**P(S-b-4VP) templated ordered ZnO nanostructures via sol-gel route**

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The high capability of diblock copolymers to self-assemble in ordered morphologies which allows to produce highly ordered nanostructures has driven the interest in these materials. In particular, the use of an asymmetric diblock copolymer template has attracted interest to synthesize inorganic nanostructures. Structuring of inorganic materials have gained consideration due to their wide range of applications in gas and chemical sensing, catalysis and energy conversion devices. [1]

In the present study, zinc oxide (ZnO) is studied for applications in hybrid photovoltaics. Poly(styrene-\(b\)-4vinylpyridine), abbreviated as P(S-\(b\)-4VP), is chosen as a template for the synthesis of ZnO nanostructures via sol-gel route. Pioneering work by Russell and co-workers to produce highly ordered P(S-\(b\)-4VP) hexagonal arrays on a grated substrate has indicated the high potential of this diblock to structure inorganic materials. [2]

![Figure 1: SEM images showing the surface morphologies of the ZnO nanocomposite films obtained by spin coating (a) before and (b) after calcination.](image)

N,N-dimethylformamide (DMF) is used as the major solvent which dissolves both blocks of the copolymer. Water is used as the selective solvent that offers poor solubility for the PS block. Mixing the diblock copolymer in the good-poor solvent pair induces micro-phase separation and formation of micelles with the hydrophobic PS block forming the core and the P4VP block constituting the corona. Addition of a suitable ZnO precursor, namely, zinc acetate dihydrate (ZAD), leads to the formation of Zn-O networks. The as-prepared solution is then spin coated on a pre-cleaned silicon substrate and studied by SEM (figure 1a). The surface morphology of the sample appears highly structured with the brighter regions indicating the semiconducting Zn-O networks. In order to convert the precursor into zinc oxide, a calcination step is performed in air at 400°C for 30 minutes. The diblock copolymer gets combusted in this process leaving behind the ZnO nanostructured morphology as shown in the SEM image of figure 1b. The morphology of the calcined film resembles the laterally and perpendicularly oriented micro-domains observed for example with P4VP (HABA) composite thin films studied by Nandan et al. [3]

In order to probe the structural dimension in the volume of the films, grazing incidence small angle X-ray scattering (GISAXS) measurements were performed at the P03 beamline of PETRA III storage ring at DESY, Hamburg. The incident angle and the sample-detector distance for all samples were kept constant at 0.38° and 2.18 m respectively. Figure 2a, 2b and 2c show the 2D GISAXS data of the pure polymer film, the as-prepared nanocomposite film and the calcined film, respectively. As seen from figure 2a, the diblock copolymer exhibits well-pronounced side maxima peaks, marked with arrows in the image. These side maxima indicate the presence of highly ordered structures in the system. In the vertical direction, along the \(q_z\) axis, the scattered intensity is modulated resulting from a height correlation of the copolymer layer. As seen from the GISAXS...
data of the as-prepared sample, the side maxima are shifted towards lower $q_y$ values as larger structures are produced in the film after incorporation of ZAD (figure 2b). This observation is attributed to a formation of Zn-O bonds inside a matrix of highly ordered P(S-$b$-4VP). For the calcined sample, as seen from figure 2c, the most side maxima stay at the same position as for the as-prepared sample. However, the scattering in the $q_z$ direction is reduced. This also indicates that the scattering along $q_z$ is largely enhanced by the presence of the diblock copolymer in the sample.

![Figure 2: 2D GISAXS data of (a) pure polymer film, (b) as-prepared nanocomposite film and (c) nanocomposite film post calcination. The arrows in image (a) indicate the peak positions with the second order being faintly visible. The specular peak is shielded by a beam stop. All the images have the same intensity scale bar as shown at the bottom.]

The characteristic size of structures inside the films are obtained by analyzing the horizontal cuts of the 2D GISAXS data for the pure polymer, as-prepared and calcined samples as shown in figure 3a and 3b. All horizontal cuts are analyzed with a model fit following the effective surface approximation of the distorted wave born approximation (DWBA). The horizontal cut obtained from the pure polymer sample shows two prominent structure factor peaks corresponding to those observed in the 2D image (figure 2a). The sharpness of the peaks resembles to the highly ordered structures in the film corresponding to distances of 23 nm and 10 nm, respectively. However, for the as-prepared and the calcined samples, the most prominent structure remains unchanged at around 37 nm. In addition, for the as-prepared sample, additional broad peaks are observed corresponding to structure sizes of 102 nm and 15 nm in the film volume. These additional peaks are further broadened upon calcination, which indicates a loss of order in the film that is explained by the loss of the highly ordered polymer matrix upon calcination.

![Figure 3: Horizontal cuts of the 2D GISAXS data at the $q_z$-value of the Yoneda peak of (a) the pure polymer film, (b) as-prepared copolymer-ZAD composite film and of ZnO film after calcination. Solid lines are fits to the data as described in the text. The arrows indicate the dominant structure peaks for each sample. The corresponding structure sizes are detailed in the text. Data are shifted along the intensity axis for illustrative purposes.]

References