GO@Fe$_3$O$_4$@CuSilicate Composite with a Hierarchical Structure: Fabrication, Microstructure, and Highly Electromagnetic Shielding Performance

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ABSTRACT: Two nanocomposites with a hierarchical structure (GO@CuSilicate@Fe$_3$O$_4$ and GO@Fe$_3$O$_4$@CuSilicate) were fabricated in this paper. These as-synthesized nanocomposites were analyzed for their structural, compositional, and morphological features by X-ray diffraction, scanning electron microscopy (SEM), Raman spectroscopy, and Brunauer–Emmett–Teller methods. SEM images showed that both nanocomposites had a core–shell structure, and their shells were composed of CuSilicate nanoneedle arrays. Further, their total electromagnetic shielding efficiency was measured and compared in a wide frequency range of 8–12 GHz (X-band). Because of the “antenna” role of CuSilicate nanoneedle arrays and the polarization at the interface between graphene oxide (GO) and Fe$_3$O$_4$, GO@Fe$_3$O$_4$@CuSilicate showed higher electromagnetic shielding performance than that of GO@CuSilicate@Fe$_3$O$_4$. With 1 mm thickness, GO@Fe$_3$O$_4$@CuSilicate showed a high electromagnetic shielding efficiency (over 40 dB) in the whole X-band (8.2–12.4 GHz) and reached a maximum value (41.8 dB) at 8.2 GHz. Its total electromagnetic shielding efficiency was mainly contributed by absorption rather than reflection. This study provided an idea for the structural design of high-performance electromagnetic shielding materials in the GHz frequency range (X band).

1. INTRODUCTION

Owing to the ever-increasing use of telecommunications and electronic devices, electromagnetic interference, and electromagnetic compatibility problems are becoming more and more serious in civil and military fields. To overcome the electromagnetic wave pollution, the development of high-performance electromagnetic shielding materials with strong absorption and weak secondary reflection, wide adsorption frequency, thin thickness, and lightweight is of great significance.

In order to realize the efficient absorption of the incident electromagnetic wave, the material must satisfy two conditions: first, the first reflection of the incident electromagnetic wave should be minimized. That is, the electromagnetic wave can enter the material to the maximum extent. Second, the electromagnetic wave energy into the material can be consumed efficiently and quickly through the electromagnetic loss mechanism inside the material.

Different materials have different electromagnetic loss mechanisms. According to their loss mechanisms, they are generally classified into two types: magnetic loss type (such as ferrite, carbonyl iron, polycrystalline iron fiber, iron nitride, etc.) and dielectric loss type (such as graphite, conductive polymer, etc.). The magnetic loss is caused by the magnetization or demagnetization of some materials with magnetic properties under the action of an electromagnetic wave and it is positive correlated with their coercivity. The dielectric loss includes polarization and conductive loss, and the polarization is mainly related to the defects and functional groups of the material which could provide dipoles and...
generate relaxation loss toward the incident wave. While the conductive loss is mainly related to the conductivity of the material, which could produce a large internal current when the electromagnetic wave enters these materials. Taking the advantage of the synergy between magnetic loss and dielectric loss is a method to improve the electromagnetic shielding performance of a material. For example, Shu18 and Li19 obtained hybrid composites which showed enhanced microwave absorption capabilities with highly efficient performance. Reducing the material’s size to the nanometer scale might also be an effective method to improve its electromagnetic shielding performance. The work of Wei,20 Kim,21 and Duan22 showed that for the same substance, nanomaterials exhibited better absorbing properties and wider absorbing frequency band than conventional materials. The authors attributed these improvements to the nanomaterial having more surface, more defects, and more functional groups.

Constructing the nanostructure, especially the three-dimensional (3D) nanostructure, may also be a promising approach to enhance electromagnetic shielding because some nanostructures could lead to multiple reflection and absorption of the incident microwaves. Tong23 prepared three different polymeric Fe3O4 nanomaterials (nanospheres, sponges, and urchins) and compared their static magnetic and microwave electromagnetic characteristics. Their results showed that Fe3O4 sponges exhibited improved saturation magnetization and coercivity compared with Fe3O4 nanospheres and urchins because the nanoporous structure in Fe3O4 sponges allowed multiple reflection and scattering, which trapped the wave and facilitated attenuation with additional dielectric loss. Similarly, because of the multiple reflection and diffuse scattering of the microwave’s behavior, flower-like particles (such as flower-like CuS hollow microspheres,24 flower-like porous Fe3O425 flower-like Co superstructures,26 and flower-like ZnO structures27) also exhibited improved microwave absorption capabilities compared with normal materials.

Recently, Cao28 constructed a nanoarchitecture with a honeycomb surface which achieved integrated advantages in electromagnetic attenuation. One of the key factors was that the honeycomb surface generated an equivalent wedge effect and most parts of the strengthened reflected wave could enter into the nanoarchitecture.

In our previous work, the 3D hierarchical GO@CuSilicate nanoarray had been prepared through a hydrothermal method.29 Based on our previous work and inspired by the above literatures, in this paper, two different nanocomposites with a multicomponent and hierarchical structure (GO@CuSilicate@Fe3O4 and GO@Fe3O4@CuSilicate) were prepared in aiming at developing an electromagnetic shielding material with a strong adsorption value, wide adsorption frequency, and thinness. Their structures, morphology, and electromagnetic shielding properties were investigated and compared as well. On these bases, the possible electromagnetic shielding mechanism of GO@Fe3O4@CuSilicate was explored.

2. RESULTS AND DISCUSSION
2.1. Structure and Morphology of GO@CuSilicate@Fe3O4. The strategy of synthesizing GO@CuSilicate@Fe3O4 was depicted in Scheme 1. First, GO was coated with a silica layer by the Stöber method30 to obtain a GO@SiO2 composite. Then, the obtained SiO2 coating was used as sacrificial templates to obtain GO@CuSilicate. Finally, the obtained GO@CuSilicate was blended with nano-Fe3O4 under ultrasonic to get GO@CuSilicate@Fe3O4. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of GO and GO@SiO2 are shown in Figure 1a–d. It could be seen that GO nanosheets are crumpled transparent nanosheets, while GO@SiO2 are a semi-transparent sheet and had a smooth surface, indicating that the SiO2 coating layer was relatively thin. Compared with that of GO@SiO2, the morphology of GO@CuSilicate was obviously different. As can be seen from Figure 1e,f, a large number of nanoneedles stood on the GO sheet, presenting a nanoarray structure. The diameter of the nanoneedles
exhibited a narrow size distribution with a mean diameter size of about 10 nm. The neighboring nanoneedles formed many V-shaped pores on the surface of GO@CuSilicate. As indicated by the circle in the inset in Figure 1h, the CuSilicate nanoneedles even had a hollow structure. Figure 1g showed the lateral structure of a broken GO@CuSilicate, it could be seen that nanoneedle arrays were distributed on both sides of the GO layer uniformly and the length of the nanoneedles was about 200 nm, forming a 3D hierarchical core–shell structure. A gap between the GO core and CuSilicate shell, which was left by the SiO2 sacrificial template, could also be observed (as indicated by the circle in Figure 1g).

Raman spectroscopy is an effective tool to characterize the structural characteristics and properties of carbon nanomaterials. Figure 2 showed the Raman spectra of GO and GO@CuSilicate. Two characteristic peaks at 1335 cm⁻¹ (D-band) and 1598 cm⁻¹ (G-band) were observed in both GO and GO@CuSilicate spectra. The D-band, which appears due to the defects in the carbon plane, reflects the disordered state of the grain boundary, vacancy, and amorphous carbon on the graphene surface. While the G-peak band, which appears due to the E₂g vibrational modeling of the sp² carbon atom, represents the ordered sp² bond structure. According to the literature, compared with GO, although rGO has more sp² region, the average size of the sp² region is smaller. This leads the fact that the intensity ratio of D-peak to G-peak (I_D/I_G) of rGO is always higher than that of GO. From Figure 2, it could be seen that compared with the I_D/I_G value of GO (1.023), the I_D/I_G value of GO@CuSilicate increased to 1.12, suggesting that GO had been partly reduced during the hydrothermal reaction.

The X-ray diffraction (XRD) patterns of GO@SiO2 and GO@CuSilicate were shown in Figure 3. It could be seen from the pattern of GO@SiO2, the sharp characteristic peak of GO disappeared at 2θ = 10.3°, while a new broad band belonging to the amorphous SiO2 diffraction peak (JCPDS card no. 29-0085) appeared at 2θ = ~22°. The disappearance of the peak at 2θ = 10.3° indicated that the stacking structure of GO was destroyed by SiO2 coating. The XRD pattern of GO@CuSilicate showed several characteristic diffraction peaks located at 20.4, 26.54, 30.54, 31.84, 36.5, 56.4, 62.7, and 71.4, which corresponds to the (130), (132), (023), (360), and (362) planes of the copper silicate crystal (JCPDS card no. 03-0219). This result indicated the successive synthesis of GO@CuSilicate.

Figure 4 showed the morphology of GO@CuSilicate@Fe₃O₄ composite prepared by different Fe₃O₄/GO@CuSilicate mass ratios. The dark dots in TEM represented Fe₃O₄ (Figure 4d–f). As can be seen from the figures, the diameter of Fe₃O₄ nanoparticles was only ~11 nm. When the Fe₃O₄/GO@CuSilicate mass ratios were low (0.2:1, Figure 4a,d), most of the Fe₃O₄ nanoparticles were loaded in the gap between two CuSilicate needles, forming a uniform coverage from the bottom to the top of the CuSilicate needle. Because of the low coverage of Fe₃O₄, the nanoneedle array structure could be clearly seen in its TEM diagram. When the Fe₃O₄/GO@CuSilicate mass ratios increased to 0.5:1, some Fe₃O₄ nanoparticles started to aggregate together (as indicated by circles in Figure 4e). Because of the higher coverage of Fe₃O₄, parts of the nanoneedle array structure seemed illegible in TEM. When the Fe₃O₄/GO@CuSilicate mass ratios continued to increase to 1:1, more Fe₃O₄ nanoparticle agglomerates appeared in the gap and on the top of the CuSilicate array (Figure 4c). In addition, more nanoneedle structures became vague and illegible (Figure 4f).

The XRD patterns of the GO@CuSilicate@Fe₃O₄ with different GO@CuSilicate/Fe₃O₄ mass ratios were shown in Figure 5. It could be seen that despite the different characteristic diffraction peaks of CuSilicate, more diffraction peaks could be observed at 30.1°, 35.4°, 43.1°, 53.4°, 62.5°, 70.9°, and 73.9°, which corresponds to the (220), (311), (400), (422), (440), (620), and (533) planes of Fe₃O₄ (JCPDS card no. 19-0629).

2.2. Structure and Morphology of GO@Fe₃O₄@CuSilicate. The synthesizing strategy of GO@Fe₃O₄@CuSilicate was slightly different from that of GO@CuSilicate@Fe₃O₄ and was depicted in Scheme 2. First, GO was covered with Fe₃O₄ microspheres by the thermal decomposition method to obtain a GO@Fe₃O₄ composite. Then, the obtained GO@Fe₃O₄ composite was coated with a silica layer by the Stöber method to obtain the GO@Fe₃O₄@SiO2 composite. Finally, the obtained GO@Fe₃O₄@SiO2 composite was hydrothermally treated in aqueous Cu(NO3)₂ and ammonia solution at 140 °C to obtain GO@Fe₃O₄@CuSilicate.

Figure 6 showed the morphology of GO@Fe₃O₄@CuSilicate. The Fe₃O₄ nanoparticles were uniformly anchored on the surface of the GO sheet with a diameter size of ~11 nm. This uniform distribution of Fe₃O₄ (Figure 6b) ensured the smoothness and integrality of SiO2 deposition coating. GO@Fe₃O₄@CuSilicate showed a similar morphology with that of GO@CuSilicate (Figure 6c) and exhibited less transmittance than GO@CuSilicate because of the existence of a large number of Fe₃O₄ (Figure 6d).

The XRD patterns of GO@Fe₃O₄@CuSilicate are shown in Figure 7. It indicated that GO@Fe₃O₄@CuSilicate also contained Fe₃O₄ and CuSilicate components.

2.3. Specific Surface Area and Pore Size Distribution of GO@CuSilicate@Fe₃O₄ and GO@Fe₃O₄@CuSilicate. Because large specific surface and the porous structures

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Figure 2. Raman spectra of GO and GO@CuSilicate.

Figure 3. XRD patterns of GO (a), GO@SiO2, and GO@CuSilicate (b).
could benefit the interfacial polarization and the multiple reflection and scattering of electromagnetic wave, the specific surface and pore size distribution of GO@CuSilicate@Fe3O4 and GO@Fe3O4@CuSilicate were measured by the Brunauer–Emmett–Teller method. Figure 8a,b were isothermal adsorption curves of GO@CuSilicate and GO@CuSilicate@Fe3O4. It could be seen that GO@CuSilicate had a specific surface area of 316.4 m²/g. When the mass ratio of Fe3O4/GO@CuSilicate was 0:2:1, the isothermal adsorption curve of GO@CuSilicate@Fe3O4 almost coincided with that of the GO@CuSilicate. Its specific surface area was 305.8 m²/g (Figure 8b). However, with the mass ratio of Fe3O4/GO@CuSilicate increased, both the specific surface area and the pore volume of GO@CuSilicate@Fe3O4 decreased. It indicated that with the increase of Fe3O4 mass, more and more gaps in CuSilicates arrays were occupied by Fe3O4. This result was consistent with that observed in Figure 4. From Figure 8c, it could be seen that all the samples (GO@CuSilicate and GO@CuSilicate@Fe3O4) had a mesoporous structure and the mesopore size was independent of Fe3O4 loading. Their mesopore size had a relatively narrow distribution and a peak value of approximately ∼31 nm. This mesoporous structure might be contributed by the hollow structure of the CuSilicate nanoneedle (as indicated in Figure 1h).

Figure 4. SEM and TEM images of GO@CuSilicate@Fe3O4 with different mass ratio of Fe3O4/GO@CuSilicate of 0:2:1 (a,d); 0:5:1 (b,e); 1:1 (c,f).

Figure 5. XRD patterns of GO@CuSilicate@Fe3O4 with different mass ratio of Fe3O4/GO@CuSilicate.

Figure 6. SEM image of GO@Fe3O4 (a); SEM image of GO@Fe3O4@SiO2 (b); SEM image (c) and TEM image (d) of GO@Fe3O4@CuSilicate.

Figure 7. XRD patterns of GO@Fe3O4 (a) and GO@Fe3O4@CuSilicate (b).

Figure 9a was the isotherm adsorption curves of GO@Fe3O4, GO@Fe3O4@SiO2, and GO@Fe3O4@CuSilicate. It could be seen that the lack of the CuSilicate nanoneedle array, the specific surface areas of GO@Fe3O4 and GO@Fe3O4@SiO2 were only 50.4 and 37.8, respectively. While the specific surface areas of GO@Fe3O4@CuSilicate reached 105.7 m²/g.
Figure 8. Typical N$_2$ adsorption–desorption isotherms of GO@CuSilicate (a); GO@CuSilicate@Fe$_3$O$_4$ (b); pore size distribution of GO@CuSilicate@Fe$_3$O$_4$ (c).

Figure 9. Typical N$_2$ adsorption–desorption isotherms of GO@Fe$_3$O$_4$, GO@Fe$_3$O$_4$@SiO$_2$, and GO@Fe$_3$O$_4$@CuSilicate (a); pore size distribution of GO@Fe$_3$O$_4$@CuSilicate (b).

Figure 10. Hysteresis loop of GO@Fe$_3$O$_4$, GO@CuSilicate@Fe$_3$O$_4$, and GO@Fe$_3$O$_4$@CuSilicate (a); $M$–$H$ curve in the range of –100 to 100 Oe (b); magnetic movement of GO@Fe$_3$O$_4$, GO@CuSilicate@Fe$_3$O$_4$, and GO@Fe$_3$O$_4$@CuSilicate by an external magnet (c).
The GO@Fe₃O₄@CuSilicate also had a mesoporous structure and its most probable aperture size was 35 nm (Figure 9b).

2.4. Magnetic and Electromagnetic Shielding Properties of GO@CuSilicate@Fe₃O₄ and GO@Fe₃O₄@CuSilicate Composites. The magnetic properties of samples were studied via a vibrating sample magnetometer (VSM) by applying a maximum magnetic field of ±20 kOe. The hysteresis loop of GO@CuSilicate@Fe₃O₄ (the mass ratio of Fe₃O₄/GO@CuSilicate was 0.5:1), GO@Fe₃O₄ and GO@Fe₃O₄@CuSilicate at 300 K are depicted in Figure 10a. It could be seen that all the hysteresis loops exhibited a typical S-curve. Figure 10b was an enlarged view of the M−H loop in the range of −100 to 100 Oe. The enlarged hysteresis showed that all the samples displayed low coercivity, suggesting that they were magnetically soft.35,36 When a magnet was placed beside, derived by Fe₃O₄, all the samples showed quick movements along the magnetic field (Figure 10c). The saturation magnetization (Mₛ) of GO@Fe₃O₄, GO@CuSilicate, GO@CuSilicate@Fe₃O₄ (0.2:1) (b); GO@CuSilicate@Fe₃O₄ (0.5:1) (c); GO@CuSilicate@Fe₃O₄ (1:1) (d); GO@Fe₃O₄ (e); GO@Fe₃O₄@CuSilicate (f).

Figure 11. Electromagnetic shielding efficiency curve of GO@CuSilicate (a); GO@CuSilicate@Fe₃O₄ (0.2:1) (b); GO@CuSilicate@Fe₃O₄ (0.5:1) (c); GO@CuSilicate@Fe₃O₄ (1:1) (d); GO@Fe₃O₄ (e); GO@Fe₃O₄@CuSilicate (f).

Scheme 3. Schematic Illustration for the Microwave Absorption of GO@Fe₃O₄@CuSilicate
Fe$_3$O$_4$@CuSilicate which was almost independent of frequency range in this paper, the shielding effectiveness of GO@CuSilicate was increased with the increase of frequency and reached the maximum (7.84 dB) at 12.4 GHz. The surface loading of Fe$_3$O$_4$ on GO@CuSilicate seemed to have little effect on improving electromagnetic shielding effectiveness, although their maximum shielding effectiveness showed a little shift compared with that of GO@CuSilicate (Figure 11b–d).

In contrast, GO@Fe$_3$O$_4$@CuSilicate displayed significantly enhanced electromagnetic absorption properties compared to the GO@CuSilicate (Figure 11f). The electromagnetic shielding effectiveness of GO@Fe$_3$O$_4$@CuSilicate was always higher than 40.6 dB in the whole X band and a maximum shielding effectiveness of 41.8 dB could be observed at 8.2 GHz, among which absorption and reflection losses are $S_E$ 36.5 dB and $S_R$ 5.3 dB, respectively. As a comparison, the electromagnetic shielding effectiveness of corresponding GO@Fe$_3$O$_4$ was also measured and shown in Figure 11e. Different from the electromagnetic shielding effectiveness of GO@Fe$_3$O$_4$@CuSilicate which was almost independent of frequency, the electromagnetic shielding efficiency of GO@Fe$_3$O$_4$ exhibited dependency on the frequency and reached a maximum shielding effectiveness of 35.6 dB at 11.4 GHz.

The better electromagnetic shielding performance of GO@Fe$_3$O$_4$@CuSilicate compared with GO@Fe$_3$O$_4$ should be attributed to the array structure of CuSilicate. It could be seen from the SEM image in Figure 6 that there existed lots of V-shaped gaps between CuSilicate nanoneedles. This array structure played similar roles as a cuneiform array which could make incident waves reflect downward (as shown in Scheme 3). In other words, the CuSilicate nanoneedle arrays acted as a microwave receiver and induced more electromagnetic waves penetrate the CuSilicate shell. Besides, the hollow mesoporous of CuSilicate nanoneedles might play a similar role. Moreover, the coexistence of different pore sizes in GO@Fe$_3$O$_4$@CuSilicate might partly explain why GO@Fe$_3$O$_4$@CuSilicate had such a broadband absorption and was almost independent of frequency. Furthermore, the gap left by SiO$_2$ sacrifice templates might also benefit the strengthened electromagnetic absorption because this gap situated between GO@Fe$_3$O$_4$ (core) and CuSilicate (shell) and could also contribute to the repeatedly scattered and multiple reflected microwaves between the core and the shell (as shown in Scheme 3).

The huge difference of electromagnetic performance between GO@Fe$_3$O$_4$@CuSilicate and GO@CuSilicate@Fe$_3$O$_4$ might attribute to the different distribution of Fe$_3$O$_4$, considering that both of them have the same components, multiporous structures, and similar morphologies. The diameter of the Fe$_3$O$_4$ particle was only about 11 nm. With such a small size, the coercivity of Fe$_3$O$_4$ was close to zero and, therefore, had little contribution to magnetic loss. However, the small size brought a lot of defects and functional groups to its surface which benefited the generation of dipoles under electromagnetic waves. When these nano-Fe$_3$O$_4$ nanoparticles were attached to the surface of GO (In the case of GO@Fe$_3$O$_4$@CuSilicate), the high-electronic mobility in conjugated regions of GO might induce asymmetric charge distribution and produced lots amounts of dipoles and polarization at the interface between graphene and Fe$_3$O$_4$. According to Cao’s literature, these dipoles together with the graphene they loaded might form a microcapacitor-like structures, which had high charge storage capacities and have great contribution to microwave attenuation (as shown in Scheme 3).

However, in GO@CuSilicate@Fe$_3$O$_4$ nanoparticles were attached on CuSilicate needles. Because of the insulate characteristic of CuSilicate, it was hard for them to induce asymmetric distribution of charge and to produce dipoles at their interface with Fe$_3$O$_4$. Although Fe$_3$O$_4$ and CuSilicate alone could also generate some dipoles and which would caused the attenuation of the electromagnetic wave, their dipole number was almost negligible compared with the large number of dipoles produced at the interface in GO@Fe$_3$O$_4$@CuSilicate. Furthermore, the attached Fe$_3$O$_4$ blocked the V-shaped gap between nanoneedle arrays and destroyed their role as of “antenna”. That is why the attachment of nano-Fe$_3$O$_4$ had little effect on the electromagnetic shielding effectiveness of GO@CuSilicate. Their independent characteristics of electromagnetic properties relative to Fe$_3$O$_4$ content should be attributed to the combined effect of the decrease of V-shaped pores and the increase of dipoles caused by the increase of Fe$_3$O$_4$ loading.

In GO@CuSilicate, GO was surrounded by the insulate CuSilicate shell. The electron-hoping between two graphene nanosheets which contribute to electrical loss was blocked. Even though a CuSilicate array could also induce large numbers of electromagnetic waves to the core layer, the attenuate of electromagnetic waves by the core was small because only dipoles contributed by the unreduced region of GO can do this. Therefore, the maximum shielding effectiveness of GO@CuSilicate was only 7.84 dB.

3. CONCLUSIONS

Two nanocomposites with different structures (GO@CuSilicate@Fe$_3$O$_4$ and GO@Fe$_3$O$_4$@CuSilicate) were fabricated and their microstructure and electromagnetic shielding performance were studied and compared. The results showed that both GO@CuSilicate@Fe$_3$O$_4$ and GO@Fe$_3$O$_4$@CuSilicate had 3D hierarchical structures. They both had a large specific surface area and magnetically soft. However, the inner and outer order of Fe$_3$O$_4$ in the hierarchical structure greatly affected their electromagnetic shielding efficiency. When Fe$_3$O$_4$ was in the outermost position (attached on CuSilicate), the attachment of Fe$_3$O$_4$ had little effect on the electromagnetic wave-shielding effectiveness, and the maximum electromagnetic wave-shielding efficiency of GO@CuSilicate@Fe$_3$O$_4$ was only 8 dB. When Fe$_3$O$_4$ was located in the middle (attached on GO), due to the superposition of various loss effects, GO@Fe$_3$O$_4$@CuSilicate exhibited excellent electromagnetic shielding performance. With 1 mm thickness, GO@Fe$_3$O$_4$@CuSilicate showed a maximum shielding efficiency of 41.8 dB at 8.2 GHz and maintained the high shielding efficiency (over 40 dB) in a wide frequency range (8.2–12.4 GHz). This work provided a new approach to prepare electromagnetic shielding materials with “wide band, strong absorption, thin thickness”.

4. EXPERIMENTAL SECTION

4.1. Materials. Tetraethyl orthosilicate (TEOS), copper nitrate ($\text{Cu(NO}_3\text{)}_2\cdot 3\text{H}_2\text{O}$), triethylene glycol, iron(III) acetylacetonate (Fe(acac)$_3$), oleic acid, oleylamine, and benzyl
ether were purchased from Aladdin Reagent Co., Ltd. Cetyltrimethylammonium bromide (CTAB) was purchased from CapitalBio Corporation. Ammonia (NH₄H₂O) was purchased from Hangzhou Longshan Fine Chemicals Co., Ltd. All chemicals were of analytical grade and used without further purification. Pristine flake graphite was purchased from Qingdao Guangli Graphite Co., Ltd. All water used in the synthesis and characterization was deionized water obtained from a Milli-Q system (Millipore, Bedford, MA).

4.2. Preparation of GO@SiO₂. First, GO was prepared according to the Hummers method. The detailed preparation process has been described in our previous paper. For preparation of GO@SiO₂, 0.16 g of CTAB was dissolved into a mixture solution containing 30 mL of deionized water, 120 mL of ethanol, and 1.5 mL of ammonia (28 wt %) at room temperature. Under vigorous stirring, 0.05 g of GO was dispersed into the above mixture followed by ultrasonication for 30 min. Then, 1 mL of TEOS was added into the above mixture and further sonicated at 40 W for 6 h. The obtained product was centrifuged, washed with ethanol and deionized water, and dried under a vacuum at 60 °C for 12 h. The dried product was gently ground for further use.

4.3. Preparation of GO@CuSilicate. For preparation of GO@CuSilicate, 10 mg of GO@SiO₂ was dispersed in a flask containing 36 mL of deionized water and was ultrasonicated for 30 min. Then, 4 mL of ammonia (28 wt %) were added under mild stirring. After 5 min, 2.4 mL of the Cu(NO₃)₂ solution (0.1 mol/L) was added dropwise and the mixture was stirred for another 5 min before the reaction solution was transferred to an autoclave and was heated at 140 °C in an electric oven for 12 h. After cooling down naturally, the product was collected by several rinse-centrifugation cycles and fully dried at 60 °C for 12 h. The obtained product was ultrasonically dispersed in n-hexane and used for further use.

4.4. Preparation of GO@CuSilicate@Fe₃O₄. First, nano-Fe₃O₄ was prepared by thermal decomposition. Briefly, 1.06 g of Fe(acac)₃ was added into a mixture solution containing 15 mL of oleylamine, 15 mL of oleic acid, and 15 mL of benzyl ether and was ultrasonicated for 30 min. Then, 10 mL of the Fe₃O₄/n-hexane dispersion (4.5 mg/mL) was mixed with 20 mL of ethanol and 45.4 mg (or 90.8, or 227 mg) of GO@CuSilicate under ultrasonication for 1 h. After separated by a magnet and washed, the GO@CuSilicate@Fe₃O₄ (Fe₃O₄/GO@CuSilicate mass ratio was 1:1 or 0.5:1 or 0.2:1) was obtained and dried in a vacuum at 60 °C for 12 h.

4.5. Preparation of GO@Fe₃O₄. First, 400 mg of Fe(acac)₃ and 100 mg GO were added into 60 mL of oleylamine and was ultrasonicated for 30 min. The reaction was carried out at 278 °C for 30 min under N₂ protection and continuously stirred. After cooling down naturally, the obtained products were separated by a magnet and washed with ethanol and dried at 25 °C in a vacuum. The obtained GO@Fe₃O₄ was gently ground for use.

4.6. Preparation of GO@Fe₃O₄@SiO₂. CTAB (0.16 g) was added to a flask containing 30 mL of deionized water, 120 mL of ethanol and 1.5 mL of ammonia (28 wt %). After stirred for 5 min, 0.05 g of GO@Fe₃O₄ was added to the mixture and was ultrasonicated for 30 min. Then, 1 mL of TEOS was added to the above mixture slowly and further sonicated for 6 h. Finally, the obtained product was centrifuged, washed, and dried in a vacuum at 60 °C for 12 h.

4.7. Preparation of GO@Fe₃O₄@CuSilicate. For preparation of GO@Fe₃O₄@CuSilicate, 10 mg of GO@Fe₃O₄@SiO₂ was dispersed in 36 mL of deionized water under ultrasonication for 30 min. Then, 6 mL of ammonia (28 wt %), 3.6 mL of Cu(NO₃)₂ solution (0.1 mol/L) were added to the mixture. After ultrasonicated for another 5 min, the reaction mixture was transferred into a Teflon-lined autoclave and was heated in an oven at 140 °C for 12 h. After cooling down naturally, the product was collected by several rinse-centrifugation cycles and washed thoroughly with ethanol. Then, it was dried at 60 °C for 12 h.

4.8. Characterization. The structure and morphology of as-prepared samples was characterized by field-emission SEM (SEM, Carl Zeiss AG, Supra S5), TEM (FEI, Tecnai G2 F30), and XRD (Rigaku, Ultima IV). Hysteresis loops in the range of −20 to 20 kOe were measured at 300 K using a VSM (Quantum Design, MPMS Squid-VSM). Nitrogen adsorption isotherm measurements were performed at 77 K using a Micromeritics ASAP 2020C+ analyzer.

4.9. Electromagnetic Shielding Measurement. GO@Fe₃O₄, GO@Fe₃O₄@CuSilicate, and GO@CuSilicate@Fe₃O₄ samples were pressed into wafer having a thickness of about 1.0 mm and a diameter of 10 mm. The mass of the sheet was about 150 mg. The electromagnetic shielding performance was tested using an Agilent N5247A model vector network analyzer and the scattering parameters, including S₁₁ and S₂₁ were measured in the frequency range of 8.2−12.4 GHz. Then, the total shielding effectiveness (SEₜ), the reflection from the material surface (SEₐ) and the absorption (SEₐ) of the material were calculated according to the following formula proposed in Yang et al.’s paper, where the same coaxial method was employed. In each test, at least three specimens were tested and the average was reported.

\[ R = 10^{0.15 A} \]  
\[ T = 10^{0.15 A} \]  
\[ A = 1 - R - T \]  
\[ SE_R = -10 \log(1 - R) \]  
\[ SE_A = -10 \log(T/(1 - R)) \]  
\[ SE_T = SE_R + SE_A \]

where \( R \) is the reflection efficient; \( A \) is the absorption coefficient; and \( T \) is the transmission coefficient.

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