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Highly conductive, mechanically strong graphene monolith assembled by three-dimensional printing of large graphene oxide

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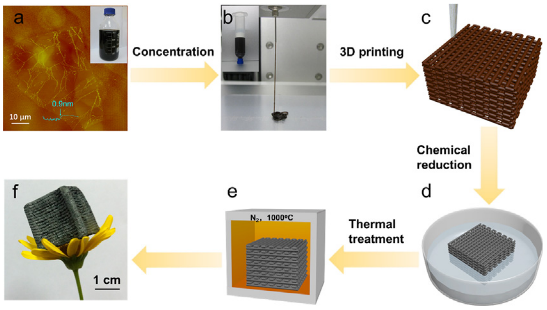
GRAPHICAL ABSTRACT



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ABSTRACT

The manufacturing of three-dimensional (3D) graphene monolith with high mechanical and electrical performance has become an urgent issue in view of their potential applications in energy and electronics fields. Due to the structure rigidity and poor liquid-phase processing capability of graphene sheets, it is challenging to fabricate 3D graphene monolith with high mechanical performance, including strength, toughness and resiliency. Graphene oxide (GO) shows an improved dispersibility and reduction-restorable conductivity, which enables it to effectively balance the processing and comprehensive performances of graphene monolith. Here, we demonstrate a strategy to fabricate high-performance, shape-designable 3D graphene monolith through a 3D printing method based on large-sized graphene oxide (LGO) fluid ink. The concentration of the LGO ink for printing is as low as 20 mg/mL. The resulting monolith exhibits low density (12.8 mg/cm^3), high electrical conductivity (41.1 S/m), high specific strength (10.7×10^3 N·m/Kg) and compressibility (up to 80% compressive strain). Such a 3D printing technique enables plenty of complicated monolith structures and broadens the application range of graphene.

1. Introduction

Over the past few years, there has been growing interest in manufacturing three-dimensional (3D) graphene structures because of their prospective applications, including supercapacitors [1,2], battery electrodes [3,4], contaminants absorption [5,6], electromagnetic shielding [7] and so on. For these functionalities, low density, high mechanical stability and electrical conductivity are essential requirements. To fully exploit the inherent properties of graphene, it is important to establish an effective approach that can transform individual graphene sheets into desired 3D macroscopic structures.

The most used routes to produce 3D graphene structures can be divided into three categories, including chemical vapour deposition (CVD) on metallic foams [8], freeze-casting methods [9,10] and hydrothermal processes [11,12]. However, these methods cannot

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effectively tune the mechanical, electrical properties and change the macrostructures for specific applications. Generally, 3D graphene monolith made by CVD-based methods exhibited high conductivity but poor mechanical properties, while the geometry of the graphene monolith prepared by the freeze-casting method is not easily controlled. Hydrothermal methods can be used to prepare 3D graphene monolith with different shapes by changing the container shape, but the final products always exhibited low mechanical strength [13]. It is thus urgent to develop simple, template-free and cost-effective processing methods that can construct highly conductive, mechanically strong and shape designable 3D graphene monolith. Recently, an extrusion-based direct ink writing (DIW) 3D printing technique has emerged as a hot field for preparing graphene monolith. For such 3D printing, the essential prerequisite lies in developing printable graphene ink; the latter would possess a proper thixotropic (shear-thinning) behavior and viscoelastic characteristics. To this end, the previous studies have tuned the rheological behavior of graphene ink primarily through adding either polymer additives [14,15] or silica nanoparticles [16]; however, this usually complicates the preparation process. Increasing the concentration of GO solutions (e.g., 80 mg/mL) [17] can avoid the use of additional additives such as polymers or nanoparticles, but concentrating GO solutions practically is a time-consuming process due to the occurrence of gelation. In addition, a synchronous freeze casting technique has been demonstrated to allow 3D printing of low concentration GO suspensions (e.g., 10 mg/mL) [18]. However, such synchronous freeze casting could be hard to implement in practical operations. Apparently, it is critical how to construct printable graphene or GO ink in a simple, cost-effective manner.

It has been demonstrated in our previous study [19] that large GO sheets (LGO) can form gel even at the concentration as low as 5 mg/mL, this provides a possible solution for room-temperature 3D printing without additional additives or freeze operations. Different from small GO sheets (SGO), LGO sheets have lower inter-sheet contact resistance and better stress transfer efficiency [19], which are important for improving the mechanical and electrical properties of 3D monolith. In this work, we employ low-concentration LGO solutions to print shape-designable, highly conductive and mechanically strong graphene monolith. Different from the ink based on SGO solutions, typically requiring 80 mg/mL, LGO solutions can be printed at a much lower concentration (20 mg/mL). The resulting monolith exhibits intriguing comprehensive performance: low density (12.8 mg/cm^3), high electrical conductivity (41.1 S/m), specific strength (10.7×10^3 N·m/Kg) and compressibility (up to 80% compressive strain). Such LGO-based ink opens a promising door for 3D printing of high-performance graphene monolith that can be applied in energy and electronics fields.

2. Experimental

2.1. Materials

Natural graphite flake (~500 μm) was purchased from Sigma. Concentrated sulfuric acid (H_2SO_4, ~98%), hydrochloric acid (HCl, 36.5%), hydrogen peroxide (H_2O_2, 30%) and potassium permanganate ($KMnO_4$) were purchased from Jiangsu Tongsheng Chemical Co., Ltd. Chromium Oxide (CrO_3) and hydroiodic acid (HI, 55%) were obtained from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received without further purification.

2.2. Preparation of LGO and SGO sheets

The synthetic procedures of LGO sheets were according to our previous report. In a typical experiment, graphite (1 g) and CrO_3 (8.5 g) were added into 7 mL of concentrated HCl solution. The mixture was stirred at room temperature for 2 h to obtain the graphite intercalation compound (GIC) flakes. Then the washed GIC flakes were immersed in 40 mL of H_2O_2 at room temperature for 20 h to obtain the wet chemically expanded graphite (CEG). For oxidation, $KMnO_4$ (2 g) was gradually added into 40 mL of concentrated H_2SO_4 in ice-water bath during 30 min, and then the CEG was added. After reacting for 4 h at 35 °C, the grey black mixture was poured into ice water and then H_2O_2 was added to decompose the insoluble manganese salts. Chemically expanded graphite oxide (CEGO) particles suspended in solution were obtained. After 4–5 times' washing by distilled water, the resulting CEGO particles can be exfoliated thoroughly by magnetic stirring for 30 min at 300 rpm to obtain stable LGO dispersion (about 2 mg/mL).

The SGO sheets were obtained through ultra-sonication of the LGO sheets. As the LGO dispersion (2 mg/mL) was subjected to sonication using an ultrasound probe (400 W, 20 kHz, with amplitude of 50% and a pulse of 5 s) for 1 h in an ice bath to break down the lateral size of LGO.

2.3. Preparation of GO ink

The as-synthesized LGO solution was concentrated to 60 mg/mL through distillation in a 60 °C water bath. The solid content of the concentrated solution was measured through freeze-drying method. Different concentrations of ink (5, 10, 15, 20, 30, 40 and 60 mg/mL) were obtained through diluting the higher concentration ink with certain amount of deionized water. In our study, the printable LGO ink had a concentration of 20 mg/mL, and the SGO ink with a concentration of 40 mg/mL was prepared in the same way.

2.4. Preparation of the graphene monolith through 3D printing process

3D printing was performed by a Biological 3D printer (Regenovo 3D Bio-Architect WS) with capability for programmable patterning in three dimensions built layer-by-layer. In our experiment, a 3D printing nozzle with diameter of 400 μm was used and the nozzle's moving speed was 10 mm/s. After printing, the printed structure was freeze-dried at −50 °C with a vacuum pressure of 0.6 Pa to remove the water solvent and maintain the 3D structure, as the obtained sample was called LGO. The reduction of LGO was divided into two steps, hydroiodic acid (HI) reduction and thermal annealing. For HI reduction, the monolith was immersed into the HI acid solution in a sealed container at 95 °C for 2 h. After reduction, the sample was washed by water and ethanol several times before vacuum-dried at 60 °C for 12 h, the resultant sample was called H-LGO. The H-LGO was then subjected to thermal annealing at 1000 °C in nitrogen to obtain T-LGO. The corresponding SGO, H-SGO and T-SGO monolith were prepared in the same way.

2.5. Characterization

Atomic Force Microscope (AFM) images of GO sheets were conducted in the tapping mode on a Multimode 8 model scanning probe microscope, for which the GO dispersion was drop-casted onto freshly cleaved mica surfaces. The microscopic characteristics of the GO sheets and monolith were carried out with an Ultra 55 mode field emission scanning electron microscope (FESEM), for which the GO solution (~0.02 mg/mL) were drop-casted onto silicon wafers. Rheological characterization of the ink was conducted with a Rotary rheometer (Thermofisher, HAKKE MARS III). A shear rate sweep was performed at 25 °C from 10^{-2} to 10^2 s^{-1} to measure their apparent viscosity. A stress sweep was performed at 25 °C from 10^{-1} to 10^3 Pa with a constant frequency of 1 Hz. X-ray photoelectron spectra (XPS) was performed on an AXIS UltraDLD system, operating at 150 W with Al Kα radiation (1486.6 eV).