Synthesis of ultrasmall magnetic iron oxide nanoparticles and study of their colloid and surface chemistry

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ABSTRACT

Colloidal nanoparticles of Fe_3O_4 (4 nm) were synthesized by high-temperature hydrolysis of chelated iron (II) and (III) diethylene glycol alkoxide complexes in a solution of the parent alcohol (H_2DEG) without using capping ligands or surfactants: $[Fe(DEG)Cl_2]^{2-}+2[Fe(DEG)Cl_3]^{2-}+2H_2O+2OH^- \rightarrow Fe_3O_4+3H_2DEG+8Cl^-$ The obtained particles were reacted with different small-molecule polydentate ligands, and the resulting adducts were tested for aqueous colloid formation. Both the carboxyl and α-hydroxyl groups of the hydroxyacids are involved in coordination to the nanoparticles' surface. This coordination provides the major contribution to the stability of the ligand-coated nanoparticles against hydrolysis.

Biomedical applications of magnetic metal oxide nanoparticles require them to form stable aqueous colloids and, therefore, largely rely on their organic coatings. The function of the coating is to stabilize the particles in colloidal form and prevent them from degradation, to decrease toxicity, and to act as a linker for the nanoparticles' biofunctionalization. It is also imperative that the coating be resistant to hydrolysis. The most popular currently used coatings are biocompatible polymers that cloister on nanoparticles, but inevitably bring a large diamagnetic contribution and thus decrease the resulting nanocomposites' magnetic response. Using a small-molecule capping ligand addresses the problem of excessive size, however requires the careful tuning of several parameters. Polymers [1–3], dendrimers [4–6], cyclodextrins [7–9] and large capping ligands [10] stabilize nanoparticles in colloidal form mostly through the steric suppression of interparticle interaction, however the small-molecule ligands like carboxylic, phosphonic and hydroxamic [11] acids engage the electrostatic mechanism in aqueous colloids. Functionalized polymers are efficient in colloid stabilization due to the cooperative effects of the binding of their polar substituents or in-chain heteroatoms to the nanocrystal's surface at multiple sites. Polydentate small-molecule capping ligands are efficient stabilizers for the same cause, however nanoparticles coated with them are more prone to entropy-driven dissociation. Therefore, in order to provide better colloidal stability for the polymer-free nanoparticle systems, the issues of molecular geometry and binding mode of the small-molecule capping ligands, must be addressed in greater detail.

The adsorption of small-molecule ligands on inorganic surfaces has been in focus with regard to their influence on crystal growth [12,13], colloid stabilization [14–16] and catalysis [17]. In this work, we report the synthesis of magnetite and maghemite nanoparticles with chemically active surfaces, studies of their complexation reactions with small-molecule polyfunctional carboxylic acids, and studies of their relative aqueous colloidal stability. One of the aims was to determine the structural features and the binding mode of the most efficient stabilizing agents. The organic substances selected for this study have significantly different molecular geometries and, therefore, different potential binding capabilities. The common feature however is their ability to bind to the same surface at several sites (polydentate bridging ligands). The studied compounds are citric, tartaric, malic, pyromellitic and 5-hydroxyisophthalic acid and β-cyclodextrin.

1. Experimental

Reagents and solvents from commercial sources were: anhydrous iron(II) chloride (99.5%) and iron(III) chloride (98%) from Alfa Aesar, diethylene glycol (DEG) (99%), 1, 2, 4, 5-benzenetetracarboxylic and 5-hydroxyisophthalic acid from Aldrich, sodium metal from Fisher Scientific, anhydrous citric, malic and L(+)-tartaric acids from ACROS Organics. All reagents were used without additional purification. Prior to use, the solvent diethylene glycol was degassed on a vacuum under stirring for at least 1 h. Synthesis and manipulations with air-sensitive materials were performed in the atmosphere of ultra pure nitrogen in a

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glovebox of the Vacuum Atmospheres Company (VAC) and by using the Schlenk technique. Dynamic light scattering (DLS) and electrophoretic mobility experiments were performed on Malvern Zetasizer Nano ZS (ZEN-3600) instrument. Powder X-ray diffraction studies were performed on Rigaku Miniflex II diffractometer (CuKα radiation). Transmission electron microscopy studies were performed on JEOL 2011 TEM instrument. Dynamic magnetic measurements on colloids were carried out using the DynoMag AC susceptometer by IMEGO in a frequency range of 5–200 kHz. The ZFC FC data was measured with Quantum Design MPMS XL (superconducting quantum interference device (SQUID)) and the hysteresis loops were measured with Quantum Design PPMS-ACMS option-using DC extraction.

For synthesis, stock solutions of $FeCl_3$ (0.500 mol/kg), $FeCl_2$ (0.500 mol/kg) and H_2O (1.00 mol/kg) were prepared in the degassed diethylene glycol. Prior to using, the iron salts solutions were purified by centrifuging or filtration. In the first step, the concentrated solution containing all precursors was prepared in a glovebox. The following components in the form of stock solutions were mixed: 3 mmols of $FeCl_3$, 1.5 mmols of $FeCl_2$ and 7 mmols of H_2O (this is a solution A). Sodium metal in a flattened form or as small pieces (13 mmols) was dissolved in 10 mL of diethylene glycol under intensive stirring (this is a solution B). Both solutions (A and B) were mixed and transferred into addition funnel equipped with a gas inlet stopcock. Next, a 500 mL three-necked reactor connected via gas inlet to the Schlenk line was set over magnetic stirrer and heating mantle and equipped with spinbar and thermometer. DEG (160 mL) was added to the reactor and degassed. The addition funnel with the reaction solution was connected to the Schlenk line and attached to the reactor. The reactor temperature was raised to 235 °C and with intensive stirring the precursor solution was injected rapidly (1–2 s) into DEG using the higher pressure of the nitrogen line. The temperature of 220–230 °C was maintained for 5–60 min and the solution was allowed to cool while stirring was continued. The resulting solution contained no precipitate, looked black in bulk, but transparent in thin layer, and showed no light scattering when illuminated with strong incident beam. Colloids exposed to heat for only 5 min and colloids heated at 225 °C for 30–60 min showed similar results in DLS spectra (peak centered at 7–8 nm).

In order to isolate the product in a powdery form for X-ray diffraction, magnetic measurements and for infrared (IR) spectrometry, aliquots of the colloid were precipitated with 1.5 volumes of ethyl acetate (assisted with centrifugation or magnetic separation), the solid then decanted, washed with methanol 2–3 times and dried at room temperature under a flow of nitrogen.

2. Results and discussion

2.1. Synthesis and characterization of magnetite nanoparticles

As we have shown previously [18,19], magnetite and other transition metal ferrites can be conveniently prepared by high-temperature hydrolysis of the chelated diethylene glycol alkoxide complexes in a solution of the parent alcohol, according to the following reaction:

$$[Fe(DEG)Cl_2]^{2-} + 2[Fe(DEG)Cl_3]^{2-} + 2H_2O + 2OH^-$$
$$\rightarrow Fe_3O_4 + 3H_2DEG + 8Cl^-$$
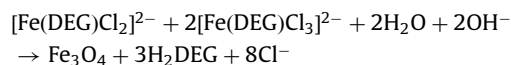
The advantage of this method is that it allows production of the surfactant-, capping ligand- and polymer-free non-aggregated particles with high yield. Surface modification with organic molecules requiring gentle conditions, can be done as a separate step from the rough conditions of the inorganic synthesis. Moreover, since organic ligands dramatically influence kinetics

and mechanism of the crystal nucleation and growth, using and changing the desired organic compounds in the first step of the synthesis would afford no reproducible results in terms of composition and morphology of the resulting nanoparticles. The known practice of ligand exchange however, is associated with lower yields, contamination and also using larger volumes of solvents and sometimes expensive chemicals.

Our original method for the synthesis of ferrite nanoparticles [18,19] uses metal chloride hydrates and sodium hydroxide as main reagents. Composition of these substances is not exact due to their hygroscopic nature and sensitivity of $FeCl_2 \cdot 4H_2O$ to oxygen. These factors lead to some stoichiometrical uncertainty, which can be critical for colloid and surface chemistry. Aiming the development of a new method, capable of providing reproducible results in colloidal and surface chemistry studies, we used the anhydrous salts and the exact amount of water according to the reaction stoichiometry. We also enhanced the protection from moisture and oxygen at all steps of the synthesis. All reagents, including water, were weighed, dissolved and quantitatively mixed into a final concentrated solution in dry glovebox to assure the exact stoichiometry of the reaction, which was performed then using the Schlenk technique. We also used the injection technique, which we did not use in [18,19], however we did not find evidence that this change was beneficial.

Crystal structure of the obtained products was examined by powder X-ray diffractometry. Samples of magnetite powders isolated from colloids after a short (10 min) and long (1 h) heating at 225 °C showed almost identical diffractograms (Fig. 1) that were consistent with the literature cubic inversed spinel pattern. The average crystal size calculated using the Scherrer's formula was 5.3 nm.

Upon exposure to open air the optical density of the original magnetite colloids decreases in several days, and the originally black solutions of magnetite become dark brown. This is attributed to the oxidation of magnetite into maghemite. We examined this reaction in more details by passing oxygen through the colloid for several hours and comparing the DLS spectra of the original and resulting fluid. No substantial difference in the position and intensity of the peak centered at 7–8 nm was found. Calculations of the expected size change, assuming that iron content in each particle is constant, and using the bulk density of Fe_3O_4 equal to 5.18 g/cm^3 and Fe_2O_3 equal to 4.87 g/cm^3, show that 4 nm particles of maghemite originate from 3.87 nm particles of magnetite. This difference is below the resolution limit of the DLS method.
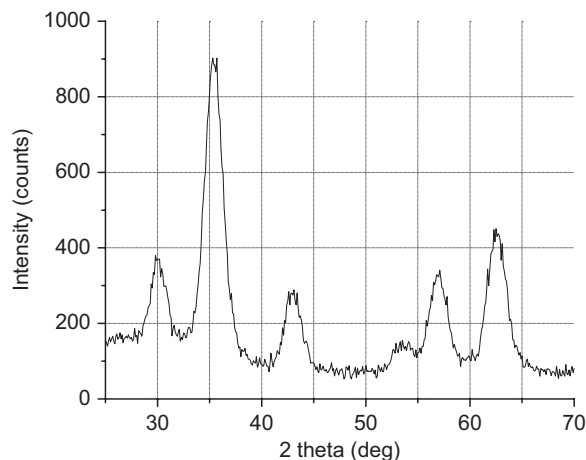

Fig. 1. X-ray diffractogram for the Fe_3O_4 DEG colloid obtained after 15 min of heating at 225 °C.