

Ferroferric oxide/polystyrene (Fe₃O₄/PS) superparamagnetic nanocomposite via facile *in situ* bulk radical polymerization

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Abstract. Organo-modified ferroferric oxide superparamagnetic nanoparticles, synthesized by the coprecipitation of superparamagnetic nanoparticles in presence of oleic acid (OA), were incorporated in polystyrene (PS) by the facile *in situ* bulk radical polymerization by using 2,2-azobisisobutyronitrile (AIBN) as initiator. The transmission electron microscopy (TEM) analysis of the resultant uniform ferroferric oxide/polystyrene superparamagnetic nanocomposite (Fe₃O₄/PS) showed that the superparamagnetic nanoparticles had been dispersed homogeneously in the polymer matrix due to the surface grafted polystyrene, confirmed by Fourier transform infrared (FT-IR) spectroscopy and thermogravimetric analysis (TGA). The superparamagnetic property of the Fe₃O₄/PS nanocomposite was testified by the vibrating sample magnetometer (VSM) analysis. The strategy developed is expected to be applied for the large-scale industrial manufacturing of the superparamagnetic polymer nanocomposite.

Keywords: nanocomposites, superparamagnetic, bulk polymerization, large-scale manufacturing

1. Introduction

Polymer nanocomposites containing magnetic metal, alloy, or oxide nanoparticles have excellent potential for applications such as electromagnetic interference shielding, magneto-optical storage, biomedical sensing, flexible electronics, biomedicine, separations, etc. Control over the dispersion of the nanoparticle phase embedded in a polymer matrix is critical and often challenging. To achieve excellent dispersion, competition between polymer-polymer and polymer-particle interactions have to be balanced to avoid clustering of particles in polymer nanocomposites [1].

By far, there are two main approaches for the preparation of the polymer-based magnetic nano-

composites: physical mixing and *in situ* polymerization. In the first approach, the magnetic nanoparticles were physically mixed into polymeric matrices after being surface-modified with polymers [2–7]. The strategy is suitable for the large-scale industrial manufacturing, however, the uniform dispersion of the magnetic nanoparticles in the polymeric matrices could not be guaranteed [2]. As for the *in situ* polymerization approach via the solution polymerization [8, 9], dispersion polymerization [10, 11], and emulsion polymerization techniques [12–18], the magnetic nanoparticles are dispersed well in the polymeric matrices. But it is not suitable for the preparation of bulk magnetic nanocomposites because of its low efficiency.

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The bulk polymerization technique is desired to be the most suitable method for the large-scale industrial manufacturing except that, if the magnetic nanofillers are used in the form of small particles, the aggregation of the nanoparticles could be avoided. Most recently, Li *et al.* [19] prepared the bulk transparent PMMA/Fe-oxide nanocomposites via the bulk radical polymerization. In the present work, the ferroferric oxide/polystyrene superparamagnetic nanocomposite (Fe₃O₄/PS) was prepared via the facile bulk radical polymerization of styrene with the incorporation of the oleic acid modified ferroferric oxide superparamagnetic nanoparticles (OA-Fe₃O₄).

2. Experimental

2.1. Materials

Ferric chloride hexahydrate (FeCl₃·6H₂O), ferrous chloride tetrahydrate (FeCl₂·4H₂O), ammonium hydroxide (NH₄OH, 25% of ammonia), and oleic acid (OA) were analytical grade reagents received from Tianjin Chemical Co. (Tianjin, China) and used without further purification and were used as received. The monomer, styrene (St, analytical reagent, Tianjin Chemicals Co. Ltd., China) was dried over CaH₂ and distilled under reduced pressure. The initiator, 2,2'-azobis(isobutyronitrile) (AIBN) (Tianjin Chemicals Ltd. Co. Tianjin, China) was re-crystallization in ethanol. Other reagents used were all analytical grade from Tianjin Chemicals Co. Ltd., China. Distilled water was used throughout.

2.2. OA-Fe₃O₄

The oleic acid modified ferroferric oxide superparamagnetic nanoparticles (OA-Fe₃O₄) were prepared according to our previous report [9]: 2.07 g FeCl₃·6H₂O and 0.81 g FeCl₂·4H₂O were dissolved into 100 ml water with stirring and bubbling with N₂. Then a mixture containing 10.0 ml ammonium hydroxide, 1.0 ml OA and 15 ml water was added dropwise to the solution after it was heated to 90°C. The reacting mixture was stirred for another 30 min after the addition. Finally, the products were collected by a magnet and rinsed with water three times and with ethanol once and dried in vacuum.

2.3. Bulk polymerization

The bulk polymerization was followed: 0.6 g OA-Fe₃O₄, 10 ml styrene, 0.15 g AIBN was added into a glass polymerization pipe, then the mixture was irradiated ultrasonically for 5 min and subsequently heated to 90°C and lasted for 8 h. After the temperature was cooled to room temperature, the polymerization pipe was broken open and the resulting superparamagnetic nanocomposite (Fe₃O₄/PS) was collected.

2.4. Analytical methods

A Bruker IFS 66 v/s infrared spectrometer was used for the Fourier transform infrared (FTIR) spectroscopy analysis. The morphologies of the superparamagnetic nanoparticles were characterized with a JEM-1200 EX/S transmission electron microscope (TEM). Thermogravimetric analysis (TGA) was performed with a Perkin-Elmer performed with a Perkin-Elmer TGA system from room temperature to 800°C in N₂ at a scan rate of 10°C min⁻¹. The magnetic properties were examined by vibrating sample magnetometer (VSM) (Lakeshore 7304).

3. Results and discussion

The properties of the inorganic nanoparticle/polymer composites definitively depend on the dispersibility of the inorganic nanoparticles in the polymer matrices. Surface modification of the inorganic nanoparticles with polymers has been validated to be the most impactful method to improve the dispersibility of the inorganic nanoparticles in the polymer matrices [20]. In the preparation of the magnetic nanocomposites via the *in situ* polymerization technique, oleic acid (OA) is the most used surface-modifier for the magnetic nanoparticles [21]. By modification with OA, the magnetic nanoparticles could be dispersed well in the monomers. Furthermore, the polymer grafted magnetic nanoparticles could be achieved by the copolymerization of the monomers and OA molecules immobilized on the surfaces of the magnetic nanoparticles. Therefore, the aggregation of the magnetic nanoparticles could be avoided and the uniform dispersion of the magnetic nanoparticles is obtained.

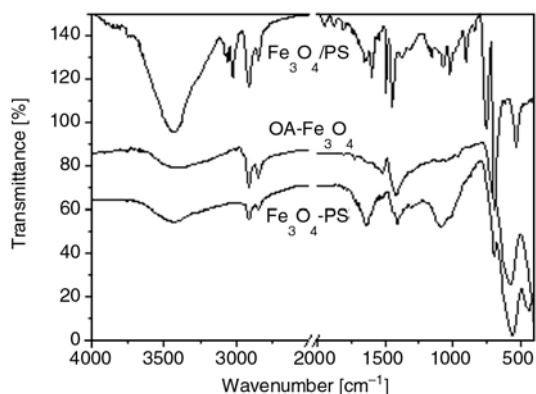


Figure 1. FT-IR spectra of the OA-Fe₃O₄ and Fe₃O₄-PS nanoparticles and Fe₃O₄/PS nanocomposite

The FT-IR spectrum reveals the nature of the bond that is formed between OA and the surface atoms. The antisymmetric and symmetric vibrations at 2920 and 2850 cm⁻¹, respectively, are clearly observed due to the aliphatic alkyl chains (Figure 1). The presence of two peaks at 1520 and 1425 cm⁻¹, attributed to the carboxylate unit vibration modes, shows that oleic acid is bound through the carboxylate anions, i.e. chemisorptions of the surfactant on the iron oxide surface. Except the chemisorbed amount, a physisorbed part was also present as evidenced by a less intense peak at 1721 cm⁻¹ (-COOH) because the miscibility of oleic acid with ethanol is low [22]. The TGA analysis (Figure 2) showed that the OA content of the OA-Fe₃O₄ nanoparticles were more than 20%.

In our previous work [9], the ferroferric oxide/polystyrene superparamagnetic nanocomposites (Fe₃O₄/PS) were prepared by the *in situ* solution polymerization of styrene in the presence of the OA-Fe₃O₄ nanoparticles. It was found that the highest percent of grafting (PG%) had been

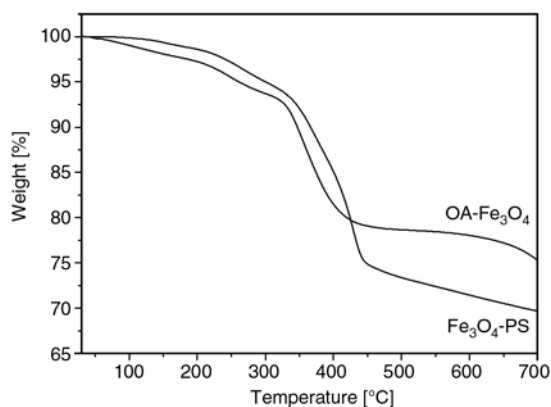


Figure 2. TGA curves of the OA-Fe₃O₄ and Fe₃O₄-PS nanoparticles

achieved in the polymerization of 10.0 ml styrene with 0.60 g OA-Fe₃O₄ nanoparticles added in 10 ml toluene. So the ratio of the magnetic nanoparticles and monomer was applied in the present work.

After the *in situ* bulk radical polymerization, the magnetic nanoparticles in the magnetic nanocomposite (Fe₃O₄/PS) were characterized with FT-IR and TGA techniques after being separated from the non-grafted PS by extracting the Fe₃O₄/PS with toluene, as reported previously [21]. Besides the same absorbance bands at 2920 and 2850 cm⁻¹ of the CH₂ antisymmetric and symmetric vibrations, the characteristic absorption peaks at 580 cm⁻¹ attributed to the lattice absorption of magnetite in the FT-IR spectra of the OA-Fe₃O₄ nanoparticles and the magnetic nanoparticles in the magnetic nanocomposite (Fe₃O₄/PS), the absorbance band at 699 cm⁻¹ attributed to the phenyl structure, which is not present in the FT-IR spectrum of the OA-Fe₃O₄ nanoparticles, appeared (Figure 1). It indicated that the polystyrene had been successfully grafted onto the surfaces of the superparamagnetic nanoparticles via the *in situ* bulk polymerization. So the uniform grey-black superparamagnetic nanocomposite was achieved in the present work. Compared with the obvious macroscopic aggregations reported [23], the vital difference is the higher OA content in the OA-Fe₃O₄ nanoparticles.

The grafting percentage (GP%, mass ratio of the organic and inorganic components) of the polystyrene grafted magnetic nanoparticles (Fe₃O₄-PS) was calculated to be about 30% from the TGA analysis (Figure 2). The main weight loss of both OA-Fe₃O₄ and Fe₃O₄-PS occurred in the temperature range of 350–450°C, attributed to the thermal degradation of OA and PS modified on the surfaces of the magnetic nanoparticles.

Compared with the small aggregations of the oleic acid modified ferroferric oxide magnetic nanoparticles (OA-Fe₃O₄) in toluene as shown in Figure 3, most of the magnetic nanoparticles had been dispersed into toluene with diameter less than 10 nm in the polystyrene grafted magnetic nanoparticles (Fe₃O₄-PS). In fact, the magnetic nanoparticles tend to form the aggregations because of their magnetic forces although oleic acid molecules had been terminated on their surface. The aggregations seen in the OA-Fe₃O₄ nanoparticles were the clusters of OA-Fe₃O₄ nanoparticles, not the real aggregations of the magnetic nanoparticles. Their magnetic

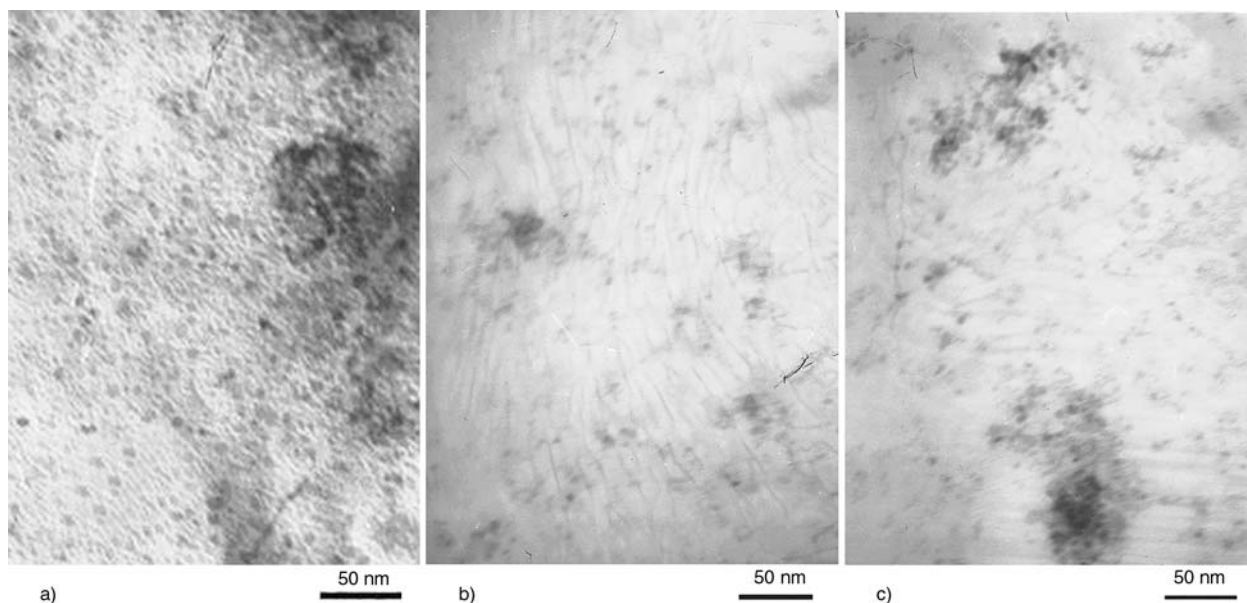


Figure 3. The TEM images of the OA-Fe₃O₄ (a), Fe₃O₄-PS (b) nanoparticles and PS/Fe₃O₄ nanocomposite (c)

forces could be conquered after the polystyrene macromolecules had been grafted. So they showed the better dispersibility in the organic solvent.

The hysteresis curves of the OA-Fe₃O₄ nanoparticles, Fe₃O₄-PS nanoparticles, and Fe₃O₄/PS nanocomposite were illustrated in Figure 4. Neither the remanence nor the coercivity was observed in the three hysteresis curves. They showed superparamagnetic with the saturation magnetization (M_s) values of 32, 40, and 2.2 emu/g at 25°C, respectively. It indicated that the polymerization did not affect magnetic properties of the nanoparticles. The saturation magnetization value of the Fe₃O₄-PS nanoparticles was higher than that of the OA-Fe₃O₄ nanoparticles because of the excellent dispersion of the magnetic nanoparticles. Furthermore, the saturation magnetization (M_s) value of the accidental sampling Fe₃O₄/PS nanocomposite was near to the

theoretic value of about 2.3 emu/g. It indicated that the monomer conversion in the *in situ* radical bulk polymerization was near to 100% and the magnetic nanoparticles were dispersed uniformly in the polymer matrix. It is expected that the superparamagnetic polymer nanocomposite with different saturation magnetization values could be prepared with the strategy developed by simply changing the magnetic nanoparticles feeding ratio.

4. Conclusions

In summary, a facile *in situ* bulk radical polymerization strategy was developed for the preparation of the superparamagnetic nanocomposite (Fe₃O₄/PS). The polymerization did not affect magnetic properties of the nanoparticles. The strategy developed is expected to be applied for the large-scale industrial manufacturing of the superparamagnetic polymer nanocomposite due to the advantages such as simple manipulation and high efficiency.

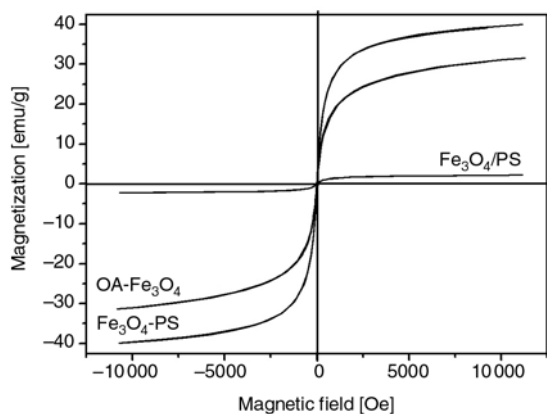


Figure 4. Magnetization curves of OA-Fe₃O₄, Fe₃O₄-PS and Fe₃O₄/PS

References

- [1] Pyun J.: Nanocomposite materials from functional polymers and magnetic colloids. *Polymer Reviews*, **47**, 231–263 (2007). DOI: [10.1080/15583720701271294](https://doi.org/10.1080/15583720701271294)
- [2] Xu C., Ohno K., Ladmira V., Composto R. J.: Dispersion of polymer-grafted magnetic nanoparticles in homopolymers and block copolymers. *Polymer*, **49**, 3568–3577 (2008). DOI: [10.1016/j.polymer.2008.05.040](https://doi.org/10.1016/j.polymer.2008.05.040)

- [3] Garcia I., Tercjak A., Gutierrez J., Rueda L., Mondragon I.: Nanostructuration via solvent vapor exposure of poly(2-vinyl pyridine-*b*-methyl methacrylate) nanocomposites using modified magnetic nanoparticles. *Journal of Physical Chemistry C*, **112**, 14343–14347 (2008).
DOI: [10.1021/jp802345q](https://doi.org/10.1021/jp802345q)
- [4] Yáñez-Flores I. G., Betanvount-Galindo R., Aquino J. A. M., Rodríguez-Fernández O.: Preparation and characterization of magnetic PVC nanocomposites. *Journal of Non-Crystalline Solids*, **353**, 799–801 (2007).
DOI: [10.1016/j.jnoncrysol.2006.12.109](https://doi.org/10.1016/j.jnoncrysol.2006.12.109)
- [5] Fang P. F., Chen Z., Zhang S. P., Wang S. J., Wang L. Y., Feng J. W.: Microstructure and thermal properties of ethylene-(vinyl acetate) copolymer/rectorite nanocomposites. *Polymer International*, **55**, 312–318 (2006).
DOI: [10.1002/pi.1957](https://doi.org/10.1002/pi.1957)
- [6] Yang T-I., Brown R. N. C., Kempel L. C., Kofinas P.: Magneto-dielectric properties of polymer-Fe₃O₄ nanocomposites. *Journal of Magnetism and Magnetic Materials*, **320**, 2714–2720 (2008).
DOI: [10.1016/j.jmmm.2008.06.008](https://doi.org/10.1016/j.jmmm.2008.06.008)
- [7] Hoppe C. E., Rivadulla F., López-Quintela M. A., Buján M. C., Rivas J., Estantes D., Baldomir D.: Effect of submicrometer clustering on the magnetic properties of free-standing superparamagnetic nanocomposites. *Journal of Physical Chemistry C*, **112**, 13099–13104 (2008).
DOI: [10.1021/jp8039548](https://doi.org/10.1021/jp8039548)
- [8] Dallas P., Georgakilas V., Dimitrios N., Komninou P., Kehagias T., Petridis D.: Synthesis, characterization and thermal properties of polymer/magnetite nanocomposites. *Nanotechnology*, **17**, 2046–2053 (2006).
DOI: [10.1088/0957-4484/17/8/043](https://doi.org/10.1088/0957-4484/17/8/043)
- [9] Liu P., Zhong W., Shi H. G., Xue D. S.: Polymer grafted magnetite nanoparticles via a facile in-situ solution radical polymerization. *Journal of Experimental Nanoscience*, **4**, 323–329 (2009).
DOI: [10.1080/17458080903108150](https://doi.org/10.1080/17458080903108150)
- [10] Gyergyek S., Huskic M., Makovec D., Drogenik M.: Superparamagnetic nanocomposites of iron oxide in a polymethyl methacrylate matrix synthesized by in situ polymerization. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **317**, 49–55 (2008).
DOI: [10.1016/j.colsurfa.2007.09.035](https://doi.org/10.1016/j.colsurfa.2007.09.035)
- [11] Fan L-H., Luo Y-L., Chen Y-S., Zhang C-H., Wei Q-B.: Preparation and characterization of Fe₃O₄ magnetic composite microspheres covered by a P(MAH-co-MAA) copolymer. *Journal of Nanoparticle Research*, **11**, 449–458 (2009).
DOI: [10.1007/s11051-008-9556-z](https://doi.org/10.1007/s11051-008-9556-z)
- [12] Qiu G. H., Wang Q., Wang C., Lau W., Guo Y. L.: Polystyrene/Fe₃O₄ magnetic emulsion and nanocomposite prepared by ultrasonically initiated miniemulsion polymerization. *Ultrasonics Sonochemistry*, **14**, 55–61 (2007).
DOI: [10.1016/j.ultsonch.2006.03.001](https://doi.org/10.1016/j.ultsonch.2006.03.001)
- [13] Jiang J.: Ultrasonic-assisted synthesis of PMMA/Ni_{0.5}Zn_{0.5}Fe₂O₄ nanocomposite in mixed surfactant system. *European Polymer Journal*, **43**, 1724–1728 (2007).
DOI: [10.1016/j.eurpolymj.2007.02.011](https://doi.org/10.1016/j.eurpolymj.2007.02.011)
- [14] Martins M. A., Neves M. C., Esteves A. C. C., Girginova P. I., Guiomar A. J., Amaral V. S., Trindade T.: Biofunctionalized ferromagnetic CoPt₃/polymer nanocomposites. *Nanotechnology*, **18**, 215609 (2007).
DOI: [10.1088/0957-4484/18/21/215609](https://doi.org/10.1088/0957-4484/18/21/215609)
- [15] Mahdavian A. R., Ashijari M., Mobarakeh H. S.: Nanocomposite particles with core-shell morphology. I. Preparation and characterization of Fe₃O₄-poly(butyl acrylate-styrene) particles via miniemulsion polymerization. *Journal of Applied Polymer Science*, **110**, 1242–1249 (2008).
DOI: [10.1002/app.28729](https://doi.org/10.1002/app.28729)
- [16] Liu H., Xu F., Li L. C., Wang Y. P., Qiu H. Z.: A novel CoFe₂O₄/polyacrylate nanocomposite prepared via an *in situ* polymerization in emulsion system. *Reactive and Functional Polymers*, **69**, 43–47 (2009).
DOI: [10.1016/j.reactfunctpolym.2008.10.009](https://doi.org/10.1016/j.reactfunctpolym.2008.10.009)
- [17] Yang S., Liu H. R., Huang H. F., Zhang Z. C.: Fabrication of superparamagnetic magnetite/poly(styrene-co-12-acryloxy-9-octadecenoic acid) nanocomposite microspheres with controllable structure. *Journal of Colloid and Interface Science*, **338**, 584–590 (2009).
DOI: [10.1016/j.jcis.2009.07.007](https://doi.org/10.1016/j.jcis.2009.07.007)
- [18] Zhang X. J., Jiang W., Li F. S., Sun Z. D., Ou'yang Z.: Controllable preparation of magnetic polymer nanospheres with high saturation magnetization by miniemulsion polymerization. *Materials Letters*, **64**, 119–121 (2010).
DOI: [10.1016/j.matlet.2009.10.002](https://doi.org/10.1016/j.matlet.2009.10.002)
- [19] Li S. H., Qin J., Formara A., Toprak M., Muhammed M., Kim D. K.: Synthesis and magnetic properties of bulk transparent PMMA/Fe-oxide nanocomposites. *Nanotechnology*, **20**, 185607 (2009).
DOI: [10.1088/0957-4484/20/18/185607](https://doi.org/10.1088/0957-4484/20/18/185607)
- [20] Liu P., Su Z. X.: Thermal stabilities of polystyrene/silica hybrid nanocomposites via microwave-assisted in-situ polymerization. *Materials Chemistry and Physics*, **94**, 412–416 (2005).
DOI: [10.1016/j.matchemphys.2005.05.023](https://doi.org/10.1016/j.matchemphys.2005.05.023)
- [21] Wu W., He Q., Jiang C.: Magnetic iron oxide nanoparticles: Synthesis and surface functionalization strategies. *Nanoscale Research Letters*, **3**, 397–415 (2008).
DOI: [10.1007/s11671-008-9174-9](https://doi.org/10.1007/s11671-008-9174-9)
- [22] Liu G., Liu P.: Synthesis of monodispersed crosslinked nanoparticles decorated with surface carboxyl groups via soapless emulsion polymerization. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **354**, 377–381 (2010).
DOI: [10.1016/j.colsurfa.2009.05.016](https://doi.org/10.1016/j.colsurfa.2009.05.016)
- [23] Xia A., Hu J., Wang C., Jiang D.: Synthesis of magnetic microspheres with controllable structure via polymerization-triggered self-positioning of nanocrystals. *Small*, **3**, 1811–1817 (2007).