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Self-standing rationally functionalized graphene as high-performance electrode materials for supercapacitors

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Abstract
Supercapacitors (SCs) have attracted much attention as one of the alternative energy devices due to their high power performance, long cycle life, and low maintenance cost. Graphene is considered as an innovative and promising material due to its large theoretical specific surface area, high electrical conductivity, good mechanical properties and chemical stability. Herein, we report an effective strategy for elaborately constructing rationally functionalized self-standing graphene (SG) obtained from giant graphene oxide (GGO) paper followed by an ultrarapid thermal-processing. This treatment results in both the exfoliation of graphene sheets and the reduction of GGO by elimination of oxygen-containing groups. The as-prepared SG electrode materials without additive and conducting agent provide an excellent combination of the electrical double layer capacitor (EDLC) and pseudocapacitor (PC) functions and exhibit superior electrochemical performance, including high specific capacitance, good rate capability and excellent cycling stability when investigated in three-electrode electrochemical cells.

Key words
functionalized graphene; supercapacitors; self-standing

1. Introduction

Supercapacitors (SCs), also known as ultracapacitors or electrochemical capacitors, have emerged as one of alternative energy devices due to their high power performance, long cycle life and low maintenance cost [1−9]. Depending on different energy storage mechanisms, SCs can be classified into pseudocapacitors (PCs) and electrical double layer capacitors (EDLCs). PCs, storing energy based on fast reversible surface redox reactions, hold much higher energy density but unsatisfied cycle stability and rate capability. Whereas EDLCs, storing energy using ion adsorption and desorption at the electrode and electrolyte interface, can perform ultra-high power density and excellent cycle life but lower energy density. Currently, from the perspective of electric vehicles and powering large industrial equipments, a major challenge in the field of SCs is to improve the energy density of EDLCs without sacrificing their power density and cycle life.

Recently, novel carbon-based materials with rational design of material composition, size and morphology have been explored for high-performance EDLCs, such as carbon nanotubes (CNTs), onion carbons (OCs) and active carbons (ACs) [10,11]. Graphene is considered as an innovative and promising material for EDLCs due to its large theoretical specific surface area (SSA) of over 2600 $m^2 \cdot g^{-1}$, high electrical conductivity, good mechanical properties and chemical stability [12−21]. As reported, a theoretical EDLCs capacitance value of 550 $F \cdot g^{-1}$ can be expected if the entire theoretical SSA of graphene is fully utilized. However, the electrochemical performance of graphene is far from the theoretical calculations because there is a high tendency to restack between neighboring sheets owing to the strong π-π interactions, which lead to a significant decrease in the electrochemically active surface area. Tremendous efforts have been made to overcome this problem, and one of promising strategies is to introduce a pseudocapacitive component as the second phase (such as RuO_2, MnO_2 and conductive polymer), which could prevent the restacking of graphene and

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improve the specific capacitance [22−32]. However, these methods suffer from more or less severe drawbacks like high cost, cycling instability and poor rate performance. An alternative strategy is to functionalize graphene with some oxygen-containing groups, such as carboxylic acid, epoxy and hydroxyl groups. However, the restacking between neighboring sheets is still severe. So the key issue here is efficient combination of both ample electrochemically active surface area and appropriate functional groups in the electrode at the same time.

Herein, we report an effective strategy for elaborately constructing rationally functionalized self-standing graphene (SG) by ultrarapidly annealing GGO paper obtained from giant graphene oxide (GGO). This treatment results in both the exfoliation of graphene sheets as well as the rationally functionalized graphene by selective elimination some of oxygen-containing groups of GGO. In addition, the as-prepared graphene could preserve the self-standing structure, which avoids the extra addition of conducting agent and binder during the preparation of electrode and provides a three-dimensional, continuous and fast electronic path in the electrode. These are much important to improve the energy density for ECs in practical application. The as-prepared SG electrode materials without additive exhibit superior electrochemical performance, including high specific capacitance ($181\ \mathrm{F\cdot g^{-1}}$ at current density of $1\ \mathrm{A\cdot g^{-1}}$), good rate capability and excellent cycling stability.

2. Experimental

2.1. Chemicals

Graphite powders (325 mesh, Alfa Aesar, AR), potassium permanganate ($KMnO_4$, Aladdin reagent, AR), sulphuric acid ($H_2SO_4^{2-}$, Beijing Chemical Works, AR), phosphoric acid ($H_3PO_4^{2-}$, Beijing Chemical Works, AR), hydrogen peroxide (H_2O_2, Aladdin reagent, AR), hydrochloric acid (HCl, Beijing Chemical Works, AR), Ni foam (2 mm thick, $420\ \mathrm{g\cdot m^{-2}}$, Changsha Lyrun New Material Co. Ltd.), potassium hydroxide (KOH, Beijing Chemical Works, AR). All reagents were used as received without any further purification.

2.2. Characterization

X-ray diffraction (XRD) patterns were collected on Bruker D8 Focus Powder X-ray diffractometer using Cu K_α radiation (40 kV, 40 mA). Scanning electron microscope (SEM) was performed on a field emission scanning electron microscope (FESEM, HITACHI, S-4800). Transmission electron microscopy (TEM) was taken on a FEI Tacnai G2 electron microscope operated at 200 kV. FTIR tests were performed on a Nicolet 6700 spectrometer. Nitrogen adsorption measurements were performed on a Micromeritics ASAP 2020 adsorption analyzer. X-ray photoelectron spectroscopy (XPS) analysis was carried on an ESCALAB MK II X-ray photoelectron spectrometer.

For three electrode systems, electrochemical measurements were carried out in 6 mol/L KOH aqueous solution. SG pressed onto Ni foam (2 cm×2 cm) was used as working electrode, Hg/HgO electrode filled with 1 mol/L KOH was used as reference electrode, and Platinum wire was used as counter electrode. For symmetrical SCs, stainless-steel coin cells with two symmetrical graphene electrodes were directly assembled in atmospheric air. Electrochemical studies including cyclic voltammetry (CV), galvanostatic charge-discharge (GC) and electrochemical impedance spectroscopy (EIS) were carried out using VMP3 electrochemical workstation (Bio-logic Inc.). Typical CV curves were measured at different scan rates of 5, 10, 20, 50, 100 and $200\ \mathrm{mV\cdot s^{-1}}$ in the potential range from -0.8 to 0 (or -0.4 to 0.4) V vs. Hg/HgO. GC tests were conducted under the current densities of 0.5, 1, 2, 4, 10, 20 and $40\ \mathrm{A\cdot g^{-1}}$. EIS tests were performed at the open-circuit voltage with a superimposed 10 mV sinusoidal voltage in the frequency range of 100 kHz–0.01 Hz.

2.3. Preparation of GGO sheets

GGO sheets were prepared according to the previous reported method [33]. Finally we obtained the GGO aqueous dispersions with a concentration of $14\ \mathrm{mg\cdot g^{-1}}$.

2.4. Preparation of self-standing graphene

The obtained GGO aqueous (100 g) was dried at 80 °C for 12 h in a glass dish to form GGO paper. Then the as-prepared GGO paper was cut into strips and heat treated at 900 °C for 30 s to obtain the self-standing graphene (SG).

3. Results and discussion

A brief summary of the synthesis procedure of SG is schematically presented in Figure 1. Typically, two steps are included for synthesizing SG. The GGO paper is firstly prepared by evaporating GGO solution in a glass dish at 80 °C. Then, the GGO paper undergoes ultrarapid thermal treatment at 900 °C for 30 s. During the heat treatment process, the oxygen-containing groups will rapidly decompose to generate CO_2 between the layers of GGO, which could exfoliate the aggregate GGO and form electrically conductive channels to facilitate the transport of electrolyte. Moreover, the as-prepared SG by this method is highly dispersible in water, which would facilitate the infiltration of electrolyte and thus offer sufficient contact interface between active materials and electrolyte. It should be noted that the GGO is used here to keep the self-standing structure after heat treatment because of its large sheet area.