



Synthesis of graphene oxide/polybenzoxazine-based nitrogen-containing porous carbon nanocomposite for enhanced supercapacitor properties



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ABSTRACT

A strategy for the fabrication of graphene oxide (GO) and nitrogen-containing porous carbon (NC) nanocomposites for high-performance supercapacitor electrodes was reported. Driven by the hydrogen bonding and covalent bonding between GO and benzoxazine, GO/NC nanocomposites with different GO content were prepared from a novel polybenzoxazine (PBZ) via a situ ring opening polymerization process coupled with KOH activation technique. The introduction of GO demonstrates a significant effect on the textural property, surface chemistry as well as the electrical conductivity of the nanocomposites, leading to remarkably improvement of the electrochemical behavior. A maximum specific capacitance of 405.6 F g^{-1} at a current density of 1.0 A g^{-1} was achieved for GO/NC nanocomposite electrode with GO content of 1.29 wt. % in 6 M KOH electrolyte solution. It also shows better rate capability (267.8 F g^{-1} at 40 A g^{-1}) and cycle durability (95.8% capacitance retention over 5000 cycles) in comparison with the activated PBZ-based nanoporous carbon without GO. Additionally, the as-fabricated GO/NCs symmetric supercapacitor devices in 1 M Na_2SO_4 can realize a wide operational voltage of 1.8 V, and displays high energy density of 38.6 Wh kg^{-1} at the power density of 180 W kg^{-1} , which still maintains 19.9 Wh kg^{-1} at 32.4 kW kg^{-1} .

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1. Introduction

Supercapacitors have attracted considerable attentions, due to their high power density, fast charge/discharge rates, long cycle lifetime, and safe operation compared with other chemical energy storage devices [1,2]. So far, carbonaceous materials are commonly regarded as promising electrode materials for electrical double-layer capacitors (EDLCs), mainly due to their high specific surface area, well-developed pore structure, controllable surface chemistry, stable physicochemical properties, and good corrosion resistance [3–5]. The carbon-based supercapacitors exhibit high power density and long cycle life, but suffer from low capacitance and low energy density. To increase their energy densities, one effective approach is incorporating pseudocapacitive materials (such as conducting polymers [13,14], or transition metal oxides [15,16]) into the carbon matrix by the synergetic effect of both EDL and faradaic capacitance. Another approach is to combine carbon

nanotubes (CNTs)/porous carbon [17,18], graphene oxide (GO) [19], or reduced graphene oxide (RGO) [20] with porous carbon to improve their inherent electrical conductivity and electrochemical performance as compared with individual constituents.

Recent studies show that the incorporation of heteroatoms into the carbon framework, such as electrochemically active nitrogen functionalities, not only enhances the polarity of the carbon surface, electrical conductivity, and the surface wettability towards the electrolytes, but also produces additional pseudo-capacitance by participating in reversible Faradaic reactions at the electrolyte/electrode interfaces [2,3,6]. Currently, it is preferable to utilize the nitrogen-containing precursors as starting materials for the synthesis of nitrogen-enriched porous carbons (NCs) in a direct and easy way [7]. Benzoxazine resins are a new class of nitrogen-containing thermosetting resins, which possess many attractive properties, including high char yield, high thermal stability, near-zero shrinkage during polymerization, low water absorption, great molecular design flexibility, excellent reactivity and compatibility with other polymer [8,9]. A three-dimension network of polybenzoxazine (PBZ) resins can be further obtained from the benzoxazine monomers through the ring opening polymerization

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reaction without the need of any hardeners or catalysts. Our previous work have demonstrated the possibility of successful synthesis of NCs derived from PBZs [10,11]. Compared with the monofunctional benzoxazine, bifunctional benzoxazine, which are prepared from the bisphenols (or monophenols), monoamines (or diamines), and formaldehyde, shows improved performance, such as higher cross linking density, better thermal and mechanical stability [11,12]. Thus, we selected a novel bifunctional benzoxazine as the nitrogen source and carbon source to prepare the NCs in this work.

Noticeably, graphene, which is consisted of two-dimensional graphite layers with one-atom-thick sheet of sp^2 bonded carbon atoms, possesses high theoretical surface area, outstanding electrical conductivity, and good chemical stability [21]. A hybrid composite of nanoporous carbons with graphene has been proved to greatly enhance the electrical conductivity and capacitive performance compared to the pure nanostructured carbon materials [19,20,22]. However, it is still a challenge to fully take the advantage of graphene's excellent intrinsic properties. The electrochemical behavior of graphene-based supercapacitors is greatly limited by the aggregation and restacking of graphene layers and poor solution processability, owing to the strong van der Waals interactions between platelets during the fabrication of graphene-based hybrid nanocomposites [23]. Remarkably, GO possesses abundant epoxide and alcohol functionalities throughout the basal plane, which can be easily dispersed in water and many organic solvents. Besides, the existence of a large number of oxygen and nitrogen functionalities in the benzoxazine monomer can reinforce the interaction between GO and benzoxazine via hydrogen bonds and van der Waals interaction, which shows good compatibility between GO surface and benzoxazine. Furthermore, the presence of $-OH$ group in PBZ can be acted as a binding site for the fabrication of GO/PBZ hybrid nanocomposites. Thus, GO as a nanofiller can be feasibly introduced into the polymer matrix at low loadings to produce hybrid materials with improved properties [24,25]. In addition, GO is an excellent precursor for the synthesis of graphene, as GO can be partially reduced to graphene-like sheets by removing the oxygen-containing groups [26]. By the combination of the intriguing properties of GO with nitrogen-containing porous carbon, graphene oxide/nitrogen-containing porous carbon (GO/NC) nanocomposite is considered to be an ideal electrode material for high-performance supercapacitors with both high power density and high energy density.

In this work, a novel GO/NC nanocomposite was fabricated by in situ ring opening polymerization of PBZ in the presence of GO. The benzoxazine with high thermal stability and char yield was firstly synthesized from phenolphthalein, urea, and formaldehyde through a solution method based on benzoxazine chemistry. Subsequently, GO was introduced into the polymer matrix through the strong hydrogen bonds by ultrasonication. The GO/NC nanocomposite was demonstrated to be a promising, high-performance supercapacitor electrode material, owing to its improved electrical conductivity, high surface area, well-developed, hierarchical pore structure, high nitrogen and oxygen content, and improved electrical conductivity.

2. Experimental

2.1. Synthesis of GO/NC nanocomposites

The nitrogen-containing PBZ polymer was synthesized as follows: In a 250 mL three-necked round bottom flask equipped with a magnetic stirrer, a thermometer, and a reflux condenser, 4.0 g of urea and 8.5 g of formaldehyde (30 wt. %) were added. The mixture was heated to 80 °C for 30 min and then cooled to room

temperature. Then, 11.9 g of phenolphthalein dissolved in absolute ethanol (150 mL) were poured into the above solution. Subsequently, the mixture was heated under reflux at 90 °C for 6 h to obtain benzoxazine monomer solution.

GO was synthesized from natural graphite by the modified Hummers method as described elsewhere [27]. 200 mg of GO powder was dispersed in 100 mL deionized water by ultrasonication for 2 h at room temperature.

For the synthesis of GO/NC nanocomposites, the method is carried out as follows: The obtained surfactant/benzoxazine solution was added into the above GO dispersion. The mixture was stirred adequately and sonicated for 4 h to form an aqueous suspension (2.0 mg GO mL^{-1}). Subsequently, the mixture was poured into the dish to evaporate ethanol at room temperature for 12 h. The obtained nanocomposites were step-heated in an oven to 100, 150, 180, 220, and 260 °C, and held at each temperature for 4 h to obtain polymerized GO/PBZ nanocomposites.

The resulting nanocomposites was chemically activated by heating a KOH-GO/PBZ mixture (weight ratio of 2:1) at 700 °C for 1 h in a tube furnace under flowing nitrogen (with a ramping rate of 3 °C min^{-1}), respectively. Then, the products were repeatedly washed with 1 M HCl and deionized water until the pH value of the filtrate reached about 7 and dried at 120 °C for 12 h. The weight feed ratio of the dry GO powder to the cured GO/PBZ nanocomposite is varied from 0.65, 1.29, 2.60, and 5.16 wt. %, and the resulting GO/nitrogen-containing porous carbon nanocomposites were denoted as GO/NC-1, GO/NC-2, GO/NC-3, and GO/NC-4, respectively. For comparison, the sample named GO/NC-0 was prepared without adding GO and was also activated at 700 °C, where 0 represents none amount of GO.

2.2. Structure characterization

N_2 adsorption isotherms were measured using a Micromeritics ASAP2020 analyzer at 77 K. Before measurements were taken, all samples were degassed at 473 K for 12 h. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific gravimetric surface areas (S_{BET}). The total pore volume values (V_{total}) were estimated from the adsorbed amount at a relative pressure P/P_0 of 0.99. The micropore pore volume (V_{micro}) and micropore surface area (S_{micro}) were estimated using the t-Plot method. The pore size distribution (PSD) curves were derived from nonlocal density functional theory (NLDFT) method assuming a slitlike pore geometry. Scanning electron microscope (SEM) investigations were carried out with a JEOL JSM-700 microscope instrument at an accelerating voltage of 10.0 kV. Transmission electron microscope (TEM) was conducted with the JEOL 2010 microscope at 200 kV. Thermogravimetric analysis (TGA) curves were recorded on a TA Q500 analyzer from room temperature to 850 °C with a heating rate of 10 °C min^{-1} under a constant nitrogen flow of 50 $mL min^{-1}$. X-ray photoelectron spectra (XPS) were obtained on a AXIS Ultra DLD spectrometer with an exciting source of $MgK\alpha$ (1486.6 eV). Elemental analysis was performed by an Elementar Vario Macro EL Cube micro-analyzer. Fourier transform infrared (FT-IR) spectroscopy was carried out using a Bruker Vertex70 spectrometer over the wavenumber range of 4000–400 cm^{-1} . X-ray diffraction (XRD) patterns were obtained on a X-ray diffractometer (XRD, Bruker D8) with $Cu K\alpha$ radiation ($\lambda=0.15406 nm$). The DC electrical conductivity (σ) of the samples was tested by the four-point probe method on a four-point probe meter (RTS-8, Guangzhou, China) at room temperature. A round HPC tablet was fabricated by pressing ($\sim 20 MPa$) 50 mg of the samples by a tablet compression machine. The thickness and diameter of the round tablet were tested using a vernier caliper.

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