Preparation of Monodispersed ZnO Nanoparticles via Thermal Growth-inhibitive Action of Polyethyleneimine (PEI) at Low Temperature

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An effective wet-chemical method to produce highly monodispersed ZnO nanoparticles (4–6 nm diameters) is presented. A thermal growth-inhibitive phenomenon of ZnO precursor by PEI was employed to generate monodispersed nanoparticles at low temperature (40 °C) and to improve the nanoparticle properties in terms of both size distribution and crystallinity.

Semiconductor nanoparticles have been a focus of photoelectronic research because of their unusual optoelectronic properties resulting from quantum size effects.[1] Numerous research groups have reported preparation techniques as well as potential or practical applications of nanoscale semiconductors such as CdS, CdSe, CdTe, ZnS, TiO_2, Fe_2O_3, and ZnO.[2–7] In particular, nanoscale wurtzite ZnO has been utilized in electrochemical fields including dye-sensitized solar cells,[8–11] photocatalysts,[12] chemical sensors,[13] and phosphors[14] owing to its wide band gap (3.37 eV) and large exciton binding energy of 60 meV.[15] Spanhel and Anderson,[16] Bahnemann and Kormann,[17] and Koch et al.[18] demonstrated nanocolloids or nanopowders of the ZnO depending on the preparation methods.

Recently, chemical methods such as sol–gel processes,[19] template growth,[20] and hydrothermal methods,[21,22] have attracted attention because of the relatively low growth temperature ($\leq$150 °C), the ease of processing, and promising scale-up fabrication. In addition, in order to obtain a monodispersed size distribution and good morphology of ZnO nanocrystals, some additives, either a surfactant or a complexing agent, have been extensively applied in the reaction process.[23] The preparation of ZnO nanoparticles by wet-chemical methods at low temperature has been commonly performed using the sol–gel process, which seems to be very attractive owing to easier processing than other preparation methods. However, the major problem of the sol–gel method is the uncontrolled reaction rates of hydrolysis and condensation steps, resulting in the formation of precipitates with a high degree of structural defects. The thermal growth of ZnO precursors may result in the creation of crystal defects that can strongly affect the physical properties of the crystals.[24] In view of industrial applications of nanoparticles as well as fundamental studies, chemically pure or compositionally well-defined ZnO nanocystals are required.

In this letter, a simple and efficient alcohol thermal technique at low temperature is introduced to control the ZnO particle distribution in terms of size and morphology by adding a cationic polymer, polyethyleneimine (PEI) as an over-growth inhibitor.

The reagents were purchased from Aldrich; Zinc acetate ($Zn(Ac)_2\cdot 2H_2O$, Ac = CH_3COO) (98+%, A.C.S. REAGENT), LiOH (98+%, A.C.S. REAGENT), ethanol (Denatured, HPLC grade) and PEI (branched, MW ≈800). $Zn(Ac)_2\cdot 2H_2O$ (13.17 g) was dissolved in ethanol (400 mL) at 70 °C (bp of EtOH 78 °C) and cooled to 0 °C. A LiOH base solution (0.525 M) was added dropwise to the zinc acetate suspension under vigorous stirring at 0 °C. The ZnO sol was stored for one day in a refrigerator (≈4 °C) not only to prevent rapid particle growth by retarding ZnO nuclei formation as suggested that the conversion of the precursor, basic zinc–lithium acetate, into ZnO nuclei was very slow at near 0 °C[7] but also to precipitate the over-grown ZnO seeds during storage step. Only the supernatant of the ZnO sol was used for the following thermal reflux process.

After adding the PEI (net concentration10 mM) as a growth inhibitor to the ZnO sol, it was refluxed for 3 h at different temperatures from 40 to 80 °C by using a rotary evaporator. The color of the ZnO sol became dense white, and aggregated substances were precipitated with time. The substances were then washed with a centrifuge (10000 rpm) with denatured ethanol five times to remove impurities such as acetate, hydroxide components, and PEI and subsequently dried at 70 °C. The yield of ZnO nanoparticles was 45.8%.

The diameter distribution of the finally produced ZnO nanoparticles was dependent on the storage time before the thermal reflux process. It became monodispersed with the storage time up to 24 h, and the particle diameter was not changed significantly after 24 h.[25] The storage experiment illustrated that a storage time less than 24 h was insufficient to precipitate the over-grown ZnO seeds, which bring a negative effect on the nanoparticle uniformity in the end.

Figure 1 confirms the temperature effect on the particle size and also shows the effect of PEI on the grown of ZnO crystals structure. Nanoparticles prepared at 40 °C with PEI (Figure 1a) were smaller than those made at 80 °C with PEI (Figure 1c). However, the ZnO crystals produced without PEI have irregular rod-like structures with different sizes and morphologies (Figures 1b and 1d). Figures 1e and 1f are a TEM image and the size distribution of the ZnO nanoparticles, respectively, that were prepared at 40 °C with 10 mM PEI. The TEM image shows the obtained nanoparticles with perfect circular crystal structure (≈5 nm diameter).

In our approach, hydrolysis and condensation of the zinc acetate hydrate precursors lead to the precipitation of ZnO crystals in the presence of LiOH base.[26,27] The strategy behind is the addition of PEI chains can restrict the area in which the ZnO nuclei can grow. PEI was sufficiently soluble in the denatured ethanol solution, formed hyperbranched chains, and defined the small region for the ZnO nuclei to grow into nanoparticles. The ZnO nanoparticles were generated and stabilized in the confined area, where the formed ZnO nuclei were surrounded by the

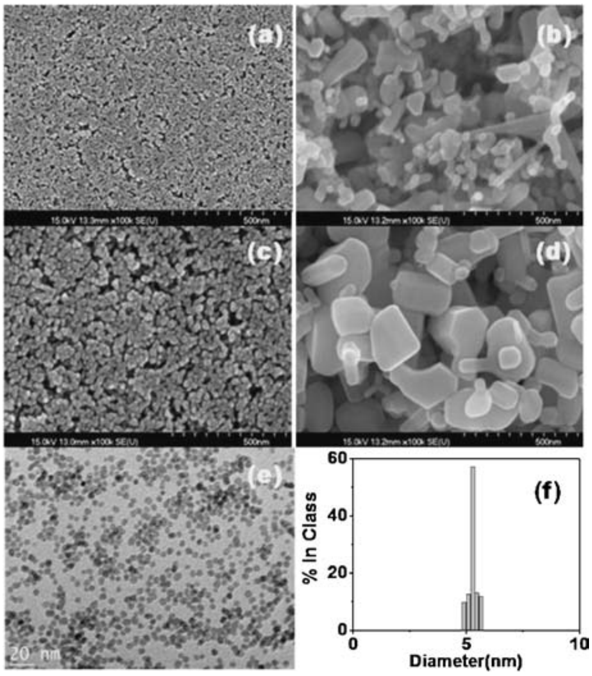

Figure 1. SEM images of the ZnO nanocrystal structures prepared (a) at 40 °C with PEI, (b) at 40 °C without PEI, (c) at 80 °C with PEI, and (d) at 80 °C without PEI. (e) TEM image and (f) size distribution of the ZnO nanoparticles made at 40 °C with PEI.

bulky hyperbranched PEI chains. However, the effect of PEI on the particle formation is not the same at all temperatures. The hyperbranched PEI chains have more mobility with increasing temperature, which provides more possibility for the $[\mathrm{Zn(OH)_4}]^{2-}$ growth units outside the bulky chains to penetrate the chains and meet the ZnO nuclei inside. The greater the chance that the growth units meet the ZnO nuclei is, the faster the ZnO nuclei grow. As the dissociation reaction proceeds more at higher temperatures, more $[\mathrm{Zn(OH)_4}]^{2-}$ growth units are formed; hence, producing larger nanoparticles eventually.

Quantum size effects such as broadening of the band gap are observed in ZnO particles with diameter less than 7 nm by PL measurements.[18] Figure 2 compares the PL spectra measured from the colloid solutions prepared at 40 and 80 °C with PEI and at 80 °C without PEI with an excitation wavelength of 290 nm. The emission peak exhibits blue shift from 367.2 (3.38 eV) to 355.9 nm (3.48 eV) with decreasing reflux temperature from 80 to 40 °C with PEI, in other words, with decreasing the size of ZnO nanoparticle, illustrating the quantum size effect. The emission peak from the ZnO nanorod-like structure prepared at 80 °C without PEI (Figure 1d) was observed at 380.5 nm (3.26 eV) which is red-shifted from the emission peak of the nanoparticles. Its PL spectrum also contains a broad emission in the visible range due to the impurities and ionized oxygen vacancies in the grown ZnO crystal structure.[24] Comparatively, the PL spectrum from the nanoparticles prepared at 40 °C with PEI does not show any emission in the visible range, which proves that ZnO nanoparticles with high purity were produced by our preparation method.

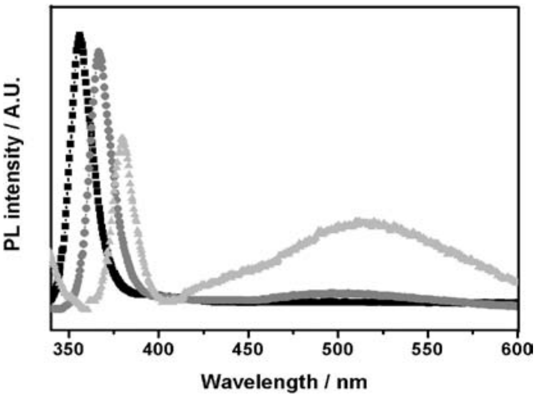

Figure 2. Photoluminescence spectrum from the colloid solution prepared at 40 °C (■), 80 °C (●) with PEI and 80 °C without PEI (▲).

In conclusion, very tiny and monodispersed (≈5 nm diameter) ZnO nanoparticles were produced in an alcoholic solution at a low reflux temperature (40 °C) by combining techniques of storing the precursor solution at 4 °C and adding PEI as a growth inhibitor. The size of the nanoparticles was found to be controlled by the reflux temperature and the quantum size effect from the nanoparticles was seen in PL measurements. In addition, this method produced pure nanoparticles which were appropriate for the device application.

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