Fish bone-derived interconnected carbon nanofibers for efficient and lightweight microwave absorption

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Abstract

In this work, we demonstrated a simple method for preparing three-dimensional interconnected carbon nanofibers (ICNF) derived from fish bone as an efficient and lightweight microwave absorber. The as-obtained ICNF exhibits excellent microwave absorption performance with a maximum reflection loss of -59.2 dB at the filler content of 15 wt%. In addition, the effective absorption bandwidth can reach 4.96 GHz at the thickness of 2 mm. The outstanding microwave absorption properties can be mainly ascribed to its well-defined interconnected nanofibers architecture and the doping of nitrogen atoms, which are also better than most of the reported carbon-based absorbers. This work paves an attractive way for the design and fabrication of highly efficient and lightweight electromagnetic wave absorbers.

Keywords Biomass · Interconnected carbon nanofibers · Microwave absorption · Highly efficient

1 Introduction

With the rapid development of electronic technology, the problem of electromagnetic radiation pollution has become prominent and cannot be ignored [1, 2]. Thus, it is urgent to develop highly efficient electromagnetic wave absorption materials. Among various absorbers, Fe_3O_4 is extensively studied due to its low cost, high Curie temperature, unique dielectric/magnetic dual-loss properties, and environmental benignity [3, 4]. However, the high weight density and relatively low impedance matching restricts its application prospect. Recently, carbonaceous materials with unique structures have attracted tremendous attention for their low density, high electrical conductivity, large specific surface area, and controllable dielectric loss [5–8]. Quan et al. designed the macrostructure of the carbon nanotube dielectric filler and achieved ultra-high microwave absorption bandwidth [10]. Zhang et al. prepared the MoS_2 -RGO composite by a one-step hydrothermal method, which exhibited strong microwave

absorption properties [10]. Despite those advantages, the fabrication route is complicated and expensive, which constrains their scalable applications. Therefore, it is still a challenge to synthesize carbon materials with outstanding microwave absorption properties through a low-price and simple approach.

Herein, fish bone, a typical kind of biomass waste, is used to prepare three-dimensional (3D) interconnected carbon nanofibers (ICNF) using a facile and simple process. It is well known that fish bone is cheaply obtained and mainly comprised of hydroxyapatite and collagen [11, 12]. Thus, fish bone can be used as the hard templates to synthesize ICNF with 3D interconnected framework architectures by a simple pyrolysis treatment and the following acidizing process. To the best of our knowledge, there has been no report on the fabrication of 3D interconnected carbon nanofibers from fish bone. The as-obtained ICNF exhibits excellent microwave absorption performance, and the minimum reflection loss is as high as -59.2 dB at 7.92 Hz with a low filler percent of 15 wt%. Moreover, the

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effective bandwidth can reach 4.96 GHz when thickness is 2 mm. These encouraging performances indicate that the as-prepared sample ICNF has great potential as an efficient and lightweight electromagnetic wave absorber.

2 Experimental details

2.1 Synthesis of ICNF

The typical process of synthesizing ICNF from fish bone is as follows. 10 g of fish bone powders was added into 80 mL of deionized water and stirred for 30 min at room temperature. Then, the above mixture was poured into a Teflon-lined autoclave for a hydrothermal treatment at 180 °C for 10 h. Subsequently, the precipitates were dried, grinded, and put into a horizontal tube furnace at N₂ atmosphere with a heat treatment at 850 °C for 2 h. After that, the obtained black powders were soaked in 2 M of HCl solution for 24 h to remove inorganic substances. Finally, ICNF powders were obtained after the treatment of centrifugation, washing and drying for use.

2.2 Characterization of the samples

The morphologies were observed by scanning electron microscopy (SEM, S-4800) and transmission electron microscopy (TEM, JEM-2100). The crystallinity was characterized by X-ray diffraction (XRD, Bruker D8-ADVANCE) with Cu K α radiation. The specific surface area of samples was examined by the nitrogen adsorption–desorption isotherms (3H-2000PS2, BeiShiDe) using the Barrett–Emmett–Teller (BET) method, and the pore diameter was calculated by the data of the adsorption branch of the N₂ isotherm plot. The Raman spectrometer (inVia, Renishaw) was used to collect the Raman spectroscopy. The microwave absorption properties of the synthesized sample ICNF were measured by a vector network analyzer (Agilent N5071C, USA) in the frequency range of 2–18 GHz. Sample ICNF was homogeneously distributed in paraffin

wax and pressed into a toroidal ring with the thickness of 2 mm, outer diameter of 7 mm, and inner diameter of 3.04 mm, respectively.

3 Results and discussion

The morphology and microstructure of sample ICNF were characterized by SEM and TEM. As presented in Fig. 1a, sample ICNF exhibits 3D interconnected nanofibers architecture with the diameter in the range of 10–50 nm and the length of a few micrometers. Figure 1b gives the TEM image of sample ICNF, which also confirms the unique 3D interconnected nanofibers network structure. The internal structure of sample ICNF is analyzed by XRD patterns, as shown in Fig. 2a. There are two broad and weak diffraction peaks at about 24.5° and 43.4°, which can be well ascribed to the (002) and (100) planes of graphitic carbon, respectively, demonstrating the low graphitization degree of sample ICNF [13]. Raman spectroscopy is measured to further investigate the graphitization degree of sample ICNF. Figure 2b shows two typical peaks centered around 1351 and 1590 cm⁻¹, consistent with the features of amorphous carbon [14].

The specific surface area and porous structure of sample ICNF are evaluated by nitrogen adsorption–desorption measurements. As depicted in Fig. 3a, sample ICNF possesses a typical IV-type isotherm curve with a H3-type hysteresis loop, suggesting the existence of mesopores [15]. Based on the adsorption branch of N₂ isotherm curve, the pore size distribution curve is calculated and illustrated in Fig. 3b. It is clear that the pore size of sample ICNF is mainly located in the range of 5–45 nm, also certifying the presence of mesopores. Moreover, sample ICNF has a large specific surface area value of 881 m² g⁻¹. The high specific surface area and the unique 3D interconnected nanofibers network architecture are suggested to be beneficial to the impedance matching, multiple microwave reflection, and interfacial polarization. Therefore, the as-synthesized sample ICNF has great potential in terms of microwave

Fig. 1 **a** A typical SEM image, and **b** a typical TEM image of sample ICNF

Fig. 2 The XRD pattern **a**, and the Raman spectrum **b** of sample ICNF **Fig. 3** N₂ absorption–desorption isotherm (**a**), and the pore size distribution (**b**) of sample ICNF. XPS spectra of sample ICNF: C 1 s (**c**), and N 1 s (**d**)

absorption. In addition, the surface composition and chemical state of sample ICNF were determined by the XPS technique. The C 1 s spectrum in Fig. 3c can be deconvoluted into four peaks around 284.8, 285.7, 286.7, and 289.4 eV, which are attributed to C–C/C=C, C–N, C–O, and C=O, respectively [16, 17]. For N 1 s spectrum in Fig. 3d, it demonstrates that the binding energies around 398.3 and 400.5 eV are assigned to pyridine N and quaternary N, respectively [18, 19]. The XPS analysis confirms the presence of nitrogen atoms in sample ICNF, which is suggested to be conducive to the dielectric loss and microwave absorption performance.

The microwave absorption performance is evaluated by the complex permittivity ϵ due to the fact that no magnetism exists in sample ICNF. The real part ϵ' and the imaginary part ϵ'' of as-fabricated ICNF/paraffin composites

with different absorbent loading are depicted in Fig. 4a and Fig. 4b, which represent the storage and dissipation capability of electromagnetic wave energy, respectively. For the filler ratio of 15 wt% shown in Fig. 4a, the ϵ' value decreases with increasing frequency. While its ϵ'' value in Fig. 4b firstly reduces slightly in the range of 2–11 GHz, then increases dramatically in the frequency range of 11–18 GHz with obvious fluctuation and a maximum peak at 17 GHz, which might be from the polarization relaxation process occurring in sample ICNF. In addition, with the increase in loading content from 10 to 20 wt%, the values of ϵ' and ϵ'' firstly increase and then decrease. Thus, there is an optimal content of ICNF, only the proper ICNF loading in ICNF/paraffin can get the best complex permittivity performance. The dielectric loss tangent ($\tan \delta_\epsilon = \epsilon''/\epsilon'$) is further calculated to assess dielectric loss capability of ICNF/

Fig. 4 The relative permittivity real part **a**, the relative permittivity imaginary part **b**, the dielectric loss tangent **c**, and the Cole–Cole semicircles **d** of ICNF/paraffin composites with different absorbent loading

paraffin composites. As illustrated in Fig. 4c, the ICNF/paraffin with 15wt% filler content also has the highest value of $\tan \delta$, which maintains almost unchanged around 0.4 in the range of 2–11 GHz, then increases sharply along with increasing frequency and has a maximum peak at 17 GHz, suggesting the occurrence of intense dielectric loss effect. Moreover, the Cole–Cole plots of ICNF/paraffin composites are applied based on the Debye relaxation theory to better investigate the polarization relaxation behaviors. As shown in Fig. 4d, there are more distorted Cole–Cole semicircles with a tail in 15 wt% ICNF/paraffin composite, suggesting the existence of more forms of relaxation process.

According to transmission line theory, the reflection loss (RL) values of as-synthesized samples are calculated based on the following formula to evaluate the electromagnetic wave absorption properties [20, 21].

$$RL \text{ (dB)} = 20 \log \left| \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \right|$$

$$Z_{in} = \sqrt{\frac{\mu_r}{\epsilon_r}} \tanh \left[j \left(\frac{2\pi f d}{c} \right) \sqrt{\mu_r \epsilon_r} \right]$$

where the parameters Z_{in} , Z_0 , f , d , and c are input impedance, free space impedance, applied frequency, absorber thickness, and light velocity, respectively. Figure 5a–c exhibits the three-dimensional patterns of ICNF/paraffin composites with different ICNF loading at different

thickness. When filler ratio of ICNF is 15% (Fig. 5b), the minimum value of RL is up to -59.2 dB at 7.92 GHz with the thickness of 3 mm, outperforming the other ICNF/paraffin composites in Fig. 5a, c. Moreover, the 15% filler loading composite possesses a broad effective absorption bandwidth of 4.96 GHz (11.04–16 GHz) at 2 mm. The above electromagnetic wave absorption performance is superior to the other outstanding absorbents reported previously, as summarized in Fig. 5d, suggesting the potential prospect of ICNF as an excellent microwave absorption absorbent with lightweight.

Figure 6 further illustrates the possible electromagnetic wave absorption mechanism of sample ICNF. Firstly, the unique interconnected carbon nanofibers conductive framework endows a lot of conductive pathways, facilitating the migration and the hopping of electrons, then boosting the conductive losses [29, 30]. Secondly, the high specific surface area is conducive to multiple reflections and scattering of microwave, which can enhance impedance matching degree, thus inducing a high dielectric loss [31, 32]. Thirdly, nitrogen element in sample ICNF can accelerate the electron transfer and also can improve the dipolar polarization and defect polarization, which are beneficial to the conduction loss and dielectric loss, respectively [33, 34]. Lastly, there are numerous defects and boundaries in sample ICNF, which can give rise to strong dipole orientation relaxation and interfacial polarization relaxation, respectively.

Fig. 5 Three-dimensional patterns of reflection loss of ICNF/paraffin composites with filler ratio of 10 wt% **a**, 15 wt% **b**, and 20 wt% **c**. **d** Comparison of microwave performance of sample ICNF with recent reported absorbents

Fig. 6 Schematic illustration of electromagnetic wave absorption mechanism of sample ICNF

4 Conclusions

In summary, three-dimensional interconnected carbon nanofibers derived from fish bone have been successfully fabricated through a facile carbonizing and the following acidizing process. The as-prepared ICNF absorbent exhibits outstanding electromagnetic wave

absorption performance with the corresponding minimum reflection loss of -59.2 dB at a low loading content of 15 wt% and the effective bandwidth of 4.96 GHz at a relatively low thickness of 2 mm, outperforming those of most carbonaceous absorbents reported previously. Moreover, the possible microwave absorption mechanism is discussed, and the excellent microwave properties are mainly attributed to its unique 3D

interconnected nanofibers network structure and the doping of nitrogen atoms. These results demonstrate that fish bone is of great potential in the synthesis of efficient and lightweight microwave absorbents by a facile and low-cost strategy.

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Compliance with ethical standards

Conflict of interest The author(s) declare that they have no competing interests.

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