



Acid-base block copolymer brushes grafted graphene oxide to enhance proton conduction of polymer electrolyte membrane



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ABSTRACT

For composite membrane, efficient mass transfer between polymer and filler can trigger synergic promotion effect through the tunable interfacial nanodomains. Herein, four kinds of functionalized graphene oxide nanosheets (FGOs) bearing polymer brushes (phosphoric acid brushes, imidazole brushes, acid-base or base-acid block copolymer brushes) are designed exquisitely, and then embedded into two typical polymer matrixes (acidic sulfonated poly(ether ether ketone) and basic chitosan) to prepare composite membranes. It is found that the strong electrostatic attractions drive the brushes insert into polymer matrix and form interconnected networks, affording enhanced thermal/mechanical stabilities and enlarged free volume. Especially, the attractions from outer segment even drag the inner segment to deeply insert into polymer matrix for FGOs with acid-base copolymer brushes, yielding wide and long-range interfacial networks. When employing as proton conductors, these networks can ultrafast transport protons between FGOs and polymer matrix using the functional groups (especially acid-base pairs), affording 6.7 times' increment of proton conductivity to polymer membrane. The synergic promotion effect is governed by the width and amount of interfacial networks (pathways). The effect of these polymer brushes on acidic membrane and basic membrane are investigated and compared extensively to explore their functions on membrane microstructure and mass transfer.

1. Introduction

Graphene oxide (GO) is a kind of ultrathin two-dimensional material, whose excellent intrinsic merits of high aspect ratio, abundant oxygen-containing groups and excellent thermo-mechanical stability render GO diverse applications in the fields of nanoelectronics and nanocomposites [1–6]. Particularly, the combination of advantages from GO and various polymers gives polymer/GO composites promising potential for the applications in many areas including membrane separation [7], photovoltaic devices [8], supercapacitors [9], and energy devices [10–12]. Hydrogen fuel cell, using proton exchange membrane (PEM) as proton conductor, is highly desired to eventually replace gasoline and diesel internal-combustion engines as an efficient power source. For PEM, it is found that the incorporation of GO can afford simultaneous enhancement of proton conductivity and mechanical stability [13–15]. Like other composites, the compatibility and dispersion of GO determine the performance of composite membrane by providing excellent mass transfer and more interfacial domains [16,17]. Particularly, if continuous transfer networks could be constructed along GO–polymer interface, the efficiency for ion transfer will be significantly improved through the synergy effect between two

components. Also, the presence of such networks would donate obvious promotion for the mass transfer in other separation membrane, especially for pressure filtration, pervaporation, and gas separation [18–20].

For effective mass transfer, surface functionalization has been demonstrated to be one powerful approach to endow GO with various chemical properties and abilities, making GO universal and active for almost all kinds of polymer materials [21–23]. For instance, grafting conducting groups promotes the proton migration between polymer matrix and GO, forming long-range conduction pathways along GO surface [24]. Although the functional groups can be grafted in form of small molecule or polymer layer, the form of polymer brushes has triggered considerable interest due to the unique features: on one hand, the brushes insert into polymer matrix to generate wide networks for synergic ion conduction; on the other hand, different from polymer layer, the high chain motion confers high diffusion/conduction abilities on polymer brushes. It has been found that polymer brush-grafted SiO₂ or GO can markedly enhance the proton conductivity of PEMs by over three times [25,26]. Clearly superior to adsorption, covalent grafting gives stable polymer brushes through the facile “grafting from” or “grafting to” approaches [27]. By comparison, the high reaction

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activation and low space steric hindrance make the former attractive to incorporate high loading polymer brushes. Among various “grafting from” techniques, surface initiated atom transferring radical polymerization (SI-ATRP) is the most versatile one as an exquisite and controllable synthesis, utilizing diverse monomers (polar or nonpolar) and reaction media (aqueous or organic) [28,29]. Despite the readily advantages, if there exists weak or none interaction between polymer bushes and polymer matrix, the brushes would shrink and attach on GO surface. Phase-separation would, thereby, emerge at GO–polymer interface with no connected networks. The ability of synergic mass transfer would decline or even lose, weakening the performance of polymer/GO composite.

Recently, block copolymer has triggered intensive attentions as it could create multifarious functional nanostructures after self-assembly in solvents via swelling-collapse transition of different blocks [30,31]. For this exquisite progress, the difference of mutual interactions between the two blocks and solvent determines the chain stacking and hence the assembled structure. Attractive interactions give a fully stretched conformation of the block through solvation process, whereas the block would collapse and agglomerate for minimal surface tension. Similarly, we can thus predict that when emerging in polymer solution, the interaction between different blocks and polymer would help to regulate the arrangement of block copolymer (either being grafted on filler or not). Also, strong attraction from polymer could induce the block to insert into polymer matrix and then form connected networks. In particular, the inner block of copolymer (being grafted on filler) would be stretched pulled by the outer block if only outer block has interaction with polymer matrix. Considering the independent controllable structure of the two blocks, grafting block copolymer brushes would make GO universal and powerful to achieve enhanced mass transfer of various polymer matrixes. For PEM, the widely-used membrane matrix is either acidic or basic polymer because of the acceptable proton conduction ability of acid or base groups. The inorganic fillers were modified with acidic brushes or basic brushes in the few previous studies [32,33]. Among acid or base groups, phosphoric acid and imidazole groups are the most attractive representatives due to their amphoteric nature, intermolecular hydrogen bonds, and high self-dissociation ability [34,35]. These features render the carrier sites fast proton hopping in a low-energy-barrier manner, especially under low humidity. Acid-base block copolymer brushes are very likely to form well-connected networks and thereby trigger synergy effect of polymer and filler, however, such brushes grafted filler is seldom developed and rarely employed as conduction reinforcer at present.

Herein, four kinds of polymer brushes grafted GO nanosheets (labeled as FGOs) were designed and fabricated through SI-ATRP technology, the brushes of which contained four conditions, i.e., acid brushes, basic brushes, acid-base block copolymer brushes, and base-acid block copolymer brushes. Dimethyl vinylphosphonate (DMVP) and vinyl imidazole (VI)

were chosen as monomers to offer acid group and base group, respectively. Two typical polymers (sulfonated poly(ether ether ketone), SPEEK and chitosan, CS) were selected, representing anionic polyelectrolyte with phase-separated structure and cationic polyelectrolyte with nonphase-separated structure, respectively. FGOs were facilely dispersed into SPEEK or CS to prepare composite membranes, the interfacial microstructures of which would be regulated with the aid of the polyelectrolyte brushes. In such a way, the microstructure-property relationship of polymer/GO composite could be comprehensively elucidated. Moreover, the mass transfer between polymer and FGOs was investigated by measuring the proton conductivity and energy barrier under hydrated and anhydrous conditions and various temperatures. By doing so, the function of block copolymer brushes on synergy effect between polymer and FGOs could be explored preliminarily.

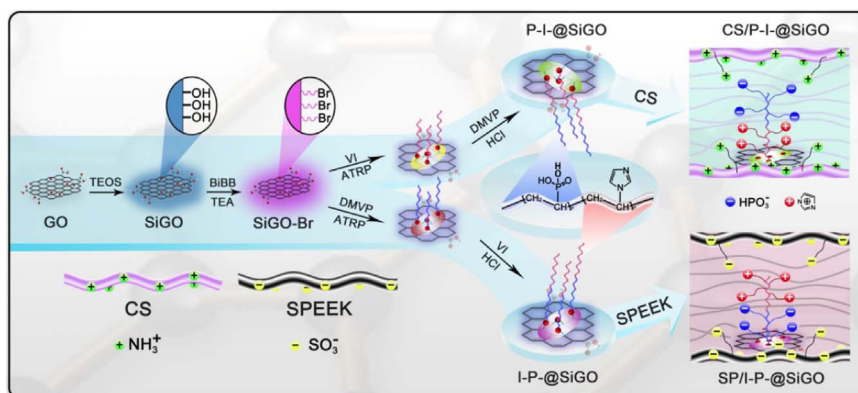
2. Experimental

2.1. Materials and chemicals

2-Bromoisobutyryl bromide (BIBB) was provided by J&K Scientific (Beijing, China). Tetraethoxysilane (TEOS), triethylamine (TEA), 2,2'-bipyridine (BPy), Copper(II) bromide (CuBr_2), azodiisobutyronitrile (AIBN), VI, and DMVP were purchased from Alfa Aesar (Shanghai, China) and used without further purification. Polyvinylpyrrolidone (PVP) was purchased from Aladin Ltd. (Shanghai, China). Natural graphite powers (45 μm) were obtained from Sigma-Aldrich (Shanghai, China). Poly(ether ether ketone) (Victrex®PEEK, grade 381G) was supplied by Nanjing Yuanbang Engineering Plastics Co., Ltd and dried overnight at 120 °C before using for reaction. SPEEK with sulfonation degree of 62.9% was synthesized according to the procedure in literature [36]. CS with the deacetylation degree of 91% was obtained by Golden-Shell Biochemical Co. (Zhejiang, China) and used as received. All the other chemicals were obtained from Kernel Chemical Reagent Co., Ltd., (Tianjin China) and used without further treatment. De-ionized water was used throughout the experiment.

2.2. Fabrication of FGOs by SI-ATRP

The detailed preparation process of FGOs was depicted in Scheme 1. Firstly, GO was synthesized from natural graphite powder using the improved Hummers method [37]. Secondly, GO aqueous solution (25 mL, 0.2 mg mL⁻¹) was added into 200 mL of ethanol, followed by the addition of PVP (1g). After stirring at room temperature for 0.5 h, TEOS (2.5 mL) was injected into the above solution under basic conditions (pH ~9.0 adjusted by ammonia) at room temperature and then treated by sonication for 0.5 h to obtain homogeneous mixture. Further, it was vigorously stirred at 25 °C for another 24 h. Finally, the final reaction mixture was centrifuged and washed with absolute ethanol for several times before being dried and then named as SiGO.



Scheme 1. Preparation of acid-base copolymer brushes functionalized GO and composite membranes.

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