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# One-Pot Synthesis and Characterization of VO<sub>2</sub>(B) with a Large Voltage Window Electrochemical Performance in Aqueous Solution

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**Abstract:** B-type vanadium dioxide (defined as VO<sub>2</sub>(B)) nanobelts were synthesized through using commercial ammonium metavanadate, oxalic acid via one-step hydrothermal technique. The structure of VO<sub>2</sub>(B) was characterized using different instruments. N<sub>2</sub> adsorption-desorption isotherms revealed that the VO<sub>2</sub>(B) nanobelts were porous structures where BET surface area was 10.4 m<sup>2</sup>·g<sup>-1</sup>, the pore volume was 0.0687 cm<sup>3</sup>/g, and the average pore size was 42.7 nm. Furthermore, the VO<sub>2</sub>(B) nanobelts as supercapacitors electrode exhibited a large voltage window ( $-0.8 \sim 1.0$  V). The measured capacitance was based on the pseudocapacitance. When the discharge current density is 0.5, 1, and 10 A·g<sup>-1</sup>, the VO<sub>2</sub>(B) shows the specific capacitance of 287, 246, and 222 F·g<sup>-1</sup>, respectively.

Keywords: VO<sub>2</sub>; nanobelts; hydrothermal synthesis; pseudocapacitance

## 1. Introduction

Recently, the strategy for systematically designing the morphology and structure of diverse inorganic materials has been a cutting-edge research focus owing to the novel physical and chemical properties essentially affected by their shapes and sizes [1–5]. Particularly, nanobelts have been paid great attention due to their novel physical and chemical properties and wide application prospects [6,7]. Moreover, supercapacitors (SCs) are considered as one of the most attractive pieces of new-generation apparatus in energy storage, and their performance is closely related to the characteristics of electrode materials. Metal oxides with novel structures show excellent specific capacitance and energy density because of their energy storage mechanism [8–10]. Meanwhile, there is a wide utilization in various fields, such as energy, biology, gas sensors, etc. [11–13].

After the discovery of VO<sub>2</sub>, it aroused great interest among scientists for its structural phase transition [14,15], and the crystallography data of VO<sub>2</sub> polymorphs were studied systemically (in Table 1) [16–21]. In the past decades, B-type vanadium dioxide (defined as VO<sub>2</sub>(B)) has attracted widespread attention to the application of lithium-ion batteries due to its chemical structural characteristics [22,23]. Nowadays, VO<sub>2</sub>(B) has arisen people's interest in the field of supercapacitors. For examples, concerning one kind of VO<sub>2</sub>(B) nanobelts, it was reported that a specific capacitance of 142 F·g<sup>-1</sup> is displayed at the voltage window limit of -0.4~0.6 V [24]. Concerning VO<sub>2</sub>(B) nanosheets, [25] reported that the particles show a high rate capability of 200 mAh g<sup>-1</sup>. Furthermore, hybrid materials related to VO<sub>2</sub>(B) were also developed to apply to the material of the electrodes. For instance, VO<sub>2</sub>(B)/C were synthesized through the hydrothermal method, which exhibited the specific capacitance of 182 F·g<sup>-1</sup> when the voltage window limit is -0.6~0.8 V. The VO<sub>2</sub>(B)/rGO composites exhibited a capacity of 456 mAh g<sup>-1</sup> [26]. According to the published data, the electrochemical

Phase	Transition Temperature (K)	a(Å)	b(Å)	c(Å)	Crystal System
VO <sub>2</sub> (M)	341	5.74	4.16	5.38	Monoclinic
$VO_2(R)$	341	4.53	4.53	2.87	Monoclinic
$VO_2(A)$	435	8.44	8.44	7.67	Tetragonal
$VO_2(B)$	—	12.03	3.69	6.42	Tetragonal

properties of  $VO_2(B)$  as SCs remains to be optimized further. Therefore, it is necessary and significant for material researchers to improve the specific capacitance or voltage window.

**Table 1.** The crystal data of VO<sub>2</sub> polymorphs.

In this paper, we designed a simple and convenient route to synthesize  $VO_2(B)$  nanobelts. That is,  $NH_4VO_3$  is reduced by  $H_2C_2O_4$ · $2H_2O$  using hydrothermal method without adding any template or surfactant. cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) tests have been applied to assess the electrochemical properties of the  $VO_2(B)$  nanobelts.

## 2. Experiment and Characterization

The chemicals (analytical grade) in the experiment need not be purified any more. The synthesis of VO<sub>2</sub>(B) nanobelts is divided into the following steps. Firstly, 0.585 g of NH<sub>4</sub>VO<sub>3</sub>, 1.103 g of H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O (NH<sub>4</sub>VO<sub>3</sub>:H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O = 1:1.75, abbreviate V:C = 1:1.75) were blended together with 35 mL distilled water. After stirring for 30 min, the mixture was kept at 180 °C for 48 h in a 50-mL Teflon-lined stainless steel autoclave. Subsequently, the products were washed and dried at 75 °C for 12–24 h.

X-ray powder diffraction (XRD) was tested in Panalytical X'Pert powder MPD with Cu Ka radiation. Fourier transform infrared spectroscopy (FT-IR) was applied to measure the products with Nicolet 6700. The Raman spectra were carried out with a 532-nm excitation line (Thermo Scientific, MA, USA). Morphology and dimensions were measured through scanning electron microscopy (SEM) on QUANTA450, and transmission electron microscopy (TEM) on FEITECNAIG220. The surface area was determined on ASAP-2020 through the Brunauer-Emmet-Teller (BET) method.

A three-electrode cell was employed in the electrochemical test. The working electrode was prepared via the following steps. Firstly, mix 10 wt% of carbon black, 10 wt% of polyvinylidene difluoride, and 80 wt% of VO<sub>2</sub>(B) together, and then put N-methyl-2-pyrrolidone into the mixture. Next, the slurries were coated on a nickel foil. After heating at 80 °C for 24 h, these nickel foils were pressed on a Ni grid under the pressure of 10 MPa. An amount of 1.0 mol·L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> aqueous solution was chosen as the electrolyte. The electrochemical characteristics using CV and GCD were performed on CHI 660D. The specific capacitance (C, F·g<sup>-1</sup>), energy density (E, W·h·kg<sup>-1</sup>) and the power density (P, W·kg<sup>-1</sup>) are determined through Equation (1) to Equation (3).

$$C = \frac{I \cdot \Delta t}{m \cdot \Delta V} \tag{1}$$

$$E = \frac{1}{7.2} C \cdot (\Delta V)^2$$
<sup>(2)</sup>

$$P = \frac{3600E}{\Delta t}$$
(3)

where, I (A) denotes the discharge current.  $\Delta t$  (s) denotes the discharge time. m (g) denotes the mass of the VO<sub>2</sub>(B).  $\Delta V$  (V) denotes the potential drop during the process of discharge.

#### 3. Results and Discussion

The synthetic conditions took a significant part in the formation of  $VO_2(B)$  nanobelts. Figure 1A demonstrates the XRD pattern of the samples at various ratio of V:C. When the ratio of V:C is 1:1.25,

an unknown solid was obtained based on our knowledge. With the increase of V:C, the characteristic peaks of VO<sub>2</sub>(B) (JCPDS, No. 81-2392) were obtained and pure phase of VO<sub>2</sub>(B) was synthesized with V:C and increased to 1:1.75. However, when V:C continued to increase (V:C = 1:2), VO<sub>2</sub>(B) was not obtained and other vanadium oxides were prepared. Thus, V:C = 1:1.75 is suitable for the synthesis of VO<sub>2</sub>(B) with pure phase. Figure 1B describes the XRD patterns of VO<sub>2</sub>(B) prepared with various hydrothermal times, which discloses the evolution process of VO<sub>2</sub>(B)'s formation. As depicted in Figure 1B, VO<sub>2</sub>(B) was obtained at 6–96 h indicating that VO<sub>2</sub>(B) could be synthesized in a short time.



**Figure 1.** XRD patterns of the samples with various conditions: (**A**) various ratio of V:C (180 °C, 48 h); (**B**) reaction time (V:C = 1:1.75, 180 °C).

Figure 2 shows the morphology of the samples obtained by SEM. When V:C = 1:1.25, it can be seen that nanosheets are obtained (Figure 2a). With V:C increasing to 1:1.75, VO<sub>2</sub>(B) nanobelts are synthesized, as shown in Figure 2b. Thus, V:C = 1:1.75 is favorable for preparation of VO<sub>2</sub>(B) with belt-like morphology. The SEM images of the samples obtained at 6 and 12 h are shown in Figure 2c,d respectively. They both reveal that VO<sub>2</sub>(B) nanobelts are formed. This result indicates that VO<sub>2</sub>(B) nanobelts can be synthesized at a short time. Figure 3 shows the TEM image of the samples. The TEM images are consistent with SEM images, which also reveals that VO<sub>2</sub>(B) with belt-like morphology could be synthesized.



**Figure 2.** SEM images of the products under various conditions: (**a**) V:C = 1:1.25, 48 h; (**b**) V:C = 1:1.75, 48 h; (**c**) V:C = 1:1.75, 6 h; (**d**) V:C = 1:1.75, 12 h. (at 180 °C).



Figure 3. TEM images of the VO<sub>2</sub>(B) nanobelts at different scales: (a) 500 nm; (b) 200 nm.

Further composition and structure information about the as-obtained VO<sub>2</sub>(B) was provided by EDS, FTIR, and Raman. The SEM image and its corresponding EDS spectrum of the as-obtained sample is shown in Figure 4, which indicates that the sample composes of vanadium and oxygen elements in consonance with the observation of XRD patterns. The IR and Raman spectra of the as-obtained VO<sub>2</sub>(B) is shown in Figure 5a. The absorption peaks among 1100 and 400 cm<sup>-1</sup> are assigned to V-O vibration band in the IR spectrum [27,28]. The peak at 535 cm<sup>-1</sup> is ascribed to the stretching modes of V-O-V, and that at 920 cm<sup>-1</sup> is ascribed to V-O bonds. Meanwhile, the characteristic absorption peak of the VO<sub>2</sub>(B) nanobelts with layered structure is observed at 998 cm<sup>-1</sup>, which is assigned to the symmetric stretching vibration in VO<sub>2</sub>(B) (V<sup>4+</sup> = O).



Figure 4. SEM image and EDS spectrum of the VO<sub>2</sub>(B) nanobelts.



**Figure 5.** (a) IR and Raman spectra of VO<sub>2</sub>(B) nanobelts; (b)  $N_2$  adsorption-desorption isotherms of the VO<sub>2</sub>(B) nanobelts at 77 K.

Raman spectrum of the VO<sub>2</sub>(B) nanobelts is shown in Figure 5a, which demonstrates a series of bands located at 100–1100 cm<sup>-1</sup> are the vibrations of V-O type of VO<sub>2</sub>(B). Specially, the intense peak at 134 cm<sup>-1</sup> corresponds with  $B_{3g}$  and  $B_{2g}$  symmetry, which is indexed to the stretching vibration pattern of  $(V_2O_2)_n$  in agreement with the chain conversion [29,30]. Therefore, the results of Raman and infrared spectroscopy are consistent with those of XRD and EDS.

The nitrogen adsorption-desorption isotherms of VO<sub>2</sub>(B) nanobelts is shown in Figure 5b. The isotherms show that the phenomenon of capillary condensation occurs at high  $P/P_0$ , which is a type IV isotherm in accordance with the IUPAC classification, and VO<sub>2</sub>(B) nanobelts exhibits mesoporous material characteristics [31]. The BET surface area of VO<sub>2</sub>(B) nanobelts is 10.4 m<sup>2</sup>·g<sup>-1</sup> and the Barrett-Joyner-Halenda (BJH) method (insert in Figure 5b) was used to obtain the sample with a pore volume of 0.0687 cm<sup>3</sup>/g and an average pore size of 42.7 nm. The porous characteristic of VO<sub>2</sub>(B) nanobelts indicates potential excellent electrochemical properties, which can be used as SC [32] or lithium ion battery electrodes [33] in the future.

The CV curves of the VO<sub>2</sub>(B) nanobelts are shown in Figure 6. The results indicate that there is a large capacity at the potential limit of  $-0.8 \sim 1.0$  V among a different potential limit. Hence, electrochemical curves of VO<sub>2</sub>(B) nanobelts were measured from -0.8 V to 1.0 V.



Figure 6. CV curves of the VO<sub>2</sub>(B) nanobelts at different potential limit (20 mV·s<sup>-1</sup>, 1 M Na<sub>2</sub>SO<sub>4</sub> electrolyte).

CV curves of the VO<sub>2</sub>(B) nanobelts at  $-0.8 \sim 1.0$  V are shown in Figure 7a, and the scan rate is from 5 to 100 mV·s<sup>-1</sup>. The results indicate that the redox peaks are seen, disclosing that VO<sub>2</sub>(B) nanobelts

storing charges are mainly on basis of a redox mechanism [34]. The corresponding redox reaction is described as follows:  $VO_2 + xNa^+ + xe^- \rightarrow Na_xVO_2$ . The *x* denotes mole fraction of inserted Na<sup>+</sup>. Original shapes of the CV curves remain almost unchanged as the increment of scan rate, which indicates there are excellent ionic and electronic conductivity in the  $VO_2(B)$  nanobelts. Meanwhile, the peak moves to a higher potential for the electrode polarization effect. Furthermore, the peak current enlarges as scan rate increases, which shows the faradic redox reactions at surface is rapid enough, as well as the rates of ionic and electronic transport [35]. Figure 7b shows GCD curves of the  $VO_2(B)$  nanobelts. When the discharge current densities are 0.5, 1 and  $10 \text{ A} \cdot \text{g}^{-1}$ , the specific capacitance are 287, 246, and 222 F·g<sup>-1</sup>. As the discharge current density increases (0.5–10 A·g<sup>-1</sup>), the specific capacitance decreases. One reason is that a lower use rate of  $VO_2(B)$  occurs at the high current density in the process of charge-discharge, and the other one is that the incremental voltage drop is involved in the redox reaction [36,37]. The value of capacitance at current density of  $10 \text{ A} \cdot \text{g}^{-1}$  remains 77% of that at current density of 0.5 A·g<sup>-1</sup>. The good rate capability is ascribed to the belt-like (Figures 2 and 3) and porous (Figure 5b) structures of the  $VO_2(B)$  nanobelts.



Figure 7. (a) CV curves of VO<sub>2</sub>(B) nanobelts; (b) GCD curves of VO<sub>2</sub>(B) nanobelts (1 M Na<sub>2</sub>SO<sub>4</sub> electrolyte).

Table 2 displays the electrochemical properties of the VO<sub>2</sub>(B) nanobelts with other materials discovered previously. Although the stability is not as good as some materials, the specific capacitance of porous VO<sub>2</sub>(B) nanobelts (287 F·g<sup>-1</sup>) outperforms other materials, for example, VO<sub>2</sub>(B) particles (136 F·g<sup>-1</sup>) [36], VO<sub>2</sub>(B) nanofibers (174 F·g<sup>-1</sup>) [38], VO<sub>2</sub>(B)/CNTs (229 F·g<sup>-1</sup>) [38], RG/VO<sub>2</sub>(B) hybrid composites (225 F·g<sup>-1</sup>) [36], etc. Furthermore, it is concluded from Table 2 that porous VO<sub>2</sub>(B) nanobelts can be used as a large voltage window compared to the previous reports. Therefore, porous VO<sub>2</sub>(B) nanobelts in this paper reveal large capacity as well as excellent rate capability. According to Figure 5b, the calculated energy density at the current density of 0.5, 1, and 10 A·g<sup>-1</sup> are 129, 111, and 100 W·h·kg<sup>-1</sup>, meanwhile the power density is 450, 900, and 9000 W·kg<sup>-1</sup>, respectively.

Figure 8 shows the cycling stability of the porous  $VO_2(B)$  nanobelts. Figure 8a displays the CV curves at various cycles, which depicts the specific capacitance fades with the cycle increasing. Figure 8b shows the GCD curves to quantitatively observe the cycling stability, which displays similar results with CV curves. During the CV and GCD tests, the solution gradually turned yellow because of the dissolution of the  $VO_2(B)$  nanobelts as electrode material in  $Na_2SO_4$  electrolyte solution. This is an experimental phenomenon that often occurs when vanadium oxides are applied in SC and lithium-ion battery electrodes [27,39,40].



**Figure 8.** (a) CV cycling curves of the VO<sub>2</sub>(B) nanobelts (20 mV·s<sup>-1</sup>, 1 M Na<sub>2</sub>SO<sub>4</sub> electrolyte); (b) Cyclic stability of the specific capacitance (GCD method, 1 M Na<sub>2</sub>SO<sub>4</sub> electrolyte).

Materials	Current/A·g <sup>−1</sup>	Potential/V	Capacitance/F⋅g <sup>-1</sup>	Literatures
VO <sub>2</sub> (B)/RG(1.0)	1	-0.6~0.4	245	[24]
$VO_2(B)$ particles	0.25	$-0.2 \sim 0.8$	136	[36]
$RG(1.0)/VO_2(B)$	0.25	$-0.2 \sim 0.8$	225	[36]
$VO_2(B)$ nanofibers	0.5	$-0.6 \sim 0.4$	174	[38]
VO <sub>2</sub> (B)/CNTs	0.5	$-0.6 \sim 0.4$	229	[38]
VO <sub>2</sub> (B)/GN (20%)	0.5	0~0.6	197	[41]
W-dopedVO <sub>2</sub> (B) nanobelts	1	$-0.4 \sim 0.6$	253	[42]
Porous $VO_2(B)$ nanobelts	0.5	$-0.8 \sim 1.0$	287	This work
Porous VO <sub>2</sub> (B) nanobelts	1	$-0.8 \sim 1.0$	246	This work

Table 2. Comparison of the VO<sub>2</sub>(B) nanobelts with other materials discovered previously.

#### 4. Conclusions

In this study, VO<sub>2</sub>(B) nanobelts with porous structures were synthesized by using NH<sub>4</sub>VO<sub>3</sub>, H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O, and H<sub>2</sub>O through a facile hydrothermal route. The VO<sub>2</sub>(B) nanobelts were characterized by different instruments. BET surface area of the VO<sub>2</sub>(B) nanobelts is 10.4 m<sup>2</sup>·g<sup>-1</sup>, the pore volume is 0.0687 cm<sup>3</sup>/g, and the average pore size is 42.7 nm. In terms of the electrochemical properties, the VO<sub>2</sub>(B) nanobelts exhibited that the measured capacitance was based on the pseudocapacitance with a large voltage window ranging from -0.8 V to 1.0 V. Porous VO<sub>2</sub>(B) nanobelts displayed specific capacitances of 287, 246, and 222 F·g<sup>-1</sup> at the discharge current density of 0.5, 1, and 10 A·g<sup>-1</sup>, respectively. The VO<sub>2</sub>(B) nanobelts with a large voltage window perform good electrochemical properties, which is an ideal cathode material in the research field of SCs.

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