Indian Journal of Fundamental and Applied Life Sciences ISSN: 2231– 6345 (Online)
An Open Access, Online International Journal Available at www.cibtech.org/sp.ed/jls/2015/01/jls.htm
2015 Vol.5 (S1), pp. 2143-2150/Kianfar et al.

Research Article

SYNTHESIS OF VANADIUM OXIDE NANOSTRUCTURES USING HYDROTHERMAL METHOD AND THE UTILIZES OF ULTRASONIC PROCESS

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ABSTRACT

Vanadium oxide nanotubes were synthesized using V_2O_5 powder as the precursor and hexadecylamineas the structure-directing template using a sol-gel reaction method followed by a one-step hydrothermal treatment. The effect of ultrasonics on the formation of nanotubes is reported. The structure and morphology of the nanotubes were investigated by X-ray diffraction, scanning electron microscopy, and transmission electron microscopy. The inner and outer diameters of the nano tubes varied from 15 to 25 nm and 50 to 90 nm, respectively. The nano tubes measured several micrometers in length.

Keywords*: *Vanadium Oxide, Nanotubes, Ultrasonics, Hydrothermal Synthesis

INTRODUCTION

The discovery of the carbon nanotubes (Mamalis *et al.*, 2004) and finding a unique structure for novel products due to physical properties and interesting shape of it has opened a new gateway to the science. There are several reports published on comprehensive development in synthetic routes and structure of nano-scaled materials since 1991 (Iijima, 1991; Ajayan,1999; Grobert *et al.*, 1999).The synthesis of different kinds of inorganic nano materials was the motivation for chemists, physicists and material researchers to focus their attention toward the design of a variety of tubular or other types of structures containing nano particles such as nano composites (Jana *et al.*, 2001; Tremel, 1999; Shenton *et al.*, 1999). Vanadium oxide nano tubes (VOx-NTS) are useful material, due to their high potential applicability in electrochemical devices and catalytic processes (Muhr *et al.*, 2000; Muhr *et al.*, 2000; Zhang *et al.*, 2006; Krumeich *et al.*, 1999). The first successful approach to make a tubular vanadium oxide was reported using carbon nanotubes as a template (Ajayan *et al.*, 1995). Different types of vanadium oxide precursor consists of vanadium penta oxide (V_2O_5), vanadium dioxide (VO_2), vanadium oxytrichloride ($VOCl_3$) and vanadic acid (HVO_3) as vanadium source where in alkyl amines ($C_nH_{2n+1}NH_2$) $4 \leq n \leq 22$ with alkyl chain length within a large size range or other types of amines ($H_2N[CH_2]nNH_2$) with $12 \leq n \leq 20$ and aromatic amine as direct structural agents, are used for successful synthesis of vanadium oxide nanotubes (Bieri *et al.*, 2001). 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 (Grigorieva *et al.*, 2008). VOx-NTs can be prepared in high yields with a unique structure of multilayer scroll. The interlayer distance can be easily controlled by a proper choice of structure-directing templates involved in a hydrothermal process. In a hydrothermal synthesis, the reaction path is sensitive to the experimental conditions such as temperature, pH and hydrothermal treatment time (Sediri *et al.*, 2007). Starting with vanadium penta oxide precursor and amine, a sol–gel reaction combined with a subsequent hydrothermal treatment could lead to the formation of vanadium oxide nanotubes. This highly ordering procedure is repeatable and leads to the tubes with minimum amounts of flake shape. The organic template molecules are embedded between the vanadium oxide layers inside the tube walls. VOx-NTs synthesized can be separated by three different methods: (1) Adding a template to V_2O_5 gels by hydrothermal treatment; (2) Grinding mixture of a template and V_2O_5; (3) Melt quenching method (Aghabozorg *et al.*, 2007; Chen *et al.*, 2004). This paper presents the synthesis of VOx-NTs using vanadium oxide powder and studies the effects of ultrasonics prior and after to mixing and distribution of hexadecylamine into the V_2O_5 slurry.

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This methodology reduces the synthesis time, and allows for the study of the effect of ultrasonics on the quality and yield of NTs. The VOx-NTs is first produced so that it could be incorporated into the alumina support material as catalytic membrane. However, before its application in catalysis, the optimum size of the nanotube is crucial. The size is fore-most important as it control the rate of reaction as well as its specificity. By using ultrasonic method it is expected that the NTs with uniform size will be produced and the yield of NTs could be enhanced by reducing its amorphous phase.

Experimental

Synthesis of Vanadium Oxide Nano Tubes

The synthesis of VOx -NT was performed in three stages. The first step consisted of the preparation of $V_2O_5.nH_2O$ gels according to an earlier publication (Düllberg *et al.*, 1903). This synthesis involves on the dissolution of crystalline V_2O_5 (Merck, 2g) in a solution of hydrogen peroxide (Aldrich, 100 ml, 30%). The exothermic reaction that occurs during synthesis leads to the partial decomposition of hydrogen peroxide that in turn leads the release of oxygen gas and the formation of V(V) peroxo complexes (Alonso *et al.*, 1999). A clear orange solution is formed after about 10 min (final $pH \approx 1.5$) that progressively turns into a red gel after ca. 24 h. This gel has been shown to correspond to $V_2O_5 \cdot nH2\ O$, where the amount of water depends on the experimental conditions. In our case, before drying, it corresponded to $n = 300$.

For the second step, About 2.66 grams of hexadecylamine was dissolved in 4 ml ethanol (under very small heating to dissolve) and then added to the $V_2O_5.nH_2O$ gel (V: amine ratio 2:1). The brown mixture was stirred for about 10 hours and aged without stirring for about 14 hours. The brown mixture turned to green after aging with pH of around 4.5. The resulting black powder was washed with150ml ethanol and 20ml n-hexane and then dried under vacuum at 80°C for about 5h.

X-ray powder diffraction patterns were recorded on a Philips PW 1830 diffractometer operating with the Cu K radiation ($\lambda = 1.5406$ Å). Scanning electron microscopy (SEM) studies were performed on a Cambridge Stereos can 120 microscope. Transmission electron microscopy (TEM) investigations were carried out on a JEOL 100 CX II microscope. One droplet of the powder dispersed in KBr was deposited onto a carbon-coated copper grid and left to dry in air.

RESULTS AND DISCUSSION

AV_2O_5 slurry was used as the vanadium precursor for the synthesis of VOx-NTs. We prepared the V_2O_5 slurry via an ultrasonic method and dispersed HDA homogeneously throughout the suspension Compared to other synthesis methods for VOx-NTs, this procedure is more cost-efficient.

Effect of Ultrasonics

Zhu *et al.,* (2010), have reported the production of silver nanorods by using ultrasonic treatment it was noticed that ultrasonic treatment plays an important role in this reaction. They found that the growth of nanorods is powerfully dependent on the ultrasonic treatment time. When the treatment time is 15 min, a huge number of small spherical silver particles were formed. With the prolonging of ultrasonic treatment time the silver nanoparticles aggregated together with a linear chain, but after 60 min treatment, the nanorods became dense, compact show ingregular shapes. The effect of ultrasonics on the morphology and structure of V_2O_5 nanotubes was studied by changing the time of ultrasonics treatment. The ultrasonic treatment was useful for the fragmentation, accelerated the reaction of amine template with the vanadium precursor at room temperature, and reduced mixing time. As reported by other researchers the mixing time, without ultrasonic treatment should be long enough so that the vanadium oxide-surfactant composite have enough time to develop a lamellar structure which is needed to enhance the yield of nanotube production (Bieri *et al.*, 2001). In this case, prolonged aging, as proven in the results, is not necessary compared to ther synthesis method which normally takes two or more days of aging with continuous stirring in order to develop the needed lamellar structure. In other words, in comparison, homogenously stirring of the V_2O_5 and amine template with the suggested condition is normally difficult to carry out. This may importantly lead to some portion of vanadium oxides which are not thoroughly intercalated with the amine template leading to some amorphous by products aside from the needed nanotubes. To verify, SEM visualizations of the VOx-NTs were carried out after they had been subjected to the typical ultrasonic treatment conditions.

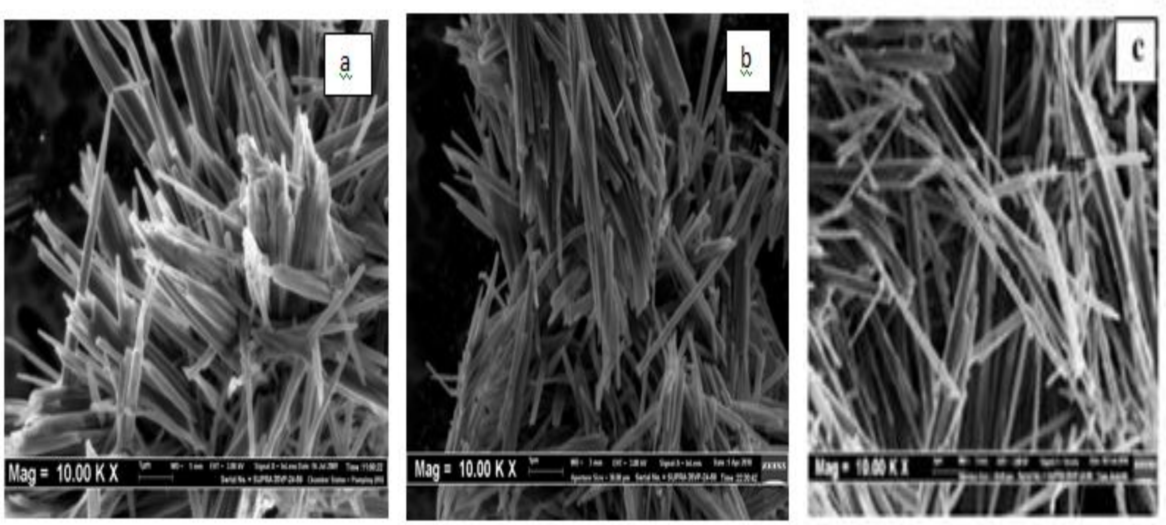

Figure 1: SEM images of the template-containing vanadium oxide illustrating its nanotubular morphology. a Without using ultrasonic; b 15 min ultrasonic; c 30 min ultrasonic

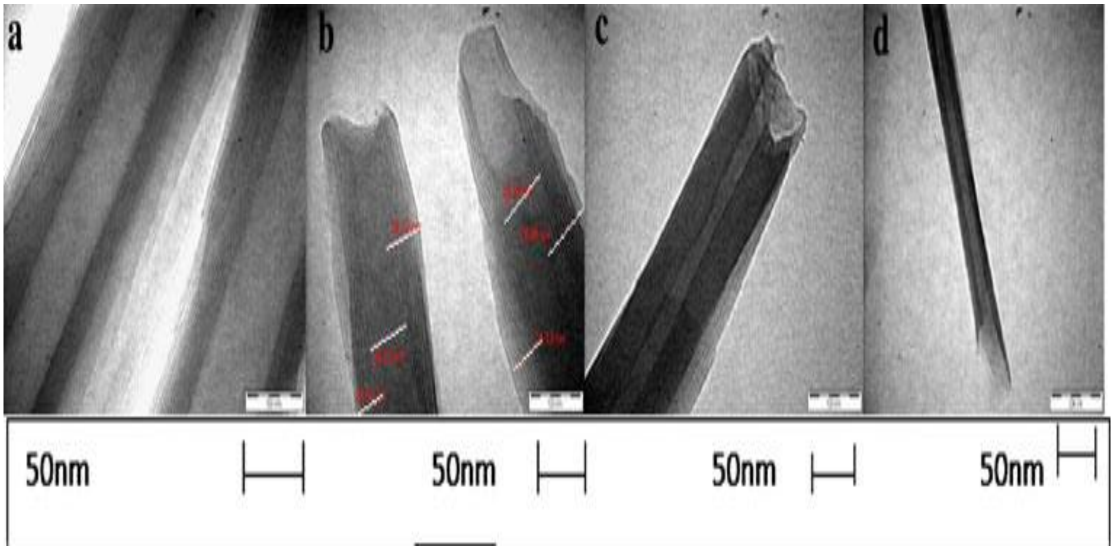

Figure 2: TEM images of vanadium oxide nanotubes forming in theV_2O_5-HDA system, b–d showing the typical open end. a, b The tube walls appear as alternating lines with dark and bright contrast

Figure 1 presents the morphology of VOx-NTS subjected to ultrasonics and without ultrasonics treatment. With ultrasonic treatmentV_2O_5 slurry can be easily intercalated with the amine template and can be easily stirred homogeneously resulting to less aging period and increase yield of nanotubes with no other amorphous by-products presence. The hydrolysis and conversion to gel, reduces the crystallization size of V_2O_5 particles between amine layers due to the fact that ultrasound produce a number of localized hot spots in the solution and inside the gel, also increased high-velocity collisions among the particles, and thus in turn preventing the formation of more ordered similar lamellar assemblies. These effects show that these are advantages of using ultrasonic irradiation for the preparation of VOx-NTS with longer length and similar diameter with minimum amount of amorphous by-product compare to other product without using ultrasonic (Neppolian *et al.*, 2008). SEM was performed using SUPRA TM 35vp ZEISS to investigate the morphology of the samples. In the case of using ultrasonic irradiation, the SEM image in Figure 1 show sreveal the resulting products obtained at different time of ultrasonic, for the synthesized material forms a homogenous phase with uniform particle sizes and displays NTs morphology. Furthermore, the material is several micrometers in length and has an outside diameter of approximately 50–90 nm. It can be noticed from the images that the VOx-NTS produced with 15 and 30 min duration time of ultrasonic treatment had affected the morphology of VOx-NTS. It can be observed that within 15 min of ultrasonic treatment could produce well developed nanotubes with smallest amount amorphous or lamellar by-products and within 30 min of ultrasonic treatment not only reduce amorphous by-product but also produce VOx-NTS with longer length and similar diameter.TEM was carried out on a Philips CM12 machine equipped with a DOCU version 3.2 image analysis system to further determine the size of the NTs. The TEM image in Figure 2 shows that the reaction product exhibits a tubular morphology similar to that of multi-walled VOx-NTs. The TEM images illustrate that the NTs are made up of concentric and open-ended cylinders. The average distance between the vanadium oxide layers in the tube walls gives rise to their corresponding reflections in the diffraction patterns. The inner diameters vary from 15 to 25 nm. The outer diameters range from 50 to 90 nm (Figure 2b). Other TEM images (Figure 2b–d) illustrate the open-ended cylindrical shape of the tubes. As shown in Figure 2, the walls of the VOx-NTs are presented with alternating margins of dark and bright regions. A schematic presentation of one layer formation and the internal interaction of the NTs is shown in Figure 3. The dark margins represent the vanadium oxide layers, while the bright margins represent amine molecules that are intercalated between the vanadium oxide layers. The contact between the organic molecules and inorganic precursors may be possibly due to coordinative interactions, electrostatic interactions, or hydrogen bonding (Mai *et al.*, 2003). The formation of the VOx-NTs appears to follow the rolling mechanism and could thus be dividedin to three steps: (1) The surfactant molecules condense with VOx to form lamellar structures; (2) Under hydro-thermal conditions, the condensation process continues and brings additional ordered lamellar assemblies; and (3) The lamellar sheets become loose at the edges and roll in to VOx-NTs (Chen *et al.*, 2002).

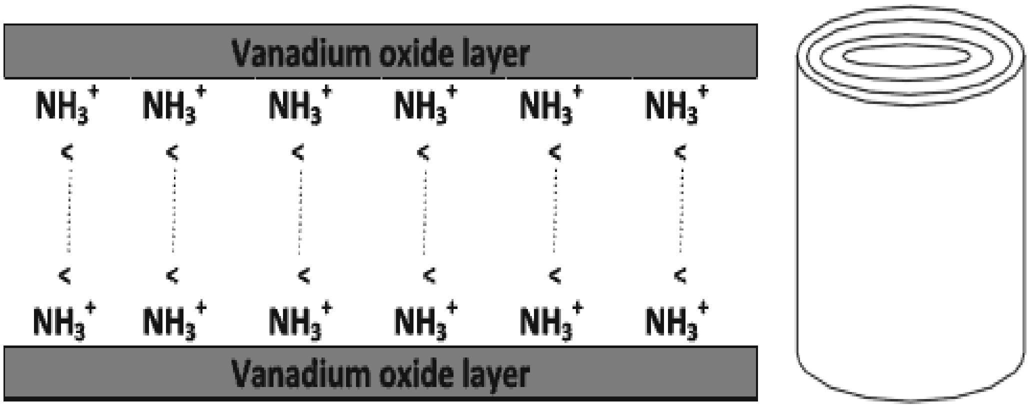

Figure 3: Schematic presentation of one layer formation V_2O_5–hexadecylamine

From the X-ray diffraction patterns of VOx-NTs (Figure 4), the ordered layers of structures are confirmed by the reflection in (00l). The layer distance of the lamellar structures from hexadecylamine is 0.8 nm (back-calculated from the peak with intensity at 2Θ = 11 corresponding to a dvalue of 0.8 nm). The peaks above 25° at 2Θ are reflections and originate mostly from the structure within the VOx layers (Reinoso *et al.*, 2000). The peak series 2Θ = 22 corresponds to the two-dimensional structure of the VOx layers, which form the walls of the VOx-NTs (Chen *et al.*, 2004). The Fourier transform infrared (FT-IR) spectrum of VOx-NTs (Fig. 5) shows strong absorptions at 2,918 and 2,850 cm^{-1}, which could be attributed to the stretching and bending modes of the different C–H vibrations in the hexadecylamine template.

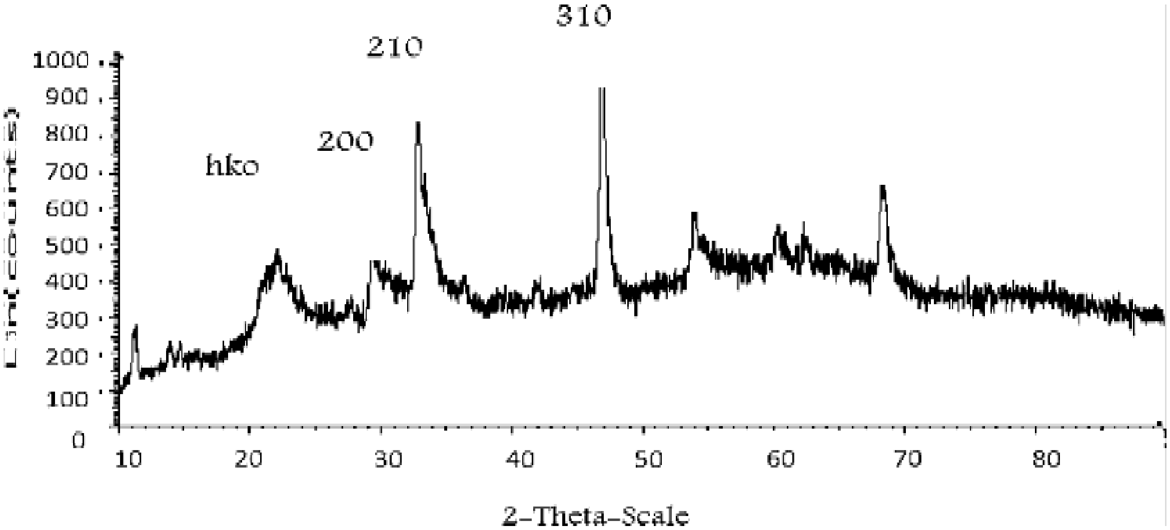

Figure 4: XRD pattern of V_2O_5–hexadecylamine

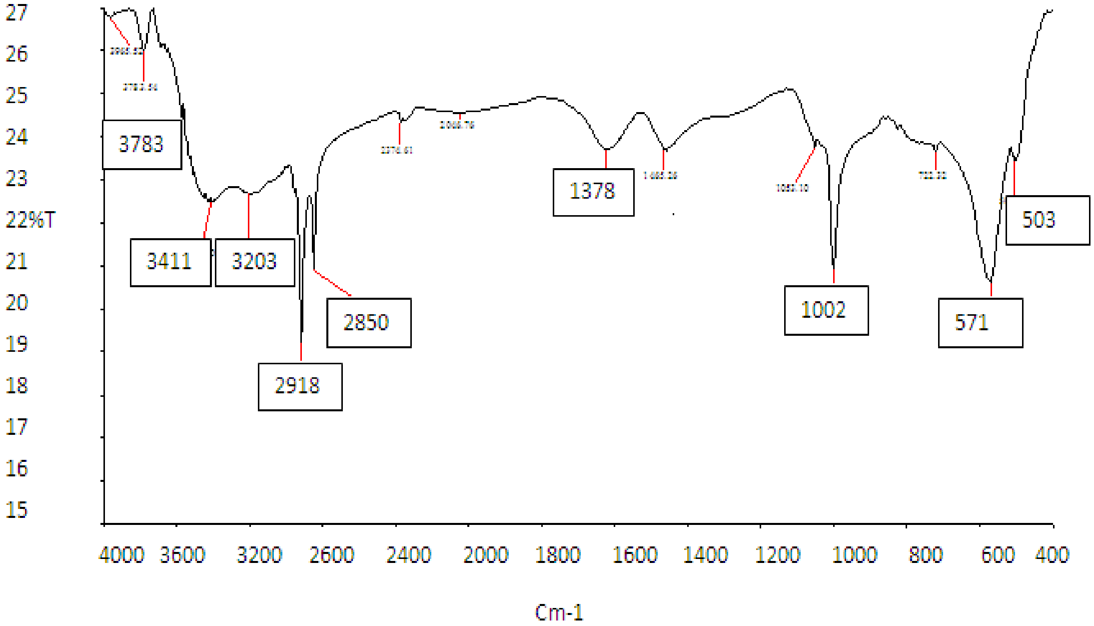

Figure 5: FT-IR spectra of VOx-NTs

The assignment of the enormous bands between 3,2033,411 cm^{-1} and 1,621 cm^{-1} correspond to O–H vibrations, thus confirming the intercalation of water molecules into the VOx layers of the VOx-NTs. the reflection in (00l). The layer distance of the lamellar structures from hexadecylamine is 0.8 nm (back-calculated from the peak with intensity at 2Ө = 11 corresponding to a dvalue of 0.8 nm).The peaks above 25at 2 Ө are reflections and originate mostly from the structure within the VOx layers (Reinoso *et al.*, 2000). The peak series 2Ө = 22 corresponds to the two-dimensional structure of the VOx layers, which form the walls of the VOx-NTs (Chen *et al.*, 2004). The Fourier transform infrared (FT-IR) spectrum of

VOx-NTs (Figure 5) shows strong absorptions at 2,918 and2,850 cm^{-1}, which could be attributed to the stretching and bending modes of the different C–H vibrations in the hexadecy lamine template. The assignment of the enormous bands between 3,2033,411 cm^{-1} and 1,621 cm^{-1} correspond to O–H vibrations, thus confirming the intercalation of water molecules into the VOx layers of the VOx-NTs. Adsorption bands between 503 and 1,002 cm^{-1} could be attributed to a range of vibrations of the V–O type. The band at 1,002 cm^{-1} might be signed to V=O vibration, in comparison with crystalline V_2O_5. These FT-IR characterization results may suggest that the compound synthesized has a lamellar formation with intercalated organic amines among various VOx groups (Chen *et al.*, 2004). The thermal stability of the VOx-NTs (Fig. 6) was studied via thermal gravimetric analysis in oxygen at a heat ingrate 15 °C/min between room temperature and 800°C. For the template containing VOx-NTs, the thermal gravity curve showed that the synthesized compound underwent a weight loss of approximately 46.25% between 190 and 486 °C. This corresponds to the decomposition of the organic template and the loss of water between the vanadium oxide layers. With continued increases in temperature past 480 °C an increase in mass was observed, which could be attributed to the oxidation of vanadium as the compound transforms in to crystalline vanadium pent oxide (Figure 7) is a schematic presentation depicting the two possible ways (bending and rolling) of the tube formation. Regardless of which way the tube forms, it both started as a lamellar product as proven by the TEM investigation. By hydrothermal treatment, the lamellar product either bends in both sides together or one side rolled-up like a carpet roll. In bending, the sheets/layers can close together or they can miss each other. However, in rolling formation, it forms one sheet scroll. It can be proposed that upon bending, when the sheets totally missed each others, they wrap or continue to bend, one on the inside and the other on the outside. Thus, it looks like that one side rolled-up to form the tubes Figure 7c. Regarding the concerns on why does vanadium oxide forms tubes instead of other forms, until now there is no known or proven driving force for it. The driving force for the bending of the sheets as well as the role of the amine template is not yet clear. There are various possibilities speculated: (1) The template has to create a certain distance between the layers (> 1.6 nm) providing high flexibility of the layers. (2) The intercalation between the amine template and the vanadium atoms results in a structural reorganization of the vanadium oxide layers leading to a polarized structure, i.e., the two sides of the vanadium oxide layers do not consist of identical atomic subunits. (3) Slight misfit between the two parts of the vanadium oxide layer is reduced by bending. Bending due to mixed valency (Niederberger, 2004).

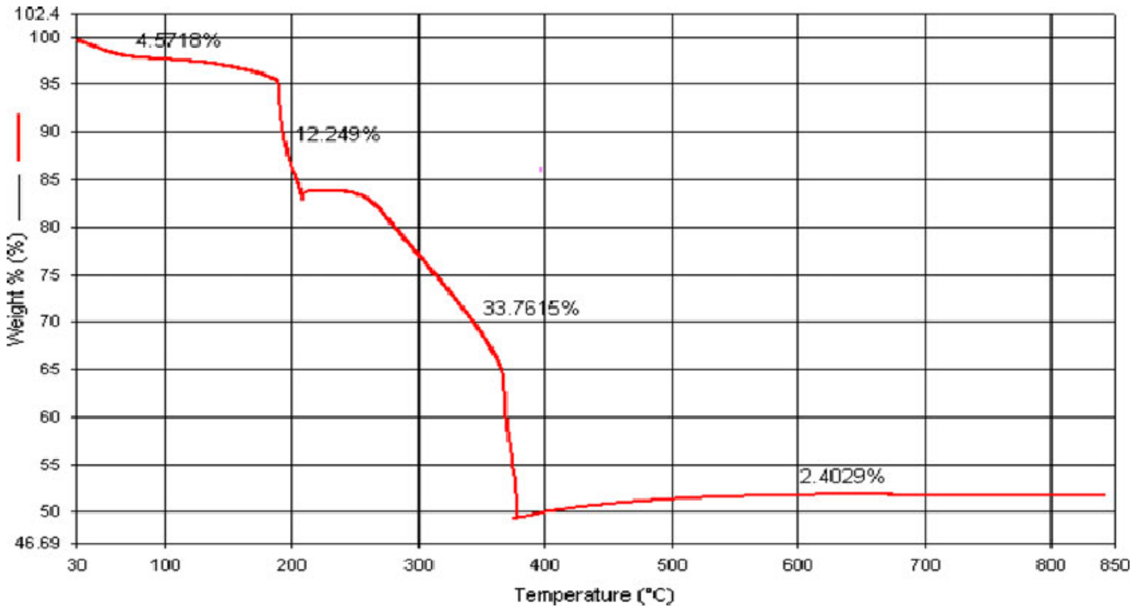

Figure 6: TGA of VOx-NTs

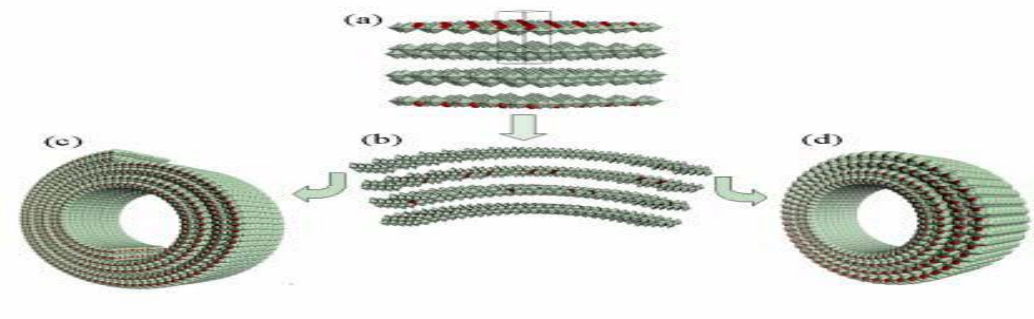

Figure 7: Possible formation structure description of V_2O_5 nano tubes. when bent (b)such layers may form nanoscrolls (c) or closed nanotubes (d)[26]

Conclusion

This paper describes an easy and cost-efficient hydrothermal method for the synthesis of VOx-NTs using vanadium oxide as precursor. This method is favorable due to its low cost and eases of handling. The use of an ultrasonic frequency of 37 kHz with an RMS power of 150 W and maximum peak power of 600 W helped to better distribute the hexadecylamine throughout the homogeneous slurry mixture. Ultrasonication did not reduce the particle size and, in fact, enhanced the suspension homogeneity of vanadium oxide with hexadecylamine for better and faster formation of NTs. The ultrasonic treatment for the duration of 15 min produced well developed nanotubes with only small amount amorphous or lamellar by-products but forthe duration of 30 min it also produced VOx-NTS with longer length and similar diameter (Zhu *et al*., 2010; Awati *et al*., 2003). The VOx-NTs were tested via SEM and TEM. An efficiency increase of 70–85% in different batches on the preparation conditions such as precursor, time of suspen sion homogenization by ultrasonic, method of distribution, and hydrothermal time was evident. The obtained product possessed a well-ordered layer-like structure and tube-like morphology. By applying ultrasonics and using acetone as the solvent for hexadecylamine, the reaction time was substantially decreased in terms of the following: (1) mixing time from 48 h (normal mixing time) to 24 h, and (2) hydrothermal conditioning from 7 days (hydrothermal treatment time normally reported) to 5 days. As a result, this method proves to be a desirable approach toward preparing VOx-NTs (Bieri *et al*., 2001; Grigorieva *et al*., 2008).

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