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Electronic Supplementary Material

Nanocasting synthesis of Fe₃O₄@HTC nanocapsules and their superior electromagnetic properties

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Experimental section

Materials

Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), D-(+)-xylose 99% anhydrous, tetraethyl orthosilicate 95% (TEOS, $\text{Si}(\text{OC}_2\text{H}_5)_4$), ammonium hydroxide solution 28% (NH_4OH), (3-Aminopropyl) triethoxysilane (APTES, $\text{C}_9\text{H}_{23}\text{NO}_3\text{Si}$), sodium hydroxide (NaOH) were purchased from Sigma-Aldrich. And all reagents were analytically pure and used as-received without further purification.

Synthesis of Fe_3O_4 nanorods@HTC nanocapsules

The well-designed Fe_3O_4 nanorod@HTC nanocapsules were synthesized using a multi-step synthetic procedure. Firstly, the β -FeOOH nanorods were synthesized by a hydrolysis process. First, the β -FeOOH nanorods were synthesized by a hydrolysis process. 0.06 mol $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 930 ml distilled water and transferred into a 1 L empty plastic bottle with a 0.8 mm needle hole. Then the bottle was kept in an oven at 100°C for 24h. After cooling down to the room temperature, the brown colour precipitates were collected and washed with distilled water and ethanol several times and finally dried at 80°C overnight. In the second step, a portion of the as-prepared β -FeOOH nanorods were coated with a layer of SiO_2 through a modified Stöber process. In a typical coating process, 1g of the β -FeOOH nanorods were dispersed in a mixture of ethanol (300ml), distilled water (100ml) and ammonium hydroxide solution (10ml). Then, 4ml of TEOS was added dropwise and the reaction was allowed to proceed for 6h under mechanical stirring. The resulting products were collected by centrifuging and then washed with ethanol four times and then dried at 60°C for 12h. Afterwards, in order to effectively attract the D-(+)-xylose on the surface of the prepared β -FeOOH@ SiO_2

nanorods, the amino-functionalization treatment was required. 1g prepared β -FeOOH@SiO₂ nanorods was immersed in a solution composed of 6.9 mL of (3-Aminopropyl) triethoxysilane (APTES) and 160 ml of ethanol and kept at the ambient temperature for 24h to produce the amino-functionalized β -FeOOH@SiO₂ nanorods. Then 1g of amino-functionalized β -FeOOH@SiO₂ nanorods was immersed into a solution containing 30 ml of deionized H₂O and 0.9g of D-(+)xylose. The suspension was then sealed into to a Teflon-lined autoclave and hydrothermally treated at 180°C for 24h. Then resultant was washed using distilled water and subsequently dried under vacuum at 80°C overnight. After heat treatment in a tube furnace under a flowing H₂/Ar (5%H₂) atmosphere at 550°C for 4h, the Fe₃O₄ nanorods@SiO₂@HTC could be gained. Finally, the Fe₃O₄ nanorods@HTC nanocapsules were obtained after removal of the SiO₂ layer using a 1M NaOH solution. For comparison, the Fe₃O₄ nanorods without the HTC shell were also prepared by directly heat treated the obtained β -FeOOH nanorods in H₂/Ar (5%H₂) atmosphere at 550°C for 2h.

Materials Characterization

X-ray diffraction (XRD, Rigaku Ultima IV with Cu K α radiation) was performed to detect the phase of as-synthesized samples. Field emission scanning electron microscope images were collected on JEOL JSM-6701F microscope. Transmission electron microscope (TEM, JOEL JEM 2010 at an accelerating voltage of 150 kV) equipped with an EDS detector were performed to acquire high resolution TEM (HRTEM) images. The thermal analyses were determined by a SDT Q600 (TA Instruments) under air atmosphere at a heating rate of 10°C min⁻¹ from room temperature to 700°C. Nitrogen

adsorption measurements were performed on a Micromeritics ASAP 2020 physisorption analyzer at 77k. BET and BJH methods were used for the surface area and pore size distribution determination using N₂ absorption data. Static magnetic properties of as-synthesized Fe₃O₄ nanorods and Fe₃O₄@HTC nanocapsules at room temperature were measured by using a vibrating sample magnetometer (VSM, ADE Magnetics EV-9). For microwave measurement, silicon resin composites were prepared by homogeneously mixing 60wt% of the prepared Fe₃O₄ nanorods and Fe₃O₄@HTC nanocapsules with silicon resin and pressed into toroidal-shaped samples with an outer diameter of 7.00 mm and an inner diameter of 3.04 mm. Complex permeability and permittivity of the composites were measured by using an Agilent VNA (Vector Network Analyzer) HP8722D with a reflection-through-line calibration, over 0.5 –18 GHz, using a set of 7 mm coaxial air-line with length of 49.96 mm. Frequency dependence of reflection loss (RL) of the composites was estimated from their complex permittivity ($\epsilon_r = \epsilon'_r - j\epsilon''_r$) and permeability ($\mu_r = \mu'_r - j\mu''_r$) according to the following equations:

$$Z_{in} / Z_0 = \sqrt{\frac{\mu_r}{\epsilon_r}} \tanh \left[j \frac{2\pi ft}{c} \sqrt{\mu_r \epsilon_r} \right] \quad (1)$$

$$RL(dB) = 20 \log_{10} \left| \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \right| \quad (2)$$

where Z_{in} is impedance of the composites backed by a ground plane, Z_0 is the intrinsic impedance of free space, c is the velocity of light in free space, t is thickness of the attenuation material, f is the frequency of the incident EM wave.

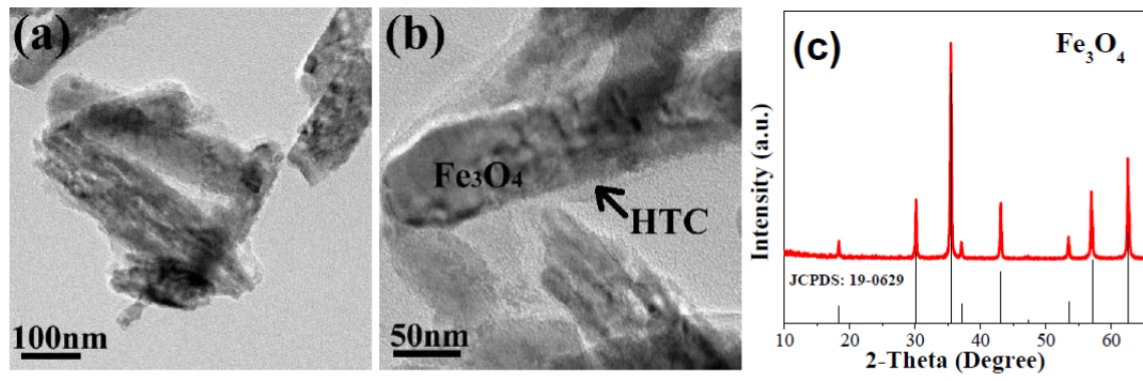


Figure S1. (a)-(b) TEM images of as-prepared Fe₃O₄@HTC nanocapsules annealed at 400°C in H₂/Ar (5%H₂) atmosphere for 4h and (b) XRD pattern of the Fe₃O₄@HTC nanocapsules sintered at 400°C.

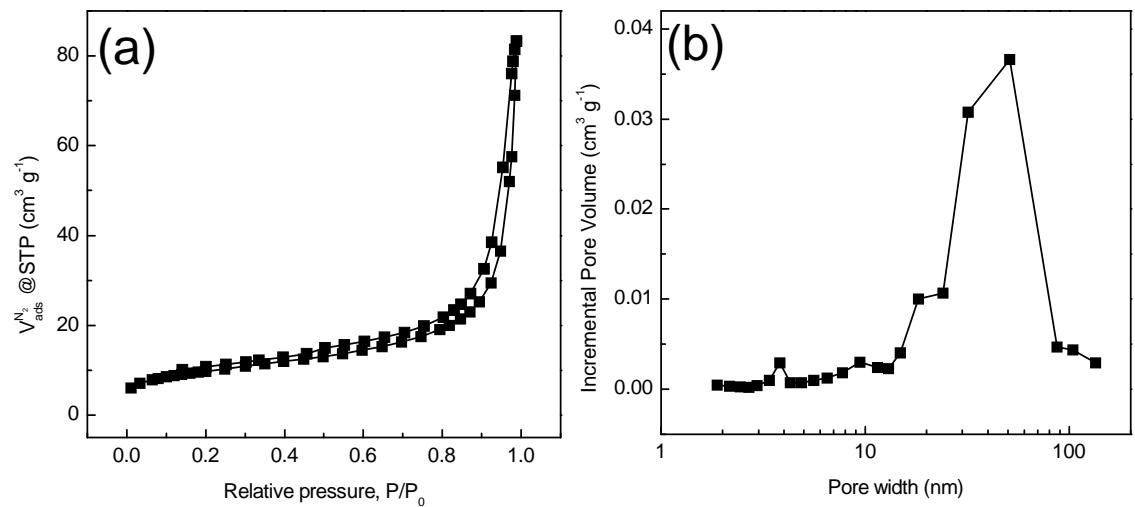


Figure S2. (a) N₂ adsorption-desorption isotherm plots and (b) corresponding BJH pore size distribution of the Fe₃O₄@HTC nanocapsules.

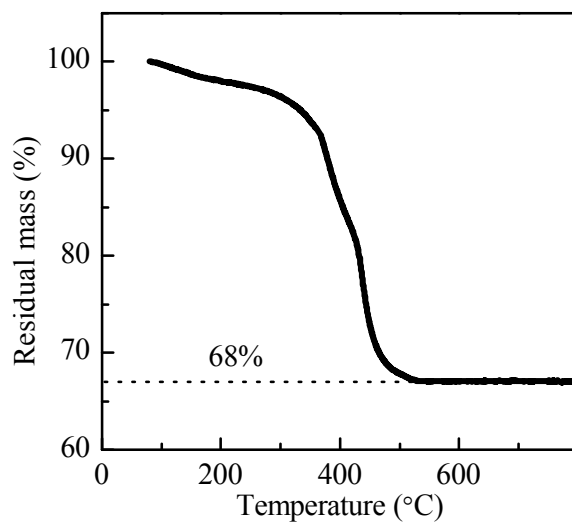


Figure S3. TGA curve of the as-prepared Fe₃O₄@HTC nanocapsules from room temperature to 700°C under the air gas flow with a temperature ramp of 10°C/min.

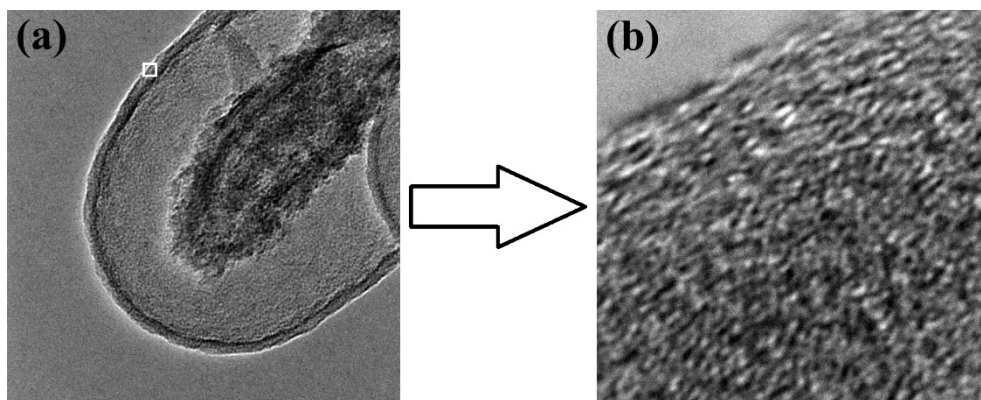


Figure S4. (a) TEM image of part of an as-prepared Fe₃O₄@HTC nanocapsule and (b) corresponding HRTEM image recording from the boxed region in (a). No lattice fringes are found in HRTEM image which reveals that the HTC shells are amorphous.

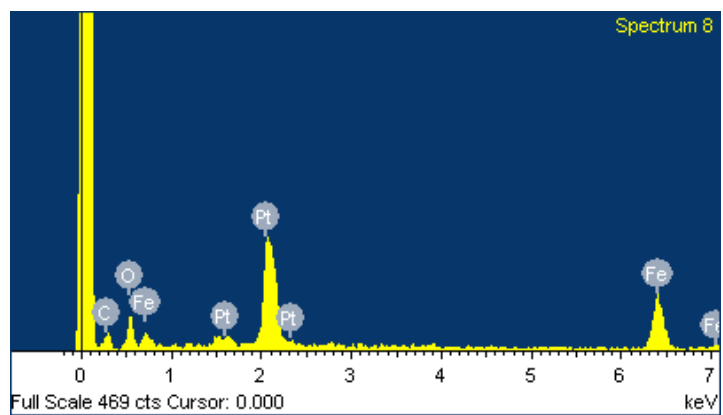


Figure S5. The EDS spectrum of obtained Fe₃O₄@HTC nanocapsules.