

Quantum confinement in ZnO nanorods

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The colloidal-synthesized ZnO nanorods with radius of 1.1 ± 0.1 nm (less than the bulk exciton Bohr radius, $a_B \sim 2.34$ nm) have been studied by optical methods combined with simple model calculations. The quantum confinement has been observed in these nanorods. The exciton binding energy is shown to be significantly enhanced due to one-dimensional confinement. Additionally, it is suggested that the green luminescence in ZnO involves free holes. © 2004 American Institute of Physics. [DOI: 10.1063/1.1811797]

ZnO has been of great interest recently because of its wide band gap ($E_g = 3.36$ eV at room temperature¹) and relatively high bulk exciton binding energy ($E_B^{3D} \sim 0.06$ eV²), which make this material a promising candidate for ultraviolet laser devices operating at room temperature (RT). Furthermore, the lasing conditions can be further improved with low-dimensional ZnO structures (quantum dots and wires), which enhance the exciton oscillator strength and quantum efficiency (see, e.g., Ref. 3). There have been many reports (see, e.g. Refs. 3–6) on the fabrication and the optical properties of ZnO nanowires (nanorods); however, no quantum confinement effects were reported since all these nanowires (nanorods) have radius (r) larger than 10 nm, while the bulk ZnO exciton Bohr radius, a_B , is ~ 2.34 nm.⁷

With a recently developed colloidal synthesis method, ZnO nanorods with radius of 1.1 ± 0.1 nm, which is smaller than a_B , have been obtained.⁸ In this letter, we show the experimental evidence of quantum confinement effects associated with these nanorods, using absorption, photoluminescence and simple model calculations. Additionally, we shall show that the binding energy of excitons in these nanorods is significantly enhanced due to one-dimensional (1D) confinement, and that the transition responsible for the “green band” often observed in ZnO is likely to involve free holes.

Details of sample preparation are given in Ref. 8. The size of ZnO nanorods ($r = 1.1 \pm 0.1$ nm, length ~ 43 nm) has been determined using high resolution transmission electron microscopy.⁸ For optical characterizations, these ZnO nanorods were dispersed in hexane stored in a quartz cell. UV-visible spectroscopy absorption spectra were recorded with an Agilent HP8453 spectrophotometer. Photoluminescence (PL) spectroscopy was performed using the 325 nm excitation from a He–Cd laser. All experiments were performed at RT.

In Fig. 1 we show the absorption spectrum together with the PL (inset). The absorption spectrum shows two broad peaks ($\sim 3.53 \pm 0.05$ and $\sim 4.59 \pm 0.14$ eV indicated by arrows). We attribute these to the ground ($n=0$) and the first excited ($n=1$) 1D excitonic states. The ground state exciton energy ($\sim 3.53 \pm 0.05$ eV) is significantly enhanced compared to the free exciton energy in the bulk (~ 3.30 eV) due to the 1D confinement. The PL spectrum (inset) is fitted with the

Gaussian functions peaked at 3.54, 3.28, 3.05, and 2.57 eV. The 3.54 eV peak is, apparently, the ground state 1D excitonic transition because it coincides with the first absorption band. The 2.57 eV peak is attributed to the transition that is usually observed as the green band in bulk ZnO; the peak energy is again enhanced compared to that from the bulk ($\sim 2.38 \pm 0.04$ eV, see, e.g., Refs. 6 and 9–12), which we attribute to the confinement effects (see also below). The 3.28 and 3.05 eV peaks are attributed to transitions associated with impurities in ZnO (see, e.g., Ref. 1).

To further understand the quantum confinement effect, we model the nanorods as cylindrical wells with infinite barriers using the effective-mass approximation.¹³ Then, excitonic absorption levels can be described by the following equation:

$$E_{ns} = E_g + \frac{\hbar^2 x_{ns}^2}{2r^2} \frac{1}{m_e} + \frac{\hbar^2 x_{ns}^2}{2r^2} \frac{1}{m_h} - E_B^{1D}(r), \quad (1)$$

where x_{ns} is the s th zero of the Bessel function, $J_n(x)$; m_e ($=0.28m_0$) (Ref. 2) and m_h ($=0.59m_0$) (Ref. 2) are the effective masses of electrons and holes, respectively; $E_B^{1D}(r)$ is the binding energy of 1D exciton, which depends on the size and geometry of the nanorods (see, e.g., Ref. 14 and references therein). Within this model, the carrier wave function does not penetrate into the surrounding media; the errors associ-

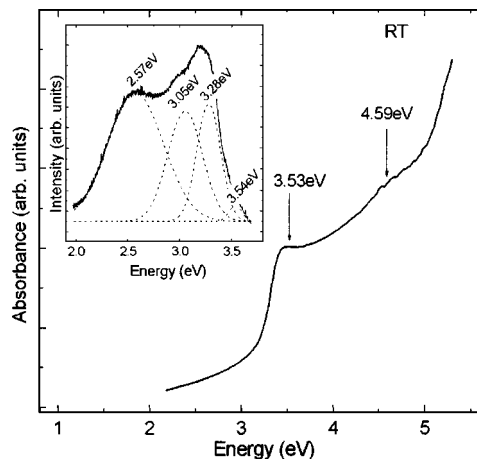


FIG. 1. The RT absorption spectrum of ZnO nanorods dispersed in hexane solution. The arrows indicate the ground and the first excited states of 1D excitons. The inset shows the RT PL (the solid line) fitted with 4 Gaussians (dashed lines) peaked at 3.54, 3.28, 3.05, and 2.57 eV.

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ated with this are usually very small and often neglected since in most cases the radius of nanorods is large. However, this is not so in our case. Indeed, the penetration length (ℓ_p) of the electron wave function into the surrounding media can be estimated as¹⁵

$$\ell_p = \frac{\hbar}{\sqrt{2m_e(V - \Delta E_e)}}, \quad (2)$$

where ΔE_e is the electron confinement energy [the second term in Eq. (1)] and V is the barrier height. For the estimation of V , we note that it has been reported that the energy between the level of the optical ligands and the conduction band of CdSe is around 4 eV.¹⁶ The bottom of the conduction band of ZnO is about 20 meV higher than that of CdSe.¹⁷ Therefore, V is estimated to be ~ 3.8 eV, giving $\ell_p \sim 0.2$ nm. For the nanorods with radius $r = 1.1 \pm 0.1$ nm, this is not negligible.

Therefore, to take the penetration length into account, we use, in a rather intuitive, qualitative way, in Eq. (1), the effective radius $r_{\text{eff}} = r + \ell_p = 1.3 \pm 0.1$ nm. With this, the only unknown term in Eq. (1) is $E_B^{\text{1D}}(r)$. Taking that the lower (higher) energy limit of the first absorption peak (the ground state, $n=0$) is associated with the largest (smallest) nanorods, we estimate the $E_B^{\text{1D}}(r)$ to be ~ 0.47 eV (0.58 eV), which corresponds to $7.8E_B^{\text{3D}}$ ($9.7E_B^{\text{3D}}$). Assuming that $E_B^{\text{1D}}(r)$ is of the same value (for an appropriate radius) for the first excited excitonic (E_{11}) state, we calculated $E_{11} = 4.61 \pm 0.21$ eV, which is in excellent agreement with the experimental value of 4.59 ± 0.14 eV. Therefore, we believe that our calculations are consistent.

The enhancement of $E_B^{\text{1D}}(r)$ compared to the bulk value as well as its increase with decreasing size observed here is consistent with both theoretical (see, e.g., Refs. 14 and 18–21) and experimental²² results. A specific enhancement factor, $\gamma = E_B^{\text{1D}}(r)/E_B^{\text{3D}}(r)$, depends on the wire size and shape. The approach of Ref. 14 is very useful for estimating the enhancement factor arising from the quantum confinement effects; in our case, this gives $\gamma \sim 6$ for $r_{\text{eff}} = 1.4$ nm, and $\gamma \sim 7$ for $r_{\text{eff}} = 1.2$ nm, which are close to the experimental values obtained here. Also, following the approach of Ref. 23 (where the dielectric confinement effect is taken into account), one can obtain $\gamma \sim 7.2$ for $r_{\text{eff}} = 1.4$ nm, and $\gamma \sim 8.1$ for $r_{\text{eff}} = 1.2$ nm. We note that in Ref. 22 (and references therein), $\gamma \sim 8$ (independent of the nanowire radius) was reported.

Finally, we discuss the green band (~ 2.57 eV) observed in our ZnO nanorods. In ZnO bulk and wires ($r \geq 10$ nm) the green band is usually observed at $\sim 2.38 \pm 0.04$ eV (see, e.g., Refs. 6 and 10–12). The origin of this band, however, remains a controversial issue: transitions associated with O_{Zn} antisites,¹⁰ oxygen vacancies,^{24–27} zinc interstitials,²⁸ ZnO antisites,²⁹ donor–acceptor pairs,³⁰ and Cu²⁺ ions³¹ have all been suggested. These proposed defects form deep centers that trap electrons (holes), which in turn recombine with holes (electrons) from the valence (conduction) band and/or hydrogenic (shallow) levels. Interestingly, our data provide a certain insight into the origin of this emission. Indeed, assuming that the energies of deep levels formed by defects do not move appreciably with the band edges, we can estimate the green band energy ($h\nu_{\text{green}}$) in our ZnO nanorods by considering two types of transitions: (1) involving electrons

from the conduction band and (2) involving holes from the valence band using the following equation:

$$h\nu_{\text{green}} = 2.38 + \frac{\hbar^2 x_{\text{ns}}^2}{2r^2} \frac{1}{m_e(m_h)}. \quad (3)$$

For the electron case we obtained ~ 2.78 eV for $r_{\text{eff}} = 1.4$ nm, and ~ 2.93 eV for $r_{\text{eff}} = 1.2$ nm; for the hole case we obtained ~ 2.57 eV for $r_{\text{eff}} = 1.4$ nm, and ~ 2.64 eV for $r_{\text{eff}} = 1.2$ nm. Apparently, the observed green band energy in our nanorods (~ 2.57 eV) corresponds to the transition involving free holes, whose energies follow the movement of the valence band due to confinement effects. This conclusion is consistent with that reached in Ref. 27.

In summary, we have shown the quantum confinement in colloidal-synthesized ZnO nanorods. The significant enhancement of the exciton binding energy has been observed due to 1D confinement. This might be significant in terms of the realization of high-temperature ZnO-based devices. Finally, it is suggested that the green luminescence in ZnO involves free holes.

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