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# High Quantum Efficiency of Band-Edge Emission from ZnO Nanowires

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**Abstract** External quantum efficiency (EQE) of photoluminescence as high as 20% from isolated ZnO nanowires were measured at room temperature. The EQE was found to be highly dependent on photoexcitation density, which underscores the importance of uniform optical excitation during the EQE measurement. An integrating sphere coupled to a microscopic imaging system was used in this work, which enabled the EQE measurement on isolated ZnO nanowires. The EQE values obtained here are significantly higher than those reported for ZnO materials in forms of bulk, thin films or powders. Additional insight on the radiative extraction factor of 1-dimensional nanostructures was gained by measuring the internal quantum efficiency of individual nanowires. Such quantitative EQE measurements provide a sensitive, non-invasive method to characterize the optical properties of low

dimensional nanostructures and allow tuning of synthesis parameters for optimization of nanoscale materials.

Nanoscale materials have shown unprecedented capabilities in emerging technologies ranging from solar energy harvesting to biosensing.<sup>1-4</sup> One-dimensional semiconductor nanostructures have garnered particular interest due to their high-crystallinity, large aspect-ratio, and enhanced electronic and optical properties as compared to their bulk counterparts. While research and development of nanoscale light emitting and harvesting devices is burgeoning, a fundamental understanding of the photoconversion efficiency based on material quality of semiconductor nanostructures remains unclear. In particular, there is a lack of quantitative information on the intrinsic efficiency of exciton-photon conversion within such nanostructures and how it scales with sample morphology and injected carrier density.

External Quantum Efficiency (EQE) of semiconductors, which measures the absolute yield within a material from exciton creation to photon emission, is inherently tied to the photonic and optoelectronic properties. Therefore, both the measurement and the understanding of EQE are critical to optimize material qualities for applications such as solar cells and LEDs. Current methods of measuring this intrinsic optical property are often based on ensemble averaging and require additional knowledge of structural dimensions to extract values indirectly, which becomes increasingly inaccurate as the dimensions of the material approach nanometer scale. Such limitations present a significant roadblock for investigating and improving the optical quality of nanostructures, which are essential to the progression of technologies based on nanoscale materials.

In this letter we present a direct measurement of photoluminescence (PL) EQE from isolated semiconductor nanowires at room temperature. In contrast to the low EQE values typically reported for bulk semiconductor materials<sup>5-7</sup>, we found that the EQE of single-crystal ZnO nanowires can be higher than 20%. The high material quality was also indicated by an internal quantum efficiency (IQE) of 62%. Interestingly, the EQE became higher as the excitation power density increased which resulted in a

considerable discrepancy between the EQE values measured from high-density nanowire arrays and isolated nanowires. In addition, the EQE of ZnO nanowires was found to be very sensitive on the synthetic conditions. Changes in growth temperature from 860 C to 950 C resulted in over 10-fold variation in the band-edge EQE. Therefore, EQE measurement can be a non-invasive measure of low-dimensional material quality, and are vital to the development of future semiconductor optical devices.

ZnO nanowire arrays were grown epitaxially on  $\alpha$ -plane sapphire substrates using chemical vapor deposition.<sup>1</sup> SEM images (Fig 1a) show uniform and aligned nanowires with length and diameter approximately 15 – 20  $\mu\text{m}$  and 100 nm, respectively. Hexagonal faceting on individual nanowires (Fig. 1a inset) indicates single crystal structures consistent with previous reports.<sup>8</sup> Nanowire arrays were transferred onto UV-fused quartz substrates (Fig 1b) to allow photoluminescence studies on isolated nanowires. Using an integrating sphere customized with a microscopic imaging system (Supporting Information), the EQE values measured under 325-nm excitation can be correlated to specific nanowires using the corresponding PL images (Figure 1c inset). Most importantly, the ability to directly correlate optical properties from EQE measurements with structural properties by electron microscopy provides a powerful method of optimizing intrinsic material quality with nanoscale morphology.

PL spectra collected inside the integrating sphere (Fig. 1d) reveals strong band-edge emission and negligible defect emission in the visible region, which suggests highly crystalline ZnO nanowires with minimal point defects.<sup>9</sup> The low density of the nanowires on quartz results in high laser transmission through the sample, as seen in Figure 1d Inset. From the measured PL signal and absorption of the laser line, the EQE is determined by the equation:

$$\text{EQE} = \frac{PL_S - (1 - L_S / L_M) PL_M}{L_O (L_S / L_M)} \quad [1]$$

where  $PL_S$  and  $L_S$  are the integrated PL and laser signals when the laser directly hit the sample,  $PL_M$  and  $L_M$  are the integrated PL and laser signals when the laser missed the sample, and  $L_O$  is the integrated laser signal when no sample was present in the sphere.<sup>10</sup> In simpler terms, the numerator represents the total number of photons emitted by the sample minus the autofluorescence of the sphere itself, and the

denominator accounts for the total number of photons absorbed by the nanowires. A more detailed description of this calculation, including measurement calibration, can be found in the Supporting Information.

The band-edge EQE of the ZnO nanowires shown in Figure 1b was calculated at  $20\% \pm 3.1\%$  with an absorption of  $16\% \pm 5\%$  using  $2500 \text{ W/cm}^2$  excitation. This EQE value is significantly higher than reported values of ZnO powders (1 – 3%) using similar excitation and measurement schemes.<sup>6, 11</sup> Not only is the measured EQE of ZnO nanowires larger than that measured from high-purity ZnO powder (Figure S4, Supporting Information), it originates from bottom-up synthesized semiconductor nanostructures that offer functional geometries for device applications. Such high EQE values were achieved by optimization of nanowire growth with reaction temperature and oxygen pressure to produce nanowires with minimal point defects that are deleterious to band-edge emission. Additional reasons for such high EQE measured from ZnO nanowires will be discussed in later sections.

The prominent optical quality of our gas-phase grown ZnO nanowires was further verified by high IQE, the ratio of radiative events to total energy relaxation processes. At room temperature, energy relaxation in semiconductors is dominated by nonradiative processes.<sup>12</sup> On the other hand, at cryogenic temperatures it is assumed that phonon-assisted transitions within a crystal are virtually eliminated and all energy relaxation events are radiative. In other words, at sufficiently low temperatures the probability of exciton recombination resulting in a photon emission is considered to be 1. As the temperature increases, additional phonon modes become available and the probability for photon emission drops below 1. Therefore, the ratio of the PL intensity at room temperature to that at cryogenic temperatures (such as  $T=6 \text{ K}$ ) is defined as the Internal Quantum Efficiency (IQE) of the material.<sup>13</sup>

The IQE of a material can be related to the EQE by the equation:

$$EQE = IQE * EF \quad [2]$$

where the Extraction Factor (EF) is the probability of emitted photons within the crystal lattice reaching the surface and escaping into the far-field.<sup>14</sup> While IQE is independent of EF, the EQE is reduced for

small EF values. For direct bandgap semiconductors the EF can be low due to their high absorption coefficients ( $\sim 2 \times 10^5 \text{ cm}^{-1}$ )<sup>15</sup>, which increases the probability of photon reabsorption within the crystal lattice. In semiconductor nanowires, however, reabsorption is drastically reduced because the nanowire diameter is roughly 1 or 2 absorption lengths. Therefore, nanowires offer an ideal platform to determine the intrinsic EQE of a semiconductor material as opposed to microscale and bulk structures which underestimate this value due to increased reabsorption.

The IQE of isolated ZnO nanowires was measured at low temperature in a cryostage coupled to an optical microscope (Figure S5). Figure 2 shows the PL emission spectra collected from T=6 K to room temperature for the nanowire sample presented in Figure 1 where EQE=20%. The noticeable increase in PL intensity at a low temperature is caused by the suppression of non-radiative transitions. Assuming a radiative recombination probability of 1 at T=6 K, the IQE of ZnO nanowires is approximately 62%, as calculated by the ratio of the area under each curve (Figure 2 Inset). Knowing the overall EQE and the IQE of ZnO nanowires, the Extraction Factor can be determined from Eqn 2 to be roughly 30%, which suggests almost one third of all photons created from exciton recombination escapes from the nanowire into the far-field. This value is larger than recent studies on ZnO powder that contain EF values of approximately 10 – 12%<sup>6, 11</sup>, however in those reports ZnO crystals with diameters of 300 – 2000 nm likely reduced the percentage of photons that escape to the surface as compared to 100 nm diameter nanowires. Fundamentally, by maximizing the EF of a material using nanostructure geometries, the measured EQE achieves greater accuracy with respect to the intrinsic value, which underscores the significance of utilizing nanostructures for investigation of material properties.

Interestingly, the band-edge EQE of ZnO nanowires was found to be highly dependent upon the excitation power density. As the incident photon flux was increased under constant beamspot size, the emission spectra showed a super-linear increase in band-edge PL intensity (Figure 3a) while the optical absorption remained roughly constant. On the other hand, the PL emission around 500 nm, typically known as defect emission from ZnO, exhibited a sub-linear trend with the excitation power density. This inverse relation between band-edge and defect emission may be related to energy relaxation

pathways from the band edge (or near the band-edge) to defect states and other non-radiative channels. As the density of photogenerated carriers and excitons increases, defect and other non-radiative states may become saturated causing more photogenerated excitons to recombine directly via radiative band-edge emission. As shown in Figure 3b, the EQE of isolated ZnO nanowires increased significantly with excitation power density, until a saturation level was reached at very high power. It is worth noting that the EQE of dye solutions and polymer films measured with the same system remained constant regardless of excitation power (Figure S6).<sup>10, 16</sup>

Because of the dependence of semiconductor EQE on excitation power, the measurement of nanowire EQE is contingent on nanowire geometry relative to the excitation beam spot. In particular, it is important to avoid measuring an EQE value averaged between high- and low-power excitation regions which would falsely underestimate the material EQE. High-density array nanowires oriented axially along a focused laser beam experience vertical non-uniformity of the excitation power density along the nanowire axis due to their high absorption coefficient, and transverse non-uniformity due to the Gaussian distribution of the beam spot. In contrast, nanowires oriented perpendicular to the focused beam experience uniform excitation density over their 100 nm diameter, and the isolation of the nanowires reduced the transverse non-uniformity of the excitation. Consequently, ZnO nanowires transferred to a thin, dilute layer on quartz exhibited EQE higher than 20%, whereas the EQE of the vertically oriented nanowire arrays (from which the thin nanowire layer was transferred) was only measured to be 4% (Fig. 3c and 3d). Hence, the configuration of isolated ZnO nanowires oriented perpendicular to the incoming laser provides more accurate measure of EQE.

The band-edge EQE of ZnO nanowires depended critically on the synthetic growth parameters, and hence, provided a sensitive method for optimizing material quality. For semiconductor nanostructure growth by CVD, high temperatures are used to minimize crystal lattice defects.<sup>9</sup> However, above a certain temperature growth conditions become unfavorable and nanostructure material quality suffers.<sup>17</sup> Therefore, determination of the optimal growth temperature is necessary for high material-quality nanostructures with functional geometries. In Figures 4a and 4b the PL spectra and EQE values of ZnO

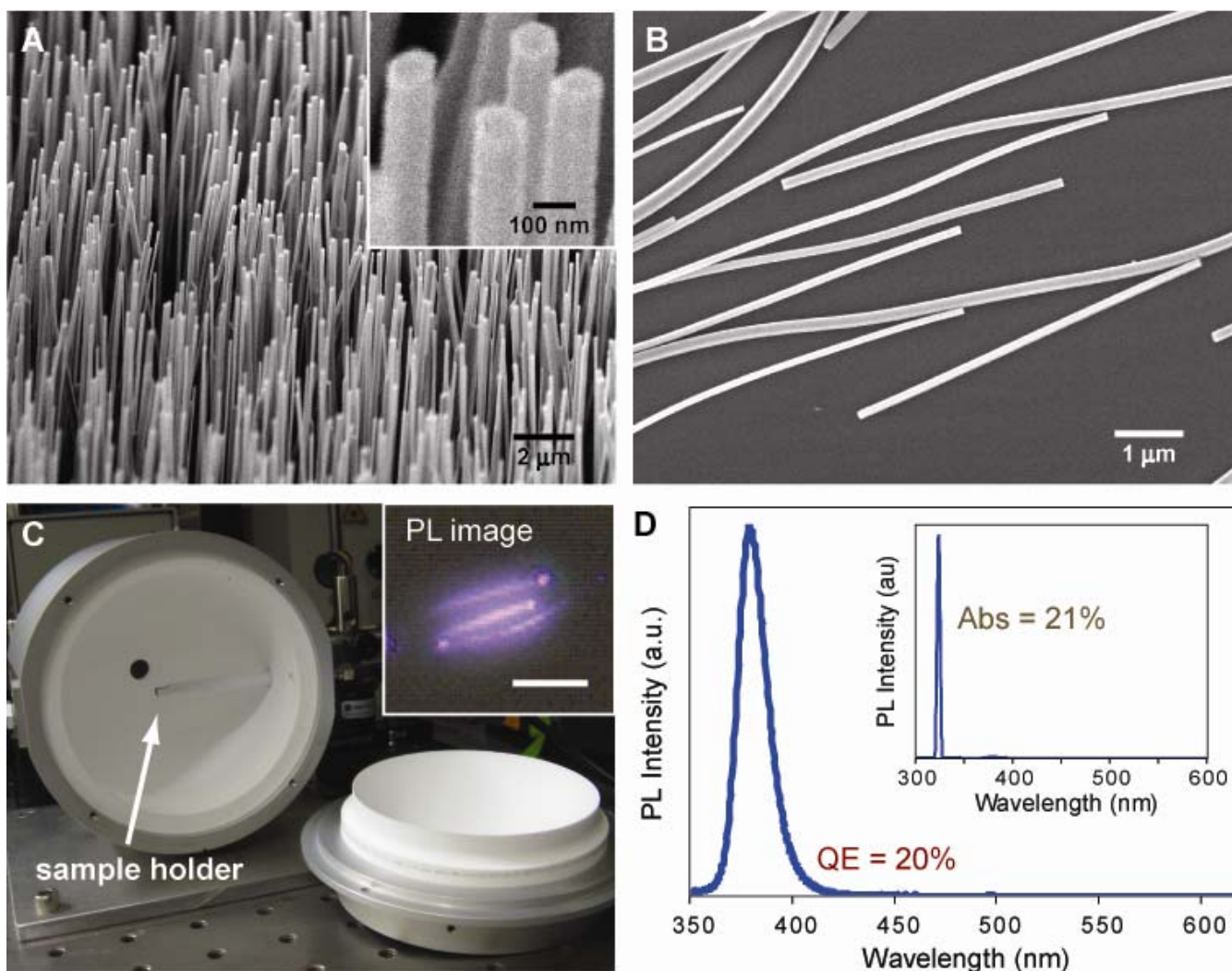


nanowires are plotted vs nanowire growth temperature, respectively. The highest EQE is observed at approximately  $T=910$  °C, which suggests the optimal conditions for crystalline nanowire growth, and minimization of non-radiative point defects, is achieved between 900 – 920 °C. Also apparent is the lower ratio of band-edge PL to defect PL at lower growth temperatures, which results from the increased density of crystal point defects and atomic vacancies. However, by optimizing local growth conditions with temperature and oxygen pressure the measured EQE of ZnO nanowires increased by an order of magnitude. This presents a powerful tool for optimizing the quality of nanoscale materials.

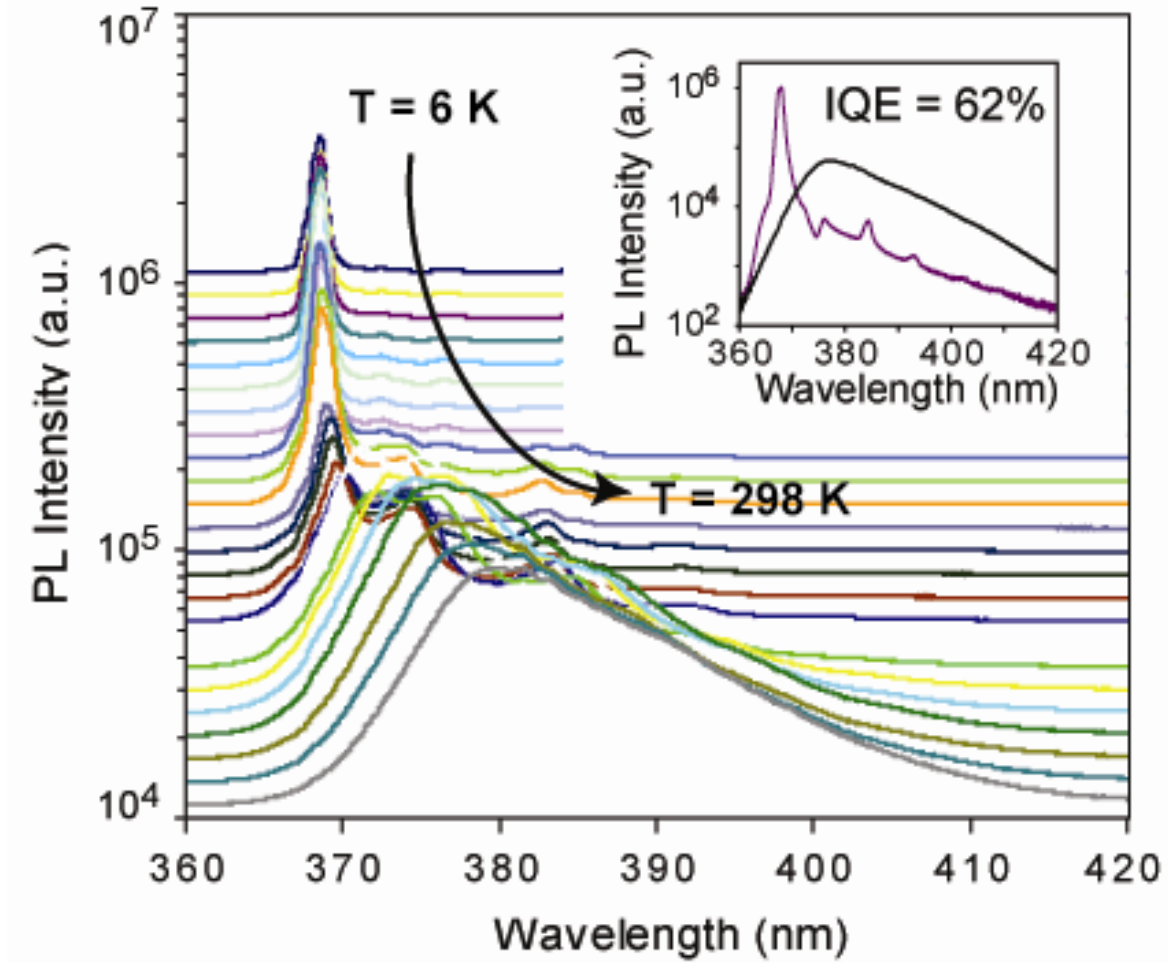
In summary, we have shown that band-edge quantum efficiency of solid-state ZnO nanowires can be as high as  $20\% \pm 3.1\%$ . This value is surprisingly higher than most previously reported values for bulk and nanostructured solid-state materials. We show the Internal QE is 62%, which suggests the Extraction Factor for photons inside a nanowire is roughly 30%. These optical quantities showed that ZnO nanowires synthesized using CVT methods are highly efficient emitters. More importantly, we found that the power dependent behavior of EQE relates as the derivative of PL intensity versus excitation power, which underscores the importance of achieving a highly uniform density of photo-generated carriers for accurate measurement of EQE. Therefore, measuring EQE from isolated nanowires provides an accurate method to characterize the intrinsic optical quality of low-dimensional materials, which may also be applied to other semiconductors showing excitation power-dependent photoluminescence.

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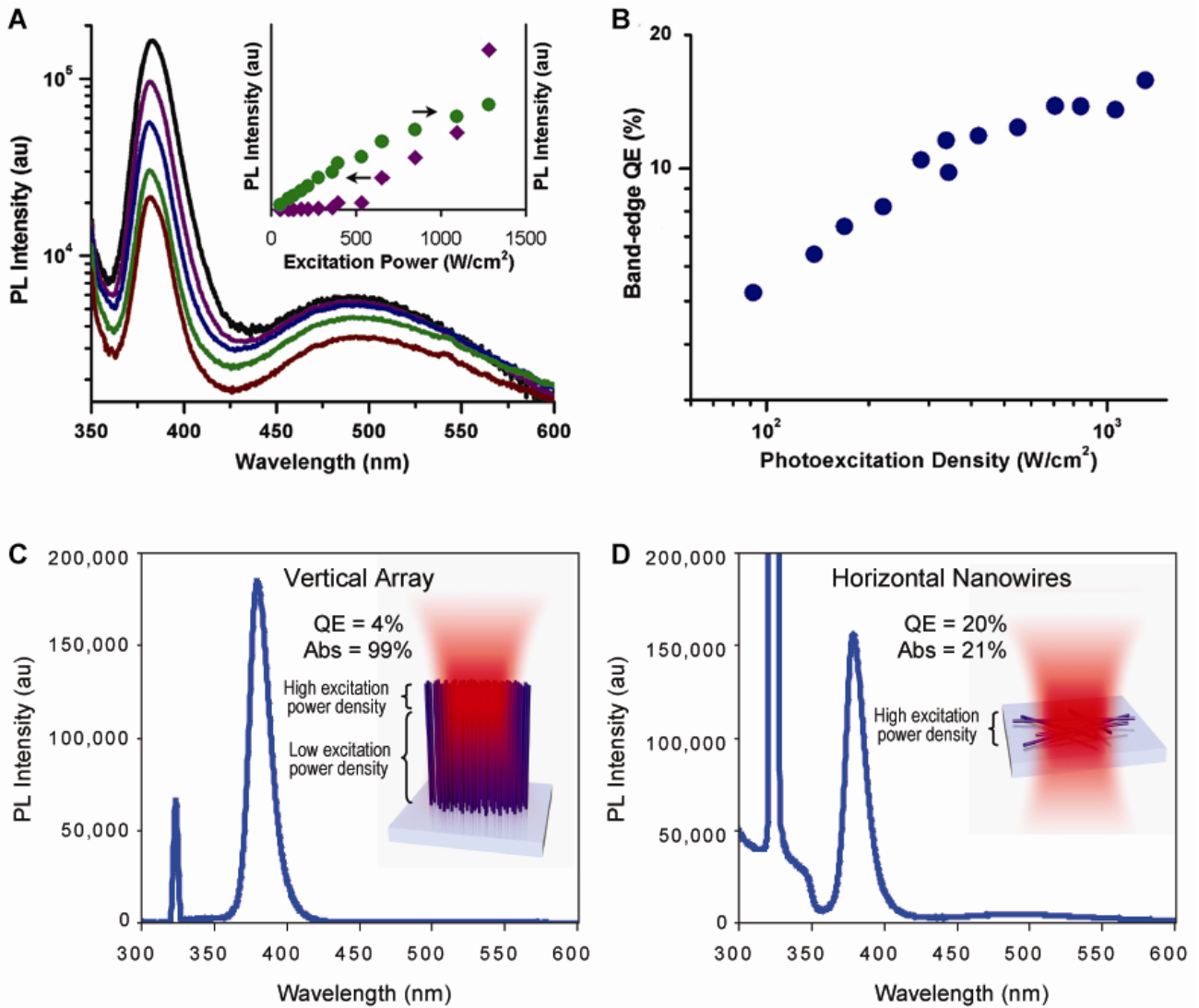
## Figure Captions



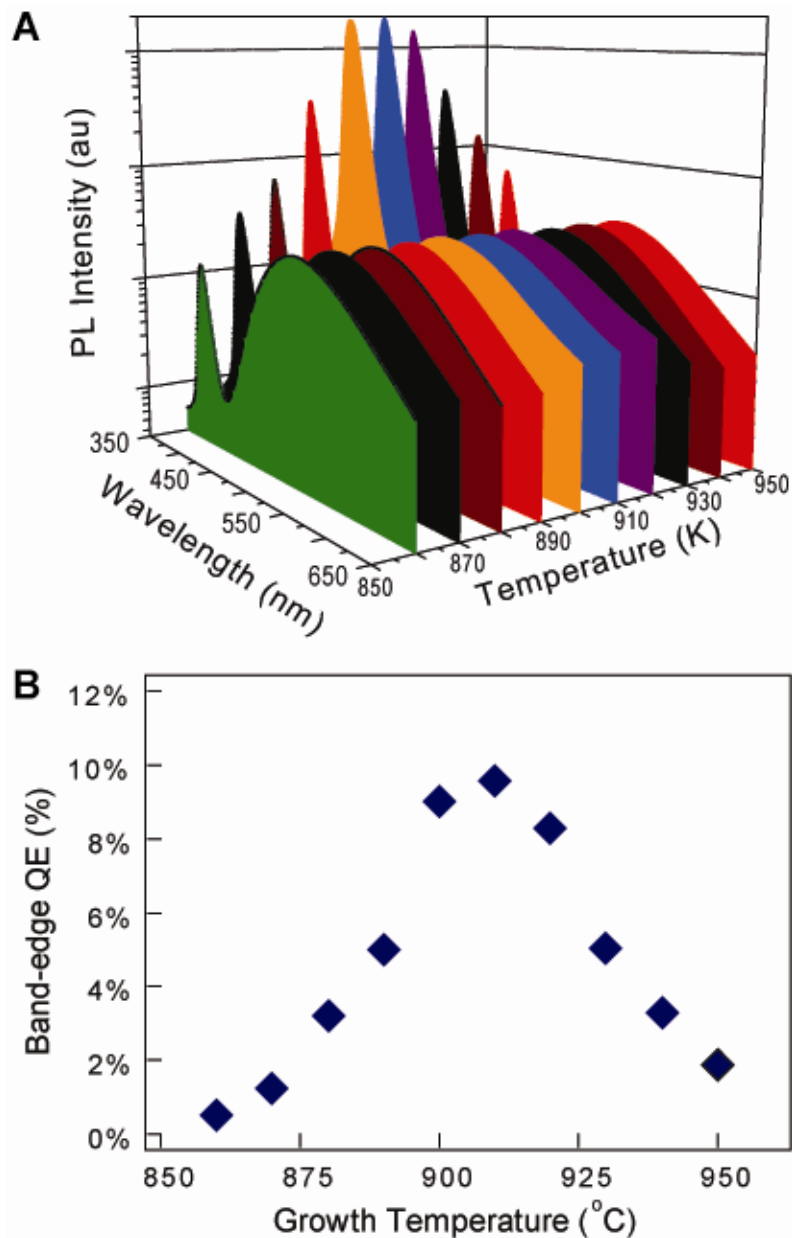
**Figure 1.** High band-edge EQE from CVT-grown ZnO nanowires. a) SEM image of vertical ZnO nanowire array grown on sapphire and b) transferred to a blank quartz substrate. c) 4" diameter integrating sphere with highly reflective coating. Inset: PL image of ZnO nanowires inside integrating sphere (scale bar: 5 μm) d) PL spectrum of ZnO nanowires collected inside the integrating sphere. Strong band-edge emission appears at 380nm, while no defect emission in the visible region is detected. Inset: PL spectrum expanded to show transmitted laser signal at 325 nm which determines the total absorption by the ZnO nanowires.



**Figure 2.** IQE measurement of a single ZnO nanowire. PL spectra (plotted on log scale) of a single ZnO nanowire collected from T=5 K to T=298 K. Inset: PL spectrum of ZnO nanowire at T=6 K (purple curve) and T=298 K (black curve). IQE is 62%.

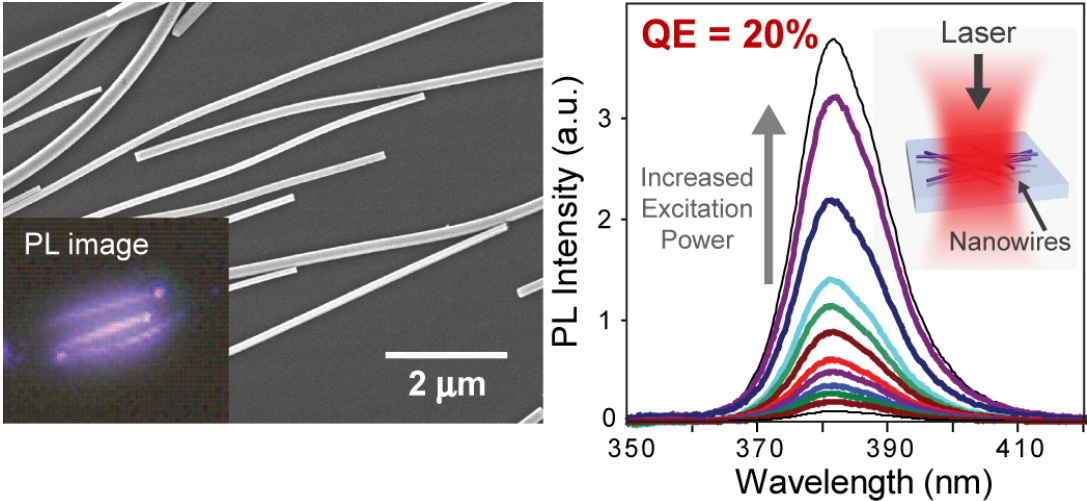


**Figure 3.** EQE of ZnO nanowires depend significantly on the excitation power density. a) PL spectra of ZnO nanowires collected at increasing excitation power density shows non-linear growth of the band-edge peak at 380 nm compared to the defect peak at 500 nm. (log scale) Inset graph shows PL intensity of band-edge peak (purple diamonds) and defect peak (green squares) vs. excitation power density. b) Band-edge EQE vs. excitation power density,  $I$ , plotted on a log-log scale. PL spectra and schematics of excitation configurations shown for c) vertical arrays and d) horizontal nanowires. EQE measured from horizontal nanowires is more accurate due to uniform excitation power density while the EQE measured from vertical array is an average of emission from high and low power density excitation.



**Figure 4.** EQE can be used to evaluate the optical properties of ZnO nanowires quantitatively. EQE dependence of growth temperature reveal optimal condition for ZnO nanowires growth at  $T=910$  °C. a) PL spectra and b) EQE plotted for ZnO nanowires grown at various temperatures. Spectra in a) were normalized to emission at 520 nm and plotted on log scale to illustrate dependence of the ratio of band-edge to defect PL on growth temperature.

TOC FIGURE



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