

Morphology-controlled large-scale synthesis of ZnO nanocrystals from bulk ZnO†

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Gram-scale, teardrop-like, monodisperse ZnO nanocrystals with a well-resolved absorption onset and a strong sharp UV emission were prepared by thermal decomposition of ZnO-oleic acid complexes in hexadecylamine.

ZnO is a wide bandgap semiconductor ($E_g = 3.37$ eV) with a large exciton binding energy (60 meV) that possesses a wide range of envisaged applications such as in catalysis,¹ for solar energy conversion,² and in optoelectronic devices.^{3,4} In particular, room-temperature UV lasing from ZnO nanorod arrays has been demonstrated,⁴ which triggers extensive activities in searching for novel, facile synthetic methods. Among them, vapour-phase catalysis-assisted transport process and thermal evaporation are the major physical methods to fabricate ZnO nanostructures.^{4,5} The chemical methods appear to be of particular interest since they offer the potential of facile scale-up, and of flexible processing chemistry. The wet-chemistry synthesis is generally carried out in water or alcohols using zinc salts as the starting material in the presence of a base.⁶ However, this synthesis makes use of ionic species, which may react with the growing oxide and thus affects material properties. Recently the thermal decomposition of organometallic precursors in coordination solvents was also explored to fabricate ZnO nanostructures.⁷

Almost all the previously reported synthetic methods are limited in the formation of the preferred spherical or one-dimensional ZnO nanostructure owing to the hexagonal lattice of ZnO with an $a : c$ axial ratio of 1 : 1.6. It is well established that the shape and size of inorganic nanocrystals control their widely varying optoelectronic and chemical properties. From this aspect, one can expect that some other types of morphologies of ZnO would be promising candidates for room-temperature UV laser utilization or other interesting phenomena. Therefore, the development of a morphologically controlled synthesis of ZnO nanoparticles is urgently needed to meet the demand for exploring the potentials of ZnO.

In our previous reports,⁸ ZnO was dissolved in carboxylic acid at high temperature to form molecular complexes and served as a precursor for the preparation of ZnS or $Zn_xCd_{1-x}S$ nanocrystals. This prompts us to add amines to the ZnO-carboxylic acid system and reconvert the formed molecular complexes into nanoscaled ZnO. Here we report for the first time a solution-phase synthesis of gram-scale, morphology-controlled single crystalline ZnO nanostructures by thermal decomposition of ZnO-oleic acid

complexes in hexadecylamine, which produces monodisperse ZnO nanocrystals with teardrop-like shape. The nanoscaled ZnO exhibits a well-resolved absorption onset, a strong sharp UV emission and shows some extent of quantum confinement effect compared with bulk ZnO.

In a typical reaction for the synthesis, 0.81 g (10 mmol) of ZnO was dissolved in a mixture containing 5.0 mL of octadecene (ODE) and 10.0 mL (30 mmol) of oleic acid (OA) at 280 °C. When the formed ZnO-OA complex solution was cooled to room temperature, 40.0 g of hexadecylamine (HDA) was loaded into the flask. The resulting mixture was heated rapidly (≈ 25 °C min^{-1}) to 310 °C and maintained at this temperature for 15 min under Ar flow. The solution gradually turned yellow and became a little cloudy, which gave rise to the uniform ZnO nano-teardrops. The particles were precipitated by adding ethanol to the reaction mixture at ≈ 50 °C. The resulting precipitate was purified by repeated centrifugation and decantation. The surfactant-coated ZnO particles were then easily re-dispersed in non-polar solvents such as CHCl_3 or hexane, and used for spectroscopic measurements and transmission electron microscopy (TEM) investigation without any size selection. The structure and morphology of the obtained ZnO were characterized by high-resolution TEM and by powder X-ray diffraction (p-XRD).

The p-XRD pattern (Fig. 1) reveals that the obtained ZnO nanoparticles possess a wurtzite hexagonal structure of high crystallinity, and all of the peaks match well with Bragg reflections of the standard wurtzite structure ($P63mc$), with the measured lattice constants of c and a of this hexagonal phase being 5.21 and 3.25 Å, respectively ($cla = 1.60$).

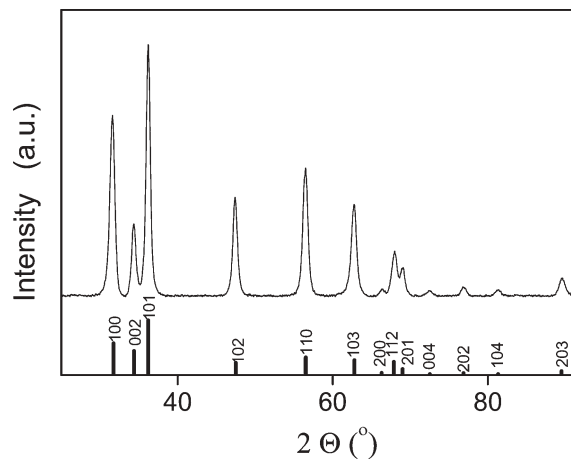


Fig. 1 p-XRD patterns of the nanoscaled ZnO teardrops. The line XRD spectrum corresponds to bulk hexagonal ZnO (bottom).

† Electronic supplementary information (ESI) available: Fig. S1: self-assembly of ZnO nano-teardrops into flower-shaped aggregates. See <http://www.rsc.org/suppdata/cc/b4/b414948c/>

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The wide-field TEM image (Fig. 2) shows the teardrop-like ZnO nanostructures, with fairly uniform shape and size. These nanoteardrops are 22 ± 1.7 nm in averaged length, and the bodies of the teardrops are 8.0 ± 0.8 nm in diameter on average. The diameter of the teardrop decreases evenly and the end point is 2.0 ± 0.3 nm in mean diameter. The monodisperse nanoteardrops can self-assemble into separate close-packed 'flowers', in which they align with their thinner end parts stacking together and the large body forming the outer circle (see Fig. S1 in the ESI[†]). The HRTEM image shows that the nanostructures are structurally uniform, and the 2D lattice fringes illustrate that the nanocrystals are single crystalline and confirm that the nanoteardrops exhibit wurtzite-type structure. The electron diffraction (ED) pattern shows the characteristic reflections of wurtzite structure, which was also found in the corresponding p-XRD.

The use of capping reagent(s) to kinetically control the growth rates of various facets of a seed for the synthesis of various architectures of nanocrystals has been realized in many materials.⁹ Undoubtedly, oleic acid plays a key role in the formation of the anisotropic shape of ZnO nanostructures in this experiment. It seems that the combination of different solvents determines the final architecture of ZnO nanoparticles. In addition, the complicated variation of the monomer concentration *versus* time should also play a role in the determination of the morphology of ZnO nanoparticles. Unlike the quick injection of precursor (or monomer) into hot solvent, where precursor concentration decreases monotonously, here the relative stable precursor ZnO–OA is gradually heated up to and then above its critical decomposition temperature, which results in the ZnO monomer concentration increasing gradually to its maximum value and keeping for a certain period, and then decreasing gradually with the depletion of the monomer. (Our experimental results show that the whole decomposition process of ZnO–oleic acid complexes lasts for ≈ 3 min. Later on, the absorbance of the reaction solution stops increasing.) The variation of monomer concentration in the nucleation and growth process should have a contribution to the development of the morphology of the ZnO nanoparticles. Usually, low monomer concentration favours the isotropic growth, while high monomer concentration favours the anisotropic

growth.¹⁰ The detailed mechanism for the morphology development of the ZnO nanoparticles is still under investigation.

In the absorption spectrum (Fig. 3), the first exciton feature ($1S_h-1S_e$) of the obtained nanoparticles is well-resolved, while the second exciton feature ($1P_h-1P_e$) is not distinguishable. This may be due to the lifted degeneracy of different hole and electron P-states arising from the odd shape or from the crystal-field. The onset of absorption is around $\lambda = 360$ nm, somewhat blue-shifted from that of bulk ZnO (373 nm), showing the effect of quantum confinement. Almost no observable absorption tail at wavelengths longer than 380 nm indicates that the colloidal dispersions scattered light does not exist. The obtained ZnO nanocrystals show a strong UV emission at $\lambda = 377$ nm (with a full width at half-maximum (fwhm) of 23 nm), which is attributed to the near band-edge emission coming from the recombination of excitons. The UV emission peak shows a similar profile by changing the excitation wavelength, which is the characteristic feature of band-edge emission. No deep-level or trap-state defect emission in the green region is detected. The disappearance of the commonly encountered green emission in the PL spectrum demonstrates the

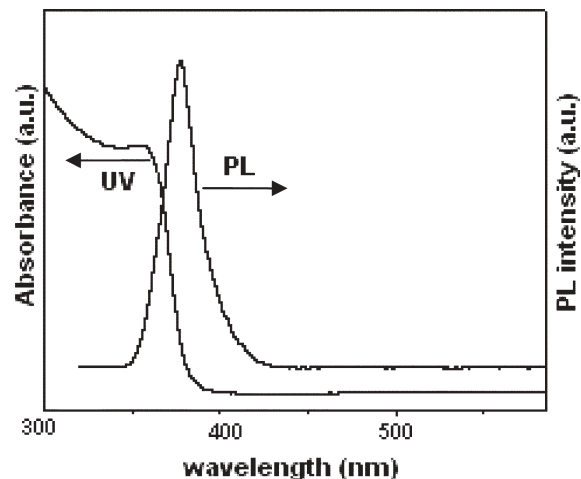


Fig. 3 UV/VIS and PL spectra ($\lambda_{\text{ex}} = 310$ nm) of the ZnO nanoteardrops dispersed in CHCl_3 .

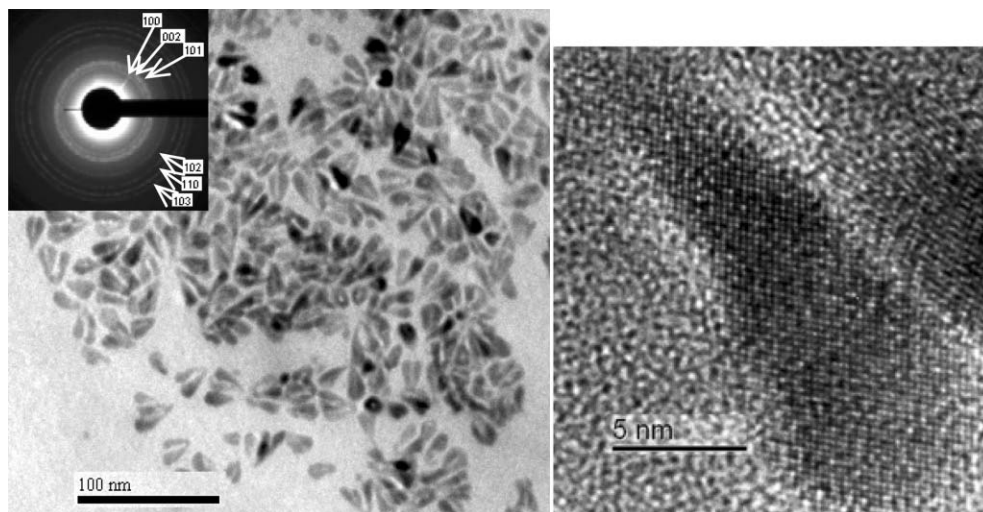


Fig. 2 Wide-field TEM images of ZnO teardrops (the insert is a wide-area SAED pattern) and the corresponding HRTEM image.

absence of oxygen vacancy in our sample.¹¹ In addition, the sharpness of the absorption and the emission peaks gives a powerful attestation that the sample shows a narrow size distribution which is consistent with the TEM observation. In the previously reported ZnO nanoparticles, due to the poor crystal quality, the UV emission of the nanoscaled ZnO is liable to be quenched and only defect emission in visible region is detected. This deficiency hinders progress in the applications of ZnO in optoelectronic and lasing devices. Therefore, our anisotropic ZnO nanocrystals with strong UV emission and the absence of the defect emission in the visible region would be a promising candidate for room-temperature UV laser utilization or other interesting phenomena such as application in optoelectronic and lasing devices. In addition, the obtained teardrop-like ZnO nanocrystals would be valuable in exploring the morphology control mechanism in the crystal formation process.

In conclusion, we reported here a facile method for the morphology-controlled gram-scale production of high-quality ZnO nanocrystals from bulk ZnO, resulting in soluble and processable ZnO nanoparticles with high crystallinity, and uniform size and shape. This approach has the potential to be extended to the production of other metal oxide nanocrystals.

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