Silica microsphere templated self-assembly of a three-dimensional carbon network with stable radio-frequency negative permittivity and low dielectric loss†

Peitao Xie, Zhongyang Wang, Zidong Zhang, Runhua Fan, Chuanbing Cheng, Hu Liu, Yao Liu, Tingxi Li, Chao Yan, Ning Wang and Zhanhu Guo

Percolative composites always suffer from their unstable and filler-loading dependent microstructures and negative electromagnetic parameters. Here, stable negative permittivity is achieved by in situ constructing a three-dimensional carbon network in the silica spherical matrix after a self-assembly and pyrolysis process. An electrical percolation phenomenon appears with the formation of a carbon network. Once the carbon network is formed, further increasing carbon loadings will only influence the porosity rather than the connectivity due to the nature of the porous carbon itself. Hence, the microstructure and plasma-like negative permittivity are not sensitive to carbon loading, leading to a negligible carbon loading dependent permittivity behavior. Moreover, negative permittivity with small values (−100 < ε′ < 0), beneficial for matching with permeability, was effectively adjusted by changing the carbonization temperature. The carbon composites with negative permittivity showed an extremely low dielectric loss (tan δ = 1–7) compared with metal composites (usually tan δ = 10–100). This work provides a convenient means to obtain stable negative permittivity properties. The carbon composites can be regarded as a promising candidate for metamaterials and will facilitate the applications of materials with negative electromagnetic parameters.

1. Introduction

Materials with negative electromagnetic parameters have gained extensive research attention in plasmons, biosensing, microwave funneling, dielectric enhancement and transistors, since they possess the key characteristics to achieve negative refraction in metamaterials. The novel property of metamaterials is fundamentally dependent on the geometrical shape of artificial periodic array structures rather than on the material components. From the viewpoint of chemistry and microstructure, a negative electromagnetic parameter can also be realized in the percolative composites with metallic fillers randomly dispersed in the insulative matrix. These percolative composites are called metacomposites or random metamaterials which have greatly expanded the scope of metamaterials.

Previous researchers have focused on metal composites to achieve negative permittivity. In fact, negative permittivity is an intrinsic behavior of all metals below their plasma frequency (usually in the ultraviolet range). However, it is an imaginary number and is difficult to measure even in the radio frequency region. Hence, several innovative research strategies have been exploited to achieve practically negative permittivity materials. Some metal–ceramic composites were prepared to obtain negative permittivity by the impregnation–reduction process in 10 MHz–1 GHz, in which the three-dimensional network consisting of metal nanoparticles was formed by the template of the porous ceramic matrix. On the other hand, metal–ceramic composites were also prepared by an in situ synthesis

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c7tc05911f
process along with a reduction reaction, where the metal nanoparticles were uniformly dispersed in the composites and gradually established continuous conductive paths with increasing metallic loading. These metal–ceramic composites usually have a high percolation threshold with the advantage of good mechanical properties.36–38 Besides, polymer composites containing copper, permalloy or amorphous alloy particles were constructed to achieve negative permittivity by a blending and hot-molding process.39–45 All these aforementioned results indicate that the negative permittivity can be obtained in the radio and microwave frequency regions by diluting the free-electron concentration in metals, also called low-frequency plasmonic state of metal networks.

Although negative permittivities could be obtained and easily be adjusted in metal composites, their values are huge and thus suffer from poor matching between electric components and magnetic components.36 Besides, when negative permittivity was used in capacitors to enhance effective permittivity, small negative permittivity values and small dielectric loss values were required to match with positive permittivity materials.3 According to the Drude model, negative permittivity comes from the response of electrons and its value has a close relationship with electron concentration. A lower electron concentration in metacomposites is preferable in order to obtain negative permittivity with small values. Hence, a carbon material with low electron concentration can be considered as a candidate for constructing metacomposites.37–40 Amorphous carbon was introduced into porous Si$_3$N$_4$ or Al$_2$O$_3$ to achieve negative permittivity by the impregnation–pyrolysis method.41,42 Besides, carbon nanofibers (CNFs), carbon nanotubes (CNTs) and graphene have been used to realize negative permittivity in polymer nanocomposites with continuous 3D conductive networks.43–45 It is worth noting that a small magnitude of negative permittivity is obtained due to the low concentration of free electrons in the carbon materials, while enormous negative permittivity in the metal composites causes poor matching when used in electromagnetic shielding and energy storage capacitors.

According to percolation theory, a conductive network could be formed with increasing conductive filler loading, hence, negative permittivity could be achieved and a negative permittivity value would also change violently with increasing conductive filler loading. This is the characteristic of percolation, which is difficult to change.36–40 In fact, when the metacomposites are used, negative permittivity properties are required to be stable and repeatable. That is, a negative permittivity value is almost a constant as the conductive filler loading changes within a small range, which is also the purpose of some giant permittivity materials.40 Thus, to obtain a stable negative permittivity in the conductive percolative nanocomposites is still a challenge.

In this research, stable negative permittivity was achieved by a novel strategy, i.e., a three-dimensional (3-D) carbon network was in situ constructed in the silica sphere matrix after a self-assembly and pyrolysis process. The microstructure and composition were analyzed by field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). The carbon content in the composites was evaluated by thermogravimetric analysis (TGA). The dielectric properties were tested in the frequency range from 10 MHz to 1 GHz. With the formed 3-D carbon network, the electrical percolation behavior was observed and stable negative permittivity was achieved. The carbon network was porous itself and confined in the channels among silica spheres; hence, the microstructure of the carbon network was not sensitive to carbon loadings, and stable negative permittivity was achieved. Besides, the dielectric loss and the negative permittivity value could be effectively adjusted by changing the carbonization temperature, showing small values of negative permittivity ($-100 < \varepsilon' < 0$) and a relatively low dielectric loss ($\tan \delta = 1–7$) in 100 MHz–1 GHz.

2. Experimental

2.1. Sample preparation

Preparation of SiO$_2$ microspheres. The monodispersed silica microspheres were prepared by using the Stöber method.49 Briefly, 25 mL of deionized water and 20 mL of ammonium hydroxide (28 wt%) were mixed with 80 mL of ethanol and stirred for 20 min at 40 °C (marked as A solution). 40 mL of tetraethyl orthosilicate (TEOS) was mixed with 80 mL of ethanol and stirred for 20 min (marked as B solution). Then, B solution was added to A solution at a constant feeding rate of 200 mL h$^{-1}$. After that, the mixture was stirred for 12 h at constant temperature. The white precipitate was separated by centrifugation and cleaned by deionized water and ethanol several times until pH = 7 and dried at 80 °C for 6 h.

Preparation of C/SiO$_2$ nanocomposites. The fabrication process of the C/SiO$_2$ microsphere composites is schematically shown in Fig. 1. Briefly, sucrose solutions of different concentrations were obtained by mixing 10, 20, 30, 35 or 40 g of sucrose to 30 mL of deionized water respectively. Only supernatant liquid was used due to the incomplete dissolution of sucrose. That is, the solubility of sucrose is less than 40 g. SiO$_2$ microspheres of 3 g were added to the sucrose solution and ultrasonically dispersed for 6 h to obtain the SiO$_2$ microsphere suspension. Then, the suspension was transferred into centrifugal tubes equipped with a disc-shaped mold. After centrifugation at 4800 rpm for 20 min, the bulk samples were obtained in the mold. After drying at 80 °C for 48 h to remove water, the bulk samples were calcined at 900 °C for 1 h under a nitrogen atmosphere to obtain C/SiO$_2$ microsphere composites.

2.2. Characterization

The microstructure of the composites was studied by field emission scanning electron microscopy (FESEM, Hitachi SU-70, Tokyo, Japan). The Raman spectra were reported on a micro-Raman spectrometer (Jobin Yvon HR800, France) with 532.05 nm incident radiation. The phase identifications of the composites were investigated at room temperature by X-ray diffraction (XRD; Tokyo, Japan) using the Rigaku D/Max-RB X-ray with Cu K$_\alpha$ radiation. X-ray photoelectron spectroscopy (XPS, Perkin-Elmer, PHI-5400, USA) was performed in order to
obtain the information about the composites and amorphous carbon. To evaluate the carbon content in the resultant composites, thermogravimetric analysis (TGA) was performed on an SDT thermal microbalance apparatus from room temperature to 900 °C with a heating rate of 10 °C min⁻¹ in air. The porosity was tested by the Archimedeans method, and N₂ sorption measurements were performed using Brunauer–Emmett–Teller (BET) calculations for the distribution of pores.

The dielectric parameters, including ac conductivity, reactance and complex permittivity of the composites, were measured using an Agilent E4991 Precision Impedance Analyzer with the 16453A dielectric test fixture. After calibration and compensation of the analyzer, the samples were put between these two planar electrodes. The samples’ dimensions was Ø 20 mm × 2 mm for dielectric and conductivity tests. The impedance data were obtained and converted to permittivity and ac conductivity using eqn (1)–(3):

\[ \epsilon' = \frac{Cd}{\varepsilon_0 A} \]  
(1)

\[ \epsilon'' = \frac{d}{2\pi\varepsilon_0 AR} \]  
(2)

\[ \sigma_{ac} = \frac{d}{RA} \]  
(3)

where \( d \) is the sample thickness, \( C \) is the capacitance, \( A \) is the electrode plate area, \( R \) is the resistance, \( \varepsilon_0 \) is the absolute permittivity of free space (8.85 × 10⁻¹² F m⁻¹), and \( f \) is the frequency.

3. Results and discussion

3.1. Thermogravimetry and carbon loading

Fig. 2 depicts the typical TGA curves of the composites with different carbon loadings in an air atmosphere. As can be seen from the plot, the weight changing process begins at about 570 °C and proceeds rapidly with increasing temperature up to 720 °C and then the weight loss decreases slowly to the final temperature. The results indicate that the carbon loadings of the composites are 0.87, 1.68, 3.12, 4.6, 5.51, 7.48, and 8.90 wt% for the C/SiO₂ composites prepared with different carbon precursor loadings.

3.2. Conductivity and percolation

Fig. 3 shows the frequency dispersion of ac conductivity \( \sigma_{ac} \) for the C/SiO₂ microsphere composites. In Fig. 3a, the \( \sigma_{ac} \) increases with increasing frequency for bulk SiO₂, composites with \( f_{\text{carbon}} = 0.87, 1.68, 3.12 \) and 4.6 wt%, attributed to the localized charge motions of isolated carbon nanosheets (microstructures in Fig. 6b) at high frequency. The localized charge motion could take advantage of high conductive regions of carbon nanosheets at high frequency because the charge transport needs a shorter distance at a higher frequency, while the charge transport needs a much longer distance at a lower frequency and thus the charge must extend over the gaps of nanosheets and thus the conduction is limited. The \( \sigma_{ac} \sim f \) curve can be fitted well by the following Jonscher power law:

\[ \sigma_{ac} = Ao^\beta \]  
(4)
where $\omega = 2\pi f$ is the angular frequency, $A$ is the pre-exponential factor and $n$ is the fractional exponent between 0 and 1. The experimental data showed good agreement with the power law (solid lines in Fig. 3a), indicating a hopping conduction behavior. For the composites with $f_{\text{carbon}} = 5.51$, 7.48 and 8.90 wt%, the $\sigma_{\text{ac}}$ decreased with increasing frequency, which can be attributed to the skin effect due to the three-dimensional carbon network (microstructures in Fig. 6c). As is well known, the skin effect is well expressed by the skin depth, which decreases with increasing frequency, leading to the decrease of $\sigma_{\text{ac}}$. Besides, the skin effect is the characteristic of typical conductors and can be described by the Drude model:\(^{51}\)

$$\sigma_{\text{ac}} = \frac{\sigma_{\text{dc}} \varepsilon_\infty \omega_\infty^2}{\omega^2 + \omega_\infty^2}$$

(5)

where $\sigma_{\text{dc}}$ is the direct current conductivity and $\omega_\infty$ is the relaxation rate. The solid lines in Fig. 3b depict the fitting results of composites with $f_{\text{carbon}} = 5.51$, 7.48 and 8.90 wt% using eqn (5) with high reliability factors, indicating a metal-like conduction behavior. Different conductivity mechanisms (hopping and metal-like conduction behaviors) indicate the percolation phenomenon, and the percolation threshold is between $f_{\text{carbon}} = 4.6$ and 5.51 wt%. The dielectric behavior of a material is very sensitive to its composition and microstructure near the percolation threshold. Hence, the dielectric properties are further investigated in the following section.

### 3.3. Dielectric properties

Fig. 4 shows the frequency-dependent real permittivity ($\varepsilon'$) for the composites with different carbon loadings. It can be seen that the permittivity has a close relationship with the carbon content. For the composites with low carbon loadings (Fig. 4a), the real permittivity is positive and obviously increases with increasing carbon content because of the enhanced interfacial polarization. The polarization across the carbon nanosheets/SiO$_2$ interface indicates that any pair of adjacent carbon nanosheets separated by an insulating gap can serve as a microcapacitor. Therefore, the composites are comprised of a network of microcapacitors, as schematically shown in the inset of Fig. 4a. Millions of microcapacitors can hold an extremely large capacity to store electric charges, enabling the composites to possess a higher permittivity.\(^{52}\) The phenomenon of dielectric enhancement is common in many composites, and the interfacial polarization, also known as the Maxwell–Wagner–Sillars effect, is responsible for the enhanced dielectric constant.\(^{51}\) It is worth noting that the real permittivity of bulk SiO$_2$, composites with $f_{\text{carbon}} = 0.87$, 1.68 and 3.12 wt%, is almost constant over the measured frequency range (10 MHz–1 GHz), suggesting potential applications as novel dielectric materials over a broad frequency range with low dielectric loss ($\tan \delta < 0.03$ in Fig. 5b).\(^{54,55}\) The real permittivity of composites with $f_{\text{carbon}} = 4.6$ wt% shows an obvious frequency dispersion.

Further increasing the carbon loading resulted in negative permittivity behavior for composites with $f_{\text{carbon}} = 5.51$, 7.48 and 8.90 wt% (Fig. 4b). Theoretically, the negative permittivity for the composites is attributed to the plasma oscillation of the electrons when the conductive fillers are above the percolation threshold. The plasma-like negative permittivity can be explained well by the Drude model:\(^{56}\)

$$\varepsilon' = 1 - \frac{\omega_p^2}{\omega^2 + \omega_\infty^2}$$

(6)

$$\omega_p = \sqrt{\frac{n_{\text{eff}}}{{m_{\text{eff}}} \varepsilon_0}}$$

(7)

where $\omega_\infty$ is the damping constant, $\omega_p \sim 2\pi f_p$ is the plasmon angular frequency, $\omega$ is the angular frequency of the applied electric field, $n_{\text{eff}}$ is the effective concentration of the electrons, $m_{\text{eff}}$ is the effective weight of the electrons, and $\varepsilon_0$ is the vacuum permittivity ($8.85 \times 10^{-12}$ F m$^{-1}$). The solid lines in Fig. 4b are the fitted results using the Drude model of eqn (6), which agree well with the experimental data. The fitted values of the parameters are summarized in Table 1. The fitting parameters of negative permittivity are approximate to those of ac conductivity using the Drude model in Fig. 3b, which further verifies the accuracy of simulation. Interestingly, the absolute values of negative permittivity are smaller than those of most
metal composites. Negative permittivity with small values is very preferable to match with impedance or permeability, and it is possibly attributed to the characteristics of carbon materials from pyrolysis of sucrose. That is, the low concentration of delocalized electrons in the carbon materials leads to a lower plasma frequency than that of the metals according to eqn (7). A similar phenomenon of negative permittivity with small values was also observed in the C/Al2O3 and C/Si3N4 composites.41,42 Besides, it is worth noting that the value of negative permittivity is almost the same for the composites with $f_{\text{carbon}} = 5.51$, 7.48 and 8.90 wt%, though the carbon loading has a relatively large difference. The carbon loading dependence of real permittivity $e'$ at different frequency points is detailed in Fig. 4c. For instance, the $e'$ of the composites at 100 MHz decreases from $-299$ to $-328$ as the carbon loading increases from 5.51 to 7.48 wt%, which is a reduction of 8.8%, and then the $e'$ decreases from $-328$ to $-369$ as the carbon loading increases from 7.48 to 9.0 wt%, which is a reduction of 11.1%. When the composites are measured at 200 MHz, the $e'$ decays from $-269$ to $-294$ as the carbon loading increases from 5.51 to 7.48 wt%, which is a reduction of 8.5%, then decreases from $-294$ to $-328$ as the carbon loading increases from 7.48 to 8.90 wt%, which is a reduction of 10.4% and so on. Importantly, the negative permittivity is almost irrelevant with the carbon loading at 600 MHz, that is to say, the $e'$ of the composites at 600 MHz increases from $-127$ to $-126$ as the carbon loading increases from 5.51 to 7.48 wt%, which is only a reduction of 0.8%, and then decreases from $-126$ to $-128$ as the carbon loading increases from 7.48 to 8.90 wt%, which is also a reduction of 0.8%. It can be observed that the negative permittivity of the C/SiO2 composites is weakly dependent on the carbon loading with increasing frequency, which is especially true in the 400–700 MHz frequency range with a variation below 10% (Fig. 4d). In fact, many metacomposites always suffer from their unstable and filler-loading dependent properties of negative permittivity, which is attributed to the percolating characteristic properties that the physical properties are usually sensitive to filler loading near the percolation threshold. Table 2 shows the comparison of variation of the negative permittivity value with filler content at different frequencies. On the one hand, in those metacomposites, the negative permittivity value obviously changed with changing filler content at the 100–700 MHz region and other tested frequency regions. In our work, the variation of the negative permittivity value is controlled within 10% with varying carbon content, and the negative permittivity even remains constant at the 500–700 MHz region. On the other hand, in those metacomposites, the magnitude of negative permittivity generally was huge, harmful to many applications of metacomposites due to poor impedance matching. In our work, negative permittivity with small values is achieved, making
Interestingly, as for the composites with negative permittivity, the tan δ values are smaller than those consisting of metal and ceramics, which is mainly attributed to the low concentration of free electrons and the low conduction loss in the carbon materials.\cite{31, 42} In the vicinity of percolation threshold, the dielectric loss consists of conduction loss and polarization loss due to the generation of leakage current,\cite{57} and the conduction loss could be described by eqn (8):\cite{28, 58}

$$\varepsilon'' = \frac{\sigma_e}{\omega \varepsilon_0}$$ \hspace{1cm} (8)

There is an apparently linear correlation between $\varepsilon''$ and frequency in the log–log plot for the composites with $f_{\text{carbon}} = 5.51$, 7.48 and 8.90 wt% (Fig. 5b), suggesting that the imaginary permittivity can be explained by eqn (8), and the conduction loss is the dominant loss mechanism in these composites.\cite{17}

### 3.4. Microstructures

The microstructures of neat SiO$_2$ microspheres and composites are shown in Fig. 6 and Fig. S1 (ESI†). The size of SiO$_2$ microspheres was measured by a Nano Measurer Software using the SEM image in Fig. S1a (ESI†). The mean size of SiO$_2$ microspheres was 527 nm. As shown in Fig. 6a, the carbon nanosheets were isolated and randomly distributed in the composites with $f_{\text{carbon}} = 0.87$ wt%. With increasing carbon loading, the carbon nanosheets enhanced the interconnection with each other and formed carbon clusters in the composites of $f_{\text{carbon}} = 1.68$ wt% (Fig. 6b). Upon further increasing the carbon loading, the channels among the SiO$_2$ spheres were filled with carbon materials and thus three-dimensional carbon networks were formed in the composites with $f_{\text{carbon}} = 5.51$, 7.48 and 8.90 wt% (Fig. 6c–e). Although the carbon loading was obviously different, i.e., $f_{\text{carbon}} = 5.51$, 7.48 and 8.90 wt%, their microstructures were similar, which was attributed to the porous structure of the carbon materials with different porosities (inset of Fig. 6c–e). As shown in the inset of Fig. 6c–e, the carbon materials consisted of many tiny carbon particles with about 10 nm in size, showing a shaggy and porous structure.\cite{59–61} The porosity and distribution of pore size are also investigated in Fig. S2 (ESI†). The pore size of the sample with 8.9 wt% carbon content was mainly within the range of 10–60 nm, while the pore size of the sample with 5.51 wt% was mainly within the range of 40–200 nm, Fig. S2b (ESI†). When the carbon content was low ($f_{\text{carbon}} = 0.87$ wt% and 1.68 wt%), the pore size was mainly above 200 nm. These could also be seen from the SEM images in Fig. 6. Fig. S2c (ESI†) shows the open porosity of the SiO$_2$ ceramics and their composites. It was found that the porosity of the composites decreased with increasing carbon content. This was because more pyrolytic carbons occupied the pores of the porous SiO$_2$ matrix. The pores had a close relationship with the stable negative permittivity. With increasing carbon content, the channels among the SiO$_2$ microspheres were filled with carbon, and the carbon network was formed, which attributed to the negative permittivity behavior. Because the carbon was porous itself, upon further increasing the carbon content, these small pores would be further filled rather than changing the big

### Table 1

<table>
<thead>
<tr>
<th>Carbon loading (wt%)</th>
<th>$f_p$ (GHz)</th>
<th>$\omega_0$ (s$^{-1}$)/10$^9$</th>
<th>Reliability factor $R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.51</td>
<td>9.12</td>
<td>3.19</td>
<td>0.99621</td>
</tr>
<tr>
<td>7.48</td>
<td>8.73</td>
<td>2.84</td>
<td>0.99956</td>
</tr>
<tr>
<td>8.90</td>
<td>8.61</td>
<td>2.65</td>
<td>0.99847</td>
</tr>
</tbody>
</table>

Fig. 5 (a) Frequency dependences of the dielectric loss tangent ($\tan \delta$) from the C/SiO$_2$ composites with different carbon loadings. (b) Frequency dependences of the imaginary permittivity ($\varepsilon''$) from the C/SiO$_2$ composites with different carbon loadings.
three-dimensional carbon network, which could be demonstrated by the decreasing pore size, Fig. S2b (ESI†). It was crucial to achieve stable negative permittivity. Besides, the carbon network came from the in situ transformation from sucrose during the pyrolysis process. The distribution of sucrose in solution was homogeneous, and hence, the distribution of pyrolytic carbon was also homogeneous. The homogeneous carbon structure contributed to the repeatable and stable negative permittivity. In previous investigations, a negative permittivity value often changed violently with changing filler content mainly due to the inhomogeneous distribution of fillers.20,21,23–25 Furthermore, the carbon content in these metacomposites was restricted by the percolation threshold and the highest content. It was indicated that the carbon content could only change between the percolation threshold and the highest content.20,21,23–25 Moreover, the relative intensity of the D band changed violently with changing filler content mainly due to the inhomogeneous distribution of fillers.20,21,23–25

Table 2 The comparison of variation of negative permittivity with filler contents in various metacomposites

<table>
<thead>
<tr>
<th>Materials system</th>
<th>Frequency region (MHz)</th>
<th>Filler content</th>
<th>Magnitude of negative permittivity</th>
<th>Average variation of negative permittivity with filler content at different frequencies</th>
<th>Other frequency</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel/alumina</td>
<td>10–1000</td>
<td>31–35 wt%</td>
<td>~10^6</td>
<td>~5%</td>
<td>~43%</td>
<td>~25%</td>
</tr>
<tr>
<td>Iron–alumina</td>
<td>10–1000</td>
<td>20–27 wt%</td>
<td>~10^6</td>
<td>~62%</td>
<td>~62%</td>
<td>~71%</td>
</tr>
<tr>
<td>Carbon–silicon nitride</td>
<td>20–1000</td>
<td>4.9–8.3 wt%</td>
<td>~10^6</td>
<td>~82%</td>
<td>~80%</td>
<td>~62%</td>
</tr>
<tr>
<td>Nickel chain–poly(vinylidene fluoride)</td>
<td>10–0.1</td>
<td>6–12 wt%</td>
<td>~10^4</td>
<td>~62%</td>
<td>~62%</td>
<td>~71%</td>
</tr>
<tr>
<td>Copper–polyphenylene sulfide resin</td>
<td>100–10000</td>
<td>21.4–22.1 vol%</td>
<td>~10^4</td>
<td>~52%</td>
<td>~44%</td>
<td>~38%</td>
</tr>
<tr>
<td>Multi-walled carbon nanotubes/polyaniline</td>
<td>1–1000</td>
<td>20–30 wt%</td>
<td>~1000</td>
<td>~98%</td>
<td>~95%</td>
<td>~96%</td>
</tr>
<tr>
<td>Copper/yttrium iron garnet</td>
<td>20–1000</td>
<td>9.8–24 wt%</td>
<td>~10^4</td>
<td>~58%</td>
<td>~66%</td>
<td>~61%</td>
</tr>
<tr>
<td>Silver/yttrium iron garnet</td>
<td>100–1000</td>
<td>37–45 wt%</td>
<td>~10^4</td>
<td>~92%</td>
<td>~85%</td>
<td>~96%</td>
</tr>
<tr>
<td>Carbon/SiO₂</td>
<td>100–1000</td>
<td>5.51–8.9 wt%</td>
<td>~10^0</td>
<td>10%</td>
<td>9.5%</td>
<td>7.7%</td>
</tr>
</tbody>
</table>

Fig. 6 SEM images of the C/SiO₂ composites with different carbon loadings: (a) 0.87, (b) 1.68, (c) 5.51, (d) 7.48, and (e) 8.90 wt%; (f) schematic diagram of the microstructure for the C/SiO₂ microsphere composites with the three-dimensional carbon network.

3.5. Raman, XRD and XPS spectra

The C/SiO₂ composites (fcarbon = 5.51 wt%) were prepared at different carbonization temperatures (i.e., 600, 700, 800, 900 and 1000 °C). Their Raman spectra are presented in Fig. 7. All the samples consist of two broad overlapping peaks at around 1330 and 1590 cm⁻¹. The peak at around 1330 cm⁻¹ is the D band, corresponding to the disordered structure of the amorphous carbon, while the peak at around 1590 cm⁻¹ is the G band which originates from the in-plane vibration of sp² carbon atoms, indicating the presence of a graphitic structure.65,66 Furthermore, the relative intensity of the D band
and the G band \(I_D/I_G\) is used to evaluate the graphitic degree in the carbon materials, i.e., the Tuinstra–Koenig (TK) equation. It is worth noting that the C/SiO\(_2\) composites show a higher intensity ratio \(I_D/I_G\) with increasing carbonization temperature, which is in contrast to the microcrystalline graphite. This phenomenon is ascribed to the complicated structure transformation from nanocrystalline graphite to amorphous carbon; the end of the transformation corresponds to a completely disordered, almost fully sp\(^2\)-bonded amorphous carbon. Most importantly, the TK equation is no longer valid in the process of structure transformation. In this process, the ratio \(I_D/I_G\) increases with increasing graphitic degree, indicating that a higher graphitic degree of carbon materials is produced for a higher carbonization temperature.

In order to further investigate the crystal structure of the carbon material in the composites, the carbon powders were prepared under different carbonization temperatures from sucrose. Fig. 8 shows their XRD patterns. The broad diffraction peak at \(2\theta = 21.45\,^\circ\) is due to the (002) plane of graphite, the typical characteristic of amorphous carbon, indicating the amorphous structure of the formed carbon materials. With increasing carbonization temperature, a new peak at \(2\theta = 44.3\,^\circ\) is observed, which can be indexed to the (101) plane of graphite (JCPDS card no. 75-1621). New broad diffraction peaks of (110) and (112) appear at \(2\theta = 80\,^\circ\) for the powders carbonized at 1000 °C. Besides, the peak intensity at \(2\theta = 44.3\,^\circ\) is higher with increasing carbonization temperature, all indicating a higher graphitic degree, which is in good agreement with the Raman results. Further detailed carbon structures of the composites were characterized by XPS. Fig. 9 shows the C\(_{1s}\) spectra of the composites \(f_{\text{carbon}} = 5.51\) wt% carbonized at different temperatures. The characteristic peak at 284.32–285.1 eV, which contributed \(\sim 64\%\) to the total integrated intensity, was ascribed to the C=C bonds. The peak corresponding to the C-C bonds at 285.11–285.30 eV contributed \(\sim 24\%\) to the total C\(_{1s}\) integrated intensity. The peaks at 285.75–286.80 eV correspond to the C-O/C-OH bonds, contributing \(\sim 11\%\) to the total integrated intensity. The XPS results indicate the existence of residual oxygen functional groups which come from the carbonization of sucrose and can enormously affect the dielectric and conductivity properties of the composites, which is discussed as follows.

### 3.6. Tunable negative permittivity by different carbonized temperatures

Fig. 10 shows the frequency dispersion of the dielectric properties for the composites with \(f_{\text{carbon}} = 5.51\) wt% at different carbonization temperatures. It can be seen from Fig. 10a that \(\varepsilon'\) is positive when carbonized at 600 and 700 °C, and increases with increasing carbonization temperature. Meanwhile, \(\varepsilon'\) shows the high frequency dispersion for the composites carbonized at 700 °C, which can be attributed to nonideal Debye-type relaxations. Negative permittivity shows an obvious easily-tuned behavior by changing the carbonization temperature: negative permittivity appears above 800 °C, and the absolute values of negative permittivity are enhanced with increasing carbonization temperature (Fig. 10b). The measured data of negative permittivity at 800 and 1000 °C also show a fairly good agreement with the Drude model of eqn (6). Moreover, negative permittivity with small values \((-100 < \varepsilon' < 0)\) is achieved at 800 °C, which is significant to the impedance matching of negative permittivity materials. Interestingly, the tan δ shows a nonlinear variation with increasing carbonization temperature (Fig. 10c). The tan δ increases as the carbonization temperature increases from 600 to 800 °C, while the tan δ decreases with the temperature increasing from 800 to 1000 °C, which demonstrates that the tan δ can also be effectively adjusted by changing the carbonization temperature. It is worth noting that the negative permittivity composites show an extremely low dielectric loss (\(\tan \delta = 1–7\)) compared with metal composites (usually \(\tan \delta = 10–100\))\(^{9,10,23–28}\) in the 100 MHz–1 GHz region. Different conductivity mechanisms indicate that a carbon structure-induced percolation phenomenon (Fig. 10d) occurred at different temperatures. That is, the conductive network (not geometrical network) can be formed by nanocrystalline graphite with a higher graphitic degree with increasing temperature, which demonstrates that the percolation phenomenon is an electrical contact behavior rather than the geometrical contact."
4. Conclusion

Silica microsphere templated 3-D carbon composites are prepared by a self-assembly and carbonization process. An electrical percolation phenomenon appears with increasing carbon loading, and a carbon network is *in situ* constructed by the template of channels among the SiO₂ microspheres. The plasma-like negative

---

**Fig. 9** XPS spectra of the composites (f_{carbon} = 5.51 wt%) carbonized at different temperatures in the C1s region.

**Fig. 10** Frequency dependences of the dielectric properties for the composites (f_{carbon} = 5.51 wt%) at different carbonization temperatures (a and b) real permittivities (ε’), (c) dielectric loss tangent (tan δ), and (d) ac conductivity (σ_{ac}).
permittivity is achieved and attributed to the low frequency plasmonic state from the conductive carbon network. The negative permittivity shows small carbon loading dependence, i.e. the negative permittivity properties are stable and repeatable, which is attributed to the porous microstructure of carbon materials with different porosities, and its microstructure is not sensitive to the variation of carbon loading. Besides, the low dielectric loss values (tan δ = 1−7) and small negative permittivity values (−100 < ϵ’ < 0) can be effectively adjusted by changing the carbon structure. The carbon material is amorphous and has a higher graphitic degree with increasing carbonization temperature. This work provides a convenient means to obtain stable and tunable negative permittivity. The carbon composites can be regarded as a promising candidate for metacomposites and will facilitate the applications of negative permittivity materials.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 51402170 and 51601105).

Notes and references
