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Experimental study on the preparation, characterization and conductivity improvement of reduced graphene-oxide papers

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ABSTRACT

In the present study, reduced graphene-oxide (r-GO) papers were prepared by vacuum filtration method using chemically obtained graphene oxide as raw materials. Different reduction methods, chemical, thermal or the combination were designed to investigate the influence of reduction process on the structure and conductivity of r-GO papers. The reducibility of the obtained papers was investigated by XPS and Raman. The structure, morphology and electrical conductivity were examined by XRD, SEM and four point resistivity test system, respectively. Results showed that chemical reduction using hydrazine or annealing in reducing ambinent alone was not sufficient to achieve maximum reduction, the highest C/O ratio and highest conductivity was obtained in paper reduced via a combination of hydrazine and thermal annealing treatment. In order to further improve the conductivity of the paper, Ag nanoparticles have been decorated into the paper.

1. Introduction

As a novel class of 2D nano-carbonaceous material, graphene has attracted increasing attention in recent years due to its outstanding electrical, thermal, and mechanical properties since the first discovery by Novoselov and Geim [1–4]. Graphene is a monolayer of carbon atoms that are tightly packed into a two-dimensional, honeycomb crystal structure. Many methods were developed to prepare graphene sheets [1,5,6]. Among them, chemical efforts, involving exfoliation starting from the oxidation of graphite and post-reduction, have received the most attention, with respect to large-scale production of graphene. This solution-based method is promising in the fabrication of graphene-based nanoelectronic devices [7–9].

Recently, vacuum filtration method involves the filtration of a graphene oxide (GO) suspension through a commercial mixed cellulose ester membrane is widely used to prepare graphene oxide-based film or paper-like materials [10–13]. Chhowalla and coworkers have demonstrated that large-area ultrathin films of reduced graphene oxide as a transparent and flexible electronic material could be obtained via vacuum filtration method using GO suspension as starting material, followed by thermal annealing [12]. In 2007, Ruoff reported that GO sheets dispersed in water could be assembled into a well ordered structure under a directional flow, yielding ultrastrong GO paper [14,15]. But to make it electric conductive, further thermal annealing must be carried out but the structure and mechanical properties were deteriorate. In 2008, Dan and coworkers demonstrated that mechanically strong, electrically conductive graphene paper could be fabricated using reduced graphene oxide (graphene) as starting materials [11].

For graphene papers, apart from the mechanical property, electric conductivity is the most important consideration for its electronic application [3,13] and would also be extensively influenced by the reduction process. In 2012, Maser and coworkers reported that the reduction process extensively influenced the structure and properties, especially the electric conductivity of the graphene papers [16]. Their direct and gentle thermal reduction allows maintaining the structural integrity and mechanical flexibility; highly reduced paper exhibited higher conductivity. But the SEM image of the cross-section showed that the restacking of graphene sheets was disordered and discontinuous in the thickness direction. Barber said that this kind of macroscopic defect is harmful to the mechanical strength [17]. It can be speculated that the discontinuity is also harmful to the conductivity, although it is not involved in Ref. 17 So, it is necessary and valuable to find an appropriate process to fabricate graphene papers with regular/continuous cross-section structure, to improve its electrical conductivity.

In this paper, vacuum filtration method was used to prepare reduced graphene oxide papers. Experiments were designed,

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concerning the process by thermal annealing, chemical reduction and combination of the two, to investigate the influence of reduction process on the structure and conductivity of the papers.

2. Experimental details

2.1. Sample preparation

All the chemical reagents were analytical grade purity without further purification. Five kinds of papers were prepared in the experiments by vacuum filtration method, paper obtained with GO sheets (GO-paper) reduced by thermal annealing (GOT-paper); paper obtained with chemically reduced grephene oxide sheets (rGO-paper), rGO-paper treated by thermal annealing (rGOT-paper), and rGO-paper further treated by decorating with Ag nanoparticles and thermal annealing (rGOT–Ag-paper).

GO was prepared according to the procedure described in the literature [18]. Exfoliation was achieved by sonication of GO with concentration of 0.1 mg/mL for 2 h. For GOT-paper preparation, 30 mL of GO suspension was vacuum-filtrated using a mixed cellulose ester membrane with 25 nm pores (Millipore). The paper was allowed to dry in a vacuum at 30 °C and further heat-treated in a tube furnace at 500 °C under Ar/H_2 atmosphere (volume ratio=5:1) for 2 h and cooled naturally.

For rGO-paper preparation, in the first step, 30 mL GO (0.1 mg/ml) was mixed with 20 μL hydrazine and then transferred into two 25 mL stainless steel Teflon-lined autoclaves. The autoclaves were sealed, kept at 90 °C for 2 h, and then naturally cooled to room temperature. A monodispersed chemically reduced graphene oxide (rGO) suspension was obtained by this hydrothermal process. In the second step, rGO-paper was prepared by vacuum filtration. If the obtained rGO-paper was further heat-treated by Ar/H_2 atmosphere, then rGOT-paper was obtained.

To further improve the conductivity, rGO paper was immersed in 1 mol/L $AgNO_3$ solution for 1 h and then heat-treated by Ar/H_2 atmosphere, and the obtained paper was marked as rGOT-Ag-paper.

2.2. Characterization

The structure of the paper was characterized by a Philips 1730 powder X-ray diffractometer (XRD) with Cu Kα radiation (λ=1.5406 Å). The morphology and microstructure of cross-section were observed by a JEOL 6460 scanning electron microscope (SEM). The XPS measurements were performed on a Thermo ESCALAB 250 spectrophotometer with Al-K_α radiation. The Raman spectra were recorded on a MXR Raman system with 532 nm (2.33 eV) excitation and with laser power at the sample below 0.5 mW to avoid laser-induced heating. The film resistance was tested on a RTS-9 four point resistivity test system at room temperature.

3. Results and discussion

In the experiment, to prepare paper-like materials via vacuum filtration method, monodispersed graphene oxide sheets or reduced graphene oxide sheets must be obtained firstly. Fig. 1(a) shows the digital images of the obtained GO and rGO suspensions. It can be seen that a sufficiently dilute colloidal suspension of GO prepared with the aid of ultrasound is clear, homogenous, and stable with a brown color. The FTIR spectrum of GO shown in Fig. S1 (Supporting information) clearly proved the introduction of oxygen-containing functional groups during the chemical oxidation process, which makes the GO hydrophilic. After surfactant free hydrothermal reduction with hydrazine as the reducing agent, a homogenous and dark-colored rGO suspension could be obtained as shown in Fig. 1(b), which could be kept stable (without precipitation) for several weeks.

The obtained colloidal suspensions were further used to prepare graphene-based paper-like materials via vacuum filtration method followed by thermal annealing if necessary. In order to observe the fracture surface, the film was cut by a scissor and the fresh fracture was stuck on the side of the substrate and then placed into the sample room of SEM instrument. In Fig. 1(c), one can see that the cross section structure of GO-paper is hardly to be observed. Soft GO sheets were curled and covered the quartz substrate under the shearing force of the scissor. The preparation process of GO-paper can be explained as an exfoliation and restacking process. During the process, functional groups and water molecules were inserted in the interlayer, which makes it become sticky under the shearing force. But in Fig. 1(d), it can be seen that rGO-paper with perfect cross-section structure could be prepared by vacuum filtration method with chemically reduced graphene oxide suspension as starting materials. The layered structure could be obviously observed through the entire cross-section and the neighboring sheets are well-distributed without close-packing.

After thermal treatment, there are several voids as shown in Fig. 1(e), illustrating that the GOT-paper might be split into pieces during the heat-treating process, caused by removing or releasing of the oxygen-containing groups. Each piece is composed of graphene sheets close-packed to each other, similar to the graphite structure, as shown in the dense region in Fig. 1(e). But rGO sheets are still well-distributed, with little re-stacking as shown in Fig. 1(f).

Fig. 2(a) shows the XRD patterns of the obtained reduced graphene oxide papers. The sensible differences between the three XRD patterns indicate that the aggregation structures of them are different. Peaks around 21.3°, 23.8° and 26.7° are caused by the raw material, which can also be found in the XRD pattern of parent graphite (Fig. 2(b)). Main peak centered at 26.2° can be assigned to the (002) plane of C and d-spacing can be calculated to be 0.34 nm according to the Scherrer equation. Compared with GO-paper before thermal reduction, main peak shifted from 10.4° (d=0.85 nm) to 26.2° (see the inset of Fig. 2(a)), suggesting the removal of the functional groups from the interlayer during the thermal annealing process [19]. In the XRD pattern of GOT-paper, the relatively strong C(002) peak suggested that during the film preparation process, the reduced graphene oxide sheets were re-stacked to form a graphite-like structure. But in the XRD pattern of rGO-paper, one can see that apart from the three peaks arising from parent graphite, it shows an amorphous structure. After thermal annealing, a broaden peak with relatively low intensity centered at 26.1° arose, indicating that the heat-treatment process promoted the re-stacking of rGO sheets. The broadening and small shift of the C(002) characteristic peak maybe due to the short-range order in the restacked structure. The XRD results are in accordance with the above SEM results.

XPS spectra were introduced to analyze the elementary composition of the reduced papers, and the results are shown in Fig. 3. In the survey spectra (Fig. 3(a)), the peak corresponding to C 1s and O 1s are separately at 285.0 eV and 529.6 eV, respectively. Obviously, there was a significant difference of carbon content in the papers. Actually, the total C/O atomic ratios of GOT, rGO, and rGOT-papers are 4.45, 4.18 and 9.58, respectively, indicating that the oxygen-containing groups could be effectively removed by the chemical treatment plus thermal treatment process. One can see that there was a peak around 399 eV in the XPS spectrum of rGO-paper, which can be assigned as N 1s [13]. The intensity of the N 1s peak is very low and indicates a minor amount of N was