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Tailoring the properties of magnetite nanoparticles clusters by coating with double inorganic layers

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ABSTRACT

New magnetic nanoparticles based on Fe_3O_4 clusters covered with a double layer of inorganic salts/oxides with high magnetization for incorporation in security materials such as security paper were synthesized. For the inorganic layers ZnO, SiO_2 and $BaSO_4$ were used. The microstructure and composition of the products were determined by scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and X-ray photoelectron spectroscopy (XPS). Magnetization measurements on the obtained samples show a straightforward correlation between the saturation magnetization (M_s) and morphology of the samples. The results obtained from color parameter assessment are discussed in relation with the morphology and microstructure of the prepared samples.

1. Introduction

Cellulose is a colorless, odorless, and nontoxic solid polymer and possesses some promising properties, such as great mechanical strength, biocompatibility, hydrophilicity, relative thermal stability, high sorption capacity, and a tunable optical appearance. These are good resons for it to be used as a “smart material” in applications like as a reinforcement material, magnetic paper, for drug delivery, in optical media, for water treatment, as biomembranes, for adsorption etc. [1].

Magnetic cellulose based materials are important for interesting applications such as information storage, fibers and fabrics for protective clothing for military use, magnetic filters, sensors, health care, biomedical applications or security paper. To get the final security material different magnetic particles (for example magnetite) are encapsulated in cellulose by different methods, for instance direct wet end addition, lumen loading, in situ synthesis of magnetic particles or fiber nanocoating [2–6].

In the literature only few examples of white magnetic paper are described because the addition of different ferrites, which are brown or black, to the paper composition results in color changes which restrict their applications, especially in white paper [7].

For a magnetic paper with a resonable magnetization as well as a relatively light color it is necessary to add a smaller amount of magnetic particles into the process. In this way, the color of the paper will not be changed too much. For this process the magnetic nanoparticles should be covered or incorporated in a white material to result in a magnetic material with light color [8,9]. In paper production, several salts or inorganic oxides like SiO_2, TiO_2, $BaSO_4$, $CaCO_3$, kaolinite, Al_2O_3 or ZnO are used as white pigments.They are incorporated into the cellulose matrix to get different materials with specific properties [10]. These inorganic salts or oxides are also known for their biocompatibility, antibacterial property or resistance to external factors (temperature, pH).

Our target was to synthesize new magnetite nanoparticle clusters covered with a double layer of inorganic salts/oxides with high magnetization and appropriate color for incorporation in security materials such as security paper. For the inorganic shells ZnO, SiO_2 and $BaSO_4$ were used. Comparison of the magnetite clusters coated with different inorganic layers is necessary for the optimization of the synthesis procedure in order to get the required properties for magnetic security paper applications.

X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), energy dispersive X-ray Analysis (EDX) and magnetization measurements were carried out to investigate the changes in morphology and chemical composition of the obtained samples.

The general scheme of reactions is presented in Scheme 1. The first inorganic layer coating the magnetite clusters stabi-

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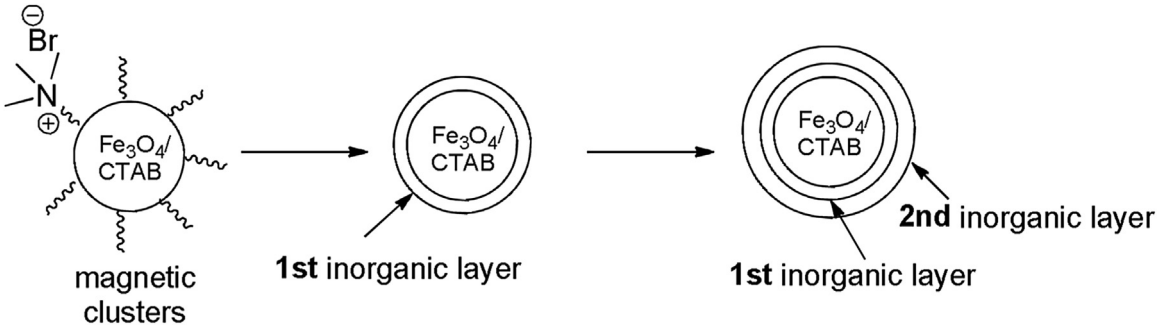

Scheme 1. General scheme of reaction for magnetic clusters MC with double inorganic layer.

lized with cetyltrimethylammonium bromide (MC) is chosen from:/$BaSO_4$,/SiO_2 and ZnO. By addition of the second inorganic layer the following nanostructured systems: MC/$BaSO_4$/ZnO, MC/ZnO/$BaSO_4$,MC/SiO_2/ZnO, MC/ZnO/SiO_2 were obtained.

2. Experimental

2.1. Materials and methods

Ferrofluid dispersed in toluene (Romanian Academia Timisoara), Cetyltrimethylammonium bromide (CTAB ≥98% Merck), tetraethylorthosilicate (TEOS) ($C_8H_{20}O_4Si$, 98%, Sigma-Aldrich), zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$ 98% Sigma-Aldrich), barium chloride dihydrate ($BaCl_2{\cdot}2H_2O$ ≥99% Sigma-Aldrich), sodium sulfate (Na_2SO_4 ≥99% anhydrous Sigma-Aldrich), ammoniumhydroxide solution (NH_4OH, 25% Chimreactiv) and absolute ethanol (≥99,5% Tunic Prod) were used as received without further purification.

The magnetic clusters were synthesized by the miniemulsion method, using a magnetic ferrofluid based on toluene provided by Academia Timisoara [11]. The obtained magnetic clusters stabilized with CTAB were covered with barium sulfate ($BaSO_4$), zinc oxide (ZnO) or silica dioxide (SiO_2).

(1) **MC/ZnO**: $Zn(NO_3)_2{\cdot}6H_2O$ (3.25 mmol, 0.615 g) and NaOH (6.5 mmol, 0.260 g) were added to a solution of CTAB magnetic clusters (0.345 g) dispersed in H_2O (10 ml) and stirred for 16 h at room temperature. The reaction mixture was separated magnetically and washed several times with methanol and water.
(2) **MC/SiO_2**: TEOS (2.5 mmol, 0.533 ml), NH_4OH (0.644 ml) and EtOH (23 ml) were added to a solution of MC(0.345 g) dispersed in H_2O (10 ml) and stirred for 3 h at room temperature. The reaction mixture was separated magnetically and washed several times with methanol and water.
(3) **MC/$BaSO_4$**: $BaCl_2{\cdot}2H_2O$ (1.76 mmol, 0.431 g) and Na_2SO_4 (3.5 mmol, 0.498 g) were added to a solution of MC(0.345 g) dispersed in H_2O (10 ml) and stirred for 3 h at room temperature. The reaction mixture was separated magnetically and washed several times with methanol and water.
(4) **MC/ZnO/$BaSO_4$**: $BaCl_2{\cdot}2H_2O$ (1 mmol, 0.235 g) and Na_2SO_4 (2 mmol, 0.257 g) were added to a solution of MC/ZnO (0.225 g) dispersed in H_2O (5 ml) and stirred for 3 h at room temperature. The reaction mixture was separated magnetically and washed several times with methanol and water.
(5) **MC/SiO_2/ZnO**: $Zn(NO_3)_2{\cdot}6H_2O$ (1.6 mmol, 0.488 g) and NaOH (3.2 mmol, 0.128 g) were added to a solution of MC/SiO_2 (0.275 g) dispersed in H_2O (5 ml) and stirred 16 h at room temperature. The reaction mixture was separated magnetically and washed several times with methanol and water.
(6) **MC/ZnO/SiO_2**: TEOS (0.8 mmol, 0.179 ml), NH_4OH (0.216 ml), EtOH (8 ml) were added to a solution of MC/ZnO (0.116 g) dispersed in H_2O (5 ml) and stirred for 3 h at room temperature. The reaction mixture was separated magnetically and washed several times with methanol and water.
(7) **MC/$BaSO_4$/ZnO**: $Zn(NO_3)_2{\cdot}6H_2O$ (1.8 mmol, 0.548 g) and NaOH (3.6 mmol, 0.8 g) were added to a solution of MC/$BaSO_4$ (0.307 g) dispersed in H_2O (10 ml) and stirred 16 h at room temperature. The reaction mixture was separated magnetically and washed several times with methanol and water.

2.2. Characterization techniques

Magnetic characterization of the samples at room temperature was performed using a Vibrating Sample Magnetometer Cryogenics.

Scanning electron microscopy (SEM) with a Hitachi SU 8230 device equipped with energy dispersive X-ray Analysis (EDX) was used to analyze the morphology and microstructure of the prepared samples. The electron energy used was 30 keV. In order to amplify the secondary electron signal, the samples prepared in the form of powders were metalized with an Au thin layer of 10 nm in an automatic Sputter Coater, in argon atmosphere.

A SPECS XPS spectrometer equipped with an Al/Mg dual-anode X-ray source, a PHOIBOS 150 2D CCD hemispherical energy analyzer, and a multichanneltron detector with vacuum maintained at 1×10^{-9}Torr was used to record the XPS spectra. The Al Kα X-ray source (1486.6 eV) was operated at 200 W. The XPS survey spectra were recorded at 30 eV pass energy and 0.5 eV/step. The high-resolution spectra for the individual elements (Fe, C, O, N, S, Si, Zn, Ba) were recorded by accumulating 10 scans at 30 eV pass energy and 0.1 eV/step. Data analysis and curve fitting was performed using CasaXPS software with a Gaussian-Lorentzian product function and a nonlinear Shirley background subtraction. Peak shifts due to any apparent charging were normalized with the C 1 s peak set to 284.8 eV. The high resolution spectra were deconvoluted into the components corresponding to particular bond types.

It is known that for an objective evaluation of color difference from sample to sample, an ordered system for the classification of color and equipment capable of quantifying the color differences is required. In this work we applied the most frequently used color classification system for research, proposed and developed by the Commission International de l'Eclairage called the CIE color system. In this system a rectangular coordinate system is placed on the central color disk the one for zero value where the hues at the edge of this disk are the most saturated. The positive *x* axis that extends out from the center toward its maximum value of +60 at red is named the a* axis. Perpendicular to this and going toward the yellow hue is the positive y axis called b*. The − a* axis extends toward green and −b* toward blue. The value (or lightness) axis which is the z axis extends upward with values ranging from 0 (black) to 100 (white) and is given the name L [19]. A standardized photographic set-up was used to record color parameters from