Supplementary Information

Superhydrophobic magnetic poly(DOPAm-*co*-PFOEA)/Fe_3O_4/cellulose microspheres for stable liquid marbles

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Synthesis of poly(DOPAm-*co*-PFOEA)

The synthesis of the *N*-(3,4-dihydroxyphenethyl) acrylamide (DOPAm) was performed using the similar method described elsewhere.[1] Dopamine hydrochloride (10.0 g, 52.8 mmol) and triethylamine (7.3 ml, 52.7 mmol) were dissolved in MeOH (100 ml), and cooled on an ice bath. THF solution (7 mL) of acryloyl chloride (5.8 mL, 71.5 mmol) and MeOH solution (10 ml) of triethylamine (9.5 mL, 68.1 mmol) were alternately added dropwise to the dopamine solution, maintaining the pH at 9.0. After adding the reagent, the reaction mixture was stirred at room temperature overnight. Solvent was removed under vacuo. The residue was dissolved in ethyl acetate and washed with 1 M hydrochloric acid (HCl) and brine. The organic layer was dried over sodium sulfate, then filtrated, and concentrated by evaporation. The precipitate was dissolved in ethyl acetate and repeatedly recrystallized, giving white product (5.6 g, yield 51 %). ^{1}H NMR (400 MHz, CD_3OD): δ 6.71-6.66 (m, 2H), 6.57-6.53 (m, 1H), 5.66 (t, 1H), 5.35 (t, 1H), 3.40 (t, 2H), 2.69 (t, 2H), 1.93 (s, 3H).

A DMF solution (3.5 mL) of DOPAm (1.9 g, 9.0 mmol), 2-(perfluorooctyl)ethyl acrylate (PFOEA, 4.7 g, 9.0 mmol), and AIBN (24.6 mg, 0.15 mmol) was deoxygenated by the argon bubbling for 30 min. The reaction vessel was sealed and stirred for 18 h at 343 K. The reaction mixture was diluted with 10 mL DMF and poured into 2.5 mL ether to precipitate the resulting polymer, which was collected by filtration and dried in vacuum.

Fabrication of poly(DOPAm-*co*-PFOEA)/Fe_3O_4/cellulose microspheres

The cellulose microspheres were regenerated using NaOH/urea as solvents described elsewhere.[2] 11 g of cellulose was first dissolved in 200 mL of NaOH/urea/H_2O (7:12:81 by weight) solution at 260 K with vigorous stirring. Then the solution was centrifuged to obtain a transparent cellulose solution. This cellulose solution was dropped into the mixed solution of 20 g Span-80 in 400 mL of paraffin oil to form cellulose solution droplets. After heated to 343 K, the cellulose solution droplets were transited into solid with spherical shape.

The magnetic cellulose microspheres (MCM) were fabricated through the situ synthesis of Fe_3O_4 in the porous of cellulose microspheres.[1] The cellulose microspheres were added to a mixture solution of $FeCl_2$ and $FeCl_3$ (mole ratio were $FeCl_3$:$FeCl_2$=2:1) by stirring under vacuum. Then ammonia was added. The mixture was washed by water to remove excess ammonia, NH_4Cl and little impurities to obtain MCM.

0.1 g of poly(DOPAm-*co*-PFOEA) was dissolved in 50 mL of 1,1,1,3,3,3-hexaflu-oro-2-propanol, and 1 g of MCM was dispersed in the above solution by stirring for 96 h at room temperature. Then the mixture was centrifuged and washed by deionized water to remove excess poly(DOPAm-*co*-PFOEA). The sample was dried at 120 °C for 2 h under vacuum to obtain poly(DOPAm-*co*-PFOEA)/Fe_3O_4/cellulose microspheres.

Magnetic properties measurement of cellulose-based microspheres

The magnetic properties were measured with a PPMS-9 vibrating sample magnetometer (Quantum Design, USA) at 300 K. Fig. S1 shows magnetization as a function of applied magnetic field for the cellulose-based microspheres containing Fe_3O_4 nanoparticles. The saturation magnetization obtained from the hysteresis loop was 9.4 emu/g, revealing that the cellulose-based microspheres possessed good magnetic properties. The small hysteresis loop and low coercivity showed that the magnetization of the composite microspheres has the characteristic of superparamagnetic behavior.[3]

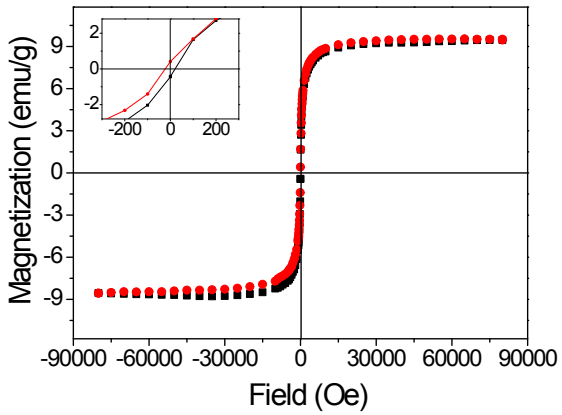

Fig. S1 The magnetic hysteresis loops of the cellulose-based microspheres at 300 K. Insert is a magnified view of the -300 to 300 Oe regions.

References

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