

## OBTAINING AND CHARACTERIZATION OF HYBRID NANOMATERIAL BASED ON SPINEL FERRITE

D.V. Brezoi

Valahia University, Targoviste, e-mail: dragosh\_brezoi@yahoo.com

**Abstract:** Cobalt-ferrite nanocrystalline powder was obtained by chemical co-precipitation. Different samples were prepared by coating cobalt-ferrite nanoparticles with an intrinsically conducting polypyrrole synthesized by a chemical route. The magnetic properties of cobalt-ferrite nanoparticles not changed significantly after encapsulation into polypyrrole shell. The electrical conductivity of the new hybrid nanomaterial obtained was measured by the four points probe method, and it shows a sudden increase in values to  $42.4 \text{ S}\cdot\text{cm}^{-1}$  at 18 %wt. polypyrrole, that could be explained on percolation theory. New poly-functional material has been developed by combining the magnetic properties of cobalt-ferrite nanoparticles and the electrical conductivity of polypyrrole.

**Keywords:** cobalt ferrite, polypyrrole, conductivity, percolation

### 1. INTRODUCTION

In 2000, the Nobel Prize in Chemistry was awarded for research on conductive polymers including polypyrrole.

Polypyrrole (PPy, figure 1), an inherently conductive polymer due to interchain hopping of electrons, has received a lot of attention in the preparation of nanocomposites due to its high stability in conducting oxidized form [1, 2].

Polypyrrole is easy to prepare by electrochemical techniques and its surface charge characteristics can easily be modified by changing the dopant anion ( $X^-$ ) that is incorporated during synthesis. Polypyrrole was the first of conducting polymers family that show high conductivity [3].

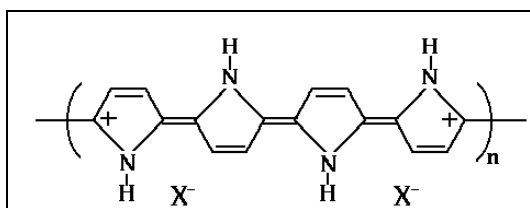


Figure 1. Polypyrrole structure

Pyrrole polymerization occurs rapidly in oxidizing environment (e.g. aqueous solution of  $\text{FeCl}_3$  or  $\text{K}_2\text{S}_2\text{O}_8$ ). Numerous studies have been reported about the polymerization of pyrrole on different surfaces. [3]

Cobalt-ferrite has attracted considerable attention because of their wide application in technological fields including permanent magnets, microwave devices, recording media [4,5].

Cubic ferrites have the inverse spinel crystal structure, which is cubic in symmetry, and similar to the spinel structure [10].

The properties of materials depend on synthesis conditions. Therefore, compared to the sintering method, the aqueous synthesis method from chemical precursors offers some advantages like molecular homogeneity and high purity of products, fine granulation, and high

specific surface area are very important features for catalytic purposes, and low energy is required to obtain.

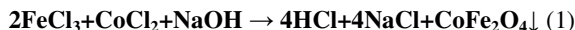
In previous papers, we have reported synthesis of iron oxide-polypyrrole nanocomposites by simultaneous gelation and polymerization process. These nanocomposites showed remarkable changes in magnetic and electrical properties with different concentrations of pyrrole [12, 13].

The purpose of this study was to obtain cobalt-ferrite nanoparticles and to encapsulate into polypyrrole shell to find an optimal composition that generate high electrical conductivity without modify the magnetic properties of spinel-like cobalt-ferrite powder.

### 2. EXPERIMENTAL

#### 2.1. Obtaining $\text{CoFe}_2\text{O}_4$ -PPy clusters in disordered media

The experimental conditions have selected based on literature [6,7]: temperature ( $70^\circ\text{C}$  for  $\text{CoFe}_2\text{O}_4$  obtaining, and  $0\text{...}6^\circ\text{C}$  for pyrrole polymerization) and  $\text{pH} = 11$  were kept constant. The synthesis shown in figure 2 is based on classic reaction of coprecipitation (equation 1), by mixing 0.2 M (50 ml) of cobalt chloride solution and 0.4 M (50 ml) of iron chloride solutions in distilled water. 50 ml solution of sodium hydroxide 3 M (precipitation agent) was prepared and slowly added to the salt solution drop wise:



It was added few drops of oleic acid (OA) like surfactant into the cobalt-ferrite suspension already prepared, and sonicated at 50 % amplitude for 100 s. Due to the presence of the surfactant, the particles will be covered by a protection layer during the mixing process and minimize the agglomeration tendency of cobalt-ferrite nanoparticles.

The precipitate was decanted with a permanent magnet, washed with distilled water, and dried in an oven at  $90^\circ\text{C}$

°C until it's formed a fine powder of constant weight ensuring the absence of water or oleic acid.

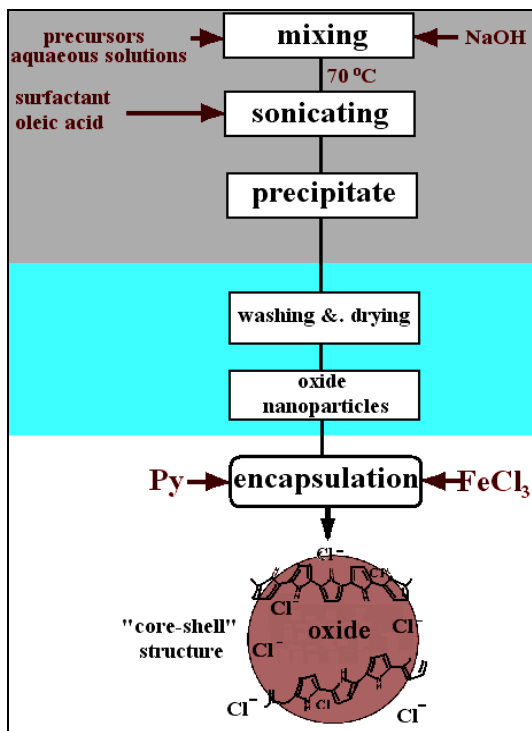


Figure 2. Obtaining scheme of  $\text{CoFe}_2\text{O}_4$ -PPy clusters in disordered media

The second step was to obtain  $\text{CoFe}_2\text{O}_4$ -PPy clusters in disordered media: encapsulation of cobalt-ferrite nanoparticles in polypyrrole shell by oxidative polymerization of pyrrole in ferric chloride solution. The cobalt-ferrite powder was dispersed in different volumes of liquid pyrrole. This mixture was added to  $\text{FeCl}_3$  in ethanol solution under stirring. Polymerization lasted for 30 min, followed by filtration and washing repeated times.

The separation between  $\text{CoFe}_2\text{O}_4$ -PPy nanocomposite and polypyrrole without cobalt-ferrite particles was done using a permanent magnet and the polypyrrole, which is not magnetic, was removed by repeated washing with ethanol and acetone. It was obtained seven samples (FP1 ... FP7) by different reaction's conditions, listed in the table 2.

## 2.2. Results and discussions

The UV/Vis spectrum from figure 3 shows that the cobalt-ferrite powder is identified by the charge transfer band at  $\lambda = 350 \text{ nm}$  ( $t_{2g} \rightarrow \pi^*$ ).

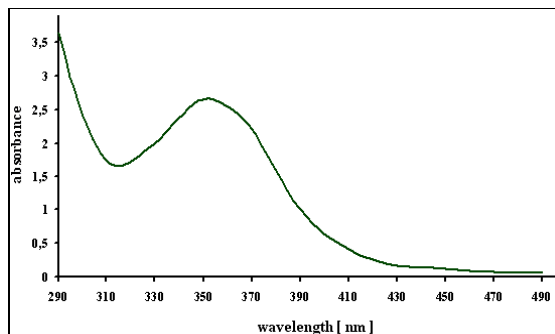


Figure 3. UV/Vis spectrum of  $\text{CoFe}_2\text{O}_4$  powder obtained

The X-ray diffraction measurements shown in figure 4.a, confirmed the formation of only nanocrystalline cobalt-ferrite structure with characteristic peaks at (111), (220), (311), (400), (422), (511), and (440) respectively. The average crystallite size of cobalt-ferrite is in the range of 8 nm to 20 nm and it was determined from XRD patterns of each sample obtained by Scherrer's equation (2) applied on (311) peak:

$$d = k\lambda [L_{1/2} \cos \Theta]^{-1} \quad (2)$$

where  $d$  = particle's average diameter,  $k = 0.9$ ,  $\lambda = 1.5418 \text{ \AA}$  (for  $\text{Cu K}\alpha$  X-Ray source at 35 kV),  $\Theta$  = peak position and  $L_{1/2}$  = effective full width half maximum of peak (311). [8]

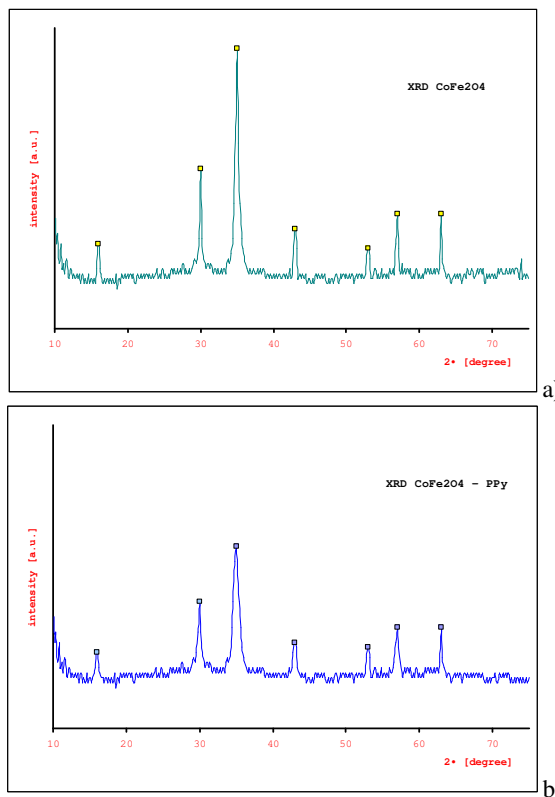


Figure 4. X-ray diffractogram of  $\text{CoFe}_2\text{O}_4$  powder (a) and  $\text{CoFe}_2\text{O}_4$ -PPy powder (sample FP7) (b)

In the figure 4.b ( $\text{CoFe}_2\text{O}_4$ -PPy – sample FP7), all peaks were observed correspond to  $\text{CoFe}_2\text{O}_4$ . Due covering with PPy amorphous shell, all peaks have reduced their intensity and became larger.

XRD data correlated with TEM images shown in figure 5 demonstrate that cobalt-ferrite nanoparticles are monocrystalline and can be magnetic monodomain. After covering with polypyrrole, there was an increase in size of cobalt-ferrite nanoparticles to an average value of 35 nm (figure 5.b).

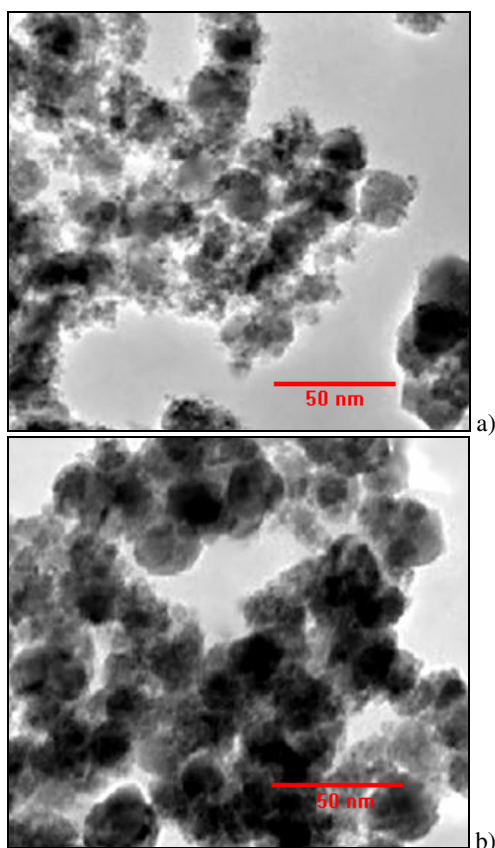


Figure 5. TEM image of: (a)  $\text{CoFe}_2\text{O}_4$  powder; (b)  $\text{CoFe}_2\text{O}_4$ -PPy powder (FP7)

In the inverse spinel crystal structure of  $\text{Co}^{2+}\text{Fe}_2^{3+}\text{O}_4^{2-}$ , there are two positions that may be occupied by the cations: half the trivalent ( $\text{Fe}^{3+}$ ) ions are situated in octahedral positions, the other half, in tetrahedral positions. The divalent  $\text{Co}^{2+}$  ions are all located in octahedral positions. The magnetic properties depend on the type of cations and their distribution between the two interstitial positions [10].

The critical factor is the arrangement of the spin moments of the ions (figure 6): the spin moments of all the  $\text{Fe}^{3+}$  ions in the octahedral positions are aligned parallel to one another; however, they are directed oppositely to the  $\text{Fe}^{3+}$  ions disposed in the tetrahedral positions, which are also aligned. This results from the antiparallel coupling of adjacent iron ions. Thus, the spin moments of all  $\text{Fe}^{3+}$  ions cancel one another and make

no net contribution to the magnetization of the solid. All the  $\text{Co}^{2+}$  ions have their moments aligned in the same direction, which total moment is responsible for the net magnetization. Thus, the saturation magnetization of a ferrimagnetic solid may be computed from the product of the net spin magnetic moment for each  $\text{Co}^{2+}$  ion and the number of  $\text{Co}^{2+}$  ions; this would correspond to a mutual alignment of all the  $\text{Co}^{2+}$  ion magnetic moments in the  $\text{CoFe}_2\text{O}_4$ .

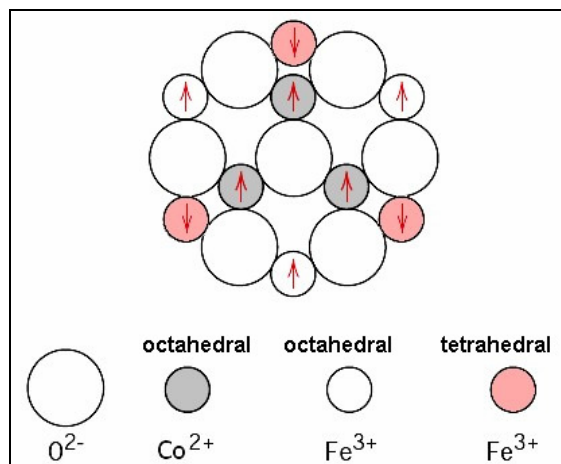


Figure 6. Schematic diagram showing the spin magnetic moment configuration for  $\text{Co}^{2+}$  and  $\text{Fe}^{3+}$  ions in  $\text{CoFe}_2\text{O}_4$  [11]

The magnetic properties (coercivity field  $H_c$ , remanent magnetization  $M_r$ , and saturation magnetization  $M_s$ ) measured with VSM (at room temperature with applied field up to 15 kOe) demonstrated that the magnetic behavior of cobalt-ferrite nanoparticles does not change significantly after encapsulation into polypyrrole shell because the polypyrrole is non-magnetic.

Table 1. The magnetic properties determined with VSM

sample	$H_c$ [Oe]	$M_s$ [emu/g]	$M_r$ [emu/g]
$\text{CoFe}_2\text{O}_4$	1175	65	17
FP7	1105	61	21

The purpose of the PPy coating was to improve the electrical conductivity of  $\text{CoFe}_2\text{O}_4$  nanoparticles. In the table 2 is shown the concentration of pyrrole (based on total reaction volume) and the weight percent of polypyrrole, which were determined from TGA analysis. The electrical conductivity ( $\sigma$ ) was measured on compressed powder samples, using the standard four probe technique at room temperature. The values of conductivity ( $\sigma$ ) determined for samples having different amounts of polypyrrole are shown in table 2 and figure 7. The sample FP1 did not have enough pyrrole to produce the targeted amount of polypyrrole coating, but increasing the amount of pyrrole to 30 wt. % of PPy (sample FP2) was excessive. A higher concentration of

pyrrole in the reaction solution may also increase the fraction of pyrrole that polymerizes in solution and can produce an uneven big coating.

The polymerization parameters that have influenced the quality of coating polypyrrole thin film deposited on cobalt-ferrite nanoparticles are: pyrrole concentration, oxidizing agent ( $\text{FeCl}_3$ ), temperature and reaction time, and all these have an important influence on electrical conductivity of  $\text{CoFe}_2\text{O}_4$ -PPy nanocomposite.

Increasing the concentration of  $\text{FeCl}_3$  should increase the polymerization yield since it initiates the reaction. This effect was demonstrated by the PPy weight of polypyrrole increased in the sample FP6.

Therefore, increasing its concentration had a similar effect as the oxidizing agent, but to a lesser degree as in the sample FP4. The higher conductivity achieved in the sample FP7 was most due to the lower reaction temperature. The reduced temperature from 5 °C to 0 °C, delayed initiation of polymerization and slowed the rate of polymerization. Furthermore, a decrease in polymerization rate can promote higher degree of order in the product, which increases conductivity.

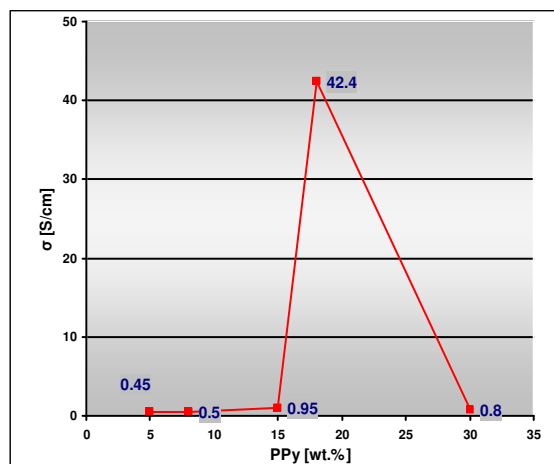
The lower temperature enhanced polymerization on the surface and produced more uniform coating of PPy on  $\text{CoFe}_2\text{O}_4$  particles, resulting in higher conductivity. The sample FP7 had the highest conductivity (table 2).

**Table 2. Experimental conditions for optimization the electrical conductivity of  $\text{CoFe}_2\text{O}_4$ -PPy nanocomposite**

Sample	$\text{FeCl}_3$ [M]	Reaction time [hours]	$t$ [°C]	PPy [wt.%] from TGA	$\sigma$ [S/cm]
FP1	$6.93 \times 10^{-2}$	4	5	5	0.45
FP2	$6.93 \times 10^{-2}$	4	5	30	0.8
FP3	$6.93 \times 10^{-2}$	4	5	8	0.5
FP4	$6.93 \times 10^{-2}$	4	5	15	0.95
FP5	$6.93 \times 10^{-2}$	14	5	18	1.7
FP6	$1.04 \times 10^{-1}$	4	5	18	1.5
FP7	$6.93 \times 10^{-2}$	4	0	18	42.4

For the samples obtained with the same parameters of polymerization process, it was observed a sudden increase in  $\sigma$  value at wt. 18 % PPy (critical concentration or percolation threshold). It was modified the polymerization's temperature to 0 °C and the result was increasing the conductivity to a maximum value determined:  $\sigma = 42.4 \text{ S/cm}$ .

The lower temperature enhanced polymerization on the surface and produced more uniform coating of PPy on  $\text{CoFe}_2\text{O}_4$  particles, resulting in higher conductivity. The sample FP7 had the highest conductivity (table 2).



**Figure 7. Variation of conductivity with concentration of polypyrrole obtained in the same condition (samples FP1, FP2, FP3, FP4, FP6)**

The sudden increase in conductivity could possibly be explained on the basis of *percolation theory* [9] which predicts that at a certain amount of polypyrrole, a full conducting path is formed for the flow of current. This has also been confirmed from TEM image (figure 5.b) which shows the formation of chained clusters with contact provided by polypyrrole shell, at a critical concentration of 18 wt. % PPy.

The mechanism of such ordering is similar to the phenomena occurring in the electro-rheological liquids. The slight ordering effect of these groups of nanoparticles consists in the mutual electrostatic interaction of the electric dipoles which are the polypyrrole shells, induced by the dopant ion  $\text{Cl}^-$  included into polypyrrole, as well as in the linear arrangement of dendritic structures with symmetry induced by external electric field direction.

A generalized effective-medium equation (GEM) has been used to model the conductivity of the nanocomposite as a function of pyrrole concentration. The nanocomposite's conductivity  $\sigma$  is the solution for the following equation (where  $\sigma_{\text{PPy}}$  and  $\sigma_{\text{oxide}}$  are, respectively, the PPy and oxide conductivity,  $\Phi_{\text{PPy}}$  is the PPy weight fraction,  $\Phi_c$  the percolation threshold,  $\rho^*$  is a correction density factor and  $t$  is a critical exponent):

$$\frac{(1/\rho^* - \Phi_{\text{PPy}})(\sigma_{\text{oxide}}^t - \sigma^t)}{\sigma_{\text{oxide}}^t + [(1/\rho^* - \Phi_c)/\Phi_c] \sigma^t} + \frac{\Phi_{\text{PPy}}(\sigma_{\text{PPy}}^t - \sigma^t)}{\sigma_{\text{PPy}}^t + [(1/\rho^* - \Phi_c)/\Phi_c] \sigma^t} = 0 \quad (3) \text{ [12].}$$

### 3. CONCLUSIONS

It was obtained cobalt-ferrite nanopowder by chemical coprecipitation with average size in the range 8-20 nm. After encapsulation in polypyrrole shell, spherical nanoparticles became bigger to 35 nm average size. The magnetic properties (coercivity field  $H_c$ , remanent

magnetization  $M_r$ , and saturation magnetization  $M_s$ ) measured with VSM demonstrated that the magnetic behavior of cobalt-ferrite nanoparticles does not change significantly after encapsulation into polypyrrole shell.

Electrical conductivity study showed a sudden increase in conductivity to  $42.4 \text{ S}\cdot\text{cm}^{-1}$  at 18 %wt. polypyrrole, that could be explained on percolation theory.

By combining the electrical conductivity of polypyrrole and the magnetic properties of cobalt-ferrite nanoparticles, new polyfunctional material has been developed.

#### 4. ACKNOWLEDGMENTS

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