UNIQUE POLARIZED LIGHT-MATTER INTERACTION IN SINGLE
ONE-DIMENSIONAL SEMICONDUCTING OXIDE NANOMATERIALS AND
APPLICATIONS OF INDIUM TIN OXIDE NANOROD NETWORKS AS SURFACE
ENHANCED RAMAN SPECTROSCOPY AND PHOTODETECTION PLATFORMS

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in Chemistry

By

Daniel So Ri Choi, M.S.

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UNIQUE POLARIZED LIGHT-MATTER INTERACTION IN SINGLE ONE-DIMENSIONAL SEMICONDUCTING OXIDE NANOMATERIALS AND APPLICATIONS OF INDIUM TIN OXIDE NANOROD NETWORKS AS SURFACE ENHANCED RAMAN SPECTROSCOPY AND PHOTODETECTION PLATFORMS

Daniel So Ri Choi, M.S.

Thesis Advisor: Professor Jong-in Hahm, Ph.D.

ABSTRACT

With increasing demand of miniaturized optoelectronic, photonic, sensors and biodetection platforms, understanding and elucidating the fundamental material properties at nanoscale is crucial for development and advancement of these devices. Specifically, one-dimensional (1D) semiconducting oxide (SCO) materials have drawn considerable interest in these fields as said materials exhibit unique, as well as highly advantageous optical and electronic properties compared to their bulk counterparts. As SCOs of interests are typically wide bandgap materials, most of the research has focused on these materials’ interaction with short wavelength light in the near UV regime. Thusly, materials’ interaction with sub-bandgap light, primarily those in the visible region, is seldom investigated.

This report presents a systematic study of elastic light scattering of four 1D SCO materials of indium tin oxide (ITO), tin oxide (SnO$_2$), zinc tin oxide (ZTO), and zinc oxide (ZnO) with visible light as the incident radiation source. The light-matter interaction is investigated by introducing incident light of a fixed polarization to a single, orientation- and position- controlled nanomaterial, then analyzing the scattered signals along the materials’ long axis as a function of the analyzer angles. The results show that under constant irradiation of polarized light, nanomaterials of all four SCO types show material independent, orientation dependent behavior
previously not reported. Furthermore, material dependent scattering phenomenon from single nanorods is validated by observing the change in the polarization state of the scattered light from one end of the NR to the other end.

Lastly, two different devices are fabricated from an array of these 1D, SCO materials to assess their potential as a surface enhanced Raman (SER) platform and a photodetector of the visible light. First, the ITO NR array as a SERS platform is established by introducing two ubiquitous fluorescing biomarkers of rhodamine 6G (R6G) and 4',6-diamidino-2-phenylindole (DAPI) and comparing the Raman signals to that of Si and AuNRs substrates. Additionally, the presented 1D SCOs as detector of visible light is realized as photoresponse is observed from networks of all four materials types upon introduction of sub-bandgap, visible wavelength light yielding comparable performance to commercially available devices for ITO NR network based device.
DEDICATIONS

I would like to dedicate this work to two most important families in my life.

First and foremost, to my parents Han & Hyun, who sacrificed everything in their own lives to provide a better one for me. Who taught me the importance of hard work, responsibility and charity. Words cannot describe how much they mean to me.

And to my younger brother and my best friend Samuel, who stood by me and supported me every step of the way growing up together in this once foreign land that we now call home.

Next, the Karnas: Shashi, Vandana, Parthesh and Molleshree, who took me in as one of their own.

Especially Dr. Shashi P. Karna, who gifted me his love of science and humanity, for giving me a chance to start my own scientific journey and to pass on his values.

Without these wonderful people, I would not be where I am today as a scientist and a person.

“Science and Peace will triumph over ignorance and war, nations will unite, not to destroy, but to build, and the future will belong to those who will have done most for suffering humanity.”

-Louis Pasteur

With Love,
Daniel So Ri Choi
ACKNOWLEDGEMENTS

This doctoral work would not have been possible without gracious guidance and support from many people in my life.

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“Alone we can do so little; together we can do so much.”
-Helen Keller

Many thanks,
Daniel S. Choi
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Chapter 1

Introduction

1.1 Background and Motivation

When a photon, propagating in a free space, comes in contact with a particle in its path, tremendous chemical and physical phenomena result from this light-matter interaction. This process is caused by the transfer of photon energy to the matter, thereby raising an electron of an atom to a higher level, or in case of a molecule, inducing higher rotational or vibrational states whereas upon this elevation of energetic state, the energy is released in several different possible forms contingent on the chemical and physical makeup of the matter. This interaction between light and matter results in phenomena such as photoelectric/voltaic effect\textsuperscript{1,2}; inelastic scattering such as photoluminescence (PL) emission\textsuperscript{3-4}, fluorescence emission\textsuperscript{5-7}, and Raman scattering\textsuperscript{8,9}; and elastic scattering such as Rayleigh\textsuperscript{10-12} and Mie scattering\textsuperscript{13,14}. When investigating such interactions, it is essential to be fully cognizant of the scatters’ chemical, optical, and electronic properties as well as their shapes and sizes, as these factors will all contribute to the type of light-matter interaction that will take place. Furthermore, the properties such as the polarization and the wavelength of the incident electromagnetic (EM) radiation, as well as the optical and dielectric properties of the propagating medium is vital in successfully understanding light-matter interaction that is taking place. Therefore, in designing optically-based devices, both the appropriate materials and the EM radiation properties must be carefully coordinated for desired operational mode.

In the realm of optoelectronics, photonics, sensors and detection platforms, utilization of low-dimension materials, compared to their bulk counterparts, have increasingly become the
dominant approach in device design due to their novel and unique optical phenomenon stemming from their reduced dimensionality. Compared to the materials’ 3-dimensional (3D) and 2-dimensional (2D) forms, 1-dimensional (1D) forms such as nanowires (NWs) and nanorods (NRs) exhibit extraordinary optical and electronic properties such as spontaneous and stimulated lasing\textsuperscript{15-18}, subwavelength waveguiding\textsuperscript{19-21} for use as optical communication probe\textsuperscript{22}, plasmonic-photonic coupling\textsuperscript{23}, and directional absorption and emission as observed in “nano-antennas.”\textsuperscript{24,25}

Unique light-matter interaction between visible light and 1D material has been demonstrated by Wang et al. through investigation of photoluminescence from single indium phosphide (InP) nanowires.\textsuperscript{26} In this study, free standing InP NW was excited with excitation lights of 488- and 514-nm, both which are significantly above the bandgap energy of InP ($E_g = 1.34$ eV, 922.5 nm) to measure the PL intensity of single NW as a function of different polarization state of the excitation light.

![Atomic force microscopy (AFM) image and polarization dependent photoluminescence (PL) characterization of InP NWs.](image)

**Figure 1.1** Atomic force microscopy (AFM) image and polarization dependent photoluminescence (PL) characterization of InP NWs. (a) Atomic force microscopy image of individual InP NWs. Scale bar, 5 µm. (b) PL spectra from single InP NW with excitation laser polarization parallel to the NW axis showing PL “on” behavior. Scale bar, 3 µm. (c) PL spectra from single InP NW with excitation laser polarization perpendicular to the NW axis showing PL “off” behavior. Inset shows incident polarization light dependence on PL intensity. This figure was adapted with permission from: Wang, J. et al. Highly Polarized Photoluminescence and Photodetection from Single Indium Phosphide Nanowires. *Science* **293**, 1455–1457 (2001).\textsuperscript{26}
Figure 1.1(a) shows the AFM image of the free standing InP NWs to ensure the signal collection from a single NW of interest. It is seen in Figure 1.1(b), under excitation light with polarization state parallel with the rod axis, strongest PL intensity is observed. Conversely, in Figure 1.1(c), when the polarization state of the excitation light is changed to be perpendicular to the rod axis, the PL becomes absent demonstrating highly polarization anisotropy behavior of photoluminescence emission. Furthermore, the inset in Figure 1.1 shows the variation in overall PL intensity as a function of excitation polarization angle with respect to the nanowire axis confirming this unique “on-off” PL behavior that has previously not been observed in bulk forms of the same material.

As a parallel effort in elucidation of inelastic phenomena in an individual 1D materials as mentioned in the previous paragraph, realizing the elastic light scattering properties from these same materials is equally crucial as it is highly beneficial for research and development of devices and spectroscopic methods that utilize such scattering modes. Elastic scattering, from a fundamental viewpoint, can be seen as the opposite of the absorption process, whereas in an absorption process, the incident photon energy is absorbed by a molecule then converted to internal energy such as thermal energy thereby causing a partial or permanent attenuation of the photon from the radiation field, the elastic scattering process essentially redirects the propagation vector of the photon. In an elastic scattering process, when the EM wave, with a specific frequency $v_0$, interacts with an obstacle particle, electrons in the particle will oscillate producing an induced dipole moment which takes form of EM radiation. When this EM radiation oscillates with same frequency as the incident frequency $v_0$, elastic scattering is observed. This EM radiation is then
propagated in directions differing from the original radiation. The overall elastic scattering process is described in Figure 1.2.

![Figure 1.2 Schematic of the elastic light scattering process by an induced dipole moment from an incident electromagnetic (EM) wave interacting with a spherical particle. Frequency of the scattered EM (\(v_o\)) is same as the frequency of the incident EM (\(v_o\)).]

Elastic scattering is often used over inelastic scattering techniques such as fluorescence, photoluminescence to obtain inherently weak signals from both metallic and semiconducting nanomaterials. Furthermore, compared to Raman scattering, elastic scattering produces stronger signal as it does not require the incident light to couple to the vibrations of the system. There are several spectroscopic and microscopic techniques that employ elastic scattering.

Rayleigh scattering spectroscopy, a technique that collects elastic scattering from polarizable objects, uses visible wavelength for excitation and detection, in which the collected signal is several magnitudes brighter, have better spatial resolution and detection sensitivity compared the aforementioned inelastic scattering techniques. This method has been employed in identifying band structures and electronic properties of quantum wires of SWCNTs as well as semiconductor nanowires of GaAs and InP. In a study performed by a group at Cornell University, a collection of SWCNTs of random chirality was investigated using Rayleigh
scattering spectroscopy scanned in the visible range from 450 to 850 nm. As seen in Figure 1.3, different CNTs have different maximum resonance peaks (λ<sub>peak</sub>) which correspond to the photon energy matching of allowed interband transitions. This information was then applied to further elucidate electronic properties of individual nanotubes of different chirality.  

![Spatial Rayleigh scattering image of single walled carbon nanotubes (SWCNTs) of various chirality.](image)

**Figure 1.3 Spatial Rayleigh scattering image of single walled carbon nanotubes (SWCNTs) of various chirality.** Spatial Rayleigh scattering image of more than 20 SWCNTs of various chirality. Various pseudo-colors correspond to various resonance λ<sub>peak</sub>. Scale bar, 20 µm. This figure was adapted with permission from: Joh, D. et al. On-Chip Rayleigh Imaging and Spectroscopy of Carbon Nanotubes. *Nano Lett.* **11**, 1–7 (2011).

Another application of elastic scattering has been demonstrated in a form of polarized Rayleigh back-scattering from individual semiconductor nanowires. Eklund group at Pennsylvania State University has probed individual GaP NWs of various diameters to better understand the physics behind the polarized light scattering from quasi-one-dimensional systems.
Figure 1.4 Schematic of polarized Rayleigh back-scattering measurement setup. The scattering geometry setup for collection of polarized Rayleigh back-scattered light from individual GaP NW. The sample plane is defined as (x, y) with incident laser coming in -Z direction. The back scattered light travels back in the Z direction where it is polarized parallel to the incident light polarization (E₀) via a polarizer. This figure was adapted with permission from: Chen, G.; Wu, J.; Lu, Q.; Gutierrez, H. R.; Xiong, Q.; Pellen, M. E.; Petko, J. S.; Werner, D. H.; Eklund, P. C., Optical Antenna Effect in Semiconducting Nanowires. Nano Lett. 2008, 8 (5), 1341-1346.⁹

In this experiment, the collection of Rayleigh back-scattered light utilized the incident light of 514.5 nm, entering via z axis, with controlled polarization E₀ which is rotated by an angle of θ with respect to the suspended nanowire on the sample plane (x, y). As described in Figure 1.4, upon interaction of the incident light with a GaP NW, elastically back-scattered light of same wavelength is passed through a polarizer set at angles of parallel (θ) to the incident light. By analyzing the back-scattered intensity from the NW at various analyzer angles, the authors were able to ascertain the intensity enhancement factors of the scattered light to the incident polarization line with respect to the NW geometry and dimensions. Furthermore, it was determined that light scattering from high length to diameter aspect-ratio NWs exhibits dipolar scattering pattern as observed in various “nanoantennas.”⁴,⁹,²⁵

While elucidating light-matter interaction with in the realm of elastic scattering has been explored through Rayleigh scattering spectroscopy and elastic back-scattering experiments, elucidating fundamental light-matter interaction at a single nanomaterial, spatial level, along each
points of the nanomaterial axis has been so far deficient. In this report, I present, for the very first time, the fundamental polarized optical response from a single, high-anisotropy, one dimensional (1D) nanomaterials of various pure and doped semiconducting oxides (SCO) of tin oxide (SnO$_2$), zinc oxide (ZnO), indium tin oxide (ITO), and zinc tin oxide (ZTO). Unlike previous methods of scattering analysis, where electric field polarization of the incident light and the collected light are set parallel to each other, my system utilizes a fixed electric field polarization of the incident light, while collecting the scattered signals over 360° analyzer angles. Using this set-up, I was able to investigate scattering behaviors from NRs/NWs of various orientations with respect to the incident electric field. Overall, my experimental approach not only helped ascertain the direction/polarization anisotropy of the elastically scattered signals from individual NRs/NWs, but also the spatial, intensity profile, as well as the polarization rotation of the scattered light along the cylinder axis, the first of its kind. The unique scattering behaviors reported in this thesis will surely have profound implications in research and development of NW-based devices and applications involving absorption and/or emission of photons in the field of optically based sensors, waveguides, optoelectronics, as well as photovoltaic devices.

1.2 Protocol for SCO Nanomaterial Synthesis

Four different types of SCO nanomaterials were utilized in completion of this study. All materials in this study were synthesized in-house, by chemical vapor deposition (CVD) method driven by the vapor-liquid-solid (VLS) growth mechanism. VLS method holds many advantages over traditional growth via direct adsorption of a gas phase onto solid surface such as requiring
significantly lower reaction energy thereby driving the growth reaction to be faster and achievable at a lower temperature.\textsuperscript{35}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure15.png}
\caption{Scheme of the vertical growth of nanorods by VLS method. This figure was adapted with permission from: Choi, H. in Semiconductor Nanostructures for Optoelectronic Devices Processing, Characterization and Applications. (Yi, G.-C.) (Springer, 2012).\textsuperscript{35}}
\end{figure}

As the name suggests, VLS is broken down into three main stages of: (1) introduction of material to be grown as vapor through carbothermal reduction, which (2) absorbs onto the liquid catalyst surface and nucleates into liquid/solid droplets, which upon (3) supersaturation at the liquid/solid interface leads to axial growth of the desired crystal as described in Figure 1.5.\textsuperscript{35} The catalyst utilized in VLS is typically gold (Au) in a thin-film or colloidal form. The thin-film utilized in VLS is typically 1-10 nm thick deposited via sputter deposition or thermal evaporation which can be quite costly. The diameter of growth crystal is controlled via thickness of the deposited thin-film; thicker the film, the larger the droplet, thus producing larger crystals.\textsuperscript{35}
Instead of utilizing Au thin-film, Au colloids can be deposited onto the silicon growth substrate. The colloidal form of the catalyst has advantages over thin-films as less amount of Au is required, as well as size and position control is significantly facilitated allowing for uniform growth of micro-patterned networks or array NWs and NRs with selective spacing. This type of deposition is achieved via utilizing micro-patterned “stamps” of specific spacing as seen in Figure 1.6.
Figure 1.7. Schematic of fabrication of PDMS stamp from a silicon master.

The patterned stamp is fabricated via coating a photoresist coating on SiO$_2$/Si growth substrate then placing a patterned mask on top of this layer. The spacing on this mask determines the periodicity of the stamped area. Then a UV radiation is applied to remove the top SiO$_2$ layer only leaving the masked pattern. This master is then placed in polydimethylsiloxane (PDMS) then cured. Upon lifting the PDMS from the master pattern, PDMS stamp with selective spacing is formed as described in Figure 1.7. This stamp can be reused repeatedly without any loss in growth quality thus proving as an effective, low-cost alternative to the thin-film deposition.

For nanomaterials utilized in completion of this report, our group has synthesized four materials of indium tin oxide (ITO), tin oxide (SnO$_2$), zinc tin oxide (ZTO), and zinc oxide (ZnO) were synthesized using the aforementioned VLS method utilizing in-house chemical vapor deposition (CVD) furnace. Silicon wafers (resistivity < 1 Ω cm, thickness: 0.017 in.) and Au colloid (20 nm in diameter) were obtained from Silicon Quest International Inc. (Santa Clara, CA) and Ted Pella Inc. (Redding, CA), respectively. A Si wafer with a thin layer of Au catalysts was then placed approximately 5 inches downstream from a 2:1 mixture of graphite and ITO powder (In$_2$O$_3$:SnO$_2$ = 90:10 wt%) which was kept at the center of a home-built chemical vapor deposition (CVD) reactor. The sample was subsequently produced in the horizontal resistance furnace under
a constant flow of 100 standard cubic centimeter per minute (sccm) of Ar, at the reaction temperature of 850 °C for 15 min. Other nanostructures of tin oxide (SnO$_2$), zinc tin oxide (ZTO), and zinc oxide (ZnO) were similarly produced. They were generated by using 1:1 mixture of graphite and SnO$_2$ heated to 850 °C for 2 h, 5:1 mixture of graphite and ZTO powder (SnO$_2$:ZnO = 50:50 wt%) at 915 °C for 10 min, 2:1 mixture of graphite and ZnO heated to 900 °C for 1 h, respectively. As-grown nanostructures form a thin layer on the Si supports for use in the scattering experiments as well as device fabrication. The overall CVD process is outlined in Figure 1.8.

<table>
<thead>
<tr>
<th>TCO material</th>
<th>Graphite:TCO ratio</th>
<th>Growth temperature</th>
<th>Reaction time</th>
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<td>ITO (90:10 In$_2$O$_3$:SnO$_2$ wt%)</td>
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<td>850 °C</td>
<td>15 min</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>1:1</td>
<td>850 °C</td>
<td>2 hrs</td>
</tr>
<tr>
<td>ZTO (50:50 SnO$_2$:ZnO wt%)</td>
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<td>915 °C</td>
<td>10 min</td>
</tr>
<tr>
<td>ZnO</td>
<td>2:1</td>
<td>900 °C</td>
<td>1 hr</td>
</tr>
</tbody>
</table>

Figure 1.8. Schematic of chemical vapor deposition (CVD) reactor with applicable growth parameters for synthesis of ITO, SnO$_2$, ZTO and ZnO nanomaterials. The inset table shows the compositions of the doped materials for ITO and ZTO, ratios of the materials with graphite, optimal growth temperature as well as the reaction times.

Upon synthesis of these nanomaterials, appropriate optical and chemical characterizations were performed tailored to each projects. The results of these characterizations are reported in the appropriate chapters of this report.
1.3 Dissertation Outline

In this dissertation work, I first present fundamental light-matter interaction between a single ITO NRs of various positions and orientations and the incoming light of specific polarizations in chapter 2. It is elucidated for the first time, the effect of orientation of a single, highly-anisotropic material on the spatial intensity and the directionality of the scattered signal obtained from an individual nanorod. In chapter 3, I expand this study further by investigating the polarized light-matter interaction in 1-dimensional material of individual ZnO NRs. In this study, in addition to elucidating intensity and directionality of the scattered light along the main body of the nanorod, results from back-aperture imaging, also known as Fourier imaging, is presented as well confirming the fundamental scattering behavior observed from these 1D materials.

In chapter 4, I consolidate the findings from the previous two chapters and expound on the results by investigating the material independent, physical parameter responsible for the observed scattering behavior. This chapter presents four different SCO materials of both doped (ITO and ZTO) and undoped (SnO₂ and ZnO) variants to elucidate the unique scattering phenomenon that is observed along the axis of 1D nanomaterials when varying the polarized light-matter interaction geometry. In chapter 5, I switch gears and present the material dependent phenomenon of rotation of electric field polarization of the scattered from one end of the nanorod to the other end in pure, highly-crystalline materials of ZnO NRs compared to doped variants of ITO and ZTO NRs.

The penultimate and the final chapters of this report present two novel Raman and photodetection platforms fabricated from the investigated materials. In chapter 6, 1D array of ITO NRs is utilized as an effective surface enhanced Raman spectroscopy (SERS) platform. First, I
validate baseline Raman spectroscopy of ITO NRs compared to typically utilized Si substrate. Then, I incorporate various concentrations of rhodamine 6G (R6G) and 4’,6-diamidino-2-phenylindole (DAPI) on both ITO NRs and Si substrate to compare the Raman intensity obtained from respective platforms to demonstrate the improved detection capabilities of the ITO NR array platform. Furthermore, I demonstrate the superior multiplexing capabilities of this platform by incorporating mixtures of various concentrations of the aforementioned molecules onto a ITO NR array platform and compared the results to traditional Si and AuNRs platforms.

Lastly, in chapter 7, I incorporate the networks of 4 different SCO materials of ITO, ZTO, SnO₂, and ZnO to develop a photodetection platform of the visible light. Unlike majority of commercially available photodetectors of the aforementioned materials, where the devices are tuned to detect near-band gap energy, ultra-violet (UV) light, I present their capabilities as a detector of the visible light through photoconduction mechanism described as the photothermoelectric effect (PTE) rather than charge separation and recombination through band-gap energy excitation. My ITO NR network device presented in this report yields comparable to a better performance compared to commercial or single NW-based devices with the added advantage of significantly lower-cost, and straightforward fabrication.
Chapter 2

Position- and Orientation-Controlled Polarized Light Interaction of Individual Indium Tin Oxide Nanorods

2.1 Background and Introduction

Attractive optical properties of one-dimensional nanomaterials have been investigated and utilized extensively in photonic, optoelectronic, as well as in biodetection devices. Especially, wide-bandgap nanomaterials such as zinc oxide, tin oxide, and indium tin oxide have demonstrated useful phenomena such as spontaneous and stimulated emission, waveguiding, evanescence field enhancement, and optical antenna effects. Such technologically desirable properties have recently contributed to the development of novel applications of the semiconducting oxide nanomaterials in nanoscale lasers, subwavelength waveguides, and biodetection platforms.

As a parallel effort to the on-going technological development of these materials, fundamental understanding of the light interaction with the metallic and semiconducting oxide materials is crucial for providing much needed insight to both the basic and applied optical research areas. The majority of the previous efforts in this regard have pertained to the bulk materials, or ensembles of nanomaterials, rather than light interaction on individual nanostructures. A limited number of research attempts to elucidate light interaction with individual nanomaterials has been made on isolated scattering systems of carbon nanotubes, gallium phosphide nanowires, and indium phosphide nanowires.

In this chapter, I investigated fundamental optical response of individual indium tin oxide nanorods (ITO NRs) when polarized light is introduced to the one-dimensional NR structure. This
approach marks the first systematic study of forward light scattering from well-defined, single ITO NRs that correlates their varying optical response to the position along the width and length of individual NRs, spatial orientation of the NRs, and the direction of the electric field vector of the incoming light. Scattering behavior of ITO NRs is elucidated from the quantitative optical measurements that discern the position, orientation, and polarization-resolved light response of single ITO NRs. Major advantages of this approach lie in the detection capability of the relatively hard-to-collect scattering signal from a single NR. With the ever increasing demand for the applications of single nanomaterials and the utilization of their optical response in miniaturized photonic and bio-optical detection, these endeavors may also provide a valuable insight into the analysis of scattering and emission signal from individual nanomaterials in such devices.

2.2 Experimental Methods

The experimental setup utilizes a measurement scheme of collecting the forward scattered signal in a dark field (DF) mode, while eliminating the incoming light via total internal reflection (TIR). This combined approach ensures that the measured signal is only from the NR under investigation and, at the same time, enables quantitative analyses of the optical signal along the length and width of the NR. This approach also permits a much needed, systematic investigation of scattered light with respect to varying NR orientations on the measurement plane as well as the angle between a polarizer and an analyzer. Such efforts can be highly beneficial in ascertaining novel and unique optical response behavior of individual nanoscale materials.

Single crystalline ITO NRs with a well-defined size and shape were synthesized by in-house chemical vapor deposition (CVD) method as reported earlier. Before performing the
scattering experiments, physical characteristics of the synthesized NR samples were characterized by scanning electron microscopy (SEM) and optical microscopy in a bright field (BF) mode as well as in a reflected dark field (RDF) mode. SEM measurements of NRs were performed by using a Zeiss SUPRA55-VP operating at 5 kV. BF and RDF analyses of the NRs were carried out with an Olympus BX51F microscope with a 100 W, 12 V halogen lamp as a light source. BF and RDF images of ITO NRs were taken at magnifications of 20x, 50x, or 100x and focused onto a CCD camera, Qimaging Exi Blue. To effectively carry out these measurements, ITO NRs were first dispersed in ethanol via sonication from their growth substrate and deposited on a clean glass slide by drop casting. Then a small drop of glycerol (refractive index, n = 1.4729) is placed on the ITO NRs on the glass slide before lowering a cover slip onto the assembly.

When making forward scattering measurements, a linearly polarized 642 nm laser (Spectra Physics Excelsior-PS-DD-CDRH with an average power of 60 mW) entered the NR plane from below the sample stage after passing through a half-lambda (HL) wave plate and a neutral density filter of optical density 3. The HL plate controlled the orientation of the electric field (E) vector of the laser on the NR plane, as seen in Figure 2.1.

The polarized laser was directed to the sample through a high numerical aperture (NA = 1.2~1.4), oil-immersion DF condenser mounted below the stage and subsequently focused onto individual NRs of investigation. The above-mentioned sample assembly, combined with the use of the oil-immersion, high NA DF condenser, ensures matching refractive index throughout all existing interfaces. This scheme also guaranteed collection of scattered signal only from the NRs by completely reflecting the incoming laser via TIR. An analyzer was placed between the microscope tube lens and the CCD detector to examine polarization anisotropy of the scattered
light from individual NRs. Scattering signal was collected by using a 40x plan apochromatic objective lens (Olympus PlanSApo, N.A. = 0.90).

Figure 2.1 describes the sample assembly to achieve TIR and the measurement geometry of individual NRs with respect to the direction of the $\mathbf{E}$ vector of the incoming light. In the measurement setting, the $\mathbf{E}$ vector lies within the $xy$ plane, the sample plane of ITO NRs. $\mathbf{E}_\parallel$ and $\mathbf{E}_\perp$ are defined as the $\mathbf{E}$ vector direction of polarized light parallel to $x$ and $y$, respectively. Forward scattering behavior is evaluated from NRs of two specific orientations; vertical NRs positioned along the $x$ direction and horizontal NRs parallel to the $y$ direction.

![Figure 2.1. Schematic of the forward dark field (FDF) optical measurement setup with nanorod (NR) measurement geometry.](image)

The figure shows the refractive index-matching sample assembly, DF detection components for the forward scattering measurement, and the orientations of the polarized light as well as NR on the sample plane.

Figure 2.2 displays (a) SEM, (b) BF, and (c) RDF panels of a typical ITO NR used in the optical measurements. The NR shown in the SEM image is 130 nm and 13.2 $\mu$m in diameter and
length, respectively. As evidenced by comparing the two images of the same NR shown in panels (b) and (c), the use of a dark field mode was critical for the collection of the scattering signal from individual NRs effectively. No contrast can be resolved from individual NRs in BF. The image displayed in the panel (d) is the elastic scattering response of the ITO NR measured with the incoming monochromatic light with controlled polarization. This DF measurement operated in a forward geometry yields much higher image contrast when compared to images obtained in RDF.

For a given NR, a set of 18 images is taken while the analyzer configuration is changed from 0\(^{\circ}\) to 170\(^{\circ}\) at an interval of 10\(^{\circ}\). Image J, a Java-based image processing program, is used to process and analyze the scattering data.

Figure 2.2. Scanning electron microscopy (SEM), bright field (BF), reflected dark field (RDF), and dark field (DF) images of a single ITO NR. (a) 12 x 12 \(\mu\)m SEM image of an ITO NR, 130 nm in diameter and 13.2 \(\mu\)m in length, synthesized in a home-built CVD reactor using 20 nm Au colloids as catalysts. (b and c) BF and RDF images of the same ITO NR. (d) Scattering panel of the same ITO NR when an incoming beam of polarized 642 nm laser is illuminated to the NR and the emission is collected in a DF mode in the forward scattering configuration, as shown in Figure 2.1.
2.3 Results and Discussion

The scattering intensity profile along a vertically oriented NR (NR||) excited by the linearly polarized laser is shown as contour plots in Figures 2.3(a) and 2.3(b). The three-dimensional maps simultaneously show the scattering intensity at each pixel (position) along the length of the NR as a function of the analyzer rotation. When an ITO NR|| is excited with the E|| polarized light as seen in Figure 2.3(a), highest scattering intensities are profiled at 0°/180° analyzer rotations with respect to the incoming E|| vector, while the lowest intensity is observed at the analyzer setting of 90°. This trend is reversed when E⊥ polarized light is used as the scattering source of the same vertical NR, as seen in Figure 2.3(b). In this case, the highest scattering signal occurs when the analyzer is configured at 90° and the lowest signal is observed at the analyzer angles of 0° and 180°. Averaged and normalized values of the scattering intensity along the vertical NR are used in order to plot the scattering intensity plots shown in Figures 2.3(c) and 2.3(d), respectively. Scattering data points, measured by using the polarized E direction of E|| (red) and E⊥ (blue) are graphed as a function of the analyzer angle. In these plots, the red and blue lines correspond to curve fits of the red and blue data points acquired from the vertical NR.

The intensity (I) of the averaged and normalized scattering signal from the NR|| follows Malus’s Law, \( I = I_0 \cos^2(\Theta) \), as the observation confirms that the ITO NR scattering intensity is directly proportional to the square of the cosine of angle (Θ) between the transmission axis of the analyzer and the polarizer (HL wave plate) of the incoming linearly polarized light. When comparing the averaged intensity values of the scattered light for the two cases of E|| and E⊥, scattering from the former is approximately eight times higher than that of the latter. For this
comparison, the exposure time is kept constant at 12 ms during all measurements for the vertically oriented NR.

The excitation and emission polarization ratios of the maximum intensities parallel ($I_{E\parallel}$) and perpendicular ($I_{E\perp}$) to the NR axis is determined as 0.77 from this measurement, by defining polarization anisotropy as the difference between the scattered light intensities for the incoming polarized light of $E_{\parallel}$ and $E_{\perp}$ divided by the sum of the two values at a given analyzer angle, $PA = (I_{E\parallel} - I_{E\perp})/(I_{E\parallel} + I_{E\perp})$. According to classical electromagnetic calculations based on Maxwell’s equation, the electric field inside the material for an infinitely long dielectric cylinder in a vacuum is the same as the incident electric field. However, when the same cylinder is interacting with $E_{\perp}$, the electric field inside the material is attenuated as a function of dielectric constant of the cylinder, $\varepsilon$. The relationship between the electric field amplitude inside the NR and the incident light of $E_{\perp}$ is a function of the dielectric constant of the NR

$$E_{NR,E\parallel} = E_{\parallel},$$

$$E_{NR,E\perp} = \frac{2\varepsilon_0}{\varepsilon + \varepsilon_0} E_{\perp}.$$ 

$\varepsilon_0$ is the dielectric constant of the vacuum. Based on this, a theoretical PA value is determined as 0.7 while using the high frequency dielectric constant of ITO of 3.8. Therefore, the classical electromagnetic approach seems to explain well, the measured PA behavior of the ITO NR in my setup. Figure 2.3(e) displays the measured polarization anisotropy (PA) values of the NR. Both the data points (dot) and the curve fit (line) in Figure 2.3(e) clearly show that the PA plot also exhibits a $\cos^2(\Theta)$ dependence. Figure 2.3(f) charts the corresponding polar plot of the
scattered light intensities when the \( E_{\parallel} \) (red) and \( E_{\perp} \) (blue) polarized lasers interact with the same vertically oriented ITO NR.

**Figure 2.3.** Scattering signal from an ITO NR\( _{\parallel} \) at various analyzer settings in response to the 642 nm laser illumination of \( E_{\parallel} \) and \( E_{\perp} \) orientations. (a) Scattering behavior of the ITO NR\( _{\parallel} \) upon illumination with the incoming light of \( E_{\parallel} \) is determined. The contour plot displays the measured scattering intensity at each point along the entire length of the NR\( _{\parallel} \) while the analyzer is rotated from 0 to 170 degrees. (b) The contour map shows the NR-position dependent scattering intensity of the same NR\( _{\parallel} \) with respect to the incoming light of \( E_{\perp} \). (c) Average scattering intensity of the NR\( _{\parallel} \) is graphed to show the difference in the magnitude of the transmitted scattering signal through the analyzer between the two cases of \( E_{\parallel} \) and \( E_{\perp} \) at various analyzer angles. (d) Normalized scattering signal from the NR\( _{\parallel} \) is displayed for \( E_{\parallel} \) and \( E_{\perp} \). (e and f) Calculated PA, \( \frac{(I_{E_{\parallel}} - I_{E_{\perp}})}{(I_{E_{\parallel}} + I_{E_{\perp}})} \), and a polar plot of the normalized NR\( _{\parallel} \) scattering signal are shown as a function of the analyzer angle in (e) and (f), respectively. In all graphs, points and lines correspond to the experimental data and curve fits of the data, whereas red and blue colors are used to denote the two circumstances of \( E_{\parallel} \) and \( E_{\perp} \), respectively.
Similarly, the scattering intensity profile along a horizontally oriented NR (NR∥) is profiled and the resulting contour maps of the scattered light from the NR⊥ are presented in Figures 2.4(a) and 2.4(b). The orientation of the linearly polarized light is \( E_\parallel \) in Figure 2.4(a) and \( E_\perp \) in Figure 2.4(b). When an ITO NR⊥ is excited by \( E_\parallel \) polarized light, highest scattering intensities are profiled at 0° and 180° analyzer rotations and the lowest intensity is at the analyzer setting of 90°. When \( E_\perp \) polarized light is used, the highest and lowest scattering signal occur when the analyzer is configured at 90° and 0°/180°, respectively.
Figure 2.4. Scattering signal from an ITO NR cells at various analyzer settings in response to the 642 nm laser illumination of E∥ and E⊥ orientations. (a) The contour plot displays the measured scattering intensity in response to E∥ at each point along the length of the NR⊥ at various analyzer orientations. (b) The contour map shows the NR-position dependent scattering intensity of the same NR⊥ with respect to E⊥. (c and d) Averaged and normalized scattering intensity of the NR⊥ are graphed for the two cases of E∥ and E⊥. (e and f) Calculated PA values as well as a polar plot of the normalized NR⊥ scattering signal are shown as a function of the analyzer angle. In all graphs, points and lines correspond to the experimental data and curve fits of the data, whereas red and blue colors are used to denote the two circumstances of E∥ and E⊥, respectively.

Therefore, the general trend for the analyzer angles yielding the maximum and minimum intensities of the scattered light is the same for the case of horizontal and vertical NRs for the two directions of the incoming polarization of E∥ and E⊥. However, a significant difference in scattering profile is observed between the NR∥ in Figure 2.3(a and b) and the NR⊥ in Figure 2.4(a and b) when their scattering behavior is compared along the length of the NR. The two ends of
the horizontally positioned ITO NR scatter the polarized light of \( E \parallel \) and \( E \perp \) much more effectively than the response along the main body of the NR\( \perp \). This interesting scattering behavior is quantitatively presented in Figures 2.4(a) and 2.4(b). Figures 2.4(c) and 2.4(d) display averaged and normalized scattering intensities of the NR\( \perp \) in response to \( E \parallel \) (red) and \( E \perp \) (blue) at different analyzer settings. In Figure 2.4(c), the scattered signal is averaged over the entire length of the NR. Comparing the average scattering intensities of the NR\( \perp \), the difference between the two laser polarizations of \( E \parallel \) and \( E \perp \) is two-fold when keeping a constant exposure time of 250 ms for the horizontally oriented NR. In general, a much higher difference between the average intensity values of \( E \parallel \) and \( E \perp \) is observed for vertically oriented NRs than for horizontal NRs. PA is calculated for the NR\( \perp \) similar to the earlier case of NR\( \parallel \) and plotted in Figure 2.4(e). In all graphs of the NR\( \perp \), the \( \cos^2(\theta) \) dependence is clearly observed from the scattered light similar to the NR\( \parallel \). The polar plot of the normalized scattered light of the horizontal NR is shown in Figure 4(f). For both the vertical and horizontal ITO NRs shown in Figures 2.3 and 2.4, the polar scattering intensity data display a tightly closed, dipole-like pattern. This phenomenon indicates that the ITO NRs under investigation exhibit a high asymmetry in scattering enhancement, i.e. signal enhancement occurring along the long axis of the NRs is much higher than the degree of enhancement parallel to the short NR axis.

### 2.4 Conclusion

Elucidating light interaction behavior of individual nanomaterials is extremely important in further understanding the nature of resulting optical response for the technologically important optical and biomedical applications of nanomaterials. This chapter showed that I have systematically characterized the light interaction profile between single ITO NRs and a beam of
linearly polarized, monochromatic light with controlled $E$ orientations. Scattering signal from individual ITO NRs of horizontal and vertical configurations was probed and the ensuing NR response, dependent on various polarization orientation of the incoming light, was quantitatively examined with respect to the analyzer angle. Such optical response of single ITO NRs was quantitatively measured with respect to the position along the length of the NRs. These efforts can be highly beneficial in identifying a unique optical behavior of individual nanomaterials for their future applications in optical and biomedical detection. As various optical phenomena of individual NRs are increasingly utilized in miniaturized optoelectronic, photonic, and bioapplications, these endeavors may also benefit position-, orientation-, and polarization-dependent analysis of the NR light signal which are further explored in the subsequent chapters.
Chapter 3

Scattering Intensity and Directionality Probed Along Individual Zinc Oxide Nanorods with Precisely Controlled Light Polarization and Nanorod Orientation

3.1 Background and Introduction

Optical properties of one-dimensional zinc oxide nanorods (1D ZnO NRs) have been extensively studied and engineered for better photonic, optoelectronic, and biosensing applications. Many studies have previously demonstrated that the incorporation of 1D ZnO materials in those applications can enable improvements in emission efficiency and/or detection sensitivity over their 2D and bulk counterparts. From these efforts, beneficial optoelectronic characteristics of 1D ZnO have been identified that have not been readily observed from the thin film or bulk form of ZnO. For instance, single-crystalline ZnO NRs have been shown to exhibit beneficial optical properties such as spontaneous/stimulated emission at room temperature and effective UV/visible light guiding. In other examples, the optical signal-enhancing capability of ZnO NRs has been used in conjunction with dye-coupled DNA and proteins for fluorescence-based biomedical detection.

Both individual and ensembles of ZnO NRs have been exploited for the aforementioned applications. Upon Subjecting 1D ZnO to incident light with different measurement configurations for excitation and detection, light can trigger various responses from the materials such as bandgap emission and elastic scattering. In this regard, the majority of previous studies on 1D ZnO has focused on ensembles of NRs for a test platform to be investigated, and on the bandgap-associated photoluminescence for a property to be examined. Several studies have attempted to elucidate
interesting light behavior specifically from individual ZnO nanomaterials instead of ensembles. Examples of these endeavors can be found in the areas of subwavelength waveguiding using 1D structures such as nanoribbons and nanobelts. Another study in the field of hybrid plasmonic/photonic coupler has demonstrated that a paired system of individual ZnO NRs and metal nanowires can be used to convert light to plasmons via direct light coupling and vice versa. Very recently, crystal facet-dependent fluorescence emission characteristics have been reported from dye-conjugated proteins on different crystal surfaces of isolated ZnO NRs. In these investigations employing single ZnO NRs as test elements, light is known to couple effectively into the ZnO NR medium and propagate predominantly along the long axis of the ZnO NR via guided- and/or surface evanescent-waves. This highly directional light guiding and propagation along the c-axis of ZnO NRs occur whether incident light is launched from another nanowire source for the cases of subwavelength waveguiding and hybrid coupling, or whether emitted light from biomolecules is coupled to the high refractive index NR medium instead.

For many optical and bio-optical applications such as those described above, quantifying how individual ZnO NRs scatter light to far field is also critical since far field observations of the light signal are commonly utilized in many optical detection schemes. Information on scattering intensity and directionality can provide much-needed guiding principles for optimizing optical device outputs and for accurate bio-optical signal interpretation in both single and ensemble ZnO NR-based devices. Therefore, scattering is another important aspect of light response that needs to be thoroughly probed to establish the fundamental light-matter relationship. However, it is not yet clearly understood how light from ZnO NRs scatter into far-field. Due to the inherently low signal intensity that can be collected from a single nanomaterial and the difficulty to remove the
background optical noise, very few studies have systematically investigated scattering from semiconducting oxide NRs, especially by addressing each NR independently.\textsuperscript{105,106}

In this chapter, I present the optical responses of individual ZnO NRs upon illumination with a linearly polarized, monochromatic beam of light (642 nm in wavelength), while specifically focusing on elucidating light polarization- and NR orientation-dependent, elastic scattering characteristics of single ZnO NRs. To circumvent the challenges of low signal and high background issues in single NR imaging, I utilized dark field (DF)-based optical measurement schemes capable of detecting the scattering intensity and, at the same time, recording the spatial distribution from individual NRs upon illumination with a well-defined incident wave vector and polarization. Specifically, DF scattering measurements in forward geometry as well as back-aperture imaging (also known as Fourier microscopy) was carried out in order to quantify systematically the position-, orientation-, and polarization-resolved optical response from individual ZnO NRs. The two investigation modes utilized in this study were designed to provide not only the scattering intensity but also scattering directionality from each NR. In the forward DF scattering mode, the scattering signal from individual ZnO NRs was both qualitatively and quantitatively discerned along the position on the NR. This measurement was systematically conducted as a function of analyzer rotation when the ZnO NRs are illuminated under different electric field orientations of the incident light. I also present distinctive, polarization-dependent scattering responses from single ZnO NRs that are arranged in different directions within the sample plane. In the back-aperture imaging mode, I identified the spatial distribution of the scattering signal from individual ZnO NRs. I resolved the polarization-dependent scattering directivity and the orientation of individual ZnO NR scatterers based on the distinctive patterns
formed at the back focal plane, which are equivalent to Fourier transforming the radiation distribution from the back-aperture of the objective lens. With the ever-growing research and development of single ZnO NRs for highly miniaturized optical, optoelectronic, and biomedical devices, this study aiming for a better understanding of fundamental light interaction with individual 1D ZnO nanomaterials may provide important insight into their potential behavior, particularly when functioning as an effective directional scatterer of polarized light to far field. Furthermore, efforts presented in this chapter may promote innovative optical, hybrid nanophotonic, and biomedical applications based on the use of ZnO NRs by harnessing the polarization dependent, highly directional optical response of the nanomaterials stemming from their high shape anisotropy.

**3.2 Experimental Methods**

1 x 1 cm Si wafer (0.017 in. thickness) obtained from Silicon, Inc was cleaned by sonication in ethanol and dried under a light stream of N₂. For individual ZnO NRs, 20 μL of 20 nm Au colloid (Ted Pella, Inc) was deposited on a Si wafer for 5 min and gently blown dry with N₂. The source materials, 0.45 grams of a 2:1 mixture of graphite (99%) and zinc oxide powders (99.999%) obtained from Alfa Aesar Inc., 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 15.6 cm downstream. The furnace was heated to 900 °C for 1 h at a ramp up/ramp down rate of 15°C/min under a constant Ar flow of 100 standard cubic centimeters per minute. Various aspect ratios of ZnO NRs were achieved by slight alterations to the distance between the source materials and the growth substrate. ZnO NRs were subsequently sonicated off their growth substrates in ethanol
and 2 μL aliquots of dispersed ZnO NRs were subsequently drop-casted onto a clean glass slide and then dried with N₂. A small drop of glycerol (n=1.4729) was placed on top of the ZnO NRs on the glass slide and a cover slip was slowly lowered onto the sample while avoiding bubble formation.

When performing the forward scattering measurements, a linearly polarized 642 nm laser (Spectra Physics Excelsior-PS-DD-CDRH with an average output power of 60 mW, Newport Corp., Bozeman, MT) was focused onto the ZnO NR plane from below the sample stage after passing through a half-lambda (HL) wave plate and a neutral density filter wheel (Thorlabs Inc., Newton, NJ). The HL plate controlled the orientation of the E field vector of the laser on the NR plane, as seen in Figure 3.1. The polarized laser was directed to the sample through a high numerical aperture (NA = 1.2~1.4), oil-immersion DF condenser mounted below the stage and subsequently focused onto individual NRs of investigation. An analyzer was placed between the microscope tube lens and the CCD detector to examine polarization anisotropy of the scattered light from individual NRs. Scattering signal was collected by using a 40x plan apochromatic objective lens (Olympus PlanSApo, N.A. = 0.90, Olympus Corp., Center Valley, PA). Scattered light from the ZnO NR sample was collected at specific analyzer angles in order to investigate the polarization dependence. For a given NR, a set of eighteen analyzer settings were used from 0° to 170° in 10° intervals. Additionally, back-aperture imaging of individual ZnO NRs was performed by adding a home-built optical attachment to the forward scattering setup. The optical addition employed to examine the spatial distribution of the scattered light contained an iris and a removable lens. Data from the forward scattering and back-aperture imaging measurements were
processed and analyzed using Origin 8.5 software (OriginLab Corp., Northampton, MA) and Image J, the Java-based image-processing program.

**Figure 3.1. Schematic of the forward dark field (FDF) optical measurement setup with light-NR geometry and light detection pathway.** Schematic illustrations showing the experimental setup to measure NR position- and NR orientation-dependent scattering signal as well as to detect back-aperture signal from individual ZnO NRs while controlling excitation and collection polarization angles. Three key measurement points in the setup indicated as (i), (ii), and (iii) are displayed in detail inside the boxed panels; (i) sample assembly to achieve refractive index matching of all measurement components and optics, (ii) two distinctive directions of the incoming polarized laser and the two different NR orientations on the measurement plane, and (iii) optical elements to perform forward DF scattering and back-aperture imaging from the same individual NRs. The diagram shown in (ii) is a 180° rotated view of the sample plane and incident light in order to describe the two polarized light directions of $E_\|_{\parallel}$ and $E_\parallel_{\perp}$. The incident angle of the laser, noted as $\theta_{in}$ in the diagram, is 62° in the experimental setup. The two orthogonal axes of the sample plane are labelled as x and y. The * sign next to E marks the projected components of the electric field onto the sample plane.
3.3 Results and Discussion

3.3.1: Optical Setup for Dark Field Scattering and Back-Aperture Imaging

Figure 3.1 describes the experimental setup to measure forward scattering signals from individual ZnO NRs with controlled orientations. The incoming light source, a linearly polarized 642 nm laser was passed through a half-lambda (HL) plate at 45° and 90° to control the orientation of the incident electric field (E) vector to achieve E|| (polarization direction lying in the plane of incidence) and E⊥ (polarization direction perpendicular to the plane of incidence) orientations, respectively. After passing through a series of mirrors and neutral density filters, the laser beam was directed to the sample stage via a dark field (DF) condenser with a high numerical aperture. The use of DF in the experimental setup is essential to resolve the inherently low amount of signal to be collected from individual NR samples. As displayed in panel (i) of Figure 3.1, multiple components involved in the ZnO NR sample assembly are refractive index-matched throughout all existing interfaces and this configuration allows for total internal reflection (TIR) of the incident laser beam after illuminating the sample.

The four experimental configurations examined in the forward scattering measurements, displayed in panel (ii) of Figure 3.1, are resultant from different combinations of the polarized laser orientations (E|| and E⊥) illuminating the NRs with the main body lying along the y- (NR||) and x- (NR⊥) directions of the sample plane as defined in the schematics. Additionally, the spatial distribution characteristics of the NR scattering signals are investigated by performing back-aperture imaging using the optical setup provided in panel (iii) of Figure 3.1. The removal of the last lens between the Fourier lens and the detector in the setup permits back-aperture imaging of the same NR directly after examination of its forward scattering behavior. Using this setup, both
forward DF mode scattering and back-aperture images were collected by examining over 20 different individual NRs. The representative scattering characteristics specific to each of the four different combinations of the NR orientation (NR∥ and NR⊥) and the incident polarization direction (E∥ and E⊥) are provided herein.
Figure 3.2. Scattering signal from a single ZnO NR\textsuperscript{\parallel} under two incident light polarizations of $E_\parallel$ and $E_\perp$. Scattering of a single ZnO NR (138 nm in diameter, 8.06 $\mu$m in length) measured by using two polarization directions of an incoming laser ($E_\parallel$ and $E_\perp$) on the NR oriented in the y direction (ZnO NR\textsuperscript{\parallel}). Scattering intensity is measured with respect to the position along the length of the 1D nanomaterial as well as the analyzer angle. (a) The 3D contour plot summarizes scattering results from a ZnO NR\textsuperscript{\parallel} under the excitation of $E_\parallel$ as a function of both the analyzer angle and the spatial position on the NR. The highest and lowest scattering is observed when the collection polarization angle is set parallel (0°) and perpendicular (90°) to the incoming polarization direction, respectively. The phenomenon is clearly seen in the 2D projection of the scattering intensity with respect to the analyzer angle at each position along the length of the ZnO NR\textsuperscript{\parallel}. Color schemes used in the 2D plot are the same as the scattering intensity level profiled in the 3D contour graph. A series of grey-scale panels is the scattering images obtained from the ZnO NR measured at the analyzer angle of 0°, 30°, 60°, and 90°, presented from left to right, respectively. (b) The same set of scattering measurements was repeated by using the orthogonal excitation of $E_\perp$ as functions of the analyzer angle and the spatial position on the same ZnO NR\textsuperscript{\parallel} shown in (a). Similar to what was observed under $E_\parallel$, highest and lowest scattering from the NR occurred when the analyzer angle was set parallel and perpendicular to $E_\perp$, respectively. In (b), those analyzer angles correspond to 90° for the former and 0° for the latter case.
3.3.2 Scattering Characteristics of NR\textsubscript{∥} under E\textsubscript{∥} and E\textsubscript{⊥}

The typical scattering behavior of individual NRs was first characterized from the y axis-oriented NRs (NR\textsubscript{∥}) by employing the two cases of polarized illumination, E\textsubscript{∥} and E\textsubscript{⊥}. Figure 3.2 summarizes the resulting data by showing 3-dimensional (3D) contour plots of the scattering intensity as a function of both the position along the ZnO NR long axis and the analyzer angle, 2-dimensional (2D) projection maps of the scattered signal with respect to the analyzer rotation along the spatial position of the NR, and DF images of the NR\textsubscript{∥} at four representative analyzer angles of 0°, 30°, 60°, and 90°. Schematics showing the orientations of the key measurement components are also provided in Figure 3.2. The set of data in Figure 3.2(a) represents typical scattering responses of ZnO NRs lying along the y-axis when they are illuminated with an incoming light oriented parallel to the long axis of the NR, i.e. E\textsubscript{∥}. The scattering intensity of the NR\textsubscript{∥} decreases as the analyzer angle is changed from parallel (0°) to perpendicular (90°) with respect to the incident polarization direction and recovers back to its full scattering intensity when the analyzer rotation is increased from to 90° to 180°. This trend in the NR\textsubscript{∥} scattering intensity is quantitatively confirmed in the 3D contour plot in Figure 3.2(a) in which the highest intensities are observed at 0° and 180° while the lowest intensity is observed at 90°. These analyzer angle-dependent changes in NR scattering intensity are further evidenced quantitatively in the 2D projection map and qualitatively in the four representative DF images of the ZnO NR sampled at the analyzer rotations of 0°, 30°, 60°, and 90°.

When the same NR\textsubscript{∥} is examined under the incident laser polarized orthogonal to the NR long axis (E\textsubscript{⊥}) instead, analyzer angles at which the maximum and minimum scattering occurs are reversed from the previously discussed E\textsubscript{∥} case. Highest NR\textsubscript{∥} scattering is observed at the analyzer
angle of 90° whilst the lowest is observed at 0° and 180°, as presented in the 3D contour plot in Figure 3.2(b). Similar to the previously discussed case, the 2D projection map of the NR scattering intensity as well as the representative DF panels further demonstrates that, under $E_{\perp}$ illumination, the highest (and lowest) scattering from the NR$_{\parallel}$ is yielded at the analyzer rotation of 90° (and 0° and 180°). For both cases of NR$_{\parallel}$ scattering using $E_{\parallel}$ and $E_{\perp}$, the highest scattering intensity is achieved when the incident $E$ field is parallel to the analyzer rotation while the lowest scattering is observed when the incident $E$ field is perpendicular to the analyzer angle. When comparing the measured scattering intensities along the position of the NR at the analyzer angles yielding the maximum signal for each of the $E_{\parallel}$ and $E_{\perp}$ case, it is seen that the scattering intensity gradually increases from one end towards the other end of the NR. This effect is not likely due to uneven illumination of the NR as the beam size (approximately 50 µm) is much larger than the NR dimensions. Rather, this phenomenon may be caused by the light coupling through the NR end located closer to the incident light wave vector which is then guided through the NR main body before coupling out through the other end of the NR.

In Figure 3.3, the scattering signal over the entire length of the ZnO NR$_{\parallel}$ is further processed and compared for the two excitation conditions of $E_{\parallel}$ and $E_{\perp}$ by plotting NR-position averaged scattering values against the analyzer rotation. Specifically, the scattering dependence of the ZnO NR$_{\parallel}$ on the incoming $E$-field polarization is evaluated by plotting the average scattering intensity, normalized scattering intensity, and polarization anisotropy (PA) as a function of the analyzer rotation in Figures 3.3(a), 3.3(b), and 3.3(c), respectively. In all graphs of Figure 3.3, data collected from the two cases of $E_{\parallel}$ and $E_{\perp}$ (and their respective curve fits) are represented as red and blue points (and lines), respectively. For the normalized intensity plots, the average
scattering intensity is normalized with respect to the highest and lowest intensity values measured at each excitation condition. The PA values plotted in Figure 3.3(c) are obtained by the equation shown below which defines PA as the ratio of the difference between the scattered light intensities for polarized light under $E_\parallel$ and $E_\perp$ to the sum of those values at a given analyzer angle.

$$PA = \frac{I_{E_\parallel} - I_{E_\perp}}{I_{E_\parallel} + I_{E_\perp}}$$

When the scattering intensity values are taken at the analyzer angles allowing the highest signals for $E_\parallel$ and $E_\perp$ (I of 6800 and 2000, respectively), then the above equation yields the PA value of 0.55 from this measurement configuration.
Figure 3.3. The NR-position dependent scattering signal from single ZnO NR\textup{\textregistered} under two incident light polarizations of \( E_{\parallel} \) and \( E_{\perp} \). The NR-position dependent scattering signals under the two excitation conditions of \( E_{\parallel} \) and \( E_{\perp} \) were collected over the entire length of the ZnO NR\textup{\textregistered} and plotted against the analyzer rotation. Red and blue symbols in all graphs are the experimental data when excitation polarizations of \( E_{\parallel} \) and \( E_{\perp} \) were used, respectively. Lines represent curve fits for the corresponding set of data. (a) The position-dependent scattering signal was averaged over the entire length of the NR\textup{\textregistered} and plotted as a function of the analyzer angle. For the same exposure of 50 ms, the overall scattering intensity from the same NR was much lower when \( E_{\perp} \) was used as excitation instead of \( E_{\parallel} \). (b) The average scattering intensity was normalized with respect to the highest intensity values measured at each excitation condition and graphed as a function of the analyzer rotation. (c) Polarization anisotropy values calculated from the data shown in (b) follow a \( \cos^2 \theta \) dependence on the analyzer angle, \( \theta \). (d and e) Polar plots of average scattering intensities from the ZnO NR\textup{\textregistered} under (d) \( E_{\parallel} \) and (e) \( E_{\perp} \) excitation are shown.
A characteristic trend of the NR∥ scattering intensity (I) as function of analyzer angle, which reveals a sinusoidal pattern, is shown in Figures 3.3(a through c). When fitting the experimental data obtained under the two cases of E∥ and E⊥, the scattered signal from the ZnO NR∥ is directly proportional to the square of the cosine of the angle (θ) between the transmission axis of the analyzer and the incident polarized light. This behavior is similar to what is known as Malus’s law which describes the angle-dependent intensity of plane-polarized light incident on an analyzer and demonstrates that the same macroscopic behavior can be carried over to explain the analyzer angle-dependent intensity of a scatter whose width is only in a few hundreds of nanometers. In these instances, the intensity of the light transmitted by the analyzer is directly proportional to the square of the cosine of the angle between the transmission axes of the analyzer and the polarizer, \( I = I_0 \cos^2(\theta) \). Furthermore, in comparing the average intensity values of the scattered light from the same ZnO NR∥ between E∥ and E⊥, the maximum NR scattering intensity under E∥ is approximately 3.5 times greater than scattering from E⊥. This value was obtained by keeping the exposure time constant at 50 ms for both orientations of the incident light. Figures 3.3(d) and 3.3(d) provide polar plots of the ZnO NR∥ in order to reveal the effect of E∥ and E⊥ on the degree of polarization in ZnO NR∥. When evaluating the corresponding polar intensity plots in Figures 3.3(d) and 3.3(e) for the effect of E∥ and E⊥ on NR∥ scattering, a stronger polarization anisotropy effect is seen under E∥ as evidenced by the narrower waist of the dipolar plot in Figure 3.3(d) in comparison to that in Figure 3.3(e). NRs with high shape anisotropy will result in dipolar scattering patterns with tightly closed center whereas the patterns will open up in the center and become circular instead when the length of the nanomaterial reaches the size of its width.
3.3.3 Scattering Characteristics of NR⊥ under \( E_\parallel \) and \( E_\perp \)

Subsequently, the scattering characteristics of \( x \)-axis oriented ZnO NRs (NR⊥) were investigated as a function of the position along the NR⊥ and the analyzer rotation for both the incident \( E \) fields of \( E_\parallel \) and \( E_\perp \). The results are provided in Figure 3.4 along with the schematics showing the orientations of the key measurement components. The 2D projection maps and 3D contour plots in Figures 3.4(a) and 3.4(b) display the typical scattering response of NR⊥ under the incident light with \( E_\parallel \) and \( E_\perp \) polarizations, respectively, as a function of the analyzer angle.

The data in Figure 3.4 reveal that the scattering behavior of NR⊥ is strikingly different than that of NR∥. The scattering signal from the NR⊥ is highly localized at the two ends (basal planes) of the NR⊥ upon illumination with either \( E_\parallel \) or \( E_\perp \). Variations in the analyzer rotation lead to changes in this highly localized scattering intensity at each end, resulting in either even brightening/dimming of the two ends under \( E_\parallel \) or alternating brightness between the two ends under \( E_\perp \). This tendency is displayed in the four DF panels provided in Figures 3.4(a) and 3.4(b). At the same time, scattering is completely absent along the main body (prismic planes) of the NR⊥ despite the variations in \( E_\parallel \) and \( E_\perp \) or in the analyzer setting. This discontinuity in scattering intensity along the position of the NR⊥ is embodied as the NR edge peaks in the 2D and 3D plots of Figure 3.4 as well as in the one (or two) bright NR end spots in the four representative DF images. In comparison, the scattering intensity from NR∥ detailed in Figures 3.2 and 3.3 is relatively uniform spatially along the length of the NR∥, regardless of the polarization of the incident light.
Figure 3.4. Scattering signal from a single ZnO NR⊥ under two incident light polarizations of E∥ and E⊥. Scattering of a single ZnO NR (184 nm in diameter, 10.15 µm in length) measured by using two polarization directions of an incoming laser (E∥ and E⊥) on a NR oriented along the x-axis (ZnO NR⊥). Scattering intensity was measured with respect to the position along the length of the 1D nanomaterial as well as the analyzer angle. (a) The 3D contour plot summarizes scattering results from a ZnO NR⊥ under the excitation of E∥ as a function of both the analyzer angle and the spatial position on the NR. A striking difference in the scattering signal was seen along the length of the NR⊥. Intense scattering occurred only on the two ends of the NR⊥ where the signal along the main body of NR⊥ was negligible. This phenomenon is also clearly seen in the 2D projection of the scattering intensity with respect to the analyzer angle at each position along the length of the ZnO NR⊥. Color schemes used in the 2D plot are the same as the scattering intensity levels profiled in the 3D contour graph. A series of grey-scale panels is the scattering images obtained from the ZnO NR measured at the analyzer angle of 0°, 30°, 60°, and 90°, respectively. (b) The same set of scattering measurements was repeated by using the orthogonal excitation of E⊥ as a function of both the analyzer angle and the spatial position on the same ZnO NR⊥ shown in (a).
Both the 2D projection maps and 3D contour plots in Figures 3.4(a) and 3.4(b) clearly present the spatially resolved, NR⊥ scattering intensity along the position on the NR as a function of the analyzer angle probed from 0° to 180° with an increment of 10°. When the analyzer setting is varied incrementally from 0° to 90° under $E∥$, a decreasing trend in NR⊥ scattering intensity is observed as seen in the DF panels in Figure 3.4(a). The data in Figure 3.4(a) display the highest intensities monitored at 0° and 180° while the lowest is observed at 90°, showing the same trend as those observed in the (NR∥, $E∥$) case. This observation is due to the maximum scattering intensity being transmitted through the analyzer when its polarization vector is aligned with the polarized direction of the incident light. On the other hand, the scattering intensity of the same NR⊥ under $E⊥$ in Figure 3.4(b) shows more complicated behaviors. In this case, a small degree of polarization demixing is observed and the scattering does not become uniformly weaker at all positions of the NR even at the analyzer angle perpendicular to the incident polarization. Although the cause is not understood yet, this effect leads to an interesting optical phenomenon evidenced in Figure 3.4(b) by the switching of the bright ends in the series of NR scattering panels at different analyzer rotation as well as in the 2D map showing the alternating analyzer angles of the two NR ends corresponding to the maximum scattering intensity. The observed rotation of the polarization from one end to the other end of the NR may be related to the fact that ZnO is a birefringent material. Further explanation of this phenomenon is presented in the latter chapters.

In order to substantiate the polarization-dependent scattering behavior of ZnO NR⊥ under the two cases of the incident laser, Figure 3.5 further displays the quantitative scattering data measured from the ZnO NR⊥ discussed in Figure 3.4. Figure 3.5(a) displays the scattering signal averaged over the entire length of the NR⊥ in response to $E∥$ (red points) and $E⊥$ (blue points)
while systematically varying the analyzer angle. Red and blue lines in the graphs are the curve fits of the respective data. Figure 3.5(b) shows the scattering intensity as a function of analyzer rotation after normalizing the signals with respect to the highest and lowest intensity values measured at each excitation condition. The exposure time was kept constant at 10 ms between the two laser polarizations. The scattering intensity of the NR⊥ is approximately 2.5 times greater under $E_\parallel$ irradiation than under $E_\perp$, yielding a PA value of 0.428. When taking the different NR orientations into consideration, a larger difference between the average scattering intensity values from $E_\parallel$ and $E_\perp$ illumination is observed for NR∥ than for NR⊥. Figure 3.5(c) presents the calculated PA values at each analyzer angle for the NR⊥. Figures 3.5(d) and 3.5(e) provide polar intensity plots of the average scattering intensities from the ZnO NR⊥ under $E_\parallel$ (red) and $E_\perp$ (blue) radiation. Similar to the behavior observed in NR∥, the polar plots show a dipole-like pattern with a tightly closed center for $E_\parallel$ excitation while the dipolar plot is slightly open at the center under $E_\perp$. 

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Figure 3.5. The NR-position dependent scattering signal from single ZnO NR⊥ under two incident light polarizations of E∥ and E⊥. The NR-position dependent scattering signals under the two excitation conditions of E∥ and E⊥ are collected over the entire length of the ZnO NR⊥ and plotted against the analyzer rotation. Red and blue symbols in all graphs are experimental data when the excitation polarizations of E∥ and E⊥ are used, respectively. Lines represent curves fits for the corresponding set of data. (a) The position dependent scattering signal averaged over the entire length of the NR⊥ is plotted as a function of the analyzer angle. The overall scattering intensity from the same NR was much lower when E⊥ was used as excitation instead of E∥ while keeping the same exposure time of 10 ms. (b) The average scattering intensity was normalized with respect to the highest intensity values measured at each excitation condition and graphed as a function of analyzer rotation. (c) Polarization anisotropy values calculated from the data shown in (b) follow a cos²θ dependence on the analyzer angle, θ. (d and e) Polar plots of average scattering intensities of the ZnO NR⊥ under (d) E∥ and (e) E⊥ excitation are displayed.
3.3.4 Further Look at the Scattering Behavior Distinctive to Each Light-Matter Pair of \((NR_{\parallel}, E_{\parallel}), (NR_{\perp}, E_{\perp}), (NR_{\parallel}, E_{\perp})\) and \((NR_{\perp}, E_{\parallel})\)

The most striking difference in scattering behaviors for the four cases shown in Figures 3.2 and 3.4 can be summarized as y- and x-axis oriented ZnO NRs give rise to continuous (relatively evenly distributed) and discontinuous (highly localized) scattering, respectively, when analyzed as a function of the position on the NR. As detailed above, scattering signal is observed only from the end(s) of NR\(_{\perp}\) regardless of the orientation of the incident polarized light and the analyzer rotation, whereas scattering signal from NR\(_{\parallel}\) is present continuously from all positions of the NR. If the incident light enters normal to the sample plane, the symmetry in measurement conditions between the NR long axis and polarization direction present in the set of \((NR_{\parallel}, E_{\parallel})\) and \((NR_{\perp}, E_{\perp})\) as well as in the set of \((NR_{\parallel}, E_{\perp})\) and \((NR_{\perp}, E_{\parallel})\) will yield identical scattering patterns for the two cases within the same set. The data summarized in Figures 3.2 and 3.4, displaying distinctively different scattering behaviors monitored from the four different cases, correspond to the glancing laser light entering with an incident angle \((\theta_{\text{inc}})\) of approximately 62°, as illustrated in Figure 3.1(ii).

Unlike the \(E_{\parallel}\) case whose polarization direction is within the plane of incidence and results in the projected component \((E^{*}_{\parallel})\) only along the y-axis of the sample plane, the projected component of \(E_{\perp}(E^{*}_{\perp})\) has elements on both the x- and y-axes. Since the two cases of the NR orientations, NR\(_{\parallel}\) and NR\(_{\perp}\) correspond to the NR oriented along y- and x-axis, respectively, light interaction with the NR in the \(E_{\perp}\) case should be considered using the main contribution from either \(E_{\perp,x}\) and \(E_{\perp,y}\) depending on the NR orientation. Hence, the scattering data set of \((NR_{\parallel}, E_{\parallel})\) and \((NR_{\perp}, E_{\perp})\) is obtained between the case involving a NR oriented along the y-axis interacting with \(E_{\parallel}\) whose projection onto the sample plane is also along the same axis and another case with a NR positioned along the x-axis leading to the interaction of \(E_{\perp,x}\) with the NR long axis, and \(E_{\perp,y}\) with the NR.
short axis. The scattering set of (NR\(\parallel\), E\(\parallel\)) and (NR\(\perp\), E\(\parallel\)) is acquired between the case of a NR oriented along the y-axis resulting in the interaction of E\(\perp\)\(_x\) with the NR short axis and E\(\perp\)\(_y\) with the NR long axis and another case of a NR positioned along the x-axis interacting with E\(\parallel\) whose projection component is only in the y-direction. The light-NR interaction nature for the four cases is categorized in Table 1.

Table 3.1. Incident light and NR interaction geometry for the four different cases of the NR orientation and polarization direction under this study.

<table>
<thead>
<tr>
<th>Varying Cases of NR orientation, Polarization direction</th>
<th>Light and NR Interaction Geometry (L: NR long axis, S: NR short axis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR(\parallel), E(\parallel)</td>
<td>L + E(\parallel)</td>
</tr>
<tr>
<td>NR(\perp), E(\perp)</td>
<td>L + E(\perp)(_x), S + E(\perp)(_y)</td>
</tr>
<tr>
<td>NR(\parallel), E(\perp)</td>
<td>S + E(\perp)(_x), L + E(\perp)(_y)</td>
</tr>
<tr>
<td>NR(\perp), E(\parallel)</td>
<td>S + E(\parallel)</td>
</tr>
</tbody>
</table>

The wavelength of the incident light is only several fold larger than the typical width of the NRs under examination. When considering both the light projection and NR orientation factors, the incident light geometry in some cases can only be effectively interacting with the short axis of the single NR. If this condition occurs, the ensuing scattering effects may be localized only at the NR ends through light coupling and guiding instead of yielding relatively even and continuous scattering throughout the entire length of the NR. The possible origin of this experimental observation for the NR oriented along the x-axis in Figure 3.4 may lie in this nature of light-NR interaction. For example, the interaction area between E\(\parallel\) and the NR\(\perp\) oriented along the x-direction will be limited to only along the NR width since E\(\parallel\) has no x-axis projection. The scattering behavior of the NR in this case may be dominated by the light coupling and waveguiding property of individual ZnO NRs. This well-known behavior of visible light guiding in ZnO NRs is categorized in Table 1.
with physical dimensions similar to the NRs in this study explains that the incident light is first coupled into the NR optical cavity, guided through the ZnO NR, and then finally couples out from the NR ends.

**3.3.5 Back-Aperture Imaging**

I subsequently examined the polarization-dependent spatial distributions of the scattering patterns from individual ZnO NRs by carrying out back-aperture imaging as shown in the schematics of Figure 3.6. Superpositioned plane waves, each defined by a unique wave vector in reciprocal space, radiate from ZnO NRs, and their directional and spatial scattering information can be accessed by back-aperture imaging. This is possible since the objective lens focuses these individual plane waves into different spots with unique spatial coordinates at the back focal plane of the lens. Hence, the back focal plane of the objective lens contains the spatial information on scattering directionality. Back-aperture imaging refers to acquiring Fourier transformed images of the scattering electric field distribution from the objective lens on the back focal plane, a plane perpendicular to the optical axis of the objective lens at its focal distance. For back-aperture imaging of the NRs, a set of optical elements containing a Fourier lens was used as displayed in the setup in Figure 3.1(iii). This setup enabled me to carry out the back-aperture imaging of the same NRs immediately after the forward scattering measurements, while collecting the signal only from the NR of interest with the use of an iris. To switch back and forth between forward scattering and back-aperture imaging modes, the removable lens which is the last lens between the iris and the detector is simply inserted into the imaging path to form a focused image on the detector for the forward DF scattering and removed to collimate the beam for the back-aperture imaging, as
indicated with the beam path in red and purple in Figure 3.1(iii), respectively. Similar to the forward scattering experiment, both directionality and intensity of the scattered radiation from individual NRs are probed with respect to the angle between analyzer and the transmission axis.

Specifically, back-aperture imaging for both NR\(\parallel\) and NR\(\perp\) under E\(\parallel\) and E\(\perp\) illumination was carried out at the analyzer setting from 0° to 170° for measurements at every 10°. The resulting scattering patterns at four representative analyzer angles of 0°, 30°, 60°, and 90° are presented in Figure 3.6 and categorized by the polarization direction of the incident E vector (E\(_{\text{dir}}\)), the analyzer angle (θ), and the orientation of the NR. For the ZnO NR\(\parallel\) in both the cases of E\(\parallel\) and E\(\perp\), the back-aperture images reveal that the scattering patterns appear as a strip of horizontal bands that are perpendicular to the NR orientation on the back focal plane. For the NR\(\parallel\), the scattering intensity is the strongest when the incident E field is parallel with the analyzer rotation at 0° for E\(\parallel\) and 90° for E\(\perp\), while the emission is weakest when the E field is perpendicular to the analyzer at 90° for E\(\parallel\) and 0° for E\(\perp\). This tendency agrees with the forward scattering intensity of ZnO NRs whose results were discussed earlier. For ZnO NR\(\perp\), a ripple-like scattering pattern is observed instead for both E\(\parallel\) and E\(\perp\) illumination. The rippled patterns are formed due to the interference patterns of the concentrically propagating waves originating from the two points that correspond to the two end scattering points of the NR\(\perp\). Although the intensity of the NR\(\perp\) back focal pattern is most pronounced when the incident E field is parallel with respect to the analyzer angle at 0° for E\(\parallel\) and at 90° for E\(\perp\), the intensity differences are not as noticeable as for the case of NR\(\parallel\). In the forward scattering measurements on NR\(\parallel\) described in Figures 3.2 and 3.3, the entire NR scatters light along the entire NR length. This position-independent presence of scattering signal results in the linear band-like pattern recorded on the back focal imaging plane.
Light response from NR⊥ in the forward scattering measurements is observed only at the two end facets of the NR as discussed in Figures 3.4 and 3.5, and the presence of its scattering signal is highly sensitive to the position on the NR. This effect is manifested into the ripple-like patterns on the back-aperture. Therefore, the back focal imaging results of ZnO NRs confirm the optical response observed in the forward scattering measurements.

| NR orientation | ZnO NR|| | ZnO NR⊥ |
|----------------|--------|--------|--------|
| E_dir Analyzer | E|| | E⊥ |
| 0 deg          | ![Image](image1.png) | ![Image](image2.png) |
| 30             | ![Image](image3.png) | ![Image](image4.png) |
| 60             | ![Image](image5.png) | ![Image](image6.png) |
| 90             | ![Image](image7.png) | ![Image](image8.png) |

**Figure 3.6.** Back-aperture images of scattered signal from ZnO NR|| and ZnO NR⊥ at representative analyzer angles under two incident light polarizations of E|| and E⊥. Back-aperture images of the scattering signal from ZnO NRs of different spatial orientations when varying the polarization direction of excitation as well as the analyzer angle. To collect the set of back-aperture images, the excitation direction of E|| and E⊥ were used at representative collection angles of 0°, 30°, 60°, and 90°. ZnO NR|| exhibited a linear radiation pattern rotated 90° from the physical orientation of the NR in the measurement plane. ZnO NR⊥ displayed ripple-like radiation patterns emanating from two focal points (the two scattering ends of the NR⊥), that mimic interference patterns seen from radially propagating waves from two different centers.
The polarization-dependent scattering response resolved in this study can provide insight into the optical signal expected from individual ZnO NRs depending on their orientation in the measurement plane. Highly increased signal confined in the NR termini has been previously reported in near band edge (NBE) photoluminescence and biomolecular fluorescence of ZnO NRs, although the effect of polarization-, orientation-, and position-dependence of the NRs was not systematically evaluated. When unpolarized light was used as an excitation source to probe NBE emission from ZnO NRs, the two NR ends exhibited stronger photoluminescence intensity when compared to the NR body. In addition, an interesting phenomenon of fluorescence intensification on ZnO NR ends was reported in recent studies involving fluorophore-coupled biomolecules on individual ZnO NRs. The outcomes of this study demonstrate that a similar, highly spatially localized scattering can be achieved by controlling the NR orientation with respect to the direction of light polarization. Therefore, the results from this study suggest that even richer and novel optical behaviors can be identified when scattering, photoluminescence, and fluorescence/Raman emission of individual nanomaterials are further examined with well-characterized light polarization and nanomaterial orientation. The efforts presented in this chapter, signifying a systematic scattering investigation of the non-trivial case of glancing incident light with controlled polarization, may be highly valuable in interpreting and predicting characteristic optical responses collected from individual NRs of specific orientations. Coupled with the capability of discerning scattering intensity along the position of the NR as well as elucidating the spatial distribution characteristics of the scattered light, these endeavors may be extremely beneficial to the optimal design of optical devices with improved sensitivity and advantageous to the accurate interpretation of the collected optical signal based on the light polarization direction and NR orientation.
3.4 Conclusion

In conclusion, I have performed forward scattering measurements of single ZnO NRs in a dark-field configuration and elucidated their characteristic, polarization-resolved optical response under well-controlled experimental parameters such as incident light polarization, NR orientation, and analyzer rotation. I have also carried out back-aperture imaging of the same individual ZnO NRs and systematically examined the spatial radiation directivity of the scattering signal and quantitatively catalogued the effect of light polarization, NR orientation, and position along the NR on both the intensity of the resulting scattering signal as well as the corresponding spatial distribution pattern of ZnO NR scattering. Since fundamental light interaction behavior of NRs will significantly affect their functional outcomes in photonics, optoelectronics, and sensor devices, the endeavors presented in this paper will not only provide much needed insight into the unique optical properties of individual 1D ZnO nanomaterials in light-matter interaction but also signify an important step forward to developing next-generation optoelectronic systems and optical biodetectors with improved device efficiency and sensitivity.
Chapter 4

Scattering Attributes of One-Dimensional Semiconducting Oxide Nanomaterials Individually Probed for Varying Light-Matter Interaction Angles

4.1 Background and Introduction

One-dimensional nanomaterials based on semiconducting oxides have demonstrated their unique and useful properties in numerous applications of photonics,\textsuperscript{108-111} electronics,\textsuperscript{112-115} optoelectronics,\textsuperscript{116,117} photovoltaics,\textsuperscript{118-122} and chemical/biological sensing.\textsuperscript{123-131} In many of these technologically important applications, the fundamental optical properties of one-dimensional semiconducting oxide nanomaterials govern their functional outcomes. Light can produce various optical and optoelectronic responses from the materials such as absorption, reflection, bandgap emission, and scattering and, therefore, light-matter interaction can be engineered to produce desirable optical properties such as spontaneous and stimulated emission,\textsuperscript{108,132-136} waveguiding,\textsuperscript{108-110} and evanescence field enhancement.\textsuperscript{111,137-139} Such examples can be seen in the research efforts previously reported for the development of semiconducting oxide nanomaterials for applications in nanoscale lasers,\textsuperscript{132,133,136} subwavelength waveguides,\textsuperscript{108-110,140,141} and biodetection platforms.\textsuperscript{124,125,127,130,131,140,142} The widely applied optical applications of these nanomaterials underscore the importance of an improved understanding of the fundamental light interaction with the semiconducting oxide nanomaterials.

Specifically, semiconducting oxide, also known as semiconducting oxide (SCO), nanomaterials of zinc oxide (ZnO), tin oxide (SnO\textsubscript{2}), indium tin oxide (ITO), and zinc tin oxide (ZTO) have been widely utilized as optical, electrical, and biological signal transduction elements
These past applications have primarily exploited the optical properties of bulk materials or ensembles of nanomaterials. With the ever-growing demand for device and sensor miniaturization, novel constructs with highly reduced dimensions have also been explored recently in the aforementioned applications. Therefore, elucidating the exact light interaction profiles with individual nanostructures can provide much needed insight and further benefit the burgeoning efforts in single optical, optoelectronic, and biosensing devices.

In this study, dark-field (DF) experiments in a forward scattering geometry was carried out to investigate the fundamental optical response of individual semiconducting nanomaterials by systematically controlling the interaction angle between the direction of an incident light oscillation and the main crystal axis of a nanomaterial. One-dimensional nanomaterials, specifically nanorod (NR) types of ZnO, SnO₂, ITO, and ZTO are examined for their interaction angle-dependent, elastic scattering profiles in a cross polarizer setting. I determined the characteristic, interaction angle-dependent scattering response from each position along the main axis of the semiconducting oxide NRs while controlling the NR orientation, incident light polarization, and analyzer rotation. These endeavors signify the first systematic investigation of forward light scattering in a DF mode, examining various individual semiconducting oxide NRs in order to determine the precise effect of the effective angle of the light-matter interaction. The angle of light-matter interaction is controlled in the experiments by varying the NR tilt angle on the sample plane as well as the direction of the incident light electric field in and out of the plane of incidence. The findings reported in this chapter demonstrate strikingly different scattering responses depending on the NR tilt angle and the polarization direction of the incident light. The
knowledge gained from this study can be used to better understand the fundamental optical responses of the technologically useful nanomaterials and, alternatively, to yield desirable spatial distributions of the optical signals from single nanomaterials. Insight from these research efforts may be also beneficial to the analysis of scattering and emission signal acquired from highly miniaturized, photonic and bio-optical devices utilizing the spatially controlled, optical responses of the one-dimensional semiconducting oxide nanomaterials.

4.2 Experimental Methods

The experimental approach employs a home-built series of optical components in addition to a commercially available optical microscope of Olympus BX51F whose setup is configured in a DF mode to optimally collect the inherently weak scattering signals from individual nanomaterials. The DF setup involves two scattering geometries, one with a forward scattering configuration and the other with a reflected scattering configuration. The forward DF (FDF) measurement layout, whose overall instrumental components are shown in Figure 4.1(a), ensures that the measured signal comes only from the NR under investigation by eliminating the source light from the collection optics via total internal reflection (TIR). It also enables facile detection of hard-to-observe signals inherent to the use of a single nanomaterial instead of ensembles, while providing a sufficient imaging resolution for evaluating the scattering intensities along different positions on an individual nanomaterial. In addition to the FDF illumination/collection pathway with precise control over the exact incident light polarization, the setup is also equipped with a reflected DF (RDF) scattering measurement pathway. This detection mode involves a wide-field,
unpolarized illumination above the sample plane and subsequent collection of the scattering signal in the backward direction towards a DF objective lens.

**Figure 4.1. Schematic of the forward dark field optical measurement setup with NR tilt angle (NR₀) and incident light (E₀) geometry.** (a) The overall schematics of the FDF measurement setup are shown. (b) A detailed view of the refractive index-matching NR sample assembly is displayed. (c) The schematic representations illustrate the key light-matter interaction parameters including the tilt angle of a NR (θ) in the sample plane (x-y) and the polarization direction of the incident light (E₀) with respect to the plane of incidence (y-z). E* marks the projected components of E onto the sample plane. The wavevector of the incoming laser is indicated as \( \vec{k} \). (d) Two example configurations of the light-matter interaction are shown to depict different θ scenarios under the same incident polarization of E₀ = 0°. The incident angle of the laser entering the sample plane, noted as θ_{inc} in the diagram, is 62° in the experimental setup.

Single crystalline NRs of ZnO, SnO₂, ITO and ZTO were synthesized by using a home-built chemical vapor deposition (CVD) method as reported earlier.¹²₂,¹²₄,¹₂₅,¹₂₇,¹₄₅,¹₄₆
morphology, and crystal structure of the as-grown nanomaterials were reported previously along with their scanning electron microscopy (SEM) and X-ray diffraction (XRD) data.\textsuperscript{122,124,125,127} The typical diameters and lengths of the NRs employed in the measurements range from 150 to 300 nm and from 5 µm to 30 µm, respectively. To carry out the single NR measurements effectively, as-grown NR samples were first dispersed in ethanol via sonication from their growth substrate and deposited on a clean glass slide by drop casting. Then a small drop of glycerol (refractive index of 1.4729) was placed on the NRs on the glass slide before lowering a cover slip onto the assembly whose layers are depicted in detail in Figure 4.1(b).

In the FDF measurements, a linearly polarized 642 nm laser (Spectra Physics Excelsior-PS-DD-CDRH) entered the NR plane via an oil-immersion DF condenser (Numerical Aperture, NA = 1.2–1.4) from below the sample stage after passing through a half-lambda (HL) wave plate. The laser was subsequently focused onto individual NRs of investigation. The HL plate controlled the incident direction of the linearly polarized laser, $E_\theta$ in Figure 4.1(c), to be between $0^\circ$ and $90^\circ$. For the polarization case referred to as $E_\parallel$ (and $E_\perp$), $E_\theta$ is $0^\circ$ (and $90^\circ$) and the polarized light direction is within (and perpendicular to) the plane of incidence. For an illumination case with an arbitrary angle of $E_\theta$, the incident polarization lies in a plane angled between $E_\parallel$ and $E_\perp$. The intersecting axis between the plane of incidence (the y-z plane) and the sample plane (the x-y plane) is further defined as y. The angle formed between the NR main axis and the y-axis is then referred to as the NR tilt angle of $\theta$. Two cases of the light-matter interaction configurations involving a NR with $\theta$ of $0^\circ$ and of an arbitrary value are displayed in Figure 4.1(d) along with the projected components ($E^*_\parallel$ and $E^*_\perp$) of the incoming polarization field. NR scattering signals were collected with a 40x plan apochromatic objective lens (Olympus PlanSApo, NA = 0.90). An
analyzer was placed between the microscope tube lens and the charge-coupled-device detector (QImaging Exi Blue CCD camera, Surrey, Canada). Unpolarized white light (a 100 W, 12 V halogen lamp) was also used to examine the scattering behavior of the semiconducting oxide NRs in a RDF mode. The wide field illumination and collection of the NR signals were carried out with 20x (Olympus MPlanFL N, NA = 0.45) and 50x (Olympus MPlanFL N, NA = 0.80) DF objective lenses. I have systematically examined the FDF and RDF scattering profiles of at least 30 NRs for each type of the nanomaterials. From these comprehensive measurements, I consistently observed a set of characteristic scattering behaviors that are nanomaterial-independent, but NR tilt angle- and incident polarization direction-dependent. Herein, this chapter present, in detail these material-indiscriminate, \( \theta \)- and \( E_\theta \)-contingent scattering responses from the semiconducting oxide NRs.

### 4.3 Results and Discussion

Figures 4.2 and 4.3 present the typical \( \theta \)-dependent scattering profiles evaluated spatially along single NRs as a function of the analyzer rotation. The representative NR scattering data are displayed in the increasing order of \( \theta \) in Figures 4.2 and 4.3, including two arbitrary NR tilt angle cases. Figures 4.2(a,b) and Figures 4.2(c,d) summarize the characteristic NR scattering behaviors determined from the NRs of \( \theta = 0^\circ \) and 25\(^\circ \), respectively. Similarly, Figures 4.3(a,b) and Figures 4.3(c,d) are acquired from those NR cases of \( \theta = 55^\circ \) and 80\(^\circ \), respectively. The particular scattering data sets shown in Figures 4.2 and 4.3 are from an ITO NR (4.2a, 4.2b), a ZTO NR (4.2c, 4.2d), a SnO\(_2\) NR (4.3a, 4.3b), and a ZnO NR (4.3c, 4.3d). Although these selective data sets are chosen to present the results encompassing all four types of semiconducting oxide NRs, the
specific scattering characteristics that will be discussed in depth below can be applied to predict and describe the scattering behavior from any of the four nanomaterial types so long as they exhibit a comparable NR tilt angle.

Panels (a, c) of Figures 4.2 and 4.3 are the scattering patterns obtained with a wide-field, unpolarized illumination under the RDF configuration. On the other hand, panels (b, d) in Figures 4.2 and 4.3 summarize the FDF NR scattering results examined under the precisely controlled polarized light. The grey panels in both the RDF and FDF data correspond to the scattering images of each NR. The colored panels of 3-dimensional (3D) contour and 2D surface plots included in the FDF data set show the NR scattering intensities analyzed as a function of the position along the NR as well as the analyzer rotation. Due to the measurement symmetry, the range of the analyzer rotation shown in the plots is from 0° to 90°. The incident polarization was kept the same as $E_\parallel$ for all FDF results shown in Figures 4.2 and 4.3 in order to pinpoint the distinct scattering behaviors from the individual semiconducting oxide NRs that are solely influenced by $\theta$. 
Figure 4.2. Optical images and spatial scattering profiles of the semiconducting NRs at NRθ=0°, 25°. Typical scattering profiles of the semiconducting NRs, categorized by the NR tilt angle of θ, are presented in the representative data sets of RDF and FDF. (a) The RDF scattering image is obtained from a θ = 0° ITO NR probed by using an unpolarized incident light. (b) The 3D contour and 2D surface profiles show the scattering intensity distributions analyzed along the NR displayed in (a) as a function of the analyzer angle. FDF scattering images measured with the 642 nm incident light of E∥ are also shown in two grey panels which correspond to the NR signal collected when the analyzer rotation is at 0 and 90°, respectively. (c) The RDF scattering pattern is from a θ = 25° ZTO NR. (d) The colored and grey panels display the typical scattering intensity profiles and images along the NR shown in (c) as a function of the analyzer rotation probed with the E∥ polarized light.
Figure 4.3. Optical images and spatial scattering profiles of the semiconducting NRs at $\theta = 55^\circ$, $80^\circ$. Typical scattering profiles of the semiconducting NRs, categorized by the NR tilt angle of $\theta$, are presented in the two additional RDF and FDF data sets. (a) The RDF image is the scattering result from a $\theta = 55^\circ$ SnO$_2$ NR. (b) The colored and grey panels display the FDF scattering intensity distributions along the length of the NR shown in (a) as a function of the analyzer rotation. (c) The RDF scattering image is taken from a $\theta = 80^\circ$ ZnO NR. (d) The FDF scattering data for the same NR presented in (c) reveal the scattering properties profiled along the NR length with respect to varying analyzer angles.
When illuminated with the unpolarized light in the RDF setup, the scattering signal is present continuously along all positions of the NRs in all \( \theta \) cases. In contrast to this uniform scattering response from the unpolarized light, the same NRs under the polarization controlled light exhibit highly \( \theta \)-correlated scattering profiles along the length which I categorize as continuous, intermittent, or discontinuous patterns. For NRs of \( \theta = 0^\circ \), the FDF scattering response is similar to that of RDF and characterized as continuously present on all positions along the NR length. An example NR case is displayed in the 3D and 2D panels of Figure 4.2(b). As expected from the cross-polarizer setting, the overall intensity of the signal is observed to be the highest (or lowest) when the analyzer rotation is parallel (or perpendicular) to the incoming polarization of \( E_\parallel \), regardless of the position on the NR. Typical scattering behaviors from NRs with \( \theta = 25^\circ \) are shown in Figure 4.2(d). Overall, the FDF scattering response is continuous along the NR whose scattering intensity is maintained above 75% of the highest signal measured on all areas of the NR. For NRs with even a larger \( \theta \) value of 55° as displayed in Figure 4.3(b), the scattering signal alters significantly from the continuous patterns and reveals an intermittent pattern along the length of the NR with alternating peaks and valleys. In this case, the intensities on the same NR fluctuate from high to low along the NR length in which at least 50% weaker signal is measured from the valleys relative to the peak points. This effect is clearly seen from the grey panel in Figure 4.3(b) taken at the analyzer rotation of 0°. The FDF image exhibits alternating bright and dark spots along the NR. For NRs with a much higher \( \theta \) value of 80°, the FDF scattering responses turn out to be highly localized and exclusively present on the two ends of the NRs, yielding a distinctively discontinuous scattering pattern as demonstrated in Figure 4.3(d). All FDF scattering intensities are from the NR end positions only, with no signal present on the NR main body. Both the NR
cases of $\theta > 45^\circ$ in Figure 4.3, the scattering results obtained under the RDF and FDF settings are strikingly different from each other.

Figure 4.4. Summary of the $\theta$-dependent scattering profiles from four types of semiconducting NRs and $E_\theta$-dependent scattering profile. (a) The $\theta$-dependent scattering profiles are examined on the four types of semiconducting NRs in order to find the NR tilt angle associated with the transition from the continuous to discontinuous scattering. NRs exhibiting continuous and discontinuous responses along the NR length are denoted as solid and open symbols, respectively. The numerical values marked around the circumference of the semicircle denote $\theta$ in degrees. (b) $E_\theta$-dependent scattering behavior is shown for the three cases of $E_\theta = 0^\circ$, $45^\circ$, and $90^\circ$ by plotting the normalized scattering intensity distributions at different positions along the same ZnO NR with a tilt angle of $10^\circ$ while changing the analyzer rotation.
These material-independent but NR tilt angle-dependent continuous to discontinuous scattering behaviors from the individual semiconducting oxides are further substantiated in the data provided in Figure 4.4(a). For each type of the four nanomaterials, the above mentioned scattering patterns examined as a function of $\theta$ are categorized as continuous (higher than 75% of the maximum intensity maintained on all positions) and discontinuous (either abruptly alternating or discretely present bright/dark spots) groups. The solid blue and open red symbol indicate the $\theta$ value of the NR determined to have a continuous and discontinuous scattering profile, respectively. When collectively evaluating all nanomaterial data in Figure 4.4(a), the continuous to discontinuous scattering transition is noted at the $\theta$ value of 45° and, additionally due to the geometrical symmetry of the NR, at 135°. From these experimental observations, it is determined that NRs exhibit spatially continuous scattering for $0^\circ \leq \theta \leq 45^\circ$ and $135^\circ \leq \theta \leq 180^\circ$, whereas NRs with $45^\circ < \theta < 135^\circ$ yield discontinuous scattering patterns.

The data indicate that the continuous and discontinuous FDF scattering behaviors are governed by the light-matter interaction geometry. In the FDF experimental setup, the light is aligned onto a single point of the ring-like light pathway of the DF condenser lens and enters the sample plane with the wavevector of $\vec{k}$ as indicated in Figure 4.1(c), rather than passing through the entire lens. Therefore, when a NR tilt angle is parallel (and perpendicular) to the incident polarization direction as depicted in the top (bottom) panel of Figure 4.1(d), the NR long axis lying in (and out of) the plane of incidence is under propagating (and standing) electromagnetic field of the incoming light. In the former case, the propagating light interacting with the many micrometer-long NR lying in the plane of incidence will produce a continuous scattering signal. On the other hand, the latter case will yield a scenario in which only a small portion of the NR directly interacts
with the light along the NR width. Since the NR has a width much narrower than the wavelength of the light, it will interact with less than one-wavelength of light in a standing wave condition as displayed in the bottom panel of Figure 4.1(d). This effectively sets up a condition of an isolated illumination to a limited portion of the NR where the number of multiple point sources along the NR long axis will depend on \( \theta \). When \( \theta \) is 90°, the number of point source that can exist along the NR length will be the largest, which will lead to two bright signal peaks analogous to the interference wave patterns expected from a linear array of multiple point sources. When angle is 90, I'm under the impression that the incident wave and the rod axis are completely perpendicular therefore have less points of intersection compared to that of an angled rod. Unless the condition is describing multiple wavevectors simultaneously being shot at 90° rod which would result in most points of interaction with the rod. When a NR is at an arbitrary angle of \( \theta \), the interplay between the projected E-field components onto the sample plane, \( E_{\parallel}^* \) and \( E_{\perp}^* \), will determine the dominance of the continuous and discontinuous scattering nature in the resulting signal. When \( \theta \) becomes greater than 45°, the dominant \( E_{\perp}^* \) component turns the NR scattering from continuous to discontinuous response under which the effective illumination is similar to the \( \theta = 90° \) circumstance but with a decreased number of point sources. In this case, additional scattering peaks of lower intensity will exist in between the bright end signals, leading to the intermittent scattering pattern displayed in Figure 4.3(c). It can also be expected that, depending on the proximity of \( \vec{k} \) with the non-normal incident angle to each end of the NR, the scattering intensities measured at the two NR ends or along the NR length will not be identical to each other or perfectly symmetric along the NR. Indeed, this is evidenced from the majority of the data whether they are of a continuous or discontinuous nature. In contrast, the RDF measurement
layout with the wide field, unpolarized illumination setting will be equivalent to a combination of all illumination scenarios mentioned above for the different $\theta$ cases in FDF. Therefore, continuous RDF scattering patterns are expected to be uniformly observed from all NRs regardless of $\theta$, as experimentally evidenced by the RDF results as discussed before.

Additionally, NR scattering responses are examined with respect to the different polarization direction of the incident light, $E_\theta$, and the results are shown in Figure 4.4(b). All three plots of $E_\theta$ equal to 0°, 45°, and 90° display the normalized scattering intensity distributions at different positions along the same ZnO NR with $\theta = 10^\circ$ plotted as a function of the analyzer rotation. Despite the change in $E_\theta$, the $\theta = 10^\circ$ NR exhibits a continuous scattering profile along its length. Therefore, $E_\theta$ does not seem to affect the $\theta$-contingent, either continuous, intermittent, or discontinuous signals yielded from the NR scattering pattern. However, regardless of the position on the NR, the maximum scattering intensity is observed when the analyzer rotation is the same as $E_\theta$ for the three cases shown in Figure 4.4(b). Hence, altering $E_\theta$ shifts the scattering intensity to peak at the analyzer rotation parallel to the $E_\theta$ of the incoming light.

4.4 Conclusion

In conclusion, I have systematically examined the light-interaction characteristics of individual ZnO, ITO, SnO$_2$, and ZTO NRs spatially along the NR length, while precisely controlling the NR tilt angle, polarization direction of the incident light, and analyzer rotation. Subsequently, distinctive and interesting scattering properties that are material-independent but NR tilt angle- and polarization direction-dependent are revealed from these semiconducting oxide NRs. Subsequently, it is determined that the effective angle of the light-matter interaction
significantly alters the resulting scattering signal distribution along the NR main axis, resulting in illumination-specific scattering patterns ranging from continuously present, to intermittently distributed, to NR ends-localized signal. These findings will be critical in specifically tuning the light-matter interaction outcomes of these semiconducting nanomaterials, especially when single nanomaterials are employed as functional device elements based on their optical properties. Furthermore, the efforts presented in this report will be highly valuable for accurately interpreting the light signal from individual NRs in many optical and bio-optical devices employing the useful semiconducting oxides. At the same time, the experimental evidences show that the spatial distribution of optical outputs from single nanomaterials in such existing devices should be interpreted with caution based on the specific light-matter interaction angle of the system.
Chapter 5

Evaluation of Polarization Rotation in the Scattering Responses from Individual Semiconducting Oxide Nanorods

5.1 Background and Introduction

Effective manipulation of optical and electro-optical signal is critical to the successful operations of optical modulators, switches, interconnects, and photodetectors in integrated photonic circuits and optoelectronic devices.\textsuperscript{148–153} In this regard, optical anisotropy of semiconductor materials has drawn considerable research interest, particularly focusing on the manipulation of polarization rotation and phase retardation of linearly polarized light.\textsuperscript{151–153} As a part of these efforts, important aspects such as device size reduction and working wavelength range are actively pursued for further improvements in advanced optical and photonic devices. Recent progresses to precisely tailor the geometry and composition of materials at nanometer length scales have continued to push miniaturization of optical components,\textsuperscript{154–156} down to the ultra-compact regime of exploiting individual nanomaterials as functional optical elements instead of their ensembles. However, only limited numbers of experimental work are available in the literature attempting to provide insight into the precise nature of light interaction with individual nanomaterials.\textsuperscript{157–162} Yet, such an understanding is imperative to tune single nanomaterial devices with desired optical functionality. As for the working wavelength range, many previous research efforts have successfully demonstrated manipulations of infrared (IR) light and operations at telecommunication wavelength ranges.\textsuperscript{148–153} However, parallel efforts are still highly warranted for the development of visible and ultraviolet light counterparts, whose modulation can be particularly useful in bio-optical imaging and sensing.\textsuperscript{163–166}
In this chapter, I evaluate the light-matter interactions of technologically important semiconducting oxide nanorods (NRs) at the single nanomaterial level, while controlling key light-matter interaction parameters such as the wavelength and polarization direction of light, the NR tilt angle, and the analyzer angle. Pure and chemically doped NRs with comparable physical dimensions are systematically characterized for their material-dependent elastic scattering responses upon interactions with visible light. Specifically, single NRs of ZnO as well as indium tin oxide (ITO) and zinc tin oxide (ZTO) are chosen due to their well-known functional benefits as lasers,\textsuperscript{167,168} light emitters,\textsuperscript{169-172} waveguides,\textsuperscript{173-177} photovoltaics,\textsuperscript{178} and biosensors.\textsuperscript{179,180} I subsequently elucidate an intriguing scattering response of rotation in the polarization direction of the scattered light from individual NRs and further identify that polarization rotation of the scattered light is material-dependent, seen only from the pure structures of ZnO NRs but not from the doped materials of ITO and ZTO NRs. I also ascertain that the polarization rotation effect of the ZnO NR-scattered light is influenced by the NR tilt angle, and the phenomenon occurs irrespective of the wavelength and incident polarization direction of the visible light. These efforts reported here provide much needed insight into the material-dependent, visible light-matter interaction behaviors of individual semiconducting oxide nanomaterials and further offer fundamental bases to modulate scattered light in single ZnO NR devices by exploiting different material types and effective angles of the light-matter interaction.

5.2 Experimental Methods

Individual NR samples of ZnO, ITO and ZTO were synthesized by using a home-built chemical vapor deposition (CVD) reactor as reported earlier.\textsuperscript{171,181-184} The sizes, morphologies,
and crystal structures of the as-grown nanomaterials were also reported previously along with their scanning electron microscopy (SEM) and X-ray diffraction (XRD) data.\textsuperscript{171,182-184} The typical diameters and lengths of the NRs employed in the measurements range from 150 to 300 nm and from 5 μm to 30 μm, respectively. A home-built series of optical components were configured in a dark-field (DF) mode on a commercially available optical microscope of Olympus BX51F in order to optimally collect the inherently weak and hard-to-detect scattering signals from individual nanomaterials. The measurement arrangement involved two scattering geometries, one with a forward DF scattering (FDF) and the other with a reflected DF scattering (RDF) configuration. In the FDF measurements shown in Figure 5.1(a), a linearly polarized diode laser with either $\lambda = 488$ nm or 642 nm (Spectra Physics Excelsior-PS-DD-CDRH) entered the NR plane via an oil-immersion DF condenser (Numerical Aperture, NA = 1.2 $\sim$ 1.4) from below the sample stage after passing through a half-lambda (HL) wave plate. The HL plate controlled the incident direction of the linearly polarized laser whose oscillation is referred to as $\mathbf{E}_\parallel$ (and $\mathbf{E}_\perp$ when the polarization direction is within (and perpendicular to) the plane of incidence, as illustrated in Figure 5.1(b). Figure 5.1(b) also displays the NR tilt angle of $\theta$ formed by the NR main axis and the y-axis, where the y-axis refers to the intersecting axis between the plane of incidence (y-z) and the sample plane (x-y). Scattering signals from individual NRs were collected with a 40x plan apochromatic objective lens (Olympus PlanSApo, NA = 0.90). An analyzer was placed between the microscope tube lens and the charge-coupled-device detector (QImaging Exi Blue CCD camera, Surrey, Canada). The RDF mode involved wide-field, unpolarized illumination (a 100 W, 12 V halogen lamp) above the sample plane and subsequent collection of the scattering signal in the backward direction towards a DF objective lens. The RDF signals were subsequently measured with 20x
(Olympus MPlanFL N, NA = 0.45) and 50x (Olympus MPlanFL N, NA = 0.80) DF objective lenses. The NR samples were prepared for the FDF and RDF investigation using a refractive index-matching assembly method described elsewhere.\textsuperscript{160,161} I have measured and analyzed the elastic scattering responses from a large number of ZnO, ITO and ZTO NRs, over 100 NRs in total. Herein, I report the material-governed, optical phenomenon pertaining to the presence and absence of the polarization rotation in the NR scattered light. The elastic scattering data reported herein are collected at the same wavelength as that of the incident light and, hence, they are not from bandgap photoluminescence or inelastic Raman scattering.
5.3 Results and Discussion

Representative scattering data obtained from individual ZnO NRs are shown in Figures 5.2 and 5.3, specifically by presenting the FDF and RDF scattering characteristics measured from a
10.15 μm-long ZnO NR with the tilt angle of 70°. The 3-dimensional (3D) contour plots simultaneously chart the scattering intensity, the position along the NR long axis, and the analyzer angle under the different incident light settings controlled by the wavelength and the polarization direction of the incoming laser. As reported earlier, the scattering response from individual NRs can either be continuous or discontinuous, depending on the NR tilt angle. With the θ of 70°, the FDF scattering patterns from the ZnO NR are expected to be discontinuous, as shown in Figure 5.2, due to the dominant component of \( E_\perp \) projected onto the sample plane, mimicking the highly localized scattering signal discretely monitored only at the two NR ends at high θ angles approaching 90°.

Furthermore, careful examination of the ZnO NR scattering profiles in the 3D contour plots in Figure 5.2 clearly reveal additional asymmetry that has never been elucidated before. Asymmetric scattering characteristics are identified not only for the scattering intensity at different positions along the NR length but also in terms of the analyzer angles corresponding to the maximum and minimum scattering intensity at each NR end. The novel observation implies that the scattered light from the ZnO NR goes through a polarization rotation effect, and the electric field oscillation changes from one to the other end of the ZnO NR, as schematically illustrated in the right panel in Figure 5.1(c). This rotation of ZnO NR-scattered light occurs irrespective of the wavelength and the polarization direction of the incident light, as evidenced by the data presented in Figures 5.2(a)- 5.2(d). However, it should be noted that the rotation effect of the polarized scattered light seen from individual ZnO NR scattering is influenced by the NR tilt angle and that no measurable rotation of the polarized scattered light from the ZnO NRs of \( \theta = 0° \) is observed, regardless of the incident polarization. Additionally, in general, the angle shift in the polarization...
oscillation of the scattered light becomes larger as the NR tilt angle of $\theta$ increases. And the polarization rotation effect in the scattered light occurs more pronouncedly on the ZnO NRs of the intermittent and discrete scattering nature$^{162}$ relative to the continuous type.
Figure 5.2. The 3D contour plots of forward dark field scattering signals from ZnO NR under 488 and 642 nm laser illuminations of $E_{\parallel}$ and $E_{\perp}$ polarizations with FDF images of NR ends “blinking” showing polarization rotation on NR ends. FDF and RDF scattering signals from a 10.15 μm-long ZnO NR oriented at $\theta = 70^\circ$ are profiled. (a-d) The 3D contour plots show the representative NR scattering responses characterized by using different combinations of incident wavelengths and polarization directions which are (a) 488 nm, $E_{\parallel}$, (b) 488 nm, $E_{\perp}$, (c) 642 nm, $E_{\parallel}$, and (d) 642 nm, $E_{\perp}$. The scattering intensity for each case is graphed as a function of the analyzer angle and the position along the ZnO NR. (e) The snapshot series of the FDF patterns display the typical scattering images taken from the ZnO NR for the specified experimental parameters of $\lambda$, E, and the analyzer angle. In addition, the RDF scattering image taken with the wide-field illumination of unpolarized light is provided in the last row.
A series of images in Figure 5.2(e) substantiates the polarization rotation effect in the scattered light monitored from the ZnO NR. The FDF scattering snapshots for the $\theta = 70^\circ$ ZnO NR unambiguously show the switching of the bright ends at different analyzer angles. For example, for the incident light setting of 488 nm and $E_\parallel$, the left end of the ZnO NR scatters the strongest when the analyzer rotation is parallel to $E_\parallel$. When the analyzer angle gradually increases, the left end of the NR scatters more weakly, while the scattering from the right NR end becomes stronger. When the analyzer angle is perpendicular to $E_\parallel$, scattering from the left NR end significantly diminishes and that of the right end becomes intense instead. Similar trends are identified in all FDF scattering snapshots shown in Figure 5.2(e). As a comparison, the RDF scattering image of the same ZnO NR is shown in the last row of Figure 5.2(e). As this RDF measurement is carried out with wide-field illumination of unpolarized light, scattering intensities along the NR long axis show a continuous pattern, unlike the discontinuous FDF scattering configurations.
Figure 5.3. The 2D surface plots of the forward dark field scattering from ZnO NR under 488 and 642 nm laser illuminations of $E_\parallel$ and $E_\perp$ polarizations showing polarization rotation at different analyzer angles. The 2D surface plots of the FDF scattering from the ZnO NR (10.15 μm-long with $\theta$ of 70°) clearly display the optical rotation phenomenon in the polarization of the scattered light revealed by varying the analyzer angle, whose oscillation rotates from one end to the other end of the ZnO NR. The incident light setting used for each measurement is (a) 488 nm, $E_\parallel$, (b) 488 nm, $E_\perp$, (c) 642 nm, $E_\parallel$, and (d) 642 nm, $E_\perp$. As a guide to the eye, the scattering maximum (and minimum) angle on each end of the NR is indicated with white (and black) arrows.

The set of 2D surface plots in Figure 5.3 is the FDF scattering responses from the ZnO NR, clearly revealing the polarization rotation effect of the scattered light. The data were gathered at different analyzer angles for each incident light setting specified. The extent of optical rotation can
be estimated by the analyzer angles corresponding to the scattering maximum/minimum at each end of the ZnO NR. As a guide to the eye, those analyzer rotations are marked with white and black arrows to indicate the scattering maximum and minimum, respectively. The degree to which the analyzer angle yielding the scattering maximum (or minimum) shifts from one to the other end of the ZnO NR is close to 90° for λ = 488 nm while that for the case of λ = 642 nm is approximately 10-25°. Therefore, the data indicate that the phase shift in the ZnO NR-triggered polarization rotation is expected to be higher for a light-matter interaction probed with a shorter wavelength of light. The observed rotation of the polarization from one end to the other end of the ZnO NR may be related to the doubly refracting nature of ZnO. The high birefringency of ZnO exhibits a difference of approximately 0.018 between the ordinary and the extraordinary refractive indices at the visible wavelength range.\textsuperscript{185,186} The ZnO NRs used in the experiments are grown exhibiting high crystallinity and chemical purity which was evidenced by the diffraction and photoluminescence spectra of the pristine crystals.\textsuperscript{165,166,187} Therefore, individual ZnO NR crystals may produce a birefringence-originated phase difference which is known to be inversely proportional to the wavelength of the light.\textsuperscript{163,188}
Figure 5.4. The 2D surface plots of the forward dark field scattering from ITO and ZTO NRs under 488 and 642 nm laser illuminations of E∥ and E⊥ polarizations. Typical FDF scattering profiles of ITO and ZTO NRs of similar tilt angles as the ZnO NR shown previously are presented. In all cases, no rotation in the polarization direction of the scattered light is observed. (a) The scattering intensities from an individual ITO NR (11.3 μm in length, θ = 70°) are graphed as a function of the analyzer angle and the position along the NR in the 3D contour plots for the incident light of (i) 488 nm, E∥, (ii) 488 nm, E⊥, (iii) 642 nm, E∥, and (iv) 642 nm, E⊥. (b) The scattering intensities from a ZTO NR (12.41 μm in length, θ = 75°) are displayed as a function of the analyzer angle and the position along the NR under the incident light of (i) 642 nm, E∥, and (ii) 642 nm, E⊥.
I further examined other related nanomaterials for their scattering behaviors at the individual NR level and assessed whether a comparable polarization rotation effect is also present in doped variants of semiconducting oxide NRs. The typical FDF scattering plots from a single ITO and ZTO NR with comparable physical dimensions and light-matter interaction angles to those of the previously discussed ZnO NR cases are displayed in Figures 5.4(a) and 5.4(b), respectively. In all circumstances of the visible wavelength and incident polarization, the resulting scattering patterns at each end of the ITO and ZTO NRs were symmetric in terms of the analyzer angles enabling the passing of the maximum/minimum scattering signals. Consequently, no rotation in the polarization direction of the scattered light occurred in the scattering from ITO and ZTO NRs. Hence, it is confirmed that the intriguing optical rotation, persistently observed from ZnO NRs, is absent in scattered signals from ITO and ZTO NRs regardless of the incident light setting. The lack of the polarization rotation phenomenon in the scattered light from these doped NRs suggests that the birefringent nature of the pure materials, through their well-ordered atomic arrangements in the crystals, is lost due to the introduction of the doping elements. Chemical dopants of In and Sn in ITO and ZTO NRs, respectively, lead to random distributions of the dopant elements in the otherwise pure and crystalline NRs of SnO$_2$ and ZnO which, in turn, can serve as chemical and structural defect sites. Such chemical and structural perturbations may explain the absence of any phase shift in the scattered responses of the ITO and ZTO NRs seen in the experiments. Compared to the presence of optical rotation in ZnO NRs, no change in the oscillation directions of the scattered electric fields from ITO and ZTO NRs is observed, as depicted in the left panel in Figure 5.1(c). Further work is underway in order to determine the exact origin of the
polarization rotation of the scattered light that was persistently observed from individual ZnO NRs but absent on ITO and ZTO NRs.

5.4 Conclusion

In conclusion, I have examined the light-matter interactions between visible light and the NRs of ZnO, ITO, and ZTO at the single nanomaterial level, while systematically controlling the key parameters such as the wavelength and polarization direction of light, the NR tilt angle, and the analyzer angle. I subsequently report the intriguing optical phenomenon of polarization rotation in the scattered light, which is confirmed to be present on the chemically pure and highly crystalline ZnO NRs, but absent on the chemically doped NR variants of ITO and ZTO with comparable physical dimensions and light-matter interaction geometries to ZnO. Also, I further elucidate that the material-dependent polarization rotation of the scattered light is affected by the NR tilt angle, although the phenomenon itself occurs irrespective of the wavelength and incident polarization direction of the visible light for ZnO NRs.

The findings reported in this chapter may serve as a new guidance to tailor material-specific, single nanomaterial-driven, optically modulating functionalities in photonic and sensing devices. These endeavors may be particularly valuable in developing biomedical sensors based on individual ZnO NRs by equipping them with additional modalities of polarization rotation and phase shift. In addition, with the demonstrated application of ZnO NRs as nanolasers and subwavelength waveguides, understanding the factors influencing their polarization rotation effect can be highly useful in building single ZnO NR-based, optically functional elements.
Chapter 6

Application of Well-defined Indium Tin Oxide Nanorods as Raman Active Platforms

6.1 Background and Introduction

Surface enhanced Raman spectroscopy (SERS) is a powerful analytical tool which has proven its usefulness as a very selective and sensitive surface measurement technique.\textsuperscript{189-194} In SERS, the majority of the substrates used for surface enhancement effects involve nanoparticles, thin films, islands, and three-dimensional constructs of coinage metals such as Cu, Au, and Ag.\textsuperscript{190,195-197} Identifying potential SERS-active substrates and understanding enhancement mechanisms for such substrates are critical to the field and, therefore, still remain a key area of SERS study. Although not as extensively explored as the aforementioned metals, some research efforts are made to obtain SERS of transition metals such as Pt, Rh, Pd, Fe, Co, and Ni.\textsuperscript{191,198-201} And more recently, other systems involving either a metal oxide thin film or a hybrid system of a metal nanoparticle/metal oxide thin film have been demonstrated as SERS-active materials.\textsuperscript{195,202-207} Plasmonic characteristics similar to those observed from noble metals are found in some transparent conducting metal oxides such as indium tin oxide, fluorine-doped tin oxide, and aluminum-doped zinc oxide.\textsuperscript{206,208}

Despite many leading efforts on this aspect, only a small subset of research discusses Raman enhancement effects observed from nanomaterials that are precisely controlled for their physical, chemical, optical, or electrical properties during synthesis. Controlling the exact size and structure of the nanomaterials has not been the primary focus of many previous SERS studies, and many of the studies involve random surface roughening of Raman substrates for desired surface
enhancement effect. Only more recently with the progress in nanoscience has it become an active subject matter of SERS investigation.\textsuperscript{192,196,210,211} When it comes to one-dimensional (1D) metal oxide nanomaterials which typically exhibit a higher aspect ratio than noble metal nanorods of a comparable diameter, concerted SERS measurements on controlled nanomaterial substrates are even scarcer. Yet, the anisotropy of 1D nanomaterials can provide a higher degree of enhancement in localized electromagnetic fields through symmetry breaking and can thus be extremely beneficial for SERS. In this chapter, the SERS activity of well-controlled, anisotropic indium tin oxide nanorods (ITO NRs) by evaluating their role in Raman spectroscopy using rhodamine 6 G and 4’,6-diamidino-2-phenylindole (DAPI) as a model system is elucidated.

6.2 Experimental Methods

ITO NRs were synthesized via methods developed in our previous study.\textsuperscript{212} The size and morphology of as-grown ITO NRs were characterized by using FEI/Philips XL 20 scanning electron microscope (SEM) operated at 20 kV. X-ray diffraction (XRD) data were acquired using Rigaku Ultima IV x-ray diffractometer (The Wodlands, Texas) using Cu K\textsubscript{a} radiation under an accelerating voltage and current of 45 kV of 44 mA, respectively. The sample was scanned at a rate of 2°/min in the range of 20 = 5°–80°. Fourier transform infrared (FTIR) spectra were taken by using a Varian 3100 FTIR spectrometer (Varian Inc.). FTIR spectra were obtained for the scan range of 400 to 8000 cm\textsuperscript{-1} in attenuated total reflectance (ATR) mode with 4 cm\textsuperscript{-1} spectral resolution co-added for 50 scans.

Two dye molecules, rhodamine 6 G (R6G) and DAPI, were purchased from VWR Inc. (Randor, PA) and diluted to desired concentrations ranging from 10 mg/ml to 1 \(\mu\)g/ml in deionized
water. In addition to the ITO NRs, two control substrates of blank Si and ITO-coated glass were employed in these measurements. A total volume of 8 μl, either pure or mixed solutions of varying concentrations of DAPI and R6G, was deposited onto different substrates. Raman spectra were obtained by Renishaw RM1000 confocal Raman microscope. Samples were illuminated through a 50× objective lens either with a Renishaw diode laser operating at a wavelength of 785 nm or with a 514 nm Argon ion laser.

6.3 Results and Discussion

Figure 6.1 displays the SEM, XRD, and FTIR data of the ITO NRs used in the Raman study. As-synthesized ITO NRs exhibit an average diameter 40 ± 1.5 nm and extend to a length of greater than 15 μm as indicated in Figure 6.1(a). These long NRs tend to orient themselves parallel to the plane of the growth substrate instead of growing vertically. The ITO NRs exhibit the cubic structure of bixbyite Mn₂O₃ I type (C-type rare-earth oxide structure). The XRD diffraction peaks at 30.45°, 35.28°, 50.80°, and 60.40° shown in Figure 6.1(b) correspond to (222), (400), (440), and (622) planes, respectively. Figure 6.1(c) displays ATR FTIR data from as-grown ITO NRs. The ITO NR samples exhibit unique peaks located at 556 and 616 cm⁻¹ which correspond to the In-O-In and Sn-O-Sn bonds in ITO NR crystals, respectively. Other nearby peaks, also observed from a blank Si, are due to symmetric and asymmetric O-Si-O vibrations of the chemical groups on the surface of the growth substrate of Si(100).²¹³
Figure 6.1. Scanning electron microscope (SEM), X-ray diffraction (XRD), and Fourier transformed infrared (FTIR) spectroscopy characterizations of ITO NR array. (a) SEM images of the ITO NRs used as SERS-active substrates. The scan size of the image is (top) 50 × 100 μm, (bottom left) 4 × 4 μm, (bottom right) 1 × 1 μm and the inset in the bottom left panel is 500 × 500 nm. (b and c) XRD (b) and FTIR (c) spectra of as-grown ITO NRs.
Deposition conditions for the two chemicals are kept identical between the three substrates. Raman intensity of each spectrum is normalized with respect to the characteristic strong Si peak appearing at 521 cm$^{-1}$. Raman shifts of blank Si and ITO NRs are characterized in Figure 6.2(a). No distinctive Raman peak is seen in the ITO NR sample where the spectrum resembles that of Si. After depositing 100 $\mu$g/ml R6G, multiple Raman scans are carried out on different substrates in order to obtain the distinctive response signal corresponding to the spectroscopic signature of the dye molecule. Figure 6.2(b) clearly displays the difference in normalized Raman intensity observed from the same concentration of R6G on an ITO NR platform versus on a Si substrate. Peaks located at 612, 776, 1132, 1188, 1314, 1364, 1510, and 1653 cm$^{-1}$ are characteristic of R6G$^{202}$ and they are clearly resolved using ITO NRs as a Raman substrate. Moreover, the pronounced Raman signal of R6G on ITO NRs indicates that as-synthesized ITO NRs can be effectively employed as a SERS-active substrate.
Figure 6.2. Raman spectra of Si and ITO NR substrates pre- and post- R6G deposition under excitation light of $\lambda_{ex} = 785$ nm. (a) Raman spectra of unmodified Si and ITO NRs. (b) Raman spectra of 100 $\mu$g/ml R6G deposited on Si and ITO NR substrates.

In order to substantiate this initial observation, Raman scattering experiments are repeated using a different molecule, DAPI. Figure 6.3(a) displays Raman signal obtained from 100 $\mu$g/ml DAPI on ITO NR, ITO-coated glass, and Si samples while exciting with a 785 nm laser. For the
same DAPI concentration, the Raman intensities of the DAPI peaks located at 1459, 1510, and 1610 cm$^{-1}$ are much higher on ITO NRs when compared to those on Si or on ITO coated glass. In order to assess a possible link between the surface-to-volume ratio of the substrate materials and the measured Raman signal, higher concentrations of DAPI are deposited onto Si substrates and the resulting Raman intensity is compared to the ITO NR sample containing a much lower DAPI concentration. In this control experiment shown in Figure 6.3(b), the characteristic peak of DAPI at 1610 cm$^{-1}$ is clearly observed from the ITO NR sample prepared by depositing 100 $\mu$g/ml of the dye molecule. However, the same peak cannot be resolved on Si even with fifty times higher concentration of DAPI. In order to ensure the reproducibility of the observation, Raman measurements are carried out further by using varying concentration of mixed chemical molecules of R6G and DAPI. The same tendency of increased Raman signals is repeatedly obtained from the mixture of DAPI and R6G on an ITO NR platform when compared to those from the same mixture on a Si substrate, Figure 6.3. Arrows (pointing upward: DAPI and downward: R6G) in Figure 6.3(c) mark those peaks located at the expected Raman shift positions of the two dye molecules. The hard-to-resolve peaks of DAPI and R6G on Si are clearly identified when ITO NRs are used as Raman substrates instead.
Figure 6.3. Raman spectra of various concentrations of DAPI and DAPI+R6G mixture on Si and ITO NR substrates pre- and post- deposition under excitation light of $\lambda_{ex} = 785$ nm. (a) Raman signal from 100 $\mu$g/ml DAPI on ITO NR, ITO-coated glass, and Si substrates. (b) Raman spectra collected from various concentrations of DAPI on ITO NR and Si samples. (c) Comparison of concentration-dependent Raman scattering signal from a mixture of DAPI and R6G molecules on ITO NR and Si substrates.
The degree of Raman enhancement observed from the presented ITO NR systems is compared to that of gold nanorods (AuNRs) by carrying out the identical deposition of DAPI and R6G on both substrates. AuNRs were synthesized and purified according to the well-established methods in the literature.\textsuperscript{214,215} UV-Vis spectra of the AuNRs were recorded on an Agilent 8453 diode-array spectrophotometer. A 5 μl droplet of the 1.6 nM AuNR solution was placed onto a clean Si substrate and left to dry in air. This procedure was repeated ten times until the surface was densely covered by AuNRs and the mixture of DAPI and R6G were drop-casted subsequently onto the AuNRs.

Figure 6.4(a) displays a color photograph and a UV-Vis spectrum of the re-suspended AuNR solution. The characteristic plasmon peak of the AuNRs appears at 735 nm along with a small peak at 510 nm. The characteristic peaks of DAPI and R6G shown in Figure 6.4 indicate that the degree of Raman scattering on ITO NRs is comparable to that obtained on AuNR substrates. The conclusion drawn from the presented comparison study between ITO NRs and AuNRs may not be applied to all AuNR systems of different geometries and configurations reported in the literature. However, the result suggests that my ITO NR systems are capable of enhancing Raman signal and serve effectively as an alternative SERS-active substrate to metallic counterparts.
Figure 6.4. UV-Vis spectra of 1.6 nM AuNRs and Raman spectra of DAPI+R6G mixture on Si, AuNRs, and ITO NR substrates pre- and post- deposition under excitation light of $\lambda_{\text{ex}} = 785 \text{ nm}$. (a) A color photograph and a UV-Vis spectrum of 1.6 nM AuNRs resuspended in deionized water. (b) Raman spectra collected with a 785 nm excitation while keeping the deposition conditions of the 100 $\mu$g/ml DAPI and R6G mixture identical on the three substrates of Si, AuNRs, and ITO NRs.
Although the charge carrier densities of metal oxides are approximately two orders of magnitude lower than those of typical metals, the surface plasmon resonance phenomena of metal oxides are similar to those of noble metals.\textsuperscript{206,207} Therefore, it is highly likely that surface plasmons play a significant role in the enhanced Raman signal observed on ITO NRs, similar to what has been extensively reported in metallic nanoparticles.\textsuperscript{216} Unlike the 2D ITO systems reported in the literature, my 1D ITO NRs present an extremely high aspect ratio, and this shape factor can be particularly useful for SERS. The Raman signal differences observed in Figure 6.3 between ITO-coated glass (2D) versus ITO NR (1D) substrates may be due to this difference in the length to diameter ratio of the support materials. Very recently, several studies have reported on the effect of nanoparticles shapes in SERS activity and have pointed out that field enhancement is very sensitive to the geometry of the nanostructures on a SERS substrate.\textsuperscript{216} For example, SERS activities of cubic or cauliflower-like particles are much greater than that of spherical ones under the same excitation condition.\textsuperscript{191,200} The three-dimensional finite difference time domain (3D-FDTD) theory, calculating local electromagnetic fields of transition metal surfaces when compared to the free electron metals, has effectively explained the experimentally observed phenomena.\textsuperscript{191,200,210,217} The increased electromagnetic fields of non-spherical particles are often referred to as the lighting rod effect near structures of high curvature on a surface. The large anisotropy of the ITO NRs (with an aspect ratio larger 1:375 (width:length)) used in my SERS measurements may intensify this effect even further, leading to higher SERS activity than their isotropic zero-dimensional counterparts and the two dimensional ITO thin films.
6.4 Conclusion

In conclusion, SERS activity observed on 1D metal oxide NRs is determined. I demonstrate that significant enhancement in Raman intensities is observed from varying concentrations of pure and mixed R6G and DAPI molecules on ITO NRs. This approach signifies the first attempt to assess the SERS capability of well-defined 1D metal oxide NRs and to further develop as effective SERS active substrates.
Chapter 7

Indium Tin Oxide Nanowire Networks as Effective UV/VIS Photodetection Platforms

7.1 Background and Introduction

One-dimensional (1D) semiconducting nanomaterials have proven their promising potential in crucial sensing applications by serving as chemical, biological, and light sensors. In particular, semiconducting oxide (SCO) nanostructures have shown their versatility in sensing various types of analytes ranging from gas species to biological molecules to light. The improved performance leading to increased signal and fast response time is often attributed to the inherently high surface-to-volume ratio of nanomaterials, when compared to the same sensing devices which are made from thin film or bulk structures.

Both individual nanostructures and their ensembles have been previously employed in constructing sensor devices. Typical fabrication processes involving individual nanostructures require the use of high-cost, low-yield, and highly specialized fabrication equipment, presenting challenges for scalability of their assembly and production. On the other hand, sensors constructed from networks of nanostructures are not subjected to the complicated fabrication processes often employed for single nanostructure devices, potentially enabling a large-scale production via facile and low-cost techniques. Nanostructure network devices may also benefit from better light trapping and suppressed reflection. In addition to these advantages, ensemble platforms have shown to provide adequate or improved performances, making them very attractive, alternative sensor devices that are easy to fabricate. Significant research efforts have so far been made to characterize single SCO nanostructure devices. Yet, it is equally important to examine
nanomaterial network devices, when considering the aforementioned overall effectiveness of sensor devices constructed from nanomaterial ensembles. In this regard, I have previously demonstrated the different uses of indium tin oxide nanowire (ITO) NW network systems in biomolecular fluorescence and surface-enhanced Raman signal detection.\textsuperscript{227,228}

Here, ITO NW network devices for photosensor applications is examined. I demonstrate that ITO NW network-based devices can function as highly effective photodetectors capable of sensing ultraviolet (UV) and visible (VIS) light with high sensitivity and fast response time. I also show that the UV/VIS sensing capability of the ITO NW mesh devices can be significantly improved by modifying the NWs with a cationic polymer, poly-l-lysine. High photovoltage and photocurrent signals are observed from these sensors, with much faster rise and decay time than those reported for single NW devices. The photoresponsivity of the ITO NW mesh devices is comparable to those of commercial UV/VIS detectors even at a low bias. In addition, the ITO NW mesh-based devices are fabricated with simple processes which do not involve lithographic patterning or thin film deposition. Therefore, this approach can be highly beneficial in developing alternative platforms for low-cost, high performing photodetectors with improved scalability.

7.2 Experimental Methods

Four materials of ITO, SnO2, ZTO and ZnO were prepared as outlined in the previous chapter as well as our earlier study.\textsuperscript{227} The size and morphology of CVD-synthesized nanomaterials were then characterized by using a FEI/Philips XL 20 scanning electron microscope (SEM) operated at 20 kV. XRD data were acquired by using a Rigaku Ultima IV X-Ray diffractometer (The Woodlands, Texas) operated with an accelerating voltage and current of 45
kV and 44 mA, respectively, under Cu Kα radiation. The samples were scanned at a rate of 2 degree/min in the range of 2θ = 5-80 degrees.

For photovoltage (PV) measurements, Ag contacts were fabricated using silver pastes (Ted Pella, Inc.) on either end of the nanomaterial layer serving as the left (L) and right (R) electrodes for subsequent, lateral photovoltage (LPV) measurements. The sample assembly was then placed in a dark housing with a small front aperture to introduce a light source to the sample while eliminating any external optical and electrical noise. At the bottom center of the enclosure, a sample holder connects the two electrodes on the sample to the 200 MHz oscilloscope through a BNC connector for voltage characterization. A 543 nm HeNe laser (Newport Corp., Santa Clara, CA) was used as a constant-wave, visible (VIS) illumination source, with a spot diameter and laser power of 1 mm and 1.14 mW, respectively. The light was sent through an optical chopper (Thorlabs, Inc., Newton, NJ) rotating with a predetermined frequency. UV illumination was delivered by a Quanta-Ray GCR-3 pulsed Nd:YAG laser (Spectra Physics, Santa Clara, CA) as a light source. The frequency-tripled output of the laser (wavelength 355 nm) has a measured pulse width of 8 ns, repetition rate of 10 Hz and maximum pulse energy of 200 mJ. The beam was attenuated to give a pulse energy of roughly 15 μJ per pulse incident on the sample with a spot size of 1 mm. In addition, current-voltage (I-V) measurements were carried out by sweeping the L-R voltage using a Hewlett Packard pA-meter/DC-voltage source, HP 4140B.

7.3 Results and Discussion

Figure 7.1(a) displays representative 4 x 4 μm SEM panels for as-grown SnO2, ZTO, ZnO, and ITO nanomaterials. Nanowire (NW)-like structures are observed from SnO2 and ITO plates.
whereas nanorod (NR) and nanobelt (NB) structures are found from the ZnO and ZTO plates, respectively. The average diameter of SnO$_2$ NWs (35.7 ± 2.0 nm) is similar to that of ITO NWs (40 ± 1.5 nm), whereas the diameter of ZTO NBs (333 ± 45 nm) is similar to that of ZnO NRs (300 ± 15 nm). Figure 7.1(b) shows a magnified SEM panel and x-ray diffraction (XRD) data of ITO NWs, the material of focus in this paper. XRD peaks positioned at 30.45°, 35.28°, 50.80°, and 60.40° correspond to (222), (400), (440), and (622) ITO NW planes in the cubic crystal structure of bixbyite Mn$_2$O$_3$ I type (C-type rare-earth oxide structure), respectively. The atomic arrangements of In, Sn, and O in the ITO NWs are depicted in the crystal structure model provided in Figure 7.1(b).
Figure 7.1. Scanning electron microscopy (SEM) images of various 1D semiconducting oxides, X-ray diffraction (XRD) spectra of ITO NRs, and experimental schematic of photovoltaic and photocurrent measurements. (a) 4 x 4 μm SEM images displaying typical CVD-grown structures of SnO$_2$ NWs, ZTO NBs, ZnO NRs, and ITO NWs. (b) A 2 x 2 μm, zoomed-in SEM panel shows the structure of individual ITO NWs. XRD data of as-grown ITO NWs are also provided along with a schematic representation of the atomic arrangements in ITO NW crystals. (c) Schematic diagram of the overall photoelectric measurement setup.

The overall experimental scheme for the nanomaterial network photoelectric measurements is displayed in Figure 7.1(c). The device schematic provided in Figure 7.2(a) displays a typical sample configuration involving networks of ITO NWs. Figure 7.2(a) also
displays a representative voltage response obtained from ITO NWs, showing a maximum photovoltage \( V_{ph} \) value of 31 mV. Down (up) arrows inserted in Figure 7.2 indicate the time when the 543 nm laser directed to the sample is on (off) through a 400 Hz chopper wheel. In comparison, Figure 7.2(b) displays typical photovoltage plots acquired from the other three types of devices consisting of SnO\(_2\) NWs, ZnO NRs, and ZTO NBs. The voltage responses upon illumination on these materials are significantly lower than what was observed from ITO NWs. Both ZnO NR and ZTO NB devices result in \( V_{ph} \) of ~3 mV whereas SnO\(_2\) NWs produce an even weaker signal of ~2 mV. Although the exact origin of the significantly larger photovoltage response observed from ITO NWs in comparison to other nanomaterials is not clear yet, inherently superior electrical properties of the materials such as greater charge carrier density, lower resistivity, and faster carrier mobility may contribute to this effect. The corresponding values for an ITO thin film, for example, are reported to be on the order of \( 5 \times 10^{20}/\text{cm}^3 \), \( 2 \times 10^{-4} \ \Omega\cdot\text{cm} \), and \( 55 \ \text{cm}^2/(\text{V}\cdot\text{s}) \),\(^{229,230}\) whereas those of a ZnO thin film are \( 10 \times 10^{19}/\text{cm}^3 \), \( 1 \times 10^{-2} \ \Omega\cdot\text{cm} \), and \( 35 \ \text{cm}^2/(\text{V}\cdot\text{s}) \).\(^{213}\) The higher charge carrier density and mobility combined with the lower resistivity of ITO may promote the photo-induced voltage signal in this experiment. The magnitude of \( V_{ph} \) varies on the same sample devices depending on the laser position. The laser spot is kept on the sample location producing the highest signal for all devices characterized in Figure 7.2. When comparing the highest \( V_{ph} \) of the different devices, the photoresponse of ITO NWs is an order of magnitude larger than other similar semiconducting oxide nanomaterials shown in Figure 7.2(b). Therefore, herein the discussion of this paper is focused on ITO NWs. The response time of the photovoltage change of the ITO NW device is determined by using the pulsed Nd:YAG laser as a light source. Figure 7.2(c) displays the typical response time of the ITO NW photodetectors which
is defined collectively by the rise \((T_r)\) and decay \((T_d)\) time. The response time of ITO NW devices is determined as \(T_r = 20 \mu\text{s}\) and \(T_d = 1.5\text{ ms}\).

![Figure 7.2](image)

**Figure 7.2.** Typical photovoltage response acquired under 542 nm laser illumination from ITO NWs, SnO\(_2\) NWs, ZnO NRs and ZTO NBs and photovoltage response of ITO NWs under 355 nm pulsed laser. (a) Typical photovoltage acquired from ITO NWs while illuminating the device with a 543 nm laser through an optical chopper is shown. (b) Photovoltage signal from SnO\(_2\), ZTO, ZnO nanostructures is recorded when using the same light source as (a). (c) Typical photovoltage signal obtained from ITO NW devices when using a 355 nm pulsed laser is provided. The inset is a zoomed-in view with the light on to show clearly the rise time.

Electrical responses in many nanomaterial-based electronic devices can be effectively tailored by a simple modification of their device channel surfaces.\(^{232-236}\) For instance, organic amines and polymers have been utilized previously as a gate and a gate modifier in chemical- and
electrolyte-gating applications, respectively. These simple methods can produce a large change in electrical signal without introducing chemical dopants or charge separating layers into the channel material. In order to test whether the light-activated, electrical response of the nanomaterial devices can be altered in a similar way, a cationic polymer of PLL was chosen as a model system and uniformly applied to the surface of the ITO NW layer. Typical photovoltage signals from the PLL-treated ITO NW (PLL/ITO NW) devices were subsequently probed by using the 543 nm laser, and the results are provided in Figure 7.3(a). When keeping the same laser spot on the sample position yielding the highest signal, a significantly increased $V_{ph}$ value of 100 mV is recorded on PLL/ITO NWs as plotted in black in Figure 7.3(a). The photoresponse decreases when it is positioned away from the edge towards the middle of the sample. Colored plots in Figure 7.3(b) display such changes in photoresponse amplitudes when varying the laser position along a line spanning from one electrode to the other (marked as L and R electrodes in the schematics) on the PLL/ITO NW device. $V_{ph}$ varies with the light position on the line between the L and R electrodes with $\Delta V_{ph}/\Delta x$ of approximately 20 mV/mm for PLL/ITO NW device. Figure 7.3(c) displays the photovoltage response of the PLL/ITO NW device upon illumination with the 355 nm pulsed laser. The response time of the PLL/ITO NW device is $T_r = 30 \mu$s and $T_d = 3.7$ ms, slightly longer than the ITO NW device, at $T_r = 20 \mu$s and $T_d = 1.5$ ms.
Figure 7.3. Typical position dependent photovoltage response acquired from PLL-modified ITO NW device under 542 nm and 355 nm laser illuminations. (a) Typical photovoltage response obtained from PLL-modified ITO NW devices upon periodic illumination with a 543 nm laser is displayed. Plots indicated as (1), (2), and (3) correspond to voltage signal changes depending on the laser position as indicated in the schematic. (b) Voltage difference ($V_{ph} - V_d$) between 543 nm light-on and -off is recorded at five different illumination positions along the middle of the PLL/ITO NW device spanning one electrode to the other. Relative laser positions are marked as (1) through (5) as shown in the schematic. (c) Typical photovoltage signal obtained from PLL/ITO NW devices probed by a 355 nm pulsed laser is shown. The inset is a zoomed-in view with the light on to show clearly the rise time.
As the excitation wavelengths of both lasers used in these experiments are below the bandgap of ITO NWs ($> 3.75 \text{ eV}$), the photoresponse is not due to the generation of charge carriers from bandgap transition. One possible cause for the photovoltage is local heating in the region of the ITO NW network irradiated by the laser. It is known that light-induced temperature gradients in single and ensemble nanomaterials can produce a photovoltage through photothermoelectric effect (PTE) in carbon nanotube, graphene, MoS$_2$, and GaAs NW devices.\textsuperscript{238-244} Upon illumination, there will be a net electrical current flowing from the hot side to the cold side until the built-up electric field balances this current. When the laser spot is positioned to one side of the network, close to one contact, the photovoltage is highest since the net current from the one contact (on the hot side) to the other contact (on the cold side) will be largest. When the laser spot is moved close to the middle of the sample, the current caused by the temperature gradient will flow from the hot middle region to both directions towards the two colder contacts, yielding a smaller net photovoltage. Therefore, for a symmetric device, photovoltage should be zero when the laser is positioned in the middle. The results shown in Figure 7.3(b) indicate an asymmetric device behavior, yielding a nonzero photovoltage at all five laser positions tested.

In order to understand this response, current-voltage ($I$-$V$) measurements were carried out by sweeping the L-R voltage from -3 to 3 V with an increment of 10 mV using the HP pA-meter/DC-voltage source. The light source used for the $I$-$V$ measurements was the 543 nm laser. Figure 7.4 displays the resulting $I$-$V$ characteristics of the ITO NW devices with and without the PLL modification. Asymmetric $I$-$V$ curves are observed from both ITO NW and PLL/ITO NW devices. Such asymmetrical $I$-$V$ curves have been reported previously on single nanomaterial
devices such as ZnO NBs and NWs as well as Ge NW mesh devices. However, the exact origin of the rectifying I-V curves in these systems is not clear and still under debate.

Figure 7.4. Current-Voltage (I-V) curve of bare and PLL-modified ITO NWs device with photoresponsivity comparison between the two devices. (a) Typical current versus voltage (I-V) plot is shown for ITO NWs. Dark current ($I_d$) and photocurrent ($I_{ph}$) are obtained while sweeping the L-R voltage from -3 to +3 V. The 543 nm laser serves as the illumination source. The I-V plot in the right panel displays a magnified view of the blue squared region in the I-V curve on the left. The open circuit voltage ($V_{oc}$) and short circuit current ($I_{sc}$) upon illumination are determined as 15 mV and 7.7 x 10$^{-8}$ A, respectively, for the ITO NWs. (b) Typical I-V characteristics are displayed for PLL/ITO NW devices. The open circuit voltage ($V_{oc}$) and short circuit current ($I_{sc}$) upon illumination are determined as 67 mV and 1.0 x 10$^{-7}$ A, respectively, as indicated in the magnified I-V panel shown on the right. (c) The photoresponsivity data of the ITO NW and PLL/ITO NW mesh devices are plotted against the bias in black and purple, respectively.
Surface charge- and oxygen adsorbate-driven mechanisms often explaining photocurrent transport behaviors of many single NW devices will lead to a much slower reset time than what I observe from ITO NW-based devices. This slow response time of single NW devices is due to a long time scale associated with surface trap charging and oxygen re-adsorption process (several minutes to hours).\textsuperscript{247,249} In contrast, the very fast response and decay time observed from my ITO NW network devices in Figures 7.2(c) and 7.3(c) strongly suggest that a different mechanism may play a key role in my NW mesh configuration. I hypothesize that these devices are governed by a barrier-dominated transport mechanism. The L and R electrodes in my devices form different contact barriers at the interface with the ITO NW network due to variations in contact conditions caused by non-uniformity of the network, yielding asymmetric \textit{I-V} characteristics. At the same time, NW-NW junction barriers existing in the NW mesh configuration may also contribute to the asymmetry of the \textit{I-V} curves. The typical rise and decay time on the order of micro and milliseconds respectively, observed from my ITO NW network devices indicate that photothermally induced charge carriers are instantaneously formed within tens of microseconds upon illumination with the pulsed laser. However, such charge carriers can be restrained at the NW-NW interfaces and/or NW-Ag electrode contact junctions, resulting in the decay time in tens of milliseconds when the light is off. Hence, an alternative ITO device fabricated with aligned NWs between the two contacts may be able to reduce the timescale gap between the rise and decay time by minimizing the carrier trap in the NW-NW interfaces. Further work is underway to measure exactly the differences in the contact barriers at the NW-metal junctions in L and R electrodes as well as in the choice of metals for electrodes.
The open circuit voltage ($V_{oc}$) and short circuit current ($I_{sc}$) were also obtained from the $I$-$V$ curves. These results are clearly seen in the zoomed-in $I$-$V$ plots of Figures 7.4(a) and 7.4(b) for the ITO NW and PLL/ITO NW device, respectively. Under the dark condition, no significant $V_{oc}$ or $I_{sc}$ is measured from the ITO NW or the PLL/ITO NW device. Upon illumination, the ITO NW device exhibits $V_{oc}$ and $I_{sc}$ of 15 mV and $7.7 \times 10^{-8}$ A, respectively. These values change to $V_{oc} = 67$ mV and $I_{sc} = 1.0 \times 10^{-7}$ A for the PLL-modified ITO NW device under the same illumination condition. Figure 7.4(c) displays the photoresponsivity, $R = \frac{(I_{ph} - I_d)}{P \times a}$, of the ITO NW and PLL-modified ITO NW devices shown in Figures 7.4(a) and 7.4(b). $I_{ph}$, $I_d$, $P$, and $a$ correspond to the photocurrent, dark current, power density of the laser, and the cross sectional area of the illumination, respectively. When using the 543 nm laser, the ITO NWs reach the $R$ value of 0.07 A/W at 3V whereas the PLL-treated ITO NWs display $R = 0.2$ A/W at the same bias. The typical photoresponsivity of most commercial UV and VIS photodetectors is in the range of 0.1-0.2 A/W and 0.1-0.5 A/W, respectively.\textsuperscript{250-252} Hence, the photoresponsivity of my ITO NW mesh-based devices is comparable to the performance of commercial UV and VIS photodetectors.

For comparison with other similar nanomaterial devices, Table 1 lists the performance characteristics of UV and VIS photodetectors made from various individual and ensemble SCO nanomaterials.\textsuperscript{253-256} Key parameters of the light sensors are also shown along with those of the presented ITO NW mesh-based devices. The high performing ITO NW mesh devices demonstrated in this study can be straightforwardly constructed without the use of intensive lithographic steps and, thus, can potentially enable a large-scale production of ITO NW-based, UV-VIS photodetectors. At the same time, my ITO NW network devices display fairly high $I_{ph}$ and $R$ values even at a low bias of 3V, while featuring very fast response time of $T_r$ and $T_d$. 

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Table 7.1. Key characteristics of UV/VIS photodetectors constructed from various SCO nanomaterials. Co-ZnO NB and SnO$_2$ NB devices contain ensembles of nanomaterials whereas ZnO NW and In$_2$O$_3$ NW systems are examples of individual nanomaterial devices. Parameters such as bias voltage ($V$), photocurrent ($I_{ph}$), rise time ($T_r$) and decay time ($T_d$) are catalogued.

<table>
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<tr>
<th>Material type</th>
<th>$\lambda_{\text{light}}$</th>
<th>$V$</th>
<th>$I_{ph}$</th>
<th>$T_r$</th>
<th>$T_d$</th>
<th>Ref.</th>
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<td>Co-ZnO NBs</td>
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<td>110 $\mu$A</td>
<td>200 s</td>
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<td></td>
<td>630 nm</td>
<td>5V</td>
<td>0.25 $\mu$A</td>
<td>500 s</td>
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<td>ZnO NW</td>
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<td>5V</td>
<td>30 $\mu$A</td>
<td>23 s</td>
<td>33 s</td>
<td>[254]</td>
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<tr>
<td>ZnO NW</td>
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<td>5V</td>
<td>~0.01 $\mu$A</td>
<td>40 s</td>
<td>300 s</td>
<td>[253]</td>
</tr>
<tr>
<td>Au NP-ZnO NW</td>
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<td>5V</td>
<td>~1 $\mu$A</td>
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<td>10 s</td>
<td>[257]</td>
</tr>
<tr>
<td>SnO$_2$ NBs</td>
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<td>-5V</td>
<td>57 nA</td>
<td>&lt; 1 s</td>
<td>&lt; 1 s</td>
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<tr>
<td>In$_2$O$_3$ NW</td>
<td>254 nm</td>
<td>0.3V</td>
<td>290 nA</td>
<td>10 s</td>
<td>~900 s</td>
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</tr>
<tr>
<td></td>
<td>365 nm</td>
<td>0.3V</td>
<td>33 nA</td>
<td>-</td>
<td>~300 s</td>
<td></td>
</tr>
<tr>
<td>ITO NW mesh</td>
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<td>-</td>
<td>20 $\mu$s</td>
<td>1.5 ms</td>
<td>this study</td>
</tr>
<tr>
<td></td>
<td>543 nm</td>
<td>3V</td>
<td>225 $\mu$A</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>PLL/ITO NW mesh</td>
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<td>-</td>
<td>-</td>
<td>30 $\mu$s</td>
<td>3.7 ms</td>
<td>this study</td>
</tr>
<tr>
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<td>3V</td>
<td>325 $\mu$A</td>
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7.4 Conclusion

In conclusion, I have shown that ITO NWs and PLL/ITO NWs configured in a network format can be effectively used as high performing UV/VIS photodetectors. The photovoltage response of ITO NWs is much higher than similarly constructed devices made from SnO$_2$ NWs, ZTO NBs and ZnO NRs. The ITO NW mesh-based devices yield substantial photovoltage and photocurrent values of 31-100 mV and 225-325 µA at 3V, respectively, under illumination with a 1.14 mW, 543 nm laser. The photoresponsivity of the ITO NW devices ranges from 0.07-0.2 A/W at a 3V bias. The response time of the devices exhibits a rise time of 20-30 µs and a decay time of 1.5-3.7 ms when probed with a 355 nm pulsed laser. These photodetectors are simple and straightforward to construct without the need of complicated fabrication steps involving highly specialized instrumentations. Therefore, efforts presented in this chapter demonstrate that ITO NW network-based photodetectors can serve as a convenient alternative to commercial or single NW-based devices as easily assembled, high performing photodetectors.
References


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