Additive-free Hydrothermal Synthesis of High Aspect Ratio ZnO Particles from Aqueous Solution

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In this work, a new hydrothermal process is described, in which, for the first time, an aquatic Zn^{2+} precursor is used for the synthesis of high aspect ratio ZnO particles, without the presence of any organic additive. Characterization of the particles is carried out by XRD, TEM, and SAED. Also the influence of different reaction times and of another reaction medium on the morphology and the dimensions of the rods is investigated.

Zinc oxide seems to be a simple ceramic material, but, because of its unique qualities, it has conquered a key role in scores of technological applications.[1–3] Its properties can either be of an electronic, optical, thermal or chemical nature, and usually combinations of these qualities make that ZnO is such a desired material.

The last years the knowledge for the production of particles with controllable size and shape has grown steadily. The next step in the fabrication of functional ceramic materials is the realization of organized, anisotropic and/or nanoscale structures.[2,4,5] Earlier investigations have demonstrated that monocrystalline ZnO rods and wires can be produced through vapour-phase methods.[1–5] Although the exact mechanism for 1D growth during gaseous synthesis is still unclear, this route is already being frequently used for the production of anisotropic ZnO for devices on lab-scale.

In view of large scale applications, simple production methods are desired, ensuring large quantities to be produced in a reasonable time and in an ecologically sustained environment, ideally water. From recent reports the hydrothermal route seems to be promising.[6–17] In these papers, the formation of high aspect ratio rods is usually attributed to the intervention of an additive, such as cetyltrimethylammonium bromide (CTAB),[9–12] polyethylene glycol (PEG),[13,14] or polyvinyl pyrrolidone (PVP).[15–17] Beside this hydrothermal method, one can find reports of the synthesis of anisotropic ZnO with the help of microemulsions,[18–21] or sol–gel strategies.[22–24] In this paper, we present a very simple, solely water-based method for the preparation of ZnO rods with a high aspect ratio, without any additive. The absence of an additive benefits the simplicity of the procedure, and the use of water as the reaction medium makes the whole process ecologically less demanding. Zhang et al. also describe the hydrothermal synthesis of ZnO with controlled morphology, without using additives.[25] In water, however, their method produces flowerlike aggregates composed of prolate particles.

The procedure for the synthesis of ZnO rods is as follows: 10 mmol of $Zn(CH_3COO)_2 \cdot 2H_2O$ and 100 mmol of NaOH are each dissolved in 10 mL of deionized water. Next the NaOH solution is slowly added to the Zn^{2+} solution under constant stirring. Subsequently the 20 mL of this resulting aquatic solution is diluted with 200 mL of deionized water, and placed in an ultrasonic bath. After 30 min a white opaque precursor is formed. The resulting mixture is transferred to a stirred, stainless steel, Parr 5521 high-pressure compact laboratory reactor, with a total capacity of 300 mL, heated at a rate of 2 °C/min, and kept at a temperature of 120 °C. After 12 h treatment, the autoclave is allowed to cool down to room temperature. The final powder is collected, repeatedly washed with small amounts of deionized water and dried for 5 h at 60 °C. To study the morphology of the products, a Philips CM 12 transmission electron microscope (TEM) is used. X-ray diffraction measurements are carried out on a Siemens D-5000 diffractometer (radiation: Cu K_{a1}).

All of the observed peaks in the X-ray diffraction patterns of the precipitate before hydrothermal treatment (Figure 1a) can be assigned to orthorhombic $Zn(OH)_2$. The XRD pattern of the sample, that did undergo hydrothermal treatment (Figure 1b), reveals that the hydroxide has transformed completely to hexagonal, wurzite-type ZnO. No impurities, such as residues of $Zn(OH)_2$, can be detected. Furthermore a high crystallinity of the powder is indicated by the sharp peaks.

In Figure 2 two typical TEM images of the ZnO sample are presented. They show that the particles have a clear rodlike morphology with an average diameter of 200 nm and an average length of 2 μm (based on TEM images of 30 particles). Diameters down to 60 nm and up to 400 nm as well as lengths down to 900 nm and up to 5 μm are observed. A high aspect ratio of about 10 remains more or less constant for all particles. An individual rod is shown in Figure 2b. It is elongated in one dimension and both ends have a pointed appearance. The inset of Figure 2b represents the SAED pattern of the rod, given in this figure. It reveals its wurzite-type structure with a single-crystalline nature, which corroborates the XRD result of Figure 1b.

In order to investigate the effects of the hydrothermal

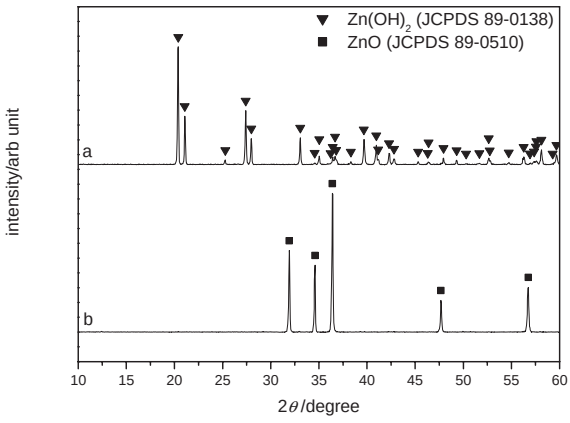

Figure 1. XRD pattern of the product obtained a) before and b) after hydrothermal treatement.

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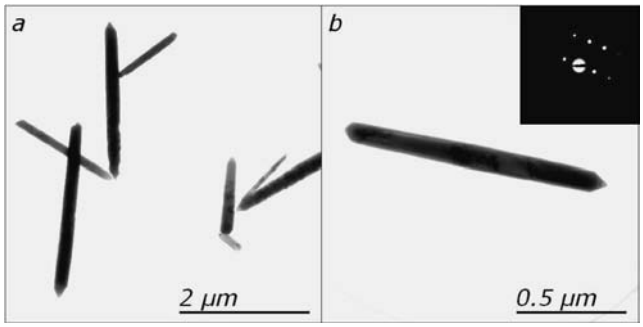

Figure 2. TEM images of the anisotropic ZnO particles a) overview b) single rod (inset: SAED pattern).

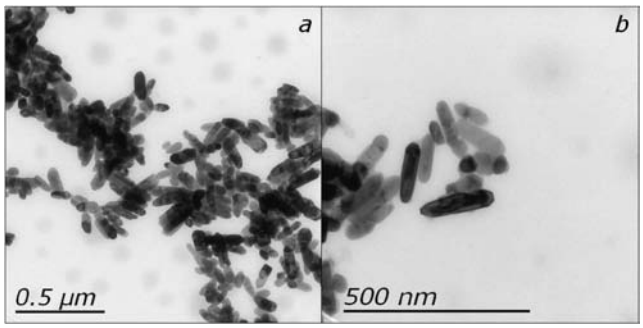

Figure 3. TEM images of the ZnO nanorods obtained in ethanol a) overview b) higher magnification.

reaction time on the structure of the particles, the time is varied from 6 to 48 h, while a constant temperature of 120 °C is maintained. XRD characterization shows that in all cases pure hexagonal ZnO is formed, as the patterns resemble that of Figure 1b. The TEM images (not shown) indicate that this variation in time does not change the morphology or influence the size significantly.

The impact of the reaction medium is examined as well. The formation of the ZnO is carried out as described above, with the exception that now 200 mL of ethanol is applied to dilute the $[Zn(OH)_4]^{2-}$ solution. On a macroscopic scale this variation is seen to change only the fact that the white suspension, originally formed after 30-min treatment in an ultrasonic bath, now developed earlier. Typical TEM images of this ZnO sample are presented in Figure 3. It is clear that the overall morphology of the particles remains rodlike. However, both ends now have a more rounded appearance. Also the dimensions of the rods have changed drastically. The diameters are now situated between 50 and 80 nm, while the typical length has fallen to 250 nm. This also implies that the general aspect ratio has diminished from above 10 to 5 or less.

In summary a new, very simple hydrothermal method is presented, in which an aquatic Zn^{2+} precursor is used for the synthesis of high aspect ratio ZnO, without the presence of an organic additive. The particles have an average length of 2 μm and a diameter of about 200 nm. The typical aspect ratio of the rods is 10 or more. When the synthesis is carried out in ethanol the particles remain rodlike, although the size has diminished drastically to 250 ± 50 nm. This means that in this reaction medium the high aspect ratio, achieved in water, has decreased to 5 or less.

On the basis of these results we can conclude that ZnO rods with a high aspect ratio can be synthesized in water without the use of extra additives. Future work will be directed towards examining the influence of other reaction parameters on the aspect ratio, and towards decreasing the size of the particles, without loosing a high aspect ratio.

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