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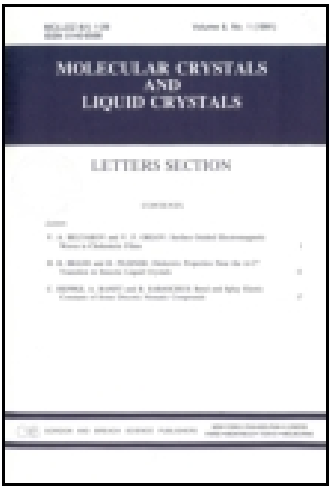

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Modification of Polymer-Magnetic Nanoparticles by Luminescent and Conducting Substances

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Modification of Polymer-Magnetic Nanoparticles by Luminescent and Conducting Substances

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The polymer encapsulated magnetic nanoparticles were obtained by suspension polymerization of styrene in the aqueous dispersion of magnetite. Functionalization of capsules was carried out by adsorption of $BaZrO_3$ *luminescent nanocrystals on the polystyrene shell. Followed oxidative polymerization of aniline on the capsule surface leading to the additional encapsulation of the microspheres by conducting substance-polyaniline. It was found that adsorption of* $BaZrO_3$ *nanocrystals on polystyrene shell leads to modification of CL spectra due to chemical interaction between polystyrene and* $BaZrO_3$ *nanocrystals.*

Keywords magnetite; polystyrene shell; barium zyrconate; polyaniline; structure; luminescence; conductivity

Introduction

Expanding the functionality of hybrid nanocomposites is realized by providing various functions-magnetic, conductive and fluorescent, etc. [1–6]. In this respect promising is the use of functionalized magnetic polymer capsules [2,4]. Marking capsules with fluorescent substances, such as semiconductor nanocrystals, makes it possible to trace their way into the tissues, capillaries, while downloading capsules magnetic nanoparticles allows you to control their movement by changing the gradient of the external magnetic field. To reduce the adverse effects of quenching the luminescence of nanocrystals, between the magnetic particles and fluorescent labels to create intermediate polymer layers, which is achieved by encapsulation of magnetic particles by the polymer shell [4]. As shown by magnetometry and Mossbauer spectroscopy data, the encapsulated magnetite particles conserve their superparamagnetic feature when they are separated in the polymer matrix [2].

Improvement of properties of the composites is also possible by providing electrical functions through the use of conducting polymers [6–9]. Such modification allows controlling the behavior of nanoparticles by both an electric and magnetic field, and tracking

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their movements in different mediums or biological environments [3,4]. Conducting polymer-magnetic composites provide a possibility of magneto switchable charge transport and bioelectrocatalysis [1,6].

However, attempts to obtain hybrid magnetic composites with both luminescence and electrical conductivity are very little. In addition, despite intensive research in the field of hybrid systems, the question of influence of the polymer matrix on the properties of fluorescent substances remains to be fully elucidated.

The aim of the work was to study the conditions of preparation, structure, luminescent and electrical properties of polymer-magnetic composites based on nanoparticles of magnetite encapsulated with polymer shells, and modified by barium zirconate and polyaniline as luminescent and conductive substances.

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Experimental

Synthesis and Characterization of the Samples

Magnetite (Mt) nanoparticles were synthesized by alkaline hydrolysis of iron (II) and iron (III) salts and stabilized by sodium oleate. Obtained magnetite in nanodispersion demonstrates typical of X-ray diffraction (XRD) powder pattern with broaden diffraction peaks of semi-amorphous samples of Fe_3O_4 shows the presence of cubic Fe_3O_4-phase of spinel-type structure [10,11] with lattice parameter $a = 8.3490(3)$ Å. Average size of grains for non-copolymer Fe_3O_4-samples was (76 ± 7) Å.

The polymer encapsulated magnetic nanoparticles were obtained by suspension polymerization of styrene in the colloidal dispersion of magnetite in the presence of peroxide initiators of polymerization – benzene peroxide and ammonium persulphate and starch as suspension stabilizer at 10–12 w.% content of magnetite. Polymerization was carried out at the temperatures of 65–80°C during 8–10 hours. Obtained polymer – magnetite capsules were separated from reaction mixture in magnetic field, rinsed by water decantation and dried to constant weight at the temperature of 60°C as described in [12]. The formation of Fe_3O_4 – polystyrene (PS) nanocomposites was confirmed by XRD analysis. Determined average size of grains for these samples (90–110 Å) can be explained as a result of magnetite encapsulated by polymer shell [12].

The commercial $BaZrO_3$ (BZO) nanopowders (grain size $d < 50$ nm) from Aldrich Company were used for modification of the surface polymer-magnetite capsules and preparation of BZO-polystyrene hybrid composites.

Functionalization of capsules was carried out by adsorption of luminescent nanocrystals on the polymer shell from colloidal solution of BZO in 1% toluene sulphonic acid (TSA), (CH_3)-C_6H_4-SO_3H using as surfactant. The dispersion of $BaZrO_3$ nanocrystals in TSA solution was treated with ultrasound for 2 hours to obtain a clear colloidal solution of BZO. This solution was introduce to water dispersion of polymer-magnetite capsules and kept for 2 hours at room temperature to complete the process of adsorption. For selection of the functionalized nanoparticles from reaction mixture the method of magnetic separation in direct magnetic field was used. For providing conductivity the polymer capsules were covered by conducting polymer – polyaniline (PANI) by oxidative polymerization of 0.1 M aniline (Aldrich Co) in the 0.1 M hydrochloride acid aqueous dispersion of polymer-magnetite nanocapsules modified by $BaZrO_3$. Obtained product was dried at the temperature of 60°C in vacuum. All investigated samples were prepared as pellets.

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Instrumentation

The data of XRD were collected on an automatic diffractometer STOE STADI P with a linear PSD detector (transmission mode; Cu $K_{\alpha 1}$ radiation, a curved germanium (111) monochromator); 2θ-range: $4 \leq 2\theta \leq 110$. X-ray phase analysis was performed using the Powder Cell [13] and LATCON [14] programs. Determination of the average apparent size and average max strain of grains was performed by simplified integral breadth methods, using the profile fitting procedure. X-ray microanalysis of the sample was carried out using local energodispersive spectroscopy (EDX) based on scanning electron microscope REMMA-102-02. The structure of nanocomposites was studied with the use of an atomic force microscope (AFM) Solver P47-PRO in the semicontact mode. To establish the shape and size of microcapsules variance was applied to the surface of a silicon single crystal (111) and dried under vacuum to complete evaporation of the solvent. Identification the chemical surface composition was studied on samples of polymer-magnetic composite pressed into tablets with a diameter of 2 mm with polished outer surface.

Investigation of molecular structure of polymer composites was carried out by means of Fourier transform infrared spectroscopy (FTIR) using AVATAR-320N spectrophotometer in the wave number range 400–4000 cm^{-1} at room temperature. Samples were obtained as thin layers on the surface of KBr crystal.

Excitation of cathodoluminescence was provided by pulse-mode electron gun with the next parameters: electron beam energy of 10 keV at current of 100 μA, pulse duration of 2 μs at frequency of 300 Hz. Luminescence spectra were recorded in the range of 1.0 – 5.0 eV at the room temperature and liquid nitrogen temperature.

Measurements of the specific volume conductivity and temperature dependence of resistance were carried out at dynamic temperature change (5 K/min) by two-probe method in the air. Powder sample was placed in quartz cylinder ($d = 2$ mm, $h = 1.8$ mm) between two nickel disc contacts with built-in thermo-couple and under pressure of 10 N/cm^2.

Results and Discussion

As shown by AFM of the obtained composites the suspense polymerization of styrene in the presence of nanodispersion magnetite and starch as surfactants provides the formation of polymer-magnetite spherical granules (microspheres) with probable diameter near 200–220 nm (Fig.1). The oxidative polymerization of aniline in the aqueous dispersion of polymer-magnetite capsules leads to the additional encapsulation of the microspheres by conducting polymer shell of polyaniline. As has been shown [2,15] polymeric nanospheres have the ability to adsorb on its surface adjacent inorganic nanoparticles. At high content of magnetite this nanoparticles may adsorb on the surface of the capsules [12] as shown by Raman spectroscopy of polymer-magnetite composites. This phenomenon we use for surface modification of polymer-magnet microcapsules by adsorption of luminescent nanocrystals $BaZrO_3$.

Adsorption of BZO nanocrystals on the surface of polystyrene capsulated magnetite was confirmed by EDX analysis. As one can see from profile of elements distribution on the surface of composite presented in figure 2, the intensive peaks from Zr, Ba and Fe are observed. With increasing of $BaZrO_3$ content in initial reaction mixture from 1 to 20 % a quantity of adsorbed nanocrystals is growing. Experimental diffraction patterns (Fig.3) indicate amorphous halo from polymer (PS), semi-amorphous reflections of magnetite [10–12] and clearly formed peaks from $BaZrO_3$ [15–17].

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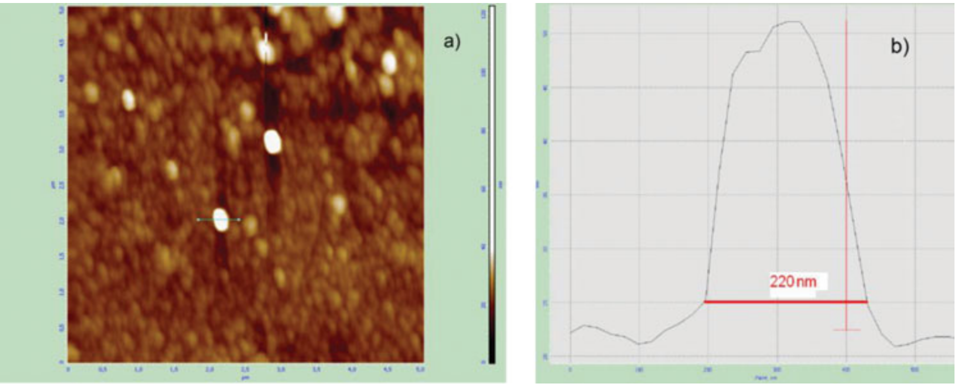

Figure 1. AFM-image (a) and the histogram of the nanoparticle size distribution (b) for the polymer-magnetite nanocomposite.

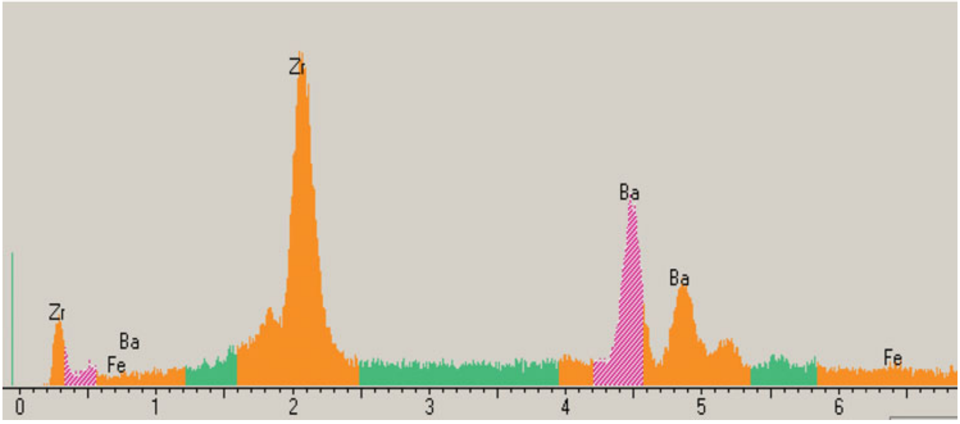

Figure 2. Profile of distribution of elements on the surface of polymer-magnetite composite, modified by nanocrystals at $BaZrO_3$ at its 10% content in initial dispersion.

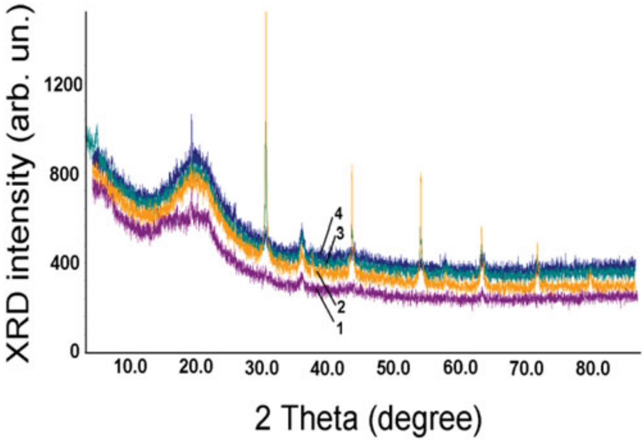

Figure 3. XPD pattern of Mt-PS-BZO-PANI composites obtained at 1(1), 5 (2), 10 (3) and 20 % (4) content of BZO in the initial dispersion.

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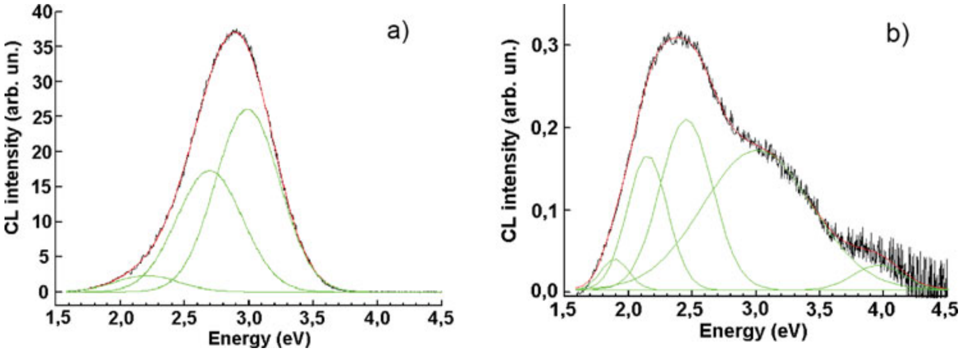

Figure 4. (a) CL spectrum of nano-BZO pellet, as prepared and (b) CL spectrum of BZO-PS composites at BZO content 5%.

Examination of polymer-magnetite nanocapsules on the ability to light radiation was carried out by cathode luminescence (CL) spectra of the pellet samples.

The CL spectrum of nano-BZO pellet at room temperature is shown in Fig. 4a, which we have presented as the respective Gaussian decomposition into three possible bands with maxima at 2.99, 2.69 eV and weak band near 2.2 eV (Fig.4a). This spectrum is similar to PL emission profile [15,16] and is typical of a multiphonon and multilevel process, i.e., a system in which relaxation occurs by several paths, involving the participation of numerous states into the band gap of the material. According to [15–17] this behavior is related to the structural disorder of BZO and confirms the presence of additional electronic levels in the forbidden band gap controlled by $[ZrO_5 \cdot V_O{}^*]$–$[ZrO_6]$ complex clusters.

It was found that adsorption of BZO nanocrystals on the surface of polymer-magnetite grains causes a significant modification in CL spectrum. By the comparison of the spectra obtained after adsorption of BZO on the surface of pure magnetite, polystyrene and polyaniline it has been found that only PS-BZO composites show the modification of CL spectrum. The Gaussian decomposition of CL curves show that the additional lowest energy

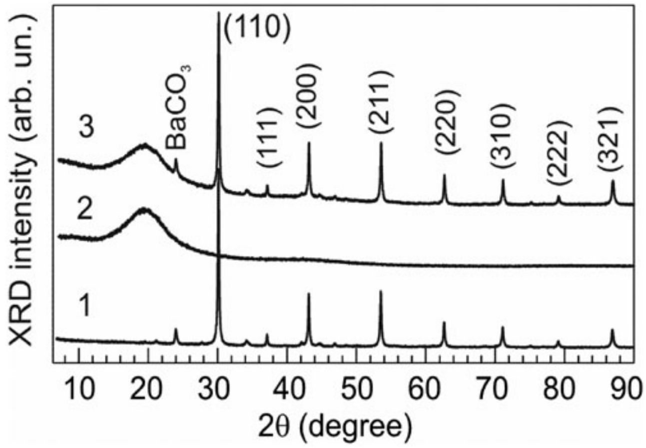

Figure 5. X-ray powder diffraction pattern for BZO nanocrystals (1, down), PS matrix (2, middle) and BZO-PS composite (3, top).

band and a highest energy band are appearance at significant reduction of the intensity CL. In the spectra of PS-BZO composites new bands at $E = 1.9$, 2.15, 2.45, 3.0 and 3.96 eV were observed (Fig. 4b).

Suggesting that blue – green emission intensity for BZO under ultraviolet excitation depends on the degree of crystal lattice disorder [18] a structure investigation has been carried out. X-ray powder diffraction pattern for nanocrystals (Fig. 5, curve 1) is typical for nanosize BZO powder described in literature [15–17]. And the presence of a small amount of $BaCO_3$ phase is observed, which can be typical for such samples [17]. By XRD analysis it is found that BZO presents a cubic perovskite-type structure in the crystalline form with space group $Pm\bar{3}m$. The lattice parameter a for BZO at room temperature is 4.19083 (6) Å, average size of domains is 23 nm. For polymer only one amorphous halo is develops on XRD pattern (Fig. 5, curve 2) with a maximum at $2\theta = 19.53°$.

Coexistence of amorphous halo with diffraction peaks of $BaZrO_3$ is evidence to formation of nanocomposites. It is found that in composite for BZO phase a parameter of elementary cell decreases to $a = 4.1879(2)$ Å while the parameters of microstructure remain similar as the pure BZO. So, for BZO phase in this composite a parameter of elementary cell (a) decreases indicating a change in the structure of nanocrystals under action of PS matrix. The described modifications of CL spectra can be connected with structural changes of BZO grains under influence of the polystyrene.

FTIR spectroscopy of PS matrix and its composite with BZO indicates that both spectra have well-defined absorption peaks at the wave numbers: 3061, 3027, 2852, 1944, 1720, 1601, 1583, 1493, 1154, 1028, 908, 698 cm^{-1} and others which are characteristic for PS [19] except an absorption band at 1720 cm^{-1} which can be attributed to the stretching vibrations of the R'R"C=O [19]. Presence of carbonyl group in the structure of suspension PS may be due to admixtures of product of peroxide decomposition formed during polymerization process or oxidation of polystyrene backbone by peroxide initiator. A decrease in the intensity of this band normalized to the intensity of the band at 1601 cm^{-1} in the FTIR

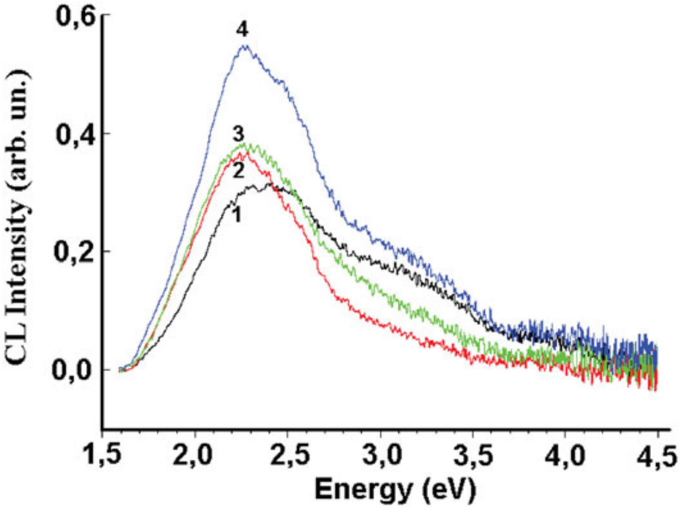

Figure 6. CL spectrum of Mt-PS-BZO-PANI hybrid composites. Content of BZO, %: 1 – 1; 2 – 5; 3-10; 4 – 20.

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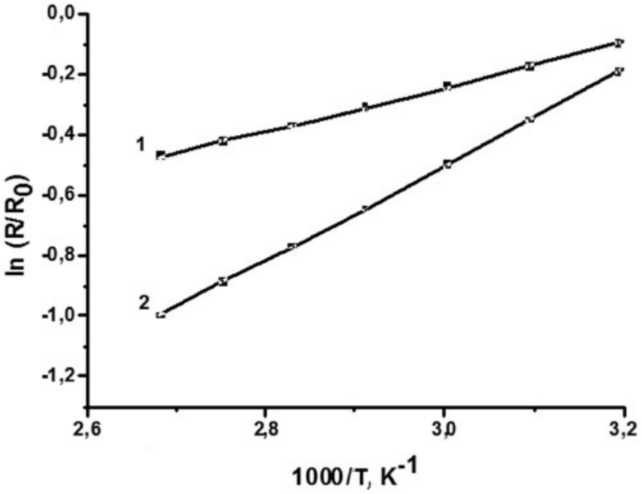

Figure 7. Temperature dependence of normalized resistance: 1 - for polymer matrix (PANI doped with HCl); 2 – for hybrid composite Mt-PS-10%BZO-PANI.

spectrum of PS-BZO nanocomposite (I_{1720} / I_{1601}) from 1.2 to 1.08 suggests that this group is responsible for the formation of chemical bonds with BZO nanocrystals.

The study of irradiative properties of composites obtained by polyaniline processing, showed preservation of the ability of composites to radiation, and the CL intensity increases with the increase of the BZO content in the composite (Fig. 6).

Simultaneously modification of the nanocapsules by polyaniline leads to significant decreasing specific volume resistance $\rho(\mathrm{T} = 293)$ of the samples – from 4×10^8 Om*m for non-modified nanocapsules to 18.2 ± 0.5 Om*m for particles modified with polyaniline.

Temperature dependence of hybrid composites resistance normalized to resistance measured at room temperature exhibits a typical semiconductor behavior and may be described by straight line in Arrhenius coordinates of equation $\rho = \rho_0 exp\ (E_a/2kT)$ in the temperature interval of 293 – 413 K (Fig.7). Calculated values of activation energy of charge transport $E_a = 0.29 \pm 0.01$ eV are higher in comparison with pure PANI doped by HCl ($E_a = 0.14 \pm 0.01$ eV). Obtained results suggest that main contribution in conductivity of hybrid composites has a matrix of polyaniline [20]. Introduction of the BZO nanoparticles would cause an increase in the activation energy of charge transport due to a morphological change in the regions of along-the-chains conductivity.

Conclusion

For the first time hybrid composites with magnetic, luminescent and conductive functions by surface modification of the magnetite-polymer nanoparticles by luminescent $BaZrO_3$ nanocrystals and polyaniline as conducting substances were obtained. It was found an influence of polymer matrix on cathodoluminescence spectrum of $BaZrO_3$ as appearance both the low energy bands and high energy band at 4 eV. Modification of CL spectra in composites may be due to changing in substructure of nanocrystals under influence of PS matrix: decreasing of lattice parameter for nano-BZO from 4.19083 (6) to 4.1879 (2) Å in BZO-PS composite; some chemical interaction between PS matrix and BZO confirmed by FTIR spectra. Proposed method of surface modification may be used for developing sensors and functional materials for diagnostic methods in medicine.

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