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Monodispersed ZnO nanoparticles from a single molecular precursor†

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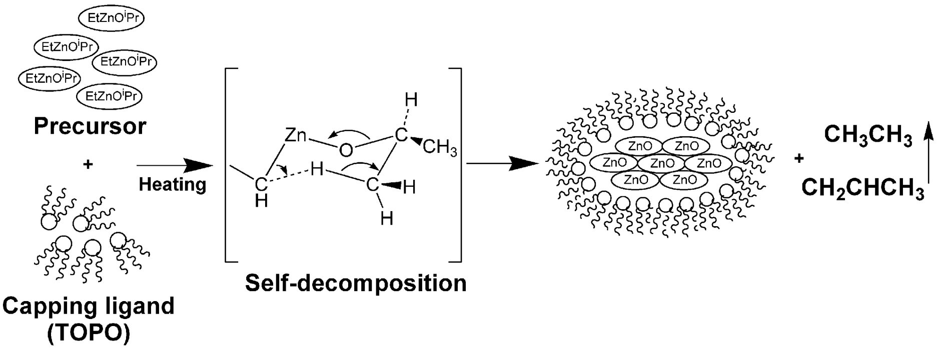
Monodispersed ZnO nanoparticles are easily prepared by the thermolysis of EtZnO^{i}Pr as a single molecular precursor and TOPO without any extra solvent as well as any oxygen source.

Semiconductor nanoparticles have attracted much interest because of their size-dependent optical and electrical properties.[1] Therefore, these properties of nanoparticles different from those of bulk materials have stimulated many researchers to investigate nanosized materials for their applications to devices such as light-emitting diodes,[2] varistors,[3] and electrochemical cells.[4] However, the properties of nanoparticles depend on the particle size as well as several other factors: structures, shapes, and surface states of the particles. Precise control of these factors in the preparation of nanoparticles is essential to the device applications in the near future.

As a wide band gap semiconductor, ZnO has found many applications such as transparent electrodes in solar cells,[5] varistors,[3] electro- and photo-luminescence devices,[6] chemical sensors, and catalysts. In many cases, multi-step processes including the use of surfactants or polymers to stabilize the surface have been required for the synthesis of ZnO nanoparticles. ZnO nanoparticles have been prepared using various methods: sol–gel techniques,[7] supercritical precipitation,[8] and colloidal synthesis.[9] Recently, the preparation of ZnO nanoparticles using surfactants or polymers has been reported. Dodecylbenzenesulfonate and polyvinylpyrrolidone have been used to stabilize the surfaces of ZnO nanoparticles.[10] However, most reported methods employed a very dilute ethanolic solution of zinc acetate and an additional base to prepare ZnO sol, the solvent of which was evaporated to produce ZnO powders, which were then washed with water. These methods require very much solvents and/or water to dilute the starting solution and purify the products. The aqueous system may be a problem to prepare ZnO nanocomposites of moisture sensitive materials like metals. For example, the preparation of Cu/ZnO nanocomposites was not possible through the reported methods.

In this report, we describe an easy non-hydrolytic route to prepare ZnO nanoparticles by the thermolysis of a single molecular precursor without any oxygen source. The solid mixture of the molecular precursor, [EtZnO^{i}Pr],[11] and 2 equivalents of trioctylphosphine oxide (TOPO) were charged into a round-bottom flask equipped with a magnetic spin bar, a condenser, and a bubbler. It was then slowly heated to dissolve homogeneously up to 80 °C. (the melting point of TOPO is *ca.* 50–54 °C) Afterward, the clear solution mixture was stirred at 160 °C for 5 h. During the stirring, gaseous products, presumably ethane and propylene, evolved. ZnO nanoparticles were separated from the clear solution by centrifugation after a simple workup, in which the solid product was dissolved in a small amount of toluene and flocculated with the addition of an excess amount of methanol. The workup could be repeated several times. The yield of the product is 78.7% based on the Zn content by ICP-AES analysis. The ZnO nanoparticles stabilized with TOPO were well dispersed in organic solvents. As shown in Scheme 1, the single molecular precursor dissolved in TOPO decomposed at 160 °C under an inert atmosphere to monodispersed ZnO nanoparticles capped with TOPO and gaseous by-products ethane and propylene, which were characterized by GC/MS. The data suggested that the precursor should self-decompose through γ-hydrogen elimination reaction as already reported in the literature.[11] Hambrock *et al.*[12] very recently reported a non-hydrolytic route to prepare ZnO nanoparticles by employing the single source precursor [MeZnOSiMe$_3$] and its derivatives with hexadecylamine as a capping ligand. Their results are very similar and may be comparable to ours. The infrared spectrum and energy-dispersive X-ray analysis (EDAX) of the dried TOPO-stabilized ZnO product show a broad band at 1050 cm^{-1} (ν_{sym} Zn–O–P) and a phosphorus peak, indicating that the ZnO nanoparticles are capped with TOPO.[13]

The X-ray diffraction pattern of the ZnO nanoparticles obtained is given in Fig. 1, showing broad peaks with low intensity due to their small sizes. However, the diffraction pattern is obviously matched with that of the standard wurzite ZnO. The size of the ZnO nanoparticles is calculated as 2.85 nm by using the Debye–Scherrer formula, $R = 0.89\lambda/(\beta \cos\theta_B)$ where $\lambda = 1.541$ Å (Cu Kα), $\beta = 0.055$ (FWHM) for the peak of $2\theta = 56.34°$.



Scheme 1 Thermolysis route of the molecular precursor to monodispersed ZnO nanoparticles without any oxygen source.

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† Electronic supplementary information (ESI) available: characterization data of the molecular precursor and thermolyzed ZnO nanoparticles and gaseous by-products. See http://www.rsc.org/suppdata/cc/b3/b306163a/

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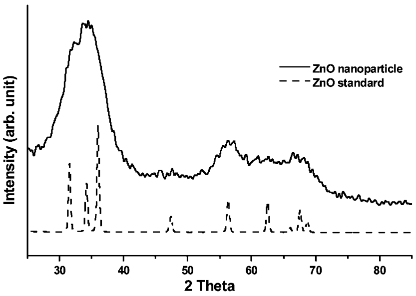

Fig. 1 X-ray diffraction pattern of ZnO nanoparticles.

Fig. 2 shows a TEM image of the ZnO nanoparticles, indicating that the nanoparticles are of monodispersed spherical shape with an average size of 3.1 ± 0.3 nm, which is in agreement with the calculated value from XRD. The selected area electron diffraction pattern shows broad diffuse rings due to the small sizes of the ZnO nanoparticles. Indexing of the SAED pattern is attributed to (100), (101), (110), (103) and (201) peaks of the hexagonal crystalline phase of ZnO nanoparticles. The HRTEM image shows that the nanoparticles are crystalline with the interplanar distance of about 3.3 Å (about 23.1 Å for 7 layers as shown in the inset of Fig. 3) and an interaxial angle of 120° in agreement with a_0 lattice parameter (3.24 Å) of wurzite ZnO.

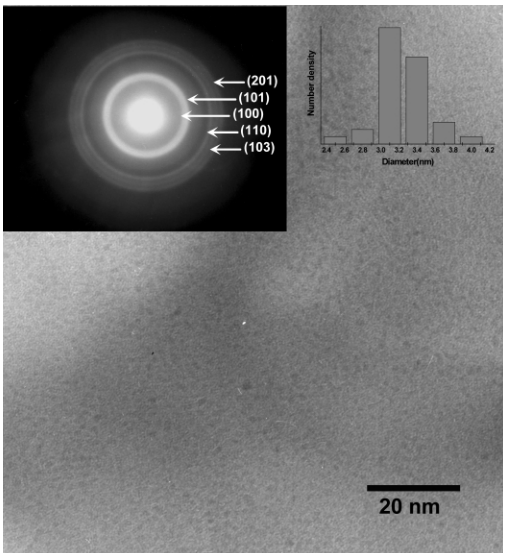

Fig. 2 TEM image and selected area diffraction pattern of ZnO nanoparticles.

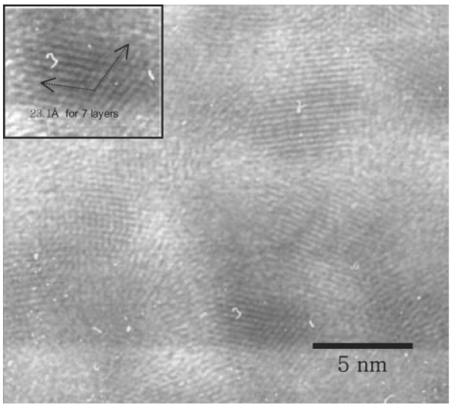

Fig. 3 HRTEM image of ZnO nanoparticles showing interplanar distance of 3.3 Å (inset).

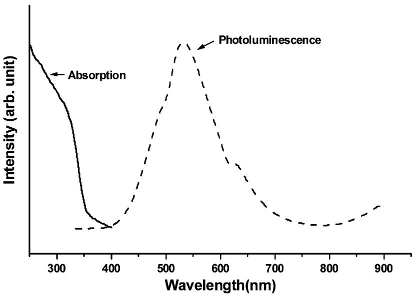

Fig. 4 Optical absorption spectrum and photoluminescence spectrum of ZnO nanoparticles.

Optical absorption and photoluminescence spectra of ZnO nanoparticles are shown in Fig. 4. The excitonic absorption peak was observed at 325 nm, blue-shifted compared to that of the bulk ZnO (375 nm) due to the quantum confinement effect.[14] The photoluminescence spectrum (λ_{ex} = 325 nm) of the ZnO nanoparticles shows a broad band at 530 nm with minor shoulders. Other research groups have already reported that a green emission band is attributed to the transition of a photo-generated electron from a dark level below the conduction band to a deeply trapped hole, induced by an oxygen vacancy for bulk ZnO as well as in nanosized ZnO.[15,16]

In conclusion, we devised a novel non-hydrolytic process for the preparation of ZnO nanoparticles by the thermolysis of the single precursor without using an oxygen source. The ZnO nanoparticles obtained at 160 °C were monodispersed with an average particle size of about 3.00 nm by a TEM image. This process could be useful to prepare nanocomposites of ZnO and metallic particles such as Cu and ZnO for catalytic application after chemical modification. We are currently investigating the possibility of preparing nanocomposites and core shells of ZnO/Cu and *vice versa*.

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Notes and references

1 A. van Dijken, A. H. Janssen, M. H. P. Smitsmans, D. Vanmaekelbergh and A. Meijerink, *Chem. Mater.*, 1998, **10**, 3513; Y.-w. Jun, J.-E. Koo and J. Cheon, *Chem. Commun.*, 2000, 1243.
2 B. O. Dabbousi, M. G. Bawendi, O. Onitsuka and M. F. Rubner, *Appl. Phys. Lett.*, 1995, **66**, 1316.
3 L. Kong, F. Li, L. Zhang and X. Yao, *J. Mater. Sci. Lett.*, 1998, **17**, 769.
4 H. Weller, *Adv. Mater.*, 1993, **5**, 88.
5 H. Rensmo, K. Keis, H. Lindström, S. Södergren, A. Solbrand, A. Hagfeldt, S.-E. Lindquist, L. N. Wang and M. Muhammed, *J. Phys. Chem. B*, 1997, **101**, 2598.
6 K. Vanheusden, C. H. Seager, W. L. Warren, D. R. Tallant, J. Caruso, M. J. Hampden-Smith and T. T. Kodas, *J. Lumin.*, 1997, **75**, 11.
7 L. Spanhel and M. A. Anderson, *J. Am. Chem. Soc.*, 1991, **113**, 2826.
8 E. Reverchon, G. Della Porta, D. Sannino and P. Ciambelli, *Powder Technol.*, 1999, **102**, 127.
9 E. M. Wong, J. E. Bonevich and P. C. Searson, *J. Phys. Chem. B*, 1998, **102**, 7770.
10 L. Guo, S. Yang, C. Yang, P. Yu, J. Wang, W. Ge and G. K. L. Wong, *Chem. Mater.*, 2000, **12**, 2268.
11 R. J. Herold, S. L. Aggarwal and V. Neff, *Can. J. Chem.*, 1963, **41**, 1368; E. C. Ashby, G. F. Willard and A. B. Goel, *J. Org. Chem.*, 1979, **44**, 1221.
12 J. Hambrock, S. Rabe, K. Merz, A. Birkner, A. Wohlfart, R. A. Fischer and M. Driess, *J. Mater. Chem.*, 2003, **13**, 1731.
13 N. Revaprasadu, M. A. Malik, P. O'Brien, M. M. Zulu and G. Wakefiled, *J. Mater. Chem.*, 1998, **8**, 1885.
14 D. W. Bahnemann, C. Kormann and M. R. Hoffmann, *J. Phys. Chem.*, 1987, **91**, 3789.
15 E. A. Meulenkamp, *J. Phys. Chem. B*, 1998, **102**, 5566.
16 S. Sakohara, M. Ishida and M. A. Anderson, *J. Phys. Chem. B*, 1998, **102**, 10169.