

Hyper-crosslinked Conjugated Microporous Polymers with Increased Micropores Promotes Confining Polymerization for Electromagnetic Absorption Application

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Electronic Supplementary Information

Abstract Conjugated microporous polymers have excellent skeleton structures but poor electrical conductivity limits their applications in microwave absorption. To solve this problem, a strategy of molecular expansion and confining polymerization is proposed in this work to synthesize conductive hyper-crosslinked conjugated microporous polymer. The topology of the conjugated microporous polymer is changed into a three-dimensional skeleton structure with high specific surface area by using molecular expansion technique, and the controlled growth of polypyrrole in the channel constructs a unique network structure. The balance of excellent composite backbone structure, proper conductivity, attenuation capability and impedance matching enable the material to exhibit electromagnetic wave absorption performance. As a result, with low filler loading of 10 wt%, a strongest reflection loss of −52.68 dB and a maximum effective bandwidth of 5.76 GHz. Additionally, CST simulations of the radar scattering cross section have been carried out to verify the excellent material properties. This study provides new concepts for new conductive polymers and broadens the application of hyper-crosslinked conjugated microporous polymer in the field of electromagnetic wave absorption.

Keywords Hyper-crosslinked conjugated microporous polymer; Electromagnetic wave absorbing; Molecular expansion; Polypyrrole

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INTRODUCTION

The rapid development of modern electronic technology and the widespread use of various types of electronic devices have generated increasingly serious electromagnetic radiation, which poses a great threat to the health of humans as well as living creatures on earth.^[1–3] In order to meet this challenge, various high-performance electromagnetic wave absorption (EMA) materials are gradually being explored, such as carbonaceous materials include graphene,^[4] carbon nanotubes,^[5] and carbon fibers;^[6] magnetic materials include carbonyl iron,^[7] core-shell α -Fe₂O₃@CoFe₂O₄,^[8] NiCu alloys,^[9] and mixtures of them.^[10–12] Organic polymers offer unique advantages over these conventional inorganic fillers in terms of porous skeletal structure, high chemical stability, low density and ease of

functionalization.^[13–16] Unfortunately, due to their insulating properties, they cannot be used as excellent electromagnetic materials.^[17] Theoretically, the EMA properties of a material are closely related to its microscopic skeleton structure, electrical and magnetic permeability, filler ratio, impedance matching and magnetic permeability.^[18,19] Therefore, giving an insulator the right electrical conductivity may be an effective approach.

Conjugated microporous polymers (CMPs) are a class of porous polymers with a π -conjugated system mesh structure assembled by organic building blocks through covalent bonding.^[20–24] The unique π -conjugated backbone, high specific surface area, permanent pores, good stability, and powerful post-functionalization have attracted extensive interests from researchers.^[25] Along with the continuous research on CMPs, there is an urgent need for the composite of different functional materials and functionalized modifications in order to achieve higher requirements for the development of the field. Related attempts have been made by researchers, only to result in a significant decrease in the specific surface area and pore number of the polymer.^[26–29] Therefore, it is necessary to find a suitable method to achieve the

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increase of specific surface area and pore optimization of polymers. Recently, Shang *et al.* prepared novel hyper-cross-linked conjugated microporous polymers (HCCPs) with tunable specific surface area and pore capacity based on covalent organic backbones (COFs) with 1,4-bis(chloromethyl)benzene and 4,4'-bis(chloromethyl)-biphenyl as expansion molecules by coupled Friedel-Crafts reaction.^[30] The results demonstrated that the process not only increased the specific surface area and total pore volume of the polymer by 2.56 and 4.68 times, respectively, but also improved the gas adsorption performance. Based on the porous skeleton and low electrical conductivity of HCCMPs, they exhibit excellent impedance matching for electromagnetic waves. When electromagnetic waves are shot in, they can easily enter the material, but the absorption performance is poor and cannot be applied to EMA.

As we all know, polythiophene,^[31] polyphenylene,^[32] polyaniline,^[33–35] and polypyrrole (PPy) are typical structural conductive polymers,^[36] which commonly used in microwave absorbing materials because of its strong conjugated π -electron system and ion doping with substantial conductivity. If a host-guest approach can be used to introduce conductive media into the massive pore channels of HCCMPs to control their growth.^[37] The pore encapsulation of conductive polymers necessarily confers increased electrical conductivity to the composite. What draws our attention even more is that the conducting polymers confined in the pores of HCCMPs exhibit completely different optoelectronic properties, which are attributed to quantum confinement effects.^[38] As a result, this strategy shows great potential for expansion.

To verify the feasibility of the above theory, the topological framework structure of CMP was firstly synthesized, and then multi-nanoporous HCCMP with the high specific surface area was formed by the swelling effect of external cross-linker. Notably, this approach changes the original 2D material into a skeletal sparse 3D material. Ultimately, the exogenous introduction strategy introduces PPy into the nanochannel and even extends it out to form a nano-coating. The conductive network formed by PPy imparts significant electrical conductivity to the composite. In addition, the properties of the composite can be tuned by modulating the mass ratio of pyrrole monomer/HCCMP. When absorbing more than 90% of the incident electromagnetic waves, a maximum bandwidth of 5.76 GHz is achieved with a thickness of only 2.3 mm, which is superior to pure PPy and PPy/CMP (direct confinement polymerization of polypyrrole by CMP without backbone expansion). This research provides new insights into new conductive polymers and significantly broadens the field of application of CMP.

EXPERIMENTAL

Chemicals and Materials

1,3,5-Tris(4-bromophenyl)benzene (97%, Energy), PdCl₂(dppf) (98%, Pd>14.5%, Energy), 4,4'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)biphenyl (98%, Energy), K₂CO₃ (98%, Energy), 4,4'-bis(chloromethyl)-1,1'-biphenyl (96%, McLean), 1,4-dioxane (99%, McLean), 1,2-dichloroethane (DCE, 99%, McLean), pyrrole (99%, McLean), ethanol (99.5%, Aladdin) (EtOH), acetone (99.8%, Aladdin), dichloromethane (DCM, 99.5%, Aladdin), methanol

(MeOH, 99.5%, Aladdin). All the purchased reagents and chemicals were used directly without further refinement.

Synthesis of CMP

A mixture of 1,3,5-tris(4-bromophenyl)benzene (1086.0 mg, 2.0 mmol), 4,4'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)biphenyl (1326.0 mg, 3.0 mmol), K₂CO₃ (2.0 mol/L in water, 5 mL) and PdCl₂(dppf) (73.2 mg, 0.1 mmol) in 1,4-dioxane (50 mL) was purged with N₂ and heated up to 90 °C for 72 h. After the mixture has cooled to room temperature, pour into 300 mL of water. The product is continuously precipitated, filtered and washed with water, ethanol, dichloromethane and acetone, followed by Soxhlet extraction with methanol for 3 days. After drying under vacuum at 60 °C, the product was obtained in grey powder form.^[39]

Synthesis of HCCMP

In 60 mL of DCE, CMP (500.0 mg) and 4,4'-bis(chloromethyl)-1,1'-biphenyl (625.0 mg, 2.5 mmol) were dispersed, then FeCl₃ (162.0 mg, 1.0 mmol) was added as catalyst. The mixture system was continuously stirred at 85 °C for 24 h under a nitrogen atmosphere. After that the mixture was cooled to room temperature and the solid product was washed with H₂O, EtOH and DCM, respectively. Then the solid product was extracted with methanol Soxhlet for 3 days. After drying in vacuum for 12 h at 80 °C, the orange loose powder product was obtained and named as HCCMP.^[20]

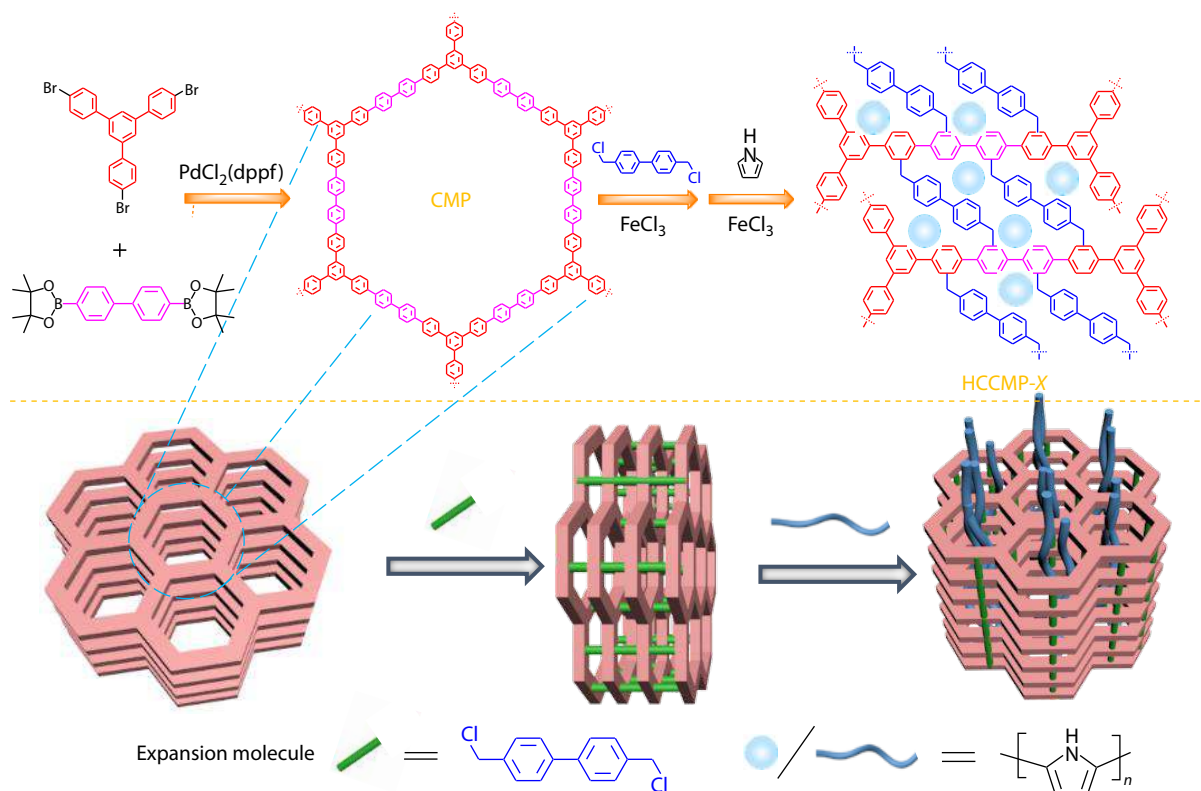
Synthesis of Conductive HCCMP-X

The synthesis of HCCMP-X is performed as follows. Taking HCCMP-1 as an example, 100 mg of HCCMP was ultrasonically dispersed in 50 mL of MeOH solution containing pyrrole monomer (100.0 mg). The solid-liquid mixture was then rotary evaporated to prepare a homogeneous blend of pyrrole/HCCMP. Precooled FeCl₃ (1 mol/L, 50 mL) aqueous solution added the pyrrole/HCCMP mixture and stirred for 4 h. The suspension was vacuum filtered to obtain a black filter cake, washed repeatedly with H₂O and EtOH and dried under vacuum to obtain CHCCMP-1. Varying the mass ratios of HCCMP and pyrrole monomer gave HCCMP-2, HCCMP-3, HCCMP-4 and HCCMP-5, corresponding to weight ratios of 1:3, 1:5, 1:7 and 1:10, respectively.

RESULTS AND DISCUSSION

Scheme 1 shows the synthesis procedures of conductive PPy/HCCMP composites. First of all, CMP with topological block structure was obtained by using Suzuki coupling reaction with simple operation and mature preparation process.^[39] To provide a broad site for propagation of polypyrrole, an exo-crosslinker (4,4'-bis(chloromethyl)-1,1'-biphenyl) was utilized to expand the spreading backbone in the CMP. The porous skeleton provides a large number of sites for the growth of PPy and also facilitates the entry of electromagnetic waves. Ultimately, PPy gradually polymerizes in the nanopore and extends to the exterior. With the increase of polypyrrole, aggregation into nanocoatings covers the surface. This strategy causes HCCMP and PPy to cross-link with each other, and PPy shuttled through the nanochannels to form a conductive network, which was observed in both SEM and TEM images.

Fig. S1 (in the electronic supplementary information, ESI)



Scheme 1 Schematic diagram of the synthesis process of HCCMP-X.

shows the scanning electronic microscopy (SEM) images of CMP and HCCMP. CMP exhibits an aggregation of indefinite nanoparticles, and HCCMP surface shows an irregular coating and a distinct porous skeletal structure, indicating effective molecular expansion support. When PPy is introduced, the extended PPy fibers can be observed on the surface of PPy/HCCMP composites. As the mass ratio of PPy and HCCMP increases, more of its surface is coated with PPy nanoparticles aggregated (Figs. S2a–S2e in ESI). Due to the limited internal pores of the polymer, the pyrrole monomer will polymerize on the surface after the internal channels are filled to full capacity. Without the restriction of the cavity wall, it grows according to the neat PPy morphology, as shown in Fig. S2(f) (in ESI). Meanwhile, the corresponding samples were observed by transmission electron microscopy (TEM, Fig. 1 and Fig. S3 in ESI). It is noteworthy that the distribution of PPy nanofibers can be observed in all five samples and show an increasing trend. For HCCMP-1, scattered several short PPy nanofibers were distributed in the HCCMP (Fig. 1a). When the mass ratio of PPy and HCCMP increases, clusters of concentrated accumulation of PPy nanofibers appear in HCCMP-2, HCCMP-3 and HCCMP-4 (Figs. 1b–1d). When the content of PPy continued to increase, the directional growth and cross-extension of PPy nanofibers appear in HCCMP-5 (Fig. 1e), forming a distinct network structure. SEM and TEM results both confirm the microstructure of the composite, the large number of pores and the loose backbone are essential for the introduction of PPy nanofibers.

The structure of the polymer was verified using FTIR spectroscopy and solid-state ^{13}C -NMR spectra. As shown in Fig. 2(a), HCCMP generates a new characteristic band around

2910 cm^{-1} , which is attributed to the C—H stretching vibration of the methylene group.^[40,41] Meanwhile, the intensity of the characteristic band of its benzene ring structure at the vicinity of 3030 cm^{-1} becomes weaker with respect to the original CMP. In comparison to the original CMP, the absorption band at 810 cm^{-1} for the C—H adjacent to the benzene ring was significantly lower, demonstrating that the H on the *para*-substituted benzene ring was mainly replaced by methylene during the exo-crosslinker expansion. Furthermore, the observation that the absorption bands of PPy/HCCMP composites with different mass ratios almost coincide with those of PPy confirms the presence of PPy. As seen in Fig. 2(b), the characteristic peaks at 27 and 40 ppm of the original CMP are attributed to the methyl and quaternary carbons of the coupling monomer 4,4'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)biphenyl, respectively. HCCMP shows a significantly enhanced absorption peak at 40 ppm compared to CMP. The enhancement of this absorption peak is attributed to the carbon atom of methylene produced by molecular expansion. The displacement of the aromatic carbon at 120–145 ppm did not change significantly before and after material expansion bracing, but the proportion of substituted aromatic carbon atoms ($\sim 130\text{ ppm}$) on the HCCMP backbone was significantly higher compared to that of nonsubstituted aromatic carbon atoms ($\sim 125\text{ ppm}$). This phenomenon is attributable to the increase in the proportion of substituted aromatic carbon atoms due to molecular expansion. The results of FTIR spectroscopy and solid-state ^{13}C -NMR spectra together confirmed the accuracy of the material. The XRD spectra of the polymers are given in Fig. 2(c). No significant peak appears for HCCMP and one peak packet appears for PPy in the range of

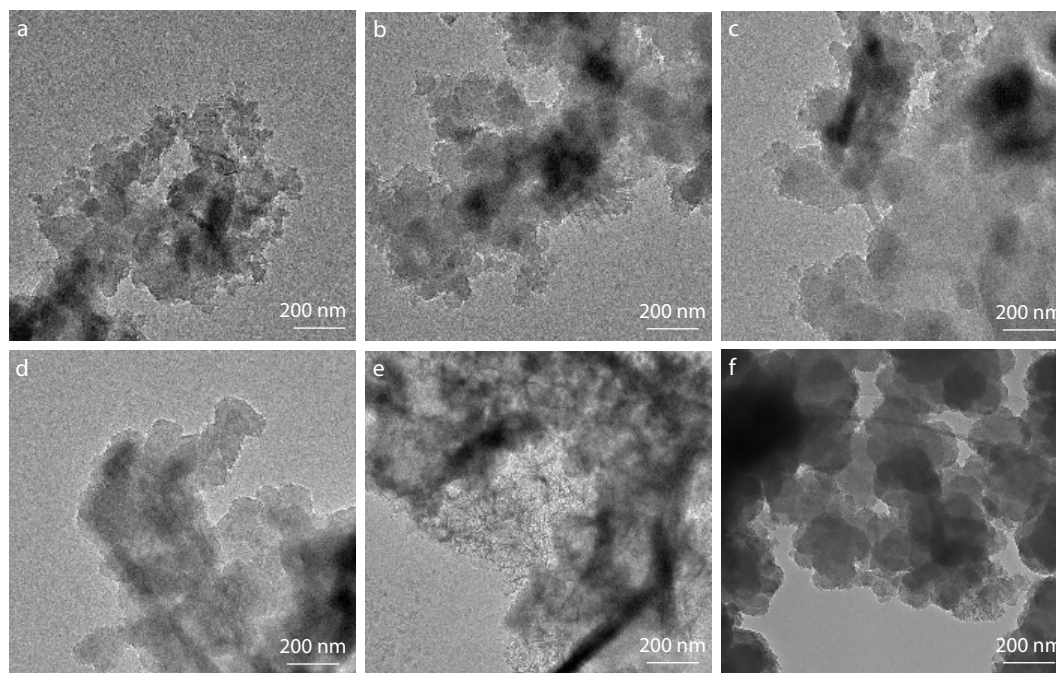


Fig. 1 TEM images of (a) HCCMP-1, (b) HCCMP-2, (c) HCCMP-3, (d) HCCMP-4, (e) HCCMP-5, (f) PPy.

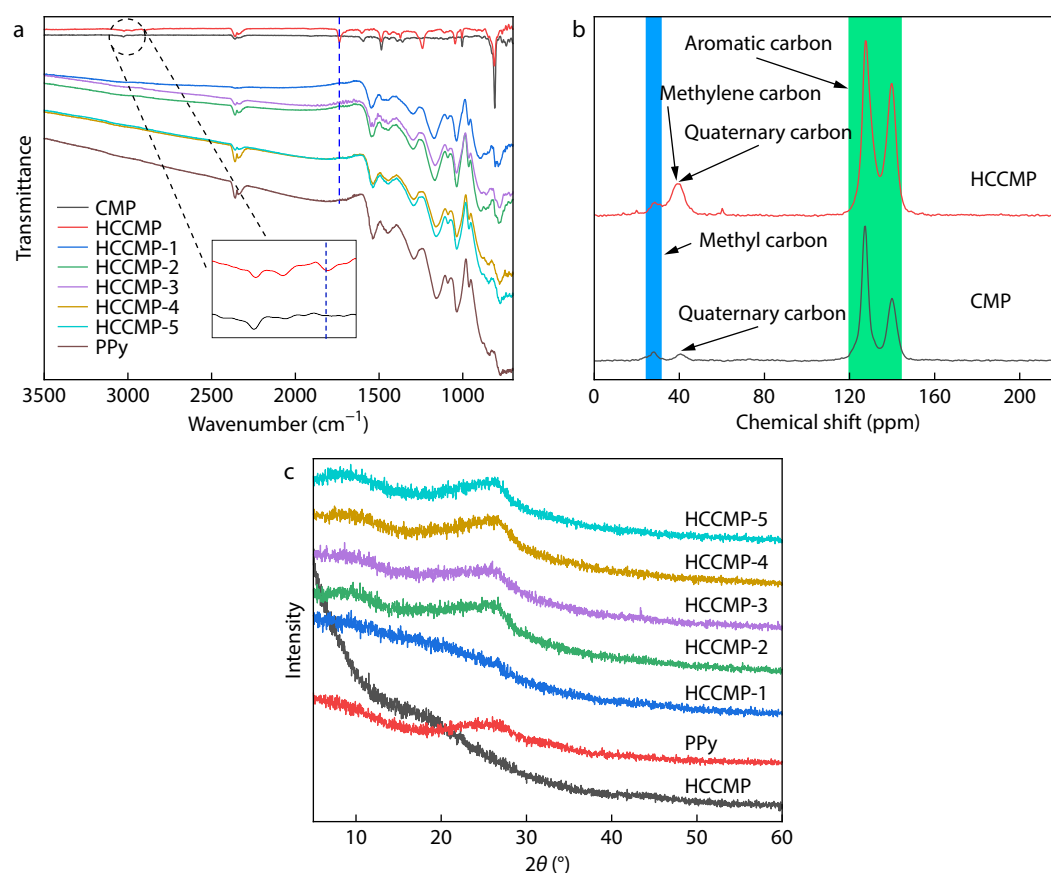


Fig. 2 (a) FTIR spectra of various polymers; (b) Solid-state ^{13}C -NMR spectra of CMP and HCCMP; (c) XRD patterns of various polymers.

20° – 30° , both indicating their amorphous structure. After loading PPy, HCCMP-1 did not show a peak packet due to low loading, while HCCMP-2, HCCMP-3, HCCMP-4 and HCCMP-5

showed a peak packet that largely coincided with PPy. In addition, Fig. S4 (in ESI) shows the thermogravimetric analysis of some of the samples. HCCMP exhibited excellent thermal sta-

bility, however, the stability of the composites decreased with the increase of the PPy/HCCMP mass ratio.

The specific surface area and pore size changes during the synthesis of the composites were investigated by adsorption-desorption experiments. A composition of type I and IV isotherms is shown in Fig. 3(a). The type I isotherm exhibits a rapid increase in adsorption at lower relative pressures, indicating the presence of a large number of micropores.^[42] The latter section of the type IV isotherm bulges again and an adsorption hysteresis loop appears in the middle section.^[43] The Brunauer-Emmett-Teller (BET) surface areas of CMP and HCCMP are 63.89 and 1426.70 m²/g, respectively. It demonstrates that molecular expansion strategy is very effective in recasting the skeleton. Remarkably, BET plummeted to 237.25 m²/g (HCCMP-3) and 184.95 m²/g (HCCMP-5) when the HCCMP was filled with PPy. It is indicated that PPy preferentially grows in the nanochannels and that the BET gradually decreases as the PPy/HCCMP mass ratio increases. From the pore size distribution curves in Fig. 3(b), a large number of microporous and mesopores were added to the HCCMP compared to the original CMP. The pores of HCCMP-3 and HCCMP-5 were substantially reduced after loading with PPy, which also followed the pattern of BET changes.

To further research the elemental composition, content and chemical bonding changes during the synthesis process, X-ray photoelectron spectroscopy (XPS) curves provided relevant information (Fig. 4). Fig. 4(a) concentrates on the full spectra of the three samples. The comparison shows the presence of the new element N in HCCMP-3 and HCCMP-5, indicating the successful introduction of PPy. The peak with a

binding energy of 284.8 eV was assigned to the C=C of the benzene ring or the C—C of the benzene ring side chain. The peaks which centred on a binding energy of 287 eV were derived from C=N or C—N in the pyrrole ring (Figs. 4c and 4d). In addition, the percentage elemental contents of all samples are summarized in Table S1 (in ESI). The progressive increase in PPy content from HCCMP to HCCMP-5 further illustrates the adjustable conductivity of the composites.

According to prior efforts,^[44,45] the reflection loss value (RL) is a crucial indicator for evaluating the EMA properties of a material. Eqs. (1) and (2) for calculating RL values are presented in transmission line theory.^[46]

$$Z_{in} = Z_0 \sqrt{\frac{\mu_y}{\epsilon_y} \tanh \left(j \frac{2\pi f d \sqrt{\mu_y \epsilon_y}}{c} \right)} \quad (1)$$

$$RL \text{ (dB)} = 20 \log \left| \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \right| \quad (2)$$

where Z_{in} denotes input impedance, Z_0 refers to impedance of free space, and c , d and f correspond to the speed of light, absorber thickness and electromagnetic pulse frequency (EMP) frequency, respectively.

In Fig. 5, the EMA properties of HCCMP and PPy/HCCMP composites with different mass ratios are mainly investigated. It can be discovered that neat HCCMP has no EMA performance in the frequency range tested (Fig. 5a). When PPy is loaded into the HCCMP, it starts to develop positively. Figs. 5(b)–5(f) and Figs. S5(b)–S5(f) (in ESI) showed the 3D RL curves of PPy/HCCMP composites with different filling ratios and the RL at different thicknesses, respectively. Effective ab-

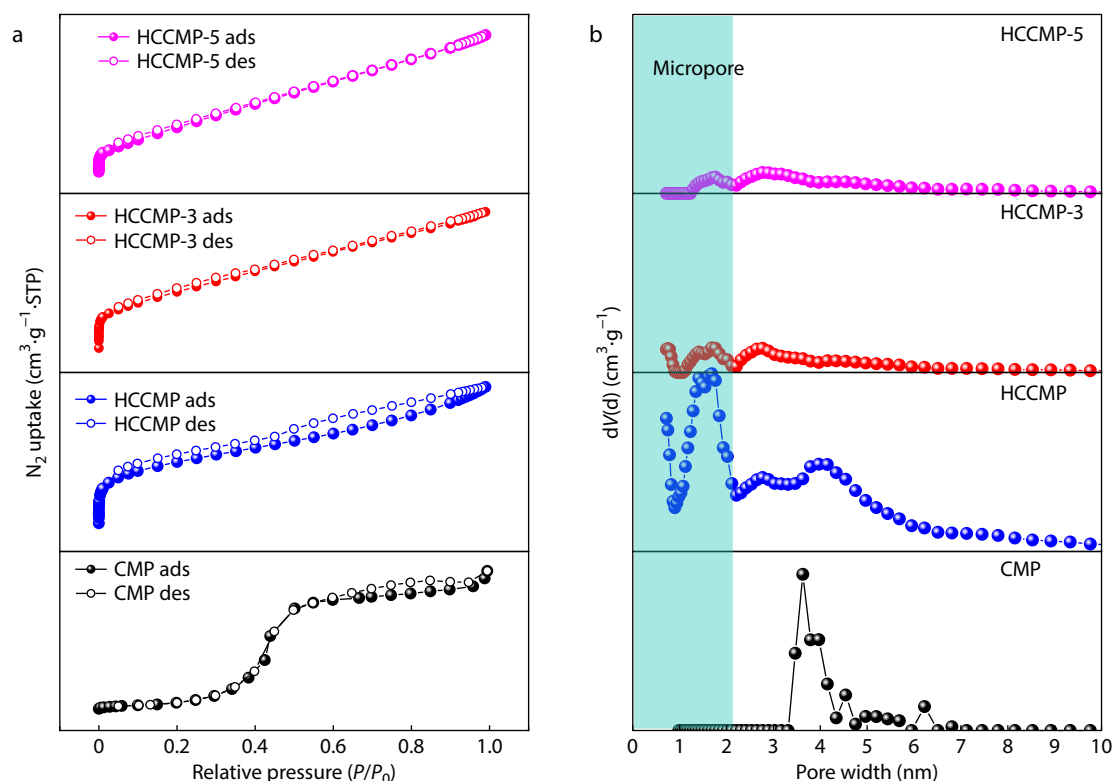


Fig. 3 (a) The N₂ adsorption-desorption isotherms of CMP, HCCMP, HCCMP-3 and HCCMP-5 were measured at −195.85 °C; (b) Pore size distributions of CMP, HCCMP, HCCMP-3 and HCCMP-5 calculated using density functional theory (DFT).

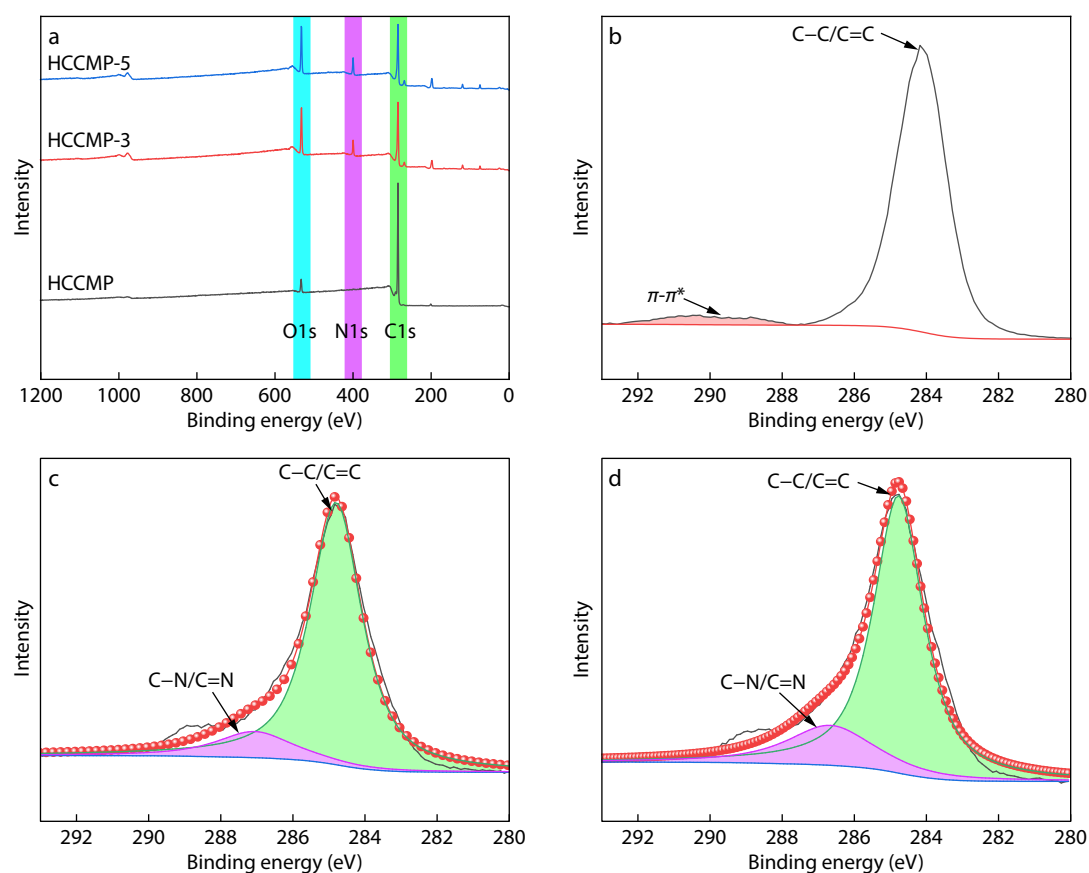


Fig. 4 XPS spectra: (a) total survey spectra of HCCMP, HCCMP-3 and HCCMP-5, (b) C 1s spectra of HCCMP, (c) C 1s core-level spectra of HCCMP-3, (d) C 1s core-level spectra of HCCMP-5.

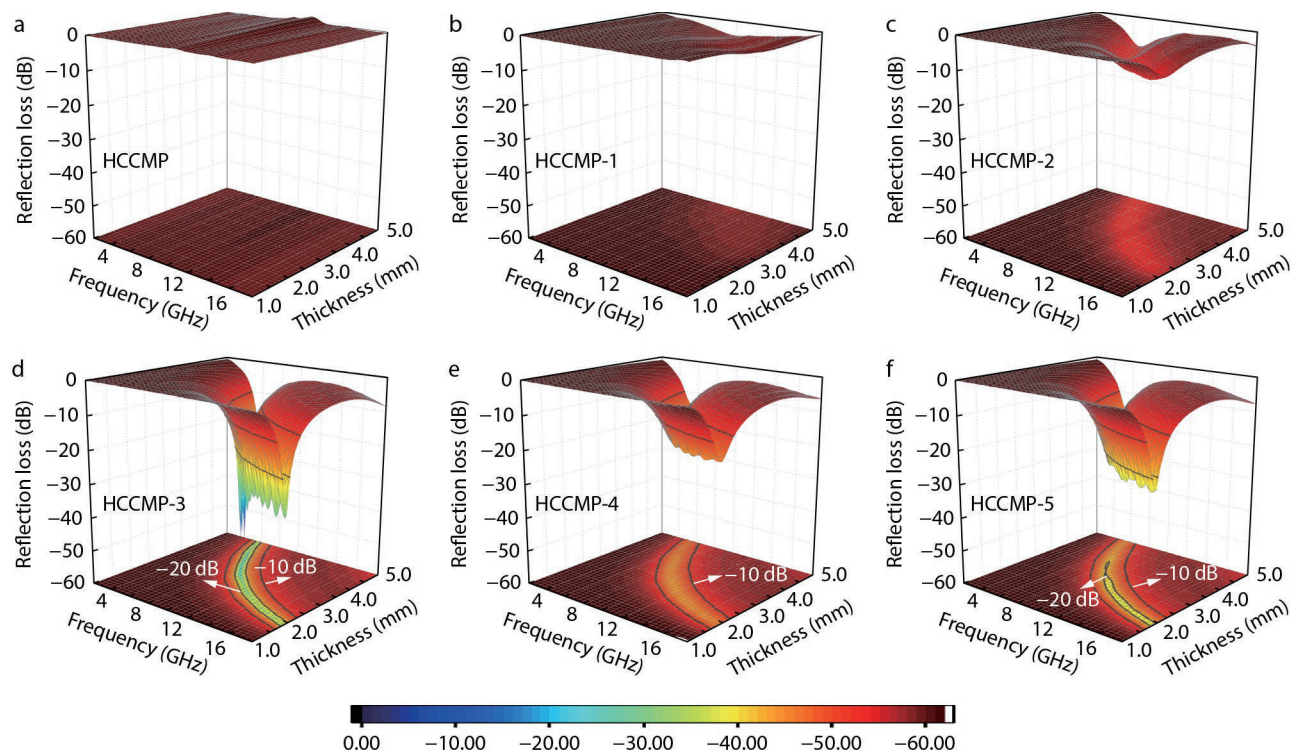


Fig. 5 3D RL of (a) HCCMP, (b) HCCMP-1, (c) HCCMP-2, (d) HCCMP-3, (e) HCCMP-4, (f) HCCMP-5 with 10 wt% filler-loading in wax.

sorption bandwidth (EAB) ($RL \leq -10$ dB) does not occur for HCCMP-1, HCCMP-2 between 2 and 18 GHz with 10 wt% paraffin fill ratio. Notably, the RL of HCCMP-3 reached -44.20 dB at 8.64 GHz with a thickness of 3.5 mm, and the EAB is 3.52 GHz (7.28–10.8 GHz) at the thickness of 2.3 mm with 10 wt% filler-loading in wax. Nevertheless, compounding too much PPy is not conducive to EMA performance. As shown in Fig. 5(e), the RL of HCCMP-4 decreases to -17.19 dB at 10.1 GHz with a thickness of 3.0 mm. In the last set of ratios, HCCMP-5 shown better EMA performance than HCCMP-4. The maximum EAB is 5.28 GHz (10.24–15.52 GHz) at the thickness of 2.3 mm with 10 wt% filler-loading in wax, even better than the HCCMP-3. Additionally, the EMA performance is much better than PPy under the same test conditions, which proves that our work has initially been confirmed (Figs. S6a and S6b in ESI). More significantly, PPy/HCCMP exhibits superior EMA performance compared to PPy/CMP prepared without molecular expansion under the same conditions of synthesis and testing (Figs. S6c and S6d in ESI). The above comparison of performance indicators between different samples demonstrates the excellent performance of our PPy/HCCMP composites and their reconcilability.

In order to optimize the performance conditions, the RL values of different thicknesses (1.0–5.0 mm) of HCCMP-3 were investigated at 5 wt%, 10 wt% and 15 wt% paraffin doping ratios, respectively. Figs. 6(a)–6(c) give a result that the maximum performance increases and then decreases as the pack-

ing ratio increases. 5 wt%, 10 wt% and 15 wt% Loaded samples show RL values of -5.45 dB (18 GHz, 2.5 mm, Fig. 6a), -42.20 dB (8.64 GHz, 3.5 mm, Fig. 6b), -17.58 dB (14.32 GHz, 2.0 mm, Fig. 6c), respectively. HCCMP-3 shows the best EMA performance at a filler loading of 10 wt%, probably attributed to its optimal conductive network and impedance matching. On the other hand, the RL absorption peak migrates from high to low frequencies as the thickness of the material increases. Consequently, the optimum performance can be achieved by regulating the thickness and filling ratio of the material. Fig. 6(d) illustrates the minimum RL ($RL_{\min}$) and maximum EAB ($EAB_{\max}$) of HCCMP-3. Specifically, the $RL_{\min}$ is -52.68 dB under a thickness of 3.9 mm and the $EAB_{\max}$ is 5.76 GHz under a thickness of 2.3 mm. It is worth noting that $EAB_{\max}$ is distributed between 11.76 and 17.52 GHz, covering almost the entire Ku-band. However, most of the reported materials of the same type are difficult to maintain such bandwidth and reflection loss intensity at such low thicknesses as shown in Table 1.^[47–53] The results confirm that conductive composites (PPy/HCCMP) have great potential in the field of electromagnetic wave absorption.

In order to dissect the EMA mechanism of conducting polymers, we first start with their dielectric properties. According to Debye's theory, the dielectric loss of absorbing materials is mainly attributed to their complex dielectric constants. The value of the complex permittivity ($\epsilon_r = \epsilon' - j\epsilon''$) depends on the real part (ϵ') and the imaginary part (ϵ''), and ϵ' and ϵ'' can be

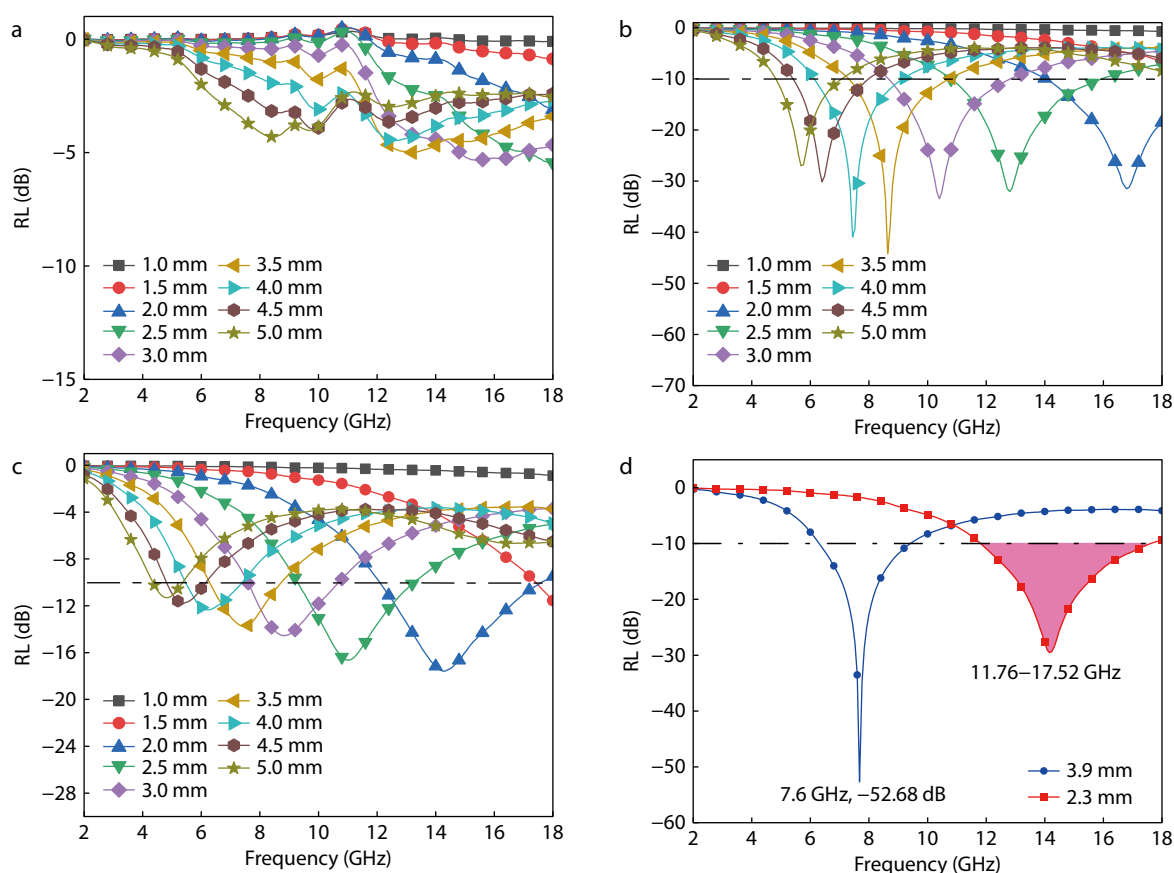


Fig. 6 The EMA performances of HCCMP-3 with the filler loadings of (a) 5 wt%, (b) 10 wt% and (c) 15 wt% in the frequency range of 2–18 GHz at different thicknesses; (d) The best EMA performances of HCCMP-3 with 10 wt% filler-loading in wax.

Table 1 The EMA performance of our absorber compared with other similar materials.

Typical materials	Thickness (mm)	EAB (GHz)	RL _{min} (dB)	Refs.
PPy/CoFe ₂ O ₄ /HGMs	2.58	4.02	−15	[47]
RGO/Fe ₃ O ₄ @PPy	2	5	−25.1	[48]
PPy@Fe ₃ O ₄ /CNTs	2.5	2.8	−51.8	[49]
Fe ₃ O ₄ @PPy	2.5	5.2	−31.5	[50]
rGO/CuS/PPy	2.5	4.88	−49.11	[51]
Fe ₃ O ₄ @PPy	2.5	5.12	−40.53	[52]
PPy/γ-Fe ₂ O ₃ /g-C ₃ N ₄	2.5	5.13	−53.66	[53]
HCCMP-3	2.3	5.76	−52.68	This work

calculated by the following equations:[54]

$$\epsilon' = \epsilon_{\infty} + \frac{\epsilon_s - \epsilon_{\infty}}{1 + \omega^2 \tau^2} \quad (3)$$

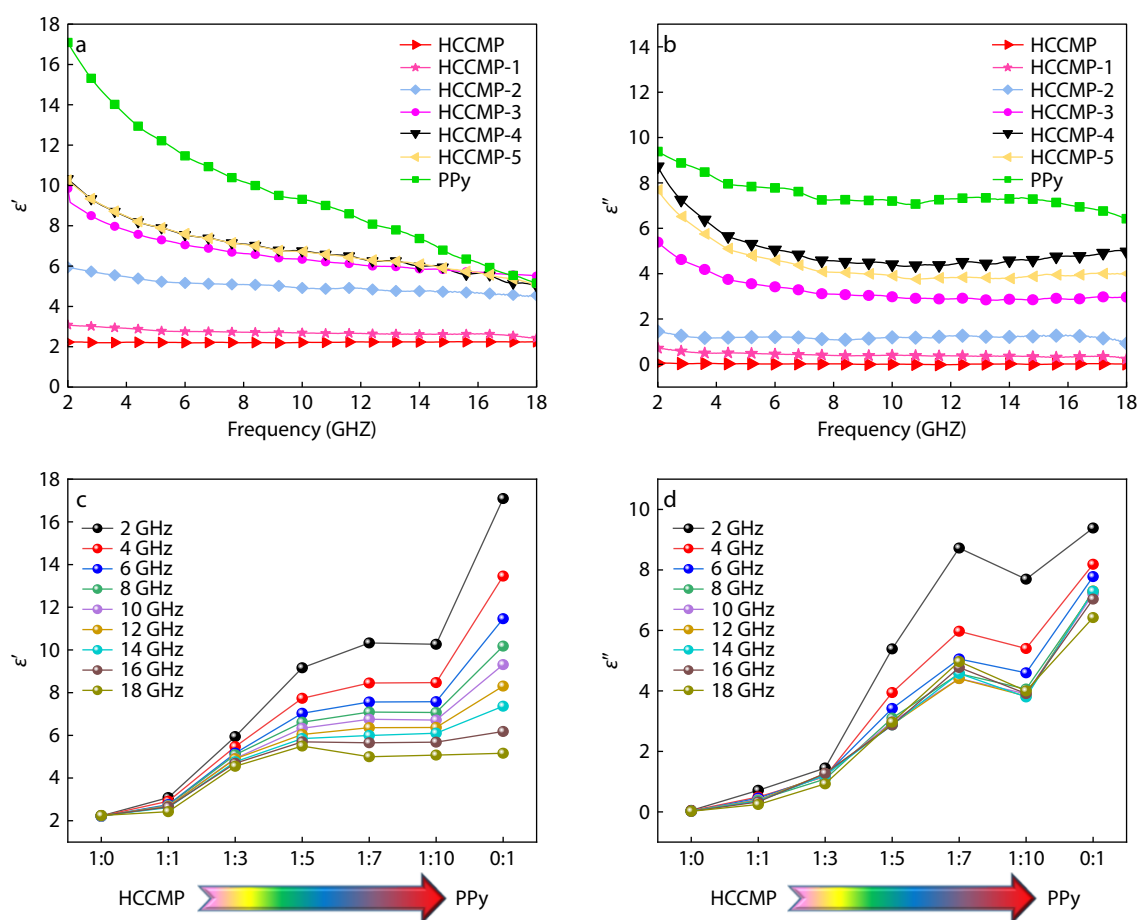
$$\epsilon'' = \frac{\epsilon_s - \epsilon_{\infty}}{1 + \omega^2 \tau^2} \omega \tau + \frac{\sigma}{\omega \epsilon_0} \quad (4)$$

where ϵ_s is static permittivity, ϵ_{∞} is the dielectric constant at infinite high frequencies. ω , τ , σ , ϵ_0 represent angular frequency, polarisation relaxation time, AC conductivity and dielectric constant in free space respectively.

Figs. 7(a) and 7(b) show the variation of ϵ' and ϵ'' curves for various samples in the range of 2–18 GHz. As the frequency increases, the values of ϵ' and ϵ'' show a gradual decrease. For a range of frequencies, the values of ϵ' and ϵ'' increase, then

decrease and then rapidly increase as the mass ratio of pyrrole monomer with HCCMP increases. The conductive composite reaches a maximum at a mass ratio of 1:7 of HCCMP to pyrrole monomer (Figs. 7c and 7d). Neat PPy shows excessively high values of ϵ' and ϵ'' , resulting in relatively poor EMA properties. In addition, the electromagnetic wave absorption loss mechanisms are mainly dielectric and magnetic losses and can be assessed by the magnitude of the dielectric loss tangent ($\tan \delta_{\epsilon} = \epsilon''/\epsilon'$) and the magnetic loss tangent ($\tan \delta_{\mu} = \mu''/\mu'$) respectively.[55] Based on the physicochemical properties of the composite, it is considered that the dielectric losses dominate. The dielectric loss of pure HCCMP is close to zero. After the introduction of PPy, the value of $\tan \delta_{\epsilon}$ in the conductive composite increases significantly and the dielectric loss is greatly enhanced, which may be attributed to the enhanced dielectric effect by the pore restriction effect (Fig. S7 in ESI).

According to Debye's theory, electromagnetic absorbing materials with multiple polarisation relaxation losses can generally be demonstrated by the $\epsilon' - \epsilon''$ curve, where a semicircle (Cole-Cole ring) proves the presence of polarisation losses.[56] As shown in Fig. 8(a), HCCMP-3 appears as several semicircles, which indicates the existence of multiple polarization relaxation. Compared to neat PPy, the PPy/HCCMP composite has a dual effect of dipolar and interfacial polarisation, showing several different semicircles (Fig. S8). Fig. 8(b) exhibits the

**Fig. 7** (a, c) The real parts of permittivity (ϵ'), (b, d) the imaginary parts of permittivity (ϵ'').

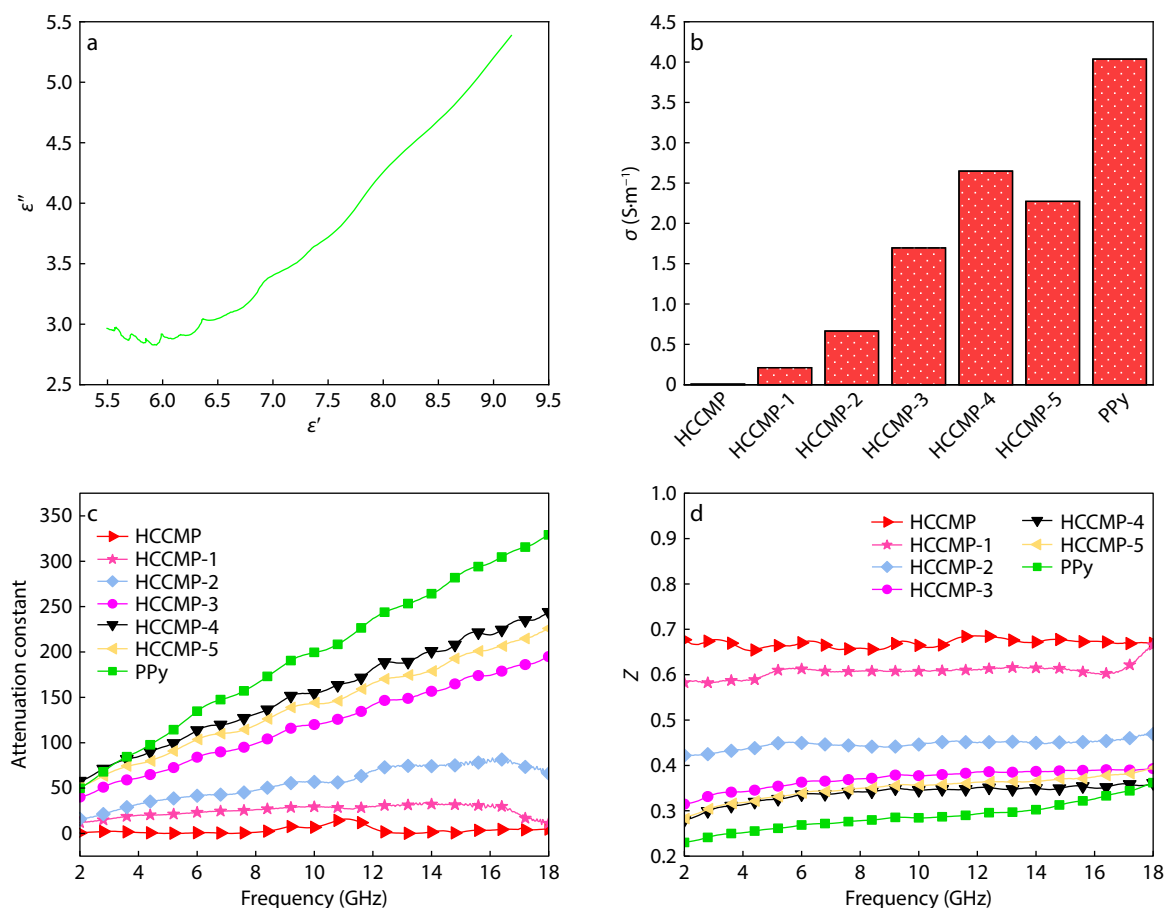


Fig. 8 (a) Cole-Cole semicircles of HCCMP-3, (b) electrical conductivity, (c) attenuation constant, (d) frequency dependences of impedance values.

electrical conductivity of the different samples. Excluding neat PPy, the conductivity of HCCMP-3 is the largest, while its EMA performance is not the best.

In order to further analyse the microwave absorption mechanism, the attenuation constant (α) and the impedance matching (Z) come to the fore as the main parameters, which can be interpreted as the following Eqs. (5) and (6):^[57]

$$6\alpha = \frac{\sqrt{2}\pi f}{c} \sqrt{(\epsilon''\mu'' - \epsilon'\mu') + \sqrt{(\epsilon''\mu'' - \epsilon'\mu')^2 + (\epsilon''\mu' + \epsilon'\mu'')^2}} \quad (5)$$

$$|Z| = \left| \frac{Z_{in}}{Z_0} \right| = \sqrt{\frac{\mu_r}{\epsilon_r} \tanh\left(\frac{2\pi jfd}{c} \sqrt{\epsilon_r \mu_r}\right)} \quad (6)$$

Compared to the original HCCMP, the conductive composite exhibits a multiplicative increase in α , following the same trend as the AC conductivity (Fig. 8c). The decay constant of HCCMP-3 is in the middle of the range and shows the best performance, indicating that the appropriate composite structure has an important influence on the performance parameters of the absorber. It is well known that the greater the ability of microwave absorbing materials to absorb incident microwaves when the value of Z is close to 1, which means maximum inhalation of incident waves. As the PPy content increases, the value of Z first decreases then increases and finally decreases (Fig. 8d). In terms of combined attenuation constants and impedance matching, the HCCMP-3 wins with its excellent composite parameters. The trend of

the attenuation constant is $HCCMP-2 < HCCMP-3 < HCCMP-4$, and the impedance matching is $HCCMP-2 > HCCMP-3 > HCCMP-4$. Hence, high performance microwave absorber materials, which need to be integrated with attenuation capability and impedance matching. In this work, HCCMP-3 as the best absorber stands out among many samples.

The two-layer structure model is designed according to the practical application requirements, where the upper layer is a 3.9 mm absorber layer for microwave absorption and the lower layer is a 2 mm perfect electrical conductivity (PEC) layer for simulating a metal backplane, as shown in Fig. 9(a). In the design, the model is placed in the x - o - y plane, with the z -axis being the direction of incidence of the plane wave and the x -axis being the direction of electrodeposition. In Fig. 9(b), a three-dimensional view of the radar scattering cross-section is shown for this absorber at a specific frequency of 7.66 GHz for incident wave angles of -90° to 90° . The 2D radar cross-section (RCS) scattering signals of the absorber at different incidence angles are shown in Fig. 9(c). The maximum RCS values are all less than 0 dB and the minimum values are around -40 dB. The simulated results are in general agreement with the microwave absorption performance results in Fig. 6(d). Overall, the data and simulation results show that the HCCMP-3 absorbers can effectively reduce the reflection and scattering of electromagnetic waves and achieve the effect of electromagnetic wave absorption and attenuation.

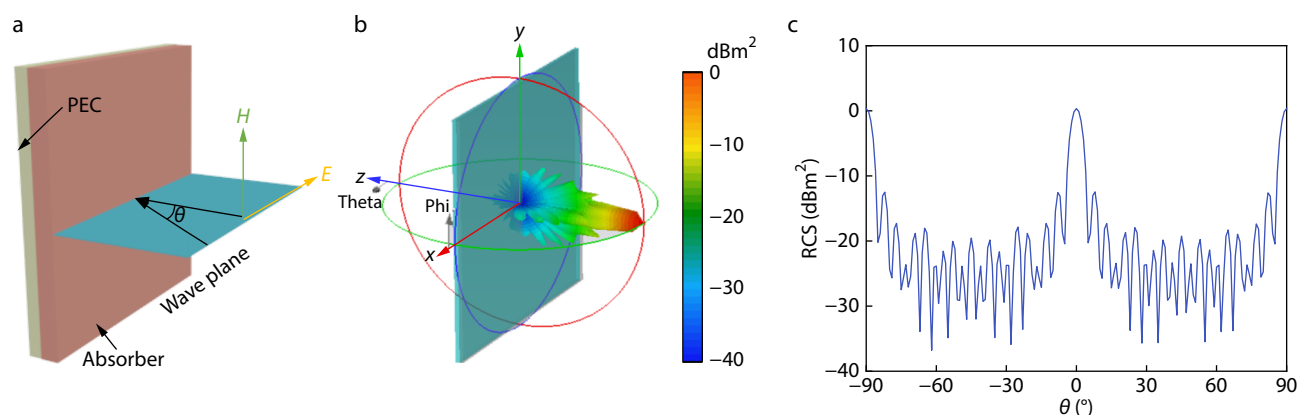
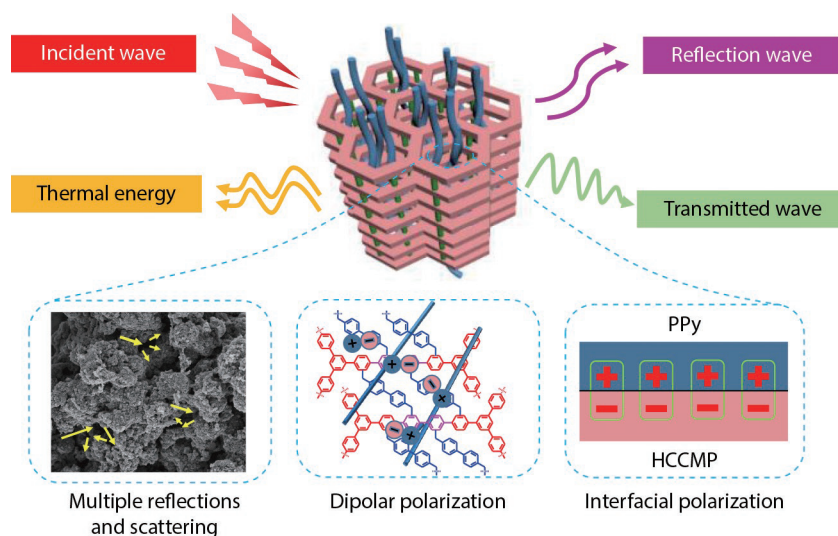


Fig. 9 (a) The radar scattering cross section (RCS) simulation schematic; (b) The 3D radar cross-section scattering signal; (c) The 2D radar cross-section scattering signal.



Scheme 2 Possible microwave absorption mechanisms for conductive HCCMP-X.

On the basis of the above investigation, the possible microwave absorption mechanism of the conductive PPy/HCCMP composite is shown in Scheme 2. Firstly, thanks to the 3D porous skeleton structure of the HCCMP, multiple reflections and scattering of electromagnetic waves occur in the material leading to extended propagation paths resulting in multiple attenuation of electromagnetic waves. Secondly, the accumulation and inhomogeneous distribution of space charge at the formed PPy/HCCMP heterogeneous interface leads to multiple interface polarisation. Thirdly, intermolecular charge transfer in microwave materials, synthetic defects and heterogeneous interfaces can all lead to the separation of positive and negative charge centres, producing dipole polarisation. Finally, the construction of PPy conducting networks also gives high speed channels for efficient electron transport and migration, leading to increased conductive losses.

CONCLUSIONS

In this work, we prepared conductive PPy/HCCMP microwave absorbing materials by a combination of molecular expansion strategy and confining polymerization strategy, and systematically researched its electromagnetic wave absorption

characteristics. In this strategy, PPy was controllably polymerized within the amplified 3D pore, providing a good conductive network and polarization loss sites for the overall structure. The results show that HCCMP-3 possesses excellent EMA performance with a maximum EAB of 7.6 GHz at 3.9 mm thickness and a strongest RL of -52.68 dB at 2.3 mm. The effective and versatile synthetic strategy broadens the scope of application of organic polymers represented by CMP in the above study.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

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