

## Electronic Supplementary Information

For

### Morphology- and defect-coordinated prominent microwave absorption, thermal exhaustion, and electrical insulation in SnO<sub>2</sub>@SnP<sub>2</sub>O<sub>7</sub>@Sn<sub>2</sub>P<sub>2</sub>O<sub>7</sub> hierarchical architectures

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Seen from Figure 8b1 and 8b2, matching constant ( $Z$ ) varies in the following trend:  $Z_{S4} < Z_{S2} < Z_{S1} \approx Z_{S5} < Z_{S4P} < Z_{S3}$  at 2~11 GHz;  $Z_{S4} < Z_{S4P} < Z_{S5} \approx Z_{S2} < Z_{S1} < Z_{S3}$  at 11~18 GHz. The  $Z$  presents an upward trend with  $f$  with large values over 4~18 GHz. The prominent matching performance is mainly ascribed to inner stress/oxygen vacancy defects caused by [Sn<sup>2+</sup>]. In addition to increasing permittivity and conductivity, P doping tunes the balance between conductivity loss and polarization loss.

While the AC takes on a weak resonance peak over 2.0~9.0 GHz and a strong resonance peak over 9.0~18.0 GHz, indicating that the EM wave absorption of the HAs mainly focuses on the 9.0~18.0 GHz. The AC values fluctuate in a small scale.

Attenuating constant ( $AC$ ) increases in the following order:  $AC_{S4P} < AC_{S5} \approx AC_{S3} \approx AC_{S4} < AC_{S1} \approx AC_{S2}$  at 2~13 GHz;  $AC_{S2} \approx AC_{S1} < AC_{S5} < AC_{S4} < AC_{S3} < AC_{S4P}$  at 13~18 GHz. The high AC corresponds to the large absorption (or low  $RL_{min}$ , Table S1), meaning that more EM waves are dampened or converted into thermal energy as they enter absorbing layers. The strong attenuation capability is due to

the cooperative effects of multiple polarization loss, conductive loss, and multiple scattering as a result of defects and hierarchical architecture.

Matching constant ( $Z$ ) and attenuating constant ( $AC$ ) are two crucial factors, which determine the wide EAB and strong absorption. The values of  $Z$  and  $AC$  usually are obtained respectively from the expressions:

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

$$Z = \left| \frac{Z_{in}}{Z_0} \right| = \left| \frac{\mu_r}{\varepsilon_r} \tan h \left( j \frac{2\pi f d}{c} \sqrt{\mu_r \varepsilon_r} \right) \right|.$$

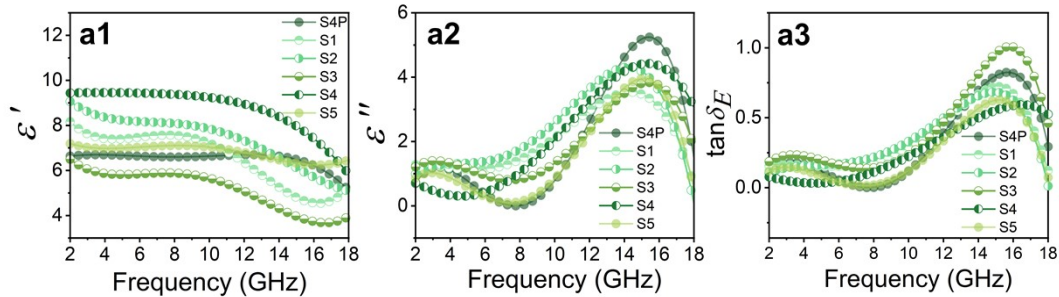
The  $Z$  presents an upward trend with  $f$ ; while the  $AC$  takes on a weak resonance peak over 2~8 GHz and a strong resonance peak over 8~18 GHz.

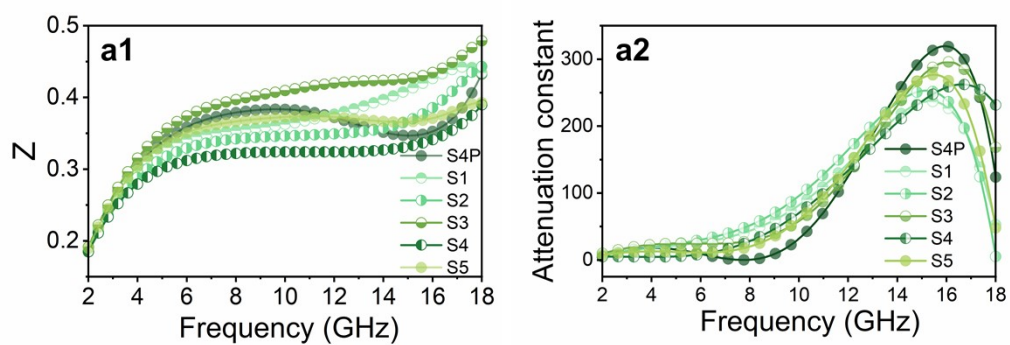
**Table S1.** MWACs summarization of SnO<sub>2</sub>-based absorption materials. <sup>2,7-20,46,47</sup>

Absorbers	Loading amount (%)	Optimal $R_L$ value (dB)	$f$ (GHz) (optimal $R_L$ )	$d_w$ (mm) ( $R_L < -10$ dB)	EAB (GHz) ( $R_L < -10$ dB)	EAB/d (GHz/mm)	Ref.
SnO <sub>2</sub> @ZnO	80	-23.5	9.20	12.0	3.50	0.29	7
Fe <sub>3</sub> O <sub>4</sub> @SnO <sub>2</sub> nanochains	50	-39.4	5.67	5.5	1.70	0.31	9
Fe-doped SnO <sub>2</sub> @RGO	60	-29.0	16.50	5.3	2.70	0.51	11
SnO <sub>2</sub> -graphene	50	-15.3	15.94	2.0	1.30	0.65	12
Ni/SnO <sub>2</sub>	70	-21.7	8.60	3.0	2.80	0.93	13
Sb <sub>2</sub> O <sub>3</sub> /SnO <sub>2</sub> /mica	20	-25.6	11.80	2.4	3.10	1.29	8
Fe <sub>3</sub> O <sub>4</sub> /SnO <sub>2</sub> nanorods	80	-27.4	16.72	2.0	2.60	1.30	10
core-shell Ni/SnO <sub>2</sub> composites	50	-45.0	13.90	1.8	3.80	2.11	14
embroidered ball-shaped SnO <sub>2</sub>	70	-45.6	12.40	2.6	6.08	2.34	20
Ni-doped SnO <sub>2</sub> @MWCNTs	33	-39.2	8.20	1.5	3.60	2.40	15
SnO <sub>2</sub> @PPy hybrid aerogels	10	-46.1	10.24	3.0	7.28	2.42	17
SnO <sub>2</sub> /Fe <sub>3</sub> O <sub>4</sub> /MWCNT	70	-42.0	10.90	1.5	3.80	2.53	16
honeycomb SnO <sub>2</sub> Foams	30	-37.6	17.10	2.0	5.60	2.80	46
Ni@void@SnO <sub>2</sub>	50	-29.7	15.20	1.7	4.80	2.82	47
AgNWs-CoNi@Sn(OH) <sub>2</sub> /SnO <sub>2</sub>	50	-37.8	6.40	2.0	5.80	2.90	18
Fe doped SnO <sub>2</sub> /C	33	-44.5	15.44	1.5	4.50	3.00	19
SnO/SnO <sub>2</sub> nanosheets	25	-37.6	15.20	1.4	4.30	3.07	2
Sn <sub>2</sub> PO <sub>4</sub> Cl S4P	50	-46.98	12.48	2.1	5.60	2.67	
SnO <sub>2</sub> @SnP <sub>2</sub> O <sub>7</sub> @Sn <sub>2</sub> P <sub>2</sub> O <sub>7</sub> -S1	50	-44.92	16.64	2.4	6.48	2.70	
SnO <sub>2</sub> @SnP <sub>2</sub> O <sub>7</sub> @Sn <sub>2</sub> P <sub>2</sub> O <sub>7</sub> -S2	50	-47.33	16.64	2.2	6.32	2.87	This work
SnO <sub>2</sub> @SnP <sub>2</sub> O <sub>7</sub> @Sn <sub>2</sub> P <sub>2</sub> O <sub>7</sub> -S3	50	-39.09	17.68	2.7	6.72	2.49	work
SnO <sub>2</sub> @SnP <sub>2</sub> O <sub>7</sub> @Sn <sub>2</sub> P <sub>2</sub> O <sub>7</sub> -S4	50	-36.61	12.96	2.0	6.48	3.24	
SnO <sub>2</sub> @SnP <sub>2</sub> O <sub>7</sub> @Sn <sub>2</sub> P <sub>2</sub> O <sub>7</sub> -S5	50	-35.01	12.16	2.2	5.92	2.69	

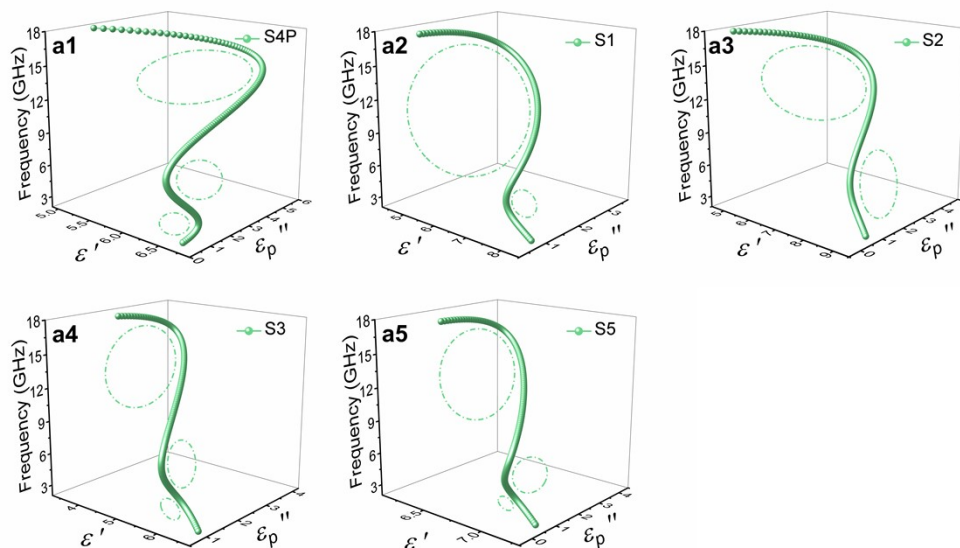
**Table S2.** Heat conductance summarization of SnO<sub>2</sub>-based composites.<sup>21–24,26–29,48–60</sup>

Filler	Matrix	Loading (%)	Heat conductance (W/m·K)	Ref.
SiO <sub>2</sub> /SnO <sub>2</sub> nanofibers	SiO <sub>2</sub> aerogel	8	0.025	48
SnO	Polystyrene / unsaturated polyester	1	0.172	49
Sb-SnO <sub>2</sub> /CM	poplypropylene	70	0.187	28
SnO <sub>2</sub> /EG nanofluids	ethylene glycol	25	0.277	26
CsCoPO <sub>4</sub>	Ceramics	100	0.35	21
MWCNTs/Sb-SnO <sub>2</sub>	Thermoplastic polyurethane	10	0.36	29
SnO <sub>2</sub> /rGO nanofluids	water	0.1	0.63	27
T-ZnO	silicone oil	70	0.83	50
b-Al <sub>2</sub> O <sub>3</sub>	epoxy resin	70	1.13	51
SnO <sub>x</sub> /Si <sub>3</sub> N <sub>4</sub> films	Ceramics	100	1.24	24
TiO <sub>2</sub> /Fe/C	silicone	45	1.87	52
SnO <sub>2</sub> /Y <sub>2</sub> O <sub>3</sub> /ZrO <sub>2</sub>	Ceramics	100	1.98	23
Al <sub>2</sub> O <sub>3</sub> /Ni/C	silicone	30	2.84	53
Ti <sub>0.8</sub> Sn <sub>0.2</sub> O <sub>2</sub>	ceramic	100	3.2	54
CNF/Fe <sub>x</sub> O <sub>y</sub>	silicone	30	3.22	55
Sn <sup>2+</sup> doped fluorophosphate glass	ceramic	100	3.25	22
Fe-doped CeO <sub>2</sub> /Ce(OH) <sub>3</sub>	silicone	45	3.442	56
MgO/Ni/MWCNT	silicone	40	3.61	57
graphene foams	silicone	5	3.95	58
MgO/Co/C	silicone	50	4.09	59
GN/PPy/Al <sub>2</sub> O <sub>3</sub>	silicone	50	4.649	60
Sn <sub>2</sub> PO <sub>4</sub> Cl S4P	silicone	20	4.003	
SnO <sub>2</sub> @SnP <sub>2</sub> O <sub>7</sub> @Sn <sub>2</sub> P <sub>2</sub> O <sub>7</sub> -S1	silicone	20	3.835	
SnO <sub>2</sub> @SnP <sub>2</sub> O <sub>7</sub> @Sn <sub>2</sub> P <sub>2</sub> O <sub>7</sub> -S2	silicone	20	4.394	This work
SnO <sub>2</sub> @SnP <sub>2</sub> O <sub>7</sub> @Sn <sub>2</sub> P <sub>2</sub> O <sub>7</sub> -S3	silicone	20	4.413	work
SnO <sub>2</sub> @SnP <sub>2</sub> O <sub>7</sub> @Sn <sub>2</sub> P <sub>2</sub> O <sub>7</sub> -S4	silicone	20	4.745	
SnO <sub>2</sub> @SnP <sub>2</sub> O <sub>7</sub> @Sn <sub>2</sub> P <sub>2</sub> O <sub>7</sub> -S5	silicone	20	4.265	

**Figure S1.** Frequency characteristics of the Sn<sub>2</sub>PO<sub>4</sub>Cl HAS (S4P) and SnO<sub>2</sub>@SnP<sub>2</sub>O<sub>7</sub>@Sn<sub>2</sub>P<sub>2</sub>O<sub>7</sub> HAS (S1–S5): (a1) the real part ( $\epsilon'$ ) and (a2) imaginary part ( $\epsilon''$ ) of relative complex permittivity, (a3) the dielectric loss ( $\tan\delta_E$ ).



**Figure S2.** Frequency characteristics of the  $\text{Sn}_2\text{PO}_4\text{Cl}$  HAs (S4P) and  $\text{SnO}_2@\text{SnP}_2\text{O}_7@\text{Sn}_2\text{P}_2\text{O}_7$  HAs (S1–S5): (a1) impedance matching ( $Z$ ); (a2) attenuation constant ( $\alpha$ ).



**Figure S3.** (a1–a5) Cole–Cole plots ( $\epsilon'$  versus  $\epsilon''$ ) of the  $\text{Sn}_2\text{PO}_4\text{Cl}$  and  $\text{SnO}_2@\text{SnP}_2\text{O}_7@\text{Sn}_2\text{P}_2\text{O}_7$  HAs.