

Full Length Article

Fabrication of polypyrrole/vanadium oxide nanotube composite with enhanced electrochemical performance as cathode in rechargeable batteries

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ARTICLE INFO

Article history:

Received 12 December 2016

Received in revised form 12 January 2017

Accepted 7 February 2017

Available online 9 February 2017

Keywords:

Vanadium oxide nanotube

Polypyrrole

Nanotechnology

Electrochemical performance

ABSTRACT

Vanadium oxide nanotubes (VO_xNTs) with hollow as well as multi-walled features were fabricated under hydrothermal condition by soft-template method. This novel VO_xNTs can be used as cathode material for lithium ion batteries (LIBs), but displaying low specific capacity and poor cycling performance owing to the residual of a mass of soft-template (C₁₂H₂₇N) and intrinsic low conductivity of VO_x. Cation exchange technique and oxidative polymerization process of pyrrole monomers were conducted to wipe off partial soft-template without electrochemical activity within VO_xNTs and simultaneously form polypyrrole coating on VO_xNTs, respectively. The resulting polypyrrole/VO_xNTs nanocomposite delivers much improved capacity and cyclic stability. Further optimizations, such as complete elimination of organic template and enhancing the crystallinity, can make this unique nanostructure a promising cathode for LIBs.

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1. Introduction

With the development of nanotechnology, a variety of nanostructures are built. Specific nanostructure realizes specific function [1–3]. In order to obtain the nanomaterials with high degree of regularity and uniformity, the hard template method always be adopted, such as anodic aluminum oxide (AAO) template method [4–6]. However, hard template method always consumes a mass of template and produces a small quantity of target nanomaterials. Certainly, the ordered nanostructures are often fabricated by other special techniques like chemical or physical vapor deposition (CVD or PVD), electrospinning et al., but these techniques generally involve sophisticated equipments and extreme conditions [7–9].

Wet chemistry and solvothermal methods based on soft template have the advantages of easy manipulation, low demand to the apparatus and facile scaling up for the products [10–12]. While the guarantee for regular and orderly nanostructure is a big challenge.

In our research, vanadium oxide nanotubes (VO_xNTs), which are easy to scale up and possess well-organized multi-walled and hollow structure as well as uniform size distribution, were

obtained via hydrothermal treatment using V₂O₅ sol as precursor and organic C₁₂H₂₇N as soft template. When VO_xNTs were applied as a novel cathode for LIBs, it delivered high initial specific capacity whereas going through severe capacity decay. To relieve this issue, structure modification was conducted by cation exchange and chemical oxidative polymerization to generate polypyrrole/VO_xNTs nanocomposite with less organic template and enhanced conductivity. As we know, polypyrrole is a kind of conductive polymer with good lithium storage property [13]. Consequently, this novel polypyrrole/VO_xNTs exhibits apparently improved specific capacity and cycling stability compared to VO_xNTs. It is very hopeful that further modification (altering cationic type or reaction condition in ion exchange process) can make this polypyrrole/VO_xNTs a promising cathode candidate with excellent electrochemical performance for application in LIBs.

2. Experimental section

2.1. Preparation of samples

A stable V₂O₅ sol was prepared by dissolving V₂O₅ powder (1.02 g) into hydrogen peroxide solution (80 ml, 30%) via continuous stirring along with intense heat and gas releases for ~1 h and followed by aging for 2 days. Then, 1.04 g dodecylamine (C₁₂H₂₇N) dissolving in 3 ml ethanol was added into the above V₂O₅ sol under sufficient agitation for 12 h. The yellow suspension obtained was

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transferred into a 100 ml of hydrothermal autoclave and kept at 180 °C for 5 days. The resulting black product was vanadium oxide nanotubes (VO_xNTs).

In the following, 0.5 g VO_xNTs was uniformly dispersed into 90 ml mixed solution of deionized water and ethanol (volume ratio, 1:8) by ultrasonic treatment for 1 h. Next, 1 g FeCl₃·6H₂O was slowly dissolved into VO_xNTs suspension and followed by the injection of 0.1 ml pyrrole monomer under stirring for another 12 h. The final sediment through rinse, filtration and drying at 60 °C was labeled as polypyrrole/VO_xNTs.

2.2. Characterizations

Scanning electron microscopy (SEM, Philips-XL-30FEG) and transmission electron microscopy (TEM, JEOL-1230) were conducted to observe the morphology and structure of VO_xNTs and polypyrrole/VO_xNTs. Qualitative elementary analysis was carried out by Energy Dispersive Spectroscopy (EDS, equipped on SEM). X-ray powder diffraction (XRD) patterns were recorded via a RigataD/max-C diffractometer with Cu K α radiation source ($\lambda = 1.5406 \text{ \AA}$). Fourier transform infrared spectroscopy (FTIR) was collected through a Bruker-TENSOR27 spectrometer at the range of 400–4000 cm⁻¹. Thermogravimetry (TG) and Differential Thermal Analyses (DTA) were performed using a SDT Q600 equipment from (~25 °C to 800 °C) and (50 °C to 700 °C) for two samples with the heating rate of 10 °C min⁻¹ in air, respectively.

2.3. Electrochemical measurements

Cathode slurry was prepared by mixing active material (VO_xNTs or polypyrrole/VO_xNTs), carbon black and polyvinylidene fluoride (PVDF) homogeneously with mass ratio of 8:1:1 in *N*-methylpyrrolidone (NMP). The formed slurry was evenly coated on aluminum foil, dried at 120 °C for 8 h under vacuum and punched into small wafer. Lithium ion coin cells were assembled in an argon-filled glove box with moisture and oxygen levels less than 1 ppm by using this wafer as working electrode, microporous polymer membrane (Celgard 2500) as separator, lithium wafer as counter electrode and 1 M LiPF₆ in ethylene carbonate (EC) and dimethyl carbonate (DMC) with volume ratio of 1:1 as electrolyte.

Galvanostatic charge–discharge tests were carried out on LAND cell-testing system between 1.5 V and 4 V at 50 mA g⁻¹. Electrochemical impedance spectroscopy (EIS) was obtained at frequency region from 100 kHz to 0.01 Hz. Zview software was applied to fit and analyze the Nyquist plots.

3. Discussion

Fig. 1(a) presents SEM image of VO_xNTs with their enlarged view at top right corner, whose length distributes between 2–5 μm

with hollow feature as observed from nanotube-end. TEM image of VO_xNTs with its single high-magnified picture in Fig. 1(b) manifests that VO_xNTs possess multi-walled and hollow nano-tubular structure with an inner diameter of 30–100 nm and outer diameter of 50–200 nm. The interlayer spacing between adjacent VO_x layers (dark lines) is $\sim 3 \text{ nm}$. Schematic drawing between VO_x layers is shown in Fig. 1(c). VO_x layer, which displays electronegativity, consists of two sheets of VO₅ square pyramids with apexes pointing toward opposite orientations and joined by VO₄ tetrahedra [14]. Every two C₁₂H₂₇N molecules under hydrothermal condition would be antiparallel-aligned and oxidized into protonated C₁₂H₂₅NH₃⁺, which was bound to VO_x layer via electrostatic interaction [15]. Consequently, VO_x layer and bi-molecule layer arranged alternately.

SEM images of polypyrrole/VO_xNTs with different magnifications were presented in Fig. 2(a) and (b), whose surface was coated by a layer of substance (polypyrrole) and obviously more rough compared to VO_xNTs. Besides, the hollow feature of polypyrrole/VO_xNTs was still retained. In order to investigate the major elementary composition qualitatively, EDS was performed as shown in Fig. 2(c). It can be seen that V, O and C were major elements in polypyrrole/VO_xNTs. Moreover, a certain amount of Fe element could be detected at the same time.

Schematic diagram of polypyrrole/VO_xNTs was illustrated in Fig. 3. Firstly, VO_x/C₁₂H₂₇N alternately lamellar composite scrolled into VO_xNTs by rolling mechanism triggered by stress variation within VO_x layer (yellow matter) when partial V⁵⁺ ions were reduced to V⁴⁺ ions under hydrothermal treatment [16,17]. Then, Fe³⁺ cation ions were employed to exchange protonated C₁₂H₂₅NH₃⁺ molecules partly, decreasing the content of organic template (blue matter) [18,19]. Meanwhile, a certain amount of Fe element would remain within nanotubes to keep charge neutrality as evidenced by EDS results. Finally, polypyrrole (green matter, n[C₄H₃N]) was formed on surface of VO_xNTs through chemical oxidative dehydrogenation polymerization in solution using pyrrole monomer (C₄H₅N) as reductant and residual Fe³⁺ ions as oxidant, resulting in polypyrrole/VO_xNTs nanocomposite.

Structure and composition of VO_xNTs and polypyrrole/VO_xNTs were characterized as shown in Fig. 4. XRD patterns of VO_xNTs and polypyrrole/VO_xNTs in Fig. 4(a) exhibited a series of (001) diffraction peaks, indicating their multilayered structure, in which the (001) peak position shifted from $2\theta = 3.12^\circ$ for VO_xNTs to 3.40° for polypyrrole/VO_xNTs. According to Bragg's law, the interlayer spacing of VO_xNTs reduced from 2.83 nm to 2.60 nm for polypyrrole/VO_xNTs. It demonstrates that polypyrrole/VO_xNTs maintained the multi-walled structure well and C₁₂H₂₇N template in it was partially removed. The (hk0) diffraction peaks (210, 310) of VO_xNTs at large angle region reflect the structural characteristics within VO_x layer. For polypyrrole/VO_xNTs, these (hk0) peaks can not be detected owing to the influence of polypyrrole on sur-

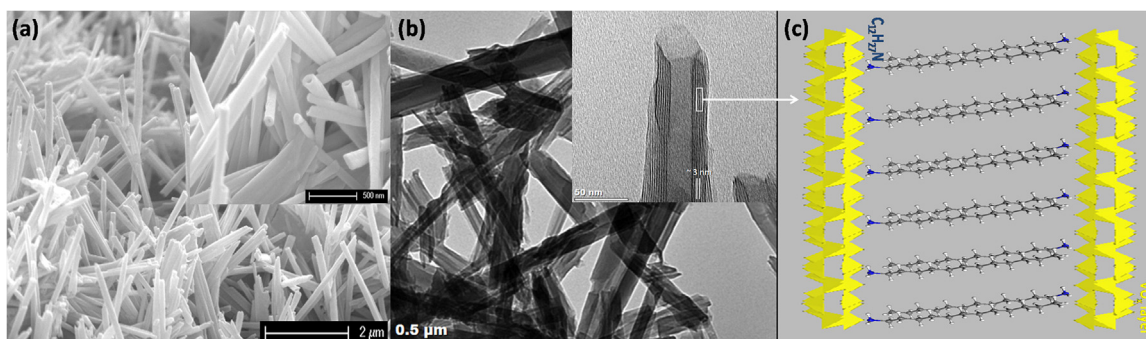


Fig. 1. TEM image (a), SEM image (b) and microstructural schematic (c) of VO_xNTs.

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