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Micro carbonaceous spheres had been successfully synthesized from watermelon, via one-pot hydrothermal reaction. After a quick annealing process to remove the surface oxygen groups, the as-prepared spheres presented an excellent microwave absorption performance at Ku band (12-18 GHz), with the loading ratio of 25 wt% in paraffin-based composite at 2.0 mm thickness.

Microwave absorption (MA) has attracted increasing attention due to their important role in blocking undesirable microwave irradiation from the electronic devices and communication apparatus, which has recently aroused a great concern with the rapid development in civil, commercial, military and airspace technology. Compared with conventional metal oxide, carbonaceous materials have more advantages in excellent corrosion resistance, light weight and low cost. During the past few years, carbonaceous nanofillers such as carbon fibers (CFs), carbon nanotubes (CNTs), carbon nanocoils(CNCs) and graphene have been considered as ideal substitute against metal oxide in electromagnetic pollution management. For example, Kong et al. grown CNTs on graphene surface, and their poly(dimethyl siloxane) (PDMS) composite showed the maximum reflection loss (RL) of ～55 dB under 2.75 mm of thickness. Wang et al. reported that CNCs or graphene coated with multi-magnetic materials by atomic layer deposition (ALD) reveal excellent potential in MA; Song et al. mixed only 5 wt% of porous carbon in paraffin-based composite, and 4.5 GHz of effective MA bandwidth (below than 10 dB) could be reached. However, CFs, CNTs and chemical vapour deposition (CVD) graphene has predominant conductivity, thus their composites are mainly used for electromagnetic interference (EMI) shielding rather than absorption. Chemical or hydrothermal reduced graphene usually reveals semi-conductivity properties, due to the remained oxygen groups. After some macro- or nano- particles were added or crystallized onto the graphene surfaces, promising MA performance had been achieved. But they are often costly, and difficult to produce on a large scale and often need complicated purification/functionolization steps.

An inexpensive carbonaceous MA material would not only provide a cost advantage over the inherently more costly inorganic materials but would also be truly green. Watermelons are globally cultivated and favourite fruit, in 2009 the output of watermelon was 26.7 million tons all over the world, reported by Food and Agriculture Organization (FAO) of the United Nations. Although researchers have prepared carbonaceous materials for multi-application, such as pollution management, EMI shielding, supercapacitor, and lithium ion battery from biomatirial, these carbonaceous materials more or less contained inorganic materials, or prepared by high temperature with hours and strong acid or base. In this work, we synthesized carbonaceous spheres (CS) from watermelon using hydrothermal method without any additives. Compared with seeds or rinds of watermelon, watermelon juice without pulp fiber only contains carbohydrate, especially small sugars, such as glucose, sucrose and fructose. According to researches of Sun et al. and Li et al., these small sugars can polymerize and intermolecular dehydrate to form micro or nano CS. With the loading ratio of 25.0 wt% in paraffin-based composite, 90% of microwave energy at Ku band (12-18 GHz) was absorbed at only 2.0 mm thickness without enhancement of any inorganic materials. The pulps of watermelon mainly contain glucose, sucrose and fructose, which have been analysed through high performance liquid chromatography (HPLC). After squeeze and filtration, these soluble small sugars were dissolved into juice. According to previous similar researches, the growth of CS seems to conform to the LaMer model. These small sugars were polymerized firstly and then dehydrated to form CS. As shown in typical SEM images (Fig. 1a), CS were found with diameter mainly around 4-5 μm. Further TEM imaging results (Fig. 1b, c and d) revealed that these spheres were separated without conglutination. EDX analysis (Fig. S1) and XPS survey (Fig. 2a and b) explained that these spheres were mainly made up by element of C and O, and the atom ratio was 4.43:1. The C 1s spectra of CS has a peak at 286.6 eV,
reflected their surface containing hydroxyl (–OH) groups. Considering the C/O ratio and the surface chemical structure of as-prepared CS, we can’t help comparing them with graphene oxide (GO).\(^\text{45}\) GO can be reduced by a quick annealing process,\(^\text{45}\) thus these CS were put into a tubular furnace at 1000 °C for only 30s under argon flow. After annealing, most of the hydroxyl groups have been removed, and the C/O ratio reached 9.76:1 (Fig. 2c and d). The Raman and XRD spectrum (Fig. S3) also illustrate that the carboxylate is improved during the annealing process.

The measured complex permittivity \((\varepsilon')\) was utilized to determine MA of the CS/paraffin composites. Considering the weak magnetic properties of CS, complex permeability \((\mu')\) was taken as 1.\(^\text{24}\) Fig. 3a and b show that the real \((\varepsilon'')\) and imaginary \((\varepsilon'''')\) part of \(\varepsilon\) measured in 2-18 GHz for the samples loading with 5.0, 15.0 and 25.0 wt% of CS in paraffin. It was found that the value of \(\varepsilon'\) obviously increased with the increasing filler loading ratio, and it can be attributed to the increment of dipolar polarization and electrical conductivity.\(^\text{16}\) The \(\varepsilon''\) is related to the dissipation of microwave energy,\(^\text{45}\) thus, when a material has relative high value of \(\varepsilon''\), it may have potential in MA. The value of \(\varepsilon''\) also increased with the increasing filler loading ratio, and the main vibration peaks were found in Ku band. We compared the dielectric loss tangent \((\tan \delta = \varepsilon''/\varepsilon'\)) , which is related to microwave attenuation in dielectric materials,\(^\text{29}\) and Fig. 3c shows the tan \(\delta\) of each sample. It is easy to find that composite with 25.0 wt% of filler loading has the maximum value in the tested frequency. The relatively high values of \(\varepsilon''\) and \(\tan \delta\) imply that this sample has the best MA performance.

The optimal thicknesses of each sample were taken into account for the higher MA and the results are exhibited in Fig. 4. It is not surprising that the composites with 5.0 and 15.0 wt% of filler loading have very poor MA performance, since the values of \(\varepsilon\) and \(\tan \delta\) explain this phenomenon (Fig. 4a and b). It can be clearly seen that composites with 25.0 wt% of filler loading exhibited effective MA performance. Fig. 4c and Fig. 5a suggest that the composite with 2.0 mm of thickness has the highest reflection loss \((RL)\) up to −37.2 dB at 13.72 GHz with an effective bandwidth of ~ 5.72 GHz (12.28-18.0 GHz). The contour plot (Fig. 5b) showed that when the thickness is between 2.0 and 2.66 mm, MA could higher than −10 dB, which means more than 90% of microwave energy has been absorbed at Ku band. The noticeable peaks of RL mainly refer to the contribution of quarter-wave-length attenuation.\(^\text{46,47}\) Observation of peak shift with thickness change could be explained by the factor that the formation of quarter-wavelength attenuation requires the absorbing thickness meet the phase match conditions.\(^\text{48}\) As shown in Tab. 1, some outstanding composites with typical carbonaceous fillers and their MA performance have been listed. Although the filler loading ratio is a little higher than previous work, facile synthesis, low thickness and large effective bandwidth make this composite an excellent MA material.

The relationship between \(\varepsilon'\) and \(\varepsilon''\) can be expressed:

\[
(\varepsilon' - \varepsilon''\tan \theta)^2 + (\varepsilon'')^2 = (\varepsilon'' + \varepsilon''\tan \theta)^2
\]

Thus, the plot of \(\varepsilon'\) versus \(\varepsilon''\) would be a single semicircle, generally denoted as the Cole-Cole semicircle. Each semicircle corresponds to one Debye relaxation process. The \(\varepsilon' - \varepsilon''\) curve is shown in Fig. 6, three semicircles imply that other kinds of relaxation occur in the CS/paraffin mixture, such as Maxwell-Wagner relaxation and electron polarization.\(^\text{15,16}\)

Furthermore, in order to evaluate the real MA performance, an epoxy based composite with 2.0 mm thickness and \(18 \times 18\) cm\(^2\) was prepared which contained 25.0 wt% of CS, placed on iron substrate and measured under NRL Arch instrument (Fig. 7a).

In Fig. 7b, the epoxy/CS composite shows lower RL \((RL_{\text{max}} = −23.4\) dB) and narrow effective MA broadband (5.1 GHz, 12.9 GHz to 18.0 GHz). It may attribute to the difference between the matrix materials and the defect during the fabrication process.

**Conclusions**

To summarize, we created a high microwave absorption (MA) based on micro carbonaceous spheres/paraffin composites. These carbonaceous spheres entirely from a single precursor of biomass, watermelon. The composites with 25.0 wt% of spheres loading have presented excellent MA performance. Especially when the thickness is 2.0 mm, 90% of microwave energy can be absorbed by this composite in Ku band. This green and low energy utilization method to synthesize order carbonaceous spheres not only can be used in MA, but also give the potential in energy transform and storage.

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**Notes and references**

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Fig. 1 SEM (a) and FE-HRTEM (b, c and d) images of CS.

Fig. 2 (a, b) XPS survey and C 1s spectra of CS; (c, d) XPS survey and C 1s spectra of CS after annealing at 1000 °C.
**Fig. 3** The real part (a) and imaginary part (b) of relative complex permittivity of CS based paraffin based composites and their dielectric loss tangent (c).

**Fig. 4** The calculated RL for paraffin composites with (a) 5.0 wt%, (b) 15.0 wt% and (c) 25.0 wt% of CS (after anealing).

**Fig. 5** 3D plot (a) and contour plot (b) of the RL versus Ku band (8-12 GHz) and thickness (1.5-4.0 mm). The composite loaded with 25.0 wt% of CS.
Fig. 6 $\varepsilon' - \varepsilon''$ curve of composites loaded with 25.0 wt% of CS.

Fig. 7 (a) Picture of NRL Arch instrument; (b) epoxy matrix by dispersing 25.0 wt% of CS, the thickness and area are 2.0 mm and $18 \times 18 \text{ cm}^2$, respectively.
Tab. 1 Typical carbonaceous composites for MA. (HOPC: highly ordered porous carbon; PVDF: polyvinylidene; PU: polyurethane)

<table>
<thead>
<tr>
<th>Filler</th>
<th>Matrix</th>
<th>Filler loading</th>
<th>RL$_{\text{max}}$ (dB)</th>
<th>Thickness (mm)</th>
<th>Frequency range (GHz) (RL below $-10$ dB)</th>
<th>Effective bandwidth (GHz) (RL below $-10$ dB)</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass-derived CS</td>
<td>Paraffin</td>
<td>25.0 wt%</td>
<td>$-37.2$</td>
<td>2.0</td>
<td>12.28-18.0</td>
<td>5.72</td>
<td>This work</td>
</tr>
<tr>
<td>RGO</td>
<td>PVDF</td>
<td>3.0 wt%</td>
<td>$-25.6$</td>
<td>4.0</td>
<td>8.48-12.8</td>
<td>4.32</td>
<td>5 (2014)</td>
</tr>
<tr>
<td>RGO/MnFe$_2$O$_4$</td>
<td>PVDF</td>
<td>5.0 wt%</td>
<td>$-29.0$</td>
<td>3.0</td>
<td>8.0-12.88</td>
<td>4.88</td>
<td>12 (2014)</td>
</tr>
<tr>
<td>RGO/ZnO</td>
<td>Paraffin</td>
<td>10.0 wt%</td>
<td>$-24.8$</td>
<td>2.5</td>
<td>11.6-18.0</td>
<td>6.40</td>
<td>25 (2014)</td>
</tr>
<tr>
<td>RGO/PEDOT</td>
<td>Paraffin</td>
<td>10.0 wt%</td>
<td>$-35.5$</td>
<td>2.0</td>
<td>11.5-16.5</td>
<td>5.0</td>
<td>15 (2014)</td>
</tr>
<tr>
<td>RGO/MWCNTs</td>
<td>PDMS</td>
<td>5.0 wt%</td>
<td>$-55.0$</td>
<td>2.75</td>
<td>8.2-11.7</td>
<td>3.5</td>
<td>16 (2014)</td>
</tr>
<tr>
<td>HOPC</td>
<td>Paraffin</td>
<td>5.0 wt%</td>
<td>$-17.4$</td>
<td>2.0</td>
<td>11.7-16.2</td>
<td>4.5</td>
<td>24 (2014)</td>
</tr>
<tr>
<td>SWCNTs</td>
<td>PU</td>
<td>5.0 wt%</td>
<td>$-18.5$</td>
<td>2.0</td>
<td>9.0-12.0</td>
<td>3.0</td>
<td>26 (2007)</td>
</tr>
<tr>
<td>MWCNTs</td>
<td>Silica</td>
<td>5.0 wt%</td>
<td>$-30.72$</td>
<td>4.0</td>
<td>unknown</td>
<td>4.2</td>
<td>27 (2013)</td>
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