

COMMENTS

Comment on “Catalysis and Temperature Dependence on the Formation of ZnO Nanoparticles and of Zinc Acetate Derivatives Prepared by the Sol–Gel Route”Dong Qian,^{*,†,‡} Leif Gerward,[†] and J. Z. Jiang^{*,†}

Department of Physics, Building 307, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark, and College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China

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In a recent paper,¹ Tokumoto et al. discussed the chemical and structural nature of powders prepared from the zinc acetate-derived precursor by the sol–gel route proposed by Spanhel and Anderson² in 1991. These authors reported that no-washed nanoparticulate powders consisted of a mixture of ZnO (wurtzite), zinc acetate ($\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$), and hydroxy double salt $\text{Zn}_5(\text{OH})_8(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ (Zn–HDS). They pointed out that the formation of Zn–HDS depended strongly on the temperature and catalysts employed in the hydrolysis step. With LiOH as a basic catalyst, powders with the highest proportion of ZnO were usually obtained at low synthesis temperature ($<20^\circ\text{C}$) and no Zn–HDS was formed at 10°C . The highest amount of Zn–HDS in the powders was obtained in the temperature range 40 – 60°C . $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ was dominant in the powders above 60°C and $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ with the proportion above 99% could be obtained at 70°C . Tokumoto et al.’s results are of considerable importance in the development of synthesis strategies and the optimization of reaction conditions for the sol–gel preparation of ZnO nanoparticles. However, there exists a difference in the formation of Zn–HDS between some results reported by Tokumoto et al. and Meulenkamp’s report³ as well as our previous findings.⁴ In 1998, Meulenkamp modified and extended Spanhel and Anderson’s procedure for preparation of ZnO nanoparticles. He found that an unexpected powder precipitated after the addition of hexane/heptane to the sol (obtained after the addition of $\text{LiOH} \cdot \text{H}_2\text{O}$ to the ethanolic $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ solution and then kept at $\leq 0^\circ\text{C}$) within 1 day. The transformation of the powder to ZnO nanocrystals was very slow and took about 1 week at $\leq 0^\circ\text{C}$. In our previous paper,⁴ we found that the ultrasonic irradiation had an enormous effect on the transformation of the powder to ZnO nanocrystals, which was finished within 10 min under sonicating at 0°C . Now the powder can be identified as the Zn–HDS phase.¹ However, the ultrasonic bath was used in Tokumoto et al.’s work¹ for the dissolution of the LiOH powder during the synthesis of ZnO nanoparticles, and the effect of ultrasonic irradiation on the formation of Zn–HDS was overlooked. As will become clear in the following, Tokumoto et al.’s results are not wrong in themselves, but there exists a negligence of the effect of

ultrasonic irradiation on the formation of Zn–HDS during the sol–gel synthesis of ZnO nanoparticles.

To avoid the effect of ultrasonic irradiation on the transformation of Zn–HDS, we did not use sonication during the preparation of Zn–HDS, which was similar to the methods described by Meulenkamp³ and in our previous paper.⁴ A 2.86 g (13 mmol) amount of $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ (Merck, reagent grade) was placed in 130 mL of absolute ethanol (Merck, reagent grade) and then the mixture was heated to dissolve $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ under magnetic stirring. When $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ was dissolved completely, the Zn^{2+} -containing solution obtained was diluted to 130 mL by the addition of absolute ethanol and was cooled to 0°C . $\text{LiOH} \cdot \text{H}_2\text{O}$ (0.754 g, 18 mmol) was dissolved in 130 mL of absolute ethanol at room temperature using magnetic stirring. The hydroxide-containing solution was then added dropwise into the Zn^{2+} -containing solution at 0°C under stirring. The sols obtained were treated under different conditions listed in Table 1. After treatments, heptane was added until white precipitates were present. The required volume ratio of heptane to the solution was 2–3:1. The mixture was kept at $\leq 0^\circ\text{C}$ for 2 h to precipitate completely. Precipitates were separated by centrifugation, dried in a vacuum freezer, and then ground to fine powders to obtain dried samples for further characterizations.

The X-ray diffraction (XRD) patterns of the as-prepared samples, characterized by a Philips PW 1050 diffractometer employing $\text{Cu-K}\alpha$ radiation, are shown in Figure 1. The peaks (marked “■”) located at about $2\theta = 31.9^\circ, 34.5^\circ, 36.2^\circ, 47.6^\circ, 56.6^\circ, 62.9^\circ, 68.0^\circ, 72.6^\circ$, and 77.0° can be indexed to hexagonal ZnO (JCPDS 36-1451). Some of these peaks are overlapped, caused by line-broadening because of the small crystal size. The peaks (marked “□”) at approximately $2\theta = 33.3^\circ, 59.1^\circ$, and 69.4° can be assigned to 100, 110, and 200 reflections of Zn–HDS (see ref 5), respectively.

In Tokumoto et al.’s experiments of studies on the formation of Zn–HDS, the ultrasonic bath was used to dissolve the LiOH powder. It is well-known⁶ that ultrasound causes high-energy chemistry, which is based on acoustic cavitation resulting from the continuous formation, growth, and implosive collapse of bubbles in a liquid. According to the results listed in Figure 1, the ultrasonic irradiation has a pronounced effect on the formation of Zn–HDS. From Figure 1a, it can be seen that a higher amount of Zn–HDS is formed after the addition of $\text{LiOH} \cdot \text{H}_2\text{O}$ into the ethanolic precursor solution (the precursor was recently identified as $\text{Zn}_4\text{O}(\text{Ac})_6$ by Tokumoto et al.⁷) at 0°C without ultrasonic irradiation. However, Zn–HDS can easily transform into the ZnO phase through ultrasonic irradiation at 0°C , which is completed within 10 min (see Figure 1a–e). Therefore, the formation of Zn–HDS after the addition of LiOH into the ethanolic precursor solution at low temperature was not observed by Tokumoto et al. probably due to the use of an ultrasonic bath for the dissolution of the LiOH powder during the synthesis of ZnO nanoparticles. In our experiments, we have found it takes more than 15 min for the dissolution by sonication, in which the transformation of Zn–HDS to the ZnO phase could have been finished.

* Corresponding author. E-mail: qiandong6@hotmail.com and jiang@fysik.dtu.dk.

[†] Technical University of Denmark.

[‡] Central South University.

TABLE 1: Treatment Conditions for Samples A–Q

| samples ^a | treatment conditions ^b |
|----------------------|--|
| A | precipitated with heptane immediately |
| B | sonicated for 1 min at 0 °C, precipitated with heptane |
| C | sonicated for 3 min at 0 °C, precipitated with heptane |
| D | sonicated for 5 min at 0 °C, precipitated with heptane |
| E | sonicated for 10 min at 0 °C, precipitated with heptane |
| F | stored at ≤−4 °C and exposed to air, precipitated with heptane after 2 days |
| G | stored at ≤−4 °C and exposed to air, precipitated with heptane after 4 days |
| H | stored at ≤−4 °C and exposed to air, precipitated with heptane after 6 days |
| I | stored at ≤−4 °C and exposed to air, precipitated with heptane after 12 days |
| J | stored at ≤−4 °C and exposed to air, precipitated with heptane after 18 days |
| K | stored at ≤−4 °C and exposed to air, precipitated with heptane after 22 days |
| L | stored at ≤−4 °C and exposed to air, precipitated with heptane after 26 days |
| M | stored at room temperature, precipitated with heptane after 10 min |
| N | stored at room temperature, precipitated with heptane after 20 min |
| O | stored at room temperature, precipitated with heptane after 40 min |
| P | stored at room temperature, precipitated with heptane after 60 min |
| Q | refluxed for 3 min, precipitated with heptane |

^a Samples A–I have been reported in our previous paper (see ref 4). ^b Sonication was carried out with a high-intensity ultrasonic horn (Branson 184V, 20 kHz, 900 W).

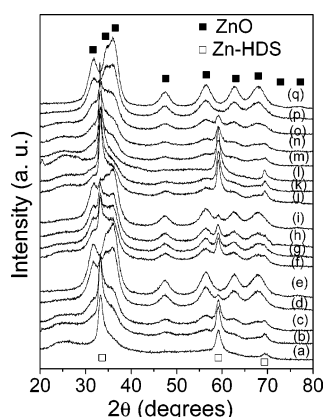


Figure 1. X-ray diffraction (XRD) patterns of as-prepared samples A–Q (from bottom to top). ZnO and Zn–HDS peaks are labeled (■) and (□), respectively.

Zinc hydroxy double salt, such as $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ or $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, can be prepared by reacting ZnO powder with a zinc salt in aqueous media.⁸ Therefore, Tokumoto et al. assumed that the formation of Zn–HDS resulted from a mechanism of dissolution/precipitation of ZnO nanoparticles, which implied that the formation of the ZnO phase was prior to the formation of Zn–HDS. The dissolution/precipitation of ZnO nanoparticles was also observed in our work. With the Zn–HDS sol exposed to air at ≤−4 °C, as shown in Figure 1f–l, the transformation of Zn–HDS to ZnO is very slow, which has not been completely finished even after 6 days. With increasing time, however, the ZnO nanoparticles can transform back to the Zn–HDS phase and peaks for the ZnO phase can hardly be found after 26 days. Moisture exposure favors the dissolution of ZnO nanoparticles due to the increase of water content in ethanol media. However, the formation of Zn–HDS through dissolution/precipitation of ZnO nanoparticles cannot rule out the fact that the formation of Zn–HDS is prior to the formation of ZnO phase during the sol–gel synthesis of ZnO nanoparticles.

The XRD patterns of the Zn–HDS sol kept at room temperature for various times are shown in Figure 1m–p. With increasing temperature, the transformation rate of Zn–HDS to the ZnO phase can be greatly enhanced. At room temperature, the transformation has been accomplished within 60 min. Therefore, Zn–HDS is reactive and sensitive to the temperature of the solution. This case is also confirmed by Figure 1q, showing the XRD pattern of a sample refluxed for 3 min, in which the transformation of Zn–HDS to the ZnO phase has been finished. Therefore, the conclusion given by Tokumoto et al. about the temperature in the range of 40–60 °C favoring the formation of Zn–HDS probably results from the formation of Zn–HDS through dissolution/precipitation of ZnO nanoparticles.

In summary, acetate Zn–HDS is formed after the addition of $\text{LiOH} \cdot \text{H}_2\text{O}$ into the ethanolic Zn precursor solution and can transform into the ZnO phase in an acetate-containing solution during the sol–gel synthesis of ZnO nanoparticles. The transformation of Zn–HDS to ZnO nanocrystals can be largely accelerated by ultrasonic irradiation and increase of temperature. ZnO nanocrystals can also transform back to acetate Zn–HDS through dissolution/precipitation of ZnO nanocrystals.

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References and Notes

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