

Supporting Information for

Structural Engineering of Hierarchical Aerogels Comprised of Multidimensional Gradient Carbon Nanoarchitectures for Highly Efficient Microwave Absorption

Yongpeng Zhao^{1, 2}, Xueqing Zuo¹, Yuan Guo¹, Hui Huang¹, Hao Zhang¹, Ting Wang¹, Ningxuan Wen¹, Huan Chen^{1, 2}, Tianze Cong¹, Javid Muhammad¹, Xuan Yang³, Xinnan Wang⁴, Zeng fan^{1, *}, Lujun Pan^{1, *}

¹School of Physics, Dalian University of Technology, Dalian, Liaoning 116024, P. R. China

²School of Microelectronics, Dalian University of Technology, Dalian, Liaoning 116024, P. R. China

³School of Materials Science and Engineering, Dalian University of Technology, Dalian, Liaoning 116024, P. R. China

⁴School of Chemical Engineering, Dalian University of Technology, Dalian, Liaoning 116024, P. R. China

*Corresponding authors. E-mail: lpan@dlut.edu.cn (L. Pan); fanzeng@dlut.edu.cn (Z. Fan)

Supplementary Tables and Figures

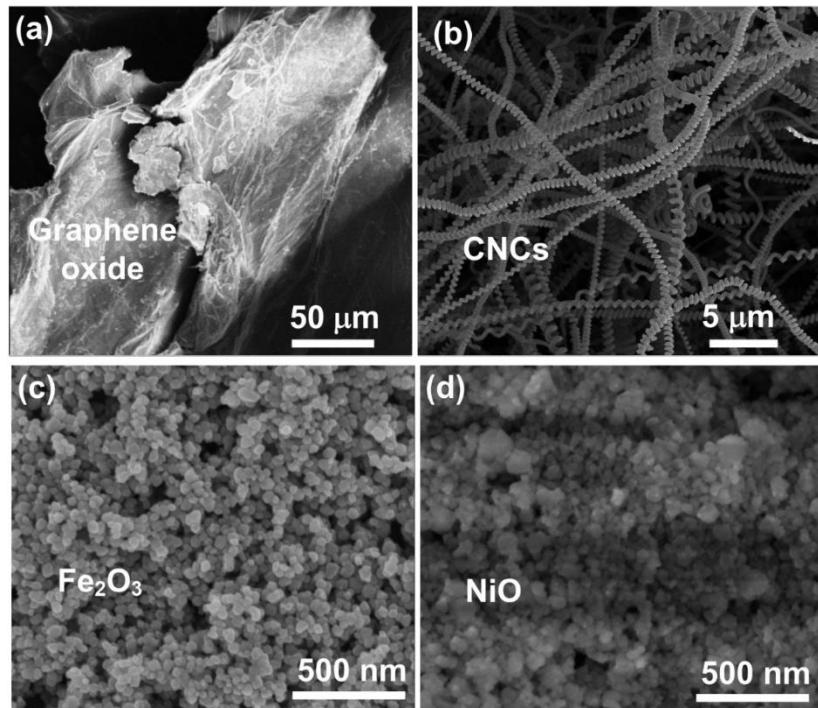


Fig. S1 SEM images of (a) graphene oxide, (b) CNCs, (c) Fe₂O₃, and (d) NiO

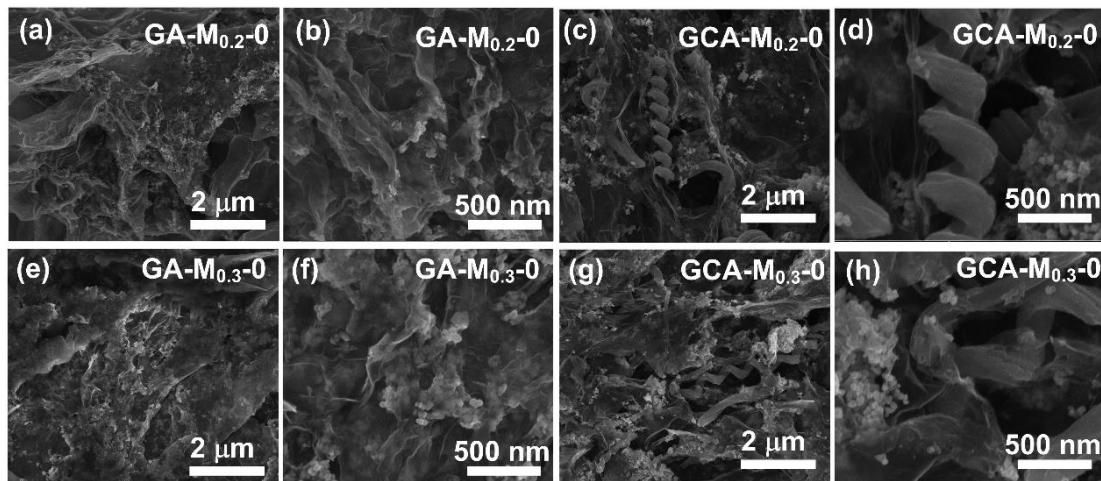


Fig. S2 SEM images of (a, b) GA-M_{0.2}-0, (c, d) GCA-M_{0.2}-0, (e, f) GA-M_{0.3}-0, and (g, h) GCA-M_{0.3}-0, respectively

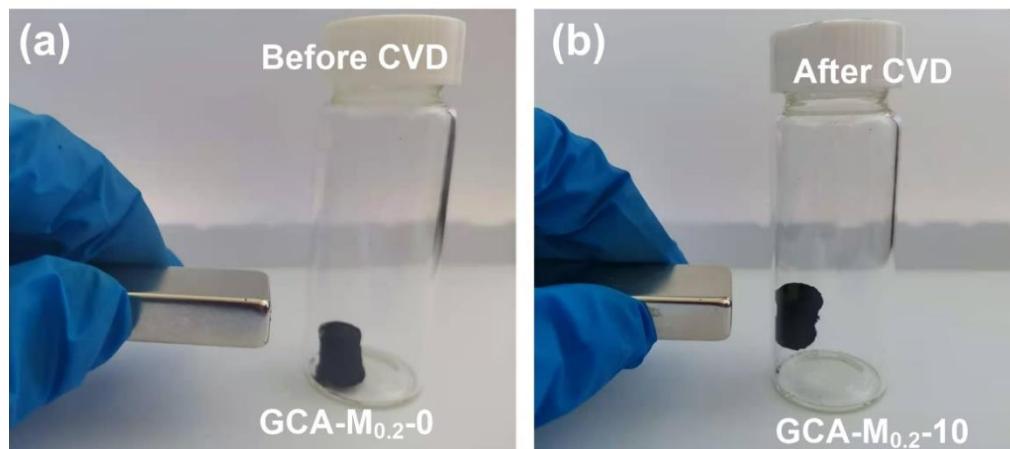


Fig. S3 Optical image of a GCA-M_{0.2}-0 aerogel before (a) and after (b) the CVD process

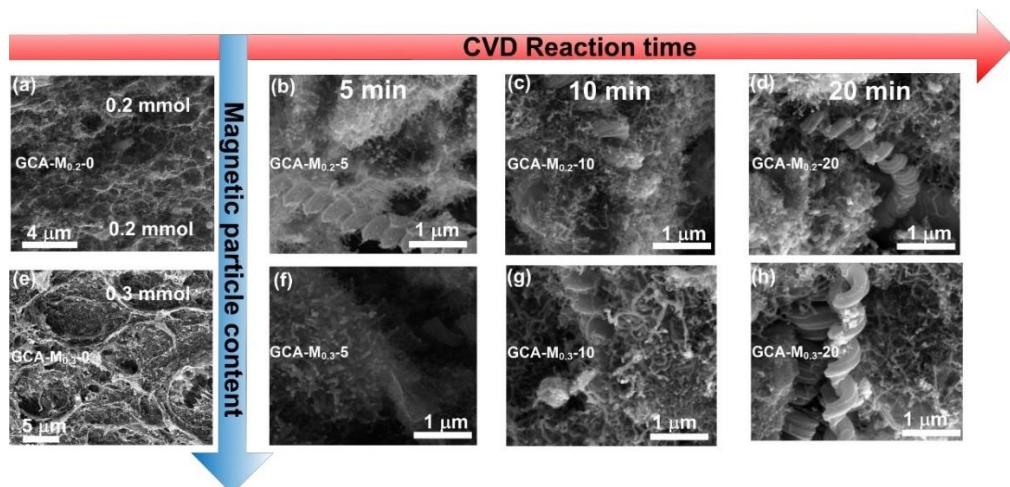


Fig. S4 SEM images of (a) GCA-M_{0.2}-0, (b) GCA-M_{0.2}-5, (c) GCA-M_{0.2}-10, (d) GCA-M_{0.2}-20, (e) GCA-M_{0.3}-0, (f) GCA-M_{0.3}-5, (g) GCA-M_{0.3}-10, and (h) GCA-M_{0.3}-20

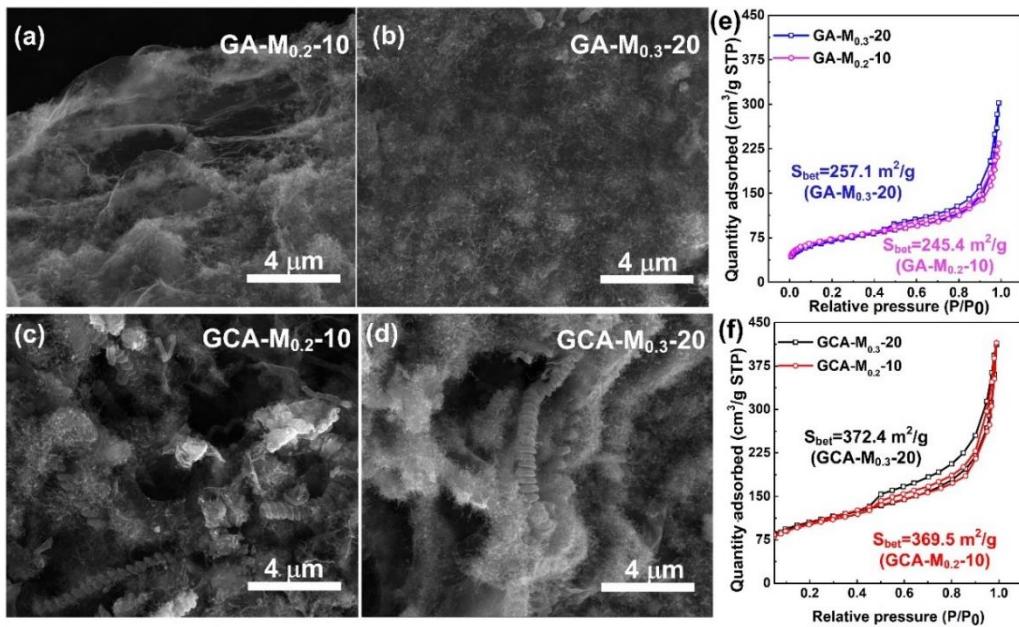


Fig. S5 SEM images of (a) GA-M_{0.2}-10, (b) GA-M_{0.3}-20, (c) GCA-M_{0.2}-10, and (d) GCA-M_{0.3}-20, respectively. The N₂ adsorption-desorption isotherms of (e) GA-M_{0.2}-10 and GA-M_{0.3}-20, (f) GCA-M_{0.2}-10 and GCA-M_{0.3}-20

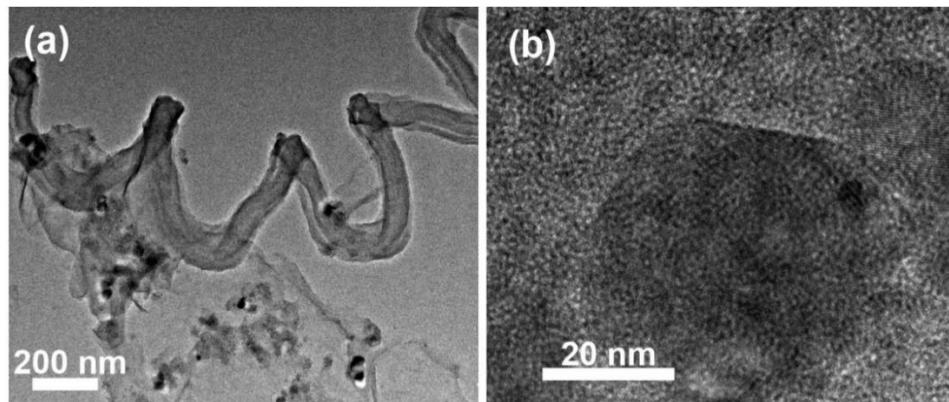


Fig. S6 (a) TEM and (b) TRTEM images of all the GCA-M_{0.2}-0 samples

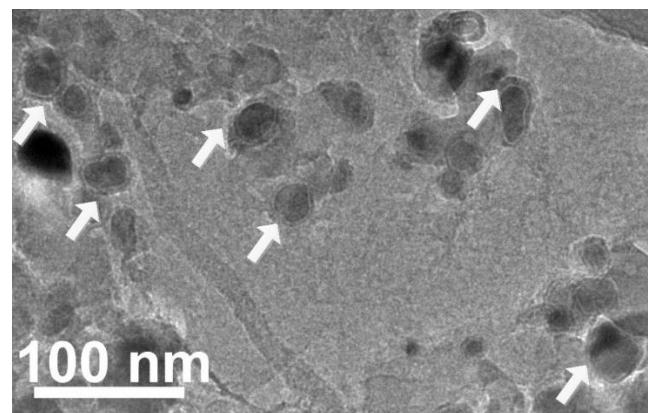


Fig. S7 Detailed TEM image of core-shell structured particles in GCA-M_{0.3}-20

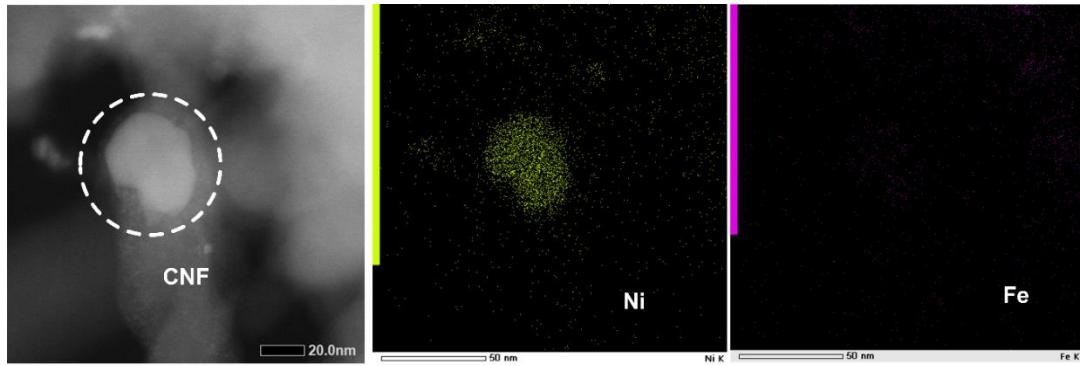


Fig. S8 Elemental maps of Ni and Fe in the tip of CNF

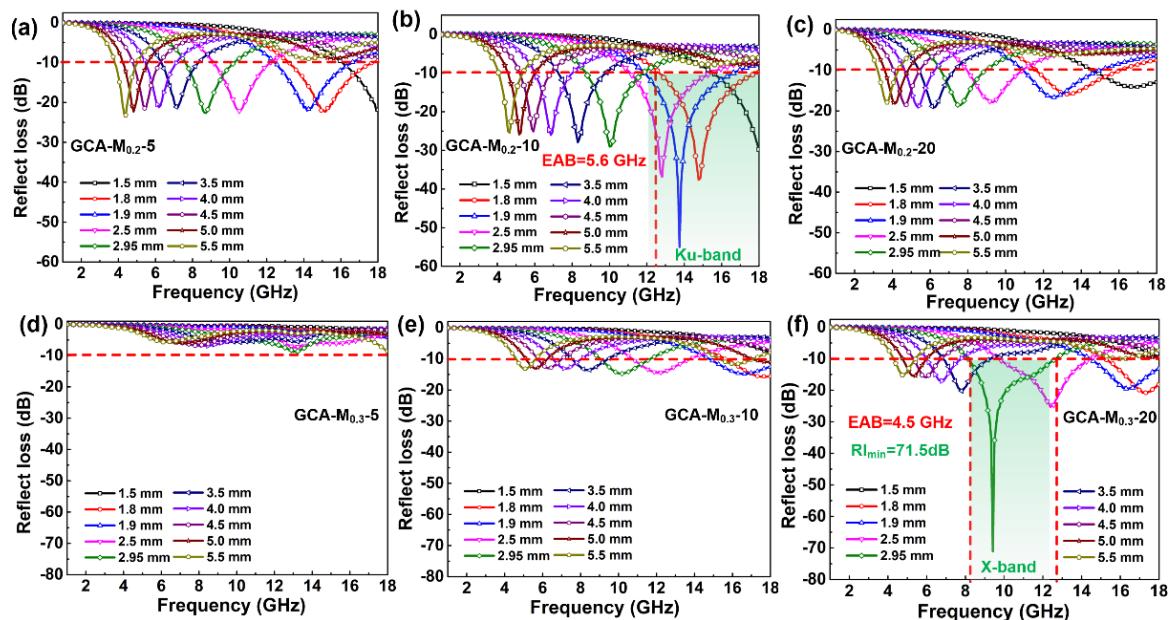


Fig. S9 Reflection loss values of (a) GCA-M_{0.2}-5, (b) GCA-M_{0.2}-10, (c) GCA-M_{0.2}-20, (d) GCA-M_{0.3}-5, (e) GCA-M_{0.3}-10, and (f) GCA-M_{0.3}-20

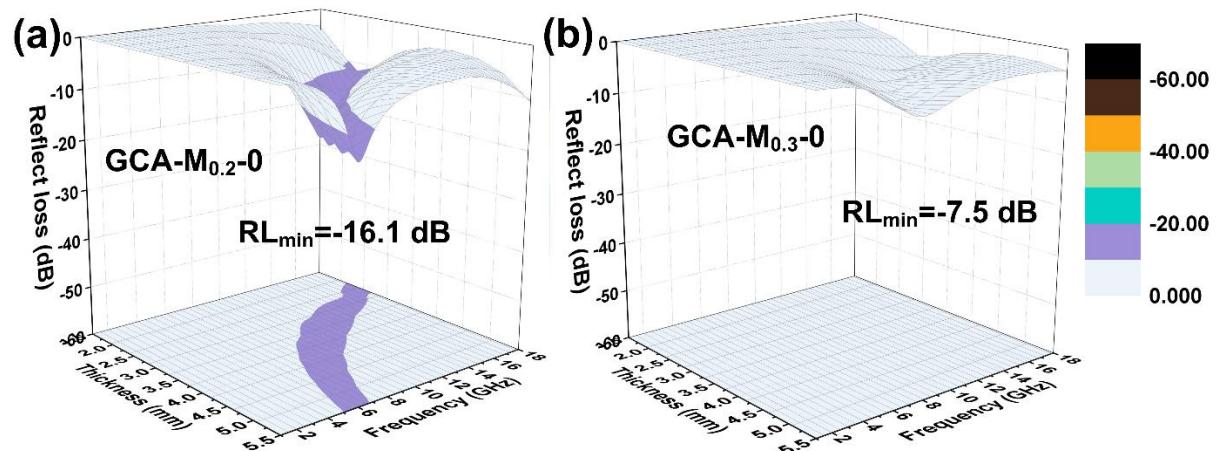


Fig. S10 3D representations of the RL of (a) GCA-M_{0.2}-0, (b) GCA-M_{0.3}-0

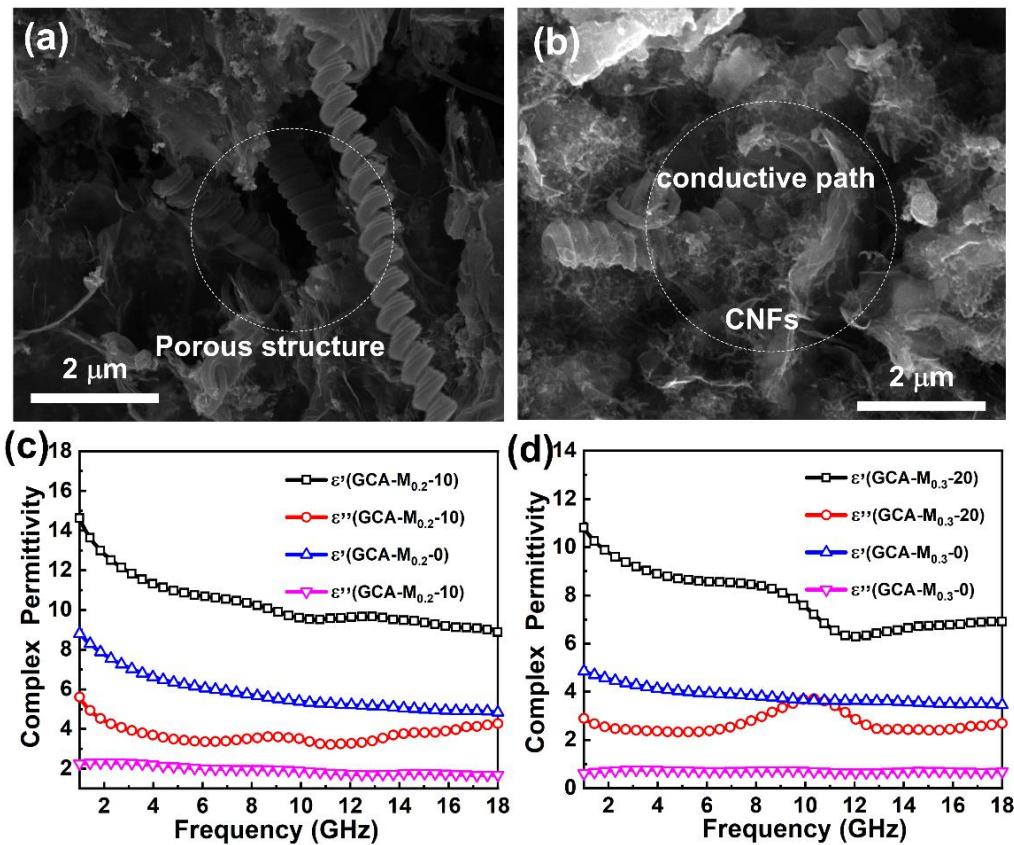


Fig. S11 SEM images of (a) GCA-M_{0.2}-0, (b) GCA-M_{0.2}-10; (c) Complex permittivity of GCA-M_{0.2}-0 and GCA-M_{0.2}-10; (d) Complex permittivity of GCA-M_{0.3}-0 and GCA-M_{0.3}-20

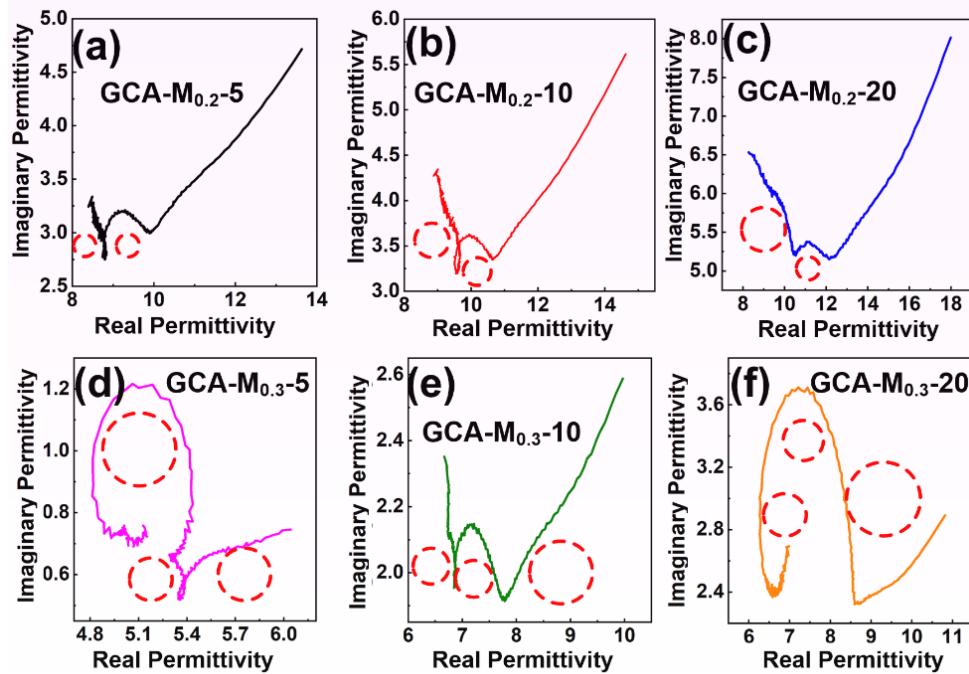


Fig. S12 Cole-Cole curves of (a) GCA-M_{0.2}-5, (b) GCA-M_{0.2}-10, (c) GCA-M_{0.2}-20, (d) GCA-M_{0.3}-5, (e) GCA-M_{0.3}-10, and (f) GCA-M_{0.3}-20

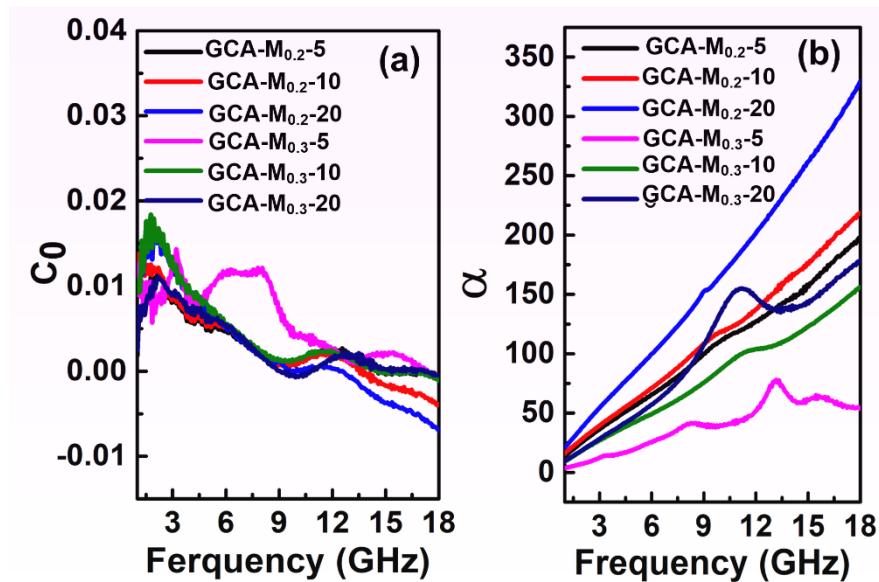


Fig. S13 Calculated C_0 (a) and α values (b) of as-obtained samples

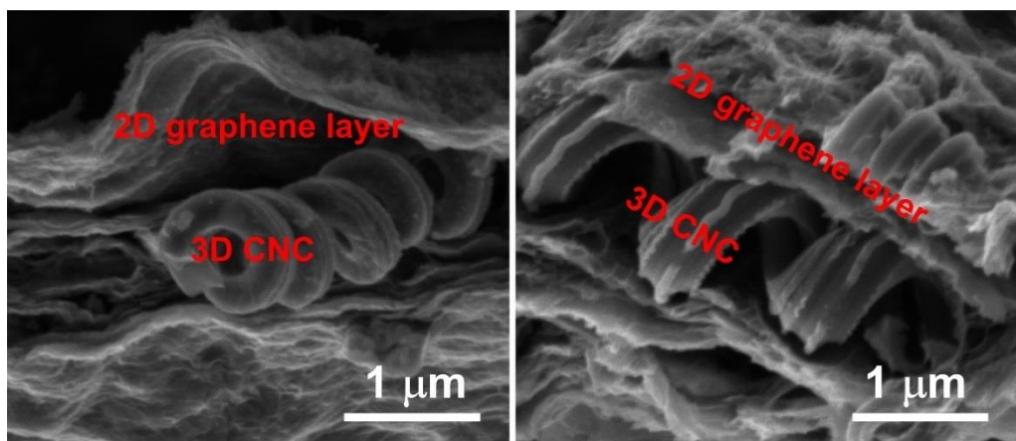


Fig. S14 Detailed SEM images of CNC and reduced graphene oxide existing in the RGO/CNC aerogel

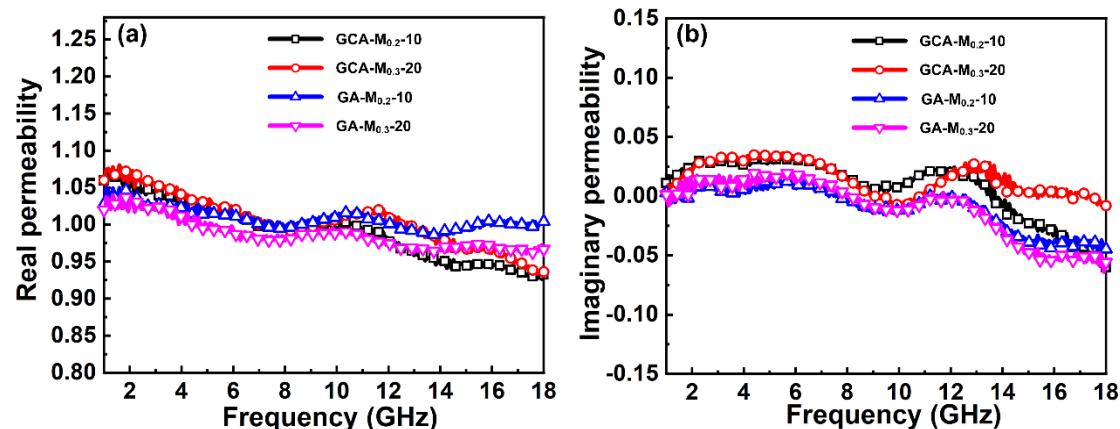


Fig. S15 (a) Real- and (b) imaginary- permeability for GCA-M_{0.2}-10-, GCA-M_{0.3}-20-, GA-M_{0.2}-10-, and GA-M_{0.3}-20-wax composites

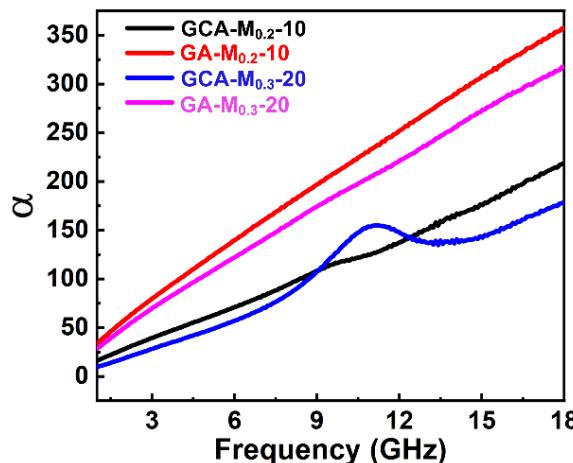


Fig. S16 Calculated attenuation constants of typical GA-M_x-Y and GCA-M_x-Y samples

Table S1 A comparison of specific surface for hierarchical RGO-based materials

Absorbers	Methods	Specific Surface Area(m ² /g)	Refs.
Porous Fe ₃ O ₄ /rGO	solvothermal	148	[S1]
Fe ₃ O ₄ @SiO ₂ @MnO ₂ -RGO	self-assembly	98.5	[S2]
Nanoporous RGO-CNT	self-assembly	231.4	[S3]
Porous Graphene Microflowers	spray-drying	230	[S4]
CNF/rGO	electrospinning	43.8	[S5]
MoS ₂ @ CNT/RGO	solvothermal	237	[S6]
Co/Co ₃ O ₄ /CNTs/RGO	solvothermal	194.6	[S7]
nitrogen-doped rGO-CNT	pyrolysis	125.29	[S8]
β -FeOOH/rGO/CNT	self-assembly	293.1	[S9]
GCA-M_{0.3}-20	self-assembly	372.4	This work
GCA-M_{0.2}-10	self-assembly	369.5	This work

Table 2 A comparison of microwave absorption performance of hierarchical carbon-based materials in X-band

Absorbers	Thickness (mm)	RL _{min} (dB)	EAB _{min} (GHz)	Filler loading	Refs.
Graphene spheres-AC	3.7	-32.4	4.2 (3.50 mm)	10 %	[S10]
RGO-NiZnFeO ₄	2.91	-63	5.4 (2.00 mm)	40 %	[S11]
RGO-SnO ₂	2.2	-53.7	3.7 (2.20 mm)	70 %	[S12]
RGO-CNT-Fe ₃ O ₄	4	-49	4.1 (2.50 mm)	15 %	[S13]
N-doped Graphene	2.9	-43.2	5.0 (2.90 mm)	40 %	[S14]
CoFe ₂ O ₄ -RGO	2.1	-60.1	4.8 (2.20 mm)	20 %	[S15]
PPY-SiC-RGO	3	-22.5	4.4 (3.0 mm)	20 %	[S16]
Co-C-MWCNTs	2.5	-50	3.6 (2.5 mm)	25 %	[S17]
N-doped Carbon aerogel	2.6	-61.7	5.3 (2.6 mm)	20 %	[S18]
GCA-M_{0.3}-20	2.95	-71.5	4.5 (2.95 mm)	15 %	This work

Table S3 A comparison of microwave absorption performance of hierarchical carbon-based materials in Ku-band

Absorbers	Thickness (mm)	RL _{min} (dB)	EAB (GHz)	Filler loading	Refs.
GCA-M_{0.3}-20	2.95	-71.5	4.5 (2.95 mm)	15 %	This work

CoFe₂O₄-RGO	2.1	-60.4	6.4 (2.2 mm)	20 %	[S15]
MnO₂-SiC-RGO	1.59	-54	7.4 (1.59 mm)	50 %	[S19]
CNC-Fe₃O₄-C	1.7	-47.5	5.0 (1.5 mm)	40 %	[S20]
CNF-CNT-Co	2.0	-52.3	5.1 (2.0 mm)	15 %	[S21]
LiFePO₄-RGO	2.4	-61.4	4.0 (2.4 mm)	30 %	[S22]
RGO-CNT-FeNi	2	-39.3	4.7 (1.8 mm)	10 %	[S23]
GRO-PEG	2.35	-43.2	5.3 (2.35 mm)	50 %	[S24]
Biomass Carbon-Ni	1.7	-52	5.0 (1.65 mm)	15 %	[S25]
Co-CNTs-Carbon Sponge	2.2	-51.2	4.1(2.2 mm)	10 %	[S26]
FeCo-C	2.8	-61.8	9.2 (2.8 mm)	10 %	[S27]
CoNi/rGO	0.8	-53	3.0 (0.8 mm)	7%	[S28]
GCA-M_{0.2}-10	1.9	-55.1	5.6 (1.8 mm)	15 %	This work

Supplementary References

- [S1] Z. Liu et al., Rational design of hierarchical porous Fe₃O₄/RGO composites with lightweight and high-efficiency microwave absorption. Compos. Commun. **22**, 100492 (2020). <https://doi.org/10.1016/j.coco.2020.100492>
- [S2] M. Ma et al., 1D flower-like Fe₃O₄@ SiO₂@ MnO₂ nanochains inducing RGO self-assembly into aerogels for high-efficient microwave absorption. Mater. Des. **188**, 108462 (2020). <https://doi.org/10.1016/j.matdes.2019.108462>
- [S3] J.H. Kim et al., 3D-interconnected nanoporous RGO-CNT structure for supercapacitors application. Electrochim. Acta **125**, 536-542 (2014). <https://doi.org/10.1016/j.electacta.2014.01.142>
- [S4] C. Chen et al., Porous graphene microflowers for high-performance microwave absorption. Nano-Micro Lett. **10**(2), 26 (2018). <https://doi.org/10.1007/s40820-017-0156-2>
- [S5] S.H. Han et al., High areal capacity of Li-S batteries enabled by freestanding CNF/rGO electrode with high loading of lithium polysulfide. Electrochim. Acta **241**, 406-413 (2017). <https://doi.org/10.1016/j.electacta.2017.05.005>
- [S6] S.H. Wang et al., Three dimensional MoS₂@ CNT/RGO network composites for high performance flexible supercapacitors. Chem. Eur. J. **23**(14), 3438-3446 (2017). <https://doi.org/10.1002/chem.201605465>
- [S7] Y. Wang et al., MOF-derived nanoporous carbon/Co/Co₃O₄/CNTs/RGO composite with hierarchical structure as a high-efficiency electromagnetic wave absorber. J. Alloys Compd. **846**, 156215 (2020). <https://doi.org/10.1016/j.jallcom.2020.156215>
- [S8] C.H. Guo et al., Space-confined iron nanoparticles in a 3D nitrogen-doped rGO-CNT framework as efficient bifunctional electrocatalysts for rechargeable Zinc–Air batteries. Micropor. Mesopor. Mat. **298**, 110100 (2020). <https://doi.org/10.1016/j.micromeso.2020.110100>
- [S9] S.W. Bokhari et al., Self-assembly of β-FeOOH/rGO/CNT for a high-

- performance supercapacitor. *Mater. Lett.* **220**, 140-143 (2018).
<https://doi.org/10.1016/j.matlet.2018.02.131>
- [S10] H.L. Xu et al., Constructing hollow graphene nano-spheres confined in porous amorphous carbon particles for achieving full X band microwave absorption. *Carbon* **142**, 346-353 (2019). <https://doi.org/10.1016/j.carbon.2018.10.056>
- [S11] R.W. Shu et al., Facile synthesis of nitrogen-doped reduced graphene oxide/nickel-zinc ferrite composites as high-performance microwave absorbers in the X-band. *Chem. Eng. J.* **384**, 123266 (2020).
<https://doi.org/10.1016/j.cej.2019.123266>
- [S12] J.B. Zhang et al., Facile fabrication and enhanced microwave absorption properties of reduced graphene oxide/tin dioxide binary nanocomposites in the X-band. *Synth. Met.* **257**, 116157 (2019).
<https://doi.org/10.1016/j.synthmet.2019.116157>
- [S13] Y. Qin et al., Preparation of graphene aerogel with high mechanical stability and microwave absorption ability via combining surface support of metallic-CNTs and interfacial cross-linking by magnetic nanoparticles. *ACS Appl. Mater. Interfaces* **11**(10), 10409-10417 (2019).
<https://doi.org/10.1021/acsami.8b22382>
- [S14] Y.L. Zhou et al., Graphene nanoflakes with optimized nitrogen doping fabricated by arc discharge as highly efficient absorbers toward microwave absorption. *Carbon* **148**, 204-213 (2019).
<https://doi.org/10.1016/j.carbon.2019.03.034>
- [S15] X.Y. Wang, et al., CoFe₂O₄/N-doped reduced graphene oxide aerogels for high-performance microwave absorption. *Chem. Eng. J.* **388**, 124317 (2020).
<https://doi.org/10.1016/j.cej.2020.124317>
- [S16] Y.H. Cheng et al., Achieving tunability of effective electromagnetic wave absorption between the whole X-band and Ku-band via adjusting PPy loading in SiC nanowires/graphene hybrid foam. *Carbon* **132**, 430-443 (2018).
<https://doi.org/10.1016/j.carbon.2018.02.084>
- [S17] R.W. Shu et al., Nitrogen-doped Co-C/MWCNTs nanocomposites derived from bimetallic metal-organic frameworks for electromagnetic wave absorption in the X-band. *Chem. Eng. J.* **362**, 513-524 (2019).
<https://doi.org/10.1016/j.cej.2019.01.090>
- [S18] P.B. Liu et al., Vacancies-engineered and heteroatoms-regulated N-doped porous carbon aerogel for ultrahigh microwave absorption. *Carbon* **169**, 276-287 (2020). <https://doi.org/10.1016/j.carbon.2020.07.063>
- [S19] S. Dong et al., SiC whiskers-reduced graphene oxide composites decorated with MnO nanoparticles for tunable microwave absorption. *Chem. Eng. J.* **392**, 123817 (2020). <https://doi.org/10.1016/j.cej.2019.123817>

- [S20] Y.P. Zhao et al., In situ construction of hierarchical core–shell Fe₃O₄@C nanoparticles–helical carbon nanocoil hybrid composites for highly efficient electromagnetic wave absorption. *Carbon* **171**, 395-408 (2021).
<https://doi.org/10.1016/j.carbon.2020.09.036>
- [S21] Z.C. Wu et al., Enhanced microwave absorption performance from magnetic coupling of magnetic nanoparticles suspended within hierarchically tubular composite. *Adv. Funct. Mater.* **29**(28), 1901448 (2019).
<https://doi.org/10.1002/adfm.201901448>
- [S22] J.J. Dong et al., Three-dimensional architecture reduced graphene oxide–LiFePO₄ composite: preparation and excellent microwave absorption performance. *Inorg. Chem.* **58**(3), 2031-2041 (2019).
<https://doi.org/10.1021/acs.inorgchem.8b03043>
- [S23] J. Xu et al., N-doped reduced graphene oxide aerogels containing pod-like N-doped carbon nanotubes and FeNi nanoparticles for electromagnetic wave absorption. *Carbon* **159**, 357-365 (2020).
<https://doi.org/10.1016/j.carbon.2019.12.020>
- [S24] H.M. Ji et al., Remarkable microwave absorption performance of ultralight graphene-polyethylene glycol composite aerogels with a very low loading ratio of graphene. *Compos. Part A: Appl. Sci. Manufac.* **123**, 158-169 (2019).
<https://doi.org/10.1016/j.compositesa.2019.05.012>
- [S25] H.Q. Zhao et al., A novel hierarchically porous magnetic carbon derived from biomass for strong lightweight microwave absorption. *Carbon* **142**, 245-253 (2019). <https://doi.org/10.1016/j.carbon.2018.10.027>
- [S26] N. Yang et al., Ultralight three-dimensional hierarchical cobalt nanocrystals/N-doped CNTs/carbon sponge composites with a hollow skeleton toward superior microwave absorption. *ACS Appl. Mater. Interfaces* **11**(39), 35987-35998 (2019). <https://doi.org/10.1021/acsami.9b11101>
- [S27] L. Wang et al., Hierarchical nest-like structure of Co/Fe MOF derived CoFe@C composite as wide-bandwidth microwave absorber. *Compos. Part A: Appl. Sci. Manufac.* **135**, 105958 (2020).
<https://doi.org/10.1016/j.compositesa.2020.105958>
- [S28] H.-B. Zhao, J.-B. Cheng, J.-Y. Zhu, Y.-Z. Wang, Ultralight CoNi/rGO aerogels toward excellent microwave absorption at ultrathin thickness. *J. Mater. Chem. C* **7**(2), 441-448 (2019). <https://doi.org/10.1039/C8TC05239E>