Microfluidic fabrication of magnetic porous multi-walled carbon nanotube beads for oils and organic solvents adsorption

Xiaojian Cao, a,b Linlin Zang, b Zhipeng Bu, a,b Liguo Sun, "b Dechao Guo a,b and Cheng Wang"a

a Key Laboratory of Functional Inorganic Material Chemistry (MOE), Heilongjiang University, Harbin, 150080, China
b Key Laboratory of Chemical Engineering Process & Technology for High-efficiency Conversion, College of Heilongjiang Province, School of Chemical Engineering and Materials, Heilongjiang University, Harbin, 150080, China

Preparation of water-soluble magnetic nanoparticles:
Typically, FeCl₃ (2 mmol) was first dissolved in 20 mL diethylene glycol, followed by the addition of 0.8 mmol sodium citrate under vigorous stirring. The solution was heated to 80 °C and sodium acetate (0.492 g) was then added to the mixture with continuous stirring to form a homogeneous solution. Subsequently, the resultant solution was transferred to the Teflon-lined autoclave and it was maintained at 240 °C for 6 h. After cooled down to room temperature, the black product was collected by centrifugation and washed with ethanol for three times. Finally, the resulting precipitate was dried in vacuum oven at 50 °C.

Preparation of polystyrene microspheres:
A typical synthesis of polystyrene microspheres was as follows: 50 mL monomer and 500 mL water were added to the three necked flask, and the stirring speed was set at 300 rpm. After the mixture had refluxed for 3 min, 0.5 g potassium persulfate powder was added to the solution. After 3 h, the product was obtained via repeatedly centrifugation.
Characterization:

**Fig.S1** SEM images of MCNTBs after solidification: (a) MCNTBs (MCNTs/polystyrene =1:3), (b) The section of a broken bead, and magnified images of (c) external structure and (d) internal structure.

**Fig.S2** Isothermal curve for nitrogen adsorption-desorption of the MCNTBs (MCNTs/polystyrene=1:3), and insert picture is the corresponding pore size distribution.
**Fig. S3** SEM images of MCNTBs after calcination: (a) external structure and (b) internal structure of MCNTBs (MCNTs/polystyrene = 1:1), (c) external structure and (d) internal structure of MCNTBs (MCNTs/polystyrene = 1:5).

**Fig. S4** (a) XRD pattern of Fe$_3$O$_4$ nanoparticles, (b) FTIR spectra of Fe$_3$O$_4$ nanoparticles.

**Fig. S5** FTIR spectra of polystyrene microspheres.
**Fig.S6** Digital photos of the state in stirring process at different speed (200, 300, 400rpm) and corresponding optical microscope images of the MCNTBs after stirring for 15 min (a) in pure water system and (b) salt water system.

**Fig.S7** Absorption velocity of magnetic porous MCNTBs (0.2g) for various solvents (1.2g).
Fig.S8 Surface tension of different oils and organic solvents.