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# Preparation and microwave absorption performance of a flexible Fe<sub>3</sub>O<sub>4</sub>/nanocarbon hybrid buckypaper and its application in composite materials†

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Graphene oxide (GO) and carbon nanotubes are promising microwave-absorbing materials. Herein, ferroferric oxide (Fe<sub>3</sub>O<sub>4</sub>)/multiwall carbon nanotube (MWCNT) and Fe<sub>3</sub>O<sub>4</sub>/GO hybrid buckypapers with excellent flexibility and manoeuvrability were coated on the surface of an epoxy substrate to fabricate microwave-absorbing composites. Fe<sub>3</sub>O<sub>4</sub>/GO buckypapers show a unique layered structure that differs from the complex network structure of Fe<sub>3</sub>O<sub>4</sub>/MWCNT buckypapers. Therefore, the Fe<sub>3</sub>O<sub>4</sub>/GO buckypapers exhibit lower tensile strength and toughness than the Fe<sub>3</sub>O<sub>4</sub>/MWCNT buckypapers, and the minimum electromagnetic reflection loss of Fe<sub>3</sub>O<sub>4</sub>/GO buckypapers is higher than that of Fe<sub>3</sub>O<sub>4</sub>/MWCNT buckypapers. Further, Fe<sub>3</sub>O<sub>4</sub>/GO buckypapers have a wider effective absorption-frequency band than Fe<sub>3</sub>O<sub>4</sub>/MWCNT buckypapers at 2.0–18.0 GHz. Although the mechanical properties of epoxy resin composites coated with Fe<sub>3</sub>O<sub>4</sub>/MWCNT or Fe<sub>3</sub>O<sub>4</sub>/GO buckypapers show a slight deterioration in comparison with those of the epoxy resin substrate, both buckypapers exhibit improved microwave-absorption performance compared with the epoxy resin substrate.

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## 1. Introduction

The rapid development of military detection technology in various countries has been accompanied by an increasing demand for high-performance absorbing materials. Through magnetic loss or dielectric loss, unwanted electromagnetic waves that are effectively absorbed by electromagnetic-wave-absorbing materials can be converted into other forms of energy.<sup>1</sup> Traditional absorbing composite materials are formed through the direct combination of magnetic loss materials—such as ferrite and carbonyl iron—with electric loss materials—such as conductive polymers, carbon nanotubes and graphene.<sup>2–4</sup> However, adding a small amount of nanoparticles significantly increases the viscosity of the matrix as the nanoparticles easily agglomerate, which is not only detrimental to practical operation but also affects the mechanical and absorption properties of composite materials.<sup>5–7</sup> Therefore, increasing the dosage of nanoparticles and evenly distributing them in the absorbing composite materials simultaneously is a key factor in determining their effectiveness in absorbing materials.<sup>8,9</sup>

Carbon nanosheets (carbon nanopapers or buckypapers), prepared from pure carbon materials or compound nanoparticles, have been widely used in supercapacitors, micro-media polarisation and flexible energy storage. In recent years, buckypapers gradually came into focus and were used as an ideal microwave-absorbing materials because of their lightness, excellent mechanical properties and high electrical conductivity.<sup>10–13</sup> The preparation methods for buckypapers can be classified into vacuum filtration assembly,<sup>14</sup> evaporation-induced self-assembly,<sup>15</sup> spin-coating,<sup>16</sup> drop-casting,<sup>17</sup> Langmuir–Blodgett (LB) methods,<sup>18</sup> spraying,<sup>19</sup> dip coating<sup>20</sup> and Langmuir–Schaefer methods. Common buckypapers include carbon nanotube,<sup>21</sup> graphene oxide (GO),<sup>22–24</sup> graphene<sup>25,26</sup> and carbon nano-fibre buckypapers.<sup>27</sup> Carbon nanotube buckypapers are made from randomly wound carbon nanotube sheets through vacuum filtration or other papermaking processes involving filtering a suspension through a thin mesh bracket. However, GO buckypapers, are self-supporting films comprising neatly arranged GO nanocrystals. GO buckypapers have a layered structure comprising individual, well-organised sheets 100–200 nm thick.<sup>22</sup> However, pure nanometre carbon buckypapers exhibit poor absorption performances owing to the large dielectric losses. Therefore, it is necessary to improve the impedance-matching performance of microwave-absorbing materials to prepare hybrid buckypapers by introducing magnetic materials.<sup>7,28</sup>

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Lu *et al.*<sup>8</sup> prepared ferric oxide ( $\text{Fe}_3\text{O}_4$ )/multiwall carbon nanotube (MWCNT) sandwich buckypapers *via* layer deposition. The results showed that the electromagnetic reflection loss (RL) of the buckypaper could reach  $-12.62$  dB at  $17.72$  GHz, making it a high-frequency-microwave-absorbing material with excellent application prospects. Ma *et al.*<sup>29</sup> prepared a rGO/F-NP hybrid film *via* an improved thermal reduction method. They studied the effects of adding carbon fibre micro-powders on the microwave absorption characteristics and mechanical properties of thin films. The results showed that when the nanoparticle content was  $200$  mg, the hybrid film had the best absorption performance, with a minimum RL of  $-22.18$  dB at  $10.64$  GHz. However, to the best of our knowledge, minimal research has been reported on applying buckypapers as microwave-absorbing coatings on epoxy resin/fibre composites.

This paper demonstrates that combining the advantages of  $\text{Fe}_3\text{O}_4$ /MWCNT and  $\text{Fe}_3\text{O}_4$ /GO flexible hybrid buckypapers and epoxy resin/fibre composites is a promising method for preparing absorbing light and thin composite materials with wide absorption frequency bands and good absorption ability. Through detailed investigation, we found that introducing flexible buckypapers significantly improves the processing performance of the composites compared with that of the traditional  $\text{Fe}_3\text{O}_4$ /carbon material powder absorbent. More importantly, the prepared  $\text{Fe}_3\text{O}_4$ /MWCNT and  $\text{Fe}_3\text{O}_4$ /GO flexible hybrid buckypapers/epoxy resin/fibre composites exhibit excellent microwave-absorption performances, which is helpful in realising applications of buckypapers as absorbing agents and absorbing materials.

## 2. Experimental

### 2.1 Materials

MWCNT (OD:  $10\text{--}20$  nm, length:  $10\text{--}30$   $\mu\text{m}$ , purity:  $>98$  wt%) were purchased from Zhongke Era Nano.  $\text{Fe}_3\text{O}_4$  nanoparticles ( $200$  nm,  $99.5\%$ ) were provided by Shanghai Macklin Biochemical Co., Ltd., China.  $\gamma$ -Aminopropyltriethoxysilane (APTES) was obtained from Nanjing Crompton Shuguang Organosilicon Specialities Co., Ltd., China. 1-(3-Dimethylaminopropyl)-3-ethyl carbodiimide hydrochloride (EDC) was obtained from Macklin Biochemical Co., Ltd., China. *N*-Hydroxysuccinimide (NHS) was purchased from Shanghai Aladdin Biochemical Co., Ltd., China. Amine-terminated polyoxyethylene ether (D230, flexible epoxy curing agent) was purchased from Guangdong Huntsman Advanced Chemical Materials Co., Ltd., China.

### 2.2 Preparation of $\text{Fe}_3\text{O}_4$ /MWCNT hybrid buckypapers

The  $\text{Fe}_3\text{O}_4$ /MWCNT buckypapers were prepared according to ref. 8. A calculated volume of suspension ( $150$ ,  $300$  or  $450$  ml) was poured into a vacuum filtration device through a  $0.45$   $\mu\text{m}$  water-based cellulose filter paper to obtain buckypapers with different thicknesses ( $0.04$ ,  $0.08$  or  $0.12$  mm). The buckypapers were labelled  $\text{C}_1$ ,  $\text{C}_2$  and  $\text{C}_3$  (corresponding to different  $\text{Fe}^{3+}$  contents) and  $\text{C}_4$ ,  $\text{C}_5$  and  $\text{C}_6$  (corresponding to different thicknesses of  $\text{C}_2$  buckypapers).

### 2.3 Preparation of $\text{Fe}_3\text{O}_4$ /GO hybrid buckypapers

The GO aqueous solution was prepared according to ref. 30.  $\text{Fe}_3\text{O}_4$  nanoparticles ( $0.4$  g) were added to the ethanol/water ( $1:1$ , volume ratio) mixed solution, and ultrasonication was performed for  $30$  min until the mixture was evenly dispersed. Then, the mixed solution was transferred to a  $250$  ml three-necked flask, and APTES was added dropwise ( $n_{\text{Fe}_3\text{O}_4} : n_{\text{KH-550}} = 1:4$ ) under a nitrogen atmosphere. The mixture was reacted at  $85^\circ\text{C}$  for  $2$  h and subsequently aged at the same temperature for  $30$  min. The brown precipitate was poured into a beaker and washed several times with deionised water and anhydrous ethanol. Finally, modified  $\text{Fe}_3\text{O}_4$  nanoparticles were obtained after vacuum drying at  $60^\circ\text{C}$  overnight.

A certain amount of GO aqueous solution was dispersed in deionised water and ultra-sonicated for  $30$  min; then,  $150$  ml of the mixed solution was poured onto a self-made PMMA plate mould and placed in a vacuum oven at  $60^\circ\text{C}$  overnight to obtain single-layer GO buckypaper. Similarly,  $300$  ml of the mixed solution was added in two equal amounts according to the aforementioned steps to obtain double-layer GO buckypaper. EDC and NHS (the mass ratio of GO : EDC : NHS was  $10:5:4$ ) were added to evenly dispersed GO aqueous solution, and continuously stirred for  $30$  min. Then, modified  $\text{Fe}_3\text{O}_4$  nanoparticles (the mass ratios of GO :  $\text{Fe}_3\text{O}_4$  were  $1:1$ ,  $8:2$ ,  $7:3$  and  $6:4$ ) were added to aforementioned mixture and further stirred for  $30$  min. The mixture obtained from this process ( $150$  ml) was poured on the self-made PMMA plate mould and placed overnight in a vacuum oven at  $60^\circ\text{C}$  to obtain single-layer  $\text{Fe}_3\text{O}_4$ /GO buckypapers with varying  $\text{Fe}_3\text{O}_4$  contents. Similarly,  $300$  ml of the mixture was added in two equal amounts according to the aforementioned steps to obtain double-layer  $\text{Fe}_3\text{O}_4$ /GO buckypaper. The single and double-layer  $\text{Fe}_3\text{O}_4$ /GO buckypapers were labelled  $\text{S}_1$ ,  $\text{S}_2$ ,  $\text{S}_3$ ,  $\text{S}_4$ ,  $\text{S}_5$  and  $\text{S}_6$ ,  $\text{S}_7$ ,  $\text{S}_8$ ,  $\text{S}_9$ ,  $\text{S}_{10}$ , respectively, corresponding to  $\text{Fe}_3\text{O}_4$  contents of  $0$ ,  $20$ ,  $30$ ,  $40$  and  $50$  wt%, respectively. The preparation mechanism and reaction scheme for  $\text{Fe}_3\text{O}_4$ /GO buckypapers are shown in Fig. 1 and 2.

### 2.4 Preparation of composites

E-51 epoxy resin and curing agent D230 were mixed in a mass ratio of  $100:35$  and uniformly coated on the surfaces of the  $\text{C}_2$  and  $\text{S}_4$  buckypapers prepared as described in Section 2.2. The flexible buckypapers were obtained when the resin was completely cured at room temperature.  $\text{Fe}_3\text{O}_4$ /MWCNT and  $\text{Fe}_3\text{O}_4$ /GO flexible buckypapers were spread on the surface layer after the fibre cloth was laid up according to the manufacturing method for the hand lay-up FRP (mass ratio of E-51 epoxy resin to D230 curing agent was  $100:35$ ). Finally, the composite materials were placed in a thermos-compressor under the pressing conditions  $60^\circ\text{C}/1$  h +  $80^\circ\text{C}/2$  h +  $100^\circ\text{C}/1$  h +  $120^\circ\text{C}/1$  h, and the  $\text{Fe}_3\text{O}_4$ /MWCNT buckypapers/EP/GF and  $\text{Fe}_3\text{O}_4$ /GO buckypapers/EP/CF composites were obtained through cooling in the furnace.

### 2.5 Characterisation

Fourier transform infrared (FT-IR) spectra of the buckypapers were obtained by using a IS10 instrument (Nicolet, USA) in the



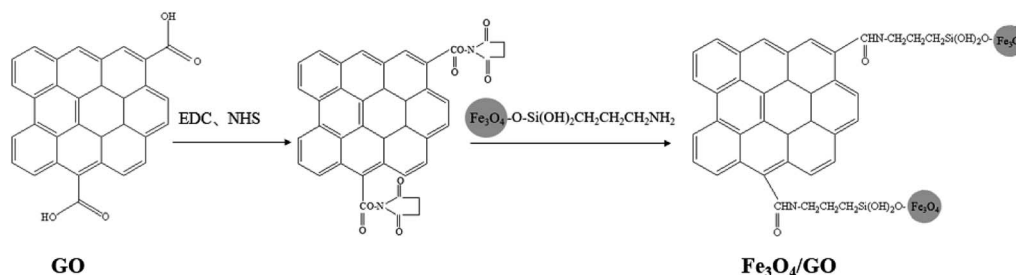


Fig. 1 Preparation mechanism of  $\text{Fe}_3\text{O}_4$  nanoparticles loaded with GO.

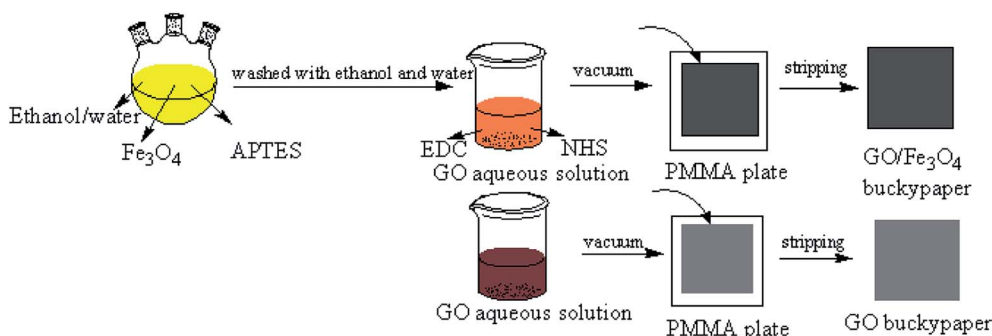


Fig. 2 Reaction scheme for GO and  $\text{Fe}_3\text{O}_4/\text{GO}$  buckypapers.

range  $4000\text{--}400\text{ cm}^{-1}$ . X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Axis Ultra DLD spectrometer with a monochromatic Al  $K\alpha$  X-ray source. The morphologies of the buckypapers and composites were characterised through scanning electron microscopy (SEM, Quanta 600FEG, FEI, USA). The lamellar structure of GO was characterised by transmission electron microscopy (TEM, FEI, USA). The tensile strengths of the buckypapers were measured using an Edberg tensiometer. The mechanical properties of the composites were determined at ambient temperatures according to the GB/T 1449-2005, GB/T 1450.1-2005 and GB/T 1447-2005 method using a UTM5000 united testing system (Xinsansi, Shenzhen). The

electromagnetic RL values of the buckypapers and composites were characterised by a Hitachi Anritsu MS4644A vector network analyser using the waveguide method in the range of  $2.0\text{--}18.0\text{ GHz}$ .

### 3. Results and discussion

#### 3.1 Structure and properties of buckypapers

The FT-IR spectra of  $\text{Fe}_3\text{O}_4/\text{MWCNT}$  and  $\text{Fe}_3\text{O}_4/\text{GO}$  buckypapers with various iron contents are shown in Fig. 3a and b. The bands at  $3433$ ,  $1631$  and  $1350\text{ cm}^{-1}$  in Fig. 3a correspond to the O–H stretching mode of water, C–C stretching vibration and the

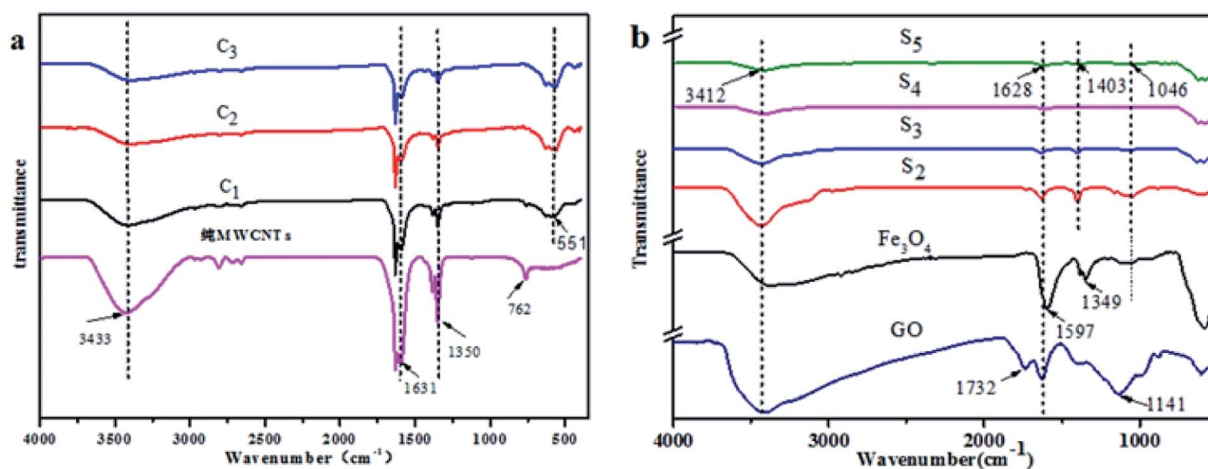


Fig. 3 FT-IR spectra of  $\text{Fe}_3\text{O}_4/\text{MWCNT}$  buckypapers (a) with different  $m_{\text{Fe}_3\text{O}_4}$  to  $m_{\text{MWCNT}}$  ratios: ( $C_1$ ) 1 : 1, ( $C_2$ ) 2 : 1 and ( $C_3$ ) 3 : 1 and  $\text{Fe}_3\text{O}_4/\text{GO}$  buckypapers (b) with different  $m_{\text{Fe}_3\text{O}_4}$  to  $m_{\text{GO}}$  ratios: ( $S_2$ ) 2 : 8, ( $S_3$ ) 3 : 7, ( $S_4$ ) 4 : 6 and ( $S_5$ ) 5 : 5.



C–H stretching vibration of the MWCNT, respectively. Moreover, an additional band at  $551\text{ cm}^{-1}$  can be ascribed to the lattice absorption of  $\text{Fe}_3\text{O}_4$ , further confirming the successful preparation of  $\text{Fe}_3\text{O}_4$  NPs. In Fig. 3b, the infrared bands of GO indicate the presence of various oxygen-containing functional groups, including bands at  $3412\text{ cm}^{-1}$  (O–H stretching vibration of water),  $1732\text{ cm}^{-1}$  (C=O stretching of carboxyl groups at the edges of the GO networks) and  $1628\text{ cm}^{-1}$  (O–H bending vibration of carboxyl), while the band at  $1141\text{ cm}^{-1}$  could be due to the C–O stretching of the carboxyl groups. However, the spectrum of  $\text{Fe}_3\text{O}_4/\text{GO}$  buckypapers differs from that of GO under the influence of electrostatic forces. Two new characteristic bands at  $1628\text{ cm}^{-1}$  (CO–NH stretching vibration) and  $1403\text{ cm}^{-1}$  (C–N stretching of amide) demonstrate the successful covalent bonding between  $\text{Fe}_3\text{O}_4$  and GO.

Fig. 4a and b shows a wide scan spectrum of  $\text{Fe}_3\text{O}_4/\text{MWCNT}$  buckypapers and the Fe 2p spectrum. The sharp peaks observed in the wide scan spectrum confirm the presence of C 1s, O 1s and Fe 2p. In the Fig. 4b, the peaks at 711.29 and 724.48 eV originate from Fe 2p<sub>3/2</sub> and Fe 2p<sub>1/2</sub> of Fe, corresponding to Fe<sup>2+</sup> and Fe<sup>3+</sup> in  $\text{Fe}_3\text{O}_4$ , respectively; however, there are no peaks at 710.35 and 724.0 eV representing  $\text{Fe}_2\text{O}_3$ . Fig. 4c shows the wide scan spectra of GO and  $\text{Fe}_3\text{O}_4/\text{GO}$  buckypapers. The peak observed in the wide scan spectrum of  $\text{Fe}_3\text{O}_4/\text{GO}$  confirms the presence of C 1s, O 1s, N 1s and Fe 2p. The C 1s spectra of GO buckypapers are shown in Fig. 4d, and these comprise three components: C=C (282.5 eV) in the aromatic rings, C–O (284.7 eV) of epoxy and alkoxy and C=O (286.5 eV) groups. On introducing  $\text{Fe}_3\text{O}_4$ , the C–N bond (285.2 eV) appears in the C 1s spectrum of  $\text{Fe}_3\text{O}_4/\text{GO}$  buckypapers and the other three parts shift to a higher binding energy, as shown in Fig. 4e, indicating the successful loading of modified  $\text{Fe}_3\text{O}_4$  nanoparticles.

The optical photos and SEM images of tensile fracture sections of C<sub>2</sub> and S<sub>4</sub> buckypapers are shown in Fig. 5. Fig. 5a shows the smooth surface of C<sub>2</sub> buckypaper, which is free-standing and black. An optical image of S<sub>4</sub> buckypaper prepared *via* evaporation-induced self-assembly is shown in Fig. 5d. Compared with  $\text{Fe}_3\text{O}_4/\text{MWCNT}$  buckypaper, the  $\text{Fe}_3\text{O}_4/\text{GO}$  buckypaper is a self-supporting thin film comprising aligned GO nanosheets, and its surface is rough and uneven. This is probably because the vacuum filtration process makes the  $\text{Fe}_3\text{O}_4/\text{MWCNT}$  buckypaper compact. The photos of bent C<sub>2</sub> and S<sub>4</sub> buckypapers in Fig. 5b and e, respectively, show that they have good flexibility and the latter bends much more easily. Fig. 5c shows a section of C<sub>2</sub> buckypaper, the cross-section appears flat and the hybrid nanoparticles are uniformly distributed. The section of buckypaper in Fig. 5f shows the well-stacked structure of GO and presence of  $\text{Fe}_3\text{O}_4$  nanoparticles in the buckypaper, unlike the cross-section of  $\text{Fe}_3\text{O}_4/\text{MWCNT}$  buckypaper.

As shown in Fig. 6, the morphologies of  $\text{Fe}_3\text{O}_4/\text{MWCNT}$  buckypapers with different  $\text{Fe}_3\text{O}_4$  contents were demonstrated through SEM. Fig. 6a–d show that the MWCNT are entangled owing to van der Waals interactions. Fig. 6b shows  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles that are uniformly attached to the MWCNT surfaces with no detectable aggregation grew around the original particles as their content increased, and more MWCNT were coated with  $\text{Fe}_3\text{O}_4$  nanoparticles. Fig. 6d shows a slight agglomeration of nanoparticles, which could be caused by their surface effects.

The structures and morphologies of single-layer GO and  $\text{Fe}_3\text{O}_4/\text{GO}$  buckypapers were characterised by SEM and TEM as shown in Fig. 7. Fig. 7a shows the folded structure of GO, which is beneficial to nanoparticle adhesion. Go has a clear layered

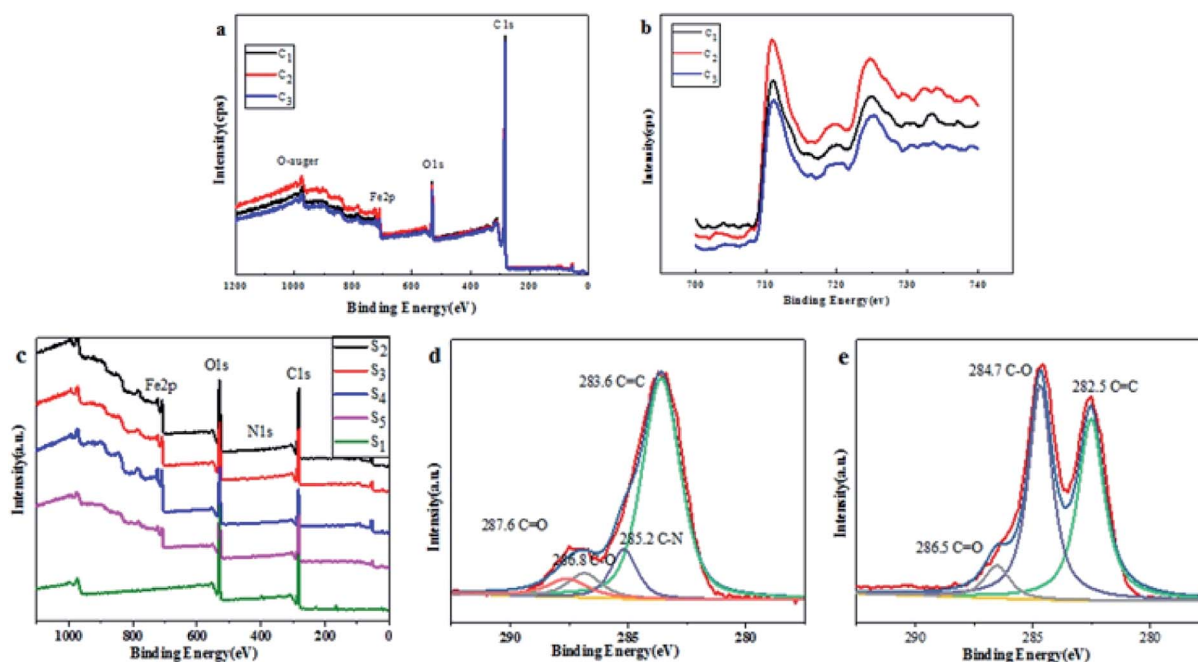


Fig. 4 XPS spectra: wide scan of  $\text{Fe}_3\text{O}_4/\text{MWCNT}$  (a) and Fe 2p spectrum of  $\text{Fe}_3\text{O}_4/\text{MWCNT}$  (b); wide scan of  $\text{Fe}_3\text{O}_4/\text{GO}$  buckypapers (c); C 1s spectra of GO (d) and  $\text{Fe}_3\text{O}_4/\text{GO}$  (e) buckypapers.





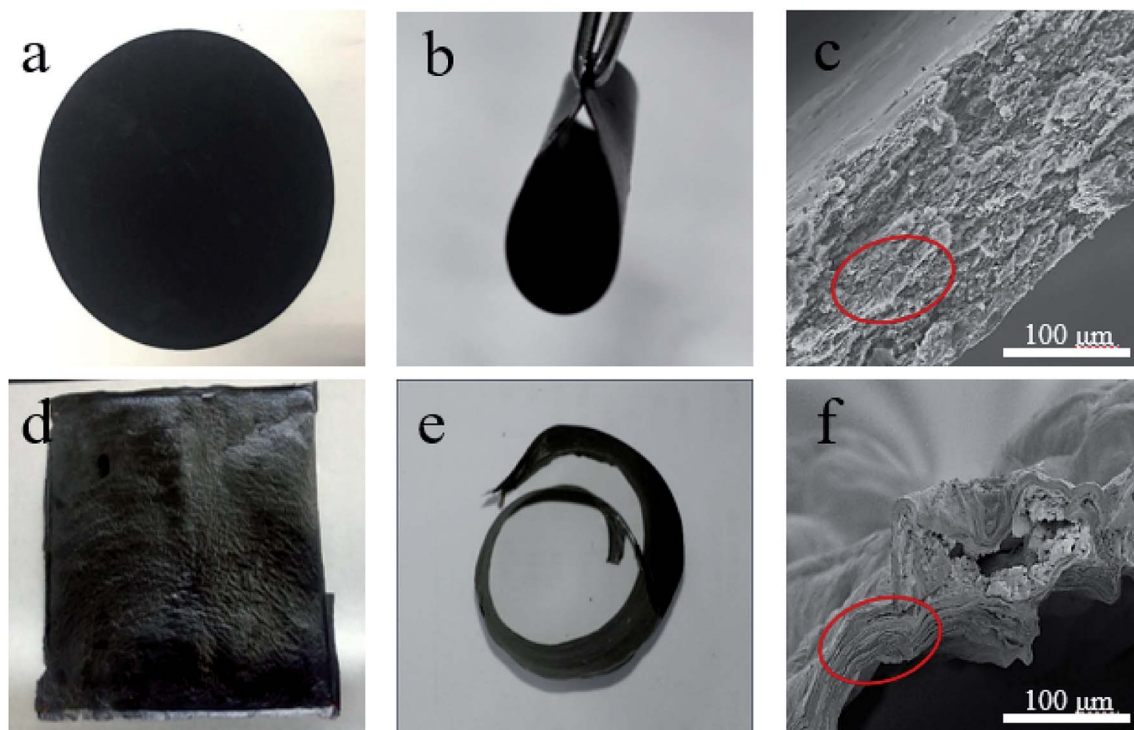


Fig. 5 Optical photos of straight and bent forms and SEM images of tensile fracture section of  $C_2$  buckypaper (a–c) and  $S_4$  buckypaper ( $m_{Fe_3O_4}$ :  $m_{GO} = 6 : 4$ ) (d–f).

structure, and Fig. 7b shows that it is a transparent film, indicating its successful preparation. As shown in Fig. 7c–f, the  $Fe_3O_4$ /GO buckypapers have a 3D mesh structure and some nanoparticles are evenly distributed on the surface of the GO sheet, indicating excellent combination between the GO sheet and  $Fe_3O_4$  nanoparticles. Additionally, a proportion of the nanoparticles were encapsulated inside the GO sheet, which partially prevented their agglomeration. The size of the nanoparticles increased with the  $Fe_3O_4$  content in the buckypapers, which helped to enhance the interfacial contact between the GO layers and  $Fe_3O_4$  nanoparticles.

To understand the relationship between the structure and mechanical properties of buckypapers, the tensile strengths of different types of buckypapers were tested using a tensiometer according to the GB/T940.3-2006 thin-film tensile-test method standard; the results are shown in Fig. 8. Fig. 8a shows the tensile strengths of  $Fe_3O_4$ /MWCNT buckypapers with different  $Fe_3O_4$  contents, the results indicate that the tensile strength of the buckypapers increased approximately threefold when  $Fe_3O_4$  nanoparticles were added, and this may be related to the denser structure of carbon nanotubes, which can be explained by the increased electrostatic forces between  $Fe_3O_4$  and carbon nanotubes stabilising the particle-coating process. Fig. 8b shows that the thickness of the buckypapers minimally affects the tensile strength of the  $C_2$  buckypapers, which may be because the unaltered structure of the buckypapers.

After adding nanoparticles, the tensile strength of  $Fe_3O_4$ /GO buckypapers was lower than that of pure GO buckypapers, as shown in Fig. 8c. The tensile strengths of single and double-

layer  $S_2$  and  $S_4$  buckypapers were 1.14 and 0.98 MPa ( $S_2$ ) and only 0.71 and 0.53 MPa ( $S_4$ ), respectively. When the mass ratio of  $Fe_3O_4$  to GO was 5 : 5, the tensile strength of the buckypapers increased slightly, which is probably related to the GO-sheet rearrangement. The presence of  $Fe_3O_4$  nanoparticles affected the layered stacking structure of GO possibly because the  $Fe_3O_4$  nanoparticles attached between graphene sheets weaken the forces between GO sheets during composite formation, and the stacking becomes slightly loose, decreasing the tensile strength of the  $Fe_3O_4$ /GO buckypapers, which is consistent with the SEM results. Conversely, carbon nanotubes are quasi-one-dimensional linear structures with a high length-to-diameter ratio. In buckypapers prepared using carbon nanotubes, these are wound around each other to form a complex network structure. Therefore, they have better mechanical properties than GO buckypapers.

The RL values of hybrid  $Fe_3O_4$ /MWCNT buckypapers with different  $Fe_3O_4$  content, which vary with frequency from 2.0–18.0 GHz, are shown in Fig. 9a. The minimum RL from  $C_1$  buckypaper can reach  $-13.4$  dB at 16.2 GHz, and the RL bandwidth below  $-10$  dB is 1.8 GHz (from 15.2 to 17.0 GHz). For the  $C_2$  buckypaper, we observed a significantly improved absorption performance compared with the former. The minimum RL can reach  $-26.4$  dB at 16.3 GHz, the RL bandwidth below  $-10$  dB ( $>90\%$  absorption) is 6.0 GHz (from 11.6 to 17.6 GHz), and RL values below  $-20$  dB ( $>99\%$  absorption) are achieved in the range 14.9–17.2 GHz. While  $C_3$  buckypaper exhibits only weak electromagnetic wave absorption, its minimum RL can reach  $-7.6$  dB at 16.4 GHz. As the mass ratio



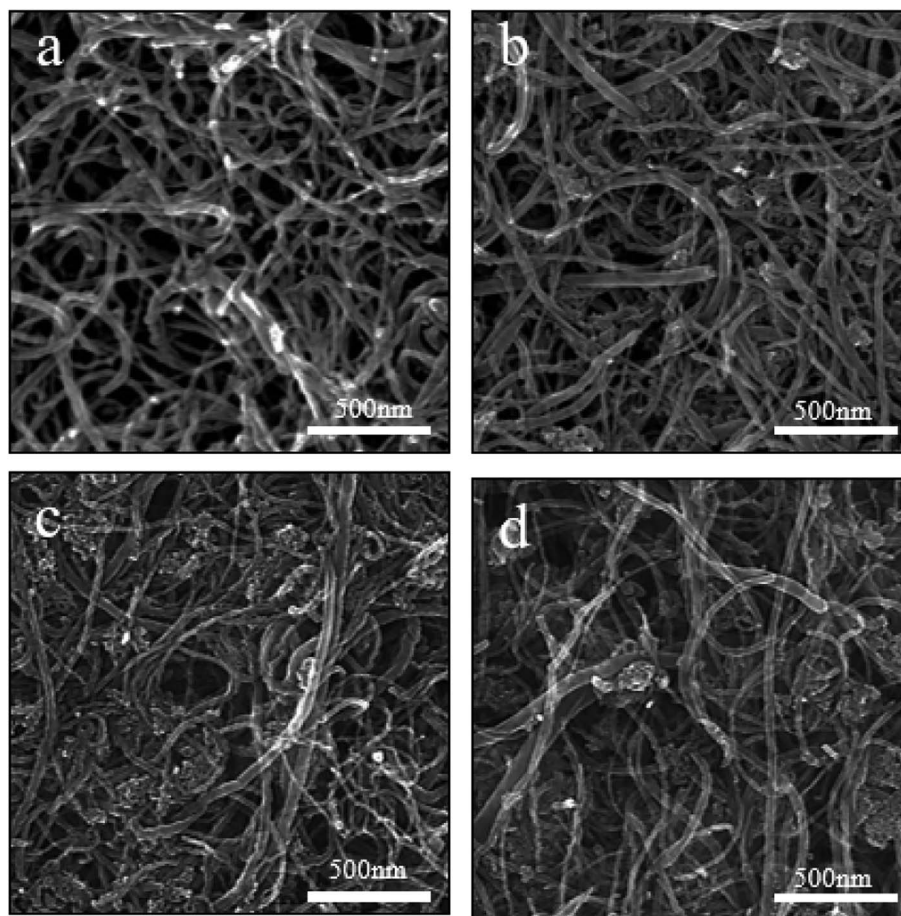


Fig. 6 SEM images of  $\text{Fe}_3\text{O}_4/\text{MWCNT}$  buckypapers with different  $m_{\text{Fe}_3\text{O}_4}$  to  $m_{\text{MWCNT}}$  ratios: (a) 0 : 1, (b) 1 : 1, (c) 2 : 1 and (d) 3 : 1.

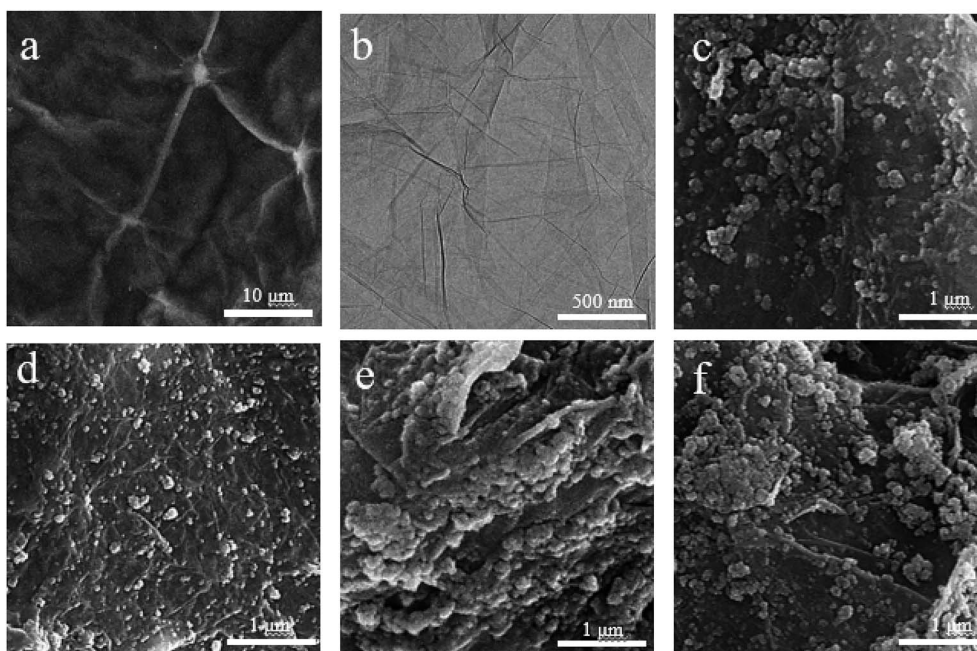


Fig. 7 TEM and SEM images of GO (a and b) and  $\text{Fe}_3\text{O}_4/\text{GO}$  buckypapers with different  $m_{\text{Fe}_3\text{O}_4}$  to  $m_{\text{GO}}$  ratios: (c) 8 : 2, (d) 7 : 3, (e) 6 : 4 and (f) 5 : 5.



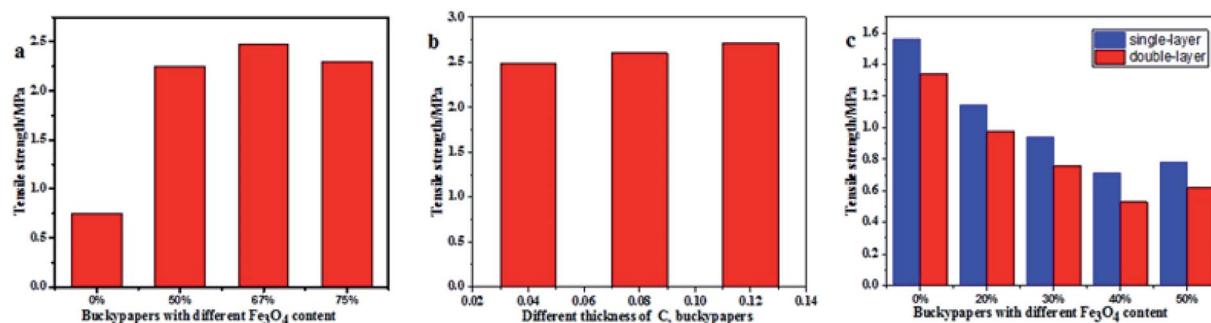


Fig. 8 Tensile strengths of Fe<sub>3</sub>O<sub>4</sub>/MWCNT buckypapers with (a) different Fe<sub>3</sub>O<sub>4</sub> contents, (b) different thicknesses of C<sub>2</sub> buckypapers and (c) Fe<sub>3</sub>O<sub>4</sub>/GO buckypapers with different Fe<sub>3</sub>O<sub>4</sub> contents.

of Fe<sub>3</sub>O<sub>4</sub> to MWCNT increases, the electromagnetic absorption properties of Fe<sub>3</sub>O<sub>4</sub>/MWCNT hybrid buckypapers showed a tendency to first strengthen and subsequently weaken. The absorption bandwidth shows the same trend; this may be due to the increase in ion displacement and electric dipole polarisation as the iron content increases.

As the interfacial area of the Fe<sub>3</sub>O<sub>4</sub>-wrapped MWCNT structures increased, the electromagnetic wave absorption performance of the hybrid buckypapers improved. When the Fe<sub>3</sub>O<sub>4</sub>

content reached 75%, aggregation of the MWCNT significantly affected the dispersion state of the Fe<sub>3</sub>O<sub>4</sub>/MWCNT buckypapers, and weakened the electromagnetic wave-absorption properties. In all the samples, C<sub>2</sub> buckypaper showed the lowest absorption peak (−26.4 dB at 16.3 GHz) and the largest bandwidth, which represents a compromise between dielectric loss (dominant role) and magnetic loss.

Fig. 9b shows the RL values of C<sub>2</sub> buckypapers with different thicknesses, which indicates that the minimum RL is −14.4 dB

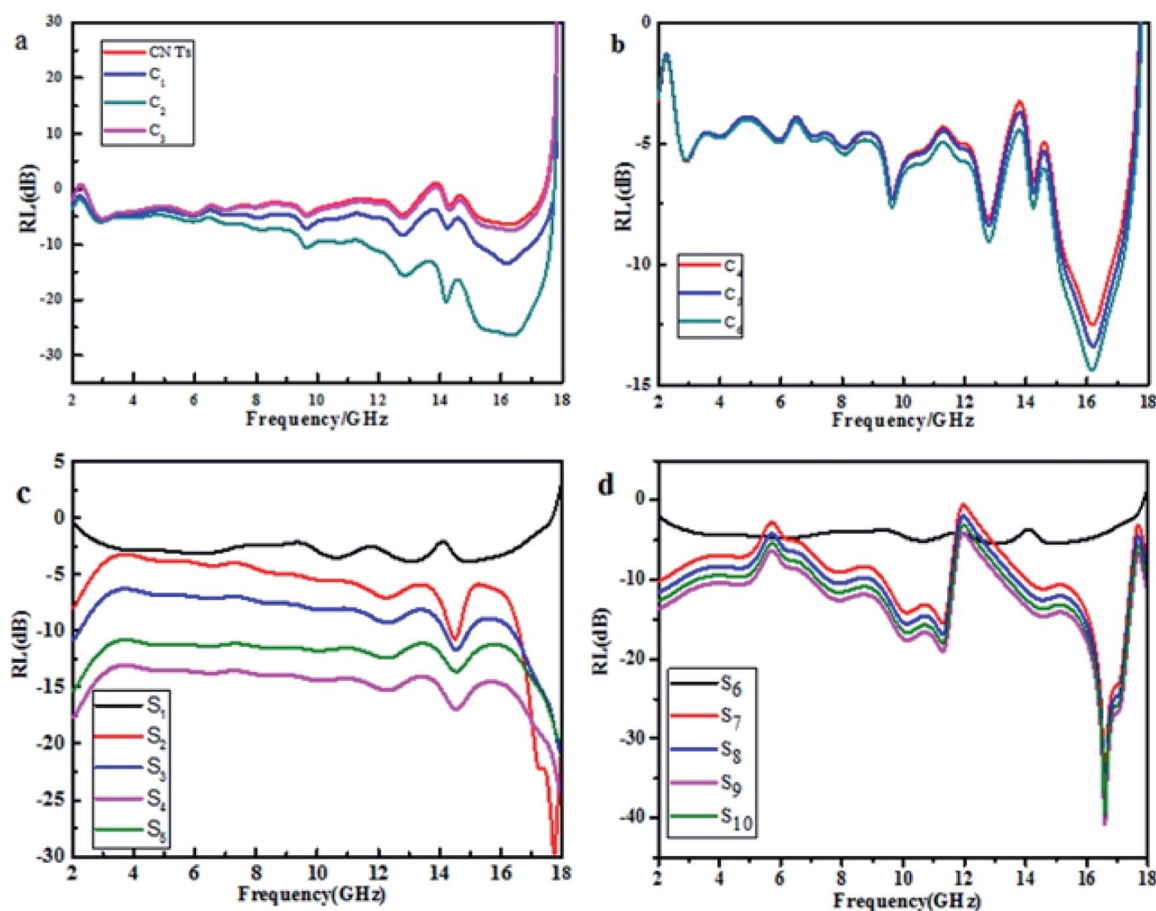


Fig. 9 Electromagnetic RL of Fe<sub>3</sub>O<sub>4</sub>/MWCNT buckypapers with different Fe<sub>3</sub>O<sub>4</sub> contents (a) and different thicknesses of C<sub>2</sub> (b), single-layer (c) and double-layer (d) Fe<sub>3</sub>O<sub>4</sub>/GO buckypapers with different Fe<sub>3</sub>O<sub>4</sub> contents (S<sub>1</sub>, S<sub>6</sub>: 0 wt%, S<sub>2</sub>, S<sub>7</sub>: 20 wt%, S<sub>3</sub>, S<sub>8</sub>: 30 wt%, S<sub>4</sub>, S<sub>9</sub>: 40 wt% and S<sub>5</sub>, S<sub>10</sub>: 50 wt%).





at 16.2 GHz and the bandwidth below  $-10$  dB can reach 2.1 GHz (from 15.1 to 17.2 GHz) for a layer 0.12 mm thick. When the thickness of buckypaper is 0.04 mm, its minimum RL is  $-12.5$  dB at 16.1 GHz, and the effective bandwidth below  $-10$  dB is 1.5 GHz. The minimum RL increases to  $-13.4$  dB at 16.2 GHz when the thickness of the hybrid buckypaper increases to 0.08 mm, and the bandwidth below  $-10$  dB for this case can reach 1.8 GHz. Therefore, the thickness is one of the main factors affecting the absorption properties of buckypapers. The absorption intensity and effective absorption bandwidth of hybrid buckypapers increased as the thickness increased.

Fig. 9c shows the difference in electromagnetic RL with frequency between single-layer GO and  $\text{Fe}_3\text{O}_4/\text{GO}$  buckypapers. This shows that pure GO buckypaper exhibits poor microwave absorption performance compared with hybrid buckypapers, with its minimum RL reaching only  $-3.9$  dB at 14.9 GHz. For the  $\text{S}_2$  buckypaper, the minimum RL reaches  $-11.8$  dB at 14.5 GHz and the RL bandwidth below  $-10$  dB is 0.3 GHz (from 14.3 to 14.6 GHz). The minimum RL of  $\text{S}_3$  buckypaper is  $-11.6$  dB, and its RL bandwidth below  $-10$  dB exceeds 0.7 GHz (from 14.2 to 14.9 GHz). For the  $\text{S}_5$  buckypaper, the minimum RL reaches  $-13.6$  dB at 14.5 GHz and the RL bandwidth below  $-10$  dB spans the entire frequency range of 2.0–18.0 GHz. However, for

$\text{S}_4$  buckypaper, the minimum RL can reach  $-17.0$  dB at 14.5 GHz; further, this incorporates over 90% of the electromagnetic wave absorption over the entire frequency range. This phenomenon possibly occurs owing to the high GO contents in the  $\text{S}_2$  and  $\text{S}_3$  hybrid buckypapers leading to higher dielectric loss and poorer impedance, matching the performance of the  $\text{Fe}_3\text{O}_4/\text{GO}$  hybrid buckypapers. Regarding  $\text{S}_4$  buckypaper, which has the most appropriate GO to  $\text{Fe}_3\text{O}_4$  mass ratio of 6 : 4, it is essential to reduce the large dielectric constant to achieve impedance matching and enhance the microwave absorption by the hybrid buckypapers.

The RL values of double-layer GO and  $\text{Fe}_3\text{O}_4/\text{GO}$  buckypapers were tested in the range of 2.0–18.0 GHz, as shown in Fig. 9d. This shows that the thickness minimally affects the absorption properties of pure GO buckypaper, for which the minimum RL reaches only  $-5.5$  dB at 14.9 GHz. The dependence curves of the RL on frequency for several  $\text{Fe}_3\text{O}_4/\text{GO}$  hybrid buckypapers are similar, the bandwidth is the main parameter affecting the absorption performance. The minimum RL of  $\text{Fe}_3\text{O}_4/\text{GO}$  hybrid buckypapers with different  $\text{Fe}_3\text{O}_4$  contents can reach  $-35.3$  dB at 16.6 GHz,  $-38.1$  dB at 16.6 GHz,  $-41.0$  dB at 16.5 GHz and  $-39.8$  dB at 16.5 GHz.  $\text{S}_4$  buckypaper has the minimum RL, which is consistent with the results shown in Fig. 9c.

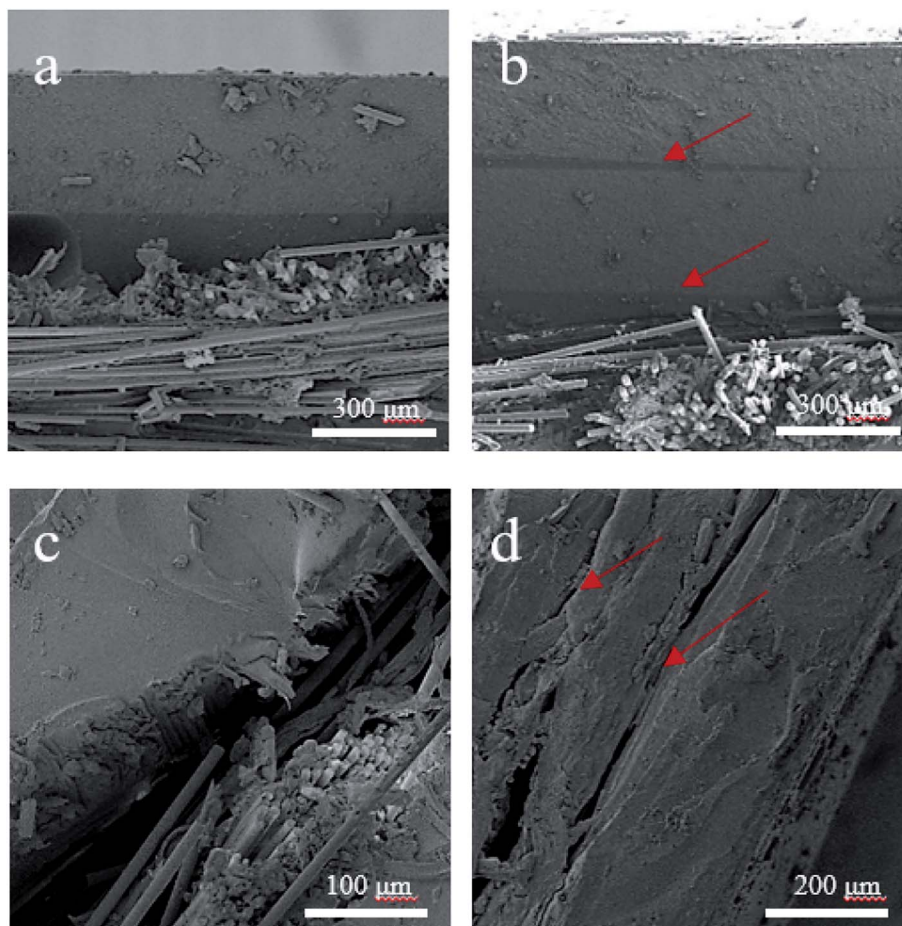


Fig. 10 SEM images of the fracture surfaces of  $\text{Fe}_3\text{O}_4/\text{MWCNT}$  buckypapers/EP/GF composites: (a) single-layer, (b) double-layer, and  $\text{Fe}_3\text{O}_4/\text{GO}$  buckypapers/EP/CF composites: (c) single-layer, (d) double-layer.





Table 1 Mechanical properties of composites

Sample	Flexural strength (MPa)	Flexural modulus (GPa)	Shear strength (MPa)	Tensile strength (MPa)
EP/GF	407.7(12.2 <sup>a</sup> )	2.9(0.3 <sup>a</sup> )	42.0(10.5 <sup>a</sup> )	188.3(14.6 <sup>a</sup> )
Single-layer Fe <sub>3</sub> O <sub>4</sub> /MWCNT/EP/GF	402.2(14.0 <sup>a</sup> )	2.7(0.5 <sup>a</sup> )	40.9(11.0 <sup>a</sup> )	185.8(12.4 <sup>a</sup> )
Double-layer Fe <sub>3</sub> O <sub>4</sub> /MWCNT/EP/GF	371.6(13.4 <sup>a</sup> )	2.5(0.2 <sup>a</sup> )	39.6(12.9 <sup>a</sup> )	182.7(13.4 <sup>a</sup> )
EP/CF	385.7(13.2 <sup>a</sup> )	5.8(0.5 <sup>a</sup> )	33.7(11.7 <sup>a</sup> )	318.6(13.6 <sup>a</sup> )
Single-layer Fe <sub>3</sub> O <sub>4</sub> /GO/EP/CF	370.6(14.5 <sup>a</sup> )	4.5(0.7 <sup>a</sup> )	28.1(11.4 <sup>a</sup> )	313.7(15.1 <sup>a</sup> )
Double-layer Fe <sub>3</sub> O <sub>4</sub> /GO/EP/CF	303.2(15.0 <sup>a</sup> )	4.1(0.3 <sup>a</sup> )	21.4(12.1 <sup>a</sup> )	315.0(11.6 <sup>a</sup> )

<sup>a</sup> Standard deviation of data.

A RL below −10 dB means that the material possesses 90% of the electromagnetic wave absorption, a RL below −20 dB means that the material possesses 99% of the electromagnetic wave absorption. It was found that as the content of Fe<sub>3</sub>O<sub>4</sub> nanoparticles increased, the RL bandwidths below −10 dB for double-layer hybrid buckypapers were 3.3 GHz (from 14.0 to 17.3 GHz), 3.9 GHz (from 13.6 to 17.5 GHz), 4.4 GHz (from 13.1 to 17.5 GHz) and 4.1 GHz (from 13.4 to 17.5 GHz), showing a tendency to first increase and then decrease. Meanwhile, the RL bandwidths below −20 dB for hybrid buckypapers were 0.8 GHz (from 16.4 to 17.2 GHz), 0.9 GHz (from 16.3 to 17.2 GHz), 1.1 GHz (from 16.1 to 17.2 GHz) and 1.0 GHz (from 16.2 to 17.2 GHz).

The electromagnetic RL and absorption bandwidth are two significant factors that affect the absorption performance. The combination of dielectric GO and magnetic Fe<sub>3</sub>O<sub>4</sub> in suitable proportions is the main reason for the improved wave-absorption performance. First, hybrid buckypapers can obtain better impedance matching, which is conducive to absorbing electromagnetic waves to the surface and thereby increasing attenuation. Second, the interface and dipole polarisation caused by the unique three-dimensional microstructure and multilayer structure of GO,<sup>31</sup> improve the absorption capacity of the hybrid buckypapers. To summarise, S<sub>4</sub> buckypaper can simultaneously obtain the minimum electromagnetic RL and maximum effective absorption bandwidth.

### 3.2 Structure and properties of composites

Fig. 10 shows the SEM images of the fracture surfaces of Fe<sub>3</sub>O<sub>4</sub>/MWCNT buckypapers/EP/GF and Fe<sub>3</sub>O<sub>4</sub>/GO buckypapers/EP/CF composites with different numbers of layers of buckypapers. Fig. 10a and b show the SEM images of the composites attached to single and double-layer of Fe<sub>3</sub>O<sub>4</sub>/MWCNT buckypapers, respectively. It is clear that there is no significant stratification, indicating good adhesion between Fe<sub>3</sub>O<sub>4</sub>/MWCNT buckypapers and the EP/GF composite matrix. An SEM image of Fe<sub>3</sub>O<sub>4</sub>/GO buckypapers/EP/CF composites coated with single-layer buckypaper is shown in Fig. 10c; the interface between the buckypaper and substrate has obvious lamination, demonstrating that the interface bonding is weak. Fig. 10d shows that the interface bonding performance between the double-layer buckypapers and substrate is poor; further, there is an obvious interface between the double-layer buckypapers, which is related to the loose-layered structure of GO.

The mechanical properties of various buckypapers/composites are summarised in Table 1. The change of tensile strength is not significant, but the flexural and shear strength of the composites deteriorated when attached to buckypapers compared with those of pure composites. The shear strength of the composites is influenced by the interfacial bonding strength between the buckypaper and matrix. Fe<sub>3</sub>O<sub>4</sub>/MWCNT buckypapers/EP/GF composites have higher shear strength than

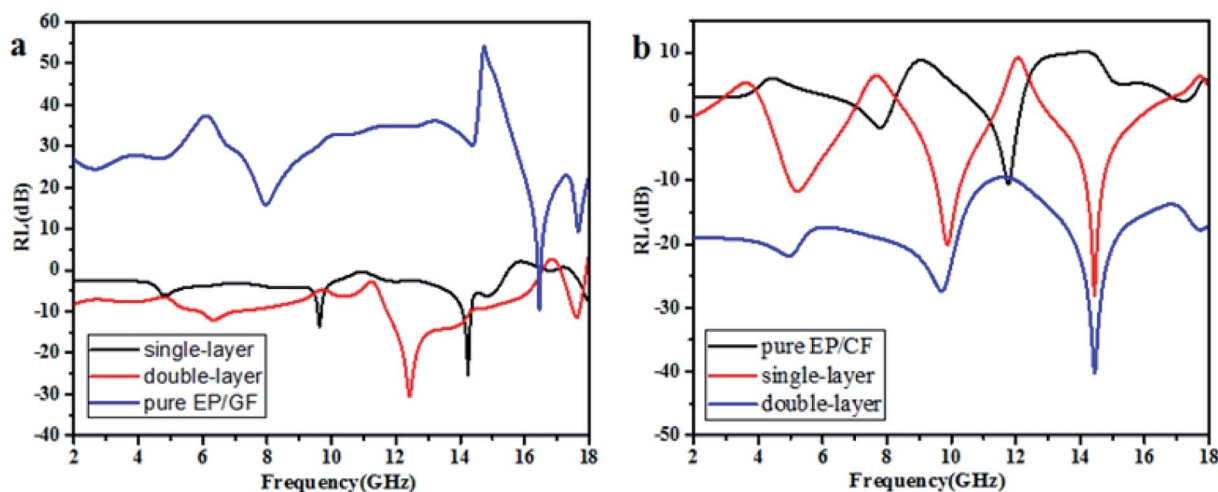


Fig. 11 Electromagnetic RL of Fe<sub>3</sub>O<sub>4</sub>/MWCNT buckypapers/EP/GF (a) and Fe<sub>3</sub>O<sub>4</sub>/GO buckypapers/EP/CF (b) composites with different numbers of layers of buckypapers.



$\text{Fe}_3\text{O}_4/\text{GO}$  buckypapers/EP/CF composites, which is because GO buckypapers delaminate easily, resulting in a weakened interaction with the matrix. It is clear that composites coated with  $\text{Fe}_3\text{O}_4/\text{MWCNT}$  buckypapers have higher flexural strength than those coated with  $\text{Fe}_3\text{O}_4/\text{GO}$  buckypapers, this is attributed to the poor mechanical properties of the  $\text{Fe}_3\text{O}_4/\text{GO}$  buckypapers, which leads to weak parts in the composite and a significant decrease in bending strength. Besides, the mechanical properties of all the composites coated with two layers of buckypapers are poorer than those of the composites coated with one layer of buckypapers, which is due to the small bonding force between the buckypapers resulting in a low interfacial force and poor mechanical properties. This is consistent with the SEM images shown in Fig. 10.

The wave-absorption properties of  $\text{Fe}_3\text{O}_4/\text{MWCNT}$  buckypapers/EP/GF and  $\text{Fe}_3\text{O}_4/\text{GO}$  buckypapers/EP/CF composites with different numbers of layers of buckypapers are shown in Fig. 11. As shown in Fig. 11a, the pure EP/GF composite has an electromagnetic RL of  $-8.6$  dB at  $16.4$  GHz. The minimum RL of  $\text{Fe}_3\text{O}_4/\text{MWCNT}$  buckypapers/EP/GF composites coated with single-layer buckypaper reached  $-25.8$  dB at  $14.2$  GHz, and the RL bandwidth below  $-10$  dB was  $0.2$  GHz (from  $14.3$  to  $14.5$  GHz). For  $\text{Fe}_3\text{O}_4/\text{MWCNT}$  buckypapers/EP/GF composites coated with double-layer buckypapers, a significant shift in the absorption band was observed compared with that of the former. The minimum RL can reach  $-31.2$  dB at  $12.4$  GHz and the RL bandwidths below  $-10$  and  $-20$  dB were  $2.5$  and  $0.4$  GHz, respectively. The results show that the electromagnetic loss performance of  $\text{Fe}_3\text{O}_4/\text{MWCNT}$  buckypapers/EP/GF composites increases with the number of layers of buckypapers, presenting a significantly broadened effective absorption band. The displacement of the frequency band can be explained through the quarter wavelength principle, which is the relation between the thickness of the absorbing agent and frequency variation required to obtain the best absorption performance.<sup>32,33</sup> Here, if the thickness ( $t_m$ ) must satisfy formula (1) at peak frequency ( $f_m$ ):

$$t_m = nc/(4f_m(|\mu_r||\epsilon_r|)^{1/2}), (n = 1, 3, 5, \dots) \quad (1)$$

where  $|\mu_r|$  and  $|\epsilon_r|$  are the moduli of  $\mu_r$  and  $\epsilon_r$ , and  $c$  is the speed of light. As the number of layers of externally attached buckypapers increases, *i.e.* the thickness of the absorbing layer increases, the double-layer buckypapers/EP/GF composite satisfies the relationship between  $t_m$  and  $f_m$  based on its attenuation-loss capability and moderate impedance matching properties. Thus, a better microwave-absorption performance is obtained at  $12.4$  GHz.

As shown in Fig. 11b, the pure EP/CF composite had a RL of  $-10.2$  dB at  $11.7$  GHz and effective absorption band of  $0.15$  GHz below  $-10$  dB. The RL of  $\text{Fe}_3\text{O}_4/\text{GO}$  buckypapers/EP/GF composites coated with single-layer buckypaper could reach  $-28.1$  dB at  $14.4$  GHz, and the RL bandwidth below  $-10$  dB was  $2.1$  GHz. The minimum RL value increased to  $-40.5$  dB at  $14.4$  GHz when the EP/CF composite was pasted with double-layer buckypapers; its electromagnetic RL values were almost all below  $-10$  dB from  $2.0$ – $18.0$  GHz, and the RL bandwidth under  $-20$  dB was  $3.8$  GHz. Generally, the minimum RL of buckypapers/EP/GF composites increased by  $17.3$  and  $29.7$  dB, and the effective absorption bands were broadened compared with those of the pure EP/CF composite.

Three absorption peaks appear for the  $\text{Fe}_3\text{O}_4/\text{GO}$  buckypapers/EP/CF absorbing composites owing to impedance matching. For multilayer absorbing materials, the surface resistance of the material and overall impedance must match the air impedance. During the matching process, two new impedances appear owing to the addition of the EP/CF composite substrate and interfacial polarisation is generated at the new interface, which improves the impedance matching and produces a strong absorption peak at the well-matched frequency.

An illustration of the principle of electromagnetic absorption by  $\text{Fe}_3\text{O}_4/\text{GO}$  hybrid buckypapers is shown in Fig. 12. A mismatch between the impedance of a single medium or magnetic composition and that of air always prevents the incoming electromagnetic wave from entering the adsorbent, resulting in low absorption efficiency. The layered interpenetrating structure of GO can generate multiple reflections, thus extending the propagation path of electromagnetic waves.

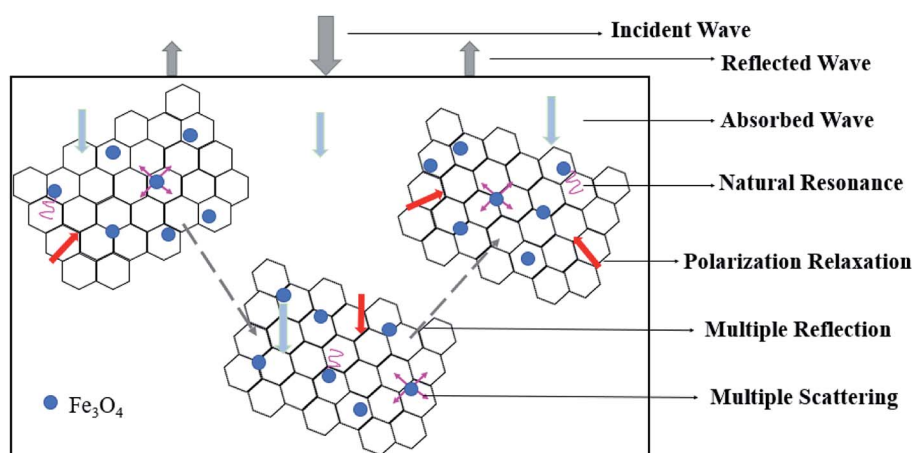


Fig. 12 Illustration of the principle of electromagnetic absorption by  $\text{Fe}_3\text{O}_4/\text{GO}$  hybrid buckypapers.



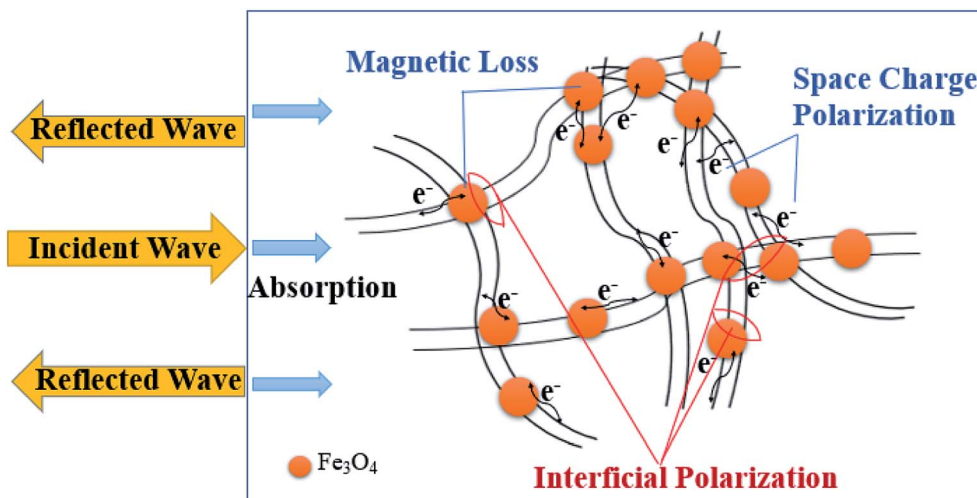


Fig. 13 Illustration of the principle of electromagnetic absorption by  $\text{Fe}_3\text{O}_4/\text{MWCNT}$  hybrid buckypapers.

The dipole polarisation is caused by the nanoparticles deposited on GO, for which the  $\text{Fe}_3\text{O}_4$  nanoparticles are regarded as the polarisation centre. Additionally, introducing GO increases the boundary and surface anisotropy of nano-crystalline iron. The rotation and displacement of the  $\text{Fe}_3\text{O}_4$  nanoparticle domain generate natural and exchange resonance.<sup>34</sup> Finally, the residual defects and groups on the GO sheet improve the polarisation relaxation and the absorption capacity of the hybrid buckypapers.

Fig. 13 illustrates the principle of electromagnetic absorption using  $\text{Fe}_3\text{O}_4/\text{MWCNT}$  hybrid buckypapers. The special helical structure and electromagnetic effects of one-dimensional carbon nanotubes lead to the dielectric relaxation of hybrid buckypapers, which contributes significantly to enhancing the electromagnetic microwave-absorption properties. The enhanced polarisation relaxation mainly originates from defects in the carbon nanotubes, which can be used as polarisation centres; further, the abundant oxygen functional groups and iron nanoparticles can produce hybrid atoms with different electronegativities, which contribute to the generation of the electron dipole polarisation.<sup>2</sup> Additionally, interfacial polarisation between  $\text{Fe}_3\text{O}_4$  nanoparticles loaded on carbon nanotubes and the carbon nanotubes improves the absorbency of the  $\text{Fe}_3\text{O}_4/\text{MWCNT}$  hybrid buckypapers.

To summarise, the structural characteristics of carbon nanotubes and GO are markedly different, leading to a difference in the absorption properties of  $\text{Fe}_3\text{O}_4/\text{MWCNT}$  and  $\text{Fe}_3\text{O}_4/\text{GO}$  buckypapers.<sup>35</sup> First, the lamellar structure of GO is more conducive to nanoparticle adhesion, enhancing the interfacial polarisation between the nanoparticles and GO. Second, the lamellar interpenetrating structure provides more opportunities for multiple reflection and absorption of electromagnetic waves, so that the electromagnetic waves are ultimately effectively attenuated. Third, many residual groups in GO can effectively improve polarisation relaxation and enhance the microwave absorption properties.

## 4. Conclusion

$\text{Fe}_3\text{O}_4/\text{MWCNT}$  and  $\text{Fe}_3\text{O}_4/\text{GO}$  hybrid buckypapers prepared *via* simple vacuum filtration and evaporation-induced self-assembly, respectively, have been successfully applied to epoxy resin/fibre substrates to fabricate absorbing composite materials. We demonstrated that owing to the structural differences in the buckypapers,  $\text{Fe}_3\text{O}_4/\text{MWCNT}$  buckypapers exhibit superior toughness and mechanical properties in comparison with  $\text{Fe}_3\text{O}_4/\text{GO}$  buckypapers and their coating on the substrate is better and much easier to operate. However, their microwave-absorption properties are inferior to those of  $\text{Fe}_3\text{O}_4/\text{GO}$  buckypapers, which is due to the effective complementarity of the dielectric and magnetic losses of the latter. Excellent absorption properties can be obtained by attaching these two hybrid buckypapers to the epoxy resin substrate, of which  $\text{Fe}_3\text{O}_4/\text{GO}$  buckypapers/EP/CF composites have better wave-absorption properties, and their mechanical properties are not significantly affected. Generally,  $\text{Fe}_3\text{O}_4/\text{MWCNT}$  and  $\text{Fe}_3\text{O}_4/\text{GO}$  buckypapers can be used as alternative microwave-absorbing coatings for preparing absorbing composites, and these are expected to meet the demand for lightweight microwave-absorbing composite materials.

## Conflicts of interest

There are no conflicts to declare.

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