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A facile and well-tailored vanadium oxide porous network for high-capacity electrochemical capacitive energy storage

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ABSTRACT

In this work, 3D interconnected porous vanadium oxide network is prepared by a facile and effective method through controlling solution polarity at room temperature. The resulted samples were systemically characterized by XRD, SEM, TEM and electrochemical measurements to study the synthesis–structure–performance correlation and further used for the electrochemical capacitive energy storage. The experimental results indicate that the microstructure of the as-prepared samples can be effectively tailored by the polarity of reaction solution and the obtained 3D interconnected network delivers a high specific capacitance of 280 F g^{-1}, providing promising potentials as an electrode material for high-performance supercapacitor.

1. Introduction

Vanadium oxides have been in the forefront of applied research in view of their multifunctional properties, which include optical, electronic, reduction/oxidation, and electrochromic properties [1,2]. In recent years, nanostructures of vanadium oxides have drawn tremendous attention because they could be employed for improving physical properties such as surface-enhanced Raman response, cathodoluminescence, field emission, spintronics and nonlinear optical studies [1] among which, the electrochemical and photochemical properties are the most significant ones for practical applications.

The properties of nanostructures are in many cases strongly size-dependent and may differ significantly from their bulk ones [3,4]. Hence, synthesis of materials with well-controlled size, morphology and chemical composition can offer great opportunities to deliver unique chemical and physical properties for specific applications. In the past 2 decades a variety of approaches have been used to prepare nanostructures of vanadium oxides including thermal evaporation, hydrothermal, surfactant-assisted, sol–gel and template based synthesis [5–9]. All these methods have tedious many steps, while requiring high temperatures for synthesis of desired nanostructures. Among of these methods, hydrothermal synthesis of vanadium oxides is widely reported. However, the complicated autoclaves operations under high temperature and high pressure for long time (sometimes even longer than 4 days) greatly limit their broad application in industry [10,11].

Here we report a novel, simple and economic method to synthesize vanadium oxides porous network under room-temperature without using any surfactant or capping agent, and is easy to scale up for industrial production. Further, different nanostructured vanadium oxides can be tailored simply by altering the polarity of the precursor solution through addition of ethanol. The possible formation mechanism of vanadium oxides porous network is also proposed. The results indicate that the 3D network could deliver a high specific capacitance due to its porous channels to facilitate ion transport to the redox-active material.

2. Experimental section

Material preparation: 2 mmol V_2O_5 and 35 mL deionized water (or 11 mL H_2O and 24 mL ethanol) were mixed under stirring at room temperature, and then 5 mL 30% H_2O_2 was added to this mixed solution and kept continuously stirring for 2 h. Subsequently the solution allowed to age for 3 days at room temperature. After that, the as-prepared products were washed with deionized water and collected by centrifugation. Finally, the as-prepared products were frozen dried and further annealed at 450 °C for 2 h.

Material characterization: The crystal structure of the product was characterized by X-ray diffraction (XRD, MAXima_X XRD-7000). Morphology and microstructure of the synthesized materials was investigated by field emission scanning electron microscopy (FESEM, JSM-6700F, Japan) and transmission electron microscopy (JEM-2010, Japan).

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Electrochemical measurements: Cyclic voltammetry and electrochemical impedance investigations of the as-prepared materials were performed on a microelectrode using three-electrode cell, which consists of the prepared vanadium oxides as working electrode, platinum flat as counter electrode, and saturated calomel electrode (SCE) as reference electrode. Charge/discharge measurements were performed using a symmetrical capacitor device. The working electrodes was prepared as following, blending 80 wt% vanadium oxides, 15 wt% activated carbon and 5 wt% polytetrafluoroethylene (PTFE) to form uniform mixture and then pressed them onto nickel foam current collectors (with diameter around 13 mm). 1 M Li_2SO_4 aqueous solution was used as electrolyte and porous polymeric (50 μm thick) as separator.

3. Results and discussion

The XRD patterns and EDS spectrum of the obtained powders are shown in Fig. 1. A few broaden and weak peaks can be observed from the samples obtained in different solutions (Fig. 1a-I and a-II), reveals their amorphous nature. After calcination at 450 °C for 2 h, it is interesting to find that all the peaks for the as-synthesized samples are in good agreement with the standard PDF card 41-1426, could be indexed as orthorhombic structure V_2O_5. No any peaks from other phases have been detected, indicating the high purity of the products. Because of the intrinsic amorphous nature of the as-prepared samples without sintering at high temperature, the use of X-ray diffraction (XRD) does not allow identification of the their structure unequivocally, hence, combined the XRD results of the sample after calcination, in our work it was denoted as $VO_x \cdot yH_2O$. Their composition was further confirmed by EDS analyses. The C signal in Fig. 1b and c come from the SEM conductive adhesive.

The morphology of the prepared samples were observed by SEM. Fig. 2a presents the sample obtained in aqueous solution composed of irregular shaped bulks, and after sintering at 450 °C, the irregular bucks get bigger, and some particles appear on their surface (Fig. 2b). While, the product formed in the ethanol aqueous solution displays a 3D interconnected network structure composed of 1D nano-ribbons (Fig. 2c), after annealing at high temperature, it still retaining their original 3D interconnected networks, although its surface turns into rough and some particles appear (Fig. 2d). The results indicated that the polarity of the
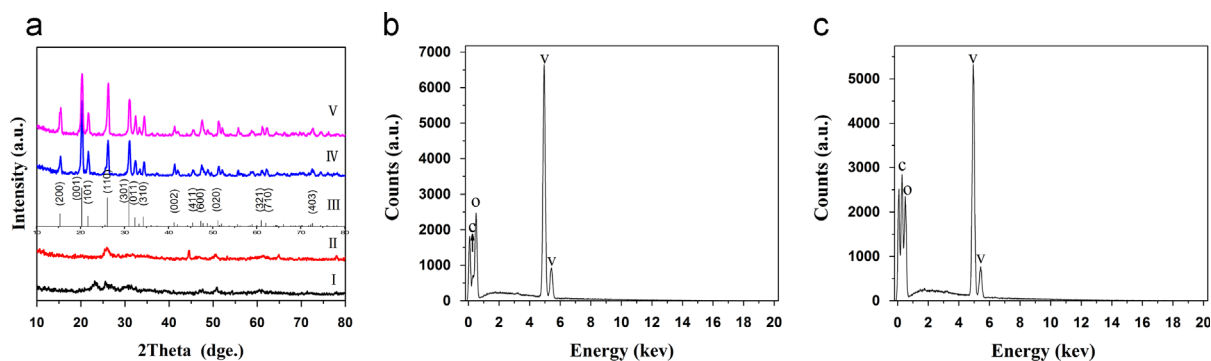
Fig. 1. (a) XRD patterns of samples: I: obtained in aqueous solution, II: obtained by ethanol aqueous solution, III: the standard values of PDF card 41-1426, IV: obtained in aqueous solution and after calcination, V: obtained by ethanol aqueous solution after calcinations; (b) EDS of $VO_x \cdot yH_2O$ obtained in aqueous solution; (c) EDS of $VO_x \cdot yH_2O$ obtained in ethanol aqueous solution.
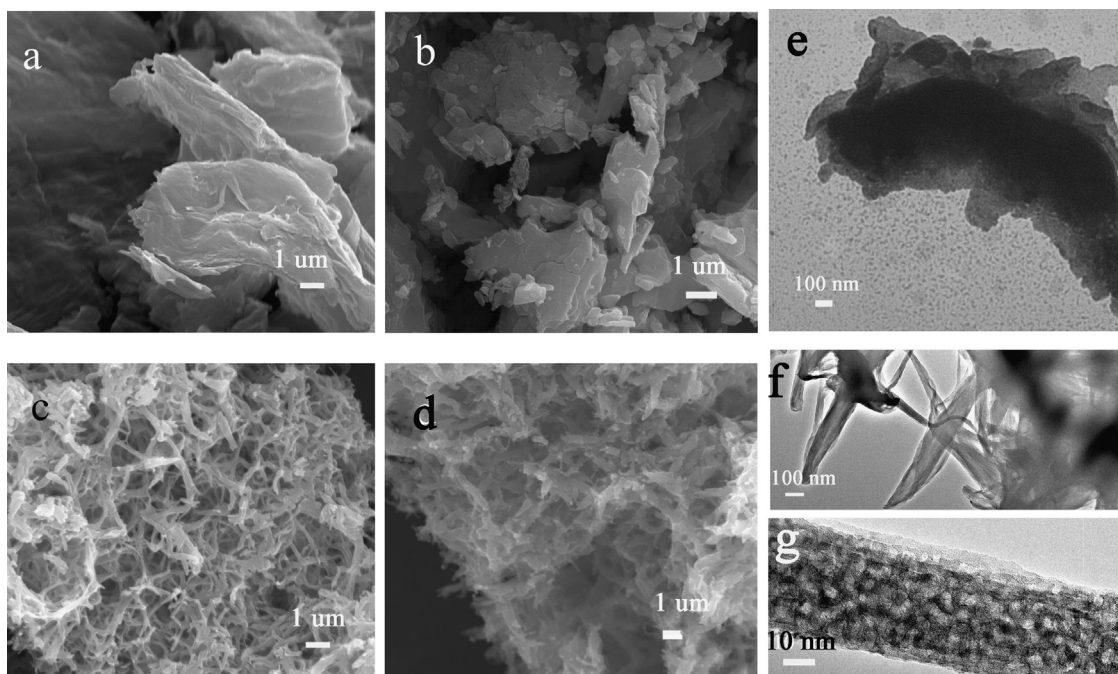
Fig. 2. ((a) and (b)) SEM images of $VO_x \cdot yH_2O$ obtained in aqueous solution before and after calcination; ((c) and (d)) $VO_x \cdot yH_2O$ obtained in ethanol aqueous solution before and after calcinations; (e) TEM image of $VO_x \cdot yH_2O$ obtained in aqueous solution; ((f) and (g)) TEM images of $VO_x \cdot yH_2O$ obtained in ethanol aqueous solution.