

Supporting Information for

## Ultrafine Vacancy-Rich Nb<sub>2</sub>O<sub>5</sub> Semiconductors Confined in Carbon Nanosheets Boost Dielectric Polarization for High-Attenuation Microwave Absorption

Zhe Su<sup>1</sup>, Shan Yi<sup>1</sup>, Wanyu Zhang<sup>1</sup>, Xiayi Xu<sup>1</sup>, Yayun Zhang<sup>1</sup>, Shenghu Zhou<sup>1</sup>, Bo Niu<sup>1,\*</sup>, and Donghui Long<sup>1,2,\*</sup>

<sup>1</sup> Shanghai Key Laboratory of Multiphase Materials Chemical Engineering, East China University of Science and Technology, School of Chemical Engineering, Shanghai 200237, P. R. China

<sup>2</sup> Key Laboratory for Specially Functional Materials and Related Technology of the Ministry of Education, East China University of Science and Technology, Shanghai 200237, P. R. China

\*Corresponding authors. E-mail: [longdh@mail.ecust.edu.cn](mailto:longdh@mail.ecust.edu.cn) (Donghui Long), [niubo@ecust.edu.cn](mailto:niubo@ecust.edu.cn) (Bo Niu)

ORCID: Donghui Long, [orcid.org/0000-0002-3179-4822](https://orcid.org/0000-0002-3179-4822)

Bo Niu, [orcid.org/0000-0003-4126-6246](https://orcid.org/0000-0003-4126-6246)

### S1 Supplementary Calculation Section

According to the transmission line theory, the values of RL are calculated via the following equations [1]:

$$R_L(\text{dB}) = 20 \log \left| \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \right| \quad (\text{S1})$$

$$Z_{in} = Z_0 \sqrt{\frac{\mu_r}{\varepsilon_r}} \tanh \left[ j \frac{2\pi}{c} \sqrt{\mu_r \varepsilon_r} f d \right] \quad (\text{S2})$$

where  $Z_0$  is the impedance of free space,  $Z_{in}$  is the normalized input impedance of the absorber,  $\varepsilon_r$  ( $\varepsilon_r = \varepsilon' - j\varepsilon''$ ) is the relative complex permittivity of the absorber,  $\mu_r$  ( $\mu_r = \mu' - j\mu''$ ) is the relative complex permeability,  $f$  represents the electromagnetic wave frequency,  $c$  is the velocity of the EM wave in free space, and  $d$  expresses the thickness of the absorber, respectively.

According to Debye dipolar relaxation (Cole-Cole model), the permittivity can be described as [S2]:

$$\varepsilon_r = \varepsilon' - j\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_\infty}{1 + j2\pi f\tau} \quad (\text{S3})$$

where  $\tau$ ,  $\varepsilon_S$ ,  $\varepsilon_\infty$ , and  $f$  stands for the polarization relaxation time, static permittivity constant, relative dielectric permittivity at the infinite frequency, and frequency, respectively. And the  $\varepsilon'$  and  $\varepsilon''$  can be deduced as follows:

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_\infty}{1 + (2\pi f\tau)^2} \quad (\text{S4})$$

$$\varepsilon'' = \varepsilon_\infty + \frac{2\pi f\tau(\varepsilon_S - \varepsilon_\infty)}{1 + (2\pi f\tau)^2} \quad (\text{S5})$$

$$\left( \varepsilon' - \frac{\varepsilon_S + \varepsilon_\infty}{2} \right)^2 + (\varepsilon'')^2 = \left( \frac{\varepsilon_S - \varepsilon_\infty}{2} \right)^2 \quad (\text{S6})$$

The attenuation constant  $\alpha$  can be evaluated through the following equation [S3]:

$$\alpha = \frac{\sqrt{2}\pi f}{c} \times \sqrt{(\mu''\varepsilon'' - \mu'\varepsilon') + \sqrt{(\mu''\varepsilon'' - \mu'\varepsilon')^2 + (\mu'\varepsilon'' + \mu''\varepsilon')^2}} \quad (S7)$$

Delta values ( $|\Delta|$ ) can be deduced by the following equations [S2],

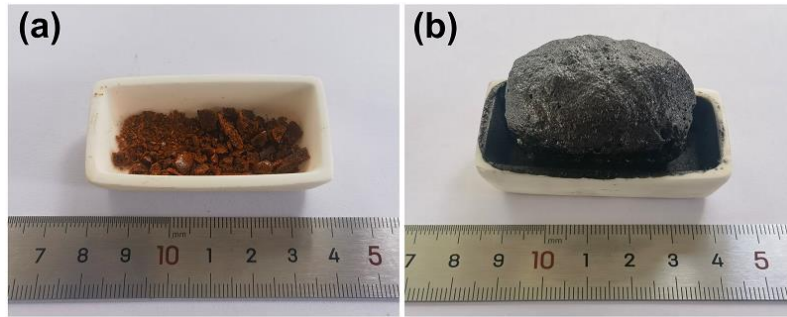
$$|\Delta| = |\sinh^2(Kfd) - M| \quad (S8)$$

where  $K$  and  $M$  can be determined by the relative complex permittivity and permeability via following equation,

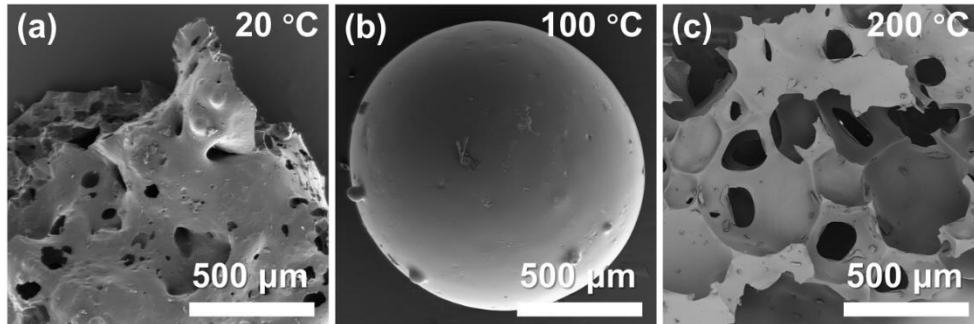
$$K = \frac{4\pi\sqrt{\mu'\varepsilon'} \cdot \sin(\frac{\delta_e + \delta_m}{2})}{c \cdot \cos\delta_e \cdot \cos\delta_m} \quad (S9)$$

$$M = \frac{4\mu'\varepsilon'\cos\delta_e\cos\delta_m}{(\mu'\cos\delta_e - \varepsilon'\cos\delta_m)^2 + [\tan(\frac{\delta_m - \delta_e}{2})]^2 (\mu'\cos\delta_e + \varepsilon'\cos\delta_m)^2} \quad (S10)$$

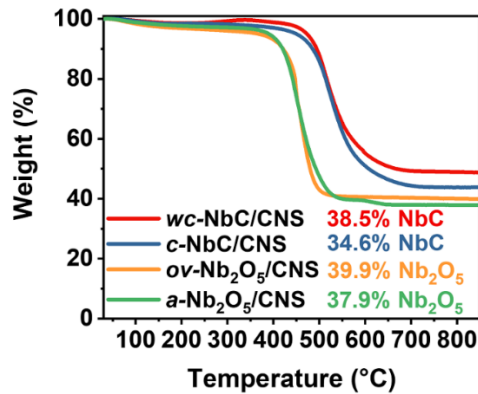
## S2 Supplementary Figures and Tables



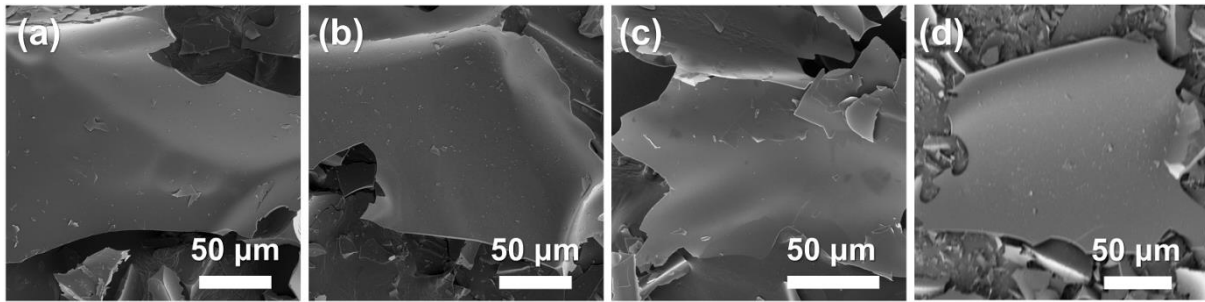
**Fig. S1** The digital photographs of **a**  $\text{Nb}^{5+}$ -gluconate precursor and **b** foamed  $\text{ov-Nb}_2\text{O}_5/\text{CNS}$



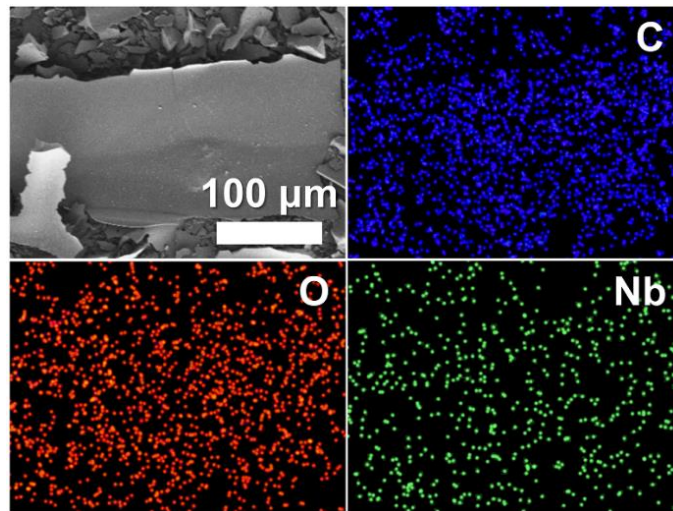
**Fig. S2.** The scanning electron microscope (SEM) images of **a**  $\text{Nb}^{5+}$ -gluconate precursor at 20 °C, **b** melted  $\text{Nb}^{5+}$ -gluconate precursor at 100 °C, and **c** foamed intermediates with closed-cell structures at 200 °C



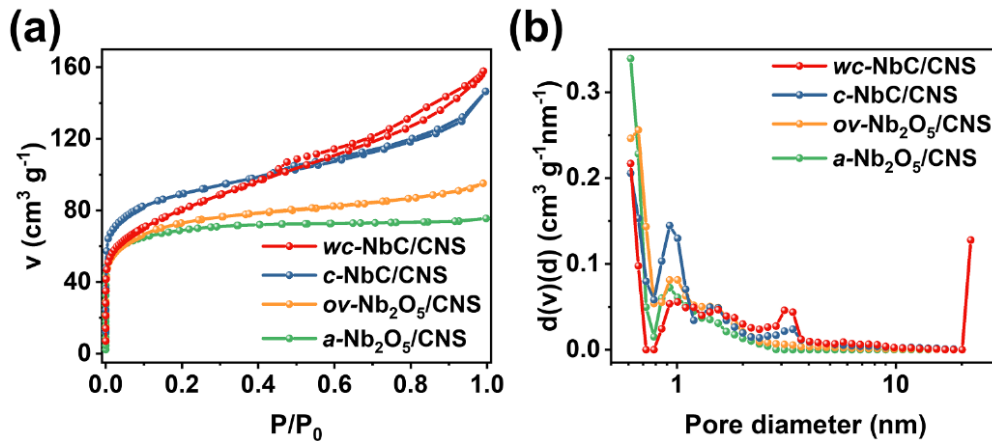
**Fig. S3** Thermogravimetric analysis (TGA) curves of *a*-Nb<sub>2</sub>O<sub>5</sub>/CNS, *ov*-Nb<sub>2</sub>O<sub>5</sub>/CNS, *c*-NbC/CNS, and *wc*-NbC/CNS composites under an air atmosphere



**Fig. S4** SEM images of **a** *a*-Nb<sub>2</sub>O<sub>5</sub>/CNS, **b** *ov*-Nb<sub>2</sub>O<sub>5</sub>/CNS, **c** *c*-NbC/CNS, and **d** *wc*-NbC/CNS composites

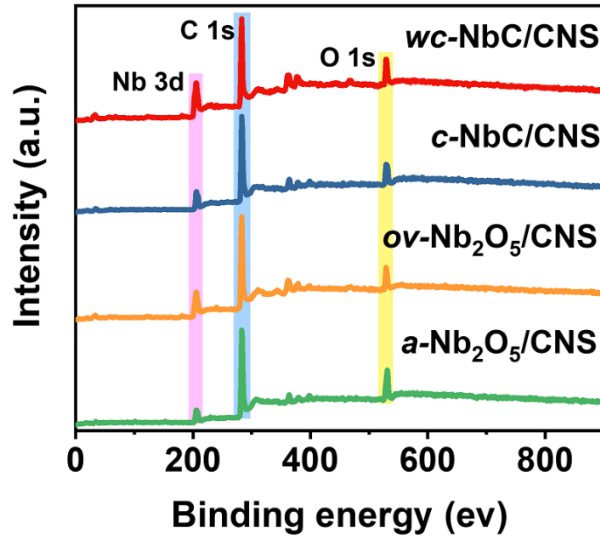


**Fig. S5** X-ray energy-dispersive spectroscopy (EDS) images of *ov*-Nb<sub>2</sub>O<sub>5</sub>/CNS

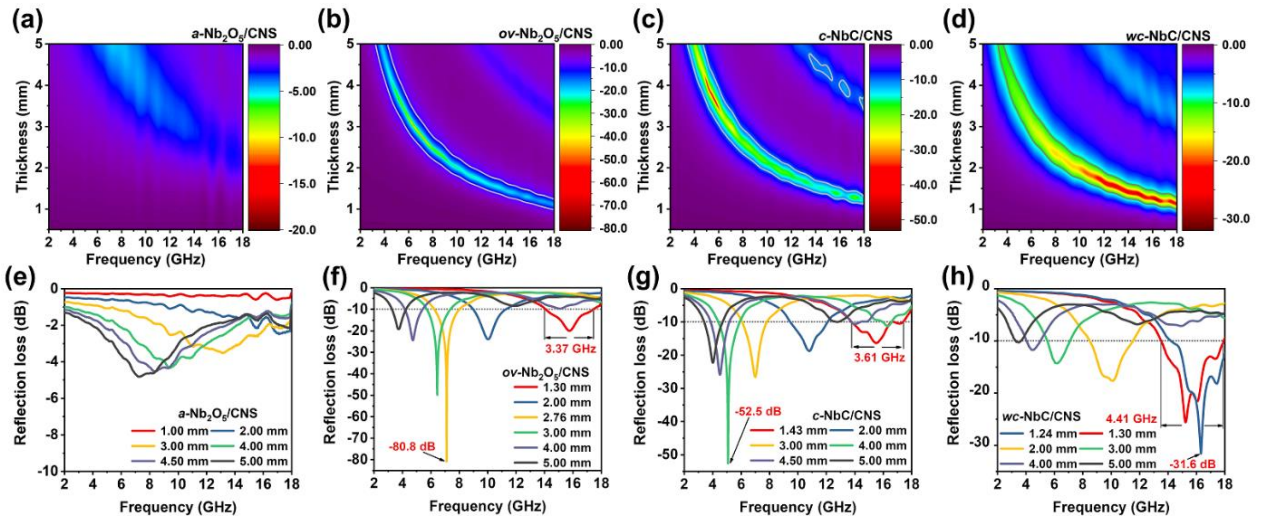


**Fig. S6** **a** N<sub>2</sub> adsorption/desorption isotherms and **b** corresponding QSDFT pore-size distribution curves of *a*-Nb<sub>2</sub>O<sub>5</sub>/CNS, *ov*-Nb<sub>2</sub>O<sub>5</sub>/CNS, *c*-NbC/CNS, and *wc*-NbC/CNS composites

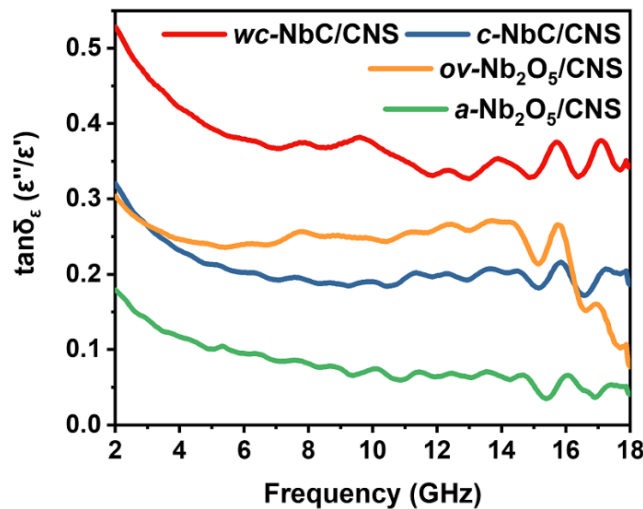
The reduction of Nb<sub>2</sub>O<sub>5</sub> by the carbon skeleton and the subsequent growth of NbC crystals results in the generation of a greater number of mesopores. This phenomenon is evidenced by the N<sub>2</sub> adsorption/desorption isotherms of *c*-NbC/CNS and *wc*-NbC/CNS composites, which display an enlarged hysteresis loop at higher relative pressures ( $P/P_0$  of 0.4-0.99).



**Fig. S7** XPS survey spectrum of *a-Nb<sub>2</sub>O<sub>5</sub>/CNS*, *ov-Nb<sub>2</sub>O<sub>5</sub>/CNS*, *c-NbC/CNS*, and *wc-NbC/CNS* composites



**Fig. S8** Reflection loss contour maps and corresponding curves of **a,e** *a-Nb<sub>2</sub>O<sub>5</sub>/CNS*, **b,f** *ov-Nb<sub>2</sub>O<sub>5</sub>/CNS*, **c,g** *c-NbC/CNS*, and **d,h** *wc-NbC/CNS* composites



**Fig. S9** Dielectric loss factor ( $\tan\delta_\epsilon$ ) of *a-Nb<sub>2</sub>O<sub>5</sub>/CNS*, *ov-Nb<sub>2</sub>O<sub>5</sub>/CNS*, *c-NbC/CNS*, and *wc-NbC/CNS*



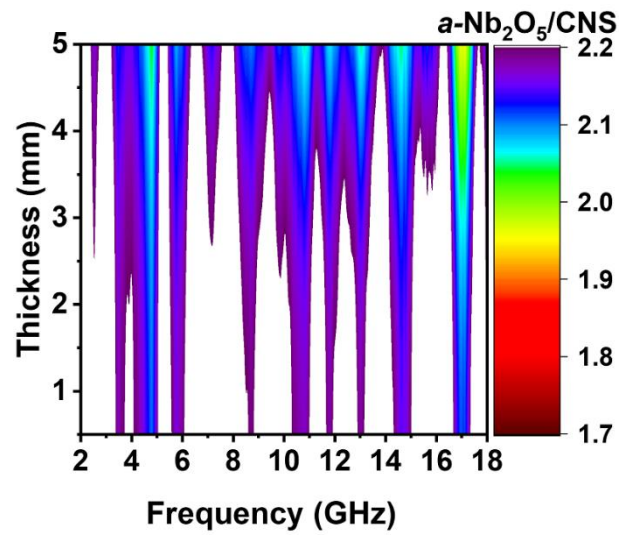


Fig. S10 2D delta ( $|\Delta|$ ) value maps of  $a$ - $\text{Nb}_2\text{O}_5/\text{CNS}$

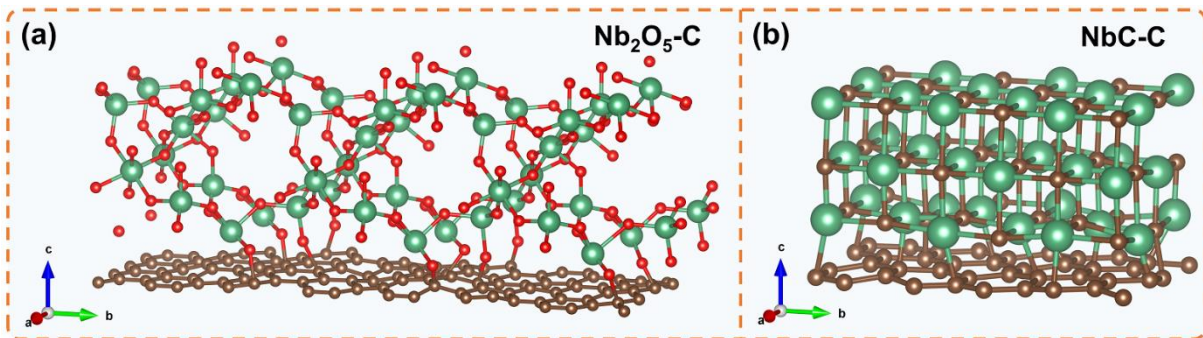


Fig. S11 Structures of **a**  $\text{Nb}_2\text{O}_5$ -carbon and **b**  $\text{NbC}$ -carbon configurations

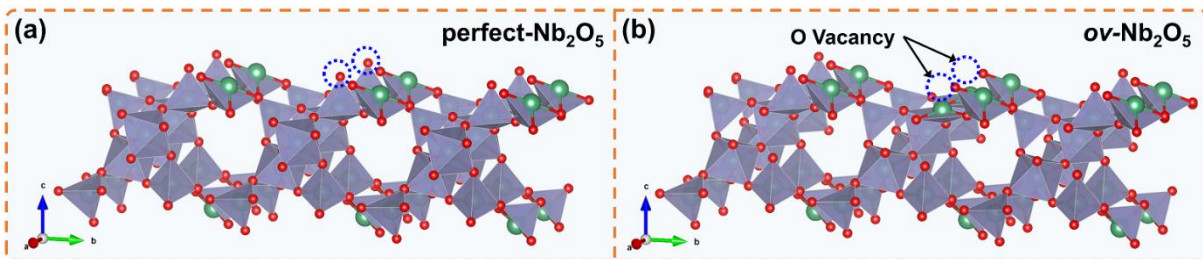
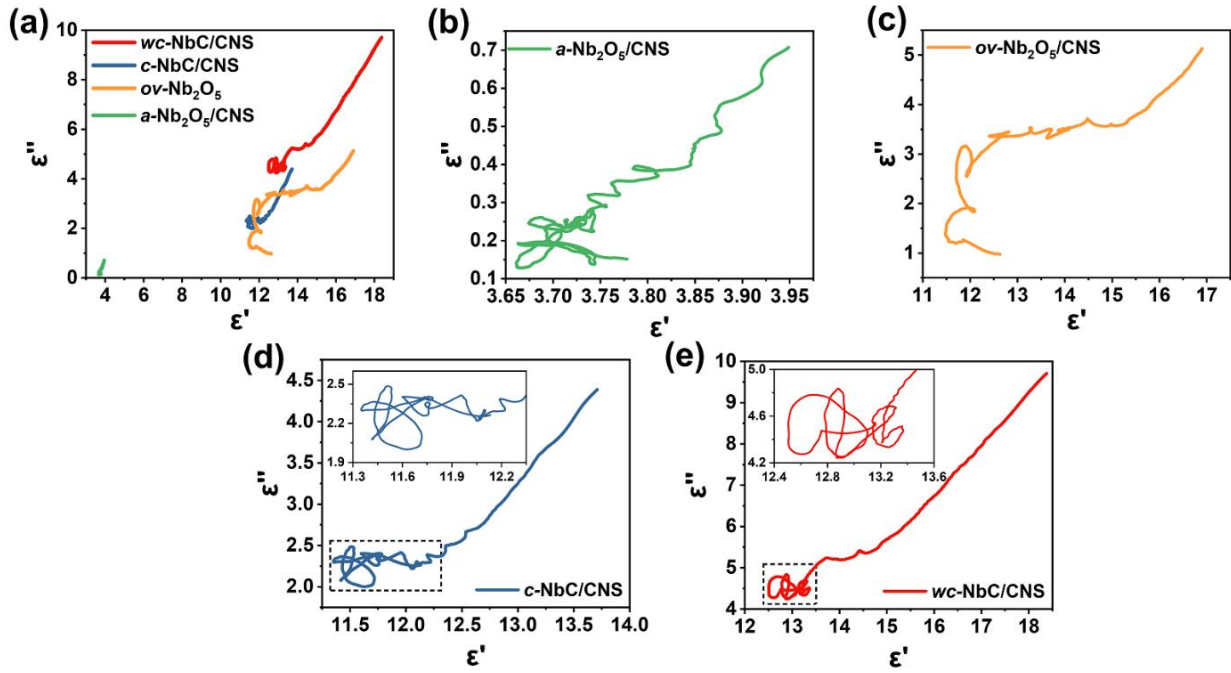


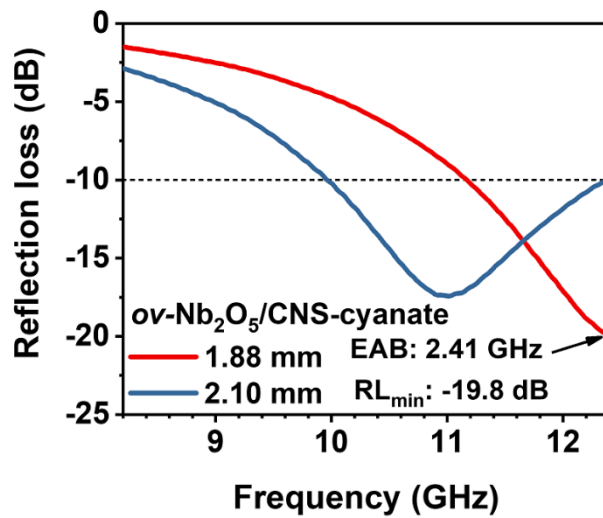
Fig. S12 Structures of **a** perfect  $\text{Nb}_2\text{O}_5$  and **b** oxygen-vacancy  $\text{Nb}_2\text{O}_5$  configurations



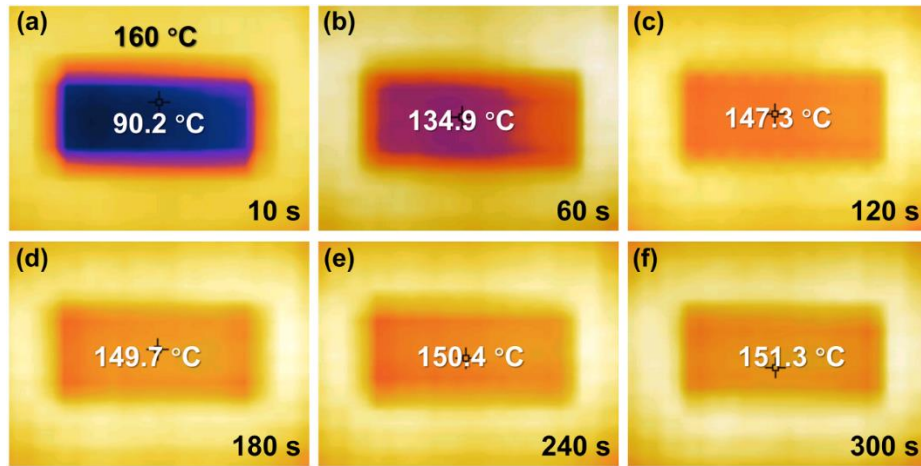
**Fig. S13** a Comprehensive and b-e individual Cole-Cole plots of  $a\text{-Nb}_2\text{O}_5/\text{CNS}$ ,  $ov\text{-Nb}_2\text{O}_5/\text{CNS}$ ,  $c\text{-NbC}/\text{CNS}$ , and  $wc\text{-NbC}/\text{CNS}$



**Fig. S14** The digital photographs of  $ov\text{-Nb}_2\text{O}_5/\text{CNS}$ -cyanate plate with a size of 22.9 mm×10.2 mm×2 mm



**Fig. S15** The detailed reflection losses curve of  $ov\text{-Nb}_2\text{O}_5/\text{CNS}$ -cyanate plate



**Fig. S16** Thermal infrared images of *ov*-Nb<sub>2</sub>O<sub>5</sub>/CNS-cyanate plate on a heating platform (160 °C)

**Table S1** Detailed pore parameters of *a*-Nb<sub>2</sub>O<sub>5</sub>/CNS, *ov*-Nb<sub>2</sub>O<sub>5</sub>/CNS, *c*-NbC/CNS, and *wc*-NbC/CNS

Sample	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	S <sub>Micro</sub> (m <sup>2</sup> g <sup>-1</sup> )	V <sub>Total</sub> (cm <sup>3</sup> g <sup>-1</sup> )	V <sub>Micro</sub> (cm <sup>3</sup> g <sup>-1</sup> )
<i>a</i> -Nb <sub>2</sub> O <sub>5</sub> /CNS	224.2	201.9	0.117	0.098
<i>ov</i> -Nb <sub>2</sub> O <sub>5</sub> /CNS	262.3	216.4	0.147	0.095
<i>c</i> -NbC/CNS	314.9	215.5	0.227	0.096
<i>wc</i> -NbC/CNS	278.3	112.0	0.244	0.054

**Table S2** Comparison of minimum reflection loss *versus* thickness among *ov*-Nb<sub>2</sub>O<sub>5</sub>/CNS and other absorbers reported in the literature

Sample	Minimum reflection loss (dB)	Thickness (mm)	References
<i>ov</i> -Nb <sub>2</sub> O <sub>5</sub> /CNS	-80.8	2.76	This work
MoS <sub>2</sub> /RGO	-50.9	2.3	[S4]
RGO/GDY	-58	2.7	[S5]
CNTs/CF	-44.46	3	[S6]
Graphene/Fe <sub>3</sub> O <sub>4</sub>	-40.4	5	[S7]
BaFe <sub>11.6</sub> Co <sub>0.4</sub> O <sub>19</sub> @Fe <sub>3</sub> O <sub>4</sub>	-48.9	3.5	[S8]
DSNTs	-54.7	2.6	[S9]
MoC <sub>1-x</sub> /C-TCN	-50.55	1.8	[S10]
NbS <sub>2</sub>	-43.85	2.5	[S11]
Cu-S-MOF	-52.8	1.69	[S12]
Fe@NCNs	-64.75	2.7	[S13]

**Table S3** Comparison of minimum reflection loss *versus* effective absorption bandwidth among *ov*-Nb<sub>2</sub>O<sub>5</sub>/CNS and other absorbers reported in the literature

Sample	Minimum reflection loss (dB)	Effective absorption bandwidth (GHz)	References
<i>ov</i> -Nb <sub>2</sub> O <sub>5</sub> /CNS	-80.8	3.37	This work
BaFe <sub>11.6</sub> Co <sub>0.4</sub> O <sub>19</sub> @Fe <sub>3</sub> O <sub>4</sub>	-48.9	2.5	[S8]
MnO@Co/C	-49.06	2.24	[S14]
MnO <sub>2</sub> @NPC-800	-54.96	3.24	[S15]
Ni/NiO	-52.15	3.22	[S16]
CoO@N/C-NCO	-61.73	2.07	[S17]
MXene bowls	-53.8	4.2	[S18]
HE-Cr-1300	-30.7	3.6	[S19]
RGO/GDY	-58	4.3	[S5]

## Supplementary References

- [S1] J. Cheng, H. Zhang, M. Ning, H. Raza, D. Zhang, G. Zheng, Q. Zheng, R. Che. Emerging materials and designs for low-and multi-band electromagnetic wave absorbers: the search for dielectric and magnetic synergy? *Adv. Funct. Mater.* **32**(23), 2200123 (2022). <https://doi.org/10.1002/adfm.202200123>
- [S2] X. Zeng, X. Cheng, R. Yu, G. D. Stucky. Electromagnetic microwave absorption theory and recent achievements in microwave absorbers. *Carbon* **168**, 606-623 (2020). <https://doi.org/10.1016/j.carbon.2020.07.028>
- [S3] M. S. Cao, X. X. Wang, M. Zhang, J. C. Shu, W. Q. Cao, H. J. Yang, X. Y. Fang, J. Yuan. Electromagnetic response and energy conversion for functions and devices in low-dimensional materials. *Adv. Funct. Mater.* **29**(25), 1807398 (2019). <https://doi.org/10.1002/adfm.201807398>
- [S4] Y. Wang, D. Chen, X. Yin, P. Xu, F. Wu, M. He. Hybrid of MoS<sub>2</sub> and reduced graphene oxide: a lightweight and broadband electromagnetic wave absorber. *ACS Appl. Mater. Interfaces* **7**(47), 26226-26234 (2015). <https://doi.org/10.1021/acsami.5b08410>
- [S5] M. Ling, F. Wu, P. Liu, Q. Zhang, B. Zhang. Fabrication of graphdiyne/graphene composite microsphere with wrinkled surface via ultrasonic spray compounding and its microwave absorption properties. *Small* **19**(7), 2205925 (2023). <https://doi.org/10.1002/smll.202205925>
- [S6] Y. Zhan, L. Xia, H. Yang, N. Zhou, G. Ma, T. Zhang, X. Huang, L. Xiong, C. Qin, W. Guangwu. Tunable electromagnetic wave absorbing properties of carbon nanotubes/carbon fiber composites synthesized directly and rapidly via an innovative induction heating technique. *Carbon*. **175**, 101-111 (2021). <https://doi.org/10.1016/j.carbon.2020.12.080>
- [S7] T. Wang, Z. Liu, M. Lu, B. Wen, Q. Ouyang, Y. Chen, C. Zhu, P. Gao, C. Li, M. Cao. Graphene-Fe<sub>3</sub>O<sub>4</sub> nanohybrids: synthesis and excellent electromagnetic absorption properties. *J. Appl. Phys.* **113**(2), 024314 (2013). <https://doi.org/10.1063/1.4774243>
- [S8] M. Yuan, B. Zhao, C. Yang, K. Pei, L. Wang, R. Zhang, W. You, X. Liu, X. Zhang, R. Che. Remarkable magnetic exchange coupling via constructing bi-magnetic interface for broadband lower-frequency microwave absorption. *Adv. Funct. Mater.* **32**(33), 2203161 (2022). <https://doi.org/10.1002/adfm.202203161>
- [S9] P. Liu, Y. Wang, G. Zhang, Y. Huang, R. Zhang, X. Liu, X. Zhang, R. Che. Hierarchical engineering of double-shelled nanotubes toward hetero-interfaces induced polarization and microscale magnetic interaction. *Adv. Funct. Mater.* **32**(33), 2202588 (2022). <https://doi.org/10.1002/adfm.202202588>
- [S10] T. Zhao, Z. Jia, Y. Zhang, G. Wu. Multiphase molybdenum carbide doped carbon hollow sphere engineering: the superiority of unique double-shell structure in microwave absorption. *Small* **19**(6), 2206323 (2023). <https://doi.org/10.1002/smll.202206323>
- [S11] H. Zhang, J. Cheng, H. Wang, Z. Huang, Q. Zheng, G. Zheng, D. Zhang, R. Che, M. Cao. Initiating VB-group laminated NbS<sub>2</sub> electromagnetic wave absorber toward superior absorption bandwidth as large as 6.48 GHz through phase engineering modulation. *Adv. Funct. Mater.* **32**(6), 2108194 (2022). <https://doi.org/10.1002/adfm.202108194>



- [S12] P. Miao, N. Qu, W. Chen, T. Wang, W. Zhao, J. Kong. A two-dimensional semiconductive Cu-S metal-organic framework for broadband microwave absorption. *Chem. Eng. J.* **454**, 140445 (2023). <https://doi.org/10.1016/j.cej.2022.140445>
- [S13] T. Gao, R. Zhao, Y. Li, Z. Zhu, C. Hu, L. Ji, J. Zhang, X. Zhang. Sub-nanometer Fe clusters confined in carbon nanocages for boosting dielectric polarization and broadband electromagnetic wave absorption. *Adv. Funct. Mater.* **32**(31), 2204370 (2022). <https://doi.org/10.1002/adfm.202204370>
- [S14] M. Liu, R. Tian, H. Chen, S. Li, F. Huang, K. Peng, H. Zhang. One-dimensional chain-like MnO@Co/C composites for high-efficient electromagnetic wave absorbent. *J. Magn. Magn. Mater.* **499**, 166289 (2020). <https://doi.org/10.1016/j.jmmm.2019.166289>
- [S15] H. Yang, Z. Shen, H. Peng, Z. Xiong, C. Liu, Y. Xie. 1D-3D mixed-dimensional MnO<sub>2</sub>@nanoporous carbon composites derived from Mn-metal organic framework with full-band ultra-strong microwave absorption response. *Chem. Eng. J.* **417**, 128087 (2021). <https://doi.org/10.1016/j.cej.2020.128087>
- [S16] Y. Shu, T. Zhao, X. Li, L. Yang, S. Cao. Enhanced electromagnetic wave absorption properties integrating diverse loss mechanism of 3D porous Ni/NiO microspheres. *J. Alloy. Compd.* **897**, 163227 (2022). <https://doi.org/10.1016/j.jallcom.2021.163227>
- [S17] W. Wang, H. Zhang, Y. Zhao, J. Wang, H. Zhao, P. Li, J. Yun, Z. Deng, Z. Zhang, J. Tian. A novel MOF-driven self-decomposition strategy for CoO@N/C-Co/Ni-NiCo<sub>2</sub>O<sub>4</sub> multi-heterostructure composite as high-performance electromagnetic wave absorbing materials. *Chem. Eng. J.* **426**, 131667 (2021). <https://doi.org/10.1016/j.cej.2021.131667>
- [S18] Q. Du, Q. Men, R. Li, Y. Cheng, B. Zhao, R. Che. Electrostatic adsorption enables layer stacking thickness-dependent hollow Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene bowls for superior electromagnetic wave absorption. *Small* **18**(47), 2203609 (2022). <https://doi.org/10.1002/smll.202203609>
- [S19] B. Zhao, Y. Du, Z. Yan, L. Rao, G. Chen, M. Yuan, L. Yang, J. Zhang, R. Che. Structural defects in phase-regulated high-entropy oxides toward superior microwave absorption properties. *Adv. Funct. Mater.* **33**(1), 2209924 (2023). <https://doi.org/10.1002/adfm.202209924>