# Foam-like ZnO nanostructured morphology for applications in photovoltaics

*K. Sarkar, M. Rawolle, E.M. Herzig, W. Wang, A. Buffet[1], S.V. Roth[1] and P. Müller-Buschbaum*

*Technische Universität München, Physik-Department, Lehrstuhl für Funktionelle Materialien, James-Franck-Str. 1, 85748 Garching, Germany*

*[1]HASYLAB / DESY, Notkestr. 85, 22603 Hamburg, Germany*

Foam-like morphology of inorganic materials such as titania is beneficial to the need of large surface-to-volume ratio in order to enhance light harvesting and minimize probabilities for electron-hole recombination in the context of photovoltaic applications. [1] Hence, inorganic foam-like network structures have been largely synthesized and investigated.

In the present study, zinc oxide (ZnO) is studied as an alternative to titania. ZnO has a wide band gap of 3.37 eV, a large exciton binding energy of 60 meV at room temperature, optical transparency, electrical conductivity, piezoelectricity and many more unique properties that make it a potential candidate for hybrid photovoltaic applications. [2]

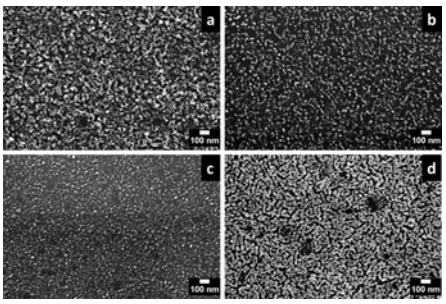


**Figure 1:** *SEM images of ZnO morphologies resembling foam-like structures obtained after calcination. (a) $W_{DMF}:W_{H2O}:W_{ZAD}$ = 0.94:0.03:0.03 (b) $W_{DMF}:W_{H2O}:W_{ZAD}$ = 0.98:0.01:0.01 (c) $W_{DMF}:W_{H2O}:W_{ZAD}$ = 0.92:0.07:0.05 (d) $W_{DMF}:W_{H2O}:W_{ZAD}$ = 0.925:0.01:0.065.*

ZnO nanostructures are synthesized via sol-gel mechanism coupled with a structure directing agent which is chosen to be a diblock copolymer namely, polystyrene-*block*-polyethyleneoxide [P(S-*b*-EO)]. The micro-phase separation of this diblock is induced by a suitable good-poor solvent pair followed by the incorporation of the ZnO precursor, zinc acetate dehydrate (ZAD) in the PEO block. Thin nanocomposite films are produced via spin coating. The final calcination step for such films is carried out in air at 400 °C for 30 minutes in order to convert ZAD into crystalline ZnO and to remove the diblock template. Tailor-made morphologies are obtained by simply adjusting the weight fractions of the good-poor solvent pair and the precursor. The predominant morphology being the foam-like structures are further investigated by scanning electron microscopy (SEM) as shown in figure 1. The surface morphology of the foams with different densities is probed using SEM.

Grazing incidence small angle X-ray scattering (GISAXS) measurements were performed at the P03 beamline of PETRA III storage ring at DESY, Hamburg to obtain better insight of the volume of the films. The 2D scattering data for the foams (see figure 1) are shown in figure 2. Although the SEM images of the samples appear very similar in their surface morphology, the 2D GISAXS images show quite distinct features from one another. Apart from the sample with $W_{DMF}:W_{H2O}:W_{ZAD}$ = 0.92:0.07:0.05, all the other samples show a strong scattering signal at the Yoneda region (figure 2) which is attributed by the dense ZnO network as also observed form the SEM images (figure 1). The sample 0.98:0.01:0.01 has the lowest ZAD weight fraction of only 0.01 indicating a very thin layer. Hence, the intensity at the Yoneda is enhanced by the underlying silicon (100) substrate, which is also visible as a dark background in figure 2b. sample 0.92:0.07:0.05 (figure 2c) shows the lowest intensity at the Yoneda position but in contrast very

prominent lateral intensity peaks indicating the presence of mesopores in the volume of the film. Mesopores of several tens of nanometers are also observed in the sample 0.925:0.01:0.065 (see figure 1d). But the corresponding prominent lateral structure peaks are shielded by the strong intensity at the Yoneda position.

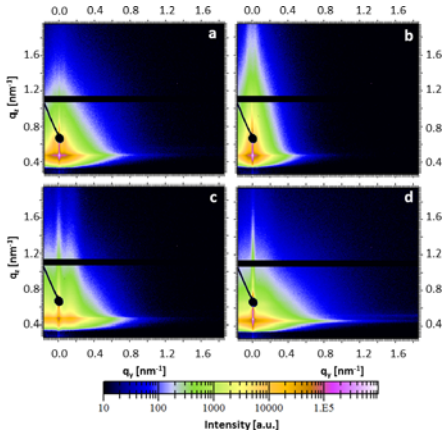


**Figure 2:** *2D GISAXS data of the calcined samples with ZnO morphologies as shown in figure 1. The circular beam stop is installed to shield the specular peak. The intensity scale bar for all the images is the same as shown at the bottom.*

Horizontal cuts of the 2D GISAXS data for all the samples are performed at the characteristic $q_z$ value of 0.47 nm$^{-1}$, corresponding to the observed Yoneda peak position. These horizontal cuts are shown in figure 3 along with the corresponding model fit obtained by following the effective surface approximation of the distorted wave born approximation (DWBA). A prominent structure factor peak for all the samples indicates the presence of ordered structures in the samples. As obtained from the fits, the predominant length scales in the samples are 20 nm, 38 nm, 60 nm and 56 nm, respectively from bottom to top of the graph. Hence, evident from the SEM images (figure 1), the values from the fit do not provide the exact size of the crystallites or the clusters, it rather resembles the distance between the clusters.

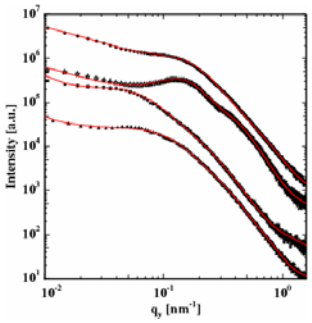


**Figure 3:** *Horizontal cuts of the 2D GISAXS data at the $q_z$-value of the Yoneda peak of the spin coated ZnO for different combinations of weight fractions of DMF, water and ZAD films after calcination. $W_{DMF}$:$W_{H2O}$:$W_{ZAD}$ from top to bottom varies as 0.925:0.01:0.065, 0.92:0.07:0.05, 0.98:0.01:0.01 and 0.94:0.03:0.03. Solid lines are the fit to the data points shown as symbols. All the data are shifted along the intensity axis for clarity.*

## References


[1] G. Kaune, M. Memesa, R. Meier, M. A. Ruderer, A. Diethert, S. V. Roth, M. D'Acunzi, J. S. Gutmann, and P. Müller-Buschbaum, ACS Appl. Mater. Interfaces **1**, 2862-2869 (2009).

[2] H. Yu, Z. Zhang, M. Han, X. Hao, F. Zhu, J. Am. Chem. Soc. **127**, 2378-2379 (2005).