Controlled embedding of semiconducting nanoparticles in a conducting polymer template


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Photoactive semi-conducting polymers have shown to be interesting candidates for photovoltaics due to their high absorption coefficient, easy processibility, mechanical flexibility and low costs. Due to the high exciton binding energy a two component system is in organic photovoltaics necessary to have efficient charge carrier separation. Furthermore, there are stringent constraints in device fabrication due to the short exciton diffusion length, i.e. the charge carrier separation has to occur in this length scale (on order of 10 nm). Therefore, the morphology of the polymer film is crucial.

Besides the inner film structure of organic photovoltaic devices, the material system used plays an important role. On the one hand, so called all polymer systems in which the active layer consist of photoactive polymers only are common. On the other hand, hybrid systems combining organic and inorganic materials have shown great potential. To obtain such hybrid systems typically a nanostructured porous inorganic basic layer is created for instance via a sol-gel approach. In a second step, these nanopores are filled with a photoactive polymer. In our new approach, we use a diblock copolymer as the structure-directing agent in which we selectively incorporate inorganic nanoparticles. We select the diblock copolymer poly(styrene-b-p-phenylene) (P(S-b-PP)) which combines a standard coil-like polymer and a photoactive rod-like polymer [1]. Titania nanoparticles coated with 4-tert-butylcatechol (TBC) where incorporated. P(S-b-PP) was dissolved in tetrahydrofurane (THF) together with different titania nanoparticle content and spin coated on pre-cleaned glass slides. By solvent annealing the micro-phase separation of the copolymer films was enhanced. To investigate the influence of solvent annealing as well as the nanoparticle incorporation grazing incidence small angle X-ray scattering measurements were performed at the beamline BW4 (HASYLAB).

![Figure 1](image_url)

**Figure 1:** a) 2d GISAXS pattern of a thin P(S-b-PP) film. b) Corresponding IsGISAXS simulation, the colour code of the 2d scattering patterns is identical. The black circle represents the specular beam stop.

In Fig. 1a the 2d GISAXS scattering pattern of a pure P(S-b-PP) film is presented. The side maxima in horizontal direction correspond to the micro-phase separation in the P(S-b-PP) film. For further analysis a 2d IsGISAXS simulation based on a full DWBA approach was performed (Fig. 1b). The selected model assumes vertically oriented cylinders of PPP embedded in a matrix of PS. The cylinder diameter is 10 nm and the distance between two neighbouring cylinders is 16 nm, which fits quit well to the length scales expected from the molecular structure [2]. The total height of the


film as well of the cylinders was fitted to 79 nm. In the simulation all basic features of the GISAXS measurement are well reproduced, however, due to the rather simple model approach (neglecting roughness on small scale) at large values of the scattering vector some small deviations are present.

In the experiment, the titania nanoparticle content was varied from 0 wt% to 20 wt%. As shown in the out-of-plane cuts of the GISAXS measurement (see Fig. 2a) the inner film structure is altered by incorporating titania nanoparticles. Two features marked with arrows change with increasing amount of embedded nanoparticles. The structure factor denoted “A” corresponds to the inter-cylindrical distance described above. From the pure P(S-b-PP) film (bottom curve) to the films with higher particle content the feature “A” is converted from a peak to a more shoulder-like shape and at a content of 20 % nanoparticles (top curve) it is strongly damped. This evolution is due to loss of contrast between the PS and the PPP domains in the polymer film. Consequently, the titania nanoparticles balance the difference in refractive index of PS and PPP. As the refractive index of PS is smaller than the one of PPP and titania has an even higher one, the nanoparticles are incorporated selectively in the PS domains. Furthermore, the structure factor “A” is slightly shifting to smaller of the lateral scattering vector component $q_y$ which means an increase of the distance of the PPP domains. The selective incorporation of titania implies the swelling of the PS domain and therefore results in an increase of the inter-cylindrical distance.

The second feature (denoted “B”) corresponds to the form factor of the spherical titania nanoparticle embedded inside the dibloc copolymer film. At a content of 20 wt% this dominates the out-of-plane scattering.

In Fig. 2b the detector cuts of the 2d scattering patterns are presented. With increasing nanoparticle content the Yoneda peak is shifting to the critical value of titania. Furthermore, the addition of nanoparticles influences the film homogeneity as the correlated roughness is getting less pronounced with increasing content. At higher nanoparticle content the wavelength of intensity oscillations changes in addition, which can be a hint for a formation of a thinner enrichment layer [3].

References