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Surfactants in the formation of vanadium oxide nanotubes

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The role of long-chain surfactants in the formation of vanadium oxide nanotubes from V_2O_5–organic additive hybrid nanocomposites seems to be connected with enforcing crystalline V_2O_5 to transform into a layered precursor giving then nanoscrolls under hydrothermal conditions.

Nanomaterials based on vanadium oxides, such as vanadium oxide nanotubes,[1,2] nanowires,[3] nanobelts[4] and even nanourchins,[5] are of great interest for modern lithium-ion batteries,[6] sensing elements,[7] catalysis[8] and microelectronics. Organic templates are routinely used for the formation of nanoscale vanadia-based objects to provide either a high yield and effectiveness of the synthesis or final structure–properties control. Vanadium oxide nanotubes can be prepared only using both organic templates and hydrothermal treatment. Unfortunately, it is not yet clear how organic molecules serve as structure-directing templates and cause such a deep structural evolution of bulk crystalline V_2O_5 into nanoscrolls. The scope of this article is a discussion of experimental findings on the processes of vanadia nanotube formation in the presence of two types of organic additives.

Vanadium oxide nanotubes have been originally synthesised in 1998,[9] and they are a classical example of multiwall tubular structures obtained using a structure-directing approach. The nanotubes are formed by scrolling up V–O layers hence the interlayer distance in such nanostructures correlates often with the chain length of surfactants applied.[1]

V_2O_5–hexadecylamine-1 (V_2O_5–HDA) nanotubes were obtained through the general procedure described elsewhere.[10,11] Initially, the homogenization of inorganic and organic compounds was performed by stirring 1.82 g of orthorhombic V_2O_5 (Sigma-Aldrich) and 2.41 g of crystalline HDA (Sigma-Aldrich) in 30 ml of distilled water for 48 h. Then, the precursor was autoclaved at 180 °C for two days. For this purpose a bomb with a special Teflon-lined cell (80% filled) was used. The same procedure was used in a separate series of experiments with ethanol added instead of HDA; in that case the hybrid composite consisted of 1.82 g of orthorhombic V_2O_5, 10 ml of 96% ethanol and 20 ml of distilled water.

All of the samples were examined by XRD (Rigaku D/MAX 2500, Japan, with a rotating copper anode, CuKα) in a 2θ range of 3–70° with a step of 0.01°. The microstructure of the samples was examined using a transmission electron microscope [Leo 912 AB Omega (Leo, Germany), LaB_6 cathode, accelerating potential of 100 kV]. Fourier transmission infrared (FTIR) spectra were recorded using a Spectrum One IR spectrophotometer (Perkin–Elmer, USA). All the samples for IR spectroscopy were prepared as KBr pellets. The measurements were carried out in the range 4000–300 cm^{-1}.

Stirring polycrystalline V_2O_5 with HDA and a small amount of water results in changing the mixture colour; orange V_2O_5 becomes greenish during the homogenization of the mixture

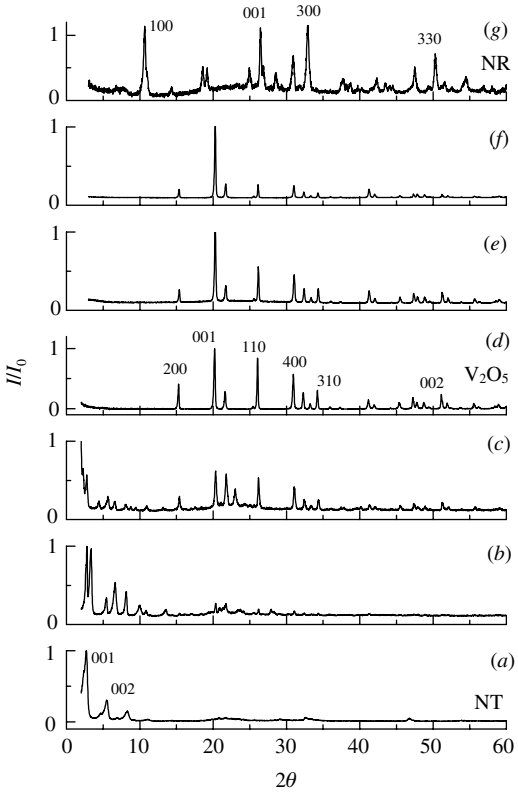

Figure 1 XRD patterns for hybrid composites obtained after the homogenization of polycrystalline V_2O_5 with organic additives in the presence of water: (*b*) and (*c*) V_2O_5–HDA mixtures after 21 and 5 h of stirring, respectively; (*d*) initial V_2O_5; (*e*) and (*f*) V_2O_5–EtOH mixtures after 5 and 21 h of mixing; (*a*) and (*g*) XRD plots for vanadium oxide nanotubes (NT) and nanorods (NR), respectively.

evidencing for reduction of V^V. The colour of V_2O_5–EtOH mixtures continues to be orange; therefore, the reduction process might not occur. Some distinct changes of crystalline structure were monitored; the corresponding XRD plots are shown in Figure 1. For the V_2O_5–HDA mixture both the patterns demonstrate a shift of reflections, meaning a deep phase transformation. In the resulting pattern for the V_2O_5–HDA precursor, all the initial reflections were reduced and some intense peaks appeared in the small-angle range. The electron diffraction data of the resulting V_2O_5–HDA precursor show the low crystallinity of V–O layers of hybrid material that could mean the structural change of the material. The electron diffraction image of a

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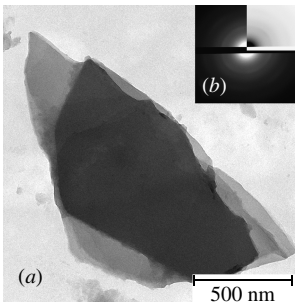

Figure 2 (*a*) TEM micrograph and (*b*) electron diffraction of the layered V_2O_5–HDA precursor.

hybrid composite is shown in Figure 2(*b*). The high intensity of reflections in the small-angle range and lowered intensity of the others is the evidence that the precursor has a layered structure with a large interlayer distance of 33 nm.

Two main processes take place during stirring: surfactant adsorption *via* NH_2 or OH groups and vanadium(V) reduction.[12] These processes start already at first minutes of stirring and continue for first 20 h according to XRD data [Figure 1(*c*),(*b*)].

For two other samples examined by XRD, the course of interaction differs strongly from the presented results of the first system. No shift of orthorhombic V_2O_5 reflections but some changes in the relative intensities of several peaks were found [Figure 1(*e*),(*f*)].

After the hydrothermal treatment of the homogenised mixtures, vanadium oxide nanotubes were observed in the V_2O_5–HDA system only while vanadium oxide nanorods were found in the V_2O_5–EtOH system. The micrographs of the resulting products in the V_2O_5–HDA and V_2O_5–EtOH systems are shown in Figure 3. The diameter of individual nanotubes is about 120 nm and the diameter of nanorods is much smaller (about 20 nm). Both of the nanostructures are layered. In the first case, the interlayer spaces are about 33 nm. In a typical nanorod structure, the interlayer spaces are less than 1 nm. It is obvious that in the first image [Figure 3(*a*)] we can see an interior tunnel while the second picture of a nanorod [Figure 3(*b*)] demonstrates a continuous nanoobject. Most probably, the precursor structure formed before autoclaving played a great role since the XRD precursor pattern in the first system is quite similar to the XRD picture of final nanotubes thus confirming that a layered structure motive might form already during mixing at room temperature while the second (hydrothermal) stage enforces the layers to scroll up thus forming 'nanotubes'.

The FTIR spectra of nanotubes, V_2O_5–HDA precursor and crystalline HDA are demonstrated in Figure 4. Some important differences between the precursor and the product spectra should be underlined. The main difference between the two spectra lies in the visible range that we can see as a greenish

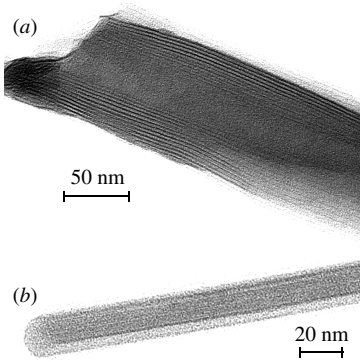

Figure 3 TEM images of (*a*) vanadium oxide nanotubes forming in the V_2O_5–HDA system and (*b*) vanadium oxide nanorods synthesised from the V_2O_5–EtOH mixture.

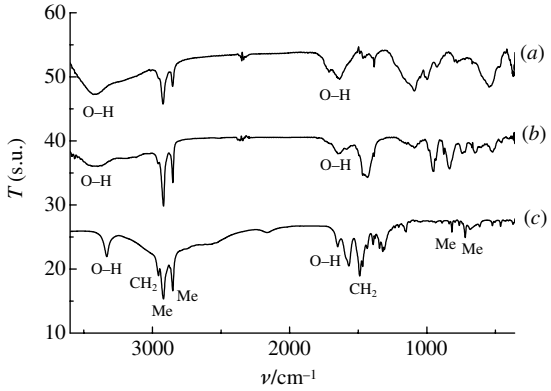

Figure 4 FTIR spectra of (*a*) vanadium oxide nanotubes, (*b*) V_2O_5–HDA precursor and (*c*) crystalline HDA.

colour of the precursor and a black colour of nanotubes. This is a result of partial reduction of V^{5+} to V^{4+} by organic compounds. The $–CH_2–$ stretching modes for nanotubes are less intensive than for the precursor; probably, because of the smaller flexibility of alkyl chains in nanoscrolls. This difference in the relative peak intensities could originate from the less vibration interaction of HDA molecules with an inorganic matrix.

Thus, we can conclude that the roles of HDA and ethanol in the formation of vanadia-containing nanomaterials are different. If HDA molecules separate V–O layers and form a lamellar hybrid material, the EtOH can only reduce vanadium pentoxide and does not change the structure of bulk V_2O_5 at room temperature. For long-chain surfactants, superficial adsorption of organic molecules occurs during the homogenization step and the crystal structure of V_2O_5 readily transforms into a layered intermediate.

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