

Synthesis of Polymer-Coated Superparamagnetic Nanoparticles Containing Chelating Ligands

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Extended Abstract

Superparamagnetic iron oxide nanoparticles (SPION) are small synthetic magnetite (Fe_3O_4) and its oxidized form maghemite ($\gamma\text{-Fe}_2\text{O}_3$) particles (Leslie-Pelecky et al., 1996). These nanoparticles have raised much interest during the recent years due to their unique properties (large specific area, superparamagnetism, high saturation field, blocking temperature, etc.) and potential applications in organic synthesis, biotechnology and medicine. The key factor in determining application of SPION in mentioned areas is the shell built around the magnetic core which: prevents cores agglomeration; provides biocompatibility and resistance to physiological conditions such as pH or enzymes; ensures dispersion and stability of these nanoparticles in various solvents, and finally delivers functional groups for further derivatization.

Magnetic nanoparticles may be coated by organic, usually polymeric (Wilczewska, Markiewicz, 2014), or inorganic: silane (Santra et al., 2001) and metallic (Ji et al., 2007) materials. Preparation of coating involves multistep synthetic procedure. It requires highly controlled synthesis protocols to ensure complete coverage of core particles with the coating material. Polymeric shells have some unique advantages over the other materials because of the flexibility in the control of chemical compositions and functions of the polymers.

Acetylacetonone is bidentate ligand able to chelate metal ions and organic compounds (Pawlicki et al., 2011). Thiosemicarbazones are an important class of N,S-donor ligands for transition metal ions because of their mixed hard-soft donor character and versatile coordination behavior (Raja, Ramesh, 2010).

The thiosemicarbazone-based and acetylacetonone-based monomers were synthesized and used to form polymeric shells. Presented monomers are bifunctional - one functionality comes from their coordination behavior (thiosemicarbazone or acetylacetonone) and the other one from their vinyl moieties. The latter enabled radical polymerization of these ligands at the surface of superparamagnetic nanoparticles. The RAFT/MADIX polymerization of synthesized monomers was chosen to obtain polymer shells around magnetic cores. Dithiocarbonates (xanthates) are a chain transfer agents (CTA) used in this polymerization technique and they were covalently anchored to nanoparticles in few step procedure.

The combination of magnetic properties of iron oxide cores and complexing abilities of thiosemicarbazone-based or acetylacetonone-based shells makes them promising materials in applications such as: heavy metal ions removal, organic catalysis or medicine.

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