Morphology evolution of ZnO nanostructures upon solvent vapour treatment

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In the present study zinc oxide (ZnO) nanostructures are synthesized using a sol-gel technique coupled with a structure-directing amphiphilic diblock copolymer, poly(styrene-block-4-vinylpyridine) in which a commercial ZnO precursor, namely, zinc acetate dihydrate (ZAD) is incorporated. Most of the diblock copolymers respond to the external stimuli such as temperature and solvent vapour [1]. An exemplary grid-like morphology of ZnO, as shown in Fig. 1, is chosen to study the morphological evolution under the influence of tetrahydrofuran (THF) vapour for different time scales. Solvent annealing is only responsible for the reorganization of the diblock copolymer. Hence, a final calcination step is performed after solvent annealing at a high temperature to ensure the effect on the final ZnO morphology as well.

Figure 1: SEM images of calcined ZnO grid-like morphology after THF solvent treatment for (a) 3 hours (b) 9 hours (c) 12 hours and (d) 48 hours.

Figure 2: Horizontal cuts shifted along the intensity axis of the 2D GISAXS data at the qz value of the Yoneda peak of the solvent annealed (bottom 5 curves) and calcined ZnO films (top 5 curves) for different solvent annealing time scales indicated on the right axis of the graph. The solid lines are the fit to the data (a). Average nanoparticle size (b) and pore size (c) in the film volume as obtained from the fits for the solvent annealed (■) and the calcined samples (●) plotted against different solvent annealing time.

As seen from the SEM images of the calcined samples in Fig. 1, there is significant difference in the ZnO morphology observed after 48 hours of solvent vapour treatment. To gain statistical relevance of the structural evolution going on in the volume of the film, grazing incidence small angle x-ray scattering is performed in the P03 Micro- and Nanofocus x-ray scattering (MiNaXS)
beamline of the PETRA III storage ring in Deutsches Elektronen-Synchrotron DESY, Hamburg on both the solvent annealed and calcined samples. The scattered signal is recorded with a Pilatus 300k pixel noise free detector with a readout time of < 5 ms (not shown here). Radiation damage is avoided by careful adjustment of the acquisition time. Horizontal cuts at the Yoneda position are performed from the 2D scattering images and plotted in Fig. 2 (a).

All the cuts are analyzed with a model fit (shown as solid lines) considering cylindrical form factor and structure factor distributed over a 1D paracrystal. A single structure and form factor is used to fit the data for all the samples. All the other peaks in the corresponding curves are the higher orders. For the solvent treated samples, it is observed that the fit using this model, agrees not so well with the data as compared to the sample which is not solvent annealed. On the other hand, the fit for the calcined sample without solvent annealing shows a poor agreement in the lower q region indicating the presence of some defects which are introduced in the sample after calcination giving rise to domains of larger structural length scales in the volume of the films which are not accessible by SEM. However, these defects are healed and the fits obtain a good agreement with the data upon solvent annealing. For the sample with the longest solvent annealing time, a structural collapse is observed which results in the loss of all the higher orders. The resulting fits yield the nanoparticle size and the pore size of the ZnO grid in the present case. These values are plotted as a function of annealing time in Fig. 2 (b) and (c) to obtain a more quantitative overview of the processes occurring in the volume of the films.

From Fig. 2 (b), smaller nanoparticle size is observed for all the samples after calcination which points to a shrinkage of the structure due to the removal of the polymer template from the films. After solvent treatment, a gradual increase in the pore size is observed, more prominently for the calcined samples, Fig. 2 (c).

![Figure 3: Schematic of structural evolution kinetics upon THF solvent vapour treatment of the ZnO spin coated films after (a) 3 hours (b) 9 hours (c) 12 hours and (d) 48 hours.](image)

The mechanism of the structural evolution hence studied by GISAXS is summarized using a schematic representation in Fig. 3. As seen from the image, the red core of the micelle represents the hydrophobic part of the template (PS block) whereas, the blue chains denote the hydrophilic block (4VP) in which ZAD (depicted by green spheres) is preferably incorporated. THF is chosen so that it is slightly preferable to the PS block forming the core of the micelles. Hence, with time, the solvent penetrates the shield of ZnO and tries to swell the PS block thereby increasing the pore size of the final ZnO grid obtained after calcination. The pore size thus increases with increasing solvent annealing time. However, if the solvent treatment is carried out for long enough time, the PS block is fairly dissolved resulting in a collapse of the micelle structure and thereby forming ZnO aggregates as also observed from the SEM images (in this case after solvent annealing for 48 hours).

Hence, the solvent treatment plays an important role in tuning the morphology of the final ZnO films synthesized by a suitable diblock copolymer.

References