MAGNETIC NANOPARTICLES COMBINED WITH NATU-RAL PROTEIN FIBRES

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ABSTRACT

Human hair and sheep wool are the natural protein fibres of complex structure, composed of α-keratin chains are analyzed as basic components for the fabrication of nanomaterials. After carrying out some successful experiments in which we demonstrate that silver nanoparticles can be immobilized on the surface and inside hair and wool fibers [1, 2], we attempted to use another type of metal-containing nanoparticles and unite in one composite material such properties as superparamagnetism of iron oxide and nonmagnetism of natural protein fiber.

The hair fibers, immersed in a reductant solution in order to break their surface disulfide groups, were placed in a α-Fe_2O_3 – nanoparticle suspension while synthesis. After some time, the fiber surface took on a brown tinge. Hematite-containig nanoparticles were found to penetrate not only into the hair cuticle but also into melanin granules inside the fibre volume. Electron magnetic resonance data (Varian Spectrometer, 9.1 GHz) indicates that the nanoparticles produced in the matrix are supeparamagnetic at room temperature. This interesting finding suggests that such a carrier can be associated with a magnetic bubble. The observed line width and effective g-factor are comparable to those reported for superparamagnetic iron oxide nanoparticles in a nonmagnetic matrix.

Key words: nanocomposite, magnetic nanoparticles, natural fibers.

INTRODUCTION

Functional metal oxide nanocrystals have been extensively investigated in the recent decade for their outstanding new properties suitable for a broad spectrum of downstream applications. Iron oxide is one of the most widely investigatednanomaterials for both biological and industrial applications. Iron oxides (Fe_2O_3) have four phases: α-Fe_2O_3 (hematite); β-Fe_2O_3; γ-Fe_2O_3 (maghemite); ϵ-Fe_2O_3. Magnetic nanocrystals of γ-Fe_2O_3 have been applied in information storage, magnetic refrigeration, bioprocessing, controlled drug delivery, and ferrofluids, while α-Fe_2O_3 is environmentally friendly and of great interest for potential applications as a gas sensor, lithiumion battery and pigment.

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The immobilization of metal-containing nanoparticles on microcarriers of various compositions is a rapidly growing area of nanomaterials research. The advantages of spheroidal microgranules as carriers for nanoparticles are well-known [3-5]. In contrast, essentially the only one dimensional (1D) carriers described in the literature are carbon nanotubes, with various nanoparticles attached to their surface. Proteins form linear structure, such as hair, wool and silk and in contrast to carbon nanotubes, such raw materials are readily available and sufficiently well studied. Wool is among the most important subjects of research for textile manufactures.

Avery limited number of studies have been concerned with the fabrication of nanoparticles inside or on the surface of hairs or wool fibres. They mainly addressed the accumulation of toxic metal ions in hair, the poisoning of the human organism with such ions, and techniques for identifying them.

A human hair and sheep wool are composite protein fibers of natural origin consisting mainly of water-insoluble α-keratincomprising hydrophobic amino acid residues (phenylalanine, isoleucine, valine, methionine, alanine) and, correspondingly, numerous functional groups including S- and N- containing ones.

The surface layer of a hair, cuticle, contains thehighest amount of cystine and consists of planar hornycells of amorphous keratin applied onto one anotherin a tile pattern and containing four layers with different contents of disulfide bonds: epicuticle on the very surface, which is a ~ 5 nm thick hydrophobic membrane; mechanically most stable α-layer; exocuticleconnected to the α-layer; endocuticle with a low cystine content (3 %). The hydrophobicity of thesurface layer, in particular, the epicuticle is caused bythe presence of an outer β-layer (2.4 nm) of acovalently bonded lipid, presumably, 18-methylarachidonic acid (18-MEA).

The natural color of the hair is caused by the granules of the pigment melanin present in its corticallayer. Melanin is insoluble in water but is rather readilysoluble in alkali or concentrated acids and consists of conjugated polymers with S- and N-containinggroups. Melanin is deposited as granules, each being astructurised body forming spheres 70 – 500 nm in diameter. The destruction of melanin occurssupposedly as separation of the disc-like granules intolayers under the action of an oxidant (which preferablyinteracts with melanin rather than with the hair keratin) accompanied by elimination of oligomer residues. The ability of melanin to reduce a solution of silver nitrate to silver metal (Masson–Fontana stain) dueto the presence of unpaired electrons is also knownfrom medical sources.

METHODS OF SAMPLE MANUFACTURING AND ANALYSIS

For binding of the obtained nanoparticles toligands within biofibers, the hair and wool were pretreated with a solution of a reducing agent (such

asNaBH$_4$) to activate the disulfide ligands on their surface, then washed with water to remove NaBH$_4$, andplaced into solutions of nanoparticles for a week.

Hematite nanoparticles were prepared by coprecipitating Fe^{2+}and Fe^{3+} ions in aqueous ammonia solution. To 200 mL of water containing ferric chloride and chlorouschloride in molar ratio 1:1, was dropped 1.5 M NH$_4$OH solution under room atmosphere while the solution was stirred rapidly. The resulting precipitate was stirred for 2 h.After triple washes with water and ethanol theprecipitates were re-suspended in water. Themagnetic nanoparticles were isolated from the solution bya magnet bar. The fibers were placed into the reaction solution directly at the beginning of the experiment.

While the experiment, the solution color gradually changed from black to brown as a result of absence of an inert atmosphere in the reactor and the surface of the fibres also became brown.

RESULTS AND DISCUSSION

The samples treated in the nanoparticle suspensionduring the reaction were examined by transmission electron microscopy (TEM) on LEO 912 AB microscope. Cross-sectional TEM specimens were prepared using a Reichert-Jung ultramicrotome. It follows from the TEM micrograph in *Figure 1* and *Figure 2* that the nanoparticles are formed not only in the cuticle of the fibre, but locally in the volume of melanin granules. The particles areless than 10nm. Electron diffraction patterns of agglomerates correspond to α-Fe$_2$O$_3$.

Thus, treatment of the hair with a reducing agent resulted in partial cleavage of cystine disulfide S–S bonds on the hair surface or (partially) in the hair bulk, some of cystine being converted to cycteine containing thiol groups S–H. These groups are known to be efficiently coordinated by Fe-containing nanoparticles to form strong bonds.
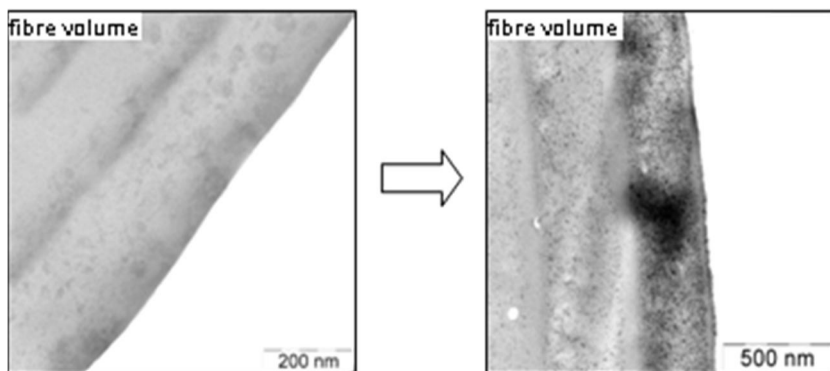

Fig. 1 – Presence of Fe-containing nanoparticles in the cuticule of the hair (on the left: the fiber before the experiment; on the right: the fiber after the experiment)
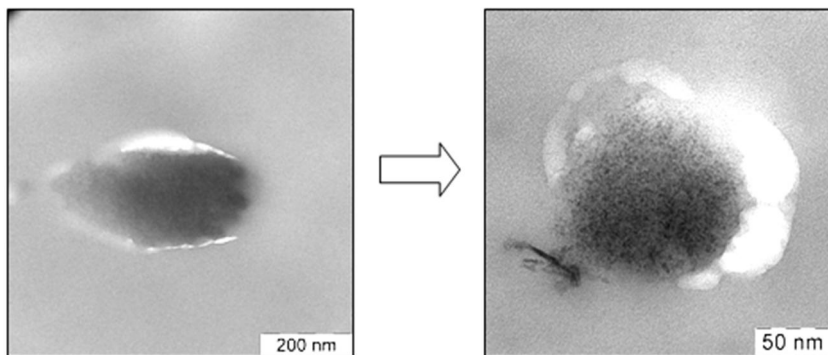
Fig. 2– Presence of Fe-containing nanoparticles in the melanine granule of the hair (on the left: the granule before the experiment; on the right: the granule after the experiment)

As for the melanine granules, we can suppose that the coordination of Fe-nanoparticles inside them occur apparently in the way of their passing through the micro and nanopores in the fibrillar structure of the protein after the treatment of a hair with a reducing agent (the cuticle flakes are partly opened). The S- and N-containing functional groups of melanin coordinate the nanoparticles thus stabilizing them and preventing them from agglomeration.

The samples also have been investigated by a method of an electronic magnetic resonance with use of the computerized spectrometer "Varian" (working frequency of 9.1 GHz). Measurements were spent at room temperature. The sample fastened on the quartz holder thus that it was possible to spend measurements at its various orientations concerning an external magnetic field. Besides, EMR spectrum in the conditions have been written down, allowing to find out a hysteresis of microwave absorption and residual magnetization of the sample [6]. As the hysteresis hasn't been found out, particles are superparamagnetic at room temperature.

EMR spectrum for two orientations of the magnetic field (a field perpendicularly and in parallel hair) are shown on *Figure 3a*. Values for width of a line (970/910 $\perp$ / $\parallel$) and the effective g-factor (1.9/2.1 $\perp$ / $\parallel$) are close to the data received for superparamagnetic nanoparticles of Fe-oxides inside not magnetic matrix [7, 8].

Value change of g-factor at turn of the sample can be explained as follows. The magnetic field operating on nanoparticles in hair, is the sum of two contributions: fields of a magnet of a spectrometer and a field caused by magnetization of the sample. In the elementary model of infinitely long homogeneously magnetized cylinder (*Fig. 3b*) in a case when hair is parallel to an external field, intensity in it is the same, as intensity of a field of magnet H_0 in absence of the sample. In the cylinder the magnetic field induction increases by size $\mu_0 M$, where M–magnetization of the cylinder. In a case when an external

field of perpendicularly axis of the cylinder, increase in a magnetic field in the cylinder for the account magnetization twice is less (*Fig. 3b*). As the resonant field registered in experiment, is the electromagnet field (equal $\mu_0 H_0$), in the second case will shift EMR spectrum to the right concerning a spectrum for parallel orientation of the sample (*Fig. 3a*).
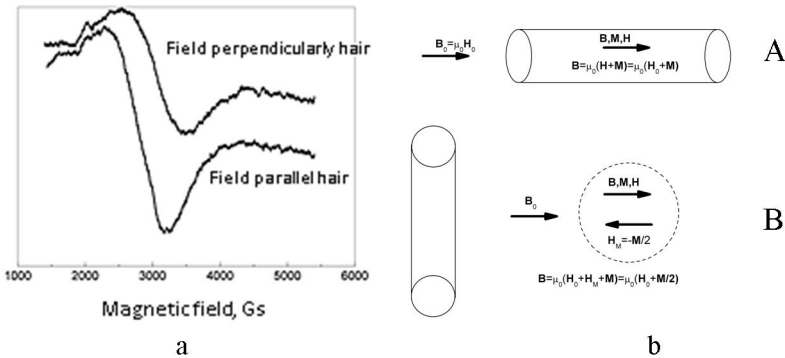

Fig. 3– *a*. EMR spectrum of the samples for two orientations of the magnetic field; b. Diagram illustrating the difference in values of the magnetic field inside the hair with nanoparticles in two orientations: (A) – the external field is parallel hair removal, (B) – the external field perpendicular to the hair (M magnetization, H – is the magnetic field, B – induction of a magnetic field)

For the investigated samples the size of shift in terms of intensity of a magnetic field is equal 0.03 T (in terms of an induction). It is 10 times less, than magnetization of a magnetite (0.6 T) or magemite (0.47 T). It is necessary to consider, however, that magnetization is a dipolar magnetic moment on volume unit, and nanoparticles occupy only insignificant part of hair. For a magnetization estimation of nanoparticles it is necessary to increase 0.03 T by a volume fraction of nanoparticles in hair.

The increase in width of EMR line approximately on 10 % at turn of the sample from parallel to perpendicular orientation is caused, basically, heterogeneity of the field caused by magnetization of the sample which smoothly decreases from the center to edge of the sample. Thus, nanoparticles in the center of hair and on its edges are in various fields (at the same current of an electromagnet of a spectrometer), and their resonant fields are displaced rather each other. It leads non-uniform widening total of EMR spectrum.

CONCLUSIONS

The present results demonstrate that the polyfunctional properties of hair and wool fibers can be successfully used to immobilize metal-containing nanoparticlesnanoparticles with various compositions and physicochemical proper-

ties (such as hematite and silver nanoparticles) on the surface and in the bulk of the fibres.

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