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Short communication

Biomolecule-assisted synthesis of nickel sulfides/reduced graphene oxide nanocomposites as electrode materials for supercapacitors

Zhicai Xing [a], Qingxin Chu [a], Xinbang Ren [a], Jingqi Tian [a], Abdullah M. Asiri [b,c], Khalid A. Alamry [b,c], Abdulrahman O. Al-Youbi [b,c], Xuping Sun [a,b,c,*]

[a] State Key Lab of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, Jilin 130022, China
[b] Chemistry Department, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia
[c] Center of Excellence for Advanced Materials Research, King Abdulaziz University, Jeddah 21589, Saudi Arabia

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ABSTRACT

The present communication demonstrates the first environmentally friendly hydrothermal synthesis of nickel sulfide nanospheres/reduced graphene oxide (nickel sulfides/rGO) nanocomposites with the use of L-cysteine as a reducing agent, sulfur donor, and linker. The nanosphere consists of ultrafine particles leading to textural pores. The resulting nickel sulfides/rGO nanocomposites were further used as an electrode material for supercapacitors and found to exhibit very high specific capacitances of 1169 F g^{-1} and 761 F g^{-1} at current rates of 5 A g^{-1} and 50 A g^{-1}, respectively, with good cycling stability.

1. Introduction

Supercapacitors (SCs) provide fast charge and discharge processes, high power performance, very long cycle life, and relatively low cost, and therefore are considered to be an important power source meeting the increasing demand of energy storage and conversion [1,2]. Graphene, a two-dimensional (2D) monolayer carbon has been largely used in SCs due to its unique properties of high specific surface area (2600 m^2 g^{-1}), high electric conductivity and high mechanical properties [3,4]. Recently, much effort has been put into the synthesizing metal sulfides-based graphene composites such as MoS_2/graphene [5], In_3S_2/graphene [6], CoS_2/graphene [7] and NiS/graphene [8] for electrochemical energy storage applications; however, the involvement of thioacetamide and thiourea as sulfur source poses environmental and health risks. Such issues can be solved by using biomolecule-assisted synthesis strategy, and indeed, metal sulfides/graphene nanocomposites, such as MoS_2/graphene [9], CoS/graphene [10] and CuS/rGO [11] have been synthesized successfully. In this study, we demonstrate an environmentally friendly, biomolecule-assisted hydrothermal synthesis of nickel sulfides nanospheres/reduced graphene oxide (nickel sulfides/rGO) nanocomposites using L-cysteine as the reducing agent, sulfur donor, and linker for supercapacitors. As an electrode material for SCs, such nickel sulfides/rGO nanocomposites exhibit very high specific capacitances of 1169 F g^{-1} and 761 F g^{-1} at current rates of 5 A g^{-1} and 50 A g^{-1}, respectively, with good cycling stability.

2. Experimental

2.1. Synthesis of nickel sulfides/rGO nanocomposites

The preparation of nickel sulfides/rGO nanocomposites was conducted by a facile hydrothermal method. In a typical synthesis, graphene oxide (GO) powders were initially prepared by a modified Hummers' method [12,13]. Then, 20 mg of GO powders was dispersed in 40 ml distilled water by ultrasonication, followed by the addition of 0.3 mM $NiCl_2 \cdot 6H_2O$ and 80 mg L-cysteine. The mixture solution was stirred for 30 min and transferred to a 50 ml Teflon-lined autoclave and heated at 160 °C for 6 h. The products were then collected, washed with water and ethanol three times each and dried in a vacuum oven at 60 °C.

2.2. Materials characterization

UV–vis spectra were obtained on a UV-1800 Spectrophotometer. Powder X-ray diffraction (XRD) datum was recorded on a RigakuD/MAX 2550 diffractometer. Scanning electron microscopy (SEM) measurements were made on a XL30 ESEM FEG microscope. Transmission electron microscopy (TEM) measurements were made on a HITACHI H-8100 microscope (Tokyo, Japan). The Brunauer–Emmett–Teller

* Corresponding author at: State Key Lab of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022 Jilin, China.
E-mail address: sunxp@ciac.jl.cn (X. Sun).

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(BET) surface area and pore volume were measured on a Quantachrome NOVA 1000 system at liquid N_2 temperature.

2.3. Electrochemical measurements

The electrodes were prepared by mixing the products with acetylene black and polyvinylidene difluoride (PVDF) (weight ratio: 8:1:1). After thorough mixing, the slurry was pressed onto Ni foam and dried at 60 °C in vacuum overnight (active material: 1 mg). The electrochemical tests were conducted on a CHI 660 C electrochemical workstation in an aqueous KOH electrolyte (2.0 M) with a three-electrode cell where Pt wire serves as the counter electrode and Ag/AgCl as the reference electrode. Electrochemical impedance spectroscopy (EIS) measurements were also carried out in the frequency range of 100 kHz–0.01 Hz.

3. Results and discussion

Fig. 1a shows the UV–vis spectra of an aqueous dispersion of GO and the prepared products. As expected, GO exhibits strong bands centered at 230 and 300 nm, corresponding to π–π* transitions of the aromatic C═C band and n–π* transitions of the C═O band in GO, respectively. It is clearly seen that the absorption peak gradually red-shifts from 230 to 266 nm, indicating the formation of rGO [13]. The XRD pattern of the products is shown in Fig. 1b. The peaks at 30.8, 34.9, 46.0, 53.6 and 65.4 are assigned to 100, 101, 102, 110 and 201 faces of NiS (JCPDS No. 02-1280). The peaks at 31.5, 35.3, 38.4, 58.6 and 61.0 can be assigned to 200, 210, 211, 230 and 321 faces of NiS_2 (JCPDS No. 11-0099). The broad peak observed at $2\theta = 20–30°$ indicates the disordered stacking of rGO sheets [13]. All these observations indicate that the nickel sulfides are complicated phases constituted of NiS and NiS_2 [14,15]. The energy dispersive X-ray spectroscopy (EDS) spectrum and the corresponding elemental analysis show the atomic ratio of Ni to S is 0.75:1 (Fig. 1c). So, the molar ratio of NiS to NiS_2 was calculated to be about 2.7:1.

Fig. 2a shows the typical SEM images of the products obtained without GO, indicating the formation of spheres about several hundred nanometers in diameter. In contrast, the involvement of GO leads to rGO decorated with nanospheres about tens of nanometers in size (Fig. 2b). The corresponding TEM image shown in Fig. 2c indicates that the nickel sulfide spheres further aggregate into bigger structures. The high magnification TEM image of one sphere reveals that the nanosphere consists of small nanoparticles (inset). Fig. 2d shows the TEM image of the composites, indicating that the rGO nanosheets can effectively prevent the aggregation of such nanospheres. The high magnification TEM image (Fig. 2e) shows that the nanosphere consists of ultrafine particles leading to textural pores. The BET surface area of the nanocomposites is determined to be 46.3 $m^2\ g^{-1}$. The pore size distribution analysis indicates that the nanocomposites have pores ranging from 1 to 7 nm.

The nickel sulfides/rGO nanocomposites were further evaluated as an electrode material for SCs. Fig. 3a shows the cyclic voltammetry (CV) analysis at various scan rates in the potential range of −0.15–0.55 V (vs. Ag/AgCl). These CV profiles clearly show pronounced pseudocapacitive characteristics different from the nearly rectangular CV shapes for conventional electric double-layer capacitors [14,16,17]. The peaks at around 0.34 and 0.23 V at the scan rate of 1 mV s^{-1} can be attributed to the redox reactions of nickel sulfides. It was proposed that nickel sulfide might have a similar mechanism to $Ni(OH)_2$ in alkaline electrolyte due to the similar redox potentials [18]. The nickel sulfides/rGO nanocomposites show one redox couple, which might be related to the following reversible process: $NiS\text{-}NiS_2 + OH^- \leftrightarrow NiS\text{-}NiS_2OH + H_2O + e^-$. However, the exact redox processes involved are not completely understood

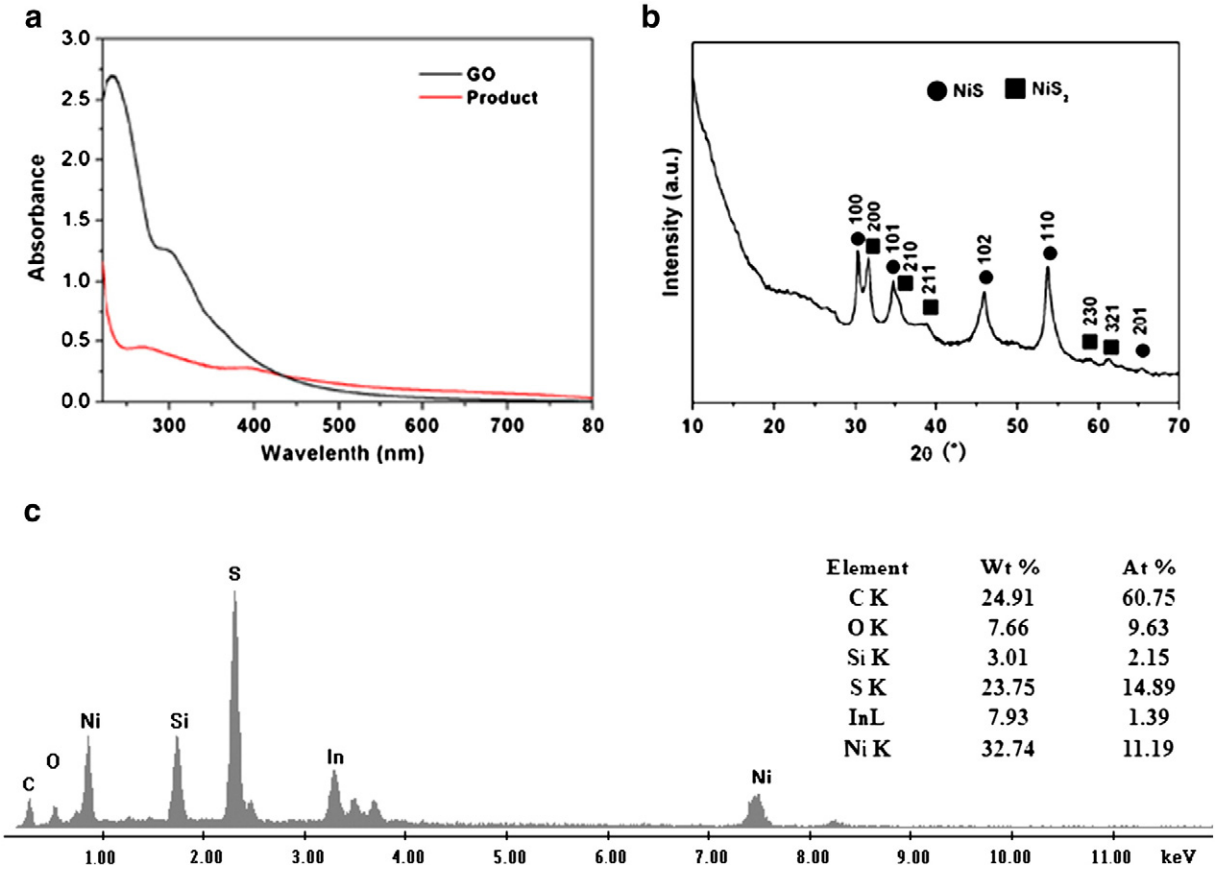

Fig. 1. (a) UV–vis absorption spectra of aqueous dispersion of GO and the products thus obtained, (b) XRD pattern, and (c) EDS of the products thus obtained.