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One-pot synthesis of 3D framework graphene via electrochemical method

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ABSTRACT

A one-pot approach of producing three-dimensional (3D) framework graphene was reported. The proposed method is based on exfoliation and reduction of graphite oxide in electrochemical reaction using pulse wave. The formation mechanism of 3D framework graphene has been investigated. The results show that graphene dendrite firstly found in our article were used as building blocks, the growing evolution of which might follow the pattern of deposition of the diffusion-limited aggregation (DLA). The flexible graphene dendrite in different structural levels overlapped or coalesced with each other, resulting in formation of cross-linking 3D framework ultimately. The 3D framework graphene as an electrode material exhibits high specific capacitance (140 F/g at 5 A g^{-1}) in an aqueous electrolyte.

1. Introduction

Graphene, a two-dimensional (2D) one-atom thick carbon, has attracted increasing attention in the past several years, mainly due to its outstanding electronic, thermal, and mechanical properties [1–4]. Furthermore, graphene has potential applications in various fields such as field-effect devices [5], energy-storage materials [6], and electrocatalysis [7].

Recently, in order to fully utilize and further explore new functions of graphene, the construction of 3D framework graphene using graphene sheets as building blocks has been extensively studied [8–10]. Taking advantages of both the graphene composition and the pore structures, 3D framework graphene materials have great application potentials in various fields [11–13]. It has been reported that this structure with unique performance can be constructed by certain methods. For example, Cheng et al. reported the direct synthesis of 3D foam-like graphene macrostructures, by template-directed chemical vapor deposition [11]. Wang et al. synthesized the 3D self-assembly of single graphene oxide sheets assisted by noble metal nanoparticles [12]. Shi and coworkers demonstrated the formation of 3D graphene hydrogel by a hydrothermal method [13].

In this paper, a green and facile strategy is reported for the fabrication of 3D framework graphene. The proposed method is based on exfoliation and reduction of graphite oxide (GO) in electrochemical reaction using pulse wave. Our approach exhibits several distinctive features over the previously reported strategies, which makes it rather attractive for practical applications: (1) It is environmentally friendly and does not need a complex procedure. (2) The exfoliation and reduction of GO were achieved simultaneously. (3) 3D framework graphene is constructed by graphene dendrite in different structural levels. Few literatures about graphene dendrite can be found in previous reports. Electrochemical reaction is normally used to synthesize graphene or graphene quantum dots. However, in our study, we used this method for constructing the 3D framework graphene. The main cause was that alternating current rather than direct current was applied. Alternating current made the graphene oxide sheets deposit onto the electrode fewer, meanwhile,it produced overpotential. The propagation process would form a dendritic structure when the exerted overpotential exceeded a critical value. The flexible graphene dendrite overlapped or coalesced with each other, ultimately resulting in the formation of cross-linking 3D framework.

2. Experimental

The GO was prepared according to the method developed by Hummers' and Offemann [14]. Fig. 1 shows the setup of the electrochemical reaction. The signal from the generator was amplified by the power amplifier and applied on the electrodes in GO aqueous dispersion, which was monitored by oscilloscope. Copper electrodes were used in the experiment. The electrode separation was 20 mm. 50 mL GO aqueous dispersion (0.5 mg mL^{-1}) was loaded in a 75 mL glass container. A pulse signal whose frequency, duty ratio and peak-to-peak voltage (V_{pp}) were 0.5 Hz, 20% and 60 V, respectively, was applied. 120 min later, the reaction product on the electrode was taken out and freeze-dried in vacuum.

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3. Results and discussion

The reduction of GO could be confirmed by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Fig. 2A and B shows the C 1s XPS spectra of GO and reaction product (graphene) separately. Four different peaks centered at 285 eV (C–C), 286.5 eV (C–O), 287.5 eV (C═O) and 288.9 eV (O═C–OH) were detected in GO sample.

After reaction, the intensities of all C 1s peaks of the carbons binding to oxygen decreased obviously, revealing that most oxygen-containing functional groups were removed.

As shown in Fig. 2C, GO exhibited a very sharp diffraction peak at $2\theta = 11.4^{\circ}$. After reaction, the regular stacks of GO were destroyed and their diffraction peaks became weak or even disappeared. Meanwhile, a new peak of graphene at $2\theta = 23.9^{\circ}$, weak and broad, was observed as the inset exhibits, indicating that graphene existed individually and highly disorderly in single or few layers [15]. The reduction of GO was also characterized using Fourier transform infrared (FT-IR) spectroscopy. As shown in Fig. 2D, after reaction, the intensities of the FT-IR peaks corresponding to the oxygen functionalities decreased dramatically, such as the C═O stretching vibration peak at 1720 cm^{-1}; the vibration and deformation peaks of O–H groups at 3395 cm^{-1} and 1410 cm^{-1} respectively; and the C–O–C stretching vibration peak at 1060 cm^{-1}. However, a new peak corresponding to C═C stretching vibration at 1500 cm^{-1} was observed as the inset exhibits, indicating simultaneous restoration of the sp^2-hybridized carbon network of graphene. It means that GO had been successfully reduced. Optical observation was also a direct way to see the changes in GO before and after reaction as shown in Fig. 3a (left: GO; right: graphene).

The GO was not only been reduced but also been exfoliated in the condition of the pulse electrical field. The exfoliation of GO could be confirmed by atomic force microscopy (AFM) as shown in Fig. 3b. It presented a relative smooth planar structure with an average thickness of 0.9 nm. In addition, a unique morphology of porous graphene dendrite was found, which looked like snowflakes. The microstructure of graphene dendrite was also demonstrated by their optical microscopic images (Fig. 4). It reflected that 3D framework graphene was constructed by graphene dendrite in different structural levels.

Fig. 4 shows optical microscopic images of graphene dendrite growing on the electrode at different times. The morphology is analogous to metal dendrite which has been prepared in previous reports[16]. The overpotential plays a crucial role in determining metal dendrite morphology [17]. The theory of diffusion-limited aggregation (DLA) was used interpret this phenomenon [18]. In our study, the graphene dendrite was not formed on the electrode when applied the applied potential was less than 37 V. This result revealed that the overpotential also played a important role in our research. Growing evolution of graphene dendrite might follow the pattern of DLA like

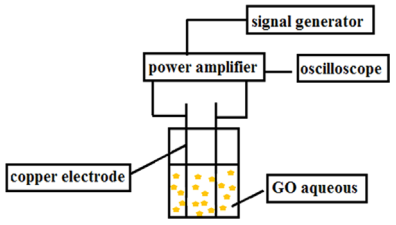

Fig. 1. The setup of the electrochemical reaction.

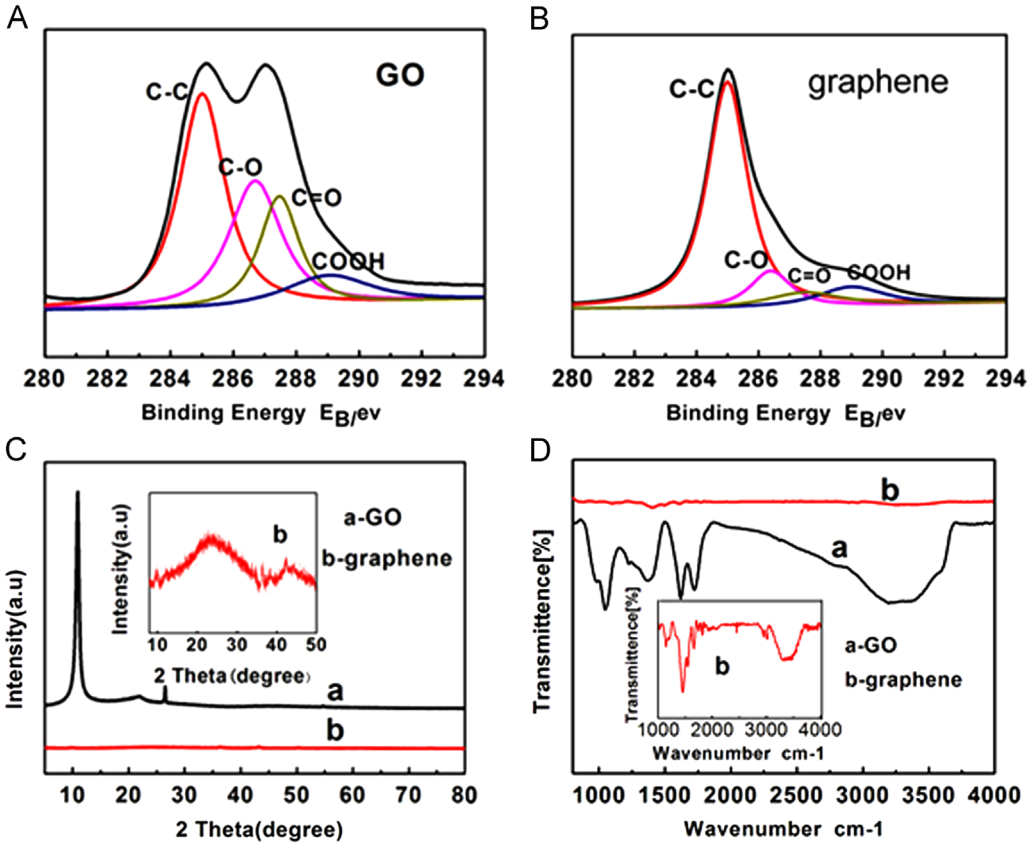

Fig. 2. XPS spectra of C 1s of GO before (A) and after (B) electrochemical reaction (graphene), XRD (C) and FT-IR (D) spectra of GO before and after electrochemical reaction (graphene).