Frontiers article

Facile syntheses of 3-dimension graphene aerogel and nanowalls with high specific surface areas

Lina Zhou [a,b], Zhongbo Yang [a], Jun Yang [a], Yonggang Wu [b,*], Dongshan Wei [a,*]

[a] *Chongqing Key Laboratory of Multi-scale Manufacturing Technology, Chongqing Institute of Green and Intelligent Technology, Chinese Academy of Sciences, Chongqing 400714, China*
[b] *College of Chemistry & Environmental Science, Hebei University, Baoding 071000, China*

ABSTRACT

We propose facile synthesis methods to prepare two three-dimension (3D) multi-porous graphene structures including graphene aerogel and graphene nanowalls. The graphene aerogel was prepared via the hydrothermal reduction and *tert*-butanol freeze-drying. The graphene nanowalls were prepared by growing the obtained graphene aerogel via a plasma enhanced chemical vapor deposition (PECVD). High specific surface areas of these two structures up to 795 m^2/g were obtained by BET analyses. The crystallized, multi-porous, and thermal stable features of these two 3D graphene structures were verified via the X-ray diffraction, SEM, Raman spectroscopy and thermal gravity analysis characterizations.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Owing to its unique mechanical characteristics, excellent electrical conductivity and large surface area, graphene has been used not only as an excellent layered material, but also as a scaffolder or a doped component composited with micro-/nano-architectures to form three-dimension (3D) structures with versatile functions [1]. Recently, many attempts have been made to assemble two-dimension (2D) graphene sheets into 3D graphene structures for promising applications in many areas including supercapacitor [2–5], conductor [6], energy storage and conversion [7], lithium ion batteries [8], field-effect transistor biosensor [9], catalysis [10], strain sensing [11], and environment [12,13]. The assembled 3D graphene materials may not only provide inherently excellent properties of 2D graphene sheets, such as high electronic, optical and catalytical properties, but also exhibit huge specific surface area (SSA), strong mechanical strength, high electron conductivity and fast mass transport kinetics [14].

As a novel kind of functional materials, the methodology for preparing 3D graphene materials has triggered tremendous interests. Until recently, a number of synthetic methods to fabricate 3D graphene materials are mainly based on the direct growth from carbon sources or by the assembly of GO/graphene sheets. Typical methods include template-guided approach [15], evaporation induced self-assembly [16], Breath-figure-templated assembly

[17], layer-by-layer deposition [18], chemical vapor deposition (CVD) [19,20], electrochemical or hydrothermal reduction [21–23]. Synthesis routes and applications of 3D graphene materials have been summarized in detail in several specialized reviews [14,24,25].

For 3D graphene, one of very important properties is the SSA. Although great progress has been made to improve the SSA of 3D graphene materials, a high SSA is always prerequisite for their wide applications in gas adsorption, catalyst, sensor and supercapacitor. A number of 3D porous graphene materials with high SSAs have been fabricated using different synthetic techniques in recent several years. Burress et al. [22] prepared porous GO frameworks with a maximum SSA of 470 m^2/g via a solvothermal reaction. Worsley et al. [26] reported the GO-R/F aerogel formed via an organic sol-gel reaction and a supercritical CO_2 drying with a high SSA of 584 m^2/g. Chen et al. [27] synthesized 3D microstructured graphene foams through a template-directed CVD approach and obtained a high SSA up to 850 m^2/g. Zhang et al. [28] prepared a self-assembled 3D porous reduced GO hydrogel by a one-step hydrothermal method with an SSA of 964 m^2/g. Despite these progresses, simple and facile preparations of 3D graphene materials with a high SSA continue to be a hot topic which attracts more and more researchers to focus on due to the wide and promising applications of these materials.

In this work, we propose new preparation methods for 3D graphene aerogel and graphene nanowalls. The synthesized 3D graphene structures have a high SSA up to 795 m^2/g and a uniform pore size distribution. The synthetic methods to fabricate 3D graphene structures are quite simple and convenient.

---

2. Materials and methods

2.1. Materials

GO was purchased from the Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences with a purity >99 wt% and an element component of 68.44 wt% C, 30.92 wt% O and 0.63 wt% S. GO has a thickness of 0.87 ± 0.32 nm, a layer number less than 4 and a lateral diameter varying from 0.5 to 3.0 μm. All other chemicals were purchased from commercial sources (Sigma-Aldrich and Alfa Aesar) and used without additional purification and refinement.

2.2. Instrumentals

Atomic force microscopy (AFM) measurement was performed using Dimension Edge (Bruker Corporation). Thermogravimetry analysis (TGA) was executed using TGA/DSC1 STARe System (Mettler Toledo) at a heating rate of 10 °C/min from 25 to 800 °C under a nitrogen atmosphere. Raman spectroscopy was measured via Raman spectrometer (Renishaw inVia ManualWiRE3.4) with 532 nm laser. Powder X-ray diffraction (XRD) analysis was carried out on a PANalytical Empyrean equipped with a PIXcel 1D detector (Cu Kα radiation, λ = 1.5406 Å). The operation voltage and current are 40 kV and 40 mA, respectively and the 2θ angle ranges from 5° to 50° with a step size of 0.0131°. The N_2 sorption BET (Brunauer Emmett Teller) analyses of the specific surface area, pore size distribution and total pore volume data were performed by BEL Belsorp-max at 77 K. All samples were degassed under vacuum at 180 °C for 10 h prior to BET analysis. Scanning electron microscopy (SEM) measurements were performed using JSM-7800F at 10 kV. XPS analysis was conducted using Kratos XSAM800 spectrometer with Al monochromatic source operated at 12 kV. Electrical conductivity and I-V mersurements were conducted by Keithley 4200-SCS semiconductor characterization system.

2.3. Synthesis of graphene aerogel

For the synthesis of self-assembled reduced graphene oxide (RGO), we adopted a direct hydrothermal reduction method similar to previous reports [5,22,23,29]. GO powder was first added into 40 mL deionized water (18.2 MΩ) and the dispersion was sonicated in an ultrasonicator surrounded by an ice bath with a power of 600 W for the duration of 1 h to form a uniform suspension. To check the effect of the sonication process on GO sample, the lateral size and the thickness of GO sheets in the suspension were measured using AFM in the tapping mode to be 0.5 ± 0.2 μm and 0.53 ± 0.18 nm, respectively, which indicates the GO sheets have a prominent reduction in the size and thickness after sonication treatment. Subsequently, the suspension was sealed in a 50 ml Teflon-lined autoclave and maintained at 180 °C for 12 h. Then the autoclave was naturally cooled to room temperature to produce the self-assembling RGO hydrogel (SRH). Lastly, the resultant SRH was tert-butanol freeze-dried [30,31] for a week to remove the impurities and water and to obtain the dried graphene aerogel (GA). To verify the performance of the tert-butanol freeze-drying, the SRH sample treated by the conventional freeze-drying was also obtained for comparison.

2.4. Synthesis of graphene nanowalls from GA

Graphene nanowalls (GWs) were prepared using a tube-style radio frequency plasma enhanced chemical vapor deposition (RF-PECVD) system [9,19,20,32]. After pulverized, GA synthesized above was placed on the substrate of Quartz boat into the center of a quartz tube. The furnace was heated to 750 °C. Under a base pressure of 50 Pa, a mixture gas of 60% CH_4 and 40% H_2 was introduced into the chamber with an RF power of 300 W. The GWs' growth was maintained for 3 h.

3. Results and discussion

3.1. Influence of GO concentration on SSAs of GA structures with different freeze-dryings

SSA is one of the most important parameters for 3D porous materials. It has been reported in previous studies that there are a few factors to influence the SSAs of 3D graphene structures. One of these factors is the concentration of GO dispersed in solution. To obtain GA sample with a high SSA, a series of GO concentrations varying from 2 to 10 mg/mL were attempted and the SSAs of the generated GA samples at different GO concentrations were measured via the BET analysis. Fig. 1 shows the variances of SSAs and the pore volumes for the GA samples obtained via the conventional and tert-butanol freeze-dryings with the GO concentration. It can be seen that there is an optimal GO concentration of 6 mg/mL to synthesize GA structures by both conventional and tert-butanol freeze-dryings and highest SSAs of 428 and 722 m^2/g are obtained, respectively. This is easily explained that at the low GO concentrations, the self-assembling of GO cannot form large and stable structures in solution, which leads to small SSAs of the GA products. While at too high GO concentrations, the formed pores are squeezed due to the increased density of GO, which results in the decrease of SSAs.

From Fig. 1, it also can be seen that the SSAs of GA from the tert-butanol freeze-drying are almost twice of those of GA from the conventional freeze-drying at different GO concentrations, which confirmed the tert-butanol freeze-drying is necessary to help to improve the SSAs of 3D graphene structures. The reason is that when the self-assembled RGO hydrogel is freeze-dried by solvent-exchange with tert-butanol, the tert-butanol in RGO will form acicular crystals which have weak surface tension ready for solvent sublimation and a much improved specific surface area of GA can be obtained in comparison to the conventional water freeze-drying [31]. Furthermore, the total pore volumes of GAs from the conventional and tert-butanol freeze-dryings are 0.242 and 2.046 cm^3/g, respectively via BET analysis. There is 8.5 times improved using the tert-butanol freeze-drying. In the following discussion, all of the 3D graphene samples were prepared at the optimal GO concentration and GA was treated via the tert-butanol freeze-drying, unless specially stated otherwise.
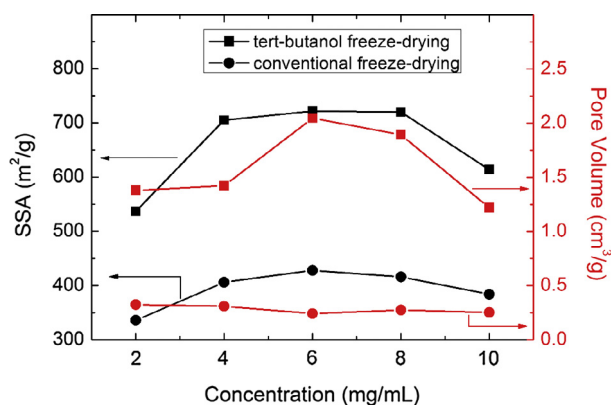

Fig. 1. GO concentration dependent SSAs and pore volumes of GA samples prepared from two different freeze-dryings.