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Polarization-Resolved Mechanistic Investigation of Fluorescence Signal Intensification on Zinc Oxide Nanorod Ends

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Abstract

The superior optical properties of zinc oxide nanorods (ZnO NRs) have continued to promote their broad use in photonic, photoelectric, light detecting, and biosensing applications. One particularly important property pertinent to biodetection is fluorescence intensification on nanorods ends (*FINE*), a phenomenon in which highly spatially localized and strongly intensified fluorescence signal with its extended photostability at the NR ends is seen from the emission profiles of fluorophore-coupled biomolecules on ZnO NRs. Therefore, understanding key parameters affecting the *FINE* phenomenon and the degree of *FINE* (*DoF*) is critical for their applications in biosensors. In this study, we describe in detail the outcomes of polarization-resolved measurements by systematically considering the polarization effects on *FINE* and *DoF* as a function of NR tilt angle and position along the NR. Specifically, we elucidate the exact roles of the different states of light polarization in *FINE* and quantitatively determine the explicit contributions arising from distinctive polarization states to the *DoF*. We confirm that the presence of the *FINE* phenomenon is ubiquitous from the fluorophore-coupled ZnO NR systems, regardless of the polarization setting. We subsequently show that *DoF* is significantly affected by the light-matter interaction geometry. We reveal the specific polarization conditions that contribute dominantly to the *FINE* effect. The highest *DoF* from a NR and the greatest NR end intensity can be achieved when both the excitation and collection polarization states are perpendicular to the NR main axis. Insights from this study provide valuable design principles for selecting the polarization state and light-matter interaction geometry to attain maximum *FINE* as well as *DoF* on ZnO NRs. The precise understanding of polarization-derived consequences on *FINE* and *DoF* manifested differently as a function of position on individual NRs can be also important for warranting accurate interpretation and quantification of the position-dependent, fluorophore-emitted signals on single ZnO NRs. Hence, our findings from this study can be extremely beneficial in fluorescence-based sensing and detection settings utilizing polarization.

Graphical Abstract

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Introduction

The optical properties of one-dimensional (1D) zinc oxide (ZnO) and other related semiconducting oxide nanorods (NRs) have been extensively studied and engineered for better photonic,^{1–4} optoelectronic,^{5–9} and biosensing applications.^{10–15} Anisotropically shaped materials can possess unique light-matter interaction phenomena different from those seen in their isotropic counterparts.^{16,17} Previous studies have shown that light interacting with anisotropic materials can result in optically distinctive responses depending on the polarization state of the light, angle of the incident light, and geometric orientation of the nanomaterial.^{16–21} Extraordinary anisotropic responses, particularly polarization-derived asymmetries, have been demonstrated in the past for tuning plasmonically enhanced fluorescence emission near metals^{17,22–24} and for influencing elastically scattering behaviors of intrinsic NRs.^{18–21,25–27}

We have previously reported on the unique optical phenomenon observed from fluorophore-coupled biomolecules on individual ZnO NRs called *fluorescence intensification on nanorod ends (FINE)*.^{10,11,14,28} When examining the temporal and spatial characteristics of enhanced biomolecular fluorescence on individual ZnO NRs, we found that both the signal intensity and photostability along the NR length show strikingly different profiles relative to those on conventional polymeric platforms.^{10,11,29} Unlike the spatially uniform signal observed on polymers, both the magnitude and temporal stability of the fluorescence signal from fluorophore-coupled biomolecules on ZnO NRs were not only much increased relative to those on polymers but also highly intensified at the NR ends relative to the NR main body. This effect was later revealed to stem from the fact that the fluorophore-emitted signals are effectively guided as surface evanescent waves along the NR and through the optical cavity of the subwavelength-waveguiding ZnO NR medium before they are finally radiated out to the far field from the two NR ends.^{10,11,28} We have subsequently determined various nanomaterial- and biomolecule-related factors influencing the degree of *FINE (DoF)*.^{10,11,28} The *DoF* serves as a measure of the degree of signal enhancement at ZnO NR ends with

respect to the NR middle. *DoF* is the ratio quantified as the difference in the average fluorescence intensity measured at the end versus the middle of the NR divided by the average intensity measured on the main body. By considering the nanomaterial factors governing *FINE*, we have shown that the *DoF* is larger for longer NRs and for NRs oriented vertically away from the underlying substrate.¹⁰ By taking the biomolecular factors into consideration for evaluating *FINE*, we have also shown that fluorophores of shorter emission wavelengths yield a higher *DoF* than fluorophores with longer wavelength emission.¹⁰ Despite these significant findings on the biomolecular fluorescence enhancement profiles on ZnO NRs, the important optical parameter of light polarization was never taken into account before. All measurements were carried out using unpolarized light in our previous studies and, therefore, the *FINE* effect was measured and discussed entirely under unpolarized settings so far.

Yet, polarization plays a very important role in the interaction of light with matter and can fundamentally change the optical measurement outcomes in elastic and inelastic scattering, absorption, and reflection. In particular, polarization has proven to be a powerful mode of sensing in biodetection. For example, molecular-level structural organizations of biomolecular assemblies (DNA or cytoskeletal protein filaments) can be revealed by performing polarized fluorescence imaging which, in turn, can provide information crucial to understanding their biological functions.³⁰ In another example, the crystallization mechanism of amyloid was construed by investigating the amyloid deposits in Alzheimer's disease plaques with polarized light microscopy.³¹ Hence, characterizing and controlling polarization-derived effects in various optical devices and sensors can be extremely useful not only for well-regulated light manipulation but also for accurate signal interpretation. Similarly, the optical phenomenon of *FINE* may be strongly affected by light polarization, but this aspect has never been systematically investigated. At the same time, recent progresses in optically promising materials have continued to push device and sensor miniaturization^{32–38} by further reducing the size of the active optical elements within the device via the employment of single nanomaterials instead of their ensembles. Therefore, it is important to elucidate the precise nature of the discrete interaction of polarized light with individual nanomaterials. However, very little information on polarized light interactions with individual semiconducting oxide nanorods is currently available to draw insight from, especially for those systems which are coupled with fluorophore emission and have important pertinent implications in biodetection.

Herein, we elucidate the exact roles of light polarization states in the optical phenomenon of *FINE* by systematically examining the optical responses of individual ZnO NRs coupled with a model fluorophore, fluorescein (Flu), under different polarization settings. The enhanced fluorescence signals observed on the ZnO NRs under varying polarized light configurations are analyzed spatially as a function of both NR tilt angle and position along the length of the NRs. The optical responses of the ZnO NRs are subsequently assessed for the presence of *FINE* and the polarization-resolved *DoF* values are quantified in order to find the optimal conditions yielding a maximum *DoF*. We unambiguously show that the *FINE* effect is present for all NRs under all polarization configurations. We then demonstrate that the *DoF* is strongly influenced by the light-matter interaction geometries between the polarization direction and the NR orientation. We reveal the precise roles of

light polarization in the mechanism of the *FINE* phenomenon and the magnitude of the *DoF*, providing the groundwork central to comprehending the extent of the *FINE* behavior observed on fluorophore-coupled ZnO NRs. These understandings can be highly beneficial and applicable to optimizing fluorescence signal outputs, quantifying fluorescence signals, and promoting new fluorescence-based biosensor applications of ZnO NRs.

Experimental Methods

ZnO NRs were synthesized in a home-built horizontal tube furnace using a chemical vapor deposition method, similar to the previously described procedures.^{39–42} Using 20 nm Au colloids (Ted Pella, Inc.; Redding, CA.) as the catalysts, subsequent growths of ZnO NRs were carried out on a Si growth substrate (Silicon Quest International Inc., San Jose, CA). The source materials, 0.45 grams of a 2:1 mixture of graphite (99%) to 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 cm downstream. The furnace was heated to 950 °C for 15 min to 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. Vertically-grown ZnO NRs were sonicated off from the growth substrate and dispersed in ethanol. A drop-wise deposition of the ZnO NRs in ethanol onto a clean Si wafer led to NRs lying flat on the Si surface. The NR samples were then treated with N₂ plasma in a Harrick PDC-32G cleaner at a setting of 18 W radio frequency. For morphological characterization of the ZnO NRs, the samples were imaged using a FEI/Philips XL 20 scanning electron microscope (SEM) operating at 20 kV. Fluorescein (Flu), one of the most common fluorophores used in bioassays, served as the model fluorophore in our polarization controlled fluorescence study on ZnO NRs. A powder form of Flu linked to biotin was received from EMD Milipore Corp. The dye molecules were then reconstituted per manufacturing recommendations and diluted appropriately to obtain desired concentrations in deionized water. The absorption and emission maxima of Flu occur at approximately 490 nm and 520 nm, respectively. A volume of 100 µL Flu solution in a desired concentration was then deposited directly on top of the ZnO NRs. The fluorescence panels summarized in this paper were all taken using 170 µg/mL Flu. The samples were kept in a humidity-controlled chamber protected from light for 5 min. The samples were subsequently rinsed with an ample amount of deionized water and dried with a gentle stream of N₂, immediately before fluorescence measurements. All optical measurements were carried out using a Zeiss Axio Imager A2M microscope (Carl Zeiss, Inc.; Thornwood, NY) equipped with a Zeiss AxioCAM HRm digital camera. All fluorescence images were acquired using a strain-free, oil-immersion, objective lens of Zeiss EC Epiplan-NEOFLUAR Oil Pol with 50x magnification (numerical aperture, NA, of 1.0). For examination in air under bright field, a dry objective lens of 50x Zeiss EC Epiplan-NEOFLUAR (0.8 NA) was used instead. The microscope setup included a polarizer and an analyzer that were removable as well as rotatable in 360 degrees (deg). The polarization controlled measurements were carried out by varying the polarizer/analyzer rotation to select for specific excitation and collection polarization states. The fluorescence excitation was provided by a 120 W Hg vapor lamp (X-Cite 120Q). The spectroscopic setting of the filter cube used was 450–490 nm excitation and 510–540 emission with 495 nm long pass filter.

The fluorescence data were collected from individual ZnO NRs coupled with Flu in a dark room with each image taken under 2 s exposure of excitation light. The images were analyzed using Zeiss AxioVision, ImageJ (a Java-based program), and Origin 8.5 (OriginLab Corp.).

Results and Discussion

Investigating *FINE* of Individual ZnO NRs under No Polarization and Polarization Control

The experimental setup for our polarization-controlled fluorescence measurements is schematically shown in Figure 1(A). Two polarizers were used in the optical setup involving a cross-polarizer setting. A polarizer (P) was placed before the fluorophore-coupled ZnO NR sample to control the polarization direction of the excitation light and an analyzer (A) was mounted after the sample to collect the fluorescence emission polarized along a specific direction. Figure 1(A) also displays our laboratory coordinates for the polarizer and analyzer angles, as defined with the arrows in the north-south (0 deg) and east-west (90 deg) directions corresponding to P0, A0, P90, and A90. The tilt angle of the NR, lying flat in the sample plane, is defined as θ and it refers to the angle formed by the long axis of the NR with respect to the north-south direction. NRs with the tilt angle of 0 and 90 deg, i.e. NR0 and NR90, are also referred to as vertical and horizontal NRs, respectively. For the measurement cases involving no polarizer and/or analyzer, the pertinent optical elements are removed from the beam path. Representative SEM images of our gas-phase synthesized ZnO NRs are displayed in Figure 1(B). The ZnO NRs exhibit a highly crystalline wurtzite structure with well-defined basal facets at the two ends of the NRs and prismatic facets on their main bodies, as shown in the left and right SEM panels at the bottom of Figure 1(B). The long axis of the NR corresponds to the c-axis of the wurtzite crystal, $\langle 0001 \rangle$, as indicated in the SEM panels. The lengths and diameters of the ZnO NRs used in our measurements are typically in the ranges of 3–10 μm and 150–350 nm, respectively.

Typical fluorescence emission profiles obtained from fluorophore (Flu)-coupled ZnO NRs are presented in Figure 2 for the cases measured with no polarizers (A) and under two polarizers (B). The fluorescence panel in Figure 2(A) with all polarizations allowed during excitation and collection clearly shows the characteristic *FINE* phenomenon we have previously reported.^{10,11,15,28,43} The unique behavior of *FINE* originates from the coupled and waveguided emission from the fluorophores placed on top of the ZnO NR which travels through the NR via the mechanisms of subwavelength waveguiding and surface evanescent wave propagation.^{10,11,28} This optical signal is highly intensified and spatially localized at the NR termini, as clearly displayed in the fluorescence intensity graph plotted as a function of the position along the long axis of the NR in the right panel of Figure 2(A).

The fluorescence panels shown in Figure 2(B), on the other hand, were acquired by precisely controlling the light polarization states both for the excitation and collection. Two individual ZnO NRs, one in a vertical and the other in a horizontal orientation, i.e. NR0 and NR90, were examined in Figure 2(B) under the settings of P0A0 (left) and P90A90 (right). The brightness and contrast of the fluorescence panels in Figure 2(B) were adjusted to show the effects of the polarizer and the analyzer more clearly. Although only qualitatively seen in the fluorescence images, the highly intensified fluorescence signal located at the NR ends

relative to that of the NR main body is more pronounced in the horizontal relative to the vertical NR under the P0A0 configuration. The vertical NR seems to have the fluorescence emission distributed relatively evenly across the entire NR. In comparison, for the polarization setting of P90A90, it is the vertical NR relative to the horizontal NR that shows stronger fluorescence emission at the NR ends relative to the main body. These observations indicate that the *FINE* phenomenon and its *DoF* may be strongly coupled to the light-matter interaction geometry defined by the NR tilt angle and the light polarization direction.

Characterization of NR Position-Dependent Signal Intensity under Polarization

We further investigated the precise effects of the light-matter interaction geometry on the spatial distribution of the fluorescence signal along the main axis of individual ZnO NRs. Raw emission intensity values, obtained from the NR0 and NR90 under the two polarization conditions of P0A0 and P90A90, were systematically evaluated by performing the operations of P0A0–P90A90 and P90A90–P0A0 in order to quantitatively compare the fluorescence signals measured along the ZnO NRs. As a result, the net fluorescence intensity variations along the different positions on each NR can be unambiguously resolved in the processed fluorescence panels. These results are summarized in Figure 3. The fluorescence emission from a vertical NR would be expected to yield the highest (the lowest) intensity under P0A0 (P90A90), since a NR with its orientation parallel as opposed to perpendicular to the excitation polarization will produce a higher signal. The A0 and A90 settings in P0A0 and P90A90 simply correspond to the analyzer conditions co-aligned with the polarizer directions, permitting the largest signal to be collected per given polarizer setting. Hence, the operation of P0A0–P90A90 is expected to yield net positive (negative) fluorescence signals for a vertical (horizontal) NR, regardless of the position along the NR. The P0A0–P90A90 fluorescence panel, therefore, is anticipated to portray a bright NR0 and a dark NR90. The reverse operation of P90A90–P0A0 is anticipated to result in net positive (negative) emission signals for a horizontal (vertical) NR, rendering a bright NR90 and a dark NR0. These trends are presumed no matter which positions on the NR are analyzed for the intensity differences between the two polarization settings.

However, as seen in Figure 3, our experimental outcomes show that the net emission signal is strikingly NR position-dependent which, under certain polarization conditions, led to a unique effect at the NR ends much different than the predictions made above. Panels provided in Figures 3(A) and (B) are the direct outcomes resultant from subtracting the raw fluorescence intensities taken under P0A0 and P90A90 from each other. As clearly evidenced in Figures 3(A) for the P0A0–P90A90 process and 3(B) for P90A90–P0A0, the trends of the fluorescence intensities measured at the two NR ends were the opposite of the signals from the NR main body. The fluorescence panel in Figure 3(A) shows that, under P0A0–P90A90, a bright signal was yielded for the main body (labelled as position 2) of the NR0 whereas the two ends of the same NR (positions 1 and 3) were dark. As for the NR90 under the same operation, the main body (position 5) was dark whereas the two NR ends (positions 4 and 6) showed strong and bright net signals. This observation suggests that, when the excitation polarization is perpendicular to the NR as is the case for the NR90 under P0A0, the emission behavior of the NR ends does not follow the expected trends. They not only exhibit net fluorescence signals but also the magnitudes are surprisingly higher than the

end signals of NR0 under P0A0. This is a very intriguing behavior since the fluorescence signal from an excitation case perpendicular to the NR long axis is expected to be much lower than the parallel polarization scenario. But, in fact, our observations clearly demonstrate that much enhanced emission can be seen at the NR ends when the excitation polarization is perpendicular to the NR.

The 2D surface map and the 3D contour plots corresponding to the fluorescence panel in Figure 3(A) further illustrate quantitatively the NR position-specific and tilt angle-dependent, net fluorescence intensities for this polarization setting. The results show that the main body signal from the NR0 coincides with the predicted outcome of having a net positive intensity under P0A0–P90A90. This can be seen by the vertical NR in the 2D and 3D graphs with its signal continuously present in the positive domain along the NR main body. More interestingly, the data also reveal that the ends of the NR0 distinctively have an opposite, net negative intensity for the same operation, unlike the expected net positive signal anticipated both on the NR main body as well as at its ends. Similarly, for the NR90 under P0A0–P90A90, the main body yielded the expected dark net intensity but the two ends of the NR90 showed markedly higher, net positive signals. In fact, the signals at the ends were very strong although the signals from the rest of the NR positions show the expected, dark emission pattern. This interesting behavior at the NR ends indicates that the two ends of the NR90, unlike the case of the main body, produce much higher fluorescence signals when the polarization excitation is perpendicular rather than parallel to the NR tilt angle.

The same unexpected effect can be seen in the P90A90–P0A0 outcomes as summarized in Figure 3(B). The end (positions 1 and 3) of the NR0 and the main body (position 5) of the NR90 showed net positive intensities whereas the main body (position 2) of the NR0 and the ends (positions 4 and 6) of the NR90 exhibited net negative intensities. As were the trends in Figure 3(A), the polarization-dependent emission of the fluorophore-coupled ZnO NRs exhibited a clear difference between the NR ends and the main body. Regardless of the NR tilt angle, the net fluorescence intensity after the operation yielded opposite signs between the main body and ends of the NR. The net signals from the NR main bodies in Figure 3(B) were as expected, resulting in the net positive (negative) intensity for the NR90 (NR0). However, at the ends of the two NRs, the same unusual behavior pertaining to a much stronger fluorescence signal was yielded when the excitation polarization was perpendicular to the NR. To sum up, when the NR tilt angle and excitation polarization are parallel to each other, the NR main body exhibits a stronger fluorescence compared to the perpendicular case, as expected. The NR ends, on the other hand, have higher fluorescence signals when the excitation polarization is perpendicular instead of parallel to the NR long axis. Although representative sets of data are shown in Figure 3, these phenomena were persistently observed from a large number of ZnO NRs used in the analysis, a total of more than 50 NRs.

NR Orientation-Dependent Intensity Profiles under Polarization

In addition to NRs with the tilt angle in the two orthogonal directions discussed above, similar analyses were carried out for NRs of arbitrary tilt angles. Figure 3(C) summarizes the NR tilt angle dependence on the fluorescence emission pattern under controlled

excitation and collection polarization configurations. Based on the characteristic fluorescence patterns after the operations of P0A0–P90A90 and P90A90–P0A0, ZnO NRs of different θ were categorized into three groups of I, II, and III. When θ of a NR is less than $\sim 40^\circ$, as for the NRs in the group I, the spatial distributions of the fluorescence emission along the NRs yield the same characteristics as the vertical NR in Figures 3(A) and 3(B). In this case, the P0A0–P90A90 operation results in a continuously present, net positive signal on the main body and net negative signals on the NR ends. Under the opposite P90A90–P0A0 operation, the positive and negative intensity areas along the NR length reverse. On the other hand, NRs with θ greater than $\sim 50^\circ$ in group II show the same trends explained for the horizontal NR in Figures 3(A) and 3(B) instead. For the NRs in II, the spatial distributions of the fluorescence emission reflect a net positive signal from P90A90–P0A0 that is continuously observed on the main bodies, whereas the NR ends have net negative signals. When θ is between 40 and 50 deg as categorized in group III, the fluorescence images of ZnO NRs show much different, intermittent emission profiles under both P0A0–P90A90 and P90A90–P0A0. Examples of these discontinuous emission signals can be seen in the P0A0–P90A90 panel (top) and P90A90–P0A0 panel (bottom) obtained from the same ZnO NR with a tilt angle of 47 deg.

***FINE* and *DoF* as a Function of NR Orientation, Polarizer, and Analyzer**

In addition to controlling the excitation polarization, we systematically varied the analyzer rotation to examine the distinctive emission polarization states as a function of the position along the NR long axis during fluorescence signal collection. The representative fluorescence intensities, measured along the different positions on fluorophore-coupled ZnO NRs while varying the polarizer and analyzer angles, are displayed in the 3D contour plots and 2D surface maps in Figure 4. The different positions along the ZnO NR axis are indicated as LE, OQ, M, TQ, and RE, denoting for the left end, one quarter of the NR length in from the LE, middle, three quarters of the NR length in from the LE, and the right end, respectively. The left and right panels in Figure 4 correspond to the data for a vertical and a horizontal NR, respectively. In each panel, 3D and 2D fluorescence profiles for the same NR are shown pairwise. The overall fluorescence intensity profiles along the NR length confirm the presence of the *FINE* behavior, regardless of the NR tilt angle or the polarizer direction. In general, as the analyzer rotates further away from the polarizer angle and, therefore, increasingly deviates from the parallel alignment between the two polarizers, the fluorescence signal decreases as expected for a cross polarizer setting. These tendencies can be seen both for the vertical (left panels) and horizontal (right panels) NR.

Although the *FINE* behavior was present ubiquitously, its degree (*DoF*) varied considerably between the different conditions specified in Figure 4. Hence, the most significant observation in Figure 4 related to *FINE* is the dramatic difference in the *DoF* between the two polarization cases. The *DoF* can be expressed as the average intensity difference between the end and the middle divided by the intensity in the middle. For both the NRs of vertical and horizontal orientations, the *DoF* observed was the highest when the NR tilt angle was orthogonal to both the excitation polarization and analyzer direction. These effects are clearly evidenced in the 2D and 3D plots shown at the bottom left (top right) panel for the vertical (horizontal) NR. Relative to the fluorescence intensity profiles on the NR

parallel to the excitation polarization, highly concentrated signals at the two NR ends compared to the main body is evident in the 3D and 2D plots of the NRs oriented perpendicular to the excitation polarization, signifying a strongly pronounced *DoF*. These results indicate that a much more pronounced *FINE* effect and the greatest contrast between the fluorescence intensities observed on the NR ends versus middle will emerge when the NR tilt angle is perpendicular to the excitation polarization.

The plots of fluorescence intensity versus analyzer rotation in Figure 5 were obtained from a horizontal ZnO NR while controlling the excitation polarization. The plots in Figures 5(A) and 5(B) display the data for the case of $P \parallel \text{NR}$ (i.e. P90 and NR90) and $P \perp \text{NR}$ (i.e. P0 and NR90), respectively, while keeping the same fluorescence intensity scales. The red symbols corresponding to the NR end signals are shown together with the blue symbols for the NR main body signals. Lines inserted through the data points are a $\cos^2\phi$ fit where ϕ is the angle between the polarizer and the analyzer. It was found that the intensities at the NR ends are always higher than those of the NR main body, regardless of the polarizer or analyzer rotation. In addition, as repeatedly seen in the previous data, the *DoF* is much larger for the $P \perp \text{NR}$ geometry than for $P \parallel \text{NR}$. This can be referred from the larger extent of separation between the NR end (red) and main body (blue) data points for $P \perp \text{NR}$ at a given analyzer angle compared to those in the $P \parallel \text{NR}$ set. Specifically for the $P \parallel \text{NR}$ setting, the fluorescence intensities both for the NR end and main body signals follow a $\cos^2\phi$ dependence as shown by the curve fits added to each set of the data, obeying Malus' law. The law predicts maximum (minimum) intensities when ϕ is 0 (90) deg. For $P \perp \text{NR}$, on the other hand, the analyzer angles producing the maximum and minimum intensities are no longer the same for the NR ends and main body, as they were for $P \parallel \text{NR}$. Under $P \perp \text{NR}$, the analyzer angle producing the largest intensity on the NR ends corresponds to the angle yielding the lowest intensity on the NR main body and vice versa. The data show a phase difference of 90 deg between the end and main body signals. Under $P \perp \text{NR}$, the fluorescence intensity of the NR ends, same as before, increased as the analyzer became more in parallel with the polarizer.

The illustrations above the data plots in Figures 5(A) and 5(B) depict the excitation polarization direction as well as the dominant emission polarization states as a function of the different position on the ZnO NR. The black arrow marked as Ex displays the excitation polarization setting of P90 and P0 in Figures 5(A) and 5(B), respectively. The white rectangle denotes for a horizontal ZnO NR. Red and blue arrows of varying strengths and directions are marked on the white rectangle to portray the emission polarization states corresponding to the fluorescence intensity data below. In Figure 5(A) for example, the leftmost schematic inside the yellow shaded area depicts the scenario of A90 (and the equivalent A270) under P90 which yielded the maximum signal intensities for the NR ends and main body. This condition corresponds to emissions polarized parallel to the NR long axis. The larger fluorescence intensity on the NR ends relative to the main body is reflected in the strength of the red arrow (three solid lines) relative to the blue (two solid and one dashed lines). The middle schematic corresponding to A180 (and its equivalent angle of A0) displays the minimum signals found on the NR ends as well as on the main body. In this case, all along the NR length, the polarization direction of the fluorescence collection is perpendicular to the NR axis and the collected intensities are weaker than the previous case,

although the end signal is still higher than the main body. The schematic drawing provided in Figure 5(B) can be similarly understood for which the direction of the arrow with respect to the NR axis shows the emission polarization state collected and the magnitude of the arrow correlates with the fluorescence intensity.

The diagram in Figure 5(C) predicts the measurement outcome for a case involving all scenarios of the analyzer angles sketched in Figure 5(A), whereas the illustration in Figure 5(D) can be considered as the sum of all analyzer angles depicted in Figure 5(B). Therefore, the resulting outcomes in Figures 5(C) and 5(D) will embody the condition with no analyzer under $P \parallel \text{NR}$ and $P \perp \text{NR}$, respectively. As seen by the much greater differences in the overall magnitude of the arrows positioned on the NR ends versus the middle in Figure 5(D) relative to 5(C), it can be deduced that the influence of the excitation direction with respect to the NR tilt angle on the *DoF* will be significant even for the no analyzer case. The analysis further implies that the same propensity, i.e. an increased *DoF* for the case of $P \perp \text{NR}$ relative to $P \parallel \text{NR}$, will be expected for the measurement setting involving no analyzer. Lastly, the illustration shown in Figure 5(E) depicts a combined polarization case involving all excitation and collected emission states shown in Figures 5(A) through 5(D). Therefore, the schematic outcome in Figure 5(E) can describe the polarization-insensitive measurement cases of the fluorophore-coupled ZnO NRs, as seen in the representative image displayed in Figure 2(A). In addition to the data in Figure 2(A), the fluorescence data in our previously reported works on *FINE* were all taken without any control over specific polarization directions of the excitation or collected emission. The systematic measurements and analyses discussed in Figure 5, hence, can provide the specific effects of polarization states on the *FINE* behavior of ZnO NRs. At the same time, by collectively considering the contributions from all polarization states, these findings also offer consistent explanations for *FINE* previously observed under no polarization control.

***FINE* and *DoF* under Polarizer Only and Analyzer Only**

As control tests based on the previous discussion, similar fluorescence measurements were carried out on Flu-coupled ZnO NRs, but this time without involving the polarizer or analyzer. The condition for no polarizer (no analyzer) permits all oscillation directions of the electric field during excitation (emission). Subsequently, the experimental data from these single polarizer experiments were compared to the predicted outcomes summarized as the schematics in Figure 5. The 2D and 3D maps in Figure 6(A) display the spatially resolved fluorescence intensity of a vertical (left) and a horizontal (right) ZnO NR while involving only the polarizer to direct the excitation polarization. The plots display the fluorescence intensity as a function of the polarizer angle and the position along the NR length. In this setting with no analyzer present in the signal pathway, the position-dependent fluorescence intensities on both the vertical and the horizontal NR in the left and right panels, respectively, faithfully show the phenomenon of *FINE* with the stronger NR end emission relative to the middle. In both the vertical and horizontal NR data with no analyzer, it is clear that the fluorescence intensification at the two ends relative to the main body is greater for the light-matter interaction geometry of $P \perp \text{NR}$. This observation agrees with the conclusions deduced from the schematic representations inclusive of all collected emission

directions in Figures 5(C) and 5(D), in which an enhanced *DoF* was found for the $P \perp$ NR case in Figure 5(D) compared to the $P \parallel$ NR setting in Figure 5(C).

The fluorescence intensity plots shown in Figure 6(B) represent the measurement cases involving only the analyzer to examine the emission polarization states, while allowing all excitation polarization directions. The 3D and 2D plots in these panels, therefore, map the fluorescence intensity as a function of the analyzer angle and the position on the NR. Under this setting with no polarizer, the fluorescence signal did not show any significant variations along the NR position or analyzer rotation. The data panels for the vertical (left) and the horizontal (right) NR exhibited the same behavior. Compared to the cases of the polarizer/analyzer or the polarizer only, these outcomes indicate that the NR position dependence on *DoF* will be reduced when the excitation light is unpolarized, irrespective of the NR tilt angle.

Quantitative Comparison of *FINE* and *DoF* between Polarizer/Analyzer, Polarizer Only, and Analyzer Only Settings

These aforementioned findings were consistently observed from NRs of all tilt angles although representative results from selected tilt angles are shown in Figure 6. Overall, the data presented in Figure 6 indicate that excitation polarization directions can significantly influence the fluorescence intensity profiles spatially along the ZnO NR, with the highest *DoF* occurring when the NR is angled perpendicular to the excitation polarization. We further quantitatively evaluated the *DoF* and its dependence on the excitation and emission polarizations. The graphs in Figure 7 chart the *DoF* on the y-axis and the two polarizer angles on the x-axis. The *DoF* values were calculated using the equation, $\frac{I_{avg,end} - I_{avg,mid}}{I_{avg,mid}}$, where I_{avg} is the average fluorescence intensity and the subscript of *end/mid* denotes for the basal/prismatic facet of the ZnO NR crystal. Figures 7(A) and 7(B) are from the measurements using both polarizers, whereas data provided in Figures 7(C) and 7(D) are from single polarizer experiments. In all data points presented in Figure 7, the *DoF* is found to be greater than zero, indicating higher end than middle signals and, accordingly, the presence of the *FINE* phenomenon in all cases. For the two polarizer measurements, regardless of the NR tilt angles, the *DoF* is the largest for $P \perp$ NR. In both panels of Figures 7(A) and 7(B), the data and curve fit for $P \perp$ NR are shown in purple as solid symbols and lines, respectively. The *DoF* values corresponding to the $P \perp$ NR case lie above those for $P \parallel$ NR in both Figures 7(A) and 7(B). In addition, the influence of the analyzer rotation on the slope change was much more pronounced when the polarization was perpendicular to the NR tilt angle. The graphs also indicate that, to achieve a larger *DoF*, the $P \perp A$ ($P \parallel A$) setting should be used for the $P \parallel$ NR ($P \perp$ NR) case. The largest *DoF* is expected when the measurement setting of both the polarizer and analyzer being orthogonal to the NR, i.e. ($P \parallel A$) $\perp$ NR. The same outcome can be deduced from the data plots provided in Figure 5(B) in which the intensity curve for the NR end inversely followed that of the main body. The fluorescence intensity observed on the NR main body was lowest for the perpendicular NR with respect to the excitation polarization while the polarizer and the analyzer are set in parallel. Therefore, combined with the fact of the NR ends having their highest fluorescence intensities under those conditions, the spatial distribution of the fluorescence emission along the NR length will yield the highest *DoF* for ($P \parallel A$) $\perp$ NR. In contrast, the *DoF* is much

lower when the polarizer is parallel to the NR. Under this condition, the fluorescence intensity on the NR main body increases considerably, especially when the setting reaches the condition of $P \parallel A$. This eventually results in smaller values for $\frac{I_{avg,end} - I_{avg,mid}}{I_{avg,mid}}$.

By varying only the excitation polarization while allowing all emitted polarization states in Figure 7(C), the same trend of larger *DoF* for $P \perp NR$ continues, reaching the *DoF* value of 0.5 ($I_{avg,end} = 1.5 I_{avg,mid}$) on average. The effect is observed regardless of the NR tilt angle. When varying analyzer rotations while allowing all excitation polarization, the *DoF* in Figure 7(D) exhibits much lower values and shows no significant changes with the different analyzer angle used. This, in turn, suggests that the *DoF* upon excitation with unpolarized light stays less affected than the case in Figure 7(C), regardless of the emitted polarization states or the NR tilt angle. This effect can be evidenced by the much shallower slopes in the data plots in both the top and bottom panels in Figure 7(D) relative to those in Figure 7(C). Overall, the *DoF* value measured under the unpolarized excitation setting is ~ 0.15 , equivalent to $I_{avg,end} = 1.15 I_{avg,mid}$.

These combined outcomes from our polarization-resolved measurements show important findings pertinent to *FINE* that have not previously been identified before when polarization effects were not considered. Our efforts of polarization-controlled measurements on fluorophore-coupled ZnO NRs unambiguously provide the different levels of excitation and emission polarization states contributing to the *DoF* for the two polarizer, single polarizer, and unpolarized cases. The varying nature and levels of contributions from the different polarization components to the *FINE* phenomenon on ZnO NRs were subsequently elucidated as a function of the position on the NRs. These results conclusively show that understanding the polarization effects is extremely important in the collection and interpretation of *FINE* signals.

Summary

In summary, we have elucidated the explicit roles that polarization plays in the enhanced fluorescence signal observed on fluorophore-coupled ZnO NR systems. By examining the spatially resolved, fluorophore-emitted signals along individual NRs under different excitation and emission polarization states, we unambiguously determine the effect of light polarization on *FINE* as well as on the *DoF*. We find that the phenomenon of *FINE* occurs regardless of the light-matter interaction geometry. However, the *DoF* is significantly influenced by polarization through its specific interaction geometry with individual ZnO NRs. The condition for producing the highest *DoF*, signifying the greatest level of fluorescence intensification observed at the NR ends with respect to the main body, is achieved when both the excitation and emission polarization states are perpendicular to the NR main axis. Measurements carried out with no polarization control yielded *DoF* values consistent with those estimated by considering collective contributions from all probed polarization states. The polarization-resolved mechanistic investigation of *FINE* and *DoF* in this study provides crucial insight into understanding the nature and extent of *FINE* observed from fluorophore-coupled, single ZnO NRs. Our efforts may advance many technologically important applications of ZnO NRs by enabling the controlled utilization of

polarization as an additional means to manipulate the propagation of optical signals through the NRs. Insights from this study may be also beneficial for custom tailoring position-dependent optical responses along the NRs and for accurately interpreting the NR-carried optical signals from analytes of interest.

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Figure 1.

(A) Schematics showing the key components of the experimental setup and the laboratory coordinates for the polarizer, analyzer, and NR tilt angles used in our polarization-controlled measurements of the fluorescence emitted from the fluorophores (Flu) coupled to the surfaces of individual ZnO NRs. (B) Representative SEM images of single ZnO NRs are displayed and the NR tilt angles as defined in (A) are marked next to a few NRs as an example. The ZnO NRs employed in our experiments exhibit wurtzite crystalline structures with well-defined, basal and prismatic facets on the NR end and main body as clearly shown in the zoomed-in SEM panels at the bottom.

(A) No Polarization Control

(B) Under Controlled Polarization

Figure 2.

(A) Typical fluorescence emission profiles obtained from Flu-coupled individual NRs are displayed. The emission signals were collected under the absence of any polarizer or analyzer in the excitation and detection pathways. The characteristic *FINE* behaviors observed from the fluorophore-coupled ZnO NRs are clearly identified from the much brighter two ends of the NRs due to the highly intensified fluorescence signal relative to the signal observed along the main body. (B) Fluorescence panels from two orthogonally located NRs, one with the tilt angle of 0 deg (vertical NR on the left in each panel) and the other of approximately 90 deg (horizontal NR on the right in each panel), were obtained by using the specific polarizer and analyzer settings of P0A0 (left panel) and P90A90 (right panel). The brightness and contrast of the fluorescence images are adjusted to show the different levels of emission at different areas on the NRs more definitively.

Figure 3.

(A) The fluorescence panel displays the outcome after the P0A0–P90A90 operation of the raw fluorescence intensity panels of the two NRs shown in Figure 2(B). Bright (dark) areas in the processed fluorescence panel, therefore, correspond to the NR regions whose fluorescence intensities under the P0A0 setting were measured to be higher (lower) than those with P90A90. The vertical and horizontal NRs exhibit drastically different behaviors. The vertical NR shows positive fluorescence intensity along its main body. In contrast, for the horizontal NR, positive fluorescence intensities are exhibited only at the two ends with a dark NR main body. The effects occurring at the two ends of the NRs, opposite of the main body results, are more clearly presented in the 2D surface map and 3D contour plot. The three key positions, the two ends and the main body, are marked on each NR with numbers for easy correlations between the results presented in the three panels. The positive, negative, and null intensities indicate the NR regions showing the raw intensity of P0A0 >

P90A90, P0A0 < P90A90, and P0A0 = P90A90, respectively, and they can be distinguished by the different colors in the plots. **(B)** The fluorescence panel displays the outcome from the P90A90–P0A0 operation of the raw fluorescence intensity from the same two NRs above. The bright and dark areas in (B) represent the reverse trend in the NR position-specific fluorescence intensity from what was described in (A). Yet, the same behavior of the main body intensity being higher (lower) for the polarizer being parallel (perpendicular) to the NR was observed. Also similar to (A), the net fluorescence intensity of the vertical NR persistently exhibited strong positive signals at the two NR ends despite the expected negative signals for the polarization case perpendicular to the NR. **(C)** Fluorescence emission patterns from the fluorophore-coupled ZnO NRs were evaluated as a function of the NR tilt angle (θ) and the results are categorized into three groups. ZnO NRs with θ less than 40 deg (group I) and greater than 50 deg (group II) exhibited continuous intensity patterns along the NR main body whose signals appeared entirely either in the positive or negative domain depending on the operation type of P0A0–P90A90 and P90A90–P0A0. On the other hand, NRs with θ in between these two angles, group III, always showed net intensity of the main body partially present in the positive (or negative for that matter) domain regardless of the operation type. NRs in group III yielded intermittent and discontinuous intensity patterns with alternating dark and bright regions along the NR main body, as shown in the two panels corresponding to the outcomes of P0A0–P90A90 (top) or P90A90–P0A0 (bottom), respectively, from the same ZnO NR of $\theta = 47$ deg.

Figure 4.

The 3D contour plots and 2D surface maps display the fluorescence signals from Flu-coupled ZnO NRs of the specified tilt angle and polarizer setting as a function of analyzer rotation and position along the NR. The polarizer settings used were 0 deg (top panels) and 90 deg (bottom panels) and two distinctive NR orientations of vertical (NR1, left panels) and horizontal (NR80, right panels) cases were examined. LE, OQ, M, TQ, and RE on the axis for NR position represent the left end, one quarter of the NR length in from the LE, middle, three quarters of the NR length in from the LE, and the right end, respectively. In these polarization-controlled measurements, the results in the 3D and 2D plots clearly show that the effect of *FINE* is much more pronounced when the polarization direction becomes perpendicular rather than parallel to the NR tilt angle.

Figure 5.

Typical fluorescence intensity profiles measured while varying the analyzer angle are displayed using a horizontal NR as an example. Fluorescence data shown in (A) and (B) correspond to the excitation polarization case of P90 and P0, respectively. The scales in the fluorescence intensity plots in (A) and (B) are kept the same. Schematics in (C) through (E) qualitatively depict the measurement cases employing only the polarizer with no analyzer (C and D) and neither the polarizer nor the analyzer (E). **(A and B)** Fluorescence intensity variations on the NR main body (open triangle in blue) and the NR end (open circle in red) are displayed in (A) as a function of the analyzer rotation while maintaining the excitation polarization parallel to the NR. Fluorescence intensity variations for the case of the excitation polarization perpendicular to the NR are shown in (B) on the NR main body (solid triangle in blue) and the NR end (solid circle in red) as a function of the analyzer rotation. The lines inserted in (A) and (B) are the $\cos^2\phi$ curve fits where ϕ is the angle between the polarizer and the analyzer. The schematic drawings above the data graphs in (A) and (B) visualize the different emission polarization states present along the different NR positions at representative analyzer angles using arrows of varying magnitudes and directions. **(C and D)** The schematic drawings represent all emission polarization states collectively per different NR position. Hence, the outcomes predict the emission intensity patterns along the NRs in the absence of the analyzer (i.e. all emitted polarization directions allowed during the fluorescence signal collection) for the excitation polarization parallel (C) and perpendicular (D) to the NR. **(E)** The schematic displays the expected fluorescence intensity profiles along ZnO NRs by combining the two outcomes in (C) and (D). Therefore, the output corresponds

to the fluorescence measurement scenario carried out with no polarization control, neither for the excitation nor for the emission.

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Figure 6. The paired, contour plots and surface maps display the fluorescence signals from the Flu-coupled ZnO NR of the specified tilt angle as a function of the position along the NR. The results correspond to the single polarizer cases involving **(A)** polarizer with no analyzer and **(B)** analyzer with no polarizer. The tilt angles for the vertical and horizontal NRs shown in (A) are NR8 and NR81, respectively, and those for the NRs shown in (B) are NR22 and NR83. When the excitation polarization was controlled while allowing fluorescence detection of all emitted polarization states, *FINE* effects at the NR ends similar to the cross polarization cases in Figure 3 were observed. Compared to the results from involving only the polarizer in (A), the fluorescence intensities observed for the no polarizer case in (B) did not show large variations either along the different positions on the NRs or with the analyzer angle.

Figure 7.

The degrees of *FINE* are charted for the two polarizer (**A and B**) and the single polarizer (**C and D**) cases. Curve fits (lines) are inserted through the data points (symbols) as a guide to the eye in all graphs. (**A and B**) The degrees of *FINE* are much higher for the polarization introduced perpendicular rather than parallel to the NR. The data showing polarization perpendicular to the NR tilt angle are plotted in purple in both (A) and (B), displaying the results from a vertical and a horizontal ZnO NR, respectively. (**C**) The *DoF* is enhanced for the excitation polarization case perpendicular to the NR and the values for the *DoF* are larger than the no polarizer case in (D). (**D**) When unpolarized light was used for the excitation instead, the analyzer rotation did not yield much difference in the *DoF*. Overall, the *DoF* was the weakest among the three cases of polarizer/analyzer, no polarizer/analyzer, and polarizer/no analyzer.