

Magnetic Separation of Polymer Hybrid Iron Oxide Nanoparticles Triggered by Temperature

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Supplementary Information

Experimental Section

Materials

Ferrous sulfate hexahydrate, ferric chloride hexahydrate, oleic acid and methacryloxypropyl-trimethoxysilane were purchased from Aldrich Chemical Co. and used as received. N-isopropylacrylamide was purchased from Acros and recrystallized in toluene. All other reagents were used as received from commercial sources.

Measurements

Transmission electron microscopy (TEM) was carried out on a JEM-100CX instrument operating an acceleration voltage of 80 kV. TEM specimens were prepared by aspirating a sample onto a copper EM grid.

Infrared spectrums were recorded by a Nicolet 200SXV-1 FT-IR spectrometer.

The hydrodynamic diameters of MNPs were measured with a Zetasizer Nano ZS90.

X-ray photoelectron spectroscopy (XPS) was carried out on an XSAM-800 electron and take-off angle of 20° was used with X-ray source.

XRD data were collected on a Shimadzu XD-D1 X-ray diffractometer employing Cu-K α radiation at 30 kV and 30 mA.

Number average molecular weights (M_n), weight average molecular weight (M_w), and molecular weight distribution (M_w/M_n) were determined using gel permeation chromatography (GPC) in THF at 30 °C with a flow rate of 1 mL min⁻¹.

Thermogravimetric analysis (TGA) was performed on a TA instrument Q50, at a scan rate of 10 °C min⁻¹, up to 700 °C under nitrogen atmosphere.

The temperature triggered magnetic separation behaviour was investigated by placing the water dispersion of PNIPAM coated MNPs with a content of 0.01 g/ml under an external magnetic

field of 1.1 T provided by a sintered Nd-Fe-B alloy permanent magnet. The temperature was switched between 25 °C and 40 °C.

Determination of the graft density

The graft density of OA, MPS and PNIPAM were calculated from TGA analysis and their molecular weight according to the following equation:

$$\text{no. of molecules per nm}^2 = \frac{W \times d_{\text{Fe}_3\text{O}_4} \times r \times N_A}{M(1-W) \times 3 \times 10^{21}}$$

W is the weight loss of sample. $d_{\text{Fe}_3\text{O}_4}$ is the density of Fe_3O_4 . N_A is Avogadro's constant. M is the molecule weight. r is the radius of MNPs

Synthesis of OA Coated MNPs

OA coated MNPs were synthesized via a two-step method (Scheme 1). First step: 2.35 g ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ >99%) and 4.1 g ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ >99%) were dissolved into 100 mL deionized water in a flask. This solution was stirred, followed by adding 25 mL 25% (w/w) $\text{NH}_3\text{H}_2\text{O}$ quickly at room temperature. The solution color could be seen to alter from orange to black, leading to a black precipitate. Then under vigorous stirring, 1 mL OA was dropped into the dispersion slowly at 80 °C in 1 hour. The whole process was carried out under nitrogen atmosphere. The as-synthesized MNPs could be well dispersed into water by the protection of the double layers of OA.

Second step was to extract MNPs from water into toluene. In a typical procedure, 50 mL MNPs' water dispersion and 50 mL toluene were mixed together in a 250 mL extractor. By adding small amount of sodium chloride, MNPs transferred into toluene phase and under the protection of single layer of OA, they had good dispersibility in toluene. Finally, the toluene dispersion was refluxed to remove the most water under nitrogen atmosphere and the content of MNPs was diluted with toluene to 10 mg/mL.

Synthesis of MPS modified MNPs

MPS coated MNPs were synthesized as follows: First, 0.01 mL MPS, 1 mL TEA (2 M in toluene), 10 mL toluene and 5 mL MNPs' toluene dispersion were added into a 50 mL round-bottom flask. The mixture was stirred for 48 h at room temperature under nitrogen atmosphere. Second, 20 mL petroleum ether was added into the mixture to precipitate the modified MNPs, followed by magnetic separation and dried in vacuum. Third, these magnetic nanoparticles were re-dispersed into toluene and re-precipitated by petroleum ether. This procedure was repeated 5 times to remove the ungrafted MPS and replaced OA followed by dried in vacuum. Finally, these magnetic nanoparticles were dispersed into acetone with content of 0.01 g/mL.

Graft Polymerization of NIPAM on the Surface of MNPs

First, 0.005 g AIBN was dissolved into 10 mL acetone in which 0.01 g MNPs were dispersed. Then 0.25 g NIPAM and 30 mL H₂O were added. Under continuous stirring, the reaction was allowed to proceed for 8 h at 70 °C under nitrogen atmosphere. After the polymerization, PNIPAM coated MNPs were separated by magnetic field of 1.1 T at 40 °C to remove the homopolymer and unpolymerized monomer.

PNIPAM coated MNPs sample were first dissolved in 10% HF for 5 h to etch the Si-O-Si network and washed to neutral by water. After the polymer was centrifuged and dried in vacuum, molecule weight measurement was performed by GPC.

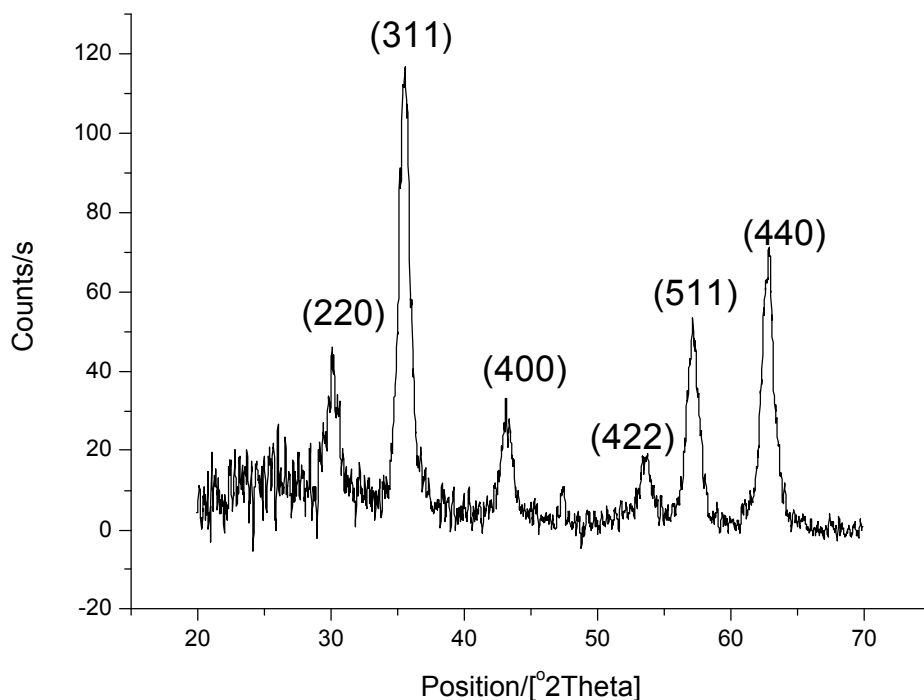


Figure 1 X-ray powder diffraction patterns of Fe₃O₄ nanoparticles

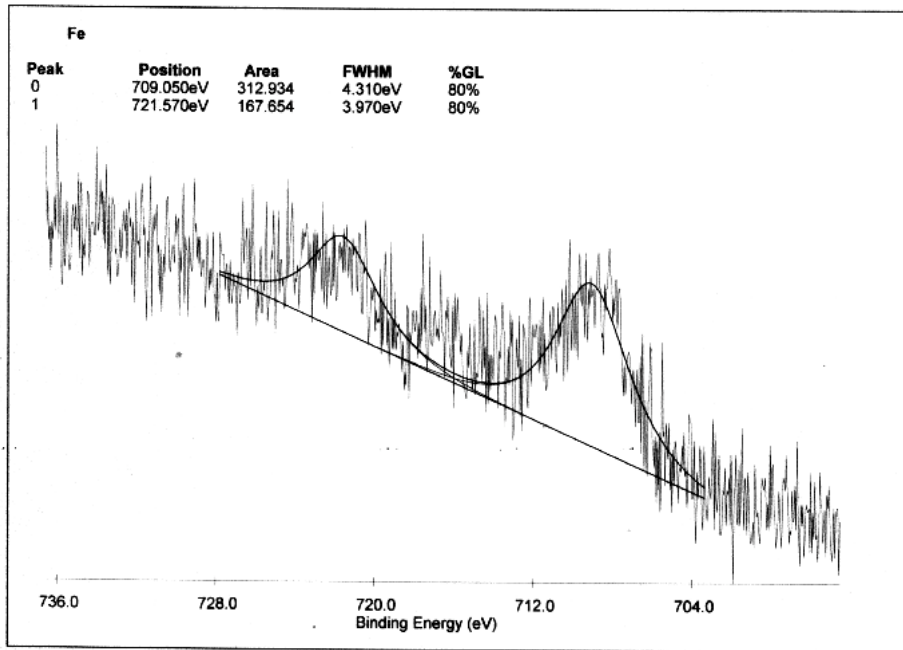


Figure 2 Fe XPS of MPS coated MNPs

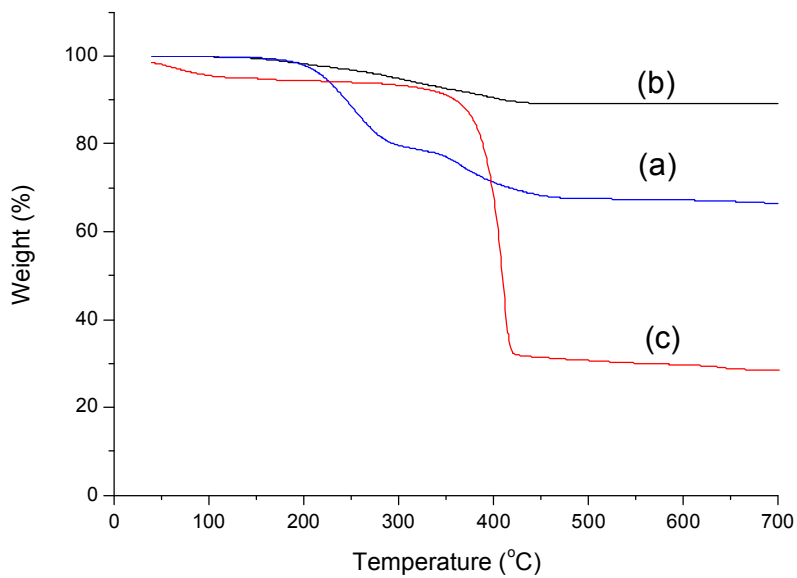


Figure 3 TGA curves of (a) OA coated MNPs; (b) MPS immobilized MNPs; (c) PNIPAM coated MNPs

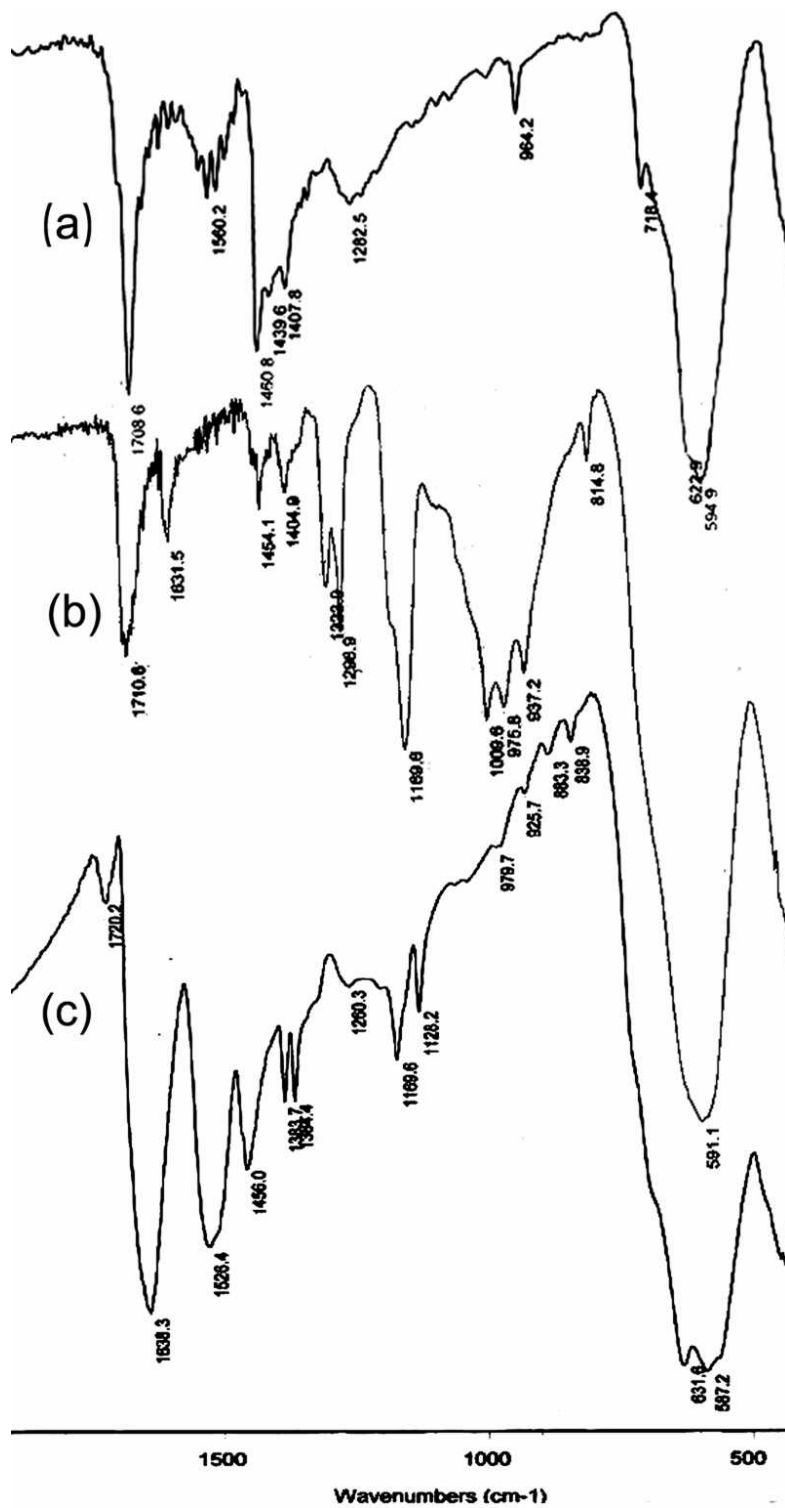


Figure 4 IR spectrum of MNPs: (a) OA coated; (b) MPS modified; (c) PNIPAM coated

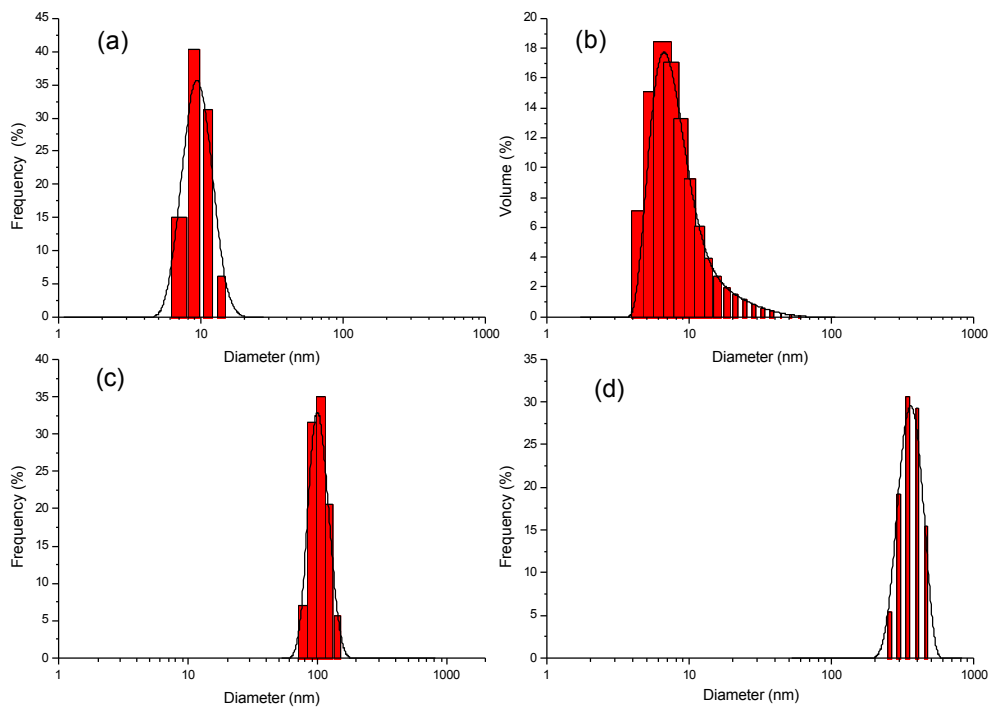


Figure 5 Size distributions of MNPs (a) OA coated in toluene; (b) MPS coated in acetone; (c) PNIPAM coated in water at 25°C; (d) PNIPAM coated in water at 40°C

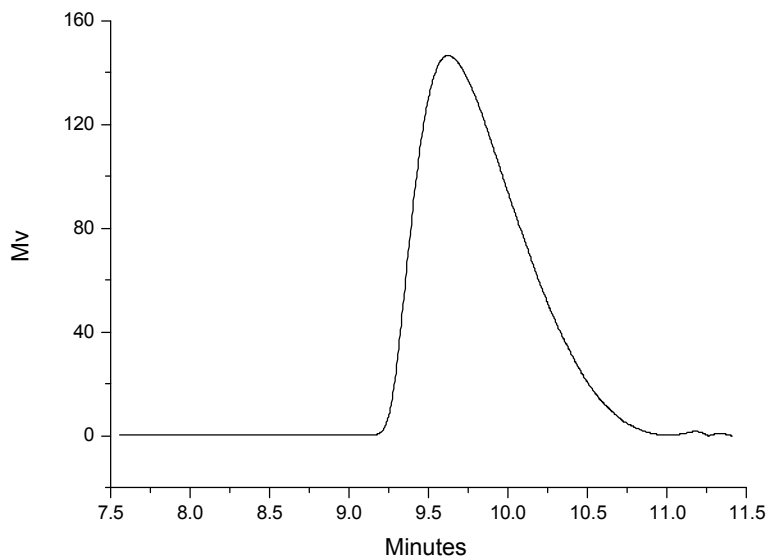


Figure 6 Gel permeation chromatography of PNIPAM on the surface of MNPs:
Mn is 4285 and Mw/Mn is 1.81