



# Synthesis and characterization of the superparamagnetic iron oxide nanoparticles modified with cationic chitosan and coated with silica shell



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## ABSTRACT

Novel method for synthesis of superparamagnetic iron oxide nanoparticles (SPION) modified with a cationic chitosan (CCh) and coated with a silica shell, SPION-CCh-SiO<sub>2</sub> was developed. The process was carried out in two steps. In the first step the chitosan coated SPIONs were obtained by co-precipitation of Fe<sup>2+</sup> and Fe<sup>3+</sup> with ammonium hydroxide in aqueous solution of CCh. In the second one, the silica shell is formed on their surfaces. The formation of SPION-CCh-SiO<sub>2</sub> was achieved by direct decomposition of tetraethoxysilane (TEOS) adsorbed on a surface of SPION-CCh dispersed in aqueous phase under sonication and mechanical stirring at room temperature. The chemical composition and physicochemical properties of the materials were determined using X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Dynamic Light Scattering (DLS) and zeta potential measurements. The morphology of the particles was evaluated by Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM). Magnetic properties were confirmed using Atomic Force Microscopy/Magnetic Force Microscopy (AFM/MFM) and magnetization measurements. The resulting products are negatively charged, rounded in shape and exhibit the superparamagnetic properties what implies their potential applications in engineering and biomedicine areas.

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## 1. Introduction

Recently, magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles (NPs) have attracted considerable attention because of their biocompatibility and remarkable magnetic properties [1–3]. Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles have an inverse spinel structure, which exhibit superparamagnetism with high saturation magnetization. These superparamagnetic iron oxide nanoparticles (SPION) can find wide range of potential applications in various areas such as: magnetic separation, magnetic resonance imaging, cell labeling, and targeted drug delivery [4–7]. Unfortunately, the practical applications of pristine SPIONs is hindered by their tendency for aggregation with formation of large clusters and rapid biodegradation when they are exposed in a biological systems. Coating the Fe<sub>3</sub>O<sub>4</sub> NPs with an inert host material, or fabrication of inert host particles containing the magnetic particles are considered as possible methods which can be applied to avoid these limitations. Various inorganic materials have been reported to form stable

shells on nano/microparticles [8,9] and among them silica is one of the most popular. This is due to its desirable properties, including non-toxicity, ease of fabrication, stability in most chemical and biological environments, and what is also very important – minimal residual magnetism [10–12]. Silica improves biocompatibility and provides a negative surface charge under physiological pH, imitating most biological species. The silanol groups make the surfaces of particles lyophilic, thus enhancing the stability for their suspensions even during changes in pH or electrolyte concentration [13]. Additionally, nanostructures derived from silica-coated SPIONs could further be directed to a specific target via the antibody–antigen recognition by conjugation of antibodies to the outer silica surface [14].

Up to date, many methods have been reported for coating of SPIONs with silica, including sol–gel process, microemulsion, and solution reaction [15–17]. According to Santra et al. [18], magnetite/silica particles can be prepared by reverse-micelle microemulsion method in organic phase such as cyclohexane and heptane. Barnakov et al. performed silica coating of magnetite nanoparticles dispersed in toluene in the presence of surfactants [19]. Zhang et al. [20] used an *in situ* reverse microemulsion micelle synthesis

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method to generate silica-coated magnetite particles dispersed in an organic solvent. Woo et al. [21] employed a technique of magnetite treatment with toluene, ammonium hydroxide, and ethanol, followed by the addition of tetraethoxysilane for 1 day. The solution was then heated to 150 °C for 1 h and cooled before 3 amino-propyl-trimethoxysilane was added and again the solution was heated to 150 °C for 1 h and subsequently cooled down to room temperature. The silica-coated magnetite particles with surface propylamine functional groups were obtained as the reaction product. Wang and co-workers examined the preparation of Fe<sub>3</sub>O<sub>4</sub>/silica composite microspheres via miniemulsion polymerization by injecting tetraethoxysilane, Triton X-100, and water into ferrofluid of Fe<sub>3</sub>O<sub>4</sub> NPs [22] and submicron-size Fe<sub>3</sub>O<sub>4</sub>/silica core/shell microspheres by sol-gel method [23]. In those syntheses considerable amounts of the organic solvents and surfactants were employed which is not desired from environmental point of view.

Very popular and widely described in literature is the silica-coating method based on the use of sodium silicate solution. Liu et al. presented the procedure for preparation of silica-coated magnetite nanoparticles by addition of an aqueous HCl solution to an aqueous mixture of the sodium silicate and magnetite nanoparticles [24]. Whereas Sun et al. [25] and Correa-Duarte et al. [26] in their papers described another, two step silica-coating method with the use of sodium silicate solution as well. They employed slow silica deposition in water from the sodium silicate solution, and as a next step the extensive growth of the silica shells through sol-gel reaction in ethanol/ammonia mixtures was carried out.

The another method for synthesis of silica-coated magnetite nanoparticles is based on Stöber synthesis and various approaches have been employed for that purpose. Chen et al. [27] proposed the way for the fabrication of monodisperse and air-stable Fe<sub>3</sub>O<sub>4</sub>/silica microspheres. They performed a direct decomposition of tetraethoxysilane in solution in the presence of freshly synthesized Fe<sub>3</sub>O<sub>4</sub> nanoparticles. Sun et al. synthesized the Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> NPs [4] by employing a combination of the mechanical stirring and ultrasonication assisted Stöber synthetic method. The resulted product was well dispersible and exhibited enhanced magnetization saturation. Yang and co-workers also prepared the Fe<sub>3</sub>O<sub>4</sub>/silica composite NPs: they introduced Fe<sub>3</sub>O<sub>4</sub> NPs into the Stöber process after formation of the primary silica particles [28]. Kobayashi et al. proposed a method for producing silica-coated magnetite nanoparticles in the presence of magnetite nanoparticles surface-modified with a silane coupling agent, carboxyethylsilanetriol. This modification was done to increase the affinity of the magnetite particles to form silica on their surface. The synthesis of the surface-modified particles was performed in the presence of magnetite colloid in aqueous sodium salt solution of the carboxyethylsilanetriol at 70 °C. The product was washed with water and ethanol, centrifuged and sonicated. In the third step the fabrication of the magnetite/silica composite particles was carried out according to the Stöber method with using tetraethoxysilane. They obtained silica particles containing multiple magnetite nanoparticles [29].

In our previous paper [30] we have presented the approach based on the modified Stöber process, in which spherical silica particles doped with iron oxide were synthesized via base-catalyzed one-pot process using tetraethoxysilane (TEOS) and iron(III) ethoxide (ITE) as co-precursors. Depending on the concentration of ITE in the starting composition, materials of various morphologies were obtained. Using magnetic force microscopy (MFM), magnetic susceptibility and magnetization measurements it was demonstrated that resulted materials have magnetic properties. It might be concluded that in comparison with the microemulsion method, the approach based on Stöber synthesis is simple and seem to be more environmentally friendly.

In the current paper we report on the new, facile and simple approach for the synthesis of the superparamagnetic iron oxide

nanoparticles (SPION) modified with cationic chitosan (CCh) and coated with silica shell, SPION-CCh-SiO<sub>2</sub>. We proposed the two-step synthesis, (1) preparation of the SPION with surface modified with CCh (SPION-CCh) by coprecipitation of Fe<sup>2+</sup> and Fe<sup>3+</sup> with NH<sub>3</sub>·H<sub>2</sub>O and (2) formation of SPION-CCh-SiO<sub>2</sub> by direct decomposition of tetraethoxysilane (TEOS) in the presence of dispersed SPION-CCh under sonication and mechanical stirring at room temperature. The cationic chitosan was used to modify the surface potential of SPION, so the base-catalyzed hydrolysis and condensation of the TEOS could occur at the surface. Chitosan is the N-deacetylated product of chitin, one of the most abundant polysaccharide in nature. Chitosan and its derivatives have been applied widely because of their non-toxicity, biocompatibility, and biodegradability. Here we utilized a cationic chitosan, N-[(2-hydroxy-3-trimethylammonium) propyl] chitosan chloride (CCh), which we have synthesized and demonstrated that it is water-soluble and shows hygroscopic property, moisture retentiveness, mucoadhesivity and permeability enhancing properties better than these characteristics for chitosan [31]. The final products (SPION-CCh-SiO<sub>2</sub>) are negatively charged, rounded in shape and exhibit the superparamagnetic properties. The morphology of the material was visualized by TEM and SEM microscopy. The chemical composition and physicochemical properties of the materials were determined using XRD, FTIR spectroscopy, DLS and zeta potential measurements. Magnetic properties were confirmed using AFM/MFM and magnetization measurements.

## 2. Experimental section

### 2.1. Materials

Cationic derivative of chitosan (low molecular weight, Sigma Aldrich), N-[(2-hydroxy-3-trimethylammonium) propyl] chitosan chloride (CCh), was synthesized and characterized according to the procedures described earlier [32]. Iron(III) chloride hexahydrate (Sigma Aldrich), iron(II) chloride tetrahydrate (Sigma Aldrich), tetraethoxysilane (TEOS, ≥98%, Fluka), ethanol (99.8%, spectroscopic grade) and ammonium hydroxide (25%, pure p.a., Chempur) were used as received. Millipore-quality water was used during the experiments.

### 2.2. Preparation of SPION-CCh-SiO<sub>2</sub>

The synthesis of SPION was carried out in an aqueous solution following the procedure which we have developed and described earlier [33]. Shortly, iron salts in molar ratio Fe(III):Fe(II) = 2:1, (0.1622 g FeCl<sub>3</sub>·6H<sub>2</sub>O and 0.0596 g FeCl<sub>2</sub>·4H<sub>2</sub>O) were dissolved in 50 ml of aqueous solution of CCh (c = 3 g/L in 0.1 M NaCl). The solution was deoxygenated by purging with argon and sonicated (Sonic-6, Polsonic, 480 W, 1 s pulse per every 5 s) for 10 min in a thermostated bath at 20 °C. In the next step, 5 ml of 2.44 M NH<sub>3(aq)</sub> was added dropwise and the sonication of the solution was continued for 30 min. Magnetic chromatography was utilized to purify the surface-modified particles and then the obtained suspension was filtered by cellulose syringe filters (0.2 μm). Finally aggregates formed in the suspension were removed with the sedimentation by centrifugating at 13,000 rpm for 60 min prior to silica-coating. Stöber method with tetraethoxysilane (TEOS) was applied to fabricate SPION-CCh-SiO<sub>2</sub> composite particles. To initiate hydrolysis of TEOS the NH<sub>3</sub> solution (25%, 0.52 ml) was added to TEOS/ethanol solution (0.112 ml/1.965 ml) at 30 °C under stirring at 300 rpm. The surface modified magnetite colloid (7.406 ml) was injected at 2 min after the initiation. The mixture was then sonicated for 60 min (amplitude 40, pulser 2 min) and after that the reaction mixture was stirring for 3 h at room temperature. The concentration of TEOS, ethanol, water and ammonia were 0.05, 3.37, 41.1 and 0.68 M, respectively.

### 2.3. Scanning electron microscopy (SEM)

SEM observations were carried out using a cold field emission scanning electron microscope (FESEM) HITACHI S-4700 equipped with a NORAN Vantage energy dispersion spectrometer. Samples for the measurements were prepared by placing a drop of solution on a silicon plate. The solvent was allowed to evaporate at room temperature and subsequently the thin film of carbon was deposited on the sample by sputtering.

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