

Light emission from a zinc oxide nanowire

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The surprising pattern of luminescence from a zinc oxide nanowire has significant implications for light-matter interaction and optoelectronic applications.

Zinc oxide (ZnO) is a wonderful material. It has found application in almost every aspect of our daily lives, from sunscreen to miniaturized lasers, sensors, and piezoelectric elements for generating power.^{1,2} ZnO has also made contributions to current nanoscience and technology. For instance, colloidal ZnO nanocrystals behave as true quantum dots, which means that the wavelength of the near-UV light they emit depends on the size of the nanocrystals.³

ZnO is also a key material in advanced optical studies. The direct optical transition that generates an exciton (composed of a so-called electron-hole pair, or negative and positive charge carriers) is very strong (3.37eV, near UV). In addition, the electron-hole attraction is huge (up to 60meV). These two elements result in a substantial interaction between the exciton and the photon that gives rise to it, resulting in a quasi-particle that is half photon, half exciton: the polariton.⁴ The energy-wave vector or (E, k) diagram of macroscopic ZnO samples has been measured.⁵ The light-matter interaction was found to be a factor of about 100 stronger than in the widely studied semiconductor gallium arsenide.

In a ZnO nanostructure, if the dimensions are of the order of the exciton wavelength (375nm, 3.3eV photon energy) theory suggests an exciton-polariton could be present as a standing wave. If so, it could enhance light-matter interaction considerably,⁶ with major implications for miniaturized lasers based on ZnO and for nanophotonic circuits. Since my group grows highly crystalline ZnO nanowires, we decided to study the optical properties of individual wires lying on a silica/silicon substrate.⁷

We set up a luminescence microscope with a pulsed 350nm laser as excitation source, lenses transparent to near-UV light, and a pinhole to detect the emission spatially resolved along the nanowire. We found that while the luminescence at and above

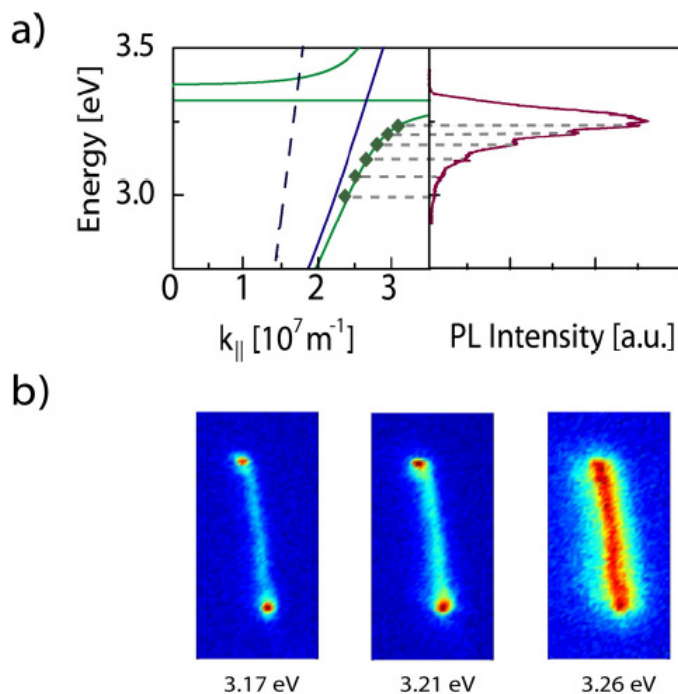


Figure 1. Luminescence spectrum of a ZnO nanowire projected onto the polariton energy-wave vector (E, k) curve. Below 3.26eV, the luminescence is emitted at the wire ends only (b). The spectrum (a, red curve) consists of a series of peaks below the exciton energy (3.3eV, green line in a, left) that fit the lower branch of the polariton curve (green dots on the green lower curve). The blue full and dashed lines represent the photon lines in the ZnO and vacuum, respectively. Note that the polariton wave vector (parallel to the wire's long axis) is much larger than that of the resonant photon in vacuum. PL: Photoluminescence.

3.26eV was emitted uniformly along the wire, nearly all luminescence below 3.26eV was emitted at the ends only, similar to the case of lasing: see Figure 1(b). The luminescence spectra at both wire ends are identical, and consist of a series of peaks extending far below the band gap of ZnO. The energy difference between

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the peaks is inversely proportional to the nanowire length, indicating that they reflect Fabry–Pérot-type modes. That is, the photons we detect at the wire ends correspond to standing-wave excitations in the ZnO nanowire, which can be seen as a natural cavity. Our analysis shows that in the lateral direction, half a wavelength or an entire one fits in the wire, while in the length direction the standing wave has 10–30 wavelength cycles. Each peak in the spectrum corresponds to a different standing wave in the nanowire, the number of cycles in the length direction (the mode number) of each wave differing by one unit with respect to the next.⁷

We found that the difference between the peaks decreases with increasing energy. Hence, the (E, k) of the luminescence peaks is strongly curved: see Figure 1(a), green data points. The data fits well to the classical polariton dispersion curve based on a model with two coupled oscillators, but only if it is assumed that the light-matter interaction is three to six times stronger than in bulk ZnO. The (E, k) diagram also shows the strength of the interaction. There is an avoided crossing between the exciton line (horizontal green line, derived from the electronic band structure) and the photon line (blue full line). The gap between the upper and lower polariton energy levels (green curves) indicates the degree of the exciton-photon coupling. Coupling weakens slightly with increasing excitation intensity. Still, it remains much stronger than in a macroscopic ZnO sample, even above the lasing threshold when stimulated emission becomes dominant. We conclude that the optical properties of ZnO nanowires are indeed governed by robust exciton-polaritons delocalized over the entire wire.

This finding has consequences that are important for optoelectronic applications. First, we note that the luminescence eigenmodes extend to 300meV below the electronic bandgap of ZnO. In other words, the optical properties are not dictated by the electronic structure, as one would expect. The strong interaction between the exciton and the photon leads to a polariton with energy levels below the electronic bandgap. Furthermore, polariton lasing is expected to start at low excitation density, reducing the electric work needed during operation.

Second, the exciton-polaritons have a wave vector directed along the nanowire. Since the polariton wave vector is larger than that in vacuum (see Figure 1), exciton-polaritons cannot leave the wire except at the wire ends. This explains the extraordinary subwavelength guiding reported previously.⁸ The high wave vector (short wavelength) of the delocalized polaritons enables them to pass sharp corners in the nanowire, which is a useful property for nanophotonic circuits.

Third, the intensity of each peak reflects its mode population. These intensities increase with the excitation density in a supra-

linear way, indicating polariton-polariton scattering. A practical consequence of this effect is that the polariton emission dominates the green (defect) emission at sufficient exciton density. We believe that nonradiative recombination is also suppressed.

The formation of one-dimensional exciton-polaritons in ZnO nanowires at room temperature could be of great importance for miniaturized lasers based on ZnO and for nanophotonic circuits. The next major step is to grow nanowires with a built-in p-n junction. That would make it possible to generate exciton-polaritons electrically.

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Daniël Vanmaekelbergh leads a research group involved in the synthesis of semiconductor nanocrystals and wires, their self-organization, and the study of their optical and electronic properties with scanning probe methods.

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