Supplemental Material

Phase-transitional Fe_3O_4/perfluorohexane Microspheres for Magnetic Droplet Vaporization

Experimental Section

Reagents

Ethylenediamine, pentobarbital sodium and agarose were purchased from Sigma-Aldrich Co. LLC. (Mainland, China). The rest of reagents applied in this study were obtained from J ＆ K Scientific Co. Ltd. (Guangdong, China).

Synthesis of Porous Magnetic Microspheres (PMMs)

Polymer microspheres of glycidyl methacrylate (GMA) cross-linked with ethylene glycol dimethacrylate (EGDMA) were synthesized using a modified swelling polymerization as literatures reported. After that, the obtained P(GMA/EGDMA) microspheres were repeatedly washed by centrifugation (3,000 g-force for 10 min) with distilled water. Then Ethylenediamine (EDA) was used to react with P(GMA/EGDMA) microspheres to generate amino groups. Two grams of P(GMA/EGDMA) microspheres was added in a flask containing 50 mL H_2O and 75 mL EDA. The mixture was stirred at 80 °C for 12 h. The obtained EDA modified P(GMA/EGDMA) microspheres were repeatedly washed by centrifugation (3,000 g-force for 10 min) with distilled water before being dried at 60 °C overnight.

Twenty grams of EDA modified P(GMA/EGDMA) microspheres were added in a flask containing 200 mL water. The mixture was cooled in a water bath under nitrogen gas bubbling. 8 g $FeCl_3 \cdot 6H_2O$ and 5.4 g $FeCl_2 \cdot 4H_2O$ were dissolved in 20 mL H_2O. Then the iron ions solution was added to the flask. A light brown color mixture was formed. The ice bath was removed and the flask was continuously evacuated with the mixture kept stirring until no further foaming in the mixture was observed. The evacuation was stopped and flask was immersed in a preheated water bath at 85 °C. 25 mL of ammonia hydroxide was added. The reaction mixture gradually turned to black. The mixture was kept stirring at 85 °C for 1 hour, then cooled to room temperature. The resultant magnetic

P(GMA/EGDMA) microspheres were obtained and thoroughly washed with distilled water.

Finally, a three-necked, round-bottomed flask equipped with a mechanical stirrer and a reflux condenser was placed 100 mL isopropanol and 20 g water. With vigorous stirring in the flask, 2 g magnetic P(GMA/EGDMA) microspheres and 5 mL ammonia hydroxide were introduced over a period of 0.5 hour. A 10% TEOS solution (in isopropanol) of 10 mL was then added drop-wise into the mixture in an hour. The sol-gel transformation of TEOS to silica in the magnetic P(GMA/EGDMA) microspheres was carried out at 30 °C for 24 h. The magnetic P(GMA/EGDMA)/silica microspheres obtained were washed repeatedly with ethanol and distilled water before being dried at 50 °C overnight. Then, the magnetic P(GMA/EGDMA)/silica microspheres were calcinated at 600 °C for 10 h at a heating rate of 10 °C/min under air. After calcination, the remaining product consisted of porous magnetic microspheres (PMMs) with loose porous inner structure were obtained. All of the fabricating process of PMMs were supported by Wuxi Knowledge and Benefit Sphere Tech. Co., Ltd.

Supplemental images

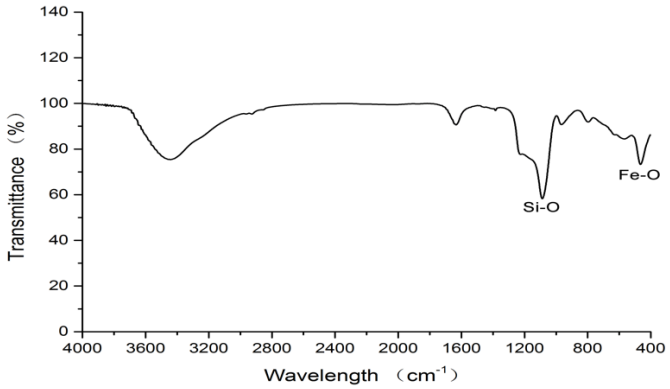

Figure S1. Fourier transform infrared (FTIR) spectrum of PMMs.

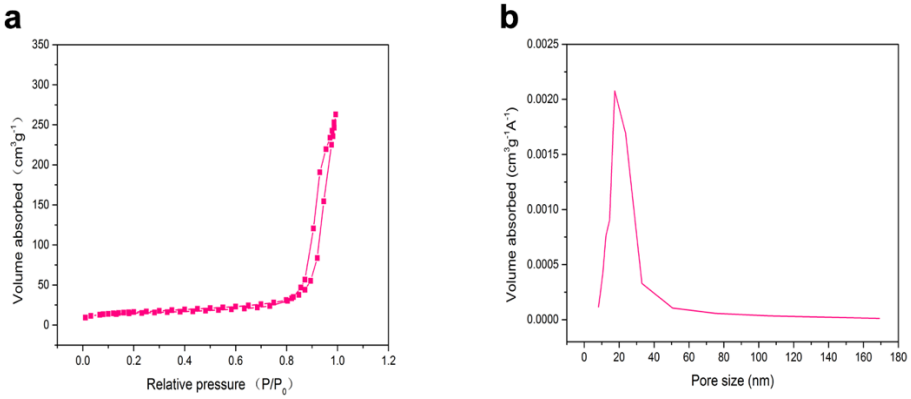

Figure S2. a. N_2 adsorption isotherms of PMMs; b. Pore size distribution of PMMs.

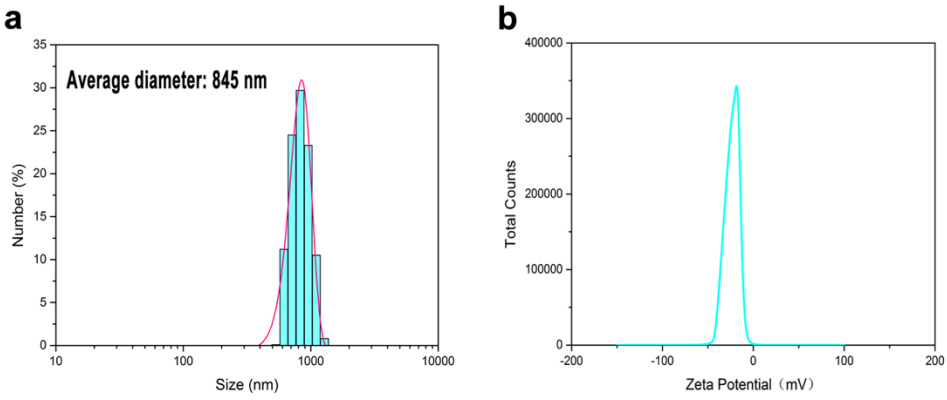

Figure S3. a. Size distribution of PMMs; b. Zeta potential of PMMs.

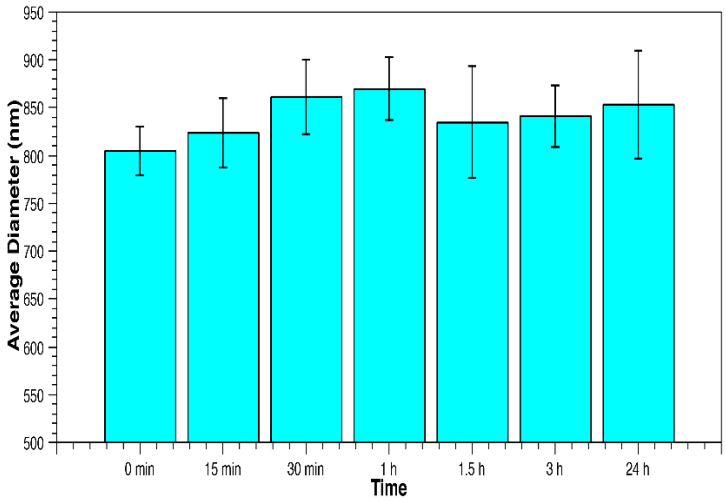

Figure S4. Average Diameters of PFH-PMMs under 37 ˚C at different time points.

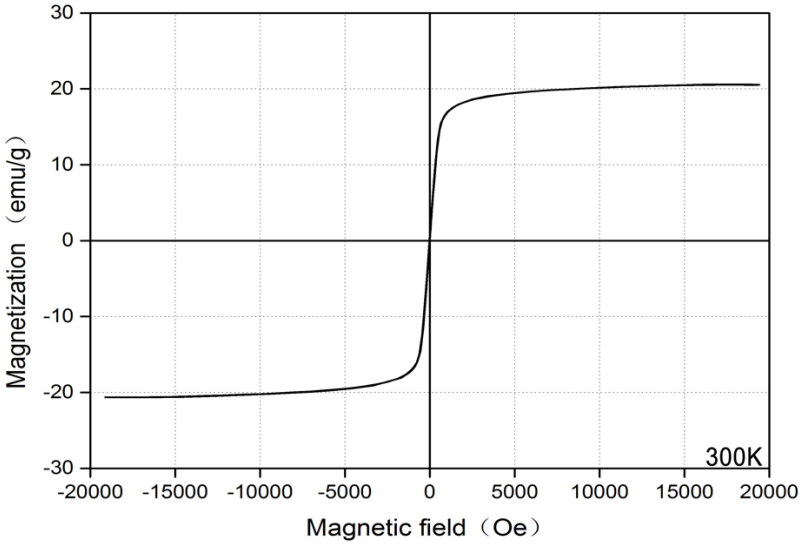

Figure S5. M-H curve of PMMs with 300K were measured by vibrating sample magnetometer.

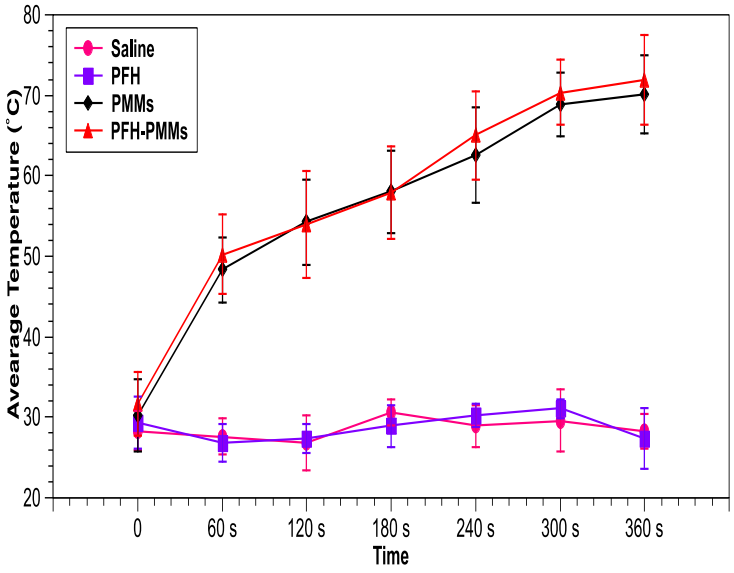

Figure S6. Temperature-time curve of tumor region obtained from the infrared thermal images of nude mice in the course of magnetic heat treatment.

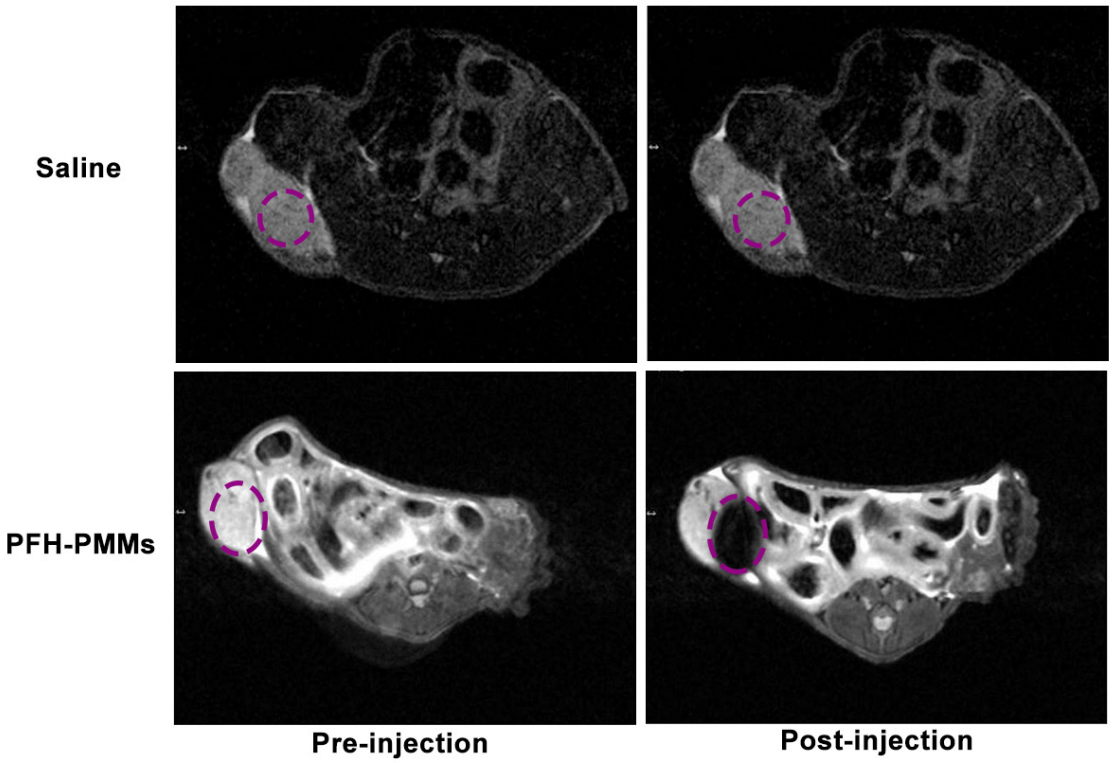

Figure S7. In vivo T2-weighted MR images of pre- and post- intratumoral injection of saline or PFH-PMMs of nude mice acquired by a 7.0 T Magnetic Resonance Imaging system.

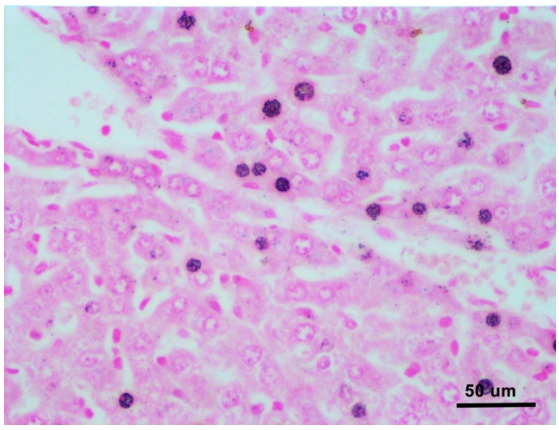

Figure S8. Prussian stain of liver tissue of nude mice 3 hour after intravenous administration of PFH-PMMs (0.125 mL, 6 mg/mL).