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Encapsulating V_2O_3 nanorods into carbon core-shell composites with porous structures and large specific surface area for high performance solid-state supercapacitors

Tao Hu, Yanyan Liu, Yifu Zhang*, Ying Nie, Jiqi Zheng, Qiushi Wang, Hanmei Jiang, Changgong Meng

School of Chemistry, Dalian University of Technology, Dalian 116024, PR China

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ABSTRACT

V_2O_3@C core-shell nanorods with porous structures and large specific surface area were synthesized using V_2O_5 nanowires as the source of core and glucose as the source of shell by a facile hydrothermal route combination of heat treatment. As-prepared V_2O_3@C nanorods comprised of core-shell structures with crystalline V_2O_3 cores and amorphous carbon shells. Nitrogen adsorption-desorption isotherms revealed that V_2O_3@C core-shell nanorods displayed BET specific surface area as high as 219 $m^2 \cdot g^{-1}$ and had hierarchical porous structures. Electrochemical properties of V_2O_3@C core-shell nanorods as supercapacitor electrode were studied and showed their measured capacitance was based on the pseudocapacitance. Specific capacitances of V_2O_3@C core-shell nanorods measured 228, 221, 207, 158 and 127 $F \cdot g^{-1}$ at current densities of 0.5, 1, 2, 5 and 10 $A \cdot g^{-1}$, respectively. Results showed V_2O_3@C core-shell nanorods displayed higher specific capacitance than values of carbon spheres (4 $F \cdot g^{-1}$ at 1 $A \cdot g^{-1}$) and V_2O_3 nanomaterials (49 $F \cdot g^{-1}$ at 1 $A \cdot g^{-1}$). Asymmetric supercapacitor device assembled from V_2O_3@C core-shell nanorods and activated carbon (V_2O_3@C//C) showed specific capacitances of 0.297, 0.274, 0.230, 0.194 and 0.169 $F \cdot cm^{-2}$ at current densities of 0.5, 1, 2, 5 and 10 $mA \cdot cm^{-2}$, respectively. It showed higher specific capacitance than that of V_2O_3//C device (0.219 $F \cdot cm^{-2}$ at 1 $mA \cdot cm^{-2}$). A capacitance retention of 86% for V_2O_3@C//C device after 1000 cycles indicated that V_2O_3@C had good cycling performance for supercapacitor application. Present findings suggested that V_2O_3@C core-shell nanorods could be considered as potential materials for high-performance energy storage materials.

1. Introduction

Ensuring the availability of energy is a crucial concern faced worldwide. Thus, alternative energy conversion systems based on renewable energy sources have been in the focus of energy innovation research recently. The transportation of that kind of sustainable energy from the point of generation to the end user is yet another challenging task which involves power grids for large-distance and high-capacity energy-storage devices for small-scale and mobile applications [1–6]. Compared to batteries, supercapacitors (SCs) are promising energy storage devices because SCs display high power density, long operating lifetimes, superior rate capability, rapid charging/discharging rate and low maintenance cost [7–12]. Generally, SCs are classified into two types originating from their storage mechanism: electrochemical double layer capacitors (EDLCs) and pseudocapacitors (PCs). EDLCs physically store charges by reversible ion adsorption at electrode-electrolyte interface, and PCs chemically store charges by redox reaction at the vicinity (a few nanometers) of electrodes' surface [13–15]. Electrode materials of SCs play an important role in their electrochemical performance [16]. Carbon-based materials, conductive polymers and transition metal oxides are widely available to SCs' electrodes [17–21]. As is well known, energy density (E) of SCs is governed by capacitance (C) and voltage (V), according to equation $E = 1/2CV^2$. Therefore, increase of device performance using novel electrode materials is an efficient strategy to improve E of SCs [22]. It was demonstrated that electrochemical performance of SCs could be significantly improved if the materials possess large specific surface area, good ion accessibility and high conductivity [23]. Just recently, metal oxides/carbon composites have attracted a considerable amount of attention because they exhibit higher capacitance than carbon-based materials and pure metal oxides [8,24–28].

Vanadium (III) oxide (V_2O_3) exhibits fully reversible temperature-

* Corresponding author.
E-mail address: yfzhang@dlut.edu.cn (Y. Zhang).

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induced metal-to-insulator transition (MIT) between rhombohedral and monoclinic phases [29,30]. Many efforts have been made to focus on synthesis, characterization, mechanism and application of V_2O_3 material with MIT in previous reports [30–36]. Recently, V_2O_3 and its derived materials (carbonaceous materials) applied to batteries have attracted increasing attention [37–46]. For examples, carbon-coated yolk-shell V_2O_3 microspheres were synthesized by a template-free polyol solvothermal method and showed a capacity of 437.5 mAh·g^{-1} after 100 cycles at a current density of 0.1 A·g^{-1} in lithium-ion batteries [44]. V_2O_3/C composites synthesized by oxygen corrosive and carbon coating process by one-pot hydrothermal method delivered an impressive capacity of 283 mAh·g^{-1} at 25 A·g^{-1} as lithium storage material [40]. V_2O_3 modified carbon microsphere was effectively prepared by a facile wet impregnation method and showed an initial discharge capacity of 1177 mAh·g^{-1} at 0.5 C when used as a cathode matrix for lithium-sulfur batteries [42]. However, researches on electrochemical properties of V_2O_3 materials as SCs have been less reported comparatively [47–49]. V_2O_3 nanoflakes@C core-shell composites comprising a carbon core with a shell layer of edge-on standing V_2O_3 nanoflakes were synthesized using a micelle-anchoring method and exhibited specific capacitance of 205 F·g^{-1} at 0.05 A·g^{-1} reported by Hong-Yi Li and his co-workers [48]. The recent report synthesized V_2O_3@C composites (V_2O_3 nanobelts) by heat treatment with $H_2V_3O_8$@C core-shell composites and exhibited capacitance of 180 F·g^{-1} at 0.5 A·g^{-1} when used as SCs electrode [49]. Therefore, it is meaningful to develop V_2O_3@C core-shell composites with V_2O_3 cores and carbon shells as well as their application to SCs.

In present work, V_2O_3 nanorods were encapsulated into carbon forming V_2O_3@C core-shell nanorods using V_2O_5 nanowires as core templates by a facile hydrothermal reaction combined with calcination. Electrochemical performance of V_2O_3@C core-shell nanorods used as SCs' electrode and solid-state SCs' device was studied.

2. Experimental section

2.1. Materials synthesis

Vanadium pentoxide (V_2O_5), hydrogen peroxide (H_2O_2, 30 wt.%) and glucose ($C_6H_{12}O_6{\cdot}H_2O$) with analytical grade were purchased from Sinopharm Chemical Reagent Co., Ltd and used without any further purification. Encapsulating V_2O_3 nanorods into carbon core-shell composites (V_2O_3@C) was adopted a facile post-synthesis method using V_2O_5 nanowires as cores, as depicted in Fig. 1. Ultra-long V_2O_5 nanowires were firstly synthesized by a hydrothermal conversion from commercial V_2O_5 based on previous reports [50,51]. Detailed synthesis and characterization were shown in *Supplementary data* (Fig. S1). In a typical synthesis of V_2O_3@C, 0.09 g V_2O_5 nanowires were dispersed into glucose solution (2.00 g glucose and 30 mL H_2O) with ultrasonic for 10 min at the room temperature. Then above mixture was vigorously stirred at 20 rpm for 1 h by the magnetic stirrer. After mixture became suspension, they were transferred into a 50 mL Teflon Lined stainless steel autoclave (KH-50, 3Mpa, Xi'an Chang Instrument Co., Ltd. equipment) and kept at 180 °C for 4 h. Glucose serves a dual role during the hydrothermal process, namely as a reductant to reduce V_2O_5 to VO_x, and as a carbon precursor for the organic carbon. Products were filtered off with a vacuum filtration pump and a sand core funnel (60 mL, G4), washed with distilled water and absolute ethanol several times to remove any possible residue, and dried for next step. Last, above products were heated in a tube furnace with 5 °C/min heating rate under a flow of N_2 (99.999%) gas at five temperatures vary from 300 to 700 °C for 2 h. After heat treatment, products cooled to room temperature in the N_2 flow. During the process of the calcination, further reduction of VO_x to V_2O_3 was facilitated on the one hand, on the other hand, crystallinity of V_2O_3 was improved. The porosity of V_2O_3@C was greatly increased by this process.

2.2. Materials characterizations

Phase of samples was identified by X-ray powder diffraction (XRD) using Panalytical X'Pert powder diffractometer at 40 kV and 40 mA with Ni-filtered Cu Kα radiation. Morphology and sizes of products were observed by field emission scanning electron microscopy (FE-SEM, NOVA NanoSEM 450, FEI) and transmission electron microscopy (TEM, FEITecnai F30, FEI). Samples for SEM observation were gold-sputtered in order to get better morphology, and samples were dispersed in absolute ethanol with ultrasonication before TEM test. Composition of products was examined by elemental analysis (EA) using a Vario EL III equipment (Germany) with a TCD detector to analyze the element of C, H and N, energy-dispersive X-ray spectrometer (EDS) and elemental mapping attached to a scanning electron microscope (SEM, QUANTA450). Fourier transform infrared spectroscopy (FTIR) was measured using KBr pellet technique (About 1 wt% of the samples and 99 wt% of KBr were mixed homogeneously, and then the mixture was pressed to a pellet) and recorded on a Nicolet 6700 spectrometer from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}. Raman spectrum was obtained using a Thermo Scientific spectrometer, with a 532 nm excitation line. Nitrogen adsorption desorption isotherms were determined by Brunauer-Emmet-Teller (BET) method using Micromeritics ASAP-2020 and samples were degassed at 150 °C for several hours.

2.3. Electrochemical characterizations

Working electrodes were prepared using a mixture of 80 wt. % of as-prepared active materials (V_2O_3@C core-shell nanorods), 10 wt. % of polyvinylidene difluoride (PVDF) and 10 wt. % of carbon black. N-

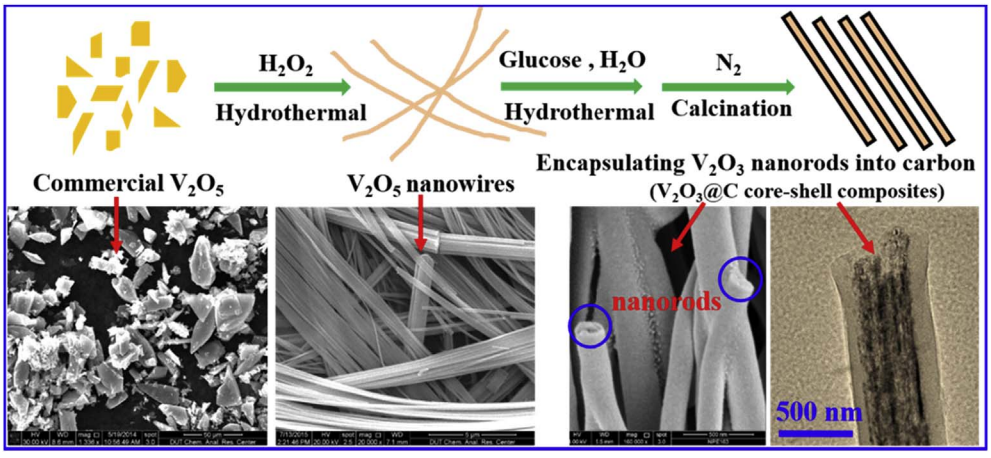

Fig. 1. Schematic illustration of encapsulating V_2O_3 nanorods into carbon core-shell structured composites (V_2O_3@C).