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Preparation of graphene oxide/polyethyleneimine layer-by-layer assembled film for enhanced hydrogen barrier property

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ABSTRACT

A super hydrogen barrier film was prepared via layer-by-layer self-assembly of graphene oxide (GO) and polyethyleneimine (PEI), and the effects of pH of the PEI solution on the performance of LBL films were studied in detail. Results show that the pH value of PEI solution has a significant influence not only on the adsorbed amount of self-assembly materials but also the stacking morphology of GO sheets. When the pH values of GO suspension and PEI solution are identical, the self-assembled film shows a superior hydrogen gas barrier performance under pH of 3.5. When the pH value of GO suspension was fixed and that of PEI solution was varied, the adsorbed amount of the film was increased and reached a maximum value when the pH of PEI solution was 12, and the film prepared under this condition had a 12.7% increase on thickness and a 55.5% decrease on its hydrogen transmission rate (H2TR).

1. Introduction

Among the burgeoning energy sources, hydrogen energy has become one of the most practical replacements for fossil fuels due to it being environment-friendly and possessing high efficiency characteristics as a secondary energy source. However, the technical bottleneck for large-scale application of hydrogen is in the question of how to safely, economically and efficiently store hydrogen gas which has not been solved [1]. Hydrogen has a high diffusion rate in the air and is also flammable and combustible, which makes it a hazardous gas. In order to enhance the pressure tolerance of the containers, materials with improved hydrogen gas barrier property are still necessary. In 2008, Bunch et al. [2] reported that even the smallest helium molecules cannot pass through a single-layered graphene, proving that graphene has an excellent gas barrier property. The graphene oxide (GO) is obtained through the oxidation and exfoliation process of graphite, and the oxygen-containing groups [3] makes the GO sheet easily exfoliated and dispersed in water. The obtained GO sheet can self-assemble into a 2D thin film on a variety of substrates with nanoscale thickness [4]. The GO films can be prepared via numerous methods such as Langmuir–Blodgett assembly electrophoresis, immersion coating, spin coating, spray coating, vacuum filtration and chemical vapor deposition [5–11]. The GO thin films have been widely used in the fields of gas separation, gas barrier, water treatment [12–16].

Except for the mentioned methods, layer-by-layer self-assembly (LBL) through electrostatic interaction has been widely reported since it is a facile route and the structure of the thin film can be precisely controlled on a nanoscale level. The GO composite material prepared by LBL method has more excellent gas barrier performance than that of the conventional filler composite due to its high exfoliation degree and orientation. The results of our research group also indicate that LBL films prepared by using polyethyleneimine (PEI) and GO on the polyethylene terephthalate (PET) film surface show an excellent hydrogen gas barrier performance [17]. Yu et al. [18] and Yang et al. [13] also reported the excellent oxygen gas barrier property of GO/PEI LBL composite film prepared via electrostatic interaction.

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Table 1
The charge density of 0.5% PEI solution with different pH values.

pH	2	3.5	5	7	8	9.5	12	13.5
Charge density (mmol g^{-1})	12.02	11.92	8.77	5.96	2.89	0.058	0	0

It's known that the charge density of the polyelectrolyte affects the adsorption efficiency of polyelectrolyte on the self-assembled thin film, while the ionization degree of the polyelectrolyte is greatly affected by the pH of its solution. Some literature reported that the thickness [19] and adsorption morphology [20,21] of a self-assembled film could be changed by adjusting the solution's pH value. Hasan et al. [22] described the microstructure of GO thin film prepared through electrostatic interaction at different pH values. Chen et al. [23] studied changes of nanostructure and oxygen barrier properties of self-assembled GO/PEI film prepared with GO dispersion of different pH values. All results indicate that the variation of the pH has valuable impact on barrier performance of GO/PEI LBL films. However, in the literature [23], only the self-assembled morphology of GO sheets after changing the pH of GO suspension was studied, the effects of the pH of PEI solution on the stretched configuration of adsorbed GO sheet during the alternating immersion process were ignored. Though GO plays a more important role in gas barrier performance of GO/PEI film, pH of PEI solution not only affects its adsorption but also may affect the GO morphology on the surface of assembled film when the film is immersed in PEI solution with a different pH value. Therefore, it is necessary to investigate the effects of pH value of PEI solution on the hydrogen gas barrier performance of GO/PEI film.

In the present study, the PEI solution and GO suspension with the same pH were used for self-assembly at first, which can exclude the effects of pH of PEI solution on GO. Subsequently, under the condition of fixed pH value of GO suspension, the pH value of PEI solution was varied for the self-assembly process. The H_2TR of $(GO/PEI)_{10}$ films prepared at different pH was measured, and the growth process and morphology variation of these films were observed as well. The comparison between these two experimental results was used to analyze the effects of pH values of PEI solution on the adsorbed amount and assembly morphology of composite films.

Table 2
Composition of the chemical groups of GO.

Material	Chemical group composition (%)			
	C–C/C=C	C–OH	C=O	C–O (epoxy)
GO	37.4	10.2	20.1	32.3

2. Experiment

2.1. Materials

GO (oxidation degree > 95%) in powder form was purchased from the Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, China. Pure PEI ($M_W = 10{,}000$ g mol^{-1}) was purchased from Aladdin Co., Ltd. (Shanghai, China). The dipping concentration of polyelectrolytes was 0.5 wt% for PEI solution, 0.05 wt% for GO suspension. The pH of the GO suspension and PEI solution was controlled by adding hydrochloric acid and NaOH solution, and the charge density of PEI solutions was measured by colloid titration method [24]. Pure industrial polyester film, PET (type 6020; thickness = 160 μm), was purchased from Yuxiang Electronic Material Co., Ltd. (Shanghai, China). The PET film was pretreated with the same method as we had reported early [17].

2.2. Multilayer membrane preparation

LBL self-assembly films were prepared on PET substrate and Si wafers respectively with the same procedure reported earlier [17], and Si wafers were pretreated with a piranha solution (70% H_2SO_4 and 30% H_2O_2) for 1 h under 90 °C. The pretreated substrate was dipped into a PEI solution for 20 min. After rinsing with pure water and drying on a spin coater, the PET film was dipped into a negatively charged solution of GO for 20 min following by rinsing and drying again. One deposition cycle involved two different layers, that is, one bilayer. This process was repeated to prepare polyelectrolytes films with different numbers of bilayers [17].

2.3. Characterization of GO

X-ray photoelectron spectroscopy (Thermo escalab 250Xi, Thermo electron, American) was used to characterize the chemical structures of GO. The thickness, size and number of layers of GO sheet were analyzed by atomic force microscopy (Bruker Multimode 8, Germany). The zeta-potential of the GO suspensions was measured by dynamic light scattering (Zetasizer Nano ZS90, Malvern, UK).

2.4. Test and characterization of films

The film thickness of the self-assembled membranes was measured using an Alpha-SE Ellipsometer (EC-400 and M-2000V, J.

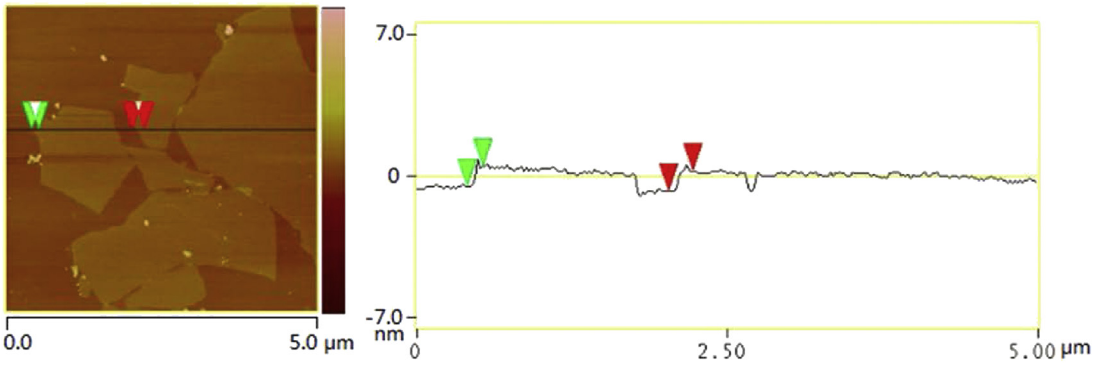

Fig. 1. AFM image of GO.