Nanocomposite materials based on ZnO and Fe$_3$O$_4$ nanoparticles in a polymer matrix

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Abstract. The techniques of sample synthesis of four types (the original liquid-phase dispersions of ZnO nanoparticles (NPs) and Fe$_3$O$_4$ NPs, solid nanocomposites ZnO-high-density polyethylene (HDPE) and Fe$_3$O$_4$-HDPE) have been developed. The dispersion of ZnO NPs was obtained by alkaline hydrolysis of zinc acetate potassium hydroxide in isopropyl alcohol. The dispersion of Fe$_3$O$_4$ NPs was prepared via the reaction of aqueous solutions of the iron salts (FeCl$_2$ and FeCl$_3$). After removal of impurity ions the dispersions were introduced into HDPE. A comparative analysis of the characteristics and properties of ZnO and Fe$_3$O$_4$ NPs in the original dispersions and in the polyethylene matrices was carried out by a complex of structural and physical methods (X-ray and electron diffraction, transmission and scanning electron microscopy, X-ray small-angle scattering, photoluminescence, electron magnetic resonance).

1. Introduction
One of the main directions of actively developed nanotechnology is to obtain stable, including to external influences, nanomaterials with reproducible properties that can be directly used in various fields of science and technology (electronics, catalysis, medicine, etc.). A promising way to create materials based on nanoparticles (NPs) is to introduce them into a polymer matrix, especially in a stable and widely available polymer such as polyethylene. However, due to the fact that the formation of a nanocomposite is carried out at relatively harsh chemical and technological conditions, the
question remains open whether it is possible to preserve the composition, structure and specific physical characteristics of the original NPs in a nanocomposite during the introduction stage.

Nanocomposite materials based on ZnO and Fe$_3$O$_4$ NPs, which attract much attention from scientific and practical points of view, have been studied in the present paper. ZnO NPs are optically active materials as well as having high brightness, narrow emission spectrum, high photostability [1]. They have the prospect of application in optoelectronics and photocatalysis as biological labels and sensors. The interest in Fe$_3$O$_4$ NPs is due to the fact that they are widely used in systems for recording and storing information, in new permanent magnets, in magnetic cooling systems, and as magnetic sensors [2].

2. Materials and methods
We obtained samples of four types: the original liquid-phase dispersions of ZnO and Fe$_3$O$_4$ NPs, and solid nanocomposites ZnO-high-density polyethylene (HDPE) and Fe$_3$O$_4$-HDPE. The dispersion of ZnO NPs was obtained by alkaline hydrolysis of zinc acetate potassium hydroxide in isopropyl alcohol. The dispersion of Fe$_3$O$_4$ NPs was prepared via the reaction of aqueous solutions of the iron salts (FeCl$_2$ and FeCl$_3$). After removal of impurity ions the dispersions were introduced into HDPE. The comparative analysis of the characteristics and properties of ZnO and Fe$_3$O$_4$ NPs in the original dispersions and in the polyethylene matrices was carried out by a complex of structural and physical methods (X-ray and electron diffraction, transmission and scanning electron microscopy, X-ray small-angle scattering, photoluminescence, electron magnetic resonance).

3. Results
3.1. ZnO samples
The analysis of X-ray (figure 1) and electron diffraction patterns revealed that ZnO NPs isolated from the dispersion in isopropanol and NPs in the polyethylene matrix are of single-phase state. NPs have the wurtzite structure (the P6$_3$mc space group).

![Figure 1. X-ray patterns of ZnO NPs.](image-url)

Transmission electron microscopy (figure 2) and X-ray small-angle scattering revealed that the ZnO samples contained NPs of spherical shape with narrow size distribution. The average size of ZnO
NPs was 5±1.5 nm in the original dispersion and 6±1.5 nm in a polyethylene matrix. Some broadening of the size distribution in the matrix is probably due to high temperature needed for the introduction of ZnO NPs into the matrix that leads to a partial agglomeration of the NPs.

To determine the effect of the HDPE matrix on the optical properties of embedded ZnO NPs, photoluminescence spectra for samples of the original dispersion of NPs and the NPs in the matrix were measured (figure 3).

The obtained spectra of two samples are largely repetitive. The positions and half-widths of both peaks (375 nm and 560 nm) look nearly identical. No significant changes in the spectra of NPs after the introduction into the composite indicate that the matrix has no appreciable effect on the exciton recombination mechanism. The matrix acts as a chemically stable preservative of NPs, retaining their spectral features.

3.2. Fe₃O₄ samples

The average size of Fe₃O₄ NPs was 8.5±2.0 nm in the original dispersion and 9±2.5 nm in the polyethylene matrix. Analysis of X-ray and electron diffraction patterns revealed that samples
containing Fe$_3$O$_4$ NPs are single-phase. The crystal structure of Fe$_3$O$_4$ NPs is described in terms of a cubic lattice (the Fd3m space group, a=8.374 Å).

Figure 4 shows the dependence of room temperature magnetization of Fe$_3$O$_4$ NPs, that were isolated from the dispersion (figure 4a) and introduced into the polyethylene matrix (figure 4b), on external magnetic field. The measurement results indicate that these two samples are of superparamagnetic behavior, since there is no residual magnetization and, consequently, a hysteresis loop.

![Figure 4](image)

**Figure 4.** Magnetic field dependence of magnetization of Fe$_3$O$_4$ NPs isolated from the dispersion (a,c) and NPs introduced into the polyethylene matrix (b,d). T=298 K (a,b), T=80 K (c,d).

The maximum magnetization of non-covered magnetite Fe$_3$O$_4$ (a) is much higher than that of magnetite in the polymer matrix (b). This is due to the fact that magnetization is directly proportional to the weight fraction of magnetic component in a sample. In converting the magnetization per atom, the results for the two samples are roughly equal, that demonstrates a conservation of the magnetic state after the transition from the dispersion into the solid matrix. The same dependence of the magnetization on the magnetic field was recorded for the two samples at liquid nitrogen temperature. The results are shown in figure 4 (c,d). There is a residual magnetization and hysteresis in this case, which suggests that the samples lose their superparamagnetic properties and become ferrimagnetics at low temperature.
The sample with magnetite NPs introduced into the polyethylene matrix was cooled in zero and an applied external magnetic field (figure 5). The blocking temperature was obtained at the intersection of two curves, it amounted to approximately 300 K for the sample. The sample is in a stable superparamagnetic state above the blocking temperature. Below this temperature, thermal energy is insufficient to overcome the magnetic anisotropy and intermolecular interactions, so paramagnetism disappears, and the sample is ferrimagnetic.

Figure 5. The temperature dependence of magnetization for Fe$_3$O$_4$ HDPE in the presence (FC) and absence (ZFC) of an external magnetic field.

4. Conclusions
The technology for production of nanomaterials based on ZnO and Fe$_3$O$_4$ NPs in a polymer matrix has been developed. The use of a complex of structural and physical methods has shown that the structure and properties of ZnO and Fe$_3$O$_4$ NPs are retained when they are introduced into a polyethylene matrix. The use of the synthesis technology of ZnO-HDPE nanocomposite is proposed for the development of standards of fluorescent emission in UV and visible ranges.

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