



Synthesis and Characterization of Barium-Vanadium Oxide Nanocomposite Using a Facile thermolysis Approach

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ABSTRACT

In this investigation, we report synthesis of new cationic-anionic Barium-Vanadium complex with 2, 6- pyridinedicarboxylic acid ligand. This compound $[\text{Ba}(\text{H}_2\text{O})_8][\text{VO}_2(\text{dipic})]_2$ (**1**) has been characterized using elemental analyses, FT-IR, UV-Vis and Cyclic voltammetry (CV) techniques. Also in this study we report facile synthesis of Barium-Vanadium Oxide nanoparticle under thermal decomposition, using precursor complex (**1**). Characterization of Barium-Vanadium Oxide nanocomposites was carried out by scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), X-ray powder diffraction (XRD) and Fourier transform infrared (FT-IR) spectroscopy. The X-ray diffraction pattern at room temperature revealed that, highly pure and crystallized $\text{Ba}_3(\text{VO}_4)_2$ with rhombohedral structure.

Key words: Cationic-anionic. elemental analyses. Cyclic voltammetry. scanning electron microscopy.

INTRODUCTION

Oxide structures with nanometric dimensions exhibit novel physical and chemical properties, with respect to bulk oxide materials, due to the spatial confinement and the proximity of the substrate. Many them have been described during the past few years^{1,2}. Like most other transition metal oxides, Vanadium, can appear in different states like: V_2O_5 , VO_2 , V_2O_3 and V_2O . Nanostructured vanadium oxides have been extensively studied^{3,4}.

Various nano compounds that capacities as catalyst with highly regarded in the field of electronics and applications⁵.

They exhibit a great variety of nanostructures, ranging from 1D to 3D^{6,7} also V_2O_5 has even been chosen as a model system for the description of nanostructured materials⁸. Vanadium oxides find major applications in the field of lithium ion batteries^{9,10}. Nanostructured vanadium oxides exhibit unusual morphologies such as nanowires,

nanobelts, nanorods, nanotubes and even flower-like or nano-urchin shapes¹¹⁻¹³.

In this study we describe preparation of the Barium-Vanadium oxide nanoparticle via synthesis of inorganic precursor metal complex. The complex were characterized by use of physicochemical methods, including spectroscopic (IR, UV-visible) studies. Cyclic voltammetry (CV) method was used to investigate the electrochemical behavior of the complex. The produced nanoparticle characterized using FT-IR, XRD, SEM and EDX. The results are presented and discussed.

EXPERIMENTAL

Materials and physical measurements

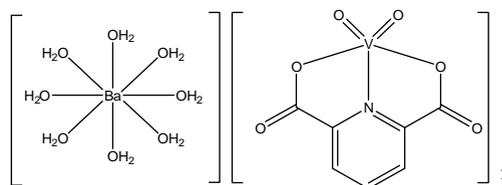
The raw materials used in this work were of purities above 99%, therefore no further purification was required. All solutions were prepared with double distilled deionized water. Elemental analyses (CHN) were determined on a Heraeus rapid analyzer. Fourier transform infrared (FT-IR) spectra were recorded using JASCO 460 FT-IR spectrophotometer in a KBr matrix. UV-Vis spectra were recorded on a JASCO 7850 spectrophotometer. The redox properties of the complexes were studied by cyclic voltammetric method. Cyclic voltammogram was recorded by using a SAMA 500 Electro Analyzer. X-ray powder diffraction (XRD) measurements were performed using an X'pert diffractometer of Philips Company with graphite monochromatic Cu K_a radiation at room temperature in the 2θ range of 10-60°. The sample characterized by using scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) techniques (Philips XL30) with gold coating. Preparation of [Ba(H₂O)₈][VO₂(dipic)]₂ (1)

For the synthesis of this complex, the cationic and anionic parts were prepared separately then added together and the final product was obtained.

To Prepare cationic part: To a salt of Barium Chloride (0.122 g, 0.5 mmol) was added double distilled deionized water (10 mL) and the mixture was stirred for 10 hour at room temperature to give a clear solution.

To prepare anionic part: To a solution of NH₄VO₃ (0.117 g, 1 mmol) in double distilled deionized water (15 mL) was added a aqueous solution (10 mL) of (NH₄)₂(dipic) (0.202 g, 1 mmol) and the mixture was refluxed at 100°C for 24 hour to give a clear yellow solution.

Then a solution of [Ba(H₂O)₈]²⁺ was added to [VO₂(dipic)] and the mixture was refluxed for 5 day. White crystals of **1** were obtained by slow evaporation of solvents and kept for further characterization. Yield 69%. *Anal. Calc.* for C₁₄H₂₂BaN₂O₂₀V₂: C, 21.63; H, 2.85; N, 3.60; Found: C, 21.58; H, 2.82; N, 3.51%. FT-IR (KBr, cm⁻¹) ν_{max}: 2600-3000 ν(O-H), 1331, 1701 ν(-COO⁻), 1530-1300 ν(C=C) and ν(C=N), 956 ν(V=O), 478 ν(V-O), 460 ν(V-N), 517 ν(Ba-O)¹⁴⁻¹⁸ (Schem. 1) .



Scheme 1: Recommended structure of complex (1)

Electronic excitation study

The UV-visible spectra of the title complex, acquired in aqueous solution. A moderately intense band observed at 215 nm that corresponding to the charge transfer (LMCT) from oxygen atom to Vanadium ion (O → V)¹⁹.

The bands in the UV region at approximately 268 nm assigned to intra-ligand transitions (n → π* and π → π*)^{20,21}. V⁺⁵ complexes have d⁰ arrangement therefore no d-d transitions are expected. Fig.1

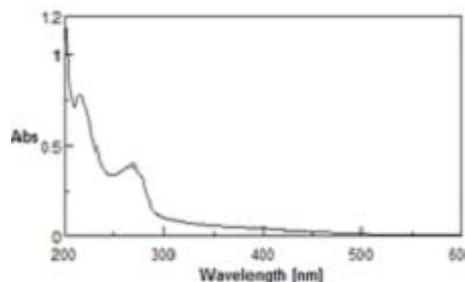


Fig. 1: UV-visible absorption spectrum of [Ba(H₂O)₈][VO₂(dipic)]₂

Electrochemical Studies

The cyclic voltammogram of complex(1) was obtained at 25°C under an argon atmosphere using DMF solution containing 0.1 M TBAH as supporting electrolyte and complexes concentration of 4×10^{-3} M at a glassy carbon working electrode. Ferrocene (Fc) was used as the internal standard, and all redox potentials are referenced to the $\text{Fc}^{+/0}$ couple.

Complex (1) shows two quasi reversible reduction waves at 0.2 V and -0.9V versus the Fc/Fc^+ couple attributed to reduction of $\text{V}^{5+}/\text{V}^{4+}$ and $\text{V}^{4+}/\text{V}^{3+}$ respectively Fig. 2. Irreversible reduction waves at negative potential -1.6 V assigned to reduction of ligand.^{22,23}

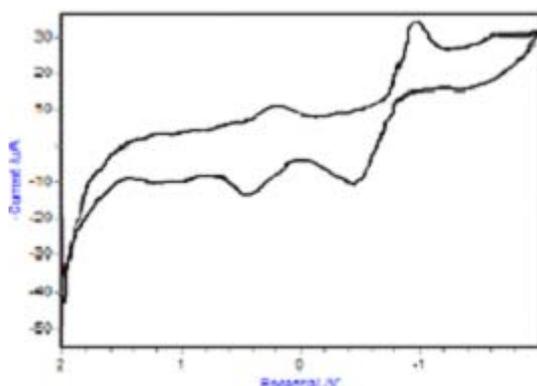


Fig. 2: Cyclic voltammogram of $[\text{Ba}(\text{H}_2\text{O})_8][\text{VO}_2(\text{dipic})_2]$ (1)

Preparation of Barium-Vanadium oxide nanoparticle $\text{Ba}_3(\text{VO}_4)_2$

Barium-Vanadium oxide nanoparticle was prepared from title compound (1) using the physical method. First 1.0 g of compound (1) dissolved in oleic acid solution (5mL) as a surfactant. Then calcinated at 1100°C for 4 h in the furnace to formed $\text{Ba}_3(\text{VO}_4)_2$ nanoparticle by thermal decomposition. The final product was collected and washed with distilled water and absolute ethanol several times, dried in air and kept for further characterization.

RESULTS AND DISCUSSION

The FT-IR spectrum precursor complex (1) is shown in Fig. 3. The broad absorption band at 2600-3000 in (1) is related to stretching vibrations of O-H group. Absorption bands at 1330 cm^{-1} and

1700 cm^{-1} are corresponding to stretching vibration of carboxylate group. Stretching band of $\text{V}=\text{O}$ group is observed at 956 cm^{-1} . Absorption bands are observed at 478, 460 and 517 cm^{-1} in (1) are corresponding to V-O, V-N and Ba-O group respectively. As shown in Fig. 4 the intensity of these bands decreases when compound (1) is heated at 1100°C. At this temperature, there is broad band at 2500-3500 cm^{-1} is representative of adsorbed water on the external surface of the sample. Absorption band at 801 related to Barium-Vanadium oxide nanoparticle and providing clear evidence for the presence of the crystalline $\text{Ba}_3(\text{VO}_4)_2$ ²⁴

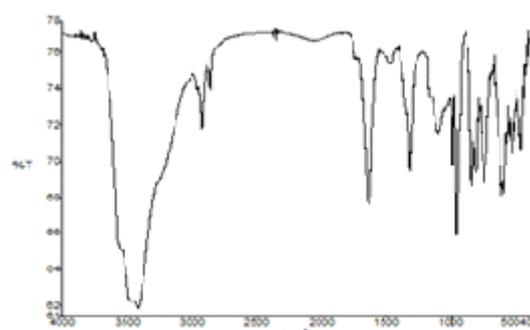


Fig. 3: FT-IR spectrum of complex (1) before thermal decomposition

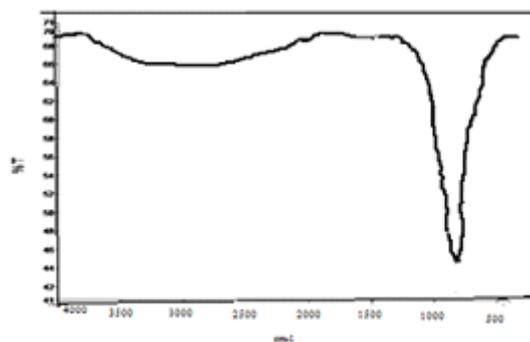


Fig. 4: FT-IR spectrum of $\text{Ba}_3(\text{VO}_4)_2$ after calcined of complex (1) in 1100°C

Fig. 5 show XRD pattern for $\text{Ba}_3(\text{VO}_4)_2$. It is obvious that all the diffraction peaks can be indexed to rhombohedral phase with space group $R\bar{3}m$ in compared with the standard XRD pattern of $\text{Ba}_3(\text{VO}_4)_2$ (JCPDS card No.00-025-1192) diffraction pattern.

materials without a need for special conditions, such as long reaction times, and high pressure. This method may be extending to synthesise other metal

nanoparticles oxide, nanowires, nanodisks, and even nanotubes.

REFERENCES

- Lee, K.; Wang, Y.; Cao, G.; *J. Phys. Chem.* **2005**, *109*, 16700-16704
- Wang, Y.; Takahashi, K.; Lee, K.; Cao, G.; *J. Adv. Funct. Mater.* **2006**, *16*, 1133-1144
- Tracey, A., Willsky, G. R. Takeuchi, E. R.; *Vanadium Chemistry Biochemistry Pharmacology and Practical applications*, **2007**, p. 217, CRC press, U.S.A.,.
- Mamedov, E.; Corberán, V. C.; *J. Appl. Catal.* **1995**, *A*, 127. (1–2)
- ÇAKIR, S.; BÝÇER, E.; *J. Chil. Chem. Soc.* **2010**, *55*, 236-239,
- Weckhuysen, B.M.; Keller, D.E.; *J. Catal. Today* **2003**, *78* (1–4)
- Gambardella P et al. *Nature*. **2001**, *416*, 301.
- Schoiswohl, J.; Sock, M.; Surnev, S.; Ramsey, M. G.; *J. N Surf. Sci.* **2004**, *555* 101.
- Tarascon, J.M.; Armand, M.; *nature*, **2001**, *414*, 359.
- Poizot, P.; Laruelles, S.; Grugéan, L.; *DuPpnt, J,M, Tarason, Powers Souces.* **2001**, 97-98-235.
- Larcher, D.; Masquelier, C.; Bonnin, D.; Chabre, Y.; Masson, V.; Leriche, J.B.; Tarascon, J.M., *J. Electrochem, Soc.* **2003**, *150*. A133.
- Wang, Y.; Cao, G.; *J. Adv. Mater.* **2008**, *20*, 2251-2269.
- Spahr, M.E.; Bitterli, P.; Nesper, R.; Muller, M.; Krumeich, F.; Nissen, H.U. *Angew. Chem. Int. Ed.* **1998**, *37*, 1263-1265.
- Nesper, R.; Muhr, H.J.; *Nanotubes—an outstanding set of nano particles. Chimia.* **1998**, *52*, 571-578.
- Angus, I.; Rudiger, K. R.; Meyer, J.; Sloan, J.; *J. Microscopy and Microanalysis.* **2005**, *11*, 401-409.
- Cakir, S.; Bycer, E.; *J. Chil. Chem. Soc.* **2010**, *55*, 236-239,.
- Dobley, A. K.; Ngala, S.; Yang, P.; Zavalij, Y.; Stanley, M.; *J. Chem. Mater.* **2001**, *13*, 4382-4386.
- K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds. PartB: Applications in Coordination, Organometallic, and Bioinorganic Chemistry*, fifth ed., John Wiley & Sons Inc, New York, **1997**.
- Gao, H.; Li, Q.; Dai, Y.; Luo, F.; Zhang, H.; *J. Corrosion Science*, **2010**, *52*, 1603–1609.
- Sung, C.; *J. Ceramic Processing Research*, **2012**, *13*, 432- 436.
- Swiderski, G.; Kalinowska, M; Wojtulewski, S.; Lewandowski. W.; *J. Polyhedron.* **2006**, *64*, 24–3
- Uc, I. Bulut, ar.; *J. Struct. Chem.* **2009**, *20*, 825–838.
- Sayyah, S.; El-Deeb, M.; Kamal, S.; Azooz, R.; *J. Appl. Poly. Sci.* **2009**, *112*, 3695–3706
- Ghosh, T.; Bhattacharya, S.; Das, A.; Mukherjee, G.; Drew, M.; *J. Inorganica Chimica Acta.* **2005**, *358*, 989–996,
- Klug, H. P.; Alexander, L. E.; *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials*, Wiley, New York, **1974**.
- Parimalagandhi, K.; Vairam, S.; *Orient. J. Chem.*, **2014**, *30*(4), 1957-1963.