

Synthesis and characterization of Fe_3O_4 magnetic particles-multiwalled carbon nanotubes by covalent functionalization

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This paper reports the synthesis of new magnetic Fe_3O_4 magnetite nanoparticles – multi walled carbon nanotubes MWCNT with amino modified surface using direct functionalization of magnetite nanoparticles with cyanuric chloride as spacer. The synthesized nanocomposites were characterized by FT-IR spectroscopy, SEM microscopy and EDAX analysis.

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1. Introduction

The synthesis and investigation of magnetic properties of nanostructured magnetic materials present interest from both fundamental and technological point of view [1]. Nanoparticles have received considerable attention in the past two decades due to the interesting properties related to their size [2]. Ferrofluids represent a special category of smart nanomaterials, consisting of stable dispersion of magnetic nanoparticles in different liquid carriers [3]. Carbon nanotubes are cylindrical carbon molecules with a few nanometers diameter which exhibit remarkable electrical, thermal, chemical and mechanical properties with applications for different domains like electronics, optoelectronics, automation, control fields, biomedicine and environmental protection [4-6]. Carbon nanotubes (CNTs)-based magnetic nanocomposites have attracted significant research interest owing to their great potentialities in various technological fields [7]. Li and collaborators [7], Fe_3O_4 /CNTs nanocomposite exhibiting good compatibility with organic solvents at the liquid-liquid interface of cyclohexane/ethanol/water mixture solvent but without a strong covalent interaction between magnetic nanoparticles and carbon nanotubes. In this paper the synthesis and characterization of novel Fe_3O_4 magnetic nanoparticles-multiwalled carbon nanotubes by covalent functionalization is reported.

2. Experimental

2.1 Materials

For magnetite nanoparticle preparation, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, NaOH from Aldrich were used without any purification. Double wall carbon nanotubes (DWCNT) with NH_2 modified surface were provided by

Nanocyl. As solvents N, N'-dimethylformamide (DMF), *iso*-propanol and deionized water (Merck) were used. For magnetic nanoparticles covalent interaction with carbon nanotubes cyanuric chloride (Fluka) was used as spacer. Carbon nanotubes were dispersed in DMF (5% concentration related to solvent) by ultrasounds in Branson 1510 ultrasound bath.

2.2 Methods

An amount of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (0,1 M) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0,1 M) at a molar ratio $\text{FeSO}_4 : \text{FeCl}_3 = 1:1$ was treated with NaOH solution 3N until pH=11 was achieved. The NaOH solution was prepared in *iso*-propanol and water (at a molar ratio 1:1). After the co-precipitation, the water was separated and removed and magnetite nanoparticles were washed with *iso*-propanol (Fig.1).

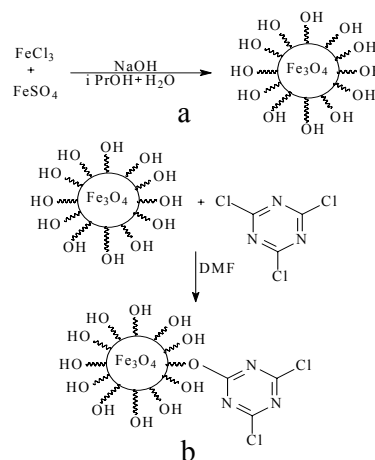


Fig. 1. Schematic representation of synthesis of magnetic nanoparticles.

The obtained magnetic nanoparticles were milled (Retsch mill) in 500 mL DMF for 1h at 260 min⁻¹. The functionalization with cyanuric chloride was performed in the tank of the mill 6h at 260 min⁻¹. For reaction between functionalized magnetite nanoparticles and carbon nanotubes, a solution of nanoparticles in DMF and a solution of carbon nanotubes in DMF (dispersed for 4 h in ultrasound bath) are milled for 3 h at 260 min⁻¹. The solvent is removed by evaporation and nanocomposites are obtained (Fig.2).

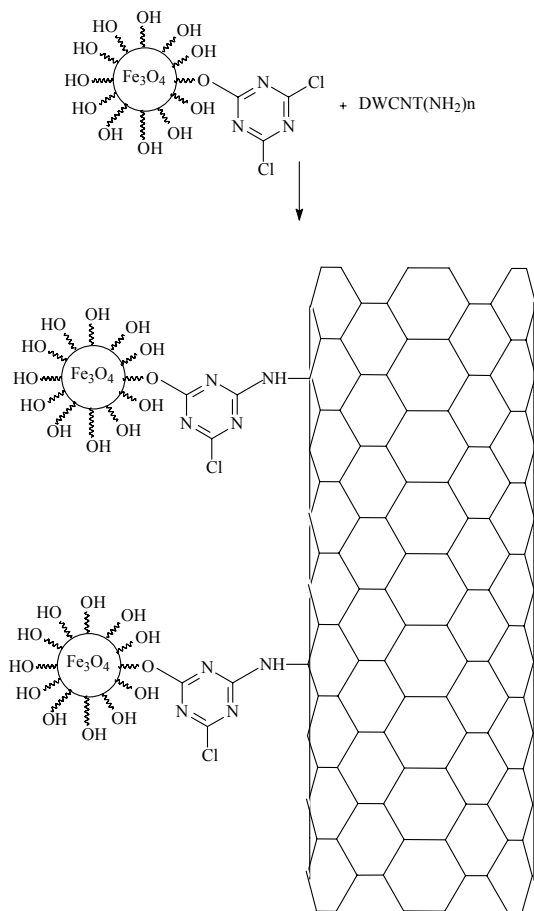


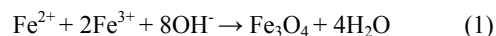
Fig. 2. Schematic representation of magnetic nanoparticles functionalization and reaction with amino carbon nanotubes.

The new magnetic nanocomposites were characterized by FT-IR spectroscopy, SEM microscopy and EDAX analysis.

3. Results and discussion

The magnetite has a reverse spinel cubic structure. The electrons can move between the Fe²⁺ and Fe³⁺ ions, at room temperature. After the surface coating, these nanoparticles can be dispersed in specific solvents, and they form ferro-fluids [8-10].

The precipitation process for magnetic nanoparticles synthesis was lead in aqueous media in accord with reaction (1).



In order to evaluate and to identify the reactions products, an EDAX elemental analysis was performed on surface of obtained nanoparticles. In Fig.3 is presented the spectra for final product and in table 1 the data are centralized. For the crude magnetic nanoparticles the preponderant elements are Fe and O. A small amount of Na is presented at all types of magnetic nanoparticles which indicate that the dialyses process was not complete.

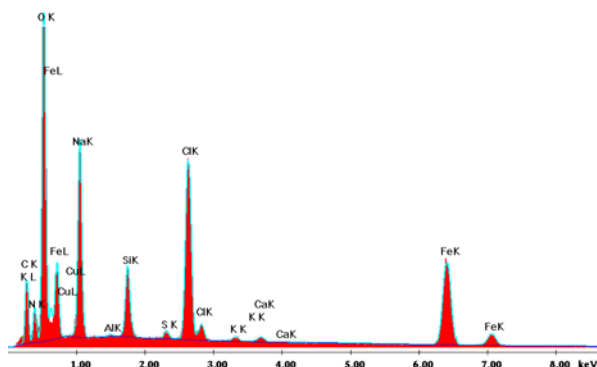


Fig. 3. EDAX analysis is spectra of magnetic nanoparticles-carbon nanotubes nanocomposites

For the functionalized magnetic nanoparticles with cyanuric chloride we can observe an increase of carbon contents form cyanuric chloride molecule. The increasing of carbon contents for magnetic nanoparticles-carbon nanotubes nanocomposites is not so spectacular; this can be explained by the fact that carbon nanotubes are intercalated between magnetic nanoparticles and only a small amount of nanotubes remain at the surface of nanoparticles.

Table 1. Elemental analysis by EDAX for synthesized compounds.

Elem.	Elem. Wt.% for:		
	Magnetic nanoparticles	Functionalized magnetic nanoparticles with cyanuric chloride	Magnetic nanoparticles-carbon nanotubes nanocomposites
C	2.21	9.11	15.07
N	0	1.24	4.56
O	49.75	39.02	34.7
Fe	44.04	42.1	37.03
Cl	0	4.65	4.71
Na	3.81	3.3	3.72
Si	0.19	0.58	0.21

The modified magnetic materials are made by an iron core covered with organic or inorganic molecules. The iron core is obtained like a nanometric particle powder with super paramagnetic properties. The functional groups with different specific scopes are deposited like a molecular layer around the core. Due to their applications, especially in biomedicine, the magnetite nanoparticles must present biocompatibility and paramagnetism and must be stable in aqueous solutions. In the case of very fine magnetic nanoparticles the big ratio between specific surface and volume lead to their agglomeration which is a problem for the obtaining of stable particles or dispersions.

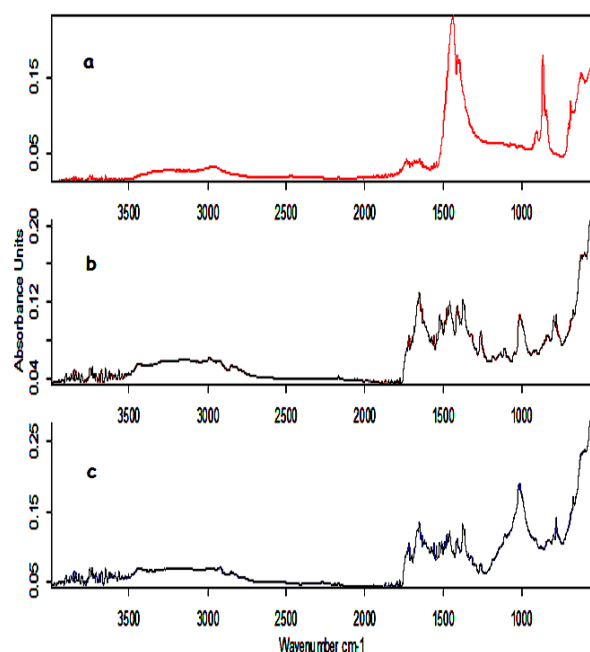


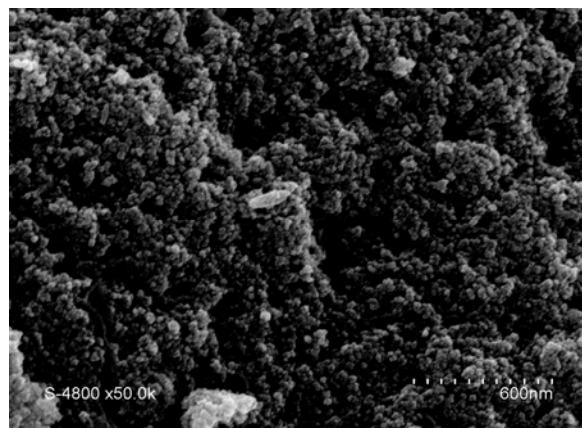
Fig. 4 FT-IR spectra of crude magnetic nanoparticles (a), functionalized magnetic nanoparticles with cyanuric chloride and magnetic nanoparticles-carbon nanotubes nanocomposites

From FT-IR spectra (Bruker Tensor 27 with diamond ATR annex) we can observe (Fig. 4) that in comparison with non functionalized magnetic nanoparticles, the functionalized ones present some new absorption bands: 1091 cm⁻¹ specific for C-N bond and 700 cm⁻¹ specific for C-Cl bond, both from cyanuric chloride molecule. 3400 cm⁻¹ and 1630 cm⁻¹ are specific absorption bands for remanent water molecules.

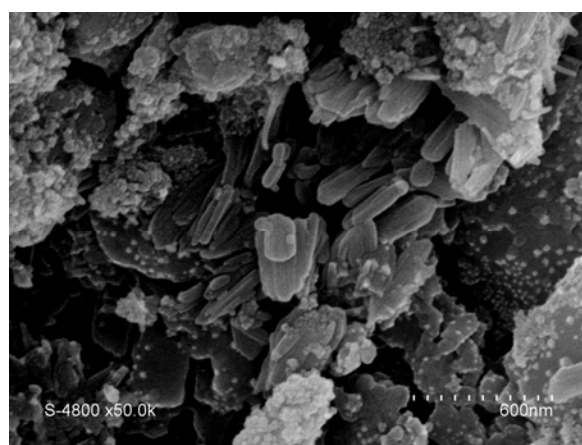
Absorption characteristic bands for Fe-O bond from Fe₃O₄ are situated in range 375-570 cm⁻¹, but these two bands are shifted higher values respectively 440 cm⁻¹ and 600 cm⁻¹. The main effect of finite dimensions of magnetic nanoparticles is represented by the breaking of large number of bonds with rearrangement of non-localized electrons on the surface of magnetic nanoparticle.

The functionalization with carbon nanotubes is demonstrated by the appearance in the spectrum of

vibration bands at 1091 cm⁻¹ specific for C-N bond. Carbon nanotubes, due to their symmetrically structure don't present absorption in infrared domain, but a shifting in the bands of magnetic nanoparticles can be observed.



(a)



(b)

Fig. 5. SEM images of magnetite nanoparticles functionalized with cyanuric chloride (a- ×50,0k), magnetic nanoparticles-carbon nanotubes nanocomposites (b-×50,0k).

In order to obtain more information related to morphology and aggregates dimensions, the nanocomposites were studied by scanning electron microscopy - FESEM Hitachi S4800 (Fig. 5). We can observe the formation of crude nanoparticles aggregates (Fig. 5 a) with dimension of approximately 30 nm. The aggregation in the case of magnetic nanoparticles-carbon nanotubes nanocomposites with dimension of 100 nm is more pronounced then in the case of uncovered ones (Fig. 5 b). This can be easily explained by the large electronic forces that appear at the carbon nanotubes surfaces which generate very stable aggregates.

Like potential applications we can suggest the magnetic collection of different heavy metals for clean

environment technologies, gas sensors and biological and biomedical uses.

4. Conclusions

New Fe_3O_4 magnetic nanoparticles – multiwalled carbon nanotubes nanocomposites were synthesized by direct covalent functionalization. Magnetic nanoparticles were obtained by precipitation method, which consists in ferric ions co-precipitation into a sodium hydroxide solution. The magnetic nanoparticles with were functionalized with amino-carbon nanotubes using cyanuric chloride as spacer.

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