International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.7, No.3, pp 1569-1573, 2014-2015

ICONN 2015 [4th -6th Feb 2015]
International Conference on Nanoscience and Nanotechnology-2015
SRM University, Chennai, India

Low temperature synthesis of Vanadium chalcogenide nanostructures from VO_x nanostructures

Naresh N[1]*, Kumuthini R[2], Helen A.T[2]

[1]Department of Physics and Nanotechnology, SRM University, Kattankulathur-603203, Tamil Nadu, India
[2]Nanotechnology Research Center, SRM University, Kattankulathur-603203, Tamil Nadu, India.

Abstract : Low-dimensional Vanadium chalcogenides in nanoscale has attracted interest due to its magnetism and as high performance functional material. The intercalation ability of layered vanadium oxide allows the insertion of various intercalant species into its structure. In this work we have demonstrated the conversion of vanadium sulfide from vanadium oxide (VOx) using dodecylamine as a growth template. The products were characterized using XRD, FESEM along with EDX and FTIR for the confirmation of conversion of vanadium sulfide nanostructures from dodecylamine intercalated vanadium oxide.
Keywords: Vanadium sulfide (VSx), Hydrothermal Method, X–Ray Diffraction (XRD), Field Emission Scanning Microscopy.

Introduction

Low dimensional nanostructures of transition metal dichalcogenides are of interest and have received much attention by researchers due to its unique electrical, optical, thermal and mechanical properties[1,2,3,4] and their application in portable electronic devices, energy storage devices due to its layered structures and sensing devices[5,6]. Among them vanadium chalcogenides nanostructures particularly vanadium sulfides (VS_2/VS_x) have attracted increasing interest since its novel magnetic properties and applications in spintronics and energy storage devices[7,8,9,10,11]. Synthesis of such materials has been achieved by few methods such as exfoliation[12,13] and chemical synthesis[14].

Literature show that a considerable amount of study on the structural and magnetic behavior of amine intercalated VO_x[15-22] nanostructures have been reported. Synthesis of various organic amines template VO_x nanostructures based on the redox intercalation ability of the layered vanadium oxide has been reported[23], where a sol-gel derived hydrothermal technique was employed. However, synthesis of stoichimetric VS_2 nanosturcures are difficult as they tend to exist most of the time as A_xVS_2 (A = alkali metal, Cu). The conversion of various amine template VO_x – NT (Nanotube) to VS_2 – NT has been first reported by[23] reductive sulfurisation using H_2S gas. Here in, we report on the synthesis of vanadium chalcogenides nanostructure from dodecylamine intercalated VO_x nanosheets prepared by one-pot hydrothermal method followed by the heat treatment with Sulfur under inert atmosphere.

Experimental

Organic amine templated vanadium chalcogenides were obtained by sulfidisation of amine templated VOx nanostrctures.

Synthesis of amine templated VO_X nanostructures

Ammonium metavanadate and dodecylamine of 2:1 mole ratio were taken in aqueous solution of 20ml and kept under stirring for whole night (around 12hrs). The pH of the solution was maintained at 7 throughout the reaction by the addition of nitric acid (HNO_3). The solution was transferred to an autoclave for hydrothermal treatment at 120◦C for 14 hrs, 24hrs and 48hrs etc., The reaction carried out for 48hrs gave us better result and we obtained VO_x nanosheets intercalated with dodecylamine at this reaction condition. Thus we have proceeded with this sample for further studies.

Sulfidisation of amine templated VOx nanostrcture

The obtained nanosheets of VO_x is mixed with sulphur powder of twice the weight of VO_x and were further subjected to the heat treatment at 250°C of 1° rate in a single zone tube furnace under Argon atmosphere for 10hrs.

Characterization

The resulting samples of VO_x & VS_2 were characterized by X-ray Diffractrometer (Xpert Pananalytical, $Cu_{k\alpha}$ radiation), FESEM (FESEM Quanta FEI 200, 20kV) along with energy dispersive x-ray analysis system (EDX). IR analysis of the samples was carried out using FTIR (ALPHA-T FT-IR Spectrometer).

Results and discussion

From XRD analysis the optimum condition or the formation of amine templated VOx was found to be better intercalation of dodecylamine into VO_x layered structure at the reaction time of 48hrs (Figure1a).

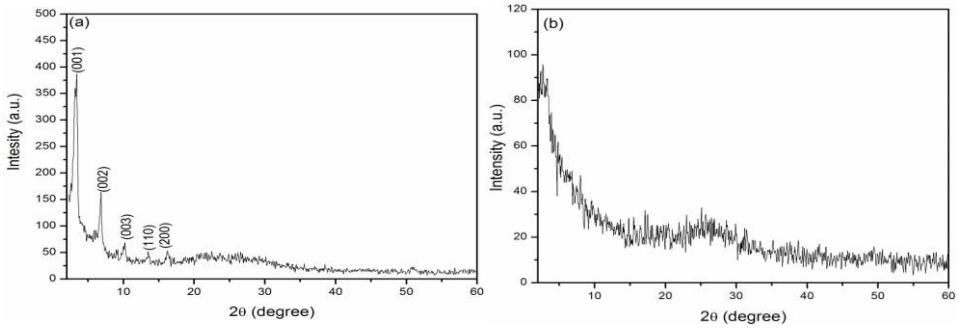

Figure 1. XRD pattern of (a) dodecylamine intercalated VO_x and (b) Vanadium sulfide

Other conditions yielded partial intercalation of dodecylamine whose are not consider for further analysis and are not reported here.Figure 1a shows the XRD patterns of dodecylamine intercalated VO_x nanosheets and Figure 1b shows the XRD patterns of heat treated vanadium sulfide. The obtained XRD pattern of VO_x [Fig.1] perfectly matches with the XRD pattern of VO_x nanotubes[15,17,24]. In XRD, no other impurity peaks were found. The d-spacing (layer distance between VO_x) value of the peaks obtained in XRD is tabulated as shown in Table1.

Table 1. 'd' spacings of vanadium oxide nanosheets.

S.No.	Peak index (hkl)	Peak position (2θ)	Interlayer spacing (nm)
1	001	3.3437	2.6
2	002	6.7989	1.3
3	003	10.0942	0.8
4	110	13.4428	0.6
5	200	16.075	0.5

The (001) reflection with high intensity at very low angle indicates the intercalation of dodecylamine into the layered vanadium oxide nanosheets (Morphology is conformed using FESEM as shown in Figure.2a); this is further confirmed by FTIR. Figure 2a shows the FESEM(Field emission scanning electron microscopy) images of dodecylamine intercalated VO_x at 3µm scale bar, bunched nanosheets of vanadium oxide due to the insufficient heat during the hydrothermal reaction.

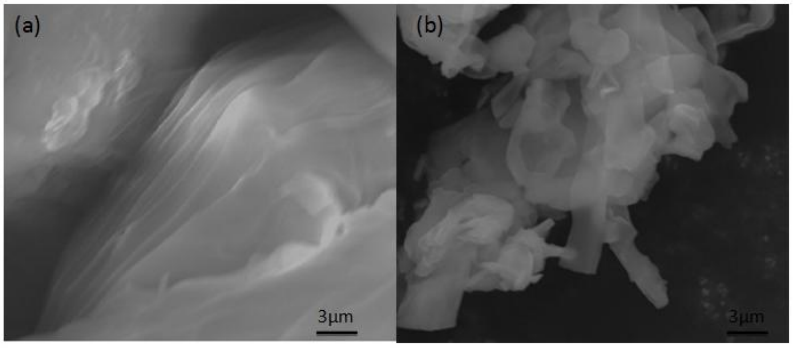

Figure 2 (a) FESEM image of VO_x – Nanosheets (b) FESEM image of Vanadium sulfide

Figure 2b shows the FESEM image of sulfurized VO_x nanosheets at 250°C. The obtained FESEM images of typical vanadium sulfide shows slightly changed morphology from nanosheets to nanoribbon like structures upon sulfidization.The crystalline nature of vanadiumoxide nanosheets turned into amorphous vanadium sulfide which is reflected by the absence of (200) peak of V_2O_5 in the XRD [24] pattern of vanadium sulfide (Figure 1b). Conversion of vanadium oxide to sulfide is further supportedby EDS (Figure 5), andFTIR analysis [Figure.3].

The FTIR Spectra of the dodecylamine intercalated VO_x nanosheets given in Figure 3(a), shows strong alkyl C-C stretching mode of vibrational band at 2851 and 2922 cm^{-1}. The vibrational band characteristics of N-H stretching mode manifest at 3451cm^{-1}, indicates the presence of dodecylamine in the layered vanadium oxide structure. The vibrational bands appear in the frequency range of 500 – 1000 cm^{-1} is corresponding to various vibration of V-O type. The bending vibrations of water molecule H-O-H also appear around the frequency 1600 cm^{-1}. The deducted intensity of the N-H stretching vibrations in figure 3(b), evidence the removal of dodecylamine from the VO_x host during the heat treatment in tube furnace.

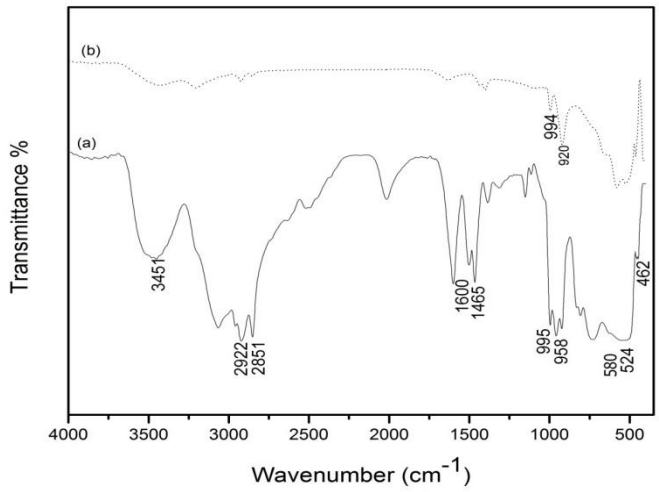

Figure 3. FT-IR Spectra for (a) Dodecyclamine Intercalated Vanadium Oxide, (b) Vanadium Sulfide

The vibration band corresponding to S-S stretching at 462, 524 and 580 cm^{-1} and the slight shift in the vibration bands characteristic of V-O at 990 cm^{-1}, 920 cm^{-1} in FTIR spectra of VS_x nanostructures indicate that the conversion of VO_x-nanosheets to VS_x at 250°C is partially achieved under Ar. The conversion of VO_x-VS_x is further confirmed by EDX spectra.

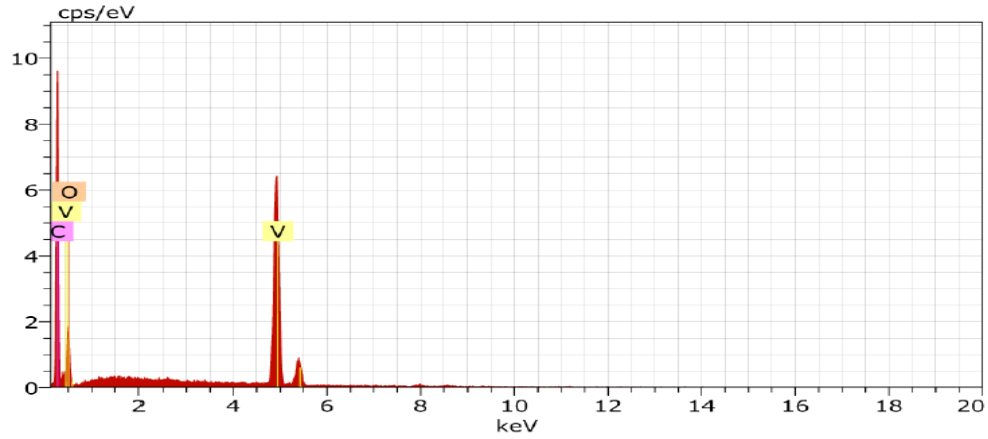

Figure 4.EDX Spectra for Vanadium Oxide

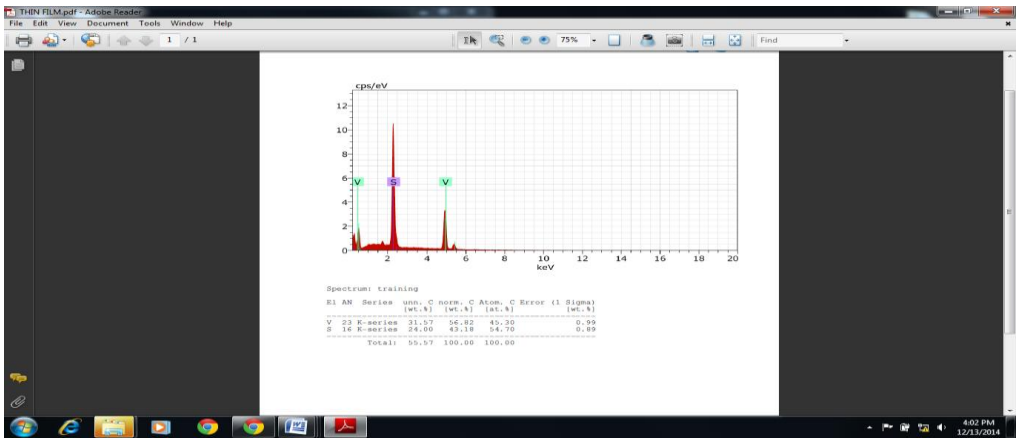

Figure 5. EDX Spectra for Vanadium Sulfide

Figure 4 and 5 shows the EDX spectra of the VO_x and VS_x samples. In Figure 5 (EDX spectra of vanadium sulfide) shows the higher intensity for sulfur denotes the presence of sulphur in the material and thus confirms the conversion of VO_x nanosheets to vanadium sulfide nanostructure.

Conclusion

In summary, we have demonstrated that the dodecylamine template VO_x nanosheet like structures are very reactive towards sulfur due to its large surface area, and can be converetd to Vanadium sulfide even in the absence of reductive atmospheres such as H_2S gas. The formation of Vanadium sulfide is confirmed by XRD, FTIR and EDS analysis. FESEM images show that the morphology of the Vanadium sulfides change from sheet- like to ribbon- like structures due to elimination of intercalated amines. Further experiments needs to be explored to obtain VS_2 nanosheets for device based applications.

References

1. Qing Hua Wang, KouroshKalantar-Zadeh, AndrasKis, Jonathan N.Colemanand Michael S.Strano1. ,Electronics and optoelectronics of two-dimensional transition metal dichalcogenides, Nature Nanotechnology, November 2012, 699-712.
2. Chai.Y, Lan.J, Zhang.G and Zhang.Y.W.,Lattice Vibrational Modes and Phonon Thermal Conductivity of Monolayer MoS2, Phy.Rev.B:Condens.MatterPhys, 2014, 89.
3. Cong.C, Shang.J, Wu.X, Cao.B, Peimyoo.N, Qui.C, Sun.L and Yu.L.,Synthesis and Optical Properties of Large-Area Single-Crystalline 2D Semiconductor WS_2 Monolayer from Chemical Vapor Deposition, Adv.Opt.Mater, 2014, 2, 131-136.
4. Radisavlijevic.B, Radenovic.A, Brivio.J, Giacometti.V and Kis.A.,Single-layer MoS_2 transistors, Nat.Nanotechnology, 2011, 6, 147-150.

5. Xiao Huang, ZhiyuanZeng and Hua Zhang.,Metal dichalcogenide nanosheets: preparation, properties and applications,Chem. Soc. Rev,2013, 42, 1934-1946.
6. Chen-Ho Lai, Ming-Yen Lu and Lih-Juann Chen.,Metal sulfide nanostructures: synthesis, properties and applications in energy conversion and storage, J. Mater. Chem, 2012, 22, 19-30.
7. Mulazzi.M, Chainani.A, Katayama.N, Eguchi.R, Matsunami.M, Ohashi.H, Senba.Y, Nohara.M, Uchida.M, Takagi.H, Shin.S., Absence of nesting in the charge-density-wave system 1T-VS2 as seen by photoelectron spectroscopy, Phys.Rev.B82, 2010, 075130.
8. Murphy.D.W,Cros.C,DiSalvo.F.J,Waszczak.J.V.,Preparation and properties of LixVS2, Inorg. Chem, 1977, 16, 3027.
9. Poddar.P,Rastogi.A.K.,Metastability and disorder effects in nonstoichiometric VS_2J.Phys.Condens .Matter, 2002, 14, 2677.
10. Therese.H.A,Rocker.F,Reiber.A,Li.J,Stepputat.M,Flasser.G,Kolb.U,Tremel.W.,VS2Nanotubes Containing Organic-AmineTemplates from the NT-VO*x*Precursors andReversible Copper Intercalation in NT-VS2, Angew.Chem.,Int.Ed.Engl, 2005, 44, 62- 265.
11. Yu Jing, Zhen Zhou, Carlos R. Cabrera, and Zhongfang Chen.,Metallic VS2 Monolayer: A Promising 2D Anode Material for LithiumIon Batteries, J. Phys. Chem. C 2013.
12. Feng.J,Sun.X,Wu.C.Z,Peng.L,Lin.C.W,Hu.S.L,Yang.J.L,Xie.Y.,J.Am.Chem.Soc, 2012, 129, 074704.
13. Feng,.J, Sun.X, Wu.C, Peng.L, Lin.C, Hu.S, Yang.J, Xie.Y., Metallic Few-Layered VS2 Ultrathin Nanosheets:High Two-Dimensional Conductivity for In-Plane Supercapacitors, J. Am. Chem.Soc, 2011, 133, 17832−17838.
14. VadivelMurugan.A, Chinnakonda S. Gopinath, Vijayamohanan.K.,Electrochemical studies of poly (3,4-ethylenedioxythiophene)PEDOT/VS2 nanocomposite as a cathode material forrechargeable lithium batteries, Electrochemistry Communications, 2005, 7, 213–218.
15. MarkusNiederberger,HansJoachimMuhr, FrankKrumeich, FabianBieri, DetlefGünther,andReinhardNesper.,Low-Cost Synthesis of Vanadium Oxide Nanotubes via Two Novel Non-Alkoxide Routes, Chem. Mater, 2000, 12 (7),1995–2000.
16. HyocheonKweon, Kyu Won Lee and CheolEui Lee.,Magnetic Phase Separation in Vanadium-oxide Nanosheets, Journal of the Korean Physical Society,April 2011, 48(2), 911-914.
17. Kyu Won Lee, HyocheonKweon and CheolEui Lee.,Structure and Magnetism in Dodecylamine-Intercalated Vanadium Oxide Gels,Journal of the Korean Physical Society, December 2008, 53(6), 3493-3496.
18. Sediria.F, Gharbi.N.,From crystalline V2O5 to nanostructured vanadium oxides using aromatic amines as templates. Elsevier,Journal of Physics and Chemistry of Solids, 2007, 68, 1821–1829.
19. HyocheonKweon, Kyu Won Lee, CheolEui Lee.,Structural coherence in dodecylamine-intercalated vanadium oxides, Current Applied Physics, 2010, 10, 1152–1155.
20. Nefzi.H,Sediria.F.,Vanadium oxide nanotubes VOx-NTs: Hydrothermal synthesis, characterization, electrical study and dielectric properties, Journal ofSolidStateChemistry, 2013, 201, 237–243.
21. HyocheonKweon, Kyu Won Lee, Eun Mo Lee, Jitae Park, I-M. Kim, and CheolEui Lee., Effect of water intercalation on VO*x*layers in dodecylamine-intercalated vanadiumoxidenanotubes, Physical Review B, 2007, 76, 045434.
22. Aihua Liu, Masaki Ichihara, ItaruHonma, Haoshen Zhou.,Vanadium-oxidenanotubes:synthesis and template-related electrochemical properties, Electrochemistry Communications, 2007, 9, 1766–1771.
23. Samuel T. Lutta, Arthur Dobley, Katana Ngala, Shoufeng Yang, Peter Y. Zavalij, and M. Stanley., WhittinghamVanadium Oxide Nanotubes: Characterization and Electrochemical Behavior, Mat. Res. Soc. Symp. Proc., 2002, 703, 323- 328.

*****