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A green method to reduce graphene oxide with carbonyl groups residual for enhanced electrochemical performance

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ABSTRACT

Reduced graphene oxide nanosheets modified with rich carbonyl groups (C=O) was obtained through a facile dehydration process by making use of the synergistic effect between phosphoric acid and monosodium phosphate. The product exhibited a high specific capacitance of 413 $F\,g^{-1}$ at the current density of 0.25 $A\,g^{-1}$ mainly owing to the high percentage of retained C=O groups which provided reversible pseudocapacitance and favored good dispersion. Additionally, the symmetric supercapacitors based on the modified graphene nanosheets showed high specific capacitance (314.2 $F\,g^{-1}$ at 1 $A\,g^{-1}$) and superior electrochemical stability with only 5.8% loss of its initial specific capacitance after 10000 cycle tests (at the current densities of 5 $A\,g^{-1}$). The present work proposed an environmentally friendly way in controlling surface structure of reduced graphene oxide which promises great potential of graphene-based electrode materials for high performance energy-storage devices.

1. Introduction

As a distinct 2D honeycomb carbon network, graphene possesses extraordinary properties such as superior optical transmittance, high electrical conductivity, inherent flexibility, high charge mobility, large specific surface area, excellent chemical stability and electrochemical activity, which promise its great potential in various application fields such as Li ion battery, catalyst engineering, transparent electrode, fuel cells, solar cells and supercapacitor [1–3].

To meet the requirements of practical applications, it is essential to realize controlled synthesis of graphene in large scale. So far, several processes have been explored to synthesize graphene, such as chemical vapor deposition [4], liquid phase exfoliation [5], vacuum thermal annealing [6], epitaxial growth [7], thermal exfoliation [8] and reduction of graphite oxide [9]. Among these methods, chemical oxidation-reduction reaction has been considered as an efficient and cost-effective approach for mass production of graphene [10]. During the oxidation step of this reaction, various oxygenic groups are introduced on its basal planes and edges, mainly epoxide, hydroxyl, carbonyl, and carboxyl groups, which could not be entirely removed in the following reduction procedure and inevitably deteriorate the electroconductivity of the obtained graphene materials [11–14]. Interestingly, unique properties of the oxygenic groups have been recently explored in reduced graphene oxide which presents extra chemical active sites and hydrophilic nature [15,16]. In addition, enhanced performance brought by oxygenic groups on graphene has been demonstrated in producing electrode materials for Li ion batteries [17], supercapacitors [18,19], photocatalysts [20,21] and fuel cell [22]. Moreover, it has been found that the amount and type of the oxygenic groups play a vital role in affecting the graphene electrode performance. Xiong et al. found out that more oxygenic functional groups on the graphene surface can improve energy density and cycling stability of Li ion battery cathodes [17]. Xu et al. reported that the oxygen-containing functional groups on the surface bestowed graphene additional pseudo-capacitance and rendered it a suitable candidate for producing electrode materials of supercapacitors [23]. Furthermore, Fang et al. addressed that hydroxyl and carboxyl groups mainly provided the quasi-reversible or irreversible pseudo-capacitance

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while carbonyl groups contributed to the observed pseudo-capacitance by storing and releasing an electron without ion exchange [24]. It is also reported that hydroxyl group affects the integral capacitance, epoxy group redox property contributes to redox property, and carbonyl, carboxyl groups mainly provide pseudo-capacitance [12,24,25]. However, it still remains a challenge and rarely reported in elaborately modifying graphene surface with desired oxygenic functional groups e.g. carbonyl group, which is regarded as the only group devoting reversible pseudo-capacitance.

In this study, we report a highly controllable and facile hydrothermal approach in modifying graphene surface with carbonyl functional groups (C=O). It is worth noting that utilizing the dilute H_3PO_4 and NaH_2PO_4 medium could easily preserve the C=O group on the graphene surface. And the results reveal that almost all the C=O group in graphene oxide (GO) was reserved after the reduction process. Based on this proposed strategy, carbonyl groups modified reduce graphene oxide was obtained with enhanced electrochemical performances in terms of high specific capacitance and excellent cycling stability which promises its potential applications for producing supercapacitor electrodes.

2. Experimental section

2.1. Materials

Graphene oxide (XFNANO, INC.), phosphoric acid (H_3PO_4, 85%, AR, Sinopharm Chemical Reagent Co., Ltd.), sodium hydroxide (NaOH, ≥96%, Tianjin Bodi Chemical Co., Ltd), potassium hydroxide (KOH, ≥85%, Tianjin Baishi Chemical Co., Ltd), home-made secondary deionized water. All chemicals were not treated with further purification.

2.2. Synthesis of reduced graphene oxide

Two kinds of samples were prepared. For sample GPN, 0.1 g of GO and 2.0 mL H_3PO_4 (85 wt%.) were dissolved into a 200 mL beaker with 70 mL H_2O existing at room temperature, and then reacted with 50 mL NaOH (0.1M). For sample GP, only H_3PO_4 (85 wt%.1.67 mL) and 70 mL H_2O were involved in the reaction. Subsequently, the both mixtures were sonicated for 30min and then stirred over 1 h. After the mixtures were uniformly dispersed, the two suspensions were transferred to an 80 mL Teflon-lined autoclave and kept in an oven at 180 °C for 24 h. Finally, the black precipitates were collected by centrifugation, washed with water, and dried in vacuum oven at 60 °C for 24 h, and two types of samples (GPN, GP) were obtained. Moreover, a spot of sodium dihydrogen phosphate was produced in the reaction medium of GPN. The reaction equation is as follows: $H_3PO_4+NaOH=NaH_2PO_4+H_2O$. In Fig. S1(Supplemental Materials), the concrete procedure for preparing G-Na, G-Na2 and G-Na3 samples in sodium phosphate media (NaH_2PO_4, Na_2HPO_4, NaH_2PO_4/Na_2HPO_4, respectively) was demonstrated.

2.3. Characterization

The surface morphology was investigated by scanning electron microscopy (SEM, Hitachi SU8010) and transmission electron microscopy (TEM, JEM 1200EX). X-ray diffraction (XRD) analysis was carried out at room temperature on a D8-FOCUS (Bruker, German) through a Cu target ($\lambda = 0.154$ nm). The Raman spectra was acquired by a RENISHAW Raman spectrometer (INVIA) with an excitation wavelength of 532 nm. Thermogravimetric analysis (TGA) was conducted under the atmosphere of nitrogen gas from room temperature to 800 °C at a heating rate of 10 °C min^{-1} via STA 409 PC (NETZSCH -Gerätebau GmbH). The specific surface area was calculated from the Brunauer-Emmet-Teller (BET) plot of the nitrogen adsorption isotherm and the pore size distribution of the samples was estimated on the basis of nitrogen absorption-desorption (Micromeritics ASAP 2020). X-ray photoelectron spectroscopy (XPS) data was obtained using a 72 w Al Ka radiation with MULT1LAB2000.

2.4. Electrochemical characterization

The capacitance properties of the samples were first evaluated at room temperature in a three-electrode systems and a 6 M KOH aqueous solution acted as electrolyte. Hg/HgO and Pt wire are used as the reference and counter electrode, respectively, and a nickel foam coated with as-prepared graphene was served as the working electrode. For preparing the electrode, composite powder (80 wt%) was homogeneously mixed with 10 wt% of acetylene black under sonication, and subsequently, 10 wt% poly tetrafluoroethylene (PTFE) was introduced. The mass and area of active material in the working electrode were ca.1.5 mg and ca.0.5 cm^2, respectively. As for the preparation of the two-electrode symmetric supercapacitor systems, the two electrodes accurately coated with the same mass were separated by polypropylene diaphragm that immersed in the 6M KOH electrolyte. Besides, the mass and area of the active material in the working electrodes were around 2.0 mg and 0.5 cm^2 in each electrode, respectively.

The cycle voltammetry (CV), galvanostatic charge-discharge (GC) and the electrochemical impedance spectroscopy in both three-electrode and two-electrode supercapacitor systems were performed on the electrochemical workstation (CHI 760E, Shanghai CH Instrument Company, China). The CV and GC were tested in the potential range from 0 to -1 V at different scan rates and current densities. The EIS measurements were performed in the frequency ranging from 100 KHz to 0.01 Hz at an open-circuit potential with a 5 mV amplitude. In the three-electrode system, the specific capacitance was estimated according to the following equation: $Cs=(I \times t)/(\Delta V \times m)$, where I(A) is the current, t(s) is the discharge time, ΔV is the potential range, and m(g) is the weight of active materials in the electrode. To further evaluate the supercapacitor performance, the prepared electrodes also were measured in the two-electrode system, and the specific capacitance was estimated according to the following equation: $Cs = 2\ (I \times t)/(\Delta V \times m)$, where I(A) is the current, t(s) is the discharge time, ΔV is the potential range, and m(g) is the weight of active materials in the individual electrode. Finally, the energy density and power density were estimated via applying the following formulas and normalizing to the mass of the two carbon electrodes: $E = Cs\Delta V^2/(8 \times 3.6)$, $P = E/t$, where E (Wh kg^{-1}) is the energy density and P (W kg^{-1}) in corresponding with the average power density.

3. Results and discussion

Morphology of the as-prepared GP and GPN samples were characterized by SEM and TEM techniques. The GP and GPN have good dispersibility in most polar or non-polar solution, which is similar to GO, and the color of GO solution changed evidently from yellow brown to black after hydrothermal treatment (see Fig. S1a, Supplemental Materials), implying the reduction of GO and partial restoration of the conjugation network within the carbon structure. From SEM images in Fig. 1a and b, it shows that GP has an obviously crumpled appearance and highly frizzy edge, while GPN exhibits a layer of gauze and slightly curly edge. The wrinkles and corrugation on graphene sheets originated from the capillary force reduce the total surface energy of the sheets, which can also effectively increase the wettability of graphene in the solution. However,