



## Characterization of nanometer-sized VO<sub>2</sub> nanoparticles prepared by an aqueous route

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We describe a convenient aqueous route to prepare VO<sub>2</sub>, based on the reductive precipitation of vanadium dioxide VO<sub>2</sub> from a vanadate solution. The effect of the reaction conditions is systematically studied, and a protocol to optimize the production of VO<sub>2</sub> while minimizing the appearance of other compounds is presented. The products were characterized using calorimetry, X-ray diffraction and high-resolution scanning electron microscopy.

### 1. Introduction

Vanadium oxides have attracted attention because of their potential or actual applications as catalysts, chemical sensors, electrodes for lithium batteries, and as the active components of various electrical and optical devices[1, 2]. Vanadium dioxide (VO<sub>2</sub>) is particularly interesting as some forms of it undergo a reversible metal/insulator phase transition at ~67°C with a large attendant change in electrical and optical properties[3]. This has suggested its application as, for example, a ‘smart’ window coating, or in optical switches[2, 4]. VO<sub>2</sub> itself has at least six known polymorphs and some hydrated VO<sub>2</sub>.nH<sub>2</sub>O compounds are also known[5, 6]; however it is the metastable monoclinic VO<sub>2</sub>-B, tetragonal VO<sub>2</sub>-R, and monoclinic VO<sub>2</sub>-M<sub>1</sub> phases that are most relevant in the present context. VO<sub>2</sub>-R is metallic and has the rutile structure, while VO<sub>2</sub>-M<sub>1</sub> is a semi-conductor, with a band gap of about 0.6 eV[7]. The latter two polymorphs are related to one another by a reversible, displacive phase transformation at about 67°C, with VO<sub>2</sub>-R being stable above that temperature and VO<sub>2</sub>-M<sub>1</sub> below it. There are several methods by which VO<sub>2</sub>-M<sub>1</sub> or VO<sub>2</sub>-R can be produced, including physical vapour deposition, ion implantation, chemical vapour deposition, sol-gel processing and lyphilization of suitable precursor solutions. Commonly, however, VO<sub>2</sub>-B is first prepared by whatever means and then it is converted to VO<sub>2</sub>-R by heat treatment in an inert environment and at a temperature in excess of 330°C. We sought a method suitable for producing VO<sub>2</sub> in relatively large quantities. Our protocol invokes the reductive-precipitation of VO<sub>2</sub>.nH<sub>2</sub>O from a vanadate solution, and is based on a process apparently first disclosed by two groups in 1998[1, 8]. Calcination of the VO<sub>2</sub>.nH<sub>2</sub>O converts it into VO<sub>2</sub>-R. We use ammonium metavanadate (NH<sub>4</sub>VO<sub>3</sub>) solution as our source of V, and KBH<sub>4</sub> as reductant.

### 2. Experimental

NH<sub>4</sub>VO<sub>3</sub> was purchased from Ajax Chemicals Ltd, Sydney, Australia. KBH<sub>4</sub> was purchased from Sigma Chemical Co., and HCl (37%) was obtained from Labscan Asia Co., Ltd.. All reagents were used without further purification. The KBH<sub>4</sub> solution was freshly produced, as needed, by dissolving the compound in ice-cold MilliQ water. The temperature must be kept low to prevent hydrolysis of borohydride ion. Concentrated HCl was first added dropwise into between 10 to 50 ml of the NH<sub>4</sub>VO<sub>3</sub> solution to adjust its pH to a selected value between 4.0 and 6.5. The reducing power of KBH<sub>4</sub> increases with the decreasing of pH value of the medium suggesting that it might be more effective at the lower end of the pH range[1].



The reduction reaction was then carried out at the desired pH by slowly adding the  $\text{KBH}_4$  solution while continuing the dropwise additions of  $\text{HCl}$  and simultaneously stirring. At the end of the reduction reaction, the brown-black precipitate of  $\text{VO}_2 \cdot n\text{H}_2\text{O}$  was collected by filtration, washed several times with a mixture of water and methanol, and dried at about  $90^\circ\text{C}$  in an air oven. The dry solid is amorphous or at best nanocrystalline at this stage, in agreement with product produced in other wet chemical reductive schemes, e.g.[1]. This phase, in turn, can be converted to  $\text{VO}_2\text{-R}$  by heating at temperatures greater than  $\sim 330^\circ\text{C}$  in an inert environment[1, 9] In the present work we used an environment of pure argon or nitrogen. Finally, on reverting to room temperature the  $\text{VO}_2\text{-R}$  transformed to  $\text{VO}_2\text{-M}_1$  by the metal-to-insulator transition.

The as-synthesized samples were characterised by X-ray diffraction (XRD, Siemens D5000 Diffractometer) with  $\text{Cu K}\alpha$  radiation ( $\lambda=0.15406\text{ nm}$ ). Scanning electron microscopy (SEM) images were taken with a Zeiss Supra 55VP SEM. A differential scanning calorimeter (DSC 2920, TA Instruments Inc., U.S.A.) was employed to test the phase transformation. X-ray diffraction patterns were calculated from the published lattice data using the program Crystallographica (produced by Oxford Cryosystems Ltd, of the United Kingdom).

### 3. Results

After systematic investigation, we found that  $\text{VO}_2\text{-M}_1$  could be reliably produced if the pH of the reaction was held at about 4.2, the ratio of  $\text{KBH}_4$  to  $\text{NH}_4\text{VO}_3$  was 5, the temperature of the reaction at about  $20$  to  $25^\circ\text{C}$ , and calcination was carried out at  $600^\circ\text{C}$ .

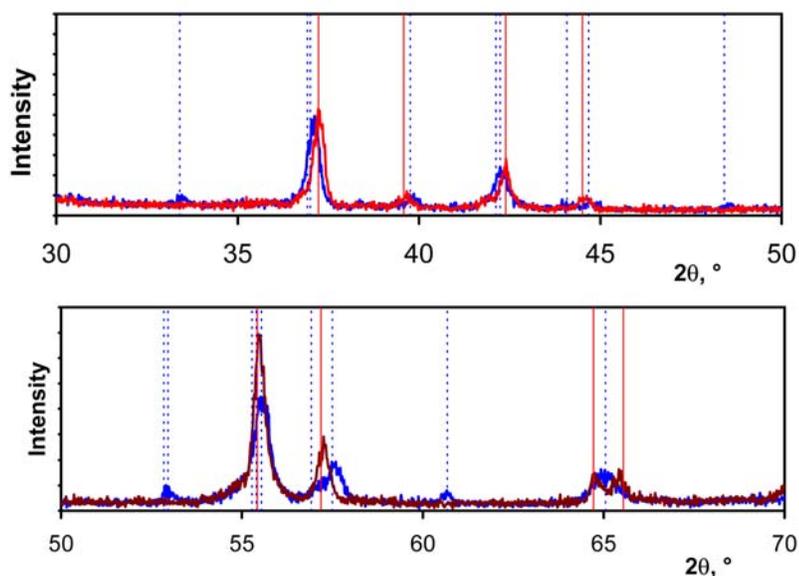


Fig. 1 XRD patterns of  $\text{VO}_2\text{-M}_1$  (blue) at room temperature and  $\text{VO}_2\text{-R}$  (red) at  $\sim 80^\circ\text{C}$ , also showing standard peak positions (coloured lines) for each phase.

Fig. 1 shows the X-ray diffraction patterns for such ‘optimum’ material, which was converted to  $\text{VO}_2\text{-R}$  (JCPDS 73-2362) by heat treatment and cycled between  $\text{VO}_2\text{-M}_1$  (JCPDS 44-0252) and  $\text{VO}_2\text{-R}$  on a hot stage. Under the optimum conditions the resulting material is almost pure, and has an XRD pattern nearly identical to the standards. The remaining small peaks in this case match the pattern of  $\text{V}_6\text{O}_{13}$ , an oxide of mixed valence. Fig. 2 shows that the diameter of the  $\text{VO}_2\text{-M}_1$  particles is about  $100\text{ nm}$ , which is about twice the diameter of the particles of precursor material, as dried in air oven at  $85^\circ\text{C}$  for  $1\text{ h}$ . The result demonstrates that crystallization of the  $\text{VO}_2\text{-R}$  is accompanied by particle coarsening. In Fig. 3 we examine the metal-insulator transition in more detail. In this case the  $\text{VO}_2\text{-M}_1$  was heated from room temperature to  $120^\circ\text{C}$  at  $3^\circ\text{C}/\text{min}$  under a flowing air atmosphere, and then back to



room temperature. The insulator-to-metal transition occurred at 66°C, and the metal-to-insulator transition at 61°C.

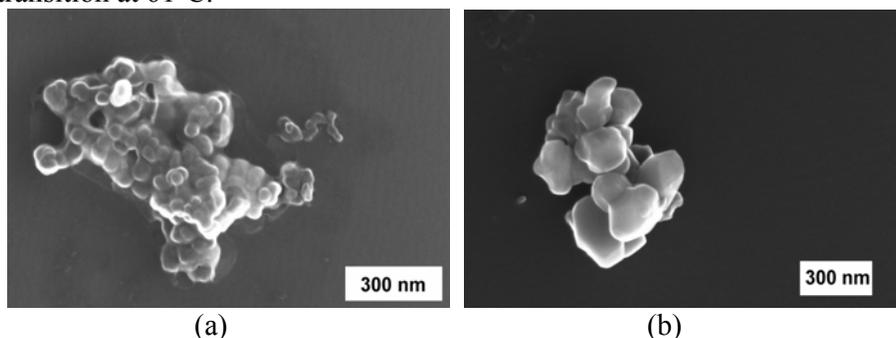


Fig.2 SEM photos of VO<sub>2</sub> nano-particles produced as described in the text. (a) Dried in air oven at 85°C for 1h. (b) Dried in tube oven at 600°C under flow of argon for 20h.

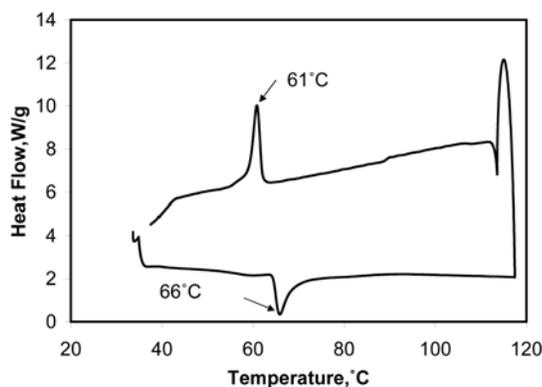


Fig. 3 DSC curve showing the reversible VO<sub>2</sub>-M<sub>1</sub> ↔ VO<sub>2</sub>-R phase transformation in the present material. There is a hysteresis of 5°C in the reaction.

## Conclusions

Nano-crystalline VO<sub>2</sub>-M<sub>1</sub> was successfully synthesized by a convenient process involving aqueous reductive-precipitation at room temperature followed by calcination. If the pH and ratio of KBH<sub>4</sub> to NH<sub>4</sub>VO<sub>3</sub> during the precipitation reaction are both kept in the range 4~5, and if the subsequent annealing temperature is 600°C, then the synthesized nano-crystals of VO<sub>2</sub>-M<sub>1</sub> are about 100 nm in size. The transition temperature of the material produced was in the range 61 to 66°C.

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