

GRAPHENE/POLYELECTROLYTE LAYER-BY-LAYER THIN FILMS FOR MULTIFUNCTIONAL COATINGS

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Abstract

A novel spray coating layer-by-layer approach was developed to fabricate thin, highly ordered and electrically conductive multilayer coatings, through alternating self-assembly of negatively charged thermally reduced graphene oxide (TRGO) and a positively charged polyelectrolyte (PEI) on a substrate to fabricate (PEI/TRGO)_n coatings (where *n* is the number of deposited bi-layers). How the microstructure and the electrical behaviour of (PEI/TRGO)_n LbL structures developed both with increasing graphene areal mass per bi-layer (keeping constant PEI content) and *n* was evaluated here. A strong effect of the lateral dimensions of graphene on the electrical properties of the coatings was found. These multifunctional LbL (PEI/TRGO)_n coatings seem promising for emerging technological applications, such as gas barrier applications or electromagnetic interference (EMI) shielding coating materials for the aerospace or defence sectors.

1. Introduction

Graphene has recently emerged as a particularly promising carbon nanomaterial for the development of multifunctional coatings, due to its lightweight, atomic thickness, bi-dimensionality, high specific surface area and excellent electrical conductivity [1-3].

The layer by layer (LbL) assembly of oppositely charged polyelectrolytes and inorganic particles represents a facile and inexpensive route for the fabrication of multilayer and multifunctional nanostructured thin films and coatings [4]. It offers important advantages, such as uniform coverages of the substrate surface, highly controllable film/coating thickness, properties and functionality. Another important advantage of the LbL coating method is its great versatility, as it can be used with a wide variety of fabrication processes.

In order to fabricate novel light-weight, thin and highly organized electrically conductive graphene based coatings for multifunctional applications we developed here a LbL assembly of oppositely charged polyelectrolytes and graphene flakes. Negatively charged and highly processable graphene materials with, at the same, high electrical conductivity to be efficient for applications such as electromagnetic interference shielding, are thus strongly required.

A method for the large scale production of highly processable and electrically conductive thermally-reduced graphene oxide (TRGO) has been recently developed [5]. In this method, the GO powder prepared using the Hummers and Offeman method [6] is annealed at high temperatures under an inert

atmosphere in order to exfoliate and partially remove functionalities from the surface of the flakes, which leads to electrically conductive graphene materials with near atomic thickness and negatively charged surfaces.

In this study, we developed a spray LbL coating technique to fabricate thin, highly organized and electrically conductive graphene based coatings on a substrate through alternating the absorption of negatively charged TRGO flakes and a positively charged polyelectrolyte (PEI), rendering (TRGO/PEI)_n coatings (with *n* being the number of deposited bi-layers), as schematically represented in Figure 1. We evaluated herein the microstructure and the electrical properties of (PEI/graphene)_n LbL coatings with increasing areal mass of graphene deposited (keeping constant the areal mass of PEI) per bi-layer, as well as with increasing number of bi-layers (*n*) in order to assess the interaction between layers.

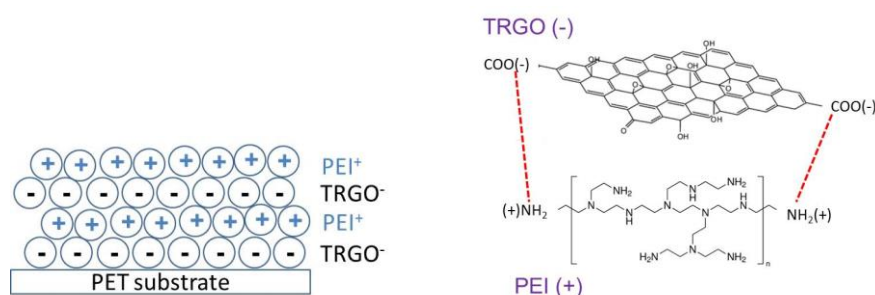


Figure 1. Scheme of the coating approach used to fabricate the LbL coatings through alternating the absorption of negatively charged TRGO and a positively charged polyelectrolyte (PEI), rendering (PEI/TRGO)_n coatings (*n* = number of bi-layers), which are established by electrostatic forces between both counter ions.

2. Experimental methods

2.1. Preparation and characterization of thermally reduced graphene oxide (TRGO)

Thermally reduced graphene oxide (TRGO) materials were prepared by annealing the GO powders at 750 °C under a nitrogen atmosphere to remove oxygen-containing functionalities from the surface of the graphene oxide flakes, following a procedure reported somewhere else [5].

In order to control the diameter of the TRGO, two different types of starting graphite were employed. A micro-graphite with a particle size distribution of $d_{50} = 17\text{-}23\ \mu\text{m}$ (SGA 20 M 99.5; AMG graphite, Hauzenberg, Germany) served as feedstock to prepare TRGO with an average diameter of $\sim 20\ \mu\text{m}$ (named here as Small-TRGO). Graphite with larger particles (Rfl 99.5; AMG graphite, Hauzenberg, Germany; min. 90% > 160 μm) was employed to produce TRGO with an average diameter of $\sim 100\ \mu\text{m}$ (named here as Large-TRGO).

2.2. Preparation of the LbL structures

Multi-layered graphene coatings were prepared by alternating self-assembly of negatively charged graphene (TRGO) and positively charged poly(ethyleneimine) (PEI), *n* times on a PET substrate, as schematically represented in Figure 1. A commercial aerosol (LindenTM H-BADG-AIRBRUSH-KIT) was employed to deposit graphene and PEI by spraying TRGO dispersions in ethanol (0.5 mg/mL) and aqueous solutions of PEI alternatively on a PET substrate. In order to evaluate the role of the lateral dimensions of graphene on the microstructure and properties of the LbL coatings, two different TRGO

materials were used, with average diameters of ~23 μm and ~100 μm, which are denoted herein as Small-TRGO and Large-TRGO, respectively, and thicknesses between 3.5 nm and 10 nm. In order to assess the formation of the LbL system, the graphene loading per bi-layer was varied by modifying the areal mass of graphene (i.e. mg per deposited layer and per surface unit) whilst the areal mass of PEI was kept constant. For each coating the graphene loading was determined from the values of areal masses of graphene and PEI. In order to assess the interaction between layers, the number of bi-layers, n , was also varied. It is important to note that the graphene loading per bi-layer depends on d_G but not on n .

2.3. Characterization of the LbL structures

A Zeiss Ultra 55 FEG-SEM was employed to analyse the fraction surface of the LbL coatings.

The impedance of the fabricated LbL (PEI/TRGO) _{n} coatings was tested on 2 mm x 3 mm specimens. All impedances were tested using a PSM 1735 Frequency Response Analyzer from Newtons4th Ltd connected with Impedance Analysis Interface (IAI) at the range of frequencies from 1 to 10⁶ Hz. The specific conductivities (σ) of the coatings were calculated from the measured impedances using the following equation (Eq. 1):

$$\sigma(\omega) = |Y^*(\omega)| \frac{t}{A} = \frac{1}{Z^*} \times \frac{t}{A} \quad (\text{Eq. 1})$$

where $Y^*(\omega)$ is the complex admittance, Z^* is the complex impedance, t and A are the thickness and cross section area of the sample, respectively.

3. Results and discussion

3.1. Microstructure of the (PEI/TRGO) _{n} LbL coatings

SEM pictures of the transversal sections of the LbL coatings (Figure 2a) revealed that the spray-on approach rendered highly ordered and well-defined multi-layered microstructures. A characterization of the fracture surface of all the coatings showed similar multi-layered structure.

3.2. Electrical properties of the coatings

In order to understand how the electrical conductance develops in LbL microstructures, the electrical properties of the fabricated LbL coatings were evaluated both with increasing graphene loading per-bilayer and with increasing n . Figure 2b shows the conductivities of the LbL structures at a frequency of 1 Hz as a function of graphene loading per-bilayer for the two graphene types studied here at $n = 2$ and $n = 10$.

We found S-shape curves typical of percolated systems in all the studied cases. The LbL coatings showed the typical behaviour of systems composed of two phases, i.e. a resistive component (graphene) and a capacitive component (PEI, i.e. a dielectric material). Below the percolation threshold the coating structures behaved as non-conductive materials. Above percolation (at higher graphene loadings) conductivities could be measured, which were found to increase with increasing amount of graphene deposited per-bilayer as well as with increasing n up to a maximum, which corresponds to the inherent conductivity of the TRGO employed for the fabrication of these LbL coatings.

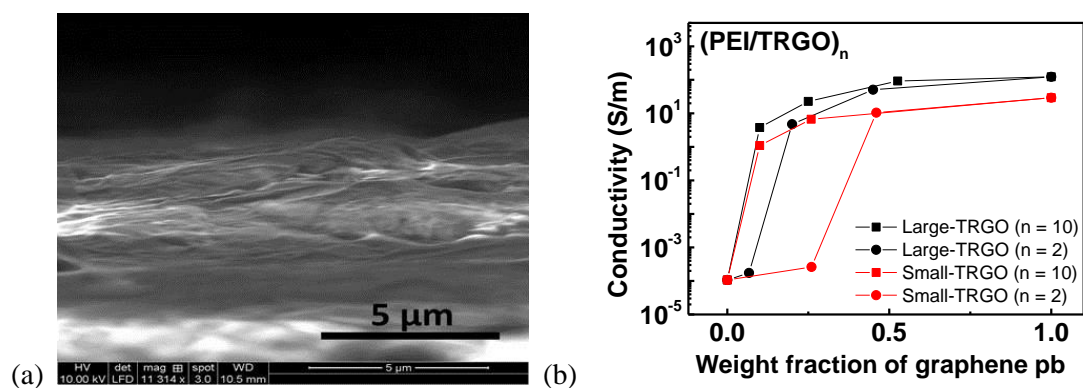


Figure 2. SEM image of the transversal section of (PEI/Small-TRGO)₅ LbL coating (a). Conductivities measured at 1Hz of frequency for (PEI/Small-TRGO)_n and (PEI/Large-TRGO)_n LbL coatings with different *n* (b).

Lower percolation thresholds were found for Large-TRGO based coatings relative to the Small-TRGO ones for identical graphene loading per-bilayer and *n*. In addition, lower percolation thresholds were found for *n* = 10 relative to *n* = 2 for identical loading of graphene and independently on the lateral dimensions. The self-assembly of graphene with larger diameters led to structures with higher conductivities and lower percolation thresholds for identical *n*, which is related to the presence of more flake-flake connections and defects in Small-TRGO deposits relative to Large-TRGO ones (also observed for the bulk papers). Both simulations and experiments have previously shown that fillers with larger aspect ratios lead to reduced percolation thresholds in systems with higher dimensionalities [7, 8] and the modelling of this effect has been further discussed [9].

Conclusions

A novel scalable spray coating layer-by-layer approach was developed here to fabricate thin, highly ordered and electrically conductive multilayer coatings through alternating self-assembly of negatively charged thermally reduced graphene oxide (TRGO) and a positively charged polyelectrolyte *n* times on a substrate to fabricate (PEI/TRGO)_n coatings (where *n* is the number of deposited bi-layers).

SEM of the transversal sections of the LbL coatings revealed highly ordered and well-defined multilayered microstructures. These LbL coating structures showed the typical behavior of electrically percolated systems. Above percolation the conductivities increased with increasing graphene loading per bi-layer and *n* up to a maximum value, which corresponds to the bulk conductivity of papers composed purely of graphene (graphene inherent conductivity). A strong effect of the lateral dimensions of the flakes on the electrical properties was found.

Due to their highly ordered microstructure and good electrical properties, these LbL coatings seem highly promising for applications as EMI shielding coatings and/or gas barrier coatings.

Acknowledgments

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