



## Conductive oxygen barrier films using supramolecular assembly of graphene embedded polyelectrolyte multilayers

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### ABSTRACT

The supramolecular self-assembly of polyelectrolyte multilayers (PEMs) provides robust bottom-up strategies to assemble a broad spectrum of nanostructures on the host substrates. In this study, we discuss the formation of graphene nanoplatelet (GNP) embedded polyelectrolyte films to enhance the oxygen barrier properties of poly(ethylene terephthalate) (PET) films. Despite cheaper costs and high mechanical strength, the diffusion of small gas molecules such as oxygen through PET films remains a matter of great concern. The simple yet robust supramolecular deposition of GNP/polyelectrolyte on PET substrates significantly increases the tortuous path the oxygen molecule has to travel, making it harder to diffuse through the PET film. With permeability coefficients in the range of 10–18 cc cm/cm<sup>2</sup> s Pa, the coatings developed in this study show three orders of magnitude reduction as compared to the permeability coefficient of the bare PET film, significantly lower than that of ethylene vinyl alcohol (EVOH) and comparable to silicon oxide thin films used in commercial gas barrier foils. The use of GNPs in the multilayered films also helped reduce the electrical sheet resistance to about 1 MΩ which is five orders of magnitude lower than the original PET substrate opening up promising opportunities for future use in semiconductor and electronics industry. Making suitable modifications in the deposition process, three configurations of GNP embedded PEM multilayers namely hydrogen bonded, electrostatic, and composite films were developed and their effect on oxygen barrier property and sheet resistance was monitored. Oxygen permeability of films was tested in accordance with ASTM D-3985 using a MOCON 2/21 ML instrument, whereas electrical sheet resistance was quantified using a Gamry Femtostat Electrochemical Impedance station.

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### 1. Introduction

In recent years, there is a growing trend toward using flexible plastic as packaging material due to its low cost, easy formability, light weight, and reasonably good durability. Glass has been traditionally used in the food packaging industry and fabrication of display panels on account of its transparency, heat tolerance, and gas shielding capability [1]. However today, flexible plastics are making rapid inroads in replacing glass in most of these applications. In order to truly compete as an alternative packaging material, flexible plastic needs to fulfill an important requirement of preserving the product from environmental degradation. Dust, oxidation and moisture are principal forces in nature that can have a deleterious effect on perishable food products and sensitive electronic components [2]. Unfortunately, flexible plastics despite their numerous advantages suffer from poor gas barrier properties [3]. Efforts have been directed to overcome this problem by depositing inorganic coatings and thin films of polymer blends to improve the

gas shielding capability. Among the inorganic materials, aluminum and silicon oxide coatings are excellent candidates to limit the permeation of gas molecules. However, inorganic coatings especially pure SiO<sub>2</sub> thin films require high temperature for effective deposition [4]. Most flexible plastics have low glass transition temperatures (*T<sub>g</sub>*) imposing a limitation on the use of inorganic coatings.

Flexible plastics are positioned to make key contributions to the electronics industry in the near future. Devices such as organic light emitting diodes (OLED) expected to corner a 40% share of the mobile phone display market by 2015 present exciting growth prospects for the plastics industry [5]. With the world rapidly moving toward miniaturization, researchers have sought to make electronic components more compact by designing new prototypes that promote improved electrical conductivity and gas barrier properties. This would be particularly useful in the fabrication of certain semiconductor materials such as the dielectric constant oxides that are frequently used in the construction of large capacitors. These devices are liable to fail in the presence of non-conducting oxide coatings [6,7]. Other devices with similar conductive gas barrier requirements include solar cells grown on flexible supports and flat panel displays [8–10]. Silicon oxide though available ubiquitously, acts

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as an electrical insulator [11]. So it cannot be directly applied for the above applications. In recent years, there has been a growing interest in the use of nanomaterials to supplement the gas barrier properties of thin polymer films. A number of theoretical models have been used to examine the critical role played by the aspect ratio of nano/colloidal materials dispersed in polymer matrix in improving the gas barrier properties [12–14]. Upon encountering a nanofiller, gas molecules are forced to adopt a tortuous pathway, producing a significant lag in the transmission. Therefore, high aspect ratio nanomaterials such as clay platelets [15–17], mica sheets [18,19], cellulose [20,21], and graphene oxide [22] have been used to build gas resistant thin films. In spite of their high gas/moisture barrier properties, these nanomaterials provide little advantage in the preparation of conductive films. On the other hand, graphene with its  $sp^2$  hybridized 2D structure has unique physical and electronic properties [23]. Thin graphene layers are impermeable to most gases and could serve as excellent nanofillers in the polymer matrix [24]. High charge mobility and ballistic transport at room temperature endow graphene with superior electrical conductivity, making it a promising candidate for applications such as electrochemical sensing, field effect transistors (FET), and supercapacitors [25].

Layer-by-layer (LbL) assembly is a versatile technique that can be used to add multiple functionalities to a host of substrates. The success of the LbL technique lies in its ubiquity and simple operation. The extension of Iler's work [26] to the polyelectrolyte multilayer assembly by Decher and Hong [27,28] has given rise to a large number of nanoscopic functional materials. The non-covalent functionalization of nanomaterials using polyelectrolytes followed by sequential assembly is a form of LbL that has successfully demonstrated its utility. A number of interactions, such as electrostatic, hydrophobic, and hydrogen bonding, are ascribed to the formation of multilayered polyelectrolyte LbL assembly [29]. Multifunctional tailor-made substrates fabricated using this route have found several applications such as in catalysis [30–32], membrane science [33,34], biosensors [35–38], and drug delivery [39–42]. Ionic strength and pH of the solution can influence the adsorption process producing films of distinct morphology and properties [43–46].

With an estimated theoretical elastic modulus of single-layered graphene projected to be 1 TPa and surface conductivity about  $50 \times 10^6$  S/cm, GNPs enjoy superior mechanical and electrical properties [47]. In recent years, methods such as thermal expansion, dielectric heating, and acid intercalation have facilitated exfoliation of graphitic flakes enabling the production of high surface area single-layered graphene nanoplatelets [48]. In this study, we report the LbL assembly of GNP embedded polyelectrolyte multilayers. Unlike inorganic coatings prepared under high temperature conditions, the GNP/PEM LbL assembly can be processed at room temperature. Similarly, compared to the recently developed fabrication methods for free standing graphite papers [49] and graphene nanoplatelet-high density polyethylene (GNP-HDPE) nanocomposite [50], the LbL process can be accomplished under milder process conditions using lower energy input. The GNP embedded polyelectrolyte films serve two purposes. Firstly, they serve as barriers to gas permeation. Secondly, graphene with its unique electronic configuration is positioned to deliver improved electrical conductance. The combination of gas barrier properties and electrical conductance make these films attractive candidates for applications in the semiconductor and electronics industry. Graphene dispersion in polyelectrolytes followed by its LbL assembly has been a subject of extensive examination [51,52]. Both strong and weak polyelectrolytes have been utilized for this purpose with varying degrees of success. While strong polyelectrolytes are fairly stable over a wide range of pH, weak polyelectrolytes are known to exhibit a remarkable variation in the charge distribution when subjected to a pH change [53]. This

can affect the film thickness, the mechanism of interaction, the adsorption kinetics, and the quality of adhesion of the films to the base substrate. Unlike other studies that utilized graphene oxide followed by its reduction [54,55], our process did not use any oxidation or reduction steps. Instead, we chose two weak polyelectrolytes namely branched polyethylenimine (BPEI) and polyacrylic acid (PAA) for LbL deposition. BPEI is rich in amino pendant groups giving it a cationic character. The abundant availability of primary, secondary, and tertiary amino residues provides ample opportunities to use BPEI to complement the anionic carboxylic group rich PAA in a multilayered assembly. Using different process conditions, three sets of GNP embedded LbL assemblies were developed. They comprised of hydrogen bonding, electrostatic, and composite interactions (combination of hydrogen bonding and electrostatic interactions).

## 2. Experimental procedures

### 2.1. Materials

Polyacrylic acid (PAA) sodium salt (35 wt% solution in water) and branched polyethylenimine (BPEI) average  $M_w \sim 25,000$  were purchased from Sigma Aldrich. Poly(ethylene terephthalate) (PET) films (Mylar A: thickness approximately 76.2  $\mu\text{m}$ ) produced by Dupont-Teijin were obtained from Tekra (New Berlin, WI). Exfoliated graphene nanoplatelets (GNP) (BET surface area: 300  $\text{m}^2/\text{g}$  and size 1  $\mu\text{m}$ , and average thickness of 2–4 nm) were purchased from XG Sciences, Lansing, MI. All aqueous solutions were prepared using deionized (DI) water ( $>18.1$  M $\Omega$ ) supplied by a Barnstead Nanopure Diamond-UV purification unit equipped with a UV source and final 0.2  $\mu\text{m}$  filter. Unless specified otherwise, all procedures were carried out at room temperature.

### 2.2. Layer-by-layer (LbL) assembly of polyelectrolyte modified GNP

For the hydrogen bonded assembly, the concentration of PAA and BPEI was adjusted to 2 mg/ml and 1 mg/ml, respectively. GNP platelets were dispersed in BPEI solution (now called BPEI-GNP) using a Fisher Scientific Ultrasonic probe (16 W) by sonicating for 1 h. GNP-BPEI solution was stirred overnight before use. The pH of the PAA and BPEI-GNP solution was adjusted to 4.0 and 7.5, respectively. For the deposition of the electrostatic layers, GNP were dispersed in 2 mg/ml BPEI solution using ultrasonication followed by magnetic stirring for at least 8 h. The excess polyelectrolyte is removed by passing the BPEI modified graphene solution through a 0.22  $\mu\text{m}$  cellulose-acetate membrane-filter systems from Nalgene. The BPEI modified graphene platelets collected on the filter membrane were washed with copious quantity of DI water and subjected to another cycle of filtration. They are finally suspended in DI water, and the pH is adjusted to 3.5–3.8. The PAA solution used for electrostatic deposition (concentration: 2 mg/ml) was adjusted to a pH of 6.0. For the preparation of composite films, the desired number of hydrogen bonded bilayers was initially deposited. This was followed by the required number of electrostatic layers.

The LbL assembly was carried out using a customized Carl-Zeiss slide-stainer. Before depositing the multilayers, the surface of the polyester films was cleaned using a Harrick plasma cleaner (Harrick Scientific Corporation, Brooding Ossining, NY). The films were subjected to air plasma for a period of 15 min. Air plasma helps in surface activation by producing hydrophilic moieties on the surface of the films. The immersion time was fixed to 15 min followed by a DI water rinse cycle of 2 min. After the deposition of each layer, the films were allowed to dry naturally for 5 min. After the

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