



Super-tough functionalized graphene paper as a high-capacity anode for lithium ion batteries



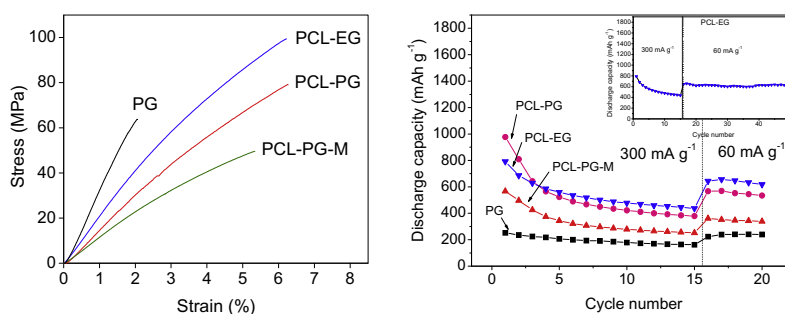
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HIGHLIGHTS

- Graphene was covalently modified to have polycaprolactone brushes on the surface.
- Functionalized graphene paper exhibited super-toughness and high flexibility.
- Lithium ion battery anode fabricated from the paper showed excellent capacity.

GRAPHICAL ABSTRACT



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ABSTRACT

A super-tough graphene paper is fabricated by vacuum filtration of functionalized graphenes dispersed in organic solvent. The graphene is functionalized with polycaprolactone (PCL) brushes on the surface by polymerization of caprolactone from functional groups on graphene. The polymer brushes effectively serve as a soft physical crosslinking system for the graphene, thus providing the graphene paper with super-toughness, 3.49×10^6 (J m⁻³), which is 5-fold stronger than paper made of unmodified graphene and surpasses the highest previous values reported for graphene oxide and graphene papers. The functionalized graphene paper exhibits excellent capacity as the anode for a lithium ion battery (LIB). The stabilized discharge capacity of the paper is around 450 mA h g⁻¹ at a constant current density of 300 mA g⁻¹. This value is approximately 2.7-fold higher than that of an anode made of unmodified graphene and is much higher than most of the values reported for LIB anodes made of graphene paper or graphene powder–polymer binder composites.

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1. Introduction

Graphene, a single-atom-thick sheet of hexagonally arrayed sp²-bonded carbon atoms, has attracted a great deal of attention because of its extraordinary electronic, electrochemical, thermal, and mechanical properties, large surface area, and high aspect ratio, providing it with potential for a variety of applications such as in electronic and energy devices, catalysis, sensors, biomedicines,

and composite materials [1–7]. The assembly of graphenes into special structures with special properties may pave the way toward their use in various potential applications. Previous work has demonstrated that graphene oxide (GO) sheets can be assembled to prepare ultra-strong GO paper with a well-ordered, layered structure by vacuum-filtration of an aqueous dispersion of GO, in which the directional flow of water helps GO sheets to be assembled layer by layer [8]. This GO paper can subsequently be converted to an electrically conductive graphene paper by thermal or chemical reduction [9,10]. Other attempts to vacuum-filter an aqueous dispersion of functionalized, water-dispersible graphene have also

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yielded well-ordered, layer structured graphene papers with good electrical and mechanical properties [9,11]. The excellent mechanical properties of GO and graphene papers have been attributed to interactions at the surface between GO or graphene sheets through π - π stacking, interlocking of the folds on the graphene surface, or physical crosslinking by intercalated water molecules or functional groups on GO sheets. The chemical crosslinking of GO sheets using divalent metal ions or polyallylamine significantly enhanced the mechanical properties of the obtained GO paper [12,13]. Such GO or graphene papers have a high tensile modulus; however, they exhibit a quite low tensile strain at break of less than 1%. In order to obtain more flexible and tougher papers, which can be used in various applications such as the fabrication of flexible, wearable electronic devices, “soft” crosslinker interlocking of the graphene sheets is necessary.

Since graphene paper prepared by vacuum filtration-induced directional flow assembly has exceptional properties including a well-ordered structure, high modulus, high electroactive surface area, high electrical conductivity and good chemical stability, it has potential for application as the flexible electrode of flexible electronic devices [14–16]. For example, several recent studies have demonstrated that graphene paper can substitute for the conventional graphite anode of a lithium ion battery (LIB) with excellent cycling ability [17]. Some authors have reported that super-flexible, highly-conductive graphene paper prepared by vacuum filtration-induced directional flow assembly with chemical vapor deposition graphene or the graphene paper incorporating one-dimensional silver nanowire, exhibited improved performance as LIB anodes or as counter electrodes of dye-sensitized solar cells [18,19]. Other types of graphene paper having novel structure have also been prepared such as the folded structured graphene paper made by compression of graphene foam, or the graphene paper functionalized by direct growth of carbon nanotubes from the paper surface, showing potential uses as a flexible electrode in high-performance, flexible energy storage and conversion devices [20,21].

However, there are some issues that need to be resolved for practical applications. Although graphene itself possesses excellent electrical and electrochemical properties, the LIB graphene paper anode prepared by vacuum filtration has a quite low discharge capacity of approximately 80 mA h g^{-1} at a current density of 50 mA g^{-1} [17,22], which has been attributed to the compact layered structure of graphene paper as well as the extremely high aspect ratio of graphene that causes a kinetic barrier to diffusion of Li ions in and out of the anode during the charge–discharge process since the basal planes of graphene sheets align perpendicular to the diffusion direction of Li ions from the electrolyte. Zhao et al. reported that holes made in graphene by controlled oxidation with acid effectively improved the cross-plane diffusivity of Li ions through the graphene sheet and thus increased the rate capability for energy storage [23]. Others reported that by intercalation of C_{60} into a few-layer graphene which caused an expansion of the (002) interlayer spacing, led to an improvement in specific capacity of the graphene powder–polymer binder composite LIB anode since lithium ions were reversibly stored between (002) planes [24,25]. A similar effect would be expected for a layer-structure graphene paper. Therefore, an appropriate modification of graphene and graphene paper structure that improved Li ion diffusion or properly expanded the interlayer spacing of the paper may result in a more optimal performance of LIB graphene paper electrodes. In addition, improvements in toughness and flexibility of graphene paper may be essential for various practical applications.

In this work, we fabricated super-tough functionalized graphene papers by a novel method and examined their capacity as a LIB anode. Graphene prepared by chemical or thermal reduction of GO normally contains oxygen functional groups such as epoxide

or hydroxyl groups that remain on the graphene surface even after reduction [26–28]. These inherent defects can be effectively utilized as anchoring sites for covalent modification of graphene while minimizing the damage to the intrinsic novel properties of graphene normally caused by covalent modification [29,30]. For example, the epoxy groups of graphene can react with amine groups, enabling the attachment of amine-containing molecules onto the graphene surface [30]. Hydroxyl groups on graphene can be used as initiating sites for ring-opening polymerization of caprolactone, which create polycaprolactone (PCL) chains grafted onto graphene [31,32]. Since PCL possesses a low glass transition temperature, high mechanical strength, and an extraordinary high tensile strain at break [33], we anticipate that PCL chains grafted onto the graphene surface may serve as a “soft” physical crosslinker making the graphene paper stronger and more flexible. In addition, since grafted-PCL chains contain oxygen atoms from ester groups distributed periodically along the polymer chain that can coordinate and conduct Li ions [34,35], the polymer would be expected not only to expand the interlayer spacing of the graphene paper but also to improve Li ion diffusion and storage in graphene paper LIB anodes during charge/discharge processes and consequently improve anode performance.

Therefore, in this work, PCL was grafted onto two types of graphenes, a thermally reduced graphene (PG) and PG additionally modified with ethanolamine (EG) to give different hydroxyl group densities on the graphene surface (Fig. 1). The PCL-grafted graphenes were then used to fabricate super-tough graphene papers using the vacuum filtration-induced directional flow assembly approach. Characteristics of the papers and their performance as LIB anodes were examined.

2. Experimental

2.1. Materials

Expandable graphite (ES350 F5, average particle size: $280 \mu\text{m}$) purchased from Qingdao Kropfmuehl Graphite Co., Ltd. (China) was used for the preparation of graphene. Ethanolamine, ammonium chloride, acetone, caprolactone, anhydrous *o*-dichlorobenzene, dimethylformamide (DMF), tetrahydrofuran (THF), chloroform, and tin (II) 2-ethylhexanoate ($\text{Sn}(\text{Oct})_2$) were purchased from Aldrich and were used as received.

2.2. Preparation and functionalization of graphene

Graphite oxide was prepared using the Brodie method as described in our previous paper [36]. Briefly, a reaction flask with 200 mL of fuming nitric acid was cooled in an ice bath to 0°C , and 10 g of graphite powder was added with stirring. Next, 85 g

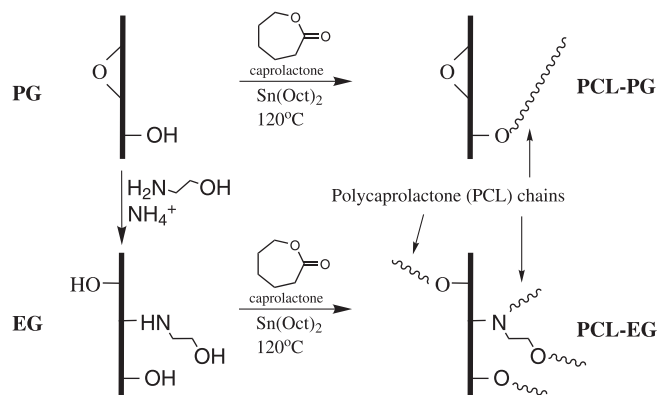


Fig. 1. Schematic representation of graphene modification reactions.

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