Preparation and Photoluminescence of ZnO Nanocrystals by a High-temperature Organometallic Route

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ZnO nanocrystals have been prepared via a high-temperature organometallic route. By XRD analysis, the effects of reaction temperature and time on the formation of ZnO were recognized. A possible mechanism was proposed. The product's size, optical absorption, and photoluminescence were also described.

ZnO is an important electronic and photonic material because of its wide direct band gap (3.37 eV) and large exciton binding energy (60 meV).[1] Particularly, ZnO nanostructures show size-dependent electronic and optical properties owing to quantum-size effects. In recent years, their potential applications in solar cells, sensors, optoelectric devices, transparent conductive films, and short-wave optics have been attracting increasing attention.[2–5]

A lot of methods have been developed for the preparation of ZnO nanocrystals, including precipitation,[6] acidic and basic routes,[7] laser ablation processes,[8] mechanochemical reactions,[9] solvo/hydrothermal processes,[10] sol–gel routes,[11] microwave irradiation methods,[12] gas-phase condensation,[13] and thermal evaporation.[14] Recently, many metal nanocrystals have been made by the thermal decomposition and/or reduction of organometallic complexes at a relatively high temperature because the resultant nanocrystals usually exhibit good monodispersity and high crystallinity.[15,16] However, few efforts have been made on the preparation of metal oxide nanocrystals by this method.[17,18] To our best knowledge, the preparation of ZnO nanocrystals via a high-temperature organometallic route has not been reported. Here, we report the preparation of ZnO nanocrystals by the thermal decomposition of zinc acetate. The temperature-dependent photoluminescence (PL) spectra were also studied.

The typical procedures for the preparation of ZnO nanocrystals were as follows. First, zinc acetate ($Zn(Ac)_2 \cdot 2H_2O$) (0.1 mol/L) and 1,2-hexadecanediol (0.15 mol/L) were dissolved in a dioctyl ether solution (10 mL) of oleic acid (0.05 mol/L) and oleylamime (0.05 mol/L). After stirring for 1 h at room temperature, the temperature was raised to 250 °C and the reaction mixture was refluxed for 1 h to form ZnO nanopaticles. Subsequently, the reaction mixture was cooled to room temperature and precipitated by the addition of ethanol (40 mL). Finally, the precipitate was washed several times with hexane and ethanol.

X-ray diffraction (XRD) measurement was carried out on a Shimadzu Model RX-III X-ray diffractometer at 40 kV with Cu Kα radiation ($\lambda = 0.1542$ nm). Transmission electron microscope (TEM) analysis was conducted on a Hitachi H-7500 transmission electron microscope at 100 kV. The UV–vis absorption spectrum was measured by a JASCO V-570 spectrophotometer. The photoluminescence spectra were obtained on a fluorescence spectrophotometer (Jobin Yvon, Labram HR) with an InGaAs laser as the excitation source at an excitation wavelength of 325 nm.

Figure 1 shows the XRD patterns for ZnO nanocrystals obtained at different reaction times and temperatures. The peaks located at about $2\theta = 31.7$, 34.3, 36.1, 47.4, 56.5, 62.8, 67.9, 72.5, and 76.8° can be indexed to hexagonal ZnO (JCPDS 36-1451). However, in addition to ZnO, the samples obtained at 250 °C for 5 h and 290 °C for 1 h showed weak peaks at $2\theta =$ 33.2, 59.2, and 69.1° which can be assigned to $Zn_5(OH)_8(Ac)_2 \cdot 2H_2O$ (Zn-HDS)[11] although the characteristic peak at $2\theta = 69.1°$ almost overlapped with that of ZnO at $2\theta = 67.9°$. This was consistent with the statement by Qian et al. who pointed out that the formation of Zn-HDS depended strongly on the temperature.[11] It was suggested that more zinc ions might be generated from the decomposition of zinc acetate by increasing reaction time and temperature, which not only accelerated their reaction with hydroxide ions to form ZnO but also was helpful for their reaction with the undecomposed zinc acetate and hydroxide ions to form Zn-HDS. A possible reaction mechanism could be expressed by reactions (1)–(3).

$$Zn(Ac)_2 \cdot 2H_2O \rightarrow Zn^{2+} + 2CH_3COO^- + 2H_2O \qquad (1)$$

$$Zn^{2+} + 2OH^- \rightarrow ZnO\downarrow + H_2O \qquad (2)$$

$$Zn(Ac)_2 \cdot 2H_2O + 4Zn^{2+} + 8OH^- \rightarrow Zn_5(OH)_8(Ac)_2 \cdot 2H_2O \qquad (3)$$

According to the above, to avoid the formation of Zn-HDS,

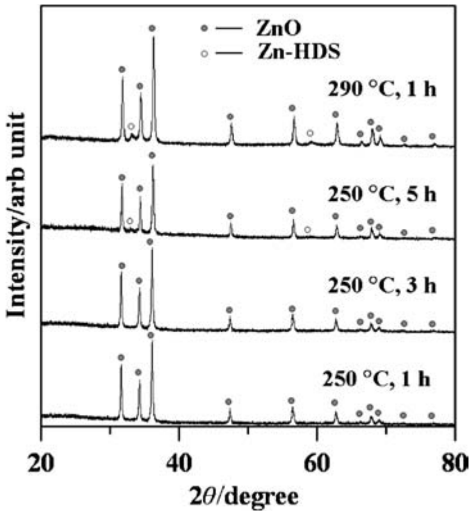

Figure 1. XRD patters of ZnO nanocrystals obtained at different reaction times and temperatures.

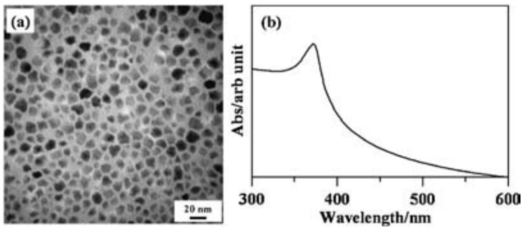

Figure 2. TEM image and UV–vis absorption spectrum of ZnO nanocrystals obtained at 250 °C for 1 h.

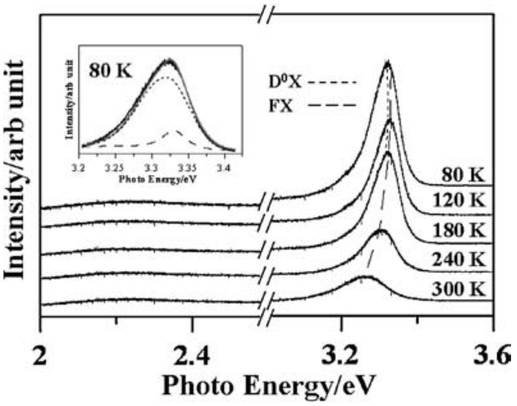

Figure 3. Temperature-dependent PL spectra of ZnO nanocrystals obtained at 250 °C for 1 h.

ZnO nanocrystals were made at 250 °C for 1 h in the following investigations. A typical TEM image of the resultant ZnO nanocrystals is show in Figure 2a. Obviously, they were roughly monodisperse with a mean diameter of 11.2 ± 1.8 nm, revealing the high-temperature organometallic route was practicable for the preparation of ZnO nanocrystals. Also, their complete discreteness was better than those by other methods.[8,9] Figure 2b indicates the UV–vis absorption spectrum for the hexane solution of ZnO nanocrystals. A significant exciton absorption feature was observed at 372 nm, from which the band gap could be estimated as 3.33 eV.

The PL spectra of the ZnO nanocrystals in the temperature range of 80 to 300 K are shown in Figure 3. Obviously, ultraviolet emission peaks occurred at 3.2–3.4 eV. When the temperature is 80 K, the dominant peak at 3.321 eV is known as the donor bound exciton (D^0X) emission, while the higher-energy shoulder peak at 3.329 eV is the free exciton (FX) emission.[19,20] With increasing temperature, intensities decreased and the intensity of D^0X emission decreased more rapidly than that of FX emission owing to the thermal ionization of bound excitons.[19] The FX emission became dominant when temperature was above about 180 K. In addition, both the exciton emission of D^0X and FX showed a red shift with the increase in the temperature. This could be attributed to the thermal expansion induced band gap shrinkage and the changes of electron–phonon interaction.[20–23] Moreover, the defect peaks around 2.25 eV were weak as compared to the ultraviolet emission peaks, revealing the high crystallinity. The intensity ratios of ultraviolet to defect emission were 20.4, 16.2, 14.8, and 7.2 at 80, 120, 180, 240, and 300 K, respectively, decreasing with increasing the temperature. All the results are in agreement with previous reports.[19–23]

In summary, ZnO nanocrystals with a mean diameter of 11.2 ± 1.8 nm have been prepared by the thermal decomposition of zinc acetate at 250 °C for 1 h. Increasing reaction time or temperature might lead to the formation of Zn-HDS. A possible mechanism was proposed. Temperature-dependent PL spectra revealed that ZnO nanocrystals showed a UV emission at 3.2–3.4 eV due to D^0X and FX emission. With increasing the temperature, both the intensities decreased with a red shift, and FX emission became dominant when temperature was above about 180 K.

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