Carbonized wood with ordered channels decorated by NiCo$_2$O$_4$ for lightweight and high-performance microwave absorber

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Abstract: Wood-derived carbon has a 3D porous framework composed of through channels along the growth direction, which is a suitable matrix for preparing electromagnetic wave (EMW) absorbing materials with low cost, light weight, and environmental friendliness. Herein, the carbonized wood decorated by short cone-like NiCo$_2$O$_4$ (NiCo$_2$O$_4$@CW) with highly ordered straight-channel architecture was successfully manufactured through a facile calcination procedure. The horizontal arrangement of the through channels of NiCo$_2$O$_4$@CW (H-NiCo$_2$O$_4$@CW) exhibits a strong reflection loss value of $-64.0$ dB at 10.72 GHz with a thickness of 3.62 mm and a low filling ratio of 26 wt% (with the density of 0.98 g·cm$^{-3}$), and the effective absorption bandwidth (EAB) is 8.08 GHz (9.92–18.0 GHz) at the thickness of 3.2 mm. The excellent microwave absorption (MA) property was ascribed to the ordered-channel structure with abundant interfaces and defects from NiCo$_2$O$_4$@CW, which could promote the interfacial polarization and dipole polarization. What is more, this advantageous structure increased the multiple reflections and scattering. Finite element analysis (FEA) simulation is carried out to detect the interaction between the prepared material and EMW when the ordered channels are arranged in different directions. This research provides a low-cost, sustainable, and environmentally friendly strategy for using carbonized wood to fabricate microwave absorbers with strong attenuation capabilities and light weight.

Keywords: microwave absorption (MA); wood-derived carbon; ordered-channel architecture; light weight; finite element analysis (FEA)

1 Introduction

Due to the serious problem of electromagnetic pollution and the urgent need of military anti-reconnaissance capabilities, a variety of electromagnetic wave (EMW) absorbing materials with excellent performance have been developed, which attenuate EMW by converting them into other forms of energy [1,2]. Among various microwave absorbing materials, the carbonaceous materials have been paid high attention due to their chemical stability, low density, and tunable electromagnetic parameters. In past reports, commonly used carbon materials for microwave absorption (MA), such...
as carbon fiber [3], carbon nanotube (CNT) [4–6], metal-organic framework (MOF) [7], and graphene [8], exhibited good MA performance. Carbon materials have greatly promoted the development of absorbing materials.

Simultaneously, the concept of sustainable development and environmental friendliness is also being valued more and more. Traditional carbon materials often rely on modern industrial techniques, which are complex and costly, and the by-products of the preparation process can damage the natural environment. Fortunately, the biomass-derived carbon overcomes the shortcomings of man-made carbon materials with many characteristics such as light weight, large natural reserves, and low cost. Nowadays, the natural wood-derived carbon materials with through channels parallel to the growth direction have been successfully applied in many fields, for example, energy storage materials, catalysts, and sensors [9–11]. The three-dimensional (3D) skeleton composed of orderly-arrangement and through channels existing in wood-derived carbon can also be applied to MA materials, which not only is favor of microwave scattering and multi-reflections to prolong the propagation path of EMW [12] and forms an efficient conductive network to enhance the conductive loss [13], but also provides a load position for magnetic materials to improve impedance matching and cause magnetic loss [14]. Hence, this 3D porous structure can be used as an ideal carbon substrate for electromagnetic interference (EMI) shielding and MA materials.

Xi et al. [15] reported that wood-based straight channel structure, which was analogous to a waveguide, exhibited excellent MA performance with maximum reflection loss (RL) of −68.3 dB at 4.28 mm and effective absorption bandwidth (EAB) (RL < −10 dB) up to 7.63 GHz at 3.73 mm. This unique structure has provided inspiration for the subsequent design of wood-derived carbon MA materials. Zheng et al. [13] have successfully fabricated the wood-derived magnetic porous carbon composites with a highly ordered anisotropic porous architecture on the foundation of the 3D ordered-channel skeleton, and this Ni/porous carbon composite exhibited an exceptional EMI shielding effectiveness of 50.8 dB at the whole X band (8.2–12.4 GHz) with the thickness of 2 mm.

In order to make full use of the 3D ordered porous framework derived from wood-derived carbon, our research introduces NiCo$_2$O$_4$ mixture on the wall of highly ordered straight channels inherited from wood. The NiCo$_2$O$_4$, a spinel-structure bimetal oxide, with high electrochemical activity, was mainly used in the electrochemistry field [16,17]. Therefore, from the point of its high electronic conductivity, NiCo$_2$O$_4$ has great potential value in the field of absorber with superior dielectric loss [14,18]. It can be foreseen that various loss mechanisms make as-prepared samples obtain excellent absorbing performance due to the natural favorable structure, improved impedance matching, and optimized conductivity. Furthermore, the finite element simulation of NiCo$_2$O$_4$@CW testifies that horizontal arrangement of the through channels leads to the excellent EMW attenuation ability. Our study provides an alternative strategy to using low-priced, environmentally friendly natural wood, and simple, efficient preparation procedure to design microwave absorbers with high absorption efficiency and wide absorption frequency. We hope that this work lays a significant foundation for the design and application of wood-derived carbon absorbers to fulfill the ever-growing demands.

2 Experimental

2.1 Preparation of CW

All reagents used in our experiments were used as received without further purification. Poplar wood was purchased from plantation (Hubei, China). To prepare the lignin removal solution, 4 g NaClO$_2$ (80%; Shanghai Macklin Biochemical Co., Ltd., China) and 1.35 mL CH$_3$COOH (99.5% AR; Tianjin Fuyu Fine Chemical Co., Ltd., China) were dissolved in 400 mL deionized water. Then a slice of poplar wood slice cut into 10 mm × 10 mm × 10 mm was immersed in the as-prepared solution in the beaker at 80 ℃ for 12 h. The lignin-removed wood (LFW) was prepared. Finally, the LFW was placed in a tubular furnace and carbonized at 400 ℃ under flowing nitrogen for 1.5 h with a heating rate of 3 ℃·min$^{-1}$. The CW was placed in a vacuum drying oven for further use.

2.2 Synthesis of NiCo$_2$O$_4$@CW composites

The CW was immersed in the solution of 1 mol·L$^{-1}$ of Ni(NO$_3$)$_2$·6H$_2$O and 2 mol·L$^{-1}$ of Co(NO$_3$)$_2$·6H$_2$O (98% AR; Tianjin Fengchuan Chemical Reagent Technologies Co., Ltd., China) in the beaker. The
beaker was placed in ultrasonic environment for 30 min, then allowed to stand for 12 h with −0.1 MPa environment, and finally heated at 50 °C for 6 h. The CW was fully saturated with Ni(NO₃)₂·6H₂O and Co(NO₃)₂·6H₂O solution. Subsequently, the CW/Ni(NO₃)₂·6H₂O/Co(NO₃)₂·6H₂O composite was placed in a drying oven for 12 h with 60 °C. Finally, the as-obtained material was placed in a tubular furnace for heating to 300 °C for 1 h in air. After the temperature dropped to room temperature, the NiCo₂O₄@CW hybrid was obtained. For comparison, the CW was also post treated by the same calcination conditions, and the post-treated CW was prepared.

2.3 Characterization

Powder XRD pattern was recorded on BRUKER diffractometer using Cu Kα radiation. The morphology and microstructure were observed using SEM images on SUPRA™55 (ZEISS, UK) at high current of 20 kV. The elemental composition was detected by energy dispersive spectrometer (EDS) spectrum deriving from the SEM, coupled with copper grids. Raman spectra were obtained by a Renishaw Raman microscope using an Ar ion laser (532 nm). Thermogravimetric analysis (TGA) measurements for the composite were carried out by a DTG-60H thermal analyzer (Japan) under flowing oxygen atmosphere and with a heating rate of 10 °C·min⁻¹. The room temperature hysteresis loop was performed on vibrating sample magnetometer (VSM; JDAW-2000C&D, Changchun Yingpu Co., Ltd., China). The conductivity measurements of all samples were carried out by the 2450 Source Meter (KEITHLEY Co., Ltd, USA).

2.4 Electromagnetic parameter measurements

The electromagnetic (EM) parameters were obtained on vector network analyzer (Agilent, N5230A, USA) by the T/R coaxial line method at 2–18 GHz band. Testing samples of MA were prepared by cutting method, which can retain the micron-level structure inside the material. Two pieces of NiCo₂O₄@CW materials were tailored into cylindrical toroidal specimens along parallel to the wood growth direction and perpendicular to the wood growth direction (called vertical and horizontal) with an outer diameter of 7.00 mm and inner diameter of 3.00 mm, and then were immersed in liquid paraffin wax; after solidification, the sample was prepared, named V-NiCo₂O₄@CW and H-NiCo₂O₄@CW. In the same way, the CW material was cut into cylindrical toroidal specimens, named V-CW (vertical) and H-CW (horizontal). The average filling ratio of coaxial sample was 26 wt% (with the density of 0.98 g·cm⁻³) and 21 wt%, obtained by weighing several times. In addition, the disordered samples (named CW and NiCo₂O₄@CW) were prepared by mixing the powders with paraffin matrix and pressed into a toroidal ring with an outer diameter of 7.00 mm and inner diameter of 3.00 mm, respectively, with the same filling ratio of ordered-channel samples. The RL values were obtained by EM parameters on the basis of transmission line theory, which can be calculated by the following equations based on the metal back-panel model [19,20]:

\[
Z_{in} = Z_0 \sqrt{\frac{\mu_r}{\varepsilon_r}} \tanh \left( \frac{j2\pi fd\sqrt{\mu_r\varepsilon_r}}{c} \right)
\]

(1)

\[
RL(dB) = 20\log \left( \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \right)
\]

(2)

where \(Z_{in}\) is the input impedance of absorber, \(Z_0\) is the impedance of free space, \(\varepsilon_r\) and \(\mu_r\) represent the complex permittivity \((\varepsilon_r = \varepsilon' - j\varepsilon''\)) and the complex permeability \((\mu_r = \mu' - j\mu'')\), respectively, \(f\) indicates the frequency of the incident microwaves, \(d\) means the thickness of the microwave absorber, and \(c\) is the velocity of the microwave. RL is smaller than −10 dB, which is implied that more than 90% of the microwave is absorbed by MA, and the frequency range can be considered as EAB [21].

3 Results and discussion

The preparation procedure of NiCo₂O₄@CW with the structure of oriented channels and standard coaxial samples is schematically illustrated in Fig. 1. The crystallographic structures of CW and NiCo₂O₄@CW were characterized by powder XRD, as shown in Fig. 2(a). The broad diffraction peaks at 26.23° and 44.35° correspond to the (200) and (101) crystal planes of graphite crystal structure, respectively, indicating that CW is partially graphitized at 400 °C, behaving as amorphous carbon. For the NiCo₂O₄@CW
Fig. 1  Fabrication process of NiCo$_2$O$_4$@CW with ordered channels, and schematic illustration to obtain vertical and horizontal standard coaxial samples.

Fig. 2  (a) XRD patterns of CW and NiCo$_2$O$_4$@CW and (b) Raman spectra of CW and NiCo$_2$O$_4$@CW; XPS spectra of NiCo$_2$O$_4$@CW: (c) O 1s, (d) C 1s, (e) Ni 2p, and (f) Co 2p.
powder sample, the diffraction peak positions were consistent with the standard XRD pattern of NiCo$_2$O$_4$ (JCPDS No. 20-0781). The diffraction peaks of NiCo$_2$O$_4$@CW composites located at 31.3°, 36.8°, 44.3°, 59.1°, and 65.1° could be corresponded to the (220), (311), (400), (511), and (440) crystal planes of NiCo$_2$O$_4$ phase, respectively. Simultaneously, the broad diffraction peaks of amorphous carbon were obtained in the spectrum of NiCo$_2$O$_4$@CW composites. These results confirmed that NiCo$_2$O$_4$ was successfully deposited in through channel of CW. The mass fraction of carbon in NiCo$_2$O$_4$@CW composites is obtained by TGA, described in Fig. S1 in the Electronic Supplementary Material (ESM), which indicated the weight ratio of CW is 56.2 wt%.

Raman spectrum was applied to demonstrate the chemical environment of carbon atoms in the CW and NiCo$_2$O$_4$@CW powder, which is an important factor for electron transportation and makes a significant impact on the electromagnetic parameters [22]. In addition, Raman spectrum was also used to characterize the existence of cobalt and nickel atoms. Two obvious peaks located at 1320 cm$^{-1}$ (D band) and 1580 cm$^{-1}$ (G band) can be demonstrated in Fig. 2(b). The intensity of the D band peak represents the number of defects or the degree of disorder in the sp$^2$-hybridized carbon atoms or amorphous carbon deposits, while the G band peak is associated with the in-plane vibrations of sp$^2$ atoms in a 2D hexagonal graphitic lattice. The degree of disorder of carbon in the material can be characterized by the ratio of D band to G band ($I_D/I_G$) [23]. As shown in Fig. 2(b), the intensity ratio value of $I_D/I_G$ was 0.87 for CW, and this result is in good agreement with the amorphous carbon in XRD pattern. The $I_D/I_G$ value of NiCo$_2$O$_4$@CW was 0.78, which suggested abundant defects exist in both CW and NiCo$_2$O$_4$@CW, and the existence of NiCo$_2$O$_4$ reduced the degree of disorder of carbon in the material, increasing the graphitization degree. The Raman spectrum of spinel Co$_3$O$_4$ has a high-frequency peak at 693 cm$^{-1}$, determined by the octahedral/Co$^{3+}$ [24]. For NiCo$_2$O$_4$, as Co$^{3+}$ (or Ni$^{3+}$) was replaced by Ni$^{2+}$ (or Co$^{2+}$), the octahedral/Co$^{3+}$ (or Ni$^{3+}$) peak weakens and shifts to lower frequency (Fig. 2(b), the band at 650 cm$^{-1}$ of NiCo$_2$O$_4$@CW is assigned to the $A_g$ phonon excitations); simultaneously, the octahedral/Ni$^{2+}$ peak was observed at 502 cm$^{-1}$ resulted from Ni$^{2+}$ substitution at octahedral sites. The peak at 460 cm$^{-1}$ was caused by tetrahedral/Co$^{2+}$ (or Ni$^{2+}$, assigned to the $E_g$ phonon excitations). This result confirms the successful synthesis of spinel structured NiCo$_2$O$_4$. It can be inferred that the Ni$^{2+}$ substitution at octahedral sites would induce the formation of dipole and dipole polarization [24,25], which is a benefit for EM wave attenuation and thus results in enhanced MA properties.

The chemical composition and the elemental valence state of the NiCo$_2$O$_4$@CW composites were further characterized by XPS. The wide span spectrum of NiCo$_2$O$_4$@CW composites indicated four typical peaks, corresponding to Ni 2p, Co 2p, O 1s, and C 1s (Fig. S2 in the ESM). The Ni 2p spectrum has two spin-orbit doublets of Ni$^{2+}$ and Ni$^{3+}$, the binding energies at 854.2, 861.2, 874.4, and 879.6 eV belonged to Ni$^{2+}$, and the peaks at 872.4 and 855.8 eV were assigned to Ni$^{3+}$. The binding energies at around 861.3 and 879.9 eV were marked to the two shake-up satellite peaks (named as “Sat.”) of nickel (Fig. 2(e)). Similarly, the Co 2p spectrum given in Fig. 2(f) consists of one spin-orbit doublet characteristic of Co$^{2+}$ (binding energies at 781.9 and 796.8 eV) and Co$^{3+}$ (binding energies at 779.9 and 795.0 eV) and two shake-up satellites (binding energies at around 787.9 and 803.7 eV, identified as “Sat.”). The high-resolution C 1s spectrum (Fig. 2(d)) consisted of three carbon peaks, which represent C–C/C=C (284.7 eV), C–O (285.8 eV), and C=O (288.7 eV) [26]. As shown in Fig. 2(c), the O 1s spectrum showed three peaks located at 529.5, 531.2, and 532.8 eV, which could be ascribed to the metal–oxygen bonds (O1, pink area), defects in oxygen (O2, blue area), and absorbed water (O3, green area) on the surface, respectively [27,28]. The defects in oxygen are due to the low oxygen coordination bond caused by the imbalance of cobalt ions and nickel ions between octahedral sites and tetrahedral sites. The existence of abundant defects in oxygen may result in the uneven distribution of local charges, thereby inducing dipole polarization under the electromagnetic field [29]. The oxygen defect ratio is expressed by the peak area ratio, and is shown in the inset of Fig. 2(c). Overall, the highly consistent characterization results of XRD, XPS, and Raman spectra collectively confirm the successful synthesis of NiCo$_2$O$_4$@CW composite.

Figure S3 in the ESM presents the room temperature hysteresis loops of NiCo$_2$O$_4$@CW (inset: enlarged view at low fields). The magnetization curve performs a typical ferromagnetic behavior, and the magnetization has been found to not saturate, even at the maximum applied field (10 kOe). The remnant magnetization and
coercivity were represented as 0.16 emu·g⁻¹ and 62.5 Oe, respectively. It should be noted that low saturation magnetization implies the poor magnetic loss capacity.

SEM images of CW and NiCo₂O₄@CW are displayed in Fig. 3. Vertical direction of CW (Fig. 3(a)) and horizontal direction of CW (Fig. 3(b)) show that the CW has through, directional, and ordered channels, and the shape of the channels presents an irregular ellipse with a pore size of 10–30 μm and channel wall thickness of 1–3 μm. Vertical direction of NiCo₂O₄@CW (Fig. 3(c)) and horizontal direction of NiCo₂O₄@CW (Fig. 3(d)) demonstrate that the high-density short cone-like NiCo₂O₄ composites uniformly distributed in the through channels in CW. The thickness of carbon channel walls is obviously thinner than that of CW, because a large number of carbon atoms are dispersed in the NiCo₂O₄ hybrid in the heat treatment process, which can be further confirmed by energy dispersive X-ray spectroscopy (EDS) mapping images (Fig. S4 in the ESM). An image in the inset of Fig. 3(c) reveals the magnified cone-like NiCo₂O₄/C. The original size of the as-prepared samples was shown by optical photograph in Fig. S5 in the ESM. Simultaneously, the through, directional, and ordered channels were retained in the NiCo₂O₄@CW, and this unique ordered pore microstructure can enable abundant multiple reflections of electromagnetic waves and interfacial polarization, which are favorable for the MA performance.

Generally, the hybrid magnetic/dielectric composites present excellent EMW absorption capabilities due to electromagnetic complementation and impedance matching effects. Our ordered-channel NiCo₂O₄@CW composites with unique microstructure perform excellent MA abilities. Impedance matching ratio ($|Z_{in}/Z_0|$) is also an important parameter for EMW absorption. The impedance characteristic of the absorber is close to that of free space (the value of $|Z_{in}/Z_0|$ lose to 1), which means that the incident EMW can enter the absorber to the greatest extent [18]. Figure S6 in the ESM presents the RL curves and the impedance matching ratio of V-CW, H-CW, and V-NiCo₂O₄@CW samples with thickness from 1.0 to 5.5 mm in the frequency range of 2.0–18.0 GHz. It is observed that these three samples showed almost no MA (Figs. S6(a)–S6(c) in the ESM), resulting from poor impedance matching performance. Nevertheless, as shown in Figs. S6(d)–S6(f) in the ESM, the impedance matching performance of the three samples is found to be quite different. The impedance matching ratio of H-CW and V-NiCo₂O₄@CW are closer to 1 than that of V-CW, which implies that the through channels arranged horizontally relative to the incident direction of EMWs have better impedance matching performance than those arranged vertically, and are more conducive to EMWs loss, and the NiCo₂O₄ introduced in through channels also achieved the same effect. The RL value, impedance matching ratio, and EM parameters of disordered CW and NiCo₂O₄@CW samples demonstrated

![Fig. 3 SEM images of (a) V-CW, (b) H-CW, (c) V-NiCo₂O₄@CW, and (d) H-NiCo₂O₄@CW.](image-url)
similar laws (Figs. S7 and S8 in the ESM). The sample of H-NiCo$_2$O$_4$@CW composites exhibited excellent EMW absorption capabilities with the NiCo$_2$O$_4$, distributed in through-channel arrangement horizontally. As observed from Fig. 4(c), the sample of H-NiCo$_2$O$_4$@CW reaches a strong absorption intensity of $-64.02$ dB at 10.72 GHz with the thickness of 3.62 mm, and the corresponding EAB value is 6.08 GHz (8.48–14.56 GHz). In particular, the maximum EAB value for the sample is 8.08 GHz (9.92–18.0 GHz) at the thickness of 3.2 mm, the super-wide EAB value could cover the entire Ku-band and the most X-band. We compare the performance of the H-NiCo$_2$O$_4$@CW sample to some similar materials reported in previous reports, the result is shown in Table 1. The excellent performance of RL, EAB, and thickness value clearly demonstrates the natural wood- derived carbon has great potential for MA. Unsurprisingly, the H-NiCo$_2$O$_4$@CW exhibits superior impedance matching at 2–5.5 mm thicknesses range with $Z_{in}/Z_0$ values between 0.75 and 1.25 in the 5–18 GHz range (Fig. 4(a)). Moreover, it is obvious that the RL peaks move to the lower frequency region as the thickness increased. This result can be explained by quarter-wavelength attenuation law, which means that when the absorber reaches the matching thickness ($t_m$), the reflected waves derived from the upper and bottom interface are out of phase by 180° and completely cancel each other in the air-absorber interface [30]:

$$t_m = \frac{n \lambda}{4} = \frac{nc}{4f\sqrt{\mu\varepsilon}} \quad (n = 1, 3, 5, \ldots)$$

where $t_m$ is the matching thickness and $\lambda$, $f$, and $c$ represent the wavelength, frequency, and velocity of the microwave, respectively. Obviously, the $t_m$ values of the H-NiCo$_2$O$_4$@CW are basically consistent with the curve of quarter-wavelength attenuation model. What’s more, by comparing the values of the $|Z_{in}/Z_0|$ and RL curve, the close correlation between them can clearly be found, that is, the closer the value of $|Z_{in}/Z_0|$ is to 1, the greater the RL value.

Generally speaking, the MA properties are not only controlled by impedance matching characteristics, but also affected by the attenuation energy capacity. Attenuation capacity is explained by that EMW is converted into other forms of energy inside absorber.

Fig. 4  (a) RL value, impedance matching ratio, actual thickness $t_m^{exp}$, and calculated thickness $t_m$ for H-NiCo$_2$O$_4$@CW; (b) 3D RL value and (c) contour map of H-NiCo$_2$O$_4$@CW.

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Table 1 MA performance of some porous carbon-based materials

| Sample                      | Filling ratio (wt%) | RLmin (dB)/thickness (mm) | EABmax (GHz) | Reference |
|-----------------------------|---------------------|---------------------------|--------------|-----------|
| PBPC\(^a\)                 | —                   | −68.3/4.28                | 7.63         | [15]      |
| NiCo\(_2\)S\(_4\)/C       | 50                  | −64.7/1.91                | 5.26         | [12]      |
| FeCo/C@WC\(^b\)           | 85                  | −47.6/1.5                 | 8.9          | [31]      |
| CoFe/BPC\(^c\)            | —                   | −53.6/2.2                 | 2.7          | [32]      |
| Fe\(_3\)N alloy/carbon     | 40                  | −65.6/2.05                | 6.76         | [33]      |
| Shaddock peel-based aerogel| 20                  | −29.5/0.3                 | 5.80         | [34]      |
| Co–CoFe\(_2\)O\(_4\)/PCHMs\(^d\) | 12.5            | −65.31/2.1                | 8.48         | [35]      |
| Ni/NiO@C                   | 20                  | −51.1/2.4                 | 5.12         | [36]      |
| H-NiCo\(_2\)O\(_4\)/CW     | 26                  | −64.0/3.62                | 8.08         | This work |

\(^a\)PBPC: porous biomass-pyrolyzed carbon.  
\(^b\)WC: wood carbon aerogel.  
\(^c\)BPC: biomass porous carbon.  
\(^d\)PCHMs: mesoporous hollow carbon spheres.

due to the existence of various loss mechanisms, such as conductivity loss, polarization loss, natural resonance, or eddy current loss, calculated as the attenuation constant (\(\alpha\)) [37]:

\[
\alpha = \frac{\sqrt{2\pi}}{c} \sqrt{\left(\mu'\varepsilon - \mu''\varepsilon\right) + \sqrt{\left(\mu'\varepsilon - \mu''\varepsilon\right)^2 + \left(\mu'\varepsilon + \mu''\varepsilon\right)^2}} (4)
\]

From Fig. 5(a), it can be observed that the H-NiCo\(_2\)O\(_4\)/CW sample shows the largest \(\alpha\) values, almost above 100 in the 2–18 GHz frequency range, indicating the stronger microwave attenuation ability of the H-NiCo\(_2\)O\(_4\)/CW sample than that of the other three samples, resulting in the NiCo\(_2\)O\(_4\) distributed in through channels arranged horizontally. In addition, as a whole, the introduction of NiCo\(_2\)O\(_4\) promoted the increase in attenuation capacity.

In order to explain the MA mechanisms of as-prepared materials, the complex permittivity (\(\varepsilon'\), \(\varepsilon''\)), permeability (\(\mu'\), \(\mu''\)), dielectric tangent loss (\(\tan\delta_e = \varepsilon''/\varepsilon'\)), and magnetic tangent loss (\(\tan\delta_m = \mu''/\mu'\)) are shown in Fig. 6. The real parts (\(\varepsilon'\) and \(\mu'\)) represent the stored capability of electric and magnetic energy while the imaginary parts (\(\varepsilon''\) and \(\mu''\)) represent the dissipated capability of electric and magnetic energy. \(\tan\delta_e\) and \(\tan\delta_m\) represent dielectric and magnetic loss capacities of the absorber, respectively [38]. From Figs. 6(a) and 6(b), it is observed that the \(\varepsilon'\) and \(\varepsilon''\) values of the H-NiCo\(_2\)O\(_4\)/CW are larger than that of the other three samples, and possess a decreased trend as the frequency increases, which is attributed to the increased polarization hysteresis versus the higher frequency electric-field variation [39]. As for V-NiCo\(_2\)O\(_4\)/CW sample, its \(\varepsilon'\) and \(\varepsilon''\) values are slightly higher than that of V-CW and H-CW, and basically do not change with the increase of frequency, showing a horizontal line relative to the frequency. The \(\varepsilon'\) values of V-CW and H-CW are the lowest, stay near 2, and do not change with frequency, and the \(\varepsilon''\) values behave the same trend as \(\varepsilon'\). The calculated \(\tan\delta_e\) of all samples are depicted in Fig. 6(c). The curve of \(\tan\delta_e\) value for the H-NiCo\(_2\)O\(_4\)/CW sample shows a trend of small fluctuations between 0.4 and 0.6, and the values are clearly higher than the other samples. As for other three samples, the trend of \(\tan\delta_e\) value is similar to that of \(\varepsilon''\) results, shown in Fig. 6(b). The H-NiCo\(_2\)O\(_4\)/CW sample presents the largest \(\tan\delta_e\) value in 2–18 GHz frequency range compared with the other samples, demonstrating the best dielectric loss performance.

Generally speaking, the dielectric loss is closely associated with conductive loss and polarization loss, and the conductive loss lies on the electrical conductivity [40]. The introduction of NiCo\(_2\)O\(_4\) could effectively enhance the conductive loss resulted from the high electrical conductivity. In detail, the NiCo\(_2\)O\(_4\) hybrid uniformly distributed in the through channels formed by amorphous carbon, which allows the NiCo\(_2\)O\(_4\)/CW composites to form an efficient conductive network; this deduction could be confirmed by the \(\varepsilon''\) curves of as-prepared samples, and the \(\varepsilon''\) values of NiCo\(_2\)O\(_4\)/CW composites are larger than that of single CW. Simultaneously, the H-NiCo\(_2\)O\(_4\)/CW sample displays the strongest conductive loss capacity, and the conductivity of all samples shown in Fig. S9 in the ESM could prove the above points. The polarization
loss comes from atomic polarization, electron polarization, dipole polarization, and interfacial polarization [41]. The atomic polarization and electron polarization could be eliminated firstly, because these two polarizations could only appear at higher frequency range. The dielectric loss for as-prepared samples should be mostly ascribed to the dipole polarization, which can be explained by the Cole–Cole model [42–44]:

\[
\varepsilon' = \varepsilon' - j\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + 2\pi f \tau}
\]

where \(\varepsilon_s\), \(\varepsilon_\infty\), \(f\), and \(\tau\) stand for the static dielectric constant, the dielectric constant at infinite frequency, the frequency relaxation time, and the polarization relaxation time, respectively. And then the \(\varepsilon'\) and \(\varepsilon^*\) can be expressed as

\[
\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (2\pi f)^2 \tau^2}
\]

\[
\varepsilon^* = \frac{2\pi f \tau (\varepsilon_s - \varepsilon_\infty)}{1 + (2\pi f)^2 \tau^2}
\]

Consequently, the relationship between \(\varepsilon'\) and \(\varepsilon^*\) can be depicted as

\[
\left(\varepsilon' - \frac{\varepsilon_s + \varepsilon_\infty}{2}\right)^2 + (\varepsilon^*)^2 = \left(\frac{\varepsilon_s - \varepsilon_\infty}{2}\right)^2
\]
loss for NiCo$_2$O$_4$@CW hybrid composites should not mainly come from the Debye dipolar relaxation, and the conductive loss and interfacial polarization should play a dominant role in dielectric loss.

Figures 6(d) and 6(e) present the changes of complex permeability in the frequency range of 2–18 GHz for the H-NiCo$_2$O$_4$@CW and V-NiCo$_2$O$_4$@CW samples. The $\mu'$ and $\mu''$ slightly fluctuated with frequency, and varied in the range of 0.90–1.05 and 0–0.17, respectively. Meanwhile, the values of the calculated magnetic loss tangent $\tan\delta_m$ of these two samples were depicted in Fig. 6(f), the values are almost below 0.2, and there is no obvious resonance peak appearing on the curves, which means that the magnetic loss does not contribute much to the MA performance. In general, magnetic loss mainly results from natural resonance, exchange resonance, and eddy current loss in the microwave frequency bands [47].

Here, the low-frequency resonance is mainly assigned to the natural resonance, while the exchange resonance almost takes place at higher frequencies [48]. The eddy current loss effect could be demonstrated by the $C_0$ curve [49]:

$$ C_0 = \frac{\mu''}{(\mu')^2 f} \tag{9} $$

If the eddy current loss is the dominated factor for the magnetic loss, the value of $C_0$ should be a constant, which makes the $C_0$ value appear as a horizontal line in $C_0$–$f$ curve. As shown in Fig. 5(b), in 2–7 GHz

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Fig. 6 EM parameters of samples: (a) real part $\varepsilon'$ and (b) imaginary part $\varepsilon''$ of permittivity, (c) dielectric loss $\tan\delta_z$, (d) real part $\mu'$ and (e) imaginary part $\mu''$ of permeability, and (f) magnetic loss $\tan\delta_m$. 
frequency range, the noticeable resonance peaks can be detected, which is assigned to natural resonance. The $C_0$ curve of H-NiCo$_2$O$_4$@CW nearly never changed in the frequency range of 7–18 GHz, while a tiny resonance peak was found in the $C_0$ curve of V-NiCo$_2$O$_4$@CW at 10.5 GHz. The huge difference of MA performance between H-NiCo$_2$O$_4$@CW and V-NiCo$_2$O$_4$@CW samples is discovered in Fig. 4 and Fig. S6(c) in the ESM, while the magnetic parameters of them behave basically similar, which implies that the dielectric loss controlled by microstructure and composition is the main influence factor on absorbing EMW.

In order to explore the influence of the arrangement direction of ordered channels on the performance of MA, the two channel arrangement directions of NiCo$_2$O$_4$@CW composite were constructed as simplified models for finite element analysis (FEA) simulation. The simplified model of V-NiCo$_2$O$_4$@CW is demonstrated in Fig. 7, with the channel diameter and channel wall thickness set to 10 and 3 $\mu$m, respectively, which is derived from the SEM pictures of actual structure shown in Figs. 3(c) and 3(d). In addition, the inside of the channels is filled with paraffin wax, and the section to be explored is marked in the model diagram. The frequency parameter of the simulation calculation process was set to 10.72 GHz. The time-average power flow ($p_{oav}$) of section 1 and section 2 are shown in Figs. 7(b) and 7(c). The $p_{oav}$ can be regarded as the propagation path and energy distribution of EMW inside the material, which is reflected in the direction and size of $p_{oav}$ arrow. Obviously, the vertical channel is less obstructive to the EMW, and the EMW can easily pass through the channel without sufficient interaction with the material. Furthermore, Figs. 7(d)–7(f) prove that V-NiCo$_2$O$_4$@CW composite has little attenuation ability to EMW. As for H-NiCo$_2$O$_4$@CW, the transmission direction and intensity of EMW change significantly near the channel walls (Fig. 8(b)), which indicates that the material has an effective interaction with microwave, due to multiple reflection and scattering caused by ordered porous structure. Simultaneously, as shown in Figs. 8(c)–8(e), strong dielectric loss occurs near the channel walls, resulted from the high-efficiency conductive network formed by CW decorated with NiCo$_2$O$_4$ hybrids and polarization relaxation. It is worth noting that the intensity distributions of total loss power density (Fig. 8(c)) and dielectric loss power density (Fig. 8(d)) are very similar and the intensity of magnetic loss power density (Fig. 8(e)) is extremely low compared to dielectric loss power density. In other words, the contribution of magnetic loss to MA is extremely small compared to dielectric loss, and this result is consistent with the previous analysis of EM parameters.

![Fig. 7](image_url)  
Fig. 7 FEA simulation of V-NiCo$_2$O$_4$@CW. (a) Schematic diagram of simplified model and section position, (b) time-average power flow $p_{oav}$ (W·m$^{-2}$), (c) time-average power flow $p_{oav}$ (W·m$^{-2}$) in section 2, (d) total loss power density $Q$ (W·m$^{-3}$), (e) dielectric loss power density $Q_e$ (W·m$^{-3}$), and (f) magnetic loss power density $Q_m$ (W·m$^{-3}$) in section 1.
In summary, the possible MA mechanism of the H-NiCo$_2$O$_4$@CW hybrid composites is described in Fig. 9. Firstly, the NiCo$_2$O$_4$ hybrids infiltrated into a large number of carbon atoms are uniformly distributed

Fig. 8  FEA simulation of H-NiCo$_2$O$_4$@CW. (a) Schematic diagram of simplified model and section position, (b) time-average power flow $p_{oav}$ (W·m$^{-2}$), (c) total loss power density $Q$ (W·m$^{-3}$), (d) dielectric loss power density $Q_e$ (W·m$^{-3}$), and (e) magnetic loss power density $Q_m$ (W·m$^{-3}$) in section 1.

Fig. 9  Schematic illustration for the EMW absorption of H-NiCo$_2$O$_4$@CW.
on the wall of the ordered channels, resulting in that the conductivity of the material is effectively enhanced, so that the 3D conductive skeleton derived from natural wood would promote the electron transportation and improve the dielectric loss ability. Secondly, the interface between carbon and NiCo$_2$O$_4$ would form non-uniform charge distribution and interfacial polarization loss because of the difference of electrical conductivity. Thirdly, the presence of defects within the amorphous carbon and NiCo$_2$O$_4$ hybrids would serve as the polarization centers to induce the multiple reflection and scattering processes. Fourthly, the magnetic loss including natural resonance and eddy current loss should also contribute to the MA property to a slight extent. Therefore, benefiting from the matched impedance and the enhanced attenuation constant, the CW with horizontally ordered channels decorated by cone-like NiCo$_2$O$_4$ hybrids (H-NiCo$_2$O$_4$@CW) exhibit the outstanding MA performance.

4 Conclusions

This work reported a wood-derived carbon-based material with ordered channels decorated by NiCo$_2$O$_4$ hybrids, which is manufactured through a facile, low-cost, and sustainable method with outstanding EMW absorption performance. The combination of 3D carbon skeleton with horizontal ordered channels derived from natural wood and NiCo$_2$O$_4$ hybrids together enable multiple EMW loss mechanisms to be effectively realized, resulting in the matched impedance and the enhanced attenuation constant. The horizontal arrangement of the through channels of NiCo$_2$O$_4$@CW (H-NiCo$_2$O$_4$@CW) exhibits a strong reflection loss value of $-64.0$ dB at 10.72 GHz with a thickness of 3.62 mm and a low filling ratio of 26\%, and the EAB is 8.08 GHz (9.92–18.0 GHz) at the thickness of 3.2 mm. The result of FEA simulation confirms that the horizontal arrangement of ordered channels allows the material to interact effectively with EMW, thereby obtaining excellent MA property. This research provides a facile and novel strategy for using CW to fabricate advanced microwave absorbers with light weight and strong attenuation capabilities.

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Electronic Supplementary Material

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