

Production and Identification of Vanadium Oxide Nanotubes

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Abstract

Lately there has been much interest in synthesizing characterizing new vanadium oxide host/ guest compounds. These compounds have open structures and the ability to intercalate atoms or molecules. They may be used as catalysts, molecular sieves, absorbents and energy storage devices. We are studying the synthesis and characteristics of vanadium oxides nanotubes. This experiment has been synthesized by sol-gel methods and based on hydrothermal treatment at temperature 150°C-180°C. For characterization of samples, SEM, XRD, TEM, and FT-IR were used. Also, we consider the effect of ultrasonic on the formation of vanadium oxides nanotubes. Results show that diameter of the vanadium oxides nanotubes are varied from 15 to 25 nm (inner diameter) and 50 to 90 nm (outer diameter). In this research, vanadium oxide nanotubes had been synthesized via gelation of V2O5 and ethanol as solvent followed by hydrothermal treatment for one (1) to seven (7) days at 180°C. The main objective of the study is to produce good quality VOX-NTS at a fastest synthesis time.

Keywords: Hydrothermal Synthesis, Ultrasonic, Vanadium Oxide Nanotubes

1. Introduction

The carbon nanotubes² have special structure with potential application, due to physical properties and interesting shape. Recently research in this subject has showed an interesting gateway to the science^{3,4}. Scientists have reported the new synthesis methods of nano-materials⁵⁻⁷. Vanadium oxide nanotubes have potential application in electro-chemical industry and catalytic processes⁸⁻¹¹. The carbon nanotubes template can be used to growth the vanadium oxide nanotubes¹².

Consists of the various kinds of vanadium oxide precursor is

1. vanadium penta-oxide,
2. vanadium dioxide
3. vanadium oxytrichloride

Also, the vanadic acid used as vanadium source. Direct structural agents for synthesis of vanadium oxide nanotubes are:

1. Alkyl amines ($C_nH_{2n+1}NH_2$) with $4 \leq n \leq 22$,
2. Amines ($H_2N[CH_2]nNH_2$) with $12 \leq n \leq 20$,
3. Aromatic Amine¹³

We don't know that how organic molecules minister as structure directing templates¹⁴. The vanadium oxide nanotubes can be synthesized in various methods with multilayer scroll as special structure. In hydrothermal method, we can control the interlayer distance by choice of structure directing templates. However, the reaction path in the hydrothermal method is related to the conditions of experiment¹⁵. For the growth of vanadium oxide nanotubes, vanadium penta oxide precursor and amine can be used. In this process, a sol-gel method combined with a hydrothermal method and in result, low amounts of flake nanotube shape can be achieved. Between the

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vanadium oxide layers inside the tube walls, the organic template molecules are embedded. We can separate the vanadium oxide nanotubes by three various methods:

1. Using hydrothermal method for adding a template to vanadium pentoxide gels.
2. Laborious mixture of vanadium pentoxide and a template.
3. Melt quenching treatment^{16,17}.

In this experimental research vanadium oxide nanotube prepared by using vanadium pentoxide powder. Also we used following process:

1. Two various types of amines as template
2. The repartition of hexylamine and hexadecylamine inside the vanadium pentoxide slurry with ethanol.

This research was conducted to fulfill the following objectives:

- To compare the morphologies and structure of

VOx-NTs by using hexadecylamine as template material.

- To determine the effect of different hydrothermal reaction time (from 1 day to 7 days) on the synthesized product^{18,19}.
- Effects of ultrasonic process the hydrothermal reaction time^{20,21}.

2. Materials Required

The chemicals used in this research are listed in Table 1. All the chemicals used in this research were of analytical grade.

2.1 Equipment

The equipments used in this research are listed in Table 2.

Table 1. List of chemicals used in the preparation of VOx-NTs by hydrothermal method

Chemicals	Formula	Mw (g/mol)	Density (g/cm ³)	Purity wt. %	Supplier
Vanadium pentoxide powder	(V ₂ O ₅)	181.88	3.357	99%	Merck
Hydrogen peroxide	H ₂ O ₂	34.0147	1.463	30%	Merck,
Hexadecylamine	C ₁₆ H ₃₅ N	241.4606	0,813	95%	Merck
Ethanol	C ₂ H ₆ O	46.07	0.789	99%	Merck
n-hexane	C ₆ H ₁₄	86.18	0.6548	96%	Merck

Table 2. List of equipments used in the preparation of VOx-NTs by hydro thermal method

No.	Equipments	Description
1	Hot plate and	Hot plate was used to heat the ethanol for better solving amine.
2	Electronic digital balance	Electronic digital balance was used to measure accurately the quantity of chemicals used in experimental and the measurement is in unit gram
3	PH meter	Ph meter was used to measure the PH of material.
4	Transmission electron micrograph(TEM)	CM 12 Philips Transmission Electron Microscopes (TEM) used for showing morphology of products.
5	X-ray diffraction(XRD)	D8 advance bruker axs Diffract meter (XRD) used for analyzed materials.
6	Thermal analysis(TGA)	For testing stability of products in different temperatures
7	Scanning electron microscope (SEM)	Zeiss Supra 35vp Scanning electron microscope (SEM) used for show shape of products.

8	Vacuum oven	Vacuum oven used for drying the product after washing.
9	Mechanical stirrer	Mechanical stirrer is a tools used to stir the sol-gel mixture
10	Parr autoclave	Used for reaction in hydrothermal condition

3. Experimental

3.1 Vanadium Oxide Nanotube Synthesis Method

The synthesis of vanadium oxide nanotube was accomplished in three processes. The first process comprised of the synthesis of $V_2O_5 \cdot nH_2O$ gels. This process includes on the dissolution of two grams crystalline vanadium pentoxide in a solution of H_2O_2 . During the process, exothermal reaction that occurs²². After 10 min, color of solution is orange. After 24 h, gradually the color of gel is red. The final pH is about 1.5. The amount of water in $V_2O_5 \cdot nH_2O$ depends on the condition of experiment. (In this work, $n = 300$, before drying).

In the second process, in 4 ml ethanol, 2.66 grams of hexadecylamine was dissolved (under very small heating to dissolve) and then added to the $V_2O_5 \cdot nH_2O$ 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. So, with 150 ml ethanol and 20 ml n-hexane, we washed the final black powder, after that under vacuum at 80°C dried for 5h.

4. Result

The preparation of vanadium oxide nano-tubes was carried out by using vanadium pentoxide powder as vanadium source and two types of template hexadecylamine ($C_{16}H_{36}N$). These two templates were chosen due to the recommendation of previous study in which hexadecylamine was used as a template²³. There was however no report on the use of hexylamine as short hydrocarbon chain. The effect of the ratio of vanadium to amine has been reported by previous researcher²⁴⁻²⁶. In this study, a ratio of 2:1 V: amine had been employed. For a better understanding and comparison of the previous result with our product, two other different molar ratios were investigated for each amine. The V: amine mixture was

aged for 24 hours to facilitate the intercalation of the amine between the layers of $V_2O_5 \cdot nH_2O$ gels. Finally, the suspension was hydrothermally treated to produce a black powder, a color indicating mixed-valent V (IV, V) oxides (e.g. V_6O_{13}). (SEM), (TEM), (XRD) (FTIR) had been employed to characterize the black powder product during different duration time of hydrothermal synthesis. In the preparation of vanadium oxide nanotube using vanadium pentoxide, amine template can be mixed directly with the vanadium pentoxide powder or gelatin of $V_2O_5 \cdot nH_2O$. Gelation of the vanadium pentoxide precursor substance prior to the addition of alkylamine template is advantageous in many aspects. Intercalation of the template is much easier, through proton-exchange with the acidic protons of the gels, as compared to direct mixing of crystalline vanadium pentoxide²⁶. With layered bulk material, the incidence of nanotubes is associated. For this process we can use graphite or WS_2 , MOS_2 ²⁷. Table 3 displays the general survey of the results of the products formed by hydrothermal method vanadium dioxide at varying time. Sample for hexadecylamine template with dissimilar synthesis situation are labeled H-NT. It can be observed for all samples that the pH of the product taken after the Hydrothermal Method (HT) would increase to become more alkaline, indicating that the amine template molecules became protonated during this procedure it can be concluded that the amine is protonated. Remarkably, a good percent product with minimum amount of flakes shape can be obtained using hexadecylamine template which form exclusively vanadium oxide nanotube according to the monitored TEM results and confirmed also by SEM images. The nanotubes morphology was analyzed by Scanning Electron Microscopy (SEM) and Tunneling Electron Microscopy (TEM). SEM will reveal the surface structure as well as the shape of the vanadium oxide produced, while the TEM will confirm whether nano tubes are produced or not. TEM analysis would also be able to determine the dimensions of the vanadium oxide nanotubes produced. Figure 1 displays the SEM micrographs of the products formed after one

Table 3. Tabulated results of the products synthesized at different conditions

Sample	Duration time (days) for hydrothermal process @180°C	PH of the mixture before and after synthesis		% VO _x -NTs produced	Observed TEM results
		before	after		
H-NTs1	1	4.82	6.19	70-75%	Tubes/lamellar
H-NTs2	2	4.75	8.97		Tubes
H-NTs3	3	4.9	9.2		Tubes
H-NTs4	4	4.6	9.1		Tubes
H-NTs5	5	4.1	9.4		Tubes
H-NTs6	6	4.15	9.1		Tubes
H-NTs7	7	4.2	9.1		Tubes
H-NTs8 15 minUS	7 7	4.5 4.4	9.3 9.2	80-85%	Tubes with longer length
H-NTs9 1g V ₂ O ₅	7	4.67	9		Tube/flake
H-NTs10 3g V ₂ O ₅	7	2.71	8.5		Flake/ribbon

to seven days of hydrothermal synthesis time using hexadecylamine as template. It can be clearly seen from the SEM images that even after two days of hydrothermal treatment, nanotubes structure can be seen. Most of the studies and related journals claimed that seven days of hydrothermal treatment is desired in order to produce well developed nanotubes²⁸⁻³⁰. However, by altering the synthesis route undertaken in this study, a quicker synthesis route of vanadium oxide nanotube can be obtained. In fact, even after one day some tubes can be observed as seen in the SEM image in Figure 1(a) but the tubes one not yet completely developed. Upon increasing the hydrothermal synthesis time, well-developed nanotubes can be achieved. After increasing the synthesis time of longer than 2 days, the nanotubes are much more developed and are isolated from one to the other. Comparing the SEM results for nonotubes and some flake products by applying 1g and 3g of V₂O₅, show more nano ribbon and some flake products. TEM images of the vanadium oxide nanotubes produced are shown in Figure 2. Images shown in Figure 2 are the products using hexadecylamine template synthesized for 1 day which shows the under-developed nanotubes. However, TEM investigations in Figure 2 show that the reaction products for 1 day to 7

days of hydrothermal treatment for hexadecylamine template consist of well-developed, multi-walled nanotubes. Fundamentally, the images obviously revealed the hollow tubular structure with open-ended. The multi-walled structure of the tubes is consisted of parallel oxide layers. It can be noted that the oxide layers which are likely to be vanadium oxide had been rolled up to form the nanotubes. The observed external tube diameters were measured to have values between 50-90 nm while the internal were between 15 to 25 nm. TEM images confirmed SEM results when 1g V₂O₅ was used, nanotubes could be produced. But by using 3g V₂O₅, the TEM results show that more nano ribbon was produced with less or none nanotubes observed.

Figure 3 shows the XRD pattern of vanadium pentoxide crystal. As can be seen, the pattern shows a variety of intense peaks occurring in between 10° to 50° 2-theta angle. In contrast, the XRD profile of the vanadium/hexadecylamine precursor can be seen in Figure 4 as can be noticed the latter had an entirely different diffraction pattern with the bulk V₂O₅. An extremely intense peak can be seen at lower diffraction angle in the case on the vanadium/hexadecylamine precursor material. The presence of the low angle reflection peaks is a typical kind of

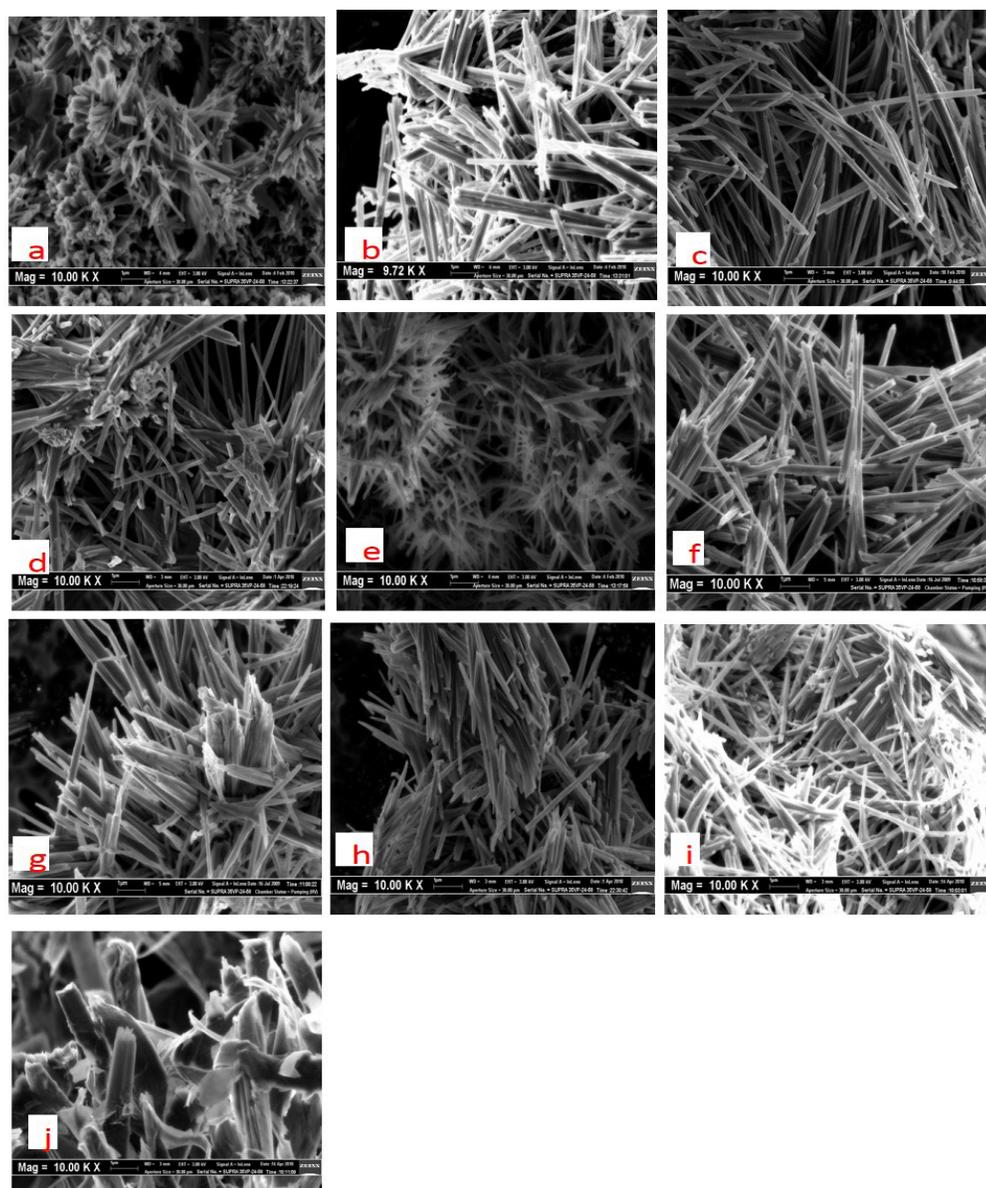


Figure 1. SEM of vanadium oxide nanotubes with hexadecylamine template at different hydrothermal synthesis time and ultrasonic condition and different molar ratio: (a) 1 day (b) 2 days (c) 3 days (d) 4 days (e) 5 days (f) 6 days (g) 7 days (h) Ultrasonic (i) 1g V_2O_5 (j) 3g V_2O_5 .

pattern which denotes a lamellar or layered compound. This observation is the same for all the V/amine precursors studied. X-ray principally interacts with electrons in atoms.

Figure 5 shows the XRD of vanadium oxide nanotubes. Two pick of diffraction patterns can be showed:

1. Series of (001) related to a well-ordered layered structure.

2. Series of (hk0) related to the two dimensional structure of the vanadium oxide layers.

As can be seen in the Figure 5, there are three distinct intense low angle reflection peaks occurring bellow 10° 2θ angle for the pattern of VO_x -NTs. This observation is true not only by the result of this study but also with the observed XRD patterns reported by previous researchers. The differences in the pattern between the nanotubes

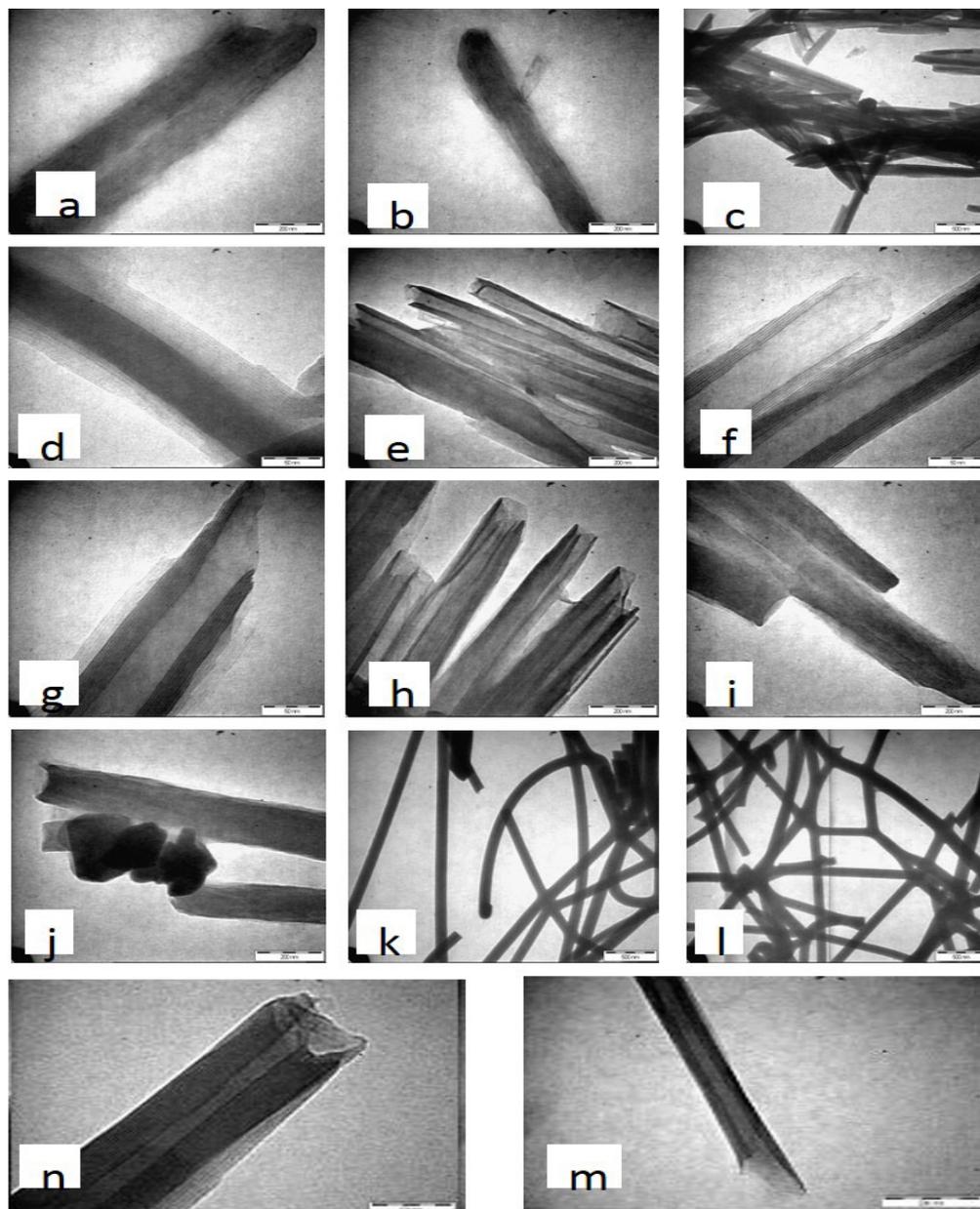


Figure 2. TEM of vanadium oxide nanotubes with hexadecylamine template at different hydrothermal synthesis time : (a,b) 1 day (c,d) 2 days (e,f) 6 days (g,h) 7 days and quantity (i,j) 1g V_2O_5 (k,l) 3g V_2O_5 (n,m) ultrasonics.

and the Vanadium/amine precursor material can simply be identified using these low angle reflection peaks. In the case of vanadium/hexadecylamine precursor, there are only two observable intense peaks at low diffraction angle. On the other hand, these three intense peaks are apparent on the pattern for the VO_x -NTs. For hexadecylamine, these three peaks of decreasing intensity happen

at d-values 3.5 nm, 1.7 nm, and 1.1 nm, correspondingly. Interestingly, even with one day, the product exhibited low angle reflections identical to that of VO_x -NTs synthesized at longer duration time; however, the hk0 series of reflections, higher angle peaks, are fewer (see appendix C for the H-NT1 peaks). It may indicate that there is not yet completely developed, that is, structural reorganiza-

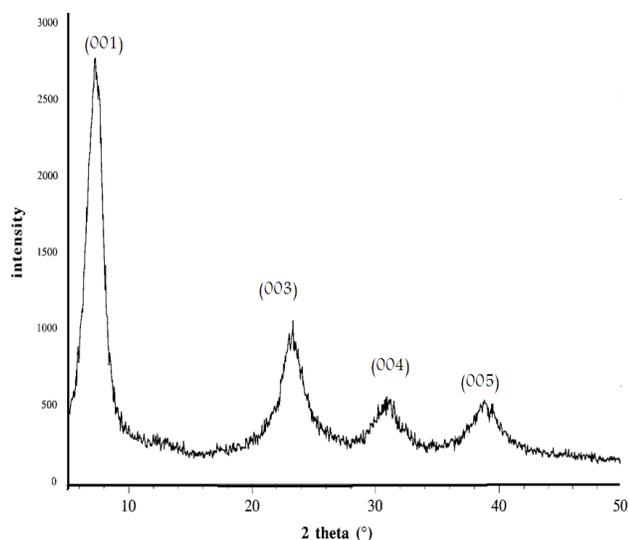


Figure 3. XRD pattern of vanadium pentoxide (V_2O_5) powder (precursor).

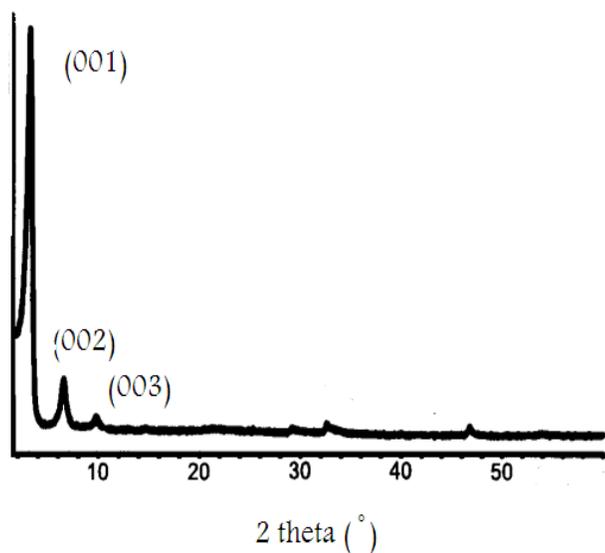


Figure 4. XRD pattern of vanadium oxide/hexadecylamine precursor.

tion is still undergoing. Certainly, SEM image of H-NT1, shown in earlier section (Figure 1)(a, b), supported that the sample is still in progress in forming a well-developed nanotubes. Within two to seven days period, it can be said that well-ordered structure of the VOX-NTs has been achieved. The highest intensity at low angle reflection (001 peak), has d- value of approximately 3.5 nm.

As seen in Figure 6 there are three major peaks centered at 1023 cm^{-1} , 617 cm^{-1} and 823 cm^{-1} . The band at

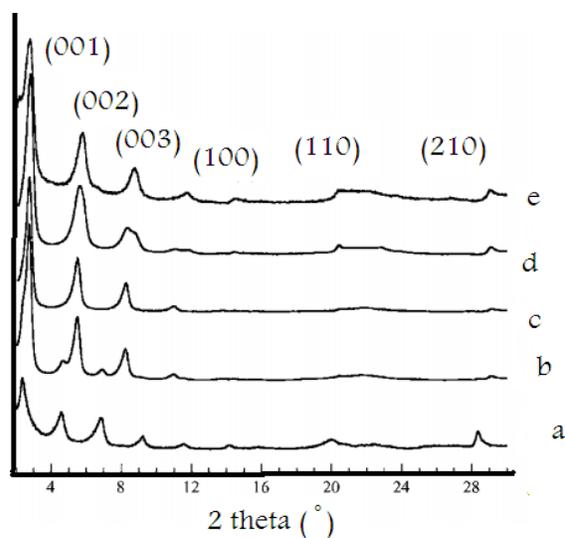


Figure 5. XRD profile of vanadium oxide/hexadecylamine hydrothermally treated for (a) 2 days, (b) 4 day, (c) 5 days, (d) 6 days, (e) 7 days.

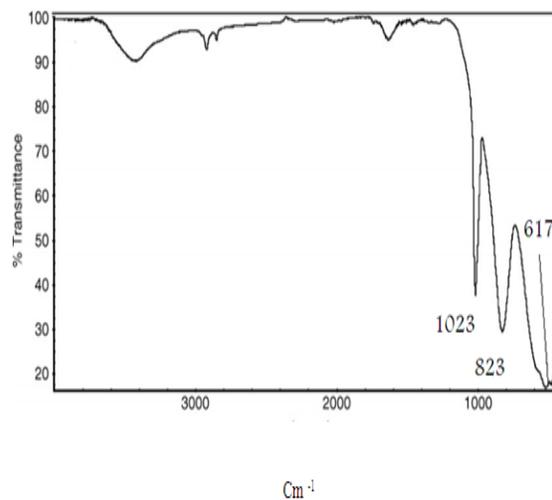


Figure 6. The IR spectrum of bulk vanadium pentoxide powder (precursor).

1023 cm^{-1} is correspond to the $V=O$ band. Also, bands at 823 cm^{-1} is related to the vibrations of $O-(V)_3$ and 617 cm^{-1} is assigned to the vibrations of $V-O-V^{25,33-35}$. Figure 7, the Fourier Transform Infrared Spectrum (FTIR) of vanadium oxide nanotubes (7 days hexadecylamine) considered the high absorptions at 2850 and 2918 cm^{-1} . Between the $3203-3411\text{ cm}^{-1}$ we show the transference of the massive bands and 1621 cm^{-1} related to $O-H$ vibrations. The band at 1002 cm^{-1} might be assigned to $V=O$

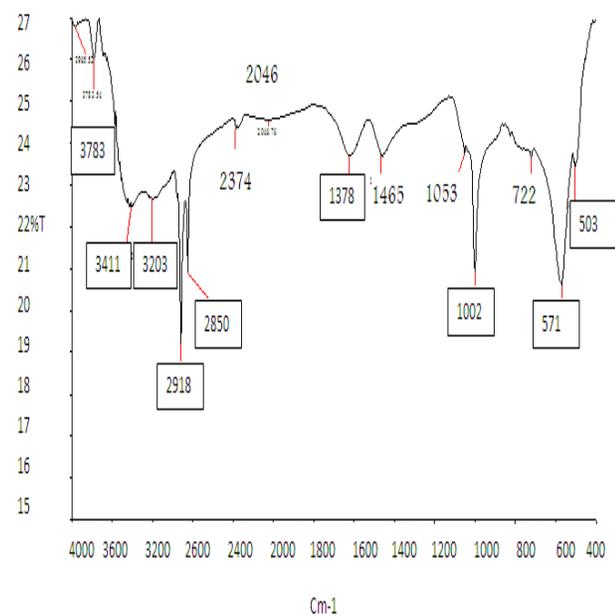


Figure 7. FT-IR spectra of VO_x-NTs (7 days hexadecylamine).

vibration, as seen with the FTIR of as well crystalline V₂O₅. The band at 2374 cm⁻¹ might be signed NH stretch, 2046 C=N=S anilysm. Stretch, 1465 Cm⁻¹ is CH₂ deformation, 1053 Cm⁻¹ CH in plane bending and 722 Cm⁻¹ CH out of plane deformation.

Figure 9 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 other, 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 9c. 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 the distance between the layers (> 1.6 nm).

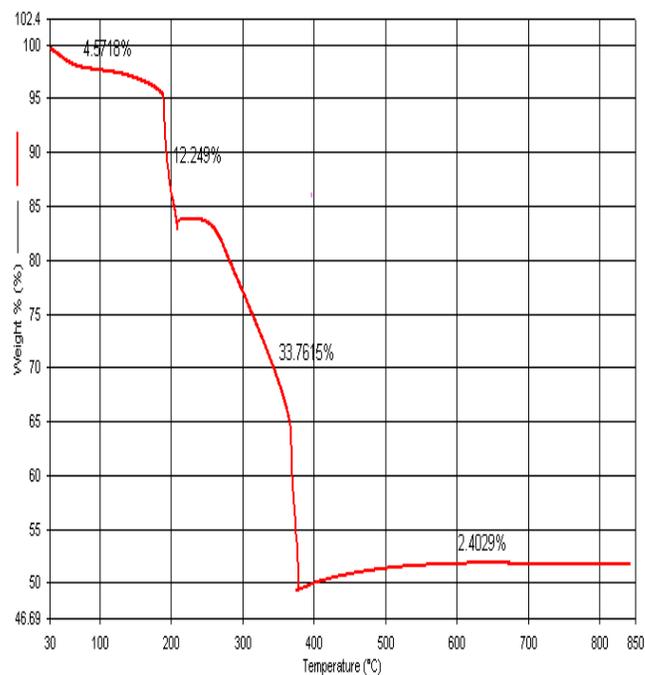


Figure 8. TGA of VO_x-NTs (7 days, hexadecylamine).

- 2) The intercalation between the vanadium atoms and the amine template, 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.
- 4) Bending due to mixed valency³⁶.

By using hydrothermal treatment, the products were regularly agglomerated or lump together. Based on the literature review, there are many types of reagents employed in order to wash the black product. Some used water, ethanol, hexane, diethyl ether or combination of two or three of these reagents^{37,38}. But, no one explained why only this reagent or why the combination of these reagents are used. In addition, they do not explain the effect of using such reagent/s on the product after washing and drying. The rule of solubility is very simple which is 'like dissolves like'. In this case, alcohol and amine compounds both contain a polar and a non-polar portion. The polar portion of these compounds varies, but the non-polar is the C-chain. For alcohols, the polar group is the hydroxyl group (-OH) while for amines, the polar group is the amino group. Amines with up to six carbon atoms are

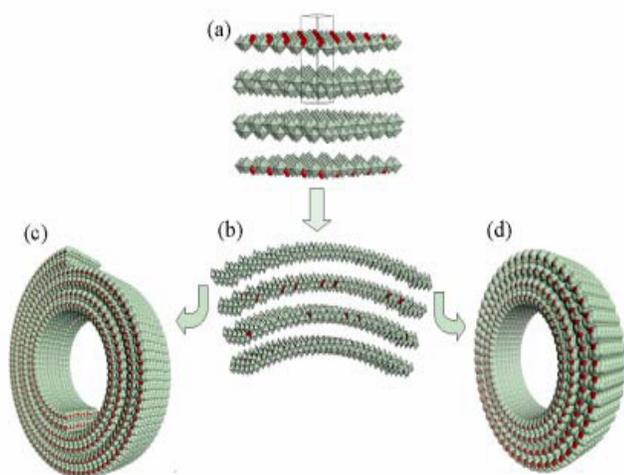


Figure 9. Possible formation structure description of V_2O_5 nanotubes. when bent (b) such layers may form nanoscrolls (c) or closed nanotubes (d).

water soluble. Increasing the carbon chain increases its non-polarity. Hexane is a non-polar which can dissolve amines with longer carbon chains. Using only ethanol, somehow dissolves the amine and other organics but addition of hexane in washing the product dissolves those other long chain organics that ethanol cannot dissolve by itself. Hence, it can be said that among the studied washing reagents, the combination of ethanol and hexane as the washing media to wash the synthesized products can produce more isolated nanotubes in addition to a much shorter duration time of drying.

5. Conclusion

The purpose of this methodology is to optimize the synthesis time, molar ratio and study the effect of amine type and the hydrothermal time on the quality and yield of VO_x-NTs.

Vanadium oxide nanotubes can be successfully synthesized starting from $V_2O_5 \cdot nH_2O$ gels with just two days duration of hydrothermal treatment. Essentially, other synthesis routes reported by other researchers need at least one week duration of hydrothermal treatment in order to produce the nanotubes. But in this study, a shortest duration time for the synthesis of exclusively vanadium oxide nanotubes had been achieved. Using different template materials affects the resulting products especially

when synthesized at longer duration time of hydrothermal treatment. Some tubes and ribbons change to flakes and others collapse when hexylamine template were used. Interestingly, using hexadecylamine with longer carbon chain length, the nanotubes can be produced within two to seven days of hydrothermal treatment with no other by-products, isolated product without agglomerated and longer length occur when was used an ultrasonic during mixing. Thus, the research output of this study, fast synthesis time, will significantly be economical on the production of VO_x-NTs.

6. References

1. Iijima S. Helical microtubules of graphitic carbon. *Nature*. 1991; 354(6348):56–8.
2. Lam E, Luong JHT. Carbon materials as catalyst supports and catalysts in the transformation of biomass to fuels and chemicals. *ACS Catalysis*. 2014; 4(10):3393–410.
3. Haffer S, Lader C. A synthesis concept for a nanostructured $CoFe_2O_4/BaTiO_3$ composite: Towards multiferroics. *Microporous and Mesoporous Materials*. 2014; 196:300–4.
4. Habibi MH, Mardani M. Co-precipitation synthesis of nano-composites consists of zinc and tin oxides coatings on glass with enhanced photocatalytic activity on degradation of Reactive Blue 160 KE2B. *Spectrochim Acta Mol Biomol Spectros*. 2015; 137:785–9.
5. Jana NR, Gearheart L, Murphy CJ. Wet chemical synthesis of silver nano rods and nanowires of controllable aspect ratio. *Chem Commun*. 2001; 7:617–8.
6. Tremel W. Inorganic Nanotubes. *Angew Chem Int*. 1999; 38:2175–80.
7. Shenton W, Douglas T, Young M, Stubbs G, Mann S. *AdvMater*. 1999; 11:253–9.
8. Chandrappa GT. Vanadium oxide: from gels to nanotubes. *J Sol Gel Sci Technol*. 2003; 26(1):593–6.
9. Solsona B. Vanadium oxide supported on mesoporous MCM-41 as selective catalysts in the oxidative dehydrogenation of alkanes. *J Catal*. 2001; 203(2):443–52.
10. Muhr HJ, Krumeich F, Schonholzer UP, Bieri F, Niederberger M, Gaukler LJ, Nesper R. *Adv Mater*. 2000; 12:231–5.
11. Zhang KF, Guo DJ, Liu X, Li J, Li HL, Su ZX. *J Power Sources*. 2006; 162:1077–82.
12. Spahr ME, Stoschitzki-Bitterli P, Nesper R, Haas O, Novak P. *J Electrochem Soc*. 1999; 146:2780–3.
13. Krumeich F, Muhr HJ, Niederberger M, Bieri F, Schnyder B, Nesper R. *J Am Chem Soc*. 1999; 121:8324–7.
14. Ledoux MJ. High-yield butane to maleic anhydride direct oxidation on vanadyl pyrophosphate supported on heat

- conductive materials b-SiC, Si₃N₄, and BN. *J Catal.* 2001; 203(2):495–508.
15. Yin H, Yu K, Zhang Z, Zeng M, Lou L, Zhu Z. Humidity sensing properties of flower-like VO₂ (B) and VO₂ (M). *Nanostructures Electroanalysis.* 2011; 23:1752–8.
 16. Ajayan PM, Stephan O, Redlich P, Colliex C. *Nature.* 1995; 375:564–8.
 17. Bieri F, Krumeich F, Muh HJ, Nesper R. *Helv Chim Acta.* 2001; 84:3015–20.
 18. Grigorieva AV, Goodilin EA, Anikina AV, Kolesnik IV, Tretyakov YD. *Mendeleev Commun.* 2008; 18:71–2.
 19. Sediri F, Touati F, Gharbi N. *Mater Lett.* 2007; 61:1947
 20. Aghabozorg HR, Mousavi R, Asckari S, Aghabozorg H. *J Nanopart.* 2007; 9:497–500.
 21. Chen W, Peng J, Mai L, Zhu Q, Xu Q. *Mater Lett.* 2004; 58:2275–8.
 22. Bouhedja L, Stenou N, Maquet J, Livage J. *J Solid State Chem.* 2001; 162:315–8.
 23. Mamalis AG, Vogtländer LOG, Markopoulos A. Nanotechnology and nanostructured materials: Trends in carbon nanotubes. *Precision Engineering.* 2004; 28(1):16–30.
 24. Iijima S. Helical microtubules of graphitic carbon. *Nature.* 1991; 354(6348):56–8.
 25. Ajayan PM. Nanotubes from Carbon. *Chem Rev.* 1999; 99(7):1787–800.
 26. Grobert N, *Nachr Chem Tech Lab.* 1999; 47:768–71.
 27. Shenton W, Douglas T, Young M, Stubbs G, Mann S. *Adv Mater.* 1999; 11:253–8.
 28. Grobert N. *Nachr Chem Tech Lab.* 2000; 49:768–71.
 29. Jana NR, Gearheart L, Murphy CJ. Wet chemical synthesis of silver nano-rods and nano-wires of controllable aspect ratio. *Chem Comm.* 2001; 7:617–8.
 30. Tremel W. *Inorganic Nanotubes.* *Angew Chem Int Ed.* 1999; 38(15):2175–9.
 31. Muhr HJ, et al. Vanadium oxide nanotubes - a new flexible vanadate nanophase. *Adv Mater.* 2000; 12(3):231–4.
 32. Spahr ME, et al. Vanadium oxide nanotubes. a new nano-structured redox-active material for the electrochemical insertion of lithium. *J Electrochem Soc.* 1999; 146(8):2780–3.
 33. Krumeich F, et al. Morphology and topochemical reactions of novel vanadium oxide nanotubes. *J Am Chem Soc.* 1999; 121(36):8324–31.
 34. Ajayan PM, Schadler O, Redlich P, Colliex C. *Nature.* 1995; 375:564–70.
 35. Bieri F, Muhr HJ, Nesper R. *Helv Chim Acta.* 2001; 84:3015–8.
 36. Cambor A, Martýnez A, Perez-Pariente J. *J Chem Soc Chem Commun.* 1992; 1:583–7.
 37. Bieri F, Muhr HJ, Nesper R. *Helv Chim Acta.* 2001; 84:3015–9.
 38. Spahr ME, Nesper R, Haas O, Novak P. *J Electrochem Soc.* 1999; 146:2780–5.