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Facile and controlled synthesis of bismuth sulfide nanorods-reduced graphene oxide composites with enhanced supercapacitor performance

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ABSTRACT

Bi_2S_3 nanorods-reduced graphene oxide nanosheet (BGNS) composites with uniform morphology have been successfully prepared via a facile one-pot hydrothermal reaction using thioacetamide (TAA) as both the sulfur source and reducing agent. The simple and versatile synthetic procedure could accomplish the controlled fabrication of BGNS hybrids with tunable size and composition through adjusting the additive amount of GO. When employed as active materials for supercapacitor electrodes, in comparison with pristine rGO and X-Bi_2S_3 that obtained in the absence of GO, the BGNS composites displayed enhanced electrochemical performance by combining desired functions of individual components and introducing extra synergistic effects into the system. It is believed that the novel BGNS composites with multifarious advantages including nontoxicity, abundant resource and low cost are promising for practical application in supercapacitors.

1. Introduction

Supercapacitors (SCs), as an indispensable and promising power source, can meet the increasing requirements for energy storage devices due to their outstanding characteristics, such as high energy and power densities, fast charge–discharge processes, long cycle life, desirable safety and relatively low cost [1–4]. Nowadays considerable attempts have been devoted to exploiting the advanced and optimal electrode materials for high-performance SCs [5–8]. Metal sulfides (MSs), which have drawn extensive attention as electrochemically active materials for SCs, possess not only higher specific capacitance than traditional carbon materials but also better cycling stability than conducting polymers [9,10]. Bismuth sulfide (Bi_2S_3), a well-known lamella-structured semiconductor with a direct band gap of 1.3 eV, has aroused tremendous interest on account of its extraordinary photoconductivity, favorable photovoltaic properties, great natural abundance and wonderful environmental compatibility [11–13]. Up to now, diverse morphologies of Bi_2S_3 nanostructures including one-dimensional (1D) nanowires, nanoribbons, nanorods, nanotubes as well as their complex assemblies such as nanofabrics, necklace architectures, disc-like networks, sheaf-like arrays, snowflake-like patterns and flower-like or urchin-like microspheres have been produced via numerous synthetic approaches with the assistance of surfactants, biomolecules, polymers, ionic liquids, organic solvents and even microwave irradiation [14–23]. Although Bi_2S_3 as the functional building block has various potential applications in electrochemical hydrogen storage, thermoelectric devices, solar cells, lithium-ion batteries, X-ray computed tomography, sensors, photocatalysis [24–30], to the best of our knowledge, the capacitive behavior of Bi_2S_3-based nanomaterials has not been previously studied and reported in detail yet.

However, similar to metal oxides, the poor intrinsic conductivity of these MSs cannot assure the effective electron transport demanded by SCs, seriously limiting their electrochemical performance and actual development [31]. It is generally accepted that one of the most valid strategies to circumvent the aforementioned drawback is to design composites with carbon matrix. Graphene, a unique planar monolayer of sp^2-bonded carbon atoms with large surface area, superior electronic conductivity, prominent chemical stability and appealing mechanical flexibility, is identified as an ideal candidate for improving the nature of other substances [32–38]. For instance, both CoS_2/graphene nanosheets (GNS) and WS_2/reduced graphene oxide (rGO) hybrids exhibited higher capacitance values than bare graphene and CoS_2 or WS_2 alone [39,40]. The ultrathin GNS or rGO which serve as a powerful support can provide conducting channels and prevent the agglomeration of

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target materials, and meanwhile, the grafting of spacers can also remarkably reduce the restacking of graphene substrate, allowing a full utilization of the surface active sites and then expediting the ion diffusion. Therefore, it is expected for MSs-rGO composites to achieve enhanced capacitive property by combining preferred functions of individual components and introducing synergistic effects into the electrode system [41,42].

Based on the above considerations, herein, we demonstrated a facile one-pot hydrothermal method to prepare Bi_2S_3 nanorods-reduced graphene oxide nanosheet (BGNS) composites. It was found that the addition of graphene oxide (GO) was fairly critical to the formation of Bi_2S_3 nanocrystals. The simple, universal and low-cost synthetic procedure could accomplish the controlled fabrication of BGNS composites with tunable size and composition. Furthermore, the as-obtained BGNS with particular construction could guarantee effective electron transport and fast ion diffusion, thus endowing themselves with more excellent electrochemical performances than naked rGO when they were employed for supercapacitor electrodes.

2. Experimental

2.1. Synthesis of materials

All the chemical reagents in this experiment were used as received without any further purification. GO was initially prepared from natural graphite powders (Sinopharm Chemical Reagent Co., Ltd) according to a modified Hummers and Offeman's method as reported elsewhere [43,44]. The typical synthetic process of BGNS composites was carried out as below: a certain quantity of GO was completely exfoliated and evenly dispersed in 45 mL of ultrapure water by vigorous ultrasonic treatment for about 2 h, and then 97 mg of bismuth nitrate pentahydrate ($Bi(NO_3)_3\cdot 5H_2O$, Beijing Chemical Works) was added, followed by magnetic stirring at normal temperature for 12 h to acquire a uniform suspension. Subsequently, the brown flocculent precipitate was collected by centrifugation and transferred into a 40 mL Teflon-lined autoclave containing 30 mL of 12 mM thioacetamide (TAA, C_2H_5NS, Sinopharm Chemical Reagent Co., Ltd) aqueous solution. The sulfuration and reduction reaction proceeded simultaneously in an electric oven maintained at 160 °C for 8 h. After cooling down, the final brownish black products with varied dosages of GO (15, 30 and 45 mg), which were designated as BGNS-1, BGNS-2 and BGNS-3, respectively, were separated by centrifugation, rinsed thoroughly with distilled water, and dried in a vacuum freeze drier for further characterization and use. For comparison, the sample fabricated through the analogous route only without the addition of GO was defined as X-Bi_2S_3. Pristine rGO was also obtained under the same hydrothermal condition just with TAA as the reducing agent in the absence of bismuth salt.

2.2. Characterization

The morphologies and structures of specimens were examined by a cold field-emission scanning electron microscopy (FESEM, Hitachi SU8020) and a transmission electron microscopy (TEM, JEOL JEM-1200 EX) operated at 3.0 and 100 kV, respectively. High resolution TEM (HRTEM) images, fast Fourier transform (FFT) pattern and energy dispersive X-ray (EDX) analysis were implemented on a FEI Tecnai G2 F20 electron microscope at an acceleration voltage of 200 kV. X-ray diffraction (XRD, PAN-alytical B.V. Empyrean) with CuKα radiation was applied to research the crystallographic structures. Fourier-transform infrared (FTIR) spectra of KBr powder-pressed pellets were acquired from a Bruker Vector 22 Spectrometer. The chemical compositions of the resulting products were characterized by an X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB250).

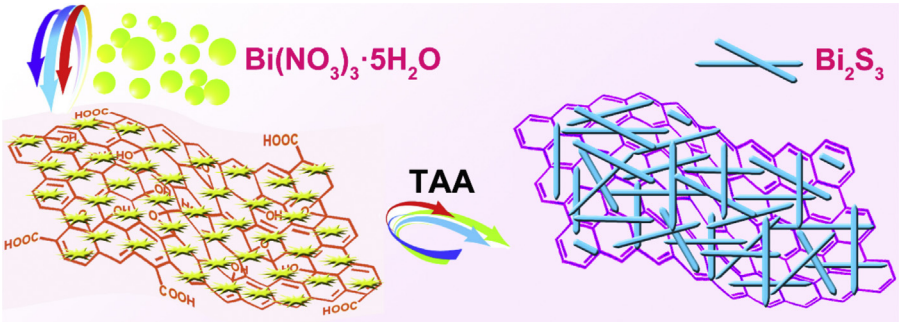
2.3. Electrochemical Measurement

Cyclic voltammetry (CV), galvanostatic (GV) charge–discharge and electrochemical impedance spectra (EIS) measurements were all conducted on a CHI 660 C electrochemical workstation (Shanghai Chenhua instrument Co., Ltd.) in the electrolyte of 2 M KOH aqueous solution using a conventional three-electrode cell, which were assembled with the as-synthesized samples acting as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a piece of platinum foil as the counter electrode. The working electrode was prepared as referred to in our early work [45], namely, the active materials (8 mg), acetylene black (commercially available) and polytetrafluoroethylene (PTFE, Aladdin) with the weight ratio of 8:1:1 were blended together by a few drops of ethanol. This slurry was then coated and pressed onto the surface of the cleansed nickel foam with an area of about 1 cm^2 followed by drying at 40 °C for 12 h. A potential window ranging from −0.2 to 0.45 V was chosen in all the CV experiments at multiple scan rates of 3, 5, 10, 20 and 50 mV s^{-1} and GV charge–discharge tests at different current densities of 1, 2, 3, 4 and 5 A g^{-1} unless otherwise stated.

3. Results and discussion

Scheme 1 vividly shows the formation process of BGNS composites. First of all, Bi^{3+} was tightly absorbed on the surface of negatively charged GO nanosheets by electrostatic interaction with the oxygen-containing functional groups attached on GO. Next, S^{2-} as both the sulfide source and reducing agent, which was derived from the decomposition of TAA, could fulfill the generation of Bi_2S_3 nanorods accompanied with the reduction of GO to rGO.

The morphologies of GO and rGO were confirmed by a transmission electron microscopy (TEM). It can be clearly seen from Fig. 1A that the as-prepared GO with a few folded regions on



Scheme 1. Schematic illustrating the in situ synthetic route of BGNS composites.