



Formation process of holey graphene and its assembled binder-free film electrode with high volumetric capacitance



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ABSTRACT

Holey graphene with abundant in-plane nanopores is achieved through a mild defect-etching reaction between graphene oxide (GO) and hydrogen peroxide (H_2O_2) then followed by a reduction process in hydrazine solution. The porosity of the obtained holey graphene is systematically investigated by optimizing the reaction conditions between GO and H_2O_2 . The optimum reaction conditions are that GO is hydrothermally treated in 0.4 mL H_2O_2 at 100 °C for 10 h and the as-prepared holey graphene oxide (HGO) is refluxed in hydrazine solution at 100 °C for 1 h, by which holey reduced graphene oxide (HRGO) suspension with good dispersity is obtained. By vacuum filtration of the HRGO suspension, the binder-free porous graphene film electrodes are successfully assembled. The obtained film electrodes exhibit high specific capacitance (251 F g^{-1} at a current density of 1 A g^{-1}), high volumetric capacitance (up to 216 F cm^{-3}), and enhanced rate capability (73% capacitance retention from $1\text{--}60 \text{ A g}^{-1}$) due to their high packing density (0.86 g cm^{-3}). The suitable porosity of the assembled porous graphene film keeps a balance between electrolyte ion diffusion rate and conductivity, which can bridge the gap between gravimetric capacitance and volumetric capacitance for the obtained electrode material.

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1. Introduction

Electrochemical capacitors (ECs) are one of the most effective and practical energy storage and conversion devices [1], which can bridge the critical performance gap between the high energy density of secondary battery and high power density of conventional dielectric capacitor, making it possible for the rapid energy storage and release [2]. The capacitive performance of the ECs lies in electrode materials, electrolyte, and assembled technology, with the most important factor being the electrode materials [3]. Among the electrode materials with different structures and morphologies, the flexible and binder-free film electrodes with high packing density have shown great promise in upcoming next-generation portable and flexible electronics such as roll-up displays, photovoltaic cells, and wearable devices [4–6]. Film architecture of the electrode materials can improve the electrolyte access, because they can show low ion diffusion length and

reduced electron transfer resistance [7–9]. According to the available literature to date, most of the working electrodes are binder-enriched ones, which are prepared by the traditional slurry-coating technology [10–12]. Evidently, the added binder will decrease the electrical conductivity of the electrode materials, hindering their potential application in high performance supercapacitors [13]. In order to obtain the ideal electrochemical performance, it is also urgent to develop flexible and binder-free film electrode materials for supercapacitors.

Graphene has attracted significant attention in recent years because of its extraordinary electrical conductivity, high surface area, chemical stability, and a distinct 2D nanostructure [14]. Graphene nanosheets can be acquired by delaminating their bulk materials with layered structure, and the obtained nanosheets are new classes of nanoscale materials, which can be used to assemble binder-free film electrodes with excellent flexibility and high packing density [15,16]. However, there are three key points remained to be solved when graphene nanosheets are used to assemble binder-free film electrodes. Firstly, the irreversible aggregation tendency of graphene nanosheets due to the strong $\pi\text{--}\pi$ stacking and van der Waals interactions between different graphene nanosheets should be prevented, because it will give rise to a significant deterioration of their properties including severely

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reduced specific surface area and much lower mass diffusion rate [17]. Secondly, the efficient ion transport pathway in the vertical direction of the film electrode is needed, which is favourable for improving the rate capability of the electrode materials [18]. Thirdly, the dispersity and processability of graphene nanosheets is needed for assembling the film electrode with high packing density [19]. Up to now, the preparation of graphene hydrogels with three-dimensional hierarchical porous network or holey graphene oxides with abundant in-plane nanopores are probably effective ways to solve the above challenges [20–22].

Porous graphene can be mainly classified into crumpled graphene, graphene foam, and graphene nanomesh [23]. The crumpled graphene with a wrinkled configuration is constructed with the bending and folding graphene nanosheets [24]. The graphene foam is a kind of 3D macroscopic graphene architecture via self-assembly of the 2D flexible graphene nanosheet or by chemical vapor deposition (CVD) [25,26]. The graphene nanomesh, also called holey graphene, is characterized as the existence of abundant in-plane pores with the pore sizes ranging from several angstroms to the nano-scale [27]. In comparison with the crumpled graphene and the graphene foam, the graphene nanomesh possesses higher surface area and much more active sites and edges for the ion diffusion shortcuts between different layers of graphene, thus they can be used to assemble outstanding electrode materials for supercapacitor [28]. The graphene nanomesh can be obtained by means of plasma etching [29,30] template direction [18,31], chemical activation [32,33] and catalytic oxidation [34,35], and so on. Although the graphene nanomesh with sufficient nanoscale periodic or quasi-periodic nanoholes can be prepared by above methods, the electrode materials assembled from these graphene nanomeshes show relatively low packing density, which generates low volumetric capacitance [1,32]. On the other hand, solution oxidation method is favourable for obtaining graphene nanomesh with good dispersity and processability, which would be able to conveniently process into holey graphene film with high packing density and bridge the gap between gravimetric capacitance and volumetric capacitance [22,36–38]. Shi and Liu groups have developed a solution approach for the production of graphene nanomesh with nitric acid, but the pollutant derived from nitric acid should be attracted more attention [37,39]. In virtue of the environmental-friendly merit of H_2O_2 used as oxidizing and etching reagent, Duan group has prepared the graphene nanomesh film with a packing density of 0.71 g cm^{-3} by mechanically compressing porous graphene hydrogel, and the prepared film shows simultaneously relatively high gravimetric and volumetric capacitances while retaining excellent rate capability [36]. However, the resultant holey graphene is in absence of dispersity and processability, which will preclude the integration of various pseudocapacitive materials into the holey graphene film to further boost its specific capacitance and energy density. From the foregoing, graphene nanomesh with abundant in-plane nanopores can be prepared by a convenient mild defect-etching reaction, while its dispersity and processability should be further improved for the high packing density and high volumetric capacitance of the film electrode.

In the present work, a mild defect-etching reaction is used to produce holey graphene with abundant in-plane nanopores by using H_2O_2 as oxidizer at relatively low temperature, and the porosity of the obtained graphene nanomesh is systematically investigated on the basis of optimizing the reaction conditions. By directly vacuum filtrating the graphene nanomesh with abundant in-plane nanopores and good dispersity, the binder-free graphene film electrodes with porous layered structure and high packing density are assembled, which exhibit enhanced volumetric capacitance, remarkable rate performance, and shortened time constant.

2. Experimental section

2.1. Samples preparation

Graphite oxide (Nanjing XFNANO Material Tech. Co., Ltd) was dispersed into ultrapure water and treated by ultrasonication in a water bath for 4 h, and the homogeneous GO suspension (1 mg mL^{-1}) was obtained. Then the GO suspension (36 mL , 1 mg mL^{-1}) was mixed with $0.4 \text{ mL H}_2\text{O}_2$ (30%) in a 50 mL Teflon autoclave under continuously stirring for 30 min and the as-formed suspension was sealed and hydrothermally treated at 100°C for 10 h, through which the holey GO abbreviated as HGO was obtained. Afterward, 0.6 mL hydrazine solution (50%) was added into the as-obtained HGO suspension and refluxed at 100°C for 1 h, and then cooled naturally to room temperature, by which HGO was reduced into holey reduced graphene oxide and the obtained sample was abbreviated as HRGO. By changing the hydrothermal treatment time, HRGO with different porosity were prepared using the same procedure, and the obtained samples were abbreviated as HRGO-x, where x represented the hydrothermal treatment time. By using a cellulose membrane with a pore size of $0.45 \mu\text{m}$, the HRGO film was finally prepared via vacuum filtration of the HRGO suspension. As a comparative experiment, the reduced graphene oxide (RGO) film was obtained under the same condition via replacing HGO with GO.

2.2. Material characterization

The morphologies of the samples were observed on Tecnai G2 F20 S-Twin Field-emission transmission electron microscopy (FETEM) operated at an acceleration voltage of 200 kV . Raman spectra were measured and collected using a Renishaw inVia Raman microscope with an excitation wavelength of 532 nm . The conductivity of the obtained RGO and HRGO film was measured by a standard four-point-probe method. Nitrogen adsorption/desorption isotherms of the resultant products were measured at 77 K on a micromeritics ASAP 2420 sorptometer. Samples were degassed at 180°C for 12 h ahead of the measurement. The apparent surface area was calculated using the Brunauer-Emmett-Teller (BET) method with the adsorption data at the relative pressure (P/P_0) range of $0.05\text{--}0.20$. The total pore volume was estimated from the amount of nitrogen adsorbed at a relative pressure (P/P_0) of 0.99 , whereas the micropore volume was analyzed from the Nonlocal Density Functional Theory (NLDFT). The pore size distribution (PSD) was also determined using NLDFT model assuming the cylinder pore geometry from the desorption data.

2.3. Electrochemical measurement

The electrochemical performance of the obtained film electrodes was characterized by cyclic voltammetry (CV), galvanostatic charge-discharge and electrochemical impedance spectroscopy (EIS) on CHI660E electrochemical workstation (CH Instruments Inc. China) via using 6.0 M KOH as electrolyte. The working electrode was prepared by directly placing the obtained film (with a weight of about 1.4 mg and an area of 0.95 cm^2) between two pieces of nickel foam without any other additives and then pressed under a pressure of 5 Mpa to make the electrode material adhere to the current collector more completely. The mass loading for each electrode is typically 1.5 mg cm^{-2} which yields an electrode with thickness about $16 \mu\text{m}$ and packing density of 0.86 g cm^{-3} . In a three-electrode system, Pt foil and Ag/AgCl electrode were applied as the counter and reference electrodes, respectively. The gravimetric capacitance, C_{wt} (F g^{-1}) of the electrode material was calculated from the galvanostatic discharge curves according to the following equation: $C_{wt} = I \times Dt / (\Delta V \times m)$, where I is the

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