Low Dimensional Materials and Catalysts

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Electron microscopy study of one-dimensional functional materials synthesized by a nonaqueous route

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Anisotropic nanoparticles such as nanofibers, nanotubes, nanorods, and nanowires are of not only scientific but also technological interest. The anisotropy inherent in these nanomaterials provides unique properties which are expected to be critical to the function and integration of nanoscale devices. Among the different families of functional materials, metal oxides play an outstanding role due to their redox activity. The possibility to change the oxidation state and the stoichiometry provides unique opportunities to tailor the chemical and physical properties. The rapidly growing number of publications in the field of metal oxide synthesis by wet chemical routes suggests that the so-called nonaqueous (or nonhydrolytic) processes are particularly successful for the size- and shape-controlled preparation of colloidal inorganic nanoparticles [1,2]. In this talk, I will present two studied anisotropical low-dimensional systems synthesized by nonaqueous route, whose structural features were elucidated by the usage of electron microscopy. First presented study [3] involves the preparation of lanthanum hydroxide and manganese oxide nanoparticles, based on a nonaqueous sol–gel process involving the reaction of $La(OiPr)_3$ and $KMnO_4$ with organic solvents such as benzyl alcohol, 2-butanone and a 1:1 vol. mixture thereof. The lanthanum manganese oxide system is highly complex and surprising results with respect to product composition and morphology were obtained. In dependence of the reaction parameters, the $La(OH)_3$ nanoparticles undergo a shape transformation from short nanorods with an average aspect ratio of 2.1(Figure 1) to micron-sized nanofibers (average aspect ratio is more than 59.5). Although not directly involved, $KMnO_4$ plays a crucial role in determining the particle morphology of $La(OH)_3$. The reason lies in the fact that $KMnO_4$ is able to oxidize the benzyl alcohol to benzoic acid, which presumably induces the anisotropic particle growth in [0 0 1] direction upon preferential coordination to the $\pm$(1 0 0), $\pm$ (0 1 0) and $\pm$ (−110) crystal facets. By adjusting the molar $La(OiPr)_3$-to-$KMnO_4$ ratio as well as by using the appropriate solvent mixture it is possible to tailor the morphology, phase purity and microstructure of the $La(OH)_3$ nanoparticles.

The second part of the presentation shows a nonaqueous liquid-phase route involving the reaction of vanadium oxychloride with benzyl alcohol leading to the formation of single-crystalline and semiconducting $VO_{1.52}(OH)_{0.77}$ nanorods with an ellipsoidal morphology, up to 500 nm in length and typically about 100 nm in diameter (Figure 2) [4]. Composition, structure, and morphology were thoroughly analyzed by neutron and synchrotron powder X-ray diffraction as well as by different electron microscopy techniques (SEM, (HR)TEM, EDX, and SAED). The data obtained point to a hollandite-type structure which, unlike other vanadates, contains oxide ions in the channels along the c-axis, with hydrogen atoms attached to the edge-sharing oxygen atoms, forming OH groups. According to structural probes and magnetic measurements (1.94 μB/V), the formal valence of vanadium is +3.81 (V^{4+}/V^{3+} atomic ratio $\approx$ 4). The temperature-dependent DC electrical conductivity exhibits Arrhenius-type behavior with a band gap of 0.64 eV. The semiconducting behavior is interpreted in terms of electron hopping between vanadium cations of different valence states (small polaron model). Ab initio density-functional calculations with a local spin density approximation including orbital potential (LSDA + U with an effective U value of 4 eV) have been employed to extract the electronic structure. These calculations propose, on the one hand, that the electronic conductivity is based on electron hopping between neighboring V^{3+} and V^{4+} sites, and, on the other hand, that the oxide ions in the channels act as electron donors, increasing the fraction of V^{3+} cations, and thus leading to self-doping. Experimental and simulated electron energy-loss spectroscopy data confirm both the presence of V^{4+} and the validity of the density-of-states calculation. Temperature-dependent magnetic susceptibility measurements indicate strongly frustrated antiferromagnetic interactions between the vanadium ions. A model involving the charge order of the V^{3+} sites is proposed to account for the observed formation of the magnetic moment below 25 K.

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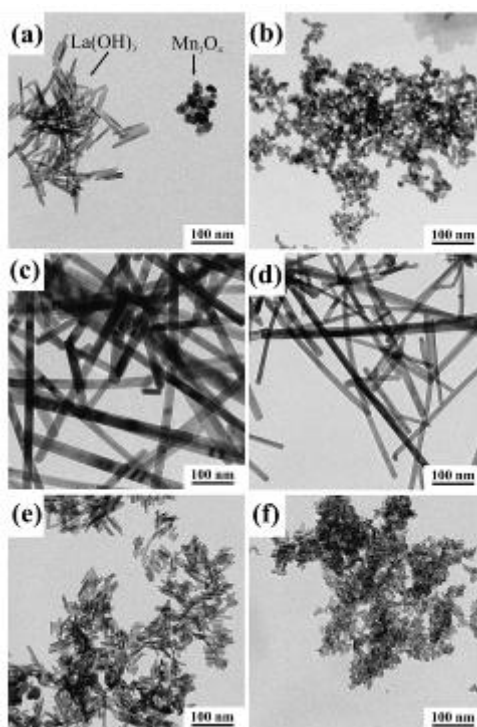
Figure 1. Representative TEM images of the nanoparticles synthesized under various conditions. (a) BA (1:1), (b) BUT (1:1), (c) BA+BUT (1:1), (d) BA+BUT (1:0.5), (e) BA+BUT (1:0.25), (f) BA+BUT (1:0). BA=benzyl alcohol, BUT=2-butanone.
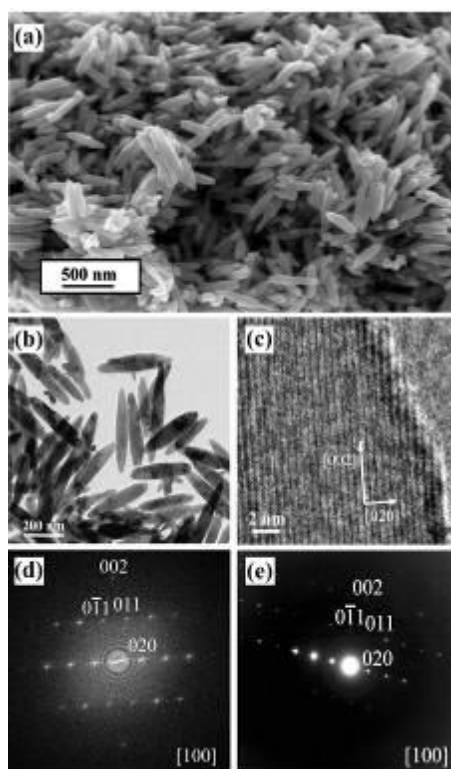

Figure 2. (a) SEM and (b) TEM overview images of $VO_{1.52}(OH)_{0.77}$ nanorods. (c) HRTEM image of a part of a nanorod. (d) Corresponding power spectrum of 2(c). (e) Corresponding SAED pattern taken from the part of the nanorod depicted in 2(c).