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EFTEM Imaging of ZnO-TiO_2 Core-Shell Nanowires and TiO_2 Nanotubes

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Dye-sensitized solar cells (DSCs) are promising devices for low-cost, large-scale solar energy conversion. The anodes of DSCs are usually made of thick films of TiO_2, ZnO or SnO_2 nanoparticles. Recently, dense arrays of oriented, crystalline ZnO nanowires have been used to replace the traditional nanoparticle film, and a power conversion efficiency of 1.5% was demonstrated with this approach.[1] Spectrally limited absorption, a low fill factor and the relatively low surface area of the nanowire array limit the device efficiency. One way to increase the efficiency of the nanowire DSC is to use core-shell heterostructures. Here we use atomic layer deposition (ALD)[2] to synthesize ZnO-TiO_2 core-shell nanowire arrays. ALD offers a unique ability to control thickness on the nanometer scale and can produce exceptionally uniform thin films. However, the uniformity, porosity and distribution of elements in these nanostructures are vitally important for the functionality of the solar cells. The aim of this work is to investigate the structure, morphology and chemical composition of the ZnO-TiO_2 core-shell nanowires using electron microscopy, XRD, spectral imaging and EDS analysis. Elemental distribution characterization was performed using a Libra EFTEM equipped with an Omega energy filter. EFTEM was performed with specific energy losses for Ti, O and Zn based on the three-windows method, in which two images are taken at energy losses below the energy loss maximum to carefully define the background signal and then subtracted from the third image. EFTEM mapping by energy-filtered imaging provides information about the distribution of oxygen, titanium and zinc at the nanometer scale with an acquisition time of 10-30 seconds and a spatial resolution of 1-2 nm. The images are focused at an energy loss of 200-300 eV. The weak intensity of EFTEM images obtained using K, L and M edges for O, Ti and Zn, respectively, is expected because small nanostructures produce weak contrast.

Fig. 1 is a typical scanning electron cross-sectional micrograph of ZnO-TiO_2 core-shell nanowires. It shows a high-density array with several billion nanowires per square centimeter. Fig. 2 is a typical XRD pattern of the ZnO-TiO_2 core-shell wires showing two sets of peaks indexed as anatase TiO_2 and wurtzite ZnO. The conventional bright-field TEM image in Fig. 3 shows that the polycrystalline TiO_2 shells (confirmed by the ring pattern in Fig. 3) are dense and nonporous. High-resolution transmission electron microscopy (HRTEM) data of TiO_2 shells (nanotubes) suggested a layer deposition mechanism (Fig. 4). Line profile EDS analysis shows clearly the presence of Zn in the TiO_2 shell and energy-filtered images in Fig. 5 confirm this finding.

In summary, the ZnO-TiO_2 core-shell nanowires is successfully synthesized using atomic layer deposition and show exceptional solar energy conversion characteristics.

1. M. Law et al., Nature Materials 4 (2005) 455.
2. M. Ritala et al., Science 288 (2000) 319.
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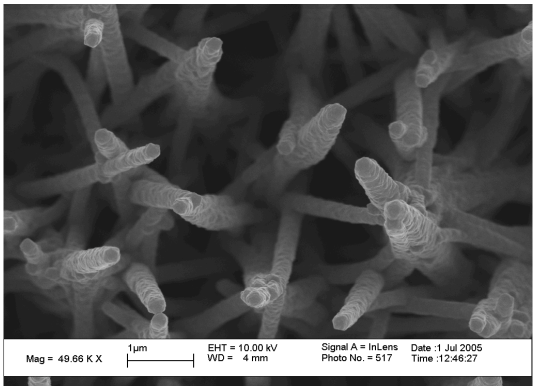


Fig. 1 - SEM image of a ZnO-TiO_2 core-shell nanowire film with a ~70 nm-thick TiO_2 shell.

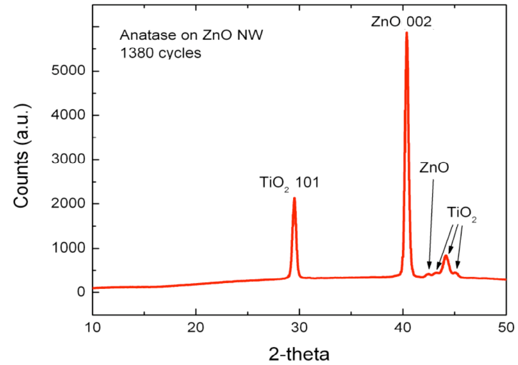
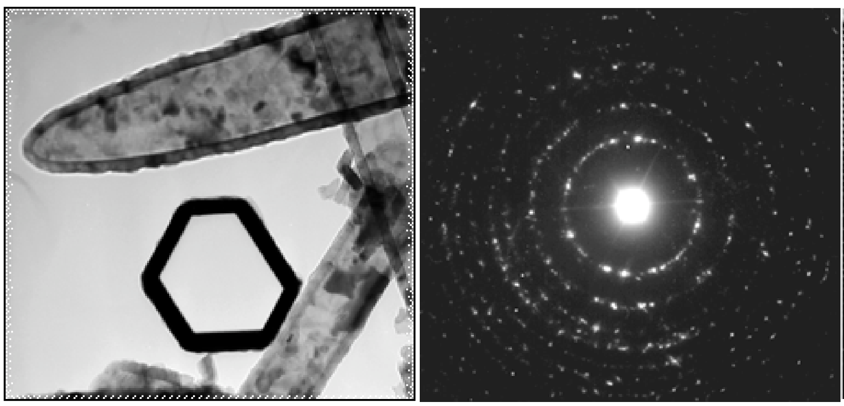


Fig. 2 - XRD pattern of a ZnO-TiO_2 core-shell nanowire array, showing two sets of peaks indexed to anatase



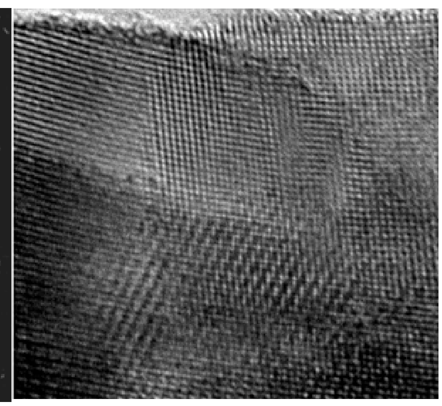


Fig. 3 – Bright field image of TiO_2 shells and selected area ring diffraction pattern.

Fig. 4 – HREM image of TiO_2 taken close to the shell surface.

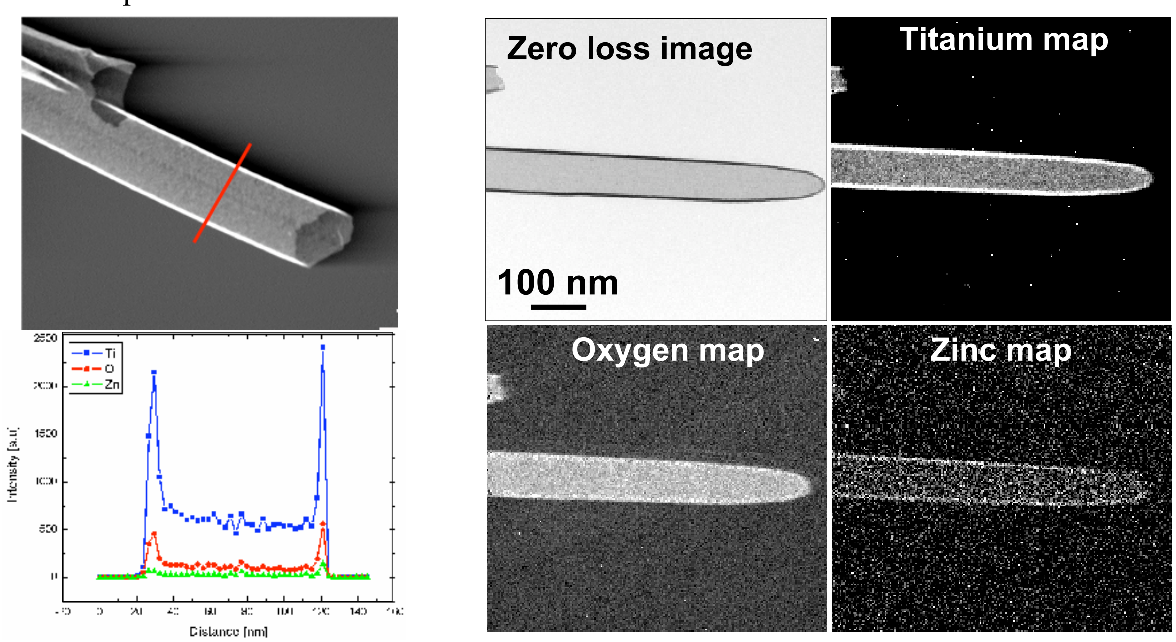


Fig. 5 – EDS profile and energy-filtered images showing elemental maps of the TiO_2 nanotubes.