Low-energy STEM and EDX investigation of polystyrene-ZnO core-shell structures

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Polystirene-ZnO core-shell structures were prepared by atomic layer deposition (ALD) at low-temperature and characterized by scanning electron microscopy (SEM) techniques[1]. Zinc oxide features a band gap of 3.37 eV, *n*-type semiconducting behavior coupled with 60 meV excitonic energy: key features which make ZnO attractive for optoelectronic, photovoltaic and sensor devices [2]. Indeed, the potential of ZnO nanocrystallites aggregated on colloidal spheres was recently proved for the enhancement of the light conversion efficiency in dye-sensitized solar cells. Therein these hierarchically organized systems take advantage of the efficient light scattering promoted by colloidal spheres to increase the light-harvesting capability of the photoelectrode. Thus, the controlled preparation of composite systems based on ZnO nanocrystals and colloidal polymers has become fundamental.

For the characterization of the core-shell structure, an approach based on scanning transmission electron microscopy (STEM) al low energy (10-20 keV beam energy) has been implemented in the SEM. The low-energy STEM technique has been demonstrated as an effective and complementary approach to high energy STEM [3, 4]. The proposed approach allows one to perform Energy Dispersive X-ray (EDX) analysis on electron transparent specimens, thus exploiting the nanometric resolving power of the SEM.

The experimental set-up has been implemented in LEO 1525 SEM with standard OXFORD EDX system and commercial KE-Developments solid-state Bright-Field (BF) – Dark-Field (DF) STEM detector. The specimen working distance, beam accelerating voltage, and detector position have been adapted for simultaneous acquisition of EDX spectra and STEM Z-contrast imaging of PS spheres supported by holey carbon grid.

The integrated intensity of carbon and zinc K-line over a line-scan across the PS sphere shown in Fig. 1 were fitted to a spherical core-shell model, and the values for the radius for the PS spheres and the thickness of the ZnO coating are comparatively reported in Table I together with the nominal values and the ones determined by STEM imaging. The estimation of the thickness does not take into account of the broadening of the 20 keV electron beam, and may result in the observed underestimation of the thickness of the ZnO layer. In Fig. 2, the contrast features of the STEM image corresponds to the ZnO layer surrounding of the sphere. The contrast features are not straightforwardly associated to the composition of the core-shell, owing to an incomplete collection of the DF component of the transmitted electrons. This detection strategy will be optimized also for STEM imaging and compared with the conventional imaging approach at higher voltages.

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Table I: Summary of the experimental values for the core-shell PS-ZnO structure.

	Nominal	*EDX profile – fit*	*STEM imaging – measure*
Radius of PS sphere (nm)	210	183±12	147
Thickness of ZnO shell (nm)	20-25	30±6	21

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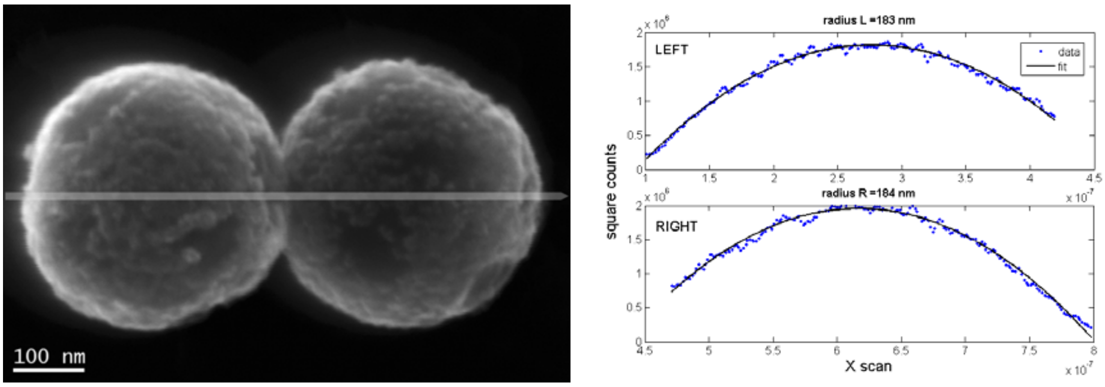

Figure 1. (left) Secondary-electrons SEM image of PS spheres covered by the ALD layer of ZnO. (right) Horizontal EDX line scan for carbon $K_{\alpha 1,2}$ across the two PS spheres (arrow).

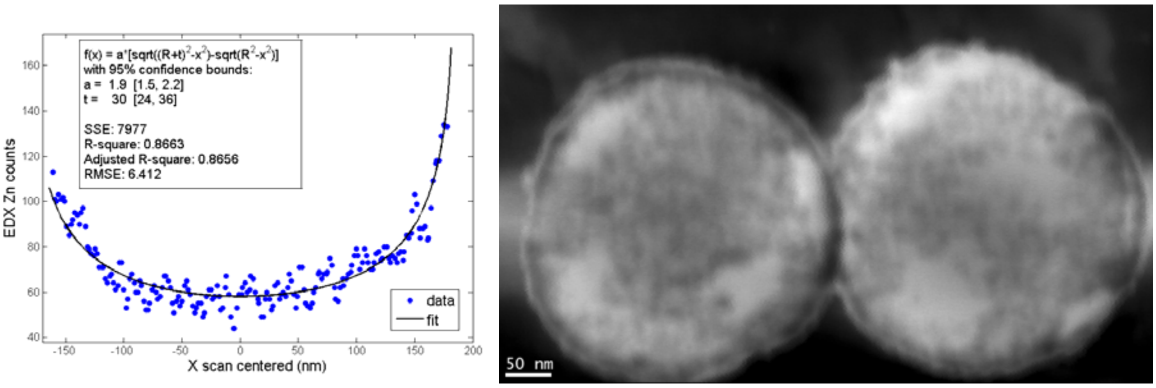

Figure 2. (left) EDX line scan for zinc K_{α} across the diameter of the left PS sphere. (right) Low-voltage STEM image of the same PS spere. Nanosized grains are clearly resolved, as well as in-homogeneities of the coverage caused by the contact between spheres in the ordered assembling.

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