Supporting Information

Electron-injection-induced Fe atomic valence transition for efficient terahertz shielding in α-Fe_2O_3@carbon microtubes

Sitao Guan,‡[a] Siying Ma,‡[a] Hengdong Ren,‡[a] Jian Chen,[b] Zhiyong Zhang,[a] Pengzhan Zhang,*[c] Xiaobing Xu*[d] and Xinglong Wu*[a]

[a] National Laboratory of Solid States Microstructures and School of Physics, Nanjing University, Nanjing 210093, China

[b] National Laboratory of Solid States Microstructures and Research Institute of Superconductor Electronics, Nanjing University, Nanjing 210093, China

[c] College of Electronic and Information Engineering, Jinling Institute of Technology, Nanjing 211169, China

[d] College of Electronic Engineering, Nanjing Xiaozhuang University, Nanjing 211171, China

****

[*] Corresponding authors

E-mail addresses: hkxlwu@nju.edu.cn (X.L. Wu), pzzhang@jit.edu.cn (P.Z. Zhang), xxb@njxzc.edu.cn (X.B. Xu).

‡S. T. Guan, S. Y. Ma, and H. D. Ren contributed equally to this work.

1. Extracting physical parameters of materials from THz-TDS spectra

Time-domain terahertz (THz) spectroscopy is a spectral technique capable of furnishing a comprehensive and intricate optical response from materials. Through the application of fast Fourier transform to time-domain signals, denoted as $E(t)$, we derive the amplitude $E(\omega)$ and phase $\varphi(\omega)$ of the wave. This process allows for the precise extraction of the complex refractive index, which encapsulates the absorption and dispersion characteristics of a material within the THz band.

2. Standard procedure of sample preparation for THz time-domain spectroscopy

To prepare the samples, we initially mixed 120 mg of composite powder thoroughly with 280 mg of ultra-high molecular weight polyethylene (PE) (particle size: 40-48 μm) by grinding them in a mortar for 30 min. Subsequently, we compressed this mixture in a hydraulic press at 10 MPa for 5 min, resulting in the formation of tablets with a 10 mm diameter. In this study, we pressed 0.15 g of α-Fe_2O_3 and (0%, 40%, 50%, 60%, and 70%) α-Fe_2O_3@CMTs mixed with PE respectively at 10 MPa, yielding tablets with respective thicknesses of 2.37, 2.39, 2.25, 2.35, 2.45, and 2.34 mm. We subsequently determined the optical parameters of these materials by subjecting the tablets to measurement using the THz-TDS system.

3. THz reflectance, absorptance, SE measurements of the composite materials using transmission and reflection modes of THz-TDS system.

The THz time-domain spectrum is Fourier transformed to acquire the amplitude spectrum, which is used to obtain the related data based on the following equations:

$$SE_{Total}\ (dB) = SE_A + SE_r = -10 \times log\ (\frac{E_t^2(\omega)}{E_{ref1}^2(\omega)}), \quad (S1)$$

$$SE_R\ (dB) = -10 \times log(1 - \frac{E_r^2(\omega)}{E_{ref2}^2(\omega)}), \quad (S2)$$

$$T(\omega) = \frac{E_t^2}{E_{ref1}^2}, \quad (S3)$$

$$R(\omega) = \frac{E_r^2}{E_{ref2}^2} \quad (S4)$$

$$A(\omega) = 1 - T(\omega) - R(\omega), \quad (S5)$$

where $E_r(\omega)$, $E_t(\omega)$, $E_{ref1}(\omega)$, $E_{ref2}(\omega)$ denote the intensities of reflection and transmission signals for samples and references, respectively. *T(ω),* R(ω), and *A(ω)* signify the transmissivity, reflectivity, and absorptivity of samples, respectively.

4. Calculations of the real and imaginary parts of permittivity:

The real and imaginary parts of dielectric constant are expressed as follows:

$$\varepsilon' = n^2(\omega) - \kappa^2(\omega) \quad (S6)$$

$$\varepsilon'' = 2 \times n(\omega) \times \kappa(\omega) \quad (S7)$$

$$tan\,\delta_e = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)} \quad (S8)$$

5. Calculation of THz shielding efficiency by a simplified modelling

The simplified model of THz wave propagation is shown in Fig. S7. According to Fresnel formula, when a THz wave is incident from media 1 to 2, the reflection coefficient (r) and transmission coefficient (t) between media 1 and 2 are given by:

$$r_{12} = \frac{n_2 - n_1}{n_1 + n_2}, \quad (S9)$$

$$r_{21} = \frac{n_1 - n_2}{n_1 + n_2}, \quad (S10)$$

$$t_{12} = \frac{2n_1}{n_1 + n_2}, \quad (S11)$$

$$t_{21} = \frac{2n_2}{n_1+n_2}, \quad \text{(S12)}$$

$$k = \frac{\omega}{c}\tilde{n}, \quad \text{(S13)}$$

where n_1 and n_2 are the refractive indexes of media 1 and 2, respectively. $\tilde{n}$ is the complex reflective index of sample. When a THz wave propagates through a distance of *"d"* within the sample, electromagnetic field intensity of the THz signal $E_d(\omega)$ can be represented as

$$E_d(\omega) = E_0(\omega) \times e^{ikd}, \quad \text{(S14)}$$

where $E_0(\omega)$ is the initial intensity of THz signal.

From the simplified model of THz wave propagation, the first, second, third, ... and nth THz wave signals reflected from sample into air can be expressed as E_{r1}, E_{r2}, E_{r3}, … and E_{rn}. Thus, the intensity of totally reflected signal can be expressed as:

$$E_R(\omega) = E_{r1}(\omega) + E_{r2}(\omega) + E_{r3}(\omega) + \cdots + E_{rn}(\omega) + \cdots \quad \text{(S15)}$$

$$= E_0 * (r_{12} + \frac{t_{12}*t_{21}*r_{21}*e^{i2kd}}{1-r_{21}*r_{21}*e^{i2kd}}) \quad \text{(S16)}$$

Analogously, the intensity of the totally transmitted signal can be expressed as:

$$E_T(\omega) = E_{t1}(\omega) + E_{t2}(\omega) + E_{t3}(\omega) + \cdots + E_{tn}(\omega) + \cdots \quad \text{(S17)}$$

$$= E_0 * (\frac{t_{12}*t_{21}*e^{ikd}}{1-r_{21}*r_{21}*e^{i2kd}}) . \quad \text{(S18)}$$

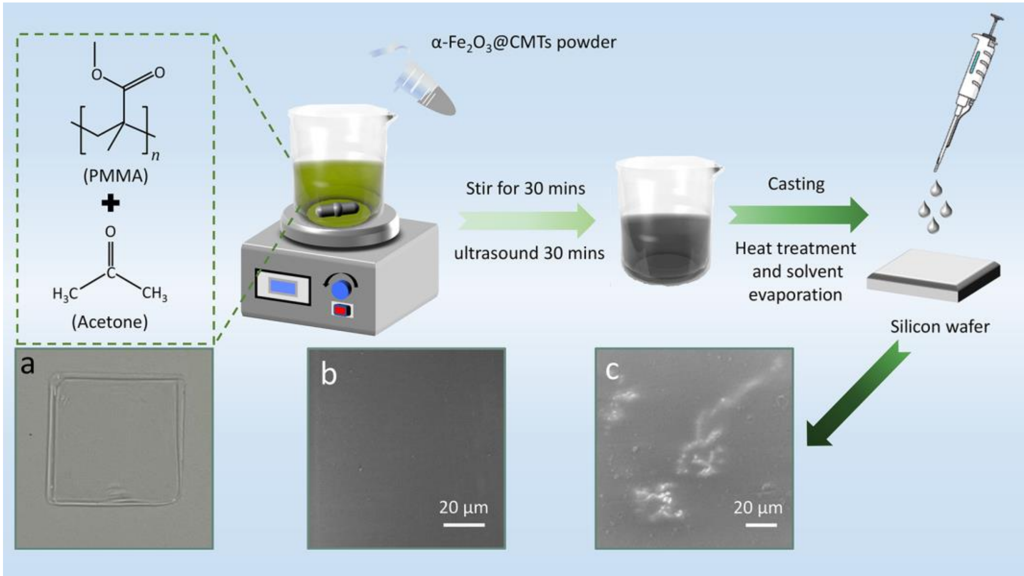

Fig. S1 Schematic diagram of the preparation process of α-Fe_2O_3@CMTs composite films. (a) Optical photograph of pure PMMA film (1 cm×1 cm). (b, c) SEM images of pure PMMA and (α-Fe_2O_3@CMTs)/PMMA composite films, respectively.

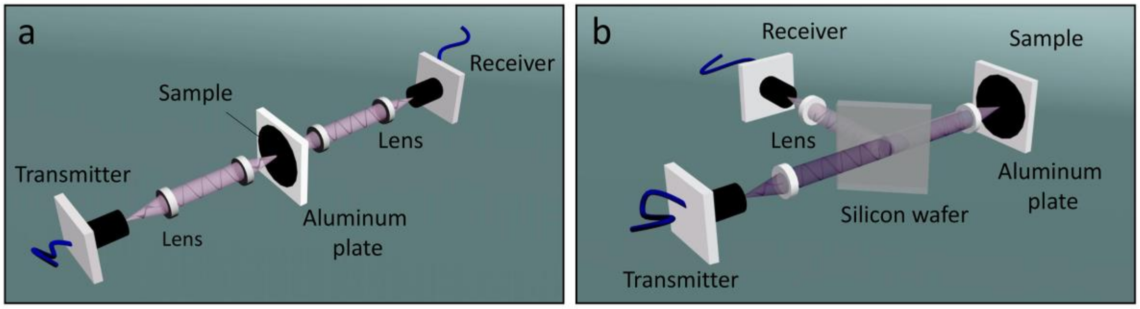

Fig. S2 (a, b) Schematic representations of the transmission (a) and reflection modes (b) of THz-TDS system.

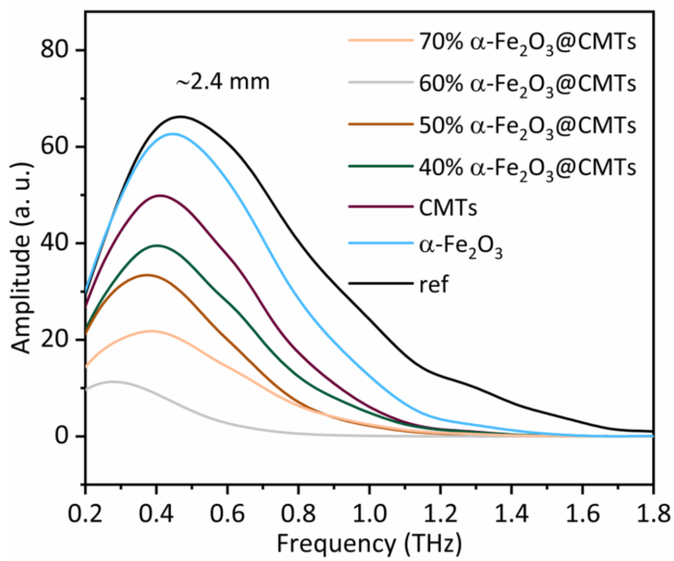

Fig. S3 Amplitude spectra of the tablet samples with different α-Fe_2O_3 proportions at a thickness of about 2.4 mm. These spectra were obtained by Fourier transform.

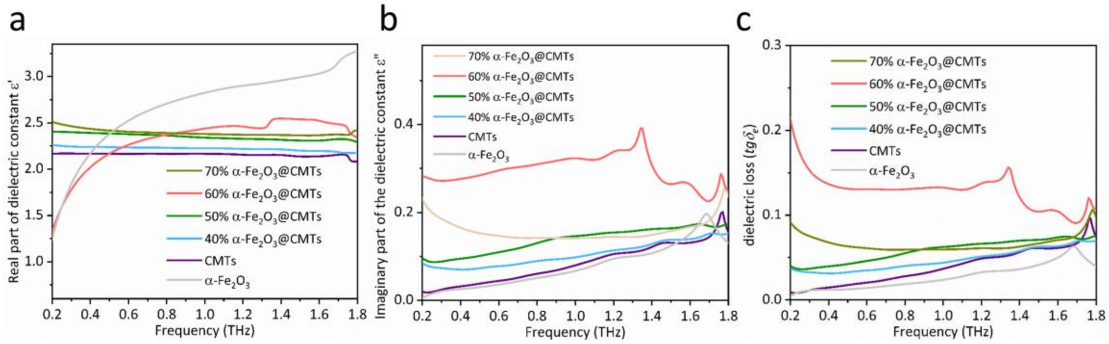

Fig. S4 (a-c) Real (a) and imaginary (b) parts of the dielectric constant and dielectric loss angle $tg\delta_e$ (c) for the α-Fe_2O_3, CMTs, 40%, 50%, 60%, and 70% α-Fe_2O_3@CMTs composites.

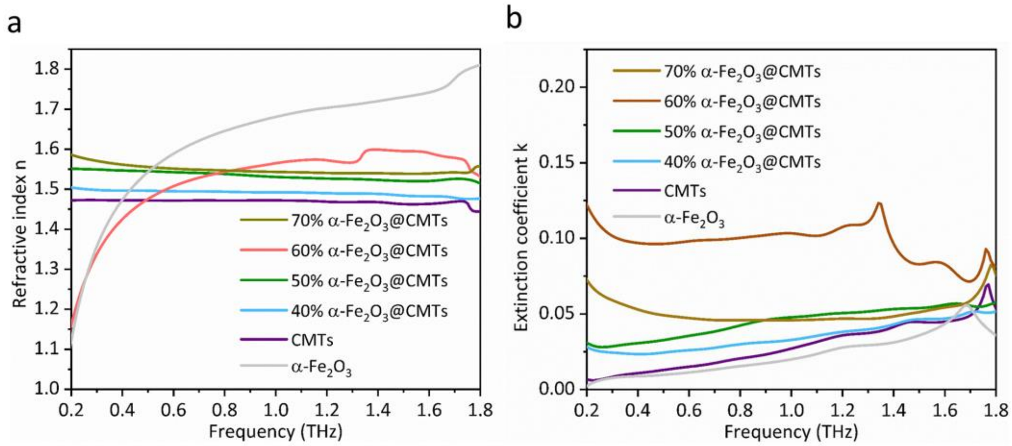

Fig. S5 (a, b) Real part of refractive index *n* (a) and extinction coefficients *k* (b) for the α-Fe_2O_3, CMTs, 40%, 50%, 60%, and 70% α-Fe_2O_3@CMTs composites.

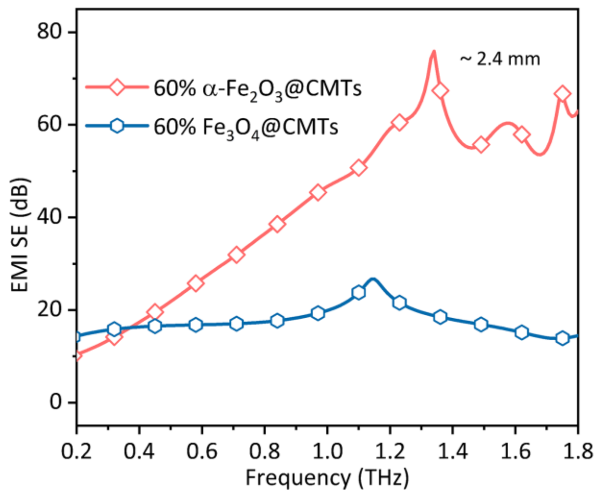

Fig. S6 Shielding effectiveness of the 60% α-Fe_2O_3@CMTs and 60% Fe_3O_4@CMTs at the thickness of about 2.4 mm.

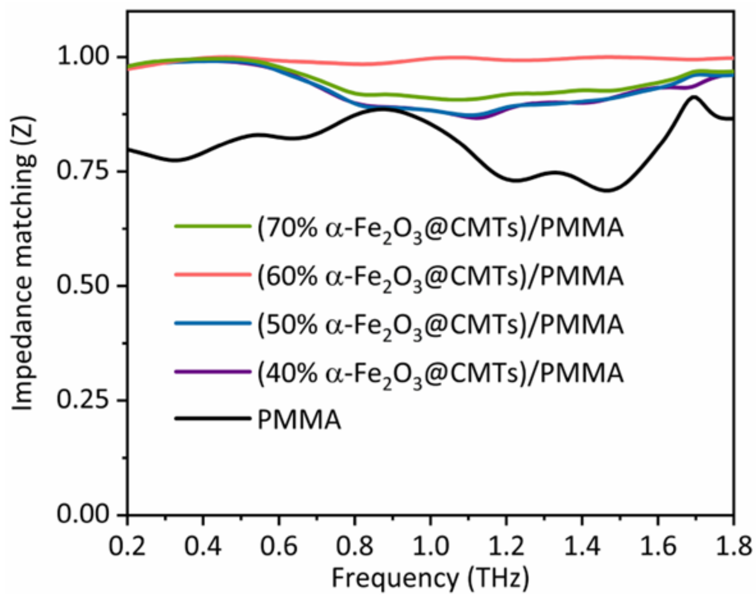

Fig. S7 Impedance matching (Z) diagram of PMMA composite films.

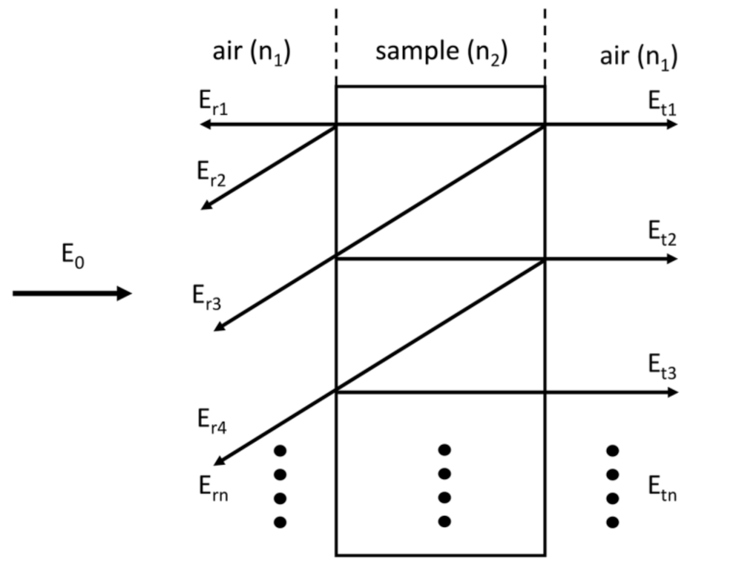

Fig. S8 Schematic diagram of a simplified THz transmission model.

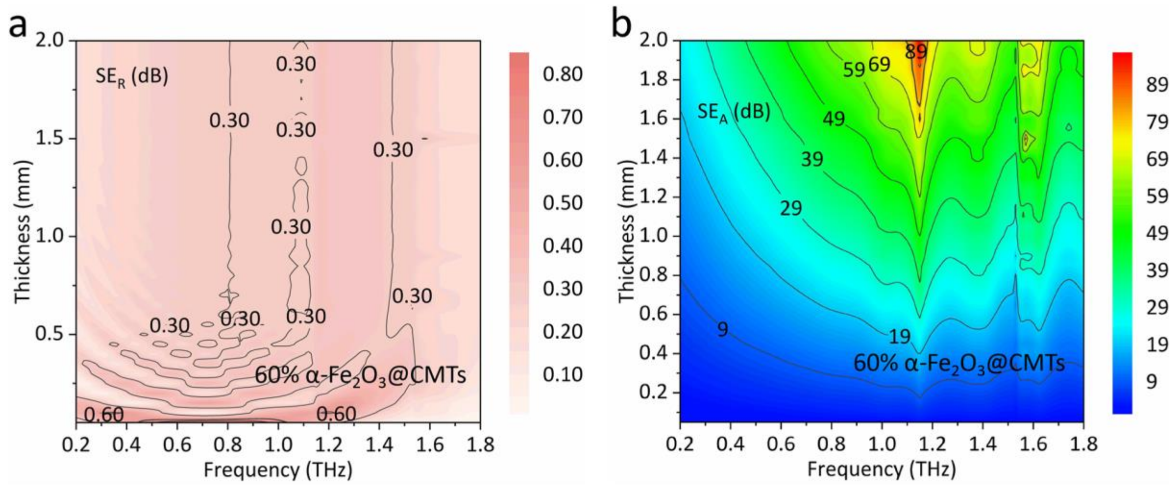

Fig. S9 (a, b) The reflection SE_R (a) and absorption SE_A (b) versus thickness and frequency for pure 60% α-Fe_2O_3@CMTs, calculated by a simplified THz transmission model.

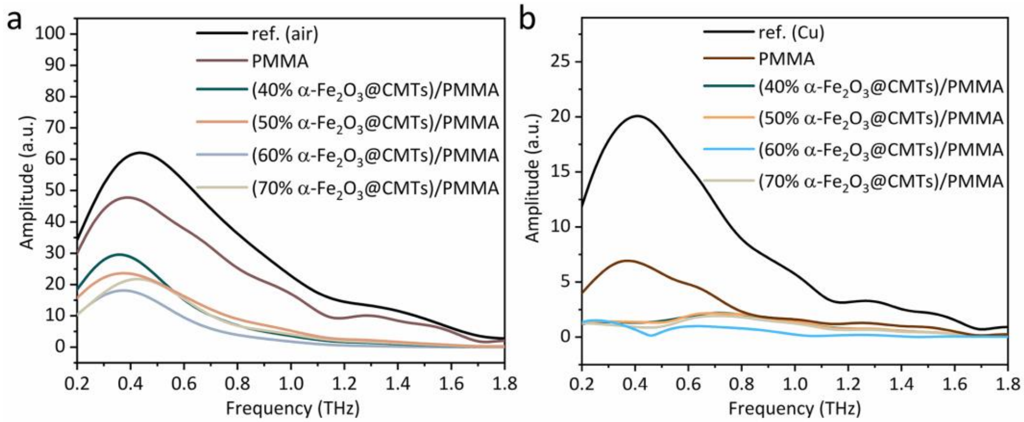

Fig. S10 (a, b) Amplitude spectra obtained from reflection (a) and transmission (b) modes for all α-Fe_2O_3@CMTs)/PMMA composite films.

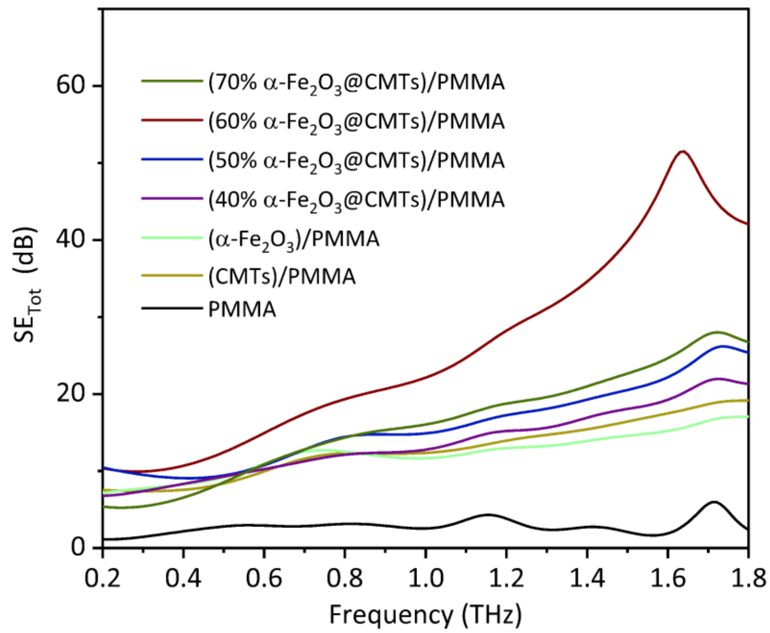

Fig. S11 THz shielding effectiveness of the (CMTs)/PMMA, (α-Fe_2O_3)/PMMA and (α-Fe_2O_3@CMTs)/PMMA composite films.

Table S1 THz shielding properties of some materials reported in the published literature.

Sample	*Thickness*	*EMI SE (dB)*	*Frequency Range (THz)*	*Refs.*
Our work α-Fe_2O_3@CMTs	3.05 mm	76.6	0.2-1.8	-
Our work (α-Fe_2O_3@CMTs) /PMMA	300 μm	51.6	0.2-1.8	-
3D $Ti_3C_2T_x$ MXene-based foam	85 μm	51	0.2-2	ACS Nano 14 (2) (2020) 2109-2117.
Graphene-based composites	3 mm	74	0.1-1.6	Adv. Opt. Mater. 6 (23) (2018) 1801165.
SiC/polydim-ethylsiloxane	0.6 mm	44.5	0.5-3	Mater. Res. Bull. 153 (2022) 111900.
3D graphene foam	4 mm	28.6	0.1-1.2	Adv. Funct. Mater. 28 (2) (2018) 1704363.
Graphene/Ion Gel/Graphene film	100 μm	10	0.1-0.25	Appl. Sci. 11(11) (2021) 5133
CNT-modified MXene/polymer composites	42 μm	36	0.2-2	Appl. Phys. A 127(5) (2021) 382.
Carbon nanofibers nanocomposite films	570 μm	44	0.2-1.2	J. Appl. Polym. Sci. 140(18) (2023) e53790.
Graphene and MXene polymer composites	700 μm	40	0.2-3	J. Appl. Polym. Sci. 138(10) (2020) 49962
Carbon nanotube polymer composites	300 μm	29	1.25-2.1	Opt. Lett. 39(6) (2014) 1541-1544.

Carbon nanofiber composite	100 µm	32	0.57-0.63	Appl. Phys. Lett., 98(17) (2011)
$Ti_3C_2T_x$ MXene sponge	10 mm	45	0.3-1.65	Adv. Opt. Mater. 8 (21) (2020) 2001120.
Ni/MXene decorated polyurethane sponge composite	8 mm	69.8	0.1-2.2	Adv. Opt. Mater. 10 (4) (2022) 2101868.