Materials Letters 229 (2018) 26–30

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

Facile hydrothermal synthesis and electrochemical properties of $(NH_4)_2V_4O_9$ sheets for supercapacitor electrode with excellent performance

Xiaoyu Liu, Yifu Zhang *, Jiqi Zheng, Changgong Meng

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

ARTICLE INFO

Article history:
Received 24 April 2018
Received in revised form 24 June 2018
Accepted 25 June 2018
Available online 25 June 2018

Keywords:
$(NH_4)_2V_4O_9$
Electrical properties
Sheets
Microstructure
Energy storage and conversion

ABSTRACT

A facile and versatile method for synthesis of novel ammonium vanadium oxide [$(NH_4)_2V_4O_9$] sheets is developed by a simple hydrothermal route. It is found that the synthetic conditions play an important role in the successful synthesis of $(NH_4)_2V_4O_9$ sheets, and the favorable condition is NH_4VO_3/$H_2C_2O_4{\cdot}2H_2O$ = 1/1 at 180 °C for 48 h. $(NH_4)_2V_4O_9$ sheets exhibit the square-like shape with several nanometers in thickness, BET specific surface area of 16 $m^2\,g^{-1}$ and pore volume of 0.16 $cm^3\,g^{-1}$. Electrochemical properties of $(NH_4)_2V_4O_9$ sheets are firstly investigated as supercapacitor electrodes by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS). $(NH_4)_2V_4O_9$ sheets exhibit electrical storage based on the faradaic mechanism with excellent capacity and rate capability. Specific capacitance of $(NH_4)_2V_4O_9$ sheets reaches to 249F g^{-1} at a current density of 0.5 A g^{-1}, suggesting that $(NH_4)_2V_4O_9$ sheets can be promising potential as electrode material applied to supercapacitors.

1. Introduction

With the rapid consumption of fossil fuels, increasing global warming and environmental pollution, huge attention has been paid to the efficient, clean, sustainable energy conversion and storage to lessen green-house gas emissions [1–3]. Supercapacitors (SCs) with high power density, long cycle life, fast charge and discharge rate, lightweight, safe operation, etc. are considered as the next generation energy-storage systems for practical applications [4–10]. The performance of SCs is mainly determined by the electrochemical properties of electrode materials. Thus, the development of new electrode materials for SCs with low cost is of decisive significance [11–13]. Recently, ammonium vanadium oxides have received increasing attention owing to their good electrochemical property used as cathode material for Li-ion and Na-ion batteries [14–21]. For examples, $NH_4V_4O_{10}$ nanobelts exhibit the capacity of 190 mAh g^{-1} at 200 mA g^{-1} applied to Na-ion battery [19]. $NH_4V_3O_8$ nanorods show good Li^+ insertion/extraction ability with the specific capacity of 238 mAh g^{-1} at 15 mA g^{-1} [15]. Among them, however, $(NH_4)_2V_4O_9$ has rarely been reported. Furthermore, the electrochemical properties of $(NH_4)_2V_4O_9$ applied to SCs' electrode for energy storage have not been studied to the best of our knowledge. Herein, we developed a facile hydrothermal route for synthesizing $(NH_4)_2V_4O_9$ sheets and investigated their electrochemical properties as a SCs' electrode.

2. Experimental

All chemicals in our experiments were used as received. In a typical procedure, 0.585 g (5 mmol) of NH_4VO_3, 0.630 g of $H_2C_2O_4{\cdot}2H_2O$ (5 mmol) (NH_4VO_3:$H_2C_2O_4{\cdot}2H_2O$ = 1:1) and 35 mL distilled water were mixed and magnetic stirred for 30 min at the room temperature. The above solution was transferred into a 50 mL Teflon-lined stainless steel autoclave and kept at 180 °C for 48 h. After the reaction, $(NH_4)_2V_4O_9$ sheets were collected and washed by distilled water and absolute ethanol for several times to remove any possible residue and dried in vacuum at 75 °C for 12 h.

The phase and composition were identified by X-ray powder diffraction (XRD), energy-dispersive X-ray spectrometer (EDS), elemental mapping, X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR) and Thermo-Gravimetric analysis (TG). The morphology and structures were observed by field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM) and nitrogen adsorption–desorption isotherms. Electrochemical properties were studied in

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

https://doi.org/10.1016/j.matlet.2018.06.116
0167-577X/

1 mol L^{-1} Na_2SO_4 electrolyte using a three-electrode method. Detail information was represented in Supplementary data.

3. Results and discussion

The synthetic conditions including the mole ratio of NH_4VO_3/$H_2C_2O_4{\cdot}2H_2O$, reaction time and temperature, play an important role in the successful synthesis of $(NH_4)_2V_4O_9$ sheets, as shown in Fig. 1a-c. $(NH_4)_2V_4O_9$ can be prepared by controlling $NH_4VO_3/H_2C_2O_4{\cdot}2H_2O$ = 1/0.9 and 1/1 at 180 °C for 48 h (Fig. 1a). When the mole ratio of $NH_4VO_3/H_2C_2O_4{\cdot}2H_2O$ is 1/0.83, the impurity of $NH_4V_4O_{10}$ is observed; however, $V_2O_5{\cdot}nH_2O$ is detected with $NH_4VO_3/H_2C_2O_4{\cdot}2H_2O$ = 1/1.1. Fig. 1b shows XRD patterns of the samples obtained with $NH_4VO_3/H_2C_2O_4{\cdot}2H_2O$ = 1/1 at 180 °C for the given times, suggesting the reaction time of 48 h is necessary for the successful formation of $(NH_4)_2V_4O_9$. Main $NH_4V_4O_{10}$ and mixture of $NH_4V_4O_{10}$ and $(NH_4)_2V_4O_9$ are synthesized for 12 h and 24 h, respectively. The influence of the reaction temperature on the products is given in Fig. 1c, revealing that the temperature at 180 °C favors the preparation of $(NH_4)_2V_4O_9$ ($NH_4VO_3/H_2C_2O_4{\cdot}2H_2O$ = 1/1, 48 h). When the reaction temperature at 160 °C, main $NH_4V_4O_{10}$ is obtained. With the reaction temperature increasing to 200 °C, $V_2O_5{\cdot}nH_2O$ is observed. Above results demonstrate that the favorable condition for synthesizing $(NH_4)_2V_4O_9$ is $NH_4VO_3/H_2C_2O_4{\cdot}2H_2O$ = 1/1 at 180 °C for 48 h.

The composition of the as-obtained $(NH_4)_2V_4O_9$ sheets is further studied by EDS, elemental mappings, XPS and FTIR. Fig. S1 and Fig. 1d-g depict EDS spectrum and elemental mappings, respectively, which confirm that the sample comprises N, O and V elements and they are homogeneous distribution. The full XPS spectrum (Fig. 1h) also verifies that the sample contains N, O and V elements (C_{1s} as charge reference [22]), which corresponds to the results of EDS and elemental mappings. Fig. 1i shows the core-level spectrum of V_{2p}, which splits two peaks: $V_{2p3/2}$ and $V_{2p1/2}$ (524.3 eV). Furthermore, $V_{2p3/2}$ can be divided into two signals including $V_{2p3/2}$(+4) at 516.1 eV and $V_{2p3/2}$(+5) at 517.4 eV [23]. These characteristics are very consistent with $(NH_4)_2V_4O_9$. Fig. 1j represents the FTIR spectrum. Various vibrations of V═O, V—O, V—O—V and N—H are detected. Fig. S2 reveals the thermal stability of $(NH_4)_2V_4O_9$, which suggests that $(NH_4)_2V_4O_9$ has good thermal stability before 330 °C. The above findings demonstrate that $(NH_4)_2V_4O_9$ is synthesized using this facile hydrothermal route.

Fig. 2a–c shows FE-SEM images of the as-prepared $(NH_4)_2V_4O_9$, which mainly consists of nanosheets. The square-like shape of the

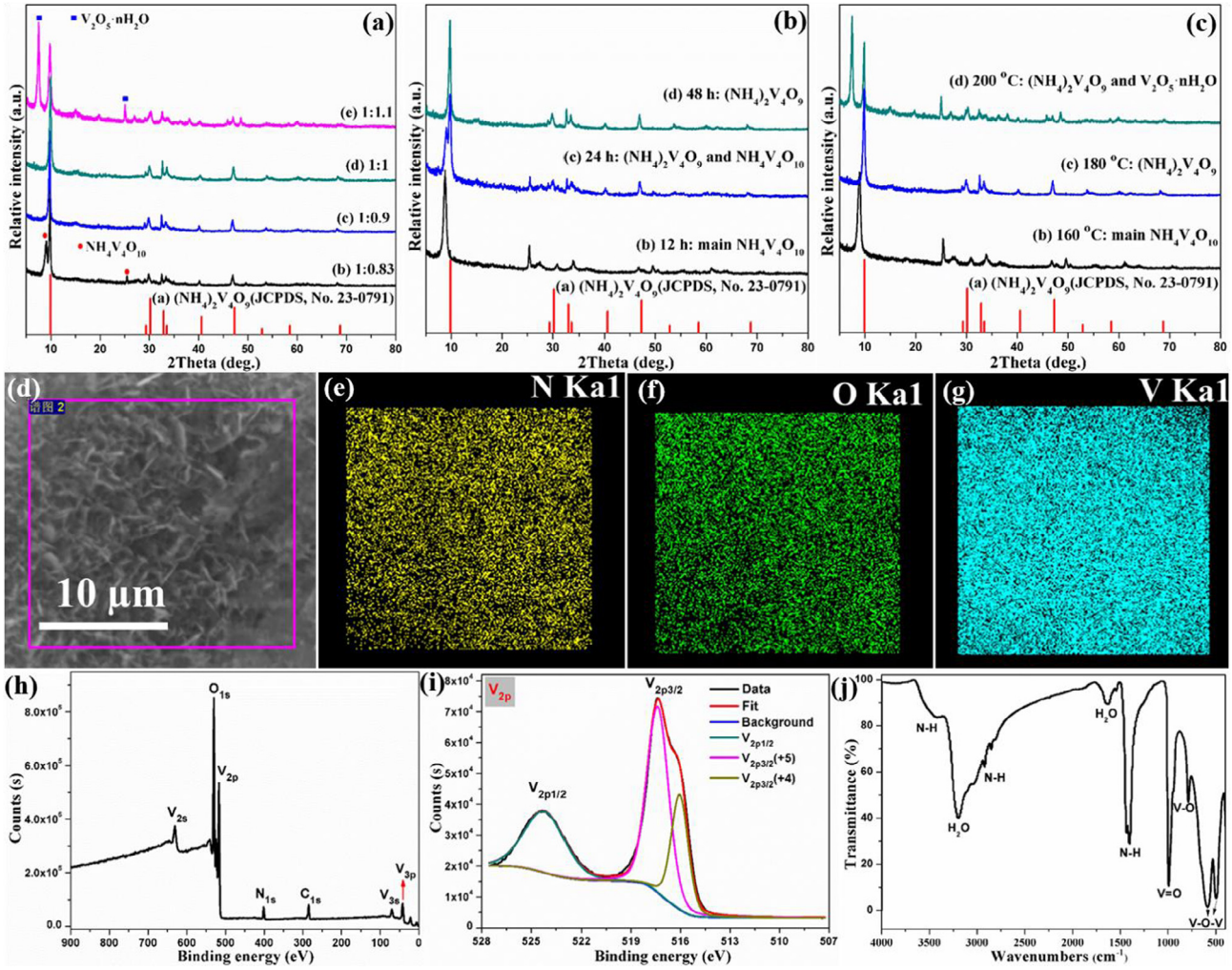

Fig. 1. Characterization of $(NH_4)_2V_4O_9$ sheets: (a) XRD patterns with various ratios of $NH_4VO_3{:}H_2C_2O_4{\cdot}2H_2O$ at 180 °C for 48 h; (b) XRD patterns with $NH_4VO_3{:}H_2C_2O_4{\cdot}2H_2O$ = 1:1 at 180 °C for different reaction times; (c) XRD patterns with $NH_4VO_3{:}H_2C_2O_4{\cdot}2H_2O$ = 1:1 at different reaction temperatures for 48 h; (d-g) Elemental images; (h) Full XPS spectrum; (i) Core-level spectrum of V_{2p}; (j) FTIR spectrum. The reaction condition of the sample for Figure (d-j) is $NH_4VO_3{:}H_2C_2O_4{\cdot}2H_2O$ = 1:1 at 180 °C for 48 h.