

Response to Comment on “Catalysis and Temperature Dependence on the Formation of ZnO Nanoparticles and of Zinc Acetate Derivatives Prepared by the Sol–Gel Route”

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In a recent paper,¹ we studied the chemical and structural nature of powders prepared from the modified Spanhel and Anderson procedure² based on the preparation in ethanolic medium of $\text{Zn}_4\text{O}(\text{Ac})_6$ precursors³ from zinc acetate solution and subsequent hydrolysis–condensation induced by thermal activation at moderate temperatures (between 10 and 70 °C), and eventually by basic (LiOH), acid (succinic acid or glacial acetic acid) or neutral (H_2O) catalysis. The hydrolysis time was varied depending on the time evolution of the turbidity reported elsewhere,⁴ typically from 30 to 240 min. The powders were separated from the solution after sedimentation by removal of the supernatant ethanolic solution and dried at 50 °C. We found that the so-isolated powders are a mixture of zinc oxide (ZnO), zinc acetate ($\text{ZnAc}_2 \cdot 2\text{H}_2\text{O}$), and zinc hydroxyacetate (Zn–HDS) and their relative amounts are dependent on the temperature and nature of catalyst used in the hydrolysis step. In particular, powders with the highest amount of ZnO are obtained at low synthesis temperature (20 °C) without catalyst or with LiOH. Powders with the highest proportions of Zn–HDS phase are obtained near 40 °C under basic catalysis or by water addition. Despite the abundant literature dealing with the formation of ZnO nanoparticles,^{2,5,6} we first addressed the formation of Zn–HDS phase as a subproduct of ZnO formation. There are two main claims in the comment made by Qian et al. on our manuscript. First, we are cogently accused of negligence about the formation of Zn–HDS, claiming that Zn–HDS is formed after the addition of $\text{LiOH} \cdot \text{H}_2\text{O}$ into the ethanolic Zn precursor solution, even at low temperature (0 °C) and can be transformed into ZnO by ultrasonic energy. Consequently, they attribute the fact that we do not observe the formation of Zn–HDS after the addition of LiOH at low temperature to the use of an ultrasonic bath for the dissolution of the LiOH powder. Second, they have done a new interpretation for their early-published results about the order of occurrence of Zn–HDS and ZnO phases. They observe that with time ZnO nanoparticles can transform back to the Zn–HDS phase through a mechanism of dissolution/precipitation as stated in our paper, but they claim that the formation of Zn–HDS is prior to the formation of the ZnO phase during the sol–gel synthesis. We now discuss each issue in turn.

Sonication and Synthesis Procedure

Our experimental procedure is far from the one used by Qian et al. in two main aspects.

First, we used a low-intensity ultrasonic bath cleaner (Branson model B1210R-DJH, 40 kHz, intensity 2.0 W/cm², bath volume 1.5 L) to dissolve $\text{LiOH} \cdot \text{H}_2\text{O}$ into the ethanol solution, whereas Qian et al. used a high-intensity ultrasonic horn (900 W) in their sonochemical synthesis. We do not know any technical or scientific paper reporting a sonochemical effect during the use of an ultrasonic bath designed for cleaning proposals in which a large area piezoelectric transducer is used to release the ultrasonic energy over a large volume, resulting in a reduced intensity of cavitation. In ultrasound assisted chemical syntheses, like that reported by Qian et al., the energy is released in a concentrated field by a probe immersed in the reactional bath, resulting in a large intensity of cavitation. Because this aspect is well-known by people working in sol–gel chemistry and in sonochemistry, we did not describe in our paper the characteristic of the ultrasonic bath used in the sol–gel synthesis of ZnO and Zn–HDS. Nevertheless, indisputable evidence of the absence of sonochemical effect in our synthesis procedure is given by the insignificant intensity of light scattering observed just after sonication (see, for example, refs 4 and 7).

The second major point is the difference in synthetic route: we have used the Spanhel and Anderson procedure whereas Qian et al. used that proposed by Meulenkamp. In the former the molecular precursor was clearly identified as the tetrameric species $\text{Zn}_4\text{O}(\text{Ac})_6$, whereas in the latter procedure the precursor is, probably, the next-higher homologue $\text{Zn}_{10}\text{O}(\text{Ac})_{12}$. Furthermore, the nominal molar ratio $[\text{OH}^-]/[\text{Zn}^{2+}]$ used by Qian et al. is more than 10 times higher ($[\text{OH}^-]/[\text{Zn}^{2+}] = 1.4$) than that used in our case ($[\text{OH}^-]/[\text{Zn}^{2+}] = 0.1$). As the condensation pathway is very sensitive to the precise conditions of hydrolysis, complexation, aging, and so on ..., it is not surprising that many differences could exist between our final product and that prepared without sonication by Qian et al.

The Sequence of ZnO and Zn–HDS Formation

One of us have already published small-angle X-ray scattering measurements aiming to elucidate the kinetic formation of the particles in solution⁷ during the synthesis at 40 °C in the presence of LiOH.

A stepped formation was evidenced, first small particles of 2 nm in diameter grow and then a second family of particles with a diameter ranging from 5 to 7 nm is observed. The same results were obtained for synthesis carried out at 60 °C with LiOH or at 70 °C without addition of catalyst. On the other hand, as already described in ref 1, a faintly different scenario in the particle growth has been observed for the reaction carried out at 60 °C after water addition. The smallest particles, which are first formed, are consumed with time whereas the second larger ones appear. These evidences of stepped kinetics motivated further investigations of the sequential process comprising the formation of the ZnO nanoparticles by EXAFS. In the case of synthesis catalyzed by LiOH between 40 and 60 °C⁸ or without catalyst at 70 °C,⁹ we have clearly evidenced, by combining UV–Vis with step-by-step EXAFS experiments carried out in situ during the early time of reaction, that the first family of particles are identified as ZnO. In the case of reaction carried out at 60 °C using water,¹⁰ UV–Vis combined with dispersive EXAFS investigations reveals the dissolution of ZnO particles and the subsequent formation of Zn–HDS particles. To our best knowledge, there is no current experimental results performed in situ in the reactive solution that

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supports the formation of Zn–HDS prior to the formation of the ZnO phase during the sol–gel synthesis, as claimed by Qian et al. As the addition of a nonsolvent like the heptane used by Qian et al. can strongly affect the equilibrium between the condensed and the dissolved species, it seems unlikely that under these conditions the nature of the incipient formed solid phase is maintained in the dried powder. Finally, because Qian et al. analyzed only the dried powders extracted from the reaction bath, their conclusion about the sequence of phase formation must be seen with some skepticism.

References and Notes

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