POLYMER-COATED IRON OXIDE MAGNETIC NANOPARTICLES – PREPARATION AND CHARACTERIZATION

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Abstract

This contribution presents the production of polymer-coated iron oxide magnetic nanoparticles carrying functional groups on their surface and their basic characterization. The preparation of polymer-coated nanoparticles was carried out by a two-step process. In the first step, magnetite (Fe₃O₄) nanoparticles were prepared by a co-precipitation method from the solutions of FeCl₂.4H₂O and FeCl₃.6H₂O using aqueous solution of NaOH. In the second step, obtained magnetic nanoparticles were coated with polymer using emulsion polymerization at high surfactant to monomer ratio. Methyl methacrylate (MMA) and acrylic acid (AAc) were used as comonomers, sodium dodecyl sulfate (SDS) as a surfactant and potassium persulfate (KPS) as an initiator.

Keywords: magnetic nanoparticles, iron oxide, polymer coating, carboxyl groups

1. INTRODUCTION

In recent years, considerable attention has been paid to iron oxide magnetic nanoparticles due to their unique magnetic properties (superparamagnetism, high coercivity, low Curie temperature, high magnetic susceptibility, etc.), non-toxicity, biocompatibility and low cost of production, which allows their usage in various nanotechnology applications in a broad range of disciplines. Magnetic ferrofluids and data storage led to the integration of magnetic nanoparticles in a numerous of commercial purposes [1]. Today, magnetic nanoparticles are also important in biomedical applications (e.g. magnetic bioseparation [2], magnetic target drug delivery [3], hyperthermia [4], magnetic resonance imaging [5], magnetofection [6], etc.). These particles have an ability to interact with various biological molecules in different ways due to their superparamagnetic properties, high specific area and wide choice of surface functionalization. Their surface can be easily modified through the creation of few atomic layers of organic (polymer) or inorganic (metal or oxide) surfaces, suitable for further functionalization with various bioactive molecules [7, 8]. In separation processes, particles would simply separate the target biomolecules with a single magnet instead of centrifugation or precipitation [9].

There are many different methods to prepare Fe₃O₄ nanoparticles such as mechanical grinding, laser ablation, chemical co-precipitation, hydrolyzation, microemulsions, etc. Among these, the chemical co-precipitation may be the most promising one because of its simplicity, productivity and low cost in the production process. This method can produce fine, high-purity, stoichiometric particles of single and multicomponent metal oxides. Furthermore, if process conditions such as solution pH, reaction temperature, stirring rate, solute concentration and surfactant concentration are carefully controlled, oxide particles of the desired sizes and shape can be produced [10, 11]. A great variety of polymers with hydroxyl, carboxylate, carboxyl, styrene or vinyl alcohol groups have been used in magnetic nanoparticles production. Coating or encapsulation of particles with polymers is the oldest and simplest method of magnetic particles preparation. Other methods include e.g. suspension, dispersion or emulsion polymerization [9].
This work is focused on the preliminary results of the two-step preparation process of polymer-coated iron oxide magnetic nanoparticles carrying carboxyl groups on their surface and their short characterization using SEM and FTIR.

2. EXPERIMENTAL

2.1 Materials
Ferrous chloride tetrahydrate (FeCl$_2$.4H$_2$O, 99%), ferric chloride hexahydrate (FeCl$_3$.6H$_2$O, 99%), tetramethylammonium hydroxide (TMAOH), sodium dodecyl sulfate (SDS) and acrylic acid (AAc) were obtained from Merck (Czech Republic) and used as received. Sodium hydroxide (NaOH), sulfuric acid (98%) and methanol were purchased from Penta (Czech Republic). Potassium persulfate (KPS) was obtained from Sigma-Aldrich (USA). The main monomer methyl methacrylate (MMA) was purchased from Fluka (Germany) and was purified by distillation before use. Milli-Q water (Millipore, USA) deoxygenated with bubbling N$_2$ for 10 min was used during particles preparation.

2.2 Preparation of iron oxide magnetic nanoparticles
Method previously published by Zhu et al. [12] and later by Sayar et al. [13] was chosen for the iron oxide magnetic nanoparticles preparation. Nanoparticles were prepared by co-precipitation of Fe$^{2+}$ and Fe$^{3+}$ salts solution and NaOH solution using peristaltic pump. Our reaction apparatus can be seen in Fig. 1. It consists of a flat bottom flask, an overhead stirrer (IKA-Werke, Germany), a heating circulator (Julabo, Germany) and a peristaltic pump (Heidolph, Germany). Two silicone tubes were used for transport and mixing of reagents. Two samples of magnetite nanoparticles were prepared with different molar ratio of Fe$^{2+}$:Fe$^{3+}$. First Fe$^{2+}$:Fe$^{3+}$ = 1:1 marked as sample 1 and second Fe$^{2+}$:Fe$^{3+}$ = 1:2 marked as sample 2. In the both cases, 25 mL of aqueous solution containing Fe$^{2+}$ and Fe$^{3+}$ salts in a total concentration of 1.25 M was mixed with 25 mL of 5 M NaOH solution. The precipitate was added dropwise into 35 mL of water at 80°C and the resulting mixture was stirred continuously for 2 hours. Prepared magnetic nanoparticles were then stabilized by the slow addition of 1.7 mL of 25 % TMAOH.

![Fig. 1 Reaction apparatus used for the iron oxide nanoparticles preparation. 1 – Heating circulator, 2 – Reactor, 3 – Stirrer, 4 – Ferrous and ferric solution, 5 – NaOH solution, 6 – Peristaltic pump](image-url)
2.3 Preparation of polymer coated magnetic nanoparticles

Previously produced iron oxide nanoparticles were coated with polymer. It was achieved by emulsion polymerization at a high surfactant to monomer ratio as described by Sayar et al. [13]. MMA and AAc were used as comonomers with a weight ratio of 9/1. The surfactant and monomer concentrations were 9.33 and 6.34% wt, respectively. In the polymerization procedure, surfactant was added to 50 mL of previously 10 min ultrasonically dispersed iron oxide nanoparticles suspension (2% wt) and 10 min dispergation was repeated. Then, the comonomer mixture was added to the dispersion and the system was mixed in an ultrasonic bath for 40 min in order to ensure dispersion of the Fe$_3$O$_4$ nanoparticles and the monomers. Prior to polymerization, mixture was transferred to the 250 mL Schott Duran reactor, initiator KPS was added and the system was shaken at constant temperature 65 °C for 24 h. After this time period, the coated magnetic nanoparticles were washed three times with mixture of methanol and water to remove the surfactant and the unreacted monomers and then three times with pure water with the help of a magnet. Then these particles were immersed in 0.1 M of H$_2$SO$_4$ solution for 48 h to separate the nanoparticles, which were not coated with the polymer. After 48 h polymer-coated nanoparticles were further washed with milli-Q water. Samples of polymer-coated magnetite nanoparticles were marked as sample 1PC and sample 2PC.

![Fig. 2 Demonstration of magnetic properties of prepared iron oxide nanoparticles dispersed in water](image)

2.4 Characterization of prepared magnetic nanoparticles

Scanning Electron Microscopy (SEM, model Mira II LMU, TESCAN, Czech Republic) was used to determine an approximate particle size of prepared nanoparticles. For SEM analysis, samples were placed on aluminium foil (thickness 0.25 mm, GoodFellow, UK) previously electrochemically polished. To study the molecular structure of Fe$_3$O$_4$ nanoparticles and their composites Fourier Transform Infrared Spectroscopy (FTIR, model Impact 400, Nicolet, USA) was utilized. The FTIR spectra were recorded using KBr pellet technique.

3. RESULT AND DISCUSSION

The motivation of our work is to prepare iron oxide based magnetic nanoparticles carrying carboxyl groups on their surface which enable further functionalization by streptavidin. Magnetic nanoparticles coated with streptavidin then allow the attachment of nucleic acid molecules. For this purpose, two-step preparation process of iron oxide magnetic nanoparticles bearing –COOH surface groups, including simple co-precipitation method and surface modification by emulsion polymerization, can be advantageous.
In this study, preparation of polymer-coated iron oxide magnetic nanoparticles was investigated. Influence of Fe$^{2+}$:Fe$^{3+}$ ratio in the initial mixture on the nanoparticles size and success of polymer coating were evaluated. All prepared samples of iron oxide magnetic nanoparticles revealed the magnetic properties in water suspension when external magnetic field was applied. It can be seen in Fig. 2. After drying, black and brownish-black powders were obtained for uncoated and coated magnetite particles, respectively (see Fig. 3).

The SEM analysis provided information about size and shape of resulting iron oxide magnetic nanoparticles. Obtained micrographs are shown in Fig. 4. The average particle size values of all produced magnetite
samples are listed in Table 1. It was observed, that the nanoparticles of all prepared samples have particle sizes below 20 nm. Bigger particles were obtained in the case of molar ratio Fe$^{2+}$:Fe$^{3+}$ = 1:1 (sample 1). However, the difference was not too significant. The change in particle sizes before and after polymer coating was also almost negligible. The produced nanoparticles were generally spherical in the shape and both type (uncoated and coated) tend to form agglomerates, as can be seen in the Fig. 4.

Table 1: Average particle sizes of all samples of iron oxide magnetic nanoparticles

<table>
<thead>
<tr>
<th>Sample</th>
<th>Particle size (nm)</th>
<th>Sample</th>
<th>Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.3</td>
<td>1PC</td>
<td>12.4</td>
</tr>
<tr>
<td>2</td>
<td>8.9</td>
<td>2PC</td>
<td>9.5</td>
</tr>
</tbody>
</table>

Fig. 5. shows vibrational spectra of magnetite particles alone and of those coated with the polymer. The fingerprint of Fe$_3$O$_4$ occurs mainly at 580 cm$^{-1}$, where a strong, sharp peak corresponds to Fe–O stretch of the magnetite nanoparticles. Broad absorption above 3000 cm$^{-1}$ typically stands for the stretch vibration of O–H bonds in hydroxyl groups; in this spectrum, this vibration can be explained by residual moistness in KBr and particles. Small narrow peak at 3315 cm$^{-1}$ can be assigned to surface and bulk OH groups in magnetite. The presence of polymer in the blend was successfully confirmed by means of FTIR; characteristic vibration bands of PMMA appear at 1726 cm$^{-1}$ for C=O and at 1440 cm$^{-1}$ C–O groups. The doublet just below 3000 cm$^{-1}$ is the well-known sign of the methyl groups (C–H stretching in CH$_3$), while shoulders at about 1300 and 1450 cm$^{-1}$ are associated with C–H symmetric and asymmetric stretching modes, respectively. At 1240 cm$^{-1}$, the torsion of the methylene group (CH$_2$) can be found and the 1150 cm$^{-1}$ band corresponds to vibration of the ester group C–O. Absorption of magnetite at the spectrum of the composite particles can be found at around 3315 and 580 cm$^{-1}$. Absence of any other significant absorption bands indicates good purity of the prepared composite.

![Vibrational spectra of magnetite nanoparticles alone and of those coated with the polymer.](image)

**Fig. 5** Vibrational spectra of magnetite nanoparticles alone and of those coated with the polymer.

4. **CONCLUSIONS**

Magnetic nanoparticles of iron oxide were prepared by two-step process. In the first step, magnetite nanoparticles were produced by co-precipitation of Fe$^{2+}$ and Fe$^{3+}$ salts solution with NaOH solution and in
the second step, formed magnetite nanoparticles were coated with the polymer using emulsion polymerization. Resulting samples of nanoparticles were analyzed utilizing SEM and FTIR. It was found that prepared nanoparticles revealed the magnetic properties in water suspension when external magnetic field was applied, that particles were generally spherical in shape and have particle size below 20 nm and that they tend to form agglomerates. The presence of the polymer in the nanoparticles blend was confirmed by means of FTIR spectroscopy.

5. ACKNOWLEDGEMENTS

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LITERATURE