

Preparation of functional composite materials based on chemically derived graphene using solution process

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Abstract. Chemically derived graphenes were assembled into functional composite materials using solution process from stable solvent dispersion. We have developed foldable electronic circuits on paper substrates using vacuum filtration of graphene nanoplates dispersion and a selective transfer process without need for special equipment. The electronic circuits on paper substrates revealed only a small change in conductance under various folding angles and maintained an electronic path after repetitive folding and unfolding. We also prepared flexible, binder-free graphene paper-like materials by addition of graphene oxide as a film stabilizer. This graphene papers showed outstanding electrical conductivity up to 26,000 S/m and high charge capacity as an anode in lithium-ion battery without any post-treatments. For last case, multi-functional thin film structures of graphene nanoplates were fabricated by using layer-by-layer assembly technique, showing optical transparency, electrical conductivity and enhanced gas barrier property.

1. Introduction

Graphene, a two-dimensional single atomic sheet of graphite [1,2], is currently attracting much attention for various applications due to its fascinating advantages of high electrical conductivity, optical transparency, gas barrier property, robustness, flexibility and environmental stability [3-6]. The combination of these remarkable electrical and mechanical properties leads us to expect that graphene can be a suitable candidate as a building block for multi-functional composite materials. Recently, even though its properties are relatively limited, chemically derived graphene-related materials such as graphene oxides (GOs), reduced graphene oxides (rGOs) and graphene nanoplatelets (GNPs) have drawn massive attention in both academic and industrial areas because of mass production and solution processibility [7,8]. Among them, especially, GNPs are few-layered graphene sheets prepared by chemical exfoliation followed by chemical/thermal reduction of natural graphite, showing excellent electrical and physical properties in itself.

In this paper, three kinds of functional composite materials based on GNPs using solution process are introduced. Self-assembly from solvent dispersion is an efficient pathway to controlling the organization of nanomaterials. These approaches would suggest potential for development towards the tailored assemblies of graphene-related materials in broad applications.

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2. Materials and methods

2.1. Foldable graphene electronic circuits based on paper substrates

Commercial GNPs (N002-PDR) prepared by chemical exfoliation and thermal reduction from natural graphite were provided by Angstrom Materials. The GNPs were dispersed in ethanol or isopropanol at a concentration of 0.1 mg/ml. Poly(4-styrenesulfonic acid) (PSS, $M_w = 75,000$, 18 wt% aqueous solution from Sigma-Aldrich) was added into the dispersions with the weight ratio of PSS/graphene, 5/1. Then, the dispersion was treated in an ultrasonic bath for 1h and filtered using a hydrophobic polytetrafluoroethylene (PTFE) membrane filter (pore size: 0.2 μm), resulting in uniform deposition of graphene on the filter. After turning this filter over and placing it on paper substrate, electronic circuits on paper could be obtained by drawing patterns on the back of the filter.

2.2. Flexible, binder-free graphene paper electrodes for lithium-ion batteries (LIBs)

GNPs were dispersed in water and stabilized using PSS solution with the weight ratio of PSS/graphene, 5/1. In order to obtain more stable dispersion of GNPs, the dispersion was sonicated for 3hrs followed by addition of GOs in ratio of 3:1 by weight to GNPs in dispersion. Then, the GNP/GO dispersion was filtered using polyvinylidene fluoride (PVDF) membrane filter (pore size: 0.45 μm), resulting in free-standing paper-like structure after drying and peeling it off from membrane filter.

2.3. Multi-functional thin film fabrication by layer-by-layer assembly of graphene

GNPs and PSS (wt. ratio 1:1) were dispersed in DI water by 30 min sonication. PET films or glass slides were used as substrates for LbL assembly of graphene. After O_2 plasma treatment, negatively charged substrates were dipped into poly(diallyldimethylammonium chloride) (PDDA, $M_w = 200,000 \sim 350,000$) solution, rinsed with DI water and dried with compressed air. Then, PDDA-coated substrates were dipped into poly(vinyl alcohol) (PVA, $M_w = 89,000 \sim 98,000$) solution and PSS-stabilized GNPs solution, alternatively for n cycles. In each deposition step, rinsing and drying processes were conducted. The assembled film was denoted as $[\text{PVA}/\text{PSS-PDR}]_n$. To reduce sheet resistance, as-assembled films were treated by dipping into 95% H_2SO_4 for 2 hrs or annealed in a vacuum oven at 160 $^\circ\text{C}$ for 10 hrs.

3. Results and Discussion

3.1. Foldable graphene electronic circuits based on paper substrates

Herein, a fabrication process and characterization of foldable graphene circuits based on paper substrates were briefly introduced according to our previous work [9]. Electronic circuits with controlled thickness/width were successfully prepared by vacuum filtration of a dispersion of GNPs and selective transfer printing which is convenient for making the circuit patterns without not only any damage to paper substrate but also pre-patterned masks.

Thickness of the graphene circuits deposited on a paper substrate was easily controlled by varying the volume of the GNPs dispersion for vacuum filtration (Figure 1). As increasing the thickness of the graphene deposition on membrane filter, surface resistance of graphene circuits after transferring to paper substrate was reduced gradually.

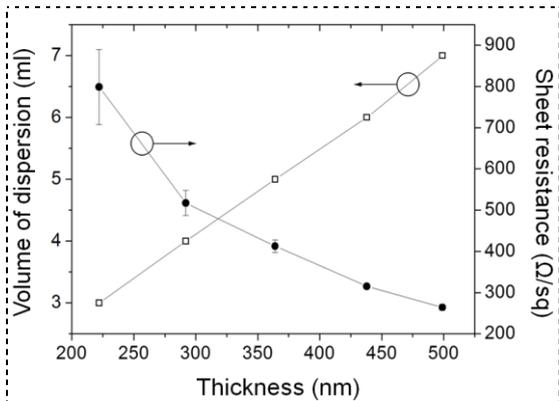


Figure 1. Thickness of the graphene circuits controlled by the volume of GNPs dispersion and sheet resistance of graphene circuits with a variance of thickness. Reproduced with permission from ref. 9.

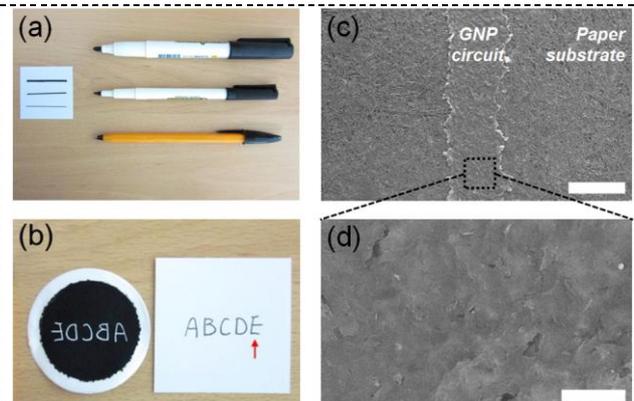


Figure 2. Optical images of a) graphene circuits with different widths and b) graphene patterns in the form of alphabet characters. c) Low- and d) high-magnification SEM images of graphene circuits. Scale bars are 500 μm for c and 10 μm for d. Reproduced with permission from ref. 9.

The width of the graphene circuits can be controlled by adjusting the thickness of the tip of the pen. Graphene circuits with different widths of about 2, 1, and 0.5 mm were obtained by employing thick (top) and thin (middle) felt tip pens and a fine (bottom) ball point pen (Figure 2a). Not only straight line patterns but also complicated patterns can be formed on substrates easily. Alphabet characters were written with filtered GNPs on a membrane filter and a pen (Figure 2b). Figure 2c and 2d shows scanning electron microscopy (SEM) images of the graphene line pattern with low- and high-magnification. Owing to good dispersion stability by contribution of amphiphilic surfactant PSS [10], well-organized graphene patterns on paper substrate can be obtained without significant aggregations of GNPs.

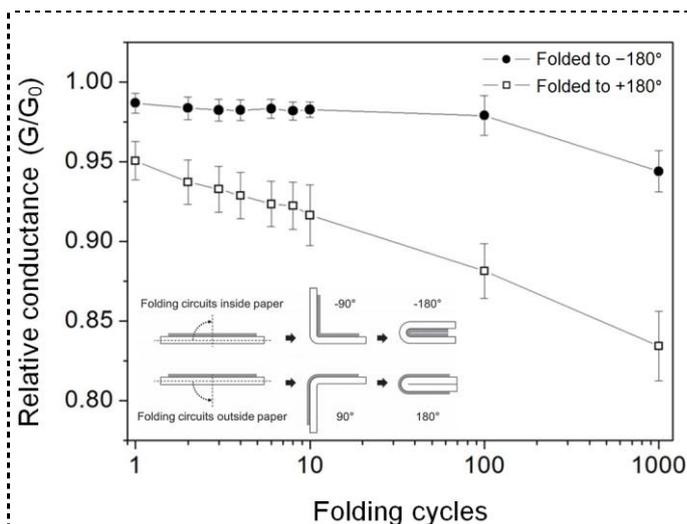


Figure 3. Relative conductance of the graphene circuits after repetition of folding and unfolding (inset: schematic diagrams of the folding angles). Reproduced with permission from ref. 9.

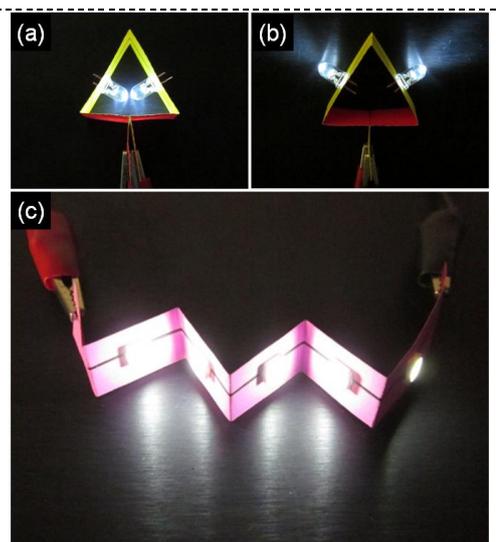


Figure 4. a) Negative, b) positive angle folded circuits and c) array of LED chips on a folded paper circuit board. Reproduced with permission from ref. 9.

In order to investigate the folding stability of the graphene circuits on paper substrates, we evaluated the relative conductance of the circuits (the ratio of measured conductance (G) to initial conductance (G_0)) with a repetition of folding and unfolding as shown in Figure 3 (negative and positive angles indicate folding of the graphene circuits inside and outside the paper substrate, respectively). The circuits with -180° folding showed higher conductance after folding due to smaller radius of curvature caused by the different deformation behaviours between the graphene circuit and the paper substrate; compression for negative angle folding and stretch for positive angle folding. The graphene circuits maintained about 94% and 83% of conductance compared to the initial conductance after 1000 cycles of -180° and $+180^\circ$ folding, respectively, which is much improved folding stability compared to foldable metallic circuits [11]. The excellent folding stability can be attributed to good adhesion between GNPs and the paper substrate as well as the outstanding mechanical properties of GNPs. This behaviour enables the demonstration of three-dimensional circuit boards including negative and positive angle folding as shown in Figure 4.

3.2. Flexible, binder-free graphene paper electrodes for lithium-ion batteries (LIBs)

In this part, flexible, free-standing graphene paper-like materials were fabricated with GNPs using simple vacuum filtration method. Generally, these graphene-based paper materials can be prepared from GOs or rGOs by chemical reduction as starting materials, resulting in limited electrical properties unless the oxidized domains in each graphene layer are restored by post-treatment such as thermal annealing, additional reduction process [12,13].

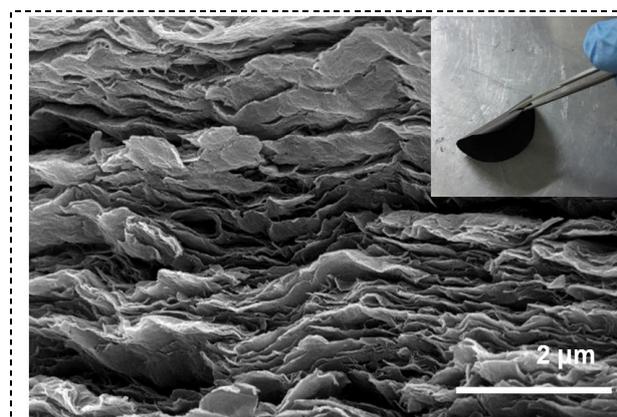


Figure 5. SEM image of the prepared graphene paper from film thickness direction (inset: optical image of the as-prepared graphene paper).

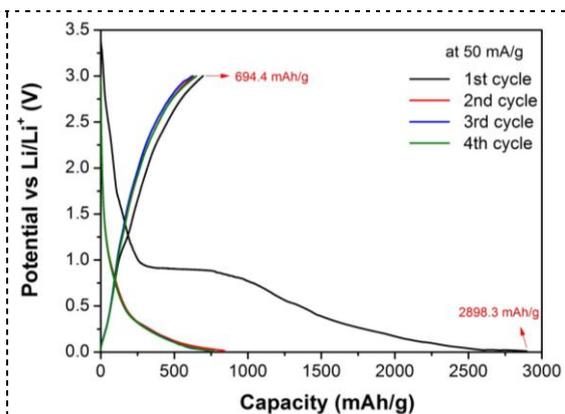


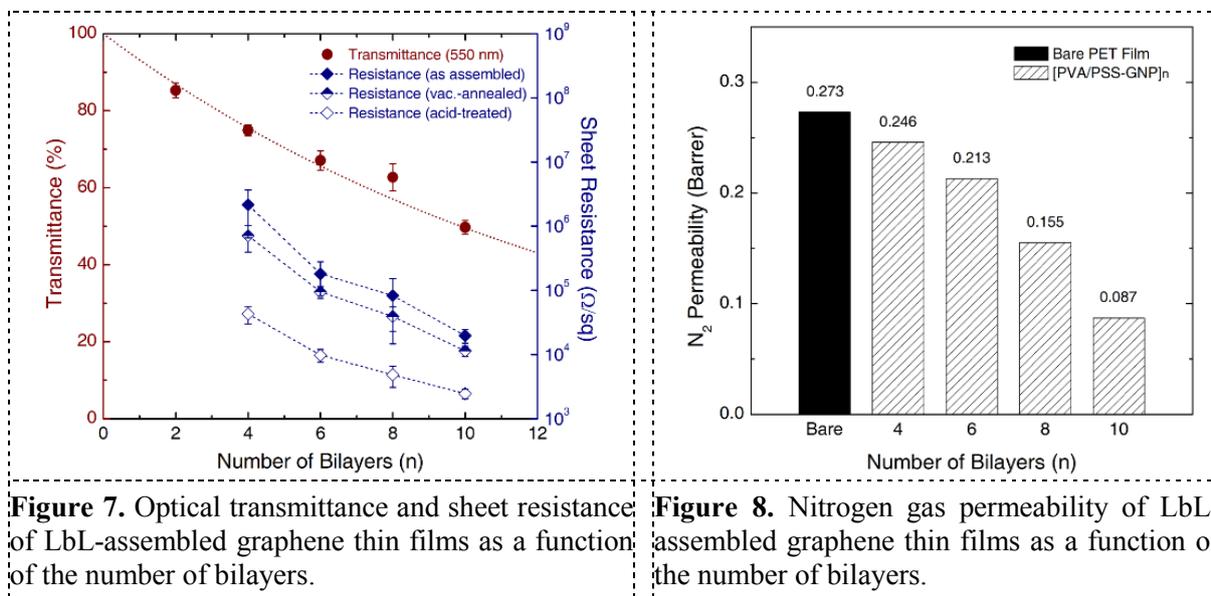
Figure 6. Discharge-charge profiles of the prepared graphene paper at a current density of 50 mA/g as a LIB anode.

Since no additional reduction process is required in case of using GNPs as a starting material for graphene paper, the as-prepared graphene papers showed outstanding electrical conductivity up to 26,000 S/m, much higher than that of graphene papers from chemical reduction of GOs [14]. The uneven layered structures (Figure 5) which were formed when the individual GNPs were assembled into layered structure during filtration are favourable to the intercalation/de-intercalation of lithium ions. These features lead to a large reversible capacity as an anode in LIBs about 700 mAh/g as shown in Figure 6, which is much higher than those of reduced graphene papers [15,16].

3.3. Multi-functional thin film fabrication by layer-by-layer assembly of graphene

Layer-by-layer (LbL) assembly is a bottom-up nano-fabrication based on alternative adsorption of materials, resulting in fine deposition of molecular multilayers [17,18]. Theoretically, a two-dimensional graphene sheet is a perfect nanoscale barrier for gas molecules, which can be a

suitable candidate as a building block for multi-functional composite films. We have successfully fabricated the LbL-assembled graphene thin films with electrical conductivity and enhanced gas barrier property, which is applicable to flexible polymer substrates, using hydrogen-bonding interaction between PVA and PSS-stabilized GNP.



The optoelectronic properties of LbL-assembled graphene thin films are shown in Figure 7. Both optical transmittance and sheet resistance were reduced by increasing number of bilayers. After post treatments, LbL-assembled graphene thin films present lower sheet resistance compared to as-assembled films. It implies that the microstructure of the films was changed by acid treatment and thermal annealing. Especially, acid treatment could remove insulating polymeric components inside the films, resulting in lower sheet resistance by ~ 2 orders of magnitude. Figure 8 presents nitrogen permeability of LbL-assembled graphene thin films. As increasing number of bilayers, nitrogen permeability was reduced gradually ($\sim 68\%$ reduction for 10 bilayers). It is known that a defect-free monolayer graphene sheet is impermeable to standard gases including helium [4]. Thus, GNPs inside the films act as impermeable walls and make longer diffusion pathway for gas molecules.

4. Conclusion

We have successfully demonstrated three kinds of functional composite materials based on GNPs using solution process, which is applicable to flexible electronic devices and multi-functional thin films. The foldable graphene circuits have been simply prepared using vacuum filtration of GNPs dispersion and a selective transfer process without special equipment. The electronic circuits show a small change in conductance under various folding conditions compared to metallic component-based circuits, resulting in realization of foldable circuit boards on paper substrates. Graphene paper-electrodes prepared by simple filtration method using stable dispersion of GNPs with GOs show high electrical conductivity and charge capacity in LIBs as an anode. Graphene thin films based on polymer substrates, assembled with PVA and GNPs, could potentially be both a transparent electrodes and gas barrier for flexible electronics. We believe that these approaches could provide a meaningful method for simple assembling of the dispersion-based graphene sheets to realize highly potential applications in flexible electronics.

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