Supporting Information

Highly compressible magnetic liquid marbles assembled from hydrophobic magnetic chain-like nanoparticles

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Part I: Preparation process of HMCNPs

Synthesis of HMCNPs is illuminated in Fig.S1, combining flame synthesis, aerosol coating and surface functionalization in a continuous gas-phase process. Fe_2O_3 nanoparticles were synthesized in an enclosed vapour assist flame synthesis (VAFS) reactor described in detail elsewhere. Precursor solution in all cases, 0.12 M Fe metal concentration of ferric chloride ($FeCl_3$) in alcohol was fed to the vaporizer at the rate of 4 ml/min by a rate-controlled syringe pump (ALC-IP900) and 1.5 m^3/h air preheated to 250℃ was used as carrier gas to transport the vaporized precursor mixture to the central tube of the nozzle. The mixed precursor vapor was ignited by O_2/H_2 (0.8 m^3/h, 0.76 m^3/h) diffusion flame in second and third rings at the nozzle base. The VAFS reactor was enclosed by a 30 cm long stainless steel tube (ID, 4 cm).

Connecting to the tube, a quench ring (ID, 4cm) made by a stainless steel torus (pipe diameter. 0.4 cm) was placed. The ring had 16 equispaced pores (ID, 0.15 cm each) as shown in Fig.S1 and was terminated by the other 30 cm long stainless steel tube. The in situ coating precursor (Tetraethylorthosilicate, TEOS) vapor was supplied by introducing N_2 through TEOS bubbler, and was injected along with an accelerated air via the 16 pores. The total flow rate through the 16 pores is preserved at 2.5 m^3/h by adjusting the accelerated air (2.5-1.9 m^3/h).

At the top of the second tube, in one side tubing sprayed 1.5 ml/min of functionalizing precursor solution dispersed by 0.3m^3 /h Air (upward 45 cm from the vertical) into the freshly flame-made Fe_2O_3@SiO_2 stream. The precursor solution was 0.1 M 3-Methacryloxypropyltrimethoxysilane (MEMO) in distilled water (10 vol %) and ethanol. The final tube of the reactor was 30 cm long. The products were collected on the filter with the aid of a vacuum pump.

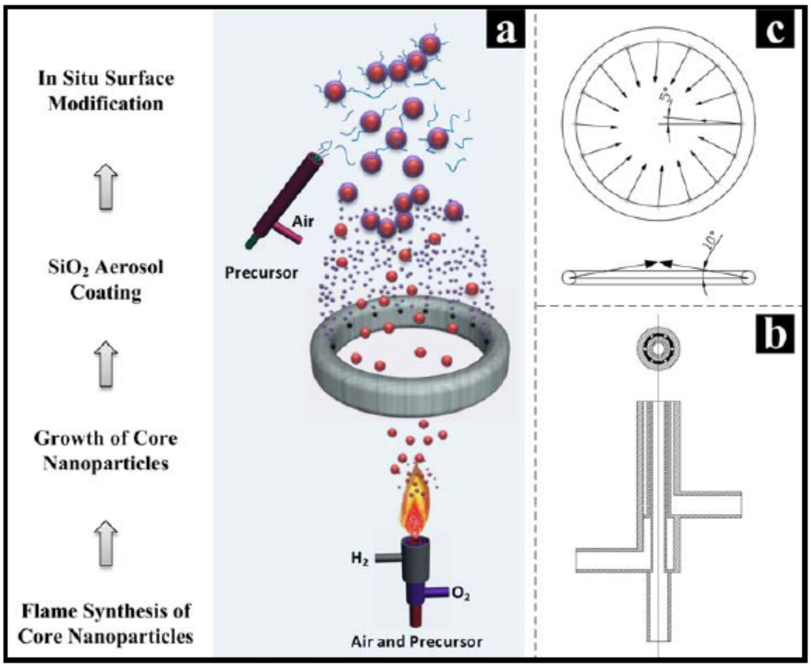

Fig.S1 Schematic of preparation process of HMCNPs via flame method

Part II. Supplementary characterizations

Fig.S2 shows the TEM images of pure and MEMO-functionalized core/shell Fe_2O_3@SiO_2 NPs dispersed in absolute alcohol. At low magnification, non-functionalized powder (Fig.S2a) has ruleless nanoparticles aggregates morphology, showing serious aggregation. In contrast, MEMO-functionalized sample (Fig.S2b) has nanoparticles chain aggregates NCA formed network structure with chain length of 200-500 nm, showing homogeneous dispersion. The MEMO chains grafted on the surface of shell-SiO_2 bring mutual exclusion and steric hindrance effect, thus the surface free energy has been reduced correspondingly, improving agglomeration. In order to represent detailed morphological information, high magnification images were shown in Fig. S2c and S2d. For both samples, core-Fe_2O_3

nanoparticles with count mean diameter of 23 nm are coated hermetically and homogeneously with an average thickness of about 3.9 nm. The detailed size of core and shell is independent of surface functionalization, as the fuctionalization precursor is introduced after core/shell NPs formation. So this gas-phase process allows independent control of particle formation and surface modification. TEM image, as shown in Fig. S1d, was used to further confirm the network nature, which agreed well with low magnification results. Meanwhile, inset in Fig. S2d shows one segment of a long chain, showing strong interaction of two neighbouring particles. In addition, Separate amorphous SiO_2 particles were not observed by TEM at any sample. So the TEM results suggested that Fe_2O_3 nanoparticles were hermetically and uniformly coated by SiO_2 with accurately controlled shell thickness, and in situ gas-phase surface functionalization can tremendously reduce agglomeration, forming network structured nanoparticles, and has no effect on the core and shell sizes, allowing independent control of particle formation and surface modification.

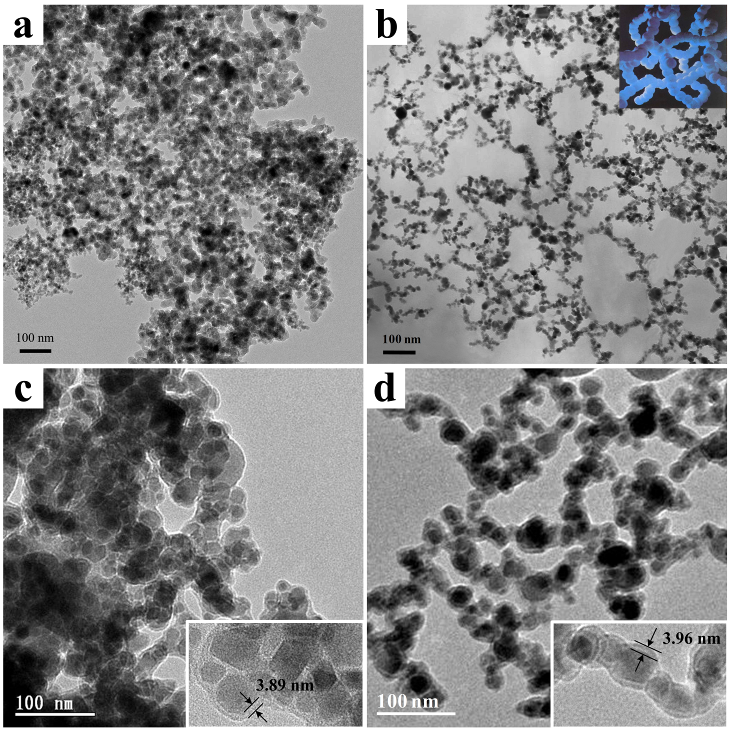

Fig. S2 TEM images of non-functionalized (a, c) and 0.1M MEMO-functionalized (b, d) core/shell Fe_2O_3@SiO_2 NPs.

X-ray diffraction (XRD) shown in Fig. S3 indicates that the present iron oxide particles in both samples are γ-Fe_2O_3 (maghemite, cubic; PDF: 039-1346), in agreement well with vapor-fed aerosol flame synthesis of Fe_2O_3. The presence of Fe_3O_4 (magnetite) cannot be ruled out by XRD as maghemite and magnetite patterns are nearly identical. However, the oxygen-rich environment in the flame reactor and the reddish-brown color of these powders suggest formation of γ-Fe_2O_3. The crystallite sizes calculated by Scherrer formula at peak (311) of γ-Fe_2O_3 are 14.5 and 14 nm for non-functionalized and MEMO-functionalized core/shell Fe_2O_3@SiO_2 nanoparticles, respectively. The XRD results indicated that surface functionalization almost has no effect on the crystalline phase and crystallite size, as the modified precursor was introduced after crystallization finished.

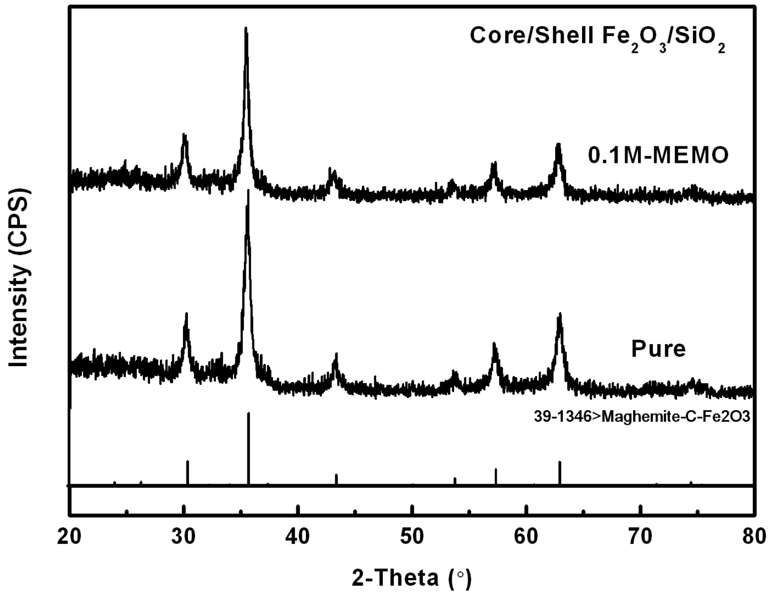

Fig.S3 X-ray diffraction patterns for HMNCPs

Fig.S4 shows typical FT-IR spectra of non-modified and MEMO-modified HMCNPs, respectively. From the FT-IR spectra of both samples, the absorptions around 1100, 810 and 470 cm^{-1} are the characteristic absorption of the silica, the characteristic band for stretching (OH) groups was found around 3400 cm−1, and the band at 1637 cm^{-1} was assigned to the bending vibration of water molecules, the high frequency bands from 500 to 750 cm^{-1} are assigned to the stretching vibrations of Fe–O groups from γ-Fe_2O_3, indicating the formation of γ -Fe_2O_3. It was noteworthy that the higher frequency bands from 850 to 900 cm^{-1} are ascribed to Si–O–Fe vibrations, indicating the strong interaction between core Fe_2O_3 and shell-SiO_2. For MEMO-modified particles, peaks visible between 3000 and 2800 cm^{-1} can be assigned toCH_3 and CH_2 asymmetric and symmetric stretching vibrations, meanwhile, the absorption peak at1735 cm^{-1} belongs to C=O. Moreover, it can be found that the peak of modified particles at 800–1150 cm^{-1} is broader and stronger than that of the non-modified particles, indicating that the surface group of shell-SiO_2 has changed from Si–OH to Si–O–C. all the FT-IR results proved that our method can successfully modified core/shell Fe_2O_3@SiO_2 nanoparticles by MEMO in a continuous gas-phase process.

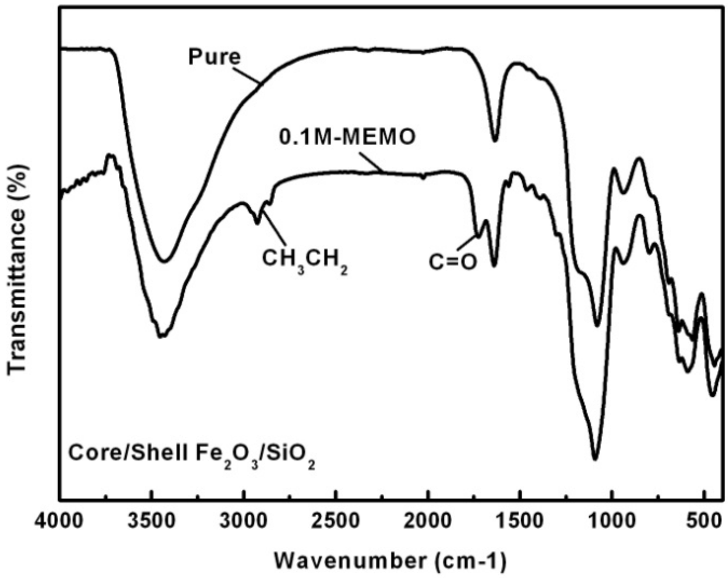

Fig. S4 FT-IR spectra for HMCNPs and non-functionalized Fe_2O_3@SiO_2 NPs.

Fig. S5 shows the dependence of contact angle on surface functionalization property of Fe_2O_3@SiO_2 NPs after water droplet deposited on a thin bed of the powders for 15 seconds. The contact angle for Non, 0.1M-MEMO modified powders increased from 54.12° and 142.50°, showing controllable surface hydrophobic and hydrophilic properties by our method. In addition, 0.1M-MEMO modified NPs showed strong repellence to water, which make such hydrophobic NPs a good candidate to act as encapsulating agent for preparation of liquid marbles.

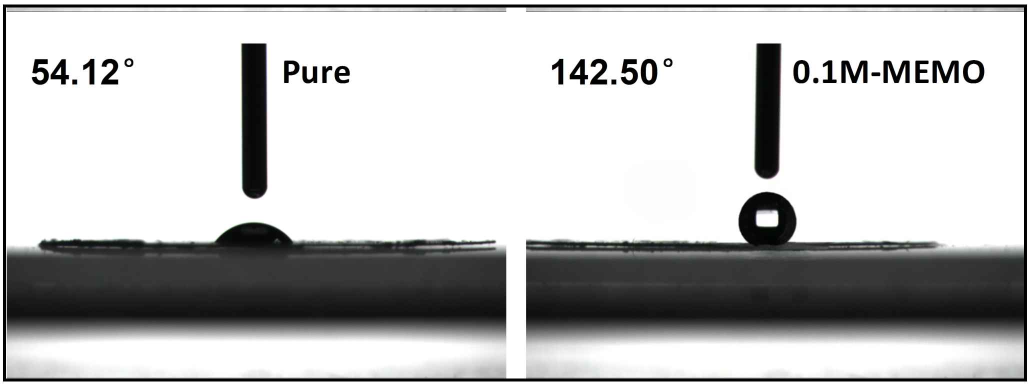

Fig. S5 Water contact angles for Non, 0.1M-MEMO modified $Fe_2O_3@SiO_2$ NPs

We also have found that the magnetic liquid marbles have the ability to be opened and closed reversibly under the action of a magnetic field. As shown in Fig.S6, when the magnet was moved slowly upward, the HMCNPs were pulled down toward the glass surface and a liquid marble, containing a water droplet, was opened up to show an exposed liquid surface on the top. As long as the magnetic field existed, the liquid marble remained in the opened state. When the magnet was removed, the HMCNPs moved rapidly back to the exposed liquid surface.

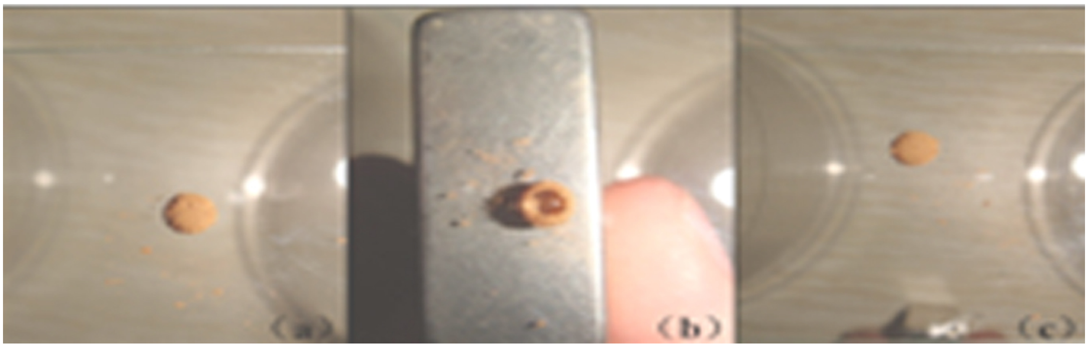

Fig.S6 Process of magnetic liquid marbles opened and closed reversibly under the action of a magnetic field.

The room-temperature magnetization curve (Fig. 7) shows that the 0.1M-MEMO modified core/shell $Fe_2O_3@SiO_2$ NPs are essentially superparamagnetic with negligible hysteresis, suggesting minimal agglomeration of magnetite nanoparticles. The saturation magnetization value is as high as 21 emu / g, showing excellent magnetic actuation performance for magnetic liquid marbles. The magnetic separability of such superparamagnetic NPs was tested in cyclohexane by placing a magnet near the glass bottle. The reddish-brown NPs were attracted toward the magnet within 30 seconds (inset of Fig. 7), and then could be easily redispersed with slight shaking, demonstrating directly that the core/shell nanospheres possess good magnetic properties.

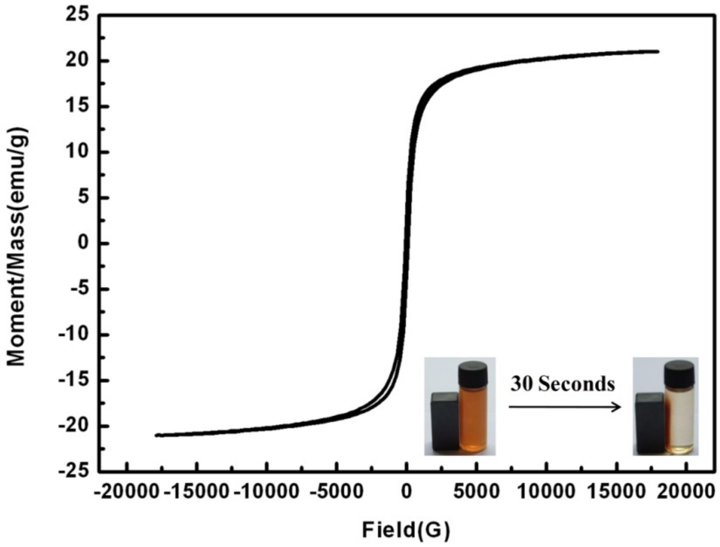

Fig. S7 Room temperature magnetization curve of 0.1M-MEMO modified core/shell Fe_2O_3@SiO_2 NPs, inset, separation from cyclohexane under an external magnetic field.