Synthesis of three-dimensional graphene architectures by using an environmental-friendly surfactant as a reducing agent

Bingying Gao, Mulenga Kalulu, Olayinka Oderinde, Jing Mei, Lili Ren[*]

School of Chemistry & Chemical Engineering, Southeast University, Nanjing, 211189, China

ARTICLE INFO

ABSTRACT

Polyvinylpyrrolidone (PVP) modified reduced graphene aerogel (PVP-GA) was prepared through hydrothermal reduction and chemical reduction of graphene oxide (GO) in the presence of PVP. The structure of PVP-GA was characterized using XRD, FTIR, SEM, TEM and BET specific surface area. The results showed that GO was reduced effectively in the presence of PVP and the PVP molecules were absorbed onto the basal plane of reduced graphene oxide (rGO) through non-covalent interactions. The preparation process was carried out in aqueous media at 120 °C for 10 h without using any toxic reducing agent, thereby making it a facile, environmental-friendly and economical approach for the synthesis of a three-dimensional (3D) interconnected graphene macrostructure. The as-prepared monolithic 3D graphene exhibits a loose and high porous structure, which may find potential applications for adsorbent, shock absorber, catalyst carrier and hydrogen storage materials. In addition, it confirmed that simultaneous hydrothermal reduction and chemical reduction routes would be of value for preparing 3D nonporous graphene-based materials via the use of cheap and environmentally-friendly PVP as a reducing agent.

© 2017 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Graphene, a flat monolayer of carbon atoms packed into a two-dimensional (2D) honeycomb lattice, possesses extraordinary chemical and physical properties [1,2] and extensive potential applications in nanoelectronics, energy storage and conversion, chemical and biological sensors, composite materials and biotechnology [3,4]. However, the applications of graphene-based materials in energy, environment, sensing and biological fields commonly require assembly of small 2D graphene sheets into three-dimensional (3D) architectures [5—9]. Li and Shi reported that the 3D graphene architectures not only possessed the inherent properties of graphene but also exhibited enhanced functions resulting from their unique microstructures [9]. In other words, the 3D architectures fabricate graphene nanosheets into macroscopic materials for practical applications. Hence, the self-assembly of graphene into a macroporous 3D structure has attracted increasing attention during the past years and considerable progress has been achieved recently [4—9], even though till now, tremendous efforts have been devoted to develop strategies for the assembly of graphene into 3D aerogels [10—12]. The assemblies of 2D graphene sheets into 3D structures have been prepared through four strategies namely chemical vapor deposition (CVD) [13,14], hydrothermal treatment [15], cross-linking [16—20] and chemical reduction [21,22] methods. In

the first strategy, where CVD method was employed, high temperature (700–900 °C) and harsh atmospheric conditions were required, which has great limitations and thus a great difficulty to realize large-scale production. The second strategy, using hydrothermal treatment, which is also an attractive technique to prepare 3D graphene materials was first reported by Shi and co-workers and was explained using the strong $\pi-\pi$ interactions between thermally reduced GO sheets [15]. However the 3D graphene structure prepared by the hydrothermal method resulted in a weak gel having a low mechanical performance [21]. Until recently, the fabrication of 3D porous graphene materials via hydrothermal reduction of GO has been reported by several groups [5,23,24], for example, Wang et al. prepared rGO aerogels via hydrothermal process with the assistance of noble-metal nanocrystals [23]. The third strategy utilized cross-linking agents such as poly(vinyl alcohol) [25,26], chitosan (CS) [27], cellulose [28], poly(N-iso-propylacrylamide) [29] and epoxy resin [30] to produce 3D structures. The mechanical strength of the graphene aerogel could be improved significantly due to the presence of cross-linking agent. Poly(vinyl alcohol) (PVA), a water-soluble polymer, was first reported as a cross-linking agent to enhance the interactions between 2D GO sheets, thereby promoting GO gelation [26]. Mixing GO and PVA aqueous solutions followed by shaking for 10 s and subsequent sonication for 20 min resulted in the formation of a GO/PVA hybrid hydrogel. The strong hydrogen bonding interaction between hydroxyl-rich PVA chains and oxygen-containing groups on GO sheets was reported to account for formation of the cross-linking sites, from where a stable GO composite hydrogel was generated. Further research confirmed that DNA [20], proteins [31], synthetic polymers with cationic charges and hydrogen bonding acceptors [32,33], small quaternary ammonium salts and metal ions [32] were all efficient cross-linkers for GO gelation, which could regulate the delicate balance between electrostatic repulsion, hydrophobic interactions and hydrogen bonding of GO-based colloid systems. Finally, with the impressive advantages, the chemical-reduction-induced self-assembly method has attracted many attentions due to the facile synthetic conditions, low requirement of equipment and convenience for mass commercial production of 3D graphene aerogels with good solution processability or high conductivity. During this approach, GO is reduced in the presence of reducing agents, in which in-situ reduced graphene sheet can spontaneously self-assemble into a 3D graphene architecture through $\pi-\pi$ interactions. Zhang et al. reported that graphene aerogel could be successfully prepared by using L-ascorbic acid as a reducing agent at mild condition [21]. However, the use of chemical reduction reagents such as hydrazine [34], hydroiodic acid (HI) [35], $NaBH_4$ and Na_2S [36,37], or some organic polymers and biocompatible molecules such as vitamin C [21] and dopamine [38] also have several limitations including toxicity, corrosiveness, relatively expensive and non eco-friendly. Therefore, there is still a challenge to develop a green approach to fabricate environmental-friendly 3D graphene aerogels under mild conditions with low-cost by adopting a non-toxic and cheap reducing agent.

Polyvinylpyrrolidone (PVP), an environmental-friendly, low-cost and amphipathic polymer has been widely used in pharmaceutical, biological and chemical species owing to its specific formation, excellent physical and chemical properties [39]. It has been reported that hydrophilic GO can form hydrogen bond with PVP, which provided an effective way to change the surface properties of GO [40]. In addition, there are limited reports about using surfactants as reducing agent to reduce GO and induce the self-assembly of graphene sheets to construct 3D architectures. We can consider combining PVP and GO to prepare composites, whose properties can be utilized to obtain different types of promising materials. The function of PVP was used as a structure-directing agent in controlling particle and shape of nanomaterials [41].

In this paper, we report a universal, green and low-cost approach to fabricate 3D graphene materials, which is based on the chemical reduction and self-assembly of GO with the aid of an environmental-friendly and cheap organic polymer, PVP. PVP plays multifunctional roles in the fabrication of 3D graphene, which acts not only as a GO reductant, but also possibly as a template during the self-assembly of graphene sheets into a 3D architecture, which is due to the presence of strong $\pi-\pi$ interactions and hydrogen bond between GO and PVP to form a network in solution. The as-prepared 3D PVP-GA has a loose and porous structure, which should be a promising candidate for efficient adsorbents in pollutant treatment. Moreover, the fabrication process does not involve toxic agent and complex synthesis procedure, hence the facile solution-processed method should be a promising candidate for fabricating other 3D carbon materials.

Experimental methods

Materials

Graphite powder and polyvinylpyrrolidone (PVP, K-30) were purchased from Shanghai Aladdin Chemical Reagents Company (China). Concentrated sulfuric acid (95–98%), hydrogen peroxide (H_2O_2), sodium nitrate, ethyl alcohol (EtOH), concentrated hydrochloric acid (36–38%), and potassium permanganate were analytically pure and bought from Sinopharm Chemical Reagent Co. Ltd. Unless otherwise specified, all other chemical reagents were of analytical grade and used as received without further purification. Deionized water was used in all experiments.

Fabrication of PVP-GAs

Graphene oxide (GO) was prepared from natural graphite by modified Hummer's method [42]. In a typical procedure, GO (0.2, 0.4 g) was first dispersed in 100 mL of deionized water by sonication for 30 min to form a homogeneous dispersion. Then a certain amount of PVP solution (9, 15 mg mL^{-1}) was added to the homogeneous dispersion of GO and the solution was mixed with constantly stirring for 20 min. The obtained mixture was sealed in a Teflon-lined autoclave by gradient hydrothermal process. Specifically, the mixture was firstly heated at 65 °C for 0.5–0.7 h, then heated at 95 °C for 1 h, and finally heated at 120 °C for 12 h. After hydrothermal reduction, the graphene hydrogel (PVP-GH) obtained was freeze-dried for