Sugar blowing-assisted reduction and interconnection of graphene oxide into three-dimensional porous graphene

Fangming Han[*], Ou Qian, Bin Chen, Haibin Tang, Meiling Wang[**]

Key Laboratory of Materials Physics, Anhui Key Laboratory of Nanomaterials and Nanostructures, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei, Anhui, 230031, People's Republic of China

ARTICLE INFO

ABSTRACT

Assembly of individual graphene sheets into macroscopic three-dimensional (3D) graphene is very important for the applications of graphene. In this paper, sugar blowing-assisted thermal reduction and interconnection of graphene oxide is developed to synthesize three-dimensional porous graphene (3D-PG). In the process, NH_4Cl added in graphene oxide solutions acts as a blowing agent, while glucose added in the solutions can enhance the bubble burst and the cross link of graphene sheets. We also describe the use of the 3D-PG films as electrodes of supercapacitor. It was demonstrated that the 3D-PG films display a high capacitance about 115 F/g at a scan rate of 10 mV/s. More importantly, because the addition of glucose could strengthen the interconnectivities among graphene sheets, further accelerating the charge transport, the 3D-PG films show better power performance than the self-assembled graphene hydrogel (SGH). Our results demonstrate that sugar blowing-assisted thermal reduction of graphene oxide is a facile and effective route for the preparation of 3D-PG with graphene sheets tightly glued.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Three-dimensional (3D) architectures and materials have received increasing attention because of their potential applications in the field of environment protection, energy storage and conversion [1–5]. As an illustration, 3D graphene is a promising material, and usually used as electrodes of the energy storage devices and environmental adsorption materials [1,2]. For high performance energy storage devices, there is a need for new electrode materials that have high specific surface area, high electrical conductivity and facilitated ion diffusion channels [6]. Nevertheless, few electrode materials simultaneously demonstrate the three excellent properties combined together. Recently, great efforts have been devoted to designing and fabricating 3D graphene in order to reach these properties [4,6–30]. Usually, 3D graphene was prepared by template-directed chemical vapor deposition (CVD) [4,8–10], sugar-blowing carbonization approach based on a polymeric predecessor [6,7] and chemical reduction of graphene oxide (GO) [2,11–19,29,30]. Among these technologies, assembly and reduction of GO into 3D graphene is one of the most extensive routes due to the mass production of graphene bulk electrodes. Unfortunately, to prevent graphene sheets from restacking, self-assembled graphene hydrogels (SGH) should experience an inconvenient and time-consuming freeze-drying process [17]. Especially, in the chemical reduction process, impurities are often introduced [12], and the chemical reduction and assembly of GO was usually carried out in liquid environment, the final product suffer from poor electrical conductivity due to the weak interactions and high inter-sheet junction contact resistance [6,8].

To enhance the interconnection between isolated graphene sheets, further increase the conductivity of 3D graphene, template-directed CVD method has been used to fabricate 3D graphene with a good connection. Nevertheless, the 3D graphene can show very good conductivity only when it has sufficient mechanical support [6]. Moreover, the recent findings show that ammonium-assisted chemical blowing method can be used to effectively produce 3D strutted graphene (SG) [6]. The SG shows high performance in an electrical double-layer capacitor because of their low resistance and facilitated ion diffusion channels [6,7]. However, a high calcination temperature (1350 °C) should be employed in the process, and the SG has a small specific surface area. Subsequently, several research groups improved the sugar blowing-assisted method. For instance, a gas-foaming method was developed to prepare 3D graphene layers in the process of reduction of GO. This technology

---

* Corresponding author.
** Corresponding author.
 E-mail addresses: fmhan@issp.ac.cn (F. Han), mlw@issp.ac.cn (M. Wang).

can prevent the face-to-face restacking of the graphene nanosheets, but the 3D graphene still has weak connections, and is inseparable with freeze-drying process [20]. Then, a developed method was used to fabricate graphene-like carbon nanosheets, with glucose acting as a carbon precursor, NH_4Cl as a blowing agent and Fe species as a graphitization catalyst [31]. But the catalyst impurities could be introduced inevitably.

Here, we present a simple strategy for the production of high-quality 3D porous graphene (3D-PG) with good interconnections between isolated graphene sheets through a sugar blowing-assisted thermal reduction of GO method. In the fabrication process, NH_4Cl, in the homogeneous mixture containing GO, NH_4Cl and glucose, can be used as gas foaming agent, while glucose in the mixture can enhance the bubble burst and the cross link of graphene sheets, which can improve the conductivity of the 3D-PG. The 3D-PG can be easily compressed to compact film, and can provide multidimensional electron transport pathways, large accessible surfaces and facilitated ion diffusion channels for high performance electrochemical supercapacitor.

2. Experimental

2.1. Preparation of 3D-PG

3D-PG was prepared using sugar-blowing assisted thermal reduction of GO (Schematically shown in Fig. 1). First, 0.4 g NH_4Cl and a certain amount of glucose were dissolved in deionized water. Next, 5 ml GO colloidal solution (2 mg/ml) were injected, and the mixed solutions were treated by ultrasonication for 5 min (Fig. 1a). Then the mixed solution was dried into a paste at 40 °C (Fig. 1b). To obtain 3D-PG (Fig. 1c), the paste-like mixture was transferred into a horizontal furnace, and the temperature was raised from room temperature to 1000 °C in 3 h and kept for 2 h under the protection of Ar.

2.2. Material characterization

The morphology and structure of 3D-PG were characterized by field-emission scanning electron microscope (FE-SEM, JEOL JSM-6700F) and high-resolution transmission electron microscopy (HRTEM, JEOL-2010). The crystallographic structures of the 3D-PG were characterized by X-ray diffractometer (Philips X'Pert). The 3D-PG was further characterized by a confocal microprobe Raman spectrometer (JY, LABRAM-HR, France).

2.3. Electrochemical measurements

Electrochemical measurements of the assembled super-capacitors were carried out using Zahner Zennium electrochemical workstation in 1 M H_2SO_4 solution. The electrochemical impedance spectroscopy measurements were performed over a frequency range from 10^5 to 10^{-1} Hz at an amplitude of 5 mV. The specific capacitance was calculated from galvanostatic discharge curves and current-voltage (CV) curves. The cycle life tests were conducted by galvanostatic charge-discharge measurements with a constant current density of 10 A/g for 10000 cycles.

3. Results and discussion

In the heating process (Fig. 1d), a molten syrup was gradually polymerized, while chemically released gases from NH_4Cl blew glucose-derived polymers into numerous little bubbles [6]. Then GO sheets were detached from each other. With the increase of the temperature, these little bubbles merged into large bubbles. GO sheets were gradually aligned along the bubble walls, and contacted with each other by the remaining glucose-derived polymers. Finally, the GO sheets and the polymers could be subsequently graphitized into 3D-PG at a high temperature. Usually, self-assembled 3D graphene is thermally unstable due to their weak interconnections [17]. In this case, the final products can exist stably at high temperature, because the graphene sheets might be glued with each other through the melt, polymerization and carbonization of glucose.

The morphology and microstructures of the as-prepared 3D-PG were characterized by FE-SEM and HRTEM. The SEM images reveal that the amount of glucose is crucial to formation of the 3D-PG (Fig. 2a and b and Fig. S1 in Electronic supplementary information (ESI)). It is difficult for the final products to form a whole (Fig. S1 in ESI), when the amount of glucose was less than about 0.2 g. Meanwhile, excessive glucose can lead to the formation of carbon
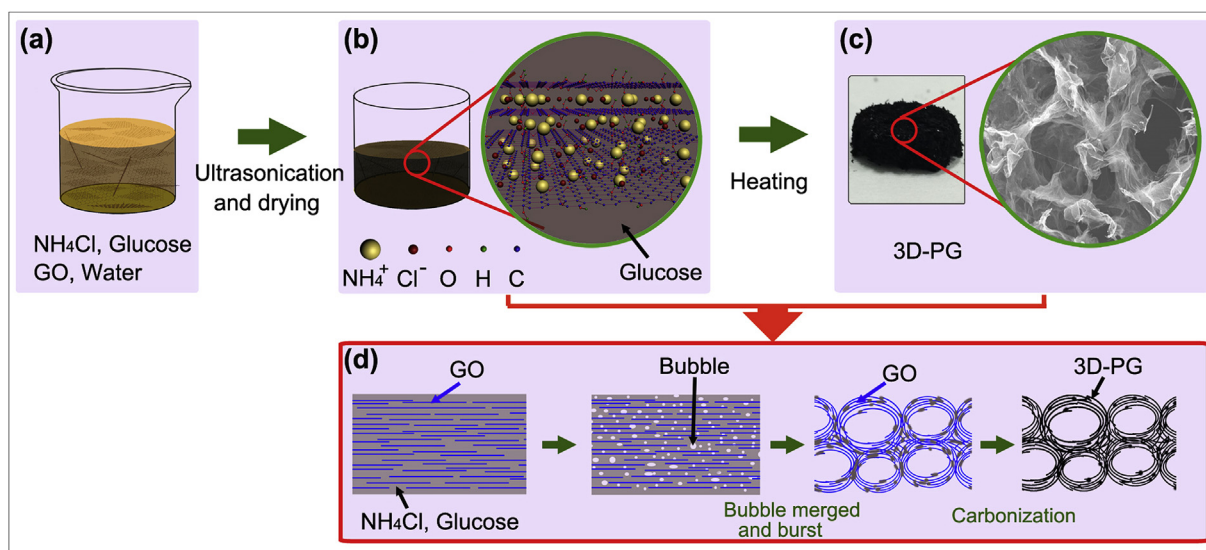

Fig. 1. A schematic show of the facile and effective process of synthesizing 3D-PG. (a) Mixture solutions containing GO, NH_4Cl, Glucose and water. (b) Paste-like mixture. (c) Photograph and SEM image of 3D-PG. (d) Transition process from the mixture to 3D-PG.