FTIR study of vanadium oxide nanotubes from lamellar structure

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Vanadium oxides and compounds derived from them have attracted interest because of their potential use as cathode materials for rechargeable lithium batteries [1–3] and their important role in catalysis [4, 5]. Depending on the nature of the species present in the reaction medium, vanadium oxides may exhibit a wide range of morphologies (lamellar structures, molecular clusters, etc.) [6, 7]. Among them, the vanadium oxide nanotubes are unique because of their strongly anisotropic geometry, which is associated with interesting chemical and physical properties. Recently, Nesper and co-workers synthesized novel vanadium oxide nanotubes using vanadium alkoxides as starting materials in a Chimia Douce route [7, 8]. However, vanadium alkoxides are very expensive. Therefore, in the present work, vanadium oxide nanotubes have been prepared by reacting vanadium oxide, instead of vanadium alkoxides, with a structure-directing agent followed by hydrothermal treatment. FTIR investigation was performed to study the structural changes of vanadium oxide before and after hydrothermal treatment to get a better understanding of nanotube formation.

10 mmol V_2O_5 (99.5%) and 10 mmol 1-hexadecylamine (ACROS CRGANICS Company) were mixed with 5 ml distilled water. After stirring for 1 h, to give an orange solution, 15 ml distilled water was added. The mixture was allowed to hydrolyze under vigorous stirring for 48 h, then a yellow composite of the organic template and the vanadium oxide component was obtained. The composite was then treated hydrothermally in a Teflon-lined autoclave with a stainless steel shell at $140\,^\circ$C for 24 h and then $180\,^\circ$C for 3 days. The obtained black product was washed with distilled water to remove the unreacted amine and decomposition product and finally dried at $70\,^\circ$C in air atmosphere for 6 h.

X-ray power diffraction (XRD) experiments were done on a D/MAX-III powder diffractometer with Cu K_α radiation ($\lambda = 1.5406\,\text{Å}$) and graphite monochrometer, with a scanning rate of $0.1\,^\circ$/s. Scanning electron microscopy (SEM) images were collected on a JSM-5610LV microscope operated at 20 kV. The transmission electron microscopy (TEM) images were obtained on a Jeol JEM-2010F microscope operated at 200 kV. The sample was deposited onto a perforated carbon foil supported on a copper grid. The Fourier transform infrared (FTIR) instrument used was a Nicolet 60-SXB spectrometer with a resolution of 4 cm^{-1}.

The XRD pattern of vanadium oxide nanotubes (Fig. 1) shows the low-angle reflection peaks, which

are characteristic of the layered structure [7]. The peak with the highest intensity is located at $d = 3.53$ nm, and this corresponds to the distance between the VO_x layers. The SEM images of the vanadium oxide-hexadecylamine composite after aging for 48 h and the final products after hydrothermal treatment indicate that the vanadium oxide-hexadecylamine composite exhibits a well-ordered lamellar structure, but this is transformed into nanotubes after autoclave reaction, as shown in Fig. 2. The final products consist almost exclusively of vanadium oxide nanotubes. Vanadium oxide nanotubes are frequently grown together in the form of bundles, but individual nanotubes with open ends can also be observed, which can be confirmed by the TEM investigations (see Fig. 3). The nanotube lengths range from 1 to 8 μm. Lengths and diameters of the nanotubes depend on the conditions of the preparation, such as different template molecules, concentration and reaction time [8].

The FTIR spectra for the vanadium oxide-hexadecylamine composites and vanadium oxide nanotubes are represented in Fig. 4a and b, respectively. For comparison, FTIR measurement of pure hexadecylamine was made, as shown in Fig. 4c. This spectrum shows two sharp peaks between 3300 and 3500 cm^{-1}, which can be associated with the $-NH_2$ vibration [9]. In the FTIR spectrum for the vanadium oxide-hexadecylamine composites, the sharp peaks between 3300 and 3500 cm^{-1} disappear while the peaks at 2956 and 1589 cm^{-1} are observed. These are assigned to the stretching vibration and asymmetric bending vibration of the N$-$H bonds in the $-NH_3^+$ group [9]. Therefore,
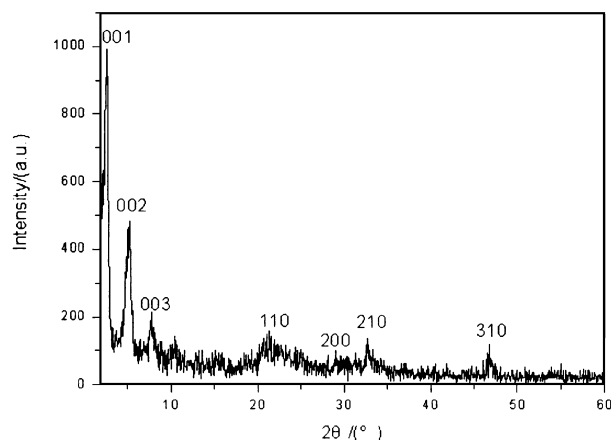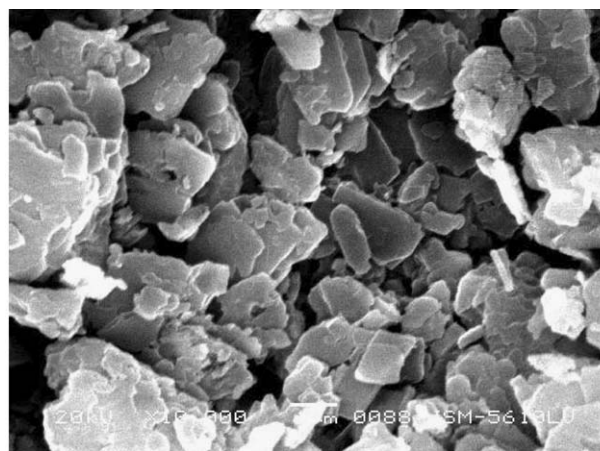

Figure 1 XRD patterns of vanadium oxide nanotubes.

(a)

(b)

Figure 2 SEM images of (a) the vanadium oxide-hexadecylamine composite and (b) the vanadium oxide nanotubes.
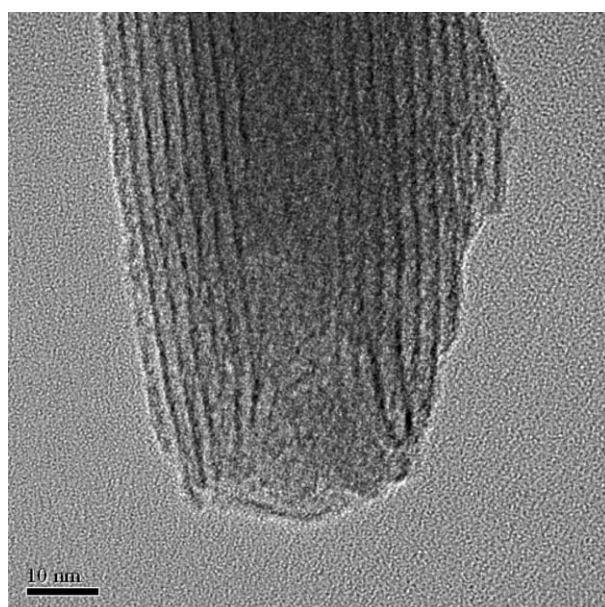

Figure 3 HRTEM image of vanadium oxide nanotube.

the 1-hexadecylamine has been hydrolyzed during the aging process. In addition, after hydrothermal treatment of the hydrolyzed material, the pH of the reaction mixture increased to 8.5 from a neutral pH, indicating that
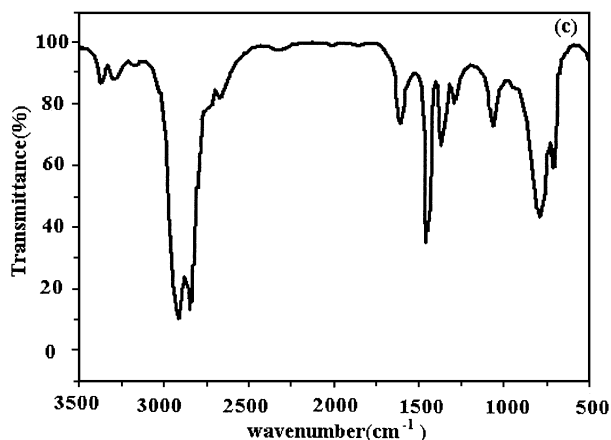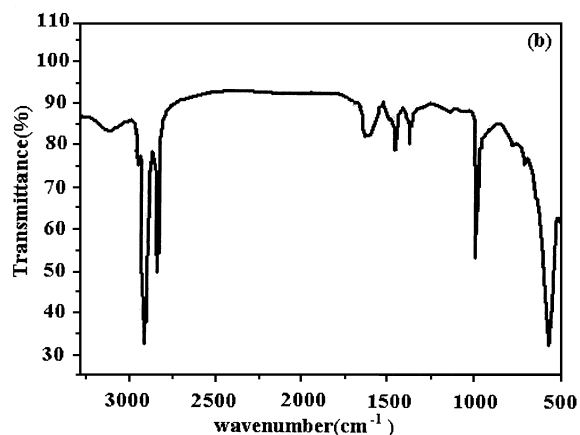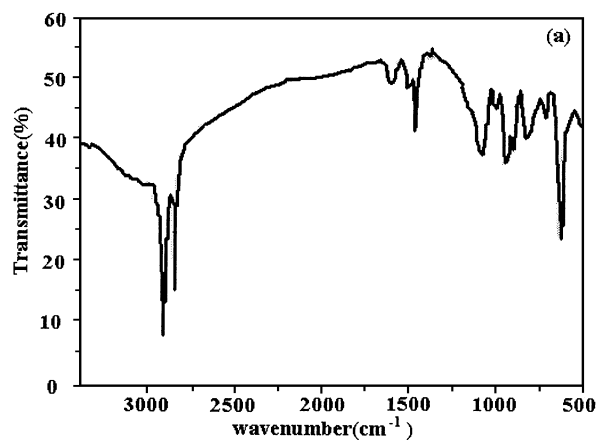

Figure 4 FT-IR spectra of (a) the vanadium oxide-hexadecylamine composite, (b) vanadium oxide nanotubes and (c) 1-hexadecylamine.

the amine template molecules became protonated during this procedure.

The FTIR spectrum of vanadium oxide nanotubes still exhibits the N—H vibration of —NH_3^+ after the hydrothermal treatment. In comparison with the FTIR spectrum for the vanadium oxide-hexadecylamine composite, the peak at 2956 cm^{-1} has not shifted while the peak at 1589 cm^{-1} is shifted to 1630 cm^{-1}, which can be associated with the strength change of hydrogen bonding from hydrothermal treatment [9]. The signals between 500 and 1000 cm^{-1} in Fig. 4a and c can be attributed to various (group) vibrations of V—O type. The vanadium oxide-hexadecylamine composite exhibits intense absorption bands at 517, 640, 720, 839, 911 and 956 cm^{-1}. In contrast, the vanadium

oxide nanotubes have only two intense peaks at 997 and 573 cm^{-1}. Smaller peaks are observed at 797 and 729 cm^{-1}. The signal at 839 cm^{-1}, which was intense before the hydrothermal reaction, has almost disappeared in the spectrum from nanotubes. This large difference in the range of the V—O vibrations of the samples before and after hydrothermal treatments clearly gives evidence that during the hydrothermal treatment a considerable rearrangement of the vanadium oxide structure takes place, which results in the transformation of the lamellar vanadium oxide-amine composite to the nanotubes. It is known that V_2O_5 displays three major absorption peaks at 617, 827 and 1022 cm^{-1}. The absorption at about 1000 cm^{-1} is associated with the V=O band. So the band at 997 cm^{-1} in the FTIR spectrum of the vanadium oxide nanotubes and the one at 956 cm^{-1} in the vanadium oxide-hexadecylamine composite belong to the V=O vibration, i.e., the vanadyl group seems to be very much influenced by hydrothermal reaction. In the V_2O_5 spectra the peaks at 617 and 827 cm^{-1} are assigned to the vibrations of V—O—V and O—(V)$_3$, respectively. These signals can be observed at 640 and 839 cm^{-1}, respectively, in the spectrum of vanadium oxide-hexadecylamine composite while they do not have corresponding peaks in the spectrum of vanadium oxide nanotubes. It can be concluded that during hydrothermal treatment, the V—O—V and O—(V)$_3$ bonds are considerably changed, whereas the V=O bond is almost unaffected. The peak at 3135 cm^{-1} in the FTIR spectrum of vanadium oxide nanotubes is difficult to assign. It belongs to O—H vibrations which are expected to spread between 3200 and 3600 cm^{-1} depending on the strength of hydrogen bonding [9]. To assign this peak accurately, nuclear magnetic resonance (NMR) investigation is necessary and this work is underway.

In summary, vanadium oxide nanotubes were successfully synthesized by using vanadium pentoxide and 1-hexadecylamine as a structure-directing template. FTIR investigations show that the amine molecules are hydrolyzed during the aging process and protonated through hydrothermal procedure. During hydrothermal treatment, a considerable rearrangement of the vanadium oxide structure leads to the formation of vanadium oxide nanotubes from lamellar structure; the V—O—V and O—(V)$_3$ bonds are considerably changed while the V=O bond is almost unaffected.

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