



A facile one-pot fabrication of flowerlike graphene-based particles for electric double-layer capacitors



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HIGHLIGHTS

- Flowerlike graphene-based particles were synthesized by one-pot hydrothermal method.
- Carbon from sucrose prompted the evolution of flat-shaped graphene to curved-shaped.
- Carbonized curved particles with considerable open edges exhibit large pore volume.
- A high specific capacitance and rate performance of the electrode were achieved.

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ABSTRACT

Flowerlike graphene-based particles had been successfully synthesized from the suspension of graphene oxide (GO) in the aqueous solution of sucrose by one-pot hydrothermal carbonization approach. Porous carbon from sucrose prompted the evolution of graphene from flat-shaped to flowerlike curved morphology, which was confirmed by the observation of scanning electron microscopy and transmission electron microscopy. The graphene-based particles possess large pore volume ($0.69 \text{ cm}^3 \text{ g}^{-1}$) and surface area ($470.5 \text{ m}^2 \text{ g}^{-1}$), which is about 6 times greater than that of carbonized graphene sheets ($79.2 \text{ m}^2 \text{ g}^{-1}$). Electrochemical investigation indicated that the specific capacitance of the particles reached 162 F g^{-1} at current density of 0.1 A g^{-1} in 30 wt% KOH aqueous electrolytes and the capacitance maintenance achieved 90% as the current density enlarged 50 times. The keys to the ideal capacitive performance are the abilities to make full utilization of specific surface area of graphene and ensure a quick kinetic process for the diffusion of ions within curved graphene particles with considerable open edges.

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1. Introduction

Electric double-layer capacitors (EDLCs), also known as supercapacitors, recently have attracted extensive attention as alternative energy storage systems owing to their remarkable power density, long cycle life (above 100,000 cycles) and broad working temperature [1]. In EDLCs, the energy is stored in an electric double layer through physisorption of electrolyte ions on the electrode surface. Thus, carbon based materials with high specific surface area are widely employed as electrode materials, such as activated

carbon, mesoporous carbon, carbon nanotubes and carbon nanofibers [2].

As a fresh member of carbon family, graphene is regarded as a promising electrode material for EDLCs because of its high theoretical specific surface area ($\sim 2600 \text{ m}^2 \text{ g}^{-1}$), excellent electrical conductivity, good chemical stability and mechanical property [3]. However, the two-dimensional (2D) graphene sheets are prone to aggregation in the process of graphene formation and subsequent electrode preparation due to the strong π – π stacking and the van der Waals attraction [4]. Restacking of graphene sheets will significantly diminish the effective surface area of the material. A successful application of graphene for high-performance EDLCs would require effectively preventing the restacking of graphene sheets and maintaining the bulk conductivity of the materials.

Recently, numerous efforts have been devoted to suppressing restacking by intercalating various molecular or nanostructured

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spacer materials to graphene sheets, such as surfactants (poly (sodium 4-styrenesulfonate (PSS) [4], dimethyldioctadecylammonium bromide (DODA·Br) [5], triblock copolymers (PEO-b-PPO-b-PEO) [6]), carbon materials (carbon nanotube [7] or carbon fibers [8]) or even inorganic salt nanoparticles (CaCO_3 [9]). Nevertheless, the composites of graphene and spacer materials are formed under noncovalent interactions such as π – π interaction and electrostatic adsorption. The as-prepared network configurations are not stable and the bulk conductivity may be lowered especially when organic molecules or inorganic compounds spacers are used.

Taking the advantage of the surface area and conductivity of porous carbon, we applied a facile hydrothermal carbonization approach to realizing mass-production of flowerlike curved carbon/graphene particles from the suspension of GO in aqueous solution of sucrose. After carbonization, porous carbon from sucrose and graphene sheets evolved to a single structure, which is very stable. The electrochemical performance in EDLCs of the flowerlike graphene-based particles was firstly investigated in a 30 wt% KOH aqueous solution. The electrochemical tests showed that the particles had a good capacitive behavior, predicting their potential application in energy storage.

2. Experimental

2.1. Preparation of graphene-based particles

GO was prepared by oxidation of natural graphite powder (average particle size of 20 μm , Qingdao Huarun Graphite Co., Ltd.) with the modified Hummers method [10]. The GO suspension (2 mg mL^{-1}) was prepared as a stable aqueous dispersion using ultra sonication. In a typical procedure: 0.8 g sucrose was dispersed in 80 mL of GO suspension (0.16 g) and the mixture was sonicated for 2 h. Then the mixture solution was put into a Teflon-lined steel autoclave with a volume capacity of 100 mL. The container was closed and maintained at 180 °C for 24 h and then cooled to room temperature. The resulting dark brown powder was washed by distilled water and dried at 120 °C for 24 h. Subsequently, the powder was further pyrolyzed in a tube furnace at 900 °C for 1.5 h under an argon atmosphere. Finally, the black carbon powder was collected after washing with abundant distilled water and denoted as C-S/GO. For comparison, pure GO suspension and sucrose solution were treated under the same recipe and procedure respectively. The obtained sample after hydrothermal process from GO was denoted as H-GO and the carbonized samples were denoted as C-GO and C-S, respectively. The total productivity of GO and sucrose after hydrothermal process and carbonization was calculated of 45% and 16%.

2.2. Characterization of the samples

The structure of the products was analyzed by X-ray powder diffraction (XRD, Bruker D8-Advanced, Germany) and Raman spectroscopy (LABRAM-010, JY Company, France). The morphology and surface features of the products were characterized by scanning electron microscope (SEM, JEOL JSM-6700F, Japan) and transmission electron microscope (TEM, JEOL JEM-3010, Japan). Nitrogen adsorption and desorption isotherms of samples were obtained at 77 K with an automatic adsorption apparatus (ASAP 3020, Micromeritics, U.S.). The BET SSA (S_{BET}) and total pore volumes (V_{tot}) were calculated using the Brunauer–Emmett–Teller equation and the single point method, respectively. The average pore diameter (D) was estimated from the equation $4V_{\text{tot}}/S_{\text{BET}}$. Micropore SSA (S_{mic}) was calculated by the t-plot method. The corresponding pore size distributions were calculated with the adsorption data based on the DFT method. Electrical conductivity

was tested by the conventional four-probe method with metal electrodes attached to the ends of circular samples (RTS-8 Four-Point probemeter, China).

2.3. Electrochemical measurements of the samples

Carbon samples (active material) and PTFE (60 wt. % solution, binder) were mixed in a mass ratio of 95:5 and dispersed in deionized water (the mass ratio of carbon to water was set as 1:2). After homogenized in a mortar, the slurry was rolled into a thin film of uniform thickness (0.5 ± 0.1 mm). From this film, 12 mm circular electrodes were punched out and pressed onto a nickel foam (as a current collector). The carbon coated nickel foam was then immersed in a 30% (wt. %) KOH solution under vacuum for ca. 3 h before testing.

Electrochemical measurements (CV, EIS) were performed on an electrochemical workstation CHI660A (Shanghai Chenhua Instrument corp. China) at room temperature, using two-electrode electrochemical capacitor cells. Cyclic voltammograms were recorded from 0 to 1 V at various sweep rates and the Nyquist plots were recorded potentiostatically (0 V) by applying an alternating voltage of 5 mV amplitude in the 100 kHz–1 MHz frequency range. The galvanostatic discharge–charge tests were conducted in the voltage range of 0–1 V with a Battery Tester (Wuhan Land, China) at different specific currents.

3. Results and discussion

3.1. Structures of samples

XRD characterizations of GO before and after hydrothermal treatment and the carbonized samples of C-GO, C-S/GO, and C-S were firstly conducted to examine the change of crystal structures, as illustrated in Fig. 1(a) and (b)), respectively. For GO, a featured diffraction sharp peak at 11.53° is observed, corresponds to the (001) crystalline plane of GO. The calculated basal spacing is 7.62 Å, which is larger than the d-spacing (3.35 Å) of pristine graphite as a result of the introduction of oxygen-containing groups on carbon nanosheets and subsequent intercalation of hydrophilic water within the stacked GO structures [11]. After the hydrothermal reaction, the sharp peak at 11.53° for GO disappears, whereas a small and broad peak at 25.2° is observed in H-GO corresponding to the interlayer spacing of 3.52 Å. These results indicate that the GO has been exfoliated largely and restack more disorderly along their stacking direction [12]. After carbonization, the pattern of C-GO exhibits a little stronger but still dispersive diffraction peak appeared around 25.8°, the interlayer spacing was calculated to be 3.45 Å. This value is lower than that of H-GO (3.52 Å) while slightly higher than that of natural graphite (3.35 Å). These results suggest that GO can't be completely recovered to the π -conjugated structure as pristine graphite even after heat treatment at 900 °C.

As illustrated in Fig. 1(b), similar to C-GO, the X-ray diffraction profile of C-S/GO exhibits a broader peak around 25.8°, indicating the poorer ordering of graphene sheets along their stacking direction. The framework of the C-S/GO is composed of fewer layer stacked graphene sheets after the introduction of porous carbon from sucrose [13].

In addition, the structures of GO before and after hydrothermal treatment and the carbonized samples were investigated by Raman technology in Fig. 2. As shown in Fig. 2(a), the Raman spectrum of GO shows a broad G band at 1590 cm^{-1} and a prominent D band at 1359 cm^{-1} with an intensity ratio $I_{\text{D}}/I_{\text{G}}$ of 0.86. This D band is ascribed to the sp^3 amorphous carbons originated by oxidation. After hydrothermal treatment, the Raman spectrum of H-GO also displays the existence of D and G bands at 1345 and 1584 cm^{-1} , but

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