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Large-Scale Synthesis of Hexagonal Pyramid-Shaped ZnO Nanocrystals from Thermolysis of Zn−Oleate Complex

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We report the large-scale synthesis of uniform-sized hexagonal pyramid-shaped ZnO nanocrystals by the thermolysis of Zn−oleate complex, which was prepared from the reaction of inexpensive and environmentally friendly reagents such as zinc chloride and sodium oleate. Under optimized reaction conditions, we were able to synthesize as much as 2.83 g using 300 mL of oleylamine and 90 mL (284 mmol) of oleic acid (OA) as both solvents and stabilizing surfactants. The UV-vis spectrum showed the absorption onset of 380 nm, and the photoluminescence spectrum showed a near band-edge emission at 387 nm and a broad blue-green emission band above 468 nm.

Nanocrystals have attracted broad attention from researchers in various areas for both their fundamental size-dependent properties and their many important technological applications.[1] For the past several years, intensive research has been conducted in an effort to synthesize anisotropic nanocrystals, owing to their unique properties that are derived from their low dimensionality combined with the quantum confinement effect.[2] ZnO is a direct gap semiconductor with a large band gap of 3.37 eV and a large exciton binding energy of 60 meV. The strong exciton binding energy can ensure an efficient ultraviolet-blue emission at room temperature. Accordingly, ZnO nanocrystals have great potential in applications such as laser diodes,[3] solar cells,[4] and sensors.[5] In particular, a large number of one-dimensional ZnO nanocrystals, including nanowires[6] and nanorods,[7] have been synthesized using various synthetic procedures.[8] For these ZnO nanocrystals to be used in a wide range of applications, an economical mass production method needs to be developed. Unfortunately, however, in most of the syntheses that have been reported so far, only sub-gram quantities of uniform-sized ZnO nanocrystals were synthesized.[9,10] Very recently, we reported the ultra-large-scale synthesis of uniform-sized nanocrystals of various transition metal oxides from the thermal decomposition of metal−oleate complexes that were prepared from the reaction of metal chlorides and sodium oleate.[11] In the continuation of the development of large-scale synthesis of uniform-sized nanocrytstals, we herein report on the synthesis of uniform-sized hexagonal pyramid-shaped ZnO nanocrystals from thermolysis of the Zn−oleate complex.

The zinc−oleate complex was prepared by reacting zinc chloride and sodium oleate. In a typical synthesis, 5.45 g of zinc chloride ($ZnCl_2$, 40 mmol, Acros, 98%) and 24.35 g of sodium oleate (80 mmol, TCI, 95%) were dissolved in a mixture solvent composed of 80 mL ethanol, 60 mL distilled water, and 140 mL hexane. The resulting solution was heated to 70 °C and kept at that temperature for 4 h. When the reaction was completed, the upper organic layer containing the zinc−oleate complex was washed three times with 30 mL distilled water in a separatory funnel. After washing, hexane was evaporated, resulting in the zinc−oleate complex in solid form. In a typical synthesis of hexagonal pyramid-shaped ZnO nanocrystals, 18 g (52 mmol) of the zinc−oleate complex was dissolved in a mixture containing 300 mL of oleylamine and 90 mL (284 mmol) of oleic acid (OA) at room temperature. The resulting reaction mixture was heated to 300 °C under an argon flow and was maintained at that temperature for 1 h. As the reaction proceeded, the solution became slightly cloudy and gray, which demonstrated the formation of ZnO nanocrystals. The solution was then cooled to room temperature, and excess ethanol was added to yield a gray waxy precipitate, which was then separated by centrifuging. The amount of the produced ZnO nanocrystals was 2.83 g (see the inset in Figure 2a). The resulting precipitate was easily redispersable in many nonpolar solvents including hexane and toluene. The ZnO nanocrystals were characterized by powder X-ray diffraction (XRD, Rigaku D/Max-3C diffractometer) and transmission electronic microscopy (JEOL EM-2010 microscope). The electronic absorption and photoluminescence spectra were obtained using a Perkin-Elmer Lambda model 20 UV-vis absorption spectrometer and JASCO FP750 spectrofluorometer, respectively.

An XRD pattern of hexagonal pyramid-shaped ZnO nanocrystals (Figure 1) revealed a wurtzite hexagonal crystal structure with high crystallinity ($P6_3mc$, $a = 3.249$ Å, $c = 5.206$ Å, JCPDS No. 36- 1451). The TEM image at low magnification, shown in Figure 2a, revealed that hexagonal pyramid-shaped ZnO nanocrystals having a side edge length of 25 ± 2.5 nm and basal edge length of 15 ± 1.5 nm were produced. The strong ring patterns from the electron diffraction pattern were indexed to the hexagonal wurtzite structure (Figure 2b), which was

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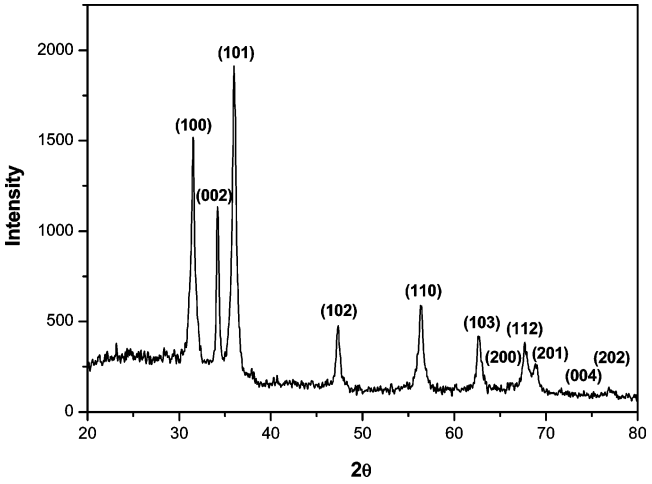

Figure 1. XRD pattern of hexagonal pyramid-shaped ZnO nanocrystals.

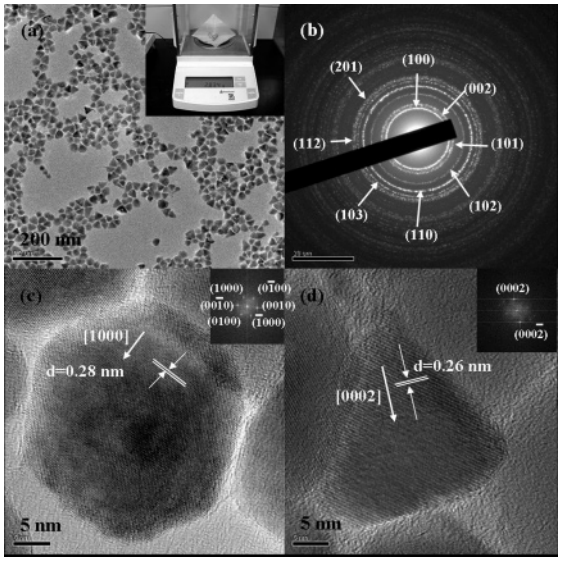

Figure 2. TEM micrographs of hexagonal pyramid-shaped ZnO nanocrystals. (a) Low-magnification TEM image. Inset: photograph of the obtained ZnO nanocrystals. (b) Electron diffraction (ED) pattern of ZnO nanocrystals. (c) HRTEM image showing the hexagon-shaped basal plane of ZnO nanocrystals. (d) HRTEM image showing the triangle-shaped side plane of ZnO nanocrystals. The insets are fast-Fourier transform (FFT) images of HRTEM images shown in (c) and (d).

consistent with the XRD data. Figure 2c shows a high-resolution TEM (HRTEM) image of hexagon-shaped basal plane with an average edge length of 15 nm. The observed lattice spacing corresponding to the (1000) lattice plane was calculated to be 0.280 nm. On the other hand, Figure 2d shows HRTEM image of triangle-shaped side plane with an average edge length of 25 nm. The lattice spacing corresponding to the (0002) lattice plane was calculated to be 0.260 nm. The insets at the right top corners of Figures 2c and 2d show the corresponding processed fast Fourier transform (FFT) images.

The hexagonal pyramid-shaped ZnO nanocrystals were confirmed by changing the tilted angle (X°, Y°), as shown in Figure 3. The TEM images showed a gradual changed from a hexagonal shape to a hexagonal pyramid shape (right) by tilting the two hexagonal ZnO nanocrystals, in which the basal plane of the hexagon was [1000], and the side plane of the hexagonal pyramid was [0002]. The figure shows a scheme of (1°, −19°) tilted angles.

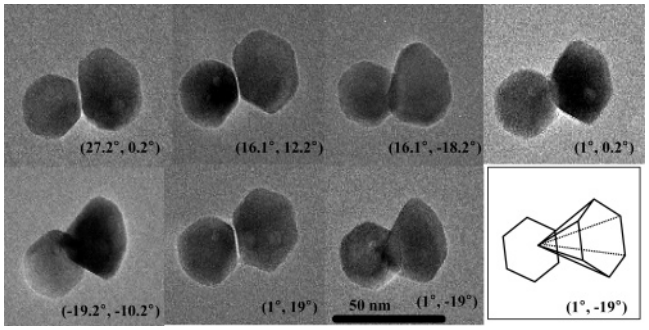

Figure 3. TEM images of hexagonal pyramid shaped ZnO nanocrystals at various tilted angles (X°, Y°) (left: hexagon shape, right: from hexagon shape to hexagonal pyramid image).

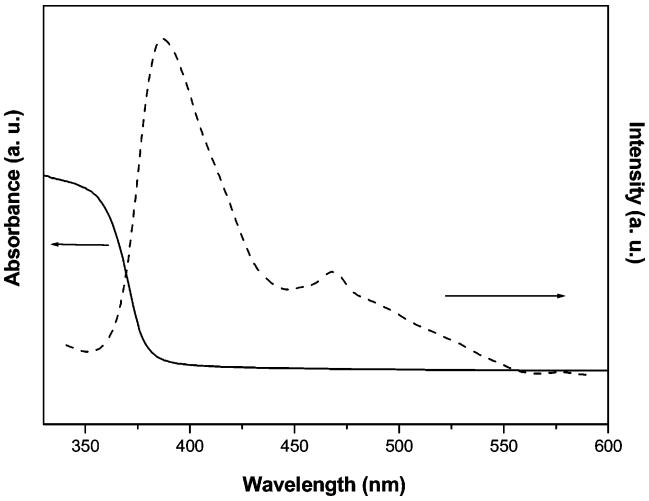

Figure 4. UV-vis. absorption and room-temperature PL spectra of the hexagonal pyramid-shaped ZnO nanocrystals.

Figure 4 shows the UV-vis absorption and the room-temperature photoluminescence (PL) spectrum of hexagonal pyramid-shaped ZnO nanocrystals. The spectra show the absorption onset of 380 nm in the ZnO nanocrystals. The PL spectra showed a near band-edge emission at 387 nm and a broad blue-green emission band at above 468 nm. The near-UV emission at 387 nm was similar to the bulk band gap at 380 nm of the ZnO, which originated from the recombination of free excitons.[12a−c] A weak and broad blue-green emission band above 468 nm was attributed to a singly charged oxygen vacancy, which results from the recombination of a photo-generated hole with a charge state of the specific defect, such as oxygen vacancies, or resulted from the surface deep traps.[12d−f]

In conclusion, large quantity of uniform hexagonal pyramid-shaped ZnO nanocrystals was synthesized from the thermolysis of Zn−oleate complex. The current synthetic method can be extended to the large-scale production of uniform nanocrystals of many metals, metal oxides, and metal sulfides.

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