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Synthesis and Characterization of Layered Vanadium Oxide Nanotubes for Rechargeable Lithium Batteries

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A range of vanadium oxide nanotubes consisting of scrolled layers of primary amine functionalized xerogel have been produced by a hydrothermal treatment of a xerogel/amine mixture. The nanotubes consist of a hollow core flanked by parallel layers of scrolled vanadium oxide layers. The interlayer spacing is varied on the sub-nm scale by intercalated amine templates of various molecular lengths. High resolution transmission electron microscopy and X-ray diffraction were used to characterize the resulting nanotubes. When the molar ratio of xerogel:amine is 1:2, a maximum yield of nanotubes is produced and the interlayer spacing can be controlled. For a molar ratio of xerogel:amine of 2:1, the product contains a low yield of nanotubes and the corresponding interlayer spacing is found to be independent of the length of the amine template. A comparison of measured interlayer distances with the actual physical length of the primary amine chains shows that interdigitation of the surface-bound amines occurs between the layers of V_2O_5 .

Introduction

Rechargeable lithium-ion batteries hold great potential for use in powering electric vehicles and hybrid electric vehicles (1) and continue to be crucial for medical and handheld portable devices owing to their high energy density, energy efficiency and long life span (2). However, power density, energy efficiency and rate performance are three important factors that need to be further improved before their wide-spread use in electric vehicles and to meet growing demands for higher performance portable electronic devices (3). Synthesizing nanoscale electrode materials has become one of the most useful methods of performance improvement as nanostructures can help to reduce the diffusion length for lithium ions during the charge/discharge process and increase the surface area of active material in direct contact with the electrolyte (4), thus leading to significantly enhanced specific power and energy densities compared with bulk materials (5).

Since it was first investigated over 40 years ago, it has been known that vanadium oxide is a very attractive layered structure for use as a battery material (6). The intercalation of ions into layered host lattices has been extensively studied because of the ability of such structures to adapt to the geometry of the intercalated ions by free adjustment of the interlaminar separation (7). Both

vanadium pentoxide crystalline powder and vanadium pentoxide xerogels exhibit a layered structure, and this enables intercalation of a wide variety of inorganic and organic guest species (8). In their bulk form however, vanadium oxides are not very useful as a cathode material due to poor cycle life and material pulverisation issues. Many of the problems associated with the bulk material can be overcome by using vanadium oxide nanostructures and in particular, vanadium oxide nanotubes (VONTs).

VONTs consist of multilayer scrolls with tube walls built up from several vanadium oxide layers. The layered tubular morphology is particularly attractive since it provides access for the electrolyte and lithium ions at the tube ends. Hence as a consequence of their scrolled structure, VONTs have a greater surface-to-volume ratio to contact with electrolyte compared to bulk vanadium oxides (9) which can shorten average Li^+ diffusion distances. The VONT geometry can in principle promote better strain relaxation during battery operation. The flexible, amine-templated scrolled layers are better able to accommodate volume changes due to lithium-ion intercalation without being pulverised as easily as the bulk material. Various exchange reactions are possible in which the tubular morphology is well preserved (10). VONTs have considerable scientific and technological significance owing to their interesting electrochemical and catalytic properties and as a result are considered as promising nanoscale electrodes for lithium ion batteries (11).

In this paper, we present an investigation of hydrothermally synthesised VONTs with various spectroscopic methods. The hydrothermal reaction is controlled by the use of primary amines which act as a template (12), and intercalate between the layers of the V_2O_5 , maintaining a constant interlayer spacing during scrolling (13). We show that sub-nm control of the interlayer spacings for VONTs is possible through the use of primary amine templates of varying molecular chain lengths. This is achieved when the molar ratio of xerogel:amine is 1:2. By changing the molar ratio of xerogel:amine from 1:2 to 2:1, a dramatic reduction in VONT yield was found and the interlayer spacing remained invariant with amine length.

Experimental

Vanadium oxide nanotubes were synthesised by hydrothermal treatment of a vanadium oxide xerogel. Initially 1 g of bulk V_2O_5 powder (Sigma Aldrich) was mixed with 90 ml of tert-butanol and heated under reflux at 100°C . The yellow solution obtained after vigorous stirring for 6 hours was then hydrolyzed by adding 30 ml of deionized water. Adding the water changed the colour of the solution from yellow to orange. The solvent was then evaporated to form a dried vanadium oxide xerogel. Mixtures of this xerogel with amines were made with xerogel:amine molar ratios of 2:1 and 1:2 using hexylamine, nonylamine, undecylamine and hexadecylamine. As an example, for the xerogel mixed with hexylamine (HA) in a molar ratio of 2:1, 0.3 g xerogel was mixed with 0.083 g of HA and 3 ml of ethanol was added per gram of xerogel. The solution was mixed vigorously for 1 hour and then hydrolyzed by adding 5 ml of deionized water per gram of xerogel before being mixed vigorously again for a further two hours. The mixture was then allowed to age for 2 days and then hydrothermally treated in a Teflon lined autoclave at 180°C for 7 days. The resulting dark paste was washed with pure ethanol and dried using a Buchner funnel, producing a dry fluffy black powder consisting of VONTs.

Specimens for transmission electron microscopy (TEM) were prepared by making a suspension of VONTs in ethanol by sonication and dropping 2 ml of the suspension on to a holey carbon grid. The TEM analysis was conducted using a field emission JEOL JEM-2100F microscope operating at an accelerating voltage of 200 kV. Interlayer distance measurements

were taken from high resolution TEM data. Specimens for scanning electron microscopy (SEM) samples were prepared by making a suspension of VONTs in ethanol. The suspension was sonicated and dropped onto a cleaved piece of silicon wafer. SEM analysis was performed using a Hitachi S-4800 at an accelerating voltage of 10 kV. X-Ray Diffraction (XRD) analysis was also used to determine the resulting VONT interlayer distances produced for each amine and for crystal structure determination. A VONT/ethanol suspension was dried on a glass slide to form the samples for XRD. In this way the sample could be treated as a thin film. XRD analysis was performed using an X'pertMRDproAnalytical instrument using CuK α radiation. (Cu K α , λ = 0.15418 nm, operation voltage 40 kV, current 30 mA).

Results and Discussion

Synthesis of High Yield Vanadium Oxide Nanotubes

Figure 1(a) – (f) show SEM and TEM images of various scrolled VONTs produced using molar ratios of xerogel:amine of 2:1 and 1:2. The reaction leads to the formation of VONTs and in some cases, some unreacted V₂O₅ xerogel remains. It can be seen that nanotubes with lengths of up to several micrometers are produced with outer diameters varying from 100 – 500 nm. Figure 1 (a), (c) and (e) shows the products of the hydrothermal treatment of a mixture of xerogel:amine in a molar ratio of 2:1 for a series of different amines. The SEM images show nanotubes as well as unreacted xerogel, which is typical at this molar ratio.

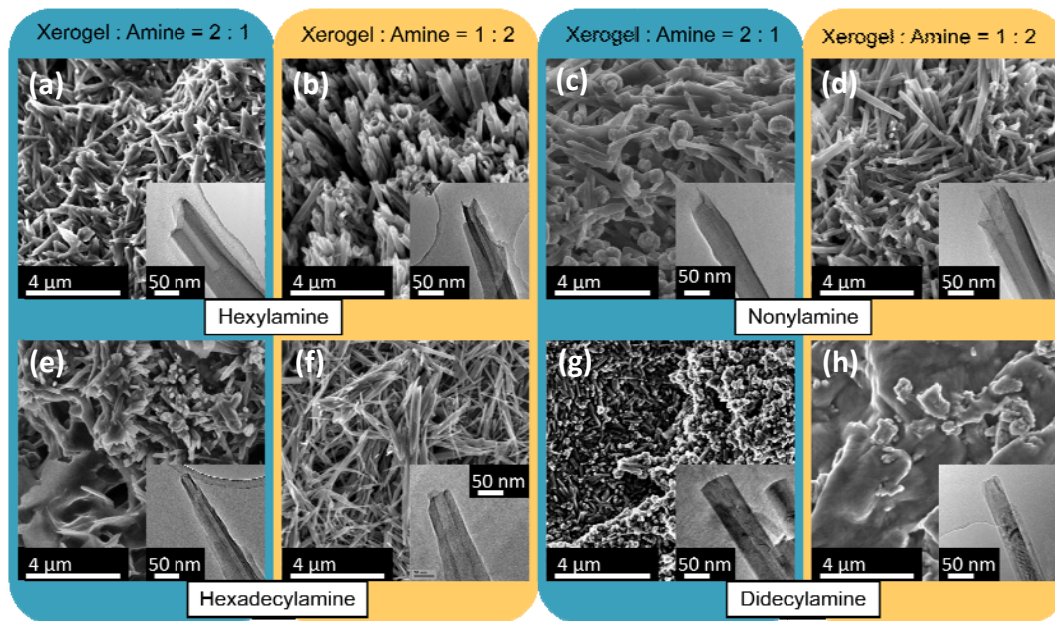


Figure 1. SEM images of VONTs formed using various primary amines, with TEM image inset. (a) hexylamine, xerogel:amine= 2:1 ; (b) hexylamine, xerogel:amine= 1:2 ; (c) nonylamine, xerogel:amine= 2:1 ; (d) nonylamine, xerogel:amine= 1:2 ; (e) hexadecylamine, xerogel:amine= 2:1 ; (f) hexadecylamine, xerogel:amine= 1:2 ; (g) didecylamine, xerogel:amine= 2:1 ; (h) didecylamine, xerogel:amine= 1:2.

It is generally found that there is less unreacted V_2O_5 xerogel in the case of the 1:2 molar ratio of xerogel:amine and consequently, a greater yield of VONTs is obtained, as illustrated in Fig. 1 (b), (d) and (f). For both molar ratios studied it was also observed that the use of didecylamine did not produce nanotubes but rather flat nanobelts. These nanobelts are seen in the TEM images insets in Fig. 1 (g) and (h).

Stages of Nanotube Formation

During hydrothermal treatment the amine templated vanadium oxide layers undergo scrolling to form the eventual nanotube (14), as shown schematically in Fig. 2(a). The various stages of this can be seen by the TEM analysis of early, intermediate and final stages of VONT formation shown in Fig. 2(b). V_2O_5 is a layered structure as depicted in Fig. 2(a) and the amines intercalate as a bilayer, sandwiched between the (010) faces of the V_2O_5 layers (15). The attachment of the amine is generally accepted to be between the oxidized amino head group (NH_3^+) and a reduced vanadyl ($V-O^-$) bond. However, it is plausible that there is competition (16) between surface Bronsted base $V=O$ and in-plane Lewis base $V-O-V$ oxygens for the amino headgroups. In any case, the opposing faces of the V_2O_5 are nominally identical (excluding localised hydration or protonation differences) and the resulting uniform tubular structure and constant interlayer spacing between pairs of V_2O_5 layers are maintained by the amine template during scrolling. In this manner the amines accommodate the curvature and eventual formation of scrolled VONTs.

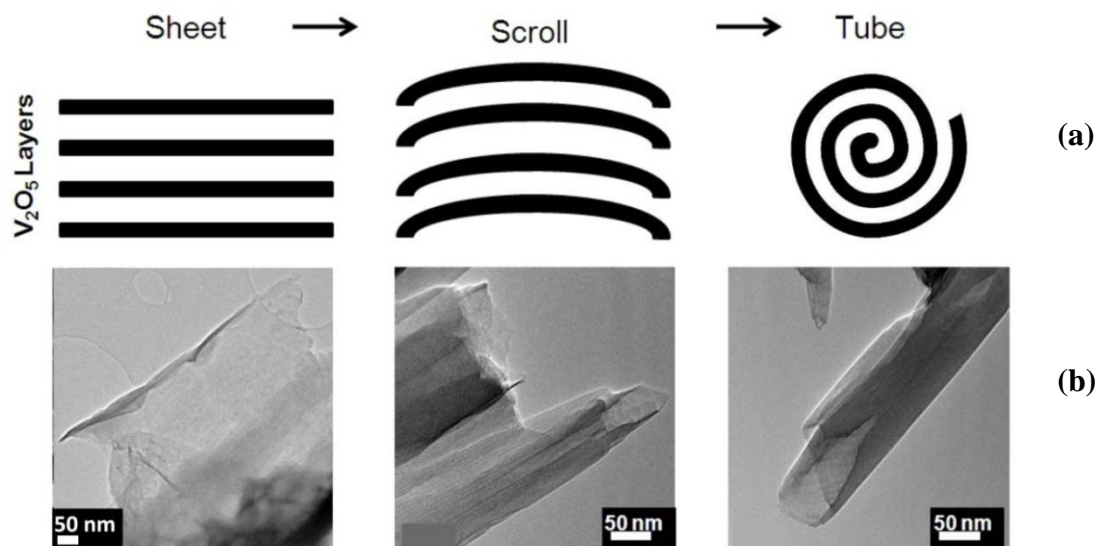


Figure 2. (a) Schematic of the growth mechanism of a scrolled nanotube. (b) Corresponding TEM images from early, intermediate and final stages of VONT formation.

An example of VONT formation with nonylamine is illustrated in Fig. 3. Figure 3(a) depicts a nonylamine molecule consisting of a linear hydrocarbon chain with an NH_2 group at one end. The length of a freely extended equilibrium-state nonylamine molecule is ~ 1.33 nm. As previously discussed, the amines intercalate between the layers of V_2O_5 , with the amino group docking to the juxtaposed $V_2O_5(010)$ faces of each interlayer space. There are several possible configurations in which this can occur. These are illustrated schematically in Fig. 3(b), (c) and

(d). Figure 3(b) shows the amine molecules aligned collinearly tail to tail, Fig 3(d) shows the amines interdigitated and perpendicular to the V_2O_5 layers and Fig. 3(c) shows the interdigitated amine molecules at an angle to the V_2O_5 layers. Each of these configurations will give a different interlayer spacing. In Fig. 3(b) the interlayer spacing is approximately twice the length of the amine molecule, *i.e.* $\sim 2 \times l_{\text{mol}}$, while in Fig. 3(c) and (d) it is less than $2 \times l_{\text{mol}}$. To distinguish between these configurations and to examine the effect of amine molecular length, we experimentally determined the interlayer spacings by two different methods.

The first technique involved analyzing TEM images of the parallellayered walls of the VONTs as seen in Fig. 3 (c) and (d). Interlayer spacing measurements were acquired from TEM images by mapping grey scale profiles of the images. Vanadium is a heavier electron scatterer and appears as periodic dark lines and in this manner the interlayer spacings could be measured. The second technique was based on XRD and involved analysis of the path length difference in Bragg reflections from a periodic layered material. XRD gives $(00l)$ and $(hk0)$ reflections; the former stemming from the layer structure and the latter from the crystal structure of the vanadium oxide. From diffractograms, the interlayer spacing and crystal structure of the vanadium oxide nanotubes can be determined and compared.

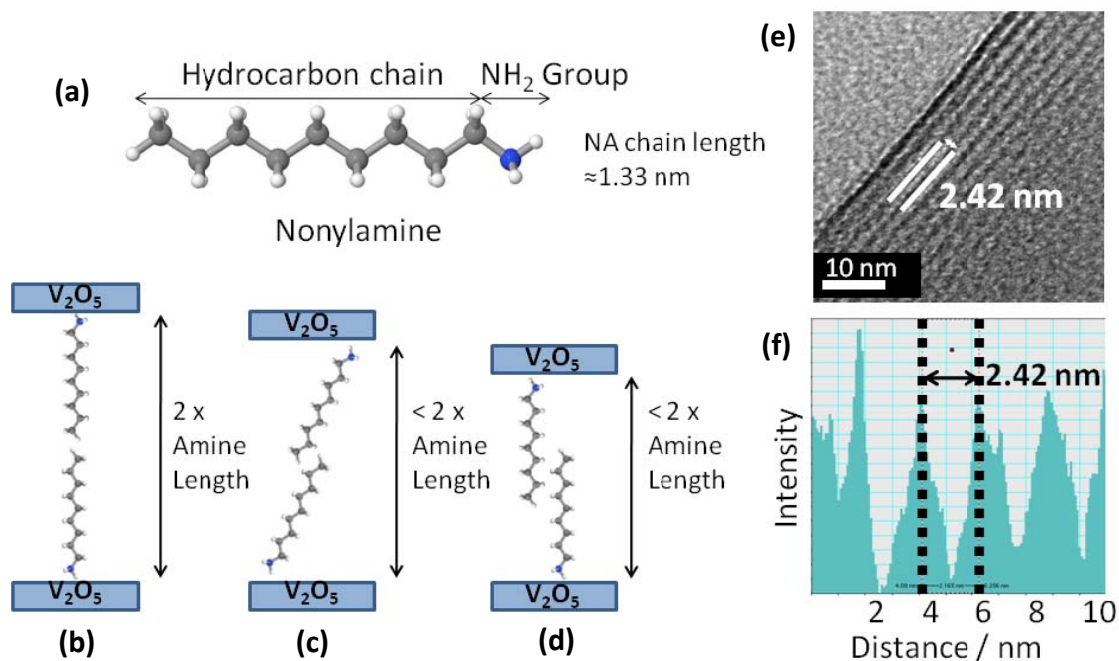


Figure 3. (a) Schematic of a nonylamine molecule. (b) Schematic of amine chains intercalated between layers of V_2O_5 (c) TEM image of the layers of a hexylamine VONT. (d) Line scan from (c) of grey-scale intensity as a function of distance.

Sub-nm Control of Interlayer Spacing in Nanotubes

The XRD patterns of VONTs shown in Fig. 4 show two characteristic regions. The first, low angle region shows the $(00l)$ Bragg reflection peaks characteristic of a well-ordered, periodic layered structure consisting of vanadium oxide sheet propped open by a bilayer of interdigitated amines, stacked periodically back-to-back in a scrolled fashion. The average distance between the parallel V_2O_5 layers in the tube walls gives rise to certain reflections in reciprocal space. As a

result, strong reflections at low diffraction angle appear in the XRD pattern. The peak with the highest intensity at lowest diffraction angle corresponds to the distance between the vanadium oxide layers. The second region comprises ($hk0$) reflections, indexed on the basis of a two-dimensional square lattice of the orthorhombic unit cell, that come from the crystal structure of the V_2O_5 . The characteristic ($hk0$) reflections indicate high structural order, and well-formed, scrolled tubes which typically exhibit characteristic ‘Fano-type’ lineshapes for ($hk0$) reflections from the crystal lattice in a curved layer; defective tubes and unreacted material do not. These two regions are shown separately in Fig. 4 for each of the two molar ratios used during synthesis and for a range of amine templates in each case. Since the organic template is incorporated between these V_2O_5 layers, XRD data gives direct determination of the interlayer spacings in the nanotubes.

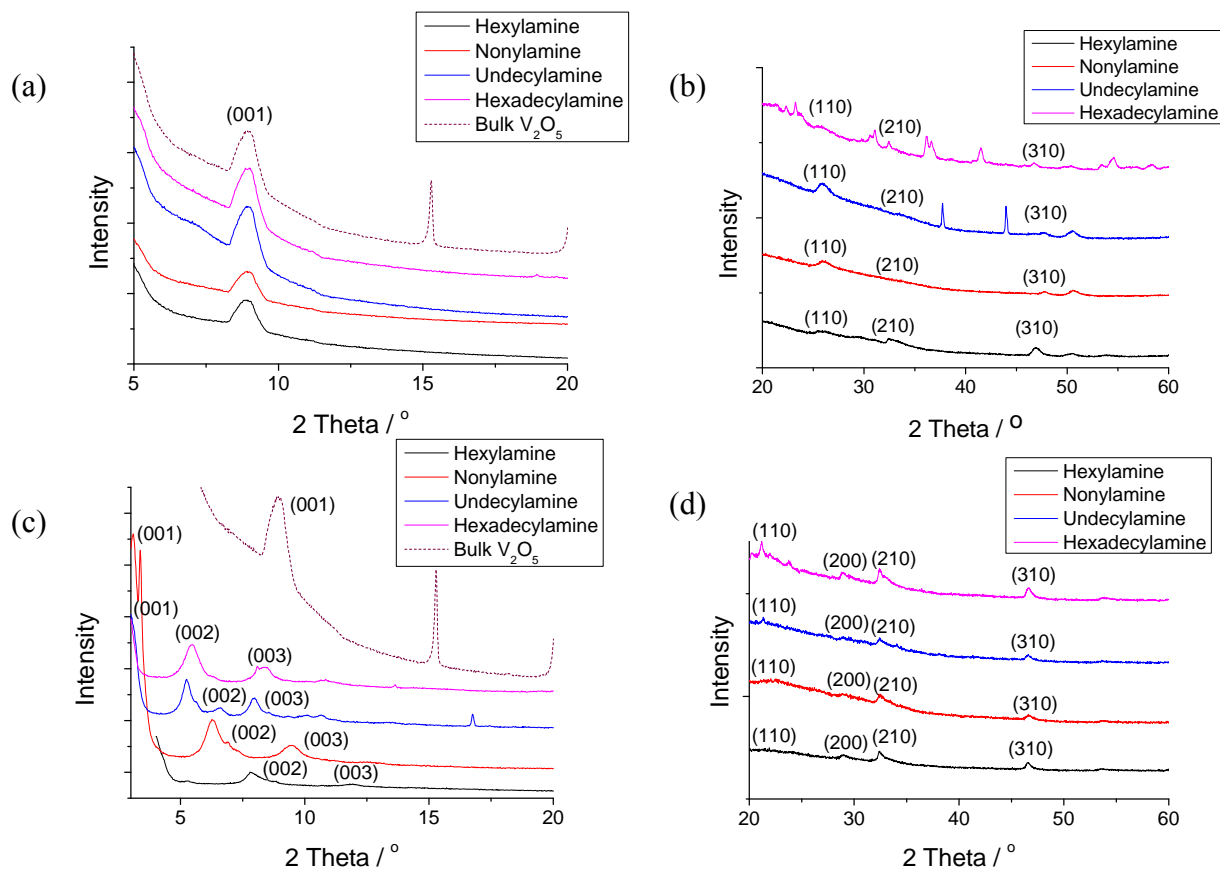


Figure 4. XRD patterns for VONTs synthesized with a molar ratio of xerogel:amine of (a) and (b) 2:1 and (c) and (d) 1:2.

Figure 4 (a) shows the ($00l$) peaks from VONTs templates with a range of amines in a synthetic 2:1 ratio of xerogel:amine. It is observed from Fig. 1 that in this case, large quantities of unreacted V_2O_5 remain after hydrothermal treatment. A single peak is observed in the XRD spectrum and the (001) peak is independent of amine used. This indicates that the diffraction stems mainly from the unreacted mixture, *i.e.* that the yield of VONTs is low. This is confirmed by the fact that the (001) peak is identical to that observed for the starting V_2O_5 powder. We note that at a molar ratio of xerogel:amine of 2:1 there is only one amine per four vanadium sites on the V_2O_5 surface. Thus, there is insufficient amine present to act as a uniform template for

maintaining and controlling interlayer spacing. By comparison, for a ratio of xerogel:amine of 1:2, the XRD data show the (001), (002) and (003) Bragg reflection peaks consistent with a periodic layered structure. Thus, for this ratio, sufficient amounts of amines are present to facilitate the formation of the tubes and as a result there is also less unreacted V_2O_5 material, in agreement with microscopy analysis of reaction products in Fig. 1. This is further confirmed by comparison of the diffraction data with that from the bulk V_2O_5 obtained in the absence of any amine additive. The periodic (00 l) reflections for each amine template in Fig. 4 (c) are shifted consistently to lower angles (wider spacings) with successively longer amines consistent with increasing interlayer separation (17). This indicates that the nanotubes being formed have interlayer distances determined by the amine molecular length.

Examination of the crystal structure of the layers also confirms the salient features of the effect of amine length and the molar ratio of xerogel and amine. Figures 4 (b) and (d) show the ($hk0$) peaks, which for all cases occur at similar diffraction angles, confirming that the V_2O_5 maintains its orthorhombic crystal structure (14). For the molar ratio at which a lot of unreacted material remains (xerogel:amine = 2:1), the diffraction contribution from the crystal structure of bulk V_2O_5 is ill-defined and some peaks arise from a mixture of monoclinic xerogel and orthorhombic V_2O_5 , which forms during hydrothermal treatment. By comparison, the ordered reflections from a xerogel:amine ratio of 1:2 in Fig. 4(d), where the yield of VONTs is much greater, show the characteristic ‘Fano’ lineshape diffraction peaks, typical of scrolled, high quality VONTs. In addition, the phase is pure and can be indexed to orthorhombic V_2O_5 with reconstructed lattice parameters of $a_0 = 1.152$ nm, $b_0 = 0.356$ nm, $c_0 = 0.437$ nm; Space Group = $Pmmm$, with no peaks found from other vanadium oxide phases.

In Fig. 5, the interlayer spacing determined from TEM is compared with the XRD data discussed above. By comparing measured interlayer spacings from TEM and XRD analyses, it was found that varying the amine chain length varies the resulting interlayer distance. For a molar ratio of xerogel:amine of 2:1 the measured interlayer spacings are almost independent of the chain length the amine used, as seen in both the TEM and XRD data. When the molar ratio of xerogel:amine is 1:2, we observe an increase in the measured interlayer spacings with longer amine molecules. Considering the XRD data at a molar ratio was 1:2, the VONTs formed with hexylamine, having 6 carbon-carbon bonds in its molecular chain, have an interlayer spacing of ~ 2.37 nm whereas nanotubes formed with hexadecylamine, having 16 carbon-carbon bonds in its molecular chain, has a interlayer spacing of ~ 3.03 nm. Thus, the use of a longer amine as the organic template consistently gives VONTs with wider interlayer distances.

From Fig. 1, it is consistently observed that no VONTs are produced using the very long didecylamine template. Didecylamine is the longest amine used in this study, having 20 carbon-carbon bonds and an NH_2 group at one end. A possible reason for the formation of nanobelts instead of nanotubes is that the didecylamine molecule may be too long to accommodate the formation of nanotubes as discussed, implying that a minimum, threshold interlayer spacing is necessary to maintain interlayer order during scrolling. The consistent observation where no nanotubes are formed using didecylamine is currently under investigation.

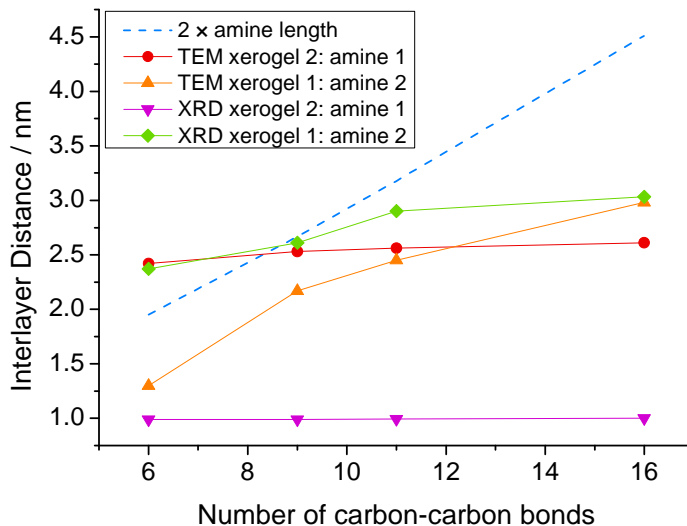


Figure 5. Comparison of measured interlayer distances determined from TEM of individual VONTs and XRD of VONT dispersions; values are plotted against the number of carbon-carbon bonds. The theoretical line corresponding to twice the amine length is also shown.

As discussed above, when the molar ratio of xerogel:amine is 1:2 the measured interlayer distance increases with the length of the amine molecule; however the relationship is not linear. From XRD measurements it was determined that for the nonylamine-templated VONTs there is a $\sim 2.25\%$ reduction in the interlayer spacing compared to $2 \times l_{\text{mol}}$, for undecylamine this reduction is $\sim 8.81\%$ and for hexadecylamine the interlayer spacing value is $\sim 32.81\%$. Thus, sub-nm control over the interlayer spacing in VONTs is possible by simply varying the amine molecular length when using a molar ratio that allows maximal packing of amines onto V_2O_5 surfaces. In the case of the VONTs produced with the hexylamine template using a molar ratio of xerogel:amine of 1:2, the observed interlayer spacings were found to be larger than $2 \times l_{\text{mol}}$. This indicates that the ends of the aliphatic chains only touch or slightly overlap (13). The VONT samples synthesized with the other amines discussed all feature interlayer spacings which are less than $2 \times l_{\text{mol}}$, confirming that interdigitation is occurring. This also implies a significant overlap of the aliphatic tails and that the amine chains may be interdigitated at large angles to each other with respect to the oxidic layers.

The ability to control interlayer spacings in lithium-ion battery materials could potentially allow for improved cycle life and high rate discharging and charging through accommodation of vanadium oxide unit cell volume changes during lithiation.

Conclusions

VONTs have been prepared by a hydrothermal treatment of mixtures of V_2O_5 xerogel and primary amines in various molar ratios. A range of primary amines with varying chain lengths were used to synthesize VONTs with varying interlayer distances and evidence is presented to support the growth mechanism for scrolled nanotubes. It was shown through microscopic analysis that longer-chain amines result in VONTs with greater interlayer distances. Through XRD analysis it was found that a molar ratio of xerogel:amine of 1:2 produces tubes with greater

interlayer distances than VONTs synthesized with a molar ratio of xerogel:amine of 2:1. Through comparison of measured interlayer distances with the length of the amine molecules it was determined that interdigitation of the amines occurs between the layers of V₂O₅ as the measured interlayer distances achieved for each amine template are less than $2 \times l_{\text{mol}}$. Furthermore, through physical examination of samples by high resolution microscopy, it was been shown that molar ratios of xerogel:amine of 1:2 produced more ordered nanotubes with higher yields and more controllable interlayer spacing. At molar ratios of xerogel:amine of 2:1, the yield was significantly reduced, the interlayer spacing is wider and is found to be independent of amine molecular length. For both of the molar ratios discussed it was found that when didecylamine was intercalated between the layers of the xerogel, nanotubes were not formed.

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17. Note: In some cases, the diffractometer was not capable of acquiring diffraction data below 4°.