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Improved synthesis of fluffy and wrinkled reduced graphene oxide for energy storage application

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ABSTRACT

In this work, we report a facile approach to synthesis of highly fluffy and wrinkled reduced graphene oxide by simple freeze-drying and microwave-expanding method in vacuum. Compared with thermal reduced graphene oxide (RGO), the as-synthesized freeze drying and microwave reduced graphene oxide (FMGO) electrodes exhibit an improved electrochemical performance with high specific capacitance of 246 F g^{-1} at scan rate 5 mV s^{-1} and good cycle stability for application in supercapacitors. The outstanding performance of FMGO as a supercapacitor is attributed to the highly fluffy and wrinkled graphene which permits the creation of three-dimensional networks to induce fast electron and ion transport, thus eventually leading the significantly improved electrochemical capacitive behaviors.

As an important next-generation energy storage device, supercapacitor has generated extensive interest because of its long life cycle, high power density, and quick charge–discharge rate [1,2]. Depending on the energy storage mechanisms, there are mainly two types of supercapacitors, pseudocapacitance which store ionic charges by reversible redox reactions and electrochemical double-layer capacitance (EDLC) [3–5]. Metal oxides such as RuO_2, MnO_2, MoO_3, SnO_2, and electronically conducting polymers, or their composites, have been used to increase specific capacitance via pseudocapacitive redox reactions. In EDLC, the capacitance comes from the charge accumulated at the electrode-electrolyte interface. Carbon materials are commonly used in EDLC because of their low cost, good electrical conductivity and high surface area [6–10]. However, their low-energy density limits their use in principal applications. Great efforts have been made to enhance the capacitor performance including developing and optimizing the electrode materials [11,12].

Graphene, a one-atom thick graphite sheet, is recognized as a promising carbon material for fabricating high-performance electrode material of EDLC because of its low mass density, excellent electrical conductivity, and high specific surface area. Graphene-based supercapacitors could achieve specific capacitance as high as 550 F g^{-1} in principle and this value now sets the upper limit for EDLC for all carbon-based materials [13]. However, graphene materials exhibit unsatisfactory performance of capacitors due to the unavoidable restacking of graphene nanosheets. Great contributions have been made to modifying graphene materials by different strategies for use in supercapcitors. For example, Ruoff et al. [14]. have activated graphene by using KOH, achieving high specific capacitance of 166 F g^{-1}. In addition, many researches focused on introducing spacers, such as metal nanoparticles [15–17], metal oxide nanoparticles, various carbon materials (i.e., carbon nanotubes, carbon black, etc) and conductive polymers, into the graphene layers to inhibit the restacking of graphen. Such composites showed an improved electrochemical capacitive performance compared to only graphene due to not only larger surface area but also pseudocapacitance introduced by the spacers' nanomaterials. Although these novel approaches were regarded to be an effective strategy for increasing their electrochemical performances, the specific capacitances are still unsatisfactory and needed to be further improved.

Freeze-drying has been applied for using to synthesize highly pores nanomaterials [18]. Cai et al. reported by freeze-drying technology and thermal reduction of GO with superior cycle stability superior cycle stability for application in lithium-ion batteries [19]. However, in current method, we fabricated an easy and cost-effective strategy for the preparation of highly fluffy and wrinkled graphene oxide via freeze drying and microwave expanded and reduced. We do not need any sophisticated process, controlled environment of H_2 or an inert gas, making this process very

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economical. The combination of freeze-drying and microwaves is simple and fast synthesis of RGO with highly fluffy and wrinkled structure. This highly fluffy and wrinkled structure can effectively avoid the restacking of graphene. The resulting of freeze drying and microwave reduced graphene oxide (FMGO) electrodes exhibit higher specific capacitance than that of thermal reduced graphene oxide (RGO), which shows an excellent material for high-performance supercapacitors applications.

Fig. 1 schematically shows the experimental preparation of FMGO materials. GO sheets were prepared by the oxidation and exfoliation of natural graphite using the modified Hummers' method. Briefly, graphite powder (3.0 g) and 80 mL of concentrated H_2SO_4 were added into a 1 L flask until the powder was completely dispersed. The flask was then cooled to 0 °C using a water-ice bath. A 9.0 g of $KMnO_4$ powder was added to the cold reaction mixture, which was allowed to warm to room temperature. The temperature was then raised to 30 °C and the mixture was stirred for 5 h. The reaction mixture was cooled with an ice bath again, which was then diluted with 200 mL of water. To the diluted mixture, about 6 mL of H_2O_2 was added until evolution of gas was ceased. The mixture is allowed to settle for about 48 h. After settling, the clear supernatant was decanted. The remaining mixture was centrifuged and washed with a diluted HCl solute (10% v/v) and a mixed solution containing CH_3OH and water (50% v/v) several times. The resulting GO was freeze drying at room temperature for 24 h, yielding about 4.0 g of dark brown powders. After filtration and freeze-drying, the sample were treated in a microwave oven in ambient conditions at 1000 W for 1 min to obtain the FMGO samples. For comparison, the as-prepared GO was thermally expanded by rapidly heating at 800 °C for 30 s under the protection of argon in a quartz tube furnace to obtain the reduction of graphite oxide (RGO).

Powder X-ray diffraction (XRD) analyses were performed on a Bruker D8 ADANCE diffractometer with Cu-Kα radiation. Raman spectra were obtained from all samples using Renishaw inVia Raman microscope with an excitation wavelength of 532 nm. The morphologies of the as-obtained samples were observed by a field-emission scanning electron microscopy (FESEM, Quanta 250 FEG) and transmission electron microscope (TEM, JEOL JEM-2100). The chemical compositions of the synthesized samples were determined by an Elementar Vario EL CHNS analyzer.

Fig. 2 presents the SEM and TEM images of FGO and FMGO. Upon microwave irradiation, a large volume expansion of the GO powders was obtained. The FGO powder in the glass vial has dramatically expanded yielding a black and fluffy FMGO powder. Fig. 2a is a typical FESEM image of the FGO. As can be seen, the space between GO sheets increased with fluffy morphology after freeze drying in vacuum. Fig. 2b and c are the SEM images of FMGO. It can be seen that the surface of the pristine GO nanosheet is very clean and wrinkled. The edges of the sheets are partially folded so that the total surface energy should be reduced. TEM image of FMGO (Fig. 2d) further indicates that the FMGO with highly fluffy and wrinkled structure are suitable for supercapacitors applications.

The structures of GO, FGO and the recovery of conjugated system from GO upon microwave reduction were studied by the XRD patters (Fig. 3a and b). After oxidation, the (0 0 2) peak of graphite powder disappears and an additional peak at ~11° is observed, which is corresponding to the (0 0 1) diffraction peak of GO. The small peaks in Fig. 3a should be the (002) of graphite at the degree of ~26° and (111) of graphite at ~42°, respectively. These small peaks come from some unoxidation of graphite. The d-spacing of GO increased to 0.779 nm from 0.335 nm of graphite powder. After freeze drying in vacuum, the d-spacing of FGO increased to 0.915 nm, which is ascribed to the induced O-containing functional groups and inserted H_2O molecules. After microwave treatment, the diffraction peak of GO disappeared and the graphene displayed a broad diffraction peak of (002) diffraction at ~24.5° (d-spacing ~0.38 nm). It is note that the intensity of FMGO is higher than that of RGO, which indicates an efficient reduction of the FGO and a high degree of exfoliation of the layered graphene sheets. These results can be also confirmed by FT-IR. As shown in Fig. 3c, the FTIR spectrum of FGO at 1728 cm^{-1} corresponds to C=O stretching vibration, 3406 cm^{-1} for O–H stretching vibration, 1052 cm^{-1} for C–O stretching, and 1612 cm^{-1} for skeletal vibration from unoxidized graphite domain. After microwave reduction and expanding, these oxygen-containing functional groups derived from the intensive oxidation were reduced significantly. The peaks for O–H and C–O are almost entirely removed, reflecting the highly reduced of F-GO. Information about the structure of F-GO and FMGO were further verified by analysis of Raman spectra. Two typical peaks appeared at ~1580 cm^{-1} (G-peak) arising from the first order scattering of the E_{2g} phonon of sp^2 C atoms, D-peak (~1350 cm^{-1}) arising from a breathing mode of photons of A_{1g} symmetry. The D-peak is related to the amount of disorder and its intensity shows the degree of edge chirality. Generally, the intensity ratio of D and G peaks (I_D/I_G) of samples indicated the degree of the disorder such as defects, ripples and edges. As shown in Fig. 3d, the I_D/I_G gradually decreased from 1.81 (FGO) to 0.54 (FMGO) indicating that the hexagonal network of carbon atoms were recovered during microwave irradiation. The G-peak at about 1600 cm^{-1} has a shoulder different in GO and FMGO. This is another defect induced peak called D′ appears at 1612 cm^{-1} and responsible for broadening of the G-band. Nitrogen adsorption–desorption isotherms measurements were carried out for examining the specific surface area of RGO and FMGO. The N_2 sorption isotherm of RGO and FMGO are shown in Fig. 3e. The BET specific surface area of FMGO is 359 m^2 g^{-1} and it has pores of sizes between 2.6 and 3.5 nm, demonstrating a mesopores structure.

In order to explore the electrochemical energy storage application of the FMGO and RGO, we investigate their electrochemical properties by a three-electrode setup with 1.0 M KOH aqueous solution. The Ni foam coated with the active materials served as the working electrode, platinum foil electrode, and a saturated calomel electrode (SCE) served as the counter and reference electrodes, respectively. The working electrode was prepared by mixing the

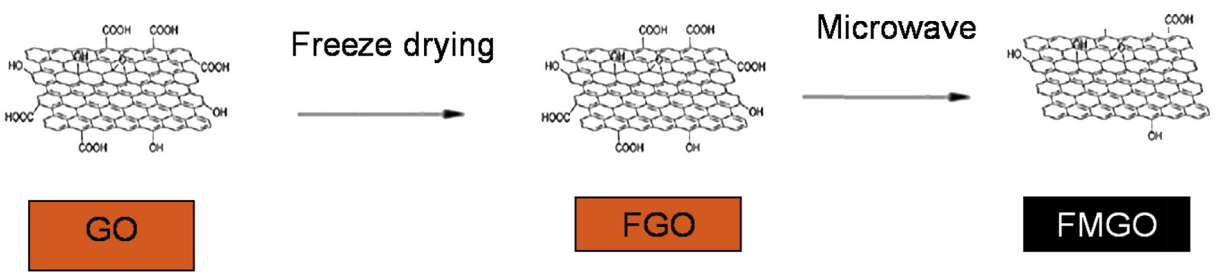

Fig. 1. Schematic diagram of preparing FMGO.