Architecture inspired structure engineering toward carbon nanotube hybrid for microwave absorption promotion

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Highlights
- Creeper-window-room-structured carbon hybrid was constructed
- Co-inheritance of frequency dependence and loss behavior was unveiled by the model
- Electromagnetic responding synergy from CNTs toward substrate was investigated
- N-AC/CNTs hybrids show impressive comprehensive microwave absorbing performance

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Architecture inspired structure engineering toward carbon nanotube hybrid for microwave absorption promotion

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SUMMARY
Constructing sophisticated 3D structure has been shown to be fruitful in developing carbon nanotubes (CNTs) microwave absorbers (MAs). However, issues with the unclear electromagnetic (EM) responding synergy of CNTs toward substrate and the limited dissipation property caused by the large dense CNTs networks throughout the reported models still need to be resolved. Inspired by the creeper-window-room-structured architecture, an analogous conformal nanostructure of amorphous carbon/CNTs (N-AC/CNTs) hybrid is constructed through an in situ autocatalytic planting approach. By this model, not only the inheritance of frequency dependence characteristic but the co-inheritance of lossy behavior and impedance matching is demonstrated. Moreover, by virtue of the unique structure, a synergistic reinforcing dielectric loss from conductive loss and dielectric polarization was introduced. Therefore, N-AC/CNTs-750 shows impressive EM performance. This work hereby unveils the synergy of EM response from CNTs toward substrate, and provides a pioneering insight into developing architecture-inspired structure engineering to construct high-performance MAs.

INTRODUCTION
The booming wireless communication technology, represented by the fifth generation (5G), as well as the proliferation of electronic devices brings society with great convenience in multiple fields; unfortunately, the consequent artificial electromagnetic (EM) pollution poses an increasing threat to both the physical health and living environment of human being (Iqbal et al., 2020; Wu et al., 2019, 2022; Wang et al., 2020a, 2020b). To address these issues, carbon nanotubes (CNTs) known by their remarkable electrical conduction ability have been extensively employed to develop state-of-the-art microwave absorbing (MA) materials (Huan et al., 2022; Xu et al., 2019; Wen et al., 2011; Che et al., 2006), by which a high conversion efficiency of transforming EM energy into Joule heat is expected. However, this peculiarity of CNTs also invites huge challenges in upgrading their MA performance toward a promising practical application owing to the intense skin effect and the ensuing easily evoked impedance mismatch. To this end, a variety of methods have been explored under the fundamental guideline of alleviating their impedance matching, primarily involving the manipulating of component (Chen et al., 2015; Hu et al., 2019; Yue et al., 2021; Han et al., 2022) and engineering of microstructure (Guo et al., 2020; Li et al., 2020; Che et al., 2004; Sun et al., 2014).

Of note, an effective strategy based on structure engineering is to composite CNTs with materials with a larger dimension such as Mxene (Li et al., 2021a, 2021b), perovskite (Wang et al., 2018a, 2018b), metal organic frameworks (Zhang et al., 2019; Li et al., 2021a, 2021b), and reduced graphene oxide (Xu et al., 2020; Zhang et al., 2020) to form sophisticated 3D structures. In these systems, CNTs spread throughout the substrates in various directions without the loading of foreign dielectrics, by which the contact area between absorber and free space can be increased to ameliorate impedance matching well. Meanwhile, the effects of CNTs from the change of morphology, the modulation of heterointerface, and the introduction of electrical conduction and magnetic coupling networks are demonstrated to be of significance on their MA performance in these models. Despite the impressive progress achieved by these studies, few of them have paid close attention to what exact role substrate plays in absorbing EM energy and how CNTs affect the EM response behavior of the integrated absorber. Exploring the relationship and interaction between...
substrate and CNTs greatly favors unraveling the underlying mechanism of their EM responding synergy. Moreover, considering that complying with gradual tapering of impedance (Kshirsagar, 2021), whether for micro-/nano-materials or flexible devices, is the golden principle of designing high-performance microwave absorber, so it actually goes against the rule to place CNTs with ultra-high impedance at the surface of composite. As a result, large dense electrically conductive network composed of CNTs formed upon the surface in these models severely retards the propagation of incident microwave into the inner medium, since such a tight and seamless structural layout of CNTs network will inevitably induce the intense shielding effect, which results in their limited MA performance. Therefore, elucidating and addressing the following three problems will be very helpful to facilitate the development of CNTs absorber toward promising practical application: i) the synergy between substrate and CNTs toward EM response, ii) whether and how CNTs impart their lossy capacity to substrate, and iii) how to excavate the MA property of CNTs to a greater level by rational structure engineering. Unfortunately, to date, these issues are still up in the air and very worth exploring.

Inspirations from nature for structure engineering like biomimetic design greatly advance the development of nanomaterials. Similarly, the architecture as an artificial combination of human art and engineering technology is also full of enlightenment in constructing nanostructure of advanced material. Inspired by one building, which is covered by crosslinked creepers crawling around the windows around the windows all over them, we realized that if CNTs can spread along the substrate in such a conformal mode rather than distribute disorderly, then CNTs can be bonded with substrate very closely and fully to enable us to investigate their interaction responding to microwave favorably. Moreover, this unique “creeper-window-room” structure can boost the entrance of microwave into the interior of system by virtue of the partially dense but integrally discontinuous layout of CNTs network. From macroscopic to microcosmic dimensions, the CNTs networks can absorb EM energy just as creepers convert solar energy to chemical energy while the windows allow the microwave further penetrate into the inner space. To ensure the full and firm combination of CNTs, multi-layered porous carbon can be selected as substrate owing to its large specific surface area and abundant active sites for the evenly distribution and nucleation of catalyst. Additionally, the highly developed porosity enables it to be a composite composed of solid and air according to the Maxwell-Garnett theory, which imparts a full contact with free space. An intrinsic advantage of decreased impedance gap between free space and absorber will follow (Huynen, 2021). Therefore, given the rationality and practicability of the above design, it is very intriguing, though comparatively unexplored, to develop the architecture-inspired structure engineering for further excavating the MA potential of CNTs.

In this work, an architecture-simulated nanostructure of carbon hybrid of amorphous carbon/CNTs (N-AC/CNTs) is constructed through an in situ autocatalytic planting approach. The creeper-like CNTs distribute uniformly but discontinuously around the macropores of AC substrate with leaving affluent penetration channel, constituting a chemically integrated hybrid of a conformal structure to AC. Interestingly, N-AC/CNTs hybrids show a conspicuous inheritance of frequency dependence characteristic from pristine AC and simultaneously a co-inheritance of impedance matching from AC and lossy behaviors from both AC and CNTs. In comparison with the physically combined AC-CNTs mixture, disparate frequency dependence characteristics and EM responding modes are demonstrated even they have electrical conductivity of the same magnitude. Moreover, by virtue of the creeper-window-room structure, not only impedance mismatch is efficiently avoided but also strong conductive loss, synergistic reinforcing polarization loss, and geometric effect-induced multi-scattering are aroused to consume EM energy. Accordingly, this work not only puts emphasis on the EM responding synergy from CNTs toward substrate for the first time but also brings an illuminating background to pioneer architecture-inspired structure engineering to design microwave absorber, which might offer insights into developing advanced functional materials.

RESULTS AND DISCUSSION

The combination of CNTs with AC substrate must be highly stable and ordered in order to acquire a conformal hybrid. To this end, a facile and low-cost in situ autocatalytic planting approach was developed as illustrated in Figure 1. Briefly, CNTs are planted onto the bio-derived multilayered porous carbon substrate with using Ni NPs as seeds and DCD as additional carbon nutrition supplement. In this approach, we firstly treated the bio-precursor via a dual pyrolysis including low-temperature heat and KOH-assisted carbonization, and a subsequent bath with concentrated HNO3 to facilitate the oxidation and hydrophilization of substrate, so as to ensure the full and uniform combination of Ni$^{2+}$ ions onto it (Zhang et al., 2021). It is worth mentioning that the KOH-assisted carbonization was adopted to induce more surface
O-containing hydrophilic groups such as hydroxyl and carbonyl. To provide the carbon source for the CNTs growth, DCD was mixed with the as-prepared substrate by mechanical stirring, which could transform into g-C3N4 and further continuously generate decomposition gases (such as, NH3 and carbon gases) as the pyrolysis temperature elevated (Zhang et al., 2019). Meanwhile, Ni2+ ions were initially reduced to Ni NPs by the carbon substrate and play a role of seeds in the growth of CNTs. During the reaction process, owing to the difference in anchoring strength of Ni NPs, some Ni NPs adhered to substrate firmly (electrostatic action) were more likely to induce a catalyst-confined graphitization for substrate, while the others having a weaker interaction with substrate (such as, physical adsorption) were prone to detach from it and thus capable of functioning as catalyst for the CNTs formation complying with the tip-growth mechanism. The force separating these Ni NPs with porous carbon is because the constantly decomposed gases can produce a thermal buoyancy vertical to the substrate, by which CNTs were lifted off while the Ni NPs were kept on the growing tips (Tessonnier and Su, 2011; Zhang et al., 2017). Hence, there would be two different configurations of Ni NPs existing in the composite, that is, one is encapsuled by carbon substrate and another is located in the tip of CNTs, as illustrated in Figure 1. With the reaction proceeds, the gaseous carbon starts to decompose on the surface of Ni NPs, and then the carbon atom turns highly supersaturated and gradually precipitates from the bottom of the catalyst, leading to the formation of tip-grown CNTs (Brukh and Mitra, 2006; Du and Pan, 2005). Finally, creeper-like CNTs were planted throughout the AC substrate and spread around the macropores, forming a kind of partially dense but integrally discontinuous network with a conformal structure.

The morphology and microstructure of samples were observed using SEM and TEM. As shown in Figure 2A, pristine AC presents an intrinsic multilayered macroporous structure with a pore diameter of submicron/micron scale. A typical amorphous structure of carbon is revealed by its XRD pattern with a broad diffraction peak at 2θ = 23.6°, indicating its low crystallinity (Figure 2B). N2 adsorption-desorption analysis unveils that the specific surface area (SBET) of AC is 56.85 m² g⁻¹, and the porosity is dominated by micropore with a pore size of ~1.99 nm (Figure 2C). The removal of small volatile components and the decomposition and rearrangement from organism to amorphous carbon after high temperature could account for the presence of these micropores. After the planting of CNTs, it can be seen in SEM, TEM, and HAADF-STEM images (Figures 2D, 2E, and S2) that CNTs cling to AC tightly, spread around the macropores, and form crosslinked dense networks while the multilayered structure of AC is basically preserved. Such a conformal integrated structure demonstrates that the duplication of the creeper-window-room structure as designed is realized. The element composition obtained by energy dispersive spectroscopy (EDS) is demonstrated to be C, Ni, O, and N. Furthermore, as exhibited in Figure 2F, the distinct diffraction peaks in XRD patterns for all N-AC/CNTs centered at 2θ = 26.2° are indexed to (002) planes of graphitized carbon (PDF#75–1621).
Compared to pristine AC, the significantly enhanced crystallinity of carbon is ascribed to two aspects, that is, the confined catalysis of Ni NPs for substrate and the combination with CNTs of a much more ordered configuration. It is also noticed that with the pyrolysis temperature elevated, the intensity of the diffraction peaks presents an increasing trend, suggesting their steadily enhanced graphitization degree (Xu et al., 2021). This structural evolution of N-AC/CNTs was further revealed through Raman spectra. As shown in Figure S3, all of the samples present two distinct characteristic peaks at 1340 cm\(^{-1}\) (D band) and 1578 cm\(^{-1}\) (G band), respectively. D band is involved with the respiratory vibration of A1g mode that aroused by the lattice un-symmetry of graphene, such as heteroatom substitution and vacancies, representing the lattice defects; while G band is associated with in-plane sp\(^2\) bond stretching vibration, which delivers the information of the order degree of carbon atoms (Sun et al., 2021; Chen et al., 2018). Accordingly, the intensity ratio of D and G bands (ID/IG) for samples is calculated to be 1.37, 1.13, and 0.96 upon the increasing pyrolysis temperature, respectively, further validating their gradually enhanced graphitization degree. Additionally, the diffraction peaks at 2\(\theta\) = 44.5\(^{\circ}\), 51.8\(^{\circ}\), and 76.4\(^{\circ}\) in XRD patterns are successively assigned to the (111), (200), and (220) planes of \(\beta\)-Ni (PDF# 04–0850). TG analysis was performed under air atmosphere to measure the Ni content. As shown in Figure S4, TG curves present three stages upon the rising temperature, including an initial slow decrease from room temperature to approximately 400\(^{\circ}\)C, a followed steep decrease until approximately 650\(^{\circ}\)C, and a smooth plateau above 650\(^{\circ}\)C. In the first stage,
the slight drop of weight below 100 °C is due to the removal of moisture, and then the gradual decrease below 400 °C is because of the loss of functional group residues and volatile small molecules. With the temperature keeping on rising, carbon matrix was gradually burned off and Ni NPs were converted to NiO, which leads to the sharp weight loss in the middle stage. Eventually, the whole reaction is completely finished with only pristine NiO left, corresponding to the last stable stage after 650 °C. According to the equation $W_{\text{Ni(N)}} = \frac{1 - W_{\text{NiO}}}{100} \times M(\text{Ni})$, where $W_{\text{Ni(N)}}$ represents the weight ratio of Ni NPs, and $W_{\text{NiO}}$ is the loss weight ratio that excludes the parts of moisture and residue, the weight ratios of Ni NPs in hybrids are successively estimated to be 22 wt.%, 21 wt.%, and 18 wt.%. Furthermore, their static magnetic properties obtained by VSM were well consistent with the above results, as shown in Figure S5. All of the samples show similar magnetic hysteresis loops with a slender S-style shape, in which both the coercivity ($H_c$) and remanence ($M_r$) are very small. In the same order, the saturation magnetization ($M_s$) values of N-AC/CNTs are as low as 7.11, 7.03, and 4.82 emu g$^{-1}$, respectively, far smaller than that of pure bulk Ni ($\approx$ 55.4 emu g$^{-1}$). On one hand, the small size effect is responsible for such a poor static magnetic property by considering that the average size of Ni NPs ($\sim$ 25 nm) is much smaller than its single-domain critical size (40 nm); on the other hand, another critical reason is the screen effect from the diamagnetic carbon shelter, which brings about Ni NPs’ surface spins with a disordered magnetization orientation. Since Ni is the sole origin of the magnetic properties for N-AC/CNTs, the close $M_s$ values of N-AC/CNTs-700 and N-AC/CNTs-750 are ascribed to the co-action between their different Ni contents and pyrolysis temperatures, while the smallest $M_s$ of N-AC/CNTs-800 is in accordance with its lowest Ni content.

XPS was further exploited to analyze the surface chemical composition of N-AC/CNTs, the results of which validates the presence of C, N, O, and Ni atoms as detected in EDS. For C 1s, its high-resolution spectrum is deconvoluted into three peaks at 284.8, 285.6, and 288.7 eV, assigned to C-C/C=C, C-N, and O=C-O groups, respectively (Figure S6A). The spectrum of Ni 2p with a weak signal discloses the presence of two valent Ni irons in addition to zero valent nickel (Figure S6B), which is attributed to the surface oxidization of Ni NPs in air. The doping of these heteroatoms is advantageous to arouse polarization loss due to the introduction of defects and dipoles. It is worth noting that though these N-containing groups bear witness to the affluent structural defects including vacancies and bonding disorders induced by the atomic arrangement in graphitic carbon, not all of them can be considered active sites to afford polarization centers to induce dielectric loss because N-Q vacancies and bonding disorders induced by the atomic arrangement in graphitic carbon, not all of them can be considered active sites to afford polarization centers to induce dielectric loss because N-Q vacancies and bonding disorders induced by the atomic arrangement in graphitic carbon, not all of them can be considered active sites to afford polarization centers to induce dielectric loss because N-Q vacancies and bonding disorders induced by the atomic arrangement in graphitic carbon, not all of them can be considered active sites to afford polarization centers to induce dielectric loss because N-Q vacancies and bonding disorders induced by the atomic arrangement in graphitic carbon, not all of them can be considered active sites to afford polarization centers to induce dielectric loss because N-Q vacancies and bonding disorders induced by the atomic arrangement in graphitic carbon, not all of them can be considered active sites to afford polarization centers to induce dielectric loss because N-Q vacancies and bonding disorders induced by the atomic arrangement in graphitic carbon, not all of them can be considered active sites to afford polarization centers to induce dielectric loss because N-Q vacancies and bonding disorders induced by the atomic arrangement in graphitic carbon, not all of them can be considered active sites to afford polarization centers to induce dielectric loss because N-Q vacancies and bonding disorders induced by the atomic arrangement in graphitic carbon, not all of them can be considered active sites to afford polarization centers to induce dielectric loss because N-Q vacancies and bonding disorders induced by the atomic arrangement in graphitic carbon. Additionally, the XPS results of Ni 2p are fully consistent with the VSM data, which strongly validates the presence of C, N, O, and Ni atoms detected in EDS. Consequently, their static magnetic properties obtained by VSM were well consistent with the above results, as shown in Figure S5. All of the samples show similar magnetic hysteresis loops with a slender S-style shape, in which both the coercivity ($H_c$) and remanence ($M_r$) are very small. In the same order, the saturation magnetization ($M_s$) values of N-AC/CNTs are as low as 7.11, 7.03, and 4.82 emu g$^{-1}$, respectively, far smaller than that of pure bulk Ni ($\approx$ 55.4 emu g$^{-1}$). On one hand, the small size effect is responsible for such a poor static magnetic property by considering that the average size of Ni NPs ($\sim$ 25 nm) is much smaller than its single-domain critical size (40 nm); on the other hand, another critical reason is the screen effect from the diamagnetic carbon shelter, which brings about Ni NPs’ surface spins with a disordered magnetization orientation. Since Ni is the sole origin of the magnetic properties for N-AC/CNTs, the close $M_s$ values of N-AC/CNTs-700 and N-AC/CNTs-750 are ascribed to the co-action between their different Ni contents and pyrolysis temperatures, while the smallest $M_s$ of N-AC/CNTs-800 is in accordance with its lowest Ni content.

N$_2$ adsorption-desorption analysis for N-AC/CNTs hybrids in Figure 2H shows the almost identically shaped isotherms of typical type IV, and obviously differ from that of pristine AC. The calculation results show that the $S_{\text{BET}}$ of N-AC/CNTs is basically unchanged with the increasing pyrolysis temperature, which are 256.49, 258.83, and 263.48 m$^2$ g$^{-1}$, respectively. These significantly higher $S_{\text{BET}}$ values than that of AC are mainly ascribed to the introduction of CNTs networks. In addition, the distinctive H4-style hysteresis loops corresponding to the capillary condensation behavior indicates that mesopore is in abundance in N-AC/CNTs (Liu et al., 2021a, 2021b). Specifically, the pore diameter distribution as displayed in Figure 2I shows that the tiny mesopore with a size of $\sim$ 3.50 nm is in overwhelming superiority. Thus, we can deduce that through enabling CNTs to spread throughout AC in a conformal manner, they can not only prevent the covering of macropores of AC but also induce a fluffy lossy surface with a higher porosity. Such a developed porous structure of the as-prepared N-AC/CNTs is favorable of bringing unexpected benefits to strengthen the interaction between absorber and microwave.

The microstructure of N-AC/CNTs was further observed. At the junction of AC and CNTs (Figure 2J), one can clearly discover that they are connected steadily even after a drastic ultrasound treatment, further confirming their strong chemically bonded nature. One can clearly observe that the presence state of Ni NPs is exactly constant with the foregoing analysis, which are divided into ones encapsuled by AC and others encapsuled by CNTs. These Ni NPs with an average diameter of approximately 14–36 nm remain after an acidic pickling and exhibit a dispersed and homogeneous distribution, suggesting that they are well protected by the carbon shelters. In this situation, the magnetic coupling network can hardly be formed. In addition, the as-synthesized CNTs show a relatively high aspect ratio with a length of micron scale
and a diameter of only about 20–25 nm (Figure 2K). This creeper-like quality favors the formation of cross-linked electrical networks throughout the substrate. Furthermore, the high-resolution TEM image in Figure 2L shows that the spacing between lattice stripes of particles is about 0.20 nm, agreeing with the (111) plane of $\beta$-Ni. Also, the interplanar distance of CNTs is around 0.33 nm, corresponding to (002) lattice plane of graphitic carbon. Due to their folded structure with high curvature, multiple defects in the wall of CNTs are observed (marked with arrows), which can be fully taken advantage of to introduce more intense dielectric polarization. The corresponding EDS elemental mapping results are displayed in Figures 2M-M4. The elemental composition of C, Ni, O, and N was further demonstrated in CNTs, and a homogeneous element distribution was presented. By considering the transition of precursors under high temperature, N dopant may be mainly attributed to the NH$_3$ gas decomposed from DCD, whereas the presence of O atom may come from the bio-derived carbon substrate that is rich in oxygen-containing functional groups (Wang et al., 2018a, 2018b). Also, the doping of N and O heteroatoms could be another reason for the lattice disorder of CNTs.

Figures 3A–3E show the microwave absorbing performance contours with changing thickness of samples over the frequency range of 2–18 GHz, which are obtained on the basis of the transmission line theory (Liu et al., 2012; Li et al., 2022a, 2022b):

$$\text{RL} = 20 \log \left| \frac{Z_n - Z_0}{Z_n + Z_0} \right|$$

(Equation 1)
\[ Z_m = \frac{Z_0}{\sqrt{\frac{\mu_0}{\epsilon_r}}} \sqrt{\frac{2\pi f t}{c}} \]  
\( \mu_0 \) is the magnetic constant, \( \mu_r \) is the relative permeability, \( \epsilon_r \) is the relative permittivity, \( f \) is the frequency, \( t \) is the thickness of absorber, \( Z_0 \) is the characteristic impedance of free space, \( c \) is the speed of light.

The electromagnetic parameters of samples were studied to unravel the underlying interaction and synergy between AC and CNTs for their variant EM responses. Based on the Debye equations, the relative complex permittivity that reflects the electronic energy storage and attenuating capacities of materials can convey their dielectric behaviors (Liang et al., 2022). As shown in Figure 4A, pristine CNTs exhibited a typical frequency dispersion behavior with a linearly steep decreasing real permittivity \( \epsilon_r' \) from 70.33 to 20.70 upon the ascending frequency, which is caused by the aggravated lag of dielectric polarization as frequency increases; while pristine AC exhibited a much gentler decrease of \( \epsilon_r' \) within a range of 12.08–10.54. Similarly, N-AC/CNTs also manifested the nearly same changing trend with N-CNTs and AC but with modest \( \epsilon_r' \) values locating between them, decreasing from 17.00 to 10.54, from 15.90 to 9.91, and from 23.01 to 12.41, respectively. Similar phenomenon is observed in the curves of imaginary permittivity \( \epsilon_r'' \) as well (Figures 4B and 4C). N-CNTs showed an ultra-large \( \epsilon_r'' \) value, monotonously declining from 87.23 to 22.77, and AC showed the smallest \( \epsilon_r'' \) that stays fluctuating within a range of 2.76–2.96. Interestingly, regarding N-AC/CNTs hybrids, it is of note that their \( \epsilon_r'' \) curves reveal an almost same dependence of frequency with that of pristine AC, which fluctuate constantly with the ascending frequency and present a similar fluctuation mode, showing an inheritance of frequency dependence characteristic from substrate. Considering that dielectric polarization behaviors are responsible for the resonances of \( \epsilon_r'' \) (Xu et al., 2021; Zhao et al., 2020a, 2020b), we are able to reasonably envisage that the as-prepared N-AC/CNTs hybrids inherited the lossy capacity of AC substrate through the elaborate conformal combination. With regard to the value gap between \( \epsilon_r'' \) of N-AC/CNTs and AC, the free electron theory that points out the huge impact of electrical conductivity \( \sigma \) on \( \epsilon_r'' \) becomes the dominant mechanism for this phenomenon when their dielectric polarization behavior is close. The \( \sigma \) values of pristine AC, N-AC/CNTs, and N-CNTs are displayed in Figure 4D. Among them, pristine N-CNTs present an ultra-high average \( \sigma \) of 8554.32 S m\(^{-1}\) due to their unparalleled innate conduction ability, while AC shows a far lower average value of 45.45 S m\(^{-1}\) for their amorphous nature. After assembly, the \( \sigma \) values of N-AC/CNTs were located at a modest level around the average value of 621.12–917.43 S m\(^{-1}\), which are still much higher than that of AC. Thus, the remarkably enhanced \( \sigma \) primarily suggests that the crosslinked CNTs networks throughout AC impart strong conduction ability to the hybrids and lead to their more intense responding toward EM energy, which is fully reflected by the increased \( \epsilon_r'' \).

Cole-Cole plots are further employed to investigate the loss behavior of samples. As shown in Figure 5A, AC delivered three distinct distorted Cole-Cole semicircles that correspond to the multiple Debye polarization processes over the middle and high frequency range, and a short tail at low frequency, which indicates that the dielectric polarization plays an important role in responding to EM energy for it (Liang et al., 2021). At the same time, AC also showed a favorable impedance characteristic with a large matched region \((0.8 \leq Z \leq 1.2)\) covering over nearly the whole frequency range by virtue of its more moderate permittivity and unique porous structure. In contrast, N-CNTs showed a Cole-Cole plots of an almost straight long line over the test frequency and a totally mismatched impedance (Figure 5B). After planting CNTs onto AC substrate, the Cole-Cole plots of N-AC/CNTs hybrids presented both the multiple semicircles and long
straight tails, manifesting that they have inherited the dielectric polarization loss from AC and the impressive conductive loss from N-CNTs simultaneously (Figure 5C). Moreover, a suitable impedance with similar matching region to that of AC in 2D contour was also delivered by N-AC/CNTs, which demonstrates that the impedance was also inherited from AC, even though their complex permittivity is significantly higher. Therefore, the as-constructed N-AC/CNTs realize the co-inheritance of impedance characteristic from AC and loss behavior from both of AC and N-CNTs, elucidating that the conformal chemical combination can induce a strong synergy responding to EM energy between them.

Dielectric loss capacity is further studied by factor tan $\delta_E$ to deliberate this synergy, as shown in Figure 4D. In conjunction with its well-matched impedance characteristic, the low tan $\delta_E$ value of AC discloses that the unbalanced contribution from lossy ability and impedance is the reason for its poor MA performance. Meanwhile, the high tan $\delta_E$ of N-CNTs also suggests a failure cooperation between remarkable conductive loss ability and awful impedance matching in terms of its negligible MA performance. Based on the transmission line theory and the testing principle of EM parameter, we can assume from the nature of low $\sigma$ and matched impedance of AC that its state is more like a circuit with large resistance (R), modest capacitance (C), as well as ignorable conductance (G), where microwave can easily penetrate and transmit out, staying at a wave traveling state; while the state of N-CNTs could belong to a circuit with remarkable inductance (L), ignorable R, and high G, in which microwave is unable to enter the interior of absorber, corresponding to a wave standing state with a total terminal reflection (Figure 4E). However, after the planting of CNTs, the modest $\sigma$ and inherited lossy behaviors indicate that the equivalent circuit model of N-AC/CNTs hybrids is featured with modulated R, L, C, and G, implying a wave traveling-standing state that can induce strong EM absorption. As a result, the tan $\delta_E$ curves of N-AC/CNTs present an enhanced dielectric loss capacity but with a similar fluctuation mode in comparison with AC, which further demonstrates that CNTs can invite the intense interaction between them and AC toward stronger EM response. In addition, it is worth noting that though N-AC/CNTs-750 shows a weaker dielectric loss capacity, its better impedance matching characteristic provides fundamental guarantee for the superior EM responding performance (Figure S8).

Moreover, the integration of conductive loss and polarization loss revealed in Cole-Coole plots can introduce a synergistic reinforcing effect of attenuating ability for N-AC/CNTs since conductive loss can
dominate the energy transformation in the low frequency, while polarization loss is activated in the middle and high frequency. According to the fundamental microwave absorption theory, the conductive loss originates from the conversion of electromagnetic energy into Joule heat that involves the transmission of induced microcurrent in the absorber, which is composed of electric field-induced current flow and magnetic field-induced eddy current. By right of the CNTs with a large aspect ratio, crosslinked electrically conductive networks without extra energy barriers are constructed throughout the surface of AC, through which the electrons can move very quickly. Energy loss thereby is aroused during the electron migration and hopping. At the same time, the conformal hybrid with macroporous structure efficiently avoids the undesirable formation of a large dense CNTs vegetation spreading over the substrate, with leaving affluent channels uncovered by CNTs, as demonstrated in Figure 2D. Such a partially compact but integrally seamless layout of CNTs networks is favorable for the elimination of in-plane macro-current, based on which the penetration of microwave into absorber is allowed to further proceed more deeply. Once microwaves enter N-AC/CNTs, the sophisticated nano/micro-scaled inner structure provides abundant sites to extend their transmission path by multi-scattering according to the geometrical effect (Zhang et al., 2015), leading to a stronger interplay between microwave and absorber and consequently a further decay. In analogy to the creeper-window-room structure, CNTs are set as “creeper” part of the as-constructed N-AC/CNTs hybrids, transforming EM energy into Joule heat just as creeper converting solar energy into chemical energy; macropores assume the role of the “window” part, affording the propagation channels for the entrance of microwave into the interior of absorber in a way like sunlight shining through the window, while the interlayers act as the “room” part, facilitating the further decay of EM energy. Additionally, on one
hand, the dipolar polarization raised by the directional arrangement of dipole under the alternating electromagnetic field (Liang et al., 2020) is one of the critical origins of dielectric relaxation considering the characteristics of heteroatoms doping and defect-ridden structure of N-AC/CNTs. On the other hand, based on the Maxwell–Wagner effect, the heterogeneous interfaces of solid/solid and solid/air provide abundant sites where charges accumulate (Qin et al., 2022; Li et al., 2022a, 2022b), by which interfacial polarization loss is induced. Moreover, considering their ultra-low permeability and magnetic loss factor (tan $\delta_d$) (Figure S9) as well as the ever-changing coefficient $C_0$ (Figure S10), the magnetic loss of hybrids can be basically neglected when compared to dielectric loss. Thereby, though these Ni NPs play an important role in reinforcing the dielectric loss capability, they have little contribution to induce magnetic loss, based on which the dominant microwave consuming mechanisms of N-AC/CNTs are proposed as illustrated in Figure 6.

The combining mode between AC and CNTs may affect the loss behavior and thus the EM responding performance. To investigate their synergy toward EM response more in depth, the frequency dependence of EM parameter and MA properties of AC-CNTs mixture counterparts prepared by simple mechanical stirring are further studied. As displayed in Figures S11A and S11B, both the $\varepsilon'$ and $\varepsilon''$ curves of them showed a disparate changing trend from those of hybrids and pristine AC. Also, different resonant mode was indicated in the dielectric loss factor tan $\delta_d$ curves (Figure S12). In conjunction with Cole-Cole plots (Figures S11E-S11G), it can be further confirmed that the loss behavior of these AC-CNTs mixtures has been significantly changed by the disordered combination. By contrast, this phenomenon reflects that the physically combined mixtures fail to induce inheritance of lossy behavior in a way as conformal combination of AC and CNTs does. Moreover, Cole-Cole plots revealed that AC-CNTs mixtures show a much weaker conductive loss and more Debye relaxation processes than N-AC/CNTs hybrids. Though these CNTs obtained with the absence of AC substrate show a much larger diameter than ones in N-AC/CNTs (Figure S13), the result in Figure S14 unveils the fact that the mixtures have $\sigma$ of an equivalent level with hybrids, which indicates that the enhanced barrier for electron motion caused by the separate layout of AC and CNTs in the insulating filler could be the dominant reason for their weaker conductive loss, as illustrated in Figure S15. Figures S16A–S16C reveal that compared to N-AC/CNTs-750, AC-CNTs mixtures present much weaker MA properties. Although the combination of AC and CNTs giving rise to complex permittivity located in a modest value range is demonstrated as well, interestingly, this physically contacted structure fails to arouse EM response as strong as chemically bonded ones do. Besides, unfavorable impedance matching characteristics with a small matched region for AC-CNTs mixtures are presented in Figures S16D–S16F. In comparison, the much more matched impedance showed by N-AC/CNTs hybrids
also testified their structural superiority in application to microwave absorption (Figure S17). In particular, the matched region of N-AC/CNTs-750 covers the frequency range from 3.7 to 18 GHz and occupies 89.38% of the whole measured frequency, 41% more than that of AC-CNTs mixtures. Therefore, based on the above discussion, it is demonstrated that thanks to the conformal creeper-window-room structure, N-AC/CNTs hybrids show more prominent advantages in absorbing microwave.

Conclusions
In summary, inspired by the creeper-window-room architecture, an analogous N-AC/CNTs hybrid was constructed through an in situ autocatalytic planting method, and by this model, the underlying synergy between substrate and CNTs toward EM response was explored. Based on the inheritance of frequency dependence characteristic, the co-inheritance of impedance from AC substrate and loss behavior from both AC and CNTs was further unveiled. CNTs could impart strong conductive loss to AC without bringing obvious negative effect on it by the conformal chemical combination. Additionally, prominent structural superiority of such a unique construction in microwave absorption was also demonstrated, which is fully reflected by its synergistic reinforcing electric energy loss capacity and well-matched impedance. Impressively, N-AC/CNTs-750 delivers a powerful RL of −61.76 dB at 1.81 mm, and an EAB of 4.64 GHz at only 1.60 mm. This work not only unravels the inheritance of EM responding synergy from CNTs toward substrate but also paves a way to design high-performance MA absorber through architecture-inspired structure engineering.

Limitations of the study
Although the EM responding synergy from CNTs toward substrate and thus the improved microwave absorbing performance were both demonstrated by the as-constructed sophisticated structure, the deeper mechanism of the interaction between components and microwave at microlevel can hardly be elaborated clearly due to the limitation of characterization technology. In the follow-up research, it is expected to develop new methods to help us understand the underlying mechanism more deeply.

STAR METHODS
Detailed methods are provided in the online version of this paper and include the following:

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SUPPLEMENTAL INFORMATION
Supplemental information can be found online at https://doi.org/10.1016/j.isci.2022.105203.

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AUTHOR CONTRIBUTIONS
X.A.L., H.J.W., and H.Y.W. supervised the project. C.Z. proposed the concept and wrote the manuscript. Y.N.S. and Y.F.S. participated in performing the experiments. W.C.G. and K.S.T. revised the manuscript. All authors participated in data analysis and manuscript discussion.
DETECTION OF INTERESTS
The authors declare no competing financial interests.

INCLUSION AND DIVERSITY
We support inclusive, diverse, and equitable conduct of research.

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STAR METHODS

KEY RESOURCES TABLE

| REAGENT or RESOURCE | SOURCE | IDENTIFIER |
|---------------------|--------|------------|
| Chemicals, peptides, and recombinant proteins | | |
| Nickel acetate tetrahydrate (AR) | Macklin | CAS: 6018-89-9 |
| Dicyandiamine (AR) | Macklin | CAS: 461-58-5 |
| Hydrochloric acid solution (AR) | Tianjin Kemiou Chemical Reagent Co., Ltd | CAS: 7647-01-0 |
| Nitric Acid (AR) | Tianjin Kemiou Chemical Reagent Co., Ltd | CAS: 7697-37-2 |
| Potassium hydroxide (AR) | Aladdin | CAS: 1310-58-3 |
| Iron chloride hexahydrate (AR) | Aladdin | CAS: 10025-77-1 |

RESOURCE AVAILABILITY

Lead contact
Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Hongjing Wu (wuhongjing@nwpu.edu.cn).

Materials availability statement
This study did not generate new unique reagents.

Data and code availability
- All data reported in this paper will be shared by the lead contact upon request.
- This paper does not report original code.
- Any additional information required to reanalyze the data reported in this paper is available from the lead contact upon request.

EXPERIMENTAL MODEL AND SUBJECT DETAILS
This study does not use experimental methods typical in the life sciences.

METHOD DETAILS

Materials
Nickel acetate tetrahydrate (Ni(CH₂COO)₂·4H₂O, 99.0%) and dicyandiamine (C₂H₄N₄, DCD) were purchased from Macklin. Concentrated hydrochloric acid solution (HCl, 12M) and nitric acid (HNO₃, 16M) were bought from Tianjin Kemiou Chemical Reagent Co., Ltd. Potassium hydroxide (KOH) and Iron chloride hexahydrate (FeCl₃·6H₂O) were purchased from Aladdin. All regents in this work are analytical purity and utilized directly without further purification.

Synthesis of N-AC/CNTs
Firstly, the bio-precursor brine shrimp eggshell was washed with deionized (DI) water and ethanol repeatedly with ultrasonic, and then dried under 60°C. Then, the evenly grinded eggshell went through a low-temperature pyrolysis under 300°C for 3 h under air. Subsequently, the brown product was physically mixed with potassium hydroxide (KOH) powder at a mass ratio of 1:1, and underwent another pyrolysis under 500°C for 4 h under an Ar atmosphere. 1.0 M hydrochloric acid (HCl) and 8.0 M hydrogen nitrate (HNO₃) solutions were successively used to treat the black product, followed by washing with DI water until neutral. The product here is denoted as amorphous carbon (AC). 200 mL Nickel acetate (Ni(OAc)₂·4H₂O, 0.02 M) solution was gradually added to the obtained carbon with stirring, and then dried by magnetic stirring after enough immersion. The product was uniformly mixed with dicyandiamide (C₂H₄N₄, DCD) powder at a mass ratio of 1:4, and then calcined in a sealed porcelain boat under Ar with a ramp ratio of 2°C min⁻¹. Last, 1.0 M FeCl₃/1.0M HCl solution and DI water were employed to wash the black product.
The as-prepared N-AC/CNTs hybrids were correspondingly marked as N-AC/CNTs-x, where x represents the pyrolysis temperature (700°C, 750°C, and 800°C).

**Synthesis of AC-CNTs mixtures**
The preparation process of AC-CNTs mixtures is shown in Figure S1. Briefly, AC was firstly prepared by the same method as described above. Then, AC was further calcined under 750°C according to the same heat profile. Pure CNTs were prepared with the same content of Ni²⁺ ions and DCD as those in preparing N-AC/CNTs hybrids. Based on the contribution of carbon atom from DCD, the mass ratio of AC to CNTs in as-obtained N-AC/CNTs hybrids could be estimated to be 87.5%. Furthermore, considering the inevitable experimental error, three mixtures with different ratios (75.0%, 87.5%, and 100.0%) were prepared, which are denoted as AC-CNTs-y, where y is the ratio of AC to CNTs.

**Characterization and EM parameter measurement**
Scanning electron microscope (SEM) and transmission electron microscope (TEM) images were obtained using a ZEISS MERLIN and a HITACHI HT7700 electron microscope, respectively. High-resolution transmission electron microscope (HRTEM) and element mapping were performed using a FEI Tecnai G2 F20 microscope. X-ray diffraction (XRD) data were collected on a Rigaku D-max-2500/PC diffractometer. Raman spectra were carried out by a Renishaw in-Via Raman spectrometer. Thermogravimetric (TG) analysis was performed on a NETZSCH STA 449 F5. A vibrating sample magnetometer (VSM, Lake Shore 7404) was used to measure static magnetic properties. X-ray photoelectron spectroscopy (XPS) data were acquired by a ESCALAB 250Xi spectrometer with an Al-Kα monochromatic excitation source. Nitrogen adsorption–desorption analysis was carried out using a Quantachrome Autosorb-1 apparatus. A four-point probe-based semiconductor resistivity of the powder tester (ST-2722, Suzhou Jingge) is employed to obtain electrical conductivity. EM parameters were recorded on a vector network analyzer (VNA, Agilent NS234A) via coaxial method. The powder product was uniformly dispersed in paraffin matrix with a filler loading of 25 wt.%, and then pressed into a coaxial ring shape with an outer diameter of 7.00 mm and an inner diameter of 3.04 mm, and a thickness of ~2.5 mm. The coaxial ring was cut into a test specimen of a thickness of 2.0 mm when measured.

**QUANTIFICATION AND STATISTICAL ANALYSIS**
This study does not include statistical analysis or quantification.