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Three-dimensional nitrogen-doped graphene hydrogels prepared via hydrothermal synthesis as high-performance supercapacitor materials

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ABSTRACT

Three-dimensional nitrogen-doped graphene hydrogel (3D NG) samples are successfully synthesized via a hydrothermal method. The synthesized 3D NG exhibits excellent mechanical properties, including the support of approximately 1165 g with three NG cylinders. The morphology, structure, component and electrochemical performance of the NG samples are characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscope, X-ray photoelectron spectroscopy, thermogravimetric analysis, N_2 adsorption-desorption, cyclic voltammetry, galvanostatic charge/discharge and electrochemical impedance spectroscopy, respectively. X-ray photoelectron spectroscopy indicates that N is present in the graphene as pyrrolic N, pyridinic N and quaternary/graphitic N, with pyrrolic N being the predominant species in all of the samples. The electrochemical results demonstrate that the 3D NG with a nitrogen content of 7.7 wt% shows excellent capacitive behavior (387.2 F g^{-1} at 1 A g^{-1}) in 6 M KOH. In addition, the specific capacitance value of this sample remains at approximately 90.5% of the maximum value (298.5 F g^{-1} at 5 A g^{-1}) after 5500 cycles. The main reason for the excellent electrochemical behavior is the incorporation of the pyrrolic and pyridinic N in the graphene, enhancing the pseudocapacitance of this material. It indicates that the 3D NG can be used as an electrode material for high-performance supercapacitors.

1. Introduction

Graphene has been the focus of extensive research efforts over the past several years due to its remarkable thermal conductivity, excellent electronic conductivity and mechanical properties [1,2]. A mass of researches explored the use of graphene in energy storage devices, electronics, catalysis, sensors and high-strength materials [2–7] because of its unique single-atom-thick two-dimensional (2D) structure and excellent properties [1,2]. However, the small surface area of graphene electrodes constructed with 2D graphene sheets, to a large extent, limits the capacitive performance. Given this, experts has turned their attention to the three-dimensional (3D) porous structures of graphene materials [8–11]. Among the numerous 3D graphene materials, graphene hydrogels [12–14] and aerogels [9] are of note. They possess a large specific surface area to make it possible for rapid diffusion of electrolyte ions and exhibit multidimensional electron transport because of the porous and interconnected nature of these unique graphene gels. Versatile 3D graphene synthetic strategies allow for the easy incorporation of heteroatoms, carbon nanomaterials, functional polymers, and inorganic nanoparticles to yield diverse macrostructures and composites with tailored structures and properties [15]. For example, Yuan et al. [11] have synthesized three-dimensional (3D) porous reduced graphene oxide (rGO) film by an intriguing replicating and an embossing strategy for electrochemical capacitors. The unique 3D porous rGO film delivered a large specific capacitance of 206 F g^{-1} at 1 A g^{-1}, and even 141 F g^{-1} at a current density of 10 A g^{-1}, owing to its appealing micro-structural feature.

Currently, graphene modified with heteroatoms is one of the most attractive materials using for an electrode due to its powerful ability to enhance capacity by faradaic reactions, in addition to maintaining the excellent cyclability of a supercapacitor. Furthermore, good results with nitrogen-doped graphene (NG) hydrogels have been prepared by graphite oxide (GO) under various thermal

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annealing conditions [12–18] and using different nitrogen [4,5,12–23]. For example, Li et al. [16] have developed a simple chemical method to obtain bulk quantities of N-doped reduced graphene oxide (GO) sheets by thermal annealing of GO in ammonia. The effect of different annealing temperatures has been studied on the formation of nitrogen functional groups. Guo et al. [21] have reported that nitrogen-doped graphene hydrogels (NGHs) with 308 $F g^{-1}$ at 3 $A g^{-1}$ prepared through a simple hydrothermal reaction of GO and urea. However, the effect on the electrochemical performance of different nitrogen functional groups has seldom been studied.

Based on the above analysis, we propose the synthesis of 3D nitrogen-doped graphene hydrogels via a mild one-pot hydrothermal process. The 3D NG samples were readily synthesized using a low mass ratio of urea and ammonia to the GO precursor. The urea and a small amount of ammonia act as reducing agents that modify the inner structure of the graphene hydrogel, which greatly improved the performance of this material as a supercapacitor. Additionally, the urea and ammonia can serve as sources of nitrogen to realize graphene doping with generation of three different nitrogen-types. Meanwhile, the different N-types in graphene play different roles in the aqueous electrolyte solution, which further enhanced the performance of our products. The structure and electrochemical performance of 3D nitrogen-doped graphene hydrogels were investigated in this study.

2. Experimental

2.1. Synthesis of Graphene Oxide (GO)

GO was prepared by a modified Hummers' method [24]. Briefly, natural graphite flake (2 g, Sigma–Aldrich) was mixed with concentrated sulfuric acid (98%, 46 mL, Chemical Reagent Ltd) and sodium nitrate (2 g, Kemiou Chemical Reagent Ltd, Tianjin), and vigorously stirred in an ice-water bath. Then, potassium permanganate (99.5%, 6 g, Kemiou Chemical Reagent Ltd, Tianjin) was slowly added to the mixture while the temperature was kept at less than 20 °C for 90 min and followed by stirring for 90 min at 35 °C. Afterwards, 80 mL of distilled water was slowly added to the mixture, which was then stirred for 30 min at 95 °C. Finally, 20 mL of H_2O_2 (30 wt%, Chemical Reagent Ltd, Tianjin) was added dropwise to the reaction system. The obtained bright yellow suspension was washed approximately 10 times with HCl (1: 6 v/v, Chemical Reagent Ltd) and water. The solid GO should be dried in a vacuum at 60 °C overnight.

2.2. Nitrogen-doped graphene hydrogels (NG hydrogels)

The GO suspension was prepared by ultrasonic (KQ-600kDE) dispersion of the GO solid in water (3 $mg\,mL^{-1}$) for 3 h to give a brown colloidal solution. Then, two drops (~0.1 mL) of ammonia (25 wt%, Chemical Reagent Ltd, Tianjin) were added for every 5 mL of GO solution to promote the complete dispersion of GO in deionized water. What's more, the ammonia can also participate in the hydrothermal reaction as a nitrogen source.

NG samples were synthesized by a hydrothermal method with the GO aqueous dispersion as the raw material and urea, as well as the ammonia from the previous step, as reducing/doping agents. In a typical process, the dispersion of GO (60 mL) and urea were mixed in a beaker with low mass ratios of 3: n (n = 0, 1, 3, 4). After sonicating for 3 h, the mixture was sealed in a 100 mL Teflon-lined autoclave and maintained at 180 °C for 24 h. Then, the autoclave should be cooled to room temperature, and the as-synthesized cylindrical solid materials were taken out with tweezers. Subsequently, the cylindrical solid materials were thoroughly washed with deionized water and ethanol to remove residual urea. The cylindrical solid materials were dried under vacuum at 60 °C for further characterization. The NG synthesized with GO: urea in mass ratios of 3: n (n = 0, 1, 3, 4) are named as NG-3: n (n = 0, 1, 3, 4).

All of the reagents were of analytical grade and without further purification in the experiments. Distilled water was needed in every step, including aqueous solution preparation and washing.

2.3. Materials characterization

X-ray diffraction (XRD) patterns were collected at room temperature with a D/MAX 2200 VPC X-ray generator using Cu-Kα (λ = 1.5406 Å) radiation and a step of 0.1° s^{-1} from 5° to 35°. Thermogravimetric analysis (TGA) data were obtained with an STA409PC Diamond TG-DTA thermal analyzer over a temperature range of 30 °C to ~800 °C in air and using ~5–8 mg at a heating rate of 10 °C min^{-1}. The morphology, microstructure and components of the NG samples were examined by scanning electron microscopy (SEM) with a ZEISS Ultra-55, and a JEM-2100HR transmission electron microscope (TEM). The specific surface area and pore size distribution of the samples were determined using the Brunauer-Emmett-Teller method (BET, ASAP-2020, Micromeritics, USA). X-ray photoelectron spectroscopy (XPS) measurements were conducted on an ESCALab250 X-ray photoelectron spectrometer.

2.4. Electrochemical measurements

The electrochemical performance was characterized in a three-electrode system with a platinum counter electrode and a standard Hg/HgO reference electrode in a 6 M KOH aqueous solution. The working electrodes were fabricated by mixing 80 wt% active material, 10 wt% conducting acetylene black, and 10 wt% polytetrafluoroethylene (PTFE, Sigma Aldrich; used as a binder); the mixture was spread on a nickel foam sheet ($1 \times 1\ cm^2$), dried at 60 °C under vacuum for a night, and pressed at 20 MPa for 10 s. The working electrodes consisted of nearly 2–3 mg of active material. Electrochemical impedance spectroscopy (EIS) measurements were carried out by applying an AC voltage with a 5 mV amplitude over a frequency range of 0.01 Hz to 100 kHz at −0.77 V (near the oxidation peak potential). Galvanostatic charge–discharge (GCD) cycling in the potential range of 0 to −1 V was performed at different current densities. All of the electrochemical measurements were performed with a CHI 660E workstation. The specific capacitance of the electrode materials was calculated from the galvanostatic discharge process according to the following equation: $C = \frac{I\Delta t}{m\Delta V}$ [17], where C is the specific capacitance ($F g^{-1}$), I is the discharge current (A), Δt is the discharge time (s), ΔV is the voltage change during the discharge process, and m is the mass of the active material in the electrodes (g).

3. Results and discussion

3.1. Mechanical property of the hydrogel

The synthesized NG is a mechanically strong hydrogel cylinder approximately 1.8 cm in diameter and 2.0 cm in height, which can be submerged in water and handled with tweezers (Fig. 1 (a–c)). Furthermore, three NG cylinders arranged in a triangle (Fig. 1(d–e)) and make it possible to support approximately 1165 g (the mass of the 1000 mL beaker is approximately 265 g) with little deformation (Fig. 1(e)). And the supported mass is significantly heavier than that reported for other graphene-based hydrogels [12,25], indicating the excellent mechanical strength of the NG.