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## Synthesis and Characterization of the Ti-Doped Vanadium Oxide Nanotubes

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### ABSTRACT

Synthesis of different kinds of nanotubes were considering after the discovery of carbon nanotubes, lately has been noticed synthesis of vanadium oxide nanotubes. Vanadium oxide nanotubes are made of multilayer scrolls with thick walls built up from several vanadium oxide layers. This compounds be used as catalysts, molecular sieves, absorbents and energy storage devices. In this research study for the first time Titanium doped vanadium oxide nanotubes (VONTs) were synthesized and characterized. These nanotubes have been synthesized by hydrothermal treatment at 180°C. Vanadium metal is known to be a catalytically active center in different molecular materials. Ti-doped VONTs were performed by using hydrothermal method. They are made of multilayer scrolls with thick walls build up from several vanadium oxide layers. The structure and morphology of the nanotubes were investigated by x- ray diffraction (XRD), scanning electron microscopy (SEM) and Brunaur Emmett Teller Theory (BET). In contrast to the undoped VONTs, the interlayer distance between oxide layers in the  $(V_{0.95}Ti_{0.05})_x$ ONTs increases owing to replacement of some V in nanotubes by Ti. The main objective of the study is to

titanium doped vanadium penta-oxide nanotubes. The results showed that Titanium 0.05wt% doped VONTs.

**Keywords:** Vanadium Oxide Nanotubes (VONTs), Titanium (Ti), Hydrothermal, Doped

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## Introduction

The discovery of the first family of nanotubes is that of carbon attributed to Ijima, following the discovery, prompted the investigation of other layered materials that may form similar tubular structures [1]. The carbon nanotubes have special structure with potential application, due to physical properties [2,3]. Research in this nanotubes has showed an interesting import to the science [4,5].

The considerable effort has been placed on the synthesis of different kinds of nanotubes. Among these one - dimensional nanostructure transition metal oxides, the vanadium oxide nanotubes (VOX-NTS) that synthesized for the first time by Spahr et al [6].

A large number of vanadium oxides have been reported [1] and these can be classified in those with a unique valance state ( $\text{VO}_x$ ,  $x=1.0, 1.5, 2.0$  and  $2.5$ ) or in those with mixed valance state, including the magneli phases [7].

Vanadium oxide nanotubes (VOX-NTS) are made of multilayer scrolls with thick walls built up from several vanadium oxide layers especially interesting with various properties [8-9].

The recently discovered VOX nanotubes (VONTs) are especially interesting due to their tunable physical and chemical properties [10] and are useful material, due to their high potential applicability in electrochemical devices and catalytic processes (chanderppa.,2003, Solsona.,2001) [10]. These nanotubes have been synthesized with various methods such as sol-gel, and hydrothermal [11,12] with  $\text{V}_2\text{O}_5$  precursors and primary amines. The amin approach to prepare vanadium oxide nanotubes and some other nanotubes was with use of organic molecules as structure- directing agents [9].

The interaction between organic molecule and inorganic precursors could be coordinative interaction, electrostatic interactions, or even hydrogen bonding [13].

Generally, the VONTs were obtained by a soft – chemistry synthesis involving an amine with long alkyl chains as an organic molecular, structure directing template. In a hydrothermal synthesis, the reaction path is deponsive to the experimental conditions such as temperature, PH and hydrothermal treatment time

[14]. Hydrothermal method used for doped- inorganic nanotubes such as vanadium oxide nanotubes. Vanadium pentoxide nanotubes are multiwalled and formed by rolling up of V-O and often have a scroll-like structure [15].

The tube walls consist of vanadium oxide layers between which the organic molecules are embedded. In contrast to the carbon nanotubes, consisting of closed concentric C layers, only a few VO<sub>x</sub>-NTs are of this type, whereas most of the tube walls comprise scrolls of layers or discorded layer arrangements. The irreversible exchange of embedded monoamines against diamines occurs readily and under preservation of the tubular morphology. A modification of the tube walls can be achieved by treatment with various metal cations [16].

The ends of these nanotubes are open, so different cations can be introduced into the inner cavity of the nanotubes [17]. Mai et al. (2003), Jiao et al. (2006), Li et al. (2007), Rouhani et al (2010), Park et al (2015) doped-vanadium oxide nanotubes with molybdenum, Tungsten, Copper, Rhenium and Nickel respectively [7,15]. In this work, Ti-doped VONTs were synthesized and characterized for the first time.

## Experimental

V<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub> and C<sub>12</sub>H<sub>25</sub>N as template were used for synthesizing the desired materials. For preparation of V<sub>0.95</sub> Ti<sub>0.05</sub> ONTS stoichiometric amounts of the desired reactant were mixed in distilled water and was stirred for 48h in air.

The resulting suspension was transferred into a Teflon- lined autoclave with a stainless steel shell. The autoclave was kept at 180°C for about a week. The final black product was washed with absolute Ethanol and Hexane and dried at room temperature. X- ray powder diffraction (XRD) patterns of the sample were obtained using a Philips pw diffraction with Cu  $\alpha$  radiation and  $\lambda=1.54059\text{\AA}$ . The morphology was studied by scanning electron microscopy (SEM) on a EM3200 KYKY and by BET Belsorp mini.

## Results

XRD analyses at low angles were used to probe the success of the exchange reaction Figure 1(VONTs). Figure 1 shows the XRD pattern of vanadium oxide nanotubes. The pattern shows the intense peaks occurring in between 10° to 60° 2-theta angle. The relationship between the wave length of the x-ray beam,  $\lambda$ , the angle of diffraction,  $2\theta$ , 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. Two sets of diffraction patterns can be observed.

Figure 1(VONTs-Ti) shows the x-ray diffraction (XRD) patterns of Ti-doped VONTs. The peaks at  $2\theta < 10^\circ$  related to the distance between the NTs interlayers.

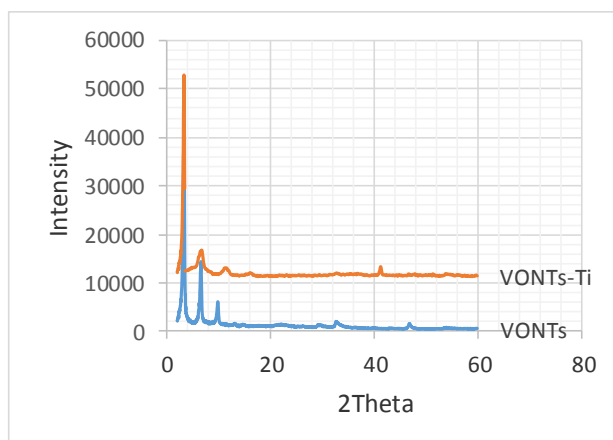
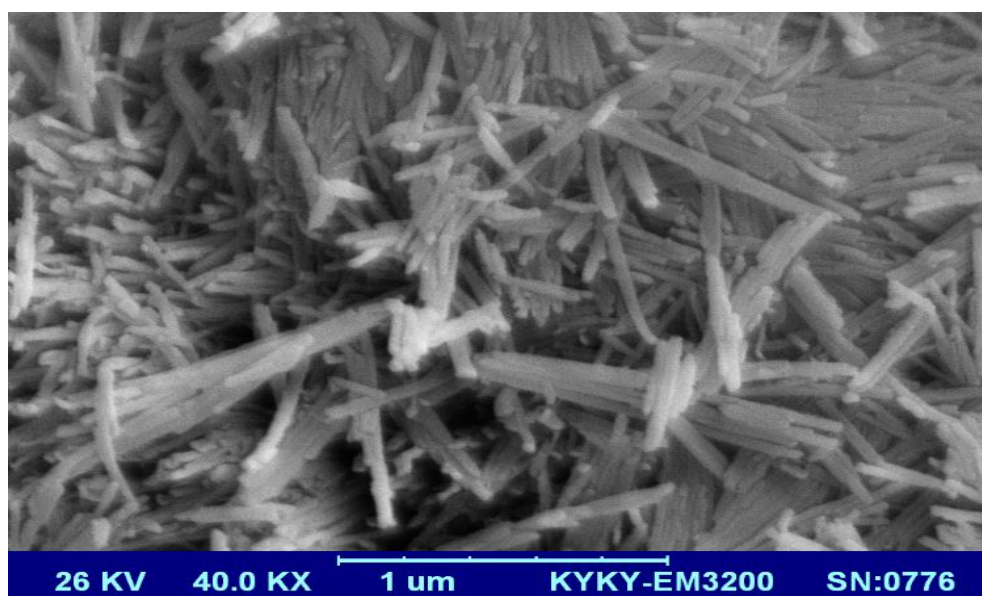
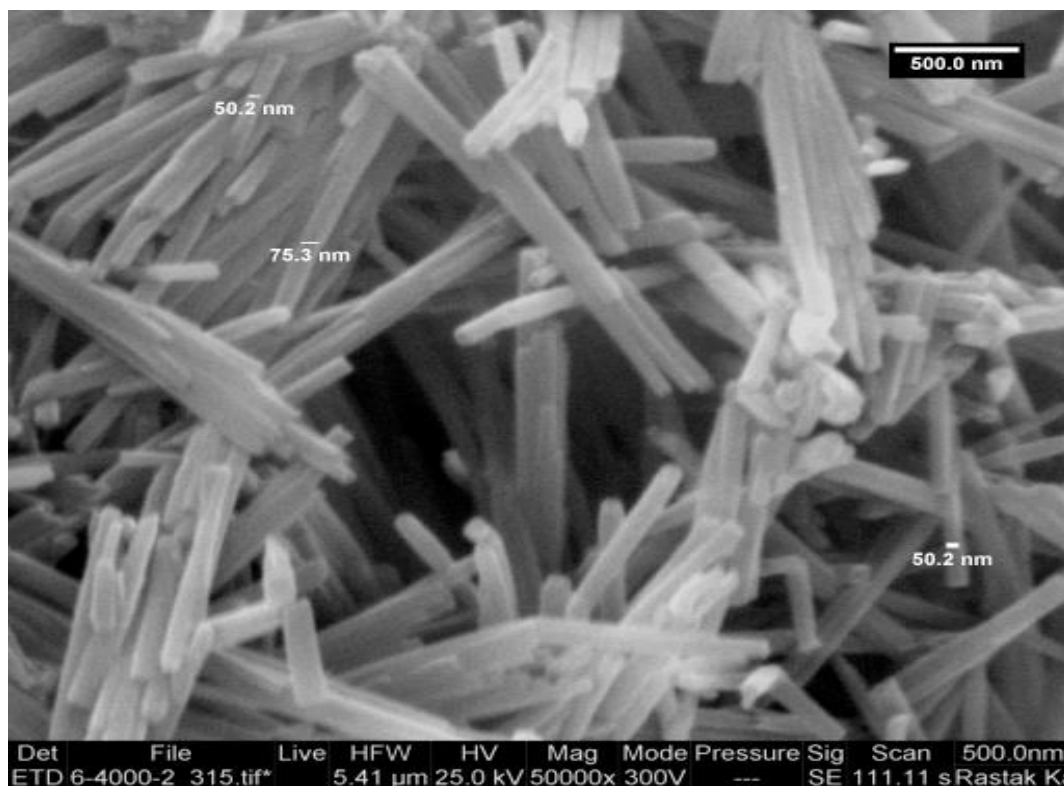


Figure 1: The XRD of VONTs and VONTs-Ti

The morphology of the samples was observed by SEM. Figure 2,3 shows the SEM images of the VONTs and  $V_{0.95}Ti_{0.05}$  ONTS. The outer diameter of the nanotubes was measured by SEM technique. The average outer diameters of VONTs and  $V_{0.95}Ti_{0.05}$  ONTS were 30-70nm.



*Figure 2: The SEM image of V ONTs**Figure 3: The SEM images of the V ONT-5%Ti*

Brunauer–Emmett–Teller (BET) theory aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of materials. In 1938, Stephen Brunauer, Paul Hugh Emmett, and Edward Teller published the first article about the BET theory in the *Journal of the American Chemical Society*.

The BET theory applies to systems of multilayer adsorption and usually utilizes probing gases that do not chemically react with material surfaces as adsorbates to quantify specific surface area. Nitrogen is the most commonly employed gaseous adsorbate used for surface probing by BET methods. For this reason, standard BET analysis is most often conducted at the boiling temperature of N<sub>2</sub> (77 K). Further probing adsorbates are also utilized, albeit with lower frequency, allowing the measurement of surface area at different temperatures and measurement scales. These have included argon, carbon dioxide, and water.

Specific surface area is a scale-dependent property, with no single true value of specific surface area definable, and thus quantities of specific surface area determined through BET theory may depend on the adsorbate molecule utilized and its adsorption cross section. The N<sub>2</sub> adsorption- desorption isotherms and

pore size distribution of Ti- doped VONTs are shown Figure 4. The specific surface area ( $S_{BET}$ ), pore volume ( $V_{por}$ ) and average pore size ( $d_{por}$ ) of VONTs and VONTs-Ti were measured by physisorption of nitrogen according to the BET method.

The BET surface area of the Ti-doped VONTs was determined from the  $N_2$  adsorption-desorption isotherm using the BJH method are summarized in table 1. The hysteresis loop of VONTs opened at a relative pressure of 0.55, whereas those of the VONTs-Ti opened at lower relative pressure (Figure 5). The BET specific surface area of the VONTs should increase with doping. The information obtained from absorbing an infrared (Absorbance or A), which changes with the track of the wavelength ( $\lambda$ ) of radiation from the source, is displayed as a spectrum. The displayed shape 6 shows the FTIR spectrum of a substance. As shown in the figure, in this shape, the width of the axis of the transmissivity (Transmittance or T) is expressed in terms of percentage and axis of the wavelengths of the waveform (Wavenumber or  $\bar{\nu}$ ) corresponding to the infrared light wavelength in  $cm^{-1}$  it shows. What can be achieved by analyzing the FTIR spectrum is that each peak in the infrared spectra represents the amount of absorption in the corresponding wave number and is generated by a given chemical bond. The Fourier transform infrared (FT-IR) spectrum of VONTs-Ti showed in figure 6.

The strong absorption at  $2920.81$  and  $2851.36\text{ cm}^{-1}$  which could be attributed to the stretching and bending modes of the different C-H vibrations in the template. The  $3465.77\text{ cm}^{-1}$  correspond to O-H vibrations. Probably finger point at Adsorption bands  $530.87\text{ cm}^{-1}$  is the Ti-O type.

Table1: The surface area determination using the BET method

	VONTs	VONTs-Ti
<b>Specimen Specific Absorption</b>	<b>12</b>	<b>15</b>
<b>(m<sup>2</sup>/g)</b>		
<b>Pore Volume (m<sup>3</sup>/g)</b>	<b>0.04</b>	<b>0.01</b>
<b>The mean diameter of the pores</b>	<b>14.48</b>	<b>15.5</b>
<b>(nm)</b>		

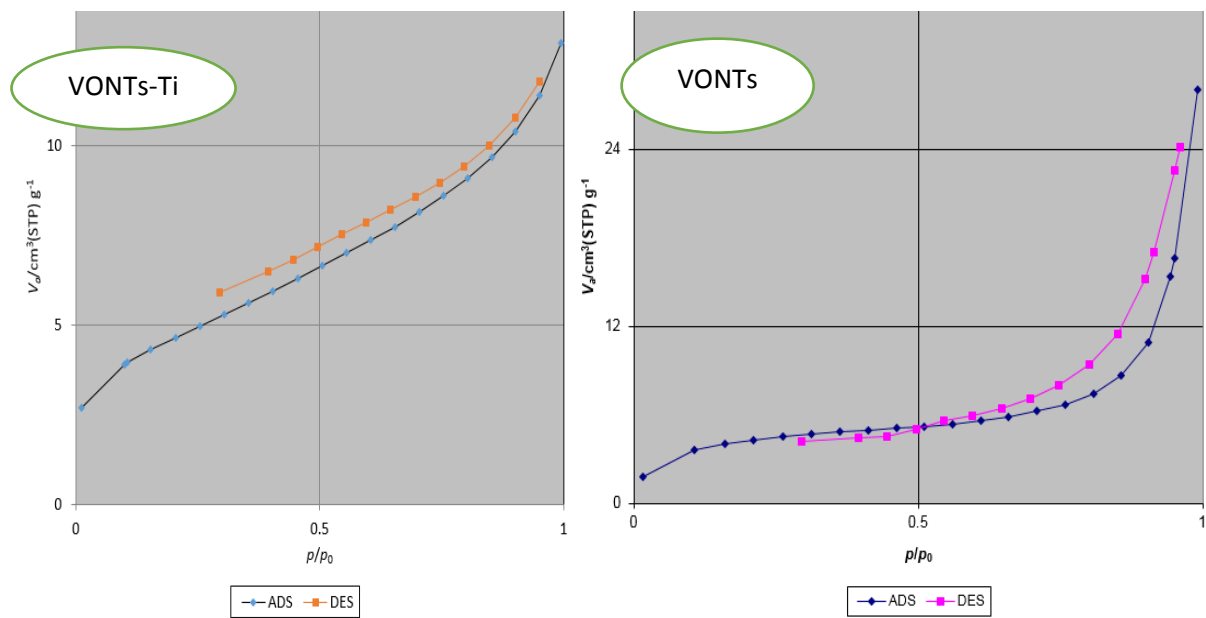


Figure 4: The  $N_2$  adsorption- desorption isotherms

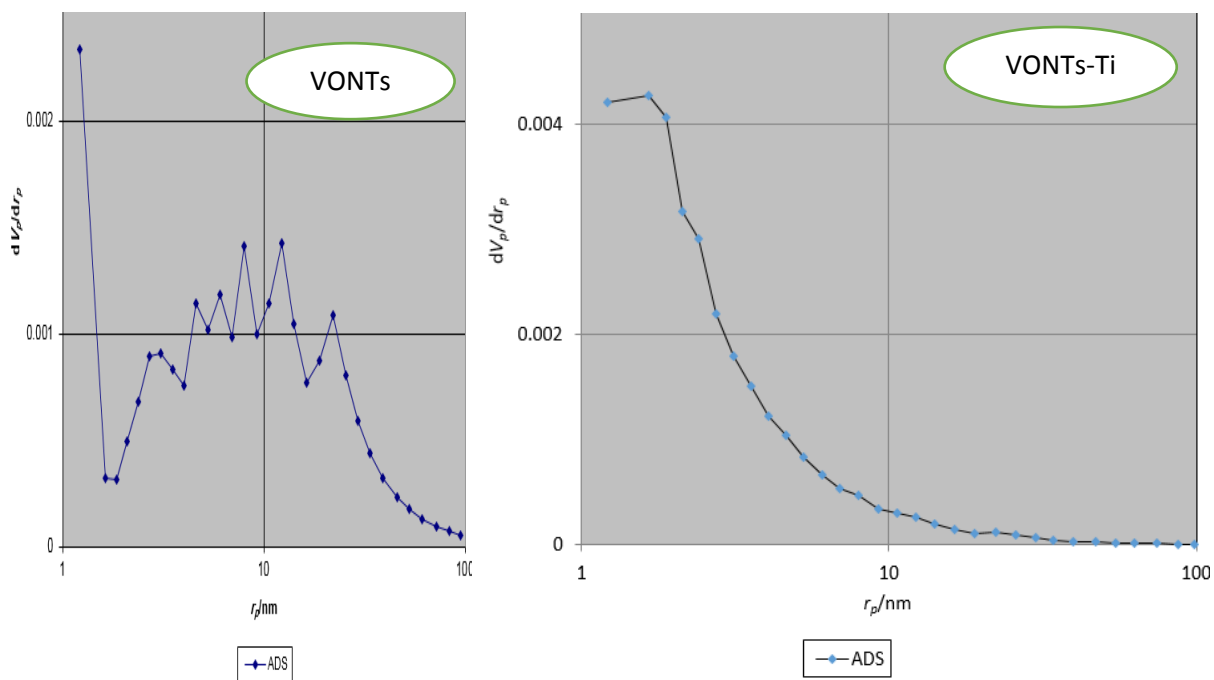


Figure 5: The BJH of VONTs-Ti and VONTs

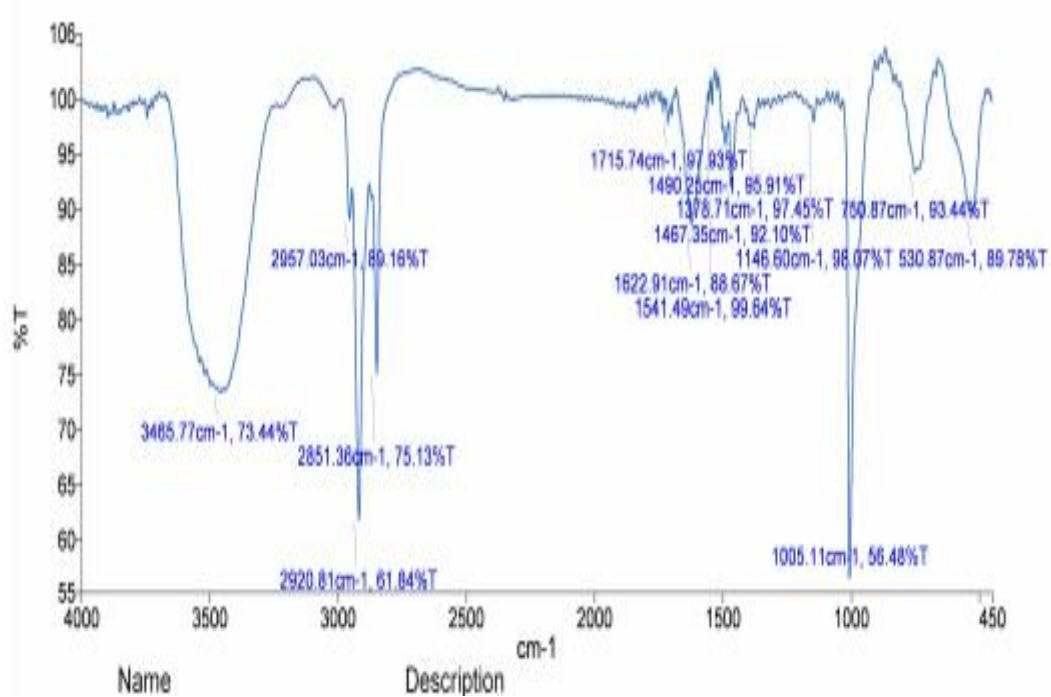


Figure 6: FT-IR Spectra of VONTs-Ti



## Discussion

XRD analyses at low angles were used to probe the success of the exchange reaction Figure 1. Two sets of diffraction patterns can be observed: The (001) set of reflection at low diffraction angles corresponds to a well-ordered layered structure and the (hko) series corresponding to the two dimensional structure of the  $\text{VO}_x$  layers which form the walls of  $\text{VO}_x$ -NTs. The d values of the (001) peaks are 2.65nm, which reflects the distance between the  $\text{VO}_x$  layers in the nanotubes.

Figure 1(VONTs-Ti) shows the x-ray diffraction (XRD) patterns of Ti-doped VONTs. In the  $\text{V}_{0.95}\text{Ti}_{0.05}$  ONTS, that Ti atoms enter the crystalline lattice of vanadium oxide layer in the nanotubes. However, in contrast with the undoped sample, there is a noticeable shift of the 001 peak toward lower diffraction angle for the Ti-doped sample corresponding to increase of the inter layer distance. The change for inter layer can be attributed to the replacement for V vanadium oxide nanotubes by Ti with a large ionic radius.

The morphology of the samples was observed by SEM in Figures 2 and 3. The SEM observations indicated that the samples had a tubular morphology and nanometric size. The outer diameter of the nanotubes was measured by SEM technique. The average outer diameters of VONTs and  $\text{V}_{0.95}\text{Ti}_{0.05}$  ONTS were 30-70 nm. The  $\text{N}_2$  adsorption - desorption isotherms and pore size distribution of Ti- doped VONTs are shown Figure 4. As shown in Fig4, the BJH pore size of Ti-doped VONTs is centered a wide distribution, broader than that of VONTs.

The BET surface area of the Ti-doped VONTs was determined from the  $\text{N}_2$  adsorption-desorption isotherm using the BJH method are summarized in table 1.

The pore volume and diameter of the pores VONTs-Ti were decreasing than VONTs. The increase in the surface area of the absorption of doped nanotubes, while diminishing the diameter and volume of the pores of these nanotubes, indicates that there are more adsorption sites. As the number of more gas molecules at this level is absorbed by larger and smaller pores.

## Conclusions

The purpose of this study was Ti-doped VONTs. Ti-doped vanadium oxide nanotubes were synthesized with  $V_2O_5$  precursors and primary amines successfully. The sample were prepared using a hydrothermal of the 5at% titanium. In the doping done, increase of the inter layer distance ( $d_{\text{value}}$ ) in the  $V_{0.98}Ti_{0.05}$  ONTs with an attributed to the replacement  $Ti^{4+}$  with  $V^{5+}$  ions. The VONTs-Ti had tubular morphology with multiwall structures. The BET specific surface area of the VONTs should increase with doping. The research output of this study, Ti-doped vanadium oxide nanotubes can be useful for catalytic processes.

## References

- [1]. C. N. R. Rao, A. Govindaraj, Nanotubes and nanowires, 2<sup>nd</sup> edition, RSC nanoscience & Nanotechnology NO.18, Royal society of chemistry (2011).
- [2] E. Kianfar, J. sci. Tech., 8, 455 (2015).
- [3] L. E. Luong, ACS. Catal., 4, 3393 (2014).;
- [4] S. Haffer, C. Lader, Microporous. Mesoporous. Mater., 196, 300 (2014).
- [5] M. H. Habibi, M. Mardani, spectrochim. Acta. Mol. Biomol. Spectros., 137, 785 (2015).
- [6]. M. E. Spahr, B. s. Bitterli, p. Nesper, R. Haaaso, P. J. Novak, Electrochem. SOC. 146, 2780 (1999).
- [7]. D. Rodolfo, M. E. Sanchez, J. Saleta, H. E. Curiale, S. R. Troiani, M. Guevara, R. Malta, R. MToresi, J. Sciencedirect., 10, 333 (2007).
- [8]. x. Liu, c. Taschner, A. Leonhard, M. H. Rummeli, T. Pichler, T. Gemming, B. Buchner, M. Knupfer, J. phys. Rev., B72, 115407 (2005).
- [9]. G. T. Chandrappa, N. Steunou, S. Cassagnon, C. Bavais, J. Lavage, J. catal. Today. 78, 85 (2003).
- [10]. E. Kianfar, M. Barghernejad, Y. Rahimdahti, J. Biol. Chem., 7, 1671 (2015).
- [11]. A. V. Grigoriera, A. B. Trasov, E. A. Goodilin et al. Mendeleev. Commun., 18, 6 (2008).

- [12] M. Roppolo, C. B. Jacobs, S. uperli, N. A. Chernova, M.S. Wittingham, *Mater. Sci.*, 43, 4742 (2008)
- [13] L. Mai, W. Chen, Q. xu, and et al, *J. solidstate. Commun., Electro analysis*, 23, 1752 (2011).
- [15] R. Rouhani, H. R. Aghabozorg, M. A. sadabad, *J. Taylor. Francis.*, 23, 1018 (2011).
- [16] J. M. Reinoso, H. J. Muhr, F. Krumeich, F. Bieri, R. Nesper, *J. Helvetica. Chem. Acta.*, 83, 265 (2000).
- [17] A. V. Grigor'eva, A. V. Ani kina, A. B. Tarasov, E. A. Gudilin, A. K. Kont'Ko, V. V. Volkov, K. A. Dembo, Y. D. Tret'yakov, *doklady. chem.*, 410, 165 (2006).