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ПОВЕРХНОСТНАЯ МОДИФИКАЦИЯ НАНОЧАСТИЦ $Fe_3O_4@SiO_2$

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Аннотация. *Работа направлена на разработку технологии амино-функциональных наночастиц $Fe_3O_4@SiO_2$. Изучены морфология и особенности магнитных и магнитооптических свойств полученных гибридных наночастиц. Рассмотрены некоторые примеры применения таких гибридных наноструктур.*

SURFACE MODIFICATION of $Fe_3O_4@SiO_2$ NANOPARTICLES

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Annotation. *The work is aimed to the development of the technology of the amino-functionalized Fe_3O_4@SiO_2 nanoparticles. The morphology and features of the magnetic and magneto-optical properties of the obtained hybrid nanoparticles are studied. Some examples of applications of such hybrid nanostructures are considered.*

Keywords: *Fe_3O_4 nanoparticles, silica coated nanoparticles, water pollutions adsorption, magnetic properties*

Silica is frequently used as a support-material in core-shell structures, it not only helps nanoparticles (NPs) to become stable at a certain condition, but also provides the opportunity to be easily modified with other functional groups and, additionally, it has high thermal and chemical stability and, most importantly, shows environmental compatibility. Furthermore, the silica coated magnetic NPs can be dispersed in water without adding other surfactants due to the negative charges on the silica shell.

The fields of application of Fe_3O_4@SiO_2 NPs functionalized with different surfactants, more frequently with amines, are varied. A number of authors have demonstrated their effective applications in biology and medicine [1, 2], in catalysis [3], and, especially, as effective adsorbents for removal of pollutants from wastewaters [4, 5, 6, 7, 8] A new type of magnetic fluorescent

nanocomposite (Fe_3O_4@SiO_2-NH_2/CQDs) was prepared by bonding of carbon quantum dots (CQDs) with Fe_3O_4@SiO_2-NH_2 nanocomposites through amine-carbonyl interactions and used as a fluorescent probe to detect Cu^{2+} [9]. Since this line of research is rather new, on the one hand, and the properties and application possibilities of nanoparticles strongly depend on the details of their synthesis, the search for optimal synthesis conditions and the study of the properties of functionalized particles by various methods can be considered as an urgent task.

In this study, we prepared Fe_3O_4 NPs and a series of nanocomposites based on them: Fe_3O_4@SiO_2, Fe_3O_4@SiO_2-NH_2, Fe_3O_4@SiO_2-NH_2-EY, conducted a comparative study of their properties, and estimated possibilities of their application as adsorbents of water pollutions.

Magnetite Fe_3O_4 NPs were synthesized by co-precipitation method using hydrolysis of iron sulfate. After that, the particles were selenized (Fe_3O_4@SiO_2) and derivatized (Fe_3O_4@SiO_2-NH_2) for covalent attachment of Eosin Y (Fe_3O_4@SiO_2-NH_2-EY). The Eosin Y is a brominated fluorescein dye derivative used as an acidic red stain for cell cytoplasm. The synthesized samples were examined with X-ray diffraction (XRD), transmission electron microscope (TEM), Fourier-transform infrared spectroscopy (FTIR), vibrating sample magnetometer (VSM), magnetic circular dichroism spectroscopy (MCD), and fluorescence measurement.

XRD patterns revealed that all the parent NPs and magnetic core of all composite NPs were of spinel ferrite crystal structure with parameters of the most intense peaks corresponding to the Fe_3O_4 phase (PDF Card # 04-005-4319). The TEM images (Fig. 1a) show that the nanoparticles synthesized by co-precipitation method are well-dispersed and have quadrangular shape. Most of the particles were 30 nm in size, and there was also a small fraction of smaller particles 5-10 nm in size. After selenized, the SiO_2 covered NPs can be observed (Fig. 1b).

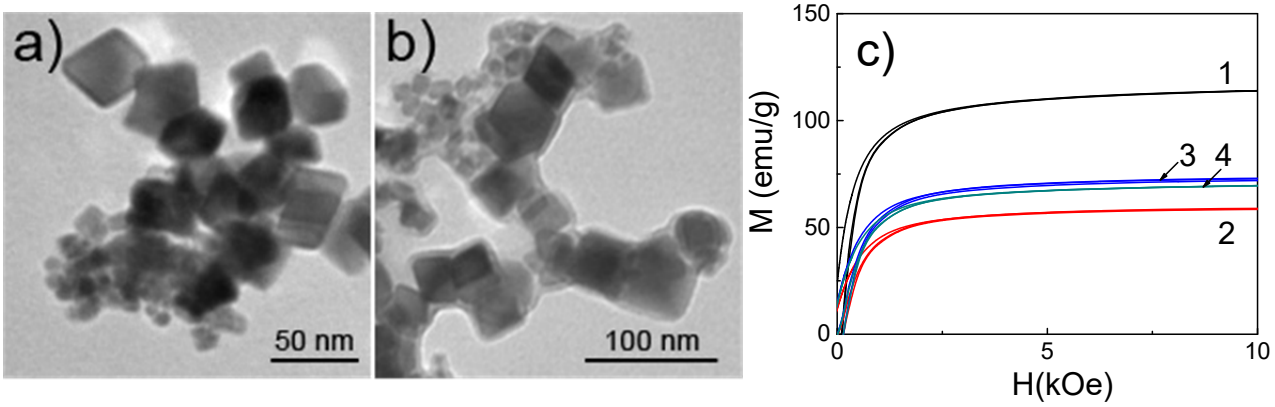

Figure 1. TEM images of Fe_3O_4 NPs (a) and Fe_3O_4@SiO_2 NPs (b), room temperature magnetization curves for magnetite nanoparticles: Fe_3O_4, Fe_3O_4@SiO_2, Fe_3O_4@SiO_2-NH_2, and Fe_3O_4@SiO_2-NH_2-EY, curves 1-4, correspondingly (c).

The FTIR spectra show the appearance of new bands upon the transition Fe_3O_4 → Fe_3O_4@SiO_2 → Fe_3O_4@SiO_2-NH_2 → Fe_3O_4@SiO_2-NH_2-EY evidencing on chemical bonds Si-O-Si, H-O-H, NH_2. Magnetic measurements (Fig. 1 c) show the saturation magnetization decrease of NPs coated with a SiO_2 shell. However, functionalization of silanized NPs with amino groups leads to some increase of their magnetization value. We ascribe this variety to the surface modification of NPs. Fluorescence measurement pumped at 2.76 eV (450 nm) was measured at room temperature.

MCD spectrum of Fe_3O_4 NPs is characteristic for this material (Fig. 2). Silanization of the samples led to a red shift in the MCD spectra. The difference in the MCD spectra of the silanized and initial samples indirectly confirms the formation of a SiO_2 shell around the Fe_3O_4 NPs. The functionalization of the silanized sample did not lead to a significant change in the spectra.

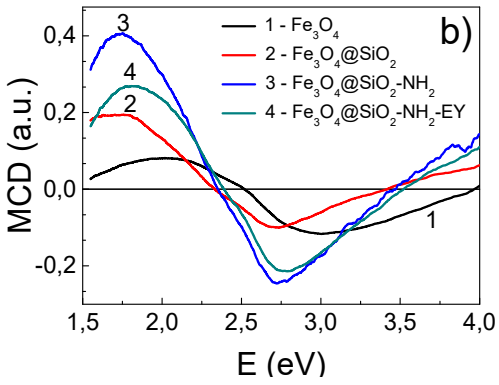

Figure 2. MCD spectra for magnetic NPs at room temperature.

So, the results described above allow concluding that our experimental process is successful and stable: Fe_3O_4@SiO_2 magnetic nanoparticles with core-shell structure were prepared and functionalized for adsorption of cationic and anionic dyes and medical imaging applications.

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