

Low Temperature Casting of Graphene into Various 3-D Shapes

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Abstract—Here we report a pH-mediated hydrothermal reduction method that combined with moulding methods, realizing fabrication of ultrahigh density graphene macrostructures with various shapes. This ‘compact graphene’ (CG) has a compressive strength of 361 MPa (6 times higher than conventional graphite products) and an excellent electrical conductivity. The processing steps are scalable and may contribute to new products. CG structures may be an ideal irradiation protection material for aerospace, atomic energy, and nuclear science due to its high density.

Keywords—graphene; compact graphene; casting; high density

I. INTRODUCTION

Graphene, a 2-dimensional, single-atom-thick layer of carbon, has attracted attention due to its fascinating properties such as high carrier mobility [1-3], high thermal conductivity [4, 5], extraordinary elasticity and stiffness [6], and other properties. While mechanical exfoliation, liquid exfoliation [7], and epitaxial growth [8] can produce pristine graphene, the yields are currently too low for large-scale production of macrostructures. In contrast, chemical reduction of graphene oxide provides “graphene” sheets in massive scale for graphene macrostructures [9-11]. Graphene-based macrostructures prepared to date have been relatively weak mechanically, given their flexible and often relatively porous or open structures, when compared with commercial graphite products. Achieving highly compacted and thus “fully dense” macrostructures based on graphene and measuring the physical properties of such material(s) is thus an important goal.

We present a new method to obtain high-density compact 3D graphene macrostructures (‘CG’) with various shapes, using a template-directed hydrothermal method from graphene oxide suspensions. The proposed method has many advantages compared to conventional strategies for forming 3D shapes with graphite powder, *e.g.*, forming of the desired macrostructure in one step, low-cost, time- and energy-saving, and low-temperature processing (180 °C). Moreover, our CG macrostructures have high density and a compressive strength of 361 MPa (over 6 times that of conventional graphite products), and thus can be expected to create new applications for graphene.

II. FABRICATION OF COMPACT GRAPHENE

A. Preparation of graphite oxide

GO was prepared by a modified Hummers method [12]. While maintaining agitation, expandable graphite powder (2 g) and sodium nitrate (1 g) were mixed with sulfuric acid (46 ml, 98 wt%) in an ice bath, and potassium permanganate (6 g) was slowly added to prevent the temperature from exceeding 20 °C. The reaction was kept at 35±1 °C for 8 h with gas release, and then deionized water (92 ml) was gradually added, bringing about violent effervescence. The temperature of the water bath was increase to 98 °C and the reaction was maintained for 15 min in order to increase the oxidation degree of the GO product. The resultant bright-yellow suspension was diluted with deionized (280 ml) water and further treated with a H₂O₂ solution (6 ml, 30%). The product was separated by centrifugation, washed with 5% chlorhydric acid (HCl) solution for 7 times until sulphate could not be detected with BaCl₂, then also washed 7 times with distilled water aiming at removing chloride ion. Then it was dried in an air oven at 60 °C overnight.

B. Fabrication of compact graphene

Colloidal dispersion of GO was hydrothermally reduced in dH₂O with different amounts of ammonia. In each case, 57 mg of graphite oxide was dispersed in 35 ml dH₂O with ammonia (25-28 v/v%) followed by sonication for 15 min. Dark brown colloidal dispersion was transferred to a sealed reactor which was then heated to 180 °C for 15 h. After heat treatment, the reactor was left to room temperature. In order to fabricate castings, plastic containers with complex shapes were designed. The reduced graphene suspension was moulded in the container and was treated in an air drier at 32 °C for at least 15 h to completely dry the casting.

III. RESULTS

The synthesis of CG is described as follows: Graphite oxide powder was dispersed in ultrapure water and sonicated, forming a brown colloidal aqueous dispersion of graphene oxide (GO) platelets. The colloid was transferred to a sealed reactor, ammonia or NaOH was added and the reactor heated sufficiently to remove many of the functional groups of GO, reducing GO into reduced graphene oxide (rGO) platelets, which we hereafter refer to as “graphene”. Graphene gel was

then taken out of the reactor and dried at a temperature slightly

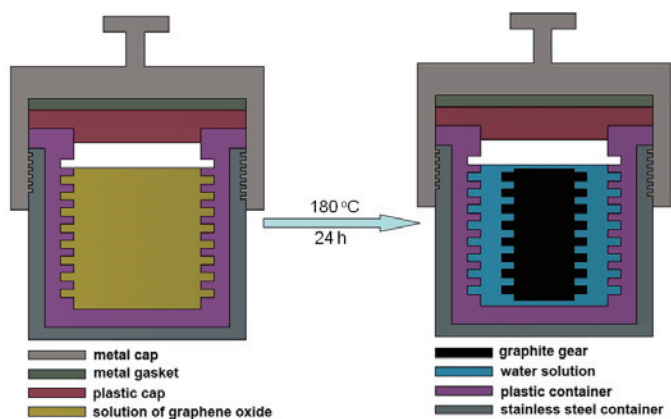


Fig. 1. Schematic diagram of graphene casting. G-O platelets are casted into a screw stem under the influence of temperature, pressure, and the container shape.

higher than room temperature. Fig. 1 illustrates the process of casting of such graphene platelets, where the dispersion of GO platelets was placed into a screw-like, sealed container and reduced at 180 °C, after which it is black or dark grey. The resulting graphene gel was formed into a screw stem. For clarity, CG with the proper, excess, and no ammonia content were abbreviated as CGP (pH=10.1), CGE (pH=11.6), and CGN (pH=5.5), respectively. When the wet gel was taken out of autoclave, and dried at temperature of 60 °C for 15 h, the gel became a compact graphene which kept its original shape of wet gel (Fig. 2).

“Graphene castings” can be easily produced by this approach compared to other methods. Different castings were made, e.g., triangular prism, quadrangular prism, joint ring, crucible, screw stem, and gear, as shown in Fig. 3. The sizes of castings range from sub-millimeter to sub-meter, depending on the moulds and the concentrations of GO dispersion. In order to be transformed into malleable graphene gel, the requirement of lowest GO concentration should be 0.5 mg/ml [13].

In order to clarify the relationship between pH and mechanical property of CG, scanning electron microscopy (SEM) was applied to study the surface morphology and structure of cross-section (Fig. 4). Images of the surfaces of CG demonstrated the importance of pH. Rugged CGN surface accompanied with pits throughout the surface (Fig. 4a). There were also many but smaller protuberances on the surface of CGE (Fig. 4c), which may imply the fact that a great deal of ammonia vapor had escaped from graphene gel during solidification. Contrarily, CGP appeared a smooth surface (Fig.

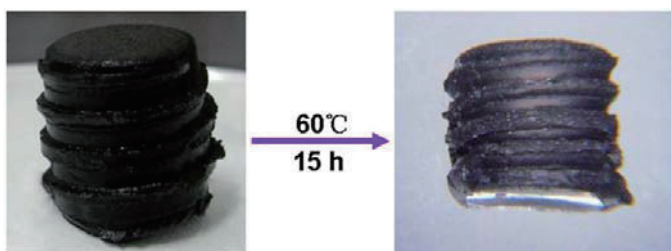


Fig. 2. The wet graphene gel can be shrunk into compact graphene after drying at temperature of 60 °C.

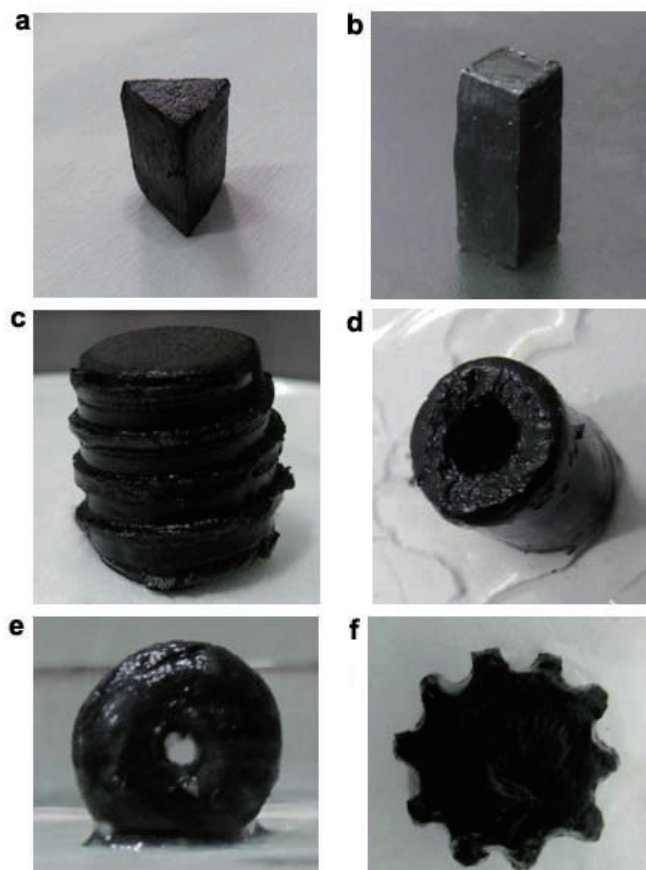


Fig. 3. Different castings of the graphene before drying. (a) triangular prism. (b) quadrangular prism. (c) screw stem. (d) crucible. (e) joint ring. (f) gear.

4e). Similar phenomenon was also observed in the digital photographs. Figs. 4b and 4d demonstrated that either shortage or excess of ammonia lead to the formation of holes and cracks within the CG during agglomeration of graphene sheets. These imperfections could decrease density, compressive strength and conductivity. A dense structure of CGP without apparent imperfection can be acquired with a proper pH (Fig. 4f). Comparisons among the cross-sections of the three CG further proved that the quantity of ammonia, in another word the pH, played a critical role during the agglomeration of graphene sheets, and had further impact on the performance of CG.

During the repetitive synthesis of CG, the impact of pH to the physico-chemical quality of castings has emerged. Relationships between compressive strength, conductivity and pH have then been studied. In this section, CG were obtained from graphene oxide dispersions with different pH values adjusted by ammonia (pH 5.5~10.1) or sodium hydroxide (pH 10.7~11.6). The details were shown in Table 1. The compressive strength of CGN (pH=5.5, 135MPa) was apparently smaller than that of CGP (pH=10.1, 361 Mpa), indicating the contribution of proper pH to improve compressive strength. According to the results, the CG would achieve maximum compressive strength when the pH of GO dispersion was adjusted to 10. Electrical conductivity of CG

was found greatly affected by pH as well. The maximum conductivity for CG (pH=10) is up to 7.6 S/cm, which was at least five times as great as that of CGN. And the value is very close to that of graphene foam [14].

In summary, a feasible method for CG fabrication has been developed, whose production showed that the pH of the graphene oxide dispersions a key factor which determined properties of its product. pH has a direct impact on surface topography, internal structure, thus electrical and mechanical

TABLE I. THE EFFECTS OF PH ON THE COMPRESSIVE STRENGTH AND ELECTRICAL CONDUCTIVITY

pH	Compressive strength (MPa)	Electrical conductivity (S cm ⁻¹)
5.5	135	1.5
7.7	150	2.7
8.5	220	3.5
9.4	248	6.8
10.1	361	7.6
10.7	30	2.1
11.6	18	1.9

compressed and super strong three-dimensional macrostructures based on graphene.

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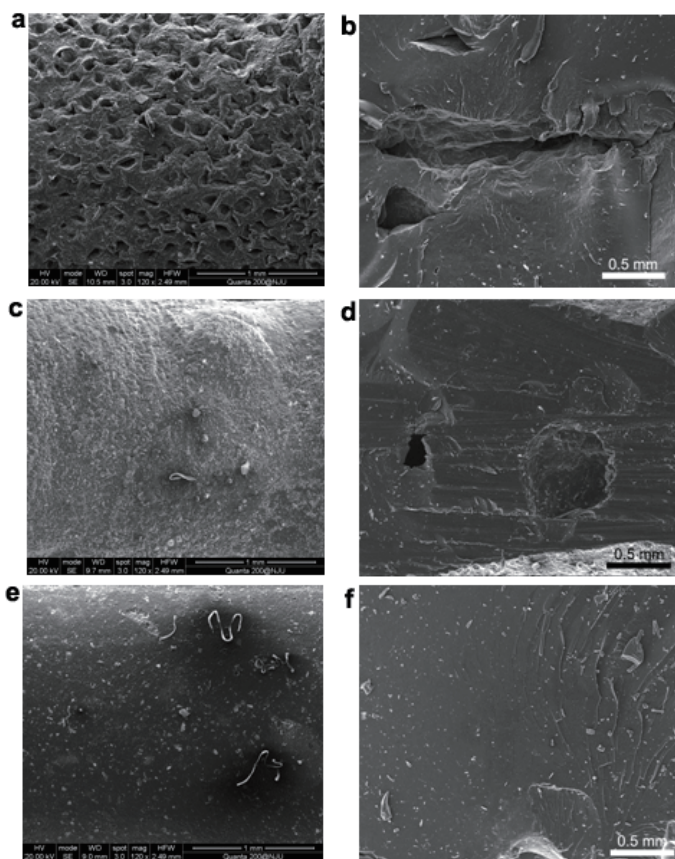


Fig. 4. SEM images of surface and cross-section of CG. (a) CGN, rough surface, holes could be observed. (b) CGN, holes and cracks inside. (c) CGE, rough surface, protuberances could be observed. (d) CGE, imperfections were observed. (e) CGP, smooth surface was produced when pH=10. (f) CGP, graphene sheets combined solidly. No imperfection was found in this case.

properties of the CG. CG has the best structure and properties when the pH of reaction was adjusted to 10, *i.e.*, smooth surfaces, dense internal structures, good electrical conductivity, and high compressive strength. Even the density, compressive strength, and electrical conductivity have been further improved (2.31 g/cm³, 361 MPa, and 7.6 S/cm, respectively) by high temperature annealing at 900 °C. All these parameters were far higher than conventional products, e.g. isotropic graphite. Meanwhile, the proposed method tended to be low-cost, environment-friendly, and energy-saving. CG have been proved a great potential to be applied to a wide range of fields from traditional graphite industry (graphite heaters, electrodes, and crystallizers) to aerospace, atomic energy and nuclear science. This work also pointed a new route to prepare highly

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