Supporting information

A General Method for Synthesis of Various Rattle-type Microspheres and Their Versatile Applications

Bin Liu, Jianchao Wang, Shuxuan Sun, Xiaoman Wang, Meng Zhao, Wei Zhang, Han Zhang, and Xinlin Yang*

Key Laboratory of Functional Polymer Materials, the Ministry of Education, Institute of Polymer Chemistry, Nankai University, Tianjin 300071, China

* **CORRESPONDING AUTHOR**

Prof. Xinlin Yang, Tel/Fax: +86-22-23502023; E-mail: xlyang88@nankai.edu.cn.

Table S1. Polymerization conditions for synthesis of different core/PMAA particles.

Entry	seeds	MAA(g)	MBA(g)	AIBN[b] (g)	Acetonitrile (mL)
Au	8 mL[a]	0.045	0.255	0.0060	80
Fe_3O_4	0.1 g	0.32	0.08	0.0080	80
Fe_2O_3	0.1 g	0.32	0.08	0.008	80

a) The as-prepared Au aqueous sol was used as seeds directly.

b) The amount of AIBN initiator was maintained at 2 wt % relative to the total monomers.

The procedure for the synthesis of the PMAA microspheres

PMAA microspheres were prepared through distillation-precipitation polymerization. The typical procedure was as follows: 0.8 g of MBAAm, 3.2 mL of MAA and 0.08 g of AIBN were dissolved in 160 mL of acetonitrile (2.5% monomers to solvent, 20% degree of crosslinking) in a 250 mL of flask. The flask attaching with a fractionating column, a Liebig condenser, and a receiver was submerged in a heating mantle. The reaction mixture was heated from ambient temperature till the boiling state within 15 min and the polymerization system was kept under refluxing state for 15 min further. Then the polymerization was carried out by distilling the solvent out of the reaction system and the reaction was ended after 80 mL of acetonitrile was distilled off the reaction mixture within 90 min. After the polymerization, the resultant PMAA microspheres were purified by repeating centrifugation, decantation, and resuspension in ethanol for three times. The products were dried in a vacuum oven at room temperature till constant weight.

Synthesis of PMAA/silica core-shell particles and the corresponding hollow mesoporous silica microspheres

0.10 g of PMAA microspheres, 0.2 mL of TEOS, 0.04 mL of C_{18}TMS and 0.6 mL of ammonium hydroxide were dispersed in water/ethanol (8 mL/40 mL) mixture with vigorous stirring. The sol-gel process was allowed to proceed for 24 h at room temperature. The resultant PMAA/SiO_2 core-shell particles were purified by centrifugation, decantation, and resuspension in ethanol for three cycles and then dried in a vacuum oven at 50 ^{o}C till constant weight. Hollow mesoporous silica microspheres

were then prepared through the calcination of the as-prepared PMAA/SiO_2 core-shell particles at 600 ^oC for 6 h.

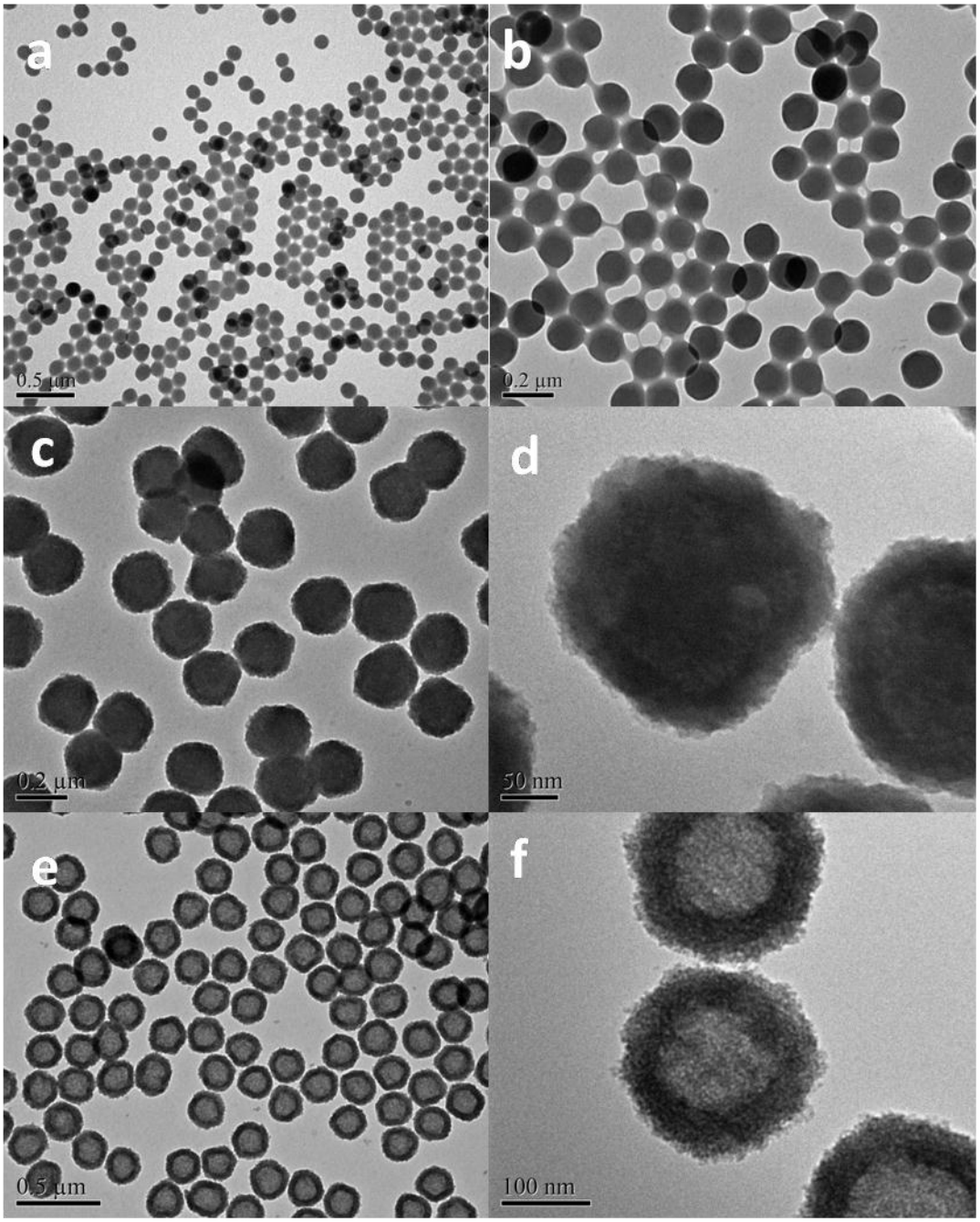


Fig. S1. TEM images: a) and b) PMAA microspheres; c) and d) PMAA@SiO_2 core-shell particles, e) and f) hollow mesoporous silica particles.

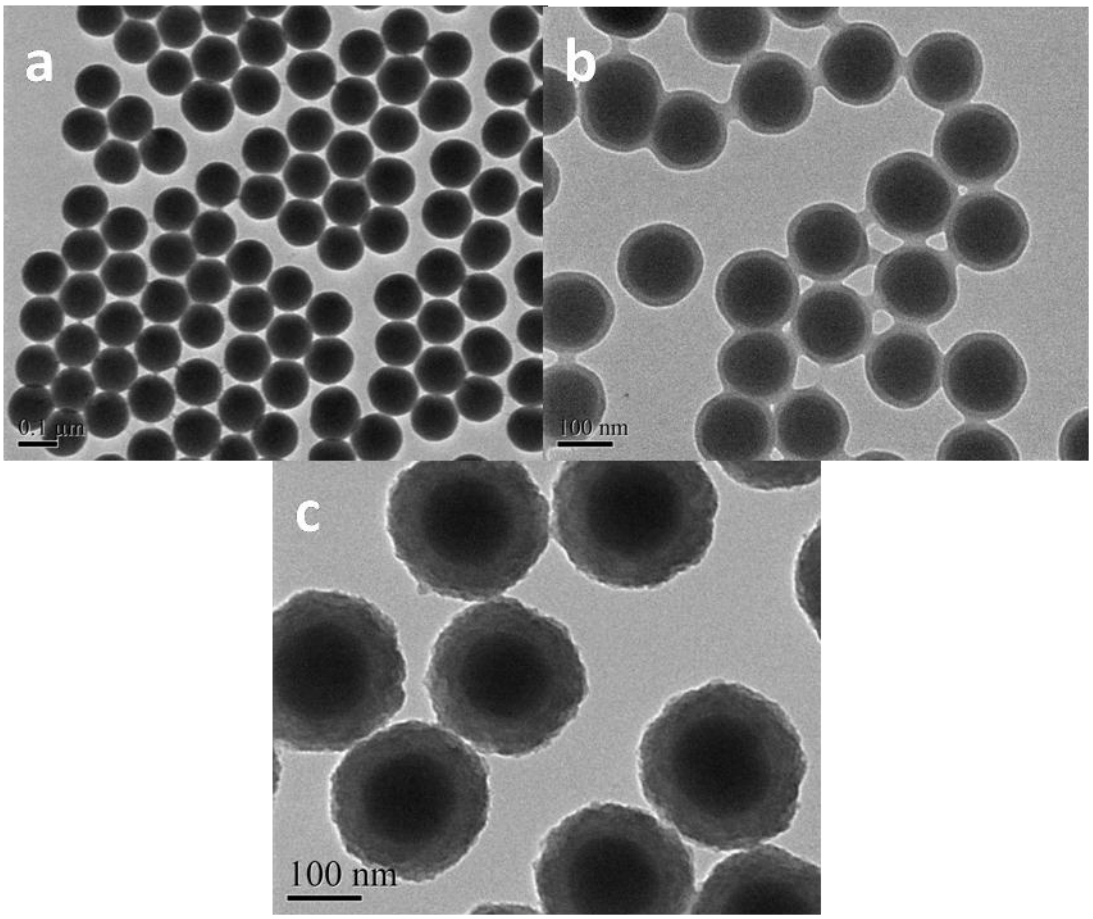


Fig. S2. TEM images: a) MPS modified silica particles, b) SiO_2@PMAA core-shell particles, c) SiO_2/PMAA/SiO_2 trilayer microspheres.

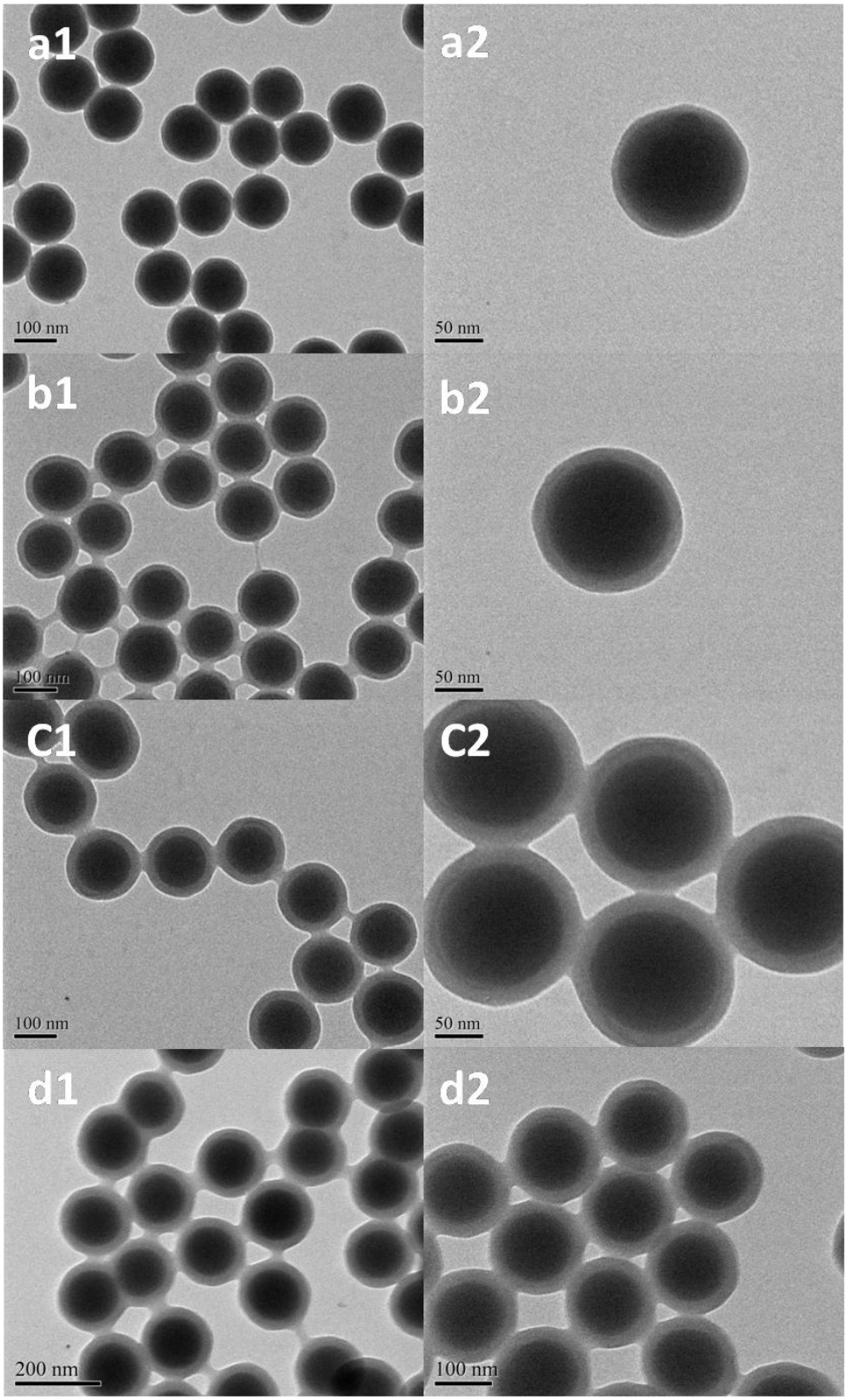


Fig. S3. TEM images: SiO_2@PMAA microspheres with different shell thicknesses from different feeds of the monomers to the seeds during the second stage of the polymerization: a1) and a2) 1:1, b1) and b2) 1:1.5, c1) and c2) 1:2.5, d1) and d2) 1:3.

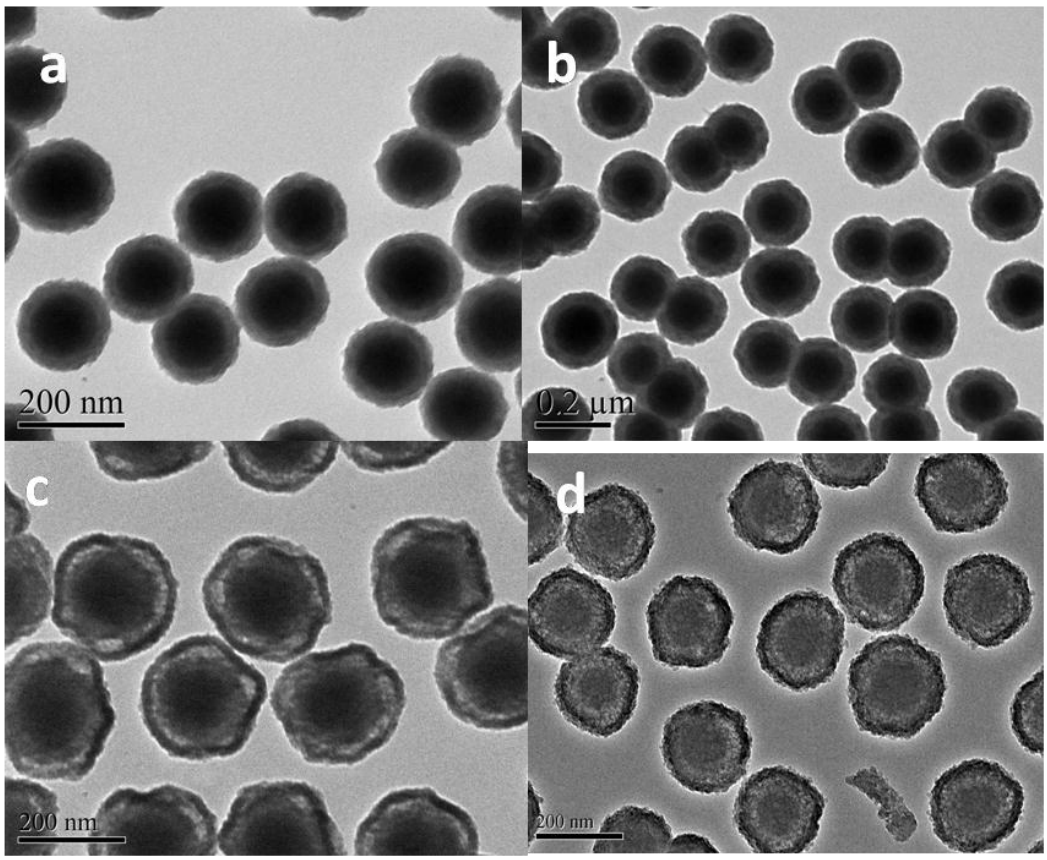


Fig. S4. TEM images of SiO_2@PMAA@SiO_2 tri-layer microspheres from SiO_2@PMAA microspheres with different shell thickness.

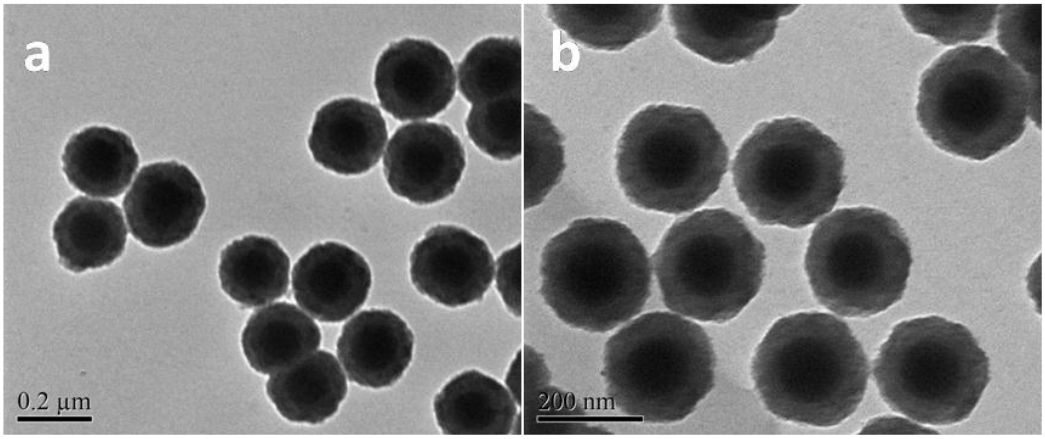


Fig. S5. TEM images of SiO_2@PMAA@SiO_2 tri-layer microspheres with different outer silica thickness from different TEOS feed: a) 0.15 mL, b) 0.1 mL.

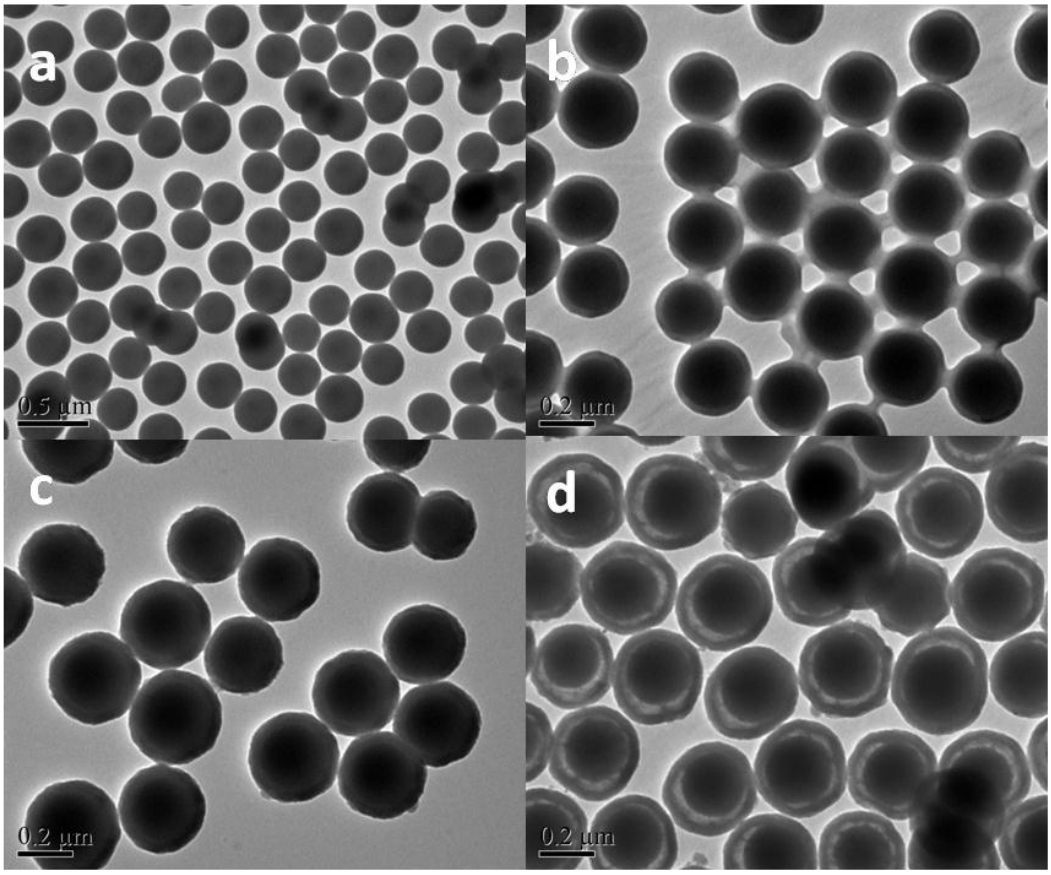


Fig. S6. TEM images: a) SiO_2 particles, b) SiO_2/PMAA, c) SiO_2/PMAA/SiO_2, d) SiO_2@mSiO_2 rattle-type microspheres from the silica with core size of 270 nm.

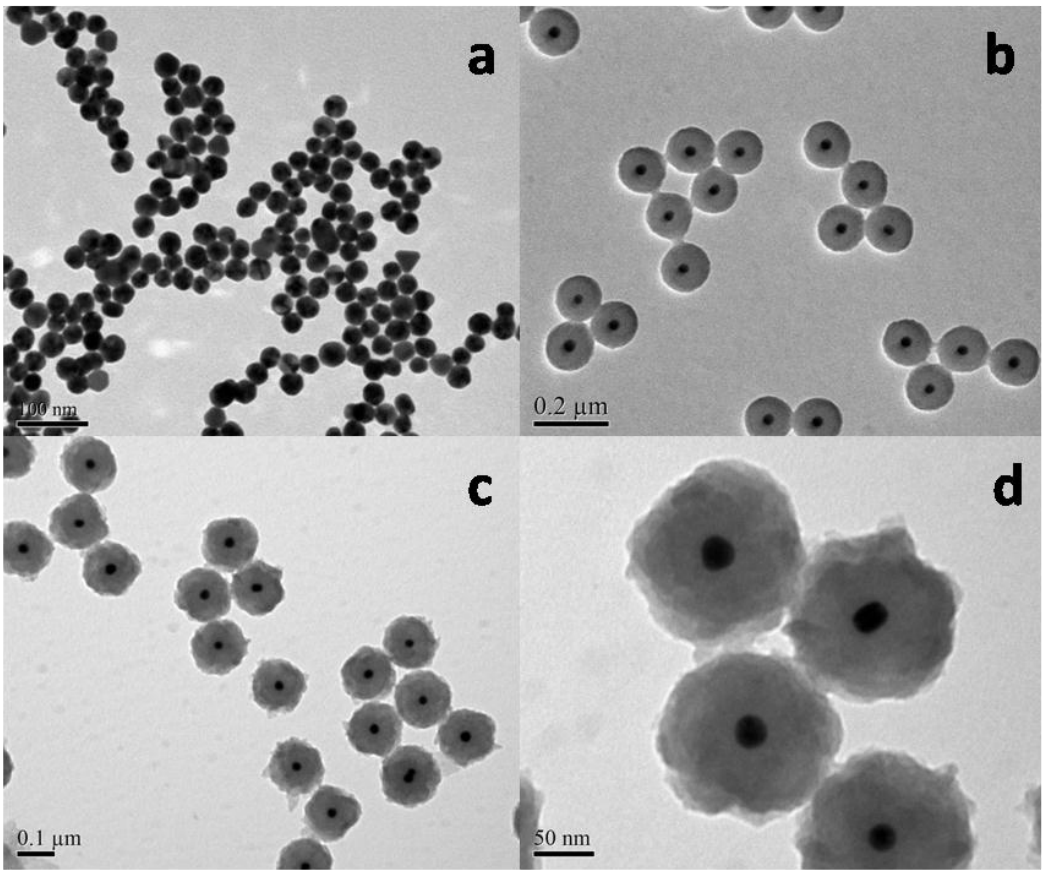


Fig. S7. TEM images: a) gold nanoparticles; b) Au/PMAA core-shell particles; c) and d) Au/PMAA/SiO_2 tri-layer microspheres.

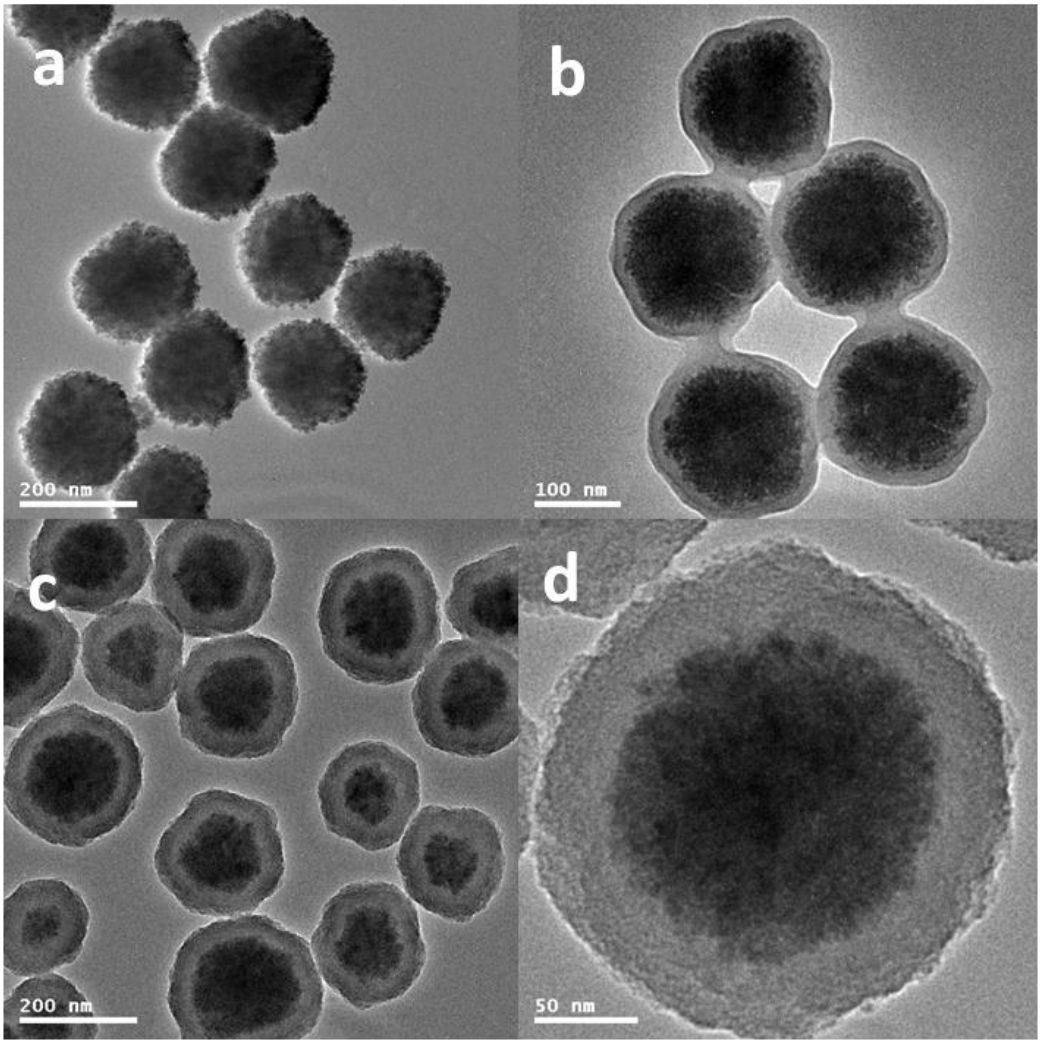


Fig. S8. TEM images: a) Fe_3O_4 microspheres, b) Fe_3O_4/PMAA core-shell microspheres, c) and d) Fe_3O_4/PMAA/SiO_2 tri-layer microspheres.

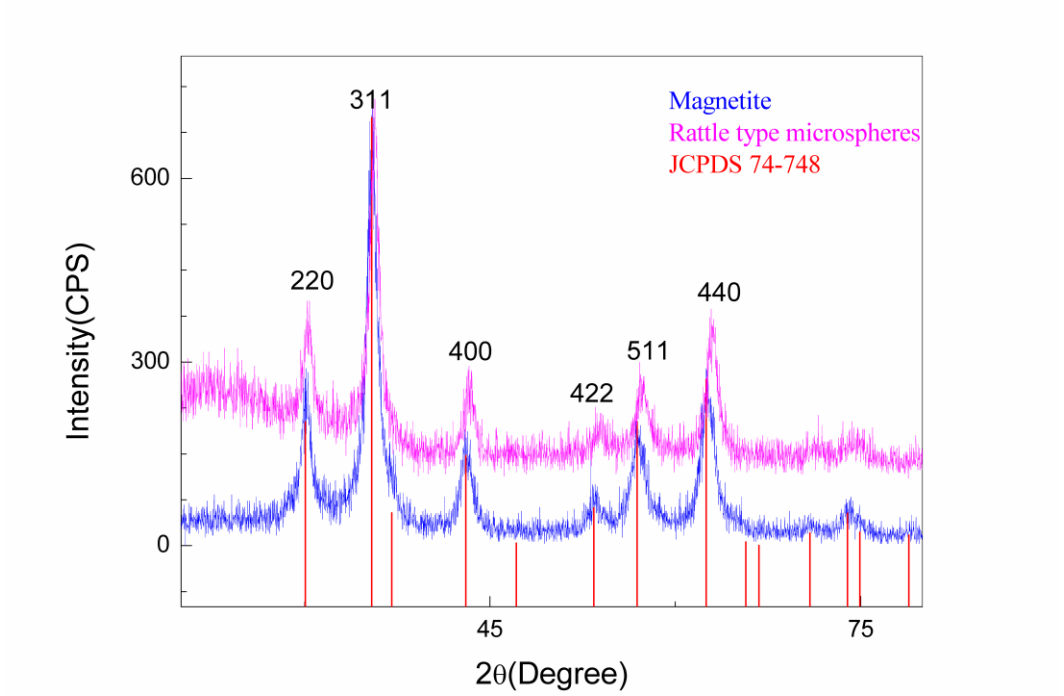


Fig. S9. XRD patterns of Fe_3O_4 microspheres (blue color), and MIO@mSiO_2 rattle-type microspheres (pink color). The red line represented the PDF card 74-0748.

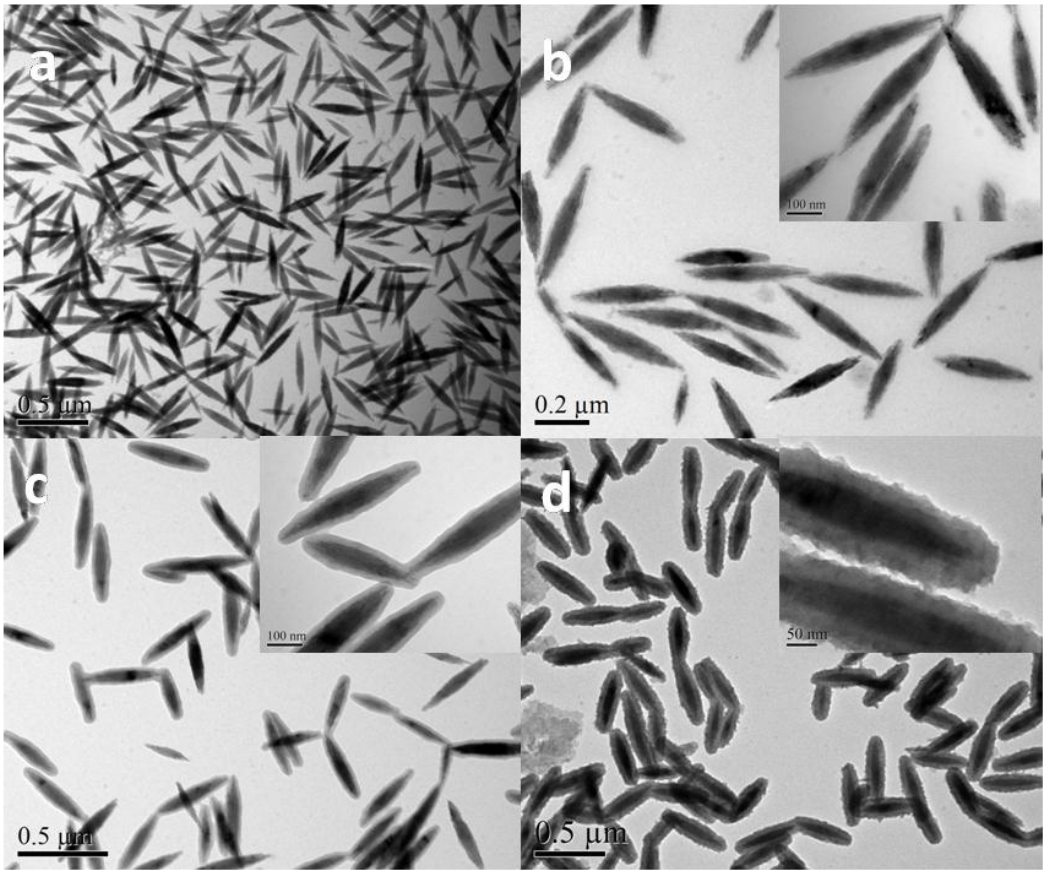


Fig. S10. TEM images: a) hematite particles; b) hematite/PMAA core-shell microspheres from the first stage polymerization; c) hematite/PMAA core-shell microspheres from the second stage polymerization; d) hematite/PMAA/SiO_2 tri-layer microspheres.

Procedures for preparation of TPI-PEG and TPI-PEG-FA

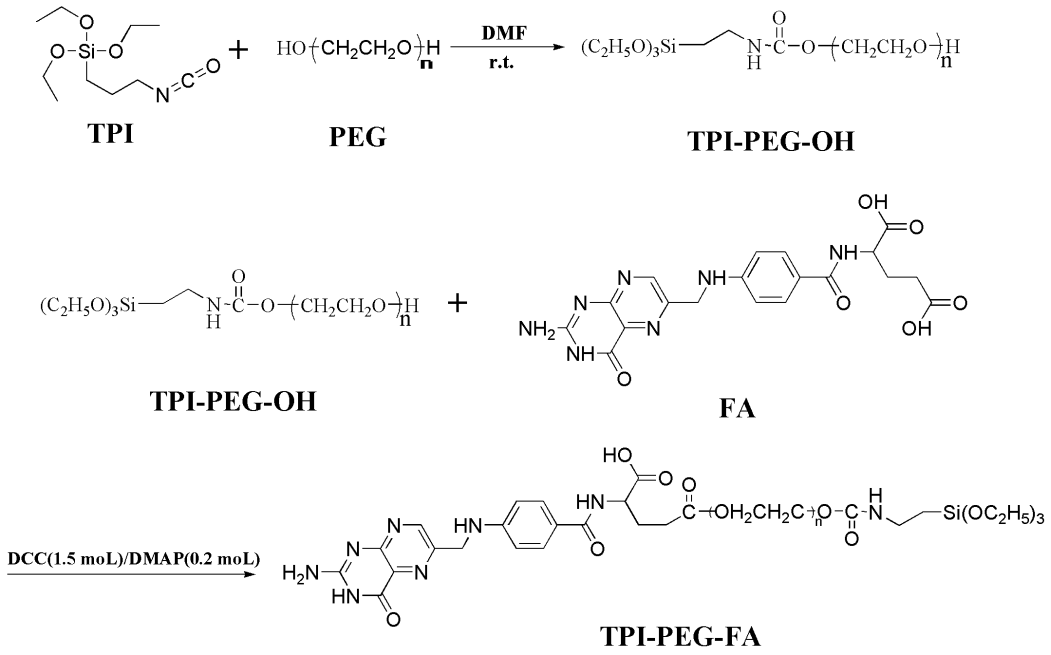
The TPI-PEG was synthesized by the addition reaction between TPI and PEG (Scheme S1). The details were as follows: 8.8 g of PEG (0.22 mmol, M_n=40000) was dissolved in 32 mL of dry DMF and then 50 μL of TPI (0.2 mmol) was added under stirring for another 24 h. This solution was used directly for the silica coupling reaction with the MIO@mSiO_2 and dominated as A.

The TPI-PEG-FA was prepared through the esterification between TPI-PEG and FA (Scheme S1). The details were as following: the TPI-PEG was prepared as described above. 0.106 g of FA (0.24 mmol) was firstly dissolved in solution A. Then, dicyclohexylcarbodiimide (DCC, 0.0743 g, 0.36 mmol) and 4-dimethylamiopryidine (DMAP, 0.006 g, 0.048 mmol) were added as catalyst into the above mentioned solution for esterification under the magnetic stirring in the ice base for another 24 h. This solution was also used directly for the silica coupling reaction with the MIO@mSiO_2 and dominated as B.

Preparation of MIO@mSiO_2-PEG and MIO@mSiO_2-PEG/FA

The PEG or PEG/FA was grafted onto the surface of the MIO@mSiO_2 rattle-type microspheres through the silica coupling reaction. The details were as follows: 0.15 g of MIO@mSiO_2 rattle-type was dispersed in 50 mL of dry DMF. Then, 50 μL of triethylamine (TEA) was added under the mechanic stirring. Finally, 10 mL of solution A or B was added for 48 h for preparation of MIO@mSiO_2-PEG and MIO@mSiO_2-PEG/FA, respectively. The resultant MIO@mSiO_2-PEG and MIO@mSiO_2-PEG/FA were purified by repeating magnetic collection, decantation,

and resuspension in ethanol for three times. The products were dried in a vacuum oven at room temperature till constant weight.



Scheme S1. The process for the preparation of TPI-PEG and TPI-PEG-FA.

Table S2. Elemental analyses of the MIO@mSiO$_2$, MIO@mSiO$_2$-PEG and MIO@mSiO$_2$-PEG/FA microspheres.

Entry	C(%)	H(%)	N(%)
MIO@mSiO$_2$	3.29	1.86	0.33
MIO@mSiO$_2$-PEG	13.66	1.79	0.90
MIO@mSiO$_2$-PEG /FA	9.04	2.53	2.29

Table S3. BET surface area and pore volume of surface MIO@mSiO$_2$ and MIO@mSiO$_2$ rattle-type microspheres

Entry	BET surface area (m^2/g)	Pore volume (cm^3/g)
MIO@mSiO$_2$	494.5	0.42
MIO@mSiO$_2$-PEG/FA	120.3	0.22