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PVP-assisted hydrothermal synthesis of $VO(OH)_2$ nanorods for supercapacitor electrode with excellent pseudocapacitance

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ABSTRACT

Vanadium oxyhydroxide $VO(OH)_2$, which may possess specific chemical and physical properties, has been paid less attention comparing with vanadium oxides. Herein, with the assistance of polyvinyl pyrrolidone (PVP) and by adjusting pH about 4.7, $VO(OH)_2$ was successfully synthesized by a facile hydrothermal method for the first time, which were short nanorods with widths of 50–130 nm and lengths of 250–500 nm. Electrochemical performance of $VO(OH)_2$ nanorods was firstly investigated as supercapacitor electrodes, which were studied by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS). $VO(OH)_2$ nanorods showed capacitive behavior based on pseudocapacitance and superior rate capability. Specific capacitance of 198 $F{\cdot}g^{-1}$ was achieved at 0.5 $A{\cdot}g^{-1}$. These findings suggested that $VO(OH)_2$ nanorods can be promising candidate as potential material for supercapacitor electrode.

1. Introduction

The rapid consumption of fossil fuels and increasing environmental pollution have led to an urgent demand for efficient, clean, sustainable energy conversion and storage. Compared with batteries, supercapacitors (SCs) receive tremendous attention due to their superiorities of excellent power output, exceptional cycling life, lightweight, and ease of handing, etc. [1–5]. SCs' performance mainly relies on the properties of electrode materials, therefore it's of decisive significance that how to develop novel materials for SCs' electrodes [6–9]. $VO(OH)_2$ is a novel V-based materials, which is scarcely reported in the literature [10]. Julie et al. [10] first studied three vanadium oxyhydroxides formation mechanisms especially for Haggite $V_2O_3(OH)_2$ and Gain's hydrate $V_2O_4(H_2O)_2$. And they first studied the electrochemical behavior of Duttonite $VO(OH)_2$ and Haggite applied for Li and Na batteries, confirming V^{4+} oxyhydroxides can bear scientific importance and promising chemical and physical properties in electrochemistry. Thus, $VO(OH)_2$ may possess scientific importance and specific chemical and physical properties compared with other V-based materials [11–13]. However, the electrochemical properties of $VO(OH)_2$ applied to SC's electrodes for energy storage have been little studied in the literature to the best of our knowledge. In this work, we focused on synthesis and electrochemical properties of $VO(OH)_2$ as SC's electrodes.

2. Experimental

All chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd and used without any further purification. In detail, 0.22 g PVP was dispersed into 25 ml distilled water under ultrasonication to form a transparent colorless solution after 20 min. Subsequently, 0.82 g $VOSO_4$ was added to obtain a transparent blue $VOSO_4$ solution (2 M). Then NaOH solution (0.5 M) was slowly dropped into above $VOSO_4$ solution to adjust pH about 4.7, and brown precipitates were formed and suspended in the solution. Last, the suspension was transferred to a Teflon-lined stainless steel autoclave, sealed, and was heated at 100 °C for 48 h. After the reaction, the resulted precipitate was filtered off, washed and dried in vacuum. Phase and composition were identified by X-ray powder diffraction (XRD), energy-dispersive X-ray spectrometer (EDS), elemental mapping, X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR). Morphology was observed by field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). Electrochemical tests were performed in 1 $mol{\cdot}L^{-1}$ Na_2SO_4 electrolyte. All detail information was seen in Supplementary data.

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3. Results and discussion

The composition of the as-obtained samples were characterized by EDS, elemental mappings, XRD, XPS and FTIR. Fig. S1 (Supplementary data) shows EDS spectrum and elemental mappings, which demonstrates that the sample contains two elements V and O with homogeneous distribution in the view. Fig. 1a shows the XRD pattern of the sample. Almost all the peaks are assigned to $VO(OH)_2$ (JCPDS, No. 11-0209) except that some small peaks are indexed to VO_2 (JCPDS, No. 09-0142), suggesting the successful synthesis of $VO(OH)_2$. The full XPS spectrum (Fig. 1b) also confirms that the sample comprises V and O (C_{1s} is used as charge reference [14]), in agreement with the observations of EDS and elemental mappings. The core-level spectrum of V_{2p}-O_{1s} is depicted in Fig. 1c. The peak of V_{2p} splits two binding energies of $V_{2p3/2}$ and $V_{2p1/2}$, which are respectively centered at 516.2 eV and 523.6 eV, in good accordance with the characteristic binding energies of V^{4+} [15]. O_{1s} peak locates at 530.5 eV in agreement with V–O [15]. Fig. 1d shows the FTIR spectrum, which can well explain the successful synthesis of $VO(OH)_2$ [16]. The bands at 3565 and 3516 cm^{-1} are attributed to the stretching vibrations of V–OH. Furthermore, the peaks at 867 and 800 cm^{-1} are assigned to the in-plane V–OH deformations. The strong peak at 963 cm^{-1} is ascribed to the typical VO^{2+} stretching vibration, which is very consistent with the molecular formula of $VO(OH)_2$. Moreover, three peaks at 619, 538 and 449 cm^{-1} are probably related to torsional modes of –OH groups [16]. The above results confirm that $VO(OH)_2$ is synthesized by the PVP-assisted hydrothermal route.

Fig. 2 shows FE-SEM and TEM images of the as-obtained $VO(OH)_2$. It can be observed that short nanorods with a diameter of 50–130 nm and lengths from 250 to 500 nm are obtained. HRTEM image (insert in Fig. 2d) displays that the lattice fringes of $VO(OH)_2$ can be seen, and the distance between neighboring planes is about 0.224 nm, which is consistent with $2\theta = 40.2°$ (Fig. 1a) of $VO(OH)_2$.

To explore the merits of the as-prepared $VO(OH)_2$ nanorods, their electrochemical properties as SC's electrodes were investigated by CV, GCD and EIS in a three electrode cell. Fig. S2 depicts CV curves of $VO(OH)_2$ nanorods at various potential limits, which suggests that it exhibits good symmetry and high capacity at the potential window of −0.2 V to 0.8 V. Therefore, CV and GCD of $VO(OH)_2$ nanorods were tested in the potential range from −0.2 V to 0.8 V. Fig. 3a presents CV curves at the scan rates from 5 $mV \cdot s^{-1}$ to 100 $mV \cdot s^{-1}$. All curves show the quasi-rectangular shape, which demonstrates that $VO(OH)_2$ has a capacitive behavior with pseudocapacitance. Furthermore, these curves maintain their original shape with the scan rate increasing, indicating good ionic and electron conduction of $VO(OH)_2$ nanorods [7]. To calculate the value of specific capacitance and understand the rate capability, GCD curves of $VO(OH)_2$ nanorods at various current densities are shown in Fig. 3b and their corresponding results are summarized in Fig. 3c. The discharge curves and the corresponding charge curves (Fig. 3b) almost displays line-like and symmetrical over the whole potential region, suggesting the good capacitive behavior of $VO(OH)_2$ in agreement with CV observation (Fig. 3a). Specific capacitances are 198, 165, 149, 134 and 120 $F \cdot g^{-1}$ at discharge current densities of 0.5, 1, 2, 5 and 10 $A \cdot g^{-1}$, respectively. Specific capacitances decrease as current densities increasing, and about 61% of specific capacitance at 0.5 $A \cdot g^{-1}$ is remained at 10 $A \cdot g^{-1}$. This decline is caused by the incremental voltage drop and involvement of insufficient active materials [17]. Besides, GCD process leading to a low utilization rate of active materials at high current densities is another reason [18]. Maximum specific capacitance of $VO(OH)_2$ nanorods as SC's electrodes reach to 198 $F \cdot g^{-1}$ at 0.5 $A \cdot g^{-1}$ in this study, which has not been reported. This value is even

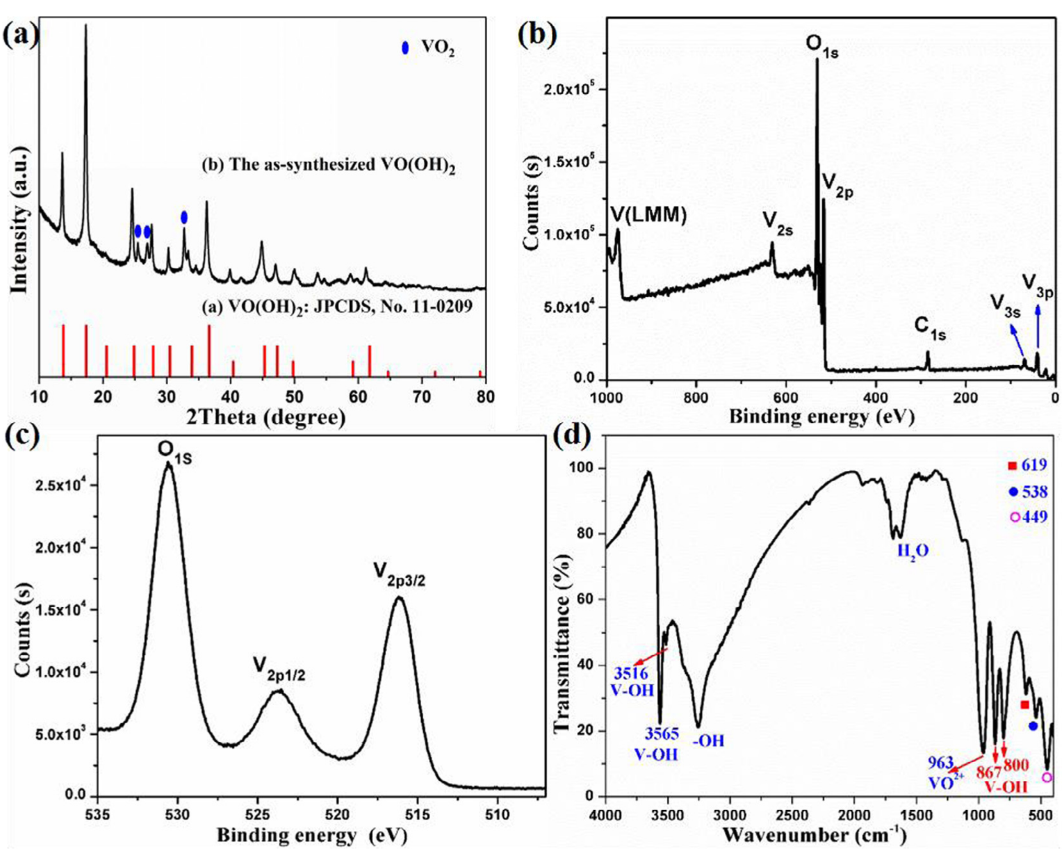

Fig. 1. Characterization of $VO(OH)_2$ nanorods: (a) XRD; (b) Full XPS; (c) V_{2p}-O_{1s} XPS; (d) FTIR.