Electronic Supplementary Material (ESI) for Nanoscale.
This journal is © The Royal Society of Chemistry 2016

Supporting information

A wormhole-like porous carbon/magnetic particles composite as an efficient broad band electromagnetic wave absorber

Jiyong Fang,[a] Tao Liu,[b] Zheng Chen,[a] Yan Wang,[a] Wei Wei,[a] Xigui Yue *[a] and Zhenhua Jiang[a]

[a]*The key laboratory for high performance polymer of the Ministry Education of China, College of Chemistry, Jilin University, Changchun 130012, People's Republic of China*

[b]*306 Institute, The third Academy of China Aerospace Science & Industry Corp., Beijing, 10010, People's Republic of China*

Corresponding author: Xigui Yue

E-mail addresses: yuexigui@jlu.edu.cn *Tel: +86 431 85168868*

SI-1: The synthesis of $Co_{0.2}Fe_{2.8}O_4$ nanoparticles

To a three-necked flask, H_2O (150 ml), $FeCl_3{\cdot}6H_2O$ (0.9731 g, 3.6 mmol), $FeCl_2{\cdot}4H_2O$ (0.2863 g, 1.44 mmol), $CoCl_2{\cdot}6H_2O$ (0.0857 g, 0.36 mmol) were added. With the protection of N_2, the solution was rapidly heated to 70 °C with a mechanical stirring (800 rpm). Subsequently, some $NH_3{\cdot}H_2O$ was added to the above mixture to make pH=10. After being heated at 70 °C for 1 hour, the products were collected by magnet and washed thoroughly by deionized water, ethanol and DMF to remove impurities. The products were then dispersed with 14 ml DMF for further use. Subsequently, the morphology of $Co_{0.2}Fe_{2.8}O_4$ nanoparticles was investigated by TEM as shown in Fig. S1. The $Co_{0.2}Fe_{2.8}O_4$ nanoparticles have an average diameter of 13 nm according to the statistical treatment of the TEM image in Fig. S1.

SI-2: The selection for the pore size

As mentioned in the main text, PVP used in this work was a hydrophilic additive with non-solvent properties and expected to adjust the pore size of the synthesized porous membrane. The wormhole-like porous carbon/magnetic nanoparticles composite with different pore sizes were synthesized using the same method shown in the main text with some modification (Scheme 1). For WPC/MNPs-150 (pore size at about 150 nm, see Fig. S2 for SEM image) and WPC/MNPs-210 (pore size at about 210 nm, see Fig. S3 for SEM image), the weight of PVP are 0.24 g and 0.35 g, while that of PAN are all 2.4 g, respectively. The EM wave absorbency of this two samples were evaluated at the same absorber loading (sample/paraffin wax=1/2). And the EM wave attenuation performance of this two synthesized absorbers were shown in Fig. S4 and S5. When compared with the EM wave absorbency of WPC/MNPs-80 (pore size at about 80 nm, see EM wave absorbency in Fig. 6 in the main text), it is not difficult to find that the WPC/MNPs with the pore size of 80 nm has the best EM wave consuming ability with the characteristics of wide absorption band, strong absorbency and thin matching thickness. Accordingly, in this work, the properties and the EM wave absorbency of WPC/MNPs-80 were investigated in detail in the main text.

SI-3: The EM wave absorption performance for wormhole-like porous carbon without magnetic nanoparticles (WPC)

Firstly, 0.08 g PVP and 1.20 g PAN were added into 7 ml DMF and the mixture was heated at 60 °C by vigorous stirring to obtain the casting solution; secondly, the casting solution was prepared as membrane by spin coating at room temperature, and the resulting solution membrane was immediately immersed in a water bath at 25 °C for 24 h; thirdly, the membrane was dried at room temperature for 30 h and then heated at 250 °C for 4 h in an oven with air atmosphere; lastly, it was pyrolyzed in a tubular furnace under a flowing argon gas atmosphere with a proper heating procedure (20 °C to 1000 °C, 5 °C/min; 1000 °C, 1 h; 1000 °C to 20 °C, 5 °C/min). Then the wormhole-like porous carbon without magnetic nanoparticles (WPC) was obtained after the carbon membrane was grinded into powder. The SEM images and the EM wave absorbency of WPC were shown in Fig. S12 and Fig. 7 in the main text, respectively. WPC has a similar wormhole-like porous structure with the average pore size of about 70.9 nm. The EM wave absorbency was calculated from the electromagnetic parameters with the absorber loading of 28.1% ((1÷3)×84.4%=28.1%, the absorber loading for WPC/MNPs-80 is 1/3, the carbon content in WPC/MNPs-80 is 84.4%).

SI-4: The EM wave absorption performance for carbon and magnetic nanoparticles composite without porous structure (C/MNPs)

Firstly, 1.20 g PAN and 3 ml DMF was added into 7 ml suspension of $Co_{0.2}Fe_{2.8}O_4$ nanoparticles (NPs, synthesized in SI-1) in DMF and the mixture was heated at 60 °C by vigorous stirring; secondly, the solution was prepared as membrane; thirdly, the membrane was dried at 60 °C for 2 h, 80 °C for 20 h, 100 °C for 2 h, 120 °C for 2 h, and then heated at 250 °C for 4 h in an oven with air atmosphere; lastly, it was pyrolyzed in a tubular furnace under a flowing argon gas atmosphere with a proper heating procedure (20 °C to 1000 °C, 5 °C/min; 1000 °C, 1 h; 1000 °C to 20 °C, 5 °C/min). Then the carbon and magnetic nanoparticles composite without porous structure (C/MNPs) was obtained after the membrane (1.24 g/cm^3) was grinded into powder. The SEM images and the EM wave absorbency of C/MNPs were shown in Fig. S13 and Fig. 8 in the main text. Unlike WPC/MNPs, C/MNPs doesn't have a porous structure. The EM wave absorbency was calculated from the electromagnetic parameters with the absorber loading of 33.3% (equal with the loading of WPC/MNPs-80).

SI-5: The content of each component in WPC/MNPs-80

The content of the magnetic nanoparticles in the wormhole-like porous carbon/magnetic particles composite was determined by EDS and weight analysis. The EDS data was shown in Figure S9 with the carbon content of 84.4%, Fe content of 14.5% and Co content of 1.1%. The weight analysis goes as following: Firstly, 0.1000 g WPC/MNPs was added into 30 ml concentrate hydrochloric acid (HCl) with mechanical stirring and the mixture was kept for 24 hours to totally remove the magnetic nanoparticles; Then the precipitate was collected by centrifugation and washed for 6 times with distilled water; Finally, the residue was dried under vacuum for 24 hours at 100 °C and weighed (0.0831 g). Accordingly, the EDS data was consistent with the weight analysis data, and the content of the magnetic nanoparticles was around 16%.

SI-6: The maintenance ability of porous structure of WPC/MNPs-80 in the paraffin and absorber composite

In the preparation of the samples for electromagnetic parameter testing, the porous absorber (WPC/MNPs-80) and paraffin composite was pressed into toroidal-shaped samples. In that process, the porous structure maybe has been destroyed. Accordingly, SEM was used to determine the condition of the porous structure in the toroidal-shaped samples. However, it is not allowed to measure the SEM image for paraffin based materials in our lab. So tetrahydrofuran (THF) was used to remove the paraffin matrix from the toroidal-shaped sample and the SEM image of the residue was measured. When the paraffin was removed from the toroidal-shaped sample by tetrahydrofuran (THF), the residue (WPC/MNPs-80) still has a porous structure as verified by SEM shown in Fig. S15. Hence, according to the above results, the wormhole structure keep unchanged without breakdown.

SI-7: The Cole-Cole semicircle of WPC/MNPs-80

According to the electromagnetic theory, it is known that the dielectric loss of the carbon materials may be attributed to natural resonance, electron polarization relaxation and Debye dipolar relaxation and so on. As for the Debye dipolar relaxation, the relative complex permittivity (ε_r) can be expressed by the following equation (1):

$$\varepsilon_r = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + j2\pi f\tau} = \varepsilon' - j\varepsilon'' \tag{1}$$

where f, ε_s, ε_∞ and τ are frequency, static permittivity, relative dielectric permittivity at the high-frequency limit, and polarization relaxation time, respectively. Consequently, ε' and ε'' can be described by the following equation (2) and (3):

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (2\pi f)^2\tau^2} \tag{2}$$

$$\varepsilon'' = \frac{2\pi f\tau(\varepsilon_s - \varepsilon_\infty)}{1 + (2\pi f)^2\tau^2} \tag{3}$$

According to the above equation (2) and (3), the relationship between ε' and ε'' can be deduced as:

$$(\varepsilon' - \frac{\varepsilon_s + \varepsilon_\infty}{2})^2 + (\varepsilon'')^2 = (\frac{\varepsilon_s - \varepsilon_\infty}{2})^2 \tag{4}$$

Thus, the plot of ε' *vs*. ε'' would be a single semicircle, generally denoted as the Cole-Cole semicircle. Each semicircle corresponds to one Debye relaxation process. The Cole-Cole semicircle of WPC/MNPs is shown in Fig. 10 in the main text.

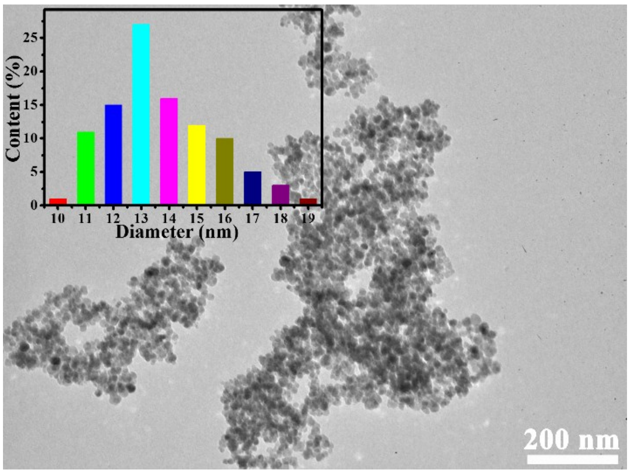

Fig. S1. The TEM image of the synthesized $Co_{0.2}Fe_{2.8}O_4$ magnetic nanoparticles and the insert is the distribution of the diameter of the $Co_{0.2}Fe_{2.8}O_4$ magnetic nanoparticles.

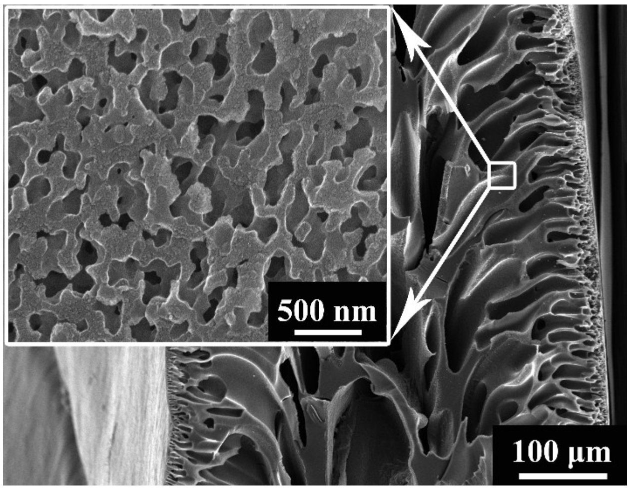

Fig. S2. The SEM images for WPC/MNPs-150.

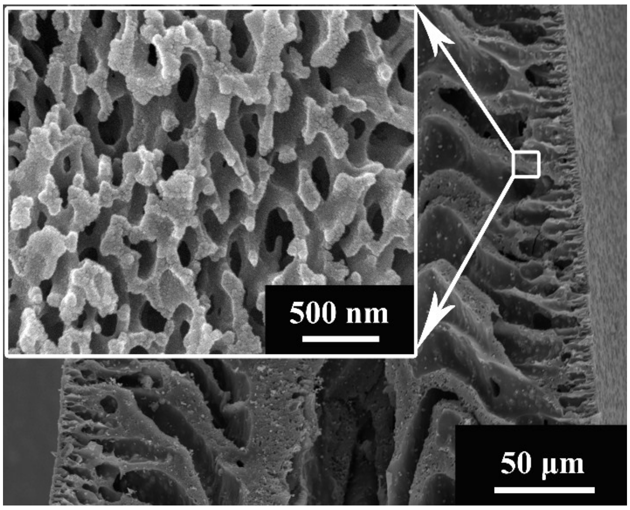

Fig. S3. The SEM images for WPC/MNPs-210.

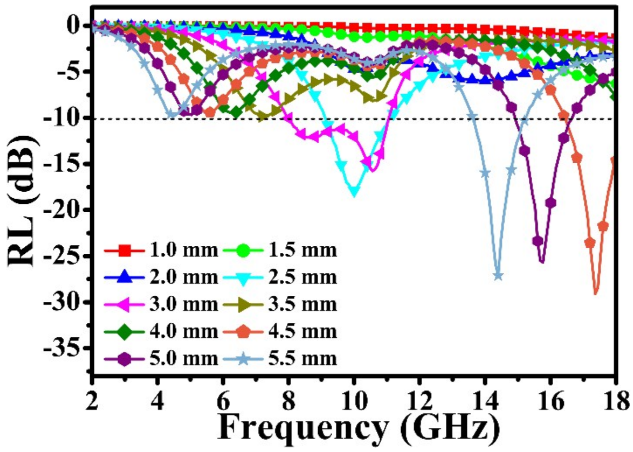

Fig. S4. The RL-F curves for WPC/MNPs-150 in 2-18 GHz with the absorber thickness from 1.0 mm to 5.5 mm.

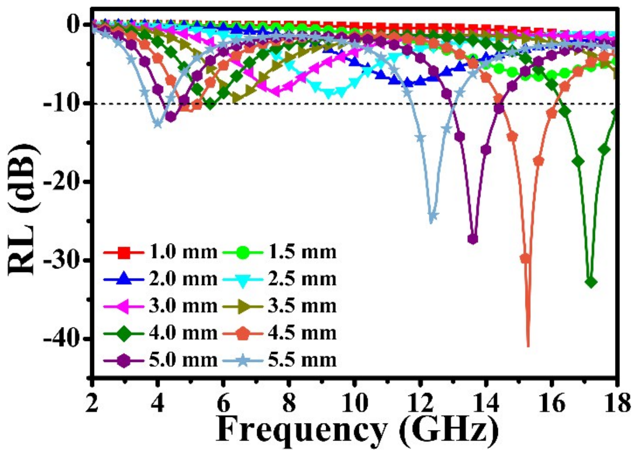

Fig. S5. The RL-F curves for WPC/MNPs-210 in 2-18 GHz with the absorber thickness form 1.0 mm to 5.5 mm.

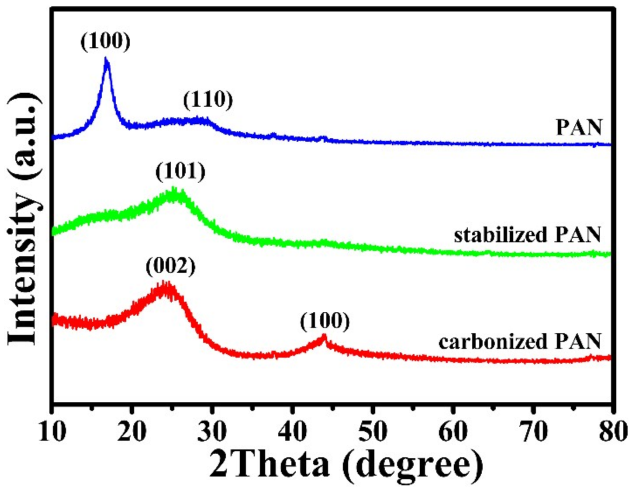

Fig. S6. The XRD patterns of PAN, stabilized PAN, carbonized PAN.

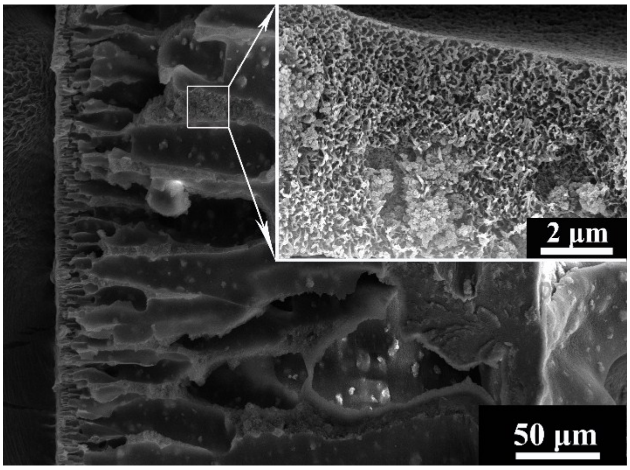

Fig. S7. The SEM images for the PAN and nanoparticles membrane corresponding to WPC/MNPs-80.

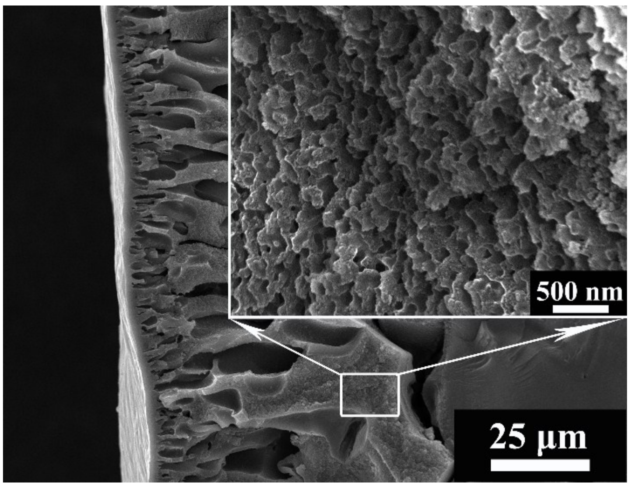

Fig. S8. The SEM images for the stabilized PAN and nanoparticles membrane (250°C for 4 h) corresponding to WPC/MNPs-80.

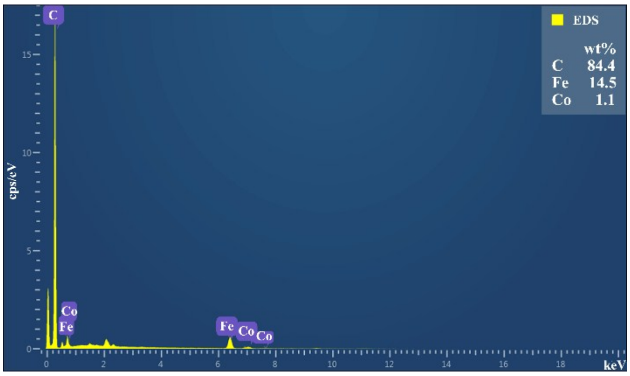

Fig. S9. The EDS elemental data for WPC/MNPs-80.

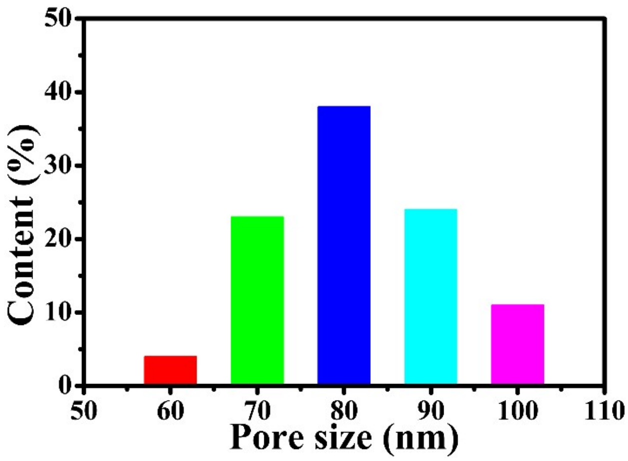

Fig. S10. The distribution of the pore size for WPC/MNPs-80.

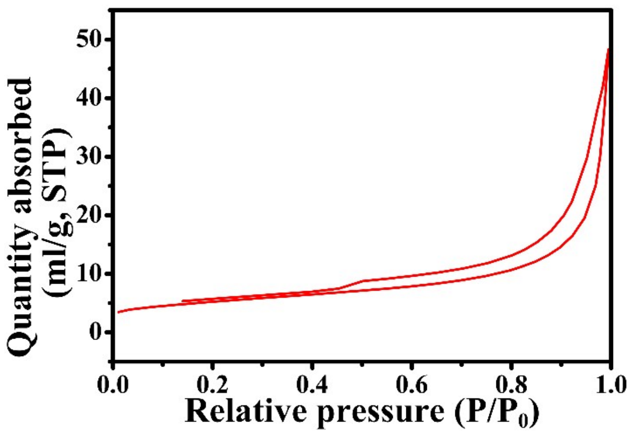

Fig. S11. The nitrogen adsorption-desorption isotherm for WPC/MNPs-80.

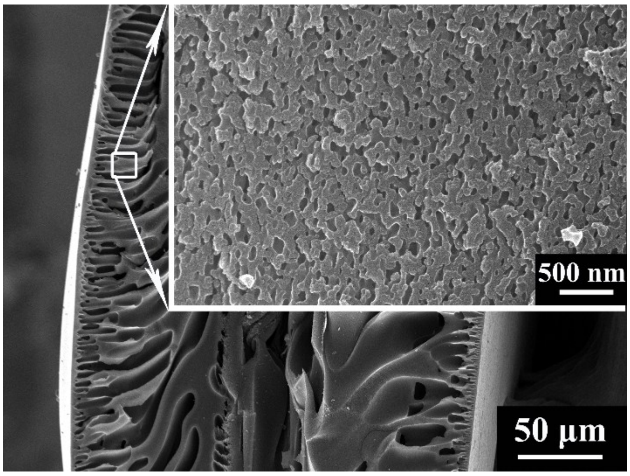

Fig. S12. The SEM images of cross-sectional view of the wormhole-like porous carbon without magnetic nanoparticles membrane (WPC) and the insert is the magnification of the corresponding finger pore wall.

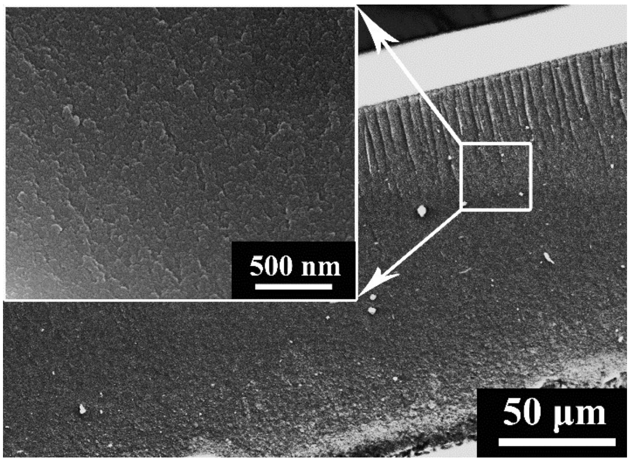

Fig. S13. The SEM images of cross-sectional view of the carbon and magnetic nanoparticles composite membrane (C/MNPs) and the insert is the magnification of the selected area.

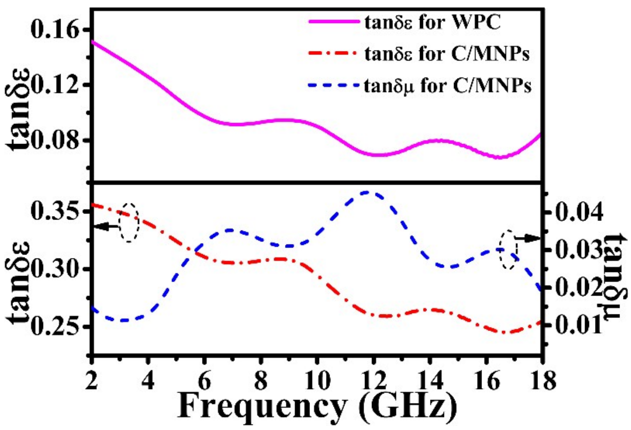

Fig. S14. The dielectric loss for WPC and C/MNPs and the magnetic loss tangent of C/MNPs in the

EM frequency range of 2-18 GHz.

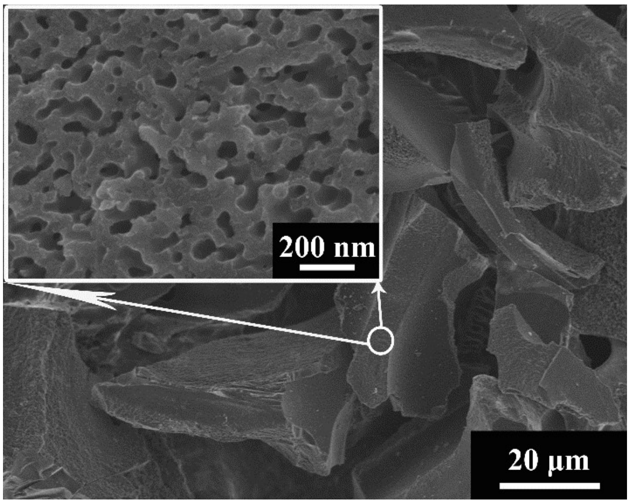

Fig. S15. SEM image for the residue of the toroidal-shaped sample after etched by THF, and the insert is SEM image for the residue of the toroidal-shaped sample after etched by THF at high magnification.

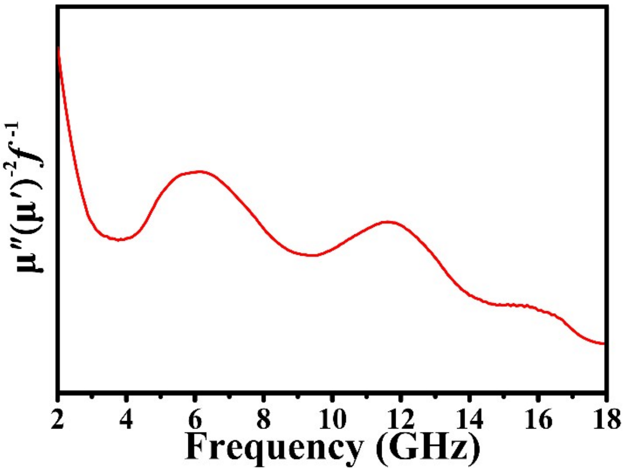

Fig. S16. Value of the eddy current (C_0, $\mu''(\mu')^{-2}f^{-1}$) for WPC/MNPs-80 *vs.* EM wave frequency.