



## V<sub>2</sub>O<sub>3</sub> 纳米粉末的固相反应合成

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## Preparation and Characterization of V<sub>2</sub>O<sub>3</sub> Nanopowder by Solid Phase Reaction

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**Abstract:** Vanadium sesquioxide (V<sub>2</sub>O<sub>3</sub>) nanopowder was successfully prepared by the solid phase reaction of the mixture of vanadyl hydroxide (VO(OH)<sub>2</sub>) and ammonium chloride (NH<sub>4</sub>Cl) at 500 °C. The as-obtained samples were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). V<sub>2</sub>O<sub>3</sub> nanoparticles were well dispersed and displayed sphere-like particles with diameters in the range of 30~50 nm.

**Key words:** vanadium sesquioxide; nanopowder; solid phase reaction

## 0 Introduction

With the growing interest in building advanced materials using nanoscale building blocks, inorganic nanomaterials have attracted considerable attention due to their strong size dependent properties and excellent chemical processibility<sup>[1~5]</sup>. As a member of vanadium oxides, pure vanadium sesquioxide (V<sub>2</sub>O<sub>3</sub>) displays a single metal-insulator transition (MIT) around 160 K, changing from a low-temperature anti-ferromagnetic insulator to a high-temperature paramagnetic phase<sup>[6]</sup>. For V<sub>2</sub>O<sub>3</sub> doped by Cr<sup>[7]</sup>, Al<sup>[8]</sup> and Mo<sup>[9]</sup>, the transition temperature may be controlled by changing the proportion of the doped metals. It's convenient for us to prepare some functional devices such as temperature sensors and current regulators<sup>[10,11]</sup>.

Furthermore, V<sub>2</sub>O<sub>3</sub> powder can be used in conductive polymer composites<sup>[12]</sup> and in catalysts<sup>[13]</sup>.

Many methods for preparing V<sub>2</sub>O<sub>3</sub> powder have been studied<sup>[14~17]</sup>. Spherical V<sub>2</sub>O<sub>3</sub> particles were prepared by O<sub>2</sub>-H<sub>2</sub> flame of V<sub>2</sub>O<sub>3</sub> at 2 000 °C; spherical and necking V<sub>2</sub>O<sub>3</sub> powders were synthesized by reducing V<sub>2</sub>O<sub>5</sub> from evaporative decomposition of solutions in H<sub>2</sub> flow at 850 °C for 6 h. Furthermore, V<sub>2</sub>O<sub>3</sub> powders were prepared by pyrolyzing the hydrazine containing vanadium salt and reducing the sol gel synthesized V<sub>2</sub>O<sub>5</sub> in H<sub>2</sub> stream. However, only micropowder could be obtained by these methods.

Thus far, there have been just two reports about the preparation of V<sub>2</sub>O<sub>3</sub> nanoparticles. Toshiyuki et al. synthesized V<sub>2</sub>O<sub>3</sub> nanoparticles by laser-induced vapor-phase reaction<sup>[18]</sup>. Zheng et al. prepared V<sub>2</sub>O<sub>3</sub>

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nanopowders in 2003 with spherical particles by reductive pyrolysis of ammonium oxovanadium (IV) carbonate hydroxide,  $(NH_4)_2[(VO)_6(CO_3)_4(OH)_9] \cdot 10H_2O$ , in a  $H_2$  flow<sup>[19]</sup>. Herein, we present a novel chemical route to prepare nanopowders by the thermal treatment of the mixture of vanadyl hydroxide ( $VO(OH)_2$ ) and ammonium chloride ( $NH_4Cl$ ). The average particle size of the as-synthesized sample is 30~50 nm. Compared with previous reports, the reaction conditions for this method are much simpler and easier to control, although high temperature was employed in the process.

## 1 Experimental

All the reagents used in this work were analytical grade and were purchased from Beijing Chemical Co. Ltd. The procedure employed for preparing  $V_2O_3$  nanopowder was as follows: vanadium pentoxide ( $V_2O_5$ ) (0.910 g, 5 mmol) and concentrated sulfuric acid (2 mL) were respectively added into 50 mL distilled water by vigorous magnetic stirring to get a suspending system, and then the system was heated to 90 °C with a flow of fresh sulphur dioxide and continuous stirring until it gave a clear blue solution. 5% ammonia was added dropwise to adjust the pH value to 6~7. The resulting gray precipitate, after being vacuum-filtered and washed five times with 100 mL distilled water, was dispersed in 50 mL supersaturated aqueous solution containing 20 g  $NH_4Cl$ . The gray and white mixture was obtained by vacuum filtration at 0 °C after the system was stirred for 2 h at 30 °C. The mixture was directly put into a quartz tube and treated thermally at 400~500 °C for 5 h under the argon atmosphere. And then, it was gradually cooled down to room temperature. A loose black powder was obtained.

X-ray diffraction (XRD) pattern was obtained on a Rigaku (Japan) D/MAX-2400 X-ray diffractometer with Cu  $K\alpha$  radiation ( $\lambda=0.154\ 178\ nm$ ), at a scanning rate of  $0.02^\circ \cdot s^{-1}$  in the  $2\theta$  range of  $20^\circ$  to  $80^\circ$ . TEM images and ED patterns were taken with Hitachi H-800 transmission electron microscopy, using an accelerating voltage of 100 kV. X-ray photoelectron spectroscopy (XPS) data were obtained by a V.G. ESCA Lab. 2201-XL photoelectron spectrometer with a Al  $K\alpha$  source, a concentric hemispherical analyzer operating in fixed analyzer transmission mode and a multi-channel detector. The pressure in the analysis cham-

ber was less than  $2.7 \times 10^{-8}$  Pa. The spectra were acquired with a 30 eV pass energy and a binding energy was calibrated with reference to the C1s level of carbon.

## 2 Results and discussion

Fig.1 shows the powder diffraction pattern of the sample prepared at 500 °C. As is shown, all the diffraction peaks are in good agreement with the bulk rhombohedral  $V_2O_3$  (JCPDS file 34-187). According to the Scherrer Equation, the grain size calculated from the data of the peaks (012), (104), and (110) is 31.1, 26.8 and 29.3 nm, respectively. Typical TEM images of the  $V_2O_3$  powder are shown in Fig.2. The crystallites display sphere-like morphology with diameters of 30~50 nm. ED patterns (Fig.2 insert) suggest that the powder is polycrystalline.

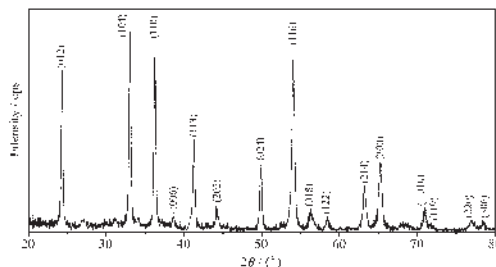


Fig.1 XRD pattern for the sample prepared at 500 °C

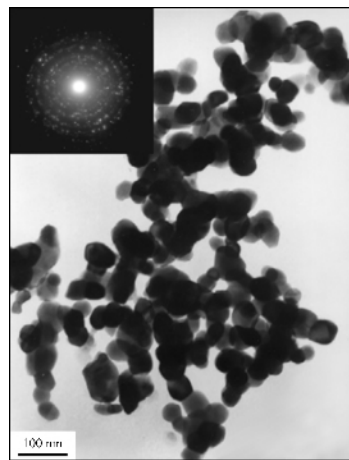


Fig.2 TEM and ED image for the sample prepared at 500 °C

The XPS result shows the existence of vanadium and oxygen without any impurities. Fig.3 is the enlarged XPS spectrum between 510.0 and 532.5 eV. The peaks at 516.8 eV and 524.2 eV are attributed to the spin-orbit splitting of the components,  $V2p_{3/2}$  and  $V2p_{1/2}$ . The binding energy of O1s in  $V_2O_3$  is located

at 530.3 eV. All assigned binding energies agree well with the literature values<sup>[19,20]</sup>.

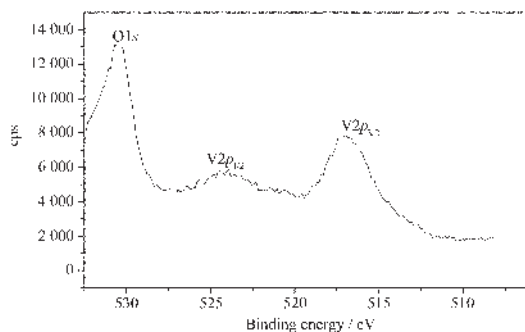


Fig.3 XPS spectrum of typical elements in the sample obtained at 500 °C

The formation of  $V_2O_3$  nanoparticles is suggested from the reactions as follows:

- (1)  $H_2SO_4 + V_2O_5 + SO_2 \rightarrow 2VOSO_4 + H_2O$ <sup>[20]</sup>
- (2)  $VOSO_4 + 2NH_3 \cdot H_2O \rightarrow VO(OH)_2 + (NH_4)_2SO_4$
- (3)  $NH_4Cl \rightarrow NH_3 + HCl$
- (4)  $6VO(OH)_2 + 2NH_3 \rightarrow 3V_2O_3 + N_2 + 9H_2O$

From vanadium(+4) in  $VO(OH)_2$  to vanadium (+3) in  $V_2O_3$ , we propose that  $NH_3$  from decomposition of  $NH_4Cl$  may play a critical role on the reduction of vanadium.

To further understand this process, some comparison experiments were conducted to explore the mechanism above.  $VO(OH)_2$  was directly treated thermally without the presence of  $NH_4Cl$  under the same reaction conditions; the results show that  $VO_2$  crystal was obtained<sup>[21]</sup>. Also, excess  $NH_4Cl$  was mixed with  $VO(OH)_2$  dried in vacuum at 80 °C for 5 h, and then the mixture, after being fully ground for a few minutes, was treated thermally;  $V_2O_3$  crystal was achieved. Additionally,  $V_2O_3$  was also obtained when  $VO(OH)_2$  was subject to thermal treatment in the flow of  $NH_3$ . Although  $V_2O_3$  crystal could be obtained from the comparison reactions above, the aggregation is very serious and there are some impurities peaks in XRD patterns. These experiments above illustrate the proposed mechanism that  $NH_3$  acted as a reductant. We believe that the obtained dispersed  $V_2O_3$  nanoparticles are related to the mixture formation method and gases' released during the thermal treatment.  $NH_4Cl$  and  $VO(OH)_2$  formed a well-dispersed mixture with continuous stirring when the system was lowered from 30 °C to 0 °C. Thus, the gases,  $NH_3$  and  $HCl$ , from thermal treatment may play a crucial role on particles' dispersion. That is to say, the gases formed a soft "shell"

surrounding the particles to prevent them from aggregating to larger particles.

### 3 Conclusion

In summary, a novel chemical route based on the thermal reaction of the mixture of  $NH_4Cl$  and  $VO(OH)_2$  for fabrication of  $V_2O_3$  nanopowder has been developed. We believe that this synthetic strategy may be potentially extendable to prepare other nanopowder materials. Intensive research is under progress in our laboratory.

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