Morphology control of ZnO nanostructures

A. MEZY, C. GÉRARDIN,* D. TICHIT,* D. RAVOT, S. SUWANBOON and J-C. TEDENAC

Université Montpellier 2, Institut C. Gerhardt, UMR 5253, Place Eugène Bataillon, 34095 Montpellier, France
*Ecole Nationale Supérieure de Chimie, Institut C. Gerhardt, UMR 5253, 8 rue Ecole Normale, 34296 Montpellier Cedex 5, France

Highly crystalline zinc oxide (ZnO) nanomaterials are synthesized using a seeded growth sol–gel method. In order to control the morphology and the dimensionality of ZnO crystals, a double hydrophilic block copolymer, the Polyacrylic acid-Polyacrylamide (PAA-PAM), was introduced during the growth step. It was shown, first, that depending on the amount of PAA-PAM copolymer, different morphologies of ZnO particles precipitated from homogeneous solutions were obtained, such as ZnO nanostructured spheres or flat hexagonal crystals. Secondly, the dimensionality of ZnO objects grown from seeds on a substrate could be tuned by varying the amount of copolymer leading to ZnO films with variable characteristics. Thus, systematic studies were done in order to investigate the influence of copolymer addition on ZnO nanomaterial morphologies and then explain the mechanisms of the morphological and dimensional modifications.

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1. Introduction
Zinc oxide is a II–VI semiconductor with an hexagonal wurtzite crystal structure, which presents a direct wide band-gap of $3.37 \text{ eV}$ at room temperature and a large exciton binding energy of $60 \text{ meV}$. ZnO exhibits a large variety of nanoscale behaviours, both in terms of structural and physical properties. Much attention has been paid to nanostructured ZnO materials, due to their potential use for electronic, photonic, catalytic, and sensor applications. Among low dimensionality (1D) semiconductors, ZnO nanorods are of special interest for their applications as high efficiency short wavelength optoelectronic nanodevices because of their large exciton binding energy and high mechanical and thermal stabilities.

Due to their physical and chemical properties, ZnO nanorods present a great economic interest. Many methods have been employed for the growth of ZnO nanomaterials, such as rf magnetron sputtering, chemical vapor deposition, spray pyrolysis, thermal evaporation etc. However, low cost and simplicity of the synthesis processes are required for commercial development. The wet chemical synthesis route seems to meet these requirements, enabling the preparation of ZnO nanorods with a high crystalline quality and a proper growth orientation. The synthesis process used in this study declines into two steps. The first one is the synthesis of ZnO nanoparticles, which once deposited on a substrate, will be used in the second step as seeds for the subsequent growth of ZnO structures. The objective is to control the morphology of ZnO structures in order to improve their properties and consequently fit to further applications. Our first objective was to grow well dispersed and individual crystals with different morphologies. The second objective was to be able to modify the dimensionality of ZnO crystals grown form seeds on a substrate. For that, a hydrophilic polyacrylic acid-b-polyacrylamide diblock copolymer was introduced during the growth step. Indeed, double hydrophilic block copolymers (DHBCs) are now well known as control agents of growth and stabilization of inorganic phases. The purpose of our study is both, investigating the influence of the addition of a polyacrylic acid-b-polyacrylamide diblock copolymer during the growing step and understanding the formation mechanisms of the obtained crystal structures.

2. Materials, method and characterization
Starting materials used in this investigation were analytical-grade $(\text{CH}_3\text{COO})_2\text{Zn} \cdot 2\text{H}_2\text{O}$ (Merck, Germany), propan-2-ol (Prolabo, France), Diethanolamine (DEA) (Prolabo, France), $(\text{NO}_3)_2\text{Zn} \cdot 6\text{H}_2\text{O}$ (Acros Organics, USA), Hexamethylenetetramine (Merck, Germany). All materials were used as delivered without further purification.

The diblock copolymer Polyacrylamide $(M_w = 30000 \text{ g mol}^{-1})$-Polyacrylic acid $(M_w = 5000 \text{ g mol}^{-1})$ used in this investigation is synthesized by Rhodia (Aubervilliers, France).

For the first step, a stock solution of zinc acetate $(2 \text{ mol l}^{-1})$, in propan-2-ol was prepared. DEA (0.2 ml) was then added in 10 ml of the zinc-containing solution. The mixture was kept under constant stirring for 30 min at room temperature. Then 0.18 ml of distilled and deionised water was added. After 30 min of new stirring, the suspension was heated at 60°C for 1 h under static conditions. The resulting suspension was aged for 24 h at room temperature.

The aged suspension was deposited onto alumino-silicate substrates (float glass) by dip-coating; substrates were previously sonicated and washed with HNO$_3$ and thoroughly rinsed with acetone, ethanol and water. The obtained films were heated up to 500°C for an hour, in order to obtain crystallized ZnO and to remove all organic compounds by calcination.

For the second step, a stock solution was prepared with an equimolar mixture of zinc nitrate and hexamethylenetetramine in distilled water. The PAA-PAM is dissolved into deionised water in order to obtain a 0.86 mol l$^{-1}$ solution and the pH of this solution is increased up to 5.5 allowing the ionisation of the acrylate functions. Different amounts of PAA-PAM copolymer, with an R ranging from 0 to 0.1 (R is...
the molar ratio between acrylate groups and Zn\(^{2+}\) ions, were added to the Zn containing solution. The coated substrates, as obtained in the first step, were dipped in the solutions with different \(R\) and left for different growth times, ranging from 15 to 25 h, and at different temperatures ranging from 60 to 90 ± 5°C.

The morphology of the ZnO nanorods was observed using scanning electron microscope (SEM) (Hitachi type S-2600N, Japan).

The crystalline phase of the materials was determined by X-ray diffraction (XRD) using a Seifert diffractometer (with a copper K\(\alpha\) anticathode and a nickel filter) in the \(2\theta\) range, with a step of 0.02° and a step time of 2s.

3. Results and discussion

During the growth step, the presence of the DHBC influences the characteristics of both ZnO crystals grown in the solution, and ZnO objects grown from the substrate. The results are then classified into two parts; each one aims at investigating the influence of the addition of the copolymer on crystal growth (i) from homogeneous solutions and (ii) from seeds on the substrate.

3.1 ZnO crystals grown in solution

Three kinds of ZnO crystal morphologies were obtained depending on the amount of the DHBC added in the solution during the growth step.

Without any PAA-PAM copolymer and after a fifteen hour growth time, ZnO nanorods are obtained (Fig. 1(a)). They present a dendritical growth of several nanorods from a common nucleus, the nanorods growing along the preferential direction of the crystalline network. The entanglement and the lack of organization of the so-obtained ZnO nanorods are detrimental to the physical properties; they lead to energy re-absorption and make them non-suitable for their use in optical devices.

We introduced the PAA-PAM copolymer in order to improve the nanoparticle characteristics by controlling the crystalline growth process. We first observe the effect of the addition of a small amount of PAA-PAM copolymer on the morphology of the synthesized ZnO nanomaterials. Due to the presence of the PAA-PAM copolymer, even in a small amount \(0 < R \leq 0.005\), a new morphology of ZnO nanomaterials appears: nanostructured ZnO microspheres (Fig. 1(b)). Nevertheless, the small proportion of the PAA-PAM copolymer does not allow the exclusive growth of nanostructured ZnO microspheres.

Then, we observed the modifications of the nanomaterial morphology when the proportion of PAA-PAM introduced during the synthesis is higher, i.e. when \(R\) ranges from 0.01 to 0.03. For a fifteen hour growth time, we observed an exclusive growth of nanostructured ZnO spheres beyond a PAA-PAM copolymer threshold of \(R = 0.01\) (Fig. 2). This new kind of ZnO nanomaterial has a great deal of interest for catalytic applications due to its large specific area.

The PAA-PAM copolymers introduced during the synthesis are ionised at a pH of 5.5. Then, the presence of negatively charged polyacrylate blocks allows the formation of complexes with zinc ions. The small complexation rate \(R\) leads to the binding of the PAA-PAM copolymers on the surface of the ZnO nuclei in a very small amount. The polymers prevent the crystalline growth due to the strong binding of the acrylate groups to zinc ions and the steric hindrance of the bigger PAM blocks (Fig. 3). In particular, the growth along one preferred direction (c-axis) becomes difficult by this configuration. Thus, no ZnO nanorods were observed in this range of PAA-PAM copolymer ratio, but rather isotropic and porous ZnO based particles where the voids must be occupied by the polymer.

The PAA-PAM copolymer ratio \(R\) was increased again, up to values ranging from 0.03 up to 0.1 and two different times of growth were considered, 15 and 25 h. For a growth
Fig. 3. Schematic view of the synthesis conduct with the presence of the PAA-PAM copolymer.

Fig. 4. The SEM images (enlargement ×7k) show the ZnO morphology when (a) $R = 0.06$ and $t = 25$ h, (b) $R = 0.08$ and $t = 25$ h, (c) $R = 0.1$ and $t = 25$ h.

Fig. 5. Diffractogram of the different ZnO morphologies (a) dendritic ZnO crystals, (b).

time of 15 h, the amount of PAA-PAM was sufficient to prevent any crystalline growth. A growth time of 25 h was necessary to observe the formation of crystals.

For $R$ equal to 0.06 and a time of growth of 25 h (Fig. 4 (a)), a partial disappearance of the nanostructuration as ZnO spheres has been observed and a new morphology of ZnO nanomaterials appeared: hexagonal crystalline ZnO particles, which are truncated in the middle. A further increase of the PAA-PAM copolymer ratio results in a further decrease of the fraction of nanostructured ZnO spheres (Fig. 4 (b)). The proportion of the hexagonal ZnO crystals increases with the PAA-PAM copolymer ratio. For $R$ equal to 0.1, the flat hexagonal crystalline structures were the only ones observed under these growth conditions (Fig. 4 (c)).

The monodispersity of these hexagonal ZnO structures has to be emphasized since it was one of the expectations, when introducing double hydrophilic block copolymer (PAA-PAM).

The PAA-PAM copolymers bind to the surface of ZnO and inhibit the crystalline growth. Consequently, the more PAA-PAM copolymers in solution, the larger the disappearance of nanostructured ZnO spheres.

From a crystallographic point of view, a crystal of zinc oxide is built up from layers of zinc atoms and layers of oxygen atoms alternatively stacked up. The PAA-PAM copolymers present negatively charged blocks at pH 5.5. The acrylate blocks will preferentially bind to a zinc atom layer, which is positively charged. If the PAA-PAM copolymers are preferentially anchored to the (001) faces of ZnO crystals, at a high PAA-PAM copolymer ratio ($R \geq 0.1$), the crystal growth becomes difficult in the direction perpendicular to this face (along the c-axis). As a consequence, for a growth time of 25 h, flat ZnO platelets are obtained (Fig. 4 (c)). Such flat ZnO hexagonal crystals were previously observed by Öner et al in their study involving other hydrophilic diblock copolymers (PEO-b-PMMA). They studied nucleation and growth processes from homogeneous zinc solutions in the presence of PEO-b-PMAA polymers. They observed that crystals grow shorter and wider with increasing polymer concentration. This observation was also made by Vayssieres et al using a negatively charged surfactant. Nevertheless, in their study the temperature is higher than in the present one, leading to different kinetics. The kinetic influences the isotropic growth of the ZnO crystals and a slow reaction will stabilize the different phases leading to the nanostructuration.

The diffractograms of the different crystal morphologies confirm the observations by SEM concerning the growth directions. A high crystalline quality is shown on the diffractogram of the hexagonal zinc structure obtained with a (AA)/(Zn) ratio equals to 0.1 and a growth time of 25 h. One can observe that the diffraction pattern (Fig. 5) corresponds to a major basal plane crystallisation, favourable to further experiments for growing ZnO nanorods.

3.2 ZnO nanorods grown from the seeds on a substrate

For a starting material concentration of (Zn) = 10^{-3} M, a very small amount of nanorods is obtained, which does not allow a correct investigation of ZnO morphology modifications induced by the addition of DHBCs. In order to obtain a sufficient amount of nanorods grown from the substrate, the starting material concentration has been increased and that leads to the synthesis of aligned nanorods perpendicu-
The synthesis process is described as a successive stacking of charged acrylate blocks bind to the positively charged layers stabilizing agents. During the growth process, the negatively charged layers relative increases compared to the one of the others crystal directions is not restricted. Under such conditions, the addition of DHBCs leads to the formation of a continuous and dense ZnO layer (Fig. 6b). The introduction of DHBCs during the synthesis seems to be a promising way to obtain films of ZnO with a good crystallinity, whose properties can be adapted to applications.

In order to meet the requirements in terms of physical properties and electronic applications, our future work will consist in studying the effect of the addition of the PAA-PAM polymer on the size of the seeds on the substrate, and the implication of the modified synthesis conditions on the growth of nanorods. Furthermore, synthesis parameters like growth time will be modified in order to control the thickness of the ZnO film. Finally, the use of some specific organic additives will be studied with the aim to obtain hybrid organic-inorganic nanomaterials.

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References
Fig. 7. SEM images (enlargement × 7k) show the ZnO nanorods stemmed from the germs for different $[\text{HMT}] = [\text{(NO}_3\text{)}_2\text{Zn}]$ concentration (a) $10^{-3}$ M, (b) $5.10^{-3}$ M, (c) $10^{-2}$ M, (d) $2.5.10^{-2}$ M.