Electrochimica Acta 180 (2015) 770–777

Contents lists available at ScienceDirect

Electrochimica Acta

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

Preparation of porous layered molybdenum selenide-graphene composites on Ni foam for high-performance supercapacitor and electrochemical sensing

Ke-Jing Huang*, Ji-Zong Zhang, Jia-Lin Cai

College of Chemistry and Chemical Engineering, Xinyang Normal University, Xinyang 464000, China

ARTICLE INFO

Article history:
Received 8 August 2015
Received in revised form 30 August 2015
Accepted 2 September 2015
Available online 8 September 2015

Keywords:
Porous layered molybdenum selenide-graphene composites
In situ preparation
Supercapacitors
Electrochemical sensing

ABSTRACT

Graphene and the flexible Ni foam substrate are used in a facile hydrothermal process to control the formation of $MoSe_2$-graphene composites. The effects of the content of graphene on the structure of $MoSe_2$-graphene composites are investigated and the results indicate a suitable proportion of $MoSe_2$ and graphene (7:1) is more beneficial to the charge transport and ion transfer owing to formation of unique porous layered structure. In this composite, abundant graphene nanosheets cover on the surface and interspace of $MoSe_2$ bars homogeneously, leading to large specific surface area and plenty of macropores. As the electrode material of supercapacitors, the composites display a high specific capacitance of 1422 $F g^{-1}$ and retain the specific capacitance of 100.7% after 1500 cycles. As expected, after charged at a current density of 5 $A g^{-1}$, the composites can light up a miniature bulb for more than 70 seconds. Moreover, the as-prepared materials exhibit a good catalytic activity toward the electrochemical oxidation of dopamine with a linear range of 0.01-10 μM and the detection limit of 1.0 nM in terms of the role of signal to noise ratio of 3:1 (S/N = 3). These results indicate that the porous layered $MoSe_2$-graphene composite *in situ* prepared on Ni foam can be applied for high-performance supercapacitors and electrochemical sensors.

1. Introduction

Recently, supercapacitors have been recognized as one of the most important energy storage appliance due to the unique properties, such as fast charging-discharging rate, high power density and good cyclic stability [1–6]. The energy stored in supercapacitors is either electrochemical double-layer capacitors (opposite charges are physically separated at the electrode/electrolyte interface to form electrochemical double layers) or pseudocapacitors (storing energy relies on chemical reactions that quick occur in the electrode materials) [7–9]. Undoubtedly, electrode materials play a very important role in the supercapacitors performance.

Molybdenum selenide ($MoSe_2$) is belonging to the family of transition-metal dichalcogenides and is a diamagnetic indirect semi-conductor [10]. Usually transition-metal dichalcogenides exhibit stacked layers. In $MoSe_2$, there are six-fold-bonded Mo atoms sandwiched between two three-fold-bonded Se atoms [11]. The interlayer atoms are bonded by covalent forces, while inter layer atoms are bonded by Van der Waals forces. Recently, $MoSe_2$ has attracted particular interest in a variety applications from solid lubricants [12] and photo-responsive device [13] to Li ion baterry [14]. As similar with the most transition metal oxides, the poor electronic conductivity limits the performance of transition metal dichalcogenides in terms of capacitance and cyclic stability. To enhance the electrochemical performance of $MoSe_2$ based supercapacitors, the electrodes that incorporate $MoSe_2$ with good electronic conductive materials seem imperative. Graphene is a two-dimensional carbon material composed with single-layer sheets. It has been reported possessing excellent conductivity, good thermal and mechanical properties [15–18]. Furthermore, graphene nanosheets have huge surface-to-volume ratio, which renders it as an striking substrate material when compounded with inorganic substances and conducting polymers for electrochemical capacitors, lithium ion batteries or others [19–22]. To some great extent, controlling over the morphologies of materials is still noted to be one of the most essential challenges for fundamental understanding of the properties induced by nanoscale [23,24]. Moreover, the selection of new substrate and facile routes to obtain novel composite is of great significance. The 3D

* Corresponding author. Tel.: +86 376 6390611.
E-mail address: kejinghuang11@163.com (K.-J. Huang).

http://dx.doi.org/10.1016/j.electacta.2015.09.016
0013-4686/

flexible Ni-foam, which may effectively affect the disperse of the materials, has been largely applied as electrode substrate due to intrinsic big surface area, good electron conductivity and low cost. What's more, Ni foam has better hydrophilicity than carbon materials and therefore is much suited for preparation of high mass loading electrodes by hydrothermal method [25,26].

The above viewpoints have inspired the present work, where the obtained $MoSe_2$-graphene composites experienced a simple hydrothermal process with the appearance of the flexible Ni-foam. Both Ni-foam and graphene were considered to be a guidance to control the morphology of $MoSe_2$. To our knowledge, reporting the preparation of $MoSe_2$-graphene grown on Ni-foam ($MoSe_2$-graphene/Ni) in this work is the first time. By taking advantage of its porous layered structure and vertically aligned orientation, the $MoSe_2$-graphene/Ni displayed high performances when used as the supercapacitor electrode material and electrochemical sensor.

2. Experimental

2.1. Preparation of $MoSe_2$-graphene/Ni composites

Graphene oxide was firstly prepared by oxidizing natural graphite powder according to the reference [27]. In short, 87.5 mL concentrated H_2SO_4 and 45 mL fuming HNO_3 were mixed. Then 5 g graphite powder was slowly added in the above mixture. Subsequently, 55 g $KClO_3$ was added and stirred. After 96 h, the mixture was washed with water and then filtered. Finally, the Graphene oxide was obtained after exfoliating the as-prepared graphite oxide in water with ultrasonic treatment.

For $MoSe_2$-graphene/Ni composites preparation, 0.158 g Se powder was first dissolved in 5 mL hydrazine hydrate under continuous vibration until homogeneous dark red brown solution was obtained. Then the mixture was laid aside for 24 hours to obtain hydrazine hydrate-Se, during which the color remained unchanged in the atmospheric conditions. In the meanwhile, 0.242 g sodium molybdate was dissolved in 50 mL water, and then the as-prepared hydrazine hydrate-Se solution was dropwise added. After that, the as-prepared graphene oxide was dispersed sufficiently in the mixture. Subsequently, the mixture and the flexible Ni-foam were transferred into a 100-mL Teflon-lined autoclave and heated at 180 °C. After 48 h, the autoclave was cooled down in the air. The black Ni-foam was collected after washed with water and dried overnight. During this procedure, the mass ratio of $MoSe_2$ and graphene varied from 5:1 to 8:1. The synthesis of pure $MoSe_2$ undergone the similar strategy with the absence of graphene oxide. The mass of the $MoSe_2$ or $MoSe_2$-graphene "grown on" the Ni-foam was reckoned up by the mass difference before and after the hydrothermal reaction.

2.2. Characterization

A Hitachi S-4800 scanning electron microscope (SEM, Tokyo, Japan) was used to study the morphologies of the as-prepared composite. The chemical compositions of the samples were determined by JEM-2100F transmission electron microscopy (TEM, JEOL, Tokyo, Japan) coupled with an energy-dispersive X-ray spectrometer (EDS, Oxford-1NCA) at an acceleration voltage of 200 kV. A RigakuD/Maxr-A X-ray diffractometer (Japan) with graphite monochromatized high-intensity Cu Kα radiation (λ = 1.54178 Å) was used for X-ray powder diffraction (XRD) analyses. A Renishaw Raman spectrometer (model 1000) with a 200 mW argon-ion laser was used to record the Raman spectra at an excitation wavelength of 514.5 nm. The thermal stability of obtained material was conducted on the thermogravimetric analyzer (TGA, STD Q600 TA) with 100 mL/min of N_2 flow from 50 to 700 °C (10 °C/min).

2.3. Electrochemical measurements

A CHI660E Electrochemical Working Station (Chenhua corp., shanghai) was use to tested the electrochemical properties of the electrode material using a three-electrode system with the Ni-foam substrate coated with active materials as the working electrode, Hg/HgO as reference electrode and platinum foil as the counter electrode. Cycle voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge-discharge (GCD) were all carried out on in aqueous KOH solution (6 M). The measurement of specific capacitance (C_s) was calculated according to the following equation:

$$C_s = It/\Delta Vm \quad (1)$$

where I,t, ΔV and m are the constant current, discharge time, the total potential difference and the weight of active materials, respectively.

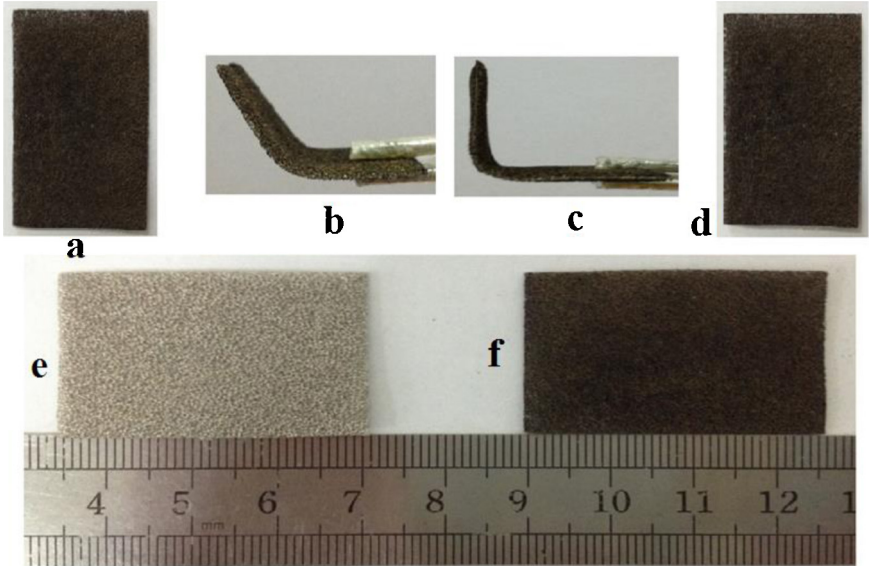

Fig. 1. Digital camera images of Ni-foam (e), $MoSe_2$-graphene/Ni (a, f), $MoSe_2$-graphene/Ni bent to about 45° (b) and 90° (c), bent-recovered $MoSe_2$-graphene/Ni (d).