



Original Research Article

Study of Saturation and Supersaturation of Zr-Doped Vanadium Oxide Nanotubes

Azita Salimian*

** Department of chemistry, North Tehran Branch, Islamic Azad University, Tehran, Iran*

*Corresponding author E-mail: azita_salimian_chem@yahoo.com

ABSTRACT

Vanadium oxide nanotubes belong to inorganic nanotubes. One inorganic nanotubes (WS_2) synthesized in 1992. Vanadium oxide nanotubes discovered by spahr in 1998. Vanadium oxide nanotubes are used in chemical, bio, electronics and catalysts industry. Many applications of these nanotubes have not yet been discovered. Especially when these nanotubes are doped with different elements. The structure of these nanotubes is flexible. This makes it possible to explore different ideas. In this research study zirconium – doped vanadium oxide nanotubes (VONTs) with different percentages were synthesized. Zr-doped VONTs were performed by hydrothermal method. Zr-VONTs prepared (0, 2, 10, 20, 30, 50 and 60) %wt. The structure and morphology of the nanotubes were investigated by x- ray diffraction (XRD), scanning electron microscopy (SEM). The results showed that zirconium 2%wt doped VONTs completely but in others amount in addition doped, was forming zirconium oxide phase. Also with increase percent of doping Zr

into vanadium oxide nanotubes were formed monoclinic structure of ZrO_2 . The increase of doping level of the ZrO_2 phase leads to change interlayer distances.

Keywords: Vanadium oxide nanotubes (VONTs), Zirconium (Zr), Hydrothermal, Doped

Introduction

nanoscale have preferably one to one hundred nanometers, and this size leads to physical and chemical properties. Nanostructured materials, are considered to be a part of nanomaterials, they have a special structure and characteristics, such as Carbon nanotubes, nanowires and nanofibres. The most important of these are: increasing the surface area and entering the particle size into the quantum effect area. The following are the uses of nanoscale materials as Solar and cosmic plates, Complex compound construction, Surface coatings, Extremely hard-to-paint tools and solvents, Environment-Fuel cells, Screens, Batteries, Additives for fuel, Magnetic materials, Medical equipment, Machine ceramics, and Clothing War. Nanotubes are nanoparticles that made on a nanoscale by nanoparticles. The nanotubes are considered to be fullerene group. The diameter of a nanotubes is about a few nanometers. While its length can reach several millimeters. Tensile strength 100 times the steel, thermal conductivity to other compounds with the exception of pure diamonds, high electrical conductivity, ability to carry a stream higher than copper, a very large magnetic moment, and the ability to emit and absorb light from the prominent features of nanotubes. Nanotubes are many applications in technology and industry. One of the most important types of nanotubes is carbon nanotubes. Carbon nanotubes have two main groups: single-wall and multi-wall. carbon nanotubes are ability to cross the plasma membranes. Nanotubes have significant properties in terms of electrical conductivity, flexibility and strength. Nanotubes are used as fillers in nano-composites. Other groups of nanotubes, are inorganic nanotubes. Inorganic nanotubes were considering after the discovery of carbon nanotubes [1]. Inorganic nanotubes are synthesized from metals and non-metals. One inorganic nanotubes (WS_2) synthesized in 1992 [2], and V_2O_5 nanotubes by Spahr in 1998 [3].

Researchers gradually realized the properties of the physical chemistry of these nanotubes. The first reports intense research for their potential as gas sensing applications [1]. Every day,

they tried to improve the quality and yield of these nanotubes. Since 2003, various elements have been doped on vanadium oxide nanotubes. Mai et al (2003) [4] reported doping molybdenum, tungsten, and copper. In particular VONTs have recently attracted attention because they offer a large active surface area and numerous channels for ionic transport owing to their multiwalled tubular structures [5-10]. The ends of these nanotubes are open, so different cations can be introduced into the inner cavity of the nanotubes [11]. Mai et al (2003) reported doping molybdenum, tungsten, and copper. Li et al (2007) and jiao et al (2006) and rouhani et al (2011) respectively [1,3,5] [12-16]. In this present work, Zr doped vanadium oxide nanotubes (VONTs) were prepared by hydrothermal method.

Experimental

The Zr doped VONTs were prepared with V_2O_5 (> 99 %, merck) ZrO_2 (>99%, merck) and dodecylamine (merck) as a template were mixed in the molar ratio $(V_{1-x}Zr_x)_y$ ONTs (x=0, 0.02, 0.1, 0.2, 0.3, 0.5, 0.6). In distilled water, and the mixture were stirred for 48 h in air. The resulting mixture was shall. The autoclave was kept at 180C for 7 days and then allowed to cool naturally. The obtained product was washed with hexan and absolute ethanol and then dried. X-ray powder diffraction (XRD) patterns of the prepared samples were obtained using pw 3064 with cu radiation (40kv,40mA). Scanning electron microscopy (SEM) using a Em – 3200 at 25 KV. The morphologies and structures of the obtained products were observed by SEM.

Results and discussion

The x-ray diffraction (XRD) patterns of $V_{1-x}Zr_x$ ONTs (X=0, 0.02, 0.1, 0.2, 0.3, 0.5, 0.6) are shown in figure 1, 2, 3 and 4 respectively. The peaks are $2\theta = 1- 60^\circ$. The peaks at $2\theta < 10^\circ$ indicated nanotubes formation. The peak with the highest intensity at the low diffraction angle indicates the inter layer distances of the nanotubes. All samples have highest intensity. Therefore, the tubular form of nanotubes is formed in all samples. As the dope reaches from 20%wt to 60%wt, the intensity of the first peak is reduced. In the angles more than 10° peaks appear. The 10%wt magnitude was then seen at 28.22° and 31.5° peaks, which indicates the presence of zirconium oxide phase. The presence of peaks at 34° , 35° , 48° , 50° Generally, the data obtained from the X-ray model indicate that: Firstly, with the increase in the amount of doping matter (zirconium oxide) and the formation of nanotubes formed, we encountered a mass

of zirconium oxide nanoparticles. Considering the zirconium oxide is monoclinic. Secondly, with increasing doping percentage, peaks of the monoclinic phase have been shown to be more intense. This process showed that by increasing the zirconium oxide phase, the distance between the walls of the vanadium oxide nanotubes increased to 20%wt. This could indicate the presence of oxide zirconium between the walls of the vanadium oxide nanotubes, without destroyed vanadium oxide nanotubes. From 30% at onwards, zirconium oxide nanoparticles sit cumulatively between the walls and act as a false wall and ultimately lead to a decrease in wall spacing. In other cases without 2%at, saturation doped was observed and in over 60% super saturation doped. In the samples of (20, 30, 50,60) %wt increased the peaks at $2\theta = 28.22^\circ$, 31.5° , 34° , 35° , 48° , 50° gradually. In the bulk region ($2\theta > 10^\circ$) grew ZrO_2 phase and indicated monoclinic structure.

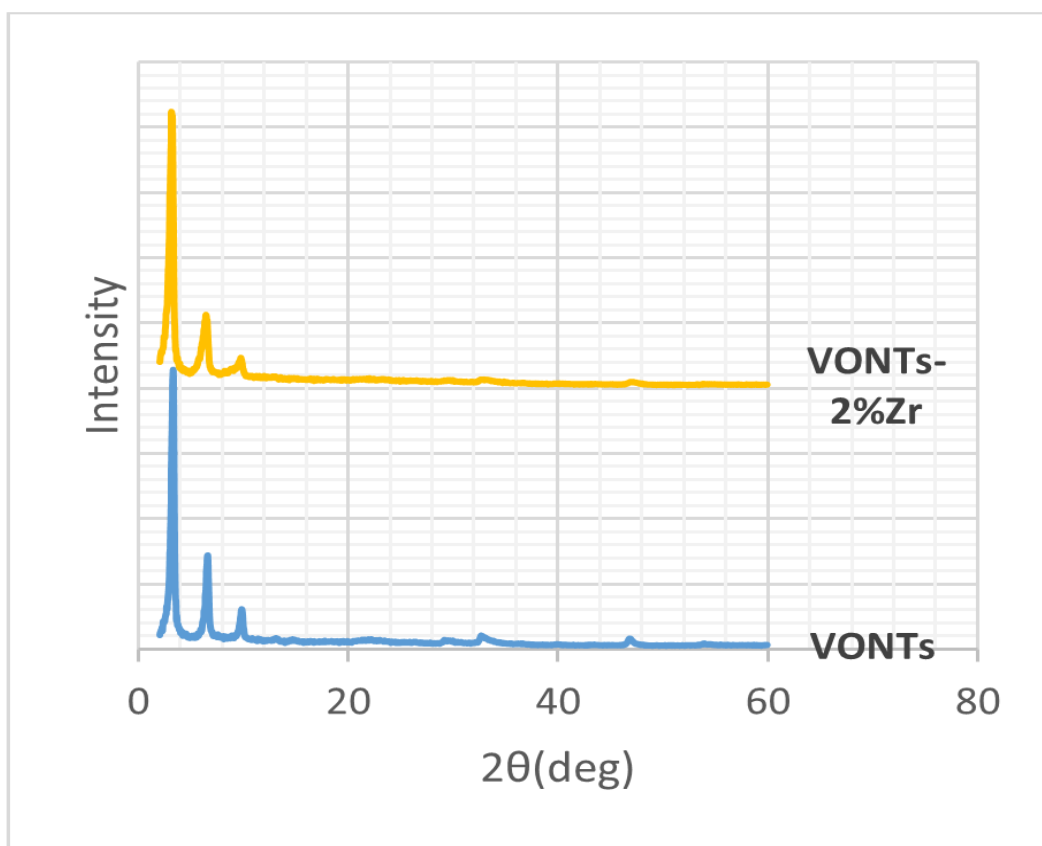


Figure 1. XRD patterns of 2%Zr-doped VONTs and VONTs ($2\theta=1-60^\circ$).

Only in the $V_{0.98}Zr_{0.02}$ ONTs perfect doping done and increase of the inter layer distance (d_{value}) in the $V_{0.98}Zr_{0.02}$ ONTs and $V_{0.9}Zr_{0.1}$ ONTs than VONTs could be attributed to the replacement of vanadium ions in VONTs by zirconium ions with larger ionic radiuses [11]. The scanning electron microscopy (SEM) shown in figure (5-8). The SEM images indicated that the $V_{1-x}Zr_x$ ONT ($x= 0, 0.02, 0.1$) have tubular morphology and other nanotubes have layers zirconia.

In the SEM images uper of 20% wt doping Zr, increased bulk and agglomeratey from. The reason that were increased zirconia phase. The outer diameter of the VZrONTs varied from 20 to 50 nm.

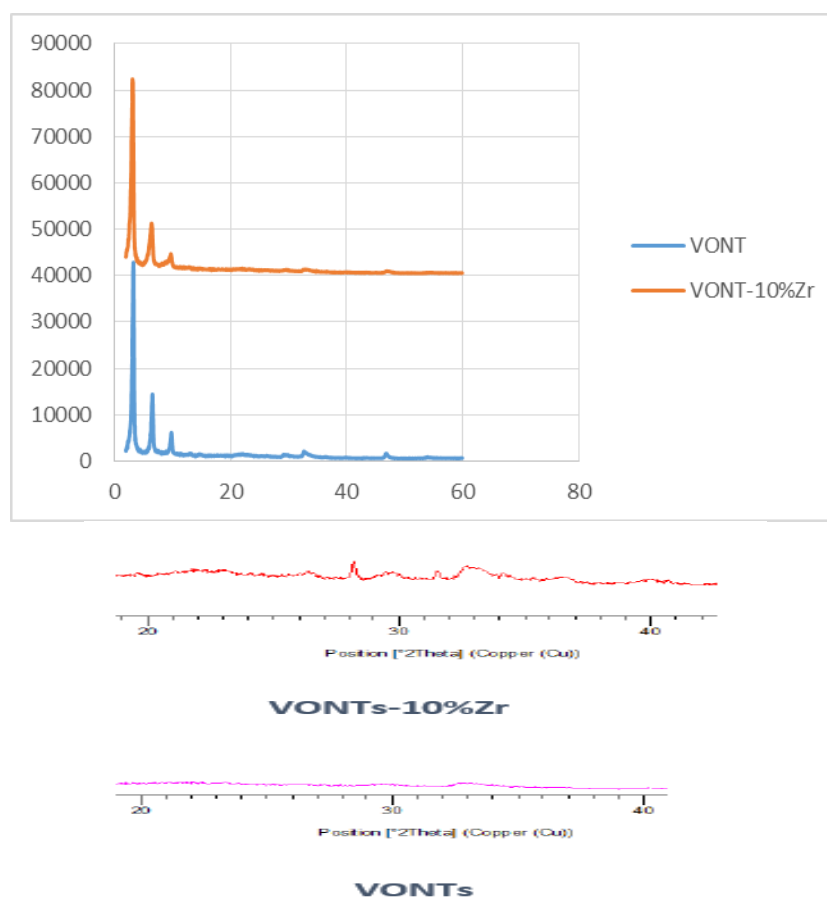


Figure2: XRD patterns of VONTs and 10%Zr-doped VONTs

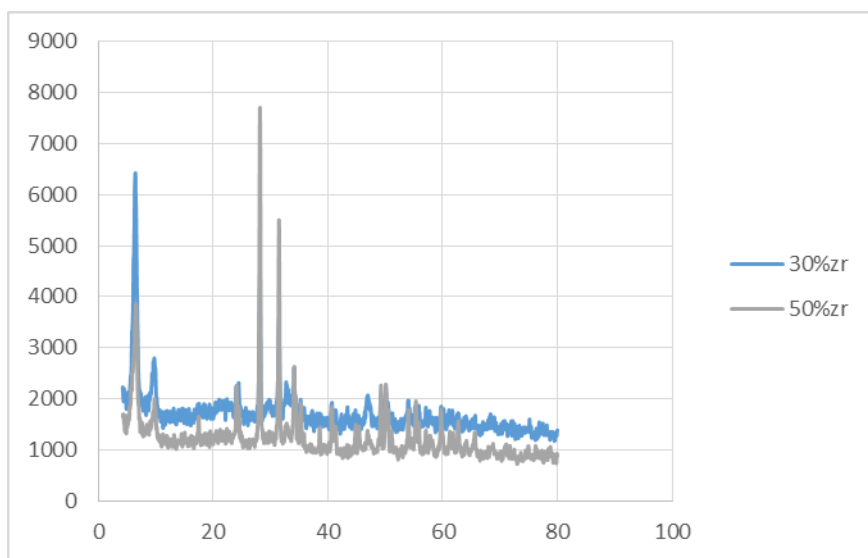


Figure3: XRD patterns of (30:50)%Zr-VONTs

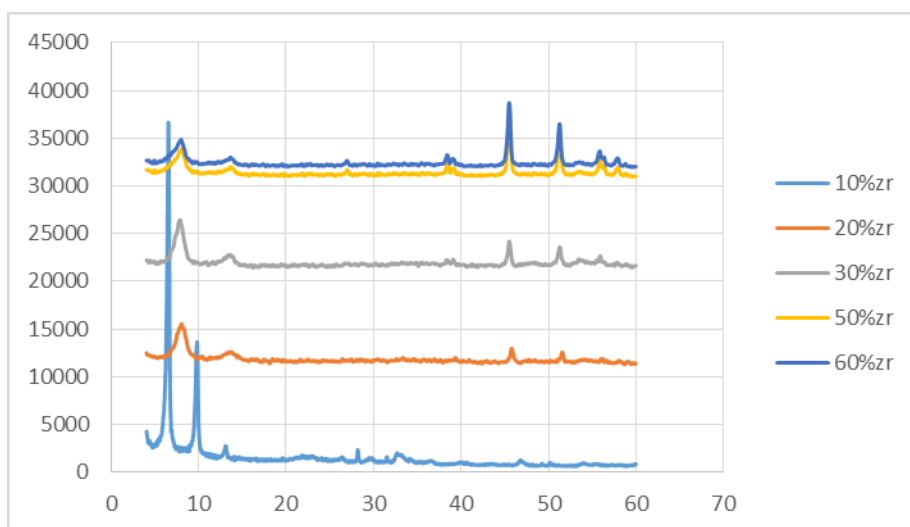


Figure4: XRD patterns of different percent Zr-doped VONTs

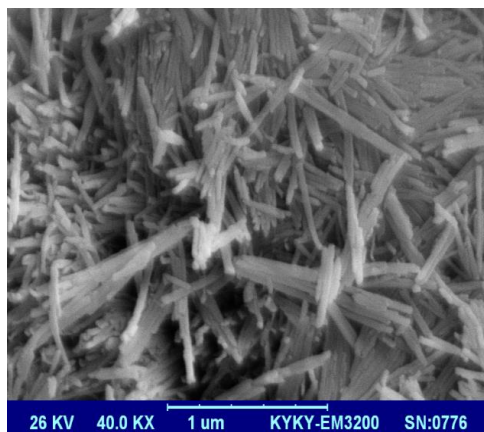


Figure 5: SEM image of VONTs

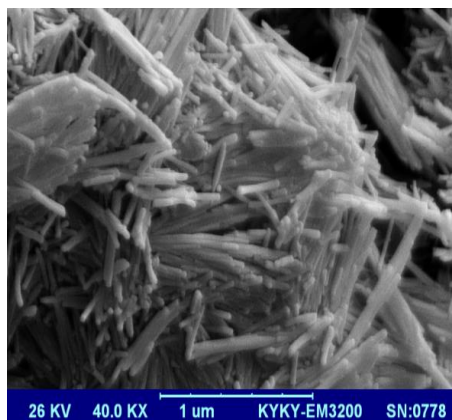


Figure 6: SEM image of 10% Zr-doped VONTs

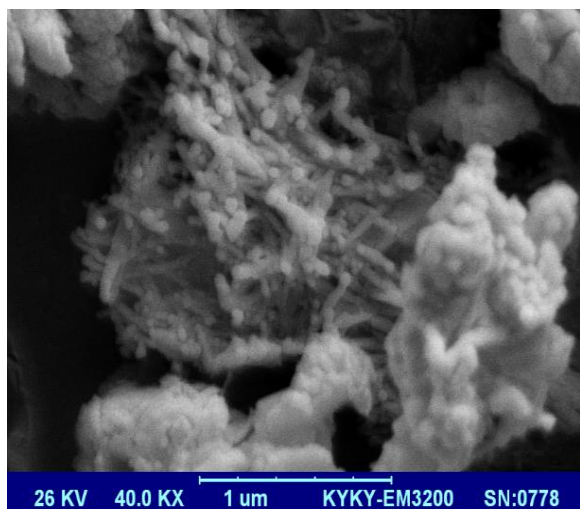


Figure 7: SEM image of 20% Zr-doped VONTs

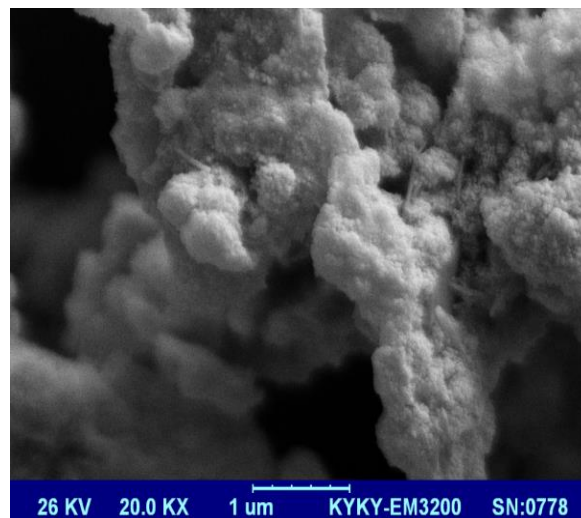


Figure 8: SEM image of 60% Zr-doped VONTs

Conclusions

According to results, doping of Zr (0, 0.02, 0.1, 0.2, 0.3, 0.5, 0.6) %wt into VONTs prepared by hydrothermal method. The results showed that doping of $V_{0.98}Zr_{0.02}$ VONTs were synthesized as whole, from doping of 20% to 60% synchronized replacement Zr^{4+} with V^{5+} ions were formed ZrO_2 phase. That increasing amount doped changed morphology zirconia gradually. The morphology changed to agglomerate form, because increased ZrO_2 phase.

References

- [1] R. Rouhani, H.R. Aghabozorg, and M.A. Asad Ababdada, synthesis and characterization of Re-, MO-, and W- doped vanadium oxide nanotubes, Taylor & Francis Groups, LLC, 1018-1021, 2011
- [2] R. Tenne, L. Margulis, M. Genut, G. modes, *Nature* 1992, 360, 444.
- [3] M. E. Spahr, P. Bitterli, R. Nesper, M. Muller, F. Krumeich, H. U. Nissen, *Angew. Chem., Int. Ed.* 37 (1998) 1263.
- [4] Mai, L. Q; chen, W; Xu, Q; peng, J. F, Zhu, Q. Y. Mo doped vanadium oxide nanotubes: microstructure and electrochemistry *chem. Phys. Let* 2003, 382, 307-312.
- [5] R. Tenne, L. Margulis, M. Genut, G. modes, *Nature* 1992, 360, 444.
- [6] Y. Feldman, E. Wasserman, D. j. Srolowitz, R. Tenne, *Science* 1995, 267, 222.
- [7] N. G. Chopra, R. G. Luyken, K. Cherrey, V. H. Crespi, M. L. Cohen, S. G. Louie, A. Zettl, *science* 1995, 256, 966.
- [8] H. Nakamura, Y. Matsui, *L. Am. Chem. Sock.* 1995, 117, 2651.
- [9] P. Hoyer, *Langmuir* 1996, 12, 1411.
- [10] M. E. Spahr, P. Bitterli, R. Nesper, M. Muller, F. Krumeich, H. U. Niessen, *Angew. Chem. Int. Ed.* 1998, 37, 1263; *Angew. Chem.* 1998, 110, 1339.
- [11] M. Kanttcheva, *Physical Chemistry Chemical Physics* 2 (2000) 3-43-3048.
- [12] D. H. Galvan, J. H. Kim, M. B. Maple, M. Avalos – Berja, E. Adem, *Fullerene Sci, Technol*, 2000, 8, 143.
- [13] M. Niederberg, H. J. Muher, F. Krumeich, F. Bieri, D. Gunther, R. Nesper, *Chem. Mater.* 12 (2000) 1995.
- [14] F. Bieri, F. Krumeich, H. J. Muher, R. Nesper, *Helv. Chim. Acta* 84 (2001) 3015.
- [15] Grigoreva, A. V, Anikina, A. V, Tarasov, A. B, Sudilin, E. A, Knotko, A. V, Volkov, V. V, Dembo, K. A, Tretyakov, Y. D micromerology and structure of vanadium oxide nanotubes. *Doklady chem*, 2006, Ulo, 165-169.
- [16] Li, Zheng, L., Zhang, K. F. Feng, X. Q, Su, Z. X. Ma, J. T Synthesis of Ag modified vanadium oxide nanotubes and their antibacterial properties. *Mater, Res. Bull.* 2008, 43, 2810 - 2817.