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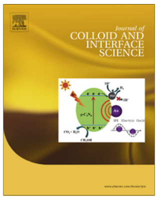

# Polydopamine decoration on 3D graphene foam and its electromagnetic interference shielding properties

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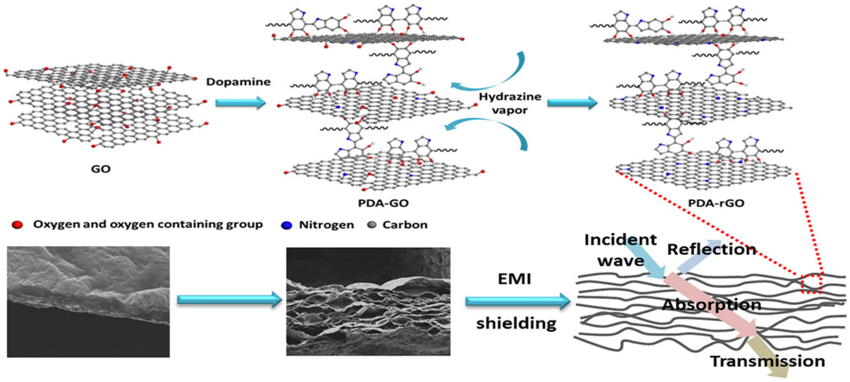
## GRAPHICAL ABSTRACT



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## ABSTRACT

3D graphene foam was recently demonstrated to exhibit excellent electromagnetic interference (EMI) shielding performance. In this work, we prepared 3D graphene foams by incorporating a surface modification process of graphene via self-polymerization of dopamine with a subsequent foaming process. The multiple roles played by polydopamine (PDA), including as nitrogen doping source and as an enhancement tool to achieve higher extent of reduction of the graphene through providing wider pathways and larger accessible surface areas were discussed in detail. Despite the presence of the PDA which acted as barriers among the graphene layers that hindered the electrons movement, the enhanced reduction of graphene sheets and the polarization effects introduced by PDA decoration compensated the negative effect of the barrier on EMI shielding effectiveness (SE). As a result, the PDA decorated 3D graphene foams showed improved EMI shielding effectiveness (SE) compared to PDA-free graphene foam (from 23.1 to 26.5 dB). More significantly, the EMI shielding performance of the PDA decorated graphene foam was much superior to all existing carbon-based porous materials when the thickness of the specimen was considered.

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## 1. Introduction

Nowadays, electronics is widely used in information processing, telecommunication, and signal processing. With the rapid development of various modern electronics, electromagnetic (EM) pollution elevates the degradation of the electronic devices performance and facilities as well as the serious threat to the work place's safety. Hence, great effort has been motivated for the development of high-performance electromagnetic interference (EMI) shielding materials to minimize the harmful effects provided by EMI. Searching for the library of EMI shielding materials, carbon-based nanomaterials, such as carbon nanofibers (CNFs), carbon nanotubes (CNTs) and graphene emerged as an excellent EM wave attenuation candidate [1–14]. Among them, graphene as the thinnest material in the carbon family [15] which have extremely high surface area and extraordinary electron mobility may be the best candidate for achieving superior EMI shielding performance.

The EMI shielding effectiveness (SE) of a material strongly depends on its electrical conductivity [16] and higher electrical conductivity tends to show better EMI shielding performance [17]. Reduction of graphene oxide (GO) which is a preferred method for large-scale production of graphene [18] aims at the recovery of the conjugated network of $sp^2$ graphitic lattice of graphene to the greatest extent to restore the intrinsically high electrical conductivity. Different reduction methods of GO introduced considerable variations of properties that affecting its final performance. Besides the reduction, chemical doping of heteroatoms such as sulfur [19] or nitrogen [20,21] into reduced GO (rGO) greatly influenced the electrical conductivity of graphene. In general, the reduction and the chemical doping process were conducted separately and usually involved high equipment costs, harsh environment, special gas precursors, or a large well-ordered template. Therefore, it is desirable to develop a low-cost and facile in situ strategy to obtain functionalized rGO for high EMI shielding performance.

In addition to high EMI SE, lightweight is another important technical requirement for practical EMI shielding materials. Through coupling rGO with high EMI SE potential and lightweight structure, a material system with superior EMI shielding performance can be expected. Recently, freestanding graphene foam was developed by different groups via a foaming process [22–24] and was used in various applications including EMI shielding. Since electrical conductivity is one of the primary requirements for EMI shielding and higher extent of reduction of the GO could increase the electrical conductivity, the EMI shielding performance can be improved through further reduction of graphene foam and/or doping heteroatoms on graphene foam. It was reported that the surface treatment of graphene by polydopamine (PDA) allowed the partial reduction of GO [25–28]. This work aims to take advantage of the duel functions of PDA, inducing partial reduction of GO and introducing chemical doping to graphene simultaneously, through a one-step in situ process before foaming. The PDA served as a reducing agent and nitrogen source that was beneficial to the EMI shielding performance. The presence of PDA molecules also assisted in the expansion of the interlayer distance between the graphene sheets in order to promote the further reduction of GO through providing wider pathways and larger accessible surface areas for reducing agent. The novel design of PDA decorated graphene foam was demonstrated for the first time for EMI shielding purpose and was proven to afford great opportunity to develop high-performance EMI shielding materials.

## 2. Experimental section

### 2.1. Raw materials

Dopamine hydrochloride (99%) and tris(hydroxymethyl)amino methane hydrochloride were purchased from Regent Chemicals Pte Ltd. Natural graphite powder, sulfuric acid ($H_2SO_4$, 95–98%), potassium permanganate ($KMnO_4$), dimethylformamide (DMF), hydrazine monohydrate (98%) and whatman® anodized aluminum oxide (AAO) membrane with a pore diameter of 0.02 μm were purchased from Sigma-Aldrich. Hydrogen peroxide ($H_2O_2$, 30%) was supplied by VWR Company. All the chemicals and materials were used as received.

### 2.2. Preparation of PDA-rGO foam

GO was obtained by oxidation of natural graphite powder according to the modified Hummers' method [29]. The synthetic procedure of PDA decorated rGO (PDA-rGO) foam production is depicted in Fig. 1. 2 mg/ml of GO was added into 250 ml 10 mM Tris buffer solution (pH 8.5), followed by adding 0.5 g of dopamine hydrochloride. The suspension was mechanically stirred for 4 h at room ambient and then centrifuged at 8000 rpm for 20 min. The centrifugation process was conducted to remove the free PDA particles. The dark slurry-like PDA-GO was washed with deionized (DI) water for 4 times in order to remove unreacted dopamine monomers and free PDA [30] and then re-dispersed into DMF to carry out the filtration. In this procedure, PDA-GO suspension (15 ml) was filtered through a porous AAO membrane. The usage of AAO membrane is an effective way to prepare freestanding GO films with compact layered structures [31]. The PDA-GO film was peeled off from the AAO membrane, followed by the foaming process to prepare PDA-rGO foam. In this process, the PDA-GO film was put into an autoclave prefilled with 90 μL of hydrazine monohydrate. The autoclave was then placed in an oven at 90 °C for 12 h. It is important to note that the PDA-GO film was suspended well above the hydrazine monohydrate since direct contact of hydrazine monohydrate caused the dissolution of the film.

### 2.3. Characterization

Morphologies of the synthesized products were observed using transmission electron microscopy (TEM) by JEOL 2100F. Microstructures of the specimens were examined using a Jeol 7600F field emission scanning electron microscope (FESEM) with an acceleration voltage of 5 kV. The FESEM specimens were sputtered with a thin layer of platinum before the examination. X-ray diffraction (XRD) patterns of the specimens were acquired by an X-ray diffractometer (Bruker D8) using CuKα radiation ($\lambda = 0.15406$ nm). Raman spectra were recorded by using a WITEC CRM200 confocal Raman microscopy at an excitation wavelength of 488 nm with spectra resolution of 1 $cm^{-1}$. A 100X objective lens with a numerical aperture of 0.95 was used. High resolution X-ray photoelectron spectroscopy (XPS) with monochromatic Al Ka as X-ray excitation source operating at 15 kV and 10 mA was used to characterize the surface compositions of specimens. The electrical conductivity was measured using the two-probe method by Hewlett Packard 4140B pA Meter/DC Voltage source. The I-V curves were measured at ambient condition over a range of 0.2 to −0.2 V with a step of −0.01 V across the pair of Au electrodes with a channel length of 100 μm. The scattering parameters, e.g., $S_{11}$ (input reflection), $S_{22}$ (output reflection), $S_{21}$ (forward transmission) and $S_{12}$ (reverse transmission) were measured using a