

# Fabrication of VO<sub>2</sub> nanopowder via direct reaction of vanadium metal and hydrogen peroxide

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A vanadium-oxide-based precursor fine powder was prepared by the reaction of vanadium metal and H<sub>2</sub>O<sub>2</sub>. A VO<sub>2</sub> powder with particles tens of nanometers in size was obtained by treatment of the precursor powder at 650°C in an H<sub>2</sub>/Ar atmosphere. The particle size of the resulting VO<sub>2</sub> powder was 40 nm, and the transition temperature of the obtained VO<sub>2</sub> powder was 68.5°C.

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## 1. Introduction

VO<sub>2</sub> exhibits a metal–insulator transition at about 68°C, accompanied by a crystallographic transition from a low-temperature monoclinic phase to a high-temperature tetragonal rutile structure.<sup>1),2)</sup> This phase transition causes abrupt changes in the electrical and optical properties, hence VO<sub>2</sub> has potential applications in thermochromic smart windows.<sup>3)–8)</sup> There have been several studies focused on applications of VO<sub>2</sub> fine particles, such as composites of VO<sub>2</sub> powders in polymeric matrices,<sup>9)</sup> and coating nanosized VO<sub>2</sub> powders on glass substrates.<sup>10)</sup>

In previous studies, VO<sub>2</sub> fine particles were fabricated by reduction of VO<sub>2</sub> (B) nanopowders,<sup>10)</sup> reduction of V<sub>2</sub>O<sub>5</sub>·xpyridine·yH<sub>2</sub>O particles,<sup>11)</sup> and reduction of vanadium oxide precursor particles from a vanadium oxyisopropoxide solution.<sup>12)</sup> We have found that a vanadium oxide nanopowder (two-dimensional V<sub>2</sub>O<sub>5</sub>-like,<sup>13)</sup> 2D-V<sub>2</sub>O<sub>5</sub>) can be obtained by direct reaction of vanadium metal and H<sub>2</sub>O<sub>2</sub>, without cooling. The 2D-V<sub>2</sub>O<sub>5</sub> powder<sup>13)</sup> can be dissolved in water, however, the vanadium oxide nanopowder obtained in this investigation cannot be dissolved in water. Since the powder in this investigation does not deliquesce with water vapor in air, it is easy to handle in experiments. In this investigation, VO<sub>2</sub> powders of nanometer size were fabricated by reduction of precursor nanopowders, and the thermal properties and microstructures of the resulting VO<sub>2</sub> powders were evaluated.

## 2. Experimental procedure

Metallic vanadium powder (Wako, Osaka, Japan) was used as the starting material. Vanadium powder (0.3 g) was mixed with 30% H<sub>2</sub>O<sub>2</sub> solution (30 mL) at room temperature, without cooling. The mixture reacted vigorously, and a dark-brown powder was obtained. The resulting powder was dried at 100°C to remove residual water, and the dried powder was heat-treated at 500–700°C for 2 h in an H<sub>2</sub>/Ar (4% H<sub>2</sub>) atmosphere.

The crystal structure of the VO<sub>x</sub> powder was determined by X-ray diffraction (XRD) using a Miniflex II diffractometer (Rigaku, Tokyo, Japan) with Cu Kα radiation. Differential scanning calorimetry (DSC) was performed on the resulting powder using a DTG-60 calorimeter (Shimadzu, Kyoto, Japan), with the temperature increasing at a rate of 10°C/min. The microstructures of the precursor and the heat-treated powders were observed by transmission electron microscopy (TEM; EM-002B, Topcon Corp., Tokyo, Japan); the powders were supported on copper grids during the observations.

## 3. Results and discussion

The precursor powder was obtained by direct reaction of vanadium metal and H<sub>2</sub>O<sub>2</sub>, and the precursor powder was obtained by heat-treatment at 500–700°C in an H<sub>2</sub>/Ar atmosphere. **Figure 1** shows the XRD patterns of the precursor powder and the heat-treated powders. The precursor powder was assigned the 2D-V<sub>2</sub>O<sub>5</sub> structure. The structures of the powders heat-treated at 500 and 550°C were the V<sub>3</sub>O<sub>7</sub> phase. The powder heat-treated at 600°C consisted of V<sub>3</sub>O<sub>7</sub> as the main phase and V<sub>6</sub>O<sub>13</sub> as a secondary phase. Above 650°C, the heat-treated powder was a VO<sub>2</sub> single phase of high crystallinity. The sample heat-treated at 700°C was also a VO<sub>2</sub> single phase, but of low crystallinity, and the resulting powder melted slightly. When the sample was heat-treated above 700°C, the sample melted completely. The precursor powder was very similar to V<sub>2</sub>O<sub>5</sub>, and the melting point of the precursor was close to 690°C (the V<sub>2</sub>O<sub>5</sub> melting point). The crystallinity of the sample heat-treated at 700°C therefore decreased. These results show that the optimal heat-treatment temperature for obtaining VO<sub>2</sub> powder was 650°C.

The crystallite size of the VO<sub>2</sub> powder heat-treated at 650°C was calculated from the full-width at half-maximum (FWHM) of the XRD peaks, using Scherrer's equation:<sup>14)</sup>

$$D = K\lambda / (B \cos \theta),$$

where  $D$  is the particle diameter,  $\lambda$  is the X-ray wavelength used,  $B$  is the FWHM of a diffraction peak,  $\theta$  is the diffraction angle,

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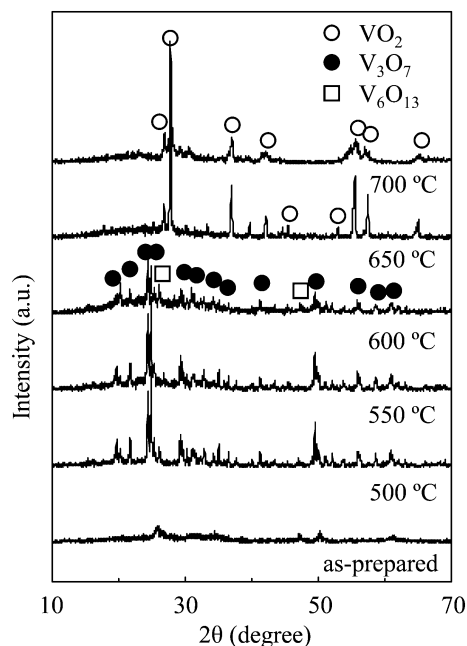


Fig. 1. XRD patterns of as-prepared powder and  $\text{VO}_2$  powders heat-treated at various temperatures.

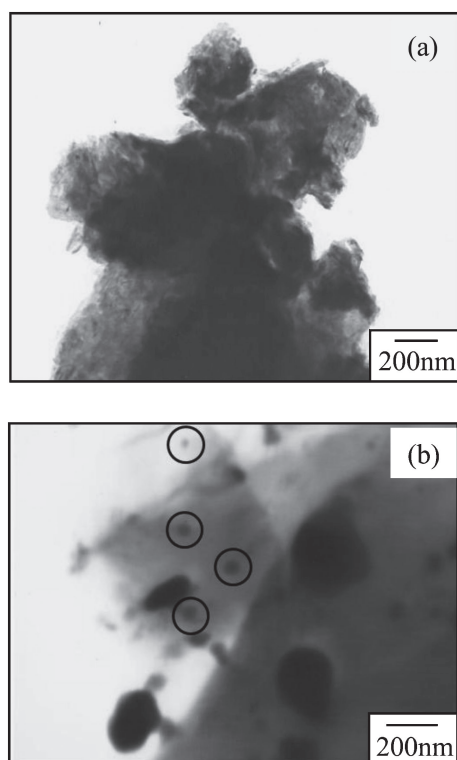


Fig. 2. TEM bright-field images of (a) the precursor powder and (b) the  $\text{VO}_2$  powder heat-treated at 650 °C in an  $\text{H}_2/\text{Ar}$  atmosphere.

and  $K$  is Scherrer's constant, which is of the order of unity for most crystals. In this investigation, the value of  $K$  used was 0.9, and the calculated size of the  $\text{VO}_2$  powder heat-treated at 650 °C was 30 nm.

To determine the particle size precisely, TEM observations were carried out on the  $\text{VO}_2$  powder heat-treated at 650 °C. **Figure 2** shows the bright-field TEM images of the precursor

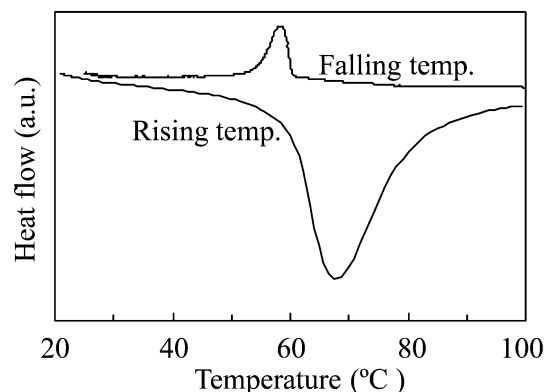


Fig. 3. DSC curve for the  $\text{VO}_2$  powder heat-treated at 650 °C in an  $\text{H}_2/\text{Ar}$  atmosphere.

powder and the resulting  $\text{VO}_2$  powder heat-treated at 650 °C; the closed circles in Fig. 2(b) denote  $\text{VO}_2$  particles. The primary particle size of the precursor powder was tens of nanometers and secondary particles were formed by aggregation of the primary particles. The primary particle size of the heat-treated powder was 40 nm, and secondary particles were also formed by aggregation of the primary particles. The secondary particle sizes before and after heat-treatment were very close to each other, therefore the secondary particle size of the  $\text{VO}_2$  powder did not change much as a result of the heat-treatment. The estimated particle size of the heat-treated powder obtained using TEM was 40 nm, which is close to the particle size calculated from the XRD measurements. These results suggest that  $\text{VO}_2$  powders of nanometer particle size can be obtained by heat-treatment of the precursor powder at 650 °C in an  $\text{H}_2/\text{Ar}$  atmosphere.

To measure the transition temperature of the resulting specimens, DSC measurements were carried out on the  $\text{VO}_2$  powder heat-treated at 650 °C. **Figure 3** shows the DSC curves for the  $\text{VO}_2$  powder. An endothermic peak was observed at 68.5 °C as the temperature increased, and an exothermic peak was observed at 57.4 °C as the temperature decreased. Generally, crystallographic transitions of  $\text{VO}_2$  show thermal hysteresis, and the transition temperature of  $\text{VO}_2$  varies depending on whether the temperature is increasing or decreasing, and is accompanied by thermal hysteresis. In this investigation, the resulting  $\text{VO}_2$  powder also showed different transition temperature for increasing and decreasing temperatures. The transition temperature of the resulting  $\text{VO}_2$  powder was 68.5 °C as the temperature increased; this was close to the previously reported values.<sup>1)–8)</sup>

#### 4. Conclusion

A vanadium-oxide-based precursor fine powder was prepared by the reaction of vanadium metal and  $\text{H}_2\text{O}_2$ , and a  $\text{VO}_2$  powder with a particle size of tens of nanometers was obtained from the precursor powder in a reducing  $\text{H}_2/\text{Ar}$  atmosphere. In order to fabricate  $\text{VO}_2$  powder with a particle size of tens of nanometers, the optimal heat-treatment temperature of the precursor powder was 650 °C. The particle size of the resulting  $\text{VO}_2$  powder was 40 nm. The resulting  $\text{VO}_2$  nanopowder exhibited a phase transition, and the transition temperature was 68.5 °C.

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