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Using organic solvent absorption as a self-assembly method to synthesize three-dimensional (3D) reduced graphene oxide (RGO)/poly(3,4-ethylenedioxythiophene) (PEDOT) architecture and its electromagnetic absorption properties

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A novel self-assembly 3D-RGO/PEDOT architecture has been synthesized through organic solvent absorption and gentle heating. It gives a new idea to obtain RGO based 3D materials, and the results also pointed that this 3D-RGO/PEDOT architecture has a promising application in electromagnetic absorption.

Electromagnetic pollution has raised an ever-increasing challenge to modern society. Electromagnetic interference (EMI) have harmful effects on electronic devices as well as organism, therefore shielding materials are intensely developed to protect electronic devices and even human beings from this hazard. A good shielding material should prevent both incoming and outgoing EMI,[1] therefore electromagnetic absorption is more important than electromagnetic reflection. The conventional electromagnetic absorption materials are based on metal oxide, especially the ferrite. Although they have a good electromagnetic absorption properties, however large content ratio in composite have limited their application. Lightweight is one of the most important technical requirements for effective and practical electromagnetic absorption applications especially in areas of stealth aircraft, aerospace, and fast-growing next-generation flexible electronics. An "ideal" electromagnetic absorption material should exhibit low density, tiny thickness, strong absorption and also broad bandwidth simultaneously.[2] Recent years, several electromagnetic absorbers has been aroused based on dielectric materials, such as CuS,[3,4] Bi_2S_3,[5] intercalated graphite,[6] α-MnO_2,[7,8] and ZnO nanorods.[9] Benefit with the nano-structure, a very low content ratio can reach an ideal electromagnetic absorption performance (less than 20 wt%).

Reduced graphene oxide (RGO) is a kind of two dimensional (2D) carbon material which was synthesized from graphene oxide (GO) through chemical,[10] thermal,[11] optical,[12,13] and hydrothermal[14] methods. Due to the intense interest of graphene all over the world in the last decade (2004-2014), RGO also catches researchers interest because of its carbon skeleton structure is highly similar with pure graphene. Although RGO can't reach the high level properties in electronic,[15] thermal,[16] mechanical[17] and optical[18] like graphene, but it is easy to synthesize, high yield, and convenient to modify. Dielectric loss and low density of RGO enable it to be used as an electromagnetic absorption material. With a suitable preparation process, pure RGO can display a good electromagnetic absorption performance.[19] In order to further enhance the apsorption property, macro or nanoparticles were added or crystallized on RGO surface, such as Fe_2O_3,[20,21] Fe_3O_4,[22,23] hematite,[24] Co_3O_4,[25] $MnFe_2O_4$,[26] polyaniline,[27,28] carbon nanotubes.[29] Furthermore, core-shell structure, for example, Fe_3O_4@ZnO,[30] SiO_2@Fe_3O_4,[31] and Fe_3O_4@Fe,[32] can also improve the absorption property. Besides, the polyvinylidene flurde (PVDF) is widely used as a matrix in electromagnetic absorbers recently. This polymer possesses a high operating temperature and dielectric strength. High permittvity of PVDF could achieve uniform distribution of a local electric field in filled materials and a low dispersion of the complex permittivity at the required frequency range at the same time.[3] This PVDF based composites exhibit better electromagnetic absorption performance than paraffin matrix in recent paper.[4,5,9,19]

Poly(3,4-ethylenedioxythiophene) (PEDOT), the conducting polymer, can be used as an electromagnetic absorber due to its high electrical conductivity.[33] Crystalline 2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT) can be facile synthesized through a facile halogenation approach (N-bromosuccinimide, NBS),[34,35] and gentle heating (50-70 °C) affords a highly conducting solid-state polymerization (SSP) of bromine-doped poly(3,4-ethylenedioxythiophene).[34] An excellent electromagnetic absorption performance was appeared when the content ratio reached 50 wt% in a paraffin matrix (see ESI).

In this study, the unique sorbent property of hydrothermal 3D RGO for organic solvent was used as a self-assembly process to build 3D-RGO/PEDOT architecture. Compared with former works, the new architecture make full use of 3D-RGO's pore. DBEDOT solution in chloroform ($CHCl_3$) was absorbed into 3D RGO easily, and after gentle heating, DBEDOT was polymerized in these pores rather than on the carbon skeleton surface (Fig. 1). Fig. 2a-b shows that 3D-RGO has a light weight, it contribute to the pores which were formed during the hydrothermal process. As revealed by field emission scanning electron microscopy (FE-SEM), the pore sizes of the 3D architecture are in the range of submicrometer to several micrometers (Fig. 2c-d). Hydrophobicity was obtained by contact angle measurements performed on the 3D-RGO and air interface, yielding a contact angle of 113.5° (Fig. 2e). But organic solvents, such as $CHCl_3$ were quickly absorbed. Due to the physical adsorption process, when the 3D-RGO was added into the solution, solvent and solute would both absorbed into this architecture. The architecture was heated up to 70 °C which was little higher than $CHCl_3$'s boiling point (61.3 °C), the liquid could be evaporated, and recollected elsewhere, and the DBEDOT monomer would be SSP in these pores. Fig. 2f-g has been shown the evidences of this phenomenon. A specific surface area was decreased from 276 m^2 g^{-1} of 3D-RGO to 29 m^2 g^{-1} of 3D-RGO/PEDOT, this result also imply that the pores has been crammed by SSP PEDOT. Due to the hydrophobic property of PEDOT, the self-assembly 3D-RGO/PEDOT expresses a higher contact angle (123.4°) than 3D-RGO under the same testing situation (Fig. 2h).

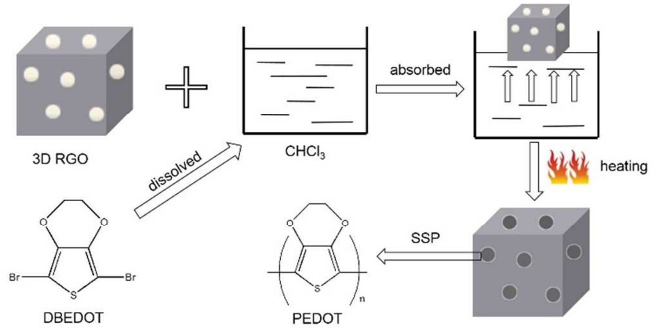

Fig. 1 Synthesis strategy of 3D RGO/PEDOT

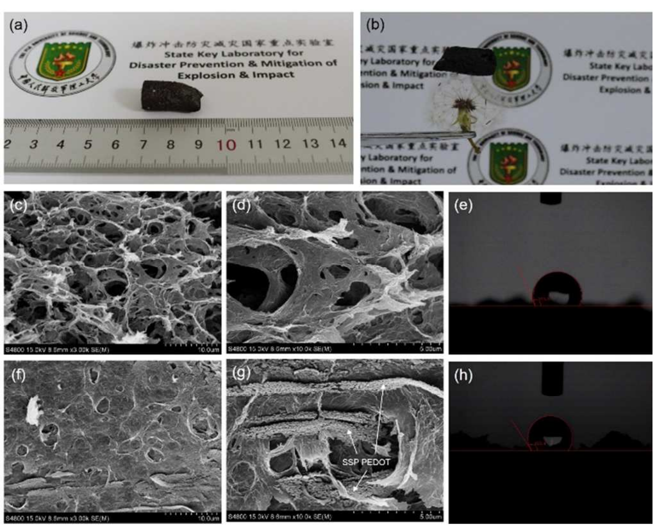

Fig. 2 (a, b) Optical image of 3D-RGO. (c, d) FE-SEM of 3D-RGO. (c) Contact angle of 3D-RGO (113.5°). (f, g) FE-SEM of 3D-RGO/PEDOT. (h) Contact angle of 3D-RGO/PEDOT (123.4°).

Electromagnetic absorption properties was tested through uniformly mixing 10 wt% of 3D-RGO/PEDOT with a paraffin matrix under coaxial wire analysis. The thickness of the sample is an important parameters which related to the intensity and the position, as well as the frequency range of electromagnetic energy absorption. As shown in Fig. 3, with the growth of the sample thickness, it obviously find that the absorbing peaks shift to lower frequency. Each one has an absorbing range deeper than −10 dB (which means it can yield a 90% of microwave attenuation). When the sample thickness is reached 2 mm, it not only has the maximum absorption value (−35.5 dB), but also has the widest bandwidth with the reflection loss (RL) deeper than −10 dB which is nearly 5 GHz (from 11.5 to 16.5 GHz). These results show that the self-assembly 3D-RGO/PEDOT predict good electromagnetic energy absorption ability in both low- and high-frequency bands with low contents.

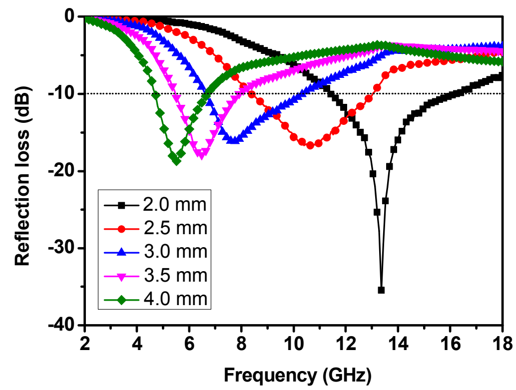

Fig. 3 Reflection loss curves for samples of 3D-RGO/PEDOT with different thicknesses (2.0 to 4.0 mm) in the frequency range of 2-18 GHz.

Conclusions

In summary, we have presented a simple method to synthesize a 3D RGO/PEDOT using organic solvent absorption as a self-assembly method. It gives a new synthesis strategy to obtain 3D RGO composites with low cost and high yield. The 3D RGO/PEDOT architecture shows excellent electromagnetic absorption properties in low contents and thickness situation. It gives a promising applications in military camouflage and electronic devices protection. Additionally, this architecture shall also warrant other novel applications, e.g., serving as an electrode in dye sensitized solar cells (DSSCs) or supercapacitors.

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Notes and references

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