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Controlled preparation of hollow zinc oxide microspheres from aqueous solution using hexamethylenetetramine and cysteine

Daniel Weinzierl^a, Didier Touraud^a, Alois Lecker^b, Arno Pfitzner^b, Werner Kunz^{a,*}

^a *Institute of Physical and Theoretical Chemistry, University of Regensburg, 93040 Regensburg, Germany*

^b *Institute of Inorganic Chemistry, University of Regensburg, 93040 Regensburg, Germany*

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Abstract

Zinc oxide particles were synthesized by precipitation from an aqueous solution of zinc nitrate tetrahydrate, *R*-(+)-cysteine and hexamethylenetetramine (HMTA, urotropine). Hollow microspheres of ZnO–cysteine hybrid material with a diameter of ca. 1 μm and a wall thickness ca. 50 nm were obtained. After heating up to 850 °C pure ZnO microspheres of roughly the same size were formed. The particles were characterized by XRD, SEM, FT-IR and TGA.

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1. Introduction

Zinc oxide crystallizes in the hexagonal wurtzite structure type having II-IV compound semiconductor properties with a wide and direct band gap of 3.37 eV and a large exciton binding energy of 60 meV [1]. It has various potential applications, major interests concern chemical sensors [2,3], varistors [4,5], transducers [6], pigments [7], components for the pharmaceutical and cosmetic industries [8,9], catalysis [10,11] and electrodes for solar cells [12]. Huang et al. [13] observed a UV-laser emission at room temperature using ZnO nanowires and thus showed the potential use as UV-laser material. All these applications make use of the unique optical, chemical and electrical properties of ZnO powders, which strongly depend on its particle size, size distribution, morphology and so on [14]. So developing new easy and cheap routes to synthesize monodispersed ZnO micro- and nanoparticles has great importance both in fundamental and application points of view. There are many reports in literature concerning the synthesis of ZnO particles [15–21]. Utilizing these methods, ZnO of a great variety of morphologies in the micro- and nanoscale has been successfully prepared, including rod-like, hexagonal prism-shaped, flower-like and needle-like. Recently, even polyhedral cages [22], nanorings and nanohelices [23] were produced. However, there are only few reports about spherical ZnO particles: Chittofrati and Matijevic [24] reported the synthesis of spherulitic ZnO particles in the presence of triethanolamine in aqueous solution. Wang et al. [25] prepared spherulitic ZnO microspheres self-assembled by hexagonal nanoplates in a methanol–water solution of zinc acetate dihydrate and hexamethylenetetramine. Finally, Andrés Vergés et al. [26] reported amorphous spherical ZnO particles in the early stages of the

* Corresponding author. Tel.: +49 941 943 4044; fax: +49 941 943 45 32.

E-mail address: Werner.Kunz@chemie.uni-regensburg.de (W. Kunz).

evolution of rod-like ZnO particles using zinc nitrate, HMTA and water. However, no attempt was made to control the sphere size and shape of the particles.

Here, we report the synthesis of spherical amorphous particles of ZnO with controllable size using zinc nitrate, hexamethylenetetramine, *R*-(+)-cysteine and water. This study is part of a systematic investigation concerning the influence of amino acids on crystallization phenomena and the structuring and morphology of the resulting material.

2. Experimental

Zinc nitrate tetrahydrate, $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, HMTA (hexamethylenetetramine) and *R*-(+)-cysteine were purchased from Merck and all were at least of reagent grade. Water was purified in a Millipore system prior to use.

In a typical experiment, 523 mg zinc nitrate tetrahydrate (2.0 mmol), 707 mg *R*-(+)-cysteine (5.8 mmol) and 280 mg HMTA (2.0 mmol) were put in a 100 mL flask and 60 mL water were added. Then the pH was adjusted to 6.3 using a 1 M NaOH solution and water added to 80 mL. This solution was filtered with 0.22 μm Millipore filters for two times. The reaction solution containing $\text{Zn}(\text{NO}_3)_2$ and cysteine was heated to 90 °C and then HMTA dissolved in 20 mL of distilled water was added to result in a total volume of 100 mL. After the solution became turbid (typically within less than 1 min), it was further kept at 90 °C for 90 min and was then immediately cooled in an ice water bath. After the reaction was finished, the flask was cooled in an ice bath for 5 min. The precipitated powder was collected by filtration (0.22 μm filters), washed several times with Millipore water and dried in an oven at 60 °C for several days.

Dried powders were analysed by scanning electron microscopy, SEM (Zeiss DSM 950), X-ray diffraction, XRD (STOE & CIE, STADI P), Fourier transform infrared spectroscopy, FT-IR (Jasco FT/IR-610) and thermo-gravimetric analysis, TGA (Perkin-Elmer TGA7). The samples were coated with gold for SEM. XRD measurements in transmission setup were performed using $\text{Cu K}\alpha_1$ radiation ($\lambda = 1.540598 \text{ \AA}$) monochromated with a germanium single crystal in the range of $8^\circ < 2\theta < 90^\circ$ at a scanning speed of $0.8^\circ/\text{min}$. The samples were spread on a mylar sample holder. For the infrared spectra, the samples were diluted with KBr and the spectra were recorded in diffuse reflection mode from 4000 to 400 cm^{-1} at a resolution of 2 cm^{-1} . TGA was performed from 50 to 900 °C at a heating rate of 10 K/min in an oxygen atmosphere.

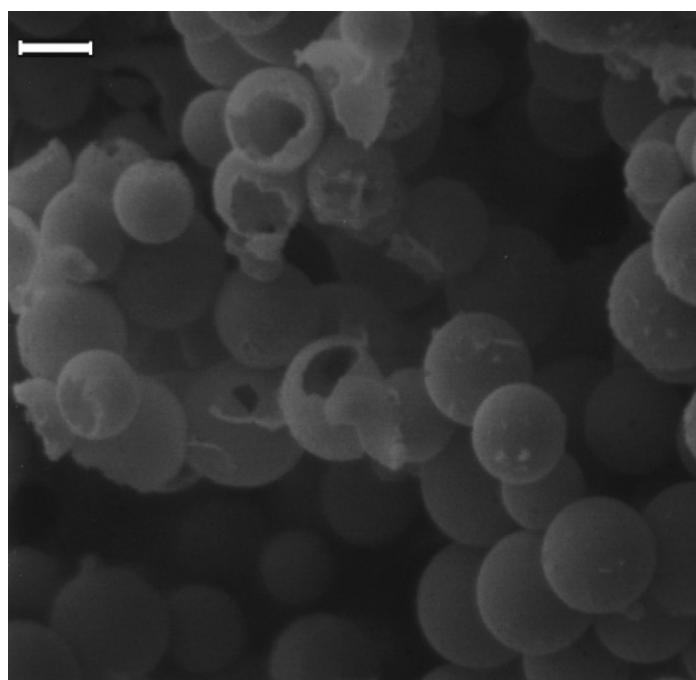


Fig. 1. SEM micrographs of monodisperse spheres synthesized at 90 °C, heated for 90 min after turbidity occurred ($c(\text{Zn}) = 0.02 \text{ mol/L}$, $c(\text{HMTA}) = 0.02 \text{ mol/L}$, $c(\text{cysteine}) = 0.05 \text{ mol/L}$), the white bar is 1 μm .

3. Results and discussion

SEM pictures like the one shown in Fig. 1 revealed the presence of hollow spherical particles with a diameter of ca. 1 μm , a shell thickness of about 50 nm and a near size distribution. Several spheres were broken so that the hollowness of the spheres clearly appeared.

To further characterize the obtained hollow spheres several other experiments were performed. Fig. 2 gives the X-ray diffraction pattern of the particles (Fig. 2a), their FT-IR spectrum (Fig. 2b), the IR spectrum of pure cysteine for comparison (Fig. 2c) and the TGA curve (Fig. 2d) of the microsphere powder formed by ZnO–cysteine complexes. XRD proves that the microspheres are completely amorphous, the maxima in the diffraction curve are due to the sample holder.

The peaks at 1350 and 856 cm^{-1} present in the IR spectrum indicate that the spheres contain NO_3^- ions. Typical IR-absorptions for NO_3^- ions are between 1380 and 1350 cm^{-1} , and another one between 860 and 800 cm^{-1} [27].

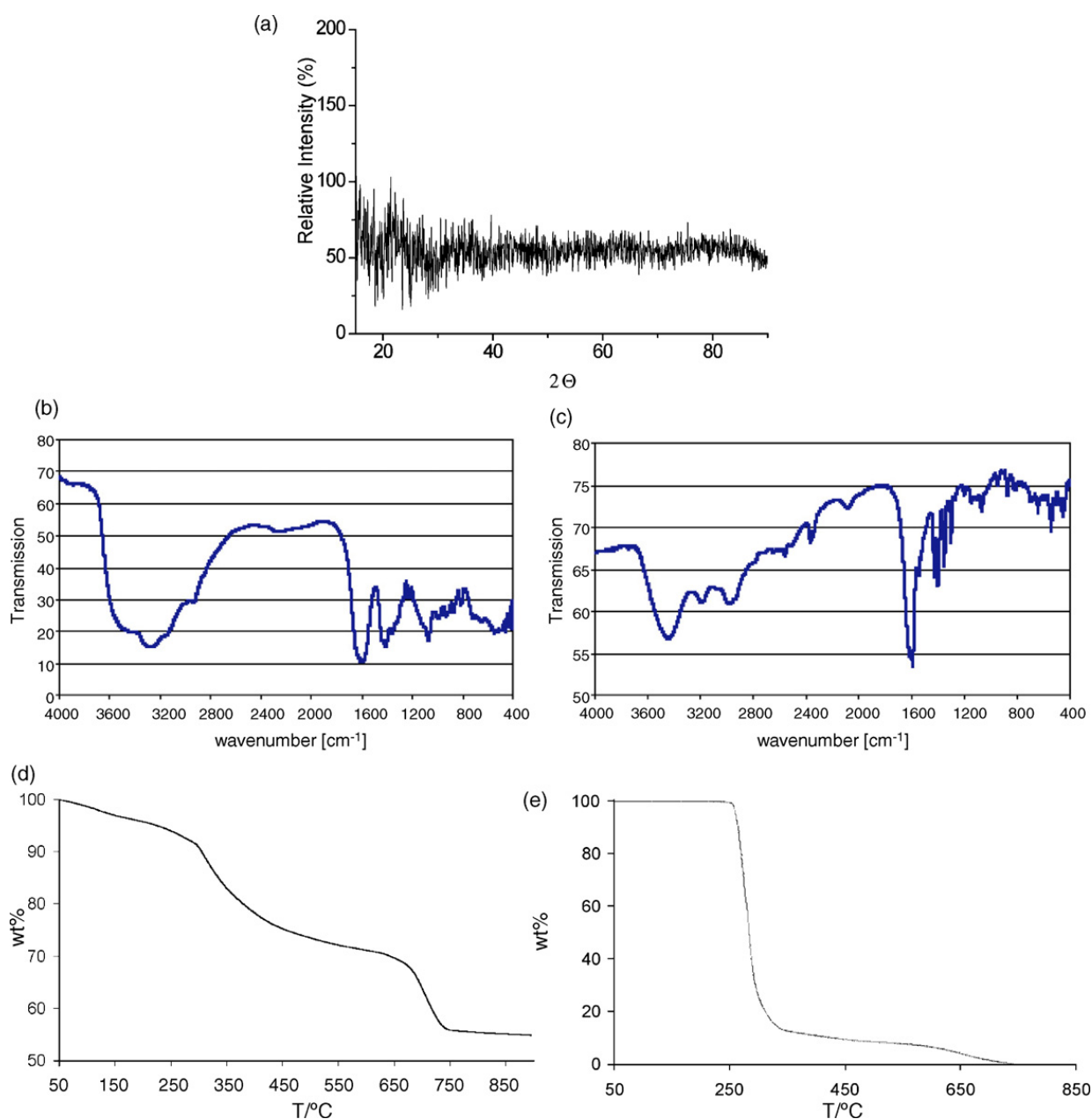


Fig. 2. (a) XRD pattern, (b) FT-IR pattern of monodisperse ZnO–cysteine powders synthesized at 90 $^{\circ}\text{C}$, heated for 90 min after turbidity occurred ($c(\text{Zn}) = 0.02 \text{ mol/L}$, $c(\text{HMTA}) = 0.02 \text{ mol/L}$, $c(\text{cysteine}) = 0.05 \text{ mol/L}$), (c) IR spectrum of pure cysteine, (d) the TG analysis of the microparticles and (e) of pure cysteine.

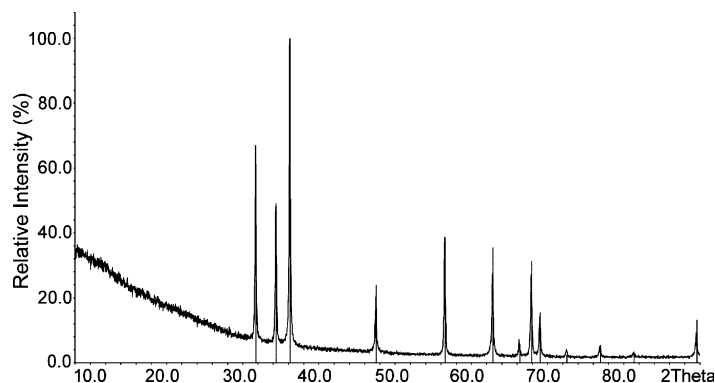


Fig. 3. The XRD analysis after heating the sample to 850 °C shows the characteristics of wurtzite type ZnO.

These nitrate absorptions are still present after thorough washing of the samples. The persistence of the characteristic nitrate absorptions in the FT-IR spectra suggests that nitrate ions are either strongly adsorbed onto the surface of the hollow microspheres or incorporated into the material. The spectrum of the particles shows also a significant contribution from cysteine, cf. Fig. 2c. Because of the superposition of signals from different components it is difficult to quantify the relative amount of each component from the IR spectrum.

Fig. 2d shows a massive weight loss of nearly 40% in the TGA, suggesting a composite material for the spheres. The TGA is qualitatively similar to the weight loss of a pure cysteine sample that was done for comparison, see Fig. 2e. It therefore can be concluded that mainly cysteine is decomposed and finally converted to CO₂ at high temperatures.

After thermal treatment XRD peaks characteristic of wurtzite type ZnO appear, see Fig. 3.

EDX analysis showed that the initial hollow microspheres (before TGA analysis) contained a significant amount of sulphur and of carbon. These results indicate that the hollow microspheres are a composite material of cysteine and zinc oxide with nitrate ions strongly adsorbed on the surface or incorporated into the material. The composite material may be made of stable complexes of zinc with cysteine as ligand. Amino acids are known to form complexes with zinc [28–30] and zinc complexes of cysteine with a composition of 1:1 are also well known in literature [31–34]. Although a quantitative EDX analysis of the powder is difficult to obtain, the EDX result is in rough agreement with such a composition.

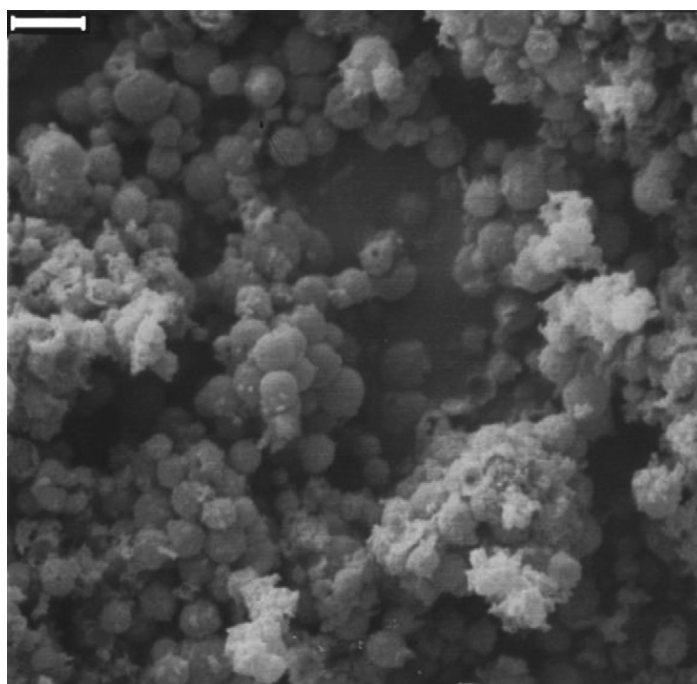


Fig. 4. SEM image of ZnO microspheres after burning the organic material at 850 °C. The scale bar is 2 μm.

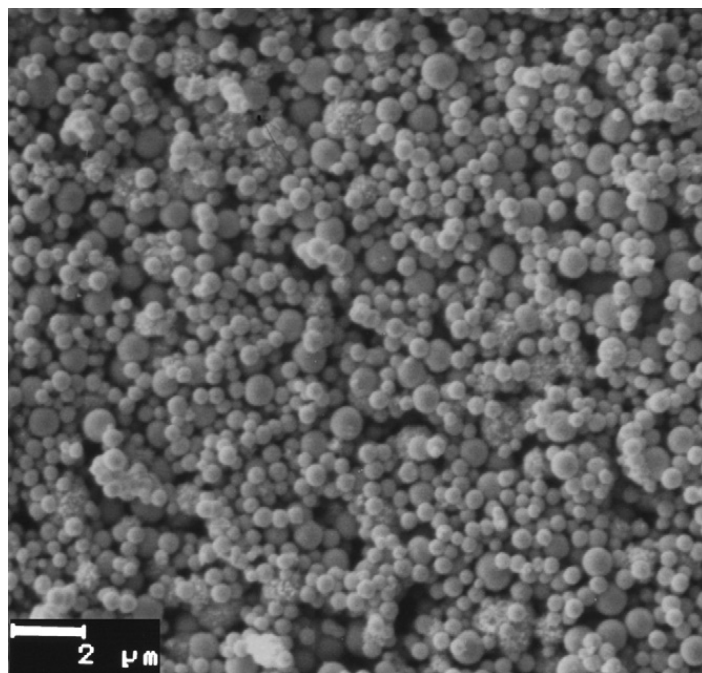


Fig. 5. SEM image of ZnO–cysteine microspheres with diameters ranging from 0.2 to 0.8 μm , synthesized at 70 $^{\circ}\text{C}$.

EDX analyses of the powder after heating to 850 $^{\circ}\text{C}$ were also performed. Only Zn and O were found in non-negligible amounts. SEM showed that the shape of the particles did not significantly change, see Fig. 4. We conclude that the remaining hollow spheres consist of more or less pure ZnO.

Further, we found that the size of the amorphous spheres depended on the precipitation temperature and time. For example, heating to 70 $^{\circ}\text{C}$ during 30 min produces a sample containing spheres with diameters of 0.2 to 0.8 μm (Fig. 5). At 90 $^{\circ}\text{C}$, the microspheres slowly grow from approximately 0.4 μm (immediately after turbidity occurs) to approximately 1 μm after 90 min of heating.

Finally, a UV spectrum of the hollow ZnO particles (after burning the cysteine at high temperatures) was recorded, see Fig. 6. The spectrum is typical for macrocrystalline ZnO [35].

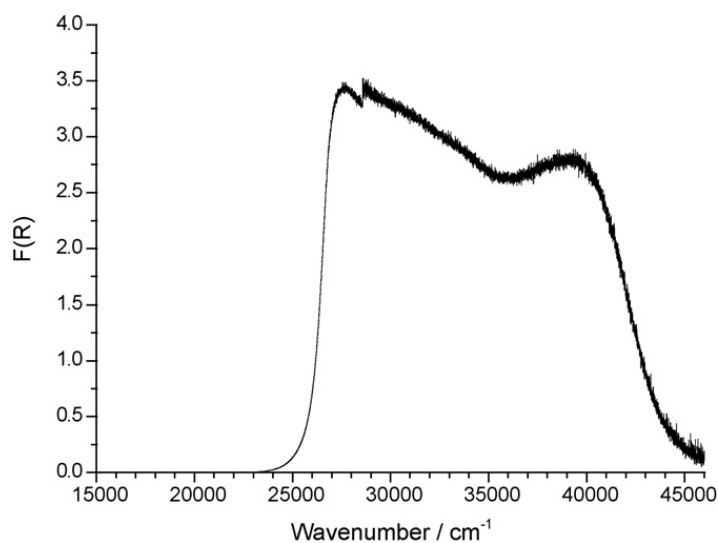


Fig. 6. UV spectrum of the ZnO particles.

4. Conclusion

Hollow, amorphous ZnO microspheres have been synthesized using a simple aqueous solution route with zinc nitrate and HMTA and taking advantage of special Zn–cysteine interactions. It is shown that the particle size depends on temperature and precipitation time.

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