



Controllable lateral contraction and mechanical performance of chemically reduced graphene oxide paper



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ABSTRACT

Graphene paper assembled from graphene oxide (GO) sheets has attracted great attention due to the intriguing physical and chemical properties. Here, we discovered that the size stability and mechanical performances of reduced graphene oxide (RGO) papers obtained by chemical reduction of the vacuum filtered GO papers are strongly dependent on the pH value of the starting GO suspensions. Moreover, it is found that RGO paper obtained from GO suspension with pH = 7 demonstrated superior performance of both flexural endurance and electrical conductivity. By investigating the structural differences of the prefabricated GO papers and their swelling behaviors during reduction, as well as the unlike microstructures of the obtained RGO papers, we interpreted the origin of the pH-mediated controllable contraction and mechanical performance of RGO papers. This study suggests a simple strategy for controlling the size stability, mechanical performance and electrical conductivity of RGO paper.

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1. Introduction

Graphene oxide (GO) is two-dimensional (2D) sheet with feature sizes at two distinct length scales like graphene [1]. In comparison with graphene which is chemically inert, GO is reactive with phenol hydroxyl and epoxy groups on the basal plane together with carboxyl and ionizable carboxylic acid moieties at the nano-sheet edge [2]. Benefiting from its molecular structure and morphological characteristics, GO presents on a unique anisotropic fashion for alignment, and special chemical properties that can be tailored to generate various graphene-based materials with structural specialities and functional novelties [3]. The difficulty of using pristine graphene nano-sheets as building blocks for the macroscopic assembly because of its low dispersibility in almost all of solvents, has led to the employment of GO as an ideal alternative [2]. Fruitful progresses have demonstrated that GO sheets could be assembled into graphene-based fibers/ribbons [4–7], membrane or foil like papers [8–11], and monoliths with 3D interconnected networks via various solution processes [12–15].

Ever since the formation of GO paper by filtration was first

reported by Ruoff and co-workers [16], this simple and efficient technique has been preferentially adopted for fabricating graphene-based paper-like materials. GO paper possesses a lamellar ordering structure and tunable mechanical properties. By enhancing the hydrogen bonding interaction or introducing chemical cross-linking between GO sheets [17,18], the mechanical property of GO paper can be improved obviously. The latest work reported by Huang's group has demonstrated that the unintentional introduction of Al³⁺ contaminant during filtration, which could lead to the cross-linking between GO sheets, was responsible for both the appearance integrity of GO membranes in water and the striking enhancement in the material stiffness [19]. GO paper can be directly reduced into an integral, electrical conductive paper via chemical or thermal methods [9,20,21]. However, the RGO papers present limited flexibility or even demonstrate brittleness [22]. Methods for improving the flexibility without doping towards obtaining RGO paper with both excellent flexibility and electrical conductivity are welcome.

In recent years, the role of pH in the assembling process of GO has been applied for obtaining macroscopic materials combined with certain solution processing [23–26]. For instance, Ruoff et al. has reported a pH-mediated hydrothermal reduction which is combined with moulding methods for controllable fabrication of high density graphene hydrogels with various shapes [25]. Material with hierarchically porous graphene nanoscroll networks has been

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fabricated through the combining of pH-tunable self-assemble technique and ice-templated method [23]. However, the relationship between pH-mediated GO paper and the properties of corresponding RGO paper have not been clarified yet. In the present study, through chemical reduction of the pre-fabricated GO papers obtained via vacuum filtration, RGO papers with controllable lateral contraction and mechanical performances were prepared using pH as a tuning parameter. Compared with those thermally reduced GO papers, the obtained RGO (pH = 7) paper demonstrates superior performance of both flexural endurance and electrical conductivity. We attempt to clarify the relationship between pH and the controllable performances of RGO papers by investigating the structural differences of the prefabricated GO papers and their various swelling behaviors during chemical reduction process.

2. Experimental

2.1. Sample preparation

GO was prepared by the modified Hummers method using natural graphite with a particle size of 325 mesh. The synthesized GO suspension was neutralized by dialysis in water. The dialyzed suspension with a concentration of 5 mg/mL was refrigerated as stock liquid. The obtained GO sheets were with a thickness of about 1 nm and the lateral size of 1 to several microns (Fig. S1, Supporting Information). Ammonia and 0.25 M HCl solution were used for adjusting the pH value of GO suspensions. In a typical procedure for obtaining chemically reduced RGO paper, 5 mL GO stock liquor was diluted to a total volume of 15 mL and sonicated for 3 min. By filtration of the diluted suspension through a cellulose nitrate filter membrane (47 mm in diameter, 0.45 μm pore size) followed by air drying, free standing GO paper with a thickness of around 20 μm could be obtained and peeled off from the filter membrane. GO paper was further subjected to direct reduction in ascorbic acid solution at 95 °C for 2 h. The obtained hydrated RGO pancake was repeatedly rinsed with deionized water and dried naturally.

2.2. Characterization

IR spectra of GO papers were collected on a Bruker Vertex70 spectrometer using the attenuated total reflectance method. UV–vis reflection spectra of the GO papers and UV–vis absorption spectra of GO suspensions were obtained through a UV–vis spectrophotometer (Shimadzu UV-2550). X-ray photoelectron spectroscopy (XPS) measurements were performed via a Thermo Scientific ESCALAB 250XI photoelectron spectrometer with Al K α (1486.6 eV) as the X-ray source. Wide angle X-ray diffraction (WAXD) patterns were collected at room temperature on a Rigaku UltimaIV diffractometer with Cu K α radiation ($\lambda = 0.154$ nm), the diffraction signals were recorded in the range of $2\theta = 5\text{--}40^\circ$ with a step interval of 0.05° and a scanning rate of 5°min^{-1} . Scanning electron microscopy (SEM) images of the samples were obtained on a JEOL 6700 SEM at an accelerating voltage of 5 kV on samples sputter-coated with gold. Atomic force microscope (AFM) image was acquired by using a Multimode V (VEECO) under contact mode. GO sheets were coated on silicon substrate for AFM measurements via spin-coating at 2000 rpm. Zeta potential data were collected on Malvern Nano ZS90.

Mechanical properties of RGO papers were evaluated by static uniaxial in-plane tensile tests using Zwick/Roell Z005. The samples were cut with a razor into rectangular strips of approximately 6*15 mm for mechanical testing. All tensile tests were conducted in controlled strain rate mode with a preload of 0.01 N and a strain rate of 0.5 mm/min at ambient conditions. At least three specimens were measured from each sample. The electrical conductivities of

the RGO samples were measured by a two-probe method. I-V curves were recorded with a CHI 660D electrochemical workstation (Chenhua, Shanghai, China), a 100 k Ω standard resistor was employed to validate the two-probe method for acquiring the bulk resistivity of sample slices.

3. Results and discussion

3.1. Fabricate RGO papers with controllable lateral contraction

The fabrication process for obtaining RGO papers with controllable lateral contraction was depicted in Fig. 1. Simply stated, after being adjusted to the desired pH values, GO suspensions were filtrated through a filter membrane, followed by air drying to produce GO papers. The GO papers were further reduced in hot solution of ascorbic acid. Then RGO pancakes were repeatedly rinsed with deionized water and dried naturally to generate free standing RGO papers.

The amounts of GO sheets in the three kinds of suspensions were kept the same by taking the same volume of raw material solution. The produced GO papers before reduction are about 25 mg in mass and roughly 20 ± 1 μm in thickness. The lateral sizes of RGO(3), RGO(7) and RGO(11) papers are 24, 33 and 38 mm, respectively. The lateral contraction rates are calculated to be 40.0%, 17.5% and 5.0%, respectively. We can see that with the elevation of pH value, RGO paper appears alleviated contraction despite of the same lateral sizes before reduction. In fact, we also prepared samples from other pH values via the same procedure (Fig. S2, Supporting Information). But the RGO samples from lower pH values than 3 were too small to be cut into appropriate shape and size for performance tests, because of the severe contraction. For example, the sample from pH value of 1 contracted to a state of briquette after drying (Fig. S2a, Supporting Information). And, the RGO samples from alkalized GO suspensions of adjacent pH values show minor variations in lateral size (Fig. S2b, Supporting Information). The photo of a series of RGO samples from GO suspensions with pH value of 2, 4, 6, 8 and 10 (Fig. S2c, Supporting Information) and the stress–strain curves of these RGO samples (Fig. S2d, Supporting Information) demonstrate that both the lateral size and the mechanical performance of the RGO papers show regular changes with the variation of pH values. Therefore, we used samples from 3 pH values for contrastive investigation to demonstrate the variation trend of properties.

3.2. Investigate the origin of pH-mediated controllable lateral contraction of RGO papers

3.2.1. Evolutions of chemical structures of GO upon pH variations

The yellowish-brown to black color change of GO aqueous dispersions upon decrease of acidity has been reported in previous literature. Zhang et al. [27] has ascribed this color change to the fast deoxygenation of exfoliated GO and the formation of graphene-based materials in strong alkaline solutions. Later, Kang et al. [28] attributed this phenomenon to a size fractionation of GO in acidic condition as well as a deoxygenate reaction initiated by basic environment. Very recently, Taniguchi et al. [29] has discovered that the brown to black color change is largely reversible over a pH range under ambient conditions, and excluded the irreversible reduction pathways of GO with a base at ambient conditions. These research works on pH related color change have enriched the knowledge on the surface chemistry of GO. Unexpectedly, this pH related surface chemistry can be further extended for controlling the lateral contraction and the mechanical properties of RGO papers. Therefore, started from the pH related surface chemistry of GO, we tried to make clear the origin of the pH mediated

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