

Synthesis of Biocompatible Feroxyhyte (δ -FeOOH) Magnetic Nanoparticles Using *in situ* Stabilization with Polyfunctional Humic Macroligands

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Biocompatible iron oxide and oxyhydroxide nanoparticles represent prospective magnetic materials for biomedical applications such as drug delivery, stem cell tracking, magnetic hyperthermia etc. Uncontrolled aggregation is a serious problem in synthesis and storage of magnetic nanoparticles, which considerably limits their application. This problem can be solved by surface modification of nanoparticles with organic macromolecules, which can prevent or inhibit aggregation. Polyethylene glycol (PEG) and its derivatives are extensively used as stabilizing coatings for magnetic iron oxide nanoparticles. However, PEG molecules coat each nanoparticle separately that leads to high concentrations of polymer needed for particles stabilization. Therefore we suggested using for this purpose humic substances (HS) which represent natural polyfunctional macroligands with branched structure rich in carboxylic and phenolic groups that allow coating several nanoparticles by each macromolecule.

In the present work *in situ* stabilization of feroxyhyte (δ -FeOOH) magnetic nanoparticles was carried out using humic acids (HA) from coal. δ -FeOOH magnetic phase was chosen due to its layered structure, which allows for incorporation of various ions and molecules into interlaminar spacing resulting in modification of magnetic properties and physiological activity of nanoparticles. The synthesis of nanoparticles included precipitation and rapid oxidation of "green rust" in HA medium. Then nanoparticles were dialyzed and dried in vacuum under room temperature. According to X-ray diffraction data, HA did not slow down oxidation of "green rust" and formation of δ -FeOOH phase. Transmission electron microscopy images (Fig. 1) show that HA effectively prevented aggregation of nanoparticles both during synthesis and after drying. δ -FeOOH nanoparticles stabilized by HA were plate-like with transverse size \sim 20-30 nm and thickness \sim 2-3 nm. The nanoparticles are partially stacked with characteristic interparticle spacing \sim 0.7 nm (Fig. 1a). On the contrary feroxyhyte synthesized without stabilization formed plate-like particles with transverse size \sim 200-300 nm and thickness \sim 30 nm (Fig. 1b).

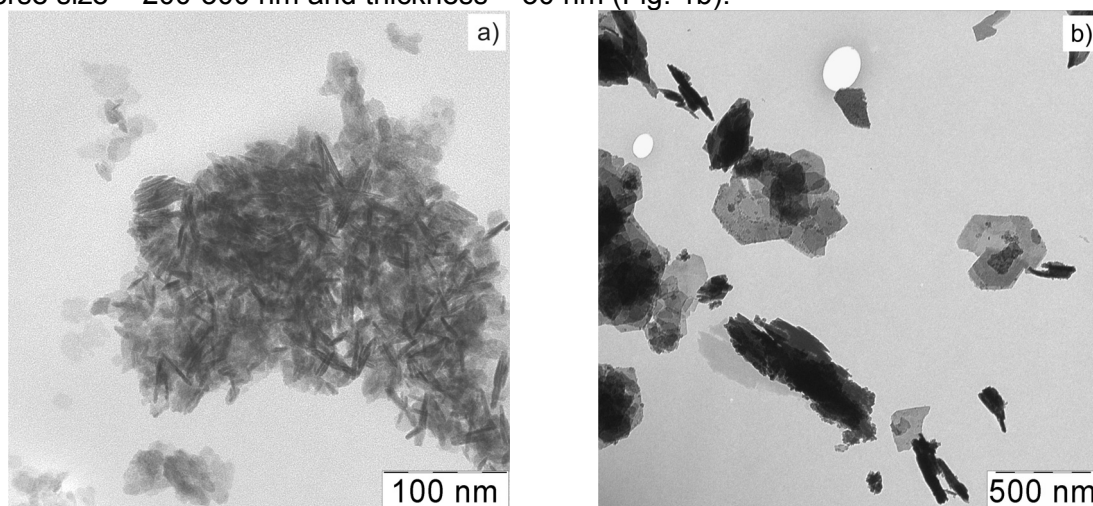


Fig. 1. Transmission electron microscopy images of feroxyhyte (δ -FeOOH) nanoparticles synthesized under different conditions: a) in the presence of HS, b) without HS.

Size reduction of δ -FeOOH crystallites was confirmed by Mössbauer spectra registered at room, liquid-nitrogen and liquid-helium temperatures. These results show a good promise for development of new generation of humic-based magnetic fluids.

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