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# Solvothermal synthesis of $Sm^{3+}$-doped $Fe_3O_4$ nanoparticles

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ABSTRACT

Magnetic iron oxide nanoparticles doped with samarium were prepared by solvothermal polyol method. An introduction of 2,2′-bipyridine during the synthesis reduces the particle diameter to about 9 nm in average. The difference in physical and magnetic properties of the samples prepared with and without capping agent was outlined on the basis of complex characterization by a number of experimental techniques. The characteristics of resulted product make it suitable for biomedical applications, for instance, as a contrast agent for MRI.

## 1. Introduction

An indubitable importance of novel, property-modified nano-sized magnetic materials for numerous demanding applications in biomedicine, electronics and catalysis has been fueling scientific research from the beginning of a nanotechnology era [1]. Among the mentioned fields biomedicine alone employs magnetic nanoparticles (MNPs) in many different ways, to mention a few as carriers for genetic materials [2], as hybrid nano-vehicles for remotely controlled therapeutic delivery [3], as vessels for drugs and contrast agents for magnetic resonance imaging (MRI) [4], as heat mediators for cancer hyperthermia treatment and labels for separation and purification of molecules in bioprocesses [5] and activators in neuronal modulation [6]. The next generation of MRI contrast agents is expected to sophistically exploit such firmly features of MNPs as enhanced magnetic moments due to high payload of Fe or other "magnetic" metals [7]. Prominent examples from the emerging field include iron oxides doped with rare earth elements [8], multi-purpose magnetic anisotropic Janus particles [9], nanoparticles incorporated into polymeric hydrogels [10]. Among them the superparamagnetic iron oxide nanoparticles (SPIONs) are produced by several routes including the hydrothermal technique, chemical co-precipitation, microwave irradiation, thermal decomposition etc. [11,12]. Since the physical properties of MNPs are strongly related to their morphology and dimension, all the synthesis methods are heading towards control over the crystallite size, shape, extent of agglomeration and their surface chemistry. And in the most cases due to inevitable drawbacks of any given method there is a need to add some surfactant for better control over particle growth, and then to stabilize MNPs by using both electrostatic and steric repulsive forces [13]. Hence, it is still a challenge to prepare MNPs of suitable and uniform size.

Motivated by a call for a simple method allowing a reproducible formation of small (~10 nm) magnetite ($Fe_3O_4$) MNPs, we have developed a novel synthesis protocol based on a solvothermal method. This method is already known to produce uniform MNPs down to 5 nm in diameter having potential for MRI application [14]. For instance, Ooi et al. [15] reports a solvothermal synthesis of $Fe_3O_4$ octahedrons with ~90 nm edge from $FeCl_3$ in ethylene glycol (EG). These anisotropic nanostructures have been obtained by studying the influence of 1,3-diaminopropane on EG/oleylamine-based solutions. Keeping EG as a traditional reliable solvent for a reaction medium, we decided to involve a new stabilization agent from the bipyridine isomers line, namely, 2,2′-bipyridine (Bpy). Being an uncommon participant to the synthesis protocols for MNPs, bipyridines as N-donor compounds have been already employed for protection of transition metal clusters against their agglomeration in solution [16].

Transition metals (Co, Ni, Mn and Pt) are known to be effective dopants of MNPs with the scope to improve their magnetic properties [17]. Compared to them, lanthanides (Ln) have much stronger potential in expressing pronounced magnetic features due to large unquenched orbital angular momentum attributed to the *f* electrons demonstrating

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higher spin-orbit coupling. This is why the substitution of $Fe^{3+}$ in magnetite with rare earth ions like $Sm^{3+}$ or $Eu^{3+}$ could improve magnetic and optical properties of Ln:$Fe_3O_4$ materials [18]. Co-precipitation in an alkaline solution and a reverse micelle method both reportedly are lacking a good control over the particle size distribution, while thermal decomposition of a mixture containing $Fe(acac)_3$ and $Ln(acac)_3 \cdot 2H_2O$ (acac = acetylacetonate) in the presence of passivating surfactants allows to obtain the diamond-shaped Sm:$Fe_3O_4$ particles with an average size of 12 nm [19].

In this work, we report the study on structural and magnetic properties of $Sm^{3+}$-doped iron oxide MNPs grown by solvothermal polyol method from a mixture of metal chlorides with particular focus on the changes in MNPs modulated by introduction of 2,2′-bipyridine into the reaction solution.

## 2. Material and methods

### 2.1. Chemicals

Iron(III) chloride ($FeCl_3$, 97%) was obtained from Sigma-Aldrich. Ethylene glycol (EG, $C_2H_6O$, 99%), 2,2′-bipyridine ($C_{10}H_8N_2$, 99 +%), sodium hydroxide (NaOH, 98%), ultra-dry samarium chloride ($SmCl_3$, 99.9%, REO) were supplied by Alfa Aesar. All chemicals were of analytical grade standards and used as received. Deionized (DI) water (18 MΩ·cm at 25 °C) was obtained by using SimplicityUV ultra-pure water system.

### 2.2. Synthesis of magnetic NPs

The two sets of $Sm^{3+}$-doped iron oxide NPs were produced by a solvothermal method without and with addition of a capping agent. In the first case, $FeCl_3$ ($4 \cdot 10^{-3}$ mol) and $SmCl_3$ ($1.35 \cdot 10^{-4}$ mol) were dissolved in 40 mL of EG. Then, NaOH ($2.4 \cdot 10^{-2}$ mol) in EG solution (10 mL) was added to reach pH ≈ 10. The solution has been purging with argon for 10 min to reduce oxygen content. Then the solution was poured in a Teflon-lined stainless-steel high pressure reactor (Berghof BR-200), where it has been maintained at 200 °C for 72 h under magnetic stirring. The reactor was cooled down to room temperature (RT). A black precipitate was washed several times with ethanol and DI water and retrieved by magnetic decantation. The powder was dried in a vacuum oven at 60 °C overnight. Another sample was prepared following the same procedure, with the only difference that 2,2′-bipyridine ($4 \cdot 10^{-3}$ mol) in 10 mL EG was added to the starting mixture of $FeCl_3$, $SmCl_3$ and NaOH in EG. The magnetic NPs prepared without a stabilization agent will be further referred as Sm:MNPs, and those obtained with addition of 2,2′-bipyridine as Sm:MNPs-Bpy.

### 2.3. Instrumentation

X-ray diffraction (XRD) patterns were collected with Ultima IV powder diffractometer (Rigaku) using CuKα radiation (α = 1.5406 Å) with a 0.02° step size and a 2 s dwell time. Operating conditions were 40 kV and 40 mA. The XRD patterns were processed by Rigaku PDXL Software: profile fitting for phase identification was performed using the WPPF (Whole Powder Pattern Fitting) method and crystallite size was calculated by Scherrer and Williamson-Hall methods [20]. For the former method the values of crystallite size obtained for each reflex in 25 to 80° 2θ interval were averaged.

TEM images were acquired using JEM-2100 microscope (JEOL) operated at an accelerating voltage of 200 kV. The samples were prepared by dropping a dilute dispersion of the sample in isopropanol onto a copper mesh coated with a carbon layer and then allowing the solution to dry at RT. The particle size distribution was obtained by direct measurements of individual particles in the complete set of TEM images, constituting a set of about 100 particles.

Thermogravimetry analysis (TGA) of samples was performed using a SDT Q600TGA/DSC analyzer (TA Instruments), allowing for simultaneous recording of weight change and differential scanning calorimetry (DSC) curves on the same sample. Samples of about 22 mg weight in alumina crucibles were heated from room temperature to 800 °C at 10 °C·min$^{-1}$ rate under argon flow.

Ultra violet–visible (UV–Vis) spectra were recorded on UV-2600 spectrophotometer (Shimadzu) with 2 nm resolution. In transmittance mode solutions of the sample against EG were measured in 2 mm cuvettes. Diffuse-reflectance (DR) spectra were recorded with integrating sphere accessory. Samples were mixed with barium sulfate and pressed into discs to be measured against pure $BaSO_4$. The obtained reflectance values (%R) were converted into Kubelka-Munk function values using the instrument's software.

The Fourier transform infrared (FTIR) spectra were collected in the air using Bruker Vertex 70 spectrometer (at 64 scans with resolution of 2 cm$^{-1}$) employing the KBr pellet technique.

Micro X-ray fluorescence (XRF) analysis was done using Bruker M4 TORNADO Micro-XRF spectrometer. The sample powder was deposited on the surface of boric acid disk. The resulted data were averaged over several measured points and presented in both atomic % (at.%) and weight % (wt%).

X-ray photoelectron spectra (XPS) were obtained using ESCALAB 250 spectrometer with excitation by monochromatized Al Kα-line radiation (hν = 1486.6 eV). A thin layer of finely powdered sample was deposed on a conductive carbon tape and fixed in a standard stainless steel sample holder. The size of an X-ray focal spot on the sample's surface was 350 × 500 μm. The elemental composition of the sample was determined by the spectra taken at an analyzer pass energy of 150 eV, while the C1s, O1s, Fe2p core lines were recorded with the pass energy of 20 eV. The spectrometer was calibrated in advance using the Ag $3d_{5/2}$ (368.2 eV) and Au $4f_{7/2}$ (84.0 eV) bonding energies lines derived from the reference metal surfaces cleaned with a flow of argon ions. The minimal energy range allowed in the experiment was measured on the full width at half maximum (FWHM) of the Ag $3d_{5/2}$ line being not worse than 0.6 eV. To remove a weak positive charge from the sample's surface it was irradiated by 2 eV "slow" electrons. XPS spectra were referenced to the C1s carbon line at binding energy of 285.0 eV. The XPS spectra

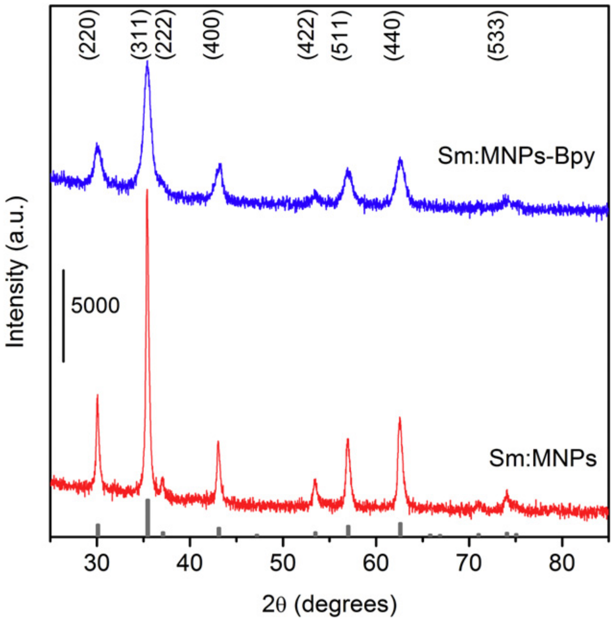

**Fig. 1.** XRD patterns of Sm:MNPs (red) and Sm:MNPs-Bpy (blue) samples prepared solvothermally. Gray bars in bottom show theoretical reflexes for $Fe_3O_4$ magnetite phase.