U.P.B. Sci. Bull., Series B, Vol. 71, Iss. 4, 2009 ISSN 1454-2331

Fe_3O_4 AND $CoFe_2O_4$ NANOPARTICLES STABILIZED IN SODIUM ALGINATE POLYMER

Cristina Ileana COVALIU[1], Cristian MATEI[2], Adelina IANCULESCU[3], Ioana JITARU[4], Daniela BERGER[5]

Nanoparticulele de magnetită şi ferită de cobalt se utilizează în imagistica de rezonanță magnetică, hipertermie, transportul magnetic al medicamentelor etc. În această lucrare se prezintă o metodă simplă şi economică de sinteză a nanocompozitelor pe bază de Fe_3O_4 şi $CoFe_2O_4$ stabilizate în alginat de sodiu polimeric. Nanoparticulele de Fe_3O_4 şi $CoFe_2O_4$ au fost sintetizate prin hidroliză forțată şi respectiv metoda combustiei. Proprietățile structurale şi morfologice au fost investigate prin difracție de raze X, microscopie electronică de baleaj şi granulometrie. Interacțiile dintre polimer şi nanoparticulele de Fe_3O_4 şi $CoFe_2O_4$ au fost studiate prin spectroscopie în infraroşu. Compozitia compozitelor a fost determinată prin spectrocopie de raze X cu dispersia energiei.

Magnetite and cobalt ferrite nanoparticles have been widely used in magnetic resonance imaging, hyperthermia, magnetic drug delivery etc. In this paper, we report a facile, low cost route to prepare nanocomposites containing Fe_3O_4 or $CoFe_2O_4$ nanoparticles stabilized in sodium alginate polymer. Fe_3O_4 and $CoFe_2O_4$ nanoparticles were prepared by forced hydrolysis and combustion method, respectively. The structural and morphological properties have been investigated by X-ray diffraction, scanning electron microscopy and dynamic light scattering measurements. The interactions between sodium alginate polymer and Fe_3O_4 or $CoFe_2O_4$ nanoparticles have been studied by infrared spectroscopy. The composition of composites was determined using energy dispersive X-ray spectroscopy.

Keywords: magnetite, cobalt ferrite, sodium alginate, composite

1. Introduction

Superparamagnetic nanoparticles are very interesting materials due to their applications in magnetic resonance imaging (MRI) [1-5], tissue repairing [4], detoxification of biological fluids [6], hyperthermia [7], drug delivery [8, 9] and

[1] PhD student, Departament of Inorganic Chemistry, University POLITEHNICA of Bucharest, Romania
[2] Reader, Departament of Inorganic Chemistry, University POLITEHNICA of Bucharest, Romania
[3] Prof., Departament of SIMONa, University POLITEHNICA of Bucharest, Romania
[4] Prof., Departament of Inorganic Chemistry, University POLITEHNICA of Bucharest, Romania
[5] Reader, Departament of Inorganic Chemistry, University POLITEHNICA of Bucharest, Romania; corresponding author: Daniela Berger, e-mail: danaberger01@yahoo.com

cell separation [9]. For biomedical applications, the nanoparticles should be non-toxic and biocompatible and for these reasons it is necessary to coat the nanoparticles with a biocompatible polymer.

The research in the field of magnetic resonance imaging contrast agents has been focused on the development of superparamagnetic nanoparticles, water insoluble, like magnetite (Fe_3O_4), maghemite (γFe_2O_3) or other ferrites. There are two commercially available iron oxide-based drugs for the clinical treatment of liver tumors: Ferumoxides (Endorem®) and Ferucarbotran (Resovist®), which contain iron oxide nanoparticles coated with dextran and carboxydextran, respectively [1].

Another polysaccharide-type polymer studied for this purpose is sodium alginate that is extracted from brown algae and is currently used in the food, cosmetics, pharmaceutical industry due to its nontoxicity and biocompatibility properties. Sodium alginate (ANa) is a linear polymer composed of α-L-guluronate (G) and β-D-mannuronate (M) units in varying proportion (Fig. 1).

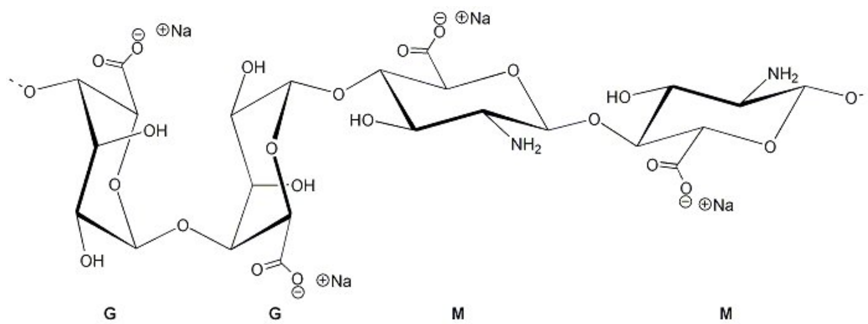


Fig.1. Structure of sodium alginate polymer

In this paper we present our results on the obtaining and characterization of Fe_3O_4 and $CoFe_2O_4$ nanoparticles coated with sodium alginate.

2. Experimental

The composites have been obtained via a two steps procedure. First, the oxide nanoparticles have been obtained and then they have been coated with sodium alginate polymer.

Synthesis of Fe_3O_4 and $CoFe_2O_4$ nanoparticles. Fe_3O_4 nanoparticles were prepared by forced hydrolysis [10] using $FeCl_2$ aqueous solution and γ-Fe_2O_3 (Sigma Aldrich, particles size < 50 nm) at a molar ratio, Fe^{2+}: Fe^{3+}, 1:2, according to equation (1). The reaction mixture was mechanical stirred for one week at 100 °C in 100 mL constant water volume. $CoFe_2O_4$ nanoparticles were obtained by combustion method using corresponding metallic nitrates and α-alanine in fuel rich conditions (20% excess of α-alanine). α-Alanine was added to the 0.2 M aqueous solution of cobalt and iron nitrates. The reaction mixture was heated under magnetic stirring to evaporate the water and then for combustion. A fine black powder, named as-prepared powder was resulted in the combustion reaction (Eq. 2), which was annealed at different temperatures to obtain $CoFe_2O_4$ single-phase compound.

$$Fe_2O_3 + FeCl_2 + H_2O \rightarrow Fe_3O_4 + 2HCl \quad (1)$$

$$2Co(NO_3)_2 + 4Fe(NO_3)_3 + 6C_3H_7NO_2 + 5/2O_2 \rightarrow$$
$$\rightarrow 2CoFe_2O_4 + 11N_2 + 18CO_2 + 21H_2O \quad (2)$$

Synthesis of Fe_3O_4-ANa and $CoFe_2O_4$-ANa nanocomposites. The Fe_3O_4-ANa and $CoFe_2O_4$-ANa composites were obtained by adding the oxide nanopowder (20% wt. theoretical content of nanoparticles in the composite) to 1% aqueous solution of sodium alginate polymer. The suspension was homogenized by mechanical stirring for 48 h at room temperature and the uncoated nanoparticles were separated by centrifugation. The water from polymeric suspension was removed by rotary evaporation.

The oxides and composites were characterized by X–ray diffraction (XRD) carried out on a Rigaku Miniflex II diffractometer with CuKα radiation, FTIR spectroscopy performed on Bruker Tensor 27 spectrometer and scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX) using a Philips Quanta Inspect F with field emission gun scanning electron microscope. Dynamic light scattering measurements (DLS) were performed on Zetasizer Malvern instruments at 25 °C in water, after 30 minutes dispersion in a ultrasounds bath.

3. Results and discussions

Fe_3O_4 and $CoFe_2O_4$ powders obtained in different conditions were analyzed by XRD. The patterns of $CoFe_2O_4$ as–prepared powder have proved a multi-phase compound formation containing $CoFe_2O_4$, $Fe_{0.294}O$ and Co_3O_4 crystalline phases (Fig. 1). In order to obtain $CoFe_2O_4$ single-phase compound, the as-prepared powder was annealed at different temperatures (Fig. 2). The average crystallite size calculated for cobalt ferrite samples annealed for 3h at 400 °C, 500 °C and 600 °C were 21 nm, 33 nm and 39 nm, respectively. XRD patterns have proved for all samples, the formation of $CoFe_2O_4$ with inverse spinel structure and cubic symmetry (ICDD 22-1086). The XRD results for $CoFe_2O_4$-ANa composite show only the main peaks of $CoFe_2O_4$ (Fig. 3a). For $CoFe_2O_4$-ANa composite obtaining, it has been used cobalt ferrite sample annealed at 500 °C.

XRD data of Fe_3O_4 synthesized by forced hydrolysis show the formation of Fe_3O_4 single-phase compound with inverse spinel structure (ICDD 82-1533) with an average crystallite size of 41 nm, as calculated by PDXL software. Unlike $CoFe_2O_4$-ANa, the XRD patterns for Fe_3O_4-ANa sample present the characteristic peaks of Fe_3O_4 besides other unknown crystalline phase (Fig. 3b), probably an induced crystallization and ordered structure formation of the polymer (seen also in SEM investigation).

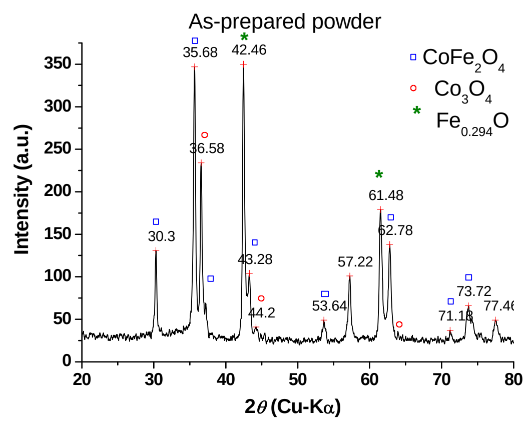


Fig.1. XRD patterns of $CoFe_2O_4$ as-prepared powder

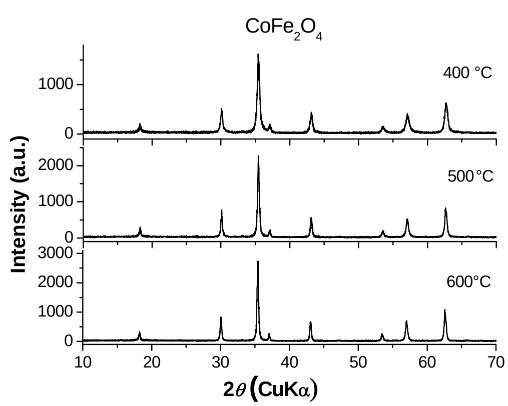
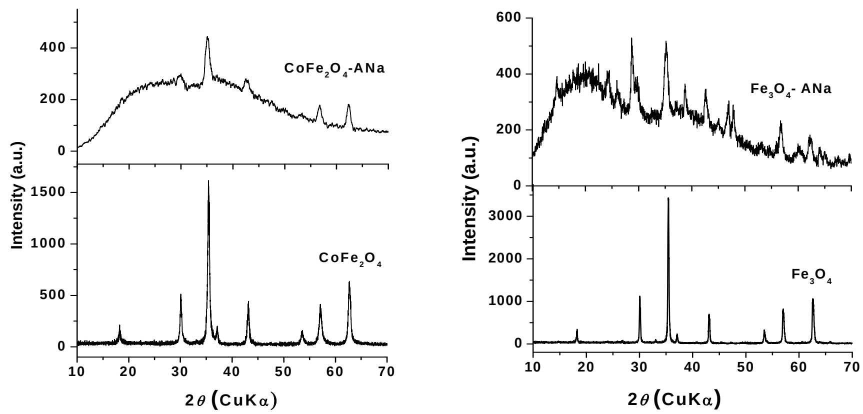


Fig. 2. XRD patterns of $CoFe_2O_4$ annealed at different temperatures.



(a) (b)

Fig.3. XRD patterns of: (a) $CoFe_2O_4$ powder and $CoFe_2O_4$-ANa;
(b) synthesized Fe_3O_4 powder and Fe_3O_4-ANa

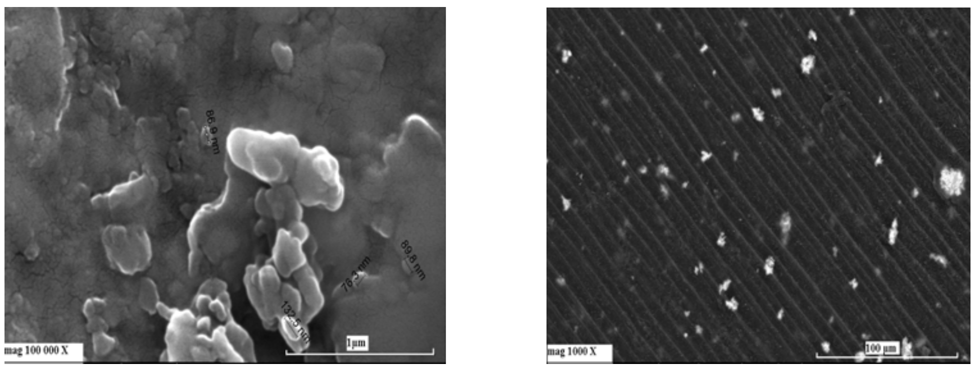
Table 1.

The main FTIR frequencies of sodium alginate (ANa), Fe_3O_4, $CoFe_2O_4$, Fe_3O_4– ANa and $CoFe_2O_4$– ANa composites

ANa [cm^{-1}]	Assignments	Fe_3O_4 [cm^{-1}]	$CoFe_2O_4$ [cm^{-1}]	Fe_3O_4– ANa [cm^{-1}]	$CoFe_2O_4$– ANa [cm^{-1}]	Assignments
		576	571	578	561	$\nu M(III)O_4$
		585	581	586	579	$\nu M(II)O_4$
1457	$\nu_s(CO)$			1457	1414	$\nu_s(CO)$
1653	$\nu_{as}(CO)^-$			1653	1609	$\nu_{as}(CO)$

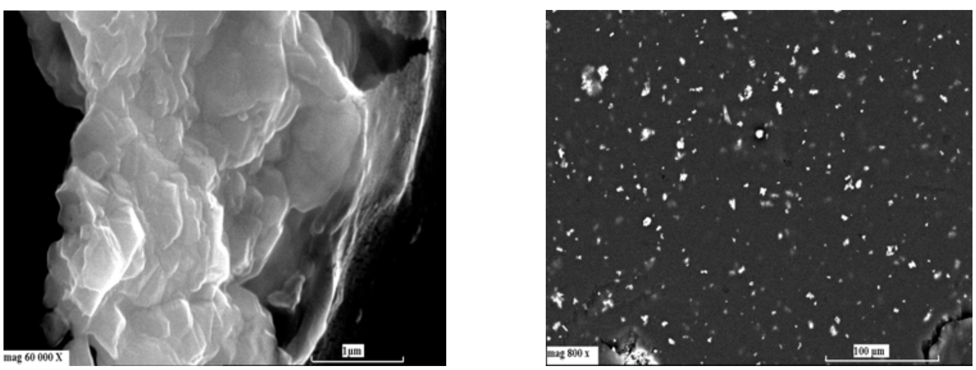
The binding of Fe_3O_4 and $CoFe_2O_4$ to sodium alginate polymer was analyzed by FTIR spectroscopy. The binding sites are the carboxyl groups of sodium alginate that could react with iron or cobalt ions. [11] The vibration bands, which appear in 385-450 cm^{-1} frequency range, correspond to the metal-oxygen bond in octahedral sites, whereas the vibration bands in the range of 550-600 cm^{-1} are assigned to the metal – oxygen bond vibration in the tetrahedral sites [12]. Also, in the case of $CoFe_2O_4$, Co^{2+} and Fe^{3+} ions exhibit preference for both octahedral and tetrahedral sites [11]. The FTIR spectrum of sodium alginate coated $CoFe_2O_4$ nanoparticles presents both asymmetric and symmetric C=O stretching vibration modes of carboxyl groups shifted to lower frequencies in comparison with sodium alginate polymer. Also, the FTIR spectrum presents spinel oxide characteristic bands shifted toward lower frequencies than for $CoFe_2O_4$ nanopowder (Table 1) that could be explained by the formation of covalent bond between metal ions from spinel structure and the carboxyl groups of sodium alginate. It is more difficult to understand how Fe_3O_4 nanoparticles are stabilized in sodium alginate. This could be because of the lower content of magnetite particles in composite (Table 2). In the case of $CoFe_2O_4$, no differences have been noticed between the main vibrations of carboxyl groups of sodium alginate and Fe_3O_4-ANa. The FTIR spectrum of Fe_3O_4-ANa shows Fe_3O_4 characteristic vibrations (Table 2). Some physical interactions between Fe_3O_4 and the polymer could be assumed.

The morphology and the chemical composition of the composite samples have been investigated by SEM-EDX. In the case of Fe_3O_4-ANa, the SEM investigation shows that the polymer has ordered domains. The spherical, 75-90 nm sized, magnetite particles form some agglomerates with irregular shapes. The magnetite particles are coated by sodium alginate.



(a) (b)

Fig. 4. SEM micrographs of the Fe_3O_4 (a) and Fe_3O_4-ANa (b)



(a) (b)

Fig. 5. SEM micrographs of $CoFe_2O_4$ (a) and $CoFe_2O_4$-ANa composite (b)

$CoFe_2O_4$ nanoparticles have a better dispersion in sodium alginate polymer than Fe_3O_4. $CoFe_2O_4$ nanoparticles form agglomerates with irregular shape, but, mainly, polyhedral agglomerates could be noticed in the SEM investigation (Fig. 5a). In aqueous suspensions, the average hydrodynamic size of oxide powders

(Fig. 6a,c) measured by DLS technique is smaller than for the corresponding composites (Fig. 6b,d), suggesting that the polymer surrounds the oxide particles. The hydrodynamic size of Fe_3O_4-ANa composite is around 500 nm (Fig. 6b), higher than 250 nm (Fig. 6d), the average value found for $CoFe_2O_4$ – ANa composite.

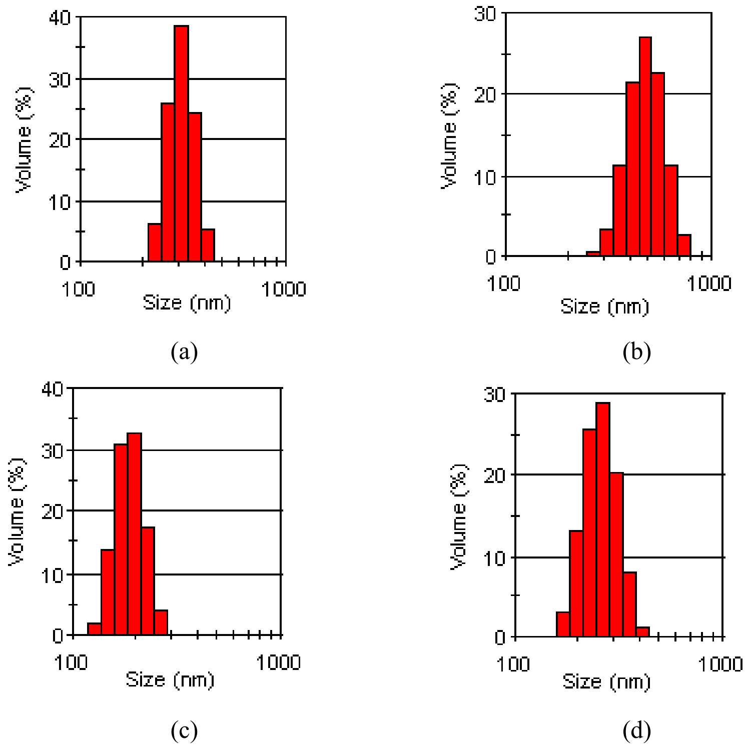


Fig. 6. Histograms of particle sizes distribution determined by DLS technique of Fe_3O_4 (a) and Fe_3O_4-ANa composite (b); $CoFe_2O_4$ (c) and $CoFe_2O_4$-ANa composite (d)

Table 2.

EDX analysis of Fe_3O_4-ANa and $CoFe_2O_4$-ANa composites

Composite composition	Elemental composition (atomic %)				
	Fe	Co	Na	C	O
$CoFe_2O_4$-ANa	3.85	1.93	35.69	1.34	55.74
Content of $CoFe_2O_4$ in composite	~ 4.0 % wt.				
Fe_3O_4-ANa	6.44	-	38.86	0.85	53.44
Content of Fe_3O_4 in composite	~ 2.9 % wt.				

Table 2 lists the average chemical composition of sodium alginate-based composite films determined by EDX analysis. The content of trapped $CoFe_2O_4$ nanoparticles is higher than for Fe_3O_4, probably due to the smaller size of $CoFe_2O_4$ particles than of Fe_3O_4. Only the fraction of small particles was trapped in the sodium alginate polymer.

4. Conclusions

A facile, low cost route to prepare nanocomposites containing oxide nanoparticles, Fe_3O_4 or $CoFe_2O_4$, stabilized by sodium alginate polymer has been proposed in this paper. Both prepared composites, Fe_3O_4-ANa and $CoFe_2O_4$-ANa are magnetic materials and present an antioxidant capacity against the oxidative stress [13] expressed as Trolox equivalent antioxidant capacity (TEAC) [14] and these results will be published elsewhere.

Acknowledgment

This work was partially supported by the Romanian grant PNCDI II no. 62-053/2008 and CNCSIS grant TD 244/2007.

R E F E R E N C E S

[1] *C.Corot, P. Robert, J.M. Idée, M. Port, A*dvanced Drug Delivery Reviews, **58**, 2006, pp. 1471-1504
[2] *D.L. Zhao, X.W. Zeng, Q.S. Xia*, *J.T. Tang*, J. Alloy Comp., **496**, 2009, pp. 215-218
[3] *J. Lu, S. Ma, J. Sun, C. Xia, C. Liu, Z. Wang, X. Zhao, F. Gao, Q. Gong, X. Shuai, H. Ai, Z. Gu,* Biomaterials, **30**, 2009, pp.2919-2928
[4] *D. Bahadur, J.Giri,* Biomaterials and Magnetism*,* **28**, 2003, pp. 639-656
[5] *C. Alexiou, W. Arnold, R.J. Klein, F.G. Parak, P. Hulin, C. Bergemann, W. Erhardt, S. Wagenpfeil, A.S. Lubbe*, Cancer Res. **60**, 2000, pp. 6641–6648
[6] *A.K. Gupta, M. Gupta,* Biomaterials, **26**, 2005, pp. 3995-4021
[7] *Y.X. Wang, S.M. Hussain, G.P. Krestin*, Eur. Radiol., **11**, 2001, pp. 2319–2331
[8] *A. Sutton, G. E .Harrison, T. E. Carr, D. Barltrop,* Br.J.Radiol. **44**, 1971, pp. 523-530
[9] *F.Y. Cheng, C.H. Su, Y. S. Yang, C.S. Yeh, C.Y. Tsaib, C.L. Wu, M.T. Wu, D.B. Shie*, Biomaterials, **26**, 2005, pp. 729–738
[10] *E. Matijevic,* Monodispersed Colloids: Art and Science, Langmuir, **2**, 1986, pp. 12-20
[11] *H.L. Ma, X.Qi, Y.Maitani, T.Nagai*, Int. J. Pharmaceutics, **333**, 2007, pp.177-186
[12] *N. Kasapoğlu, A. Baykal, Y. Köseoğlu, M.S. Toprak,* Sprita Materialia*,* **57**, 2007, pp. 441-444
[13] *A. Meghea, M.S. Drăgoiu, C. Neagu, R. Olinescu, M. Giurginca,* , U.P.B. Sci. Bull., Series B, **65**, 2003, pp. 3-8
[14] *R. Re, N. Pellegrini, A. Proteggente, A. Pannala, M. Yang, C. Rice-Evans,* Free Rad. Biol. Med., **26**, 1999, pp.1231-1237.