



Mixed solvent-mediated exfoliation of graphene invoked by synergistic effect of steric hindrance and hydrogen bond for improved electrochemical performance on its polymeric composites

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ABSTRACT

Graphene is considered as a promising candidate electrode materials for the high-performance energy-storage devices due to its desirable combination of advantages such as excellent electrical conductivity, large specific surface area, good electrochemical stability and controlled pore size distribution. However, the adjacent graphene sheets are tend to irreversibly forming agglomerates under electrostatic force, which seriously limit their further applications. Here, a simple, low-cost, eco-friendly, yet highly efficient approach to the exfoliation of bulk graphite into good dispersibility of few-layer graphene- Na^+ is achieved by sodium hydroxide-prompted exfoliation process. As a result, an extremely high yield up to 2.72 g/L h is achieved, and the resultant graphene is of intact crystallographic structure and large aspect ratio of 6.5×10^3 . Moreover, the as-received graphene- Na^+ nanosheets with hierarchical porous microstructures and high specific surface area of $900 \text{ m}^2/\text{g}$, are beneficial for diffusion of the active ions. Meanwhile, Density functional theory calculations result was further adopted to verify the effectiveness of this strategy. Besides, the as-obtained graphene/PVDF composite exhibits a low percolation threshold value of 0.06 vol %. When employing as the electrode materials, the graphene/PVDF composites possess a high energy density of 7.77 mWh cm^{-3} and power density of 2.86 W cm^{-3} respectively, along with an outstanding long-term stability.

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1. Introduction

Supercapacitors have emerged as a new category of promising energy storage devices for potential applications in portable electronic devices, electronic facilities, hybrid electrical vehicles and energy back-up system, due to their high energy density, power density and long cyclic life. Electrode material is a critical component in determining the performance of a supercapacitor [1]. Thus, there is an imperative need to develop new electrode material with high performance. Up to now, various materials, such as carbon-based materials, different metal oxides and various electroactive electro-conductive polymers have been employed as supercapacitor electrode materials [2–5]. However, their drawbacks, such as high internal resistance of various metal oxides, small

effective surface area of active carbon, and poor life of electroactive conducting polymers, limits the further application in supercapacitors. While graphene is a dominant candidate for the high-performance energy-storage electrode material owing to a particular combination of properties such as excellent electrical conductivity, remarkable mechanical stiffness, large specific surface area, good electrochemical stability and controlled pore size distribution. However, the adjacent graphene sheets are prone to irreversibly forming agglomerates or even restacking to be graphite under electrostatic force, especially in the separation and purification process, which seriously limit their further applications. Moreover, the graphene is easily decomposed into little fragments under ultrasonic, resulting in the loss of the surface area for energy storage when it is achieved by ultrasonic treatment or high shear in surfactant, ionic liquids, some certain acid, aromatics and its ramification or solvents. Besides, the molecules adsorbed on the surface will significantly increase the series resistor of the graphene nanosheets [6–8]. In order to develop graphene-based electrode

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materials with high-performance, it is still a big challenge to achieve the desirable properties of graphene with ultra-large specific surface area, good conductivity along with efficient porosities in micro-, meso- or macropores [9–13]. In this regard, achieving monolayer or few-layered high quality graphene sheets with less stack and easier ion entrance into interlayers, will be look forward to have better supercapacitor performance [1,14,15].

Herein, we report an accessible method to strip pristine graphite into graphene in urea/glycerine/sodium hydroxide dispersion. The excellent exfoliated dispersion system made of urea/glycerine at the mole ratio of 1:2, could lead to a high output of high quality, unoxidized few-layered graphene with a rate as high as 2.72 g/L·h. Such a high graphene concentration could lead to a high production rate. The urea as the electron donor forms π - π stacking effect with the graphite in glycerine, and the sodium hydroxide acts a part of liquid controlling agent and inserts into the graphite. The graphite was successfully exfoliated into thin sheets. This inspiring result was further certified by Density functional theory (DFT) calculations, is mainly attributable to the strong interaction between urea/glycerine molecules and graphene, and steric hindrance effect between urea and glycerine through the formation of hydrogen bond. The obtained graphene nanosheets possessing hierarchical porous microstructures and high specific surface area of 900 m²/g, are beneficial for diffusion of the active ions. Furthermore, the electrical conductivity of as-received graphene was less influenced by this strategy. To fully exploit its practical values, we have designed two kinds of graphene-based polymeric composites. We found that the graphene-PVDF composite exhibits a low percolation threshold value, high capacitance, superior rate performance and excellent long-term stability.

2. Experimental

2.1. Materials

Sodium hydroxide, urea and glycerine was bought from Sino-pharm Chemical Reagent Co., Ltd. Polyvinylidene fluoride (PVDF) was purchased from 3F Corporation (Shanghai FR902). Ordinary graphite was supplied by XFANO Materials Tech Co., Ltd. (purity 99.8 wt %, 325 mesh, Nanjing).

2.2. Preparation for the urea/glycerine/sodium hydroxide dispersion

123.6 g urea, 300 mL glycerine and 0.2 g sodium hydroxide were added into a 1 liter beaker in sequence, then stirred at 150 rpm for 12 h at 60 °C before further use.

2.3. Production of few-layer graphene

30 g ordinary flake graphite was added into 300 mL urea/glycerine/sodium hydroxide dispersion in a 500 mL beaker, then stirred at 600 rpm for 12 h. The dispersed resultant was centrifugalized through 4000 rpm for 30 min (TG16-WS centrifuge, Hunan Xiangyi). 80% of the supernatant liquid was collected as the few-layer graphene dispersion, which was redissolved in a mixed solvent of water and ethanol with a volume ratio of 1:1. The residual urea or glycerin was washed and filtered for 5 times. The remaining precipitation was collected as the pure graphene by vacuum drying at 120 °C overnight. The concentration of graphene can be confirmed as 32.64 mg/mL by careful measuring the collected mass. During the centrifugalization and vacuum drying, a new 3000 mL of graphite dispersion can be handled at one time, thus, a production rate of graphene can be calculated to be as high as 2.72 g/L·h.

2.4. Fabrication of graphene/PVDF composites

The as-obtained graphene was mixed and pulverized with 1.5 g PVDF powder in 30 mL DMF and stirred overnight to form a homogeneous solution. After vigorously stirring overnight, the suspension was casted onto a clean watch glass and dried at 60 °C for 12 h and 220 °C for 15 min. The as-received films were dried at 80 °C in a vacuum drying chamber overnight, then the films was pressed by a hydraulic hot press at 15 MPa with a temperature of 180 °C for 20 min. As a result, graphene/PVDF composites disks with a diameter of 12.7 mm and a thickness of about 2.3 mm were obtained. The volume fraction ratios of graphene in graphene/PVDF composites can be precisely regulated from 0.01% to 5 vol%.

2.5. Fabrication of working electrodes

The as-prepared graphene and polytetrafluoroethylene were completely mixed and further dispersed in ethanol at a mass ratio of 9: 1. The Nickel foam is cleaned continuously through ethanol, water and acetone. Then the graphene-PVDF mixture was overlaid onto the Ni foam (1 × 1 cm², thickness: 0.1 cm) through a scraping knife, followed by drying at 80 °C for 8 h in a vacuum drying chamber. Finally, the nickel foam containing graphene-PVDF mixture was pressed with a hot press at 10 Mpa. Each electrode contains about 3 milligrams of active substance. The coin cells were packaged in an Ar-filled glove box (MBraun Unilab), where lithium metal foil as a counter electrode, and polypropylene film (Celgard 2300) as a separator. 1.0 M LiPF₆ solution in a mixture solvent of ethylene carbonate (EC), dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC) (1:1:1 by volume), is employed as the electrolyte.

2.6. Characterization

The transmission electron microscopy (TEM) images were obtained with a JEOL JEM-2001. The graphene samples are obtained by the following methods, A drop of diluted graphene was dispersed on a carbon-coated copper micro-grid so that it evaporated naturally before the inspection. Scanning electron microscopy (SEM) images were obtained with a Carl Zeiss, Zeiss Ultra Plus field emission scanning electron microscope. The atomic force microscopy (AFM) images was obtained from Dimension Icon (Bruker, Germany). The samples were made by depositing one or two drops of diluent onto freshly cleaved mica plate (Peking Xinxingbairui, INC.). Raman spectra were acquired using INVIA RENISHAW spectrometer with a 532 nm argon laser. The electrical conductivity of graphene/PVDF composites were tested with a d.c. power supply (Hp6612C), digital multimeter (HP34401A) and picoammeter using a standard four-point probe technique (KEITHLFY, America) with a threshold detection of 0.1G. Nitrogen adsorption and desorption isotherms were determined by nitrogen physisorption at 77 K on a Micromeritics ASAP 2020M analyzer. Electrochemical performances and electrochemical impedance spectroscopy (EIS) for the as-prepared graphene were accomplished by a CHI 660E electrochemical workstation. The electrochemical capacitive performance of graphene supercapacitor was indagated using a three-electrode system of CHI-660E electrochemical workstation in 6 M KOH electrolyte. The Ni foam coated with active material was classified as the working electrode, the Hg/HgO electrodes and platinum foil were used as the reference and counter electrodes, respectively. Galvanostatic tests were regulated using a cell test instrument (LAND CT21001A, Wuhan corrttest instruments Co. LTD., CS150) at the voltage range of 0.005–1.4 V (vs Li/Li⁺). Cyclic voltammetry was carry out using an electrochemical station (CHI 660E, Shanghai Chenhua) in the voltage range of 0.002–1.4 V at a scan rate of

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