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Preparation and characterization of V_2O_3 micro-crystals via a one-step hydrothermal process

Yunyu Bai[a,b], Ping Jin[a,c,*], Shidong Ji[a], Hongjie Luo[a], Yanfeng Gao[a]

[a] *State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics (SIC), Chinese Academy of Sciences (CAS), No. 1295 Dingxi Road, Shanghai 200050, China*
[b] *Graduate University of Chinese Academy of Sciences, Yuquanlu 19, Beijing 100049, China*
[c] *National Institute of Advanced Industrial Science and Technology (AIST), Japan*

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Abstract

Phase pure V_2O_3 micro-crystals with a hexagonal dipyramid morphology were fabricated for the first time via a facile one-step hydrothermal method. The crystals were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and differential scanning calorimetry (DSC). A hexagonal dipyramid structure of V_2O_3 enclosed by well-grown {012} facets was obtained by hydrothermally reducing $VO(acac)_2$ precursor with $N_2H_4 \cdot H_2O$ at 220 °C for 48 h. The results indicated that V_2O_3 can be well crystallized up to micron size with distinguished facets by only one step hydrothermal treatment. The formation mechanism and morphology evolution for V_2O_3 micro-crystals were discussed. Based on our experiments, the V_2O_3 nuclei formed and grew by a phase transformation through a dissolution–recrystallization process of VOOH, and the formation of the hexagonal dipyramids was ascribed to the specific adsorption of Hacac to the {012} facets restraining the growth in the directions normal to the {012} facets. The present work provides a facile method for preparing phase pure V_2O_3 micro-crystals with hexagonal dipyramid morphology, which can be used as a new powder material for ceramic fabrication.

Keywords: V_2O_3; Hexagonal dipyramid; Morphology; Hydrothermal; Phase transition

1. Introduction

To synthesize and design inorganic materials with novel and special morphologies have always been of great interest and one of the key tasks towards application. Controlling the morphology of materials particularly at the nano- to macro-scale is necessary and it is always a challenge to material research scientists, because well-controlled morphologies may generate unique and in most cases useful electronic, magnetic, optical and catalytic properties [1,2]. The morphology of a material can also be designed according to the requirements of the devices, which is of significant value for the practical application.

Over the last few decades, vanadium oxide-based materials have attracted much attention in the scientific and industrial communities because of their unique physical and chemical properties [3,4]. As a typical and prominent example, lots of investigations were carried out on V_2O_3 due to a temperature-induced reversible metal–insulator transition (MIT) and a magnetic transition that occurred at the same temperature [5]. Below 150 K, it is antiferromagnetically ordered and an electric insulator with monoclinic crystal structure. With increasing temperature to above 150 K, the crystal structure changes from monoclinic to rhombohedral (corundum-type), accompanied by a change from antiferromagnetic to paramagnetic and a sharp increase in electrical conductivity (up to 10^7) [6–9]. It is the reversible abrupt changes of electric and magnetic properties that makes V_2O_3 a desirable material to meet the demand of potential wide ranges of applications, such as low temperature sensors, field-effect transistors, catalysts and cathode materials for lithium batteries [10–13].

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[*] Corresponding author at: State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics (SIC), Chinese Academy of Sciences (CAS), No. 1295 Dingxi Road, Shanghai 200050, China. Tel.: +86 21 6990 6208; fax: +86 21 6990 6221.
E-mail addresses: p-jin@mail.sic.ac.cn, p-jin@aist.go.jp (P. Jin).

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Although V_2O_3 has already been discovered by Foex in 1946 and a number of methods have been reported to prepare V_2O_3; it is still a challenge to synthesize high quality V_2O_3 crystal with well-developed morphology for the practical application [14]. Traditionally, V_2O_3 powders were synthesized by thermal decomposition of V_2O_5 or other vanadium-containing precursors at a temperature range from 450 to 2000 °C [15–24]. However, the formation of V_2O_3 powders by thermal decomposition requires high temperature with precise atmospheric control, and the morphologies are almost limited to a sphere shape. There were only a few studies on the synthesis of V_2O_3 particles by the solvothermal methods, using the reaction of metal alkoxide vanadium (V) triisopropoxide and benzyl alcohol at 200–220 °C [25,26]. However, the methods do not seem suitable for practical application because the raw materials are quite expensive and the solvent is not environmentally friendly.

Since there a large amount of literatures reported the synthesis of other V–O compounds, such as VO_2, with precise control of the morphology and stoichiometry by soft chemical methods, it is reasonable to consider that the formation of V_2O_3 nano- or micro-powders in aqueous solution is a more preferable method against the thermal decomposition or solvothermal method, which may result in a low temperature, low cost and environment-friendly fabrication process normally with diverse morphology control. It was reported by Blagojevic et al. that the V_2O_3 crystals can be hydrothermally formed [27]. However, the reported method requires an additional ligand as additive and cannot produce single-shaped and well-crystallized morphology.

It is still a meaningful challenge to develop a simple approach for producing V_2O_3 with single and well-developed morphology in aqueous solution. In this work, we report a facile one-step hydrothermal method to synthesis V_2O_3 micro-crystals using raw materials of $VO(acac)_2$, $N_2H_4 \cdot H_2O$, and H_2O without additional ligand as additive representing the first case for directly synthesizing single-shaped V_2O_3 hexagonal dipyramids with well-developed {012} facets in liquid condition by the hydrothermal treatment.

2. Experiment

2.1. Raw materials

$VO(acac)_2$ (vanadium oxyacetylacetone, Alfa Aesar Corporation) was used as the vanadium source and $N_2H_4 \cdot H_2O$ (67 wt%, Sigma-Aldrich Corporation) was adopted as the reducing agent. Deionized water was used in all our experiments. All chemicals were used as received without further purification.

2.2. Synthesis of V_2O_3 micro-crystals

In a typical experiment, 2.5 g $VO(acac)_2$ was added to a solution of 40 ml deionized water and 1 ml hydrazine monohydrate under constant stirring. The mixture was then transferred into a 100 ml Teflon-lined autoclave, sealed and maintained at different temperatures for different time durations. After cooling to room temperature, the precipitate was collected by centrifugation, washed with deionized water and ethanol several times and dried at 70 °C to obtain the V_2O_3 powder products.

2.3. Characterization

The structure of the samples were characterized with a D/max-2500 X-ray diffractometer (Rigaku, Japan), using Cu Kα radiation ($\lambda = 0.15406$ nm) operated at 40 kV and 40 mA. The morphologies of synthesized powders were observed by field emission scanning electron microscopy (FE-SEM, HITACHI, S-3400). The microstructure was investigated with transmission electron microscopy (TEM, JEOL, JEM2010). The phase transition behavior was measured by differential scanning calorimetry (DSC, NETZSCH, DSC200F3) in nitrogen flow in the temperature range from −140 to 20 °C at a heating/cooling rate of 10 °C min^{-1} using a liquid nitrogen cooling unit.

3. Results and discussion

3.1. Crystal structure

The XRD pattern of a sample obtained at 220 °C for 48 h is shown in Fig. 1 as a representative. All peaks can be indexed as a single phase V_2O_3 (JCPDS Card no.34-0187). It can also be seen that all of the peaks are sharp and strong with relatively narrow peak widths, indicating the good crystallinity of V_2O_3. The result indicates that phase-pure and well-crystallized V_2O_3 powders can be synthesized by such a simple one-step hydrothermal method.

3.2. Crystal morphology

Fig. 2 shows the corresponding FE-SEM image of the synthesized sample. When the precursor of $VO(acac)_2$ was reduced by $N_2H_4 \cdot H_2O$ at 220 °C for 48 h, well defined

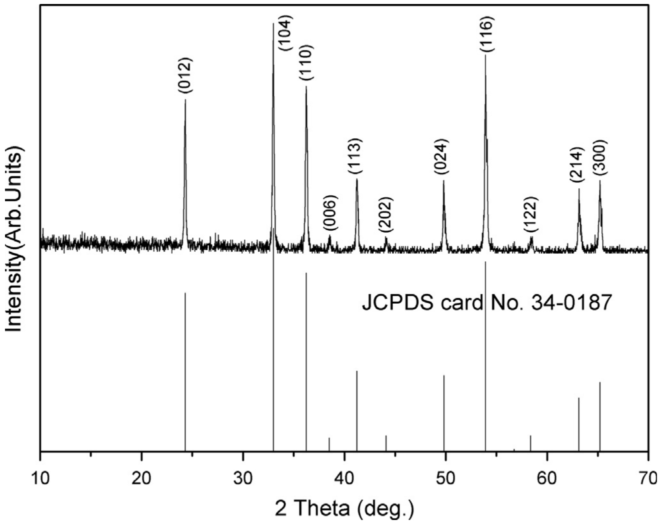

Fig. 1. XRD pattern for one sample obtained at 220 °C for 48 h, the bottom showed the simulated pattern according to the JCPDS Card (No. 34-0187).

hexagonal dipyramids of V_2O_3 micro-crystals with approximately 200–500 nm in diameter could be obtained. Herein, we highlight that the hexagonal dipyramids are of unusual crystal shapes of rhombohedral corundum-type oxides, representing the first case for synthesizing V_2O_3 hexagonal pyramids with well-grown, distinguished facets.

The morphology and crystallinity of the V_2O_3 hexagonal dipyramids were further observed by TEM, and the results are shown in Fig. 3. The TEM image in Fig. 3a clearly shows the size and shape of the hexagonal dipyramids. The SAED pattern in Fig. 3b demonstrates that they are all single crystals. As shown in the HRTEM of Fig. 3c, the interplanar spacing of 0.36 nm corresponds to the d spacing of (012) plane and the corresponding dihedral angle of 82° is consistent with the calculated angle between (012) and (10−2) planes.

3.3. Phase transition

The phase transition behavior of the micro-crystals was investigated using DSC which records the latent heat during phase transition. Fig. 4 shows the DSC curves of the V_2O_3 crystals of the hexagonal dipyramid. Upon cooling, the sample exhibits an exothermic peak at −130 °C, and upon heating during the cooling–heating circle, it shows an endothermic peak at −115 °C, with a temperature hysteresis width of approximately 15 °C. Our results are consistent with the research of Zheng et al. who determined the DSC of the V_2O_3 powder for the first time and observed that the phase transition temperature of V_2O_3 is −120 °C on cooling and −99 °C on heating with a temperature hysteresis width of approximately 20 °C [28].

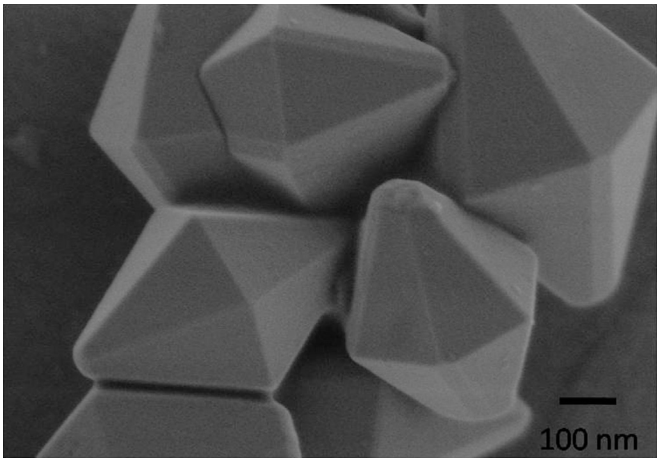

Fig. 2. SEM image of hexagonal dipyramid V_2O_3 crystals hydrothermally synthesized at 220 °C for 48 h.

3.4. Crystal growth process

To understand the growth mechanism of V_2O_3 during the hydrothermal process, serial experiments with various heating time were conducted. Products obtained at 220 °C for 6 h, 12 h, 24 h and 48 h were taken as examples for representing the four typical growth stages.

Fig. 5 shows the typical XRD patterns of the reaction products with increasing heating time. After heating at 220 °C for 6 h, the reaction product has already been crystallized as shown by the diffraction peaks in Fig. 5a. At a reaction time of 12 h, the peaks increased in intensity but were kept at almost

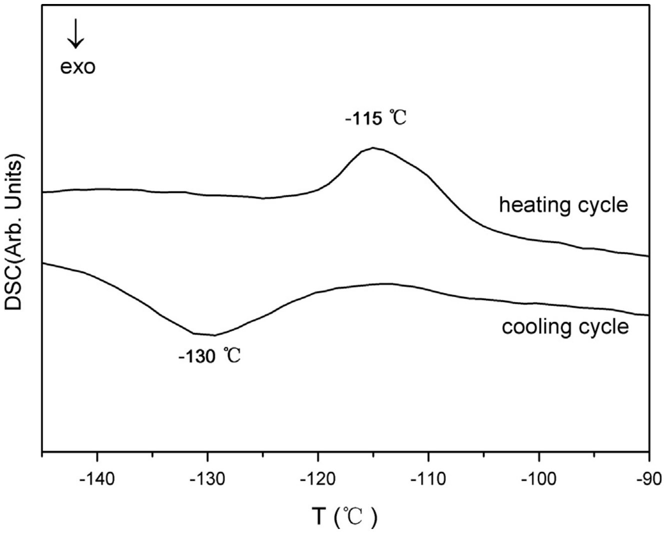

Fig. 4. DSC curves of the V_2O_3 micro-crystals of the hexagonal dipyramid.

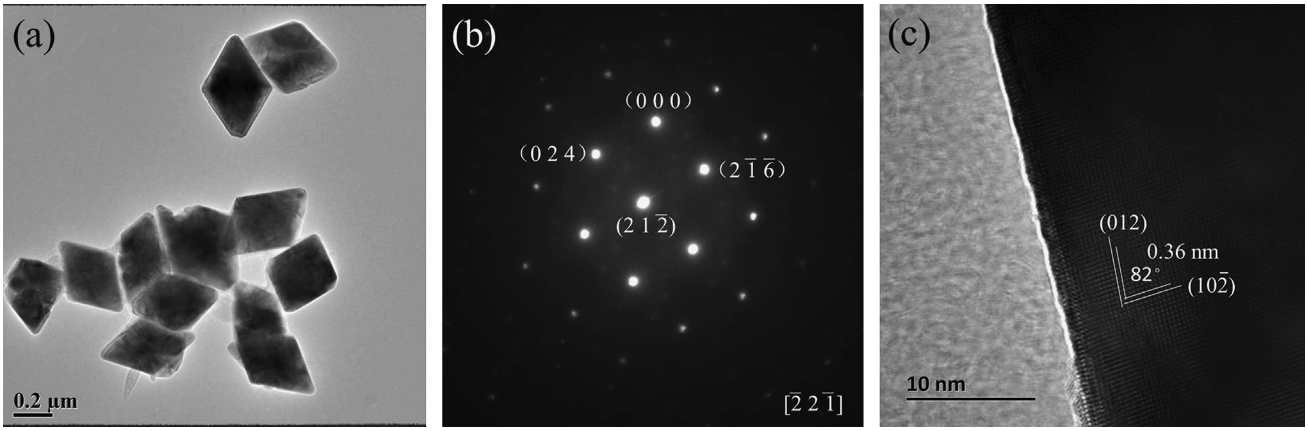

Fig. 3. TEM image (a) and the related SAED pattern (b) of hexagonal dipyramid V_2O_3 crystals, and the HRTEM image (c) of a single rhombohedral V_2O_3 hexagonal dipyramid enclosed by {012} facets.

the same position (Fig. 5b). According to the characterization and analysis of Wu et al. [29], we could identify such a vanadium oxide phase in patterns (a) and (b) as VOOH. The heating for 24 h gives a mixture of VOOH and V_2O_3 as shown in Fig. 5c. On heating for 48 h, the VOOH transforms totally into a single phase V_2O_3, as shown in Fig. 5d.

Fig. 6 demonstrates the typical FE-SEM images which illustrate the morphology change with increasing heating time during the growth process of the V_2O_3 hexagonal dipyramids. When heated for 6 h, the reaction products were composed of small particles and sheets (Fig. 6a). When the reaction time increased to 12 h, small particles disappeared and the sheets became larger and thicker (Fig. 6b). Obviously, the smaller particles aggregated into bigger sheets to satisfy the spatial requirements of the crystal growth during the “Ostwald ripening” process. The thicker sheets disappeared gradually after been heated for 24 h, and hexagonal dipyramids (though incomplete and with flaws) were formed (Fig. 6c). It is clearly seen that the hexagonal dipyramids were generated by a large number of sheets gradually appearing on their surfaces, which is consistent with the XRD pattern in Fig. 5c. Finally after been heated for 48 h, hexagonal dipyramids surrounded by almost perfect and smooth crystal facets were formed as shown in Fig. 6d.

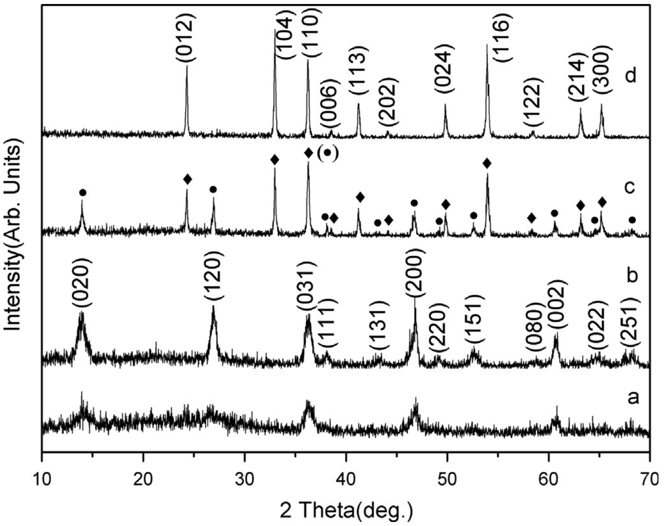

Fig. 5. XRD patterns of the reaction products with different reaction time (a) 6 h, (b) 12 h, (c) 24 h, and (d) 48 h.

3.5. Discussion

Based on the results of XRD and FE-SEM in Figs. 5 and 6, the evolution in structure and morphology by changing the heating time could be used to investigate the formation mechanism of V_2O_3 hexagonal dipyramids, the main chemical reactions involved in the hydrothermal processes are proposed as follows:

$$VO(acac)_2 + 2H^+ \rightarrow VO^{2+} + 2Hacac$$

$$4VO^{2+} + N_2H_4 + 8OH^- \rightarrow 4VOOH + N_2 + 4H_2O$$

$$2VOOH \rightarrow V_2O_3 + H_2O$$

Total reaction

$$4VO(acac)_2 + N_2H_4 + 2H_2O \rightarrow 2V_2O_3 + N_2 + 8Hacac$$

Eq. (1) is the equilibrium shift from the complex of vanadium to vanadyl cation group under hydrothermal conditions. Due to the consumption of H^+ and the formation of N_2, the reaction (2) would proceed to the right side; a high amount of VO^{2+} could be dissociated and reduced by N_2H_4 into

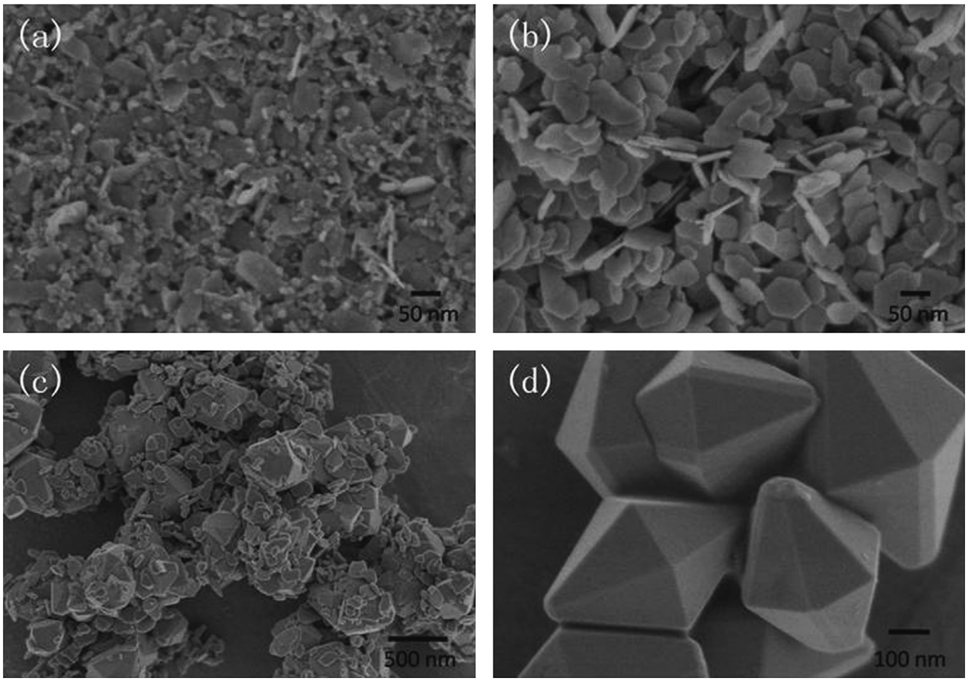

Fig. 6. SEM images of the morphology evolution of V_2O_3 samples heated at 220 °C for (a) 6 h, (b) 12 h, (c) 24 h, and (d) 48 h.

VOOH. It is a reduction and hydroxylation process that N_2H_4 is responsible for the reduction of V^{4+} to V^{3+} and OH^- is responsible for the hydroxylation of VO^{2+} to VOOH. The XRD patterns in Fig. 5 clearly illustrate the reaction process of Eq. (2). Then in reaction (3), the freshly formed VOOH monomers which have high surface energy tended to redissolve and then aggregated and dehydrated with each other in the hydrothermal process (evidently show in Fig. 6c), leading to the increase of the V_2O_3 solute concentration. When the concentration of V_2O_3 solutes was higher than its saturation solubility, the nucleation and growth of V_2O_3 crystals in the solution started. On the whole, the reduction and hydrolyzation of $VO(acac)_2$ into V_2O_3 by N_2H_4 and H_2O in the hydrothermal process are not directly and relatively complicated. It is a dissolution–recrystallization process through a phase transformation from VOOH to V_2O_3 in a given condition.

Regarding the morphology formation of unusual hexagonal dipyramids, the ligand Hacac that dissociated from $VO(acac)_2$ must play a key role in the morphology of V_2O_3 micro-crystals, since no other reagents are involved in the reaction process besides N_2H_4. According to the research work of Blagojevic et al. [27], addition of different ligands to the reaction of hydrothermal reduction in $VO(OH)_2$ using N_2H_4 as a reducing agent produces V_2O_3 particles with the morphologies of rod and platelet. However, the ligands they used cannot produce a specific morphology completely. By comparison, when NH_4VO_3 was used as the vanadium source and reduced by $N_2H_4 \cdot H_2O$ in water at 220 °C for 48 h, the mixed morphology of both hexagonal dipyramids and truncated cubes V_2O_3 was formed. The results indicated that both ligand (Hacac) and simple inorganic ions (NH^{4+}) affect the V_2O_3 crystal morphology, while ligand Hacac shows a more pronounced effect on morphology control. In general, Hacac is a more selective ligand based on morphology in the experiment.

It is found that the Hacac has a great influence on the morphologies of V_2O_3 particles by participating in the nucleation and growth. Hexagonal dipyramids V_2O_3 with the size of 200–500 nm were synthesized using $VO(acac)_2$ as the precursor in the hydrothermal solution. Hacac is a bidentate ligand that profoundly affects the crystallization of V_2O_3 by altering the deposition rate of VOOH on specific surfaces, possibly by binding to surface sites. It is noted that the dentate structure of acetylacetone ligand matches almost ideally to the arrangement of binding sites (density and spacing) of the {012} surfaces. The adsorption of Hacac to the {012} facets causes the crystal planes to grow slower compared with other planes which restrained the growth in the directions normal to the {012} facets resulting in the V_2O_3 particles with the morphology of hexagonal dipyramids enclosed by {012} facets.

4. Conclusion

Phase pure V_2O_3 micro-crystals with controlled morphology were fabricated by a facile one-step hydrothermal method. Hexagonal dipyramids of V_2O_3 with well-grown facets were obtained by reducing $VO(acac)_2$ precursor with $N_2H_4 \cdot H_2O$ in water at 220 °C for 48 h. The results indicate that V_2O_3 can be well crystallized in hydrothermal solution up to micron size with distinguished facet in one step without additional treatment. We found that the reaction mechanism is a dissolution–recrystallization process through a phase transformation from VOOH to V_2O_3 in a given condition. The Hacac dissociated from $VO(acac)_2$ has a decisive effect on the formation of hexagonal dipyramid morphology. The present work provides a facile method for preparing phase pure V_2O_3 micro-crystals with a hexagonal dipyramid morphology, which can be used as a new powder material for ceramic fabrication.

Acknowledgments

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References

[1] M.P. Pileni, The role of soft colloidal templates in controlling the size and shape of inorganic nanocrystals, Nature Materials 2 (2003) 145–150.

[2] Y.N. Xia, Y. Xiong, B. Lim, S.E. Skrabalak, Shape-controlled synthesis of metal nanocrystals: simple chemistry meets complex physics?, Angewandte Chemie International Edition 48 (2009) 60–103

[3] Y.F. Zhang, M.J. Fan, X.H. Liu, C. Huang, H.B Li, Beltlike V_2O_3@C core–shell-structured composite: design, preparation, characterization, phase transition, and improvement of electrochemical properties of V_2O_3, European Journal of Inorganic Chemistry 10 (2012) 1650–1659.

[4] C.Z. Wu, Y. Xie, Promising vanadium oxide and hydroxide nanostructures: from energy storage to energy saving, Energy and Environmental Science 3 (2010) 1191–1206.

[5] Y. Ishiwata, S. Suehiro, T. Kida, H. Ishii, Y. Tezuka, H. Oosato, E. Watanabe, D. Tsuya, Y. Inagaki, T. Kawae, M. Nantoh, K. Ishibashi, Spontaneous uniaxial strain and disappearance of the metal–insulator transition in monodisperse V_2O_3 nanocrystals, Physical Review B 86 (2012) 035449.

[6] J. Brockman, M.G. Samant, K.P. Roche, S.S.P. Parkin, Substrate-induced disorder in V_2O_3 thin films grown on annealed c-plane sapphire substrates, Applied Physics Letters 101 (2012) 051606.

[7] M.K. Stewart, D. Brownstead, S. Wang, K.G. West, J.G. Ramirez, M. M. Qazilbash, N.B. Perkins, I.K. Schuller, D.N. Basov, Insulator-to-metal transition and correlated metallic state of V_2O_3 investigated by optical spectroscopy, Physical Review B 85 (2012) 205113.

[8] A.L. Tiano, J.B. Li, E. Sutter, S.S. Wong, M.V.F. Serra, Effects of electronic correlation, physical structure, and surface termination on the electronic structure of V_2O_3 nanowires, Physical Review B 86 (2012) 125135.

[9] M.K. Liu, B. Pardo, J. Zhang, M.M. Qazilbash, S.J. Yun, Z. Fei, J. H. Shin, H.T. Kim, D.N. Basov, R.D. Averitt, Photoinduced phase transitions by time-resolved far-infrared spectroscopy in V_2O_3, Physical Review Letters 107 (2011) 066403.

[10] Y.F. Zhang, M.J. Fan, H. Ling, W.B. Wu, J.C. Zhang, X.H. Liu, Y. L. Zhong, C. Huang, Fabrication of V_2O_3/C core–shell structured composite and VC nanobelts by the thermal treatment of VO_2/C composite, Applied Surface Science 258 (2012) 9650–9655.

[11] Y. Wang, H.J. Zhang, A.S. Admar, J.Z. Luo, C.C. Wong, A. Borgna, J. Y. Lin, Improved cyclability of lithium-ion battery anode using encapsulated V_2O_3 nanostructures in well-graphitized carbon fiber, RSC Advances 2 (2012) 5748–5753.

[12] G. van der Lee, B. Schuller, H. Post, T.L.F. Favre, V. Ponec, On the selectivity of Rh catalysts in the formation of oxygenates, Journal of Catalysis 98 (1986) 522–529.

[13] Y. Xu, L. Zheng, C.Z. Wu, F. Qi, Y. Xie, New-phased metastable V_2O_3 porous urchinlike micronanostructures: facile synthesis and application in aqueous lithium ion batteries, Chemistry: A European Journal 17 (2011) 384–391.

[14] M. Foex, Comptes Rendus 223 (1946) 1126–1128.

[15] S. Kittaka, S. Sasaki, T. Morimoto, Spherical particles and their surface properties, Journal of Materials Science 22 (1987) 557–564.

[16] J.R. Sullivan, T.T. Srinivasan, E.R. Newnham, Synthesis of V_2O_3 powder by evaporative decomposition of solutions and H_2 reduction, Journal of the American Ceramic Society 73 (1990) 3715–3717.

[17] J.S. Piao, S.J. Takahashi, S. Kohiki, Preparation and characterization of V_2O_3 powder and film, Japanese Journal of Applied Physics Part 1: Regular Papers, Short Notes, and Review Papers 37 (1998) 6519–6523.

[18] C.M. Zheng, X.M. Zhang, S. He, Q. Fu, D.M. Lei, Preparation and characterization of spherical V_2O_3 nanopowder, Journal of Solid State Chemistry 170 (2003) 221–226.

[19] K.F. Zhang, X.Z. Sun, G.W. Lou, X. Liu, H.L. Li, Z.X. Su, A new method for preparing V_2O_3 nanopowder, Materials Letters 59 (2005) 2729–2731.

[20] D.S. Su, R. Schlogl, Thermal decomposition of divanadium pentoxide V_2O_5: towards a nanocrystalline V_2O_3 phase, Catalysis Letters 83 (2002) 115–119.

[21] C.V. Ramana, S. Utsunomiya, R.C. Ewing, U. Becker, Formation of V_2O_3 nanocrystals by thermal reduction of V_2O_5 thin films, Solid State Communications 137 (2006) 645–649.

[22] Z.H. Yang, P.J. Cai, L.Y. Chen, Y.L. Gu, L. Shi, A.W. Zhao, Y.T. Qian, A facile route to VN and V_2O_3 nanocrystals from single precursor NH_4VO_3, Journal of Alloys and Compounds 420 (2006) 229–232.

[23] X.H. Liu, Y.F. Zhang, S.P. Yi, C. Huang, J. Liao, H.B. Li, D. Xiao, H. Y. Tao, Preparation of V_2O_3 nanopowders by supercritical fluid reduction, Journal of Supercritical Fluids 56 (2011) 194–200.

[24] A.C. Santulli, W.Q. Xu, J.B. Parise, L.S. Wu, M.C. Aronson, F. Zhang, C.Y. Nam, C.T. Black, A.L. Tiano, S.S. Wong, Synthesis and characterization of V_2O_3 nanorods, Physical Chemistry Chemical Physics 11 (2009) 3718–3726.

[25] N. Pinna, M. Antonietti, M. Niederberger, A novel nonaqueous route to V_2O_3 and Nb_2O_5 nanocrystals, Colloids and Surfaces A: Physicochemical and Engineering Aspects 250 (2004) 211–213.

[26] Y.F. Sun, B.Y. Qu, S.S. Jiang, C.Z. Wu, B.C. Pan, Y. Xie, Highly depressed temperature-induced metal–insulator transition in synthetic monodisperse 10 nm V_2O_3 pseudocubes enclosed by {012} facets, Nanoscale 3 (2011) 2609–2614.

[27] V.A. Blagojevic, J.P. Carlo, L.E. Brus, M.L. Steigerwald, Y.J. Uemura, S.J.L. Billinge, W. Zhou, Magnetic phase transition in V_2O_3 nanocrystals, Physical Review B 82 (2010) 045104.

[28] C.M. Zheng, X.M. Zhang, S. He, Q. Fu, D.M. Lei, Preparation and characterization of spherical V_2O_3 nanopowder, Journal of Solid State Chemistry 170 (2003) 221–226.

[29] C.Z. Wu, Y. Xie, L.Y. Lei, S.Q. Hu, C.Z. OuYang, Synthesis of new-phased VOOH hollow “dandelions” and their application in lithium-ion batteries, Advanced Materials 18 (2006) 1727–1732.