A MECHANISM FOR THE ADSORPTION OF CARBOXYLIC ACIDS ONTO THE SURFACE OF MAGNETIC NANOPARTICLES

MEHANIZEM ADSORBCIJE KARBOKSILNIH KISLIN NA POVRŠINO MAGNETNIH NANODELCEV

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The unique properties of magnetic nanoparticles, which are dominated by superparamagnetism, and the size dependence of those properties have led to a number of technological and biomedical applications of these materials and to the preparation of stable magnetic fluids or ferrofluids. The main problem relating to the stability of ferrofluids is the difficulty in controlling the dispersion of magnetic nanoparticles inside a liquid medium. To overcome this problem, functionalization of the nanoparticle surface is required. The efficiency of the functionalization process depends on the adsorption mechanism, which involves interactions of the surface-active agent molecules with the nanoparticle surface. The adsorption mechanism for oleic acid onto the surface of maghemite (γ-Fe$_2$O$_3$) nanoparticles prepared with the classic coprecipitation method was followed in solution using *in-situ* infrared spectroscopy (*React*IR). The synthesized maghemite nanoparticles were characterized using transmission electron microscopy (TEM), X-ray diffractometry (XRD) and specific surface area measurements (BET). The specific magnetization of the prepared samples was measured at room temperature with a DSM-10 magneto-susceptometer.

Key words: nanoparticles, precipitation, adsorption, infrared spectroscopy, surface active agent, carboxylic acid

Zaradi edinstvenih lastnosti magnetnih nanodelcev, ki izvirajo iz njihove superparamagnetne narave in so odvisni od velikosti nanodelcev, so magnetni nanomateriali zanimivi za vrsto tehnoloških in biomedicinskih aplikacij ter pri pripravi stabilnih magnetnih tekočin. Za doseganje stabilnosti magnetnih tekočin je potrebno magnetne nanodelce v nosilni tekočini površinsko funkcionalizirati. Učinkovitost procesa funkcionalizacije je odvisna od adsorpcijskega mehanizma, le-ta pa od interakcij med površinsko aktivno snovjo in površino nanodelca. Mehanizem adsorpcije oleinske kisline na površino maghemitnih (γ-Fe$_2$O$_3$) nanodelcev, ki smo jih pripravili z metodo koprecipitacije, smo spremljali v raztopini z uporabo *in-situ* infrardeče spektroskopije (*React*IR). Sintetizirane magnetne nanodelce smo karakterizirali z uporabo presevnega elektronskega mikroskopa (TEM), rentgenske praškovne difrakcije (XRD) in merjenjem specifične površine (BET). Specifično magnetizacijo (magneto-susceptometer, DSM-10) v odvisnosti od magnetnega polja smo merili pri sobni temperaturi.

Ključne besede: nanodelci, obarjanje, adsorpcija, infrardeča spektroskopija, površinsko aktivna snov, karboksilna kislina

1 INTRODUCTION

Magnetic nanoparticles are of great fundamental and technological interest because of their unique magnetic properties, which are dominated by superparamagnetism [1]. Magnetite (Fe$_3$O$_4$) and maghemite (γ-Fe$_2$O$_3$) nanoparticles represent the most often used magnetic materials due to their great potential in current and future technological and biomedical applications [2].

Numerous applications require the magnetic nanoparticles to be well dispersed in a liquid media, chemically stable and uniform in size. For this reason, many studies have focused on the preparation of magnetic fluids or ferrofluids, which represent a stable colloidal suspension of superparamagnetic nanoparticles with a narrow particle size distribution of around 10 nm, coated with a thin layer of surfactant molecules and stably dispersed in a polar or non-polar carrier liquid.

According to the type of carrier liquid, two main groups of ferrofluids are distinguished: *ionic aqueous-based ferrofluids*, if the nanoparticle surface is electrically charged, and a *surfacted organic-based ferrofluids,* if the nanoparticle surface is sterically or electrosterically stabilized [3].

The surfactants used for steric stabilization have to be compatible with the carrier liquid and must overcome the attractive van der Waals and magnetic forces, which are usually present between the magnetic nanoparticles. Due to the magnetic dipolar attractions, unmodified magnetic nanoparticles tend to aggregate and inhibit the advantage of the specific single-domain properties. To prevent magnetic nanoparticles from aggregating, steric stabilization of their surface has to be performed [4].

A variety of monocarboxylic acids have been most often used for the steric stabilization of magnetic nanoparticles in an organic liquid medium. Monocarboxylic acids consist of a polar head, with an affinity for the hydrophilic particle surface, and a non-polar tail, with an affinity for the non-polar liquid medium.

Carboxylic functional groups can be adsorbed onto the surface of maghemite nanoparticles in different modes of coordination. In this regard, spectroscopic techniques such as infrared spectroscopy (IR) are most

often used to obtain information about the nature of the surface species and their mode of coordination.

The main goal of this work was to develop, characterize and optimize the process for the surface functionalization of superparamagnetic maghemite (γ-Fe$_2$O$_3$) nanoparticles with an organic coating and to determine the optimum amount of oleic acid for the most effective steric stabilization of nanoparticles.

With this aim, the mechanism of adsorption for surfactant molecules onto the nanoparticle surface in solution was carefully controlled using *in-situ* infrared spectroscopy (*React*IR), which provides a real-time, dynamic picture of the chemistry under actual reaction conditions and includes the possibility of analyzing the changes in the solution during the chemical reaction.

2 EXPERIMENTAL

Only commercially available reagents were used in this investigation. Iron (II) sulfate heptahydrate (FeSO$_4$ × 7H$_2$O, ACS, 99 + %; AlfaAesar), iron (III) sulfate hydrate (Fe$_2$(SO$_4$)$_3$ × xH$_2$O, Reagent Grade; AlfaAesar) and ammonium hydroxide solution (25 %, puriss p. a.; Fluka) were used as the starting reagents for the preparation of the nanoparticles. Oleic acid (cis-9-Octadecenoic acid, tech. 90 %, AlfaAesar) was used to provide the steric stabilization of the nanoparticles. *n*-Decane (CH$_3$(CH$_2$)$_8$CH$_3$; 99 + %; Alfa Aesar) served as the organic carrier liquid.

Maghemite (γ-Fe$_2$O$_3$) nanoparticles with an average particle size of around 12 nm were prepared using a classic coprecipitation method. Aqueous solutions of iron ions with a molar ratio x(Fe(II))/xFe(III)) = 1.5 were prepared by dissolving of an appropriate amount of iron (II) sulfate heptahydrate, FeSO$_4$ × 7H$_2$O, and iron (III) sulfate hydrate, Fe$_2$(SO$_4$)$_3$ × xH$_2$O in acidic conditions.

The synthesis occurred in a two-step process. In the first step, iron hydroxides were precipitated in an alkaline medium during the reaction between the aqueous solution of metal salts and an aqueous solution of ammonium hydroxide. In the final step of the synthesis the samples were oxidized and maghemite nanoparticles with a spinel structure were obtained. The temperature and the time of the reaction were kept constant at 25 °C and 1 h, respectively.

The synthesized maghemite nanoparticles were characterized using transmission electron microscopy (TEM, Jeol 2000–FX), X-ray diffractometry (XRD,
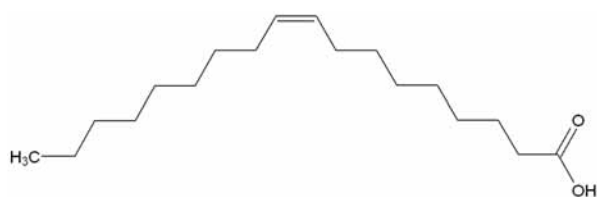
Brucker D4 Endeavour) and specific surface area measurements (BET, Micromeritis, Tristar 3000). The specific magnetization (Magneto – Susceptometer, DSM10) as a function of applied magnetic field at room temperature was also measured for all the prepared samples.

The functionalization process of the maghemite nanoparticle surface with oleic acid (OA) was performed in a solution of maghemite nanoparticles at room temperature within 30 minute intervals using *in-situ* infrared spectroscopy (**Figure 1**). The concentration of the surfactant was varied from the mass fraction 1.5 % to 4.0 % per mass unit of maghemite nanoparticles.

The mechanism of the adsorption of carboxylic acid onto the nanoparticle surface was investigated in solution using *in-situ* infrared spectroscopy.

The coated maghemite nanoparticles were finally dispersed into a small amount of carrier liquid ($\approx$18 % of *n*-decane per mass unit of maghemite nanoparticles) to obtain a stable and magnetically strong ferrofluid. *n*-Decane was used as the carrier liquid because of its low viscosity, low vapor pressure and chemical inertness.

The prepared ferrofluid samples were characterized using transmission electron microscopy and magnetometry.

3 RESULTS AND DISCUSSION

Figure 2 shows the characteristic XRD pattern of the maghemite nanoparticles obtained during the synthesis. The prepared maghemite samples showed very broad diffraction lines, in accordance with their small particle size and high specific surface area.
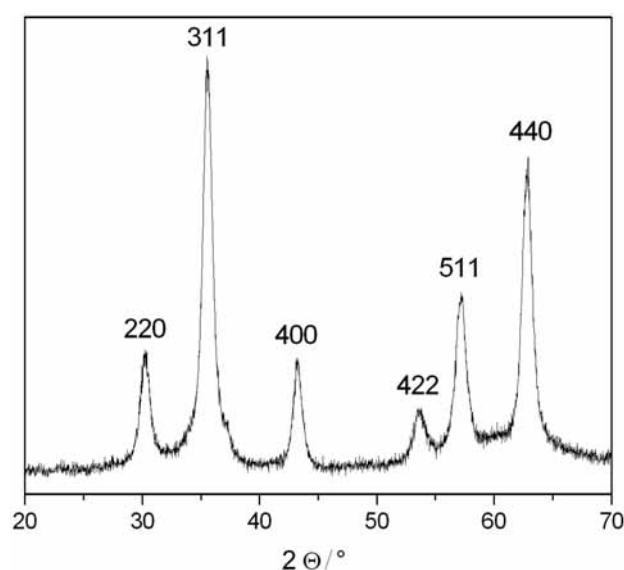

Figure 2: X-ray diffraction pattern of maghemite (γ-Fe$_2$O$_3$) nanoparticles
Slika 2: Rentgenski difraktogram nanodelcev maghemita (γ-Fe$_2$O$_3$)

Figure 1: Chemical structure of oleic acid
Slika 1: Kemijska struktura oleinske kisline

The average particle size determined from the specific surface area measurements (BET), was a little higher than the average particle size established from the (311) diffraction line broadening (**Table 1**), indicating that the particles were slightly agglomerated (**Figure 3**).

Table 1: Specific surface area (BET) and average particle size obtained from BET (D_{BET}) and XRD (D_{XRD})
Tabela 1: Specifična površina (BET) in povprečna velikost delcev določena z BET (D_{BET}) in XRD (D_{XRD})

Sample	$BET/(m^2/g)$	D_{BET}/nm	D_{XRD}/nm
γ-Fe$_2$O$_3$	68 ± 0.2	17 ± 0.1	12 ± 2

Figure 3 shows TEM images of uncoated partially agglomerated maghemite nanoparticles (a), and of maghemite nanoparticles obtained after the functionalization process (b), with a thin organic layer preventing the particles from agglomerating.

Figure 4 shows the IR spectra of pure oleic acid (OA) and maghemite (γ-Fe$_2$O$_3$) nanoparticles coated with OA. The spectrum of γ-Fe$_2$O$_3$ nanoparticles coated with OA was imitated after the functionalization process, 1 h after the addition of the mass fraction 3.4 % of OA per mass unit of γ-Fe$_2$O$_3$ nanoparticles in the solution of the synthesized nanoparticles.

It is worth noting that the C=O stretch presented at 1713 cm^{-1} in the spectra of pure OA was absent in the spectra of the coated nanoparticles and acid adsorbed onto their surface. Furthermore, there were two bands at 1646 cm^{-1} and 1351 cm^{-1}, characteristic for the symmetric $\nu_s(COO^-)$ and the asymmetric $\nu_{as}(COO^-)$ stretch, respectively [5].

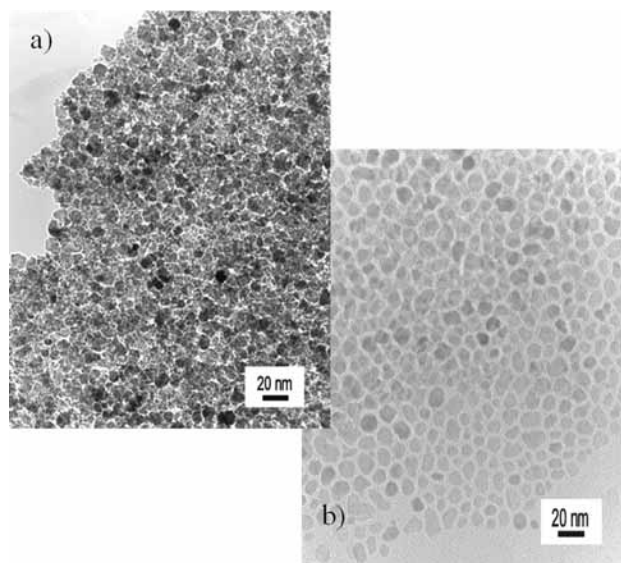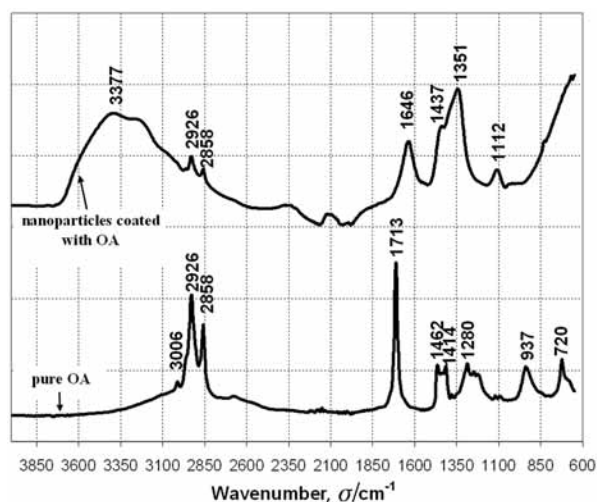This finding indicates that carboxylic acid is chemisorbed onto the nanoparticle surface in carboxylate form

Figure 4: IR spectra of pure OA and maghemite (γ-Fe$_2$O$_3$) nanoparticles coated with OA
Slika 4: IR-spektri čiste OA ter nanodelcev maghemita (γ-Fe$_2$O$_3$), oblečenih z OA

Figure 5: Chemisorption of carboxylic acid onto the maghemite nanoparticle surface
Slika 5: Kemisorpcija karboksilne kisline na površino maghemitnih nanodelcev
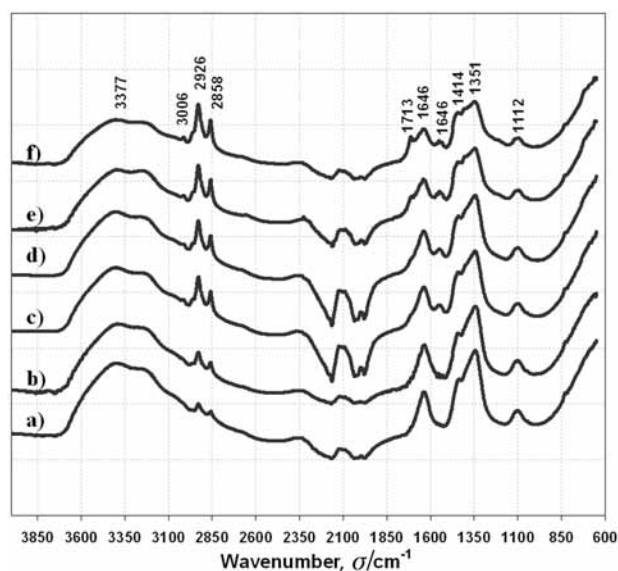

Figure 3: TEM images of a) uncoated and b) coated maghemite (γ-Fe$_2$O$_3$) nanoparticles
Slika 3: TEM-posnetek a) neoblečenih in b) oblečenih nanodelcev maghemita (γ-Fe$_2$O$_3$)

Figure 6: IR spectra of γ-Fe$_2$O$_3$ nanoparticles coated with different amounts of OA in mass fractions: a) 1.5 %, b) 2 %, c) 2.9 %, d) 3.4 %, e) 3.7 %, f) 4 % OA per mass unit of maghemite nanoparticles
Slika 6: IR-spektri maghemitnih γ-Fe$_2$O$_3$ nanodelcev po oblačenju z različnimi masnimi deleži OA: a) 1,5 %, b) 2 %, c) 2,9 %, d) 3,4 %, e) 3,7 %, f) 4 %
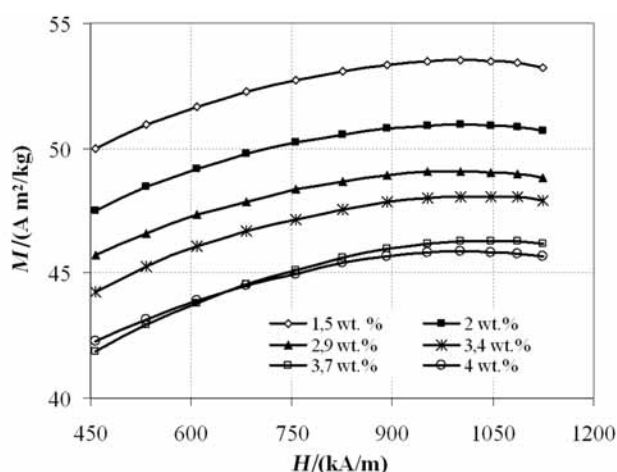
Figure 7: The specific magnetization of the prepared maghemite nanoparticles coated with different amounts of oleic acid
Slika 7: Specifična magnetizacija maghemitnih nanodelcev oblečenih z različnimi masnimi deleži oleinske kisline

(**Figure 5**), with two oxygen atoms that are symmetrically coordinated to the nanoparticle surface [6,7,8].

These results reveal the significance of surface interactions between the surfactant molecules and the nanoparticle surface for the preparation of organic-based ferrofluids. Furthermore, the appropriate amount of OA required for the most effective steric stabilization of the nanoparticles was also investigated.

Figure 6 presents the infrared spectra of γ-Fe$_2$O$_3$ nanoparticles coated with different amounts of OA, imitated after the functionalization process in the solution. The most characteristic peak of pure OA at 1713 cm^{-1} in Figure 4 was absent in **Figure 6** for a content of OA below the mass fraction 3.4 % per mass unit of γ-Fe$_2$O$_3$ nanoparticles, indicating that all the OA molecules were chemisorbed onto the nanoparticle surface.

With further increases of the OA content above 3.7 % per mass unit of γ-Fe$_2$O$_3$ nanoparticles, the characteristic peak of pure OA appeared, indicating that free molecules of OA were present in the solution.

From this we can conclude that a content of 3.7 % of OA per mass unit of γ-Fe$_2$O$_3$ nanoparticles represents the maximum content of OA to obtain the most effective steric stabilization of γ-Fe$_2$O$_3$ nanoparticles in order to prepare an organic-based ferrofluid with a high specific magnetization.

The specific magnetization of the prepared γ-Fe$_2$O$_3$ nanoparticles was around 59 A m^2/kg. **Figure 7** shows the specific magnetization of the prepared γ-Fe$_2$O$_3$ nanoparticles coated with different amounts of OA. With an increasing content of OA, the specific magnetization of the coated γ-Fe$_2$O$_3$ nanoparticles decreased from 53 A m^2/kg for the samples prepared with 1.5 % of OA per mass unit of γ-Fe$_2$O$_3$ nanoparticles to 46 A m^2/kg for the samples prepared with 4 % of OA per mass unit of

γ-Fe$_2$O$_3$ nanoparticles due to the increasing thickness of the nonmagnetic carboxylate shell. With an increasing content of OA above 3.7 % of OA per mass unit of γ-Fe$_2$O$_3$ nanoparticles, the nanoparticles were completely coated and the specific magnetization was stabilized at 46 A m^2/kg.

The specific magnetization of the ferrofluid sample, prepared from γ-Fe$_2$O$_3$ nanoparticles coated with 3.7 % of OA per mass unit of γ-Fe$_2$O$_3$ nanoparticles and dispersed in n-Decane as a carrier liquid, was around 38 A m^2/kg.

4 CONCLUSIONS

The adsorption of oleic acid (OA) onto the surface of maghemite (γ-Fe$_2$O$_3$) nanoparticles, which is of great importance for the preparation of ferrofluids, was investigated in solution using *in-situ* infrared spectroscopy. The results indicated that hydrophilic head–groups of oleic acid were chemisorbed onto the nanoparticle surface in a carboxylate form with two oxygen atoms that are symmetrically coordinated to the nanoparticle surface.

The most effective steric stabilization of γ-Fe$_2$O$_3$ nanoparticles was obtained in the range between mass fractions 1.5 % and 3.4 % of OA per mass unit of γ-Fe$_2$O$_3$ nanoparticles. In-situ IR spectroscopy was shown as an applicable method for determining the appropriate amount of surfactant molecules required for the steric stabilization of maghemite nanoparticles in a carrier liquid.

The specific magnetization of the prepared g-Fe$_2$O$_3$ nanoparticles was around 59 A m^2/kg and decreased to 46 A m^2/kg for the γ-Fe$_2$O$_3$ nanoparticles coated with 4 % of OA per mass unit of γ-Fe$_2$O$_3$ nanoparticles due to the nonmagnetic carboxylate shell. The specific magnetization of the ferrofluid sample, prepared from γ-Fe$_2$O$_3$ nanoparticles coated with 3.7 % of OA per mass unit of γ-Fe$_2$O$_3$ nanoparticles and dispersed in n-Decane as a carrier liquid, was around 38 A m^2/kg.

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