Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.
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Aligned fluorinated single-walled carbon nanotube as transmission channel towards attenuation of broadband electromagnetic wave

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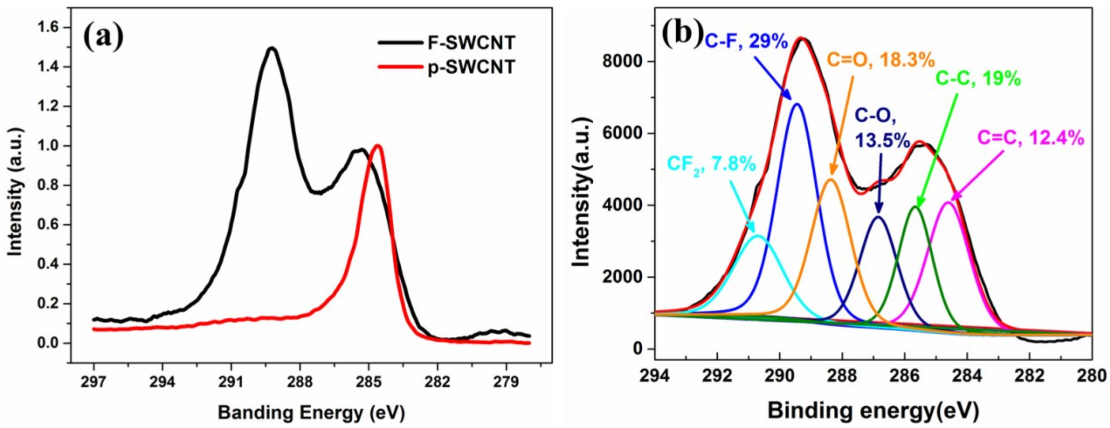

Figure S1. (a) Superimposed C 1s spectra of F-SWCNT and p-SWCNT; (b) XPS spectra of electrons from the C 1s orbital for F-SWCNT and its composition.

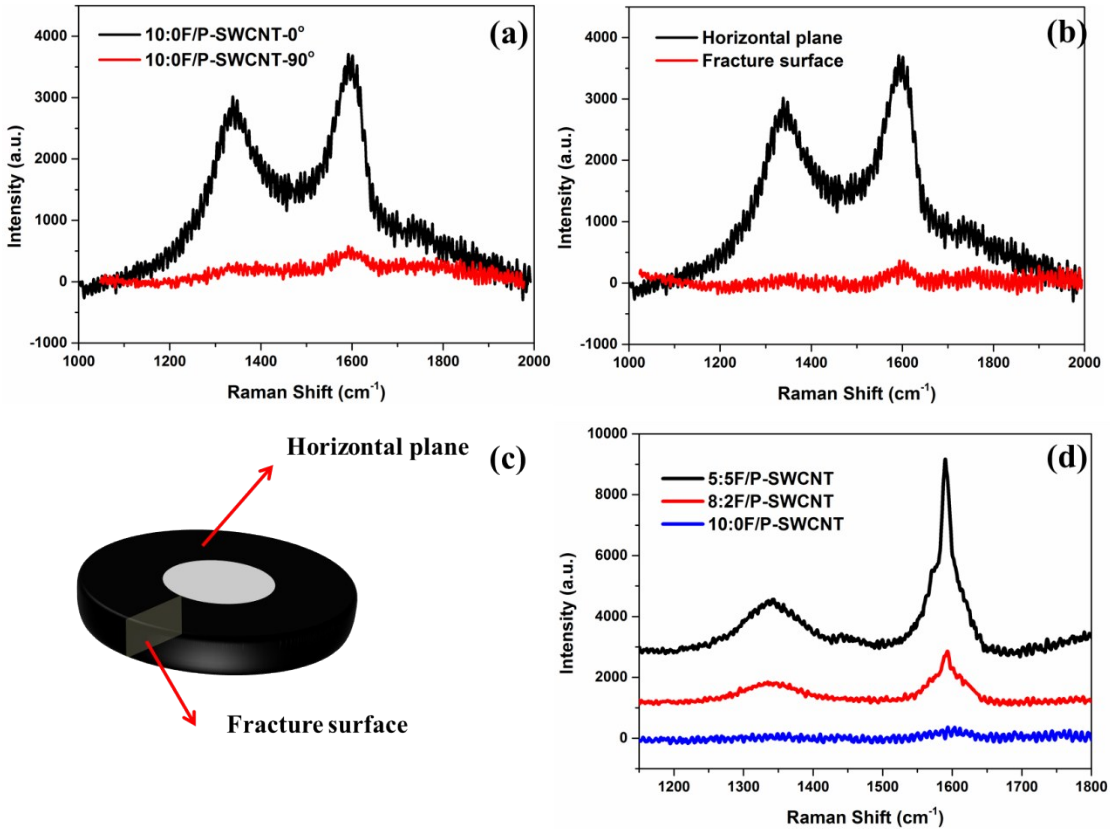

Figure S2. (a) Polarization Raman of 10:0F/P-SWCNT with polarization of the incident light parallel (0°) or vertical (90°) to the tangential direction in the horizontal plane; (b) Comparison of polarization Raman of 10:0F/P-SWCNT in the horizontal plane and fracture surface; (c) Schematic of the toroidal shape for electromagnetic parameter test. The horizontal plane and fracture surface were pointed out by red arrows; (d) the effect of F-SWCNT content on polarization Raman results in the fracture surface.

Firstly, the orientation direction of F-SWCNT in wax was determined by the combination of polarization Raman results in horizontal surface and fracture surface (Figure S2c). In horizontal plane, the Raman signal intensity with polarization direction parallel to the tangential direction is obviously stronger than the perpendicular direction, indicating that F-SWCNT prefer to be aligned along the tangential direction. Simultaneously, the Raman signal of 10:0F/P-SWCNT in the fracture surface almost cannot be detected, while it is evident in the horizontal plane, manifesting that F-SWCNT are horizontally arranged. From the above, it can be determined that F-SWCNT tends to be aligned in the horizontal surface along the tangential direction.

As a result, the influence of F-SWCNT proportion on orientation degree can be easily determined qualitatively by probing the polarization Raman sign in the fracture surface because F-SWCNT tends to be aligned in the horizontal surface. According to Figure 1b in manuscript, P-SWNCT exhibits almost no D band in Raman spectrum. After fluorination, the obvious D band of F-SWCNT demonstrates the damage of aromatic structure. As a result, the intensity of D band can reflect the orientation degree of F-SWCNT. As shown in Figure S2d, the 5:5F/P-SWCNT exhibit highest intensity of D band. With the increase of F-SWCNT, the intensity of D band decrease. Almost no Raman signal can be detected for 10:0F/P-SWCNT. These results demonstrate that more F-SWCNT lead to increased orientation degree of F-SWCNT in the horizontal surface. From the other side, the presence of P-SWCNT weakens the orientation degree of F-SWCNT, which may be due to the steric hindrance of P-SWCNT.

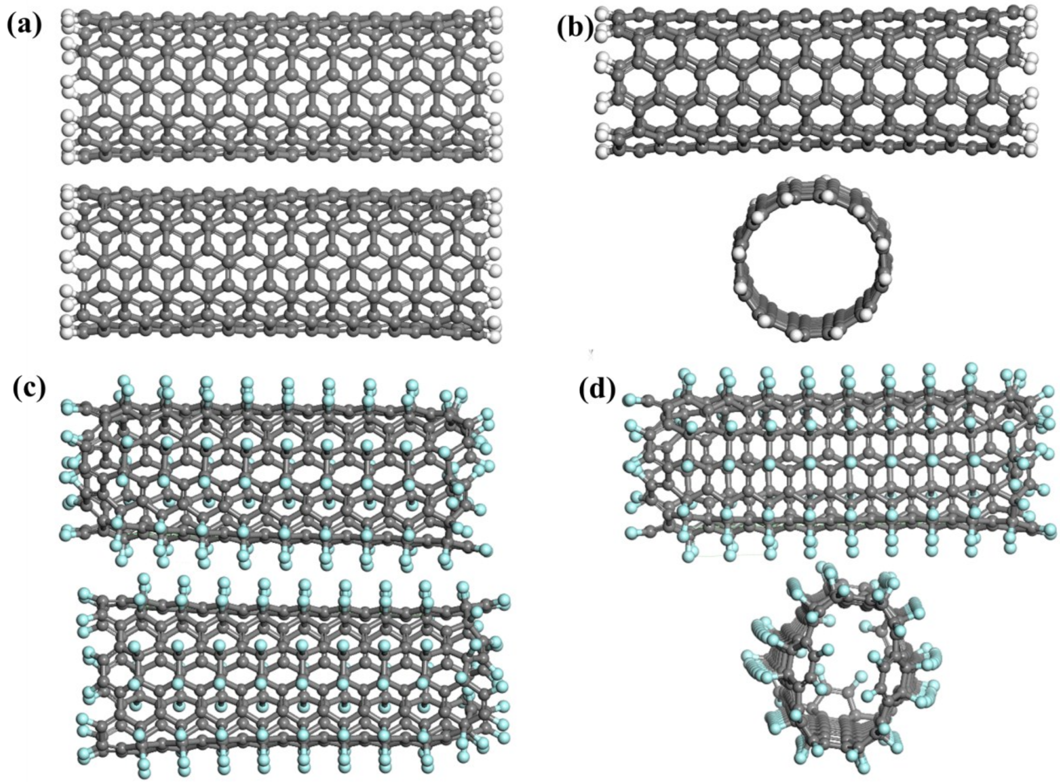

Figure S3. Snapshots of P-SWCNT (a, b) and F-SWCNT (c, d) with different intersection angle: (a) 1.2^{o}, (b) 89.5^{o}, (c) 0.9^{o}, (d) 89.5^{o}.

Table S1. Interaction energy of two P-SWCNT with different intersection angle.

Intersection angle (^{o})	Interaction energy (kcal/mol)	Electrostatic interaction energy (kcal/mol)	vdW interaction energy (kcal/mol)
1.2	-61.4	3.0	-66.3
18.8	-65.6	2.3	-71.6
29.9	-62.3	1.7	-67.0
46.0	-53.1	1.9	-60.7
51.1	-48.9	0.7	-63.6
62.7	-44.8	0.5	-49.1
71.8	-42.5	0.5	-48.7
89.5	-40.6	0.4	-45.4

Table S2. Interaction energy of two F-SWCNT with different intersection angle.

Intersection angle (^{o})	Interaction energy (kcal/mol)	Electrostatic interaction energy	vdW interaction energy (kcal/mol)

		(kcal/mol)	
0.9	-73.9	-12.2	-60.0
15.0	-52.3	-2.3	-51.9
20.0	-42.6	-1.3	-41.9
33.0	-35.7	1.1	-37.1
39.3	-32.5	1.2	-31.9
48.9	-28.1	0.6	-29.0
56.7	-26.5	-0.2	-27.6
77.9	-25.6	-0.1	-25.9
89.5	-28.1	-0.8	-27.7

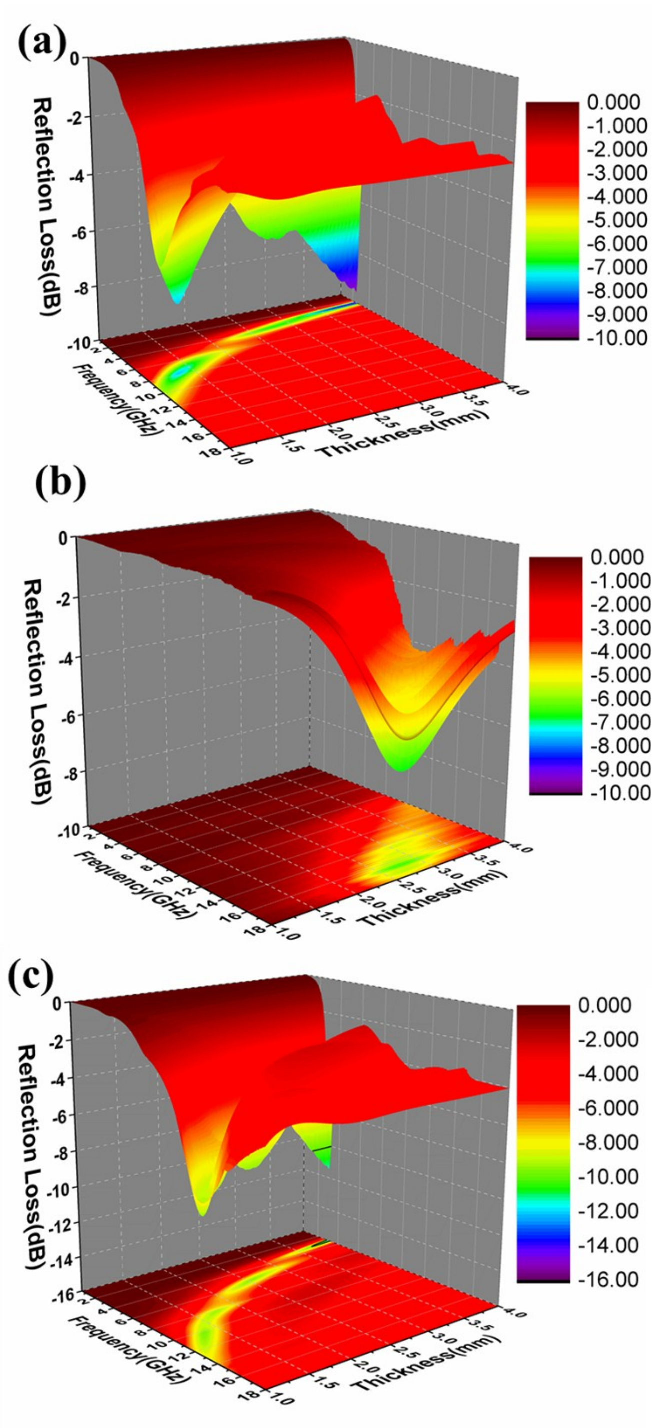

Figure S4. 3D RL plots of (a) 0:10F/P-SWCNT, (b) 10:0F/P-SWCNT and 2:8F/P-SWCNT versus frequency ranging from 0.5 to 18GHz with thickness ranging from 1 to 4 mm.

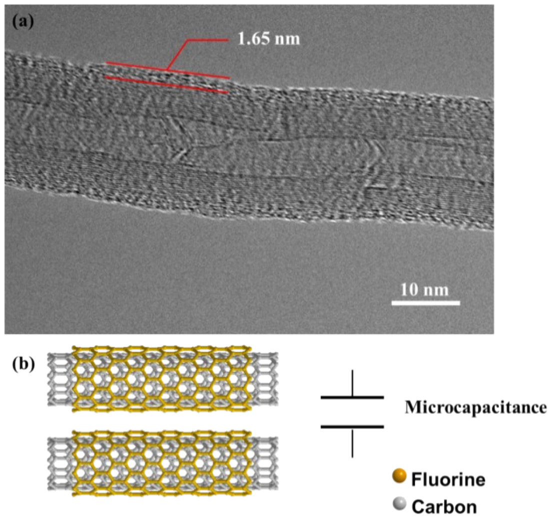

Figure S5. (a) HR-TEM image of F-MWCNTs with skin-core structure, (b) Schematic for the formation of microcapacitance structure between neighboring F-MWCNTs.

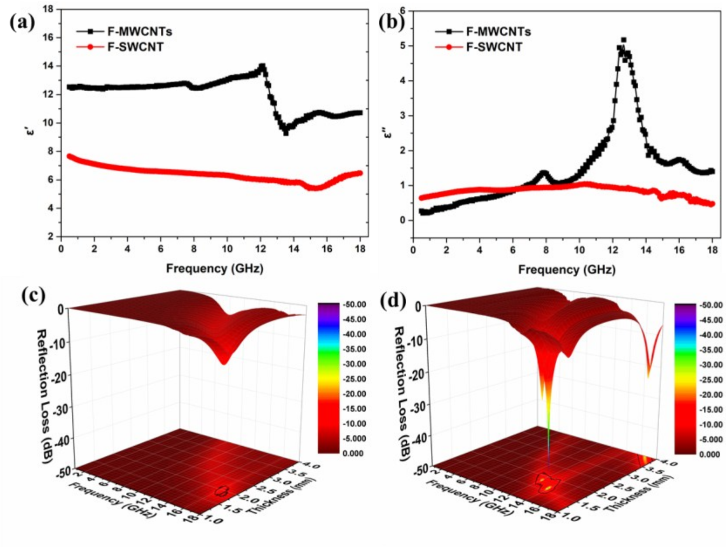

Figure S6. Frequency dependence of real (ε′; a) and imaginary (ε″; b) parts of complex dielectric permittivity for F-SWCNT and F-MWCNTs; 3D RL plots of F-SWCNT (c) and F-MWCNTs (d) versus frequency varying from 2 to 18GHz with thickness varying from 1 to 4 mm

MWCNTs are composed of 10-20 coaxial tubes. In the process of fluorination, the outer several tubes of MWCNTs are fluorinated with inner tubes intact. As a consequence, F-MWCNTs exhibit skin-core structure with outer fluorinated skin enwrapping intact inner tubes as shown in Figure S5. However, SWNCT can be fluorinated sufficiently because all carbon atoms are exposed to fluorine gas.

According to the XPS result, the F/C ratio of F-SWCNT in the present manuscript is about 0.53, which approximate the theoretically maximum fluorination degree for side wall fluorination of SWCNT. Similarly, highly fluorinated MWCNTs with F/C ratio 0.57 was prepared through long time of fluorination. The TEM image in Figure S5a demonstrates the skin-core structure of F-MWCNTs with fluorination depth about 1.65 nm.

Figure S6a-b show the frequency dependent real and imaginary part of the complex relative permittivity of F-MWCNTs and F-SWCNT with filler content 9.1 wt%. It is obvious that F-MWCNTs possess both higher ε′ and ε″ than F-SWCNT. A more important phenomenon is the obvious ε′ drop and ε″ peaks for F-MWCNTs, while similar drop and peaks are not perceived in F-SWCNT. The appearances of ε′ drops and ε″ peaks for F-MWCNTs are attributed to nonlinear resonance, which is in accord with the existence of intact aromatic structure in F-MWCNTs. On the contrary, aromatic region in F-SWCNT are depressed by fluorine, bringing about almost unchanged ε′ and ε″ with the variation of frequency. Benefiting from the particular skin-core structure, F-MWCNTs exhibit relatively better MA property than F-SWCNT. Specifically, F-SWCNT behaves poor MA property with RL_{min} higher than -10 dB, while the RL_{min} of F-MWCNTs can reach up to -45 dB. It is also noted that the main microwave absorption peak of F-MWCNTs is located within 12-14 GHz, which is just around the nonlinear resonance peak in Figure S6b. The results demonstrate the importance of constructing heterogeneous structure in the preparation of efficient microwave absorbers.

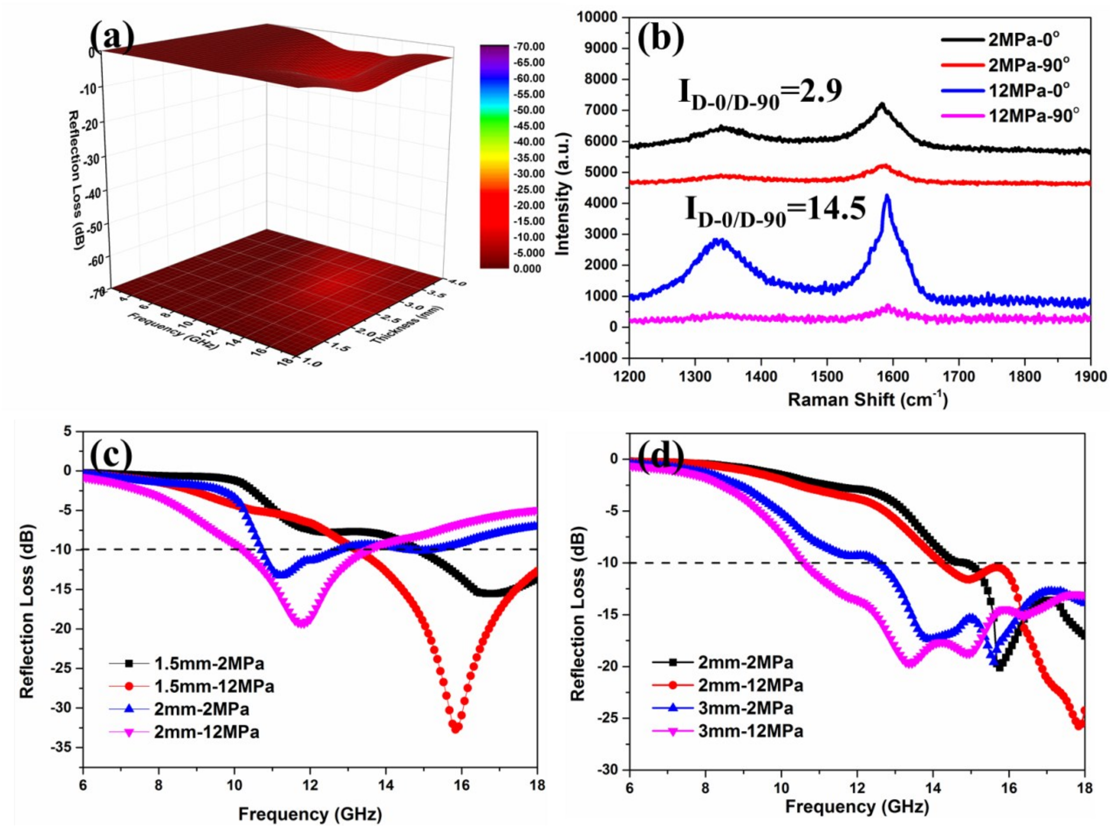

Figure S7. (a) 3D RL plots of P-SWCNT/wax (3mg P-SWCNT in 300 mg wax) versus frequency varying from 2 to 18GHz with thickness varying from 1 to 4 mm; (b) The effect of pressure on orientation degree with polarization of the incident light parallel (0^{o}) or vertical (90^{o}) to the tangential direction in the horizontal plane. The effect of orientation degree on MA property for 5:5F/P-SWCNT (c) and 8:2F/P-SWCNT (d) with different thickness.

Firstly, we proved the indispensible role of F-SWCNT in the enhancement of MA property for F/P-SWCNT. Only 3 mg P-SWCNT was mixed with 300 mg wax without addition of F-SWCNT. The MA property was supplied as shown in Figure S7a. The RL values are all higher than -10 dB with thickness varying from 1.0 to 4.0 mm, manifesting the poor MA property. However, 8:2F/P-SWCNT possessing the same composition of P-SWCNT exhibit excellent MA property with strong absorption and wide absorption bandwidth (Figure 8 in manuscript). This difference validates the indispensible role of F-SWNCT in MA property.

The orientation of F-SWCNT is controlled under different stress. F-SWCNT/P-

SWCNT with ratio 8:2 was mixed with wax. The composites were then pressed into toroidal shape with inner diameter 3 mm and outer diameter of 7 mm under the pressure of 2 MPa and 12 MPa, respectively. Polarization Raman detected in the horizontal surface was firstly measured to evaluate the orientation degree. The intensity ratio of D band at 0^o and 90^o ($I_{D-0/D-90}$) for 8:2F/P-SWCNT-12MPa is higher than that of 8:2F/P-SWCNT-2MPa, manifesting higher orientation degree of 8:2F/P-SWCNT-12MPa.

The influences of different orientation degree in MA property are supplied in Figure S7d. It is obvious that 8:2F/P-SWCNT-12MPa exhibit broader and stronger MA property than 8:2F/P-SWCNT-2MPa in thickness of both 2mm and 3mm. It is surprising that the efficient absorption bandwidth can reach 7.4 GHz. We also examined the conclusion for 5:5F/P-SWCNT and the result agree well with the result of 8:2F/P-SWCNT.

Because P-SWCNT is hardly orientated under pressure, the above results validate the indispensible role of F-SWNCT orientation in MA property. We deduced that aligned F-SWNCT arrays are beneficial to the directional propagation of electromagnetic wave, which is conductive to the effective attenuation of electromagnetic wave.

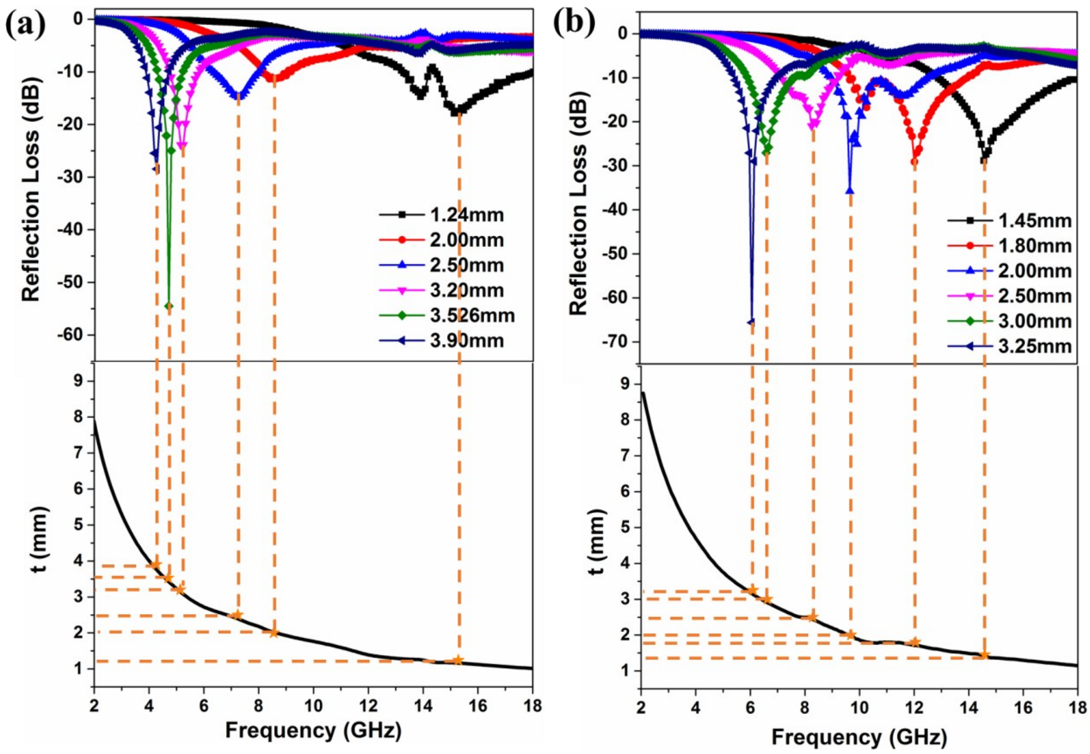

Figure S8. Dependence of matching thickness (t_m) on matching frequency (f_m) of 5:5F/P-SWCNT (a) and 8:2F/P-SWCNT (b) composites at wavelengths of λ/4.

It was also noticed that the RL peaks gradually shifted to lower frequency with the increase of thickness. This phenomenon can be explained by quarter-wavelength cancellation model ascribed as following equation:[1]

$$t_m = \frac{nc}{4f_m\sqrt{|\varepsilon_r||\mu_r|}} \quad (n=1, 3, 5\ldots) \qquad (1)$$

from which, the matched RL_{min} thickness (t_m) is inversely proportional to matched RL_{min} frequency (f_m), namely gradual increase of t_m with the f_m decreasing. It was found that the orange symbols (representing experimental matching thicknesses at the peak frequency) are located around the l/4 curves, demonstrating that the hybrids obey the quarter-wavelength matching conditions.

1. N. Li, G. W. Huang, Y. Q. Li, H. M. Xiao, Q. P. Feng, N. Hu and S. Y. Fu, *ACS Appl. Mater. Interfaces*, 2017, **9**, 2973-2983.