

Preparation of ZnO nanocrystals *via* ultrasonic irradiationDong Qian,^a J.Z. Jiang*^a and Poul Løvng Hansen^b^a Department of Physics, Building 307, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark.

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Received (in Cambridge, UK) 6th February 2003, Accepted 6th March 2003

First published as an Advance Article on the web 28th March 2003

A simple and rapid process has been developed for the preparation of nanometer-sized ZnO crystals *via* ultrasonic irradiation, by which pure ZnO nanocrystals with an average size of 6 nm and narrow size distribution can be synthesized in a short time and without using any solvents for the precipitation of ZnO.

ZnO nanocrystals have been intensively studied during the past years because of their promising physical and chemical properties, which could lead to a wide range of technologically important applications. Therefore, the preparation of ZnO nanocrystals of high quality is receiving much attention.^{1–4} Here a novel and simple procedure for preparing ZnO nanocrystals with narrow size distribution *via* ultrasonic irradiation based on Meulenkamp's preparation procedure has been developed. Pure ZnO nanocrystals with an average size of 6 nm and standard deviation about 10% can be obtained in 1 hour after preparation of ZnO sol and without using any solvents, e.g., alkanes, for the precipitation of ZnO.

Sonochemical synthesis, which has become a routine method for preparing a wide variety of nanostructured materials,^{5–9} is based on acoustic cavitation resulting from the continuous formation, growth and implosive collapse of bubbles in a liquid.^{10,11} Gedanken and coworkers¹² synthesized crystalline nanoporous ZnO spheres with a diameter of *ca.* 500 nm and 20 nm pore size *via* ultrasonic irradiation. In the present work, we found that ultrasonic irradiation can greatly enhance the conversion rate of precursor to nanometer-sized ZnO crystals and induce the precipitation of ZnO under suitable conditions without addition of solvents.

In a typical experiment, 2.86 g of Zn(Ac)₂·2H₂O was placed in 130 mL of absolute ethanol and then the mixture was distilled under magnetic stirring. When the volume of the mixture was concentrated to *ca.* 60 mL, the Zn²⁺-containing suspension obtained was diluted to 130 mL by addition of absolute ethanol and was cooled to 0 °C. The distillation process required *ca.* 30 min. 0.754 g of LiOH·H₂O was dissolved in 130 mL of absolute ethanol at room temperature using magnetic stirring. The hydroxide-containing solution was then added dropwise into the Zn²⁺-containing suspension at 0 °C under vigorous stirring. The addition procedure took *ca.* 40 min. The ZnO sol obtained was treated under different conditions listed in Table 1. After treatment, the precipitates were separated by centrifugation, dried in a vacuum freezer and then ground to a fine powder to obtain dried samples.

The X-ray diffraction (XRD) patterns of the as-prepared samples, characterized by a Philips PW 1394 diffractometer employing Cu-K_α radiation, are shown in Fig. 1. The reflections of pure ZnO [Fig. 1(i)–(o)] can be indexed to hexagonal ZnO (JCPDS 36–1451). The peaks are overlapped, caused by line-broadening because of the small crystal size. It was reported⁴ that the precursor for preparing ZnO nanocrystals is a basic Zinc-Lithium-Acetate, which further transfers to ZnO over about 1 week at ≤ 0 °C. Therefore, samples A–H are the mixtures containing ZnO and basic Zinc-Lithium-Acetate [Fig. 1(a)–(h)]. From Fig. 1(a)–(e), the conversion of the precursor to ZnO nanocrystals is very slow without sonication. The conversion has not completely finished even after 12 days since

preparation of ZnO sol. On the other hand, the transition of the precursor to ZnO nanocrystals can be largely accelerated by ultrasonic irradiation and it is completed within 10 min at 0 °C

Table 1 Treatment conditions for samples A–O

Sample	Treatment conditions ^a	Crystal size ^b /nm
A	Stored at ≤ 0 °C, precipitated with heptane immediately	—
B	Stored at ≤ 0 °C, precipitated with heptane after 2 days	4.0
C	Stored at ≤ 0 °C, precipitated with heptane after 4 days	4.2
D	Stored at ≤ 0 °C, precipitated with heptane after 6 days	4.3
E	Stored at ≤ 0 °C, precipitated with heptane after 12 days	4.5
F	Sonicated 1 min at 0 °C, precipitated with heptane	—
G	Sonicated 3 min at 0 °C, precipitated with heptane	3.8
H	Sonicated 5 min at 0 °C, precipitated with heptane	4.5
I	Sonicated 10 min at 0 °C, precipitated with heptane	4.7
J	Sonicated 60 min at 0 °C, precipitated with heptane	5.6 (~ 5.4)
K	Sonicated 120 min at 0 °C, precipitated with heptane	6.4 (~ 7)
L	Sonicated 80 min at 20 °C in a water bath without precipitation by heptane	6.4
M	Sonicated 15 min at 60 °C in a water bath without precipitation by heptane	6.4
N	Sonicated 15 min at room temperature in air without precipitation by heptane	6.4
O	Sonicated 25 min at room temperature in air without precipitation by heptane	6.5 (~ 6.2)

^a Sonication was carried out with a high-intensity ultrasonic horn (Branson 184V, 20 kHz, 900 W). ^b Average crystal size for ZnO was estimated by XRD using the Scherrer formula for the (102) reflection. The crystal sizes of samples J, K and O in parentheses were determined by TEM.

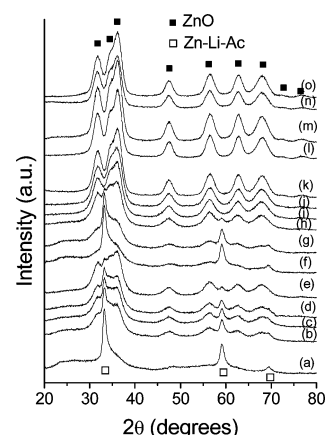


Fig. 1 XRD patterns of as-prepared samples A–O (from bottom to top).

[Fig. 1(f)–(i)], resulting in an average crystal size of 4.7 nm for sample I which is comparable to 4.5 nm for sample E prepared without ultrasonic irradiation. With increasing irradiation time, the crystal size increases to 5.6 nm in sample J for 60 min and 6.4 nm in sample K for 120 min. The effects of sonication may be understood as follows. At the beginning of ultrasonic irradiation, the cavitation enhances the nucleation rate during hydrolysis and condensation in a sol–gel process. With further increasing the irradiation time, crystals will grow due to local heating arising from cavitation.

To obtain clean ZnO nanocrystals, a precipitation and wash process is required. The method, developed by Meulenkamp⁴ using alkanes, e.g., heptane, to precipitate ZnO nanocrystals and then wash with absolute ethanol, is expensive and time-consuming. We found that sonicating ZnO sol can also precipitate ZnO nanocrystals without using any solvents, as shown in Table 1 for samples L–O, followed by washing with absolute ethanol. This sonication precipitation process strongly depends on the sonication temperature. Sonicating ZnO sol for 120 min at 0 °C (sample K) did not effect the precipitation of

ZnO. Sonicating at 20 °C in a water bath, the ZnO sol began to show turbidity after *ca.* 47 min and sample L was sonicated over a period of 80 min in order to precipitate ZnO crystals completely. With the sonication at 60 °C in a water bath, the ZnO sol showed turbidity after *ca.* 13 min and sample M was sonicated for 15 min. However, sonicating ZnO sol at room temperature without a bath resulted in turbidity after only *ca.* 10 min, which may be due to the fact that the temperature of the ZnO sol increases promptly without a bath. Sample N was sonicated for 15 min at room temperature without a bath. Samples L–O, which were sonicated under different conditions without precipitation by solvents, have almost the same crystal size. Transmission electron microscopy (TEM) measurements of samples J, K and O carried out on a Philips CM200 FEG with an ultratwin lens at 200 kV reveal that ZnO nanocrystals obtained have a narrow size distribution with a standard deviation of about 10% and single hexagonal structure. Their average crystal sizes determined by TEM, listed in Table 1, are in good agreement with the sizes estimated by XRD. An example for sample O is presented in Fig. 2 with an average crystal size of 6.2 nm, standard deviation of about 9%, and a hexagonal structure.

DQ and JZJ thank the Danish Technical Research Council for financial support.

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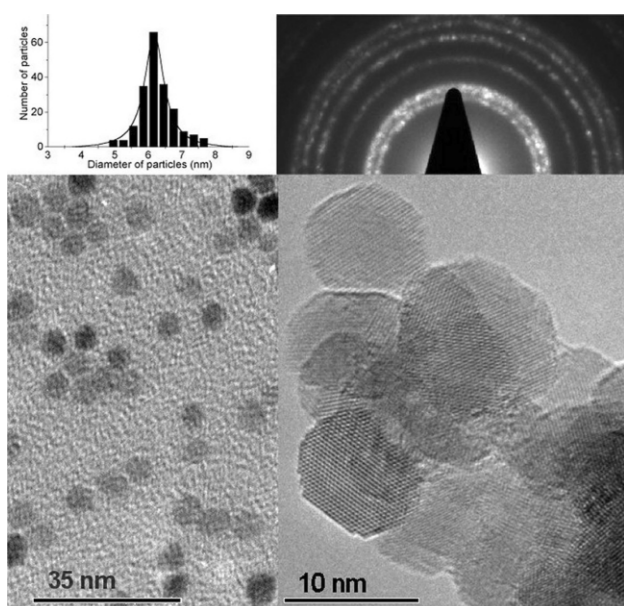


Fig. 2 TEM images, particle size distribution, and electron diffraction pattern of sample O.