Journal of International Scientific Publications:
Materials, Methods & Technologies, Volume 6, Part 1

NANOCOMPOSITE DISPERSED MAGNETIC MATERIAL AND THE METHOD OF OBTAINING IT

Igor S. Eremeev, Sveta Zh. Ozkan, Galina P. Karpacheva
Russian Academy of Sciences A.V. Topchiev Institute of Petrochemical Synthesis,
Leninsky pr. 29, Moscow, 119991, Russia

Abstract

Magnetic nanoparticles based on Fe_3O_4 and polydiphenylamine-2-carbonic acid (PDPhACA) with core-shell structure, where Fe_3O_4 is the core and PDPhACA is the shell, were obtained for the first time. Influence of polymerization conditions (reagents concentration, their ratio, temperature of the reaction) on the yield and structure of polymers was studied. Formation of nanoparticles was proved by X-ray diffraction analysis and transmission electron microscopy. On X-ray images one can clearly identify diffraction peaks of Fe_3O_4 nanoparticles. Fe_3O_4/PDPhACA nanoparticles dimensions fall in the limits of $4<d<14$ nm. Magnetic properties of Fe_3O_4/PDPhACA nanoparticles were studied. It was found that obtained nanoparticles are superparamagnetic.

Key words: *magnetic nanoparticles, Fe_3O_4, polydiphenylamine-2-carbonic acid, core-shell structure.*

1. INTRODUCTION

In recent years materials based on polymers with a system of polyconjugation and magnetic nanoparticles attract special interest due to their unique electric, magnetic and optical properties. Such materials find a wide range of applications in various areas of modern life (medicine, ecology, information storage, sensors etc.) [1-7]. Magnetic nanoparticles have attracted significant interest because of their unique properties, such as their low toxicity and biocompatibility, which enables one to apply them as magnetic components in ferrofluids. One of the main problems in the field of ferrofluids is aggregation of magnetic nanoparticles. In this research work a method of synthesis of nanoparticles based on Fe_3O_4 and PDPhACA was developed.

2. EXPERIMANTAL

Diphenylamine-2-carbonic acid of the analytical grade, ammonium persulfate of analytic grade, sulfuric acid of the reagent grade, ammonia of the reagent grade, DMF (Acros Organics), iron (II) chloride (Acros Organics), iron (III) chloride of the reagent grade and methyl alcohol (JT Baker) were used as received. Aqueous solutions of reagents were prepared with the use of distilled water.

The synthesis of Fe_3O_4/PDPhACA nanoparticles was performed as follows. Firstly the synthesis of Fe_3O_4 nanoparticles was carried out through hydrolysis of a mixture of iron (II) and (III) chlorides in ratio 1:2 in ammonium hydroxide solution at 60°C. For monomer fixation on the surface of Fe_3O_4 nanoparticles, ammonia solution of monomer with the needed concentration was added to the obtained suspension. Process was carried out at 80°C with constant intense stirring for 30 minutes.

To carry out the oxidative polymerization of DPhACA on the surface of Fe_3O_4 nanoparticles, aqueous solution of ammonium persulfate was added dropwise to the previously cooled to 0°C suspension of Fe_3O_4/DPhACA. Synthesis was being held for 3 hours under intense stirring at 0°C. When the process

was complete, the reaction mixture was precipitated into a 2-fold excess of 1M H_2SO_4, then filtered off and washed many times with distilled water to a neutral reaction of the filtrate. The obtained product was dried under vacuum over KOH to a constant weight. According to atomic-absorption spectroscopy content of Fe is 37% and Fe_3O_4 – 51%.

The polymerization of DPhACA in a sulfuric acid solution was performed as follows. To the stirred sulfuric acid solution of the monomer of the desired concentration, the solution of ammonium persulfate in the same solvent (1/4 of the total volume) was added dropwise at 0°C. Polymerization was conducted at 0°C under constant intense stirring. When the process was complete, the reaction mixture was precipitated into a 10-fold excess of ice water. The product was filtered off and washed many times with distilled water initially to remove the residues of reagents and then to a neutral reaction of the filtrate. After low-molecular-mass oligomers were extracted with methanol, the product was dried in vacuum to a constant weight.

The FTIR-spectra were recorded using "IFS 66v" FTIR spectrophotometer in the range 4000 – 400 cm^{-1}. The samples were prepared as KBr pellets.

An X-ray analysis of Fe_3O_4/PDPhACA nanoparticles and PDPhACA was performed at the room temperature with a Rigaku diffractometer in a continuous mode (FeK_α source, Bragg-Brenato geometry).

Microphotographs of Fe_3O_4/PDPhACA nanoparticles were made on a transmission scanning microscope EM-301 "Philips" (Holland), acceleration voltage 60-80 kV.

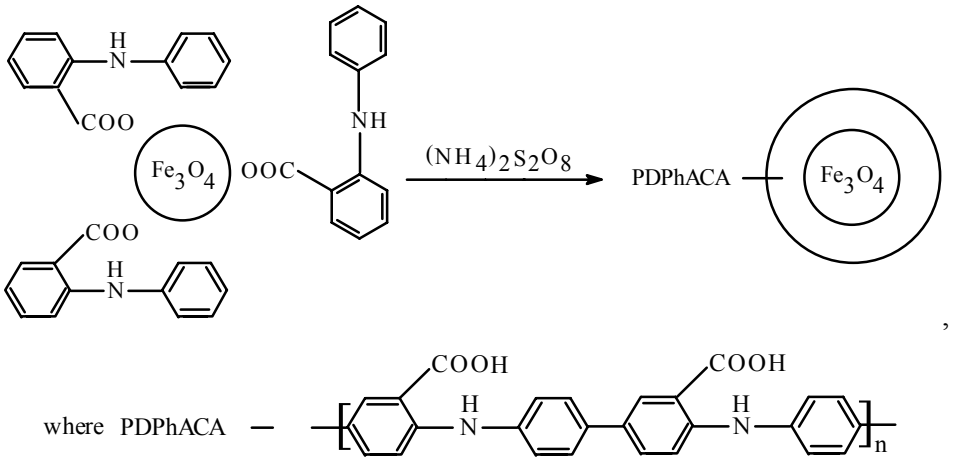
Quantity of metal in Fe_3O_4/PDPhACA nanoparticles was found with the use of atomic-absorption spectrophotometer AAS 30, "Carl Zeiss JENA".

The thermal analysis of Fe_3O_4/PDPhACA nanoparticles and PDPhACA was performed on a TGA/DSC1, "Mettler Toledo" instrument under dynamic heating in the temperature range 30–1000°C in air and in a flow of nitrogen. The test sample was preliminarily thermostated at 30°C for 15 minutes and then, after polymer being heated to 1000°C, for 30 minutes. The sample weight was 100 mg, the heating rate was 10°C/min, the nitrogen flow rate – 10 ml/min. Calcined aluminium oxide was employed as a reference. The samples were analyzed in an Al_2O_3 crucible.

The hysteresis curve was measured by vibrating sample magnetometer (VSM). The in-plane anisotropy field was found from a numerical analysis of the magnetization curve, based on the law of approach to the saturation. The microwave permeability was measured by the coaxial technique [8] in the frequency range of 0.1–10 GHz.

3. RESULTS AND DISCUSSION

Materials based on polyconjugated polymers and magnetic nanoparticles attract special interest due to their unique electric, magnetic and optical properties. Magnetic nanoparticles based on Fe_3O_4 and PDPhACA were obtained for the first time [9]. Formation of Fe_3O_4/PDPhACA nanoparticles involves synthesis of Fe_3O_4 nanoparticles through a hydrolysis of mixture of chlorides of Fe (II) and (III) in relation 1:2 in ammonium hydroxide solution [10], monomer fixation on the surface of Fe_3O_4 nanoparticles with further in situ polymerization with the addition of ammonium persulfate. As a result nanoparticles with core-shell structure are formed, where Fe_3O_4 is the core and PDPhACA is the shell. The polymeric shell, that has positively charged groups in its structure, prevents the aggregation of nanoparticles.



Structure of Fe_3O_4/PDPhACA nanoparticles was proved by XRD and TEM. On X-ray images one can clearly identify diffraction peaks of Fe_3O_4 nanoparticles (Fig. 1).

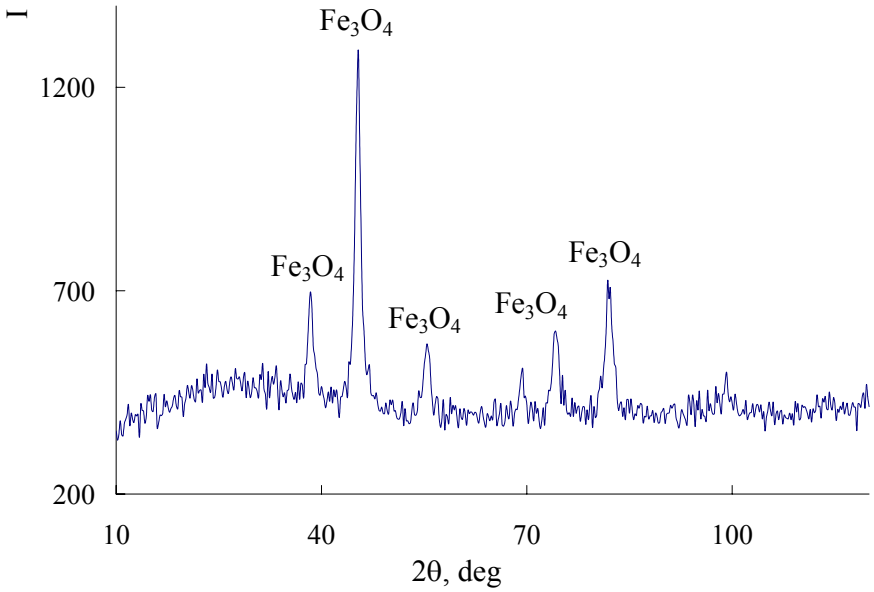


Fig. 1. XRD pattern of Fe_3O_4/PDPhACA nanoparticles.

According to TEM data, Fe_3O_4/PDPhACA nanoparticles dimensions fall in the limits of $4<d<14$ nm (Fig. 2).

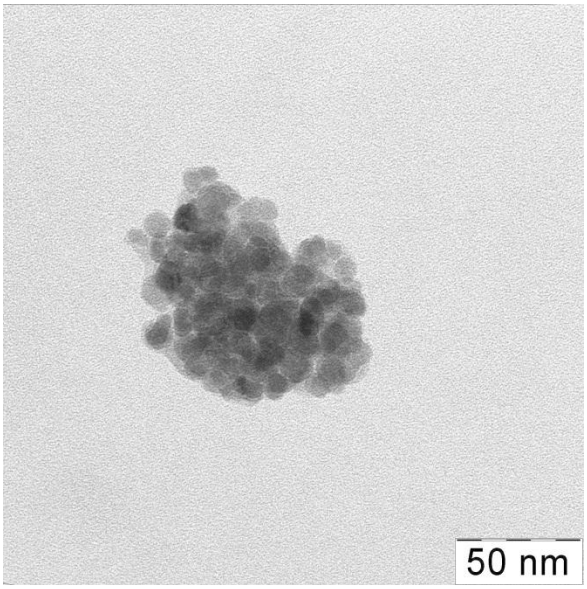
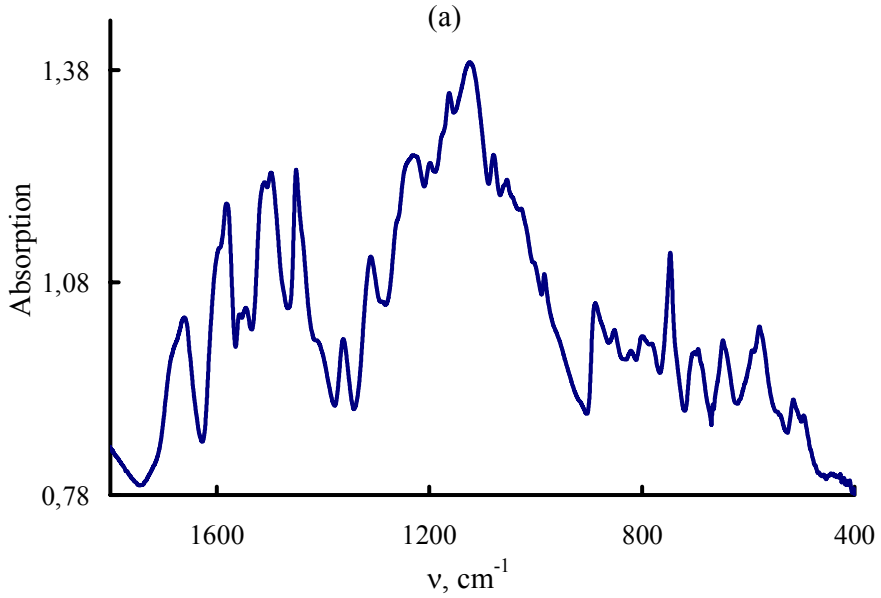


Fig. 2. Microphotograph of Fe_3O_4/PDPhACA nanoparticles.

IR-spectroscopy results have proved monomer fixation on Fe_3O_4 nanoparticles and formation of PDPhACA. In IR-spectra there is an adsorption band at 572 cm^{-1}, which is associated with stretching vibrations of Fe-O bond. It was shown that polymeric shell is formed by means of C-C joining into para-position of phenyl rings with respect to nitrogen.



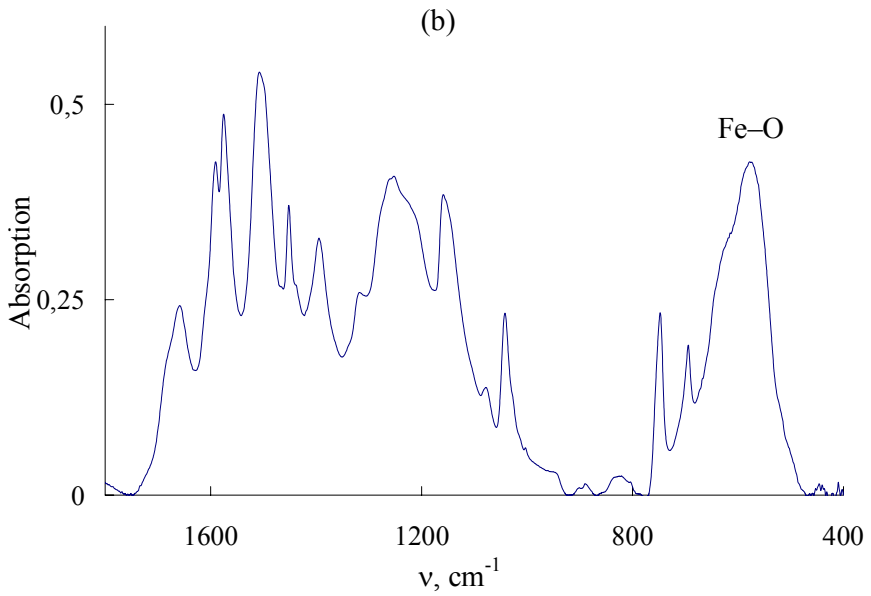


Fig. 3. IR-spectra of PDPhACA (a) and Fe_3O_4/PDPhACA nanoparticles (b).

Absorption bands near 884 and 800 cm^{-1} are due to nonplanar deformation vibrations δ_{C-H} of 1,2,4 and 1,4-substituted aromatic rings [11].

Thermal stability of Fe_3O_4/PDPhACA nanoparticles was studied (Fig. 4.). Curves of weight loss have stepped character. For Fe_3O_4/PDPhACA nanoparticles one can observe 5% weight loss at 285°C in the air. Thermal stability of nanoparticles in the inert atmosphere is higher. Basic processes of thermal destruction of Fe_3O_4/PDPhACA nanoparticles proceed at 770°C. For nanoparticles in the inert atmosphere 5% weight loss is observed at 250°C, and 50% weight loss – at 950°C.

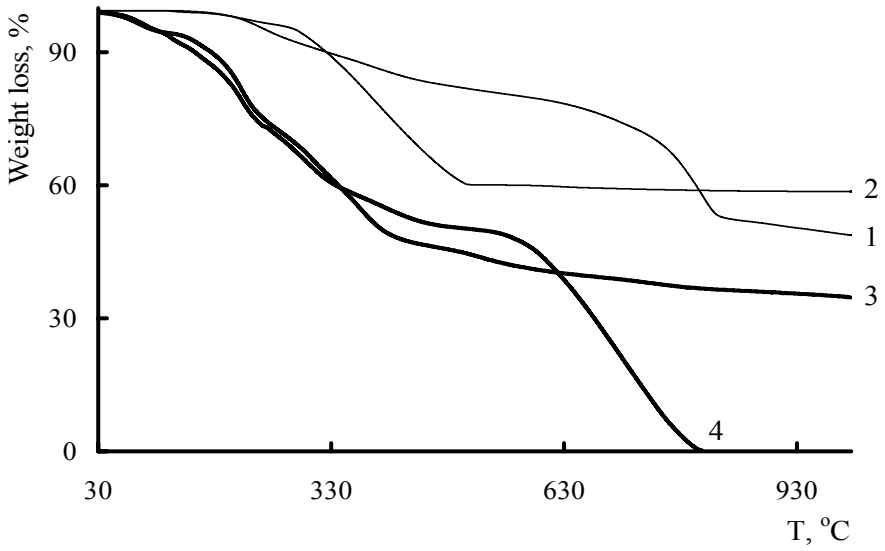


Fig. 4. Fe_3O_4/PDPhACA nanoparticles (1, 2) and PDPhACA (3, 4) weight loss while heating till 1000°C at rate of 10°C/min in nitrogen flow (1, 3) and in the air (2, 4).

Investigation of magnetic properties of Fe_3O_4/PDPhACA nanoparticles at room temperature (Fig. 5) has shown that the obtained nanomaterial is superparamagnetic (Ms = 33.5 emu/g, Hc = 76 Oe, Mr/Ms = 14.9%).

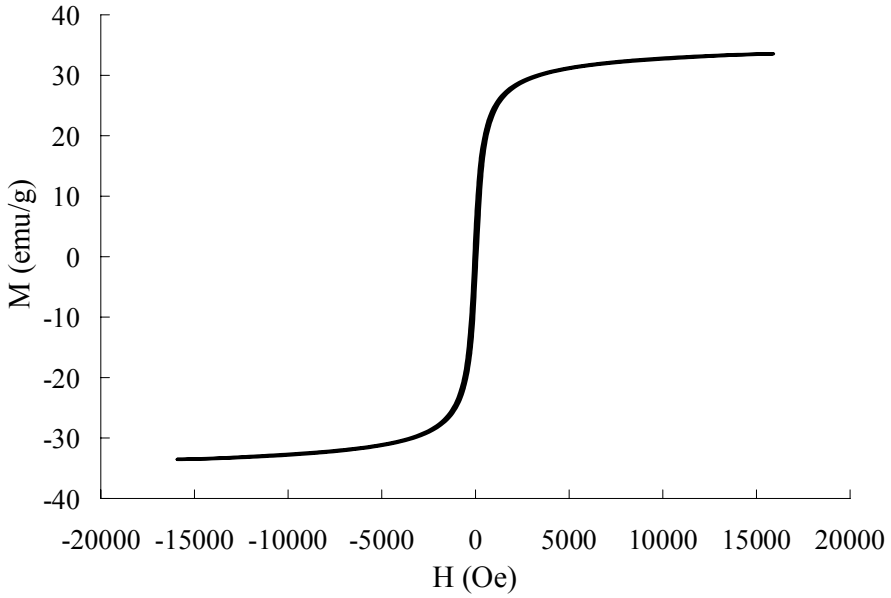


Fig. 5. Magnetization of Fe_3O_4/PDPhACA nanoparticles as a function of applied magnetic field at room temperature.

4. CONCLUSIONS

Nanocomposite dispersed magnetic material with core-shell structure, where Fe_3O_4 nanoparticles form the core and PDPhACA forms the shell, was proposed for the first time. The obtained superparamagnetic Fe_3O_4/PDPhACA nanoparticles have size $4<d<14$ nm and can be used as magnetic components in aqueous and organic ferrofluids, self-stabilization of which will be provided by polymeric shell.

ACKNOWLEDGEMENTS:

The work has been supported in part by the Russian Foundation for Basic Research, project 11-03-00560a.

REFERENCES

1. Tang B.Z., Geng Y., Larn J.W.Y., Li B., Jing X., Wang X., Wang F., Pakhomov A.B., Zhang X.X. Processible Nanostructured Materials with Electrical Conductivity and Magnetic Susceptibility: Preparation and Properties of Maghemite/Polyaniline Nanocomposite Films. // Chemical Materials. 1999. V. 11. P. 1581-1589.

2. Lu X., Yu Y., Chen L., Mao H., Zhang W., Wei Y. Preparation and characterization of polyaniline microwires containing CdS nanoparticles. // Chemical Communications. 2004. V. 13. P. 1522-1523.

3. Dorman J., Fiorani D. Magnetic Properties of Fine Particles. // Amsterdam. North-Holland. 1991. P. 309-423.

4. Zhang Z.M., Wan M.X. Nanostructures of polyaniline composites containing nano-magnet. // Synthetic Metals. 2003. V. 132. P. 205-212.

5. Deng J., He C, Peng Y., Wang J., Long X., Li P., Chan A. Magnetic and conductive Fe_3O_4–polyaniline nanoparticles with core–shell structure. // Synthetic Metals. 2003. V. 139. P. 295-301.

6. Lu X., Yu Y., Chen L., Mao H., Gao H., Wang J., Zhang W., Wei Y. Aniline dimer–COOH assisted preparation of well-dispersed polyaniline–Fe_3O_4 nanoparticles. // Nanotechnology. 2005. V. 16. P. 1660-1665.

7. Chao D., Lu X., Chen J., Zhang W., Wei Y.J. Anthranilic acid assisted preparation of Fe_3O_4–poly(aniline-*co*-*o*-anthranilic acid) nanoparticles // Journal of Applied Polymer Science. 2006. V. 102. P. 1666-1671.

8. I.T. Iakubov, A.N. Lagarkov, S.A. Maklakov, A.V. Osipov, K.N., Rozanov, I.A. Ryzhikov, S.N. Starostenko. Microwave permeability of laminates with thin Fe-based films. // Journal of Magnetism and Magnetic Materials. 2004. V. 272-276. P. 2208-2210.

9. Karpacheva G.P., Ozkan S.Zh. RF patent for the invention of "Dispersed nanocomposite magnetic material and method of its obtaining", № 2426188 from 10.08.2011.

10. Massart R. Preparation of aqueous magnetic liquids in alkaline and acidic media. // IEEE Transactions on Magnetics. 1981. Mag-17. V. 2. P. 1247-1248.

11. Ozkan S.Zh., Bondarenko G.N., Karpacheva G.P. Oxidative Polymerization of Diphenylamine-2-carboxylic Acid: Synthesis, Structure, and Properties of Polymers.// Polymer Science. B. 2010. V. 52. № 5. P. 263-269.