

# Magnetic separation of polymer hybrid iron oxide nanoparticles triggered by temperature†

Yabin Sun,<sup>ab</sup> Xiaobin Ding,<sup>\*a</sup> Zhaohui Zheng,<sup>a</sup> Xu Cheng,<sup>a</sup> Xinhua Hu<sup>a</sup> and Yuxing Peng<sup>\*a</sup>

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The water dispersion of poly-*N*-isopropylacrylamide hybrid nanoparticles exhibited temperature-triggered magnetic separation behaviour: if the temperature switched between below and above 32 °C, the nanoparticles could be dispersed into water and reversibly separated by a magnetic field of 1.1 T.

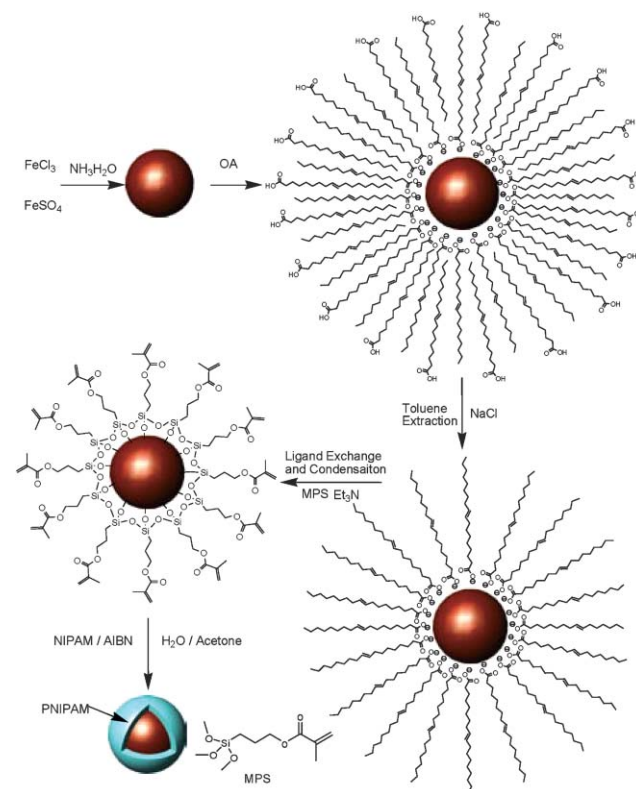
As a result of anisotropic dipolar attraction, pristine nanoparticles of iron oxides tend to aggregate into large clusters and thus lose the specific properties associated with single-domain magnetic nanostructures. Therefore, surface modification of magnetic nanoparticles (MNPs) is an essential and challenging step for most of their applications and fundamental studies. Polymeric shells have some unique advantages because of the flexibility in the control of chemical compositions and functions of the polymers. Several groups have reported the synthesis of the polymeric core/shell MNPs, such as Fe<sub>2</sub>O<sub>3</sub>/PS,<sup>1</sup> MnFe<sub>2</sub>O<sub>4</sub>/PS<sup>2</sup> and Fe<sub>3</sub>O<sub>4</sub>/P3VP<sup>3</sup> *etc.* As yet no paper has reported the synthesis of MNPs with smart polymer chains, such as poly-*N*-isopropylacrylamide (PNIPAM).

PNIPAM is a polymer well-known to undergo dramatic temperature-induced changes in chain conformation. It has a lower critical solution temperature (LCST) of about 32 °C.<sup>4</sup> Numerous reports describing the synthesis and the use of PNIPAM in diverse areas have appeared. For instance, Fu *et al.* coat crosslinked PNIPAM on silica encapsulated MNPs to synthesize thermo-responsive magnetic microspheres with core/shell structure.<sup>5</sup> However, the PNIPAM shell can only change the diameter of microspheres in water when the temperature switches between above and below 32 °C and has no effect on the magnetic separation behaviour.

In this communication, MNPs with thermo-sensitive PNIPAM chains on their surface were synthesized. The water dispersion of as-synthesized polymer hybrid nanoparticles exhibited temperature-triggered magnetic separation behaviour. The synthesis strategy that was designed is presented in Scheme 1. First, a stable colloidal dispersion of MNPs was prepared by co-precipitation method using oleic acid (OA) as surfactant. In short, 2.35 g ferrous sulfate heptahydrate and 4.1 g ferric chloride hexahydrate were dissolved into 100 mL deionized water in a flask. This solution was stirred, followed by the rapid addition of 25 mL (w/w)

NH<sub>3</sub>H<sub>2</sub>O at room temperature. Then under vigorous stirring, 1 mL OA was slowly dropped into the dispersion at 80 °C over the course of 1 hour. The whole process was carried out under nitrogen atmosphere. These MNPs were extracted into toluene by simply adding a salt such as NaCl, KCl, KI, NaBr *etc.* as inducer, similar to the technique used with nanosized silver colloids.<sup>6</sup> After having been extracted into toluene, the particles exhibit a diameter of 9 nm as determined by transmission electron microscopy (TEM) (Fig. 1(a)) and 9.1 nm by dynamic light scattering (DLS), which suggests that the MNPs are dispersed well in toluene. X-ray diffractometer (XRD) and X-ray photoelectron spectroscopy (XPS) analyses indicate that magnetite (Fe<sub>3</sub>O<sub>4</sub>) is the resulting material and the particle size calculated by analyzing XRD peaks using the integral-breath method is 9 nm (see supplementary information†).

The IR spectrum indicates that OA ligands are bonded onto the surface of MNPs through COO<sup>-</sup> functionality (see supplementary information†). Similar results are also observed for OA adsorbed

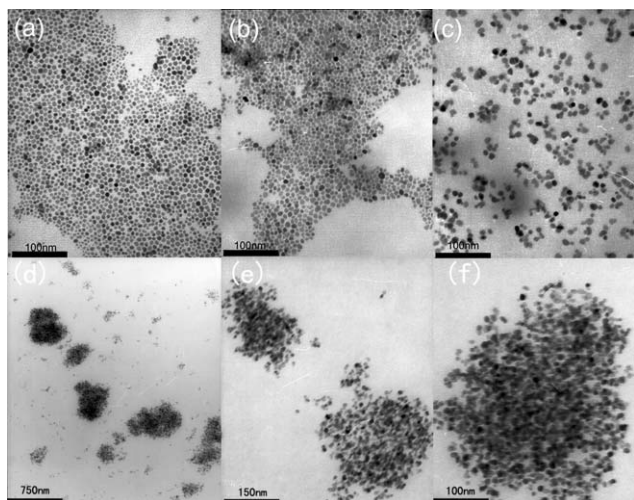


**Scheme 1** Illustration of the synthesis route for PNIPAM-coated magnetic nanoparticles.

<sup>a</sup> Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu 610041, P. R. China. E-mail: xbding@cioc.ac.cn; Fax: 86-028-85233426; Tel: 86-028-85233426

<sup>b</sup> Graduate School of the Chinese Academy of Sciences, Beijing 100081, P. R. China. Fax: 86-028-85233426; Tel: 86-028-85233426

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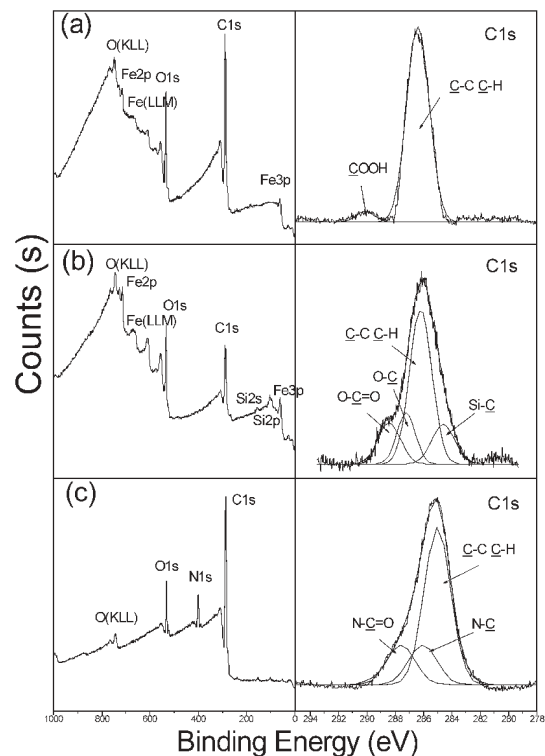
**Fig. 1** TEM images of MNPs: (a) OA-coated in toluene; (b) MPS-modified in acetone; (c) PNIPAM-coated in water at 25 °C and (d) (e) (f) 40 °C.

cobalt<sup>7</sup> and Fe<sub>2</sub>O<sub>3</sub> nanoparticles.<sup>1</sup> To further analyze the chemical composition of the surface of MNPs, XPS analysis was carried out. The photoelectron lines at binding energies of about 53, 284, 530, and 710 eV which are attributed to Fe3p, C1s, O1s, and Fe2p respectively, are observed in the wide scan spectrum of OA-coated MNPs (Fig. 2(a)). The content of Fe on the surface is only about 4%, indicating that MNPs are well covered with an OA layer. Two peak components are observed in their C1s core-level spectrum. The peak at 285.1 eV is attributed to C–C and C–H, and the peak at 288.8 eV is attributed to C=O. The area ratio of the two peaks is 16.8 : 1 which is close to the theoretical ratio of 17 : 1 for OA (Fig. 2(a)). XPS results also confirm the presence of an OA layer on MNPs.

Secondly, methacryloxypropyltrimethoxysilane (MPS) was used to modify surface of the MNPs with methacrylate double bonds. Our novel approach to the immobilization of MPS on the surface of MNPs is the combination of condensation of trimethoxysilane and ligand exchange reaction,<sup>8</sup> which takes advantage of the two methods: covalent linkage between MPS and MNPs and no aggregates formed during the modification. In short, MPS, triethylamine (TEA), toluene and OA-coated MNPs were mixed and stirred for 8 hours at room temperature under nitrogen atmosphere. When the modification was completed, petroleum ether was added into the mixture to precipitate the modified MNPs, followed by magnetic separation and drying in vacuum. Finally, the MNPs were re-dispersed into acetone and re-precipitated by petroleum ether. This procedure was repeated 5 times to remove the ungrafted MPS and replaced OA.

The diameter of MPS-modified MNPs is 9.3 nm determined by DLS measurement, which is similar to that of OA-coated MNPs. The TEM picture Fig. 1(b) indicates that the morphology of MNPs remains almost unchanged from their original state (Fig. 1(a)) and that each particle is separated from its neighbours. Both DLS and TEM analyses confirm that there are no aggregates formed during the modification.

FT-IR (see supplementary information†) and XPS investigations were carried out to characterize MPS-modified MNPs. XPS analysis in Fig. 2(b) confirms the immobilization of MPS on the



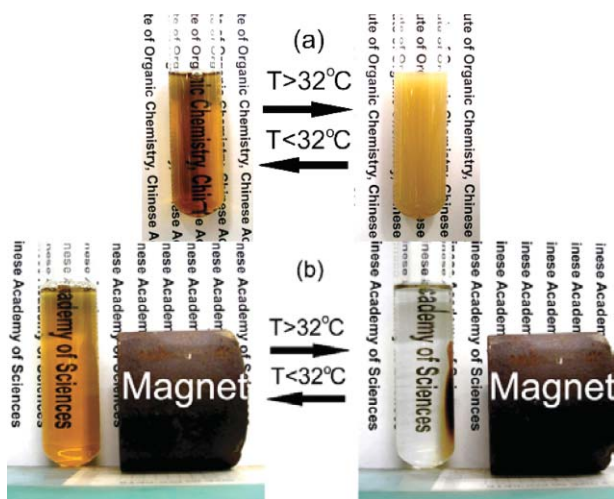
**Fig. 2** XPS of the MNPs: (a) OA-coated; (b) MPS-modified; (c) PNIPAM-coated.

surface of MNPs. The characteristic signals for silicon (Si2s at 155 eV and Si2p at 103 eV), oxygen (O1s at 533 eV) and carbon (C1s at 285 eV) are clearly observed in the wide scan spectrum and the molar ratio of the carbon : silicon is 6.96 : 1 which is close to the theoretical ratio of 7 : 1 for MPS. Four peaks are observed in the C1s core-level spectrum of the MPS-modified MNPs. The peak at about 284.6 eV is attributed to C–C and C–H, the peak at 288.7 eV is attributed to O–C=O, the peak at 283.2 eV is attributed to Si–C and the peak at 286.2 eV is attributed to O–C. The area ratio of the four peaks is 3.9 : 0.9 : 0.8 : 1 which is close to the theoretical ratio of 4 : 1 : 1 : 1 for MPS. The appearance of the C–Si and C–O species, as well as the O–C=O, confirms the presence of methacrylate double bonds on the surface of the MNPs. Furthermore, both FT-IR and XPS analyses suggest that OA absorbed on the MNPs has been completely replaced by MPS.

TGA and element analyses were carried out to estimate the amount of MPS on the MNPs. High graft densities of 4.6 and 4.9 molecules nm<sup>-2</sup>, respectively, were calculated according to TGA and element analyses, which could provide PNIPAM more sites to graft from.

Finally, the graft polymerization of NIPAM from the surface of MNPs was carried out in water–acetone mixed solvent. In detail, AIBN was first dissolved in acetone, followed by the addition of deionized water and monomer. Then the mixture was stirred for 7 hours at 70 °C under a nitrogen atmosphere. Finally, PNIPAM-coated MNPs were magnetically separated at 40 °C.

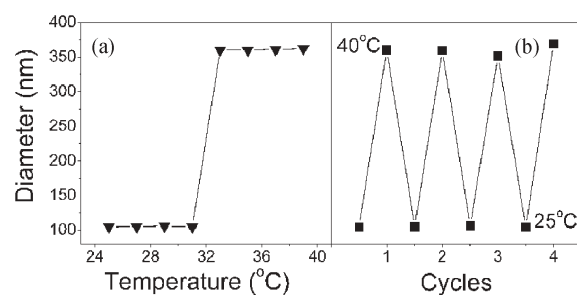
The IR spectrum confirms that PNIPAM has been grafted from the surface of MNPs (see supplementary information†). XPS analysis was also carried out to characterize the surface composition of PNIPAM-coated MNPs. As shown in Fig. 2(c),



**Fig. 3** Photos of responsive behaviour of PNIPAM-coated MNPs' water dispersion: (a) response to the temperature; (b) response to both the temperature and magnetic field.

the characteristic signals for nitrogen (N1s at 403 eV), oxygen (O1s at 530 eV) and carbon (C1s at 285 eV) are clearly observed in the wide scan spectrum and the molar ratio of the carbon : nitrogen is 6.2 : 1 which is close to the theoretical ratio of 6 : 1 for NIPAM. Compared to OA- and MPS-coated MNPs, signals for Fe disappear, indicating that MNPs are well covered with PNIPAM. Three peaks are observed in the C1s core-level spectrum of PNIPAM-coated MNPs. The peak at about 284.6 eV is attributed to C–C and C–H, the peak at 288.2 eV is attributed to N–C=O and the peak at 286.0 eV is attributed to N–C. The area ratio of the three peaks is 3.9 : 0.8 : 1 which is close to the theoretical ratio of 4 : 1 : 1 for NIPAM. PNIPAM graft density on MNPs is calculated to be 2.5 chains nm<sup>-2</sup>, which is lower than the MPS graft density.

The thermo and magnetic sensitivity of PNIPAM-coated MNPs water dispersion was investigated. When an external magnetic field of 1.1 T was applied, an interesting phenomenon was observed. As shown in Fig. 3(b), when the temperature is 25 °C, PNIPAM-coated MNPs can not be separated from their water dispersion. Whereas at 40 °C, these polymer hybrid nanoparticles can easily be separated from their water dispersion. If the temperature is decreased to 25 °C again, MNPs can be re-dispersed well into water reversibly. As far as we know, particles separated by a large distance can be considered non-interacting and the resultant magnetic properties are based solely on the physical characteristics of the particles (*e.g.*, volume, crystallinity, *etc.*). As particles are forced together they exhibit a more collective behavior due to magnetic coupling.<sup>9</sup> Magnetic coupling between adjacent particles alters the magnetic properties of a material through magnetostatic interactions. That is the reason for the temperature-triggered magnetic separation of PNIPAM-coated MNPs. As shown in Fig. 4(a), when the temperature is increased from 25 to 40 °C, the diameter of MNPs increases from 104 nm to 360 nm, which suggests that PNIPAM-coated MNPs get together to form big aggregates. And Fig. 4(b) shows us that the diameter of MNPs changes reversibly with the temperature fluctuation. TEM pictures



**Fig. 4** (a) Relationship between diameters of PNIPAM-coated MNPs and temperature; (b) diameter of PNIPAM-coated MNPs changes with respect to the temperature fluctuation.

also confirm the separated and aggregated states. As shown in Fig. 1(c) taken at 25 °C, MNPs separate from each other, while Fig. 1(d)(e)(f) taken at 40 °C show us that MNPs form big aggregates with a size of about 300 nm. This is because the conformation of PNIPAM chains on MNPs surface changes with the temperature fluctuation. When the temperature is below 32 °C, the hydrophilic PNIPAM chains stretch into water to separate every particle from its neighbours by steric force, while the temperature is above 32 °C, the hydrophobic PNIPAM chains collapse on the surface of the MNPs. Due to the lost of steric force of the PNIPAM chains, MNPs get together to form big aggregates.

In conclusion, methacrylate double bonds have been immobilized on the surface of MNPs without the formation of any aggregates through our novel approach, which is the combination of ligand exchange and condensation of MPS. From the double bonds on the surface, PNIPAM chains graft through precipitation polymerization. The as-synthesized polymer hybrid nanoparticles exhibit temperature-triggered magnetic separation behaviour. When the temperature is below 32 °C, MNPs are dispersed in water so well that they can not be separated under an external magnetic field of 1.1 T. While the temperature is above 32 °C, they can be separated from their water dispersion under the same magnetic field. If the temperature switches between below 32 °C and above 32 °C, MNPs can be re-dispersed into water and re-separated by magnetic field reversibly.

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