



# Amorphous vanadyl phosphate/graphene composites for high performance supercapacitor electrode



Ningna Chen<sup>a</sup>, Jinhua Zhou<sup>a</sup>, Qi Kang<sup>b</sup>, Hongmei Ji<sup>a</sup>, Guoyin Zhu<sup>a</sup>, Yu Zhang<sup>a</sup>, Shanyong Chen<sup>a</sup>, Jing Chen<sup>c</sup>, Xiaomiao Feng<sup>b</sup>, Wenhua Hou<sup>a,\*</sup>

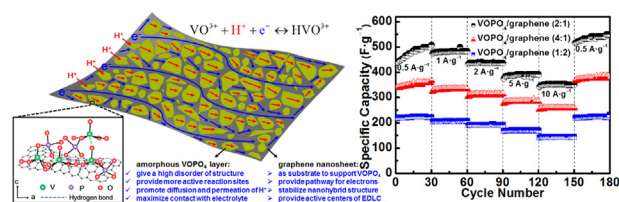
<sup>a</sup> Key Laboratory of Mesoscopic Chemistry of MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210023, PR China

<sup>b</sup> Key Laboratory for Organic Electronics & Information Displays, Institute of Advanced Materials, School of Materials Science & Engineering, Nanjing University of Posts and Telecommunications, Nanjing, 210046, PR China

<sup>c</sup> College of Chemistry and Molecular Engineering, Nanjing Tech University, Nanjing, 211816, PR China

## GRAPHICAL ABSTRACT

Amorphous vanadyl phosphate/graphene composites with a unique layer-on-sheet hybrid nanostructure show excellent performances as supercapacitor electrode materials.



## ARTICLE INFO

### Article history:

Received 24 November 2016

Received in revised form

19 January 2017

Accepted 29 January 2017

### Keywords:

Vanadyl phosphate

Graphene

Nanohybrid

Supercapacitor

Amorphous

## ABSTRACT

Amorphous vanadyl phosphate/graphene nanohybrids is successfully synthesized by first exfoliating bulk layered vanadyl phosphate ( $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ ) into nanosheets, and then hydrothermal treatment with graphene oxide (GO). The electrochemical properties of the resulted materials are systematically investigated. It is found that a phase transformation from crystalline to amorphous is occurred to  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ . As supercapacitor electrode material, the amorphous  $\text{VOPO}_4$ /graphene composite exhibits a high specific capacitance ( $508 \text{ F g}^{-1}$  at  $0.5 \text{ A g}^{-1}$ ), an excellent rate capability ( $359 \text{ F g}^{-1}$  at  $10 \text{ A g}^{-1}$ ), and a good cycling stability (retention 80% after 5000 cycles at  $2 \text{ A g}^{-1}$ ). Particularly, it simultaneously has a greatly enhanced energy density of  $70.6 \text{ Wh} \cdot \text{kg}^{-1}$  with a power density of  $250 \text{ W kg}^{-1}$ . The outstanding energy storage performance mainly originates from the generation of amorphous  $\text{VOPO}_4$  phase that facilitates ion transport by shortening ion diffusion paths and provides more reversible and fast faradic reaction sites, the hybridization with graphene that greatly improves the electric conductivity and structure stability, and the unique layer-on-sheet nanohybrid structure that effectively enhances the structure integrity. This work not only provides a facile method for the preparation of amorphous  $\text{VOPO}_4$ /graphene composites, but also demonstrates the enhanced energy density and rate capability of amorphous  $\text{VOPO}_4$ -based materials for potential application in supercapacitors.

© 2017 Elsevier B.V. All rights reserved.

## 1. Introduction

The supercapacitor (also called electrochemical capacitor), as a new type of green energy storage devices, has the advantages of high power density of traditional electrostatic capacitor and high

\* Corresponding author.

E-mail address: [whou@nju.edu.cn](mailto:whou@nju.edu.cn) (W. Hou).

energy density of rechargeable batteries, giving rise to a promising application in the fields of mobile communication, electric vehicle, energy storage and so on [1,2]. However, the relatively low energy density and fast attenuation under high rate conditions greatly limit its application.

As a main component in the supercapacitor, the electrode material has a great influence on the performance of the supercapacitor. Therefore, much effort has been devoted to the development of novel electrode materials with a high energy and power density simultaneously [3–5]. As a layered material,  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ , which is formed through vertex-sharing  $\text{VO}_6$  octahedra and  $\text{PO}_4$  tetrahedra, is an attractive pseudocapacitive material [6–8]. Because of the existence of  $\text{V}^{4+}/\text{V}^{5+}$  redox couple, it is granted with a higher redox potential of 1.0 V (and thus higher pseudocapacitance and energy density) than simple vanadium oxides [9]. Moreover, the exfoliation of layered  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$  into  $\text{VOPO}_4$  ultrathin nanosheets can be feasibly achieved due to the weak hydrogen bonds between  $\text{VOPO}_4$  layers [10,11]. The exfoliated 2D  $\text{VOPO}_4$  ultrathin nanosheets have a high specific surface area and surface atom ratio, being beneficial to the ion diffusion and charge transfer and the maximized contact between electrode and electrolyte.

Recently, it has been reported that amorphous materials with nano-architectures, including metal oxides (such as  $\text{MnO}_2$  [12],  $\text{MoO}_x$  [13],  $\text{ZnO}$  [14], and  $\text{NiWO}_4$  [15]) and metal hydroxides (such as  $\text{Ni}(\text{OH})_2$  [16] and  $\text{Co}(\text{OH})_2$  [17]), present good pseudo-capacitive performance and environmental benignity. Compared with crystalline materials, amorphous counterparts usually have a large number of structure defects (*i.e.*, vacancies) which can be served as reversible active sites and thus contribute to a high capacitance [18], large channels which can facilitate the diffusion and reaction of electrolyte ions [19], and the isotropic nature which can sustain high strain of volume change along with the redox reaction [20]. It was claimed that non-crystalline  $\text{VOPO}_4$  had greatly improved catalytic activities compared with crystalline  $\text{VOPO}_4$  [21–24]. Nevertheless, the electrochemical pseudocapacitor performance of amorphous  $\text{VOPO}_4$  has not yet been reported.

Although transition metal oxides usually have a high theoretical capacitance and a wide voltage window, the poor conductivity prevents them from having a superior cycle stability [6]. Among them,  $\text{VOPO}_4$  is no exception. In order to prolong the cycle stability, researchers combined  $\text{VOPO}_4$  with the highly-conductive carbon materials [18,25,26]. For example, Xie's group fabricated a flexible ultrathin-film supercapacitor based on  $\text{VOPO}_4/\text{graphene}$  nanosheets [27]. Lee et al. adopted an ice-templated self-assembly process to prepare a three-dimensional (3D) porous nanocomposite of layered  $\text{VOPO}_4$  and graphene with a high capacitance and a superior capacitance retention [28]. Among the above reports, the existence of graphene greatly improved the conductivity of the integrated material. Moreover, the formation of composite also reduces the need for an adhesive, thereby eliminating the possibility of nanostructure aggregation and other side effects [29]. However, the preparation process of the composites is generally cumbersome and costly. Besides, these methods generally result in the crystalline  $\text{VOPO}_4$  rather than the amorphous structure.

Currently, the preparation methods of amorphous  $\text{VOPO}_4$  are quite complicated, such as adopting suitable templates [19], using supercritical  $\text{CO}_2$  as an anti-solvent [30,31], or involving solvent evaporation in vacuum [31]. The controlled synthesis of amorphous  $\text{VOPO}_4$ , especially its nanocomposites with conductive materials for high performance supercapacitors via a simple and facile method, still remains a great challenge. On the other hand, the electrochemical performance of  $\text{VOPO}_4$ -based materials is still not good enough, such as the relatively low energy density and poor rate capability [32,33]. In order to meet the requirements of practical

application, the performance of  $\text{VOPO}_4$ -based materials should be further improved, especially the energy density and rate capability.

Here in this work, with the aim of fabricating excellent supercapacitor electrode materials with both a high energy density and a good rate capability, we developed a simple and facile method for the preparation of amorphous  $\text{VOPO}_4/\text{graphene}$  nanocomposites. Owing to the generation of amorphous  $\text{VOPO}_4$  phase and the unique layer-on-sheet nanohybrid structure, the resulted  $\text{VOPO}_4/\text{graphene}$  composites exhibited the outstanding energy storage performance. Based on the experimental results, the corresponding charge-discharge mechanism was also discussed in detail.

## 2. Experimental

### 2.1. Materials

Graphene oxide (GO) was prepared by the Hummers method, according to the procedure described in the literature [34]. A detailed description of the procedure is provided in supporting information.  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$  was obtained in the light of previously reported [35]. To prepare amorphous  $\text{VOPO}_4/\text{graphene}$  composites, the as-prepared  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$  (60 mg) was firstly dispersed in isopropanol (25 mL) by ultrasonic treatment in an ice bath for 30 min, and then GO (30 mg) was added into the solution. For bulk  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ , the weak hydrogen bonds between  $\text{VOPO}_4$  layer and  $\text{H}_2\text{O}$  molecule are easily destroyed by the applied external force [36]. After sonication for another 30 min, the dispersion was transferred to a Teflon-lined stainless pressure vessel and maintained at 170 °C for 20 h. After cooling down to room temperature, the resulting suspension was separated by centrifugation and washing with ethanol for several times. Then the resulting precipitate was dried overnight at 60 °C under a vacuum to get amorphous composite  $\text{VOPO}_4/\text{graphene}$  (2:1), in which the irregular  $\text{VOPO}_4$  layers were deposited on graphene nanosheets to give a layer-on-sheet nanohybrid structure. Besides, a phase transformation from the crystalline  $\text{VOPO}_4$  to amorphous  $\text{VOPO}_4$  was accomplished. By changing the mass of  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$  (72 mg and 30 mg) and that of GO (18 mg and 60 mg), another two samples with different mass ratios of  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$  and GO were obtained. The resultant samples were denoted as  $\text{VOPO}_4/\text{graphene}$  (4:1) and  $\text{VOPO}_4/\text{graphene}$  (1:2). For comparison, pure graphene and amorphous  $\text{VOPO}_4$  were also prepared through a similar process except that only GO (90 mg) or  $\text{VOPO}_4$  (90 mg) was mixed with isopropanol (25 mL) in the ice bath system.

### 2.2. Structure and morphology characterization

Powder X-ray diffraction (XRD) patterns of the obtained samples were measured on a Philip-X'Pert X-ray diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at a scanning rate of  $0.2^\circ/\text{s}$  in a  $2\theta$  range of  $5\text{--}80^\circ$ . The morphologies of the products were examined by scanning electron microscopy (SEM, JEOL JEM-6300F) and transmission electron microscopy (TEM, JEOL JEM-200CX, operating at an accelerating voltage of 200 kV). For TEM observation, the sample was dispersed in ethanol by ultrasonic treatment and then dropped onto carbon-coated copper grids. FT-IR spectra of products in KBr pellets were recorded using a Bruker model VECTOR22 Fourier transform spectrometer. X-ray photoelectron spectroscopic (XPS) measurements were carried out on an X-ray photoelectron spectrometer (Thermo Fisher Scientific, K-Alpha) equipped with a hemispherical electron analyzer (pass energy of 20 eV) and an  $\text{Al K}\alpha$  ( $h\nu = 1486.6 \text{ eV}$ ) X-ray source. A combination of Gaussian and Lorentzian functions was used to fit the curves.

Download English Version:

<https://daneshyari.com/en/article/5149820>

Download Persian Version:

<https://daneshyari.com/article/5149820>

[Daneshyari.com](https://daneshyari.com)