Designed Fabrication and Characterization of Three-Dimensionally Ordered Arrays of Core–Shell Magnetic Mesoporous Carbon Microspheres

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ABSTRACT: A confined interface coassembly coating strategy based on three-dimensional (3-D) ordered macroporous silica as the nanoreactor was demonstrated for the designed fabrication of novel 3-D ordered arrays of core–shell microspheres consisting of Fe3O4 cores and ordered mesoporous carbon shells. The obtained 3-D ordered arrays of Fe3O4@mesoporous carbon materials possess two sets of periodic structures at both mesoscale and submicrometer scale, high surface area of 326 m2/g, and large mesopore size of 19 nm. Microwave absorption test reveals that the obtained materials have excellent microwave absorption performances with maximum reflection loss of up to −57 dB at 8 GHz, and large absorption bandwidth (7.3−13.7 GHz, < −10 dB), due to the combination of the large magnetic loss from iron oxides, the strong dielectric loss from carbonaceous shell, and the strong reflection and scattering of electromagnetic waves of the ordered structures of the mesopores and 3-D arrays of core–shell microspheres.

KEYWORDS: interface coassembly, mesoporous carbon, magnetic nanomaterials, core–shell structures, microwave absorption

INTRODUCTION

Magnetic nanomaterials, due to their outstanding properties such as paramagnetism, magnetic separability,1−3 and Neel relaxation effect,4 have captivated tremendous research interests for applications in various fields, including magnetic resonance imaging (MRI),5 bioseparation,6−9 catalysis,9 energy storage,10 and microwave absorption.11 Particularly as a typical microwave absorber, magnetite (Fe3O4) nanoparticles have gained much attention due to their significant advantages in microwave absorption, such as the strong absorption characteristics, wide absorption frequency range, and low cost.12,13 Magnetite nanoparticles with diversified morphologies, including the nanodendrites,14 nanorods,15 two-dimensional nanolamellar and microspheres,16 have been extensively studied to reveal the dependency of microwave performance on the morphology. Dendrite-like Fe3O4 nanoparticles synthesized via hydrothermal reactions have been proved to possess a good microwave absorption performance in the low and middle frequency range (2−9 GHz).14 Wang et al.17 adopted a templating synthesis method for Fe3O4 nanolamellars that exhibit a strong microwave absorption with a reflection loss of −46.6 dB at 3 GHz.

According to the basic principle of microwave absorption, the loss mechanism of microwave absorber consists of magnetic loss and dielectric loss.18−20 Magnetite as the microwave absorber mainly contributes the magnetic loss due to its intrinsic magnetic property. Therefore, to develop high-performance microwave absorbers with both magnetic loss and dielectric loss, many fabrication strategies have been explored to combine magnetite nanomaterials with other nanomaterials that can contribute remarkable dielectric loss and electromagnetic impedance balance. To date, various multicomponent Fe3O4-based nanomaterials have been investigated.21−25 In this regard, owing to their strong dielectric loss, metal oxides26 and carbon nanomaterials such as carbon nanotubes (CNTs),25 reduced graphene oxide (rGO),26 and carbon nanocoils27 have been widely used as complementary components for Fe3O4 as microwave absorbers. On the other hand, ordered mesoporous materials, due to their regular arrays of mesopores that are tunable pore sizes of 2−50 nm, have recently been demonstrated to possess excellent performance as microwave absorbers.28−31 Guo et al.32 synthesized sandwich-like magnetic mesoporous silica microspheres by coating iron oxide particles successively with nonporous silica and mesoporous silica. Compared to the parent iron oxides, the obtained composites displayed improved microwave absorption performance with stronger absorption characteristics and broader absorption frequency range, which is due to the strong reflection and scattering of electromagnetic waves in the pore.
channels of mesoporous silica and their multilayered core–shell structure.

Wiley and co-workers reported that ordered arrays of magnetic microspheres exhibit unique magnetic phenomena, including angle-dependent magnetization, due to their ordered structures.\(^{35}\) In light of this finding, it could be expected that the microwave absorption performance of Fe\(_2\)O\(_3\)-based multi-component nanomaterials with well-aligned structures may possess unique microwave absorption enhancement. So far, much effort has been devoted to synthesizing magnetic nanomaterials-based microwave absorbers; however, most of these nanomaterials were utilized in the form of nanocomposites with ill-defined structures, and little work has been done to study the microwave absorption behaviors of the periodically arranged magnetic nanocomposites, especially carbon-coated magnetite microspheres with well-defined core–shell structure.

Herein, we report a confined interface coating strategy for the fabrication of novel three-dimensionally ordered arrays of core–shell microspheres consisting of Fe\(_2\)O\(_3\) cores and ordered mesoporous carbon shells. Three-dimensionally ordered macroporous silicas (3DOM-SiO\(_2\)) were employed as the nanoreactor for deposition of single iron oxide particle with controlled size in each macropore and further coating iron oxide particle individually with a layer of mesoporous carbon. The subsequent removal of 3DOM-SiO\(_2\) template leads to three-dimensional (3-D) arrays of mesoporous carbon-coated magnetic particles (denoted as 3DOA-Fe\(_2\)O\(_3\)@mesoCarbon) monolith with high surface area of 326 m\(^2\)/g and large pore size of 19 nm. The obtained 3DOA-Fe\(_2\)O\(_3\)@mesoCarbon materials exhibit excellent microwave absorption performance with maximum reflection loss of up to −57 dB at 8 GHz and large absorption bandwidth (7.3−13.7 GHz and −10 dB). Such an excellent performance is mainly attributed to the combination of individual merit of each component and the ordered nanostructure, that is, the large magnetic loss from iron oxides, the strong dielectric loss from carbonaceous shell, as well as the strong reflection and scattering of electromagnetic waves of the ordered structures of microsphere arrays and mesopore channels.

### EXPERIMENTAL SECTION

**Chemicals.** The Pluronic block copolymer poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) (F127, \(M_n = 12,600, EO_{106}PO_{70}EO_{106}\)) was purchased from Aldrich Corporation. Phenol (AR), tetraethyl orthosilicate (TEOS, AR), absolute ethanol (AR), hydrochloric acid (AR), ferric nitrate (Fe(NO\(_3\))\(_3\),9H\(_2\)O, AR), sodium hydroxide (NaOH, AR) were purchased from Shanghai Chemical Reagent Corporation. All chemicals were used as received without further purification, and in all experiments, purified water (Millipore) with the resistivity larger than 18 MΩ-cm was utilized. Resol, a soluble phenolic resin with relatively low molecular weight of ~500 g/mol, was first prepared according to previous report\(^{34}\) and dissolved in ethanol to form a solution with the resistol concentration of 20 wt %.

**Fabrication of Three-Dimensionally Ordered Macroporous Silicas.** For the fabrication of 3DOM-SiO\(_2\), monodispersed polystyrene (PS) microspheres with different sizes (900−1200 nm) were synthesized via a soap-free emulsion polymerization process.\(^{35,36}\) After washing with ethanol and water three times, the purified PS spheres were redispersed in ethanol and allowed to form sedimentation for a week under gravity to form colloidal crystals. Afterward, the supernatant ethanol was removed carefully, and the obtained colloidal crystals were dried at 35 °C for 4 h to obtain the solid PS microspheres. Then, the monolithic PS colloidal crystals were prepared for further use. A typical procedure for making 3DOM-SiO\(_2\) is described as follows. An ethanol solution of TEOS precursor (2.08 g of TEOS, 0.3 g of H\(_2\)O, 0.9 mL of 2 M HCl, and 15 g of ethanol) was drop-casted on several pieces of the colloidal crystals (1 cm × 1 cm × 1 cm) made of 1200 nm PS microspheres. After evaporation of ethanol at 30 °C for 24 h, the composite monolith was scratched carefully with a blade to remove the excess gel precursors. Finally, the impregnated colloidal crystals were calcined in air at 550 °C for 6 h using 1 °C/min of ramping rate to remove PS microspheres, and thus the 1200 nm-3DOM-SiO\(_2\) monolith was obtained.

For the synthesis of Fe\(_2\)O\(_3\)@3DOM-SiO\(_2\) monoliths with a porous Fe\(_2\)O\(_3\) particle filled inside each macropore, the obtained 1200 nm-3DOM-SiO\(_2\) monolith was impregnated in the Fe(NO\(_3\))\(_3\) ethanol solution (4.04 g of Fe(NO\(_3\))\(_3\) dissolved in 10 mL of absolute ethanol) for 3 h at 30 °C for evaporation of ethanol in 6 h. This impregnation process was repeated three times. At last, the excess gel precipitant of the composite monolith was scraped off carefully, and the obtained composites were finally calcined in air at 550 °C for 4 h to obtain the 1200 nm-Fe\(_2\)O\(_3\)@3DOM-SiO\(_2\) sample.

**Templated Fabrication of Three-Dimensionally Ordered Arrays of Microspheres with Core–Shell Structure.** For the
synthesis of 3DOA-Fe2O3@Carbon microspheres, small pieces (~0.5 g) of 1200 nm-Fe2O3@3DOM-SiO2 monoliths were placed in a Petri dish, and then a clear precursor solution containing resol (5.0 g) and ethanol (15 g) was dropwise added into the petri dish. Time was allowed for a complete evaporation of ethanol completely at 80 °C for 24 h for thermosetting resin into phenolic formaldehyde (PF) resin. The obtained Fe2O3-PF@3DOM-SiO2 composite was afterward carbonized at 500 °C for 3 h under N2 atmosphere with the ramping rate of 5 °C/min. Finally, the obtained composite was treated in NaOH aqueous solution (5 M) at 80 °C to remove silica, followed with thorough washing with water and ethanol six times, and thus the 1200 nm-3DOA-Fe2O3@Carbon sample was prepared.

The 1200 nm-3DOA-Fe2O3@mesoCarbon sample was fabricated via the similar procedure except that the precursor solution containing of resol (5.0 g), ethanol (15 mL), and F127 (2.5 g) was utilized instead. For the fabrication of 800 nm-3DOA-Fe2O3@Carbon and 800 nm-3DOA-Fe2O3@mesoCarbon, the synthesis procedures are the same as those for 1200 nm-3DOA-Fe2O3@Carbon and 1200 nm-3DOA-Fe2O3@mesoCarbon, except that 800 nm-3DOM-SiO2 derived from colloidal crystal of 900 nm PS microspheres was used as the template.

Measurements and Characterization. Transmission electron microscope (TEM) characterization was carried out on a JEOL 2100F field-emission TEM (Japan) operating at 200 kV of the working voltage. Scanning electron microscope (SEM) characterization was conducted on a Hitachi S-4800 field-emission SEM (Japan). Also, wide-angle X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance powder X-ray diffractometer (Germany) with Ni-filtered Cu Kα radiation (40 kV, 40 mA, 1.5406 Å). Nitrogen adsorption−desorption isotherms were measured at 77 K with a Micromeritics Tristar 3020 analyzer (USA). The samples were previously degassed under vacuum at 180 °C for at least 6 h before measurements, and the specific surface areas were calculated using the Brunauer−Emmett−Teller (BET) method. The pore volumes and distributions of pore sizes were calculated correspondingly utilizing the Broekhoff−De Boer sphere model from the adsorption branches of the isotherms. Besides, the total pore volumes (V) were evaluated according to absorbed amounts at 0.995 of the relative pressure (P/P0).

RESULTS AND DISCUSSION

Scheme 1 illustrates the synthesis protocol for 3DOA-Fe2O3@mesoCarbon based on the confined interface coating process. In the first step, 3DOM-SiO2 monolith synthesized by replicating 3-D ordered colloidal crystal of polystyrene (PS) microspheres was impregnated in the ethanol solution of Fe(NO3)3 and then the iron precursor was in situ converted into Fe2O3 particles in the macropores via calcination in air, resulting in a unique ordered mesoporous carbon@3DOM-SiO2. For the fabrication of 800 nm-3DOA-Fe2O3@Carbon and 800 nm-3DOA-Fe2O3@mesoCarbon, the synthesis procedures are the same as those for 1200 nm-3DOA-Fe2O3@Carbon and 1200 nm-3DOA-Fe2O3@mesoCarbon, except that 800 nm-3DOM-SiO2 derived from colloidal crystal of 900 nm PS microspheres was used as the template.

Monodisperse PS microspheres with a diameter of 1400 nm were synthesized via a dispersion polymerization method available in previous reports and were used to construct 3-D ordered colloidal crystals through the gravimetric sedimentation (Figure 1). With the obtained colloidal crystals as templates, silica precursor can be filled in the interstitial voids among the closely packed PS microspheres by impregnation in a siliceous solution. After removing PS microspheres via calcination, 3DOM-SiO2 monolith with intense opalescence and uniform macropores of ~1200 nm was obtained (Figure 2a and inset). The macropore size is a

![Figure 1. SEM images (a, b) of the highly ordered arrays viewed along [100] directions of the face-centered cubic structured colloidal crystals of 1400 nm PS microspheres.](image)

![Figure 2. SEM images of (a) the 3-D ordered macroporous SiO2 (3DOM-SiO2) and (b, c) Fe2O3@3DOM-SiO2 obtained after deposition of Fe2O3 particle in the macropore. (d) The structure model of Fe2O3@3DOM-SiO2. (insets) The photographs of the corresponding monolithic samples.](image)
macropores of 800 nm and window size of 100 nm can be obtained (Supporting Information, Figure S1a,b). The uniform and well-connected macropore of 3DOM-SiO$_2$ is an ideal “nanofactory” for the confinement fabrication of ordered arrays of uniform guest nanomaterials. In this study, iron oxide precursor was introduced into the macropores by repeated impregnation of 3DOM-SiO$_2$ in Fe(NO$_3$)$_3$/ethanol solutions, followed with evaporation of ethanol. After calcination at 450 °C in air, brown Fe$_2$O$_3$@3DOM-SiO$_2$ monolithic materials were obtained (Figure 2b, inset). Clearly, in the scanning electronic microscopy (SEM) image, the macropores were individually filled with iron oxide microspheres, which form ordered arrays throughout the entire 3DOM-SiO$_2$ monolith (Figure 2b). The iron oxide microspheres have diameter of ~900 nm, which is smaller than the macropore size (1200 nm) due to the significant volume shrinkage during conversion of iron precursor into iron oxides, and interestingly, the iron oxide microspheres exhibit porous structure (Figure 2c). The generation of porous iron oxides in this confined synthesis is probably due to the unique solid-phase conversion of iron precursor confined in the macropores that possess numerous nucleation sites in the curved surface of 3DOM-SiO$_2$ monolith for the growth of iron oxide. Besides, the release of NO$_3$ during the calcination treatment can also contribute to the formation of disordered nanoparticles.

Since the porous Fe$_2$O$_3$ particles are smaller than the macropores, the voids between iron oxide microspheres and silica framework is accessible for deposition of mesostructured resol-F127 composites through impregnation of Fe$_2$O$_3$@3DOM-SiO$_2$ composites in the precursor solution. Thus, after thermosetting and pyrolysis treatment, the iron oxide microspheres can be in situ coated by a layer of mesoporous carbon in the macropores of 3DOM-SiO$_2$; meanwhile, iron oxides can be converted into magnetite (Fe$_3$O$_4$) by carbon species. The successful formation of mesoporous carbon on the iron oxides is mainly attributed to two factors. First, both the porous iron oxide and 3DOM-SiO$_2$ are hydrophilic, which is favorable for the impregnation of ethanolic precursor solution. Second, the resol molecules possess lots of phenolic hydroxyl groups, which can interact with both iron oxides through chelating with iron species$^{34}$ and F127 via hydrogen binding.$^{37}$ Furthermore, the resol/F127/ethanol precursor solution can invade all the remaining space of the macropores in the Fe$_2$O$_3$@3DOM-SiO$_2$ composites, resulting in a complete encapsulation of the porous Fe$_2$O$_3$ particle and stable “sintering” of Fe$_2$O$_3$@PF-F127 microspheres located in the adjacent macropores due to the thermal polymerization of glue-like resol molecules. After carbonization treatment, Fe$_2$O$_3$@mesoCarbon core–shell microspheres binding with each other were left in the macropores (Figure 3a). Further removal of the silica framework in NaOH solutions leads to 3DOA-Fe$_3$O$_4$@mesoCarbon monolith (Figure 3b). To gain detailed structural information, the monolithic composites were slightly ground for electron microscopy observation. As shown in the SEM image (Figure 3b), the obtained Fe$_2$O$_3$@mesoCarbon microspheres have a uniform diameter of ~1200 nm (denoted as 1200 nm-Fe$_2$O$_3$@mesoCarbon), and they retain the ordered arrays of the 3DOM-SiO$_2$, indicating a faithful replication process. High-magnification SEM image reveals the presence of irregular stubbles with a diameter of ~150 nm in the surface of microspheres (Figure 3c). Such stubbles are originated from the mechanical cleavage of sintering points (boxed area in Figure 3a) that correlate with connecting windows of the macropores (Figure 3b, inset).

TEM observation clearly indicates that the obtained Fe$_3$O$_4$@mesoCarbon microspheres have a mesoporous carbon shell of 120 nm in thickness (Figure 3d), and ordered pore channels with a mean diameter of ~18 nm can be clearly seen in the shell (Figure 3d, inset).

Scanning TEM (STEM) observation further reveals a typical core–shell structure of the obtained Fe$_3$O$_4$@mesoCarbon microspheres (Figure 4a). The energy-dispersive X-ray (EDX) element mapping results (Figure 4c,d) indicate the presence of Fe, O, and C elements, and the diameter of C-mapped spheres in Figure 4d is much larger than those of Fe- and O-mapped spheres (Figure 4b,c), confirming the presence of iron oxide core and carbon shell. X-ray diffraction (XRD) patterns of the as-made Fe$_3$O$_4$@3DOM-SiO$_2$ composites display well-resolved characteristic diffraction peaks that can
be indexed to the hematite phase with a rhombohedral structure (Figure 5a). The XRD patterns of 1200 nm 3DOA-

Fe₃O₄@mesoCarbon microspheres reveal typical diffraction peaks assigned to maghemite (Figure 5b,c), which reflects a phase transformation of α-Fe₂O₃ into Fe₃O₄ in the composites during pyrolysis.

The N₂ absorption−desorption isotherms of the 1200 nm-3DOA-Fe₃O₄@mesoCarbon sample (Figure 6A) show a type IV curve with a sharp capillary condensation step in the P/P₀ range of 0.8−0.9, which implies uniform and large mesopores. The BET surface area was calculated to be 293 m²/g. The pore size distribution derived from the adsorption branch using the Barrett−Joyner−Halenda (BJH) method reveals a pore size of 19.2 nm (Figure 6A, inset), much larger than the pore size (~6 nm) of FDU-16. It is mainly due to the retarded structure shrinkage by the protection of rigid silica walls of 3DOM-SiO₂ during pyrolysis for removal of F₁₂₇ and carbonization of PF.

Similarly, by using 3DOM-SiO₂ with macropores of 800 nm as the nanoreactor, Fe₂O₃@3DOM-SiO₂ composites with porous iron oxide microspheres of 600 nm in the macropores can be readily fabricated (Figure 7a,b). Through further impregnation with resol/F₁₂₇/ethanol precursor, 3DOA-Fe₂O₃@mesoCarbon microspheres with a diameter of 800 nm (denoted as 800 nm-3DOA-Fe₂O₃@mesoCarbon) were synthesized via the same synthesis strategy and procedure (Figure 7c,d), and the obtained sample has a BET surface area of 326 m²/g and pore size of 19.0 nm. It is worth noting that the synthesis strategy is applicable for directly coating iron oxide particle with carbon shell in the Fe₂O₃@3DOM-SiO₂ composites via the impregnation procedure similar to that for fabricating 3DOA-Fe₃O₄@mesoCarbon microspheres, except that no F₁₂₇ copolymers were used. By using Fe₂O₃@3DOM-SiO₂ composites containing Fe₂O₃ particles of 600 and 800 nm, respectively, 3-D ordered arrays of carbon-coated Fe₂O₃ microspheres with a diameter of 800 and 1200 nm can be fabricated, respectively (Supporting Information, Figure S2). High-

Figure 5. XRD patterns of (a)1200 nm-Fe₂O₃@3DOM-SiO₂, (b) 1200 nm-3DOA-Fe₃O₄@mesoCarbon, and (c) 1200 nm-3DOA-Fe₃O₄@Carbon. The green patterns correspond to the standard XRD diffraction peaks of α-Fe₂O₃ (lower) and Fe₃O₄ (upper), respectively.

Figure 6. (A) Nitrogen adsorption−desorption isotherms and pore size distribution (inset) of the 1200 nm-3DOA-Fe₃O₄@mesoCarbon microspheres. (B) Magnetic hysteresis loops of (a) 1200 nm-3D-Fe₃O₄@mesoCarbon, (b) 1200 nm-3DOA-Fe₃O₄@Carbon, (c) 800 nm-3DOA-Fe₃O₄@mesoCarbon, and (d) 800 nm-3DOA-Fe₃O₄@Carbon measured at 300 K.

Figure 7. SEM images of (a, b) the Fe₂O₃@3DOM-SiO₂ obtained after replication of the 3-D colloidal crystal of 900 nm PS microspheres. (c) SEM and (d) TEM images of 800 nm 3DOA-Fe₂O₃@mesoCarbon microspheres.
Microspheres were fabricated ordered arrays of magnetite-carbon composites, the Carbon and 800 nm-3DOA-Fe3O4@Carbon are reversible hysteresis behavior at 300 K due to the large ferromagnetism as evidenced by the coercivity and the besides, all these iron oxide/C composites possess distinct due to their slightly higher content of magnetic component. Carbon microspheres with the same diameters, which is mainly calculated to be 47.0 and 52.0 emu/g for 800 nm- and 1200 nm-3DOA-Fe3O4@Carbon, respectively, and (c) 800 nm- and (d) 1200 nm-3DOA-Fe3O4@ mesoCarbon, respectively; (B) the frequency dependence of dielectric loss tangents of the 3DOA-Fe3O4@mesoCarbon and 3DOA-Fe3O4@Carbon; (C, D) 3-D representations of RL of 800 nm-3DOA-Fe3O4@ mesoCarbon (C) and 1200 nm-3DOA-Fe3O4@mesoCarbon (D).

Table 1. Saturation Magnetization (Ms) and Coercivity (Hc) for 3DOA-Fe3O4@Carbon and 3DOA-Fe3O4@mesoCarbon Microspheres

<table>
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<tr>
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<th>Saturation Magnetization (Ms)</th>
<th>Coercivity (Hc)</th>
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<tbody>
<tr>
<td>800 nm-3DOA-Fe3O4@Carbon</td>
<td>34</td>
<td>295</td>
</tr>
<tr>
<td>800 nm-3DOA-Fe3O4@mesoCarbon</td>
<td>47</td>
<td>182</td>
</tr>
<tr>
<td>1200 nm-3DOA-Fe3O4@Carbon</td>
<td>50</td>
<td>200</td>
</tr>
<tr>
<td>1200 nm-3DOA-Fe3O4@mesoCarbon</td>
<td>52</td>
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calculated to be 47.0 and 52.0 emu/g for 800 nm- and 1200 nm-3DOA-Fe3O4@mesoCarbon microspheres, respectively. Furthermore, 1200 nm-3DOA-Fe3O4@mesoCarbon microspheres possess larger Ms than 1200 nm-3DOA-Fe3O4@Carbon microspheres with the same diameters, which is mainly due to their slightly higher content of magnetic component. Besides, all these iron oxide/C composites possess distinct ferromagnetism as evidenced by the coercivity and the reversible hysteresis behavior at 300 K due to the large crystalline sizes of iron oxides.

To study the microwave absorption properties of the fabricated ordered arrays of magnetite-carbon composites, the reflection loss (RL) values of 3DOA-Fe3O4@mesoCarbon were calculated using the relative complex permittivity and permeability at a given frequency and thickness layer according to the transmit line theory, which are summarized by the two equations below

\[
\text{RL (dB)} = -20 \log_{10} \left( \frac{|Z_{in} - 1|}{|Z_{in} + 1|} \right)
\]

\[
Z_{in} = \sqrt{\mu_r / \varepsilon_r} \tanh\left( -j \frac{2\pi fd}{c} \sqrt{\mu_r / \varepsilon_r} \right)
\]

where \( \varepsilon_r, \mu_r, f, d, \) and \( Z_{in} \) corresponds to the relative complex permittivity, permeability, velocity of light, microwave frequency in free space, coating thickness, and input impedance of the absorber, respectively. The calculated RL curves for all of the four samples with the thickness of 2 mm in the frequency range of 2–18 GHz were summarized in Figure 8A. (Experimental details for fabricating absorption coating is available in Supporting Information.) The maximum RL values (RLmax) of 3DOA-Fe3O4@mesoCarbon samples comprising 1200 nm- and 800 nm-3DOA-Fe3O4@mesoCarbon are −35 dB at 10 GHz and −37 dB at 11.5 GHz, respectively (Figure 8Aa,b). It suggests these 3DOA-Fe3O4@mesoCarbon microspheres possess comparable RLmax values at a coating thickness of 2 mm. By contrast, the RLmax values of 1200 nm-3DOA-Fe3O4@Carbon and 800 nm-3DOA-Fe3O4@Carbon are −23 dB at 11.2 GHz and −17 dB at 9.5 GHz, respectively (Figure 8Ac,d), both much less than those of the corresponding 1200 nm- and 800 nm-3DOA-Fe3O4@mesoCarbon samples. It suggests that the presence of mesoporous carbon shell can significantly enhance the performance of microwave absorption of iron oxides. The dielectric loss tangents (\( \tan \delta = \varepsilon''/\varepsilon' \)) of all the samples were calculated and summarized in Figure 8B. The values of \( \tan \delta \) for 3DOA-Fe3O4@mesoCarbon samples are larger than 3DOA-Fe3O4@Carbon samples in the whole frequency range of 2–18 GHz, implying that the mesoporous carbon shell contributes a stronger dielectric loss. Such a strong dielectric loss of 3DOA-Fe3O4@mesoCarbon microspheres is mainly due to the high surface areas of the ordered mesoporous carbon shells that bring about more defects and dangling-bonded atoms in the pore wall and thus leads to stronger interface polarization compared to carbon shells without mesopores. Moreover, the 3-D representations (Figure 8C,D) of RL values at different coating thicknesses (2–5 mm) for the 800 nm- and 1200 nm-3DOA-Fe3O4@Carbon samples reveal a broader and stronger reflection loss in the whole thickness range, as compared to their counterpart sample of 800 nm- and 1200 nm-3DOA-Fe3O4@Carbon samples (Supporting Information, Figure S3). It is worth noting that the RLmax value of 1200 nm-3DOA-Fe3O4@mesoCarbon microspheres can reach −55 dB at a absorption coating thickness of 2.5 mm, which is much larger than those of most carbon-Fe3O4 composites reported.

Supporting Information, Figure S4 depicts the complex permittivity real part (\( \varepsilon' \)) and imaginary part (\( \varepsilon'' \)) and the permeability real part (\( \mu' \)) and imaginary part (\( \mu'' \)) of the four samples measured in the frequency range of 2–18 GHz. For 3DOA-Fe3O4@mesoCarbon, \( \varepsilon' \) and \( \varepsilon'' \) values are, respectively, less than and higher than those of 3DOA-Fe3O4@Carbon microspheres in the whole frequency range. Meanwhile, the frequency dispersion values of \( \mu' \) and \( \mu'' \) remain almost constant at 2–18 GHz for the 3DOA-Fe3O4@mesoCarbon and 3DOA-Fe3O4@Carbon microspheres, without evident decay even at high frequency band (12–18 GHz). Therefore, it can be concluded that both magnetic loss of Fe3O4 and dielectric loss of carbon shell contribute to the absorption dependency on frequency of our samples. In particular, the ordered structure of mesoporous carbon shell and 3-D ordered array of 3DOA-
Fe₃O₄@mesoCarbon materials bring about a strong reflection and scattering of electromagnetic waves in the mesoporous carbon channels and their core–shell structure.²³,³³

**CONCLUSIONS**

In summary, for the first time, we report a confined interface coating strategy for the fabrication of novel three dimensionally ordered arrays of core–shell microspheres comprising Fe₃O₄ cores and ordered mesoporous carbon shells, that is, 3DOA-Fe₃O₄@mesoCarbon, by using 3-D ordered macroporous silica as the nanoreactor for deposition of single iron oxide particle and for further coating iron oxide particle with mesoporous carbon shells. The obtained 3DOA-Fe₃O₄@mesoCarbon materials have high surface area up to 326 m²/g and large pore size of ~19 nm. Because of the combination of the merits of the large magnetic loss of iron oxides, the strong dielectric loss of carbon shell, as well as the strong reflection and scattering of electromagnetic waves of ordered structures of microsphere arrays and mesopore channels, the obtained 3DOA-Fe₃O₄@mesoCarbon materials exhibit excellent microwave absorption performances with maximum reflection loss of up to ~57 dB at 8 GHz and large absorption bandwidth (7.3–13.7 GHz). Because of the versatility of this confined interface coating strategy, it is expected that the design concept can be used for fabrication of a variety of topologically complicated and functionally integrated ordered structures for applications in electronic nanodevices, nanobiosensors, nano-optical systems, etc.

**ASSOCIATED CONTENT**

Supporting Information Experimental details for the electromagnetic measurements, SEM images of the colloidal crystal based on uniform PS microspheres of ~900 nm as building blocks and their templated 800 nm 3D-ordered macroporous SiO₂ (800 nm-3DOM-SiO₂), SEM images of 800 nm-3D-Fe₃O₄@C and 1200 nm-3D-Fe₃O₄@C microspheres. Three-dimensional representations of RL of the 800 nm 3D-Fe₃O₄@Carbon and 1200 nm-3DOA-Fe₃O₄@Carbon. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.

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