Nanoscale phase segregation driven magnetic properties of 3D hierarchical self-assembled microstructures formed from α-MnO2 nanotubes

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In recent years, many hierarchically structured metal oxides with various morphologies have been reported, and their potential applications, for instance include catalysis, sensors and energy conversions [1]. The formation of hierarchical structures is generally considered to be a self-assembly process, in which building blocks (nanoparticels, nanorods, …) self-assemble into regular higher level structures. The self-assembly on nanoparticels into two- or three-dimensional architectures is driven by weak interactions. On the account of increased number of active sites [1] it is believed that these structures could significantly improve sensing or catalytic properties.

For many years, MnO_2 and derivative compounds have been attracting special attention. MnO_2 is a porous material which exists in different polymorphic forms [2]. In combination with its redox capability between manganese ions in oxidation states 4+ and 3+ makes it efficient in a wide range of technological applications like in energy storage as cathode material in alkaline and rechargeable batteries [3], molecular sieves [4], and in catalysis [5]. It is widely accepted that chemical, catalytic, electrical and magnetic properties of MnO_2 phases strongly depend on their structure and morphology [6]. The synthesis of MnO_2 nanotubes [7,8] is rarely reported compared to other morphologies [9–12].

We report on a synthesis of single crystalline α-MnO_2-type nanotubes. Nanotubes were synthesized under hydrothermal conditions by a decomposition of $KMnO_4$ in acidic environment. Nanotubes with typical outer diameter of 30−40 nm and lengths between 250−370 nm are self-assembled into 3D hollow microspheres (figure 1a) with the shell thickness corresponding to the length of the nanotubes (inset in the figure 1a). Structure and composition of nanotubes were investigated by means of XRD and EELS. The XRD profile matches well with the α-MnO_2 phase.

Measurements of electrical conductivity reveal a complex behavior that could not be explained by a unique model which suggests that an additional parallel conductivity channel, such as fluctuation-induced tunneling, has to be also considered Magnetic susceptibility (figure 2) and electron paramagnetic resonance measurements reveal a complex temperature dependence with a broad transition in χT and EPR signals at around 200 K and

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antiferromagnetic ordering at T_N = 12 K. We speculate that the transition at 200 K is due do to the charge localization.

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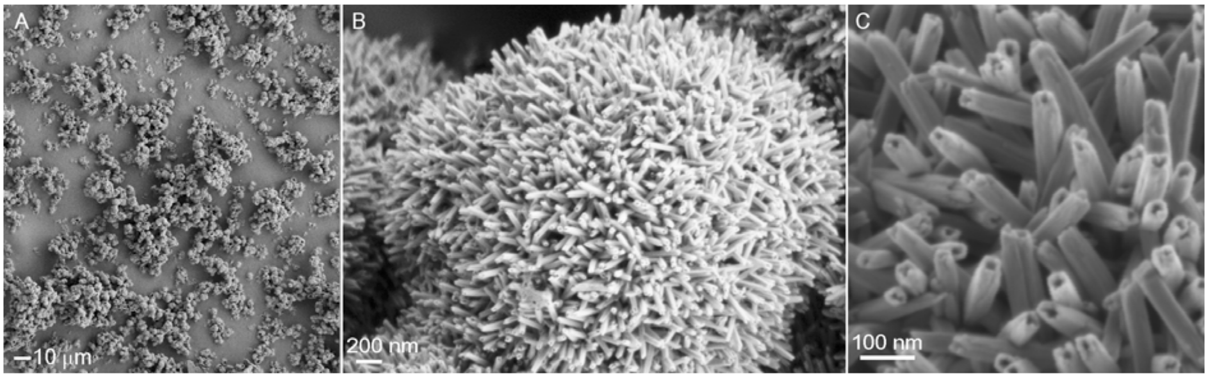

Figure 1. FE-SEM images of α-MnO_2 product: A) a panoramic view at smaller magnification reveals that the product is composed of microspheres that in diameter reach between 2–3 µ. B) an individual microsphere with a typical diameter of 3 µm and c) a top view on the microsphere shell which is composed from nanotubes. Nanotube's cavities have tetragonal shape.

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