# A new route to single crystalline vanadium dioxide nanoflakes via thermal reduction

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Large-area single-crystalline vanadium dioxide nanoflakes were first fabricated via a thermal reduction method in a tube furnace. The sample was characterized by x-ray diffraction, x-ray photoelectron spectroscopy, scanning electron microscopy, and transmission electron microscopy. The results show that VO<sub>2</sub> nanoflakes are single-crystalline with a monoclinic structure. The VO<sub>2</sub> nanoflakes have a width of 200–300 nm, a thickness of 50–100 nm, and a length up to 1–2  $\mu$ m. It is found that single-crystalline VO<sub>2</sub> nanoflakes show a novel and complicated 5-7-step Li-storage behavior for an insertion amount of <0.6 mol lithium per mol of VO<sub>2</sub>.

# I. INTRODUCTION

Transition metal oxides in nanoscale represent a unique class of functional materials with interesting electrical, magnetic, and chemical properties.<sup>1-5</sup> Vanadium. in the oxide structure, can show various valence states, forming a variety of oxides in V<sub>2</sub>O<sub>5</sub>, VO<sub>2</sub>, V<sub>2</sub>O<sub>3</sub>, and VO. Among these oxides, vanadium dioxide has attracted much attention due to its metal-to-insulator transition or semiconductor-to-metal transition,6,7 and has shown great potential for applications in Mott field-effect transistors,<sup>8,9</sup> electrical and optical switch devices,<sup>10</sup> and lithium batteries.<sup>11</sup> Previously, synthetic efforts have been devoted to the bulk materials of vanadium dioxide.<sup>6,12,13</sup> However, nanometer-scale VO<sub>2</sub> is predicted to have novel properties that can be easily tuned by size, shape, crystallinity, and morphology of the oxide. Recent developments in the syntheses have led to various approaches to the preparation of nanostructured  $VO_2$ ,<sup>14–17</sup> including the hydrothermal technique,<sup>18,19</sup> the softtemplate method,<sup>20</sup> radio frequency reactive sputtering,<sup>21</sup> and the ion implantation technique.<sup>22</sup> The syntheses have

also yielded single-crystalline metastable  $VO_2$  nanobelts<sup>16</sup> and nanowires with cross sections of rectangular shape.<sup>23</sup> Despite this progress, a simple synthetic method is still needed for producing VO<sub>2</sub> nanomaterials with enhanced chemical and physical properties for application in advanced devices.

In this article, we report on a high-yield synthesis of VO<sub>2</sub> nanoflakes using a simple thermal-reduction method. Different from any other previous syntheses, our method operates at a low temperature of about 550 °C without using catalysts. At room temperature, the yielded VO<sub>2</sub> nanoflakes are single crystals with a monoclinic crystalline structure. A possible growth mechanism of VO<sub>2</sub> nanoflakes has also been proposed. Furthermore, as-prepared material shows a complex Li-storage behavior. It was observed in voltage profiles and cyclic voltammograms (CVs) that the storage of lithium in monoclinic VO<sub>2</sub> occurs in 5-7 steps for an insertion amount of <0.6 mol lithium per mol of VO<sub>2</sub>, such a complicated behavior has not been observed before.

## **II. EXPERIMENTAL SECTION**

The experiment was carried out using a thermalreduction method. Ammonium metavanadate and vanadium powder with masses of 0.255 and 0.315 g, respectively, were mixed. The precursors were thoroughly

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FIG. 1. The morphologies and the structure of VO<sub>2</sub> nanoflakes: (a) a low-magnification SEM image; (b) a side-view image; (c) a cross-sectional SEM image showing the rectangular cross section; (d) a typical EDX spectrum showing that only O and V elements exist in the product; (e) a low-magnification TEM image of a single VO<sub>2</sub> nanoflake; (f) a TEM image of a part of one VO<sub>2</sub> nanoflake and its SAED pattern; (g) an HRTEM image of the VO<sub>2</sub> nanoflake showing that the nanoflake is a single crystal. The inset is an IFFT image from the central region of the VO<sub>2</sub> nanoflake obtained from the HRTEM image.

milled and then put into a quartz boat, which was placed in the inlet of the horizontal tube furnace. High-purity argon gas was purged at a flow rate of 300 sccm for 0.5 h in advance to remove air, and then was changed to a flow rate of 100 sccm. When the temperature at the furnace center was increased to 500–600 °C, the quartz boat was transferred into the center quickly. After 2 h, the furnace was cooled down to room temperature naturally, and black product was formed. It was found that if the quartz boat was put at the furnace center at the beginning of the heating, the flake-like VO<sub>2</sub> could not be obtained. Thus, the rapid-growth process is essential to growing crystalline VO<sub>2</sub> nanoflakes.

The VO<sub>2</sub> electrode for electrochemical measurements was composed of 75 wt% VO<sub>2</sub> nanoflakes, 15 wt% carbon black, and 10 wt% polyvinylidene fluoride. Metallic lithium was used as the anode, and 1.0 mL<sup>-1</sup> LiPF<sub>6</sub> in ethylene carbonate/dimethyl carbonate (EC/ DMC ratio = 1:1, v/v) was the electrolyte. Celgard 2340



FIG. 2. XRD pattern of as-synthesized VO<sub>2</sub> nanoflakes.

(Celgard Inc., Charlotte, NC) was used as the cell separator. The cell was assembled in a glove box filled with dry argon and cycled between 1.5 and 4 V under the current density of 30 m  $Ag^{-1}$  on a Land automatic batteries tester (Land CT 2001A, Wuhan, China). The CV measurement for VO<sub>2</sub> was performed using a CHI 627C electrochemical workstation (CHI Instrument Inc., Shanghai, China) with a scanning rate 0.05 mV/s at room temperature.

A field-emission-type scanning electron microscope (SEM; Model XL-SFEG; FEI Corp., Hillsboro, OR) was used to observe the morphologies of the vanadium dioxide nanostructures. A transmission electron microscope (TEM; Model 200CX; JEOL, Tokyo, Japan) and a high-resolution TEM (HRTEM; Tecnai F20; FEI Corp.) were used to provide TEM images of vanadium dioxide nanostructures. An x-ray diffraction (XRD) spectrometer (D/MAX 2400; Rigaku, Tokyo, Japan) with Cu K<sub> $\alpha$ 1</sub> radiation (wavelength 1.5406 Å) was used to determine the structure of the as-grown products. The as-prepared sample was also analyzed by x-ray photoelectron spectroscopy (XPS) using a VG ESCALAB MK2 (VG Inc., UK) system.

#### **III. RESULTS AND DISCUSSION**

From the low-magnification SEM image shown in Fig. 1(a), one can see that large-scale VO<sub>2</sub> nanoflakes are self-assembled into three-dimensional superstructures. The nanoflakes are uniform and well distributed in the bundles. The side-view image of the VO<sub>2</sub> nanoflakes is shown in Fig. 1(b). It can be seen that the VO<sub>2</sub> nanoflakes have an average thickness of 80 nm and a length of up to 2  $\mu$ m. Figure 1(c) shows the cross-sectional SEM image of one VO<sub>2</sub> nanoflake, which has a rectangular shape (~90 × 270 nm). The energy-dispersive x-ray (EDX) spectrum [Fig. 1(d)] shows that the products consist of only V and O elements.

The TEM images of the  $VO_2$  nanoflakes are shown in Figs. 1(e), 1(f), and 1(g). Figure 1(e) provides a typical TEM image of an individual VO<sub>2</sub> nanoflake. The HRTEM image in Fig. 1(g) was obtained from the center of the  $VO_2$  nanoflake shown in Fig. 1(f), which is the same as other regions of the nanoflake. As shown in the inset of Fig. 1(g), the inverse-fast Fourier transform (IFFT) image matches the crystalline VO<sub>2</sub> lattice structure very well. The HRTEM image shows that this nanoflake is a single crystal with many fewer defects. The corresponding selected-area electron diffraction (SAED) pattern seen in Fig. 1(f) presents the bright and sharp diffraction spots, which also confirms that the VO<sub>2</sub> nanoflake is a single crystal and can be indexed to a monoclinic VO<sub>2</sub>. Combining the SAED pattern with the HRTEM image, it can be concluded that the structure of the as-grown  $VO_2$  products is single crystalline with a

monoclinic structure and that the growth direction of  $VO_2$  nanoflakes is along the [010] direction.

Figure 2 is an XRD spectroscopy image of as-grown products. It can be seen that the diffraction peaks are sharp and have a narrow full width at half-height. These peaks match well with the pattern of VO<sub>2</sub> (JCPDS Card No. 82-0661).<sup>24</sup> Thus, it has been further demonstrated that the products are VO<sub>2</sub> nanoflakes with a monoclinic crystalline structure (space group P  $2_1/c$ ).

The as-prepared sample was also analyzed by XPS, as shown in Fig. 3. No peaks of elements other than C, O, and V are observed on the survey spectrum [Fig. 3(a)]. In Fig. 3(b), the XPS spectrum of the VO<sub>2</sub> nanoflakes shows double peaks with binding energies of 515.90 and 523.50 eV, respectively, corresponding to V2p<sub>3/2</sub> and V2p<sub>1/2</sub>. This difficulty in obtaining the degree of oxidation of these materials has led us to utilize three parameters, with promising results. These parameters are: the energy difference ( $\Delta$ ) between the binding energy of the O Is level (530.35 eV) and that of V 2p<sub>3/2</sub> (515.90 eV); and the full width ( $\lambda$ ) at half-maximum (FWHM) of each



FIG. 3. XPS image of  $VO_2$  nanoflakes: (a) survey spectrum; and (b) core-level spectra of V 2p and O1s.



FIG. 4. The possible growth process for the formation of VO<sub>2</sub> nanoflakes.

of the former XPS peaks. In this case, the energy difference ( $\Delta$ ) was 14.45 eV, and the FWHMs of O 1s and V 2p<sub>3/2</sub> peaks were 2.7 and 4.0 eV, respectively, which are characteristic of vanadium in the +4 oxidation state. These values are in excellent agreement with those of VO<sub>2</sub> that have been reported in the literature.<sup>25</sup>

To advance this approach further for nanoflake synthesis requires a clear study of the formation mechanism. We suggest that a possible model in our case obeys a vapor–solid mechanism that was proposed by Dai et al.<sup>26</sup> In their experiment, the basic reaction used for the synthesis of VO<sub>2</sub> nanoflakes can be formulated in Eq. (1), which is composed of two half-reactions [Eqs. (2) and (3)]. The vanadium introduced in this reaction was used as a reducer, avoiding other impurities being imported into the final product:

$$V + 4NH_4VO_3 \xrightarrow{\Delta} 5VO_2 + 4NH_3 \uparrow + 2H_2O \uparrow ,$$
(1)

$$NH_4VO_3 \xrightarrow{\Delta} 4NH_3 \uparrow +2V_2O_5 + 2H_2O \uparrow ,$$
(2)

 $V + 2V_2O_5 \rightarrow 5VO_2 \quad . \tag{3}$ 

To understand the detailed growth mechanism of the nanoflakes, a schematic draft of the possible growth process is shown in Fig. 4. When the precursors were transferred at the furnace center, ammonium metavanadate was thermally decomposed into  $V_2O_5$ , NH<sub>3</sub>, and H<sub>2</sub>O with astonishing velocity. The  $V_2O_5$  was completely deoxidized by vanadium, while NH<sub>3</sub> and H<sub>2</sub>O were removed by the carrier gas [Fig. 4(a)]. The source material is assumed to vaporize into molecular species. Then, VO<sub>2</sub> molecules were favored to form a small nucleus in the lower temperature regions of the reaction boat [Fig. 4(b)]. The VO<sub>2</sub> molecules would continue to be absorbed on the formed nucleus. To balance the local charge, the total energy, and the structural symmetry, the newly formed molecules would be deposited on the



FIG. 5. (a) The voltage profiles of a  $\text{Li/VO}_2$  cell at the first discharging/charging cycle. (b) Cyclic performance of a  $\text{Li/VO}_2$  cell showing a good cyclic performance.

growth fronts of the formed nucleus while the lowenergy surfaces started to form [Fig. 4(c)]. The newly arriving molecules were prevented from being deposited onto these surfaces, resulting in the fast growth of the



FIG. 6. CVs of VO<sub>2</sub> nanoflakes obtained at a scan rate of  $0.05 \text{ mVs}^{-1}$ . The numbers 1, 2, and 3 in the curves signify the cycle number.

nanoflakes. If the mobility of molecules was high enough, the low-energy surfaces would tend to be flat [Fig. 4(d)]. After some hours of growth and cooling, these single-crystalline nanoflakes were formed [Fig. 4(e)]. In the whole process, the size of the cross section and the length of the nanoflake were determined by the growth temperature and supersaturation ratio in the kinetics of crystal growth.

Figure 5(a) shows the voltage profiles of the  $VO_2/Li$ cell at the first discharging/charging cycle. The Li insertion capacity is 194 mAh/g, corresponding to 0.6 mol Li per mol of VO<sub>2</sub>. The Li extraction capacity is 145 mAh/ g, which is equal to the extraction of 0.45 mol Li. Both values are far less than the theoretical value of 323 mAh/ g, presuming that  $V^{4+}$  is fully reduced into  $V^{3+}$ . However, at least five voltage plateaus for the first Li insertion and four plateaus for the first lithium extraction can be observed clearly in Fig. 5(a). This indicates that complex multiple-step phase transitions should occur. Such a multiple-plateau phenomenon has not been observed in the case of VO<sub>2</sub> nanocrystals and nanorods,<sup>11,27</sup> for which only one voltage slope appeared, probably due to the poor crystallinity of the reported samples. In addition, single-crystalline VO<sub>2</sub> nanoflakes show a good cyclic performance in Fig. 5(b). The complicated electrochemical behaviors can be observed more clearly in CVs (Fig. 6). In the first reduction process (i.e., Li insertion), five peaks with two shoulder peaks can be observed. And five redox couples can be distinguished in the rest of the curves. It is known that a group of  $Li_X VO_2$  materials (i.e., Li<sub>0.19</sub>VO<sub>2</sub>, Li<sub>0.37</sub>VO<sub>2</sub>, Li<sub>0.9</sub>V<sub>2</sub>O<sub>4</sub>, LiV<sub>2</sub>O<sub>4</sub>, Li<sub>0.59</sub>VO<sub>2</sub>,  $Li_{0.7}VO_2$ , and  $LiVO_2$ ) exist. It is reasonable that the reaction depth for each VO2 nanoflake cannot be equivalent. Therefore, it confirms that multiple-step redox processes should correspond to the gradual formation of these phases.

### **IV. CONCLUSIONS**

In summary, we have presented a very simple thermalreduction method with which to synthesize VO<sub>2</sub> nanoflakes, and a possible growth mechanism was discussed. This method has the following advantages: (i) the low temperature used, without the need for a catalyst in the reaction process; and (ii) the high yield of the VO<sub>2</sub> nanoflakes in the synthesis. Furthermore, the finding of interesting 5–7-step Li-storage behaviors for singlecrystalline VO<sub>2</sub> nanoflakes indicates the complicated nature of the existence of a series of Li<sub>x</sub>VO<sub>2</sub> materials and their promising electrochemical performance.

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