Supplementary Information

3D Fe_3O_4 nanocrystals decorating on carbon nanotubes to tune electromagnetic properties and enhance microwave absorption capacity

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Experimental section

Materials

All reagents used were of analytical pure grade: multi-walled carbon nanotubes (MWCNTs of 5–15 nm in length and 20–40 nm in diameter) fabricated by the catalytic decomposition of CH_4 was purchased from Shenzhen Nanotech Port Co. Ltd. (China). Ferric ammonium sulfate ($NH_4Fe(SO_4)_2$•$12H_2O$) was obtained from Tianjin Fuchen Chemical Reagents Factory. Ferrous ammonium sulfate (($(NH_4)_2Fe(SO_4)_2$•$6H_2O$), tetrahydrofuran (THF), ammonia water and nitric acid (HNO_3 65-68 wt. %) was purchased from Beijing Chemical Factory. Anhydrous ethanol was purchased from Beijing Tong Guang Fine Chemicals Company.

Preparation of modified MWCNTs

To obtain modified MWCNTs, 1 g of MWCNTs were refluxed in the mixture including 80 ml of nitric acid and 420 ml of deionized water at 140℃ for 24 hours, followed by washing with deionized water until neutral pH value in the washing solution. The acquired neutral solution of the precipitate was treated by ultrasonic cell disruptor for 1 hour. The modified MWCNTs had been prepared.

Preparation of 3D Fe_3O_4-MWCNTs

In a typical fabrication experiment, 20 ml of modified MWCNTs (~100 mg) were dispersed in 20 ml of aqueous solution with 1.6 mmol of $NH_4Fe(SO_4)_2$•$12H_2O$ and 0.8 mmol of $(NH_4)_2Fe(SO_4)2$•$6H_2O$. Then 5 ml of NH_3•H_2O (25 wt. %) was dropwise added into the suspension. The co-precipitating reaction was maintaining 30 min at 50℃ with vigorously mechanical stirring. The resulting suspension was centrifuged and washed with deionized water and anhydrous ethanol. The precipitations was drying in an oven at 80℃. In order to investigate the possible growth process of 3D Fe_3O_4-MWCNTs, we get the products of different reaction time (5 min, 15 min and 30 min) and named Sample 1, Sample 2 and Sample 3, respectively.

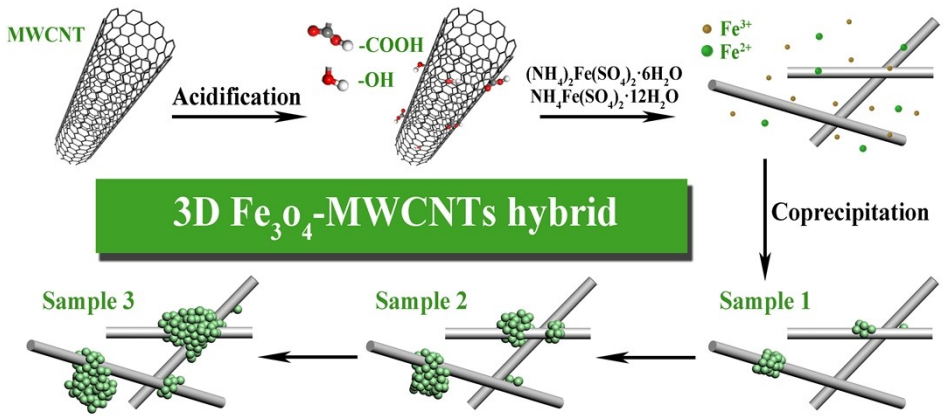
Characterizations and measurements

The results of X-ray power diffraction (XRD) spectra were performed on an X´Pert PRO system (Cu-Kα). Raman

spectra were obtained on a HORIBA Jobin Yvon HR800 Raman spectrometer. SEM images were performed on a Hitachi S-4800 SEM system. TEM images were got on a JEM-2100 TEM system, coupled with carbon- or holey carbon-coated copper grids. In order to measure the complex permittivity and permeability, different amounts of 3D Fe_3O_4-MWCNTs powders (5, 10, 15, 20 and 25 wt. %) and paraffin (95, 90, 85, 80 and 75 wt. %) were dispersed uniformly in the tetrahydrofuran, respectively. After the tetrahydrofuran was completely evaporated, the mixture was cooled to room temperature. A portion of the resulting mixture was pressed into toroidal shape (Φout 7.05 mm; Φin 3.0 mm; Thickness ~1.5mm). The complex permittivity and permeability were measured on an Anritsu 37269D vector network analyzer.

Table S1. Microwave absorption comparison of representative work

Samples in matrices	**Wt. %**	**Min RL [dB]**	**Effective bandwidth [GHz] (RL ≤ -10 dB)**	**Thickness [mm]**	**Refs**
3D Fe_3O_4-MWCNTs in wax	20	-11.1~-52.8	1.7~3.0	2.0~6.8	This work
SWCNTs in SCPU	5	-21.9	2.6	2.0	1
Fe-CNT in epoxy	10	-31.7	2.9	1.0	2
γ-Fe_2O_3/MWNTs/PBO in wax	12	32.7	2.7	2.7	3
MWCNT/Fe_3O_4 nanohybrid in wax	50	-41.6	1.5	3.4	4
r-GO/Fe_3O_4 in wax	30	-24.0	4.9	2.0	5
GO/CNT-Fe_3O_4 nanohybrid in wax	30	-37.2	1.0	5.0	6
Fe_3O_4@TiO_2 microspheres in epoxy	20	-23.3	5.5	2.0	7
Fe_3O_4@ZnO nanohybrid in wax	50	-22.7	5.8	3.5	8



Scheme S1. The illustration of the fabrication of 3D Fe_3O_4-MWCNTs

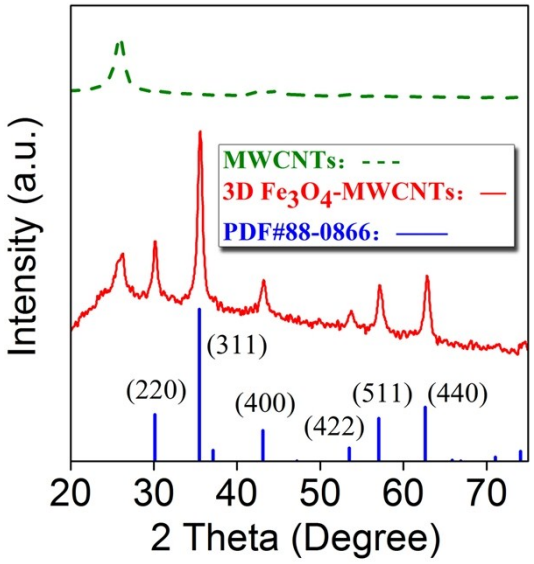


Figure S2. The XRD spectrum of neat MWCNTs and 3D Fe_3O_4-MWCNTs

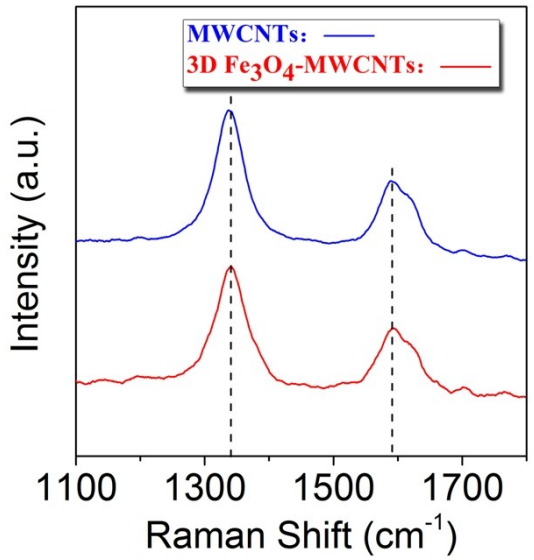


Figure S3. The Raman spectrum of 3D Fe_3O_4-MWCNTs and neat MWCNTs

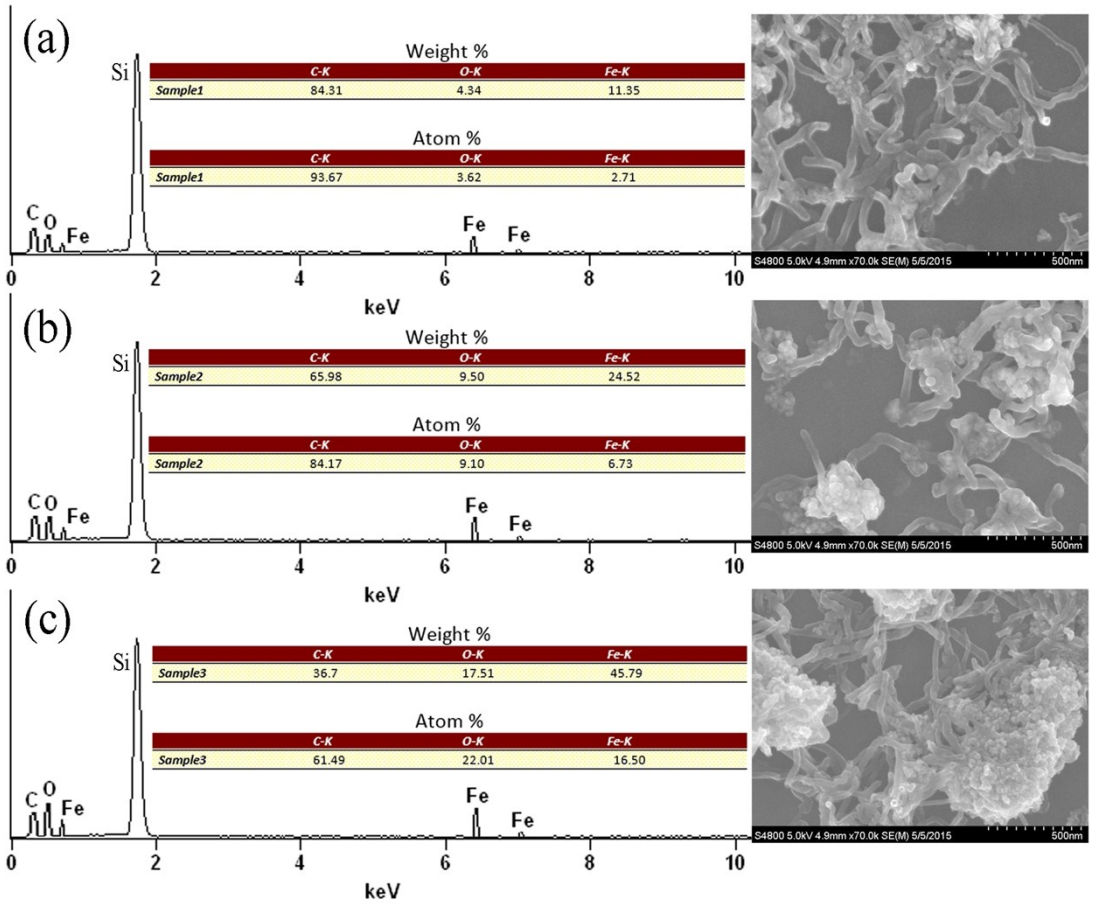


Figure S4. The energy dispersive spectroscopy (EDS) analysis of Sample 1 (a), Sample 2 (b) and Sample 3 (c); the mass percent and atom percent is in the inset

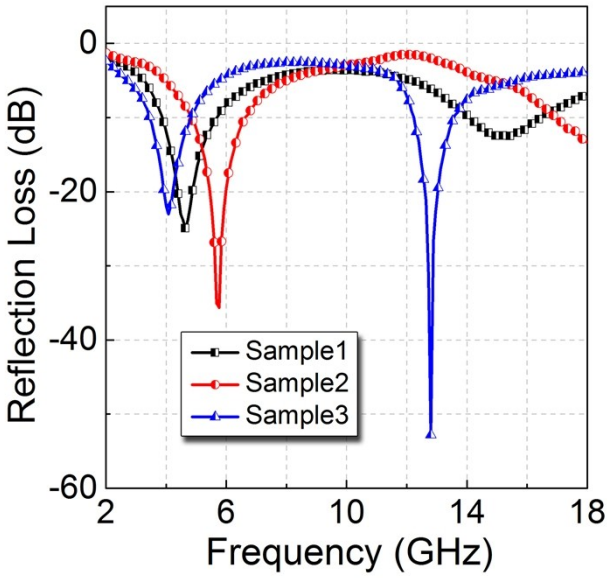


Figure S5. The RL values of Sample 1, Sample 2 and Sample 3

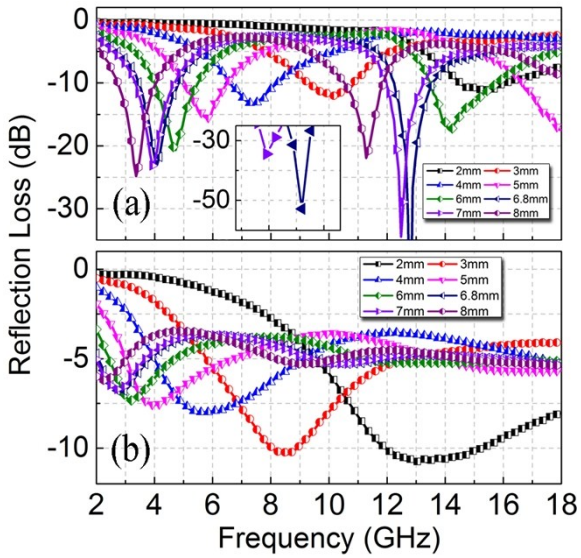


Figure S6. The RL of 3D Fe_3O_4-MWCNTs (a) and Fe_3O_4/MWCNTs blend (b)

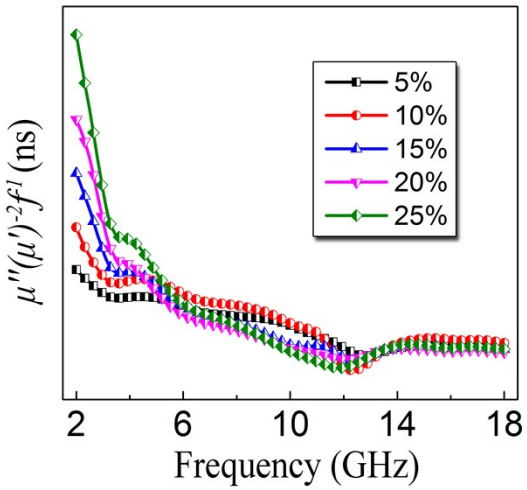


Figure S7. Frequency dependence of $\mu''(\mu')^{-2}f^{-1}$ for 3D Fe_3O_4-MWCNTs

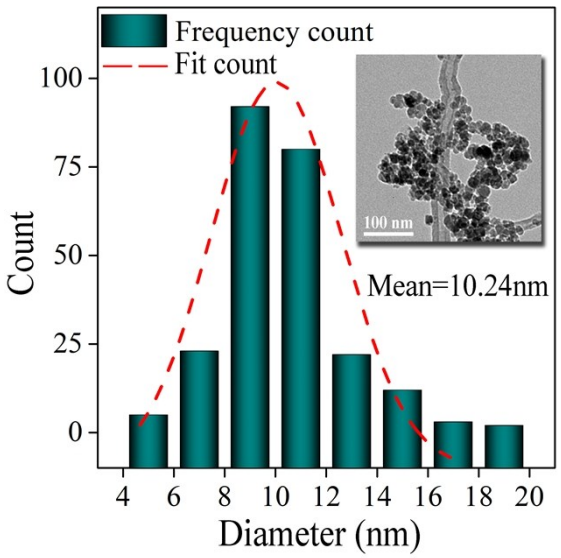


Figure S8. The size distribution histogram of Fe_3O_4 nanocrystals from the inset

Notes and References

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