

Magnetoresponse hybrid microgels: close packed magnetite nanoparticles core - double layer polymeric shells with anionic or cationic functionalities

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Abstract

Magnetic nanoparticles (MNPs) well separated or in clusters, with proper surface functionalization usually dispersed in liquid carriers or embedded/encapsulated in polymeric networks, are the basic building blocks of a large variety of multifunctional carriers. The encapsulation of magnetic nanoparticles into polymeric micro/nanogel systems gives rise to hybrid magnetic carriers that combine the features of a polymeric gel with the interesting properties of magnetic nanoparticles and make them suitable for applications such as magnetically targeted drug delivery, hyperthermia treatments, magnetic resonance imaging contrast enhancement, magnetic carriers in bioseparation equipments [1-2].

We report the synthesis and characterization of magnetic microgels based on controlled clustering of hydrophobic magnetite nanoparticles and coating with different polymeric shells of poly(N-isopropylacrylamide), polyacrylic acid, poly(3-acrylamidopropyl)-trimethylammonium chloride.

The oil in water miniemulsion method [3] was applied for the preparation of magnetic nanoparticles clusters (NPCs) using toluene based magnetic nanofluid (MF) containing Fe₃O₄ nanoparticles stabilized with a hydrophobic layer of oleic acid. The MF was added to the aqueous solution containing sodium dodecyl sulphate (SDS) as surfactant and treated ultrasonically to obtain small stable droplets with NPCs. The as prepared magnetic miniemulsion was heated to remove the toluene and then was carefully washed several times with methanol-water mixture, magnetically separated and redispersed in water. Stable aqueous dispersions of magnetic nanoparticles clusters coated with the surfactant SDS were used for encapsulation into polymers. Magnetic microgels with cation exchange (CEX) or anion exchange (AEX) functionalities have been obtained by coating the NPCs with two polymer shells using layer by layer free radical polymerization of either N-isopropylacrylamide and acrylic acid (M-NIPA-AAc) or N-isopropylacrylamide and 3-acrylamidopropyl)-trimethylammonium chloride (M-NIPA-APTAC) in the presence of the crosslinker N,N-methylene bis-acrylamide and oxidant ammonium persulfate.

The TEM image of NPCs coated with SDS, figure 1 shows that magnetite nanoparticles stabilized with oleic acid are densely packed into spherical clusters coated with SDS with sizes in the range 100-500 nm. Dynamic light scattering and zeta potential measurements of the microgels gives values of the mean hydrodynamic diameter, Dh in the range 517-914 nm and zeta potential values between -23mV and -37mV for CEX microgels and between +35 mV and +39 mV for AEX microgels. The magnetization vs. applied magnetic field at room temperature for NPCs stabilized with SDS and for magnetic microgels shows superparamagnetic behavior, the saturation magnetization has relatively high values in the range 46-56 emu/g, figure 2.

The chemical surface analysis of magnetic nanoparticle clusters and magnetic microgels was performed by X-ray Photoelectron spectroscopy (XPS). The coating of NPCs stabilized with SDS with double layer of polymers poly(N-isopropyl acrylamide) and polyacrylic acid is evidenced by the characteristic peaks in XPS spectra: (i) amide group N-C=O (286 eV) in C1s spectrum, NH (399 eV) in N1s spectrum, C=O (532.5 eV) in O1s spectrum, which are specific for pNIPA; (ii) carboxyl group O-C=O in C1s and O1s spectrum, specific for pAAc. XPS spectra of AEX magnetic microgel, confirm the double layer polymer coating of SDS stabilized NPCs with poly(N-isopropyl acrylamide) and poly(3-Acryloamido-propyl trimethylammonium chloride), figure 3.

The CEX and AEX magnetic microgels exhibit good stability, high saturation magnetization/large magnetic moment, response to moderate magnetic fields, being promising materials for applications in high gradient magnetic separation and nanomedicine.

References

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- [3] P. Qiu, C. Jensen, N. Charity, R. Towner, C. Mao, J. AM. CHEM. SOC. **132** (2010) 17724–17732

Acknowledgements

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Figures

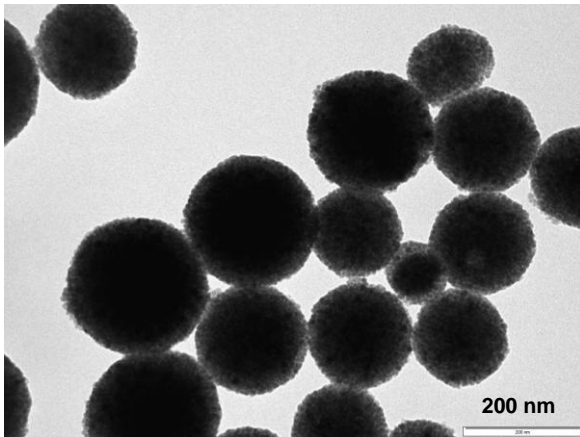


Figure 1. TEM images of NPCs stabilized with SDS prepared by oil in water miniemulsion method

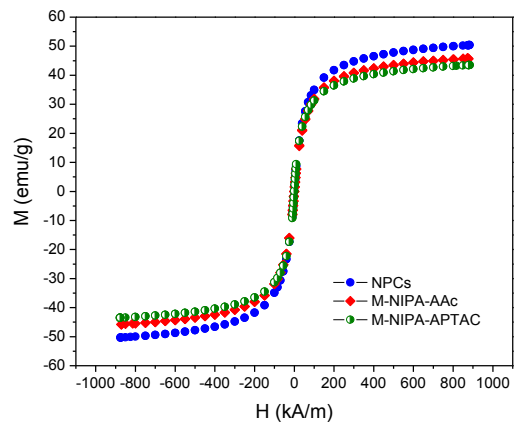


Figure 2. Magnetization curves at room temperature for NPCs and magnetic microgels M-NIPA-AAc (CEX), M-NIPA-APTAC (AEX).

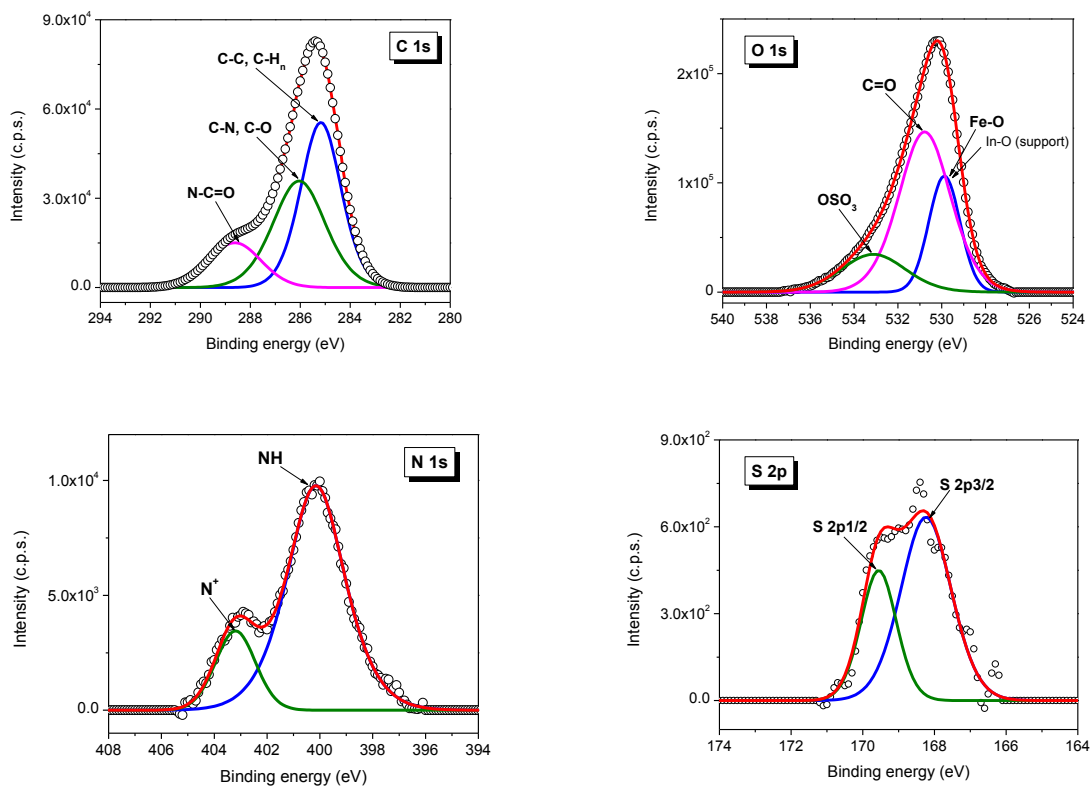


Figure 3. High resolution XPS spectra for C1s, O1s, N1s, S2p, core levels from AEX microgel M-NIPA-APTAC obtained by coating of SDS stabilized NPCs with poly(N-isopropyl acrylamide) and poly(3-Acrylamido-propyl trimethylammonium chloride).