

## A New Reaction to ZnO Nanoparticles

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A new reaction was developed to synthesize ZnO nanoparticles with nearly uniform, spherical morphologies and controlled size range from 25–100 nm via esterification between zinc acetate and ethanol under solvothermal condition. The ZnO nanoparticles were characterized by X-ray diffraction and transmission electron microscopy. The reaction mechanism was directly testified by the existence of ethyl acetate in the finished reaction liquid.

ZnO is a II–VI compound semiconductor with a wide and direct band gap of 3.37 eV and a large excitation binding energy of 60 meV,<sup>1</sup> and has been attracting increasing attention from scientists because of its importance in fundamental studies and their numerous potential applications. ZnO is widely used in pigments,<sup>2</sup> cosmetics,<sup>3</sup> varistors,<sup>4</sup> chemical sensors,<sup>5</sup> and optoelectronics.<sup>6</sup> Recent researches show that ZnO is another promising candidate for photonic crystals because of its higher refractive index and an efficient emitter in the near UV.<sup>7</sup> So the finding of new reactions to synthesize uniform ZnO nanoparticles has profound significance both in fundamental and applied aspects. Then, various approaches had been chosen to obtain ZnO nanoparticles with uniform morphologies and structures. Spanhel et al. reported ZnO clusters with crystallite sizes in 3–6 nm synthesized via sol–gel process.<sup>8</sup> Spherical monodisperse ZnO particles were prepared by Jezequel and co-workers by hydrolysis of zinc acetate dihydrate in diethyleneglycol at 180 °C.<sup>9</sup> Recently, Seelig et al. developed Jezequel's method and obtained periodic arrays of ZnO spheres.<sup>7</sup>

Herein, we proposed a new reaction to synthesize ZnO nanoparticles with nearly uniform, spherical morphologies and controlled size via esterification between zinc acetate and ethanol under solvothermal condition. The starting reagents used in the present work include zinc acetate dihydrate and absolute ethanol. Both were of analytical grade and used without further purification. The procedures were as follow: 2.5-g zinc acetate dihydrate and 25-mL absolute ethanol were added into a 40-mL Teflon-lined stainless steel autoclave and sealed tightly. Thermal treatments were carried out at 100–200 °C for 24–48 h in an autocontrolled oven. Then the autoclave was allowed to cool to room temperature. The upper clear aromatic liquid was decanted off, and the white slurry products were collected by filtration and washed by absolute ethanol and deionized water for several times. After that, the products were dried at 60 °C for 6 h.

The XRD patterns were recorded from 20 to 100° in  $2\theta$  with a scanning step of 0.02° on a D8 Advance Bruker X-ray diffractometer with Cu K $\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) radiation. Figure 1 shows the typical XRD pattern of the as-synthesized ZnO nanoparticles. The Miller indices were specified above the corresponding peaks. All the peaks were well indexed to hexagonal crystalline ZnO (JCPDS card No. 36-1451) with no impurities detected. The

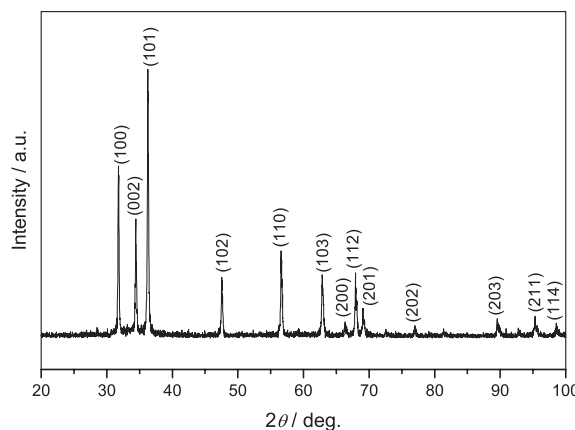


Figure 1. XRD pattern of as-synthesized ZnO nanoparticles.

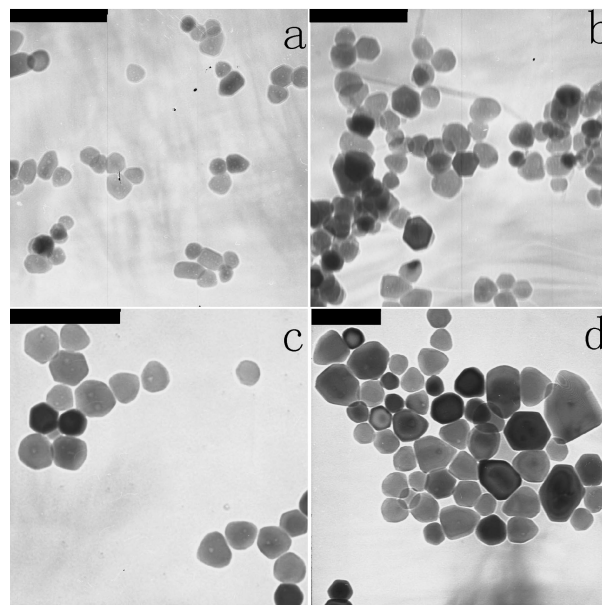


Figure 2. TEM images of as-synthesized ZnO nanoparticles under different synthesis conditions: (a) 120 °C 24 h, (b) 120 °C 48 h, (c) 180 °C 24 h, and (d) 200 °C 24 h, the black bar represented 200 nm.

sharp diffraction peaks indicated that the as-synthesized ZnO nanoparticles were with high crystallinity.

The morphologies of the ZnO nanoparticles were characterized by transmission electron microscopy (TEM) observation on an H-800 with an accelerating voltage of 200 kV. Figure 2 gives typical TEM images of the ZnO nanoparticles. It can be seen that all the ZnO nanoparticles were nearly uniformly spherical and nonagglomerate. By changing the reaction temperature

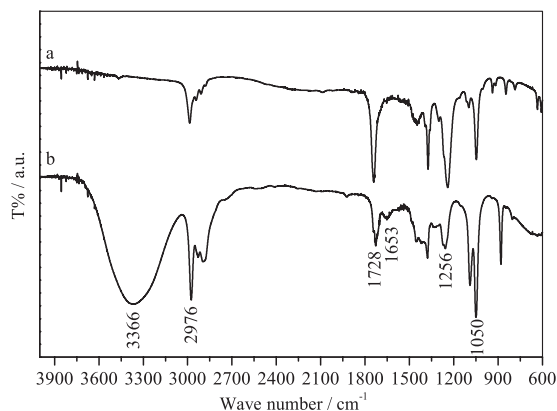
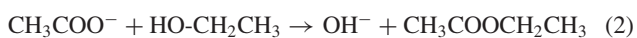
and time, the nanoparticles size can be easily controlled. The ZnO nanoparticles about 25 nm in diameter were synthesized at 120 °C for 24 h (Figure 2a). When the reaction time extended to 48 h (Figure 2b) the diameters slightly increased to about 40 nm. On the other hand, the ZnO nanoparticles size can also be influenced substantially by reaction temperature. The ZnO nanoparticles were near 60 nm in diameter as the temperature increased to 180 °C with the reaction time 24 h (Figure 1c). And the diameters became larger than 100 nm when the temperature increased to 200 °C with the reaction time 24 h unchanged (Figure 1d).

We proposed a plausible reaction mechanism wholly expressed as Eq 1:



It was testified by the evidence of the presence of ethyl acetate in the finished reaction liquid. The infrared (IR) absorption spectra of the finished reaction liquid were tested by a PE-2000 FT-IR spectrometer and shown in Figure 3. Plots (a) and (b) were the IR spectra of ethyl acetate and the finished reaction liquid respectively. In the plot (b), the strong absorption at about 1728 cm<sup>-1</sup> was attributed to the typical absorption of C=O. The strongest absorption peak at 1050 cm<sup>-1</sup> could be indexed to the C–O–C symmetric stretch vibration, while the slight broad strong peak at 1256 cm<sup>-1</sup> was of C–O–C unsymmetric stretch vibration. All these absorption peaks were well in accordance with the IR spectra of ethyl acetate as shown in plot (a), which proved the generation of ethyl acetate during the reaction. On the other hand, the strong aromatic odor would provide additional evidence to support the proposed reaction mechanism. The absorption peak at 1653 cm<sup>-1</sup> was attributed to the –COO<sup>-</sup> of the unreacted CH<sub>3</sub>COO<sup>-</sup> while the broad peak centered at 3366 cm<sup>-1</sup> were typical absorption of –OH, which implied the existence of unreacted ethanol and the production of water.

The reaction was possibly contained some coupling reactions. First, OH<sup>-</sup> anions were produced by esterification between CH<sub>3</sub>COO<sup>-</sup> and ethanol as given in Eq 2:



**Figure 3.** FT-IR absorption spectra of (a) ethyl acetate and (b) the finished reaction liquid.

Secondly, Zn<sup>2+</sup> cations reacted with OH<sup>-</sup> anions to form ZnO under solvothermal condition:



In this case the reaction mechanism is radically different from the reported reaction between zinc acetate and NaOH in aqueous and in ethanol solution.<sup>10–12</sup> The esterification (Eq 2) acted as OH<sup>-</sup> reservoir and released OH<sup>-</sup> gradually, which might be an important factor to synthesize ZnO nanoparticles with uniform shape and size. The presence of ethanol and the ester could help to improve the dispersibility of the synthesized ZnO nanoparticles. Compared with using NaOH as OH<sup>-</sup> source, there was no problem of contamination caused by the residues and impurities of Na<sup>+</sup> cations.

Besides ethanol, other homologous alcohol such as *n*-octanol could also be used. Moreover, this reaction can be extended to a versatile method to synthesize many other oxides.

In summary, we have developed a novel reaction to ZnO nanoparticles with nearly uniform spherical morphologies and high dispersibility by esterification between zinc acetate and ethanol under solvothermal condition. By change the reaction temperature and time, the particles size was easily tailored from 25 to 100 nm. Similarly, many other oxide nanoparticles could be synthesized via esterification between metal acetates and ethanol.

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