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Study Synthesis of Vanadium Oxide Nanotubes with two template hexadecylamin and hexylamine

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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.Vanadium oxide nanotube (VO_X-NT) is a new type of nanotublar material which open new horizons for application in many areas. The important catalytic and electrochemical property of vanadium oxide as well as the unique shape of the nanotubes has been the impetus for studying this novel type of nanostructured material.In this research, vanadium oxide nanotubes had been synthesized via gelation of V_2O_5 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 VO_X-NTS at a fastest synthesis time. Two template materials were studied: hexadecylamin and hexylamine. The products obtained were characterized for its morphology and structure in the nanotubes using SEM, TEM, XRD. TG and FTIR analyses were also used. As exposed by transmission electron microscopy and scanning electron microscopy images, well-developed vanadium oxide nanotubes using hexadecylamine template can be obtained even with just two days duration of hydrothermal treatment, the shortest time achieved yet and reported for the synthesis of VO_x. X- ray diffraction patterns showed the low angle reflection peaks which are characteristic for the well-ordered layered structure of the nanotubes. TEM and SEM images also, interestingly, revealed and verified the speculated rolling-up formation mechanism of the vanadium oxide nanotubes. Hence, in this research study, the gelation of the V_2O_5 and the used of ethanol as a solvent instead of acetone had circumvented the problem of longer duration time of hydrothermal treatment leading to a fast synthesis of VO_X-NTS.

Keywords: Vanadium Oxide, Nanotubes, Ultrasonics, Hydrothermal, hexadecylamine, hexylamine

INTRODUCTION

Nanotechnology is the understanding and control of matter at dimensions between approximately 1 and 100 nanometers, where unique phenomena enable novel applications. Nano-scale science, engineering and technology, involves imaging, measuring, modeling, and manipulating matter at this length scale (Iijima, 1991). One nanometer is one-billionth of a meter. A sheet of paper is about 100,000 nanometers thick; a single gold atom is about one third of a nanometer in diameter. Dimensions between approximately 1 and 100 nanometers are known as the nanoscale. Unusual physical, chemical, and biological properties can emerge in materials at the nanoscale. These properties may differ from the properties of bulk materials and single atoms or molecules. The discovery of the carbon nanotubes (Lam and Luong 2014) 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 (Haffer and Leder, 2014, Habibi and Mardani (2015).

The synthesis of different kinds of inorganic nanomaterials 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 nanoparticles such as nanocomposites (Jana *et al.*, 2001,Tremel, 1999, Shenton *et al.*, 1999). Vanadium oxide nanotubes (VOx-NTS) are useful material, due to their high potential applicability in electrochemical devices and catalytic processes (Chandrappa, 2003, Solsona, 2001, Muhr *et al.*, 2000, Zhang *et al.*, 2006). The first successful approach to make a tubular vanadium oxide was reported using carbon nanotubes as a template. 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 (Spahr *et al.*, 1999, Krumeich *et al.*, 1999).

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 [14]. 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 [15]. 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 [16, 17].

This research presents synthesis of VOx-NTs using V_2O_5 powder and effect of two different kinds of amines as template and the distribution of hexadecylamine and hexylamine inside the V_2O_5 slurry with ethanol. 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 VOx-NTS. This research was conducted to fulfill the following objectives:

(i) To compare the morphologies and structure of VOx-NTs by using hexadecylamine and hexylamine as template material.

(ii) To determine the effect of different hydrothermal reaction time (from 1day to 7 days) on thesynthesized product.

(iii) To determine the effect of different molar ratio of vanadium /amine on the synthesized product.

MATERIAL AND METHODS

The chemicals used in this research are listed in Table 1. All the chemicals used in this research were of analytical grade. 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_2O_5)	181.88	3.357	99%	Merck
Hydrogen peroxide	H_2O_2	34.0147	1.463	30%	Merck,
Hexadecylamine	$C_{16}H_{35}N$	241.4606	0,813	95%	Merck
Hexylamine	$CH_3(CH_2)_5NH_2$	101.19	0.766	96%	Merck
Ethanol	C_2H_6O	46.07	0.789	99%	Merck
n-hexane	C_6H_{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 microgeraph(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

EXPERIMENTAL

A. Synthesis of Vanadium Oxide Nano Tubes

Gelation or preparation of $V_2O_5.nH_2O$ gels. The first stepincludes the dissolution of crystalline V_2O_5 in a solution of hydrogen peroxide.

Two grams of crystalline V_2O_5 was added to 100 ml hydrogen peroxide (H_2O_2). The exothermic reaction that occurs during synthesis lead to the partial decomposition of hydrogen peroxide that lead to the release of oxygen and the formation of V(V) peroxo complexes [18].

The orange mixture formed turned to a dark red gel upon standing just after the reaction. The dark red gel was aged for about 24 hours.

Intercalation of the template. The second step was to perform the intercalation of monoamine into the $V_2O_5nH_2O$ gels. There were two types of template materials under study: hexadecylamine ($C_{16}H_{36}N$), hexylamine ($C_6H_{16}N$). The following were the steps undertaken.

Hexadecylamine ($C_{16}H_{36}N$) template. About 2.66 grams of hexadecylamine was dissolved in 4 ml ethanol (under very small heating to dissolve) and then added to the $V_2O_5nH_2O$ 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.

*Hexylamine ($C_6H_{16}N$) template.*About 1.47 ml (1.12grams) of hexylamine with 2 ml ethanol was added to the $V_2O_5nH_2O$ gel (molar ratio V: amine = 2:1). The resulting brown mixture was stirred for about 10 hours and then left to age without stirring for about 14 hours. After aging, the colour of the mixture changed to green suspension with Ph around 6.3.

Hydrothermal Treatment. At last the resultant suspension, vanadium oxide-amine composite, was after that transferred in to a borosilicate glass vessel-lined autoclave (Parr) with a stainless steel shell and hydrothermally treated at 180ºC for one to seven days Fig.1. The resulting black product was washed by about 150 ml ethanol and 20 ml n-hexane next dried in vacuum oven at 80ºC for five hours.

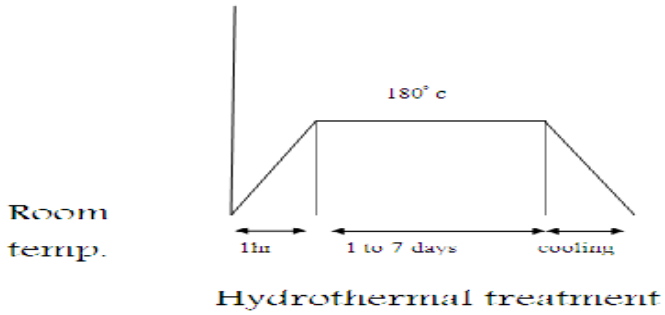

Fig.1. Hydrothermal Treatment treatment graph for the synthesis of VOx-NTs.

RESULT AND DISCUSSION

The synthesis of vanadium oxide nanotubes was carried out by using V_2O_5 powder as vanadium source and two types of template hexadecylamine ($C_{16}H_{36}N$) and hexylamine ($C_6H_{16}N$). These two templates were chosen due to the recommendation of previous study in which hexadecylamine was used as a template. 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 researcher. It is known that nanotubes excluding the flake by-products can be obtained using initial molar vanadium to monoamine ratio (V:template ratio) in the range of 3 to 2. 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 ratio 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 $V_2O_5nH_2O$ 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 synthesis of VO_X-NTs using V_2O_5, amine template can be mixed directly with the V_2O_5 powder or gelatin of $V_2O_5nH_2O$. Gelation of the V_2O_5 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 V_2O_5. As previously reported, aging or the reaction of monoamine template through the vanadium precursor at room temperature should be long enough so that the vanadium oxide-surfactant composite develops a lamellar structure wanted to produce the nanotubes. Vanadium oxide depending on the nature of the species present in the reaction exhibit a wide range of morphologies (lamellar, molecular or cluster). The occurrence of nanotubes is normally associated with layered bulk material, such as graphite, BN, or transition metal dichalcogenides (WS_2,MOS_2), which has strong in-plane forces within the layer plane, but weak interplanar vander waals forces. In this case, extensive aging, as investigated in the results, is not necessary compared to other synthesis route (i.e. alkoxide, $VOCl_3$, or HVO_3 materials) which usually takes two or more days of aging through continuous stirring so that expand the needed lamellar structure.

This means that, in similarity, homogenously stirring the V_2O_5 crystal and monoamine template with the suggested condition in general carried-out (i.e. amount of water) is complicated. This might significantly lead to a number of portions of vanadium oxides who are not comprehensively intercalated with the monoamine template leading to some flake by-products aside from the needed nanotubes. Table 3 displays the general survey of the results of the products formed by hydrothermal treated vanadium dioxide at varying time. Sample for hexadecylamine and hexylamine template with dissimilar synthesis situation are labeled H-NT and h-NT, correspondingly. It can be observed for all samples that the pH of the product taken after the hydrothermal treatment (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 VO_X-NTs according to the monitored TEM results and confirmed also by SEM images.

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

Sample	**Duration time (days)for hydrothermal process @180ºC**	**PH of the mixture before and after synthesis**		**% VOx-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 V2O5	7	4.67	9		Tube/flake
H-NTs10 3g V2O5	7	2.71	8.5		Flake/ribbon
h-NTs1	1	5.98	6.05	~40%	Tubes/amorph
h-NTs2	2	6.09	6.13		belt
h-NTs3	3	5.03	6.72		ribons
h-NTs4	4	5.88	9.66		Ribbons /tube
h-NTs5	5	5.29	8.55		flake
h-NTs6	6	5.22	9.66		flake
h-NTs7	7	6.1	9.22		flake
h-NTs8	4	8.22	9.78		
h-NTs9 3g V2O5	4	4.52	8.93		

A. Morphology

The morphology and microstructure of the products were analysed by SEM and 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 (e.g. inner and outer diameters, number of layers) of the vanadium oxide nanotubes produced. Fig. 1 displays the SEM micrographs of the products formed after one 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 nanotubes (Sediri *et al.*, 2007, Aghabozorg *et al.*, 2007).

However, by altering the synthesis route undertaken in this study, a quicker synthesis route of VOx-NTs can be obtained. In fact, even after one day some tubes can be observed as seen in the SEM image in Fig. 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 form one to the other. Comparing the SEM results for nonotubes and some flake products by applying 1g and 3g of V_2O_5, show more nano ribbon and some flake products.

B. Effect of utrasonics

The effect of ultrasonics on the morphology and structure of V_2O_5 nanotubes was studied by using an ultasonics treatment for 15 min during mixing. The ultrasonic maybe useful for the acceleration of the reaction of amine template with the V_2O_5 precursor at room temperature. This could further reduce the mixing time. As mention in previous studies (Chen *et al.*, 2004, Bouhedja *et al.*, 2001, Mamalis, *et al.*, 2004, Iijima, 1991, Ajayan, 1999) times synthesis should be long enough so that the vanadium oxide-surfactant composite could developed into a lamellar structure needed to yield the nanotubes.

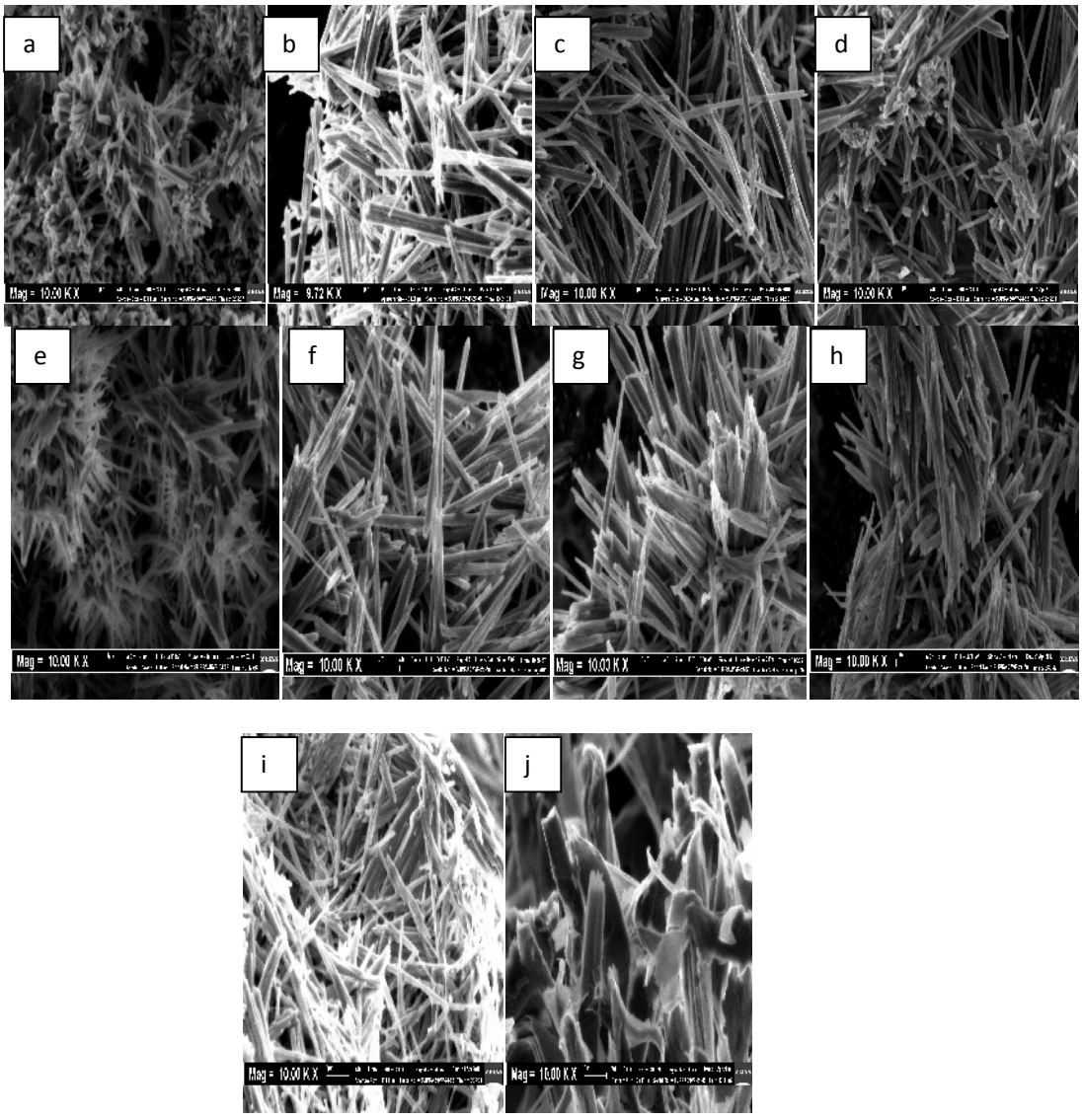

Fig. 2: SEM of vanadium oxide nanotubes with hexadecylamine template at different hydrothermal synthesis time and ultrasonic condition and different molar ratio :(a) 1 day (b) 2 days (c) 3 days (d) 4 days (e) 5 days (f) 6 days (g) 7 days (h) Ultrasonic (i)1g V_2O_5 (j) 3g V_2O_5.

In this case, prolonging the synthesis time, as proven in the results is not necessary to produce the nanotubular material. Normally it takes two or more days of aging with continuous stirring in order to develop the needed lamellar structure. Homogenously stirring of the V_2O_5 and amine template must be done for a long time and this may be done. Fig. 1 (h) are shows the morphology of VOx-NTS after being treated to ultrasonics and Fig. 1 (a-g) without ultrasonics treatment. With ultrasonic V_2O_5 slurry can be easily intercalated into the amine template. This leads to the less aging period but increase of the yield of nanotubes formation (Grobert, 1999, Shenton, *et al.,* 1999, Grobert, 1999, Jana, *et al.*, 2002, Tremel, 1999, Muhr, 2000, Spahr, 1999, Krumeich, 1999, Ajayan *et al.*, 1995, Bieri *et al.*, 2001, Niederberger, 2004, Camblor *et al.,* 1992, Bieri et al., 2001, Spahr *et al.,* 1999). These effects are important advantages of using ultrasonic irradiation for the preparation of VOx-NTS with longer length and similar diameter compare to other product without using ultrasonic. Fig. 3 shows the SEM micrograph using hexylamine as template. After 2 days of hydrothermal treatment, flake and nano ribbon products were produced. After 3 days of hydrothermal treatment, more nanoribbons are observed as shown in Fig. 3. c. After four days of hydrothermal treatment nanotubes and nanoribbons were produced. Increasing the duration time to 7 days had damaged the nanotubes and flake structure was produced as confirmed by TEM results as shown in (Fig. 5). It can be safe to note that due to shorter interlayer distance created with hexylamine template, as compared to hexadecylamine, longer duration time of synthesis may have induced instability of tubular formation. By using just 1g V_2O_5, nanotubes and some flakes products were observed in comparison to using 3g V_2O_5, in which SEM results show flake produced.

C. TEM Results

TEM images of the VOx-NTs produced are shown in Fig. 4 and 5. Images shown in Fig. 4 are the products using hexadecylamine template synthesized for 1 day which shows the underdeveloped nanotubes. However, TEM investigations in Figure 4show 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 between15 to 25nm. TEM images confirmed SEM results when 1g V_2O_5 wasused,nanotubes could be produced. But by using 3g V_2O_5, the TEM results show that more nano ribbon was produced with less or none nanotubes observed. Figure 5 are TEM images of oxide made by using hexylamine as template.

As can be seen, three days of hydrothermal treatment the image observed was a nanobelt where the nanotubes are not yet formed. After 4 days, a few nanotubes are seen and irregular shape oxide can also be seen. After 6 days of duration, the majority products observed are flakes. Upon increasing the days of the synthesis, the tubes had collapsed to form a flakes phase products. The numbers of layers are few which are difficult to be determined. TEM micrograph confirmed the SEM result, by applying 1g V_2O_5 with 1.47 ml hexylamine, nanotubes can be produced. When using 3g V_2O_5 with 1.47 ml hexylamine, only nano ribbon was seen and no nanotubes were produced.The major difference between hexadecylamine and hexylamine as used template are number of carbon in molecules. Table 4 to summarize the results and to indicate the difference in the dimensions of the nanotubes produced using hexadecylamine and hexylamine as templates. In general, it can be seen, that the nanotubes produced by the hexadecylamine have wider outer and inner and longer length compared to hexylamine template. However, hexadecylamine nanotubes have bigger number of layers. In the case of hexylamine, since the nanotubes formed by this type of amine are not well-formed, it is difficult to make a comparison between one another based from the layering obtained from the TEM analysis. The inter layer distance may have been affected by the length of the hexylamine carbon chain which is lesser compared to hexadecylamine template. The length of template has an effect on the final structure of the vanadium oxide nanotubes. Using hexadecylamine template, VO_X-NTs can be obtained even within two days of hydrothermal treatment and does not collapse upon increase in the duration time. In comparison, using the other template, hexylamine, which has a shorter carbon chain (only six carbons), the nanotubes can be formed just in four days. Besides the flake, lamellar by-products also been produced which is not desirable in this particular case. Increasing the reaction time of synthesis, cause the collapsed of the nanotubes or form flake products. It can be inferred from the observations that the flexibility of the layers upon the tube formation, bending or rolling (see section 5, formation mechanism), due to the inter layer distance formed by the template is significantly affected by the length of carbon chain. Because the hexadecylamine template is able to support the VOx-NTs sheet during the formation of the tubes.

D. X-ray diffraction results

Fig. 6 shows the XRD pattern of vanadium pentaoxide crystal. As can be seen, the pattern shows a variety of intense peaks occurring in between 10^o to 60^o 2-theta angle. In contrast, the XRD profile of the vanadium/hexadecylamine precursor can be seen in Fig. 7. As can be noticed the latter had an entirely different diffraction pattern with the bulk V_2O_5. An extremely intense peak can be seen at lower diffraction angle in the case on the vanadium/hexadecylamine precursor material.

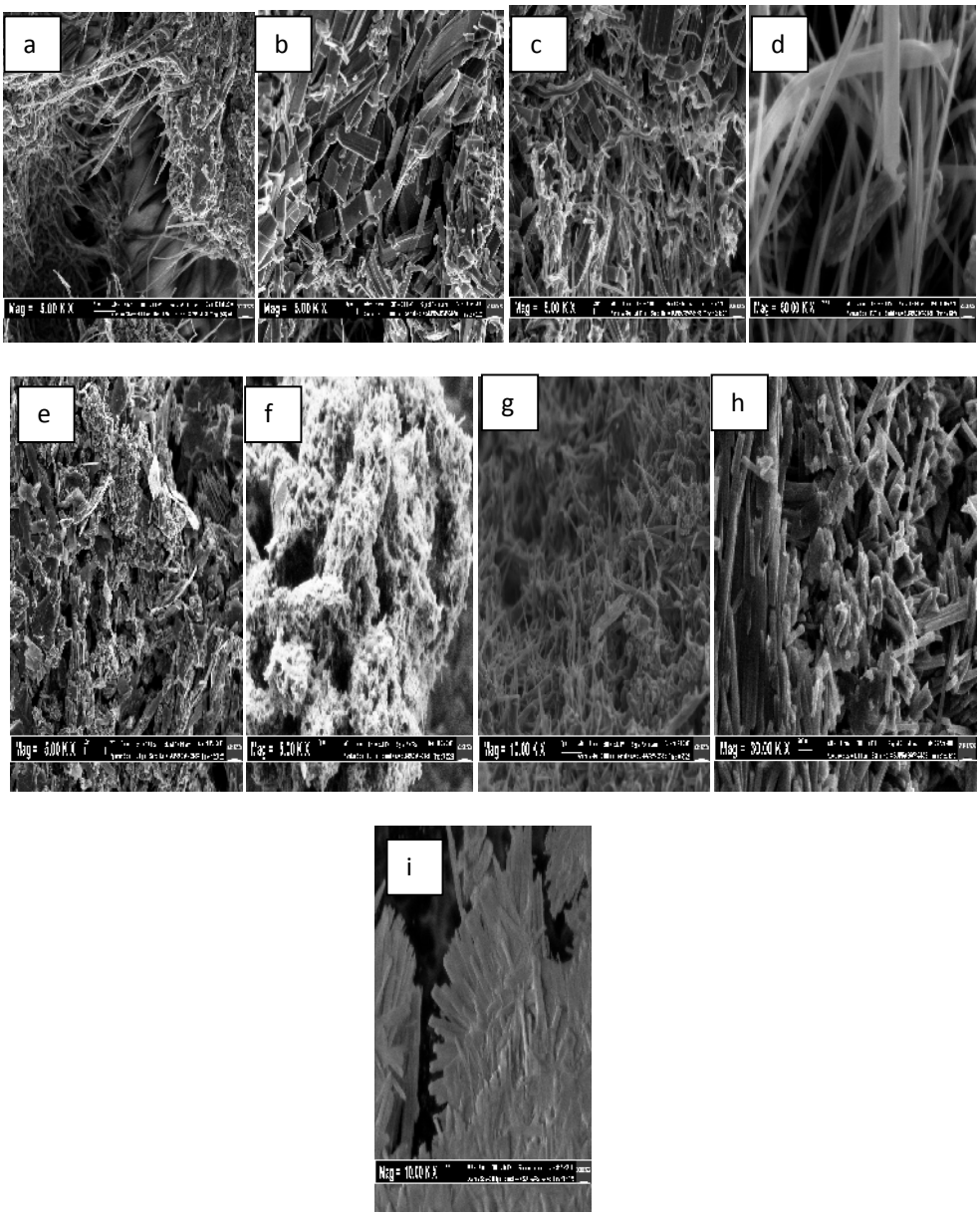

Fig. 3. Various SEM of vanadium oxide nanotubes with hexylamine template at different hydrothermal synthesis time:(a) 1 day (b) 2 days (c) 3 days (d) 4 days (e) 5 days (f) 6 days (g) 7 days ;amount of precursor (h)1 g V_2O_5 (i) 3g V_2O_5.

The presence of the low angle reflection peaks is a typical kind of 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.

If a beam of monochromatic x-radiation is directed at a crystalline material and the distances between the atoms are of the same magnitude as the wavelength of the x-ray, constructive and destructive interferences occur. These consequences in diffraction where x-ray are emitted at characteristics angles based on the spaces between the atoms organized in crystalline structures called planes. The majority crystals can have many sets of planes passed through their atoms. Each set of planes has a specific interplanar distance and will give rise to a characteristic angle of diffracted x-rays. The relationship between the wavelength of the x-ray beam, λ, the angle of diffraction, 2θ, and the distance between each set of atomic planes of the crystal lattice, d, is given by Bragg condition $\lambda = 2d\sin\theta$ Where n represents the order of diffraction. From this equation, we can calculate the interplanar distances of the crystalline material being studied. The interplannar spacing depends solely on the dimension of the crystal's unit cell while the intensities of the diffracted x-rays are a function of the placement of the atoms in the unit cell. Fig. 8 shows the x-ray diffraction patterns of VO_X-NTs.

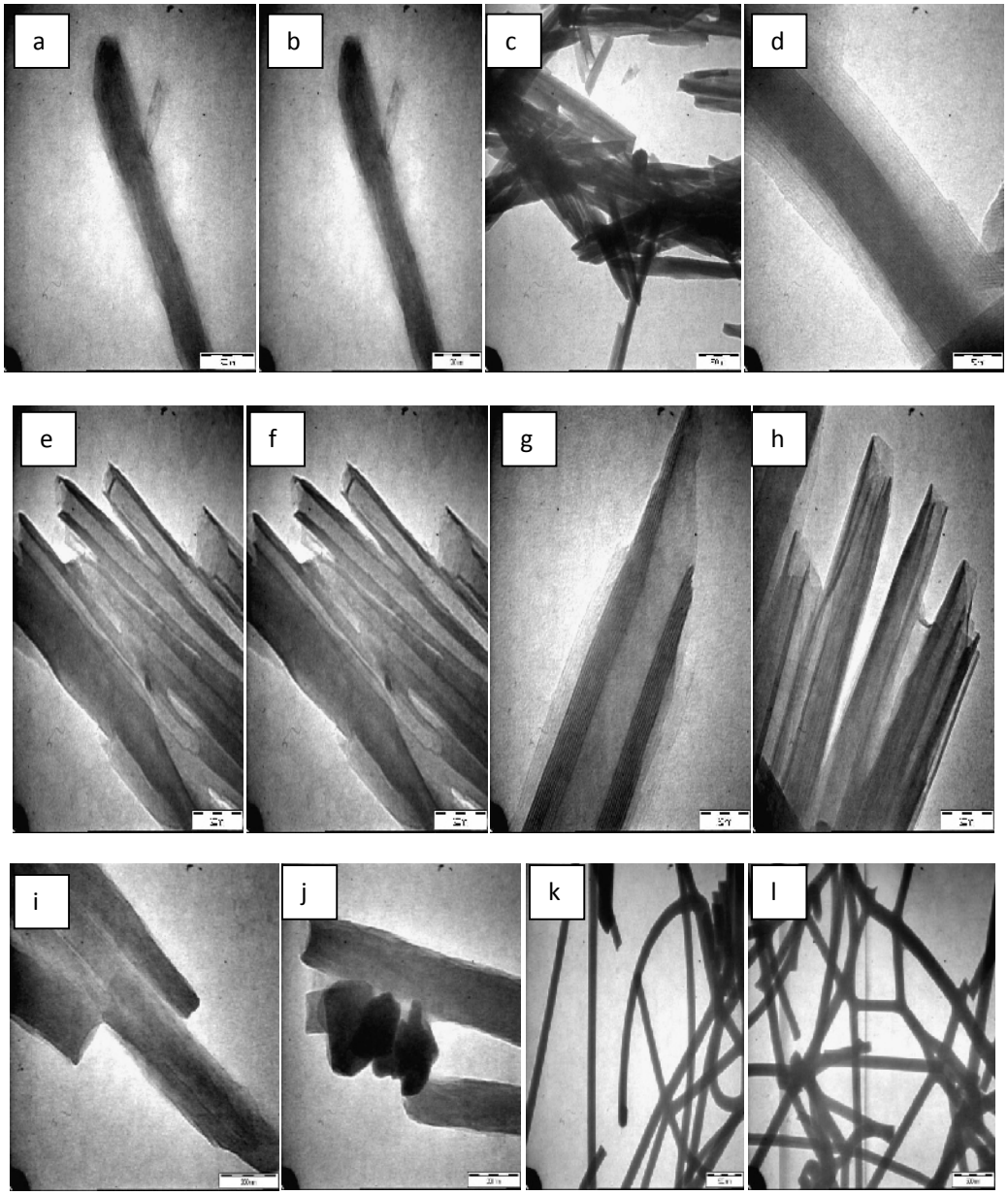

Fig. 4. TEM of vanadium oxide nanotubes with hexadecylamine template at different hydrothermal synthesis time: (a,b) 1 day (c,d) 2 days (e,f) 6 days (g,h) 7 days and quantity (i,j)1g V_2O_5(k,l) 3g V_2O_5.

Two sets of diffraction patterns can be observed: (001) series corresponding to a well-ordered layered structure and the (hk0) series corresponding to the two dimensional structure of the VOx layers which form the walls of VO_X-NTs. The (001) reflection is caused by the regular interlayer distance while the less intense peaks at smaller d-values are caused by the structure with in the layers as studied by other researchers using electron diffraction. The (kh0) set of reflections can be indexed on the basis of a two-dimensional square lattice with α~~0.61 nm. There are three distinct intense low angle reflection peaks occurring bellow 10º 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 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 1.1nm, 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).

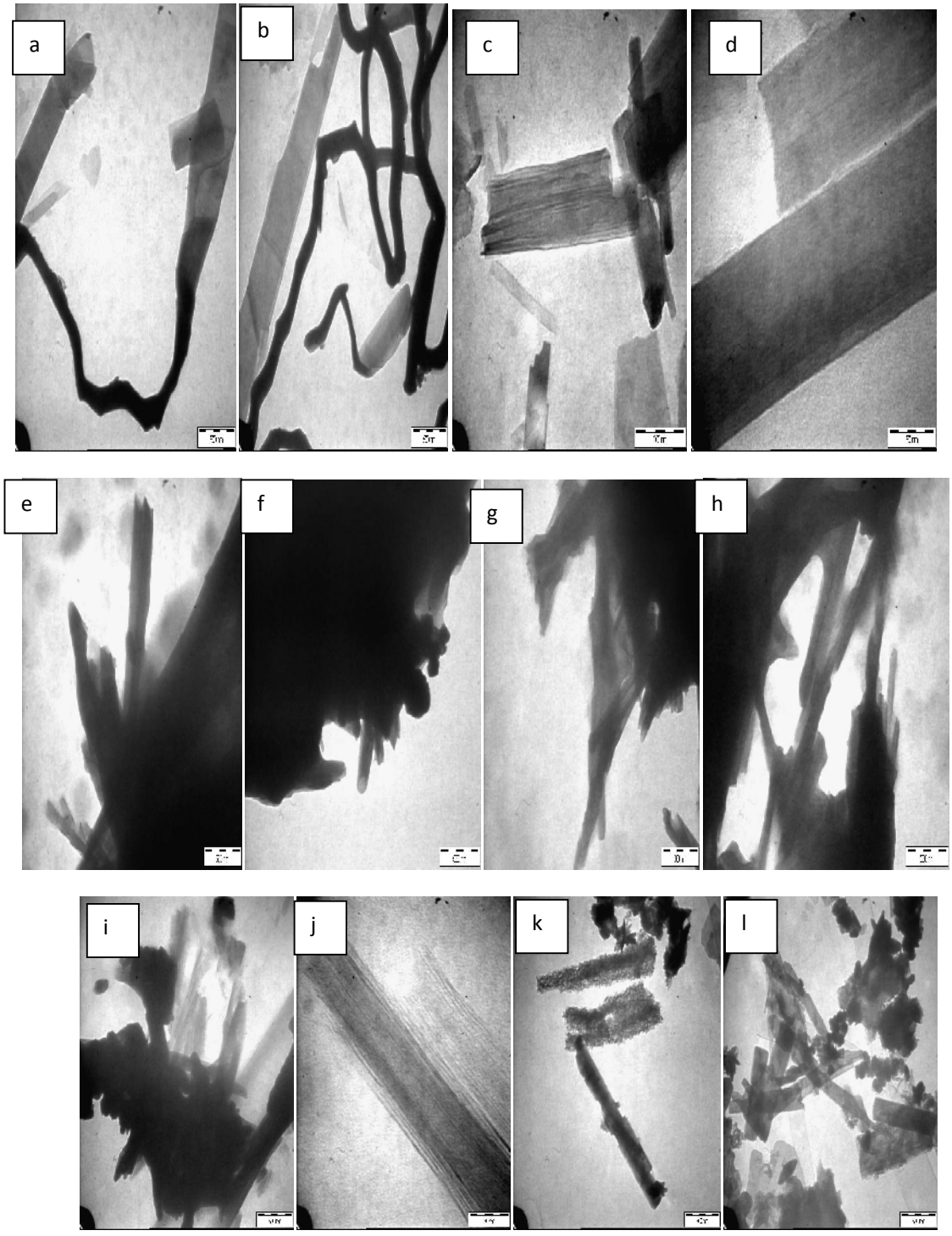

Fig. 5. TEM of vanadium oxide nanotubes with hexylamine template at different hydrothermal synthesis time (a,b) 3 days (c,d) 4 days (e,f) 6 days (g,h) 7days and quantity (I,j) 1g V_2O_5 (k,l) 3g V_2O_5.

Table 4: Dimensions of VOx-NTs formed used 2 different templates.

Template	No. of carbons In amine	Duration of HT(days)	Inner (nm)	Outer (nm)	Length (µm)	No. of layers
hexadecylamine	16	1-7	15-25	50-90	1-2.5	4-10
hexylamine	6	1-7	20-30	30-80	0.4-1.5	----

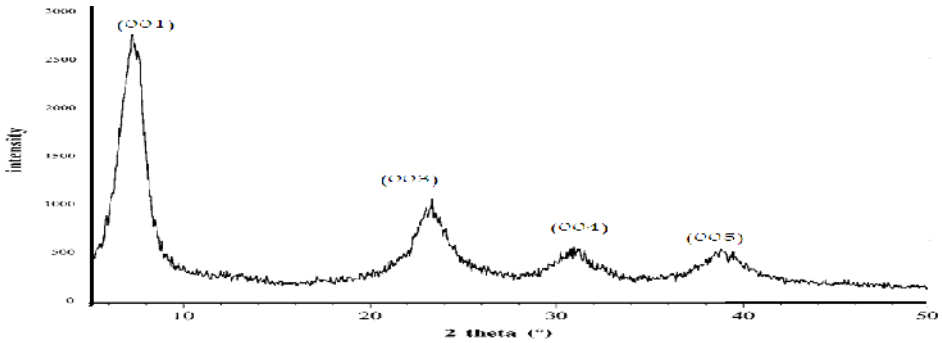

Fig. 6. XRD pattern of vanadium pentaxide(V_2O_5) powder(precursor).

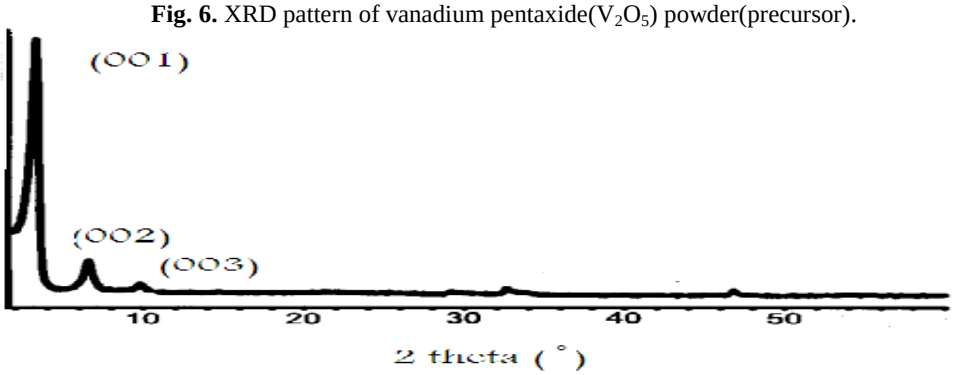

Fig. 7. XRD pattern of vanadium oxide/hexadecylamine precursor.

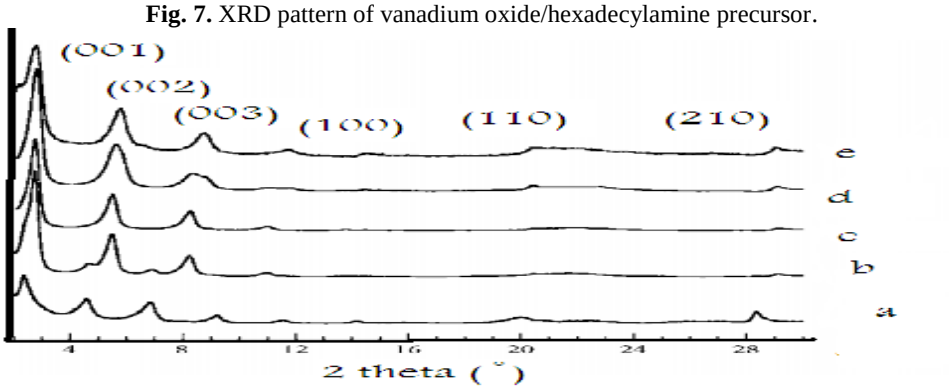

Fig. 8. XRD profile of vanadium oxide/hexadecylamine hydrothermaly treated for (a) 2 days, (b) 4 day, (c) 5 days, (d) 6 days,(e) 7 days[ICDD No.00-027-0940,V_3O_7].

It may indicate that there is not yet completely developed, that is, structural reorganization is still undergoing. Certainly, SEM image of H-NT1, shown in earlier section (Fig. 2.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 VO_X-NTs has been achieved. In addition, the distance between the vanadium oxide layers in the nanotubes is reflected with the peak with the highest intensity at low angle reflections. The highest intensity at low angle reflection (001 peak), has d- value of approximately 3.5 nm. Fig. 9 and 14 shows the XRD profiles for the sample with hexylamine as template.

The precursor material only shows one intense peak at low reflection angle also the synthesized products profile in figures 10-12 reveal one intense peaks. Significantly, according to the earlier discussion of the VO_X-NTs XRD pattern, the three distinct low angle reflection peaks are not present. Therefore, it can be inferred based on this XRD profiles that these products are not exclusively nanotubes which was confirmed previously by the SEM and TEM images taken. The (001) peak observed for h-NT2 can be the diffraction peak of some nanotubes formed and other lamellar products. It can be said that the d-value for this peak could still give us the inter layer distance of those nanotubes observed in the SEM and TEM results.

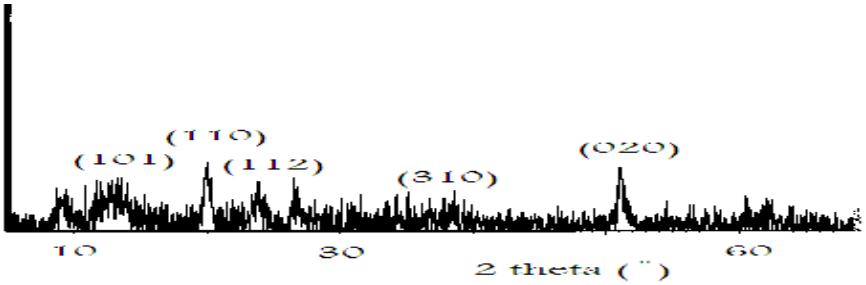

Fig. 9. XRD pattern of hexylamine template 1day HT [ICDD No.01-071-0454, V_3O_7].

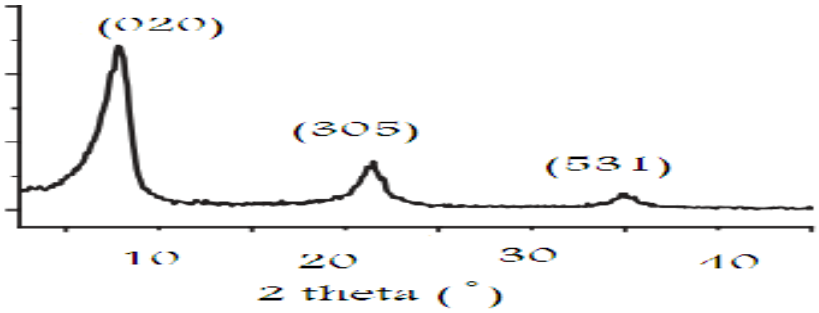

Fig. 10. XRD pattern of hexylamine template 2 days HT[ICDD No.01-078-0983, beta-V_6O_{13}].

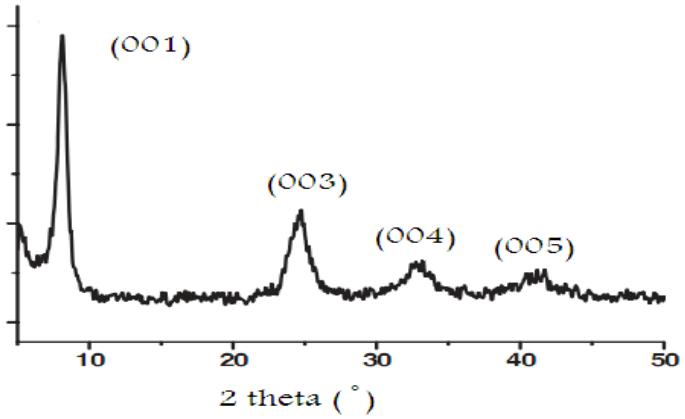

Fig. 11. XRD pattern of hexylamine template 3days HT[ICDD No.01-078-0983, beta-V_6O_{13}].

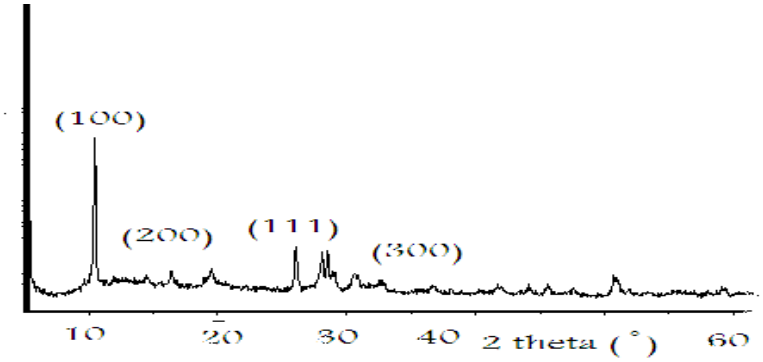

Fig. 12. XRD pattern of hexylamine template 4 days HT [ICDD No.01-078-0983, beta-V_6O_{13}].

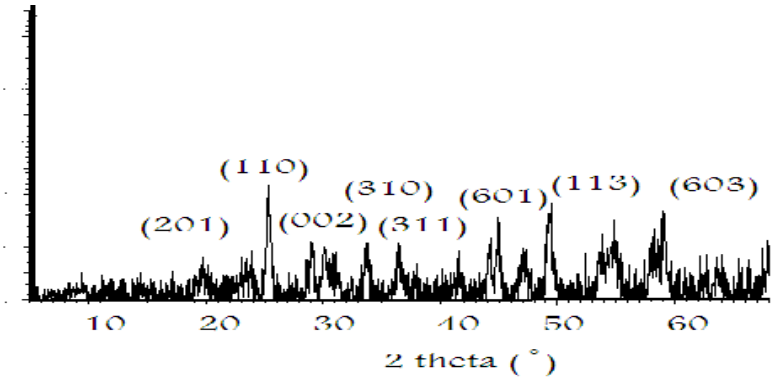

Fig. 13. XRD pattern of hexylamine template 5 days HT[ICDD No.01-081-2392,VO_2].

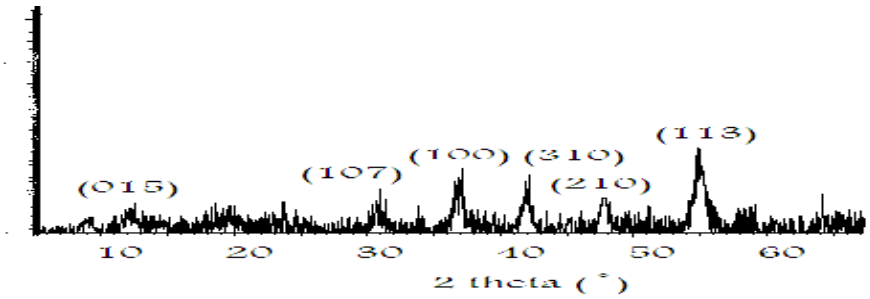

Fig. 14. XRD pattern of hexylamine template 7 days HT [ICDD No.01-071-0041, V_7O_{13}].

Table 5: The interlayer distance of VO_X-NTs. produced with 2 different templates.

Template	No. of carbon	Layer distance(nm) d_{001} XRD data
Hexadecylamine	16	3.5
Hexylamine	6	2

From the XRD pattern showed in Fig. 11, the layer spacing of phase in enlarged and can also understand this is for producing wide belts that confirm SEM and TEM result. By increasing the duration time it can be observed that the intense peak at low angle completely disappeared indicating the tubes and belt have transformed to flake phase. Table 5 shows the interlayer distance of the VO_X-NTs using different types of structure-directing template. The interlayer distance, as observed by other researchers (Oka *et al.*, 1990, Weeks *et al.* 2003, Weeks *et al.*, 1997, Li *et al.*, 2005, Chang, 2007, Chirayil and Whittingham, 1998, Laad and Muller-Hartmann, 2006, Chirayil and Whittingham, 1996, Wentzcovitch, and Allen, 1994, Morin, 1959, Goodenough, 1971) has been found to be proportional to the chain length of the organic template. From the XRD d_{001} results of this study, it confirms the observed trend. Thus, as the number of carbon atoms in the alkylamine chain increases, the corresponding interlayer distance of the nanotubes also increases. In addition, the theoretical calculated chain length of hexadecylamine is about 3.3 nm. This value is less than the observed interlayer distance. This can be attributed to the water molecules intercalated together with the protonated amines thereby increasing the basal distance.

The presence of water molecules had been confirmed by the FTIR results shown in the next section. Furthermore, there is a difference between the interlayer distances observed by different researchers. According to the results of Nesper, the inter layer distance for hexadecylamine template is about 3.35nm while other researcher found it to be 3.53nm to 3.7nm. This can be attributed to the difference between synthesis methods as well as embedded water molecules.

E. FTIR results

The Fourier transform infrared (FT-IR) spectrum of VOx-NTs (7 days hexadecylamine) shows strong absorptions at 2918 and 2850 cm^{-1}, which could be attributed to the stretching and bending modes of the different C-H vibrations in the hexadecylamine template. The assignment of the enormous bands between 3203–3411 cm^{-1} and 1621 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 1002 cm^{-1} could be attributed to a range of vibrations of the V-O type. The band at 1002 cm^{-1} might be assigned to V=O vibration, as seen with the FTIR of as well crystalline V_2O_5.The band at 2374 cm^{-1} might be signed NH stretch, 2046 C = N = S anilysm.

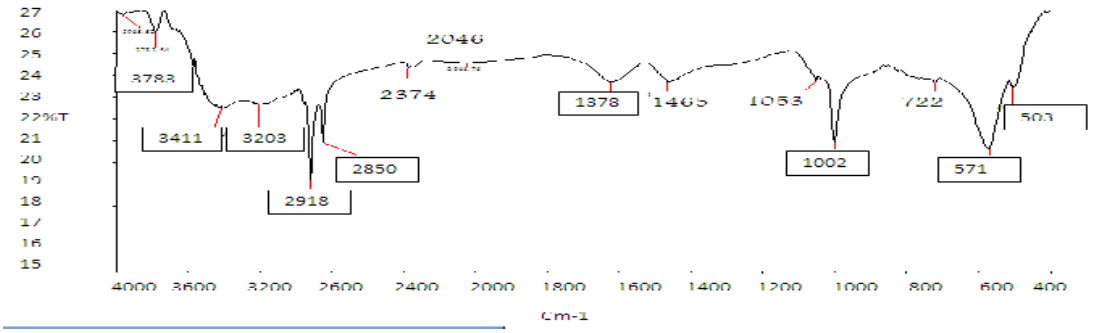

Fig. 15. FT-IR spectra of VOx-NTs (7 days hexadecylamine).

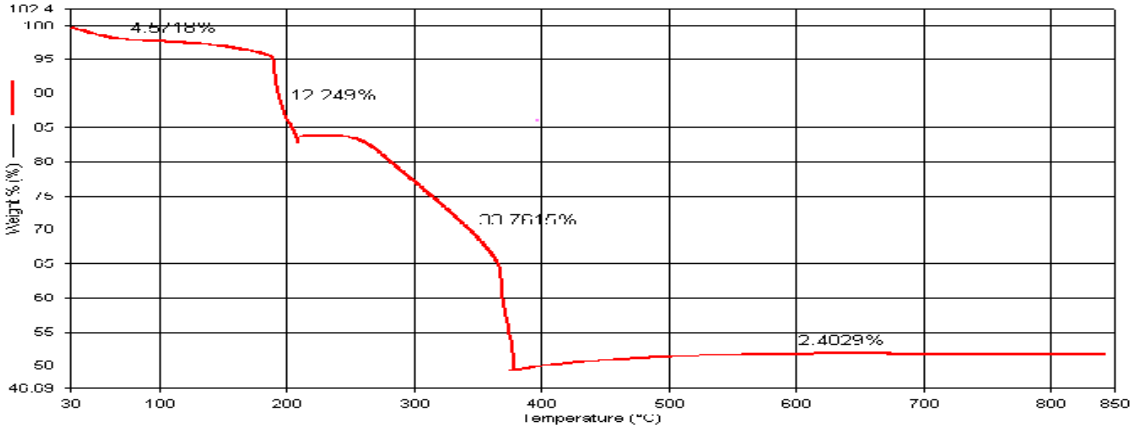

Fig. 16. TGA of VOx-NTs (7days, hexadecylamine).

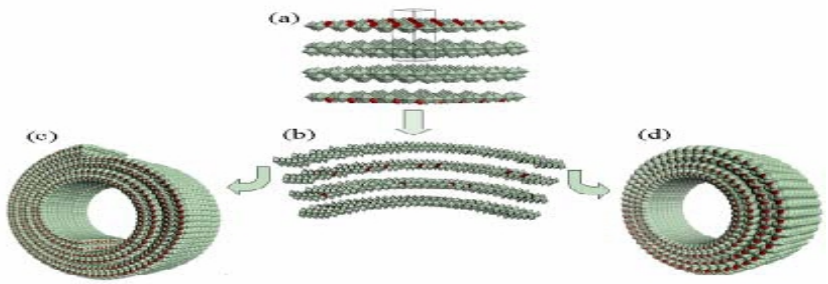

Fig. 17. Possible formation structure description of V_2O_5 nanotubes when bent (b) such layers may form nanoscrolls (c) or closed nanotubes (d).

Stretch, 1465 Cm^{-1} is CH_2 deformation, 1053 Cm^{-1} CH in plane bending and 722 Cm^{-1} CH out of plane deformation. These FT-IR characterization results may suggest that the compound synthesized has a lamellar formation with intercalated organic amines among various VOx groups.

F. Thermogravimetric analysis

The thermal stability of the VOx-NTs 7days hexadecylamine (Fig. 16) was studied via thermal gravimetric analysis in oxygen at a heating rate 15ºC/min between room temperature and 800º 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 486ºC. 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 480ºC, an increase in mass was observed, which could be attributed to the oxidation of vanadium as the compound transforms into crystalline vanadium pentoxide.

G. Formation mechanism and driving force

While the formation mechanism of the vanadium oxide nanotubes stays an open question. The gathered experimental data and morphological investigation make it possible to suggest a model for the tube formation. Fig. 17 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 Fig.17c. 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:

(i) The template has to create a certain distance between the layers (> 1.6 nm) providing high flexibility of the layers.

(ii) 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.

(iii) Slight misfit between the two parts of the vanadium oxide layer is reduced by bending.

(iv) Bending due to mixed valency (Gu *et al.*, 2003).

CONCLUSION

Vanadium oxide nanotubes can be successfully synthesized starting from $V_2O_5nH_2O$ 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 VO_X-NTs 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 changes 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 VOx-NTs.

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