

## Zinc Oxide Quantum Rods

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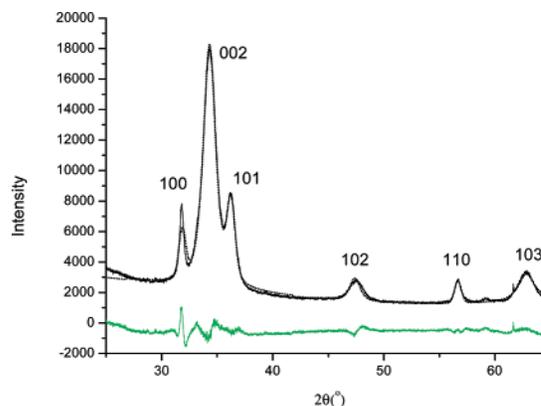
Zinc oxide, ZnO, is a wide band-gap semiconductor with a wide range of possible applications including blue/ultraviolet (UV) optoelectronic devices and piezoelectric devices.<sup>1</sup> ZnO nanostructures have attracted great interest because of their potential applications in UV laser technology.<sup>2,3</sup> The large ZnO exciton binding energy of 60 mV makes this material an attractive candidate for room-temperature lasing,<sup>4,5</sup> and low dimensional nanostructured ZnO offers the possibility of further improving lasing conditions due to quantum confinement effects.<sup>5</sup> Within the physical science community, several investigations on the fabrication of ZnO nanostructures and on the optimization of their optical performance have been carried out in the past few years.<sup>4–8</sup>

We report a new synthesis of ZnO nanorods by thermal decomposition of zinc acetate in organic solvents in the presence of oleic acid, which produces relatively monodisperse ZnO nanorods (ZnO quantum rods) with diameters of 2 nm and lengths in the range 40–50 nm. The diameter is an order of magnitude smaller than previously reported ZnO nanorods prepared by a variety of other methods<sup>8–13</sup> and shows strong evidence of quantum confinement when compared to bulk crystalline ZnO optical properties.<sup>14</sup> Our recent progress in the synthesis of transition metal oxide nanocrystals prompted our experiments to prepare nanoscale ZnO.<sup>15</sup>

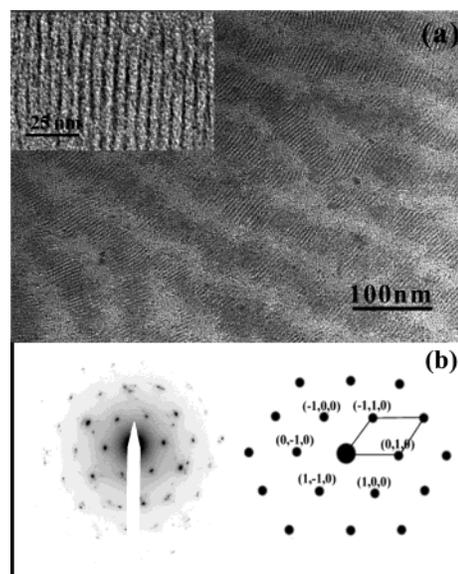
Zinc(II)acetate (ZnAc<sub>2</sub>), trioctylamine (TOA), oleic acid (OA), hexane, acetone, and ethanol were purchased in high grade from Aldrich. In a typical reaction, 4 mmol of dry Zinc acetate (Zn(CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>, Aldrich) is added to a mixture containing 15 mL of trioctylamine and 3 g of oleic acid (12 mmol) at room temperature. The resulting mixture is heated rapidly to 286 °C over 10–15 min, and the mixture changes to a yellowish solution. When the temperature is maintained at 286 °C for 1 h under N<sub>2</sub> flow, the solution gradually turns yellow and a little cloudy, which gives rise to uniform ZnO nanorods. The particles are precipitated by adding ethanol after cooling the reaction mixture to room temperature and are separated and cleaned by repeated precipitation of the hexane solution with ethanol. The final products are redispersed in hexane without further size selection.

ZnO nanorods were structurally characterized by transmission electron microscopy (TEM, JEOL 100cx) with an accelerating voltage of 100 kV and X-ray powder diffraction (Scintag X2). TEM samples were prepared by placing a drop of a dilute hexane dispersion of nanocrystals on the surface of a 400 mesh copper grid backed with Formvar and were dried in a vacuum chamber for 1 h. XRD samples were prepared by drying a hexane dispersion of nanocrystals on a piece of Si (100) wafer. Multiple layers of the rods were laid down on the wafer.

A typical X-ray diffraction (XRD) pattern (Figure 1) shows a high degree of crystallinity, and all of the peaks match well with



**Figure 1.** X-ray powder diffraction patterns of wurtzite ZnO nanorods. The fit to the pattern (dots) was performed using GSAS and the March Dollase model assuming preferred growth along the *c* axis.



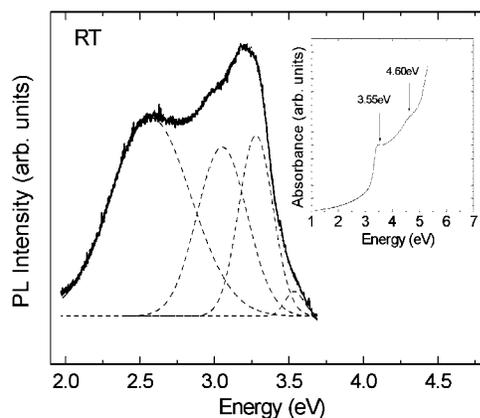
**Figure 2.** (a) Transmission electron micrograph of self-assembled 2 nm diameter ZnO nanorods (inset: higher resolution image showing the oriented stacking; rods are dark contrast). (b) Selected area electron diffraction pattern of ZnO nanorods.

Bragg reflections of the standard wurtzite structure ( $P6_3mc$ ,  $a = 3.25$  Å,  $c = 5.21$  Å, JCPDF # 36-1451). The pattern was modeled using the General Structure and Analysis Software, GSAS, with the March Dollase model for preferred growth along the *c* axis (see Supporting Information for further details).

TEM images (Figure 2a) show uniform ZnO nanorods with average diameter 2.2 nm and average length 43 nm, ranging between 40 and 50 nm. Strong preference for self-assembly of these

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**Figure 3.** The photoluminescence at room temperature of a hexane dispersion of ZnO nanorods together with the absorbance (inset).

quantum rods into separate close-packed “stacks”, in which they align with their long axis parallel to each other, is observed in all cases, suggesting the possibility for preparing ordered ZnO nanorods on substrates, which may be useful when considering the ZnO rods for optical applications. Selected area electron diffraction patterns (SAED) confirm a high degree of crystallinity over very small ( $>0.01 \mu\text{m}^2$ ) regions of the sample (Figure 2b indicates each rod is highly crystalline (possibly single crystal) and can be indexed to the hexagonal structure identified by XRD (Figure 1)). High-resolution TEM (HRTEM) was performed at Brookhaven National Laboratory (JEOL 3000F). HRTEM enabled the viewing of lattice planes, confirming crystallinity within the nanorod (see Supporting Information). HRTEM also permitted the accurate measurement of the average nanorod thickness, found to be  $2.2 \pm 0.2$  nm. This lateral size is comparable to the exciton Bohr radius ( $\sim 1.8$ – $2.0$  nm) in bulk ZnO.<sup>17</sup>

We performed optical studies of the rods in solution to determine the potentially unique optical properties and observe if quantum confinement effects play an important role in the photoluminescence.

The ZnO nanorods dispersed in hexane were stored in a quartz cell. The room-temperature (RT) photoluminescence (PL) was obtained with the excitation from the 325 nm emission from a He–Cd laser with 10 mW maximum power (the intensity is approximately  $28 \text{ W/cm}^2$ ). In Figure 3, we show such a PL (solid line) together with the absorbance (solid circles). The PL is very well fitted with Gaussian (dashed lines) peaks at 3.53, 3.28, 3.07, and 2.57 eV. Three of these PL peaks can be attributed to imperfections associated with zinc oxide (see Supporting Information). The 3.53 eV peak is close to the first absorption peak ( $\sim 3.55$  eV, Figure 3, inset) and thus can be assigned to an excitonic transition. This peak (and the absorption peak) is notably higher than the free excitonic transition in bulk ZnO at RT ( $\sim 3.30$  eV), indicating quantum confinement effects. The nanorod diameter can be calculated using a model of a cylindrical well with infinite barriers (full calculation in Supporting Information). This yields the radius of  $\sim 1.3$  nm, which is in close agreement with the TEM

results (thickness/diameter = 2.2 nm). Moreover, the penetration length of the electron wave function into the surrounding media is calculated to be  $\sim 0.2$  nm; thus the “real” radius of these nanorods is  $\sim 1.1$  nm, the exact same value obtained from TEM. Given that the rods are coated with a monolayer of oleic acid, the model is commensurate with some wave function penetration into the ligand. Furthermore, the calculations show that the first excited-state transition lies at 4.60 eV, in excellent agreement with the absorbance results (Figure 3, inset). The results clearly indicate the existence of quantum confinement effects associated with these ZnO nanorods.

Nanosized ZnO rods of diameters  $\sim 2$  nm can be prepared from a simple acetate precursor, resulting in ligand-capped rods of crystalline ZnO, monodisperse in diameter and highly dispersible in nonpolar solvents. We observed the self-assembly from hexane into uniform stacks of nanorods aligned parallel to each other with respect to the long axis. Preliminary near-UV absorption and PL measurements were able to determine that quantum confinement effects are present in these rods, with an excitonic ground state of  $\sim 3.55$  eV.

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**Supporting Information Available:** Excitonic transition/cylindrical well model calculation, further structural characterization (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- Xu, C. X.; Sun, X. W.; Chen, B. J.; Shum, P.; Li, S.; Hu, X. *J. Appl. Phys.* **2004**, *95*, 661.
- Bimberg, D.; Grundmann, M.; Ledentsov, N. *Quantum Dot Heterostructures*; Wiley-VCH: Chichester, 1998.
- Johnson, J. C.; Yan, H.; Schaller, R. D.; Haber, L. H.; Sayakally, R. J.; Yang, P. *J. Phys. Chem. B* **2001**, *105*, 11387.
- Madelung, O.; Poerschke, R. *Data in Science and Technology, Semiconductors, Other than Group IV Elements and III–V Compounds*; Springer: Berlin, 1992.
- Yang, P.; Yan, H.; Mao, S.; Russo, R.; Johnson, J.; Saykally, R.; Morris, N.; Pham, J.; He, R.; Choi, H. *Adv. Funct. Mater.* **2002**, *12*, 323.
- Haupt, M.; Ladenburger, A.; Sauer, R.; Thonke, K.; Glass, R.; Roos, W.; Spatz, J. P.; Rauscher, H.; Riethmuller, S.; Moller, M. *J. Appl. Phys.* **2003**, *93*, 6252.
- Pacholski, C.; Kornowski, A.; Weller, H. *Angew. Chem., Int. Ed.* **2002**, *41*, 1188.
- Vayssieres, L. *Adv. Mater.* **2003**, *15*, 464.
- Kawakami, M.; Hartanto, A. B.; Nakata, Y.; Okada, T. *J. Appl. Phys.* **2003**, *42*.
- Lyu, S. C.; Zhang, Y.; Lee, C. J. *Chem. Mater.* **2003**, *15*, 3294.
- Xia, Y.; Yang, P.; Sun, Y.; Wu, Y.; Mayers, B.; Gates, B.; Yin, Y.; Kim, F.; Yan, H. *Adv. Mater.* **2003**, *15*, 353.
- Kong, Y. C.; Yu, D. P.; Zhang, B.; Fang, W.; Feng, S. Q. *Appl. Phys. Lett.* **2001**, *78*, 407.
- Jeong, S.-H.; Kim, B.-S.; Lee, B.-T. *Appl. Phys. Lett.* **2003**, *82*, 2625.
- Yin, M.; O’Brien, S. *J. Am. Chem. Soc.* **2003**, *125*, 10180.
- Hamby, D. W.; Lucca, D. A.; Klopstein, M. J.; Cantwell, G. *J. Appl. Phys.* **2003**, *93*, 3214.
- Cho, S.; Ma, J.; Kim, Y.; Sun, Y.; Wong, G. K. L.; Ketterson, J. B. *Appl. Phys. Lett.* **1999**, *75*, 2761.
- Shim, M.; Guyot-Sionnest, P. *J. Am. Chem. Soc.* **2001**, *123*, 11651.

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