overall, the Raman scattering peaks of the NR indicated the combined contributions of ZnO and ZnS. The ZnS E$_{2L}$ peak at 70 cm$^{-1}$ has grown substantially and additional ZnS peaks have developed at 150 cm$^{-1}$, 261 cm$^{-1}$, and 349 cm$^{-1}$. At the same time, the intensities of the two dominant ZnO modes of E$_{2L}$ and E$_{2H}$ have decreased considerably to the intensity levels of the minor ZnO peaks of E$_{2H}$–E$_{2L}$, A$_{1T}$, and E$_{1T}$. A zoomed-in SEM view of the NR region marked with an asterisk clearly displays the structural changes that the NR underwent during the sulfidation reaction, which yielded an outer shell separated from the core by a gap layer. (C) High magnification SEM images are additionally provided for NRs that underwent a moderate sulfidation reaction similar to the NR shown in (A and B). The additional NRs also exhibit shell-like structures due to the formation of void regions just beneath the NR surface. All scale bars are 100 nm.
The data set provided in Fig. 16 represents highly sulfidated ZnO NRs. The ZnO NR in Fig. 16 underwent significant reaction to the point of developing completely hollow regions in the NR, as seen in the SEM panel in Fig. 16(A). The magnified SEM view in the inset of Fig. 16(B) is presented to display the tube-like structure of the NR with no core material inside. Fig. 16(C) presents high magnification SEM images taken from additional, highly reacted NRs in order to clearly show the tube-like structures formed inside highly sulfidated NRs. The fluorescence profile of the highly reacted NR in Fig. 16(A) exhibits intense green emission to the largest extent of all the individual NR cases discussed so far. The Raman spectra from the middle (blue) and end (red) positions of the highly reacted NR in Fig. 16(B) further confirm this increased level of ZnO to ZnS conversion. ZnO scattering signals from all phonon modes are found to be substantially weaker than in the previous cases. Additionally, compared to the NR in Fig. 15, there is generally a loss of ZnS spectral features. The reduction of not only ZnO but also ZnS signals in the highly reacted NR sample may result from the overall material loss as well as the destruction of any ordered ZnO or ZnS structures that were previously present. Such a loss of NR matter and structural integrity is observed in the SEM panels in Fig. 16 as the largely deformed NR ends and the hollow spaces formed in the NR. For ZnS Raman peaks, it is the higher order modes such as those at 150 cm$^{-1}$ and 261 cm$^{-1}$ that become more pronounced at this stage, rather than the 1$^{st}$ order peaks. This is consistent with the results presented in Fig. 12(C) where it was the higher phonon modes of ZnS that was predominantly found in the more sulfidated NR ensemble sample.
Figure 16: A representative set of correlated bright field, scanning electron microscopy, fluorescence emission, and Raman scattering data from highly reacted zinc oxide nanorods. (A) The SEM micrograph of a highly reacted ZnO NR indicates that the void regions seen in the moderately reacted NR in Fig. 4 are no longer confined just beneath the NR surface and have penetrated into the core section in some parts of the NR, forming tube-like structures towards the two NR end regions. The fluorescence panel displays intense green emission along the NR. (B) The corresponding Raman spectra of the highly reacted NR in (A) are presented. The spectra of the NR middle (blue) and end (red) positions were taken with 532 nm incident light with its polarization perpendicular to the NR c-axis. The grey scale image marked with an asterisk is the zoomed-in SEM viewgraph to show the hollow structure formed inside the highly reacted NR. Overall, both ZnO and ZnS signals were found to decrease in the highly reacted NR relative to the previous cases. As for the ZnS related Raman peaks, the higher order modes were found to be more persistent with more NR sulfidation. (C) Additional, high magnification SEM images are provided for highly reacted NRs. The characteristic, tube-like structures with no core materials inside the NR can be clearly seen in all panels. The scale bar in each panel is 100 nm.
When examining the effects of varying sulfidation degrees on the individual NR cases in Fig. 14 through 16, higher sulfidation reactivity seems to be expected for the end (basal) than for the main body (prismic) facets of the ZnO NRs. Qualitatively from the combined fluorescence emission, SEM, and Raman data of the NRs at the various sulfidation stages, the NR end facets of {0001} seem more susceptible to the sulfidation reaction with H₂S than the side facets of {10−10}. From the viewpoint of the dangling bond scenario in wurtzite ZnO, the atoms on the end facets of the ZnO crystal are only bound to one atom in the underlying layers, leading to easier removal of the atoms at the end once the surface layer is disrupted. In contrast, the atoms on the main body (side) facets have alternating Zn and O atoms on the more stable surfaces of {10−10}, where the Zn and O atoms are attached to multiple adjacent atoms. This would suggest that dissolution of ZnO by H₂S at the side facets can be favored over the end facet reaction only under circumstances of a defect-triggered reaction. However, the highly crystalline, optical quality ZnO NRs used in our experiments ensured that the crystals were free of such defects on the side facets, which, in turn, makes the end facets more vulnerable to the chemical reaction as explained above.

The mechanism of the sulfidation reaction seen on the NRs in Fig. 14 through 16 may be understood by S/Zn atoms diffusing into/out of the NRs. The S²⁻ from H₂S can react with Zn²⁺ on the ZnO NR surface, leading to the build-up of ∼35 nm ZnS NPs on the NR in Fig. 14. This initial ZnS NP formation is likely to be driven by the more thermodynamically stable ZnS formation energy and the lower solubility of ZnS in water compared to ZnO. The NR sulfidation reaction may then continue via a Kirkendall effect, forming the void layer separating the outer ZnS shell from the inner ZnO core in Fig. 15. Fig. 15 also shows small gaps and channels appearing between the ZnS shell and the ZnO core, preserving contact points between the two materials. Those ZnO core parts still in physical contact with the ZnS shell may serve as transportation channels for Zn²⁺ ions to diffuse out and reach the reaction interface to further react with S²⁻ ions. As the sulfidation reaction proceeds, the ZnS shell continues to thicken since the smaller size of Zn²⁺ relative to that of S²⁻ will make the cations move readily through the ZnS shell to react with S²⁻ in solution. This Kirkendall process may lead to the eventual formation of a hollow space in the NR core observed in Fig. 16, transforming the more reactive
NR end facets and the neighboring NR parts into tube-like regions, leaving them only with thick ZnS shells.

We further investigated the ZnO NR facet-specific reactivity towards H₂S in a quantitative manner, while ruling out any geometric effects in sulfidation of the vertically oriented NRs on the growth substrate. Hence, for this set of experiments, we employed individual ZnO NRs prepared by the ‘dispersed NR reaction’ method. Lying flat on the reaction substrate in this case, all parts of the individual ZnO NRs were allowed to equally react in TAA. We then characterized the sulfidated NRs to obtain spatially resolved Raman spectra under both 405 and 532 nm excitations. Furthermore, we systematically analyzed the intensities of the various ZnS phonon modes measured from both the middle and end positions of the same NRs and quantitatively determined the differences in the NR facet reactivity.

Fig. 17 shows the summary bar graphs of the NR facet reactivity evaluated by spatially resolved Raman spectroscopy. The bar graphs in Fig. 17(A) compare the Raman intensities of different ZnS peaks, one for the combined 2nd order modes at 261 cm⁻¹ and the other for the A₆/E₆ modes at 349 cm⁻¹, from the two distinctive positions on the NRs discussed in Fig. 15 and 16. The results in the bar graphs show that ZnS signals are substantially higher for the NR end than for the middle of the same rods. EDX measurements and elemental analysis performed on the two distinct positions of a moderately sulfidated NR also showed a similar trend to the Raman results summarized in Fig. 17(A), see Fig. S1 in Appendix B. To substantiate these findings, we profiled the Raman scattering behaviors of an additional set of 20 ZnO NRs prepared via the dispersed NR reaction method. Representative bar graphs from these measurements are shown in Fig. 17(B) for 10 independent NRs. It is apparent from the data that, regardless of the excitation wavelengths used or particular ZnS Raman modes analyzed, higher Raman intensities of ZnS are found at the NR ends versus the middle. To verify the reactivity trends associated across the 20 NRs studied, we averaged the end versus middle data for the same NRs for the three characteristic ZnS peaks of 70, 261, and 349 cm⁻¹ collected under 532 nm illumination. The Raman intensity values at the NR ends were obtained by considering only the higher intensity end of the two termini for the left panel in Fig. 17(C), while the data shown in the right panel resulted from
considering the mean of the two NR end intensities. The middle and end intensity values were normalized to the end intensity in all cases. The outcomes were then constructed into bar graphs as displayed in Fig. 17(C), which confirmed no substantial reactivity difference between the two NR termini. Clearly visible from all comparison graphs in Fig. 17 is that the sulfidation-induced Raman signals are greater at the end versus the middle of the NR for all ZnS phonon mode and excitation cases. Hence, by quantitatively comparing the position-resolved Raman chemical fingerprinting data from the same NRs, we conclusively show that the conversion from ZnO to ZnS occurs more readily at the two ends than on the main body of the NR.
Figure 17: Nanorod facet-specific sulfidation reactivity examined by position-resolved Raman scattering experiments on individual zinc oxide nanorods. (A) The Raman intensities of the two ZnS phonon modes at 261 cm\(^{-1}\) and 349 cm\(^{-1}\) are quantitatively compared between the NR middle (blue) and end (red) positions and the summary bar graphs are presented for the two NRs discussed in Fig. 15 and 16. The degree of chemical reactivity towards sulfidation was revealed to be higher at the end than at the middle positions of the NRs. (B) Representative bar graph for 10 independent sulfidated NRs showing the Raman intensities measured from the middle (blue) versus the end (red) on the same NRs. The left panel contains the Raman intensities at 261 cm\(^{-1}\) measured under 532 nm incident light. The right panel charts the peak intensities at 349 cm\(^{-1}\) collected with 405 nm incident light. Regardless of the incident laser wavelength used or the ZnS phonon mode analyzed, the overall NR reactivity towards sulfidation was determined to be higher in the end relative to the side facet. (C) The bar graphs show normalized and averaged Raman intensities corresponding to all three ZnS peaks (70 cm\(^{-1}\), 261 cm\(^{-1}\), and 349 cm\(^{-1}\)) collected using 532 nm light. The bar graph results were obtained by examining 20 independent NRs. Only the higher NR end of the two termini was used for the analysis in the left panel whereas, in the right panel, the mean value at the two NR termini was considered before normalizing the intensity values from each position against the end intensity. In all cases, the reactivity towards sulfidation was found to be higher at the end than the middle position of the NRs.
To better understand how the sulfidation reaction proceeds, we carried out subsequent Raman scattering measurements by directly tracking the same ZnO NRs before and after reaction with TAA. For these sets of NRs, positional Raman data were collected from both the middle and end locations of the pristine as well as S-reacted ZnO NRs for the same NRs with 405 nm excitation. We then analyzed the ZnS peak at 349 cm\(^{-1}\) and the SO mode centered at 334 cm\(^{-1}\). Fig. 18(A) and (B) display representative Raman spectra of ZnO NRs taken before and after the sulfidation reaction from the NR's middle and end positions. In each graph, the black spectrum represents the pristine ZnO NR signals at the given NR position. The blue and red spectra correspond to the data taken from the middle and end positions, respectively, of the same NR after sulfidation. In the ‘before’ spectrum showing the Raman frequency window of 280–460 cm\(^{-1}\) in Fig. 18(A) and (B), the NR displayed ZnO phonon modes of \(E_{2H} - E_{2L}\), \(E_{1T}\), and \(E_{2H}\). After sulfidation, the Raman spectra of the same NR yielded a broad peak spanning the region of 320–360 cm\(^{-1}\). The inset in each figure represents a peak fitting of this broad feature whose overall intensity is contributed by two ZnS phonon modes, one at 334 cm\(^{-1}\) due to the SO mode and the other at 349 cm\(^{-1}\) corresponding to the \(A_{1L}/E_{1L}\) modes. The bar graphs in Fig. 18(C) and (D) present the normalized intensities of the SO and \(A_{1L}/E_{1L}\) peaks of ZnS, respectively, obtained from 10 separate NRs after performing position-resolved Raman investigations on the same NRs before and after the TAA reaction. The outcomes in Fig. 18(C) and (D) also show that the NR ends exhibit higher ZnS signal than the middle, suggesting that the NR end facets have a higher reactivity towards ZnS formation. Combined with the results discussed in Fig. 18, the Raman scattering results in Fig. 18 unambiguously show that the higher NR end reactivity relative to the middle is persistent regardless of the excitation wavelength, ZnS phonon peak, or the specific NR terminus analyzed.
Figure 18: Nanorod facet-specific Sulfur-reactivity further substantiated by tracking the same nanorods before and after sulfidation with nanorod position-resolved Raman spectroscopy. The same ZnO NRs were examined before and after the reaction at the NR middle (blue) and end (red) locations under 405 nm illumination. (A and B) The representative data sets show typical Raman spectra and the associated peak fittings when tracking ZnO NRs before and after their reaction with TAA. The Raman data acquired from the middle and end positions of a ZnO NR are shown in (A) and (B), respectively. The insets display peak fitting of the new Raman feature detected in the 320–360 cm$^{-1}$ frequency region following sulfidation, which is attributed to the co-located SO and $A_{11}/E_{11}$ modes of ZnS. (C and D) Bar graphs displaying the normalized intensities for the peak at (C) 334 cm$^{-1}$ and (D) 349 cm$^{-1}$ from 10 exemplar NRs by tracking their Raman scattering intensities from the NR middle (blue) and end (red) locations before and after sulfidation. For both the phonon modes analyzed, the reactivity of the end facets on the NR is determined to be higher than that of the side facets towards sulfidation.
3.4. Summary

In summary, we have successfully demonstrated that position-resolved Raman spectroscopy can be used to reveal the different crystal facet-dependent reactivities associated with the sulfidation reaction of ZnO NRs at the single nanomaterial level. We have conclusively shown that the end (basal) facets of ZnO NRs are more prone to sulfidation than the middle (prismic) facets by quantitatively comparing various S-induced phonon scattering intensities measured from different positions on the same ZnO NRs and by tracking the same NRs with Raman spectroscopy before and after the sulfidation reaction. The sulfidation trends found in the NR facet-resolved Raman scattering results were further substantiated by the electron microscopy and fluorescence emission data taken on the same NRs. Such single crystal level insight on the facet-dependent sulfidation reactivity of ZnO NRs may furnish fundamentally guided, nanomaterial design principles beneficial to many technological and industrial applications exploiting the conversion of ZnO NRs to ZnS. Together with the wealth of knowledge in the literature for producing ZnO nanomaterials in a variety of crystal shapes and structures, our endeavors in this work may be broadly applicable in developing more effective, low-dimensional, ZnO-based sorbents and scrubbers for H₂S removal. More generally, the position-resolved Raman spectroscopy approach we demonstrate in this paper can be applied to quantify distinct, facet-dependent chemical reactivities of other technologically important nanomaterials. It can also be used to determine chemical reaction-triggered phonon modes from the given nanomaterial crystal planes. Owing to the exquisite chemical sensitivity of Raman spectroscopy, the approach will be particularly beneficial for examining nanomaterials at the single crystalline facet level and at a low chemical reaction state whose weak chemical signals and reaction degrees may be difficult to quantify otherwise.
3.5. References


Chapter 4. Spatially Correlated, Single Nanomaterial-Level Structural and Optical Profiling of Copper-Doped Zinc Oxide Nanorods Synthesized via Multifunctional Silicides

4.1. Introduction

Optical properties of one dimensional (1D) zinc oxide nanowires and nanorods (ZnO NWs and NRs) have been extensively studied and optimized for photonic\textsuperscript{4}, optoelectronic\textsuperscript{5-11}, and biosensing applications\textsuperscript{12-14}. One particularly effective strategy for tuning the intrinsic properties of ZnO is to introduce dopants of transition metal ions such as copper (Cu). Many studies have previously demonstrated that the incorporation of Cu into the ZnO lattice can significantly alter the structural, chemical, optical, and electrical properties of ZnO\textsuperscript{15-28}. These endeavors have been largely focused on thin film and powder structures of ZnO\textsuperscript{15-18, 20-21}. For instance, Cu doping into ZnO thin films can reduce their bandgaps\textsuperscript{15} and induce ferromagnetic behaviors unlike neat ZnO or Cu\textsuperscript{16-17}. In other examples, Cu doping of ZnO can produce highly nonlinear current–voltage characteristics used in varistors\textsuperscript{21} and, together with Ga, Cu-incorporated ZnO thin films have been constructed as cathodoluminescent screens\textsuperscript{20}.

More recently, some efforts have been made to produce 1D forms of Cu-doped ZnO. They have been produced via hydrothermal\textsuperscript{23}, chemical vapor deposition (CVD)\textsuperscript{19, 25-28}, thermal diffusion\textsuperscript{24}, and electrochemical deposition\textsuperscript{22} methods. Among these, CVD has often been the method of choice, since the gas phase approach can minimize unwanted incorporation of chemical impurities during synthesis that may otherwise arise from the presence of counter ions and bystander species in solutions. In previous CVD approaches, reactions were carried out by using source mixtures of Cu/Zn, CuO/ZnO, CuI/ZnI\textsubscript{2}, Cu(C\textsubscript{5}H\textsubscript{7}O\textsubscript{2})\textsubscript{2}/Zn/(Zn(C\textsubscript{2}H\textsubscript{3}O\textsubscript{2})\textsubscript{2}·2H\textsubscript{2}O)\textsubscript{2}, or Cu
film coating ZnO. Regardless of the dimensionality of the synthesized materials, the development of Cu-doped ZnO has so far been geared towards magnetic, electrical, and optoelectronic functions to create better luminescence activators, dilute magnetic semiconductors, and multispectral photodetectors. For reasons, Cu-doped ZnO in previous studies has been largely examined for its properties associated with ferromagnetism, near-band-edge-related photoluminescence, and photon-induced current–voltage relationships.

We have previously demonstrated that ZnO NRs can be successfully employed in bioanalyte detection. In these efforts, pristine ZnO NRs served as efficient subwavelength waveguides and surface evanescent wave carriers, which subsequently permitted ultrasensitive detection of DNA- and protein-derived fluorescence signals. Being utilized as passive waveguides of non-intrinsic light generated by fluorophore-conjugated biomolecules, ZnO NRs in these applications were designed to be optical quality single crystals, free of chemical and crystalline defects. The undoped ZnO NRs exhibited optical transparency in the visible range needed in fluorescence-based bioassays with no absorption or emission under commonly used visible excitation settings. However, rather than simply utilizing them as passive components, transforming ZnO NRs into active waveguides of visible light by augmenting their optical properties can be highly beneficial in biodetection. Exemplar uses of active visible light waveguides include in vivo bioprobes, luminescent markers, and local light sources in integrated optical biosensors.

In this study, we devise a straightforward and effective method to synthesize Cu-doped ZnO NRs using a novel multifunctional platform of copper silicide nanoblocks (Cu$_3$Si NBs). The Cu$_3$Si NBs play multiple roles, serving as catalysts for the ZnO NR growth, a local Cu source for doping
the NRs, and prepatterned guides to aid the local assembly of the NRs on the growth substrate. The Cu$_3$Si bases are first formed into square or rectangular nanoblocks (NBs) on Si in well-defined directions. Subsequent ZnO NR growth yields a forest of Cu-doped ZnO NRs vertically grown from the base of each Cu$_3$Si NB. The resulting assembly of ZnO NRs on the Cu$_3$Si NB resembles thick bristles on a brush head. The crystalline structures, optical properties, and spectroscopic signatures of the resulting Cu-doped ZnO NRs on the NBs are then ascertained at both the ensemble and individual block levels. Among the different material characterization methods that were used, fluorescence emission and Raman scattering profiles are particularly sensitive to Cu incorporation into ZnO NRs. With the use of Cu$_3$Si NBs as an effective Cu dopant source, we also show that the optical properties of the NRs are significantly altered from pristine ZnO materials. ZnO NRs synthesized on Cu$_3$Si NBs emit strong fluorescence in the visible range that is not seen from either Cu$_3$Si NBs or undoped ZnO NRs. Cu-doped ZnO NRs also exhibit phonon modes forbidden by the Raman selection rule of wurtzite ZnO and cause large peak shifts in Raman scattering. Distinct from many previous studies investigating macroscopic or ensemble-averaged behaviors of Cu-doped ZnO, we ascertain the structural and optical characteristics of Cu-doped ZnO NRs on Cu$_3$Si NBs by spatially correlating fluorescence and Raman data collected from individual NBs.

4.2. Experimental Methods

Cu$_3$Si NBs were first synthesized on clean Si(100) substrates (Silicon Quest International Inc., San Jose, CA, USA) in a CVD reactor. A mixture of 0.9 g of CuO and 0.6 g of graphite, obtained from Alfa Aesar (Ward Hill, MA, USA), was placed on a source boat at the center of a horizontal resistance tube furnace. A target boat containing the Si(100) substrate was placed at the
downstream side, 12 cm away from the center. The temperature of the furnace was then raised to 800 °C for 1 h under a constant Ar flow of 100 standard cubic centimeters per minute (sccm). During the CVD reaction, CuO was reduced to Cu which further reacted with Si, producing Cu$_3$Si nanostructures along the Si atom directions on Si(100). ZnO NRs were subsequently grown using the Cu$_3$Si NBs as catalysts. The Cu$_3$Si NBs/Si(100) sample was cleaned with a 1:5 mixture of NH$_3$/HF–deionized water (DI) for 25 min and then in 0.01 N HNO$_3$ for 40 min. ZnO NRs were synthesized in a CVD reactor kept under 100 sccm of Ar flow, similar to the setup described above. The source and target boats contained a 1:2 mixture of ZnO (99.999%) and graphite (99%) powder (Alfa Aesar Inc., Tewksbury, MA, USA) by weight and the Cu$_3$Si NBs/Si(100) sample, respectively. The CVD reaction was held at 1000–1050 °C for 4 h. Alternatively, for synthesizing undoped ZnO NRs, 20 nm Au nanoparticles (Au NPs) from Ted Pella, Inc. (Redding, CA, USA) on a Si wafer were used as catalysts. The source materials, a 1:2 mixture of ZnO to graphite powder (0.45 g total), were placed in a quartz boat at the furnace center. The furnace was heated to 950 °C for 40 min under a 100 sccm Ar flow. Upon synthesis, the growth plate contained a dense mat of undoped ZnO NRs from which the NRs were sonicated off and dispersed in ethanol. Reconstituted ZnO NRs were then deposited onto a clean Si substrate via drop casting.

The Cu$_3$Si NBs as well as doped and undoped ZnO NRs were subsequently characterized using a scanning electron microscope (SEM), FEI Nova NanoSEM 450 (FEI Company, Hillsboro, OR, USA), operated at 20 keV. For all optical measurements, a Zeiss Axio Imager A2M (Carl Zeiss, Inc., Thornwood, NY, USA) microscope equipped with an AxioCAM HRm digital camera (Carl Zeiss Microscopy GmbH., Jena, Germany) was employed. Reflected bright-/dark-field illumination and unpolarized fluorescence excitation were produced using a 12 V/100 W halogen
lamp (Carl Zeiss Microscopy GmbH., Jena, Germany) and a 120 W mercury vapor lamp (X-Cite 120Q, Carl Zeiss Microscopy GmbH., Jena, Germany), respectively. Various spectroscopic settings were employed in order to check fluorescence emission of the nanomaterials in the visible window. Images were acquired with EC Epiplan-NEOFLUAR 50X (numerical aperture, NA = 0.8) and 100× magnification (NA = 0.9) objective lenses using a 2 s exposure. X-ray diffraction (XRD) measurements were made using a Rigaku Ultima IV X-ray diffractometer (Rigaku Corp., Tokyo, Japan), operated with an accelerating voltage of 40 kV under Cu Kα radiation (1.542 Å, 1.5104) and scanned in the range of 2θ = 30–70° at a rate of 1°/min. Ultraviolet–visible (UV–vis) absorption spectroscopy data were collected using an Agilent 8453 UV–vis spectrometer (Agilent Tech, Santa Clara, CA, USA). Fourier transform infrared (FTIR) spectroscopy measurements were taken using an Agilent Technologies Cary 670 Spectrometer (Santa Clara, CA, USA) with a home-built attenuated total reflectance (ATR) attachment. Raman spectra and maps were acquired using a LabRAM HR Evolution Raman confocal microscope (Horiba Instruments Inc., Sunnyvale, CA, USA) with a long working distance and 100× objective lens of 0.8 NA (Olympus Corp., Waltham, MA, USA). Raman signals upon 532 nm laser excitation were collected in the wavenumber range of 50–500 cm\(^{-1}\) using an 1800 lines/mm grating and a charge-coupled-device detector.

4.3. Results and Discussion

The bright-field optical image in Figure 19A and SEM panels in Figure 19B display low- and high-magnification views, respectively, of the as-synthesized Cu\(_3\)Si NBs. The Cu\(_3\)Si NBs on Si(100) were aligned in two specific crystal directions along [011] and [01-1] as previously reported\(^{34-35}\), consistent with the underlying Si atom arrangement. The Cu\(_3\)Si NBs shown in Figure 19 are approximately 750–800 nm in diameter and 11–14 μm in length. The Cu\(_3\)Si NBs typically
exhibit an aspect ratio much greater than 1:10. In addition, square-shaped Cu$_3$Si nanocrystallites (NCs) can also be seen in Figure 19A,B. The small Cu$_3$Si NCs are the dominant form on samples grown only for a short time (5–10 min), making them early-stage structures before developing into the highly elongated constructs of NBs. With increasing growth time, the NCs become lengthened along either [011] or [01-1] on the substrate of Si(100), sometimes merging with other NBs growing nearby.

Figure 19: Images of copper doped zinc oxide nanorods grown on copper silicide nanoblocks. Bright-field and SEM images showing the structures of Cu$_3$Si nanoblock (NB) catalysts, ZnO nanorods (NRs) grown on Cu$_3$Si NBs (Cu-doped ZnO NRs), and ZnO NRs grown on Au nanoparticles (NPs) (undoped ZnO NRs). (A,B) As-synthesized Cu$_3$Si NBs on Si. Upon CVD, Cu$_3$Si NBs nucleate and self-assemble into NBs on the Si(100) growth substrate, as shown in the optical (A) and SEM (B) panels; (C,D) As-synthesized Cu$_3$Si NBs on Si such as the ones displayed in (A,B) were used as catalysts to directly grow ZnO NRs on the NBs. Cu-doped ZnO NRs can be successfully produced on Cu$_3$Si NBs, seen as brushlike structures in the bright-field image in (C); The wire-like shape of the Cu-doped ZnO NRs extended from a Cu$_3$Si NB base can be clearly seen in the zoomed-in SEM panels in (D); (E,F) The optical and SEM panels in (E,F), respectively, are typical images of undoped ZnO NRs produced by using Au NP catalysts. The second row of panels shown in (B–F) displays zoomed-in views of the nanostructures shown in the first-row images.
Figure 19 C,D display the bright-field and SEM images of the ZnO NRs grown on the Cu$_3$Si NBs. The panels clearly show that the resulting NR growths occurred on Cu$_3$Si NBs but not in other areas on the substrate. Thus, Cu$_3$Si NBs can serve as effective catalysts for the nucleation and growth of the ZnO NRs. The as-grown structures of ZnO NRs jutting out of each Cu$_3$Si NB resemble dense bristles on a brush head. The assembled structures of multiple modules of NRs/NB as well as a single module of NRs/NB can be clearly seen in the zoomed-in SEM panels in Figure 19D. The NRs shown in Figure 19D are approximately 160–300 nm in diameter and 10–12 μm in length, grown vertically from the NB base with one end free and the other end attached to the Cu$_3$Si NB. Figure 19E,F show the bright-field and SEM images of undoped ZnO NRs. The undoped NRs were reconstituted and redeposited onto a clean Si from the growth plate containing a dense mat of NRs. The basal (hexagonal end) and prismic (rectangular side) facets of the pristine ZnO NR crystals can be clearly seen in the high-magnification SEM image in Figure 19F.

After examining the physical dimensions and morphologies of the nanostructures, we then investigated the optical properties of the undoped and Cu-doped ZnO NR samples. ZnO NRs synthesized using Au NPs versus Cu$_3$Si NBs exhibited vastly different fluorescence emission behaviors under visible excitation. Figure 20A,B display representative fluorescence panels collected from the samples of Cu$_3$Si NBs alone and neat ZnO NRs grown on Au NPs, respectively. Excitation and collection wavelength ranges ($\lambda_{ex}/\lambda_{col}$) used were 450–490/540–552 and 510–540/575–640, all in units of nm. Cu$_3$Si NBs and undoped ZnO NRs did not show any fluorescence under these settings. Contrastingly, as-grown ZnO NRs produced on Cu$_3$Si NBs yielded strong, stable fluorescence in the specified emission wavelength range as displayed in Figure 20C, which was due to Cu doping into the NRs. Fluorescence from vertically grown NR ensembles yielded
furry green patches that span along the nonemitting Cu$_3$Si NBs. The hazy fluorescence pattern is due to the collective emission of many m-long doped ZnO NRs vertically straddling the focal plane. In contrast, those NRs lying in the imaging plane unmistakably appear as fluorescing rods in the same fluorescence images. Similar fluorescence emission was also confirmed in the red range for the ZnO NRs grown on Cu$_3$Si NBs.

Figure 20: Fluorescence panels of the copper silicide nanobeams, copper-doped zinc oxide nanorods on copper silicide nanobeams, and neat zinc oxide nanorods samples shown in Figure 19. No fluorescence emission was seen in the visible range from the samples containing (A) Cu$_3$Si NBs and (B) undoped ZnO NRs; (C) In contrast, strong fluorescence from the samples of ZnO NRs grown on Cu$_3$Si NBs was observed due to the doping of ZnO NRs with Cu from Cu$_3$Si NB catalysts. The fluorescence images in (A,B) are 300 μm × 300 μm in size. The left and right panels shown in (C) are 160 μm × 160 μm and 50 μm × 50 μm, respectively.
We subsequently employed various diffraction and spectroscopic techniques to examine the
different nanomaterials. Figure 21A displays XRD data of pristine ZnO NRs, Cu-doped ZnO NRs,
and Cu₃Si NBs as grown on Si wafers. The topmost spectrum shown in 21A, corresponding to as-
synthesized, undoped ZnO NRs, agrees well with the characteristic diffraction peaks of wurtzite
ZnO crystals. The peaks at \(2\theta = 31.8^\circ, 34.5^\circ, 36.5^\circ, 47.5^\circ, 56.5^\circ, \) and \(63^\circ\) belong to (110), (002),
(101), (102), (110), and (103) of the ZnO NR crystal, respectively, and the unassigned peaks in
the spectrum belong to the Si substrate. The middle spectrum in Figure 21A is taken from Cu-
doped ZnO NRs grown on Cu₃Si NBs, showing the same diffraction patterns as undoped ZnO
NRs. We did not observe any significant deviations in terms of new peaks or peak shifts in the
undoped versus Cu-doped ZnO NR samples. No peaks related to Cu or CuO appeared and only
the overall peak intensities of the Cu-doped ZnO NRs decreased. This was due to the lower
amounts of ZnO NRs synthesized as they form only on the Cu₃Si NBs areas. The absence of CuO
phase in the spectra indicates that the incorporated Cu level in our NR samples has not exceeded
the solid solubility of Cu in ZnO which is ~1 atomic percent\(^{36-37}\). The bottommost diffraction panel
in Figure 21A is from Cu₃Si NBs self-assembled along the two preferential growth directions on
Si(100). The peak appearing at \(45.5^\circ\) is indicative of Cu₃Si (120)/(210) and the other peaks present
are from Si\(^{34-35}\).
Figure 21: Diffraction and spectroscopic data of the nanobeams and nanorods. (A) XRD data of Cu$_3$Si NBs (black), Cu-doped ZnO NRs on Cu$_3$Si NBs (red), and undoped ZnO NRs (blue); (B) ATR-FTIR spectra of undoped (blue) and Cu-doped (red) ZnO NRs; (C) UV–vis spectra of undoped (blue) and Cu-doped (red) ZnO NRs.

Data in Figure 21B,C display the IR and UV–vis spectra, respectively, of undoped and Cu-doped ZnO NRs. Relatively broad peaks centered at 350 and 550 cm$^{-1}$ in the fingerprint region of ZnO were found in the ATR FTIR spectra of both undoped and Cu-doped ZnO NRs in Figure 21B. These peaks are associated with Zn–O stretching$^{38-40}$. No additional absorption peaks were identified from the Cu-doped ZnO NRs. Unlike the XRD and ATR FTIR outcomes, the UV–vis absorption profiles characterized from the two samples showed a small change in the 400–500 nm range, noticeable in Figure 21C. The absorption profile of neat ZnO NRs center in the UV region and show a sharp decrease at 390 nm. In contrast, the decrease in this region becomes more gradual and extends towards the visible range in the absorption spectrum for the Cu-doped ZnO NRs. The increased absorbance into the visible region of the Cu-doped ZnO NR sample coincides with the appearance of visible fluorescence emission from the NRs in Figure 20.
Figure 22 displays the Raman scattering results from undoped and Cu-doped ZnO NRs. Wurtzite ZnO, according to group theory, has the optical modes of \( I_{\text{opt}} = A_1 + 2B_1 + E_1 + 2E_2 \) at the point of the Brillouin zone\(^{41,42}\). \( A_1 \), \( E_1 \), and \( E_2 \) are Raman active whereas \( B_1 \) is a silent mode in pristine ZnO. The atomic arrangements of Zn and O in a wurtzite crystal structure as well as the vibrations associated with the characteristic ZnO phonon modes are depicted in Figure 22A,B. As seen from the Raman scattering data of pristine ZnO NRs in the left panel of Figure 22C, the Raman modes of \( E_{2L}, E_{2H} - E_{2L}, A_{1T}, E_{1T}, \) and \( E_{2H} \) were resolved at 98, 331, 378, 413, and 437 cm\(^{-1}\), respectively. These peaks are expected from wurtzite ZnO NRs belonging to the \( C_{4h}^{6v} \) space group\(^{41,43}\). The strong peaks of high and low \( E_2 \) reflect the chemical composition of Zn (\( E_{2L} \)) and O (\( E_{2H} \)) in the high-quality wurtzite ZnO NR sample. Contrarily, the Raman signals from Cu-doped ZnO NRs in the right panel of Figure 22C indicate significant deviations from the scattering behaviors of pristine ZnO NRs. Large peak shifts were observed for the \( E_{2H} - E_{2L} \) and \( E_{2H} \) modes by 8–12 cm\(^{-1}\) to the left of those from pristine ZnO. In addition, the forbidden \( B_{1L} \) mode newly appeared at around 280 cm\(^{-1}\) in the Cu-doped ZnO NR Raman spectra as did the second-order \( E_{2L} \) peak centered at 196 cm\(^{-1}\). A clear indication of Cu incorporation into the Zn–O lattice was the new peak at 220 cm\(^{-1}\), which originates from the presence of Cu(I)–O in the Zn–O lattice\(^{44,45}\). The Cu(I)–O peak is marked with an asterisk in the Raman spectrum of Cu-doped ZnO NRs in Figure 22C. Although appearing small in the ensemble-averaged Raman spectra of Cu-doped ZnO NR samples, the Cu(I)–O peak was identified prominently in the Raman measurements examining single modules of NRs/NB, which will be discussed in Figure 23. Regardless, we successfully revealed additional Raman peaks and peak shifts specifically related to Cu doping of ZnO NRs, which could not be identified previously under low doping regimes. The Cu
incorporation in our samples neither altered the dominant growth direction of the NRs nor changed the wurtzite crystals to an amorphous or another crystalline state, as evidenced by the XRD data in Figure 21A. However, the Cu dopant resulted in significant disruptions in the long-range order of the NR crystal, as seen by the pronounced downshift as well as the broadening and weakening of the Raman peaks. The perturbed Raman spectra of the doped relative to the pristine ZnO NR samples indicate that the symmetry of the allowed phonons is broken due to Cu introduction into the host ZnO lattice. The Cu-induced, long-range disorder in the ZnO lattice is likely to cause the contribution of $q \neq 0$ phonons to the Raman features such as the additional second-order peaks, not observed from pristine ZnO NRs.
Figure 22: Raman spectra of undoped and copper-doped zinc oxide nanorods, as synthesized on silicon substrates using gold nanoparticles and copper silicide nanobeam catalysts, respectively. (A) A ball-and-stick model of atomic arrangements of Zn and O is displayed for an undoped, wurtzite ZnO crystal; (B) Characteristic Raman vibration modes of wurtzite ZnO are schematically depicted; (C) The differences in the Raman scattering behaviors between the undoped (blue) and Cu-doped (red) ZnO NR samples are clearly resolved. The Raman spectra are ensemble-averaged signals acquired from a collection of undoped ZnO NRs (blue) and concentrated modules of Cu-doped ZnO NRs on NBs (red). The inset in the Cu-doped ZnO spectrum is the magnified view of the curve fit (red) and the peak fits (black) of the scattering data between 160 and 260 cm$^{-1}$. The Cu(I)–O peak is marked with an asterisk.
Figure 23: Representative panels displaying spatially correlated data between optical, fluorescence emission, and Raman scattering profiles measured from individual nanobeams with copper-doped zinc oxide nanorods. (A,B) The optical panel in (A) displays a superimposed, bright- and dark-field image of Cu-doped ZnO NRs on a Cu$_3$Si NB. The corresponding fluorescence emission profiles along the NB are shown in panel (B) where the top and bottom frames display the emission collected at wavelength ranges of 510–540 nm and 575–640 nm, respectively; (C) Exemplar Raman spectra spatially resolved along the length of the NRs/NB module are presented; (D) The E$_{2H}$ peak shift, characteristic of Cu-doped ZnO NRs grown on a Cu$_3$Si NB, is mapped along the NB via NB position-resolved Raman spectroscopy; (E) The top and bottom panels are the merged view of bright-field and E$_{2H}$ Raman peak shift (top) and that of fluorescence and E$_{2H}$ Raman peak shift (bottom). All bright-field, fluorescence, and mapped Raman images shown are 4.5 μm by 20 μm in size.

Our results indicated that fluorescence emission and Raman scattering were particularly sensitive to Cu addition to ZnO NRs. Hence, in addition to those collectively acquired from a group of NRs/NBs, we further examined the fluorescence emission and Raman scattering profiles of Cu-doped ZnO NRs on Cu$_3$Si NBs at the individual nanostructure level. Specifically, individual NRs/NB modules were studied via spatially correlated optical, fluorescence, and Raman measurements along the length of the NB. Figure 23 displays typical, correlated data acquired by examining individual NRs/NB modules. Figure 23A is a merged bright- and dark-field image of
Cu-doped ZnO NRs on a NB. Figure 23B is the corresponding fluorescence emission collected in the green (top) and red (bottom) wavelength ranges. The spectra presented in Figure 23C correspond to the spatially resolved Raman scattering signals taken from the NRs/NB module. Although overall features were similar, Raman scattering profiles from individual NRs/NB modules differed from those of NRs/NB ensembles, whose representative data are shown in Figure 22C and Figure 23C, respectively. For individual NRs/NB modules, the characteristic peaks associated with Cu doping of ZnO NRs such as the Cu(I)–O and B1L modes appeared more prominently, whereas the contribution of the second-order E2L mode was reduced. The location of the Cu(I)–O peak is found at 225 cm⁻¹ in individual NRs/NB spectra, moved from 220 cm⁻¹ for the ensemble samples. The peak shifts of the E2H–E2L and E2H modes seen in the ensemble samples were also observed in the individual NRs/NB modules.

To construct NB position-resolved Raman scattering profiles, two-dimensional (2D) Raman mapping was carried out for which a laser beam of approximately 1 µm in diameter was rastered in the vicinity of a NRs/NB module of interest. Depending on the size of the NB, the steps taken in the beam walk ranged 550–750 nm and 270–440 nm along the long and short axes of the NB, respectively. The resulting Raman map, corresponding to the E2H peak shift of the NRs/NB sample in Figure 23A, is presented in Figure 23D. The two panels in Figure 23E are a superimposed view of the bright-field and Raman data (top) with that of the fluorescence and Raman data (bottom). As evidenced in the top panel of Figure 23E, the NB areas of NR growths in the optical microscopy image match with the regions of large E2H peak shifts in the Raman map. As observed in the bottom panel of Figure 23E, the NB areas of large fluorescence and Raman peak shift signals are co-located. As both the visible fluorescence and the Raman peak shift are indicative of Cu doping,
the correlated data set further confirms that the resulting ZnO NRs on the Cu$_3$Si NB are indeed doped with Cu.

The inherent property of neat ZnO NRs showing optical transparency in the visible range has so far limited their applications to luminescence and active guiding in the spectral region of UV. Even for the limited cases employing ZnO NRs as passive waveguides in the visible region, the endeavors were largely in optoelectronic fields$^{1-2,5,46}$. Yet, these ZnO NRs and their derivatives have potential to be engineered into biodetection modules$^{47-51}$ for measuring protein activities and cell differentiation/growth using visible light. For such biological applications, visualization of the NRs is essential because determining the exact placement and distribution of the NRs in tissues and cells/cellular components is critical for interpreting results. Our efforts demonstrated in this study may be significant in this regard. For instance, the visible luminescence from vertically grown Cu-doped ZnO NRs on NBs that are self-aligned laterally on a Si wafer may be used in the streamlined fabrication of nanophotonic circuitries in integrated biosensors for bioanalyte detection via fluorescence resonance energy transfer$^{52-53}$ and fluorescence anisotropy$^{54-55}$. The intense green fluorescence produced by the Cu-doped ZnO NRs on Cu$_3$Si NBs may enable precise determination of their location once coupled with cellular systems. In addition, our approach demonstrated in this paper can greatly increase the versatility of ZnO-derived NRs in fluorescence-based biodetection by promoting them to effectively function as an active, not just passive, guiding element for visible light. For example, highly controlled spatial delivery of the green light from the Cu-doped ZnO NRs can be enabled by actively waveguiding the inherent light to the NR termini and, subsequently, to the bioanalytes of interest for exclusive excitation, without affecting nearby species whose unwanted excitation can contribute to background interference. Therefore,
our efforts can be highly valuable in paving the way for new applications of ZnO-derived NRs in basic biological research and in biomedical detection which is relatively unexplored so far, particularly for the development of integrated optical biosensors and miniaturized bioprobes.

4.4. Summary

In summary, we have demonstrated a straightforward and effective method to synthesize Cu-doped ZnO NRs using a novel system of Cu$_3$Si NBs pre-aligned laterally on a Si wafer. We showed that the unique platform of Cu$_3$Si NBs can play multifunctional roles in the CVD synthesis. They functioned as a catalyst for ZnO NR growth, a local Cu dopant source, and a pre-assembled guide for NR assembly on the Si substrate. As a result, dense, bristle-like, Cu-doped ZnO NRs were nucleated and vertically grown from each Cu$_3$Si NB base. We subsequently characterized their structural, optical, and spectroscopic characteristics at both the ensemble and individual nanostructure levels. In particular, we have successfully performed spatially correlated structural and optical measurements at the level of each NRs/NB module, including NB position-resolved fluorescence and Raman spectra. We have ascertained the augmented optical properties of doped ZnO NRs relative to those of pristine ZnO NRs and Cu$_3$Si NBs, and further discussed their potential biodetection applications. Specifically, Cu-doped ZnO NRs showed an extended absorption edge and strong luminescence in the visible range. The inclusion of Cu into ZnO NR crystals induced the emergence of the forbidden $B_{1L}$ and the second-order $E_{2L}$ modes as well as considerable peak downshifts for the $E_{2H}$–$E_{2L}$ and $E_{2H}$ phonon modes in Raman spectra. Coupled with the facile assembly of inherently fluorescing NRs on the bases of self-aligned NBs and the widespread use of fluorescence in solid-state biodetection, our Cu-doped ZnO NRs/NB
architectures may be particularly advantageous for use in active visible waveguiding, nanobiophotonics, bioprobes, and luminescent markers.

4.5. References


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Chapter 5. Conclusion and Future Outlook

The fundamental physical and chemical properties of ZnO have been studied to gain a better understanding of the role they can play as high index of refraction Raman nanoprobes. In Chapter 2, the Raman properties of ZnO NRs were studied, specifically with the understanding that minimizing the material to the nano-regime and introducing a high shape anisotropy may influence the inelastic scattering profile of the material. I demonstrated that the small size and high shape anisotropy led to unique scattering properties affecting the Raman signature at the ends of the NRs. This unique phenomenon manifested as an enhancement of Raman signals for the allowed modes at the ends of the NRs, and more importantly, gave rise to intense scattering from the forbidden Raman modes of ZnO. By comparing the Raman spectra from NRs to MPs, I unequivocally show that this phenomenon is due to the high shape anisotropy of the material.

In Chapter 3, I looked at the chemical reactivity of ZnO to H2S, an important industrial and agricultural chemical reaction in order to understand better the chemical properties of ZnO. Using mild reaction conditions and spatially resolved Raman spectroscopy, I demonstrated that the ends of the NRs were more susceptible to sulfidation than the middle of the NRs, due to the unique chemical surface of the end facets. Furthermore, because I had thoroughly studied the positional effects of waveguiding on the pristine ZnO NRs in Chapter 1, I was able to rule out this increase being a result of increased Raman intensity at the ends of the NRs. Understanding different reactivities of the ZnO surface will be important for building better H2S sorbents and better nanoprobes and allow for the tailoring of the materials to fit the particular needs of the application.
Finally, in Chapter 4, I demonstrated the effects of copper doping on the Raman spectrum of ZnO NRs. Raman mapping was used to monitor the amounts of doping in the material by tracking both the peak shift of the $E_{2h}$ Raman peak, and by the sudden appearance of the $B_1$ modes due to symmetry breaking of the material. Fluorescence and Raman proved to be sensitive techniques for determining doping amounts, however, Raman provided structural information that fluorescence could not. Raman showed that the wurtzite structure remained intact, the peak shifts and new peaks being brought about by small changes in the force constant and pockets of new symmetries in the overall crystal structure. Doping ZnO may become a key technique for adjusting the optical properties of ZnO NRs in development as nano spectroscopic probes. Controlled levels of doping could alter the physical properties of the NRs in controlled ways, tuning them for such applications as light generation or light delivery. A facile way of determining the levels of doping, and changes to the underlying crystal structure will be important for development of these probes.

All of the physical and chemical properties outlined in this dissertation lead to some interesting possibilities for using ZnO NRs as nanoprobès for Raman spectroscopy. The higher intensity of signals at the ends of the NRs demonstrates that the signal collected there is most likely due to the area effect of waveguiding signals, and if external analytes can be coupled into the waveguiding modes of ZnO they may also benefit from this enhancement. There is some evidence of this happening already as seen in both literature$^1$ and observed in my own experiments, where the Raman peaks from the underlying silicon (Si) substrate displays enhanced intensity when a ZnO NR is atop the Si. Further experimentation is needed to substantiate this finding. As of the writing of this dissertation, I have completed experiments which have set out to further study this phenomenon. I will introduce some preliminary findings along with a few figures explaining what
we have seen so far, but I will refrain from drawing any conclusions. Figure 24 contains a brief overview of what I have observed while studying this phenomenon. In these studies, polymer substrates were chosen to study the enhancement effects of ZnO on underlying substrates due to their optical clarity which allows for the study of two orientations; one in which ZnO is on top of the polymer, and one in which the polymer is on top of ZnO. For these studies, z-mapping was performed, in order to ensure that the same focal depth was captured by Raman in each orientation and over the bare substrate. Figure 24A demonstrates the condition when the ZnO NR is on top of the polymer, polydimethylsiloxane (PDMS). Overall, there is a decrease in the signal of the PDMS as can be expected when there is material between the polymer and the excitation source. However, there is a sudden and apparent increase in the PDMS signal corresponding to the area where the ZnO NR is present in the z-depth profile.

![Figure 24: Z-depth Raman profiles of various particles on polydimethylsiloxane. (A) Z-Depth profile of ZnO NR on top of PDMS showing the sudden increase in signal corresponding to the position of the NR. (B) Z-Depth profile of Ag NR on PDMS. (C) ZnO powder on PDMS. In each of the graphs, the light grey line indicates where the ZnO NR is located in the depth profile, the dark grey line indicates the PDMS signal from the 2906 cm$^{-1}$ peak when the ZnO NR is located on top of the polymer, the green line is blank PDMS. In (B) there are only two lines present since Ag has no Raman active peaks.](image-url)
This phenomenon is most likely due to the waveguiding properties of ZnO brought about by the material’s physical properties as well as its high shape anisotropy. In Figure 24C, the same experiment was conducted where the material was kept the same (ZnO), but the shape of the material was chosen to be more isotropic. As a result, the observed a z-depth profile more closely matches one in which a portion of the beam path is occupied by something other than polymer, leading to an overall decrease in polymer signal through the entirety of the map. Figure 24B demonstrates that shape anisotropy alone is not responsible for the phenomenon. Here the ZnO has been substituted with a Ag NR of similar length and width. Again, there is the similar profile where the portion with the NR has a lower polymer signal that is consistent and smooth as it decreases through the z-map. Furthermore, I have observed this phenomenon consistently for multiple ZnO NRs on top of multiple polymer surfaces.

Further experimentation is necessary before integration of ZnO NRs into a waveguiding Raman platform. Looking at surface bound molecules will also need to be studied, to rule out if there are multiple pathways of enhancement from the materials. Furthermore, a more detailed approach needs to be conducted into the properties of the forbidden peak enhancement I observed at the ends of the NRs. This will be paramount to understand how to exploit this phenomenon. Insight into the degree of waveguiding to the ends of the NRs using offset Raman detection, or looking at the depolarization of the Raman spectrum from different positions of the NRs compared with bulk ratios will be important for better understanding this phenomenon, especially in light of evidence that polarization and propagation vectors are important for evanescently excited analytes.1-3
The work in this dissertation represents a foundational understanding of the properties of ZnO NRs which make them ideal nanoprobes for Raman spectroscopy. Due to their high refractive index, small size, and large shape anisotropy, they display many characteristics necessary to be effective waveguide probes for Raman spectroscopy. The additional promise of enhanced Raman signals capable of detecting small amounts of analytes through entirety of the NRs makes them particularly appealing, since Raman spectroscopy is a rather powerful spectroscopic technique that suffers greatly from its weak signal generation.

5.1. References


Appendix A: Supplementary Figures for Chapter 2

Figure S1. (A) Raman spectrum taken from as-synthesized ZnO NRs on the Si growth wafer before the transfer of individual NRs on a clean Si substrate for use in the polarization-controlled Raman measurements. (B) Raman spectra taken from a vertically oriented ZnO NR by focusing the laser beam at the NR end (top) and the NR middle position (bottom). In both spectra, the $E_{2H}$ and $A_{1T}$ peaks, corresponding to the allowed Raman modes for the specified light-matter interaction geometry, can be seen as predicted. Unlike the selection rule predictions, the forbidden modes of $E_{2L}$ and $E_{2H}$ peaks (circled in purple) were clearly detected in the Raman spectrum of the NR end position. In contrast, the Raman spectrum acquired from the middle position of the same ZnO NR did not show any scattering from these two forbidden modes.
Figure S2. (A) Typical X-ray diffraction data of ZnO NRs used in our experiment displaying a highly crystalline, wurtzite ZnO crystals predominantly grown along the crystal’s c-axis direction. The prominent diffraction peak at $2\theta = 34.5$ deg, indicated as (0002), corresponds to the c-axis of the ZnO NRs. (B) When ZnO NRs were excited with a pulsed nitrogen laser (3.5 ns, $\lambda_{ex} = 337$ nm) with the excitation (ex.) energy greater than the ZnO bandgap, they showed a very strong, bandgap photoluminescence at 338 nm. In contrast, no emission in the visible range typically associated with the presence of atomic defects was observed. (C) When ZnO NRs were excited with 540-552 nm light ($\lambda_{ex}$ smaller than the bandgap energy and similar to the Raman measurements), the NRs exhibited no emission in the visible range. The absence of visible emission can be evidenced qualitatively from the fluorescence panel of ZnO NRs collected at 575-640 nm (left) and quantitatively from the emission spectra spanning 520-600 nm (right).
Appendix B: Supplementary Figures for Chapter 3

Figure S3. EDX elemental maps and spectra acquired from the middle (A) and end (B) position of a mildly sulfidated ZnO NR. The colored panels correspond to the EDX channels of Zn, O, and S as well as the merged view of the three channels, as specified in each frame. The merged elemental map from the NR middle data in (A) shows more clearly that the distribution of O, compared to that of S, tends to be closer to the NR core, whereas more S populates near the outer part of the NR. From the Zn: O : S atomic ratios determined from the EDX spectrum of the NR middle (A) versus end (B) position, NR end shows a higher S/O value than NR middle. These outcomes agree with the Raman results in Figures 6 and 7, as discussed in the paper.