Supporting Informations:

Chemoselectivity induced multiple interfaces in MWCNT/Fe₃O₄@ZnO heterotrimers for whole Xband microwave absorption

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1. EXPERIMENTAL SECTION

Materials. MWCNTs with a diameter of 20-30 nm and length of 5-15 mm were supplied by Shenzhen Nanotech Port Ltd. Co. (China). Triethylene glycol, 1,3-Diisopropyl carbodiimide, *N*,*N*-dimethylaminopyridine, *p*-toluene sulfonic acid monohydrate, zinc acetate, and *L*-glutamine were obtained from Aldrich. Iron(III) acetylacetonate were purchased from Acros. All chemicals were of analytical grade and used without further purification. Deionized water of high resistivity (18.2 $M\Omega$ •cm) was collected through a TKA GenPure ultrapure water system.

Synthesis of MWCNT/Fe₃O₄ nanowires. The MWCNT/Fe₃O₄ nanowires were fabricated by a modified polyol method. Initially, MWCNTs (100 mg) were dispersed in a TREG solution (30 mL) in an ultrasonic bath to obtain a dispersed suspension. Iron(III) acetylacetonate (400 mg) was then added into the suspension. This mixture was further sonicated to give a black-colored stable solution, and subsequently heated to 287 °C at a rate of 3 °C min⁻¹ under argon protection. After cooling to room temperature, the products were magnetically separated by a magnet and washed with ethanol several times.

Synthesis of MWCNT/Fe₃O₄-ZnO nanohybrids. The obtained MWCNT/Fe₃O₄ nanowires (100 mg) were dispersed in a TREG solution (25 mL) in an ultrasonic bath to give a dispersed suspension. Subsequently, 311 mg of zinc acetate was added into the suspension, and this mixture was further sonicated for at least half an hour to make zinc acetate well resolved in the solvent. This mixture was heated to 287 °C at a

rate of 3 °C min⁻¹ under argon protection. After cooling to room temperature, the products were magnetically separated by a magnet and washed several times.

Amination of MWCNT/Fe₃O₄ nanowires. The amination was preceded with the DIPC and DPTS. DPTS was prepared by mixing the saturated tetrahydrofuran solutions of *N*,*N*-dimethylaminopyridine (1 equiv) with *p*-toluenesulfonic acid monohydrate (1 equiv) at room temperature, and then dried under vacuum. Firstly, the dried MWCNT/Fe₃O₄ nanowires (100 mg) were dispersed in 18 mL of dichloromethane. Then, DPTS (24 mg) dissolved in 2 mL of dichloromethane was added into the vessel. Dropwise addition of 30 mg of DIPC was done after 5 min, followed by addition of 2.0 mL of DMF to bring the *L*-glutamine (20 mg) into solution. The reaction was completed after 12 h at room temperature. Lastly, the aminated MWCNT/Fe₃O₄ nanowires were magnetically separated.

Synthesis of MWCNT/Fe₃O₄@ZnO heterotrimers. The strategy for the fabrication of MWCNT/Fe₃O₄@ZnO heterotrimers is similar with that of MWCNT/Fe₃O₄—ZnO nanohybrids. Initially, the aminated MWCNT/Fe₃O₄ nanowires (100 mg) and zinc acetate (311 mg) were well dispersed in a 25 mL triethylene glycol solution. Then the solution was heated to 287 °C at a rate of 3 °C min⁻¹ under an argon protection and kept at reflux for 30 min. Lastly, the products were magnetically separated and dried in a vacuum oven.

Synthesis of Fe₃O₄@ZnO core-shell nanoparticles. The Fe₃O₄@ZnO core-shell nanoparticles were synthesized by our previous reported method.³⁵ Firstly, Fe₃O₄

nanocrystals are prepared by heating a 30 mL TREG solution resolved 2 mmol iron(III) acetylacetonate. 2 mmol Zn(AC)₂ was then added slowly into the mixture formed at first step, which was subsequently heated to 287 °C under a protection of argon. The ZnO shell of Fe₃O₄@ZnO core-shell nanoparticles has a thickness of about 3 nm, which is similar with that of MWCNT/Fe₃O₄@ZnO heterotrimers. The comparison of Zn L-edge XANES between Fe₃O₄@ZnO core-shell nanoparticles and MWCNT/Fe₃O₄@ZnO heterotrimers was studied, figuring out whether or not there were C-O-Zn bondings formed at the interface.

Characterizations. XRD patterns of samples were carried out on a Rigaku D/max- γ B diffractometer equipped with a rotating anode and a Cu K α source. TEM images were obtained on a Tecnai G2 F30 electron microscope under an accelerating voltage of 300 keV. Magnetic measurements were performed on the physical properties measurement system (PPMS) in a vibrating sample magnetometry mode (Quantum Design Inc.) with a magnetic field up to 5 T. FT-IR spectra were recorded on a Perkin-Elmer Spectrum One spectrometer. Thermogravimetric analysis was performed on a TA Instruments TGAQ50. Samples (3.0-6.0 mg) were placed in platinum sample pans and heated under an air atmosphere at a rate of 10 °C/min. The XANES were obtained on the spherical grating monochromator (SGM) beamline ($\Delta E/E$: ~10⁻⁴) at the Canadian Light Source (CLS) in a surface-sensitive, total electron yield (TEY) mode with use of specimen current. **Microwave absorption measurements.** The electromagnetic parameters of samples were measured on a vector network analyzer (Agilent, N5230A) with the transmission-reflection mode in the 2-18 GHz band. Samples containing 50 wt.% prepared heterotrimers was pressed into a shape with an outer diameter of 7.0 mm, inner diameter of 3.0 mm and thickness of about 3.5 mm for microwave measurement, in which paraffin wax was used as the binder. All the reported values were obtained by averaging over the data measured from three samples for each kind of nanomaterials.

The microwave absorption properties of the samples were evaluated by the reflection loss on the basis of the transmission line theory. The equations are as following:

$$Z_{in} = Z_0 (\mu_r / \varepsilon_r)^{1/2} \tan h[j(2\pi fd/c)(\mu_r \varepsilon_r)^{1/2}]$$
(1)

$$R_{L}(dB) = 20 \log \left| \frac{Z_{in} - Z_{0}}{Z_{in} + Z_{0}} \right|$$
(2)

where *f* is the frequency of the electromagnetic waves, *d* is the thickness of the absorber, *c* is the velocity of electromagnetic waves in free space, μ_r and ε_r are, respectively, the relative complex permeability and permittivity, Z_0 is the impedance of air, and Z_{in} is the input impedance of the absorber.

2. Microstructure of MWCNT/Fe₃O₄@ZnO heterotrimers



Figure S1. SEM characterizations and EDX analysis of (a) MWCNT/Fe₃O₄, (b) MWCNT/Fe₃O₄-ZnO, and (c) MWCNT/Fe₃O₄@ZnO. Both MWCNT/Fe₃O₄ and MWCNT/Fe₃O₄-ZnO have similar average diameter size of around 40 nm. The nanowires in the SEM image of MWCNT/Fe₃O₄@ZnO heterotrimers become thicker, average diameter size being around 46 nm, which confirms that ZnO nucleates on Fe₃O₄ surface.

3. Amination of MWCNT/Fe₃O₄ nanowires



Figure S2. FT-IR spectra of MWCNT/Fe₃O₄ nanowires before (a) and after amination (b). After the amination was processed, some new peaks were observed in the spectrum of the sample #b. Among these peaks, the peak locating at 881 cm⁻¹ is credited to NH_2 group out-of-plane deformation vibration. The peak at 1052 cm⁻¹ is attributed to NH_2 group in-plane deformation vibration. The peak at 1340 cm⁻¹ is ascribed to C-N stretching vibration.



Figure S3. TG analysis of MWCNT/Fe₃O₄ nanowires before and after amination. Obvious weight loss of the nanowires has been found in the temperature ranges of 20-200 °C, 200-420 °C, and 420-580 °C. The first slight amount of weight loss is attributed to the evaporation of adsorbed water and ethanol or ethyl acetate. The second stage of weight loss at range of 200-420 °C corresponds to the removal of ligands (TREG and aminated TREG) anchored on Fe₃O₄. The Third stage of weight loss is induced by the decomposition of MWCNT. The increase of weight loss in the second stage give a strong support that the function groups have been aminated by the process illustrated in Figure 1.

4. Reaction mechanism between aminated MWCNT/Fe₃O₄ nanowires and Zn(AC)₂



Figure S4. Proposed reaction mechanism between aminated MWCNT/Fe₃O₄ nanowires and $Zn(AC)_2$ as the heating temperature increased from room temperature to 287 °C.



5. Microwave absorption characterization of materials

Figure S5. Three-dimensional representations of reflection loss of (a) MWCNT/Fe₃O₄, (b) MWCNT, (c) Fe₃O₄, (d) ZnO, (e) physical mixture of MWCNT/Fe₃O₄ and ZnO, (f) MWCNT/Fe₃O₄-ZnO, and (g) MWCNT/Fe₃O₄@ZnO. Among these samples, MWCNT/Fe₃O₄@ZnO heterotrimers possess the best microwave absorption.



Figure S6. Hysteresis loops of MWCNT/Fe₃O₄@ZnO heterotrimers measured at 300 K; insert showing the response of heterotrimers to an external magnet and dispersion state in water after slight shaking. The magnetization curves show that the synthesized MWCNT/Fe₃O₄@ZnO heterotrimers exhibit superparamagnetic behavior at room temperature without coercivity and remanence. The value of saturation magnetization of the heterotrimers is 20.2 emu/g. Upon placement of a magnet beside the vial, MWCNT/Fe₃O₄@ZnO heterotrimers were attracted to the side of the vial within a few minutes, leaving the solution transparent. The heterotrimers could be well redispersed again by shaking or ultrasonic vibration, which further illustrates their superparamagnetic nature.



Figure S7. Permittivity and permeability characterizations of MWCNT/Fe₃O₄, ZnO, physical mixture of MWCNT/Fe₃O₄ and ZnO, MWCNT/Fe₃O₄-ZnO, and MWCNT/Fe₃O₄@ZnO in the 2-18 GHz range: (a) real and (b) imaginary parts of complex permittivity spectra; (c) real and (d) imaginary parts of complex permeability spectra.