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Polymer-metal hybrid structures based on polydiphenylamine and Co nanoparticles

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Abstract

Polymer-metal hybrid structures based on polydiphenylamine (PDPhA) with Co nanoparticles homogeneously distributed in polymer matrix have been prepared for the first time. In situ synthesis of Co/PDPhA hybrid structure is carried out during condensation of diphenylamine crystalline oligomers in the presence of Co acetate ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) under the conditions of IR-irradiation. As a result, polymer chain growth occurs and hydrogen molecules are eliminated. Reduction of Co^{2+} up to Co^0 takes place under IR-irradiation with participation of hydrogen. The structure, content and morphology of obtained hybrid materials were characterized by Fourier-transform IR-spectroscopy, X-ray powder diffraction patterns, atomic-absorptive spectroscopy and transmission electron microscopy (TEM). Co nanoparticles appeared to exist in α -Co and β -Co modifications. Their relationship depends on IR-light intensity and time treatment. Co nanoparticles dimensions fall inside the limits of $2 < d < 8$ nm as it is indicated from TEM microphotographs. Magnetic properties of Co/PDPhA were investigated and superparamagnetic behavior was proved. Thermal properties of nanocomposites were evaluated by thermogravimetric analysis and excellent thermal stability was shown.

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Keywords: polydiphenylamine, magnetic nanocomposite, IR-irradiation, Co nanoparticles

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1. Introduction

Interest to hybrid nanomaterials is explained by the fact that they may possess both new and improved physical and chemical properties due to the synergic effect of organic and inorganic components which interact at a molecular level. It causes a high potential of their practical applications.

Metal-polymer hybrid nanomaterials based on polymers with a system of polyconjugation are have become of great interest because of their potential applicability for organic electronics and electrorheology, microelectromechanical systems, supercapacitors, sensors and biosensors, solar cells, displays, etc.

In this research work the method of synthesis of metal-polymer hybrid nanomaterial based on PDPhA and Co nanoparticles was developed for the first time. The results of the study of process of nanocomposite formation by chemical transformations of PDPhA in the presence of cobalt (II) acetate $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ in IR-heating in Ar atmosphere at 250–600 °C are presented. Magnetic and thermal properties of the obtained nanomaterials were investigated.

2. Experimental

Commercially available solvents and chemicals were used without further purification unless otherwise stated. Ammonium persulfate was additionally subjected to crystallization (Karyakin and Angelov, 1974). The monomer and other reagents were prepared as described earlier (Orlov et al., 2006). PDPhA was synthesized by the interphase (water / toluene) oxidative polymerization of diphenylamine monomer ($[\text{M}] = 0.2 \text{ M}$) using ammonium persulfate, ($[(\text{NH}_4)_2\text{S}_2\text{O}_8] : [\text{M}] = 1.25$) and hydrochloric acid ($[\text{HCl}] : [\text{M}] = 5$) (Orlov et al., 2006).

The synthesis of Co/PDPhA hybrid nanocomposite was performed by dissolving PDPhA (2 wt %) in DMFA solution containing 5–30 wt % of $\text{Co}(\text{OOCCH}_3)_2 \cdot 4\text{H}_2\text{O}$ (with respect to M_w of polymer) followed by the removal of the solvent at 85 °C. The residue was then treated at $T = 250\text{--}600 \text{ }^\circ\text{C}$ for 5–90 min under an Ar atmosphere using laboratory device for pulse photon annealing (Zemtsov et al., 2006; Ozkan et al., 2010; Ozkan et al., 2011).

The FTIR spectra were recorded using a «IFS 66v» spectrometer in the range 4000–400 cm^{-1} on samples prepared in KBr pellets.

An X-ray analysis of obtained materials was performed with a “Difrey” diffractometer in a continuous mode (CrK_α source, Bragg-Brentano geometry).

TEM images were obtained with Phillips EM-301 (acceleration voltage 60–80 kV). Cobalt content was estimated with atomic adsorption spectrometer (AAS 30, Carl Zeiss Jena).

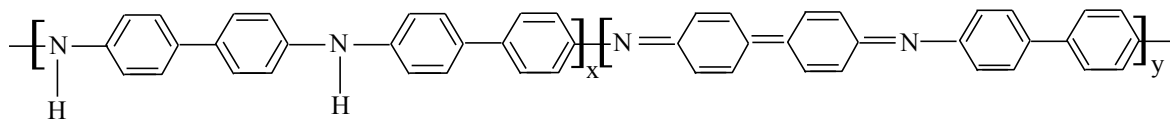
Magnetic characteristics of Co/PDPhA nanocomposite were investigated with a vibrational magnetometer (Chernavskii et al., 2006) at room temperature. The absolute value of the magnetic moment was measured by the cobalt standard with a mass of 2 mg.

A thermogravimetric analysis (TGA) was carried out using a Mettler Toledo TGA/DSC1 thermobalance under the dynamic mode in a stream of nitrogen or air in the temperature range 30–900 °C. The sample was first kept at the temperature of 30 °C for 15 min and then for the second time at 900 °C for 30 min. The TG experimental parameters were as follows: a heating rate of 10 °C/min, a nitrogen flow rate of 10 ml/min, a sample weight of 100 mg, and a standard alumina made crucible.

DSC-analysis was performed on a DSC823° Mettler Toledo calorimeter. Sample heating was carried out at the rate of 10 °C/min, in an argon atmosphere at its feeding rate 70 ml/min. Analysis of experimental results was carried out using a STARE program, which comes with the device. The accuracy of the measurements was $\pm 0.3 \text{ K}$ for the temperature determination and $\pm 1 \text{ J/g}$ for the enthalpy determination.

3. Results and discussion

PDPhA is an aromatic polyamine with a system of polyconjugation in which diphenylene units are divided by amino groups. Molecular mass of PDPhA $M_w = (9-11) \times 10^3$ (Karpacheva et al., 2004; Orlov et al., 2006; Ozkan et al., 2007).



The choice of the polymer is caused by its high thermal stability (up to 450 °C in the air and up to 600–650 °C in the inert atmosphere (Ozkan et al., 2007)).

The growth of the polymer chain of PDPhA occurring under IR-irradiation in the presence of cobalt (II) acetate $\text{Co}(\text{OOCCH}_3)_2 \cdot \text{H}_2\text{O}$ was shown via FTIR spectroscopy (Fig. 1). This fact is proved by the increase of intensity of the absorption band at 810 cm^{-1} , which characterizes non-planar deformation vibrations of $\delta_{\text{C-H}}$ 4,4'-substituted aromatic rings (Orlov et al., 2006). As the temperature of the sample increases, the intensity of the absorption band at 695 cm^{-1} of the monosubstituted phenyl ring decreases. It means that the amount of end groups of the polymer significantly decreases.

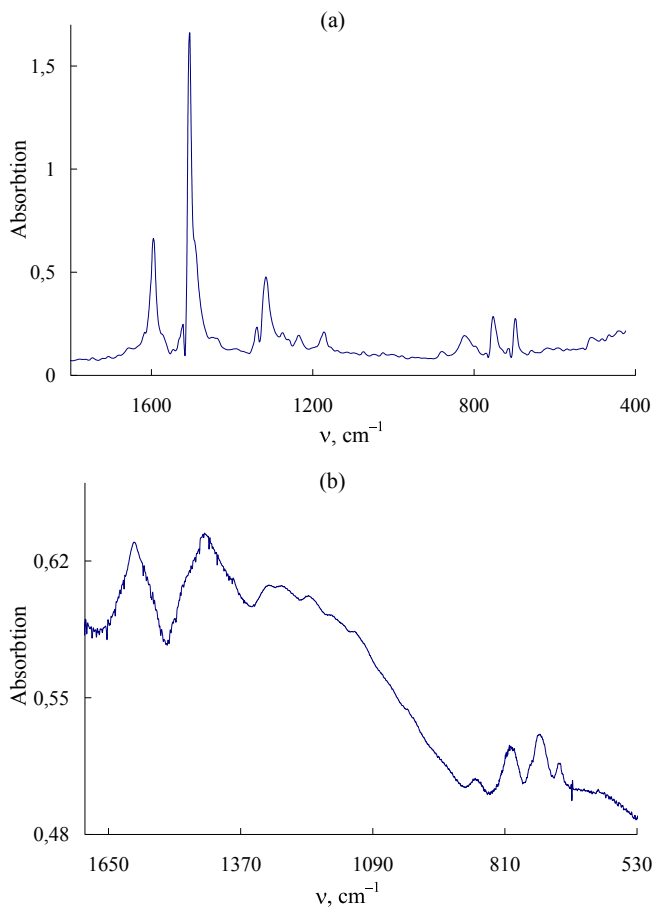


Fig. 1. IR spectra of PDPhA (a) and Co/PDPhA nanocomposites obtained by heating at 450 °C (b) for 10 min.

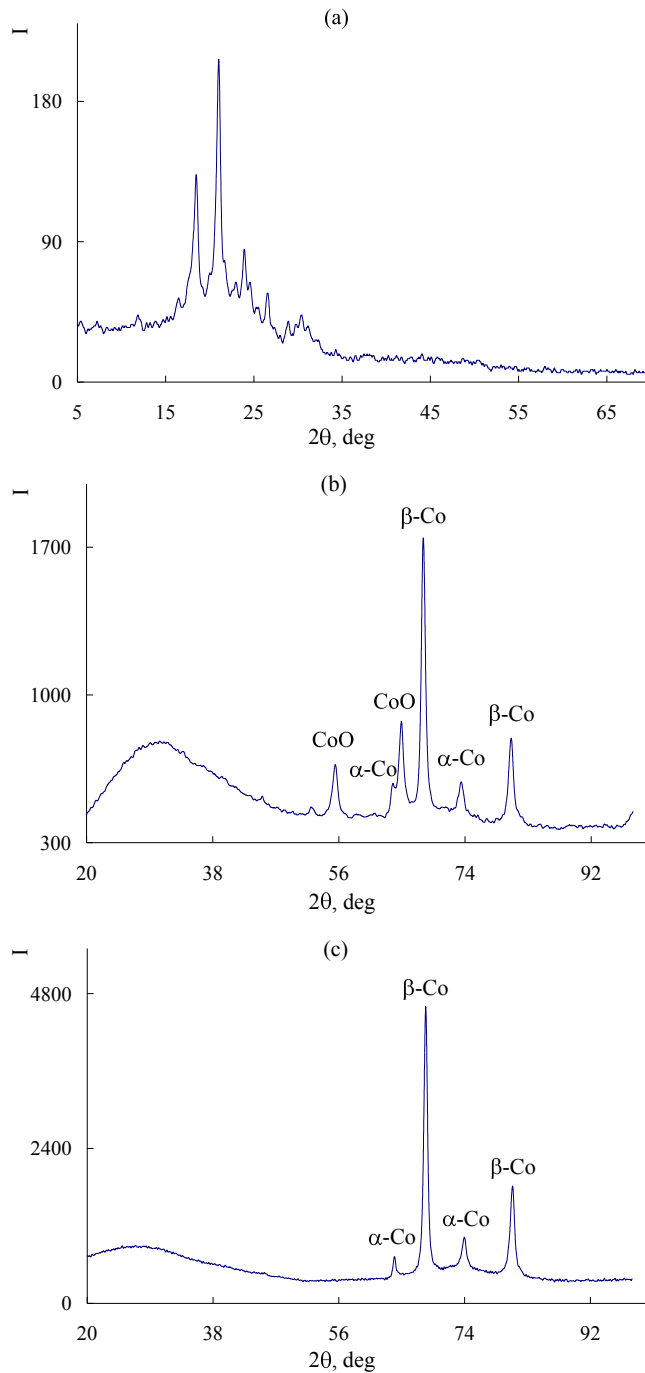


Fig. 2. XRD spectra of PDPPhA (a) and Co/PDPPhA nanocomposites obtained by heating at 400 °C (b) and 450 °C (c) for 10 min.

Fig. 2 shows diffractograms of PDPPhA (a) and Co/PDPPhA nanocomposite, obtained at 400 (b) and 450 °C (c). It was found that under IR heating of PDPPhA in the presence of Co (II) acetate the growth of the polymer

chain occurs. It's caused by means of crystalline oligomers of diphenylamine condensation (Fig. 2a) with the release of hydrogen, contributing to the reduction of Co^{2+} to Co^0 . Increasing of the preparation temperature leads to the decrease of crystalline fraction content in the polymer. This is evidenced by the absence of reflection bands in the range of scattering angles $2\theta = 5\text{--}35^\circ$, characterizing crystalline oligomers of diphenylamine. As a result, a nanostructured composite material is formed, in which Co nanoparticles are dispersed in polymer matrix. Metal-polymer Co/PDPhA nanocomposite is a black powder, insoluble in organic solvents.

The effect of IR heating conditions (preparation temperature and heating time, and also Co concentration) on the yield of hybrid nanocomposite was studied. Fig. 3 shows the yield of the nanocomposite decreases with the increase of heating time and preparation temperature. It is due to the fact that while the preparation temperature increases, the crystalline oligomers, participating in the growth of the polymer chain, are partially carried away by the argon current, in which the synthesis of the nanocomposite is carried out.

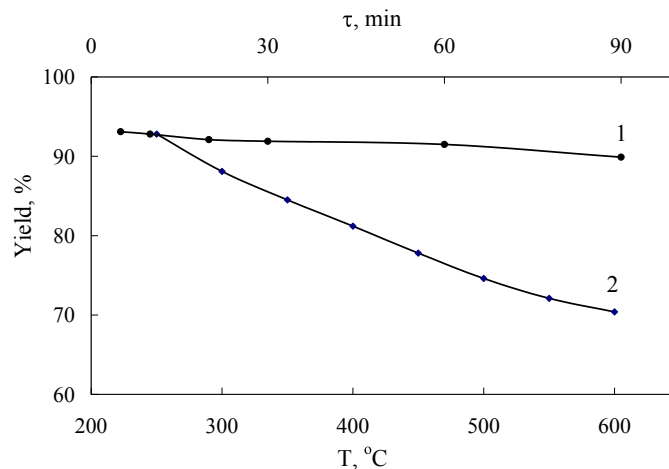


Fig. 3. The dependence of the yield of Co/PDPhA nanocomposite from the heating time (at 250 °C) (1) and preparation temperature (heating time 10 min) (2).

On the diffractogram of Co/PDPhA nanocomposite (Fig. 2) reflection bands of α -Co nanoparticles with a hexagonal close-packed lattice and β -Co with a cubic face-centered lattice are shown. Their ratio depends on the preparation temperature and heating time. It was found that at preparation temperatures below 450 °C in the nanocomposite there are both Co and CoO nanoparticles. It was shown that at the temperature of 250 °C the increase of heating time in the range of 5–90 minutes does not lead to the full reduction of Co. In the inert atmosphere at the preparation temperature in the range of 450–600 °C and the duration of the IR heating equal to 10 minutes only metallic Co nanoparticles are observed. According to AAS, cobalt content in the Co/PDPhA nanocomposite obtained at 450 °C is 13.1 wt. %.

Investigation of magnetic properties at the room temperature has shown that all of the obtained hybrid Co/PDPhA nanocomposites exhibit hysteresis nature of remagnetization. In Fig. 4 the hysteresis loop of the nanocomposite obtained at 300 °C is given as an example. Its magnetic characteristics are: $H_C = 142$ Oe, $M_S = 0.984$ emu/g, $M_R = 0.076$ emu/g, $M_R/M_S = 0.08$. The obtained value M_R/M_S is typical to uniaxial, single-domain particles (Madsen, 2002). Such the squareness ratio of the hysteresis loop implies a significant part of superparamagnetic cobalt nanoparticles. At the room temperature the transition to superparamagnetic state proceeds at Co particles size less then 7–8 nm (Bagrets et al., 2004). In our case, according to TEM, Co nanoparticles have dimensions $2 < d < 8$ nm (Fig. 5).

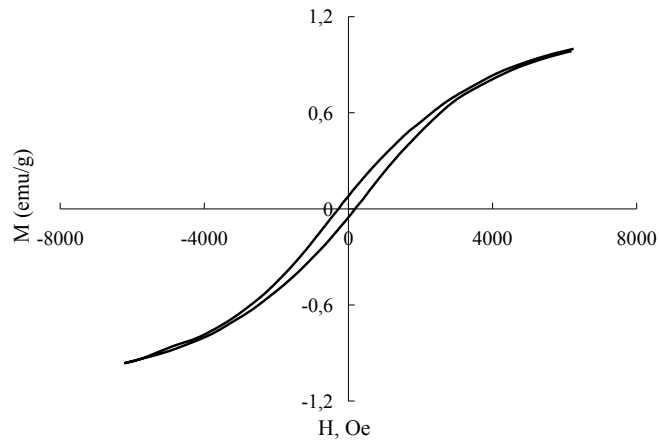


Fig. 4. Magnetization of Co/PDPhA nanocomposite, obtained at 300 °C (heated for 10 min), as a function of applied magnetic field at room temperature.

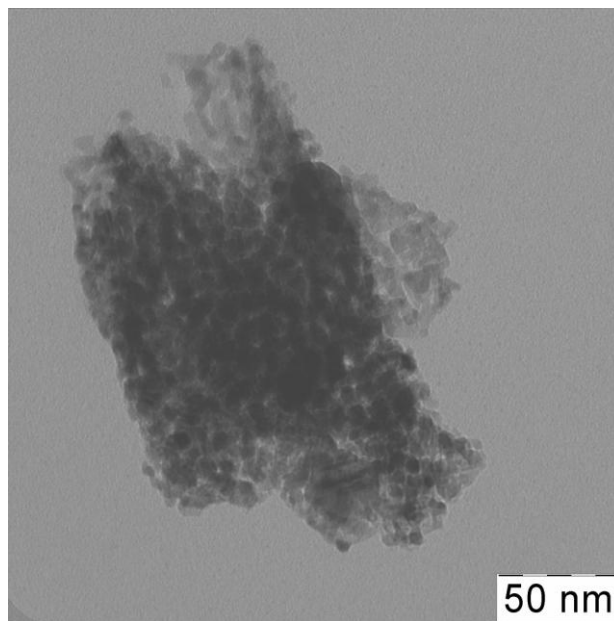


Fig. 5. The TEM image of Co/PDPhA nanocomposite obtained by heating at 300 °C.

Thermal stability of Co/PDPhA nanocomposite was studied by TGA and DSC. Fig. 6 shows the temperature dependence of weight loss of Co/PDPhA nanocomposite while heating up to 900 °C in the nitrogen and air flows. Weight loss at ~ 108 °C is associated with the removal of moisture (Yue et al., 1991; Kulkarni et al., 1989; Boyle et al., 1992; Amano et al., 1994). This is also confirmed by DSC (Fig. 7). On the DSC thermogram of Co/PDPhA nanocomposite there is an endothermic peak in this temperature range. When reheating, this peak is absent. Thus, the weight loss of 5% occurs because of the presence of moisture in the nanocomposite. After moisture removal, the weight of the nanocomposite remains the same until 410 °C.

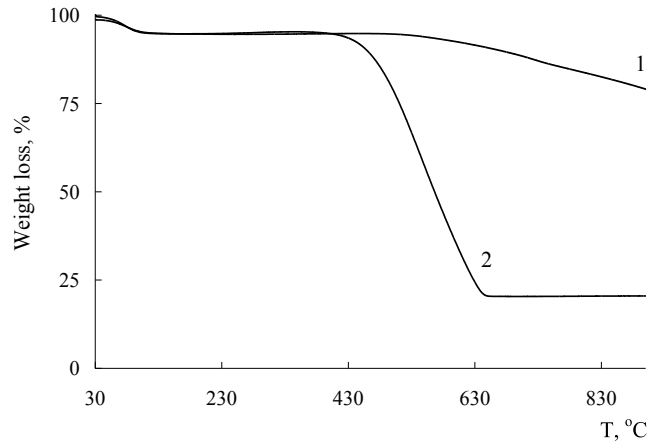


Fig. 6. Sample weight loss of Co/PDPhA nanocomposite as a function of temperature when heated up to 900 °C at a heating rate of 10 °C/min in a flow of nitrogen (1) and air (2).

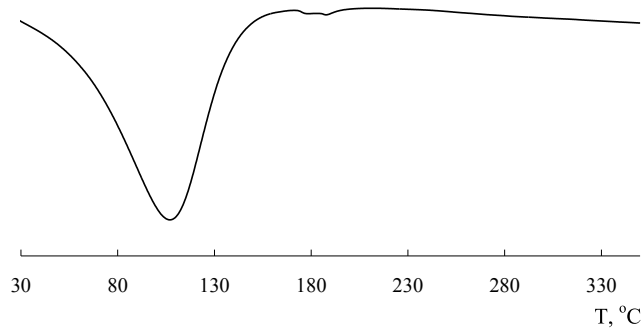


Fig. 7. The DSC spectrum of Co/PDPhA nanocomposite when heated up to 350 °C in a flow of nitrogen with a heating rate of 10 °C/min.

The main processes of thermooxidative destruction of Co/PDPhA nanocomposite start at 450 °C. Nanocomposite loses half of its original weight at 566 °C. In the inert atmosphere there is gradual loss of weight of Co/PDPhA nanocomposite and finally at 900 °C the residue is 79%.

4. Conclusions

The method of preparation of polymer-metal nanostructured hybrid material based on PDPhA with dispersed Co nanoparticles in the conditions of IR-heating of PDPhA in the presence of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ was developed. In hybrid material Co nanoparticles with sizes $2 < d < 8$ nm are dispersed in PDPhA matrix as it was shown under the investigation of structure and morphology. Nanomaterials obtained are characterized with the excellent thermostability.

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