nature portfolio

Peer Review File

Carbon nanolayer-mounted single metal sites enable dipole polarization loss under electromagnetic field

Corresponding Author: Professor Weijin Li

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The manuscript is one of many papers proposing the way how to enhance absorption ability to improve shielding efficiency of the material.

The description of the electromagnetic part does not present sufficient details. The system has a surface layer, which is the main player in electromagnetics. But the surface layer sits on the thick graphite. There is no discussion on what will be the contribution of graphite in the overall shielding performance. The thin metallic layer should be considered effectively. What do “epsilon and mu” in EQu 2 mean then?

The electromagnetic experimental part is very limited. There is no description at all of how authors measured epsilon.

Throughout the article, it is unclear where authors discuss reflection coefficients (RL) and where they discuss true absorption. What authors mean by absorption? The system transmission drop is presented in decibels. But reflection losses are also taken into account there.

There are strange formulas EQ S3 and EQ S4, where the contribution from dipoles to the real and imaginary parts are the same.

To summarize, I do not see real novelty in these results. The paper contains a lot of misprints, typos and factual mistakes. I do not think it can be published in its present view.

Reviewer #2

(Remarks to the Author)
Recommendation: Reject
Comments:
Cheng et al. fabricated a single metal atom anchored N-doped carbon for EMW absorption and attributed the EMW absorption performance to dipole polarization loss. Advanced techniques were used for material characterization and simulation, and the universality of the preparation method was verified. However, these characterizations and simulations are intended to illustrate the successful synthesis of materials and the existence of dipoles, instead of giving direct evidence of dipole polarization loss. So in fact, the authors have not further broken through on how to confirm the existence of these EMW absorbing mechanisms. The current experimental design cannot completely exclude the influence of possible interfacial polarization loss. Therefore, the contribution of dipole polarization loss to polarization loss cannot be verified. In addition, there are still some problems in logic and material characterizations. After careful consideration, I have decided to reject this manuscript.

1. There are several control samples and complex sample code names in this manuscript, which is not conducive to readers' reading. It is recommended to simplify these complex code names. In addition, since the reaction mechanism from SUR-sNi-N4@NC to SUR-sNi-N4@NC-60/-80/-100 is not shown in the mechanism diagram, it makes readers struggle to understand the relationship between these four samples, and it's not clear what happens from UR-sNi-N4@NC to SUR-sNi-N4@NC-60/-80/-100, it is suggested to further improve the mechanism diagram to make it clearer and more detailed.

2. AC-HAADF-STEM images are not clear enough and should be re-photographed with corresponding element mapping to prove the existence of single-atom metals. Furthermore, in what form do the metals on SUR-sNi-N4@NC-60/-80/-100 exist? Single atom or cluster? Evidence of impact should be given.
3. It is recommended to put the dielectric constants of all samples together to facilitate comparison and reading by readers or summarize a statistical graph including ε', ε", ε"p and ε"c "values of all samples. The legend of Supplementary Fig. 15 contains errors in color.
4. Why does the ε"p of HMO@NC appear negative values in the low-frequency area? Is it because the conductivity of HMO@NC is overestimated?
5. Why does SUR-sNi-N4@NC-100 have a lower ε', ε" and ε"c despite its higher conductivity, compared with SUR-sNi-N4@NC-60 and SUR-sNi-N4@NC-80? Please check whether the conductivity test results are reliable.
6. All Cole-Cole plots should be square and must be on the same X- and Y-axis scale to evaluate conduction loss for different samples.
7. The authors point out that by comparing SUR-sNi-N4@NC-80 and SUR-sNi-N4@NC-100, it shows that HMO only plays a supporting role. However, there is another explanation here. The complete dissolution of HMO leads to an increase in the conductivity of UR-sNi-N4@NC-100, which causes the impedance mismatch of UR-sNi-N4@NC-100. Therefore, HMO may not only provide a supporting role. Furthermore, theoretically, the existence of HMO may also bring considerable heterogeneous interfaces and possible interfacial polarization loss. So this conclusion is too hasty.
8. The author did not explain clearly how to exclude interfacial polarization loss. Theoretically, there are a large number of heterogeneous interfaces between HMO, NC and Ni atoms. Please explain how to eliminate the interfacial polarization loss contribution. More importantly, as the amount of Ni increases, the heterogeneous interfaces will also increase. If the contributions of interfacial polarization loss and dipole polarization loss cannot be effectively distinguished, the existence of dipole loss cannot be proven.
9. I don't think it is scientific and reasonable to introduce electrochemical testing methods such as EIS and Tafel plots. First of all, this confuses the concepts of electrochemical polarization and polarization under electromagnetic fields. In electrochemical tests, the usual scenario is that charge is transferred between the electrolyte and the electrode, which is completely inconsistent with the actual use scenario of EMW absorption materials. Secondly, in EIS testing, the test frequency is typically 1 MHz to 0.01 Hz, which completely deviates from the frequency used for EMW absorbing materials. Therefore, in my opinion, these tests are inapplicable and meaningless. The authors should carefully consider whether to abandon these experiments unless sufficiently convincing theoretical evidence can be provided.

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Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
I am satisfied with the revised version of the manuscript and think it can be published as it is.

Reviewer #2

(Remarks to the Author)
The authors have revised the manuscript accordingly and some issues have been addressed. After the author's additional explanation, the logic of the paper is largely self-consistent. Some suggestions for improving this paper are still worth considering before publication.
1. I suggest the authors recheck misprints in abstract and other sections.
2. It seems that the introduction of HMO complicates the study of the EMW absorption mechanism. The different degrees of HMO dissolution bring about changes in the HMO/NC interfaces. The resulting hollow structure may also introduce additional air/NC interfaces. So, the necessity of introducing HMO should be given at the beginning of the paper, avoiding readers' confusion. And whether the hollow structure has any influence on the conclusion of this paper needs to be clarified.
3. For the academic rigor, I still disagree with using electrochemical methods to verify the DFT calculation results. Because Rct actually describes the charge transfer between the the active materials (sNi(N4)@NC) and electrolyte, which is deeply affected by the conductivity and specific surface area of the active material, etc. It is far-fetched to support the DFT results. A similar problem exists in the discussion of Tafel slopes. I suggest that the authors should use these data as evidence cautiously.

RESPONSE TO REVIEWERS' COMMENTS

For Reviewer #1

Q1. The manuscript is one of many papers proposing the way how to enhance absorption ability to improve shielding efficiency of the material.

Answer: *We thank the reviewer for the critical comments. However, we humbly disagree for scientific reasons as we justify below.*

In the field of electromagnetic wave (EMW) absorption, the majority of research findings still concentrate on composite materials comprising metal nanoparticles/metal oxides and carbon. This is because precursor materials, such as metal-containing MOFs, undergo high-temperature thermal treatment, causing the metals to migrate and aggregate into clusters or nanoparticles. A recent review/perspective suggested that "However, despite the increasing number of developed methods for the synthesis of carbon-based derived M-SAs, several challenges persist and require solutions: i) developing more types of carbon-based precursors to broaden the range of carbon-based derived M-SAs for metals, ii) conducting more research to unveil the effect of the increase in metal loading of carbon-based precursors for M-SAs derivatives without aggregation, iii) exploring the role of the coordination environment." poses a significant challenge (Adv. Funct. Mater. 2024, DOI: 10.1002/adfm.202405972). Our developed surface-mounted single-atoms strategy is precisely the innovative approach aimed at tackling the aforementioned challenges.

In this study, we employed a click reaction to confine metals on the surface of carbon materials, preventing migration. By introducing a model of surface-mounted single-atoms onto cost-effective and industry-practical carbon materials, we effectively eliminated the contributions of conduction loss and interfacial loss to the absorption performance. We identified dipole polarization *loss induced by surface single atoms as the primary factor in enhancing wave absorption performance and demonstrated that EMW absorption primarily occurs at the surface of micro/nanomaterials.*

Moreover, most wave-absorbing materials display multiple loss mechanisms in synergy, making it difficult to determine the dominant loss mechanism using current materials models. The majority of composite materials consist of irregular combinations of metal and carbon phases, making it challenging to ascertain whether EMW loss primarily occurs at the material's surface or within its interior. However, the established model here by surface-mounting single atoms onto a carbon layer could eliminate the contributions of conduction loss and interfacial loss to the absorption performance. This model provides an identified dipole polarization loss induced by surface single atoms as the primary factor for enhancing wave absorption performance and demonstrates that EMW absorption predominantly occurs at the surface of micro/nanomaterials.

Q2. The description of the electromagnetic part does not present sufficient details. The system has a surface layer, which is the main player in electromagnetics. But the surface layer sits on the thick graphite. There is no discussion on what will be the contribution of graphite in the overall shielding performance. The thin metallic layer should be considered effectively.

Answer: *We thank the reviewer for the critical comments and suggestions.*

(1) Firstly, regarding the HMO/NC interface, we synthesized HMO@NC material and found that it exhibited no electromagnetic wave absorption performance ((we assumed that if the reflection loss of a material is larger than -10 dB, then it can be assumed that the materials have no effective absorption according to literatures, e.g., Adv. Funct. Mater. 2024, DOI: 10.1002/adfm.202405972). This indicates that the interfacial loss between HMO and NC, as well as the NC layer itself, did not significantly contribute to the materials' absorption capability. However, after introducing single atoms on

the surface (sM(N_4)@NC), the charge redistribution disrupted the symmetry of the local microstructure, generating more dipole polarization loss, which greatly enhanced the materials' electromagnetic wave absorption performance (Fig. 3).

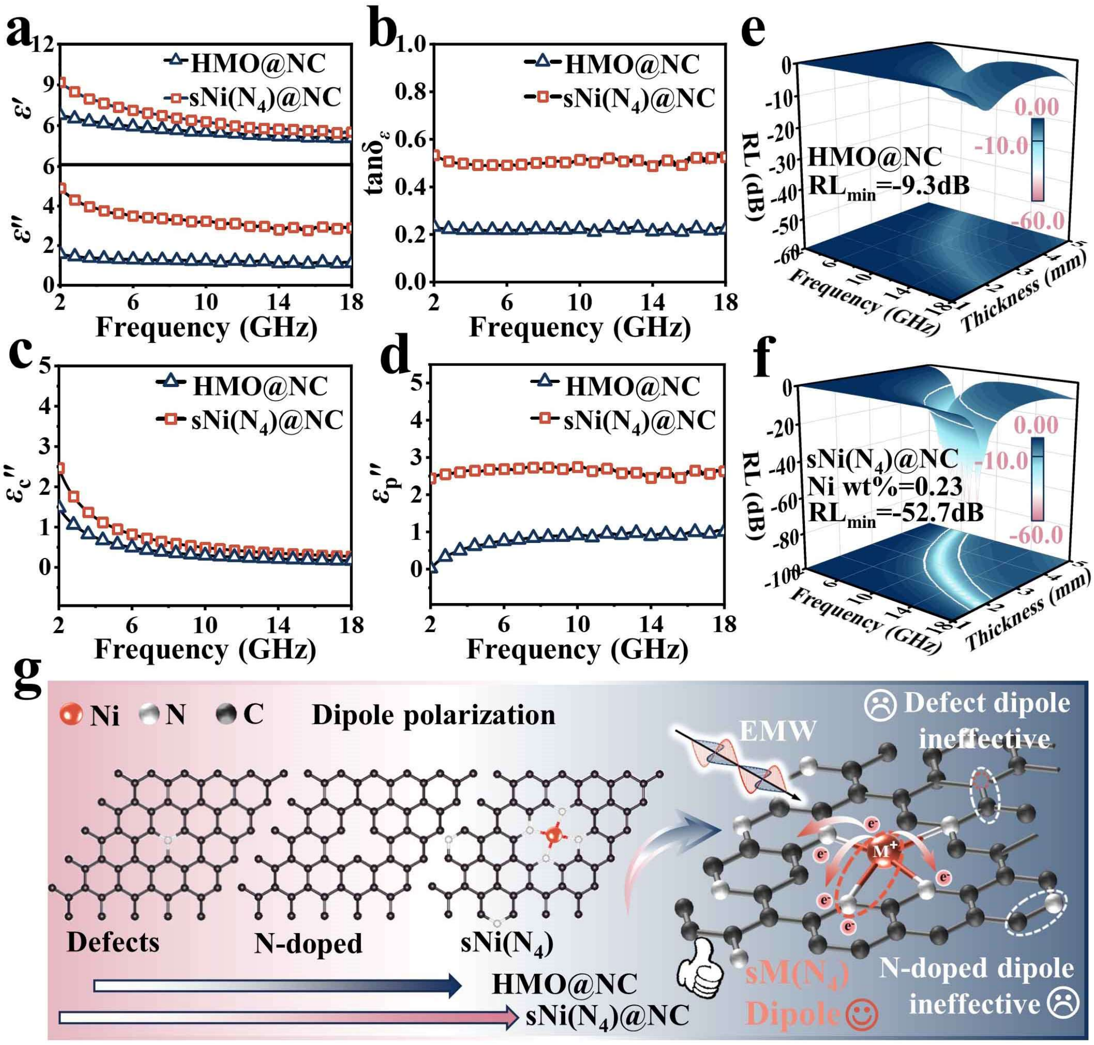
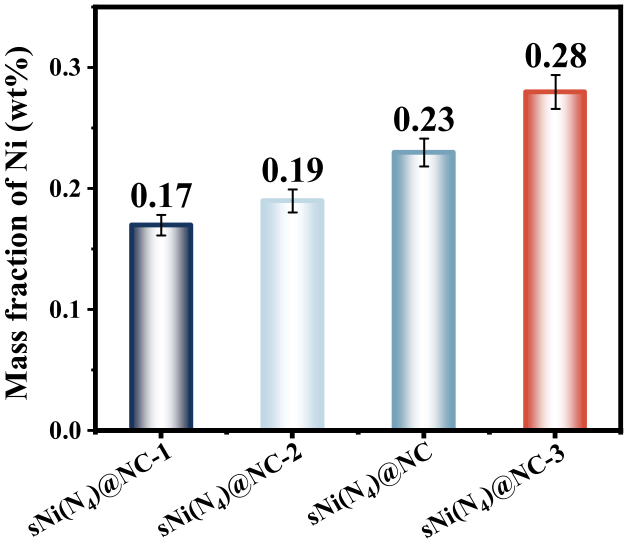


Fig. 3 | EMW absorption measurements: (a) Real (ε') and imaginary (ε'') parts of permittivity, (b) Tan δ_ε, (c) Conduction loss (ε_c'') and (d) Polarization relaxation loss (ε_p'') of HMO@NC and sNi(N_4)@NC. 3D RL plots of (e) HMO@NC and (f) sNi(N_4)@NC. (g) Dipole polarization species for HMO@NC and sNi(N_4)@NC.

(2) In our studied materials system, metals exist in the form of single atoms with a content of only about 0.2 wt%, which is inadequate to create a thin metallic layer (Supplementary Fig. 9). The metals are dispersed on the carbon surface as individual atoms rather than forming a continuous metallic layer. The presence of these isolated single-atom metals disrupts the symmetry of the

local microstructure, generating additional dipoles and enhancing dipole polarization loss. Unlike metallic layers that tend to provide electromagnetic wave (EMW) shielding rather than absorption, our material model behaves differently.



Supplementary Fig. 10 | ICP-OES spectrum of sNi(N$_4$)@NC-1, sNi(N$_4$)@NC-2, sNi(N$_4$)@NC and sNi(N$_4$)@NC-3.

Q3. What do “epsilon and mu” in EQu 2 mean then?

Answer: *We appreciate the reviewer for raising this question. Epsilon and mu in the formula represent complex permittivity (($\varepsilon_r = \varepsilon' - j\varepsilon''$) and permeability ($\mu_r = \mu' - j\mu''$), which are crucial parameters in describing the materials' response to electromagnetic waves. The dielectric constant (εr) indicates the material's ability to react to an electric field. When electromagnetic waves interact with the surface of absorptive materials, the molecules or lattices within the material undergo polarization due to the influence of the electric field. The magnetic permeability (μ_r) illustrates the material's response to a magnetic field. The magnetic permeability of the materials demonstrates their magnetization behaviour under an external magnetic field. Both permittivity (εr) and permeability (μ_r) are expressed in complex form and comprise real (ε' and μ') and imaginary (ε'' and μ'') parts, where the real part signifies the ability to store energy, and the imaginary part indicates the ability to dissipate energy. To* *provide clearer explanations of these terms to the readers, we have included term descriptions in the revised Supplementary Information (Supplementary Table 11). To improve the readers' understanding of these terms, we have included the term descriptions in the updated Supplementary Information (Supplementary Table 11).*

Supplementary Table 11 | Electromagnetic parameters and physical significance.

Electromagnetic parameter	**Physical significance**
ε_r	Complex permittivity (the material's ability to respond to an electric field)
μ_r	Complex permeability (the materials' response to a magnetic field)
ε' and μ'	Real part (the ability to store energy)
ε'' and μ''	imaginary part (the ability to lose energy)
Z_{in}	impedance of absorbers
Z_0	impedance of free-space
f	incident EMW frequency
d	thickness of absorbers
c	velocity of light
ε_s	static permittivity
ε_∞	optical dielectric constant
ω	angular frequency
τ	polarization relaxation time
α	attenuation constant

Q4. The electromagnetic experimental part is very limited. There is no description at all of how authors measured epsilon.

Answer: *We appreciate the reviewer for highlighting this. We have amended the manuscript and enhanced the electromagnetic experimental section in the revised manuscript. Specifically, we have included descriptions of the testing methods and instrumental details in the revised manuscript.*

"**Electromagnetic Measurements**: Utilizing a vector network analyzer (N5222B) to record the electromagnetic parameters containing complex permittivity ($\varepsilon_r = \varepsilon' - j_{\varepsilon}''$) and permeability ($\mu_r = \mu' - j\mu''$) by a typical coaxial-line method. Beforehand, all samples (40 wt.%) were pressed into rings-like (Φin = 3.04 mm, Φout = 7.00 mm) in paraffin.”*(Page 20)*

Q5. Throughout the article, it is unclear where authors discuss reflection coefficients (RL) and where they discuss true absorption. What authors mean by absorption? The system transmission drop is presented in decibels. But reflection losses are also taken into account there.

Answer: *We thank the reviewer for the comments.*

(1) We methodically outline the electromagnetic wave absorption properties, including minimum reflection loss and effective absorption bandwidth for all various samples in the Figure 4 section of the article (Pages 13-14 and Fig. 4). The article elaborates on the electromagnetic wave absorption properties, along with the accompanying figures, as the following:

“As one might expect, across the sM(N_4)@NC platform of materials, the minimum RL and maximum bandwidth of -55.9 dB and 4.8 GHz is registered by sCo(N_4)@NC, whereas -38.6 dB and 4.6 GHz were recorded for sCu(N_4)@NC, higher than those for sNi(N_4)@NC (-17.8 dB and 4.7 GHz)”

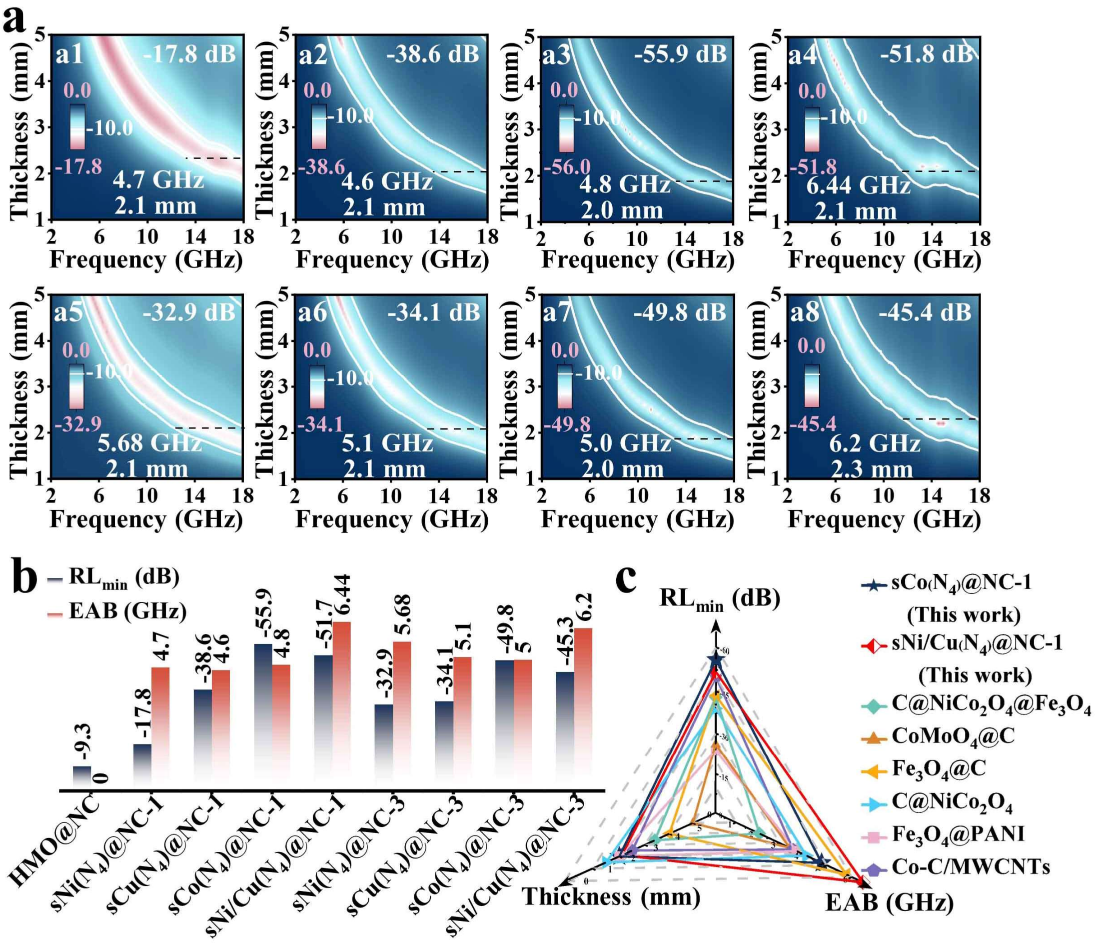
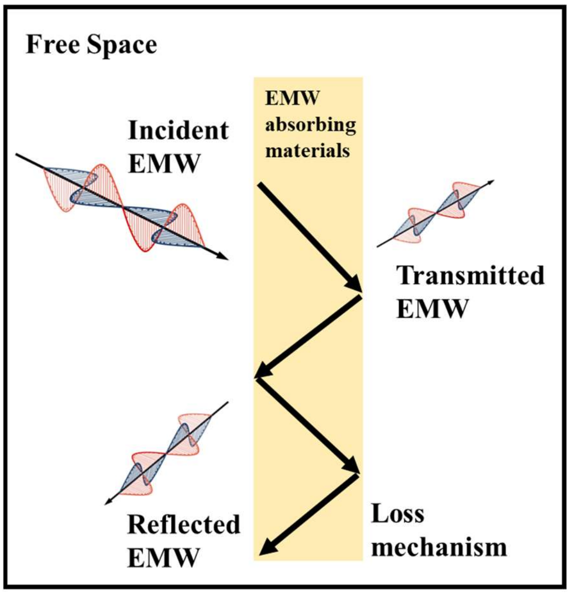


Fig. 4 | EMW absorption properties of sM(N$_4$)@NC with different single metal sites: 2D plots, reflecting loss (RL) of (a1) sNi(N$_4$)@NC-1, (a2) sCu(N$_4$)@NC-1, (a3) sCo(N$_4$)@NC-1, (a4) sNi/Cu(N$_4$)@NC-1, (a5) sNi(N$_4$)@NC-3, (a6) sCu(N$_4$)@NC-3, (a7) sCo(N$_4$)@NC-3 and (a8) sNi/Cu(N$_4$)@NC-3. (b) Summary of RL$_{min}$ and EAB of the samples with different metal single atoms. (c) Comparison of EAB, thickness, and RL$_{min}$ for the EMW absorption performances of some representative carbon-based absorbers.

(2) In the study of electromagnetic wave (EMW) absorbing materials, the primary focus is on the transmission process of electromagnetic waves in the microwave band within these materials (lossy medium). When a beam of electromagnetic waves strikes the surface of the medium, a portion of the waves is reflected on the surface while another portion penetrates into the interior of the medium. Inside the medium, the electromagnetic waves split into two components: one component undergoes attenuation through various loss

mechanisms, resulting in energy dissipation such as heat release, and the other component continues to propagate through the medium. The schematic representation is shown below (Supplementary Figures provided for reviewers, Fig. R1):



Supplementary Figure R1 (only for reviewer): The propagation of electromagnetic wave in EMW absorption materials.

(3) In the realm of electromagnetic wave absorption, the critical parameters for assessing a material's performance in absorbing electromagnetic waves include the minimum reflection loss (R_L) and the effective absorption bandwidth (EAB). The minimum reflection loss signifies the smallest amount of energy that gets reflected when an electromagnetic wave interacts with the absorbing material. A lower reflection loss value indicates a stronger ability of the material to absorb electromagnetic waves. When the reflection loss value falls below -10 dB, it signifies that the material has absorbed over 90% of the electromagnetic wave; the frequency range where the reflection loss value is below -10 dB is termed the effective absorption bandwidth. A wide effective absorption bandwidth is crucial for absorptive materials as it enables them to cover a broad spectrum of electromagnetic frequencies. A broader effective absorption bandwidth allows the material to absorb electromagnetic waves

across varied frequencies, enhancing its versatility and applicability in diverse scenarios.

Q6. There are strange formulas EQ S3 and EQ S4, where the contribution from dipoles to the real and imaginary parts are the same.

Answer: *We thank the reviewer for pointing this out.*

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1+\omega^2\ \tau^2} \qquad (Equ.S3)$$

$$\varepsilon'' = \frac{\varepsilon_s - \varepsilon_\infty}{1+\omega^2\ \tau^2} + \frac{\sigma}{\omega\varepsilon_0} \qquad (Equ.S4)$$

The Debye theory was first employed to analyse the polarisation relaxation characteristics of polar molecules, but it is now extensively utilised to examine polarisation relaxation phenomena in electromagnetic wave (EMW) absorbing materials. When polarisation relaxation occurs within the medium without taking into account the conductive current, the Debye theory expresses ε' and ε" using the following two equations, respectively.

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1+\omega^2\ \tau^2}\ , \qquad \varepsilon'' = \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{1+\omega^2\ \tau^2}$$

*However, for EMW absorbing materials used in practice, conductive currents cannot be ignored in general, making the above conclusions subject to large errors and leading to the limitations of the above equations. Therefore, the above conclusion needs to be optimized. When both polarization relaxation and conductive current exist in the medium, ε" of the medium is modified to the following equation (**Supplementary Ref. 2**):*

$$\varepsilon'' = \varepsilon_c'' + \varepsilon_p'' = \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{1+\omega^2\ \tau^2} + \frac{\sigma}{\omega\varepsilon_0}, \qquad \varepsilon_c = \frac{\sigma}{\omega\varepsilon_0}$$

Where ε_c'' denotes the conductivity loss due to conducting current; ε_p'' denotes the polarization loss due to polarization relaxation ε_s, ε_∞, ω and τ are static permittivity, optical dielectric constant, angular frequency and polarization relaxation time, respectively. σ and ε_0 correspond to conductivity and the permittivity in a vacuum.

Therefore, the formulas, after optimization, contain $\frac{(\varepsilon_s-\varepsilon_\infty)\omega\tau}{1+\omega^2\ \tau^2}$ *in both* ε'

and ε'' *expressions. But* ε' *is not equal to* ε''*.* ε' *is the sum of* ε_∞ *and* $\frac{(\varepsilon_s-\varepsilon_\infty)\omega\tau}{1+\omega^2\ \tau^2}$*.* ε'' *is the sum of* $\frac{\sigma}{\omega\varepsilon_0}$ *and* $\frac{(\varepsilon_s-\varepsilon_\infty)\omega\tau}{1+\omega^2\ \tau^2}$*.*

Q7. To summarize, I do not see real novelty in these results. The paper contains a lot of misprints, typos and factual mistakes. I do not think it can be published in its present view.

Answer: We appreciate the reviewer for providing valuable feedback.

(1) We would like to highlight the key aspects of this study, with the following four major findings:

1. *This work introduces a pioneering method of surface-mounting single atoms onto carbon layers, departing from the conventional practices of doping, implanting, or encapsulating single atoms into carbon materials for applications in electromagnetic wave (EMW) absorption. A recent review highlighted several challenges in the synthesis of carbon-based derived M-SAs, emphasising the need for broader precursor options and understanding the impact of increased metal loading without aggregation, along with exploring the coordination environment (Adv. Funct. Mater. 2024, DOI: 10.1002/adfm.202405972). Our surface-mounted single-atoms strategy presents a novel approach to tackle these challenges. Our research confirms that EMW interactions with materials at the micro/nanoscale primarily occur at the material's surface rather than within the bulk, a previously unexplored aspect. Using mathematical statistical modelling, we excluded conduction and interfacial losses, revealing that dipole polarization loss induced by surface-mounted nitrogen-confined single atoms is the key factor enhancing the EMW absorption performance of materials. This study offers theoretical insights and models for designing future EMW absorbing materials with enhanced efficiency.*
2. *Altering metal atoms with different electronegativities results in varying polarization strengths. Through a combination of experimental outcomes and theoretical calculations, we have established a structure-property*

relationship at the atomic level regarding the influence of diverse single-atom metal surface modifications on wave absorption performance.

3. *The innovative approach of surface-mounting single atoms onto cost-effective and industry-applicable carbon layers in this study serves as a significant reference for the development of highly efficient wave-absorbing materials for industrial purposes. To further highlight the novelty, the following text has been included in the introduction:*

"In this study, we propose an electromagnetic wave (EMW) dipole-dominated loss model that eliminates other unnecessary EMW losses (such as conductivity, defects, and interfacial polarization loss), showcasing promising EMW absorption characteristics. This offers a fresh perspective for designing and conducting a detailed analysis of EMW absorbers. The focus is on the straightforward surface mounting of single atoms onto cost-effective and industrially viable carbon materials, paving the way for the exploration of future EMW absorbing materials suitable for academic research and industrial applications."

(2) *We appreciate the reviewer for the suggestions. We have carefully reviewed the manuscript once more, rectifying all misprints, typos, and factual errors.*

For Reviewer #2

Cheng et al. fabricated a single metal atom anchored N-doped carbon for EMW absorption and attributed the EMW absorption performance to dipole polarization loss. Advanced techniques were used for material characterization and simulation, and the universality of the preparation method was verified. However, these characterizations and simulations are intended to illustrate the successful synthesis of materials and the existence of dipoles, instead of giving direct evidence of dipole polarization loss. So in fact, the authors have not further broken through on how to confirm the existence of these EMW absorbing mechanisms. The current experimental design cannot completely exclude the influence of possible interfacial polarization loss. Therefore, the contribution of dipole polarization loss to polarization loss cannot be verified. In addition, there are still some problems in logic and material characterizations. After careful consideration, I have decided to reject this manuscript.

***Response**: We thank the reviewer for critical comments and suggestions. The most significant innovation of this work lies in the surface-mounted single atoms onto carbon layer, which greatly enhances the materials' wave-absorbing performance. This directly proves on a microscopic scale that the dissipation of electromagnetic waves (EMW) primarily occurs on the surface of the material. Firstly, HMO@NC (without single-atom site modification on the carbon shell surface) exhibits almost no EMW absorption performance (RL > -10 dB), indicating that the surface carbon layer and Heterogeneous interface between HMO and carbon layer have a minimal impact on wave absorption. However, after introducing single-atom sites on the HMO@NC surface, the effective absorption bandwidth (RL < -10 dB, EMW absorption efficiency up to 90%) of sNi(N_4)@NC-1, sCu(N_4)@NC-1, and sCo(N_4)@NC-1 was significantly enhanced to 4.7 GHz, 4.6 GHz, and 4.8 GHz, respectively (**Fig. 3e and 4a**).*

Following the high-temperature etching of HMO to form hollow materials (sM(N_4)@NC-3), the heterointerface between the HMO and the carbon layer was eliminated, resulting in an increase in absorption performance. The *effective absorption bandwidths of sNi(N_4)@NC-3, sCu(N_4)@NC-3, and sCo(N_4)@NC-3 were 5.68 GHz, 5.1 GHz, and 5.0 GHz, respectively (Fig. 4). Furthermore, the effect of the hollow structure on EMW absorption performance is negligible. The primary reason for the enhanced EMW absorption performance is the increased surface single-atom content, which leads to strengthened dipole polarization (**Supplementary Fig. 21**). Consequently, this elimination process demonstrates that polarization loss induced by surface metal single atoms is the main factor enhancing EMW absorption performance.*

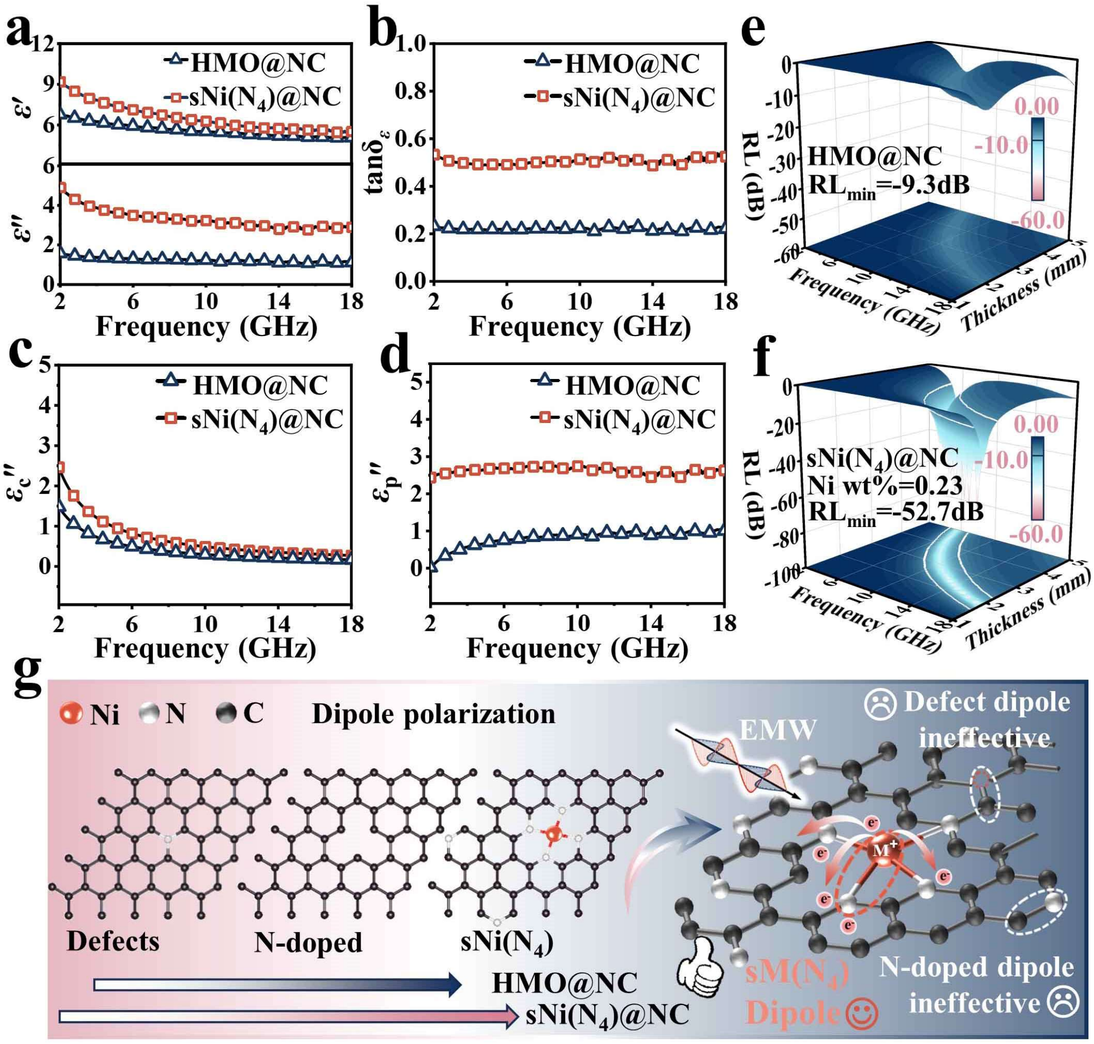


Fig. 3 | EMW absorption measurements: (a) Real (ε') and imaginary (ε'') parts of permittivity, (b) Tan δ_ε, (c) Conduction loss (ε_c'') and (d) Polarization relaxation loss (ε_p'') of HMO@NC and sNi(N_4)@NC. 3D RL plots of (e) HMO@NC and (f) sNi(N_4)@NC. (g) Dipole polarization species for HMO@NC and sNi(N_4)@NC.

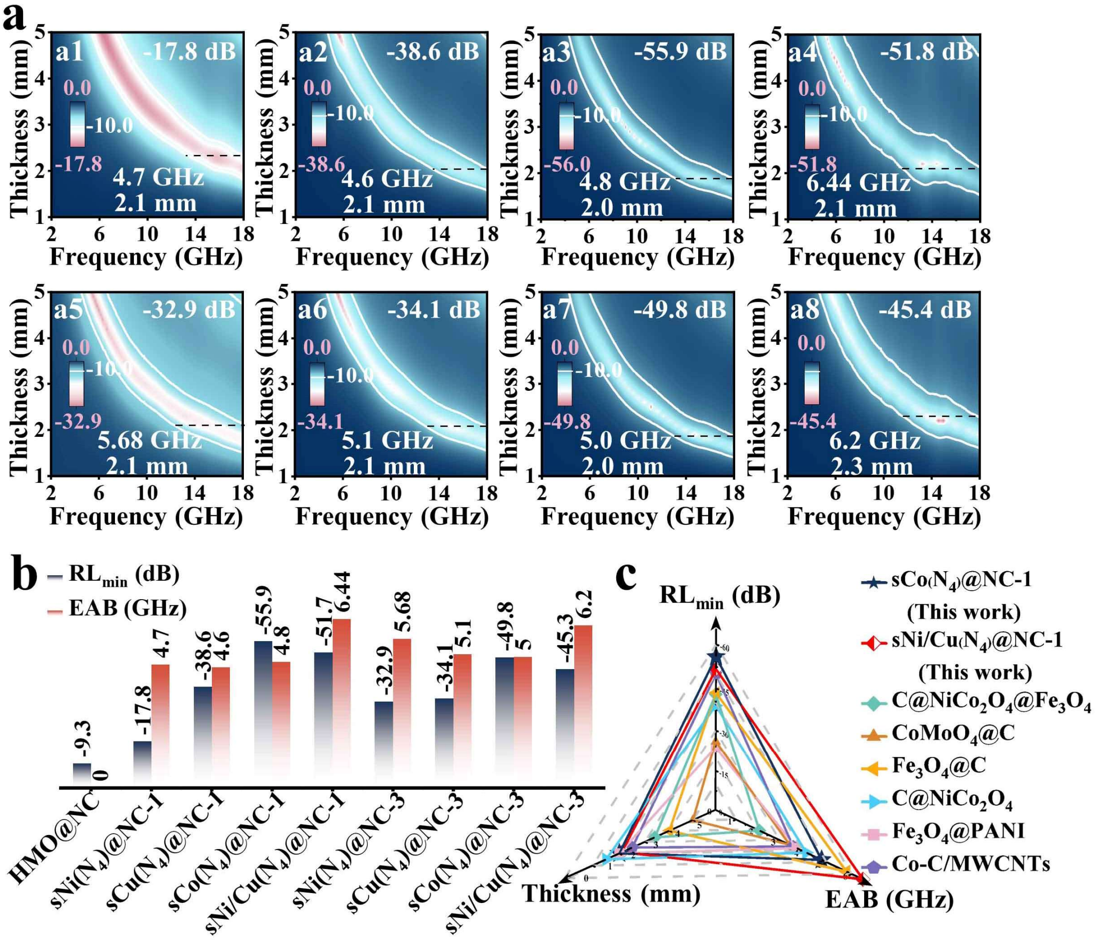
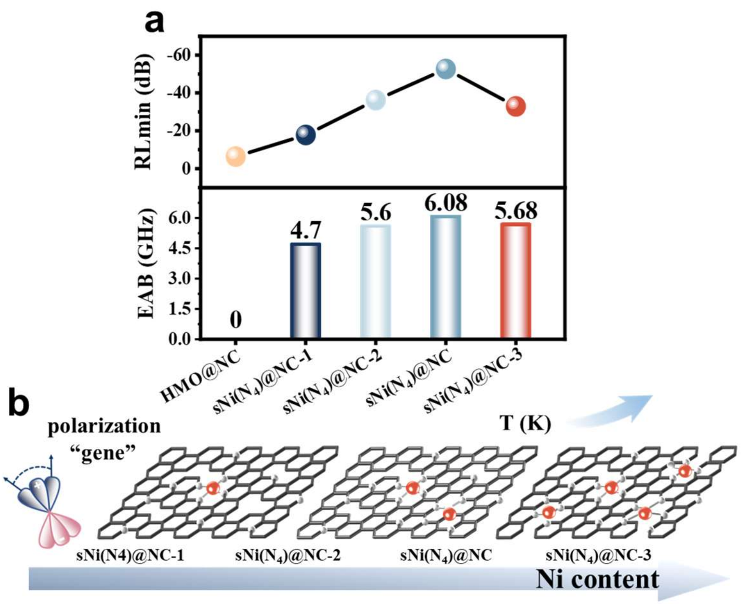


Fig. 4 | EMW absorption properties of s$M(N_4)$@NC with different single metal sites: 2D reflecting loss (RL) plots of (a1) s$Ni(N_4)$@NC-1, (a2) s$Cu(N_4)$@NC-1, (a3) s$Co(N_4)$@NC-1, (a4) s$Ni/Cu(N_4)$@NC-1, (a5) s$Ni(N_4)$@NC-3, (a6) s$Cu(N_4)$@NC-3, (a7) s$Co(N_4)$@NC-3 and (a8) s$Ni/Cu(N_4)$@NC-3. (b) Summary of RL_{min} and EAB of the samples with different metal single atoms. (c) Comparison of EAB, thickness, and RL_{min} for the EMW absorption performances of some representative carbon-based absorbers.



Supplementary Fig. 21 | **a)** Summary of EAB and RL$_{min}$ for all the samples. b) As the reaction temperature increases, the content of Ni increase.

Here, we would like to re-emphasize the highlights of this work, and the four major findings are listed below:

1) In this work, we have pioneered to use the surface-mounted single atoms onto carbon layers rather than doping/implanting/encapsulating single atoms into carbon materials for the applications in the field of electromagnetic wave (EMW) absorption. Latest review/perspective proposed that "However, despite the increasing number of developed methods for the synthesis of carbon-based derived M-SAs, several challenges remain and require solutions: i) developing more types of carbon-based precursors to expand the range of carbon-based derived M-SAs for metals, ii) doing more research to reveal the effect of the increase in metal loading of carbon-based precursors for M-SAs derivatives without aggregation, Iii) exploring the role of the coordination environment." is of great challenge (Adv. Funct. Mater. 2024, DOI: 10.1002/adfm.202405972). While our developed surface-mounted single-atoms strategy here is exactly the novel approach to address the above-mentioned challenges. Our studies confirm that interactions between EMW and materials on the micro/nano scale *level predominantly occur at the material's surface rather than inside the bulk materials, which un-studied before. By utilizing mathematical statistics modeling approach, we excluded conduction loss and interfacial loss, disclosing that dipole polarization loss induced by surface-mounted nitrogen-confined single atoms is the primary factor enhancing the materials' EMW absorption performance. This study provides a theoretical reference and models for the design of future EMW absorbing materials with high efficiency.*

2) The modification with metal atoms of different electronegativities results in varying polarization intensities. Through experimental results and theoretical calculations, we have established a structure-property relationship at the atomic level for the effect of different single-atom metal surface modifications on wave absorption performance.

3) The surface-mounted single-atom onto economical and industry-practicable carbon layer in this work provides a novel reference for future designing highly efficient wave-absorbing materials for industrial applications.

To clarify the novelty more clearly, we have added the following text in introductions as follows:

In this study, we elegant build a unique EMW dipole dominated loss model excluding other redundant EMW loss (e.g., conductivity, defects, and interfacial polarization loss) with promising EMW absorption properties, providing a new approach for the design and in-depth loss study of EMW absorbers. Such approach focuses on the simply surface-mounted single atoms onto economic-budgeted and industrially practical carbon materials, opening an avenue for exploring future academic studied and industrial applicable EMW absorbing materials.”

Q1. There are several control samples and complex sample code names in this manuscript, which is not conducive to readers' reading. It is recommended to simplify these complex code names. In addition, since the reaction mechanism from SUR-sNi-N_4@NC to SUR-sNi-N_4@NC-60/-80/-100 is not shown in the mechanism diagram, it makes readers struggle to understand the relationship between these four samples, and it's not clear what happens from SUR-sNi-N_4@NC to SUR-sNi-N_4@NC-60/-80/-100, it is suggested to further improve the mechanism diagram to make it clearer and more detailed.

Answer: *We thank the reviewer for the constructive suggestions. We have changed SUR-sNi-N_4@NC-60, SUR-sNi-N_4@NC-80, SUR-sNi-N_4@NC-100 to sNi(N_4)@NC-1, sNi(N_4)@NC, sNi(N_4)@NC-3 in the revised manuscript and supplementary information. Additionally, we have included the reaction mechanism from sNi(N_4)@NC to sNi(N_4)@NC-60/-80/-100 (now sNi(N_4)@NC-1/-2/-3) in the mechanism diagram.*

Q2. AC-HAADF-STEM images are not clear enough and should be re-photographed with corresponding element mapping to prove the existence of single-atom metals. Furthermore, in what form do the metals on SUR-sNi-N_4@NC-60/-80/-100 exist? Single atom or cluster? Evidence of impact should be given.

Answer: *Thank you very much for the constructive suggestion.*

*(1) We have re-imaged sNi(N_4)@NC and sNi(N_4)@NC-1/-2/-3 using AC-HAADF-STEM and clearly observed some individual small bright spots instead of larger bright spots (**Fig. 1c-1e and Supplementary Fig. 9**). Furthermore, XANES revealed that the peak shapes of Ni in sNi(N_4)@NC-1 are completely different from those in Ni-foil (Ni-Ni), indicating that Ni in sNi(N_4)@NC-1 does not have Ni-Ni bonds and is not in the form of metal clusters. The peak shapes match perfectly with NiPc (Ni-N) (**Fig. 2**). Additionally, by calculating the coordination number, we confirmed that Ni in sNi(N_4)@NC-1 exists in a Ni(N_4) coordination environment.*

(2) We have also characterized the metals in sNi(N_4)@NC-1/-2/-3 by using the HAADF-STEM and elemental mapping. Experimental data confirm that the metals in sNi(N_4)@NC-1/-2/3 are in the form of single metal sites. New sentences and data are added in the revised manuscript. ("Additionally, the aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC-HAADF-STEM) images exhibited uniform dispersion

*of bright dots over the the prepared samples surface (**Fig. 1c,d and Supplementary Fig. 9**). Simply put, these dots correspond to the heavy Ni atoms and uniformly dispersed on the surface of carbon (**Fig. 1e**).")*

*(3) Besides, We have systematically investigated the XAFS data of sNi(N4)@NC and sNi(N4)@NC-1/-2/-3 (**Supplementary XAFS data for reviewer, Fig. 2**). The data shows that the isolated Ni atoms to be carrying positive charge each, and the valence state of isolated Ni atoms to be close to +2 each (**Supplementary XAFS data for reviewer, Fig. 2a**). The FT-EXAFS spectra display one main peak at about 1. 48 Å, similar to the Ni-N peak in NiPc (**Supplementary XAFS data for reviewer, Fig. 2b**). All samples do not exhibit characteristic peaks corresponding to Ni-O (2.54 Å) and Ni-Ni (2.17 Å).*

In summary, the results of AC-HAADF-STEM and XAFS demonstrated that Ni was present in all samples as highly dispersed monoatomic sites.

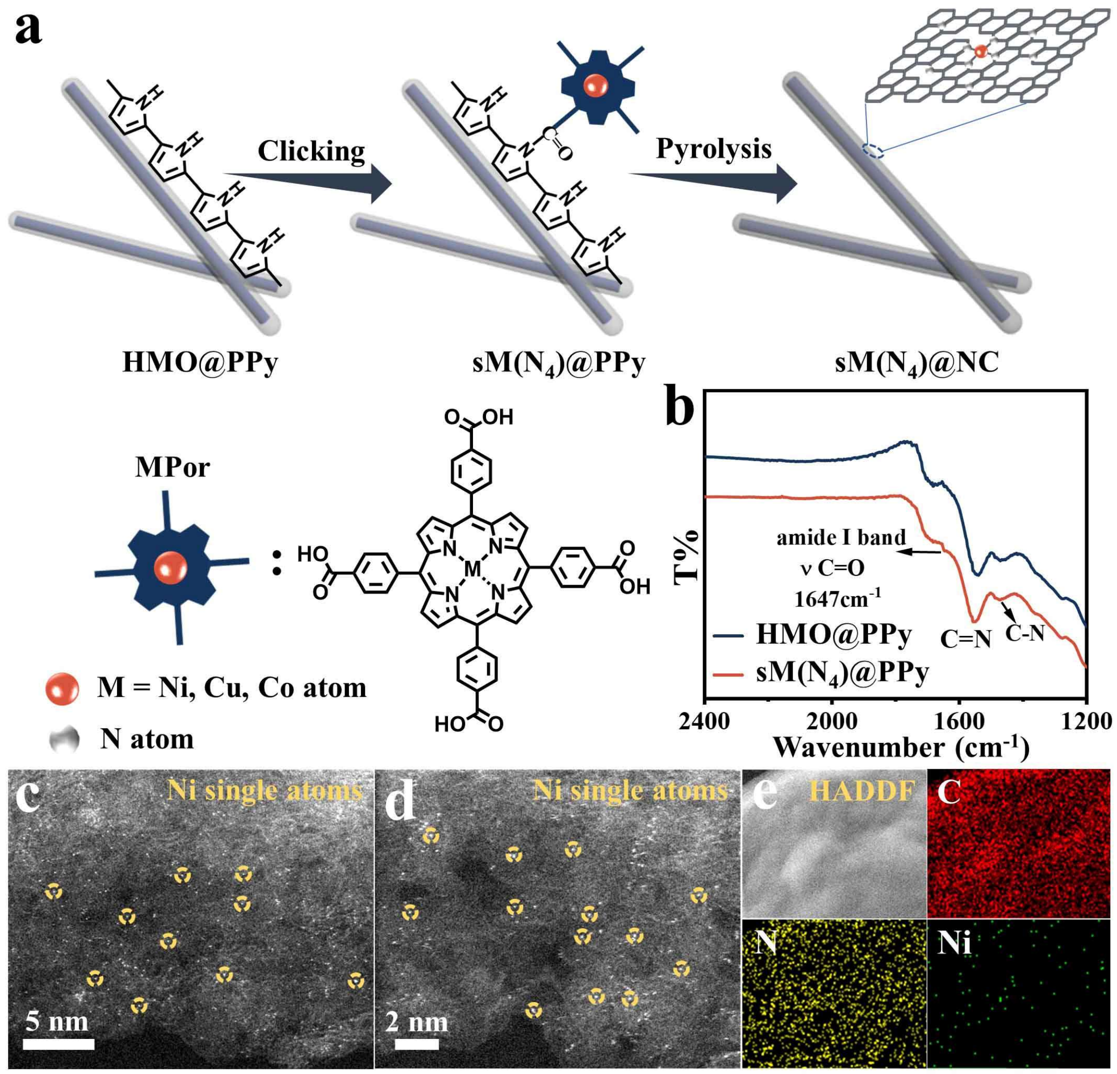
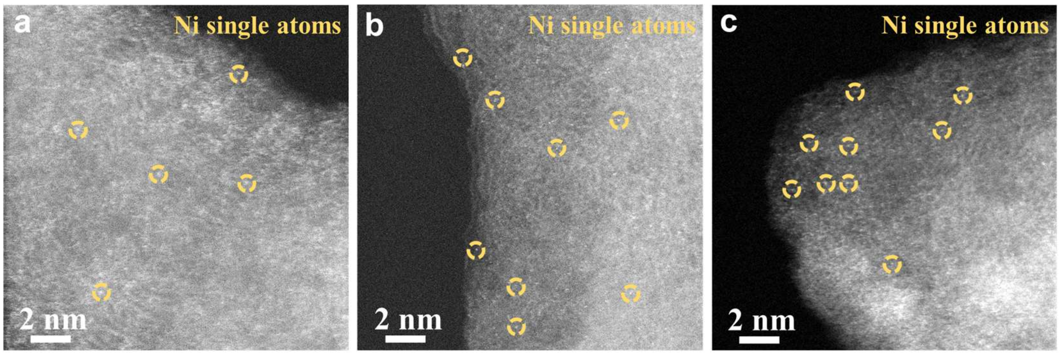


Fig. 1 | Synthesis and Characterization of sM(N$_4$): (a) Schematic illustrating the surface modulation of 4-nitrogen surrounded single metal sites on a nitrogen-doped carbon layer (exemplified across the sM(N$_4$)@NC family, M=Ni, Cu, Co and Ni/Cu); (b) FTIR spectra of HMO@PPy and sNi(N$_4$)@PPy; (c,d) Aberration-corrected high-angle annular dark-field scanning TEM images of sNi(N$_4$)@NC-3 and (e) corresponding EDX mapping of C, N, Ni.



Supplementary Fig. 9 | Aberration-corrected high-angle annular dark-field scanning TEM images of a) sNi(N_4)@NC-1, b) sNi(N_4)@NC-2, c) sNi(N_4)@NC

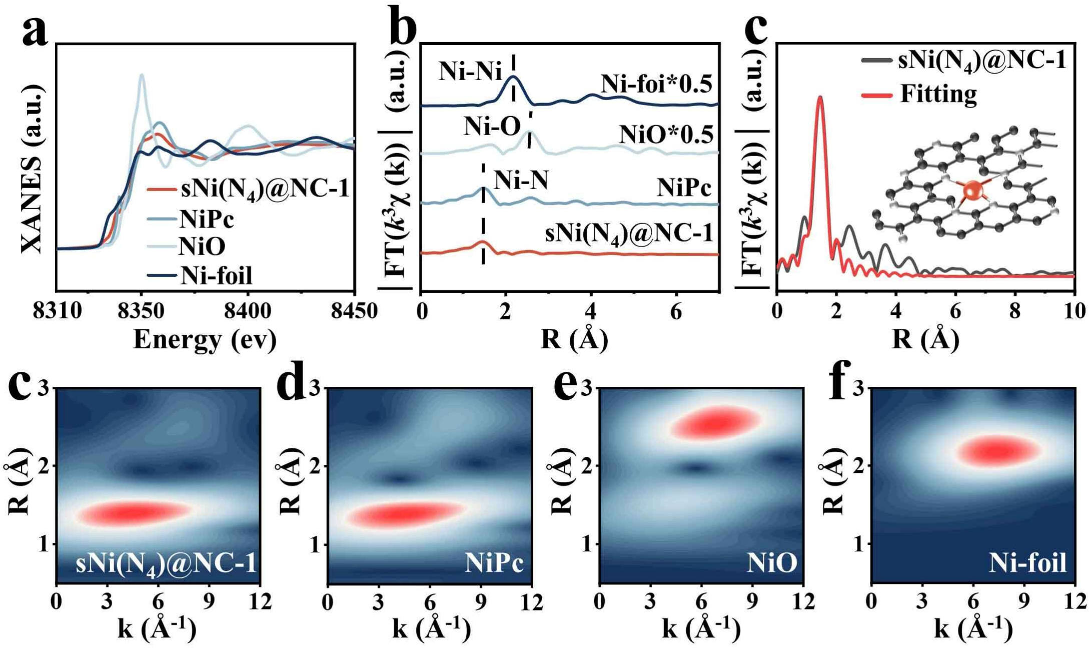
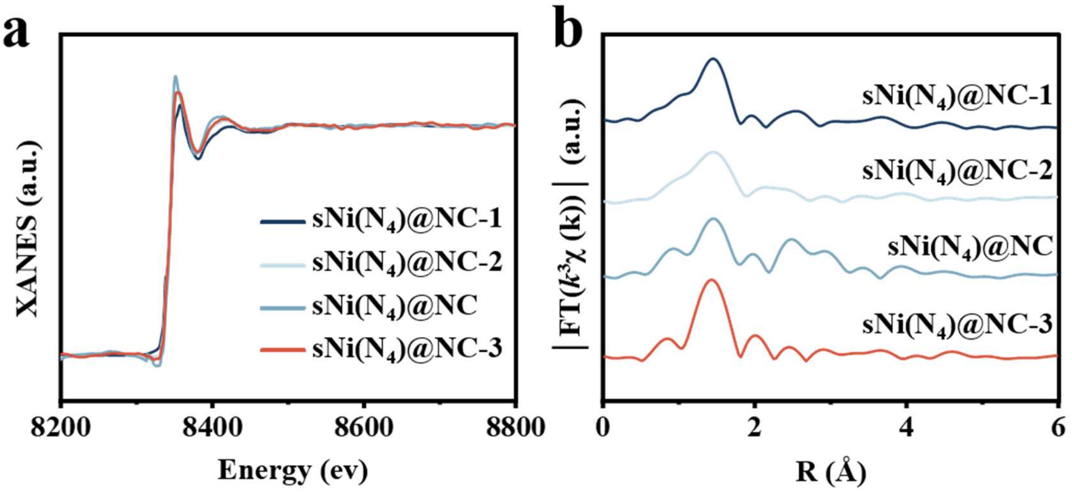


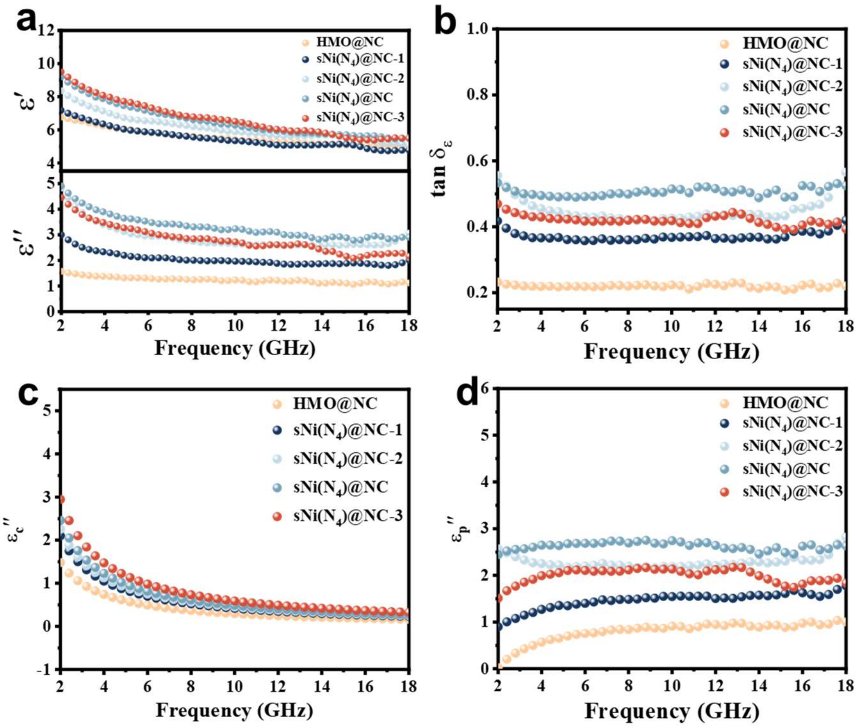
Fig. 2 | Synchrotron X-ray absorption spectrum characterization: (a) XANES spectrum at the Ni K-edge, (b) EXAFS spectra in reciprocal space, (c) EXAFS fitting results of sM(N_4)@NC (Inset: illustration of the NiN_4). Wavelength transformations observed in (d) sM(N_4)@NC-1, (e) NiPc, (f) NiO, and (g) Ni-foil.



Supplementary XAFS data for reviewer, Fig. 2 | (a) XANES spectrum at the Ni K-edge, (b) EXAFS spectra in reciprocal space.

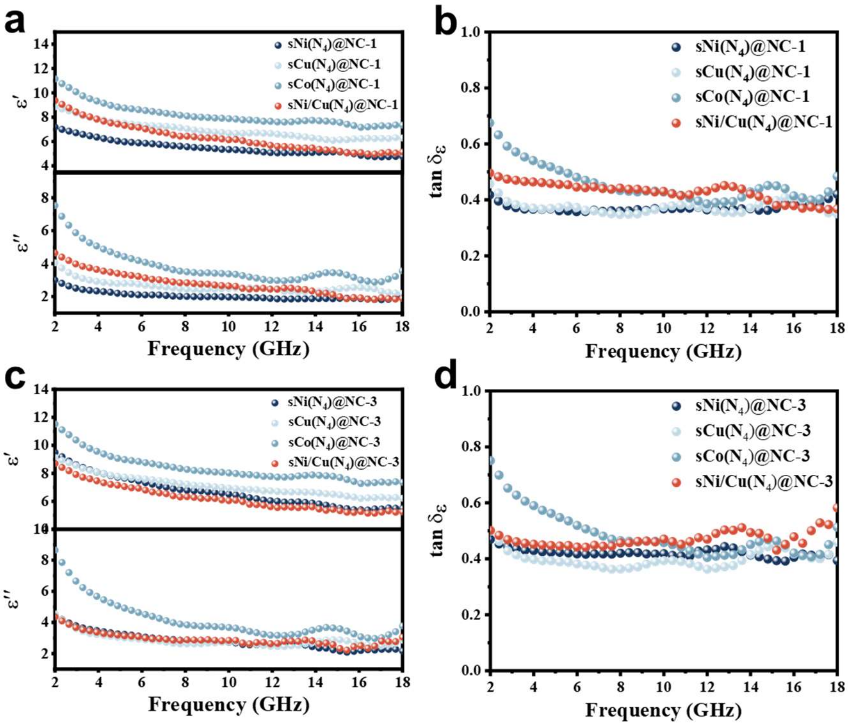
Q3. It is recommended to put the dielectric constants of all samples together to facilitate comparison and reading by readers or summarize a statistical graph including ε', ε'', ε''p and ε''c "values of all samples. The legend of Supplementary Fig. 15 contains errors in color.

Answer*: We thank the reviewer for the suggestions. We have presented the ε', ε'', ε''p, and ε''c values of all samples together for easier comparison and readability (****Supplementary Fig. 16****). Besides, we have reorganized the tables accordingly in the revised supplementary information. (****Supplementary Table12-14****)*



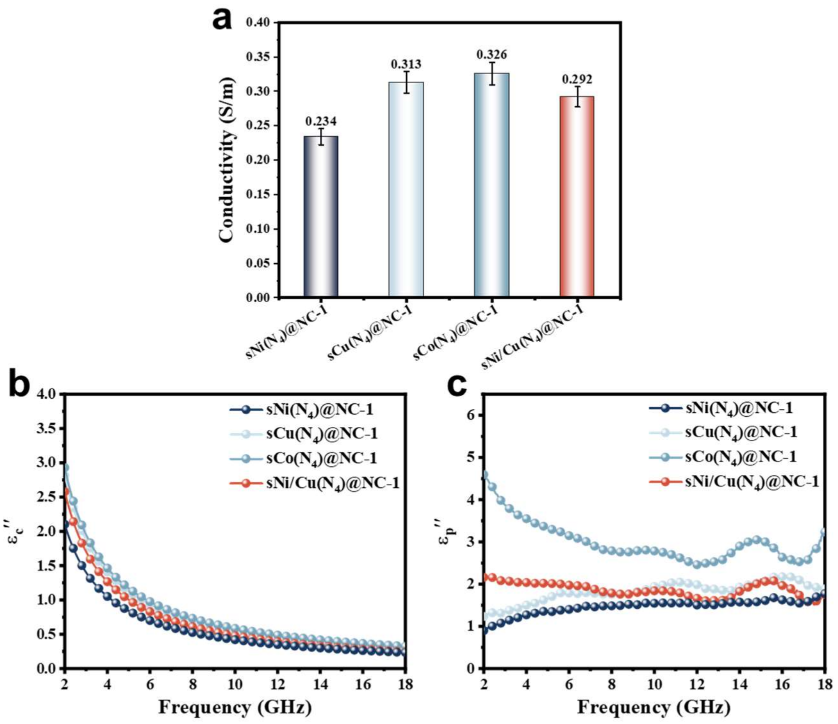
Supplementary Fig. 16 | Electromagnetic parameters of HMO@NC, sNi(N_4)@NC-1, sNi(N_4)@NC-2, sNi(N_4)@NC and sNi(N_4)@NC-3 tests: a) Real (ε′) and imaginary (ε″) part of permittivity, b) Tan δε, c) Conduction loss (ε_c'') and d) Polarization relaxation loss (ε_p'') of HMO@NC, sNi(N_4)@NC-1, sNi(N_4)@NC-2, sNi(N_4)@NC and sNi(N_4)@NC-3.

The results show there is a slight increase in the conductivity of the samples with increasing single-atom loading, which is in agreement with work that has been reported (Adv. Funct. Mater. 2023, 33, 2212604). Therefore, the increase in the EMW absorption performance of sNi(N_4)@NC/-1/-2/-3 and sNi(N_4)@NC is due to the increase in dielectric losses (including conduction and dipole polarization losses) due to the increase in Ni content.



Supplementary Fig. 24 | Dielectric loss mechanism analysis. a) Real and imaginary part of permittivity, and b) Tan δε of sM(N_4)@NC-1 (M= Ni, Cu, Co and Ni/Cu). c) Real and imaginary part of permittivity, and d) Tan δε of sM(N_4)@NC-3 (M= Ni, Cu, Co and Ni/Cu).

*Further, comparing the data of sM(N_4)@NC-1 (M : Ni, Cu, Co, Ni/ Cu), we find that the conduction loss is not the main reason for the difference in the EMW absorption performance (**Supplementary Fig. 25**), and by separating out the polarization loss, we can find that the dipole polarization loss caused by different electronegative metal atoms is the main reason for the difference in the EMW absorption performance. This conclusion is verified by the DFT calculations in the article.*



Supplementary Fig. 26 | a) Conductivity, b) Conduction loss and c) Polarization relaxation loss of sM(N_4)@NC-1 (M= Ni, Cu, Co, Ni/Cu).

Supplementary Table 12 | ε', ε'', ε_c, ε_p average values of HMO@NC, sNi-N_4@NC-1, sNi-N_4@NC-2, sNi-N_4@NC and sNi-N_4@NC-3.

	ε'_{av}	ε''_{av}	$\varepsilon_{c,\ av}$	$\varepsilon_{p,\ av}$
HMO@NC	5.47	1.24	0.41	0.81
sNi-N_4@NC-1	5.52	2.05	0.58	1.47
sNi-N_4@NC-2	6.46	2.90	0.62	2.28
sNi-N_4@NC	6.55	3.31	0.68	2.63
sNi-N_4@NC-3	6.67	2.81	0.81	2.0

Supplementary Table 13 | ε′, ε″, ε_c, ε_p average values of HMO@NC, sNi-N_4@NC, sCu-N_4@NC, sCo-N_4@NC and sNi/Cu-N_4@NC.

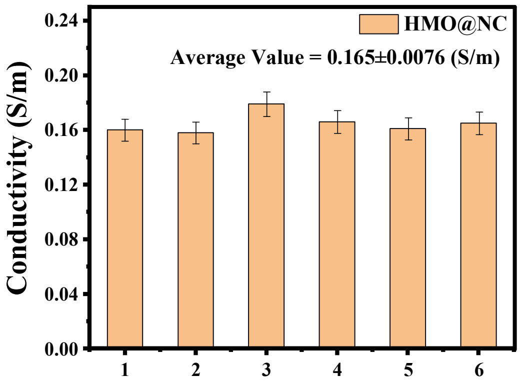
	ε'_{av}	ε''_{av}	$\varepsilon_{c,\,av}$	$\varepsilon_{p,\,av}$
HMO@NC	5.47	1.24	0.41	0.81
sNi-N_4@NC-1	5.52	2.05	0.58	1.47
sCu-N_4@NC-1	6.94	2.60	0.77	1.82
sCo-N_4@NC-1	8.19	3.80	0.81	3.0
sNi/Cu-N_4@NC-1	6.33	2.75	0.72	1.87

Supplementary Table 14 | ε′, ε″ average values of HMO@NC, sNi(N_4)@NC-3, sCu(N_4)@NC-3, sCo(N_4)@NC-3 and sNi/Cu(N_4)@NC-3.

	ε'_{av}	ε''_{av}
HMO@NC	5.47	1.24
sNi(N_4)@NC-3	6.35	2.71
sCu(N_4)@NC-3	7.13	2.84
sCo(N_4)@NC-3	8.36	4.15
sNi/Cu(N_4)@NC-3	6.22	2.91

Q4. Why does the ε"p of HMO@NC appear negative values in the low-frequency area? Is it because the conductivity of HMO@NC is overestimated?

Answer: *We thank the reviewer for pointing this out and helpful suggestions. We reexamined the conductivity of HMO@NC several times and obtained an average conductivity of 0.165±0.0076 S/m according to the reviewer's suggestions. The conductivity data is presented below.*



Supplementary Figures only for reviewer, Fig. 3 | Conductivity of HMO@NC.

We have carefully analyzed the data again and found the negative values in the low frequency is not existing anymore. The re-analyzed and revised figures are added to the revised manuscript.

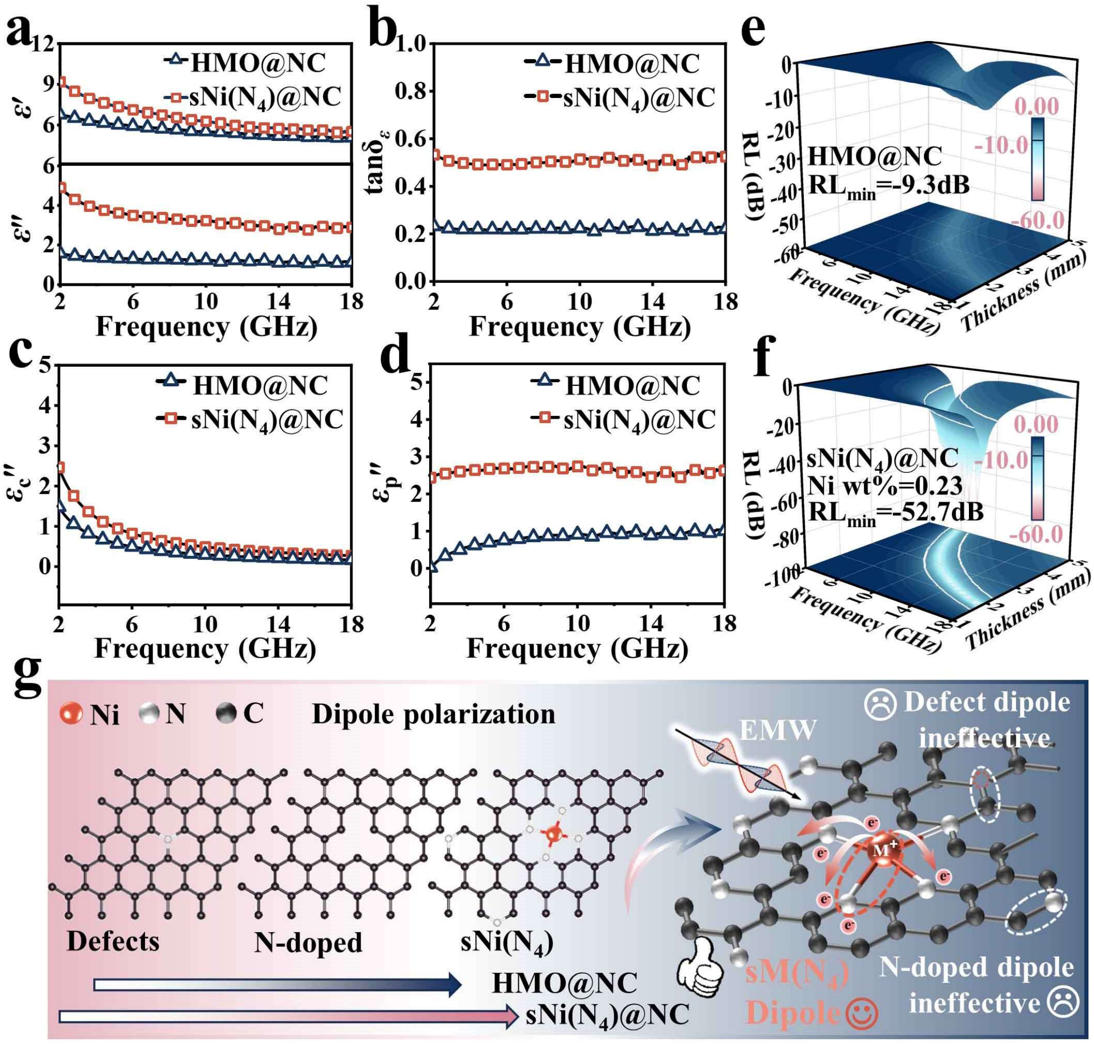
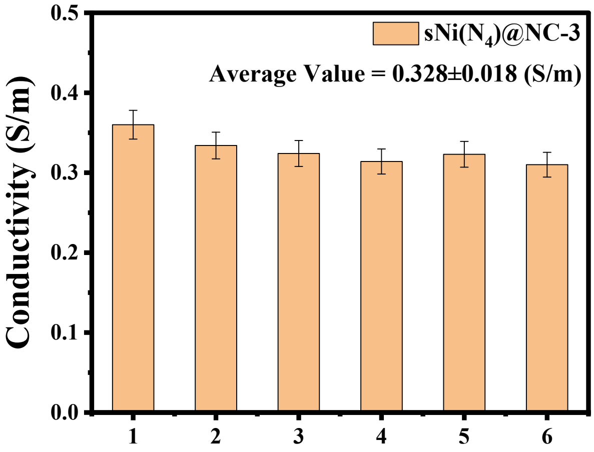


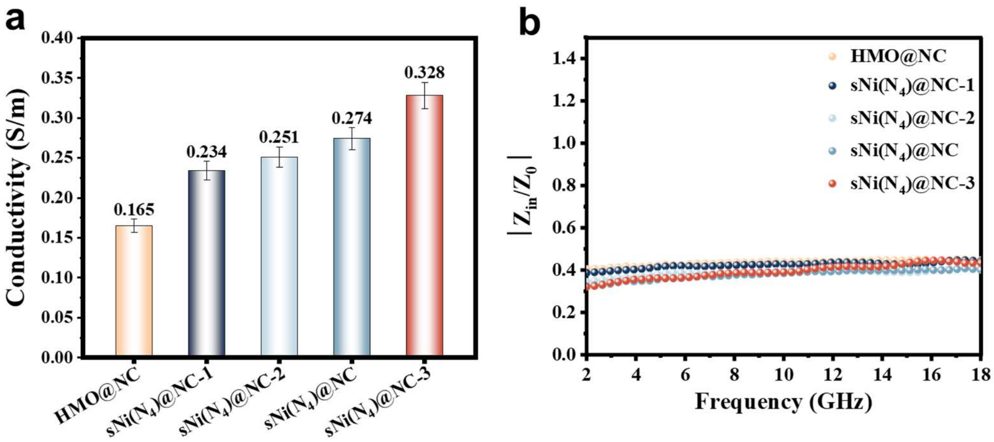
Fig. 3 | EMW absorption measurements: (a) Real (ε') and imaginary (ε'') parts of permittivity, (b) Tan δ_ε, (c) Conduction loss (ε_c'') and (d) Polarization relaxation loss (ε_p'') of HMO@NC and sNi(N_4)@NC. 3D RL plots of (e) HMO@NC and (f) sNi(N_4)@NC. (g) Dipole polarization species for HMO@NC and sNi(N_4)@NC.

Q5. Why does SUR-sNi-N_4@NC-100 have a lower ε', ε'' and ε''c despite its higher conductivity, compared with SUR-sNi-N_4@NC-60 and SUR-sNi-N_4@NC-80? Please check whether the conductivity test results are reliable.

Answer: *We thank the reviewer for the comment. We are sure that the conductivity test results are reliable. To make the data more solid. We retested the conductivity of the samples several times. The average conductivity of* *sNi(N_4)@NC-100 (sNi(N_4)@NC-3) is 0.328±0.018 S/m, which is still higher than sNi(N_4)@NC-1 and sNi(N_4)@NC-2.*



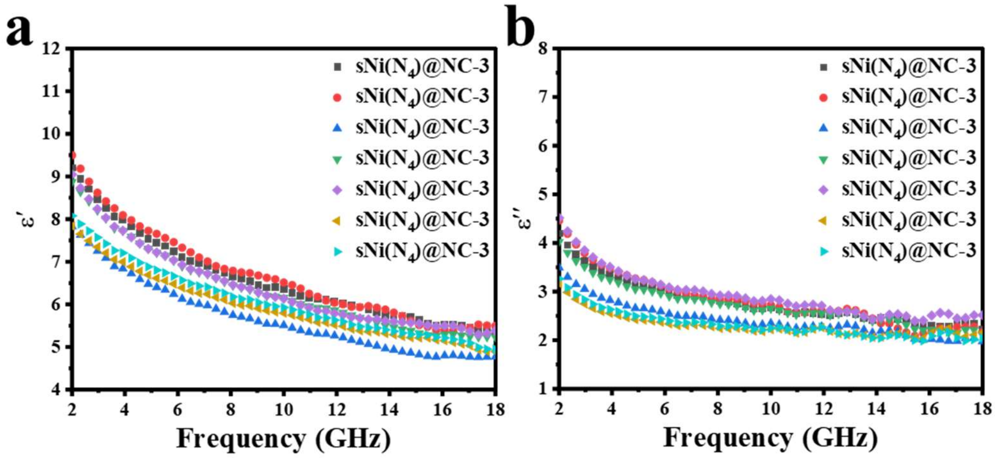
Supplementary Figures only for reviewer, Fig. 4 | Conductivity of sNi(N_4)@NC-3.



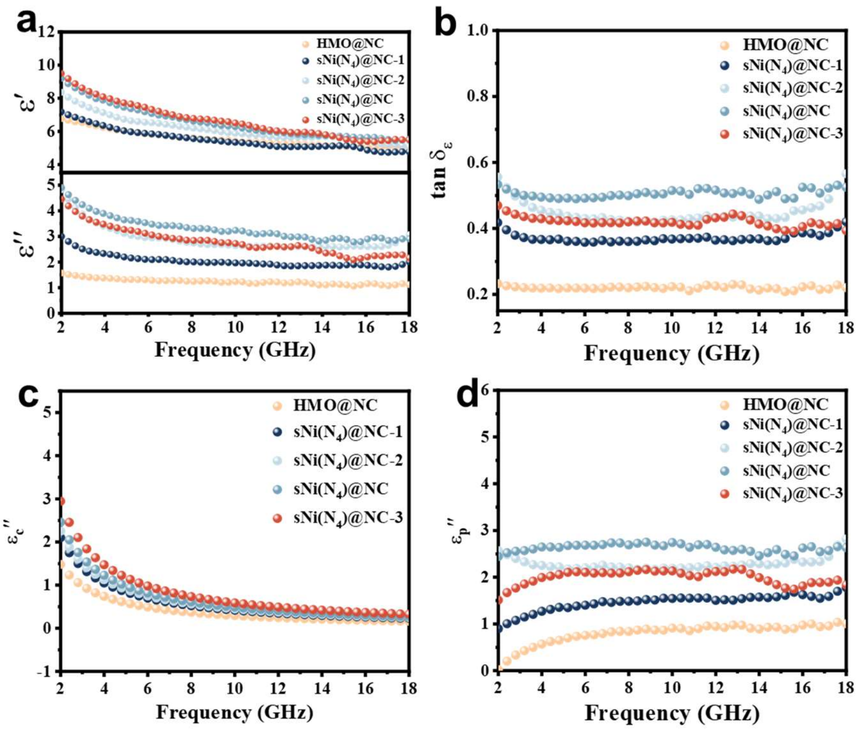
Supplementary Fig. 18 | a) Conductivity and b) Impedance matching of HMO@NC, sNi(N_4)@NC-1, sNi(N_4)@NC-2, sNi(N_4)@NC and sNi(N_4)@NC-3.

Then, the electromagnetic parameters of sNi(N_4)@NC-3 were retested several times. Due to the need to calibrate the instrument state before each test, after several measurements, the results show that the electromagnetic parameters will go up and down in a small range under different test states

*(**Supplementary Figures only for reviewer, Fig. 5**). Therefore, sNi(N_4)@NC-3 have a lower ε' and ε'' may due to different test batches.*



Supplementary Figures only for reviewer, Fig. 5 | Electromagnetic parameters of sNi(N_4)@NC-3 tests: a) Real (ε′) and imaginary (ε″) part of permittivity.

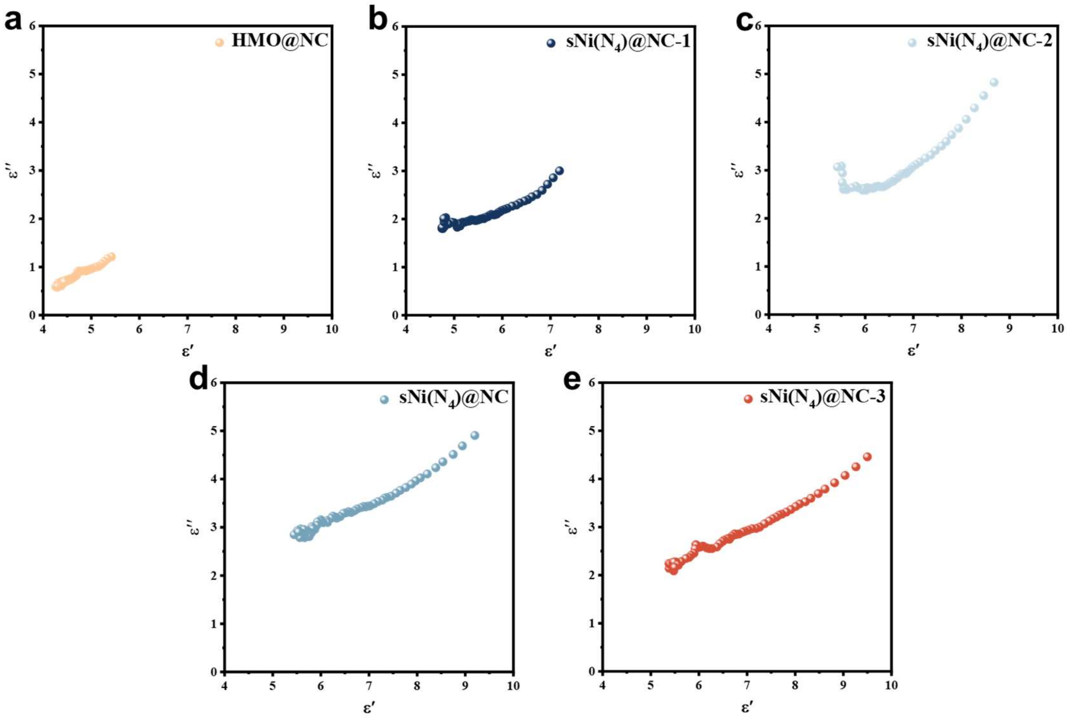


Supplementary Fig. 16 | Electromagnetic parameters of HMO@NC, sNi(N_4)@NC-1, sNi(N_4)@NC-2, sNi(N_4)@NC and sNi(N_4)@NC-3 tests: a) Real (ε′) and imaginary (ε″) part of permittivity, b) Tan δε, c) Conduction loss

(ε_c'') and d) Polarization relaxation loss (ε_p'') of HMO@NC, sNi(N_4)@NC-1, sNi(N_4)@NC-2, sNi(N_4)@NC and sNi(N_4)@NC-3.

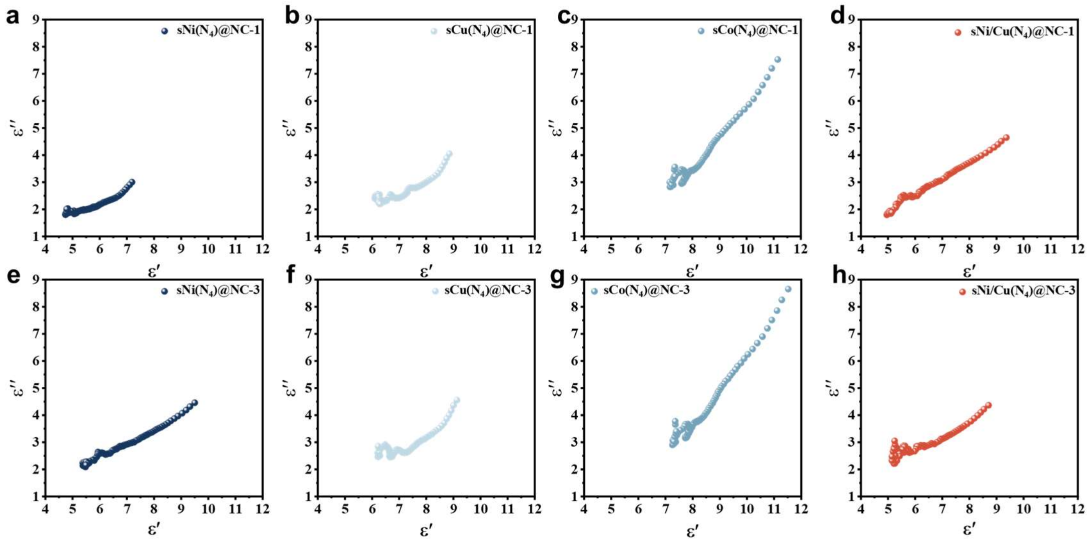
Q6. All Cole-Cole plots should be square and must be on the same X- and Y-axis scale to evaluate conduction loss for different samples.

Answer: *We appreciate the reviewer for bringing up these questions. We have adjusted all Cole-Cole plots to squares and standardized the X- and Y-axes of all samples to conduct a more thorough evaluation of the samples' conductance loss. The relative contents have been included in the updated supplementary information for further clarity.*



Supplementary Fig. 17 | Cole-Cole semicircles of a) HMO@NC, b) sNi(N_4)@NC-1, c) sNi(N_4)@NC-2, d) sNi(N_4)@NC and e) sNi(N_4)@NC-3.

"According to the Debye theory, the semicircle observed in the Cole-Cole plot corresponds to the polarization relaxation process, while the straight tail represents the conduction loss. As shown in **Supplementary Fig. 17**, it is evident that the dielectric losses of HMO@NC, sNi(N_4)@NC-1, sNi(N_4)@NC-2, sNi(N_4)@NC, and sNi(N_4)@NC-3 are attributed to the conduction loss and polarization relaxation process. As the Ni content increases, the samples exhibit higher slopes at the tail of the Cole-Cole curves as well as more semicircles, implying the existence of conduction loss and polarization loss. And more semicircles mean more polarization relaxation processes occur in the alternating electromagnetic field favoring the absorption of electromagnetic wave."

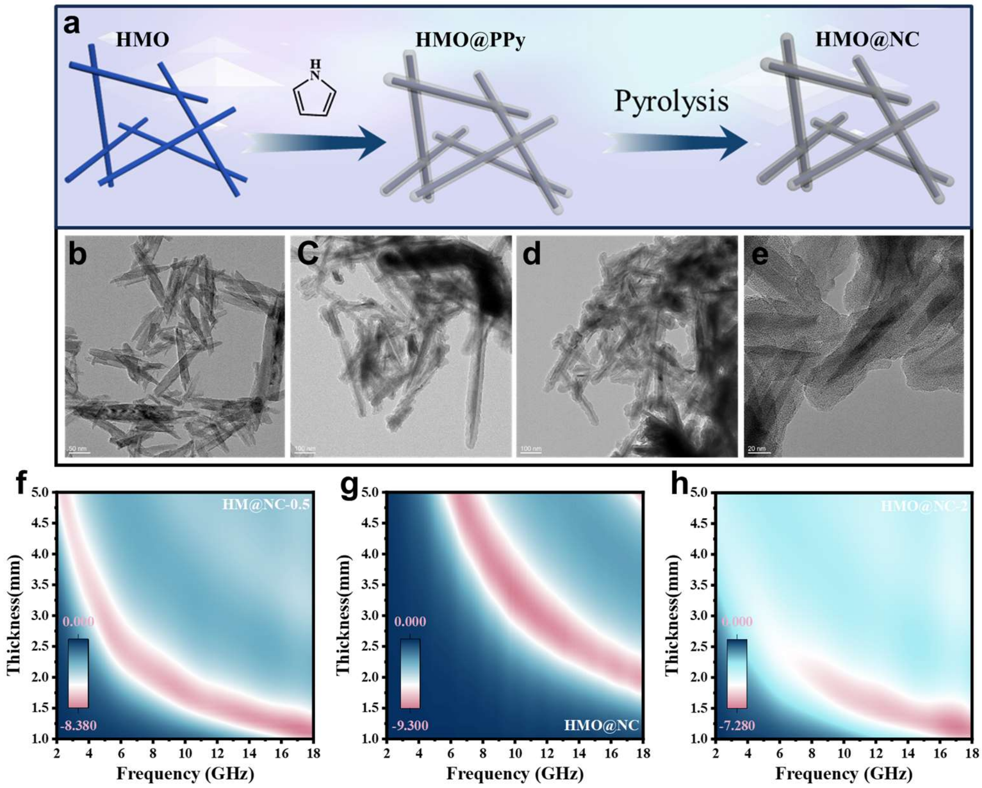


Supplementary Fig. 25 | Cole-Cole semicircles of a) sNi(N$_4$)@NC-1, b) sCu(N$_4$)@NC-1, c) sCo(N$_4$)@NC-1, d) sNi/Cu(N$_4$)@NC-1, e) sNi(N$_4$)@NC-3, f) sCu(N$_4$)@NC-3, g) sCo(N$_4$)@NC-3 and h) sNi/Cu(N$_4$)@NC-3.

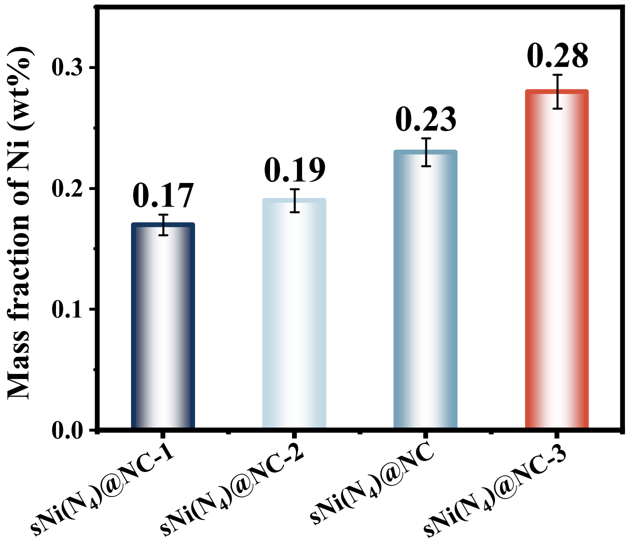
"sCo(N$_4$)@NC-1 show the most semicircles in the Cole-Cole plots, indicating that sCo(N$_4$)@NC-1 has the most polarization loss. Moreover, the number of semicircles in the Cole-Cole plots is in the order sCo(N$_4$)@NC-1 > sNi/Cu(N$_4$)@NC-1 > sCu(N$_4$)@NC-1 > sNi(N$_4$)@NC-1, which is consistent with their EMW absorption properties."

Q7. The authors point out that by comparing SUR-sNi-N$_4$@NC-80 and SUR-sNi-N$_4$@NC-100, it shows that HMO only plays a supporting role. However, there is another explanation here. The complete dissolution of HMO leads to an increase in the conductivity of SUR-sNi-N$_4$@NC-100, which causes the impedance mismatch of SUR-sNi-N$_4$@NC-100. Therefore, HMO may not only provide a supporting role. Furthermore, theoretically, the existence of HMO may also bring considerable heterogeneous interfaces and possible interfacial polarization loss. So this conclusion is too hasty.

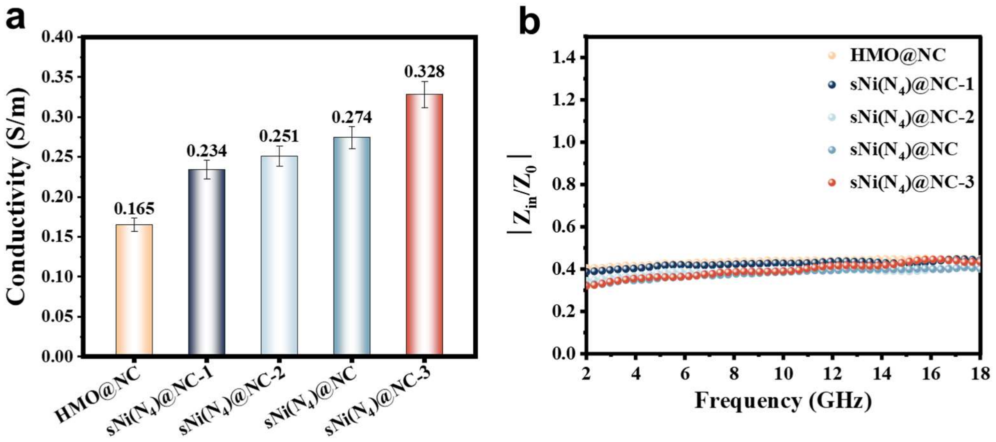
Answer: *We thank the reviewer for the critical comments. Theoretically, heterogeneous interfaces formed by HMO and carbon may introduce interfacial polarization loss. However, HMO@NC has no EMW absorption performance (**Supplementary Fig. 1g**), which helps us to initially exclude the contribution of the polarization loss from the interface between HMO and carbon to the EMW absorption performance. Moreover, the data show an increase in the efficiency of the click reaction as the reaction temperature increases, an increase in the content of Ni atoms (**Supplementary Fig. 10**), which increases the conductivity of the samples (sNi(N_4)@NC, sNi(N_4)@NC-1/-2/-3), as well as the dissolution of HMO, which induces an increase in the conductivity of the sample (sNi(N_4)@NC-3) (**Supplementary Fig. 18a)**. However, the difference between the conductivity of sNi(N_4)@NC-2 and sNi(N_4)@NC-3 is small, so the conductivity of sNi(N_4)@NC-3 is not sufficient to cause impedance mismatch (**Supplementary Fig. 18b)**, which can be verified by the fact that after HMO dissolution, there is no significant degradation of the EMW absorption performance of sNi(N_4)@NC-3 (RL_{min} = -32.9 dB, EAB = 5.68 GHz) compared to sNi(N_4)@NC (RL_{min} = -52.7 dB, EAB = 6.08 GHz) (**Supplementary Fig. 21a**). Therefore, we conclude that the interfacial polarization generated by the heterogeneous interface between HMO and carbon can be neglected and is not the main reason for the superior EMW absorption performance of sNi(N_4)@NC/-1/-2/-3. The increase in the EMW absorption performance is due to the increase in dielectric losses (including conduction and dipole polarization losses) due to the increase in Ni content (**Supplementary Fig. 16c,d**).*



Supplementary Fig. 1 | HMO@NC preparation and characterization: a) Schematic diagram of the preparation of HMO@NC. TEM image of HMO@NC with different mass ratios of PPy: b) 2:1, c) 1:1 and c, d) 1:2. f) EWM absorption performance diagram of HMO@NC-0.5, g) HMO@NC and h) HMO@NC-2.



Supplementary Fig. 10 | ICP-OES spectrum of sNi(N_4)@NC-1, sNi(N_4)@NC-2, sNi(N_4)@NC and sNi(N_4)@NC-3.



Supplementary Fig. 18 | a) Conductivity, b) Impedance matching of HMO@NC, sNi(N_4)@NC-1, sNi(N_4)@NC-2, sNi(N_4)@NC and sNi(N_4)@NC-3.

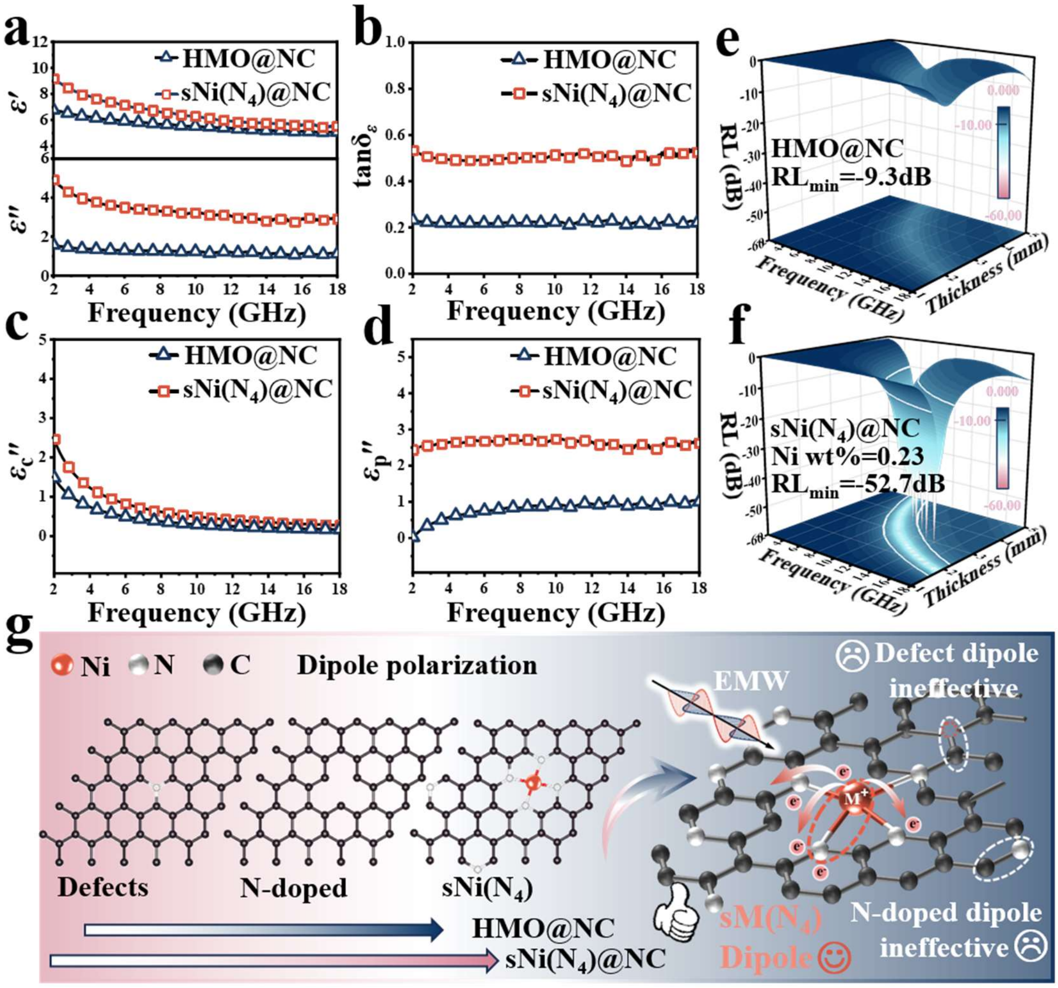
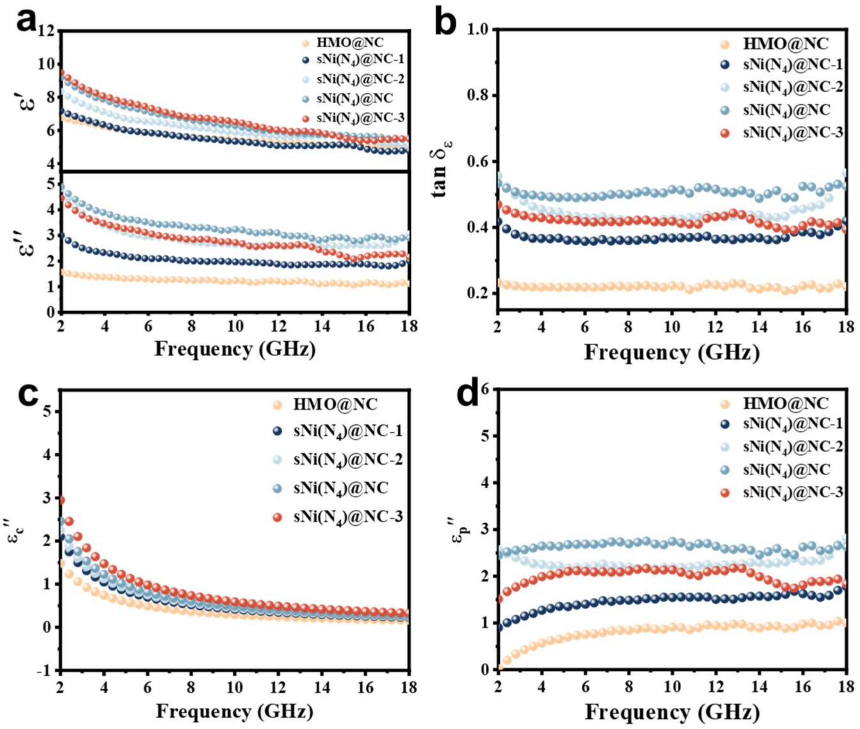
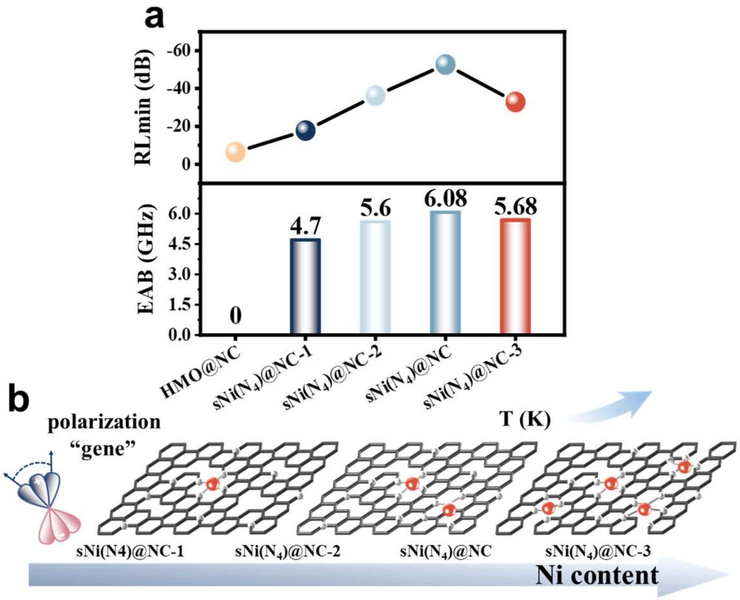


Fig. 3 | EMW absorption measurements: (a) Real (ε') and imaginary (ε'') parts of permittivity, (b) Tan δ_ε, (c) Conduction loss (ε_c'') and (d) Polarization relaxation loss (ε_p'') of HMO@NC and sNi(N_4)@NC. 3D RL plots of (e) HMO@NC and (f) sNi(N_4)@NC. (g) Dipole polarization species for HMO@NC and sNi(N_4)@NC.



Supplementary Fig. 16 | Electromagnetic parameters of HMO@NC, sNi(N_4)@NC-1, sNi(N_4)@NC-2, sNi(N_4)@NC and sNi(N_4)@NC-3 tests: a) Real (ε′) and imaginary (ε″) part of permittivity, b) Tan δε, c) Conduction loss (ε_c'') and d) Polarization relaxation loss (ε_p'') of HMO@NC, sNi(N_4)@NC-1, sNi(N_4)@NC-2, sNi(N_4)@NC and sNi(N_4)@NC-3.



Supplementary Fig. 21 | a) Summary of EAB and RLmin for all the samples. b) As the reaction temperature increases, the content of Ni increase.

*To verify this conclusion, we prepared samples loaded with different metal atoms at 30°C ($sM(N_4)@NC$-1, M: Ni, Cu, Co, Ni/Cu) and 100°C ($sM(N_4)@NC$-3, M: Ni, Cu, Co, Ni/Cu), respectively. The data show that compared with $sM(N_4)@NC$-1, the RL_{min} of $sM(N_4)@NC$-3 is only slightly decreased, while the EAB of $sM(N_4)@NC$-3 is wider than that of $sM(N_4)@NC$ (**Fig. 4b**). This further proves that the polarization from the interface between HMO and C is not the main reason for its excellent EMW absorption performance. And by comparing the data of the samples at the same temperature, we find that the conductivity of the samples does not increase significantly when loaded with different metal atoms at the same temperature, which means that the enhancement of the conduction loss is not the main reason for the difference in the EMW absorption performance (**Supplementary Fig. 26a,b**), and by separating out the polarization loss, we can find that the dipole polarization loss caused by different electronegative metal atoms is the main reason for the difference in the EMW absorption performance (**Supplementary Fig. 26c**). This conclusion is verified by the DFT calculations in the article.*

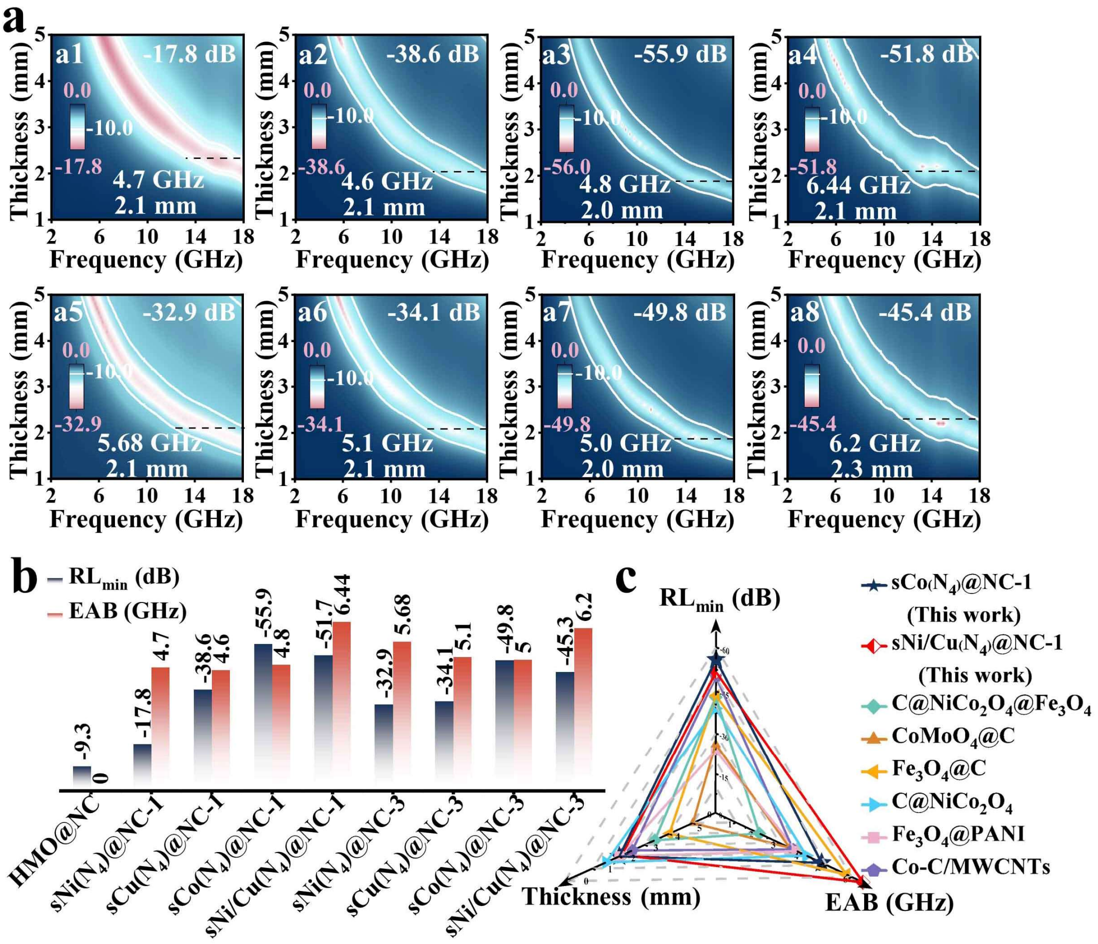
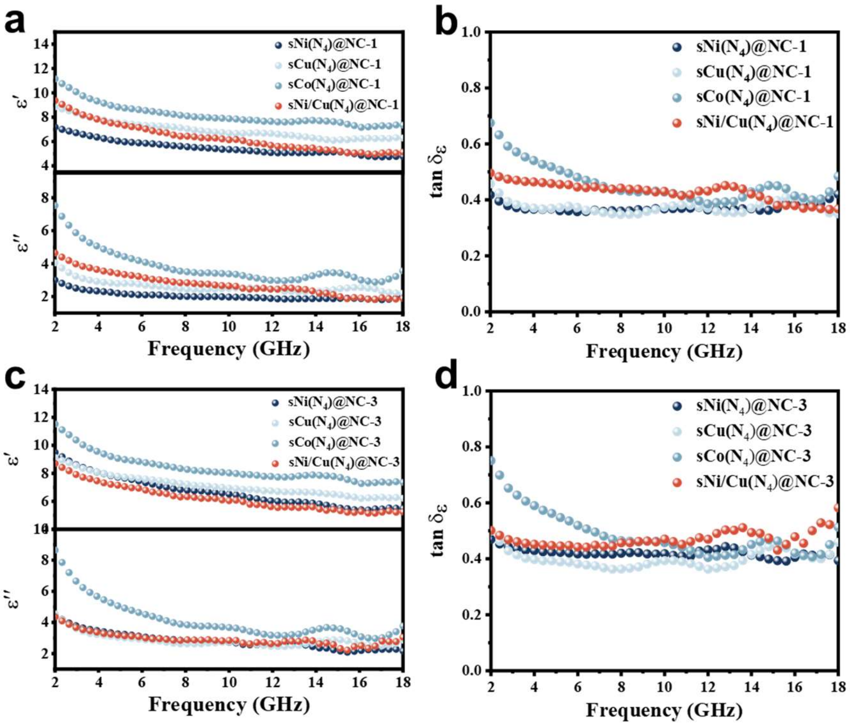
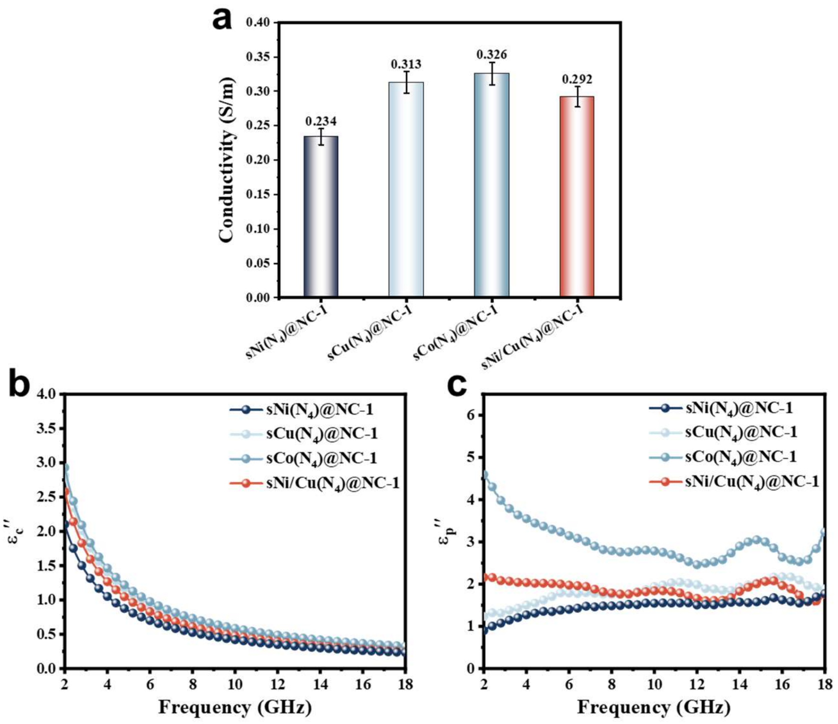


Fig. 4 | EMW absorption properties of sM(N_4)@NC with different single metal sites: 2D reflecting loss (RL) plots of (a1) sNi(N_4)@NC-1, (a2) sCu(N_4)@NC-1, (a3) sCo(N_4)@NC-1, (a4) sNi/Cu(N_4)@NC-1, (a5) sNi(N_4)@NC-3, (a6) sCu(N_4)@NC-3, (a7) sCo(N_4)@NC-3 and (a8) sNi/Cu(N_4)@NC-3. (b) summary of RL_{min} and EAB of the samples with different metal single atoms. (c) comparison of EAB, thickness, and RL_{min} for the EMW absorption performances of some representative carbon-based absorbers.



Supplementary Fig. 24 | Dielectric loss mechanism analysis. a) Real and imaginary part of permittivity, and b) Tan δε of sM(N_4)@NC-1 (M= Ni, Cu, Co and Ni/Cu). c) Real and imaginary part of permittivity, and d) Tan δε of sM(N_4)@NC-3 (M= Ni, Cu, Co and Ni/Cu).



Supplementary Fig. 26 | a) Conductivity, b) Conduction loss and c) Polarization relaxation loss of sM(N_4)@NC-1 (M= Ni, Cu, Co, Ni/Cu).

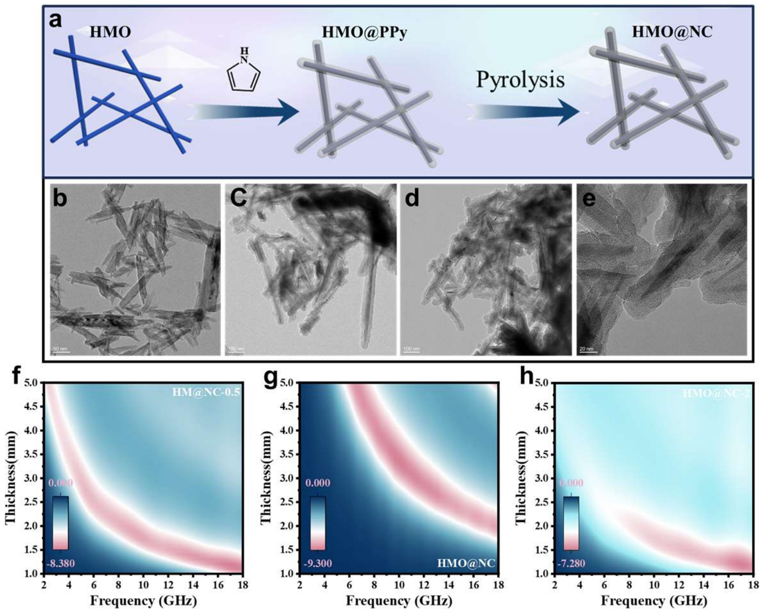
Overall, the conclusions are drawn after comprehensive testing and systematic analysis of a large number of samples.

Q8, The author did not explain clearly how to exclude interfacial polarization loss. Theoretically, there are a large number of heterogeneous interfaces between HMO, NC and Ni atoms. Please explain how to eliminate the interfacial polarization loss contribution. More importantly, as the amount of Ni increases, the heterogeneous interfaces will also increase. If the contributions of interfacial polarization loss and dipole polarization loss cannot be effectively distinguished, the existence of dipole loss cannot be proven.

Answer*: We thank the reviewer for the comments.*

(1) Theoretically, I agree with the reviewer that there probably have two heterogenous interfaces, however, in our case, based on extensive experimental data, characterization analyses, and the development of mathematical models, we conclude that interfacial loss can be considered negligible.

__a）Regarding the HMO/NC__：HMO@NC has been demonstrated to lack wave-absorbing capabilities, indicating that the heterojunction between HMO and NC does not generate significant interfacial loss affecting the material's absorption performance (__Supplementary Fig. 1__). Furthermore, when HMO is etched away at high temperatures (sM(N_4)@NC-3), it is observed that the removal of the HMO and NC interface still results in an enhanced effective bandwidth (__Fig. 3__). This further suggests that interfacial loss between HMO and NC plays a minimal role in this model. Thus, our simplified model implies that the interfacial loss between HMO and NC can be considered negligible.



Supplementary Fig. 1 | HMO@NC preparation and characterization: a) Schematic diagram of the preparation of HMO@NC. TEM image of HMO@NC with different mass ratios of PPy: b) 2:1, c) 1:1 and c, d) 1:2. f) EWM absorption performance diagram of HMO@NC-0.5, g) HMO@NC and h) HMO@NC-2.

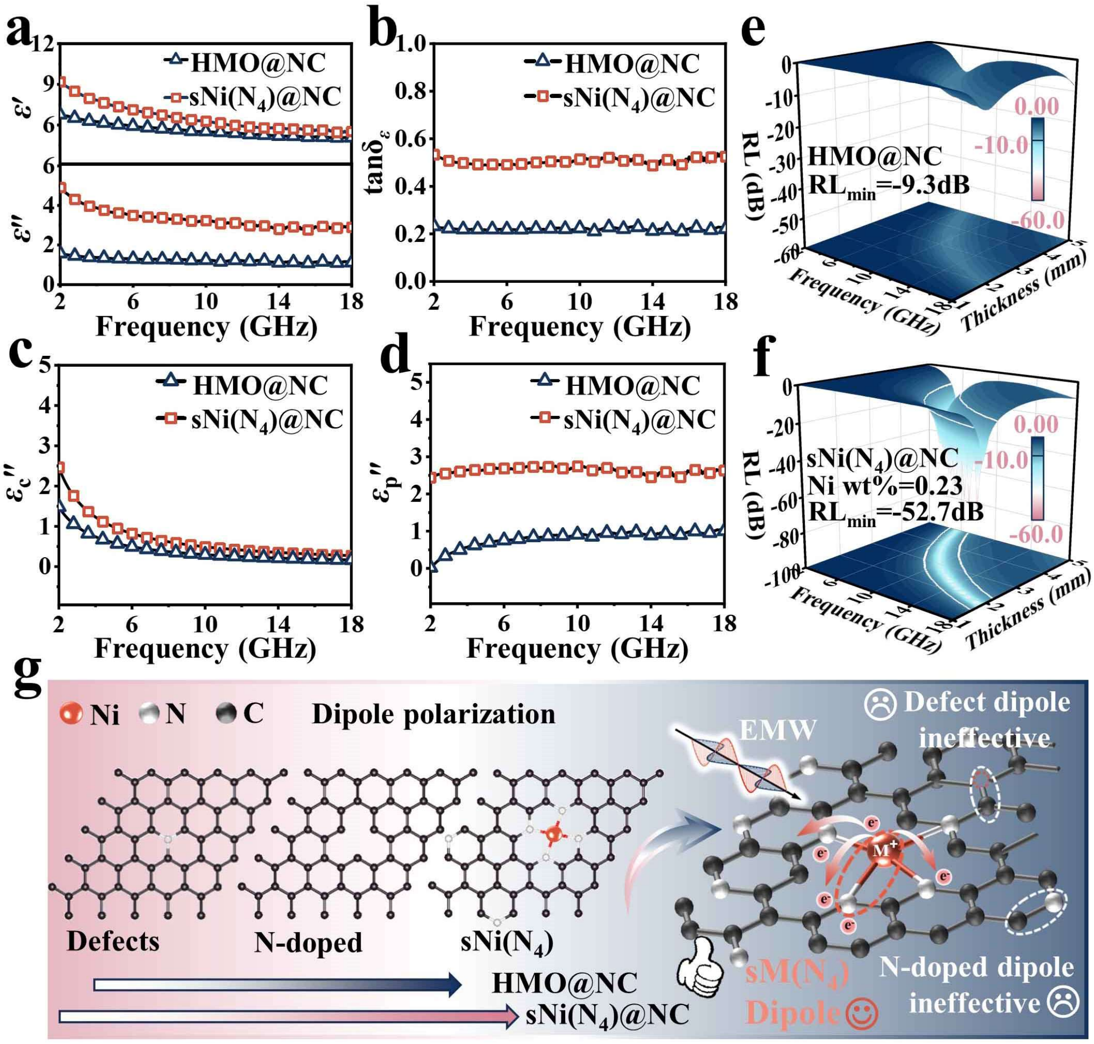


Fig. 3 | EMW absorption measurements: (a) Real (ε') and imaginary (ε'') parts of permittivity, (b) Tan δ_ε, (c) Conduction loss (ε_c'') and (d) Polarization relaxation loss (ε_p'') of HMO@NC and sNi(N_4)@NC. 3D RL plots of (e) HMO@NC and (f) sNi(N_4)@NC. (g) Dipole polarization species for HMO@NC and sNi(N_4)@NC.

***b) Regarding the NC and Ni atoms*：** *XANES analysis reveals that Ni atoms form only Ni(*N_4*) bonds, indicating that Ni does not form a metal layer (**Fig. 2**). Since the single Ni atoms are embedded in the carbon layer and their content is only about 0.2 wt%, we believe they cannot form a continuous layer (**Supplementary Fig. 10**). Instead, the relationship between the Ni atoms and the NC layer is a point-to-plane interaction. The introduction of Ni atoms leads to charge redistribution, disrupting the symmetry of the local microstructure and creating new dipole polarization losses (**Supplementary Fig. 21**).*

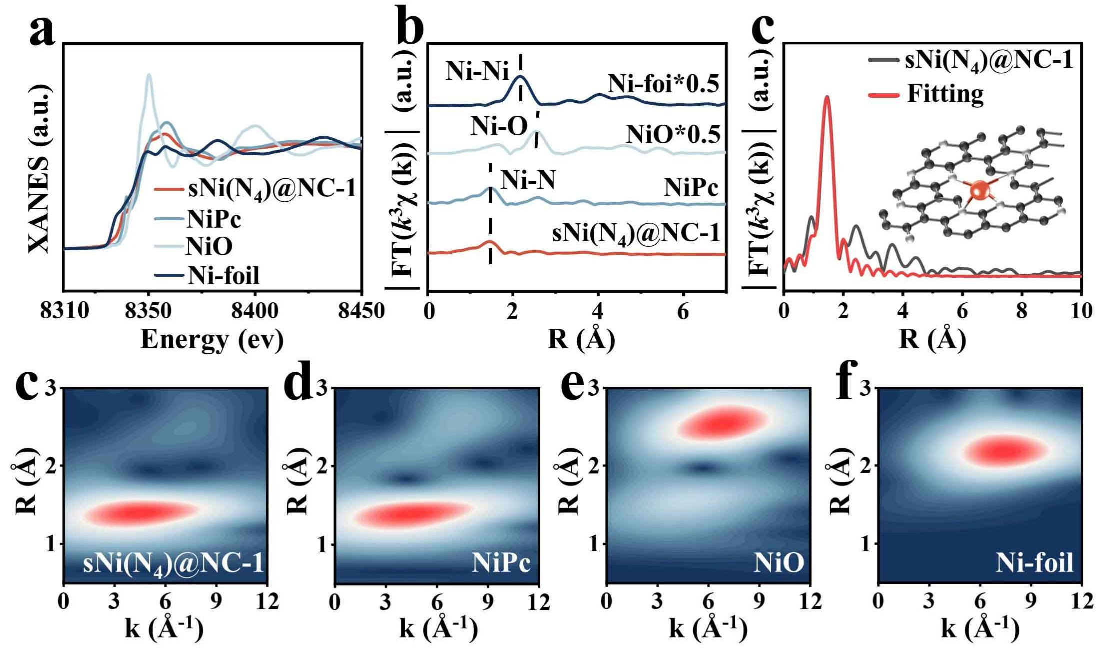
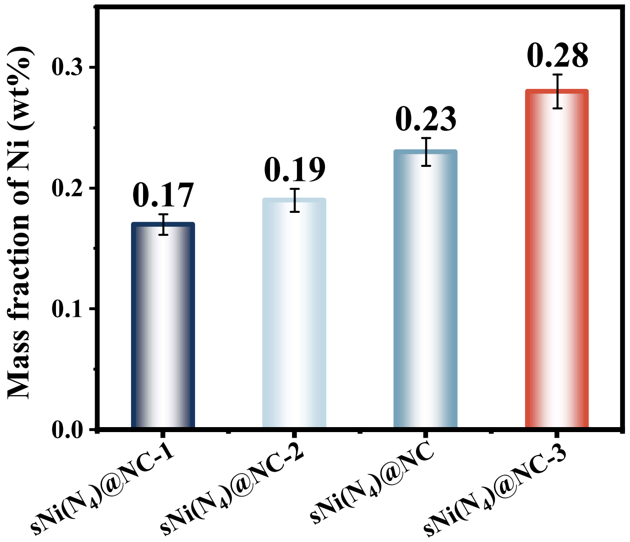
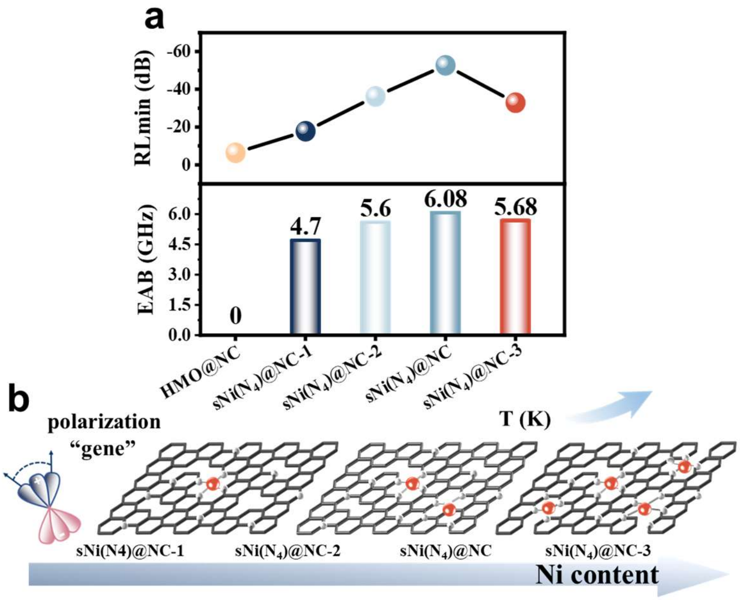


Fig. 2 | Synchrotron X-ray absorption spectrum characterization: (a) XANES spectrum at the Ni K-edge, (b) EXAFS spectra in reciprocal space, (c) EXAFS fitting results of sM(N$_4$)@NC (Inset: illustration of the NiN$_4$). Wavelength transformations observed in (d) sM(N$_4$)@NC, (e) NiPc, (f) NiO, and (g) Ni-foil.

*(2) XANES analysis reveals that Ni atoms form only Ni(N$_4$) bonds, indicating that Ni does not form a metal layer. As the click reaction temperature increases, while the reactant concentration remains constant, the grafting rate of NiPor and the single-atom loading rate increase (****Supplementary Fig. 10****). However, even at 100°C, the Ni single-atom content is only 0.28 wt%, insufficient to form a heterojunction between Ni and NC. Nonetheless, the increased Ni content disrupts more local microstructural symmetry and induces additional dipoles, resulting in more dipole polarization loss (****Supplementary Fig. 21****). Consequently, this enhances the material's electromagnetic wave absorption performance.*



Supplementary Fig. 10 | ICP-OES spectrum of sNi(N_4)@NC-1, sNi(N_4)@NC-2, sNi(N_4)@NC and sNi(N_4)@NC-3.



Supplementary Fig. 21 | a) Summary of EAB and RLmin for all the samples. b) As the reaction temperature increases, the content of Ni increase.

Q9, I don't think it is scientific and reasonable to introduce electrochemical testing methods such as EIS and Tafel plots. First of all, this confuses the concepts of electrochemical polarization and polarization under electromagnetic fields. In electrochemical tests, the usual scenario is that charge is transferred between the electrolyte and the electrode, which is completely inconsistent with the actual use scenario of EMW absorption materials. Secondly, in EIS testing, the test frequency is typically 1 MHz to 0.01 Hz, which completely deviates from the frequency used for EMW absorbing materials. Therefore, in my opinion, these tests are inapplicable and meaningless. The authors should carefully consider whether to abandon these experiments unless sufficiently convincing theoretical evidence can be provided.

Answer*: We are grateful for the reviewer's guidance on this matter. Our references include the studies of several articles, such as Gogotsi et al., who delved into the correlation between the electrochemical behaviour of MXenes and their interaction with electromagnetic radiation using electrochemistry (Nat. Nanotechnol. 18, 373–379 (2023)), and Wu et al., who examined the polarisation state and carrier behaviour of samples through electrochemical detection (Adv. Funct. Mater. 2022, 32, 2112294, Adv. Funct. Mater. 2022, 32, 2112294).*

Furthermore, we did not directly confirm the conclusions of this work through electrochemical testing methods; instead, we validated the samples' charge migration properties through electrochemical tests. The results from the electrochemical tests aligned with the electron migration properties obtained from DFT theory calculations. It was observed that samples modified with different metal atoms exhibited similar electron migration properties across various test ranges.

RESPONSE TO REVIEWERS' COMMENTS

Reviewer #1

1. I am satisfied with the revised version of the manuscript and think it can be published as it is.

Answer: *We greatly appreciate the reviewers for their overall positive feedback and helpful suggestions, which have improved our manuscript.*

Reviewer #2

The authors have revised the manuscript accordingly and some issues have been addressed. After the author's additional explanation, the logic of the paper is largely self-consistent. Some suggestions for improving this paper are still worth considering before publication.

Answer: *We sincerely appreciate the reviewer's constructive points, which have greatly enhanced the quality of our paper.*

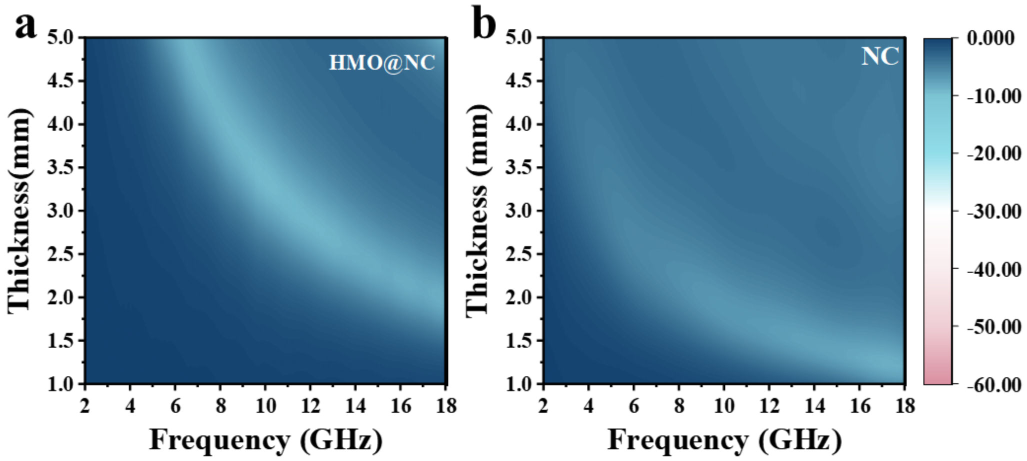
Q1. I suggest the authors recheck misprints in abstract and other sections.

Answer: *Thank you very much for the suggestions. We have thoroughly reviewed the manuscript for typographical errors and made the necessary corrections as below (the yellow-highlighted sections refer to the revisions introduced).*

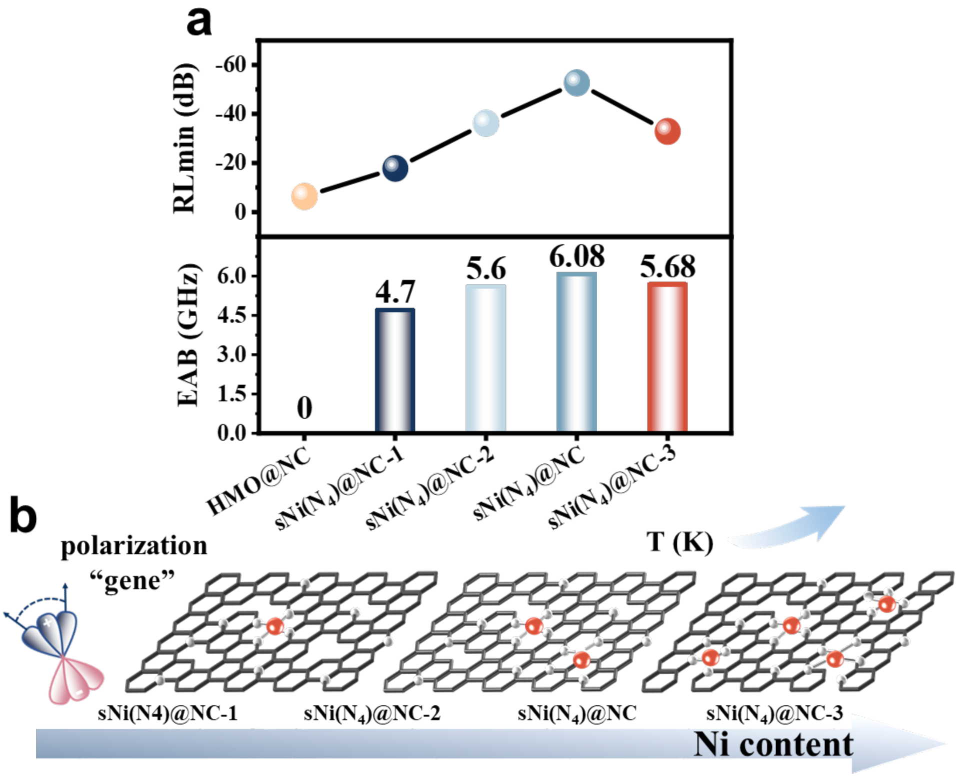
"Surface modulation strategies have spurred great interest with regard to regulating the morphology, dispersion and flexible processability of materials. Unsurprisingly, customized modulation of surfaces is primed to offer a route to control their electronic functions. To regulate electromagnetic wave (EMW) absorption applications by surface engineering is an unmet challenge. Thanks to pyrolyzing surface-anchored metal-porphyrin, here we report on the surface modulation of four-nitrogen atoms confined single metal site on a nitrogen-doped carbon layer (sM(N_4)@NC, M=Ni, Co, Cu, Ni/Cu) (sM=single metal; NC= nitrogen-doped carbon layer) that registers electromagnetic wave absorption. Surface-anchored metal-porphyrins are afforded by attaching them onto the polypyrrole surface *via* a prototypical click reaction. Further, sM(N_4)@NC was experimentally found to elicit an identical dipole polarization loss mechanism, overcoming the handicaps of conductivity loss, defects, and interfacial polarization loss among the current EMW absorber models. Significantly, the sM(N_4)@NC exhibit an effective absorption bandwidth of 6.44 and reflection loss of -51.7 dB, preceding state-of-the-art carbon-based EMW absorbers. This study introduces a surface modulation strategy to design EMW absorbers based on single metal sites that enable fine-tunable and controlled absorption mechanism with atomistic precision."

Q2. It seems that the introduction of HMO complicates the study of the EMW absorption mechanism. The different degrees of HMO dissolution bring about changes in the HMO/NC interfaces. The resulting hollow structure may also introduce additional air/NC interfaces. So, the necessity of introducing HMO should be given at the beginning of the paper, avoiding readers' confusion. And whether the hollow structure has any influence on the conclusion of this paper needs to be clarified.

Answer: *We thank the reviewer very much for this suggestion. In this study, HMO serves mainly as a support for PPy, and our experimental results suggest that the presence or absence of HMO has only a minimal impact on the material's electromagnetic wave absorption performance. This is why we humbly submit that it may not be essential to emphasize HMO in the introduction. First, experiments demonstrate that the HMO/NC interface loss has little effect on electromagnetic wave absorption. As the temperature increases, HMO partially dissolves, reducing the HMO/NC interface. At 100°C, a hollow NC structure forms, and experiments confirm that NC lacks electromagnetic wave absorption capability, indicating that the hollow structure does not enhance the electromagnetic wave absorption of HMO@NC (Supplementary Figure R1). Additionally, by adjusting the reaction temperature, we can tune the HMO/NC interface and the single-atom Ni content in the* *material. It was observed that as the metal content increases, both RL_{min} and EAB improve. However, in the hollow sNi(N4)@NC-3, RL_{min} and EAB decrease compared to sNi(N4)@NC (Supplementary Fig. 21), suggesting that the hollow structure does not play a significant role in electromagnetic wave loss in this material.*



Supplementary Figure R1 (only for reviewer): EWM absorption performance diagram of a) HMO@NC and b) NC.



Supplementary Fig. 21 | a) Summary of EAB and RL$_{min}$ for all the samples. b) As the reaction temperature increases, the content of Ni increases.

Q3. For the academic rigor, I still disagree with using electrochemical methods to verify the DFT calculation results. Because Rct actually describes the charge transfer between the the active materials (sNi(N4)@NC) and electrolyte, which is deeply affected by the conductivity and specific surface area of the active material, etc. It is far-fetched to support the DFT results. A similar problem exists in the discussion of Tafel slopes. I suggest that the authors should use these data as evidence cautiously.

Answer*: We are grateful for this thoughtful suggestion. We have very carefully conducted the literature research again, thinking about the "effectiveness" of using "the electrochemical method" as an auxiliary support. The goal of the electrochemical method used here is to demonstrate that the polarization trends align with those observed in the DFT calculations, rather than to provide the exact polarization values within the frequency range of 10 mHz to 105 Hz or 2 GHz to 18 GHz. The polarization characteristics often exist both in low* *frequency (10 mHz to 105 Hz) and high frequency (2 GHz to 18 GHz). We totally agree with the reviewer that the polarization values in different frequency ranges will demonstrate different polarized values. To avoid misunderstanding and unnecessary confusion for the readers, we have removed any language suggesting that electrochemical methods were used to validate the DFT results. We sincerely appreciate your feedback/suggestions in helping us avoid this misunderstanding. Accordingly, our revised text in the manuscript is written below:*

The carrier behaviors were further analyzed by electrochemically derived Tafel curves. The Tafel plots revealed that surface-modification of single metal atoms leads to a decrease in the Tafel slope, which can be attributed to the improvement of charge carrier behavior (Supplementary Fig. 30a-30c). As the loading of sM(N4) increases and the electronegativity of the metals decreases, the overpotential gradually increases, indicating that electrode polarization is primarily due to dipole polarization induced by sM(N4) (Supplementary Figs. 30a-30c). The electrochemical impedance spectra (EIS) further confirm that the modification of sM(N4) reduces charge transfer resistance (R_{ct}) (Supplementary Figs. 30d, e). This suggests an order of increasing carrier mobility from sNi(N4)@NC-1 to sCu(N4)@NC-1 to sCo(N4)@NC-1, demonstrating how this trend facilitates interfacial charge transfer.