Position- and orientation-controlled polarized light interaction of individual indium tin oxide nanorods

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We have systematically investigated the position, orientation, and polarization angle dependence of scattered light from well-characterized, indium tin oxide nanorods (ITO NRs) upon illumination with monochromatic light. Scattering signals from individual ITO NRs of horizontal and vertical configurations are probed quantitatively by examining signal response with respect to the analyzer angle and position along the length of the NR. Our efforts can be highly beneficial in providing fundamental understanding for the light interaction behavior of ITO NRs. Our results can provide valuable bases for comprehending optical emission from individual NRs, with their ever-growing applications in optoelectronics, photonics, and biosensing. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4866794>]

Attractive optical properties of one-dimensional nanomaterials have been investigated and utilized extensively in photonic,¹ optoelectronic,² as well as in biodetection devices.^{3–5} Notably, wide-bandgap nanomaterials, such as zinc oxide, tin oxide, and indium tin oxide, have demonstrated useful phenomena such as spontaneous and stimulated emission,^{6–9} waveguiding, evanescent field enhancement,^{10–12} and optical antenna effects.^{13,14} Such technologically desirable properties have recently contributed to the development of semiconducting oxide nanomaterials for applications in nanoscale lasers,^{6,15,16} subwavelength waveguides,¹⁷ and biodetection platforms.^{18–21}

As a parallel effort to the on-going technological development of these materials, a fundamental understanding of the light interaction with the metallic and semiconducting oxide materials is crucial for providing much needed insight to both basic and applied optical research. Light can produce various optical and optoelectronic responses from the materials such as absorption, reflection, bandgap emission, and scattering. In this Letter, our discussion is focused on scattering behavior of one-dimensional nanomaterials. The majority of previous studies in this regard pertains to the bulk materials or ensembles of nanomaterials, rather than light interaction with individual nanostructures.^{21–29} A limited number of research attempts to elucidate light interaction with individual nanomaterials have been made on isolated scattering systems of carbon nanotubes,^{30,31} gallium phosphide nanowires,¹⁴ and indium phosphide nanowires.³²

In this Letter, we investigate the fundamental optical response of individual indium tin oxide nanorods (ITO NRs) when polarized light is introduced to the one-dimensional NR structure. Our approach marks the first systematic study of forward light scattering from well-defined, individual ITO NRs that correlates the varying optical response with respect to position (both width and length) of individual NRs, spatial orientation of the NRs, and the direction of the incident

electric field. Scattering behavior of single ITO NRs is elucidated from our quantitative optical measurements that discern the position, orientation, and polarization-resolved light response of single ITO NRs. Our experimental approach utilizes a previously described, forward-detection approach which collects the scattered signal in a dark field (DF) mode³⁰ while eliminating substrate scattering with index-matching media and the incident light via total internal reflection (TIR). This method ensures that the measured signal comes 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. As our efforts permit 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 fundamental study can be highly beneficial in ascertaining unique optical response behavior of individual nanoscale materials. 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, our endeavors may also provide valuable insight into the analysis of scattering and emission signal from individual nanomaterials in such devices.

Single crystalline ITO NRs with a well-defined size and shape were synthesized by using a simple chemical vapor deposition (CVD) method as reported earlier.²⁰ 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 20×, 50×, or 100× and focused onto a CCD camera, Qimaging Exi Blue. To carry out the single NR measurements effectively, ITO NRs were first dispersed in ethanol via sonication from their growth substrate and

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deposited on a clean glass slide by drop casting. Then a small drop of glycerol (refractive index, $n = 1.4729$) was placed on the ITO NRs on the glass slide before lowering a cover slip onto the assembly.

When performing 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. The HL plate controlled the orientation of the electric field (E) vector of the laser on the NR plane, as seen in Figure 1. The polarized laser was directed to the sample through a high numerical aperture ($NA = 1.2\text{--}1.4$), oil-immersion DF condenser mounted below the stage and subsequently focused onto individual NRs of investigation. The above-mentioned sample assembly scheme, combined with the use of the oil-immersion, high NA DF condenser, ensured refractive index-matching conditions throughout all existing interfaces and 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 (PA) of the scattered light from individual NRs. Scattering signal was collected by using a $40\times$ plan apochromatic objective lens (Olympus PlanSapo, N.A. = 0.90). The use of the high NA oil-immersion DF condenser is to prevent any direct light from the laser entering the objective lens and, at the same time, to focus effectively the laser onto the NRs.

Figure 1 displays our sample assembly to achieve TIR and the measurement geometry of individual NRs with respect to the direction of the E vector of the incoming light. In our measurement setting, the E vector lies within the xy plane, the sample plane of ITO NRs. $E_{\parallel}$ and $E_{\perp}$ are defined as the 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 displays (a) SEM, (b) BF, and (c) RDF panels of a typical ITO NR used in our optical measurements. The

FIG. 1. Schematic of the optical measurement setup to examine individual ITO NRs. 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 the NR on the sample plane.

NR shown in the SEM image is 130 nm and $13.2\ \mu\text{m}$ 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 effective collection of the scattering signal from individual NRs. 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 yielded much higher image contrast when compared to images obtained in RDF. For all NR scattering data reported in this paper, the polarizer angle was fixed either at 0° ($E_{\parallel}$) or 90° ($E_{\perp}$) while varying the analyzer angle by a predetermined increment. For a given NR, a set of images was taken, while the analyzer configuration was changed from 0° to 180° at an interval of 10° . Image J, a Java-based image processing program, was used to process and analyze the scattering data.

The scattering intensity profile along a vertically oriented NR ($NR_{\parallel}$) excited by the linearly polarized laser is shown as contour plots in Figures 3(a) and 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 $NR_{\parallel}$ is excited with the $E_{\parallel}$ polarized light as seen in Figure 3(a), highest scattering intensities are profiled at $0^\circ/180^\circ$ analyzer rotations with respect to the incoming $E_{\parallel}$ vector, while the lowest intensity is observed at the analyzer setting of 90° . This trend is reversed when $E_{\perp}$ polarized light is used as the scattering source of the same vertical NR, as seen in Figure 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 3(c) and 3(d), respectively. Scattering data points, measured by using the polarized E direction of $E_{\parallel}$ (red) and $E_{\perp}$ (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 $NR_{\parallel}$ follows Malus's Law, $I = I_0$

FIG. 2. SEM, BF, RDF, and DF panels of a single ITO NR. (a) $12 \times 12\ \mu\text{m}$ SEM image of an ITO NR, 130 nm in diameter and $13.2\ \mu\text{m}$ in length, synthesized in a home-built CVD reactor using 20 nm Au colloids as catalysts. (b) and (c) BF and RDF panels of the same ITO NR. (d) Scattering panel of the same ITO NR when an incoming beam of 642 nm is illuminated to the NR and the emission is collected in a DF mode in the forward scattering configuration.

FIG. 3. Scattering signal from an ITO NR_{||}. (a) The contour plot displays the measured scattering intensity of an ITO NR_{||} upon illumination with $E_{||}$ at each point along the entire length of the NR_{||}, while the analyzer is rotated from 0° to 180°. (b) The contour map shows the NR-position dependent scattering intensity of the same NR_{||} with respect to the incoming light of $E_{\perp}$. (c) Average scattering intensity of the NR_{||} is graphed to show the difference in the magnitude of the transmitted scattering signal through the analyzer between the two cases of $E_{||}$ and $E_{\perp}$ at various analyzer angles. (d) Normalized scattering signal from the NR_{||} is displayed for $E_{||}$ and $E_{\perp}$. (e) and (f) Calculated PA and the polar plot of the normalized NR_{||} 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 $E_{||}$ and $E_{\perp}$, respectively.

$\cos^2(\theta)$, as our observation confirms that the ITO NR scattering intensity is directly proportional to the square of the cosine of angle (θ) between the transmission axes of the analyzer and the polarizer (HL wave plate) of the incoming linearly polarized light. When comparing the averaged intensity values of the maximum scattered light for the two cases of $E_{||}$ and $E_{\perp}$, 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 in all measurements for the vertically oriented NR.

The excitation and emission polarization ratios of the maximum intensities parallel and perpendicular to the NR axis is determined as 0.77 from this measurement, by defining polarization anisotropy as below

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

According to classical electromagnetic calculations based on Maxwell's equations, 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 the dielectric constant of the cylinder, ϵ . The relationship between the electric field amplitude inside the NR and incident light of $E_{\perp}$ is a function of the dielectric constant of the NR³²

$$E_{NR,E_{||}} = E_{||},$$

$$E_{NR,E_{\perp}} = \frac{2\epsilon_0}{\epsilon + \epsilon_0} E_{\perp}.$$

ϵ_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 3.8.³³ Therefore, the classical electromagnetic approach seems to explain well the measured PA behavior of the ITO NR in our setup. Figure 3(e) displays the measured polarization anisotropy values of the NR_{||} at various analyzer angles. Both the data points (dot) and the curve fit (line) in Figure 3(e) clearly show that the PA plot also exhibits a $\cos^2(\theta)$ dependence. Figure 3(f) charts the corresponding polar plot of the scattered light intensities when the $E_{||}$ (red) and $E_{\perp}$ (blue) polarized laser interacts with the same vertically oriented ITO NR.

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 4(a) and 4(b). The orientation of the linearly polarized light is $E_{||}$ in Figure 4(a) and $E_{\perp}$ in Figure 4(b). When an ITO NR_⊥ is excited by $E_{||}$ 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. Therefore, the general trend for the analyzer angles yielding the maximum and minimum intensities of the scattered light is the same for the two cases of horizontal and vertical NRs with respect to the direction of the incoming polarization of $E_{||}$ and $E_{\perp}$. However, a significant difference in scattering profile is observed between the NR_{||} in Figures 3(a) and 3(b) and the NR_⊥ in Figures 4(a) and 4(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 $E_{||}$ and $E_{\perp}$ much more effectively than the response along the main body of the NR_⊥. This interesting scattering behavior is quantitatively presented in Figures 4(a) and 4(b). Figures 4(c) and 4(d) display averaged and normalized scattering intensities of the NR_⊥ in response to $E_{||}$ (red) and $E_{\perp}$ (blue) at different analyzer settings. In Figure 4(c), the scattered signal is averaged over the entire length of the NR. Comparing the average scattering intensities of the NR_⊥, the difference between the two laser polarizations of $E_{||}$ 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 is observed for vertically oriented NRs than for horizontal NRs. PA is calculated for the NR_⊥ similar to the earlier case of NR_{||} and plotted in Figure 4(e). In all graphs of the NR_⊥,

FIG. 4. Scattering signal from an ITO NR. (a) The contour plot displays the measured scattering intensity in response to $E_{\parallel}$ 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 $E_{\perp}$. (c) and (d) Averaged and normalized scattering intensity of the NR are graphed for the two cases of $E_{\parallel}$ and $E_{\perp}$. (e) and (f) Calculated PA values as well as the 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 $E_{\parallel}$ and $E_{\perp}$, respectively.

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). The origin of the slightly rotated polar curve seen from many NR $_{\perp}$ under $E_{\perp}$ is not clear yet and on-going study is underway. For both the vertical and horizontal ITO NRs shown in Figures 3 and 4, the polar scattering intensity data display a dipole-like pattern. Note that the angles shown in the polar plots of Figures 3(f) and 4(f) correspond to the analyzer rotation angle. The detector is configured directly above the sample plane at a fixed angle in our measurements. This dipole phenomenon indicates that our 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 along the short NR axis.

In summary, elucidating light interaction behavior of individual nanomaterials is extremely important in engineering the nature of resulting optical response for the technologically important optical and biomedical applications of nanomaterials. We 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 is probed and the ensuing NR response, dependent on various polarization orientation of the incoming light, is quantitatively examined with respect to the analyzer angle. Such optical response of single ITO NRs is quantitatively measured with respect to the position along the length of the NRs. Our efforts can be highly beneficial in identifying 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, our endeavors may also benefit position-, orientation-, and polarization-dependent analysis of the NR light signal.

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