Supporting Information

Dual nanocomposite multihollow polymer microspheres prepared by suspension polymerization based on a multiple Pickering emulsion

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Experimental:

Materials:

The hydrophobic modified amorphous fumed silica (H30) was a gift from Wacker-Chemie (Burghausen) whose primary particles are approximately spherical of diameter between 5 and 30 nm. The primary particles can aggregate into larger units of about 200-500 nm in diameter, and these aggregates are loosely bound together in larger agglomerates which can easily be destroyed by sonication in styrene. Synthetic hectorite clays Laponite RD (Rockwood Ltd.) were used as-received. 2'-azobisisobutyronitrile (AIBN) was purified by recrystallization, and styrene was distilled under a reduced pressure before use. N,N'-methylenebisacrylamide (BIS, Acros), 2,2-azobis(2-methylpropionamidine)dihydrochloride (V-50, Guangzhou Exhibition Biotechnology Company, China), fluorescein isothiocyanate (FITC,Alfa) were used as received. Water used in all experiments was purified by deionization and filtration with a Millipore purification apparatus to the resistivity higher than 18.0 MΩ·cm.

Preparation of γ-Fe_2O_3 nanoparticles.

A 0.5 g portion of $FeCl_3 \cdot 6H_2O$ was added to 50 mL of nitrogen-purged HPLC grade 2-propanol. Then, 0.25 g of $FeCl_2 \cdot 4H_2O$ was added while the solution was continuously stirred. The solution color was yellowish-orange after complete dissolution of the iron precursors. Then, the solution temperature was gradually raised to 50 ^oC and concentrated aqueous ammonia was added to the solution in excess, <10 mL. The color of the solution changed to dark brown after 15 min of continuous stirring. To speed up the precipitation of the Fe_2O_3 nanoparticles, the resulting solution was placed in a refrigerator for 5 h. The products were subsequently washed with methanol 3 times and settled by centrifugation at 10000 rpm for 5 min. A 10 mM oleic acid solution, in 50 mL methanol, was then added to the products, and this mixture was stirred for 3 h. After completing the synthesis, the products were thoroughly washed with methanol to remove excess surfactant and finally dispersed in 50 mL hexane. This Fe_2O_3 suspension was used as synthesized. The resulting oleic acid-stabilized Fe_2O_3 were single crystalline and uniform with diameters of ~5 nm.

Fluorescence labeled laponite RD with rhodamine B

A solution of rhodamine B (1 mL, 240 mg/L) was added dropwise under strongly stirring to a suspension of laponite RD (9 mL, 10 g/L). For removal of unbound rhodamine B, the suspension was filtered through cellulose nitrate filters.

Suspension polymerization based on multiple Pickering emulsion.

In a typical experiment of Pickering suspension polymerization based on w/o/w emulsion, water (0.5 mL) was emulsified into a dispersion of silica nanoparticles (10 mg) in styrene (2 mL) with

AIBN (20 mg) by ultrasonification to form the primary w/o emulsion. Multiple w/o/w Pickering emulsion was prepared by re-emulsifying the simple w/o emulsion just made (0.4 mL) into an aqueous dispersion (2 mL) of Fe_2O_3 nanoparticles (2 mg) using hand shaking. Suspension polymerization was carried out for 8 h at 60 ^oC with no stirring help after multiple Pickering emulsion was bubbled through with argon for 5min.

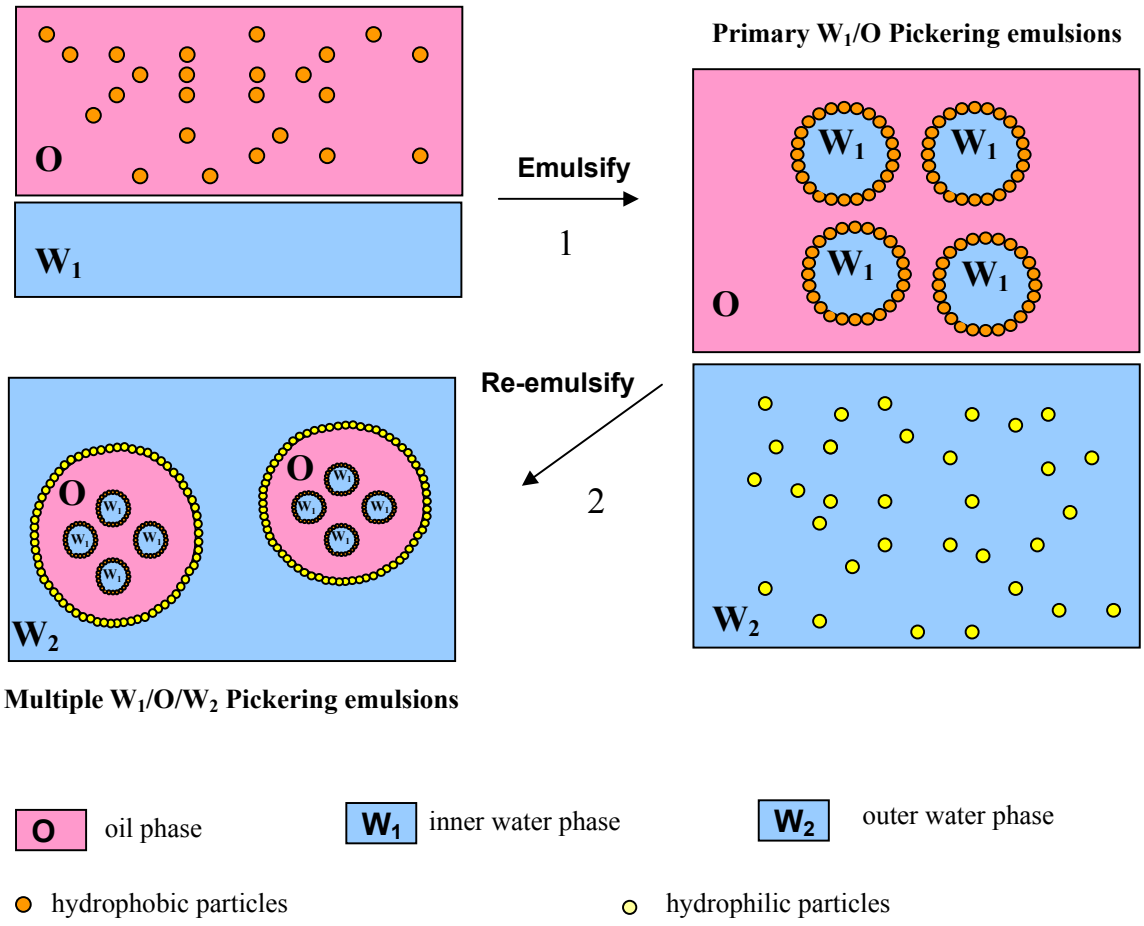
Moreover, multiple o/w/o Pickering emulsion was obtained in a similar method. Am (200 mg), BIS(20 mg), V-50(10 mg), clay (20 mg) and NaCl (11 mg) were dissolved in water (2 ml). The primary o/w emulsion was prepared by emulsifying toluene (0.5 ml) in aqueous solution (2 ml) via ultrasonification. This primary emulsion (0.4 ml) was dispersed in a toluene phase (2 ml) containing silica nanoparticles (10 mg). Suspension polymerization was also carried out in an ice-water bath under 30 mW/cm^2 UV radiation for 5 min because water-soluble V-50 is a photo-initiator. After polymerization, the microspheres were transferred into 10 ml $NaCO_3$–$NaHCO_3$ buffer (pH=9.9). The fluorescent dye, FITC, was dissolved in DMSO at a concentration of 1 mg/ml. 100 ml of the dye solution were added to the buffer and oscillated for 24 h. After reaction, hybrid microspheres were washed with water until no free FITC was detected in the supernatant.

Characterization

The structures of microspheres were observed using a Philips XL 30 scanning electron microscopy (SEM) at the acceleration voltage of 20 kV. The dried samples were sputtered with gold. Fourier transform infrared (FTIR) spectra were obtained on a Bruker Vector33 FTIR spectrometer using the KBr method. Thermo-gravimetric analysis curves of the dry microcapsules were collected with a thermo-analyzer (TG 209, NETZCH Co.) within a temperature range of 20–600 ^oC and with the rate of increasing temperature of 10 ^oC/min. The

molecular weight and polydispersity of the resultant polystyrene (PS) after filtering out inorganic particles were measured by gel permeation chromatography (GPC, Waters 2410) with tetrahydrofuran as the solvent (1.0 ml/min) at 35 ^{o}C. Calibration was established using polystyrene standards. The confocal micrograph was taken with a Leica TCS SPE confocal laser scanning microscope (CLSM). Elemental analysis of Si and Fe was performed by means of inductively coupled plasma atomic emission spectroscopy (ICP-AES) using Thermo Jarrell Ash IRIS (HR).

Figure S1. The procedure for preparing multiple w/o/w emulsions by a two-step method.



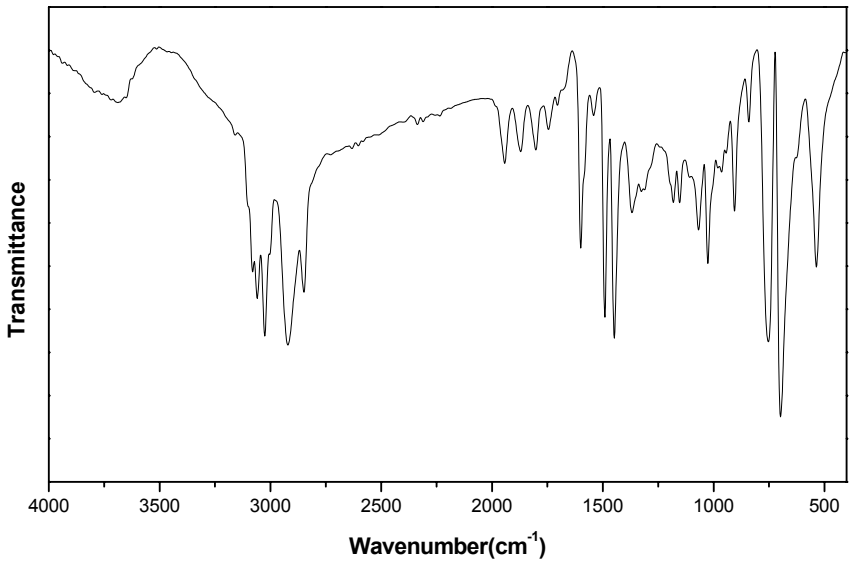


Figure S2. FTIR spectrum of nanocomposite PS microparticles.

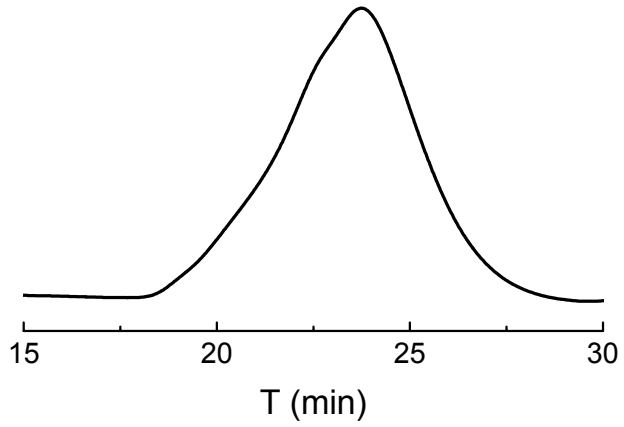


Figure S3. GPC of PS in the nanocomposite.

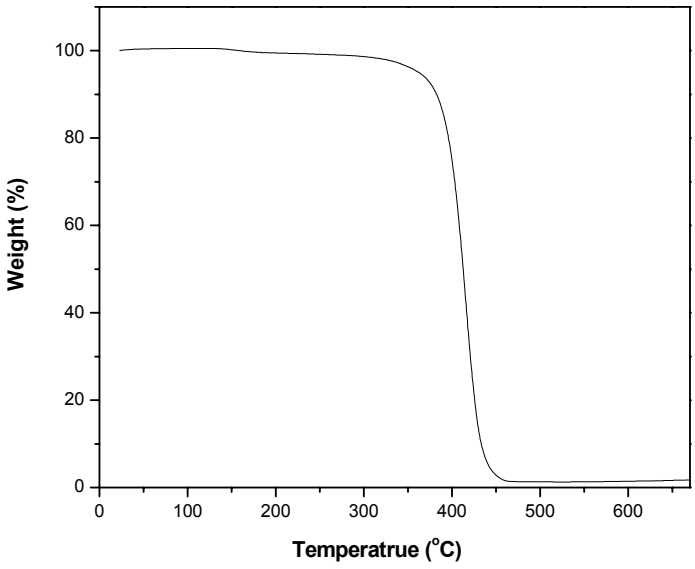
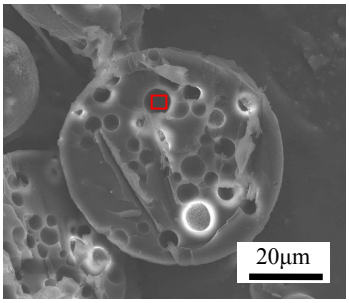
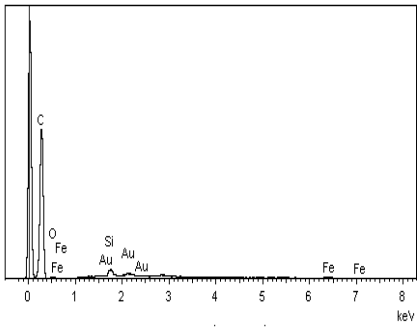
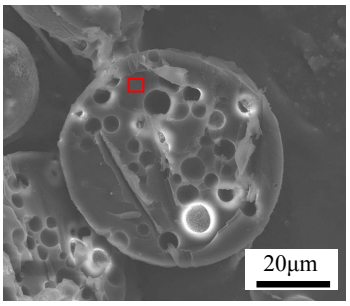


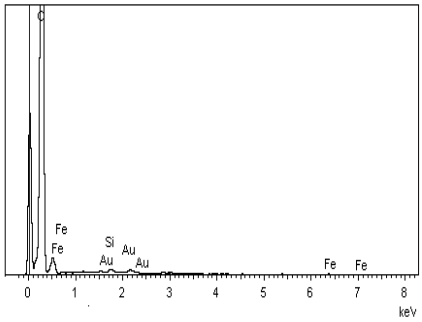
Figure S4. TGA curve of nanocomposite PS microparticles.



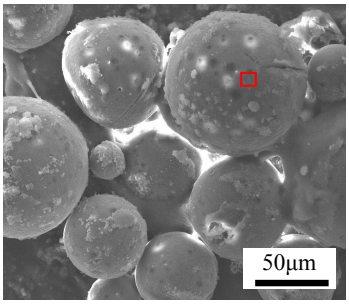


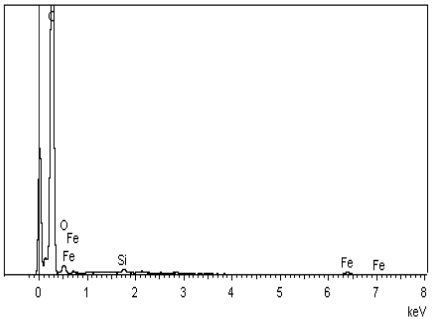
Element	Atom percentage
C K	96.14
O K	2.81
Si K	0.62
Fe K	0.32
Au K	0.11





Element	Atom percentage
C K	99.77
Si K	0.12
Fe K	0.07
Au K	0.04





Element	Atom percentage
C K	93.22
O K	6.44
Si K	0.09
Fe K	0.24

Figure S5. EDX analysis of the different areas of the multihollow PS beads

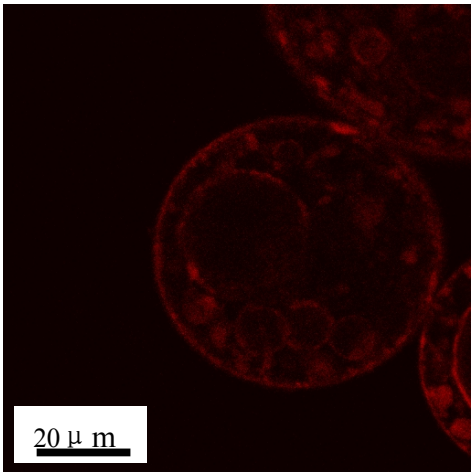


Figure S6. Fluorescence image of nanocomposite PAm microgel with aqueous multi-cores;

The clay nanoparticles stained with the fluorescent dye rhodamine B.

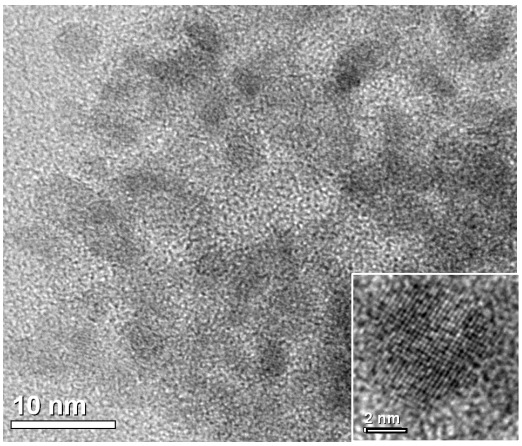


Figure S7. Characterization of the synthesized γ-Fe_2O_3 magnetic nanoparticles: high-resolution TEM images (inset scale bar = 2 nm)