Ultrathin Active Layer for Transparent Electromagnetic Shielding Window

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ABSTRACT: Recently, electromagnetic (EM) shielding (EMS) window, especially the ultrathin, transparent EMS active layer, has been the primary objective of extensive studies because of its widely potential applications in stealth technology, high radiation pollution, and others. However, several defects, including opacity and large thickness, have severely restricted the application in optical EMS devices. Herein, we developed an ultrathin and highly transparent EMS active layer on a rigid glass and a flexible polyethyleneterephthalate substrate by chemical doping CVD (chemical vapor deposition) graphene with nitric acid (HNO₃) as the P-type dopant, which has a 91% transmittance and 1/1000 thickness compared to the conventional EMS active layer. The HNO₃-treated graphene shows excellent EMS efficiency by a factor of 4.5, significantly compensating for the adverse effects of the grain boundaries between CVD graphene crystals. Additionally, 55% HNO₃ is the most suitable for achieving high EMS effectiveness, which can be significantly improved by treating for only 5 min. This unique chemical-doping CVD graphene holds potential for being exploited as a transparent active layer in numerous EMS applications.

1. INTRODUCTION

Electromagnetic (EM) pollution has become a serious problem because of the rapid development of electronic equipment, which has attracted enormous attention to invent efficient EM shielding (EMS) materials. Conventional EMS materials contain metal foil, metal mesh, conductive coating, and conductive composite materials, although they can achieve high EMS effectiveness (EMSE), but these materials are more than tens of microns in thickness and opaque, which are greatly limited by the application in some special fields such as aerospace, microelectronics, and ultrathin. The EMSE of the conventional conductive coating is only 3 dB μm⁻¹.²

Considering the unique features such as corrosion resistance, lightweight, and easy processing, much attention has been attracted to develop new graphene composite and their applications in EMS materials.¹⁻³ The EMSE of PS/graphene composite with 3.47 vol % graphene can reach 48 dB.¹ For the lightweight polyetherimide (PEI)/graphene composite foams, its EMSE varies from 17 to 44 dB/(g/cm³) in the range of 8−12 GHz.³ The graphene-based lightweight shielding materials are of outstanding EMS performance. The addition of magnetic particles such as Fe₃O₄ can increase the absorption efficiency.³⁻⁴ The thickness of the graphene composite is too high to be used in ultrathin devices.

Generally, most of the EMS active layers are currently black, opaque, and thick in micron scale. The contradiction between thickness and transparency of the conventional shielding material restricts its application in nanoelectronic devices¹⁵,¹⁶ and transparent conductive windows by which not only EM waves can be shielded, but also the situation inside the shielded room can be observed. So, it is necessary to develop ultrathin and transparent EMS materials. For instance, Batrakov et al. successfully proposed a ~241 nm thick pyrolytic carbon film which can absorb about 50% microwave.¹⁷ In addition, Wu et al. also fabricated a 4 μm carbon nanotube film, and its EMSE can achieve 61−67 dB.¹⁸ In addition, Kim et al. deposited silver nanowires in polyimide surface to produce a conductive network, the EMSE of the fabricated film is 55 dB with a transmittance of 58%, and the thickness of the film is less than 10 μm.³ The materials reported above are expected to be used in ultrathin devices, but these materials are difficult to produce in large scale, which seriously hinders its application. The materials reported above are expected to be used in ultrathin devices. Furthermore, it is still difficult to produce such graphene EMS on a large scale which still constitutes a major obstacle in the practical applications, especially for excessive use.

Graphene is a two-dimensional material with only a carbon monolayer composed of sp² hybrid carbon atoms with a honeycomb-like lattice. Its electrical conductivity at room temperature and monolayer transmittance are as high as 2 × 10⁴ cm² V⁻¹ s⁻¹ and 97.7%,¹⁹,²⁰ Graphene is expected to be an excellent shielding material because of its excellent electric property. For example, Song et al. have fabricated conductive graphene paper used as an ultrathin shielding material,²¹ the EMSE of the graphene paper can reach 19.0 dB with 0.1 mm in...
thickness and can reach 46.3 dB with 0.3 mm in thickness. Shen et al. developed an ultrathin graphene oxide film with 8.4 μm in thickness which shows excellent EMSE of 20 dB.22 Kim et al. introduced the EMSE effectiveness (SE) of the reduced graphene oxide (RGO) sheets interleaved between PEI films fabricated by electrophoretic deposition.23 Lu et al. investigated the EM interference (EMI) shielding performance of multilayer graphene (without doping)/polyethylene terephthalate (PET) structure at 18−26.5 GHz.24 Zhao et al. designed an optically transparent shielding enclosure by integrating indium tin oxide with graphene/quartz substrates, which effectively suppresses the cavity-resonant modes, and the shielding enclosure may cause EMI.25 Wen et al. reported high-efficiency EMI shielding of light-weight RGOs at elevated temperatures.26 Cao et al. found that ultrathin and lightweight graphene composites exhibit high-efficiency microwave absorption at elevated temperatures.27 The chemical vapor deposition (CVD) method is an efficient way to grow graphene in large scale. It is expected to be used as an ultrathin and transparent EMS material. Hong et al. demonstrated that the EMSE of the monolayer CVD graphene is 2.27 dB which can shield 40% of the incident waves.28 The EMSE value per unit thickness of graphene is 7.73 dB nm−1 which is more than 7 times greater than that (1.04 dB nm−1) of the gold film. The theoretical conductivity of ideal monolayer graphene, estimated by using the plane-wave theory, is known to be $10^8$ S m−1.19 They calculated that the theoretical value of EMSE for ideal monolayer graphene should be 16.5 dB, which can shield 97.8% waves. However, the migration of carrier is hindered because of the grain boundary or other defects, which reduces the EMSE of CVD graphene.

Chemical doping method has been used to improve the conductivity of the carbon-based materials such as graphite and carbon nanotube film.29,30 The previous work shows that doping with nitric acid (HNO₃) can significantly increase the conductivity of graphite.31 In our work, we used HNO₃ as the P-type dopant to improve the EMSE of the CVD graphene. Results show that the EMSE of the trilayer graphene is increased by a factor of about 4.5 after 55% HNO₃ doping for 30 min, and the thickness of the EMS active layer, with a transparency of up to 91%, is reduced to about one-thousandth of the thickness of the usual EMS active layer. We also discussed the best doping conditions of HNO₃ for achieving high EMSE.

2. RESULTS AND DISCUSSION

The schematic diagram of the polymethyl methacrylate (PMMA)-assisted transfer method is shown in Figure 1. As shown in Figure 1, graphene was successfully transferred onto transparent PET films and glass substrates by the PMMA-assisted method. The transferred 1–3-layer graphene on PET was denoted as PET/graphene-N (N = 1, 2, and 3). PET/graphene-N-PMMA and PET/graphene-N (N = 1, 2, and 3), respectively, denoted graphene with preserving and removing PMMA on the surface of transferred graphene. The transferred graphene is of high transmittance, as shown in Figures 2 and 3. For the light with the wavelength of 1000 nm, the transmittance of PET/graphene-1-PMMA is up to 91%,...
which is slightly lower than that of ideal monolayer graphene.\textsuperscript{20} Figure 2d indicates that the graphene stack on glass substrate also shows higher transmittance.

Figure 4 shows the Raman spectra of the 1−3-layer graphene EMS active layer on the PET film. The ratio of the intensity of 2D and G bands ($I_{2D}/I_G$) is used to identify the layers of graphene.\textsuperscript{32,33} As shown in Figure 4, $I_{2D}/I_G > 1$ for once transferred graphene (Figure 4a), $I_{2D}/I_G = 1$ (Figure 4b) for twice transferred graphene, and $I_{2D}/I_G < 1$ for thrice transferred graphene (Figure 4c). These values of $I_{2D}/I_G$ indicate that the graphene stacks in Figure 4a−c include monolayer, bilayer, and trilayer graphene, respectively.

PMMA was used to assist the transfer of graphene in this work. The effect of removing PMMA on the EMSE of graphene was considered, and the graphene stacks preserving PMMA were first studied. Figure 5 shows the EMSE properties of PET/graphene-1/PMMA, PET/graphene-2/PMMA, and PET/graphene-3/PMMA. The results show that both PET and PET/PMMA films have almost no EMSE in the range of 8.2−12.4 GHz. In the same test band, the EMSE of the stack PET/graphene-1/PMMA with one layer of graphene varies in the range of 2.8−5.1 dB, which indicates that only one layer of graphene in the test band has obvious EMSE. In the same test band, the EMSE ranges of PET/graphene-2/PMMA and PET/graphene-3/PMMA are 5.0−7.2 and 6.8−9.2 dB, respectively. Each stacking of one layer of graphene, the EMSE increases by about 2 dB, which suggests that the EMSE approximately increases linearly with the number of graphene layers. The stacks with 1−3 layers of transferred graphene can, respectively, shield ~50, ~70, and ~80% EM waves under the test band.

For PET/graphene-N/PMMA stacks, we found that three ways can contribute to the attenuating EM waves: (1) PMMA impedance is close to that of air, but the impedance of PMMA is very different from that of graphene. Therefore, when the EM wave reaches the surface of graphene through PMMA layer, the reflection attenuation of EM wave occurs on the surface of graphene. (2) An unreflected EM wave undergoes absorption attenuation when passing through graphene. (3) When the EM wave passing through a layer of graphene reaches the surface of another layer of graphene in the multilayer graphene stacks, the reflection attenuation occurs again within the stacks because of the differential impedance between PMMA and the graphene. Multiple reflection attenuations of this part of the EM wave will take place within the stacks. In addition to the protection of graphene in the transfer process, the PMMA layer sandwiched between two layers of graphene can also act as an impedance mutation layer between graphene layers, causing the EM wave to be reflected multiple times within the stacks.

Figure 6 shows the EMSE value of multilayer graphene stack is significantly higher than that of monolayer graphene. However, PET/graphene-N/PMMA needs to be superimposed layer by layer. Alternatively, we stacked three PET/graphene-1/PMMA stacks together and tested their EMS properties. The results indicate that the EMSE value of three sheets of PET/graphene-1/PMMA is higher than that of PET/graphene-3/PMMA, indicating that the transfer process for a three-layer stacking of PET/graphene-1/PMMA has a relatively lower damage to the integrity of graphene.

There are grain boundaries in CVD graphene because of the different crystal orientations of the Cu substrate and the growth patterns of CVD graphene.\textsuperscript{34} As one kind of defect, the grain boundary hinders the migration of carrier, and then reduces the

Figure 3. Transmittance of the PET/PMMA and PET/graphene-N/PMMA (N = 1, 3).

Figure 4. Raman spectra of the PET/graphene-N-PMMA (N = 1, 2, and 3).

Figure 5. EMSE of PET, PET/PMMA, and PET/graphene-N/PMMA (N = 1, 2, and 3).
carrier concentration,\textsuperscript{35,36} resulting in a lower conductivity of CVD graphene compared with that of the ideal graphene. The EMSE of graphene is related to its conductivity,\textsuperscript{37} and the EMSE is calculated as follows:

\begin{equation}
SE = SE_R + SE_A + SE_B
\end{equation}

\begin{equation}
SE = 20 \log \left( \frac{E_0}{E_1} \right) = 20 \log \left( \frac{H_0}{H_1} \right)
\end{equation}

\begin{equation}
SE_R = 168 - 10 \log \left( \frac{\mu_r}{\sigma_r} \right)
\end{equation}

\begin{equation}
SE_A = 1.314d \sqrt{\mu_r \sigma_r}
\end{equation}

where, $SE_R$, $SE_A$, and $SE_B$ are the reflection loss, the absorption loss, and the reflection loss inside the shield, respectively. $E_0(H_0)$ and $E_1(H_1)$ are the electric fields (magnetic field) intensity at the point with and without shields, respectively. $\mu_r$ is the magnetic permeability of the shielding material relative to the vacuum. $\sigma_r$ is the conductivity of the shielding material relative to the ideal copper. $f$ is the EM wave frequency (Hz). $d$ is the thickness of the shielding material (cm). Equations 3 and 4 indicate that the EMSE of the shielding material increases with the conductivity.

Chemical doping method is one of the effective ways to improve the conductivity of carbon materials. HNO$_3$ has been demonstrated to be an effective P-type dopant to improve the conductivity of graphite and carbon nanotube film.\textsuperscript{31,38,39} The doping mechanism is described as follows:\textsuperscript{30,40}

\begin{equation}
6\text{HNO}_3 + 2\text{C} \rightarrow \text{C}_2\text{S}_2\text{NO}_4^- \cdot 4\text{HNO}_3 + \text{NO}_3^- + \text{H}_2\text{O}
\end{equation}

Because graphene and graphite (or carbon nanotube) essentially have the same chemical component and structure, HNO$_3$ was used to dope CVD graphene to improve its EMSE. As a P-type dopant, the electron is transferred from the graphene to the HNO$_3$, creating a hole in graphene. The carrier concentration of graphene increases for the shift of the Fermi level, thus improving the conductivity.

Before HNO$_3$ doping, we first use acetone (according to section 4.3) to remove PMMA from the surface of graphene so that the surface of graphene becomes the outermost layer for easy doping. After the removal of PMMA, the EMSE of graphene with and without HNO$_3$ doping is shown in Figure 7. The results show that the EMSE of the graphene with removing PMMA is lower than that of the graphene without removing PMMA. The EMSE of three layers of graphene without PMMA is one third of the EMSE of three layers of graphene covered with PMMA. In addition, after removing PMMA, the EMSE decreases with an increase in the amount of transferred graphene, which is opposite to the effect laws of the number of transfer layers on the EMSE when PMMA is not removed (Figures 5 and 8). This diametrically opposed phenomenon is mainly because of the damaging effect of the removal of PMMA on the integrity of graphene, which can be observed from the optical micrographs of graphene stacks (Figure 8).

Figure 9 shows the effect of HNO$_3$ doping on the EMSE of graphene stacks. The results indicate that HNO$_3$ doping is an
efficient way to improve the EMSE of graphene. After doping, the EMSE of the PET/graphene-1 improved from 3.0−5.2 to 4.5−7.5 dB (increased by about 1.5 times); the EMSE of the PET/graphene-2 is improved from 1.7−3.7 to 5.6−7.9 dB (increased by about 3 times); and the EMSE of the PET/graphene-3 is improved from 1.9−3.2 to 9.8−12.6 dB (increased by about 4.5 times). The EMSE increases non-linearly with the number of the graphene layer. From 1 layer to 3 layers, the increasing amplitudes vary from 1.5 to 4.5 dB, which means the more the number of transferred graphene layers, the more obvious the effect of HNO_{3} doping on the enhancement of the EMSE. The doping efficiency of monolayer graphene is relatively lower because HNO_{3} molecules can only dope on the graphene surface. For multilayers graphene, HNO_{3} molecules can dope between the graphene layers, so the doping efficiency is high. In addition, to further clarify the EMS mechanisms, the coefficients of absorption A, reflection R, and transmission T were investigated. Considerable efforts have been devoted to investigating these factors by Wen et al. and Cao et al., who have proposed the corresponding relationships to obtain these factors from the measured S-parameters (dB) in previous studies. In their work, the scattering parameters, including S_{11} and S_{21}, were determined by a vector network analyzer both using the wave-guide method. In this work, the S-parameters of the samples between 8.2 and 12.4 GHz were measured through the coaxial method by a PNA-X network vector analyzer. Hence, we calculated the reflection coefficient R, absorption coefficient A, and transmission coefficient T using an alternative method proposed in Yang et al. and Khanum et al.’s papers, where the same coaxial method was employed. The related equations are described as follows

\[ R = 10^{0.1S_{11}} \]  

(6)

\[ T = 10^{0.1S_{21}} \]  

(7)

\[ A = 1 - R - T \]  

(8)

\[ \text{SE}_{R} = -10 \log(1 - R) \]  

(9)

\[ \text{SE}_{A} = -10 \log \left( \frac{T}{1 - R} \right) \]  

(10)

\[ \text{SE} = \text{SE}_{R} + \text{SE}_{A} \]  

(11)

Subsequently, the effect of HNO_{3} doping on the \( \text{SE}_{A} \) and \( \text{SE}_{R} \) parameters of graphene stacks is shown in Figure 7d−f. After doping, both \( \text{SE}_{A} \) and \( \text{SE}_{R} \) values of all of the PET/graphene-N increase, which is attributed to the improved conductivity. The results are in accordance with eqs 3 and 4, indicating that chemical doping using HNO_{3} (as a P-type dopant) is one of the effective ways to improve the conductivity and EMSE of CVD graphene.

The removal of PMMA can damage the integrity and the EMSE of graphene. In particular, the more the number of transferred graphene layers with removing PMMA, the more serious is the damage to graphene. However, HNO_{3} doping can increase the EMSE of these damaged graphene stacks PET/graphene-3 by 4.5 times. Therefore, the effect of HNO_{3} doping on the improvement of the EMSE of graphene is expected to be more obvious with improving the integrity of graphene in the
process of removing PMMA. The thickness of 1–3-layer graphene EMS active layer varies from 3.4 to 10.2 Å, which is only about 1/1000 of the thickness of the conventional EMS active layer. Therefore, the HNO₃ doping graphene can be used to prepare ultrathin electronic devices and transparent EMS window.

Figure 9a shows the EMSE of PET/graphene-2 doped by 15, 35, 55, 65, and 95% HNO₃ for 30 min. The EMSE did not have a significant improvement after doping by 15% HNO₃ (Figure 9a). The EMS performance increased with the HNO₃ concentration. With increasing the HNO₃ concentration, more and more HNO₃ molecules react with graphene, thus resulting in the increase of the carrier concentration. The EMSE of PET/graphene-2 reaches the maximum value for 55% HNO₃ doping, and it declines for the higher HNO₃ concentration (65 or 95%). This might be attributed to the fact that the high HNO₃ concentration may induce defects on graphene and the deformation of PET film, thus affecting the shielding performance of graphene.

The effect of doping time on the EMS performance of graphene was studied and shown in Figure 9b. For all samples in this section, the concentration of HNO₃ was fixed at 55%. PET/graphene-2 was doped for 5 min, 30 min, 1 h, 3 h, and 6 h. The EMSE of PET/graphene-2 has been significantly improved after doping for only 5 min, demonstrating the high doping efficiency of HNO₃. The EMSE of graphene increased with the doping time, and it changes very little after 3 h of doping.

Figure 10 shows the transmittances of PET/graphene-N (N = 1, 2, and 3) before and after doping. All graphene stacks on PET films have a high transmittance at 400–1100 nm. It is found that the HNO₃ doping almost has no effect on the transmittance of graphene. For PET/graphene-2, the transmittance even increases slightly after HNO₃ doping. The residuals between graphene layer may be rinsed by HNO₃, thus resulting in the increase of the graphene transmittance.

3. CONCLUSIONS

In this work, we have used HNO₃ as a P-type dopant to improve the EMS performance of CVD graphene. It has been found that the HNO₃ doping increases the EMSE of PET/graphene-3 by a factor of 4.5, which indicates that HNO₃ doping is an effective way to improve the EMSE of graphene. The effect of HNO₃ doping on the improvement of the EMS performance of graphene is expected to be more obvious with improving the integrity of graphene in the process of removing PMMA and transferring graphene. Besides, graphene by HNO₃ doping has high transmittance by rinsing the residuals between graphene layers. The thickness of graphene EMS active layer is only about 1/1000 of the thickness of the conventional one. HNO₃-doping CVD graphene has wide potential applications in ultrathin electronic devices and transparent EMS window.

4. EXPERIMENTAL SECTION

4.1. Materials. Graphene (ratio of monolayer ≥95%) grown by the CVD method on copper foil was purchased from 2D Carbon Tech Inc. Ltd (Changzhou). FeCl₃·6H₂O, acetone (analytical reagent), HNO₃ (analytical reagent), anisole (analytical reagent), and HCl (analytical reagent) were obtained from Kelong Inc. Ltd (Chengdu). PET films and PMMA with a molecular weight of 9000 were purchased from 2D Carbon Tech Inc. Ltd (Changzhou). The Cu etchant was 15 wt % FeCl₃ aqueous solution.

4.2. Characterization. The EMSE of the samples between 8.2 and 12.4 GHz is tested through the coaxial method by a PNA-X network vector analyzer (Agilent Technologies Inc.).
The samples for the test were 13 mm in diameter. To avoid the EM waves generated by the port spill test error, both ends of the port were calibrated before testing. The transmittances of graphene were tested by UV-3600 UV-visible spectrophotometer (Shimadzu Corporation, Japan). To avoid the influence of the substrate on the light transmittance of graphene, graphene was first transferred to a transparent substrate (PET), and a blank substrate (PET) was used as a reference. Raman spectrum was tested by a Raman spectrometer (DXRxi, Thermo Fisher Scientific, United States) imaging microscope using a 532 nm excitation laser source. To avoid damage to the graphene by the laser source, laser energy is set to 4.5 mW. Each sample was tested in three areas. Optical microscope: first, the graphene was transferred onto PET films. Then, the CMM-20 metalliclographic optical microscopes (Shanghai Changfang Optical Instrument Co., Ltd.) was used to characterize the graphene transferred onto the PET films by analyzing the color contrast between graphene and silicon wafers.

4.3. Transfer and Doping Process. PMMA has many prominent features, such as the relatively low viscosity, excellent wetting capability, flexibility, and good dissolubility in several organic solvents. Moreover, the high transparency of PMMA makes it easy to observe the process of Cu removal. Therefore, PMMA was used as the supporting layer to transfer graphene grown by CVD. PMMA anisole solution (50 mg/mL) was spin-coated on graphene by a spin-coating apparatus at room temperature; then, the samples were cured at room temperature for 3 h. CVD graphene was grown on both sides of the copper substrate. To facilitate the etching of the copper substrate and maintain the quality of transferred graphene, the graphene on one side of the copper substrate was removed by oxygen plasma at 50 W for 1 min. The metal substrate was etched with a 15 wt % aqueous solution of ferric chloride for 2 h until the metal substrate was completely etched away. Then, the PMMA/graphene stack was transferred to a Petri dish containing 10% HCl to wash off the residual HCl for 10 min. PET film, glass, and silicon wafers were cleaned using ultrasound for 5 min in acetone and isopropyl alcohol to remove the remainings on its surface. The PMMA/graphene stacks were picked from the water with the prepared PET film (or glass or silicon wafers) and were dried at room temperature for 12 h. PMMA was removed with acetone for 3 h; then, the graphene was transferred onto the PET film (or glass, SiO2/Si wafers), as shown in Figure 1. Multilayer graphene was transferred by stacking the transfer of monolayer graphene. Graphene was doped by immersing the samples into HNO3 aqueous solution at room temperature with various concentrations and reaction times.

Notes
The authors declare no competing financial interest.

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