

# Growth of magnetic graphene films with higher electromagnetic interference shielding at moderate annealing temperatures

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## ABSTRACT

Ultrathin, highly conductive, and free-standing graphene films have been seen as promising electromagnetic interference (EMI) shielding materials for portable electronic devices. However, they are still expensive. In this paper, a magnetic graphene film decorated with  $Fe<sub>3</sub>O<sub>4</sub>$  nanoparticles was prepared through in situ wet chemical synthesis followed by catalytic graphitization. A graphitic structure was obtained at a moderate annealing temperature (1000  $^{\circ}C$ ), after introducing  $Fe<sub>3</sub>O<sub>4</sub>$  nanoparticles. This temperature is much lower than the conventional graphitization temperature, which reduces the synthesis costs of graphene film. In addition,  $Fe<sub>3</sub>O<sub>4</sub>$  also behaved as microwave absorbers, enhancing the EMI shielding performances. The resulting ultrathin film ( $\sim$  50 µm) provided a high EMI shielding effectiveness (SE) of  $\sim$  52.76 dB in the X-band (8.2-12.4 GHz). This is found to be higher than that of bare graphene films ( $\sim$  33.45 dB) prepared under the same temperature and sufficient to screen about 99.999% of microwave radiation. Furthermore, absorption was the dominant shielding mechanism for the prepared film owing to the contribution of Fe3O4 nanoparticles that reduced the electromagnetic pollution resulting from secondary reflections. The catalytic graphitization strategy could provide a lowcost approach for fabricating efficient graphene-based EMI shielding materials for portable electronic device applications.



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# 1 Introduction

The rapid development of information technology and electronic devices has inevitably caused serious pollution through electromagnetic radiation, which not only interferes with the normal operation of electronic components but also threatens the environment and human health [\[1–4](#page-9-0)]. Electromagnetic interference (EMI) shielding is one of the most important and effective approaches for reducing the negative impact of stray electromagnetic radiation [\[5](#page-9-0)]. Metals and alloys are traditional choices for EMI shielding materials because of their high conductivity; however, they suffer from high density, easy corrosion, and rigidity, which are undesirable in portable and wearable electronic devices [[6,](#page-9-0) [7\]](#page-9-0). Moreover, metals provide EMI shielding predominantly through reflection, which can cause secondary electromagnetic pollution. Therefore, it is necessary to develop new lightweight and flexible EMI shielding materials to reduce the impact of EMI on portable and wearable electronic devices.

Graphene, a new type of two-dimensional carbon nanomaterial, is becoming a promising candidate for EMI shielding due to its low density, corrosion resistance, high carrier mobility, and modifiable surface properties [[8–10\]](#page-9-0). Several efforts have been made to introduce graphene into polymer matrices. However, poor dispersion of graphene in polymer matrix limits its use as composite filler [[11–14\]](#page-9-0). In addition, the thickness of polymer-based composites is usually more than 1 mm, which is difficult to meet the requirement of EMI materials for portable and wearable devices. Recently, free-standing graphene films derived from graphene oxide (GO) have attracted significant interest from researchers because of their exceptional properties, such as low density, ultrathin thickness, flexibility, good processability, ultrahigh thermal and electrical conductivity [[15–18\]](#page-9-0). There are numerous oxygen-containing functional groups and structural defects on the surface of GO, which makes its conductivity very poor [\[16](#page-9-0), [18\]](#page-9-0). Most functional groups can be removed by chemical reduction or moderate thermal annealing  $(< 2000 \degree C)$ , but such prepared reduced graphene oxide (RGO) films still have a large number of structural defects, which can be repaired through further high-temperature graphitization to highly crystalline graphene film. For example, Shen et al.

[ $15$ ] fabricated an 8.4-µm-thick graphene film by the direct evaporation of a GO suspension followed by graphitization at 2000  $^{\circ}$ C; the film exhibited an EMI shielding effectiveness (SE) of 20 dB in the X-band. Lin et al. [[19\]](#page-9-0) modified GO with ethylenediamine to obtain amine-modified GO films, which was subsequently graphitized at 2600  $\degree$ C to prepare a nitrogendoping graphene film with an EMI SE of 58.5 dB. Furthermore, Wang et al. [\[20](#page-9-0)] annealed GO film at an ultrahigh temperature of  $3000$  °C and deposited a copper layer on graphene film via magnetron sputtering; the EMI SE of this composite film can reach as high as 63 dB. However, ultrahigh-temperature graphitization consumes substantial energy and time, which increases the production cost of the graphene films. Moreover, the achievement of such high annealing temperature also requires special equipment. It is still a big challenge to prepare highly crystalline graphene films at a relatively low temperature  $(< 2000 \degree C)$ .

Catalytic graphitization is an effective method to obtain a graphitic structure at a moderate temperature in the presence of various catalysts, such as boron [\[21](#page-9-0)], nickel [[22,](#page-9-0) [23\]](#page-9-0), or iron [\[24](#page-9-0), [25](#page-9-0)]. The graphitization temperature of carbon precursors can be remarkably decreased using this strategy, thereby reducing the production cost of graphitic materials. The catalytic graphitization effect of  $Fe<sub>3</sub>O<sub>4</sub>$  has been demonstrated by previous works [[25–27\]](#page-9-0). For instance, Zhang et al. [\[25](#page-9-0)] discovered the graphitic structure in polyacrylonitrile-based carbon nanofibers carbonized at 800 °C with the aid of Fe<sub>3</sub>O<sub>4</sub>. Mordina et al.  $[26]$  $[26]$  revealed that  $Fe<sub>3</sub>O<sub>4</sub>$  increased the graphitization degree and the conductivity of nanofibers at a carbonization temperature of 900 C. Although there were already some reports on  $Fe<sub>3</sub>O<sub>4</sub>/$ RGO composite materials [\[28–30](#page-9-0)], highly crystalline graphene films have not been obtained due to the absence of graphitization process. To our best knowledge, using catalytic graphitization effect to fabricate highly crystalline graphene films has not been reported so far.

In the present work, we used catalytic graphitization induced by  $Fe<sub>3</sub>O<sub>4</sub>$  nanoparticles to prepare EMI shielding graphene films at moderate annealing temperatures (1000 °C), wherein Fe<sub>3</sub>O<sub>4</sub> nanoparticles were embedded onto graphene films via in situ wet chemical synthesis. Furthermore, we characterized the microstructure, thermal and electrical conductivity and EMI shielding performances of the grown

 $Fe<sub>3</sub>O<sub>4</sub>@graph$ ene films (Fe<sub>3</sub>O<sub>4</sub>@GF) and discussed the catalytic graphitization effect and EMI shielding mechanism. The  $Fe<sub>3</sub>O<sub>4</sub>@GF$  exhibited a high thermal conductivity of 973 W  $m^{-1}$  K<sup>-1</sup> and an electrical conductivity of  $\sim 2.0 \times 10^3$  S cm<sup>-1</sup>. Moreover, the EMI SE of  $Fe<sub>3</sub>O<sub>4</sub>@GF$  can reach as high as 52.76 dB in the X-band, and absorption is the dominant shielding mechanism.

# 2 Experimental procedure and investigation

#### 2.1 Preparation of  $Fe<sub>3</sub>O<sub>4</sub>@GO film$

The  $Fe<sub>3</sub>O<sub>4</sub>@GO$  film was prepared by in situ wet chemical synthesis followed by vacuum filtration. First, a GO aqueous suspension ( $\sim 2$  mg/mL) was obtained by sonicating a mixture of graphite oxide that was prepared by the Hummers method and distilled water at 100 W for 5 min. Subsequently, a 50 mL of aqueous solution containing 2 mmol of  $FeCl<sub>2</sub>$  and 4 mmol of  $FeCl<sub>3</sub>$  was added into 150 mL of the above GO suspension and stirred for 8 h. Then, 8 mL of ammonia solution with the concentration of 25–28 wt% was added dropwise into the mixture with continuous stirring to synthesize  $Fe<sub>3</sub>O<sub>4</sub>$ . These processes were performed in an argon atmosphere. A black precipitate was obtained by centrifuging the resulting mixture, which was washed several times with distilled water before redispersion. Finally,  $Fe<sub>3</sub>O<sub>4</sub>@GO$  film was prepared by filtering the redispersed suspension through a Teflon film with a pore size of 200 nm, followed by drying and peeling from the substrate.

## 2.2 Preparation of  $Fe<sub>3</sub>O<sub>4</sub>@GF$

 $Fe<sub>3</sub>O<sub>4</sub>@GO$  film was placed into a common tubular furnace and annealed at 1000  $^{\circ}$ C for 2 h under an argon atmosphere with the heating rate of  $2 \degree C/min$ . The obtained black film was  $Fe<sub>3</sub>O<sub>4</sub>@GF.$  For comparison, the RGO film (RGF) was prepared by annealing bare GO film under the same preparation condition. Moreover, highly crystalline graphene film (HCGF) was prepared at  $2800$  °C under an argon atmosphere.

The structure and morphology of the  $Fe<sub>3</sub>O<sub>4</sub>@GF$  were observed by a field emission scanning electron microscopy (FE-SEM, JEOL JSM-7001F) and transmission electron microscopy (TEM, FEI Tecnai G2 F30). The crystalline structure of the  $Fe<sub>3</sub>O<sub>4</sub>@GF$  was tested by powder X-ray diffraction (XRD) using a Bruker D8 Advance Diffractometer with Cu Ka  $(\lambda = 1.54184 \text{ Å})$  radiation. The X-ray photoelectron spectroscopic (XPS) was performed an X-ray photoelectron spectrometer (Thermo Fisher, ESCALAB 250Xi) equipped with a monochromatic Al K $\alpha$  X-ray source. The Raman spectra were recorded from 500 to  $3000 \text{ cm}^{-1}$  on a confocal Raman Microprobe (Labram Aramis) using the 532 nm excitation line of an Argon-ion laser. Thermal degradations were investigated by a thermogravimetric analyzer (TGA, PE STA8000) under an oxygen atmosphere with a heating rate of 10  $^{\circ}$ C min<sup>-1</sup>. The electrical conductivity of the samples was measured by a digital four-probe tester (ST-2258A). The thermal conductivity of the samples was calculated by using the equation  $\kappa = \alpha \times C_p \times \rho$ , where  $\kappa$ ,  $\alpha$ ,  $C_p$ , and  $\rho$  represent thermal conductivity, thermal diffusivity, heat capacity, and sample density, respectively. The thermal diffusivity and heat capacity were measured using a laser flash method (Netzsch, LFA-447) at room temperature. The EMI SE of samples in the frequency of 8.2–12.4 GHz was tested by a vector network analyzer (Agilent, N5247A) based on waveguide method.

#### 3 Results and discussion

## 3.1 Growth mechanism of  $Fe<sub>3</sub>O<sub>4</sub>$ on graphene film

The  $Fe<sub>3</sub>O<sub>4</sub>@GF$  was prepared through in situ growth of  $Fe<sub>3</sub>O<sub>4</sub>$  nanoparticles on GO film followed by the graphitization of GO. The growth mechanism of  $Fe<sub>3</sub>O<sub>4</sub>$  nanoparticles and formation of  $Fe<sub>3</sub>O<sub>4</sub>@GF$  are illustrated in Fig. [1.](#page-3-0) Initially, the GO suspension mingles with the  $Fe^{2+}/Fe^{3+}$  solution, following which excessive ammonia is added to the resulting solution.  $Fe<sub>3</sub>O<sub>4</sub>$  nanoparticles are synthesized via the following reaction [[28,](#page-9-0) [29](#page-9-0)].

<span id="page-3-0"></span>

Fig. 1 Schematic representation of the growth mechanism of  $Fe<sub>3</sub>O<sub>4</sub>$  nanoparticles on graphene film

 $\text{Fe}^{2+} + 2\text{Fe}^{3+} + 8\text{OH}^- \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2\text{O}$  (1)

The presence of oxygen-containing functional groups, such as carboxyl (–COOH), hydroxyl (C– OH), and epoxy (C–O–C) groups, negatively charges the GO surface; hence, it can electrostatically attract cations (Fe<sup>2+</sup> and Fe<sup>3+</sup>) in the solution [\[29](#page-9-0), [30](#page-9-0)]. Subsequently, these oxygen-containing functional groups evolve into active sites for the nucleation and growth of Fe<sub>3</sub>O<sub>4</sub> nanoparticles [[30\]](#page-9-0). Finally, with the removal of oxygen-containing functional groups by annealing treatment, we obtained  $Fe<sub>3</sub>O<sub>4</sub>@GF$  that can be strongly attracted by a magnet, showing a ferromagnetic characteristic.

#### 3.2 Morphologies of  $Fe<sub>3</sub>O<sub>4</sub>@GF$

To investigate the distribution of  $Fe<sub>3</sub>O<sub>4</sub>$  nanoparticles on the graphene surface, the morphological features of RGF, HCGF, and  $Fe<sub>3</sub>O<sub>4</sub>@GF$  were observed by SEM. Compared with the rough surface and loose structure of RGF (Fig. [2a](#page-4-0), d), HCGF exhibits a smooth surface and well-stacked multilayer structure (Fig. [2](#page-4-0)b, e), which can be attributed to the repair of structural defects on graphene film during hightemperature graphitization. In the case of  $Fe<sub>3</sub>O<sub>4</sub>@GF,$ plenty of spherical nanoparticles are uniformly anchored on the surface of the graphene film (Fig. [2c](#page-4-0)) and intercalated between graphene layers (Fig. [2f](#page-4-0)). These spherical particles are identified as  $Fe<sub>3</sub>O<sub>4</sub>$  by energy-dispersive spectrum (Fig. S1). The

intercalation of  $Fe<sub>3</sub>O<sub>4</sub>$  nanoparticles hardly affects the well-stacked multilayered structure of the graphene film.

The morphologies of  $Fe<sub>3</sub>O<sub>4</sub>@GF$  were further observed by TEM. TEM images of  $Fe<sub>3</sub>O<sub>4</sub>@GF$  also reveal that the graphene sheet is homogeneously decorated by numerous  $Fe<sub>3</sub>O<sub>4</sub>$  nanoparticles with diameters ranging from 5 to 15 nm (Fig. [3a](#page-4-0)). Note that  $Fe<sub>3</sub>O<sub>4</sub>$  nanoparticles remain firmly attached to the surface of the graphene sheets even after severe ultrasonic oscillation during TEM sample preparation, indicating strong interfacial bonding between graphene nanosheets and  $Fe<sub>3</sub>O<sub>4</sub>$  nanoparticles. Furthermore, high-resolution TEM images of  $Fe<sub>3</sub>O<sub>4</sub>$ crystalline grains reveal a lattice spacing of  $\sim 0.25$ nm (Fig. [3](#page-4-0)b), corresponding to the (311) plane of  $Fe<sub>3</sub>O<sub>4</sub>$  [[31\]](#page-9-0).

#### 3.3 Structural evolution of  $Fe<sub>3</sub>O<sub>4</sub>@GF$

To explore the catalytic graphitization mechanism of  $Fe<sub>3</sub>O<sub>4</sub>$  nanoparticles, the phase compositions of samples were tested by XRD. Figure [4](#page-4-0) shows the XRD patterns of samples. For  $Fe<sub>3</sub>O<sub>4</sub>@GO$  film, a strong diffraction peak can be observed at  $2\theta = 11.8^{\circ}$ , which can be ascribed to GO. In addition, several weak diffraction peaks appear at  $2\theta = 30.2^{\circ}$ , 35.6°, 43.2°, 53.6°, 57.2°, and 62.8°, corresponding to the  $(220)$ , (311), (400), (422), (511), and (440) planes of facecentered cubic  $Fe<sub>3</sub>O<sub>4</sub>$  [[28–31](#page-9-0)]. After thermal annealing, the strong diffraction peak shifts from 11.8 to

<span id="page-4-0"></span>





Fig. 3 a High-resolution TEM image of Fe<sub>3</sub>O<sub>4</sub>@GF. **b** Close view of lattice fringe of  $Fe<sub>3</sub>O<sub>4</sub>$  nanoparticles



Fig. 4 XRD pattern of bare Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>@GO film, Fe<sub>3</sub>O<sub>4</sub>@GF, RGF and HCGF

 $26.1^{\circ}$ , owing to the removal of oxygen-containing functional groups. The diffraction peaks of  $Fe<sub>3</sub>O<sub>4</sub>$ become sharper and stronger compared with Fe<sub>3-</sub> O4@GO film, indicating that the grain size and crystallinity of  $Fe<sub>3</sub>O<sub>4</sub>$  are increased after thermal treatment. Moreover, a new diffraction peak appears at  $2\theta = 44.7^{\circ}$ , which could be corresponding to the  $(110)$  plane of iron  $[32]$  $[32]$ . The generation of the iron is related to the catalytic graphitization reaction. Based on previous reports, the catalytic graphitization due to  $Fe<sub>3</sub>O<sub>4</sub>$  might be explained by the formation of carbide and its decomposition. During the thermal annealing process, the amorphous carbon of GO reacted with  $Fe<sub>3</sub>O<sub>4</sub>$  nanoparticles to form its carbide  $(F_{e_3}C)$ ; then,  $Fe_3C$  was decomposed into iron and graphitic carbon [\[25–27](#page-9-0)], which was why the prepared Fe<sub>3</sub>O<sub>4</sub>@GF contains iron. The resulting iron could also act as a catalyst for graphitization of GO. Under the synergy of  $Fe<sub>3</sub>O<sub>4</sub>$  and iron, the highly ordered graphitic structure was obtained at a low calcination temperature.

The elemental composition and chemical state of the samples were further investigated via XPS testing. The C 1s and O 1s peaks can be observed in the XPS spectra of all tested samples (Fig. [5a](#page-5-0)); in contrast, the Fe 2p peak only appears in the XPS spectrum of Fe3O4@GF. For the GO film, the intensity of the O 1s peak is considerably higher than that of the C1s peak because of the abundant oxygen-containing functional groups on the GO film. The removal of oxygencontaining functional groups during graphitization significantly decreases the intensity of the O 1s peak.

<span id="page-5-0"></span>Fig. 5 a XPS survey spectra of GO, RGF, HCGF and Fe<sub>3</sub>O<sub>4</sub>@GF. **b** XPS spectrum of Fe 2p peak of Fe<sub>3</sub>O<sub>4</sub>@GF. c XPS spectrum of fitted Fe 2p peak of Fe3O4@GF. d Raman spectra of GO, RGF, HCGF and  $Fe<sub>3</sub>O<sub>4</sub>(*a*)GF$ 



Moreover, the O 1s peak of  $Fe<sub>3</sub>O<sub>4</sub>@GF$  is less intense than that of RGF, which implies that introducing  $Fe<sub>3</sub>O<sub>4</sub>$  may facilitate the removal of oxygen-containing functional groups on the GO surface. This conclusion is also supported by the fitted C 1s peak (Fig. S2).

The C 1s spectra of all samples are composed of two components, which are ascribed to the C–C ( $\sim$  284.8 eV) and C–O ( $\sim$  286.4 eV) groups [[33,](#page-10-0) [34\]](#page-10-0). The intensity of the peaks corresponding to the C–O groups clearly decreases after thermal reduction, which is consistent with the results of XPS survey spectra. The area ratio of the deconvoluted C–C peak to C–O peak can be calculated as  $3.33:1$  for  $Fe<sub>3</sub>O<sub>4</sub>@$ GF, 2.55:1 for RGF, and 3.51:1 for HCGF, which indicates that  $Fe<sub>3</sub>O<sub>4</sub>@GF$  can be reduced more easily than RGF.

Figure 5b shows the Fe  $2p$  XPS spectrum of Fe<sub>3-</sub> O4@GF, wherein two peaks appear at 724.5 and 711.1 eV, corresponding to the Fe  $2p_{1/2}$  and Fe  $2p_{3/2}$ orbitals of Fe<sub>3</sub>O<sub>4</sub> [[30,](#page-9-0) [33](#page-10-0)], respectively. The weak satellite peak at 707.0 eV is induced by  $Fe^{0}$  [[32\]](#page-9-0), indicating the presence of iron in  $Fe<sub>3</sub>O<sub>4</sub>@GF$ . The Fe  $2p_{3/2}$  peak can be deconvoluted into two peaks at 711.7 and 710.4 eV (Fig.  $5c$ ), which are ascribed to

 $Fe<sup>3+</sup>$  and Fe<sup>2+</sup> of Fe<sub>3</sub>O<sub>4</sub> [[26,](#page-9-0) [30\]](#page-9-0), respectively. The area ratio between the deconvoluted  $Fe<sup>3+</sup>$  peak and the  $Fe<sup>2+</sup>$  peak is calculated as 2.09:1, which matches well with the atomic ratio of  $Fe^{3+}/Fe^{2+}$  in  $Fe_3O_4$ . Finally, we investigated the O 1s XPS spectra of the samples. Unlike the single peaks of GO, RGF, and HCGF, the O 1s XPS spectrum of  $Fe<sub>3</sub>O<sub>4</sub>@GF$  exhibits distinct double peaks due to C–O and Fe–O bonds (Fig. S3).

Raman spectroscopy was conducted to estimate and compare the graphitization degree of the samples. Figure 5d reveals two characteristic peaks at 1352 cm<sup>-1</sup> (D band) and 1579 cm<sup>-1</sup> (G band), which are induced by lattice defects and the tangential stretching mode of sp<sup>2</sup>-hybridized carbon atoms [[35,](#page-10-0) [36\]](#page-10-0), respectively. The  $I_D/I_G$  ratio can be used to evaluate the graphitization degree of carbon-containing materials. Compared with GO, the  $I_D/I_G$  ratio of Fe<sub>3</sub>O<sub>4</sub>@GF significantly decreases from 1.29 to 0.06, suggesting that numerous defects are repaired during calcination process. Moreover, the D band of  $Fe<sub>3</sub>O<sub>4</sub>@GF$  is much less intense than that of RGF, which indicates that  $Fe<sub>3</sub>O<sub>4</sub>@GF$  can obtain higher graphitization degree than the bare graphene film at the same annealing temperature. This phenomenon can be attributed to the catalytic graphitization effect of  $Fe<sub>3</sub>O<sub>4</sub>$  and Fe. The D band of HCGF almost disappears, indicating its higher graphitization degree than  $Fe<sub>3</sub>O<sub>4</sub>@GF.$  This can be attributed to the ultrahigh graphitization temperature of HCGF, which enable more structural defects to be repaired. Furthermore, 2D bands located at  $\sim 2715$  cm<sup>-1</sup> show an increasing trend from GO, RGF,  $Fe<sub>3</sub>O<sub>4</sub>@GF$  to HCGF, which also demonstrates that the structure of Fe<sub>3-</sub> O4@GF is more ordered than RGF, but more disordered than HCGF.

## 3.4 Thermal and electrical properties of  $Fe<sub>3</sub>O<sub>4</sub>@GF$

The thermal and electrical conductivity of carbon materials significantly increases after graphitization owing to deoxygenation, structure rearrangement, and defect repair [\[15](#page-9-0), [16](#page-9-0)]. Herein, we compare the thermal and electrical properties of  $Fe<sub>3</sub>O<sub>4</sub>@GF, RGF,$ and HCGF with similar thicknesses of  $\sim$  50 µm to further verify the catalytic graphitization effect of  $Fe<sub>3</sub>O<sub>4</sub>$ . As presented in Fig. 6, the thermal conductivity of Fe<sub>3</sub>O<sub>4</sub>@GF (973 W m<sup>-1</sup> K<sup>-1</sup>) is substantially higher than that of RGF (729 W  $m^{-1}$  K<sup>-1</sup>), indicating that catalytic graphitization assisted by  $Fe<sub>3</sub>O<sub>4</sub>$  repairs more defects than graphitization without catalyst. The thermal conductivity of  $Fe<sub>3</sub>O<sub>4</sub>@GF$  is no match for that of HCGF (1278 W  $m^{-1}$  K<sup>-1</sup>), owing to its more disordered structure than HCGF and the increasing phonon scattering at the interfaces between graphene sheets and  $Fe<sub>3</sub>O<sub>4</sub>$  nanoparticle. The measured electrical conductivity mirrors the thermal conductivity (Fig. 6), further confirming catalytic graphitization by  $Fe<sub>3</sub>O<sub>4</sub>$  and Fe.



 $Fe<sub>3</sub>O<sub>4</sub>(Q)$ GF

## 3.5 EMI shielding performance of Fe<sub>3</sub>O<sub>4</sub>@GF

It is well known that the EMI shielding performance is associated with the electromagnetic parameters. Therefore, the relative permittivity and permeability of the samples were investigated in the X-band (8.2– 12.4 GHz) based on the coaxial transmission line method. As shown in Fig. [7](#page-7-0)a, the mean relative permittivity of Fe<sub>3</sub>O<sub>4</sub>@GF, RGF, and HCGF is 7.56, 6.62, and 7.48, respectively. The enhanced relative permittivity of  $Fe<sub>3</sub>O<sub>4</sub>@GF$  is attributed to strong interfacial polarization caused by the introduction of  $Fe<sub>3</sub>O<sub>4</sub>$  nanoparticles. Figure [7](#page-7-0)b displays the relative permeability of all samples. The mean relative permeability of RGF and HCGF is close to 1, owing to their nonmagnetic properties. In contrast, the mean relative permeability of  $Fe<sub>3</sub>O<sub>4</sub>@GF$  is increased to 1.51 due to the introduction of magnetic  $Fe<sub>3</sub>O<sub>4</sub>$  nanoparticles. The increased permeability causes a remarkable decrease of skin depth  $\delta$  according to Eq. (2) [[37,](#page-10-0) [38\]](#page-10-0),

$$
\delta = (\pi \sigma f \mu)^{\frac{-1}{2}} \tag{2}
$$

Here,  $\sigma$  represents the electrical conductivity of the material, and  $f$  is the frequency of the electromagnetic wave. The skin depth is defined as penetrating distance of electromagnetic wave in materials at which electromagnetic energy is attenuated to 1/e of the initial value. A small skin depth means a good shielding performance of the material.

The EMI SE of  $Fe<sub>3</sub>O<sub>4</sub>@GF$  was investigated, which is widely used in radar detection, weather monitoring, and satellite communication. The EMI measurement setup is displayed in Fig. [7c](#page-7-0). The EMI SE was measured experimentally via commonly used vector network analyzer equipped with waveguide section. Because the thickness affects the EMI SE of materials, we used samples of similar thicknesses ( $\sim$  50  $\mu$ m) for the measurements. Figure [7](#page-7-0)d shows that the average SE of HCGF ( $\sim$  46.20 dB) is higher than that of RGF ( $\sim$  33.45 dB), which is attributed to the superior electrical conductivity of the former. Moreover, Fe<sub>3</sub>O<sub>4</sub>@GF has an average EMI SE of 52.76 dB, which is higher than that of HCGF and RGF due to the contribution of  $Fe<sub>3</sub>O<sub>4</sub>$  nanoparticles. For comparison, the EMI SE and thickness of recently reported carbon-based EMI shielding materials Fig. 6 Thermal and electrical conductivity of RGF, HCGF, and [[6,](#page-9-0) [15](#page-9-0), [17,](#page-9-0) [33,](#page-10-0) [39–42](#page-10-0)] in the X-band are presented in



<span id="page-7-0"></span>Fig. 7 a Relative permittivity and b relative permeability of RGF, HCGF, and  $Fe<sub>3</sub>O<sub>4</sub>(a)$ GF in the X-band; c photograph of EMI shielding measurement setup based on waveguide method; d EMI SE of RGF, HCGF, and  $Fe<sub>3</sub>O<sub>4</sub>(@GF)$  in the X-band; e EMI shielding performance of recently reported graphene-based materials; f schematic representation of EMI shielding mechanism of  $Fe<sub>3</sub>O<sub>4</sub>(*a*)GF$ 



Fig. 7e. The EMI SE of  $Fe<sub>3</sub>O<sub>4</sub>@GF$  is superior to most of relevant shielding materials ever reported. Moreover, the thinner thickness makes our prepared materials have wider applications in portable electronic devices.

As well known, the electromagnetic waves can be shielded by a material through reflection mechanism and absorption mechanism. The total EMI SE is the sum of attenuation from reflection  $(SE_R)$  and absorption ( $SE_A$ ). As shown in Fig. 7f, the  $SE_R$ depends on the impedance mismatch between the film and free space (air) in which the incident electromagnetic wave travels.  $SE_A$  represents the ability of the film to convert electromagnetic energy into thermal energy  $[43]$  $[43]$  $[43]$ , including conductive loss caused by graphene, magnetic loss caused by  $Fe<sub>3</sub>O<sub>4</sub>$ ,

interfacial polarization as well as multiple reflection and scattering.

To explore the shielding mechanism of  $Fe<sub>3</sub>O<sub>4</sub>@GF$ , we calculate  $SE_R$  and  $SE_A$  from the scattering parameters using Eqs. (3) and (4) [[44,](#page-10-0) [45\]](#page-10-0),

$$
SE_R = -10 \log(1 - R) = -10 \log(1 - S_{11}^2)
$$
 (3)

$$
SE_A = -10 \log \left( \frac{T}{1 - R} \right) = -10 \log \left( \frac{S_{21}^2}{1 - S_{11}^2} \right) \tag{4}
$$

where  $T$  and  $R$  are the transmittance and reflectivity of the electromagnetic waves, respectively. The scattering parameters  $(S_{11}$  and  $S_{21})$  were measured using the vector network analyzer. Figure [8](#page-8-0)a shows that both reflection and absorption contribute to the EMI SE of Fe<sub>3</sub>O<sub>4</sub>@GF. The mean value of  $SE<sub>A</sub>$ 

<span id="page-8-0"></span>

( $\sim$  40.68 dB) is much higher than that of  $SE_R$ ( $\sim$  12.08 dB), indicating that absorption is the dominant shielding mechanism for  $Fe<sub>3</sub>O<sub>4</sub>@GF.$  Furthermore, the high conductivity of HCGF deteriorates the impedance match between the air and the film, resulting in a higher  $SE_R$  value than that of RGF and Fe<sub>3</sub>O<sub>4</sub>@GF (Fig. 8d). Moreover,  $SE_A$  of Fe<sub>3</sub>O<sub>4</sub>@GF is higher than that of the bare graphene film, which means that  $Fe<sub>3</sub>O<sub>4</sub>@GF$  can absorb more electromagnetic energy than the other samples. The enhanced  $SE_A$  of  $Fe_3O_4@GF$  results from the contribution of  $Fe<sub>3</sub>O<sub>4</sub>$  nanoparticles. On the one hand,  $Fe<sub>3</sub>O<sub>4</sub>$ nanoparticles can attenuate electromagnetic waves through magnetic loss, such as natural resonance and eddy-current loss [\[46](#page-10-0), [47](#page-10-0)]. On the other hand, charges are prone to accumulate at the interface between graphene and  $Fe<sub>3</sub>O<sub>4</sub>$  under an alternating electromagnetic field, resulting in interfacial polarization and dielectric loss [[48–50\]](#page-10-0).

#### 4 Conclusion

In summary,  $Fe<sub>3</sub>O<sub>4</sub>$  nanoparticles anchored graphene films were successfully prepared via in situ wet chemical synthesis followed by catalytic graphitization at a moderate annealing temperature of 1000  $^{\circ}$ C. The magnetic film exhibits a high thermal conductivity of 973 W  $m^{-1}$  K<sup>-1</sup> and an electrical conductivity of  $\sim 2.0 \times 10^3$  S cm<sup>-1</sup>. The EMI SE of Fe<sub>3</sub>O<sub>4</sub>@GF can reach as high as 52.76 dB in the X-band at a thickness of  $\sim$  50  $\mu$ m, which is superior to most of carbon-based shielding materials. The good EMI shielding performance is attributed to the introduction of  $Fe<sub>3</sub>O<sub>4</sub>$  nanoparticles and high graphitization degree of graphene sheets. With these excellent properties,  $Fe<sub>3</sub>O<sub>4</sub>@GF$  is expected to be a promising candidate for EMI shielding application in portable electronic devices, such as mobile phones and notebook computers.

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# Author contributions

WL did methodology, investigation, formal analysis, data curation, writing—original draft, and funding acquisition. KJ was involved om validation, formal <span id="page-9-0"></span>analysis, and funding acquisition. DW performed formal analysis, writing—review and editing. XW contributed to conceptualization, methodology, writing—review & editing. PW done writing—review and editing. KZ performed resources and writing—review and editing.

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## Data availability

All data generated or analyzed during the current study are available from the corresponding author on reasonable request.

# **Declarations**

Conflict of interest The authors declare that they have no conflict of interest.

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