



Layer-by-layer assembled polyelectrolyte-decorated graphene multilayer film for hydrogen gas barrier application



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ARTICLE INFO

Article history:

Received 17 December 2016

Received in revised form

2 February 2017

Accepted 7 February 2017

Available online 9 February 2017

Keywords:

Thin films

Thermal properties

Surface analysis

Assembly

ABSTRACT

A facile approach for the fabrication of chemically-modified reduced graphene oxide (RGO) based multilayer films was developed for gas barrier applications. Polyethyleneimine (PEI) and poly(sodium 4-styrenesulfonate) (PSS) were utilized as surface modifiers to yield water-dispersible RGO with opposite charges. Altering the deposition pH of PEI-RGO layer resulted in different phase morphology and bonding of the multilayer films. PEI-RGO and PSS-RGO were assembled into multilayer films via a layer-by-layer (LbL) assembly method through electrostatic and hydrogen bonding interactions, respectively. The LbL assembly of polymer-decorated RGO based multilayer films were characterized by various characterization techniques. Hydrogen gas transmission rate (H₂GTR) of the hydrogen bonding interaction based LbL film with 24 bilayers was 5.8 cc/m²·d·atm; and H₂GTR value was 46.2 cc/m²·d·atm for the corresponding LbL film based on electrostatic interactions. Hydrogen bonding interaction based multilayer films exhibited very low H₂GTR values compared to electrostatic interaction based multilayer and bare polyethylene terephthalate films.

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1. Introduction

Graphene has attracted tremendous attention due to its variety of potential applications including areas of energy, sensors, nano-electronics, gas barriers, and etc. [1–7]. The unique properties of graphene, such as its excellent electrical conductivity, mechanical properties, and impermeability to any gas/liquid, account for its multitudinous applications [8–11]. The poor gas barrier properties of commercially available polymers limit their application as flexible electronics and packaging materials although the polymeric materials are lightweight, flexible, inexpensive, and easily

processable. Triggered by the success of impermeable graphene sheets, studies on gas barrier applications have been extensively conducted with different polymer materials, including thermoplastic polyurethane, polyethyleneimine, poly(vinyl alcohol), polystyrene, polynorbornene dicarboximide, and polyimide [12–18]. However, graphene sheets tend to form irreversible agglomerates during processing due to their strong π - π stacking and Van der Waals attractive interactions. Hence, high surface to volume ratio makes this material difficult to work with; therefore, most of the graphene-related work uses chemically or thermally modified graphene material. Another issue is that the composites obtained by mixing (melt or solution) usually yield a random dispersion of graphene sheets in polymeric matrices. However, fully exfoliated and homogeneous dispersions of graphene are extremely desirable to get enhanced gas barrier properties [19,20]. To date, great attention has been paid to prepare graphene-based

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gas barrier materials via various novel approaches [3,8,9,20,21]. Gas barrier low-cost thin films have found extensive application for a variety of packaging applications including the food/pharmaceutical, flexible electronics, and fuel cell industries. The design and fabrication of hydrogen gas (H_2) storage container is very crucial in various engineering and industrial applications [9,15,22]. Besides, H_2 is used as a carrier gas for trace elements which are used for fabricating semi-conducting layers in integrated circuits and to cool the electrical generator [22]. Metallized films, SiO_x coatings, and nanoplatelet-filled polymer composites have been utilized as gas barrier materials to protect various items, e.g., food, electronics, etc. [23,24]. These materials display excellent barrier properties towards different gases and moisture but they show poor substrate adhesion, undesirable optical quality, and limited flexibility. On the contrary, layer-by-layer (LbL) assemblies constructed with nanoplatelets (clay, graphene, etc) can overcome these restrictions [22–26]. It is also reported that polymer based composite thin films with barrier more than inorganic oxides have been fabricated by LbL assembly [27,28]. LbL assembly technique can be tailored through adjustment of concentration, pH, temperature, and exposure time to prepare ultrathin gas barrier films with precisely controlled thickness and transparency. Besides, LbL assembly is a well-constructed, facile, and time-saving technique that can be used to fabricate ultrathin barrier film via electrostatic interactions, hydrogen bonding, covalent bonding, or coordination interactions [25–28]. LbL-deposited films have been successfully utilized to transport drugs, purify hydrogen gas, prevent reflection, modify wettability, and protect polymeric substrates from fire [22–26]. Clay platelets have already been assembled by LbL methods for the improvement of gas barrier properties [25,26]. R. Rajasekar et al. fabricated multi-layered films using poly(diallyldimethylammonium) chloride (PDDA) and sulfonated poly(vinylidene fluoride) (SPVDF)-graphene oxide (GO) composites through layer-by-layer (LbL) assembly to improve the hydrogen gas barrier properties [22]. Yang et al. reported that GO and polyethyleneimine (PEI) can be assembled via the LbL technique with covalent-bonding interactions. The resultant films, with 10 and 20 bilayers, can reduce the H_2 transmission rate by 38 and 41%, respectively [24]. Yu et al. assembled GO and PEI via the LbL process for O_2 barrier applications [29]. A large decrease in the oxygen permeation rate was obtained, decreasing from $8.119 \text{ cc m}^{-2} \text{ day}^{-1}$ for the bare PET substrate to $0.05 \text{ cc m}^{-2} \text{ day}^{-1}$ for the LbL film with five bilayers of PEI/GO. Although, the electrochemical and sensing applications of reduced GO (RGO) have been studied extensively, but, only a few reports on the gas barrier applications of RGO have been found in literature [5–7,10,30,31]. In the present work, a series of super gas barrier multilayer films were prepared from graphene based aqueous composite solutions using layer-by-layer (LbL) assembly. Herein, the assemblies of two kinds of polyelectrolytes-modified RGOs have been used for the fabrication of multilayer films via the LbL method. Polyethyleneimine modified graphene oxide (PEI-RGO) and poly(sodium 4-styrenesulfonate) modified graphene oxide (PSS-RGO) are employed as precursors to yield graphene-based super gas barrier multilayer thin film with precisely controlled thickness, and transparency. Two types of tunable assemblies of multilayers were achieved by taking advantage of electrostatic interactions and hydrogen bonding interactions, respectively. These two kinds of multilayers can be easily obtained by transforming the pH of modified graphene. Efforts were made to determine how the driving forces (electrostatic interactions and hydrogen bonding interactions) influence the LbL film assembly and gas barrier properties.

2. Experimental

2.1. Materials

Expanded graphite was obtained from TIMCAL, Ltd., Switzerland. Concentrated sulfuric acid (H_2SO_4 , 95%), hydrochloric acid (HCl), and hydrogen peroxide (H_2O_2) were purchased from Samchun Pure Chemical Co. Ltd., Korea. Potassium permanganate ($KMnO_4$) was obtained from Junsei Chemical Co. Ltd., Japan. Sodium nitrate ($NaNO_3$), poly(sodium 4-styrenesulfonate) (PSS, Mw ~ 70,000), and polyethyleneimine (PEI, Mn ~10,000) were purchased from Sigma-Aldrich. Hydrazine monohydrate was obtained from TCI, Tokyo, Japan. The materials were used as received without further purification. Polyethylene terephthalate (PET) substrate was purchased from DuPont (Mylar(R) 500), USA. The details for the modification of the PET surface are provided in [Supporting Information](#).

2.2. Precursor preparation

Graphite oxide was prepared from expanded graphite by a modified Hummer's method [15,32]. PEI-RGO was prepared as described in our previous report [11]. PSS-RGO was prepared as reported in the literature [33]. Preparation procedures of PEI-RGO and PSS-RGO have been depicted briefly in [Supporting Information](#).

2.3. Layer-by-layer deposition

All the modified PET substrates were initially dipped into a 1 wt % PEI solution (unaltered pH of ~8) for 10 min and then rinsed with DI water to generate a cationic surface (i.e., a primer layer). This PEI coating ensures that the surface charge is uniformly decorated on the PET surface, thereby, improving the adhesion of the next polyelectrolyte modified graphene layer. Afterwards, a rinsing process was conducted to remove excess PEI. Then PET substrates were dipped into the PSS-RGO dispersion (1 mg/ml, pH = 7) for 10 min, after that rinsed with DI water, and dried with a stream of filtered air. This procedure was followed by an identical dipping, rinsing, and drying procedure with the PEI-RGO dispersion (1 mg/ml, pH = 4) solution. The PET substrate with one bilayer of oppositely-charged RGO was designated as (PSS-RGO/PEI-RGO)1. These procedures were repeated until the desired number of layers was obtained. After the initial bilayer was deposited, additional layers were added using identical dipping, rinsing, and drying conditions. The cyclic procedure was repeated to obtain LbL films with the desired numbers of deposited bilayers. In another case, LbL films were obtained by identical dipping and rinsing procedures but the pH of PSS-RGO was 7 and the pH of PEI-RGO was changed to 10. These changes of pH values were done using aqueous hydrochloric acid or an ammonia solution as regulators. The schematic of the LbL assembly technique is shown in [Fig. S1](#).

2.4. Characterization

Fourier transform infrared (FT-IR) spectroscopy was performed on a Nicolet 6700 spectrometer at room temperature over a frequency range of $4000\text{--}400 \text{ cm}^{-1}$. The powder samples mixed with KBr were pressed into disks for the FT-IR study. Ultraviolet visible (UV-vis) spectroscopy was carried out at ambient temperatures using a UVS-2100 SCINCO spectrophotometer. X-ray diffraction (XRD) analysis was carried out using a D/Max 2500V/PC diffractometer (Rigaku Corporation, Japan) with $CuK\alpha$ targets ($\lambda = 0.154 \text{ nm}$) at a scanning rate of $2\theta = 2^\circ \text{ min}^{-1}$ under a voltage of 40 kV and a current of 100 mA. Field emission scanning electron microscopy (FE-SEM) measurements were carried out with a JSM-

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