Supporting Information

Preparation of Multi-Shelled Conductive Polymer Hollow Using Fe_3O_4 Hollow Spheres as Sacrificial Templates

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Experimental Section

Materials. All reagents were analytical grade and purchased from Sinopharm Chemical Reagent Beijing Co. Ltd., and used without further purification unless otherwise mentioned.

Preparation of PEDOT multi-shelled hollow microspheres. Fe_3O_4 microspheres were synthesized by a one-pot hydrothermal route as described elsewhere.[38] The as-prepared hollow Fe_3O_4 microspheres（0.1 g）were dispersed into 50mL of PVA (0.2 g) aqueous solution with ultrasonic for 5 min. Then 25mL of *p* -TSA (20 mmol) was added into the mixture with vigorous stirring for 20 min. After this, 4 mmol of EDOT was introduced with stirring at 40 oC for 12 h. At last, 25 mL of ammonium persulfate (APS) (4 mmol) was purred into the above solution. The temperature was maintained at 40 oC for 24 h. The mixture was centrifuged and washed by deionized water/ethanol (1/1, v/v) for several times until the supernatant fluid was colorless and transparent. The resulting precipitate was dried under a vacuum at 60 oC for 24 h. PPy multi-shelled hollow microspheres were also synthesized by a similar procedure.

The solid PEDOT particles and single-shelled PEDOT microspheres used in microwave absorbing tests were fabricated by following procedure:

Synthesis of PEDOT solid spheres. 1 mmol EDOT was added into 50mL PVA (0.2 g) aqueous and vigorous stirring for 20 min. After this, 25mL ammonium persulfate (APS) (1 mmol) was purred into the above solution and reacted for 24 h. The mixture was centrifuged and washed by a solvent of deionized water/ethanol (1/1, v/v) several times until the supernatant fluid was colorless and transparent. The resulting products were dried under a vacuum at 60 C for 24 h.

Synthesis of PEDOT hollow spheres. Firstly, Fe_3O_4/PEDOT compounds were synthesized as the synthesis of multi-shelled PEDOT hollow microspheres but reacted in room temperature, then using concentrated hydrochloric acid etched the as-prepared Fe_3O_4/PEDOT compounds for 5 mins, The products were centrifuged and washed by a solvent of deionized water/ethanol (1/1, v/v) several times and dried under a vacuum at 60 oC for 24 h.

Measurement. The morphology of the products was characterized using JEM-2100F transmission electron microscope (TEM) and S-4800 scanning electron microscope (SEM) (Japan). Electron Dispersive Spectrometer (EDS) was tested by S-4800 (Japan) operated at 15 kV. Powder X-ray diffraction (XRD) was carried out on a D8 Focus Diffractometer (Germany). Fourier transform infrared (FTIR) spectra were conducted on sample pellets with KBr by means of an infrared spectrophotometer (Excalibur 3100, America, Varian). Conductivity measurements of the double-shelled PEDOT samples (compressed into rectangular block) were

performed using a Keithley 220 Source Meter four-point probe instrument. The composites samples for electromagnetic parameter measurement were prepared by mixing the double-shelled PEDOT microspheres and paraffin wax at different volume fraction of the multi-shelled PEDOT microspheres. The mixture was then pressed into a toroidal shape with the thickness of 2 mm by a HP8722ES network analyzer at the frequency range of 2-18 GHz.

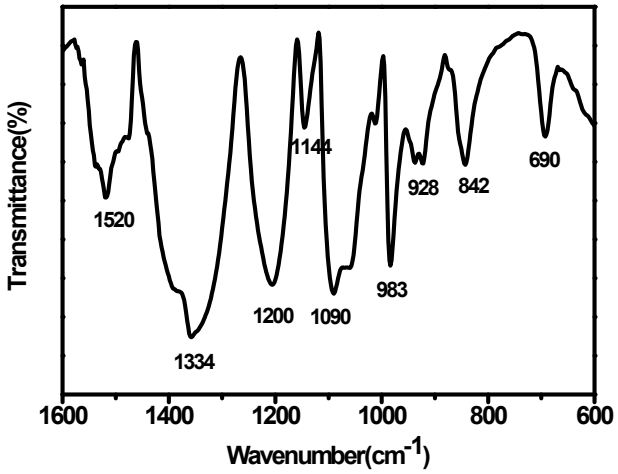


Figure S1. FTIR spectrum of the multi-shelled PEDOT at 40 oC for 24 h.

The FTIR spectrum as shown in Figure S1 confirms the component of product is PEDOT. The peak at about 1520 cm^{-1} are due to the C=C stretching of quinoidal structure of thiophene ring, and the peak near 1334 cm^{-1} is assigned to C–C stretching vibrations of the quinoidal structure of the thiophene ring. Peaks at 1200 cm^{-1}, 1144 cm^{-1}, 1090 cm^{-1} to 1058 cm^{-1} and 928 cm^{-1} originate from C–O–C bond stretching in the ethylene-dioxy ring deformation mode. Vibrations at 983, 842 and 690 cm^{-1} are attributed to the C–S bond in the thiophene ring.

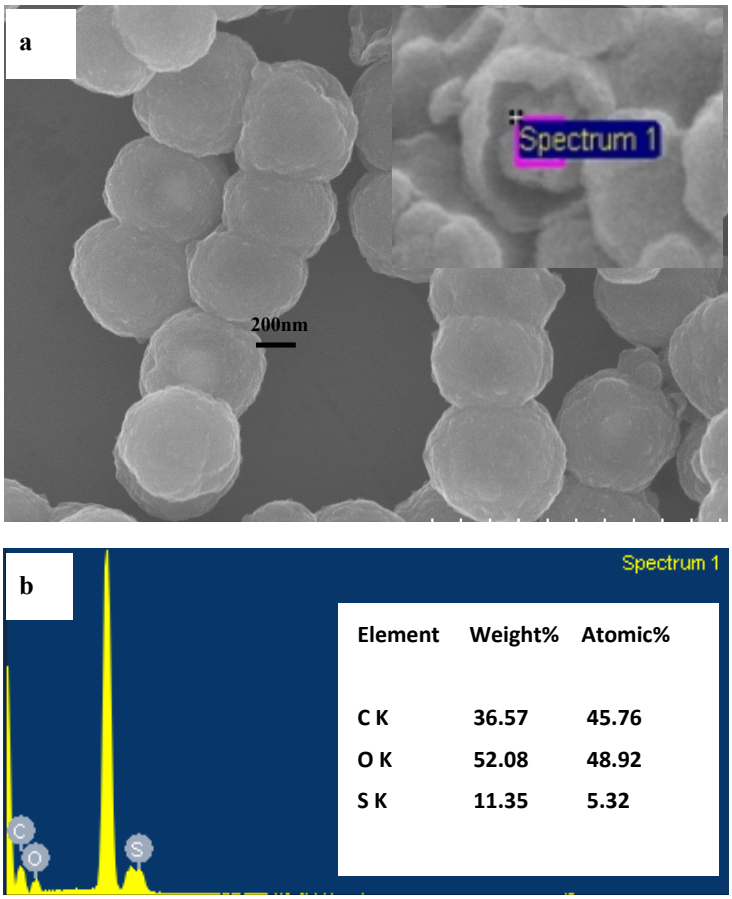
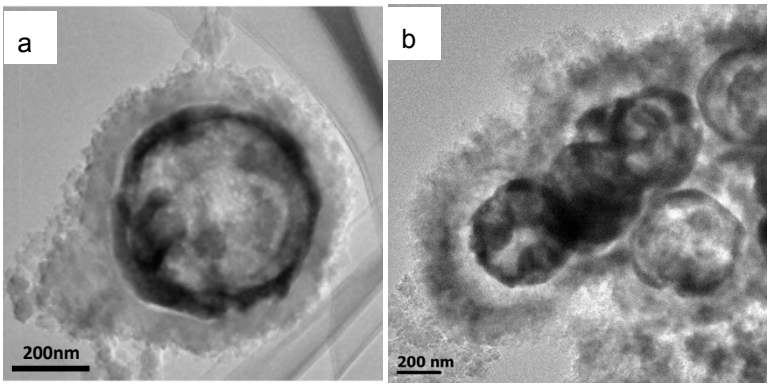


Figure S2. a) SEM image of the multi-shelled PEDOT products (include insert image); b) EDS analysis of the multi-shelled PEDOT at 40 oC for 24 h.



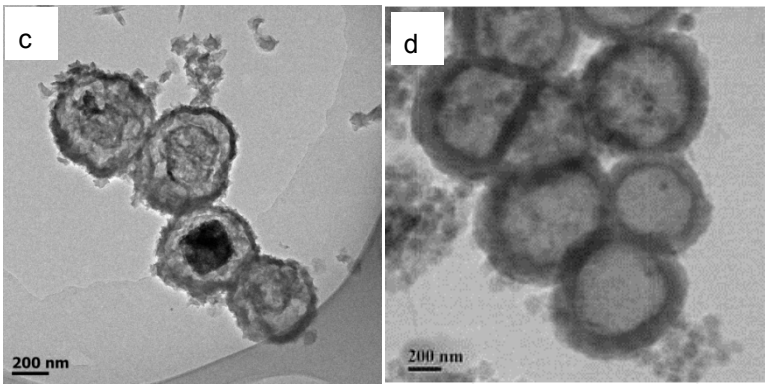


Figure S3. TEM image of the obtained products prepared with different HCl concentrations at room temperature for 24 h: a) 0.5; b) 1; c) 5; d) 7.5 mol L^{-1}.

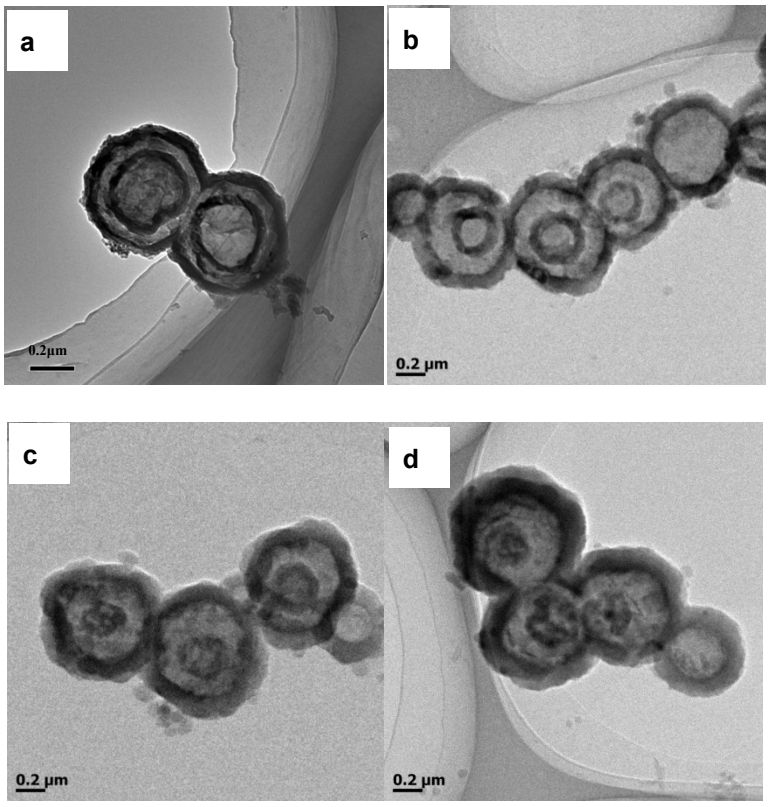


Figure S4. The morphology of the obtained multi-shelled PEDOT with different（EDOT/(Fe_3O_4) ratios at 40 oC for 24 h: a) 10; b) 20; c) 30; d) 50.

Temperature (oC)	(EDOT)/(Fe_3O_4) ratios	Conductivity (S cm^{-1})
40	**10**	**0.92**
40	**20**	**1.34**
40	**30**	**1.82**
40	**50**	**2.74**

Table S1. The conductivity of multi-shelled PEDOT microspheres with different (EDOT)/(Fe_3O_4) ratios at 40 oC for 24 h.

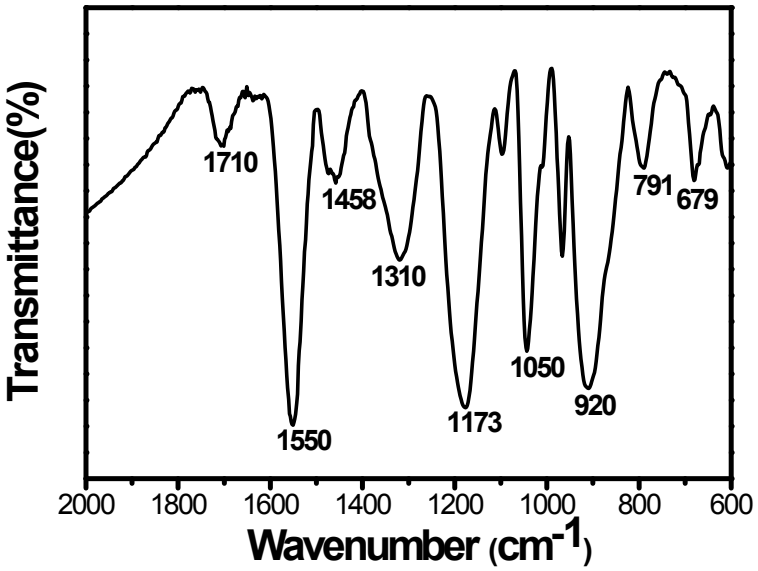


Figure S5. FTIR spectrum of the double-shelled PPy at 40 oC for 24 h.

Figure S5 shows the FTIR spectrum of double-shelled PPy. The main vibration region is in the range from 2000 to 600 cm^{-1}. The peak at 1550 cm^{-1} results from C=C and C–C stretching vibrations of the pyrrole ring. The peak at the 1458 cm^{-1} corresponds to ring breathing with contributions from C=C/C–C and C-N. The peaks at 1317, 1173, 1050 and 907 cm^{-1} are associated with the vibrations from C-H in-plane bend. Vibrations at 966 cm^{-1} is due to the part of polymer unaffected by

reduction, e.g. terminal rings away from influence of dopant. Peaks at 791 and 679 cm^{-1} originate from the vibration of C-H out-plane bend. The absorption band at 1707 cm^{-1} is assigned to C=O bond stretching vibration, which indicates this polypyrrole particles are a bit peroxided.

The transmit line theory is summarized as the following equations:

$$Z_{in} = \sqrt{\frac{\mu_r}{\varepsilon_r}} \tanh\left[j\frac{2\pi}{c}\sqrt{\varepsilon_r \mu_r}\, f d\right] \quad \text{S1}$$

$$RL(dB) = 20log\left|\frac{Z_{in} - 1}{Z_{in} + 1}\right| \quad \text{S2}$$

Where Z_{in} is the input impedance of the absorber, ε_r and μ_r are the relative complex permittivity and permeability of the absorber medium, c is the velocity of light in free space, f is the frequency of microwave, d is the coating thickness.

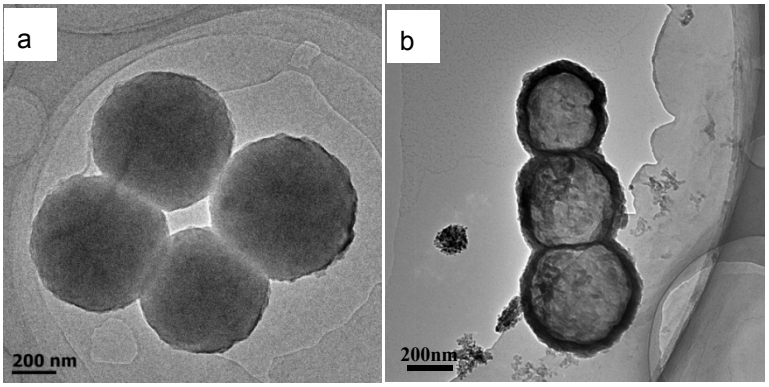
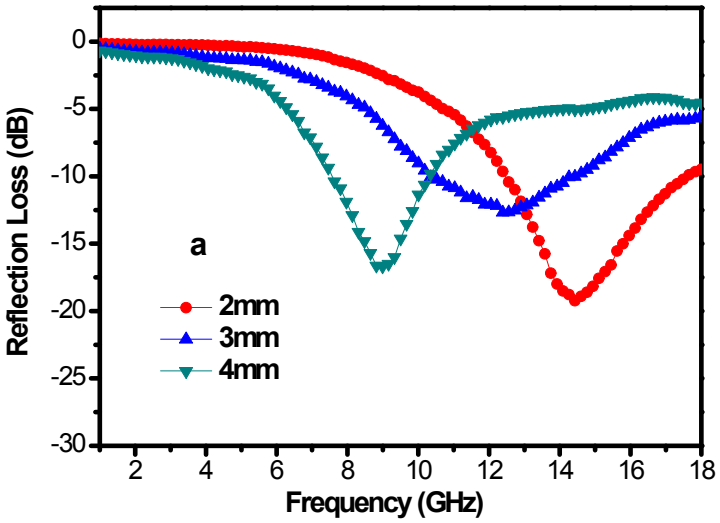


Figure S6. TEM image of a) PEDOT solid spheres; b) single-shelled PEDOT hollow spheres.


Reflection Loss (dB)
0
-5
-10
-15
-20
-25
-30
a
2mm
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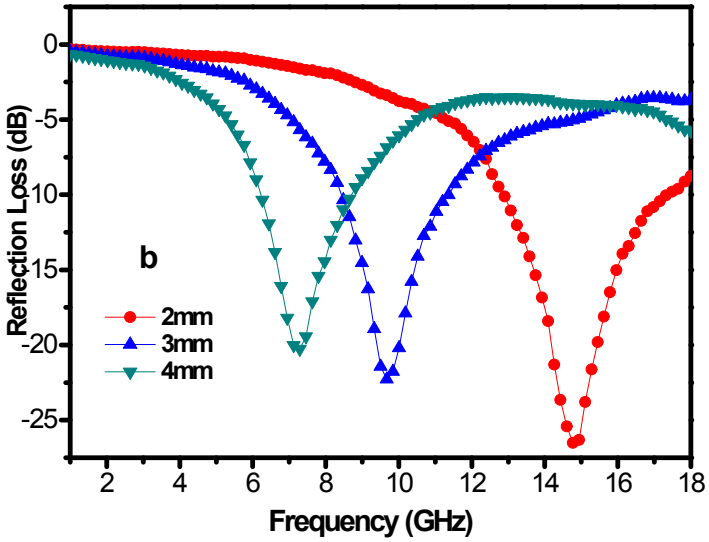
4mm
2
4
6
8
10
12
14
16
18
Frequency (GHz)


Reflection Loss (dB)
0
-5
-10
-15
-20
-25
b
2mm
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2
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6
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16
18
Frequency (GHz)

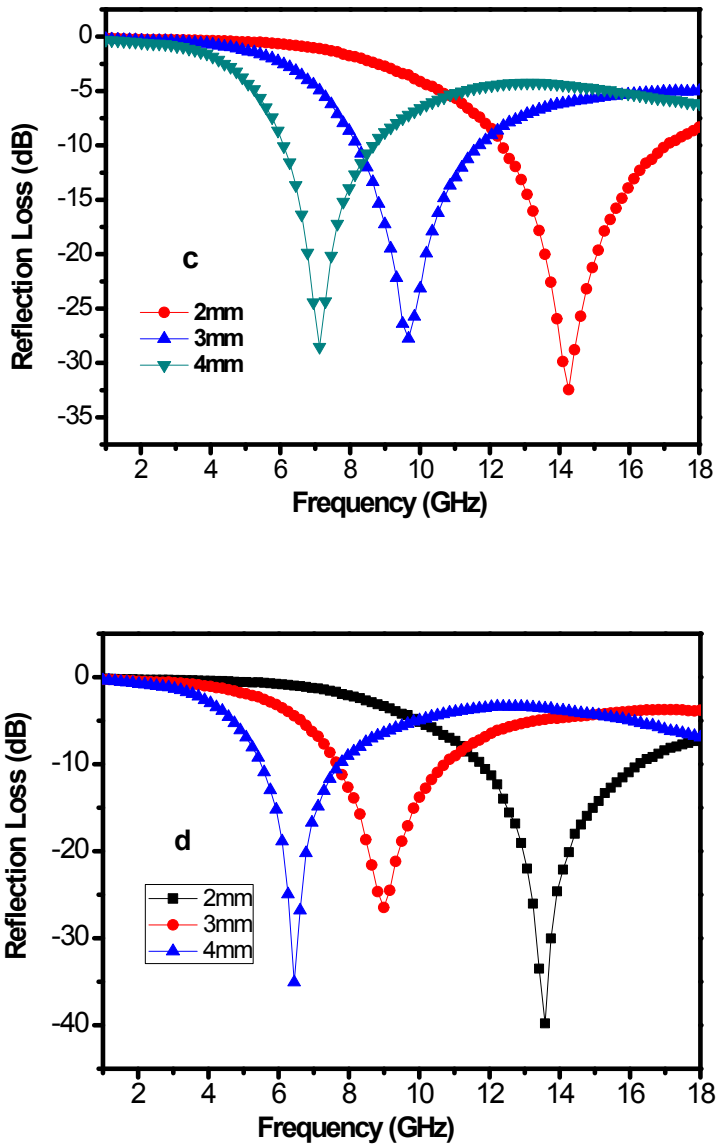

Figure S7. Reflection losses with different morphology of PEDOT in the frequency range of 2-18 GHz at 20% volume fraction: a) solid PEDOT; b) single-shelled PEDOT; c) double-shelled PEDOT; d) triple-shelled PEDOT with a thickness of 2-4 mm.

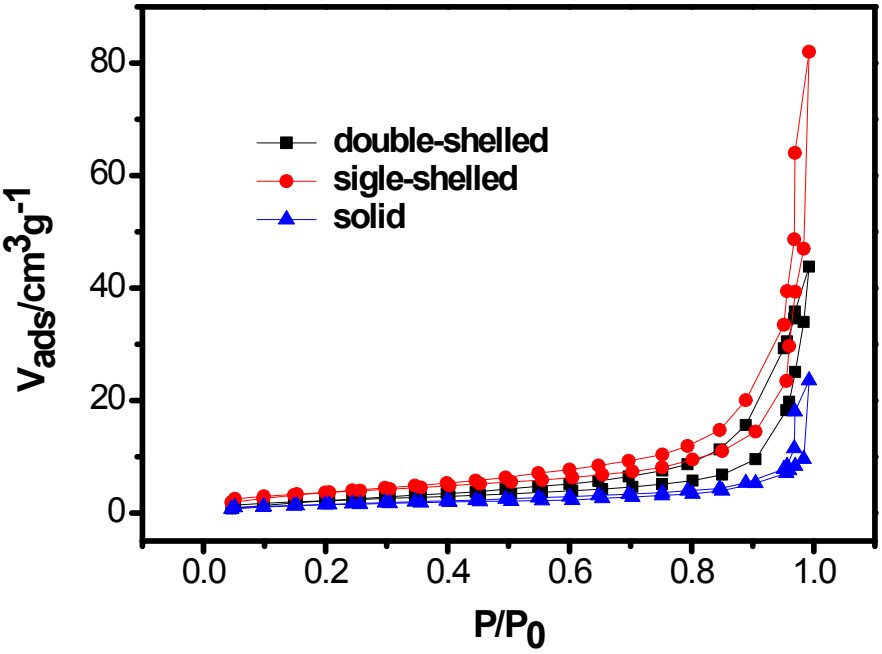

Figure S8. Typical nitrogen adsorption–desorption isotherms for different morphology of PEDOT microspheres.