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# Preparation of Monodisperse and Spherical Rutile $VO_2$ Fine Particles

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Fine particles of metal oxides have been widely investigated not only because of their technological applications as pigments and catalysts but also because of their potential uses as raw materials for advanced ceramics.[1−3] They have also attracted attention recently in opal-based photonic crystals (i.e., three-dimensionally ordered arrays of spherical particles),[4−6] but only a few such crystals have been reported because it has not been easy to prepare spherical metal-oxide fine particles with a sufficiently narrow size distribution.[7−14] Developing a new method of preparing monodisperse and spherical metal-oxide fine particles is thus a challenging issue and a key to success for the opal-based photonic crystal applications.

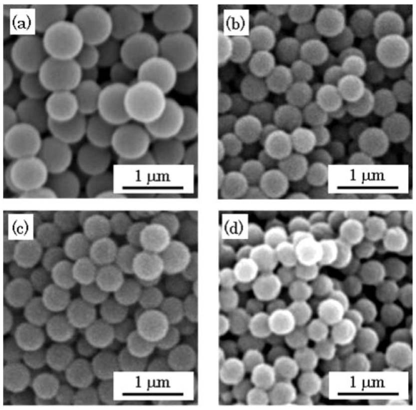

**Figure 1.** SEM images of VOPs (a) before and after annealing for 2 h in flowing $H_2$ at (b) 300 °C, (c) 400 °C, and (d) 500 °C.

Vanadium dioxide with a rutile structure ($VO_2$(R)) shows a reversible metal−insulator transition at about 70 °C.[15−19] This transition, associated with a structural transition from monoclinic to tetragonal and also causing abrupt changes in infrared transmission and electrical resistivity[15,17] will be useful in various applications.[20−22] $VO_2$(R) has been prepared in several forms such as sintered powders, single crystals, and thin films, but few works have focused on preparation of fine particles.[23−28] $VO_2$(R) has been formed into rods[23,25] and wires,[24] but it has not been possbile to obtain fine spherical $VO_2$(R) particles with a narrow size distribution.

We recently succeeded in preparing $V_2O_5 \cdot x\mathrm{Py} \cdot yH_2O$ ($x \approx 0.8$, $y \approx 0.9$) particles (VOPs) by a hydrolysis of vanadium isopropoxide ($VO(O\mathit{i}Pr)_3$) in acetone/pyridine/$H_2O$ mixture solutions.[29] The fine particles we obtain had a narrow distribution of sizes, were almost perfectly spherical, and were not agglomerated. More important, their size could be easily adjusted anywhere between 200 and 800 nm by changing the pyridine concentration. Here we report that monodisperse and spherical $VO_2$(R) fine particles can be obtained by reducing these VOPs and that the fine particles obtained this way show a reversible metal−insulator transition at about 70 °C.

Figure 1 shows SEM images of VOPs 469 ± 52 nm in diameter (mean ± standard deviation) before and after 2 h of annealing at various temperatures in flowing $H_2$. We can clearly see that although particle size decreases with increas-

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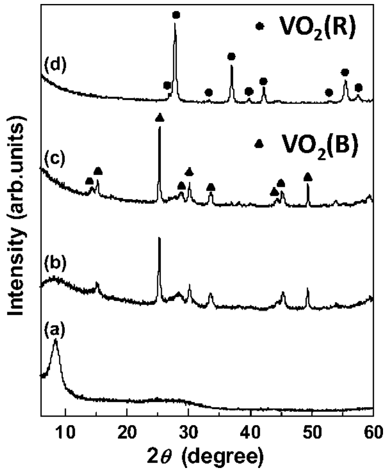

**Figure 2.** XRD patterns of VOPs (a) before and after annealing for 2 h in flowing $H_2$ at (b) 300 °C, (c) 400 °C, and (d) 500 °C.

ing annealing temperature, VOPs annealed at temperatures up to 500 °C remain monodisperse and spherical. The decrease in the particle size can be largely attributed to deintercalation of $H_2O$ and pyridine molecules, which was confirmed by infrared measurements of VOPs annealed at various temperatures (Figure S1, Supporting Information).

The XRD patterns of the samples obtained by the same annealing conditions used for the SEM measurements (Figure 1) are shown in Figure 2. The XRD pattern of the VOPs before annealing shows a diffraction peak at about $2\theta = 8.4°$, which corresponds to the characteristic *d*-spacing of the layered structure of VOP.[29] A metastable $VO_2$(B) phase was formed at 300 °C, and a $VO_2$(R) phase was formed at 500 °C. This annealing condition thus produced $VO_2$(R) but did not cause sintering nor cause losing their original spherical morphology as clearly shown in Figure 1d. Annealing VOPs in flowing $H_2$(5%)/Ar(95%) gas at 500 °C for 2 h, on the other hand, yielded mixed phases and did not produce single-phase $VO_2$(R): weak diffraction peaks from $VO_2$(R) and intense diffraction peaks from $V_6O_{13}$ with high-oxidation-state $V^{5+}$ ions were observed (Figure S2, Supporting Information). The result implied that reduction of $V_2O_5$ to $VO_2$ did not complete within 2 h in flowing $H_2$(5%)/Ar(95%) gas at 500 °C, and annealing at a higher temperature or longer time should be necessary for preparing the single-phase $VO_2$(R). However, extensive annealing caused sintering of the particles, resulting in the losses of their narrow size distribution and the spherical shape, because the annealing at 500 °C for 2 h already caused sintering (Figure S3, Supporting Information).

Unlike the sample annealed in the pure $H_2$ gas, the sample annealed in flowing $H_2$(5%)/Ar(95%) gas showed no sign of the metastable $VO_2$(B). This result strongly suggests that metastable $VO_2$(B) plays an important role to form $VO_2$(R) structure without losing spherical morphology of VOPs. This is consistent with previous reports that annealing $VO_2$(B) particles is an effective route to produce $VO_2$(R) fine particles with less sintering.[26−28] Appropriate reducing conditions enable single-phase $VO_2$(B) to be produced, which could be a key to maintain the spherical morphology of the precursory VOPs while forming $VO_2$(R) phase.

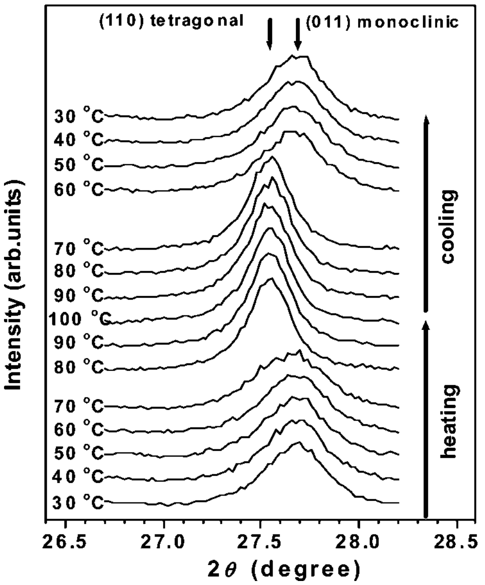

**Figure 3.** Variable-temperature XRD patterns of $VO_2$(R) fine particles.

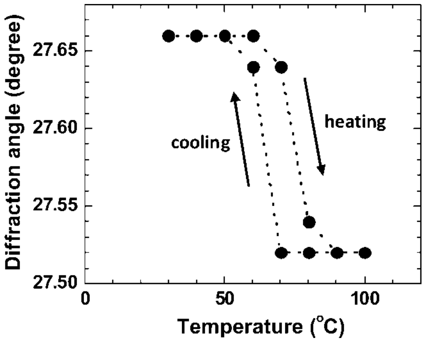

**Figure 4.** Diffraction angle of the main peak of $VO_2$(R) fine particles plotted as a function of temperature.

All the above results indicated that the reducing condition range in temperature, atomsphere, and time was very limited for forming monodisperse and spherical $VO_2$(R) particles because the reduction of VOPs took place simultaneously with the deintercalation of $H_2O$ and pyridine molecules. It should be noted here that we obtained monodisperse and spherical $VO_2$(R) fine particles ≈ 200 nm in diameter by annealing VOPs 270 nm in diameter at 500 °C for 2 h in flowing $H_2$ and obtained monodisperse and spherical $VO_2$(R) fine particles ≈ 400 nm in diameter by annealing VOPs 652 nm in diameter at 500 °C for 2 h in flowing $H_2$ (see Figures S4 (Supporting Information) and 5b).

An important feature of $VO_2$(R) is a metal−insulator transition associated with the structural phase transition. Figure 3 shows variable-temperature XRD patterns of $VO_2$(R) fine particles prepared by the annealing at 500 °C for 2 h in flowing $H_2$. From the reversible change of the diffraction peak it is clear that the low-temperature monoclinic $VO_2$ phase changes to the high-temperature tetragonal phase. The diffraction angles of (110) tetragonal and (011) monoclinic reflections are plotted in Figure 4 as a function of temperature. The structural transitions took place between 70 and 80 °C upon heating and between 60 and 70 °C upon cooling, and the changes are very sharp with little hysteresis. These transition temperatures are similar to those reported

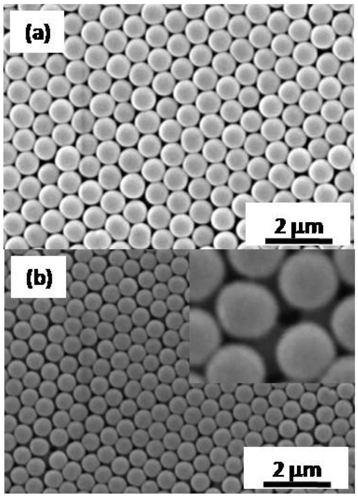

**Figure 5.** SEM images of colloid crystals of (a) VOPs and (b) $VO_2$(R) fine particles. Inset in part b is an enlarged image showing three-dimensional structure.

for bulk samples.[15−17] Since the metal−insulator transition of $VO_2$(R) is associated with the structural phase transition, the observed changes in the variable-temperature XRD measurements clearly indicate that our $VO_2$(R) fine particles show the metal−insulator transition at the same temperature that the bulk material does.

Having prepared $VO_2$(R) fine particles without losing the fairly narrow size distribution and almost perfectly spherical shape of the VOPs, we thought it would be interesting to fabricate a colloid crystal of $VO_2$(R). As shown in Figure 5a, spherical VOPs with a sufficiently narrow size distribution (652 ± 34 nm) can be self-assembled by a sedimentation method to form a three-dimensionally ordered colloid crystal. Annealing the VOP colloid crystal at 500 °C for 2 h in flowing $H_2$, we obtain a three-dimensionally ordered colloid crystal of $VO_2$(R) shown in the SEM image of Figure 5b. Although the annealing decreased the size of the fine particles, their three-dimensionally ordered structure was intact after the annealing. XRD study confirmed that the colloid crystal consisted of the $VO_2$(R) phase (Figure S6, Supporting Information). Our present result clearly demonstrates that we can fabricate a colloid crystal of spherical $VO_2$(R) particles.

In conclusion, we have developed a method for preparing spherical $VO_2$(R) fine particles with a narrow size distribution by annealing VOPs at 500 °C for 2 h in flowing $H_2$. At about 70 °C these particles showed a reversible monoclinic-to-tetragonal structural transition thought to be accompanied by a metal−insulator transition. We also demonstrated that colloid crystals of $VO_2$(R) fine particles can be fabricated by reducing colloid crystals of VOPs. We think that these monodisperse and almost perfectly spherical fine particles will allow us to explore new applications of $VO_2$(R), though discussion on optical properties of our $VO_2$(R) is beyond the scope of the present work.

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**Supporting Information Available:** Detailed experimental procedures, infrared spectra of VOPs annealed in flowing $H_2$ at various temperatures (Figure S1), SEM images (Figure S2) and XRD patterns (Figure S3) of VOPs annealed for 2 h in flowing $H_2$ (5%)/Ar (95%) at various temperatures, SEM image and XRD pattern of the $VO_2$(R) fine particles with an average size of ≈200 nm (Figure S4), variable-temperature XRD patterns of $VO_2$(R) fine particles (Figure S5), and XRD pattern of a $VO_2$(R) colloid crystal (Figure S6). This material is available free of charge via the Internet at http://pubs.acs.org.

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