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# Conducting Polypyrrole Shell as a Promising Covering for Magnetic Nanoparticles

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## 1. Introduction

Conducting polymers are a recent generation of polymers, opening the progress in understanding the fundamental chemistry and physics of  $\pi$ -conjugated macromolecules. Among conducting polymers, polypyrrole (PPy) has attracted great interest owing to its high conductivity and relatively high environmental stability, therefore the potential applications of polypyrrole are numerous. The combination of PPy with other inorganic materials in order to prepare composites which combine the properties of both materials is a very promising way to extend the application field of PPy but also of the inorganic materials. In order to improve the poor processability of polypyrrole a lot of methods have been explored in the preparation of soluble or swollen PPy (Masuda et al., 1989; Stanke et al., 1993) and dispersible fine powdered PPy (Bjorklund & Liedberg, 1986; Armes, et al., 1987; Cawdery et al., 1988; Aldissi & Armes, 1991). To extend the application field of polypyrrole, sterically stabilized PPy colloids were synthesized in aqueous media by chemically polymerizing pyrrole monomers in the presence of a suitable water-soluble polymer, such as methyl cellulose or poly(vinyl alcohol) (Armes et al., 1987; Armes & Vincent, 1987). The preparation of core-shell structures based on polypyrrole were first reported by Yassar et al. long before polypyrrole based magnetic core shell nanoparticles were developed. The authors coated latex particles by conducting polypyrrole (Yassar et al., 1987). After this many research groups reported the preparation of colloidal conducting polypyrrole by coating particles with a thin layer of conjugated polypyrrole to form conducting composites with a core-shell structure. Most of them were non-magnetic. Different types of polymers, metals and metal oxides were used as shells. Many papers describe the polymerization of pyrrole in the presence of different polymers structure, polystyrene being the most often used. (Lascelles & Armes, 1995; Lascelles et al., 1997; Lascelles & Armes, 1997; Cairns & Armes 1999; Lu et al., 2003; Bousalem et al., 2003; Bousalem et al., 2004a; Bousalem et al., 2004b; Bousalem et al., 2005; Benabderrahmane et al., 2005; Mangeney et al., 2006; Yip et al., 2006; Lee et al., 2009; Wang et al., 2009).

Latex particles having a poly(butyl methacrylate) (PBMA) core of about 700 nm and a very thin polypyrrole (PPy) shell were reported by Huijs & Lang 2000. Further studies illustrated the effect of the thickness of the polypyrrole shell on latex properties (Huijs et al., 2001). Other ways to water-based processable conducting polypyrrole are based on the preparation of colloidal core-shell polypyrrole nanoparticles by oxidative polymerization of pyrrole in the presence of ultrafine silica nanoparticles. (Maeda & Armes, 1994; Azioune et

al., 1999; Yang et al., 2006; Marini et al., 2008; Liu et al., 2008; Pourabbasa et al., 2010) or the copolymerization of pyrrole and functionalized pyrroles in the presence of the such silica nanoparticles (McCarthy et al., 1997; Goller et al., 1998; Azioune et al., 2004).

In 1995 Maeda & Armes presented a study about the chemical polymerization of pyrrole in the presence of various other ultrafine inorganic oxide sols such as tin(IV) oxide, zirconium, antimony(V) oxide, yttrium, and titanium(IV) oxide. It turned out that only the tin(IV) oxide sols act as effective particulate dispersants; the other four oxide systems failed to prevent macroscopic precipitation. SiO<sub>2</sub>@CdSe/polypyrrole multi-composite core-shell structures were synthesized by cationic polymerisation of pyrrole (Hao et al., 2006).

A simple non-template one-step method for the synthesis of 2.0-2.5 nm palladium nanoparticles encapsulated into a polypyrrole shell is based on direct redox reaction between palladium(II) acetate and pyrrole in acetonitrile medium (Vasilyeva et al., 2008). They stipulated that palladium nanoparticles are found to be able to self-organize into spherical Pd/PPy composites.

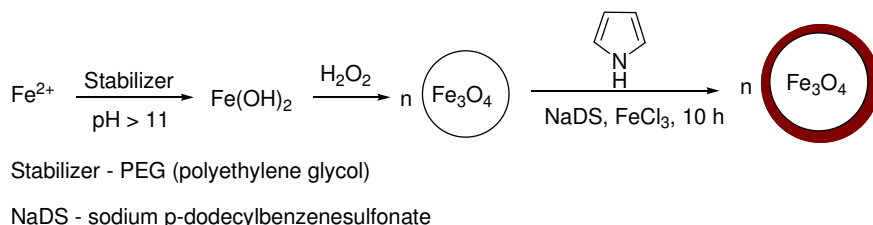
Selenium-polypyrrole core-shell nanostructures fabricated by *in-situ* polymerization process and functionalized with transferrin can be used for targeting and imaging of human cervical cancer cells (Li & Liu, 2008). Silver is another type of metal which was used as a core for polypyrrole shells (Feng et al., 2007; Wang & Shi 2007; Rojas et al., 2008; Ye & Lu et al., 2008; Ye et al., 2009). Coating gold nanoparticles with conductive polypyrrole resulted in uniform core-shell nanoparticles with tailored core aggregation and shell thickness (Xing et al., 2009).

An extremely important class of core-shell nanoparticles based on polypyrrole are magnetic nanoparticles. Although such composites share many aspects with non-magnetic nanoparticles they exhibit magnetism a unique property which is extremely important for many applications. In the present review the synthesis, characterization and applications of this class of magnetic core shell nanostructure are illustrated.

## 2. Preparation of magnetic core-shell nanostructure based on conducting polypyrrole

### 2.1 Preparation of magnetic core-shell nanostructured based on unfunctionalized polypyrrole

First publication which reported about the preparation of magnetic core-shell nanoparticles based on conducting polypyrrole appeared in 1994. Later on a promising approach using the direct polymerization of pyrrole in the presence of Fe<sub>3</sub>O<sub>4</sub> nanoparticles as reported by Deng et al. (Scheme 1) (Deng et al., 2003). The magnetite was obtained by partial oxidation of iron(II) followed by the polymerisation of the pyrrole using iron(III) chloride as oxidant. In this way novel nanocomposites with a well-defined core-shell microstructure were obtained



Scheme 1. Preparation of magnetic-conducting polypyrrole core-shell structure

Core-shell nanostructures based on the same polypyrrole and spherical hydroxyl iron (Fe[OH]) cores were prepared by Li et al. through the polymerization of pyrrole in the presence of *p*-toluenesulfonic acid (*p*-TSA) as dopant and Fe[OH] with a diameter 0.5-5  $\mu\text{m}$  (Li et al., 2006). They obtained a micro/nanostructure which exhibit high conductivity ( $\sim\sigma_{\text{max}} = 50.6 \text{ S/cm}$ ) and superparamagnetic behaviour.

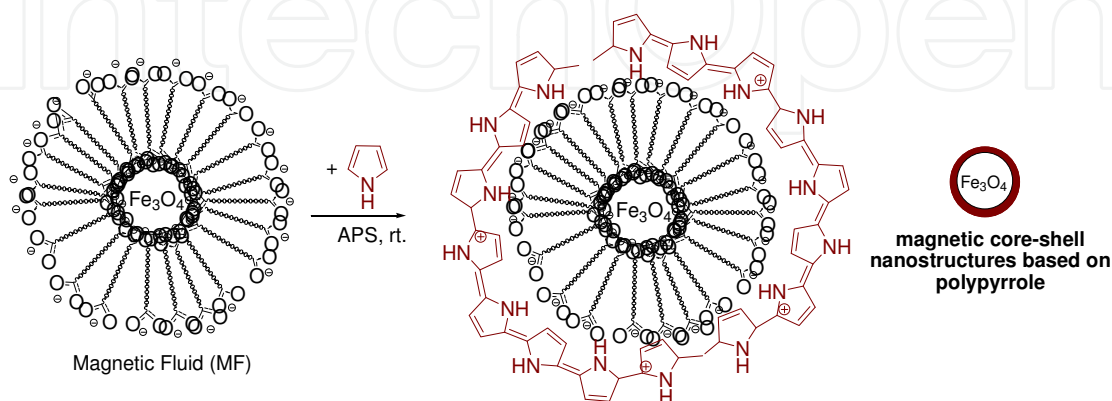
Ultrasonic irradiation technique was applied to polypyrrole/Fe<sub>3</sub>O<sub>4</sub> nanocomposite preparation, for a better dispersion of the Fe<sub>3</sub>O<sub>4</sub> nanoparticles resulting in nanocomposite with high conductivity. Again, the polymerization of pyrrole was mediated by FeCl<sub>3</sub> as oxidant (Qui et al., 2006).

An efficient DNA retrieval system was developed based on Fe<sub>3</sub>O<sub>4</sub> polypyrrole nanoparticles. Here, the surface of the magnetite was modified with pyrrole-2-carboxylic acid followed by free radical polymerization of unsubstituted pyrrole., The resulting Fe<sub>3</sub>O<sub>4</sub>@polypyrrole showed excellent high affinity to DNA (Park et al., 2008). Superparamagnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles were successfully encapsulated inside polypyrrole via an emulsion polymerization using polyvinyl alcohol as a surfactant, yielding magnetic core-shell nanostructures of spherical shape with a diameter of 80-100 nm. These products exhibited high magnetization values and good electrical conductivities (Wuang et al., 2007). Cell targeting nanostructures were obtained when the surfaces of these nanoparticles were further functionalized with folic acid. Their potential for targeting of cancer cells was investigated revealing that the uptake by MCF-7 breast cancer cells is significantly enhanced as compared to non-functionalized precursors (Wuang et al., 2007).

Uniform Fe<sub>3</sub>O<sub>4</sub> nanospheres with a diameter of 100 nm could be obtained by the microwave solvothermal method. When these nanospheres were covered with a polypyrrole shell followed by the electrostatic interactions with citrate stabilized gold nanoparticles (Au NP) a type of three-component Fe<sub>3</sub>O<sub>4</sub>/polypyrrole/Au nanocomposites with core/shell/shell structure were obtained (Zhang et al., 2008).

Another important application of the core-shell magnetic nanoparticles based on magnetite and unfunctionalized polypyrrole is the removal of fluoride ions from aqueous solution. The magnetic property makes the material easy to retrieve from solution using external magnetic field (Bhaumik et al., 2011).

As shown by our group polypyrrole magnetite core shell nanoparticles can efficiently be synthesized if pyrrole is polymerized by ammonium persulfate (APS) as oxidant in water based magnetic nanofluids (MF) (Scheme 2) (Turcu et. al., 2006).



Scheme 2. Preparation of magnetic core-shell nanostructure based on polypyrrole and magnetic fluid

These nanofluids used in the polymerization reaction, consist of magnetite nanoparticles which are covered and thus stabilized by fatty acid shells rather than of "naked" nanoparticles. The preparation of the magnetic fluid starts with coprecipitation of  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$  ions in  $\text{NH}_4\text{OH}$ -solution to give magnetite nanoparticles. The temperature was maintained at 80–82 °C, in order to obtain entirely magnetite nanoparticles and to optimize the following chemisorption of the surfactant (Bica et al., 2007). Combinations of surfactants with different chain lengths: myristic acid (MA), lauric acid (LA) and dodecylbenzenesulphonic acid (DBS) were used, such as MA+MA, LA+LA, MA+DBS, DBS+DBS, LA+DBS for the preparation of polypyrrole based nanocomposites (Turcu et al., 2008). The electrical conductivity of the nanocomposites can be controlled by the ratio of the starting materials.

Tubular  $\text{Fe}_3\text{O}_4$ /polypyrrole nanocomposites can be synthesized by in situ polymerization of pyrrole in the presence of the monodispersed 4 nm  $\text{Fe}_3\text{O}_4$  nanoparticles (Wu et al., 2007). The monodispersed 4 nm  $\text{Fe}_3\text{O}_4$  nanoparticles which served as cores were synthesized using the thermal decomposition of a mixture of iron (III) acetylacetonate and oleic acid in the presence of high boiling solvents. The resulting nanoparticles were further dispersed in an aqueous solution with the anionic surfactant sodium bis(2-ethylhexyl)sulfosuccinate to form micelle/ $\text{Fe}_3\text{O}_4$  spherical templates that avoid the aggregation of  $\text{Fe}_3\text{O}_4$  nanoparticles during the further preparation of the nanocomposites. The  $\text{Fe}_3\text{O}_4$ /PPy nanocomposites were then synthesized via in situ chemical oxidative polymerization on the surface of the spherical templates.

A new type of magnetic core-shell nanostructures based on polypyrrole was developed by using iron-gold (Fe@Au) nanoparticles instead of magnetite as magnetic cores. The gold-coated iron nanoparticles generally were obtained by reverse micelle method, wherein cetyltrimethylammonium bromide (CTAB) acted as surfactant and 1-butanol as co-surfactant (Pana et al., 2007). The resulting Fe@Au nanoparticles were covered by the surfactant and were further coated with polypyrrole by APS-mediated polymerization of pyrrole.

Another type of core-shell nanoparticles were obtained with flaky  $\text{BaFe}_{12}\text{O}_{19}$  nanoparticles (10–20 nm in thickness) as polymerization seeds, functionalized and microstructured quasi-spherical  $\text{BaFe}_{12}\text{O}_{19}$ /polypyrrole organic-inorganic composites were prepared by a conventional in situ chemical oxidative polymerization (Xu et al., 2008; Birsöz et al., 2010). Magnetic core-shell nanoparticles based on polypyrrole and  $\text{SrFe}_{12}\text{O}_{19}$  nanoparticles composites were prepared by *in situ* polymerization method; the morphology of such magnetic nanoparticles could be modified from sphere-like to conglomeration-like and arborisation-like structure increasing the pyrrole/ $\text{SrFe}_{12}\text{O}_{19}$  mass ratio (Zhang et al., 2009).

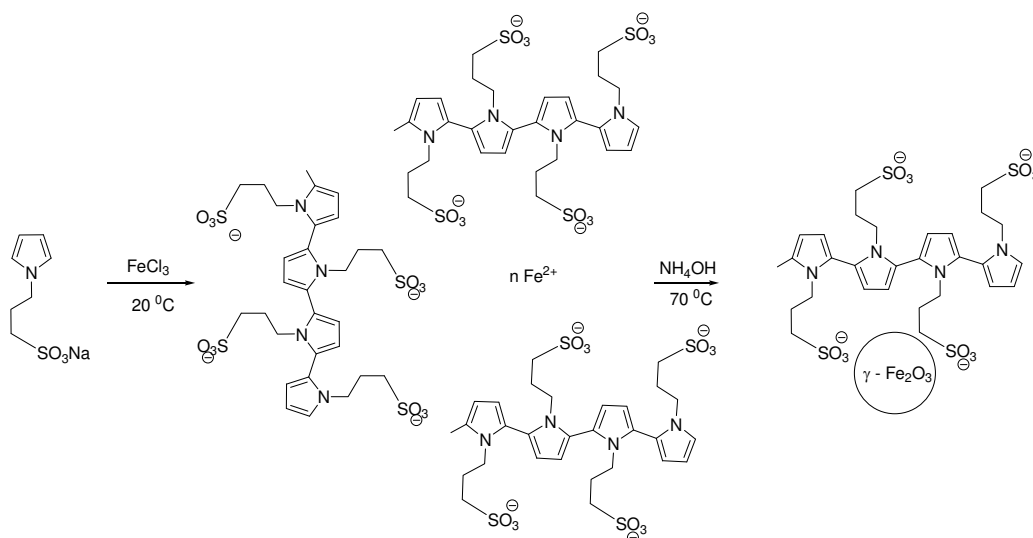
A polypyrrole/ferrospinel ( $\text{NiFe}_2\text{O}_4$ ) nanocomposite with a core-shell structure was prepared by the in situ chemical polymerization of pyrrole in the presence of  $\text{NiFe}_2\text{O}_4$  nanoparticles in water-in-oil microemulsion (Jiang et al., 2010).

$\text{ZnFe}_2\text{O}_4$ /polypyrrole core-shell nanoparticles could be subsequently synthesized via in situ chemical oxidative polymerization of pyrrole monomers on the surface of  $\text{ZnFe}_2\text{O}_4$  nanoparticles using ammonium persulfate as oxidant at relatively low temperature 80 °C. The shell thickness of core-shell nanoparticles could be easily controlled by adjusting the amount of pyrrole monomer. The synthesis was shown to be inexpensive, nontoxic and reproducible solvothermal method (Li et al., 2009).

## 2.2 Preparation of magnetic core-shell nanostructured based on functionalized polypyrrole

By using functionalized pyrrole instead of unsubstituted pyrrole the applicability of magnetic core shell nanoparticles can be extended considerably. Corresponding pyrrole monomers are available either commercially or by various chemical reactions.

The first publication about the preparation and characterization of core-shell magnetic nanostructured appeared in 1994 when Nguyen and Diaz reported a simple route to poly(pyrrole-*N*-propylsulfonate) polymer containing nano-sized  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> particles (Nguyen & Diaz, 1994). The preparation occurred in two steps by first polymerization of sodium pyrrole-*N*-propylsulfonate using excess of FeCl<sub>3</sub> as oxidant resulting a black powder poly(pyrrole-*N*-propylsulfonate). In the second step, the magnetic-polypyrrole nanostructures were formed by adding an ammonia solution to the preformed polymer and keeping the reaction under stirring and at 70 °C for 30 minutes while the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> is formed (Scheme 3).



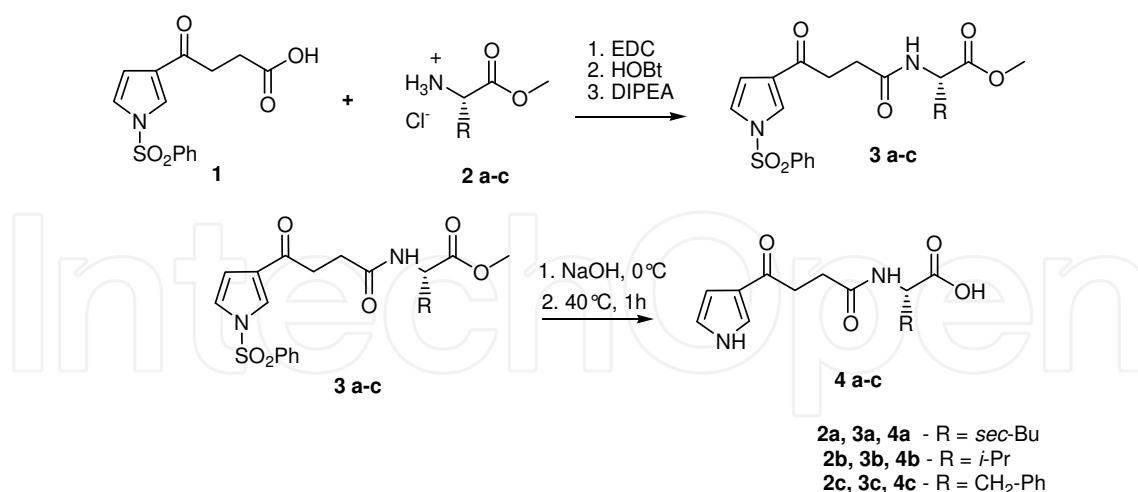
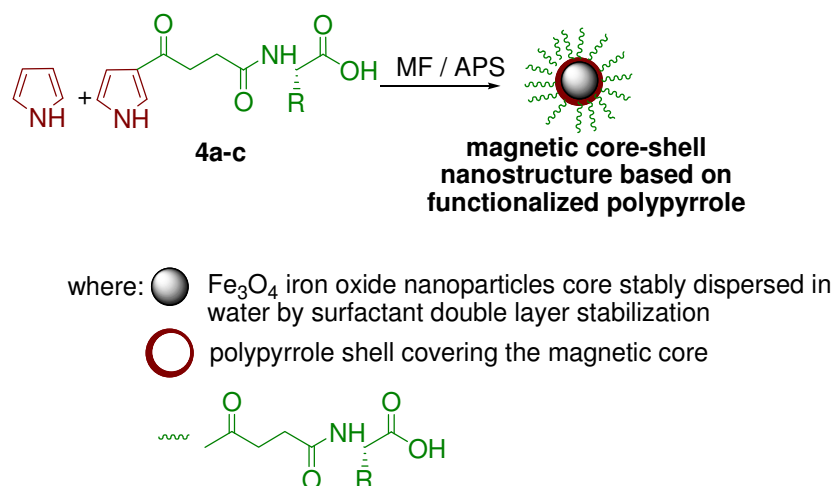
Scheme 3. Preparation of magnetic nanoparticles based on  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and poly(pyrrole-*N*-propylsulfonate)

Although Fe<sub>2</sub>O<sub>3</sub>-poly(pyrrole-*N*-propylsulfonate) nanostructures have been successfully prepared they still have low room-temperature conductivity ( $10^{-4}$ - $10^{-1}$  Scm<sup>-1</sup>) and low coercive force. In addition, their structures and properties are difficult to control owing to the complicated synthetic method involved, therefore further development of synthetic methods to produce novel electrical-magnetic nanostructures with high room-temperature conductivity and coercive force was highly required.

External magnetic field was applied to affect assembling of functionalized polypyrrole-coated latex particles. Here  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> superparamagnetic nanoparticle-containing polystyrene cores were coated by a functionalized polypyrrole shell. The polystyrene particles provide a rigid, non-deformable and nonporous support for the polypyrrole coating (Mageney et al., 2007).

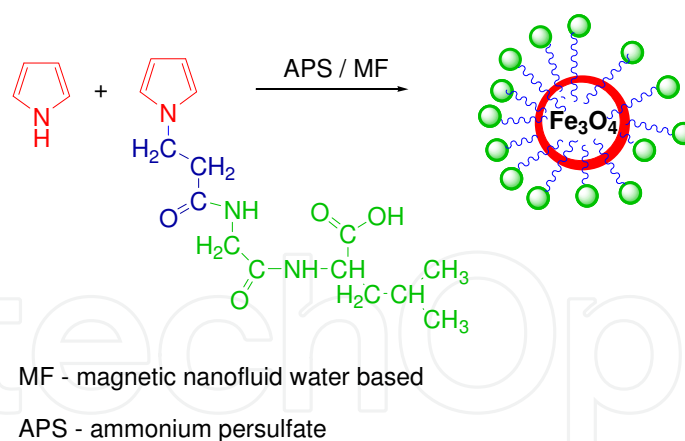
Thus Nan et al. synthesized pyrroles which are linked to amino acids at the  $\beta$ -position of the pyrrole ring (Scheme 4) (Nan et al., 2008).

These amino acid pyrrole conjugates were successfully used in the synthesis of novel functionalized magnetic nanostructures by chemical oxidative polymerization in aqueous solutions in the presence of Fe<sub>3</sub>O<sub>4</sub> nanofluids (Scheme 5) (Nan et al., 2008).

Scheme 4. Synthesis of new pyrrole monomers functionalized by  $\alpha$ -amino acidsScheme 5. Preparation of magnetic core-shell nanostructures functionalized by  $\alpha$ -amino acids

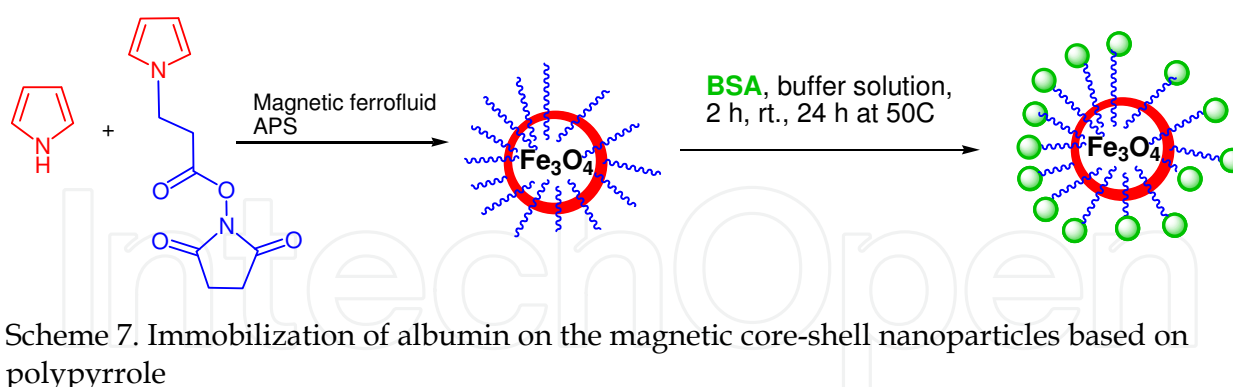
Glycyl-leucine dipeptide and bovine serum albumin were also used for the functionalization of the polypyrrole shell which covered the magnetic nanoparticles (Nan et al., 2010) using N-hydroxysuccinimide as activating reagent. In the case of the dipeptide, this were first covalent attached on the pyrrole ring and after that the polymerization of functionalized pyrrole monomer in the presence of a ferrofluid based on water were performed (Scheme 6).

The BSA-functionalized magnetic core shell nanoparticles were synthesized starting from the polymerization of 3-(Pyrrol-1-yl)-propanoyl-N-hydroxysuccinate in the presence of double layer stabilized magnetic ferrofluid in water, issuing a N-hydroxysuccinate surface active magnetic nanoparticles. The resulted magnetic nanoparticle based on functionalized polypyrrole with N-hydroxysuccinate was dispersed in phosphate-buffered saline solution (PBS, pH 7.4) and then, BSA was added. In this way BSA substituted a part of the N-hydroxysuccinate groups while the others survived and gave propionic acid moieties by hydrolysis.



Scheme 6. The functionalization of magnetic nanoparticles based on functionalized polypyrrole with glycyL-leucine dipeptide

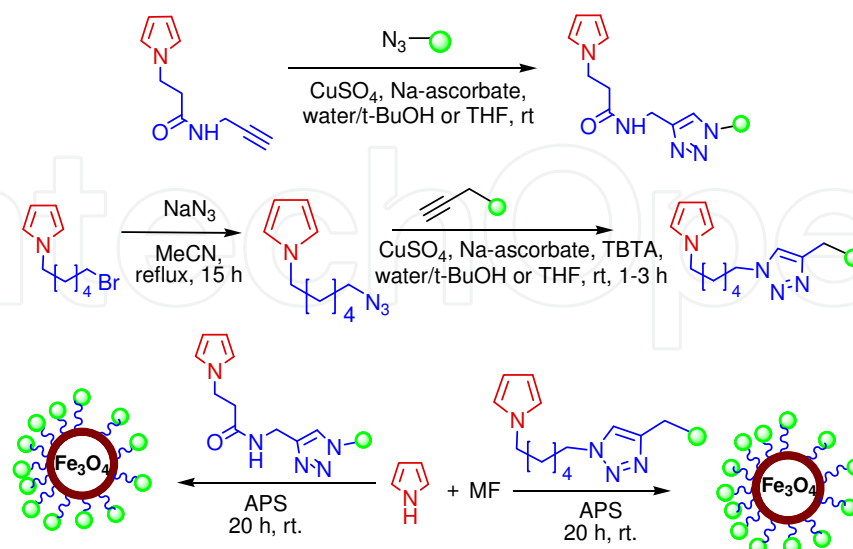
For instance, the popular *N*-hydroxysuccinimide ester is prone to hydrolysis before and during the coupling reaction, which can both reduce coupling yields and make the yields and the material irreproducible. Therefore, it is highly desirable and useful to develop new reactions which can be easily performed under mild conditions, with high yields and without by-products. These requirements are met by the Meldal-Sharpless cycloaddition. This 1,3-dipolar cycloaddition reaction is recognized as the best example of click chemistry and can be performed to give a quantitative yield, in multiple solvents (including water) and in the presence of various functional groups, as well as under mild reaction conditions. As compared with other tethering tools, the Meldal-Sharpless cycloaddition method tolerates many functional groups allowing the omission of protective groups and thus was also widely applied to biological molecules.



Scheme 7. Immobilization of albumin on the magnetic core-shell nanoparticles based on polypyrrole

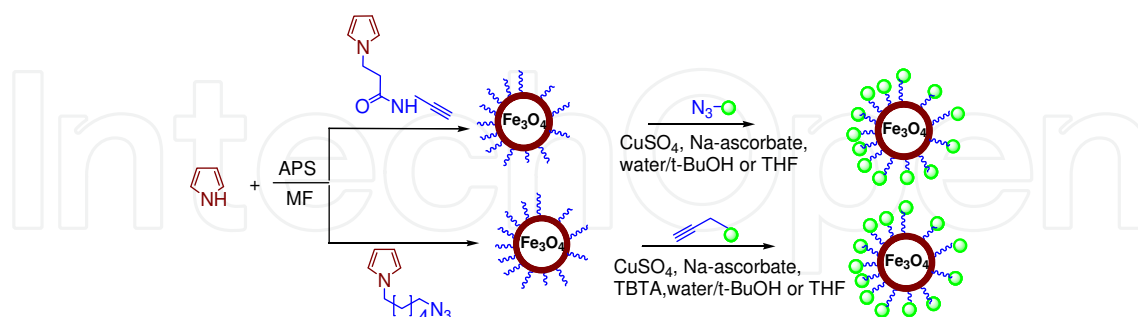
The mild and versatile method based on Cu-catalyzed [3+2]-cycloaddition was developed to tether biomolecules, such as monosaccharides, biotin, cholesterol or uridine to the *N*-atom of pyrrole. The required azido and alkyne function can be placed in either reactant, i. e. in the pyrrole or the biomolecule. The resulting products were employed as precursors for functionalized superparamagnetic polypyrrole core-shell nanoparticles (Karsten et al., 2010). The functionalizations of the core-shell nanoparticles were prepared in two ways. First, the biomolecules are attached on the pyrrole monomer via “click-reaction” and after this take place the polymerization of the preformed pyrrole monomer in the presence of the magnetic fluid (scheme 8).





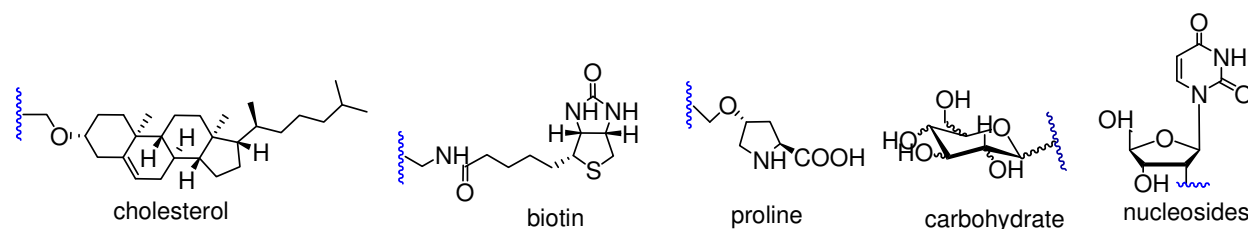
Scheme 8. Preparation of magnetic core-shell nanoparticles based on biofunctionalized polypyrrole

Another way to obtain magnetic core-shell nanoparticles based on functionalized polypyrrole using “click-chemistry” occurs in two steps. In the first step, the polymerization of the pyrrole monomer which has attached on the ring azide group or alkyne group in the presence of magnetic nanofluid. The second step consists in the execution of the Cu-catalyzed [3+2]-cycloaddition with different biomolecules on the beforehand prepared magnetic core-shell nanoparticles based on functionalized polypyrrole with azide or alkyne groups (scheme 9).



Scheme 9. Preparation of magnetic core-shell nanoparticles based on biofunctionalized polypyrrole

As was mentioned before using Cu-catalyzed [3+2]-cycloaddition reaction, many types of biomolecules with interesting application can be attached on different substrates; this principle was applied also for the magnetic core-shell nanostructured based on polypyrrole. In the scheme 10 are shown which types of biomolecules were attached on the magnetic core-shell nanoparticles (Karsten et al., 2010).



Scheme 10. Biomolecules which were attached on the magnetic core-shell nanostructures based on polypyrrole using the „click-chemistry“

### 3. Methods for characterization of magnetic core-shell nanoparticles based on polypyrrole

For magnetic core-shell nanoparticles based on polypyrrole the characterization methods which can be applied for a better structural investigation are: morphological investigation, FTIR spectroscopy, X-ray diffraction, X-photoelectron spectroscopy and the magnetic properties.

#### 3.1 Morphologic characterization of magnetic core-shell nanoparticles based on polypyrrole

The size and morphology of the magnetic core-shell nanoparticles were mainly characterized by Transmission Electron Microscopy (TEM), High-Resolution Transmission Electron Microscopy (HRTEM), field-emission scanning electron microscopy (FESEM), but in some cases is also used Scanning Electron Microscopy (SEM).

The SEM microscopy gives more an overview of the size and shape of the magnetic core-shell nanoparticles based on polypyrrole. A very clear SEM image (figure 1) in which the coating phenomenon can be clearly observed is presented in the case of  $ZnFe_2O_4$  cores surrounded by polypyrrole shells. In the SEM images can be see that the  $ZnFe_2O_4$  core diameter is around 80 nm and after polymerization of pyrrole monomer the diameter increased at about 100–300 nm (Li et al., 2009).

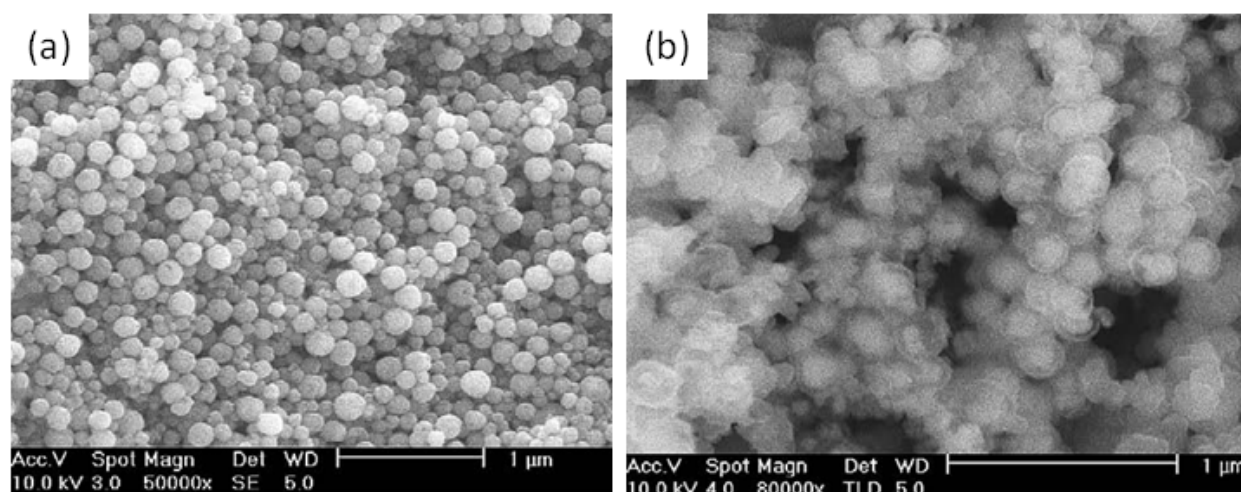


Fig. 1. The SEM images of (a)  $ZnFe_2O_4$  nanoparticles and (b) magnetic core-shell nanoparticles based on  $ZnFe_2O_4$  and polypyrrole by using 1 ml of pyrrole at 80 °C for 8 h

The TEM microscopy provides more clear information about the size and shape than SEM microscopy. In the literature TEM microscopy is a useful tool to determine the magnetic core diameter and the thickness of polypyrrole shell, but in the same time TEM allows the comparison between the former magnetic nanoparticles and magnetic core-shell nanoparticles based on polypyrrole. Figure 2 shows the difference between the TEM image of the ferrofluid used for the polymerization of unfunctionalized pyrrole monomer and the TEM image (figure 2a) of the magnetic core-shell nanoparticles based on polypyrrole and magnetite (figure 2b).

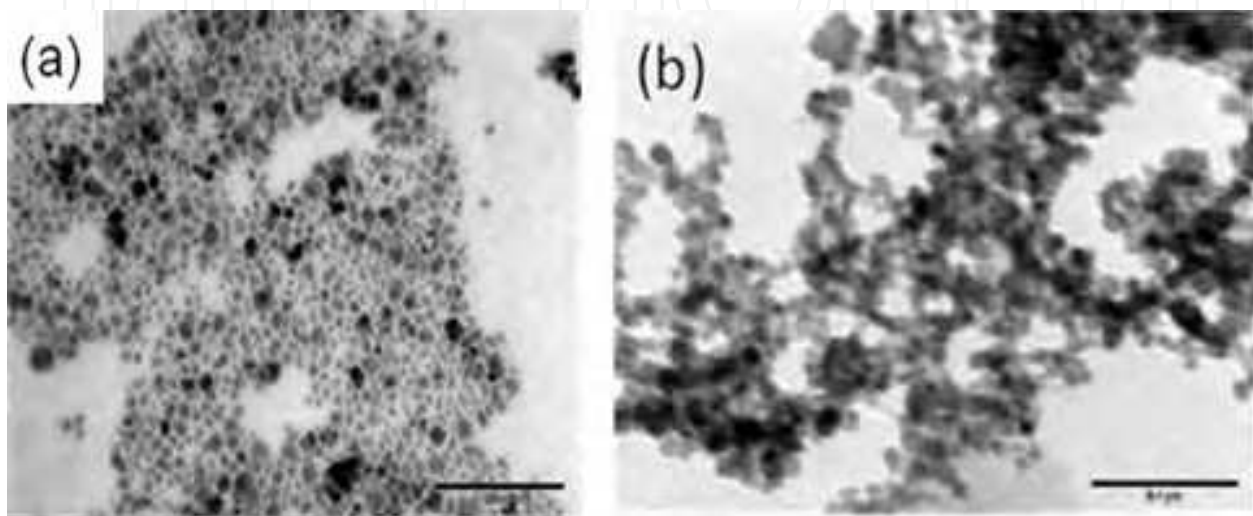


Fig. 2. The TEM images of (a) magnetic ferrofluid and (b) magnetic core-shell nanoparticles prepared based on the ferrofluid and unfunctionalized polypyrrole

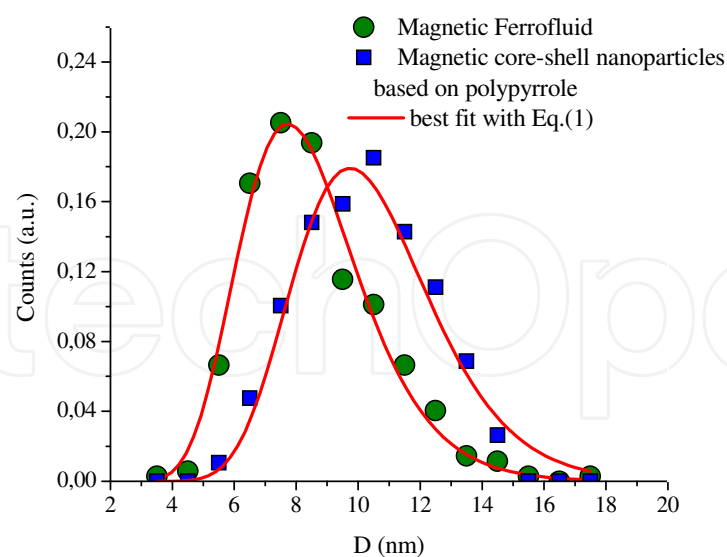


Fig. 3. The corresponding distributions of diameters for magnetic ferrofluid and of the magnetic core-shell nanoparticles based on polypyrrole

The analysis of the TEM images presented above enabled the determination of the diameters distributions of the nanoparticles, as shown in the figure 3. The normalized distribution of diameters is well described by a lognormal distribution function (equation 1):

$$f(D) = \frac{1}{D\sigma\sqrt{2\pi}} \exp\left[-\frac{1}{2}\left(\frac{\ln^2 D / D_0}{\sigma^2}\right)\right] \quad (1)$$

where  $D$  is the diameter,  $D_0$  is the mean diameter and  $\sigma$  is the standard deviation.

From the diameter histogram were obtained a mean diameter  $D_0 = 8.2$  nm for the magnetic ferrofluid and a mean diameter  $D_0 = 10.2$  nm for the magnetic core-shell nanoparticles based on polypyrrole, that means that the thickness of the polypyrrole shell it is about 2 nm (Turcu et al., 2008).

Nevertheless HRTEM with it high resolution makes it ideal for imaging materials on the atomic scale. The HRTEM images given in Figure 4 presents the core-shell nanoparticles based on unfunctionalized polypyrrole (Figure 4a), with a thin shell around 2 - 3 nm, which is similar to those found in the magnetic core-shell nanoparticles formed with substituted pyrrole (Figure 4b) (Nan et al., 2008).

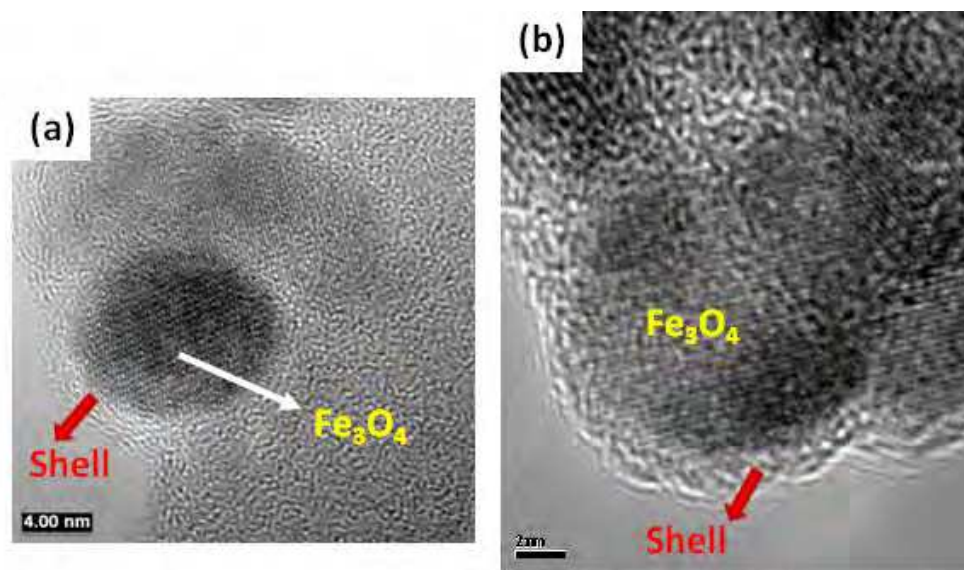


Fig. 4. HRTEM images of (a) magnetic core-shell nanoparticles based on unfunctionalized polypyrrole and (b) magnetic core-shell nanoparticles based on functionalized polypyrrole

The HRTEM microscopy point out also that the polymer which surrounds the magnetite nanoparticles seems to be strongly adhesive onto the surface of the nanoparticles resulting in a very intimate connection between the two components.

### 3.2 X-ray diffraction of the magnetic core-shell nanoparticles based on polypyrrole

An X-ray diffraction method is capable to determine average particle size, microstrains, probability of faults as well as the particle size distribution of magnetic nanoparticles. By XRD method one can be obtain the crystallite size that has different values for the different crystallographic planes. There is a large difference between the grain size and crystallite size due to the physical meaning of the two concepts. Practically speaking, it is not easy to obtain accurate values of the crystallite size and microstrain without extreme care in experimental measurements and analysis of XRD data. In the figure 5 presented the XRD of two samples of magnetic core-shell nanoparticles based on polypyrrole prepared by the oxidative polymerization of pyrrole monomer in the presence of magnetic ferrofluid (Aldea et al., 2009). The characteristic peaks for  $\text{Fe}_3\text{O}_4$  can be clearly observed in the XRD spectra from

figure 5. In addition, the characteristic peak (200) for FeO appears. Moreover, the intense peak at  $2\theta = 35.4$  degrees could be due to the superposition of Fe<sub>3</sub>O<sub>4</sub> characteristic peak (311) and FeO characteristic peak (111).

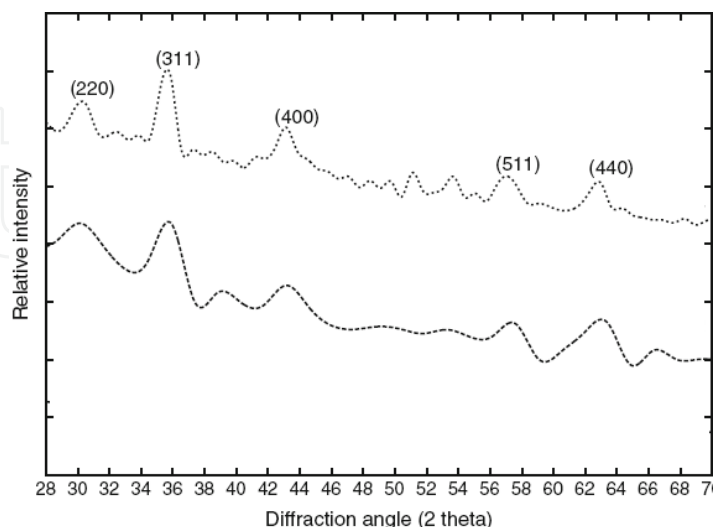


Fig. 5. XRD spectra of magnetic core-shell nanoparticles prepared by the oxidative polymerization of pyrrole monomer and magnetic ferrofluid

XRD analysis can add more information for understanding the nanostructure of the magnetite surrounded by the PPY shell. The studies made on this samples presented in the figure 5, is that the diminution of the number of atoms from the first and the second coordination shells of Fe atoms point out the existence of an electronic interaction between the magnetite nanoparticles and the surrounding PPY.

Another type of material which was investigated by X-ray diffraction is the magnetic core-shell nanoparticles based on NiFe<sub>2</sub>O<sub>4</sub> and polypyrrole (figure 6). The XRD scan on this type of material shows a broad amorphous diffraction peak centred at around  $2\theta = 23^\circ$ , which correspond to the scattering from the polymer chain at the interplanar spacing of protonated

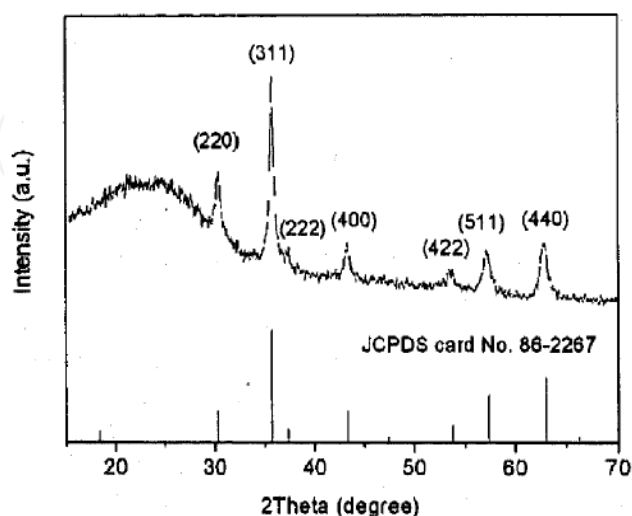


Fig. 6. XRD patterns of the magnetic core-shell nanoparticles based on polypyrrole and NiFe<sub>2</sub>O<sub>4</sub>

polypyrrole. The other seven diffraction peaks presented in the figure at  $2\theta = 30.1^\circ, 35.6^\circ, 37.3^\circ, 43.4^\circ, 53.7^\circ, 57.4^\circ$  and  $62.8^\circ$  corresponding to the (220), (311), (222), (400), (422), (511) and (440) reflections of the ferrosipinel  $\text{NiFe}_2\text{O}_4$  are consistent with the reference standard data.

### 3.3 FTIR spectroscopy of the magnetic core-shell nanoparticles based on polypyrrole

Magnetic core-shell nanoparticles based on polypyrrole are materials which combine two components: an anorganic core and an organic shell, therefore the FTIR spectroscopy is one of the most important tool for structural investigation of this type of material.

Figure 7 compares the FTIR spectrum of a pure polypyrrole sample doped with DBS and the FTIR spectrum of magnetic core-shell nanoparticles based on functionalized polypyrrole with phenylalanine. The FTIR spectra of the nanocomposites contain the characteristic absorption bands of both constituents, namely, oxidized polypyrrole shell and  $\text{Fe}_3\text{O}_4$ . The intense absorption band located around  $580\text{ cm}^{-1}$  is characteristic of  $\text{Fe}_3\text{O}_4$ . In the FTIR spectrum of magnetic core-shell nanoparticles the absorption bands which belongs to the polypyrrole chain at  $914, 1190, 1465\text{ cm}^{-1}$  are shifted to higher wave numbers. The position of this bands are correlated with the conjugation length of the polypyrrole chain, the shift to higher frequencies indicates a decrease of the conjugation length of the functionalized polypyrrole chain in the functionalized magnetic nanoparticles as compared to unfunctionalized polypyrrole. The band presented at  $1711\text{ cm}^{-1}$  ascribed the C=O bond, demonstrating that the function (phenylalanine) is attached on polypyrrole chain and incorporated in the magnetic core-shell nanoparticles (Nan et al., 2008).

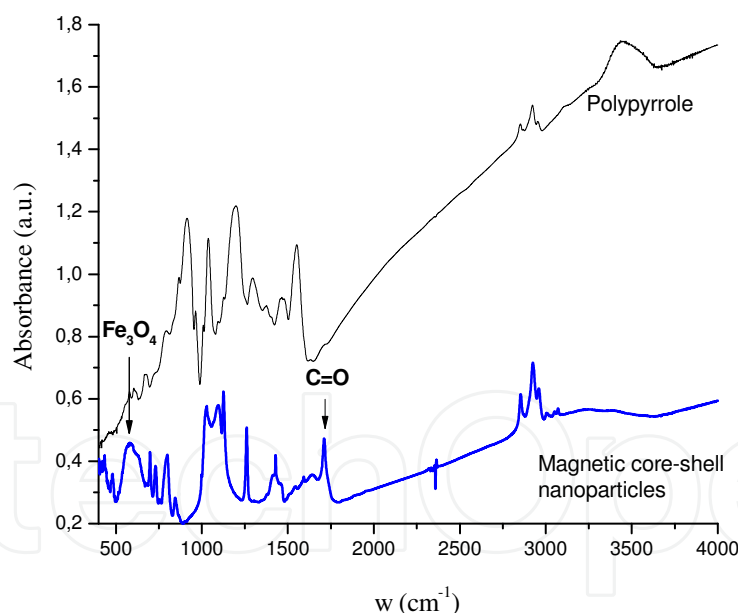


Fig. 7. The FTIR spectra of a pure polypyrrole sample doped with DBS and of the magnetic core-shell nanoparticles based on functionalized polypyrrole with phenylalanine

The FTIR spectra of polypyrrole and magnetic core-shell nanoparticles based on  $\text{ZnFe}_2\text{O}_4$  and polypyrrole is presented in the figure 8. The fundamental vibration of pyrrole ring, peak observed at  $1569\text{ cm}^{-1}$  in figure 2(a), has shifted to higher wavenumbers compared with  $1543\text{ cm}^{-1}$  of pure polypyrrole. This may be due to the interaction between PPy and  $\text{ZnFe}_2\text{O}_4$  nanoparticles and influence the skeletal vibrations, consequently delocalizing  $\pi$ -electrons. The peaks at  $1289\text{ cm}^{-1}$  and  $1046\text{ cm}^{-1}$  correspond to C-H in-plane vibration, while C-N

stretching vibration and C-C out-of-plane ring deformation vibration are found at  $1217\text{ cm}^{-1}$  and  $931\text{ cm}^{-1}$ , respectively. C-H ring out-of-plane bending mode shows at  $789$  and  $631\text{ cm}^{-1}$ . The appearance of peak at  $1694\text{ cm}^{-1}$  is attributed to the overoxidization of polypyrrole. Additionally, a strong band at  $572\text{ cm}^{-1}$  appears in the spectrum of  $\text{ZnFe}_2\text{O}_4$  nanoparticles, which is assigned to the Fe-O stretching vibration mode. The conclusion which can be drawn from the FTIR spectroscopy in this case is that the  $\text{ZnFe}_2\text{O}_4$  nanoparticles only serve as the nucleation sites for the polymerization of pyrrole because there is no chemical interaction between  $\text{ZnFe}_2\text{O}_4$  and polypyrrole in the magnetic core-shell nanoparticles (Li et al., 2009).

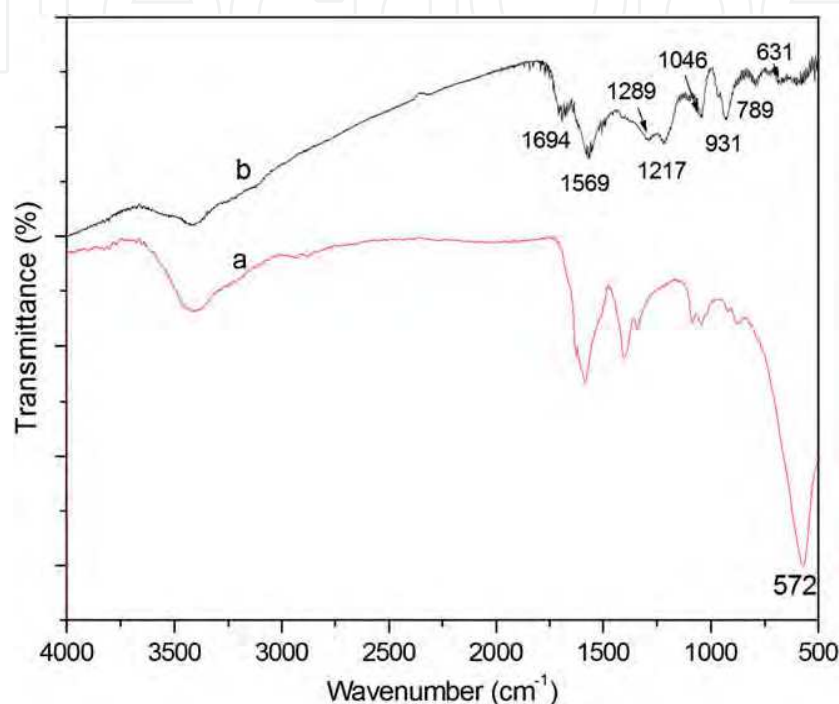


Fig. 8. FTIR spectra of (a)  $\text{ZnFe}_2\text{O}_4$  nanoparticles and (b) magnetic core-shell nanoparticles based on  $\text{ZnFe}_2\text{O}_4$  and polypyrrole nanoparticles

### 3.4 X-photoelectron spectroscopy of the magnetic core-shell nanoparticles based on polypyrrole

XPS is a surface-analysis method, consisting of the irradiation by X-rays of the investigated material, detection of the ejected photoelectrons, and their analysis by the kinetic energies ( $E_{kin}$ ). The method provides information concerning the element composition (atomic concentration) of the surface, as well as the chemical state of the emitting atoms (valence states, oxidation degree, chemical ligands etc). The former information is inferred from the areas delimited by the photoelectron peaks. The latter one relates to the chemical shifts of the peaks with respect to the elemental state, induced by the chemical surrounding of the atoms. Chemical shift represents a change in  $E_b$  of a core electron of an element due to a change in chemical bonding of that element. Core binding energies are determined by electrostatic interaction between electron and the nucleus and are reduced by the electrostatic shielding of the nuclear charge from all other electrons in the atom. Removal or addition of electronic charge as a result of changes in bonding will alter the shielding: withdrawal of valence electron charge (oxidation) increase in  $E_b$ ; addition of valence electron charge decrease in  $E_b$ .

Chemical shift information is a very powerful tool for functional group, chemical environment, oxidation state. According to the type of chemical bond and to the neighbor atoms, the binding energy of a given state can be shifted from a fraction of eV up to several eV. When several chemical bonds types are present, the spectrum peaks are splitted into several peaks which are sometimes almost merged. Using the appropriate software the peaks are deconvoluted into the components, each component corresponding to a particular bond type.

The high-resolution XPS spectra of C 1s, O 1s, N1s and Fe 2p core levels from the magnetic core-shell nanoparticles based on functionalized polypyrrole with cholesterol units, are given in the figure 9.

The spectrum of C 1s can be deconvoluted into three peaks corresponding to carbon atoms from different groups. The higher binding energy component at 288.7 eV correspond to carbon atoms from the group O-C=O present in the structure of the lauric acid double layer coating the magnetite nanoparticles from the magnetic fluid. The component peak located at 286 eV is ascribed to carbon atoms from the groups C-N, C-O from the structure of substituted pyrrole (see figure 9). The component at 285 eV corresponds to C-C, CH<sub>n</sub> groups.

The oxygen spectrum in the figure 1 exhibit three components assigned to the oxygen atoms from C-O-C, O-C=O groups from the structure of the substituted pyrrole and lauric acid, respectively and from Fe-O located at 530 eV.

The N1s core-level spectrum, figure 1 shows four components ascribed to the nitrogen atoms in different chemical states characteristic for unsubstituted and substituted pyrrole structures (Kang et al., 1993): the component at 398 eV corresponds to C=N group, the more intense component located at 400 eV is ascribed to N-H, C-N groups, the component at 402 eV is attributed to the positively charged nitrogen N<sup>+</sup>-H from unsubstituted pyrrole ring and the high binding energy component 403 eV ascribed to N-N group from the substituted pyrrole.

The Fe 2p spectrum contains the doublet Fe 2p<sub>3/2</sub> and Fe 2p<sub>1/2</sub> with binding energy values of 710 and 723.6 eV, typical for magnetite (Bhargava et al., 2007). Each peak from Fe 2p spectrum can be deconvoluted into two components corresponding to Fe<sup>3+</sup> and Fe<sup>2+</sup> ions from magnetite. One can observe the contribution of the Fe 2p<sub>3/2</sub> satellites located at 714.19 eV and 719.6 eV which correspond to Fe<sup>2+</sup> and Fe<sup>3+</sup> species (Brundle et al., 1977).

### 3.5 Magnetic properties of the magnetic core-shell nanoparticles based on polypyrrole

The most important property of these magnetic core-shell nanoparticles based on polypyrrole is the magnetic properties. The magnetic properties for almost all type of magnetic nanoparticles are determined by vibrating sample magnetization (VSM) at theroom temperature. The magnetic properties of magnetic core-shell nanoparticles based on polypyrrole depend very much on the type of core but also on the polymerization condition applied for pyrrole monomer.

The magnetic curves for ZnFe<sub>2</sub>O<sub>4</sub> nanoparticles and magnetic core-shell nanoparticles based on polypyrrole and ZnFe<sub>2</sub>O<sub>4</sub> are presented in the figure 10, the authors determined that the magnetization saturation value Ms for magnetic core-shell nanoparticles based on ZnFe<sub>2</sub>O<sub>4</sub> and polypyrrole is 17.8 emu/g, and the coercivity values Hc is about 130 Oe. However, the magnetization saturation value Ms of ZnFe<sub>2</sub>O<sub>4</sub> nanoparticles is 31.92 emu/g, and the coercivity value Hc is 94 Oe. These results can be attributed to the fact that non-magnetic



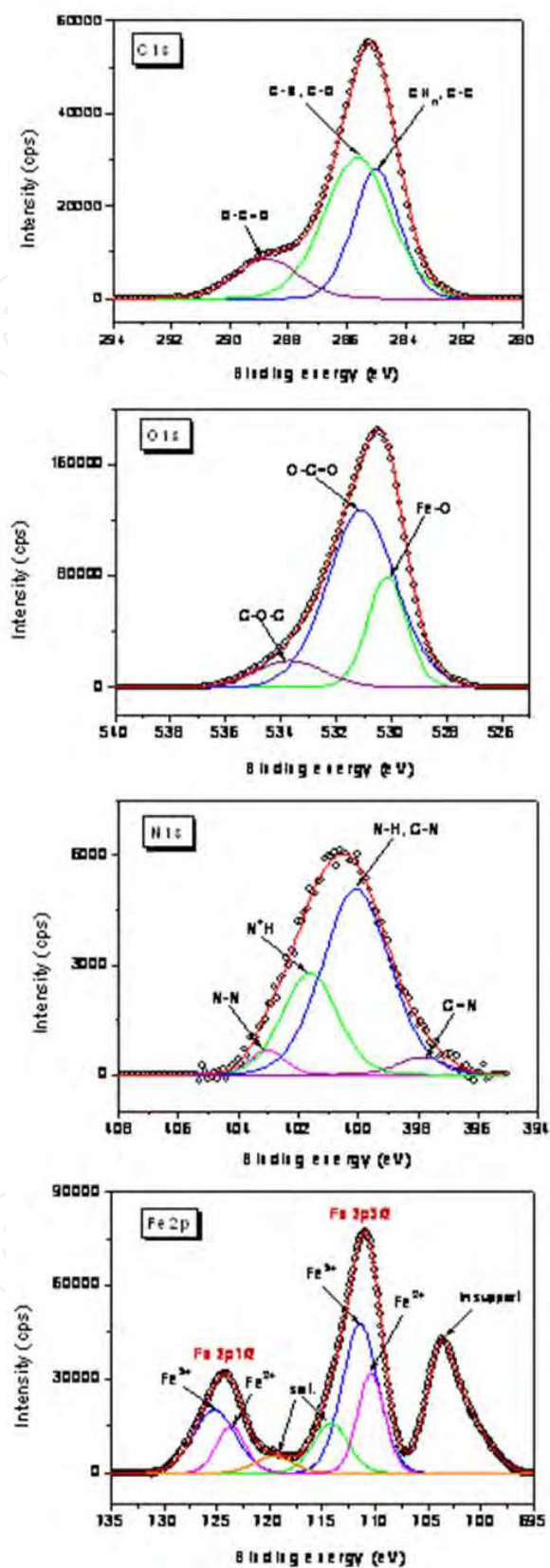


Fig. 9. High resolution XPS spectra C 1s, O 1s, N1s and Fe 2p core levels from the magnetite nanoparticles based on functionalized polypyrrole with cholesterol unites

polypyrrole coating layer on the surface of magnetic particles can decrease the magnetism of magnetic materials, while coercivity of nanocomposites increases due to the surface anisotropy upon coating and external morphology transformation (Li et al., 2009).

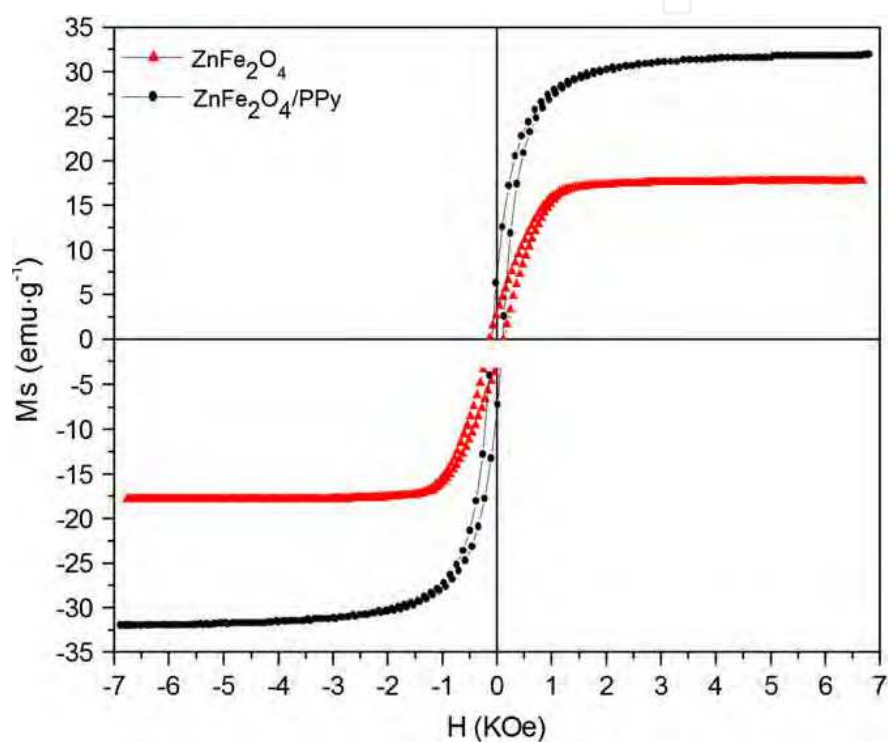


Fig. 10. Magnetic hysteresis loops of ZnFe<sub>2</sub>O<sub>4</sub> nanoparticles and magnetic core-shell nanoparticles based on polypyrrole and ZnFe<sub>2</sub>O<sub>4</sub> (ZnFe<sub>2</sub>O<sub>4</sub>/PPy).

In the case of magnetic nanoparticles based on functionalized polypyrrole prepared starting from magnetic ferrofluid the temperature magnetization show no hysteresis loop. For exemplification in the figure 11 we show the behavior of the magnetization at room temperature for magnetic core-shell functionalized polypyrrole with valine. The magnetization curves at room temperature of all investigated samples did not show hysteresis loops, thus proving the superparamagnetic behavior of the particles, the magnetization saturation value Ms is 63 emu/g. For such systems, the magnetic moment of the particle is free to rotate in response to the applied magnetic field when the blocking temperature is exceeded (Nan et al., 2008).

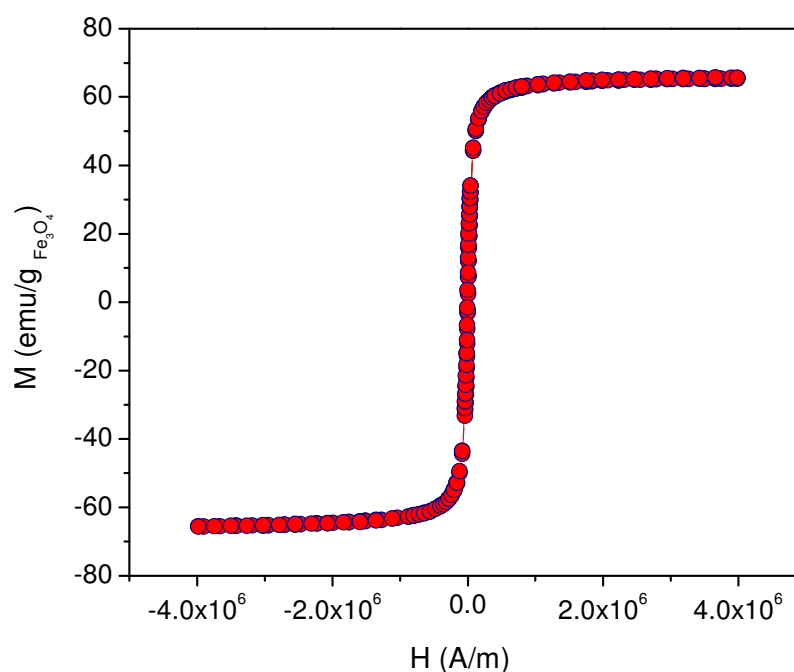


Fig. 11. Magnetization vs. applied magnetic field at room temperature of magnetic core-shell nanoparticles based on functionalized polypyrrole with valine

#### 4. Conclusion

The magnetic core-shell nanoparticles based on polypyrrole in most cases are obtained via chemical oxidative polymerization in the presence of different types of magnetic nanoparticles. The future applications of this kind of materials requires a deep understanding of the nanostructure-properties relationship which implies a complex physical chemical characterization correlated with the synthesis parameters.

This review focused on polypyrrole which is one of the most used conducting polymers for applications due to its high electrical conductivity, relatively good stability and the easy polymerization by low cost and environmentally friendly methods.

The combination of conducting polypyrrole with different magnetic nanoparticles is a successful way to provide composite materials with improved processability and greater potential applicability. The nature of the component materials and the synthesis parameters allow the control of some magnetic core-shell nanoparticles properties such as colloidal stability, electrical conductivity, and magnetic susceptibility.

Due to the discovery of new tools for an easy functionalization of polypyrrole simultaneously the functionalization of magnetic nanoparticles a large utilization of this materials are expected in the future for many applications as: biomolecular recognition, diagnosis, organocatalysis and separation of biological material.

#### 5. Acknowledgment

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code 76/2010, Surface and interface science: physics, chemistry, biology, applications and project POS CCE ID 550/ SMIS-CSNR 12025, contract financing: nr. 235/16.08.2010.

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