SYNTHESIS AND CHARACTERIZATION OF NANOSTRUCTURED POLYPYRROLE-MAGNETIC PARTICLES HYBRID MATERIAL

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Abstract. We report the synthesis and characterization of the nanocomposites obtained by the combination between a well-known conducting polymer polypyrrole (PPY) and magnetic nanoparticles Fe_3O_4. The properties of the composites were investigated by TEM, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), FTIR spectroscopy, d.c. conductivity and magnetization measurements.

Key words: nanocomposite, polypyrrole, conducting polymer, magnetic nanofluid, polymerization, superparamagnetism, electrical conductivity, magnetization, X-ray diffraction, X-ray photoelectron spectroscopy.

1. INTRODUCTION

Conducting polymers are the most recent generation of polymers, opening the way to progress in understanding the fundamental chemistry and physics of π-bonded macromolecules. Among conducting polymers, polypyrrole (PPY) has attracted great interest owing to its high conductivity and relatively high environmental stability. The potential applications of PPY are numerous and will grow as the improvement in the characteristics of this material continues [1, 2]. The association of PPY with other materials in order to prepare composite which combine the properties of both materials is one very promising way to obtain the specific requirements of physical properties for each type of application [2, 3].

In this paper we present the structural, electrical and magnetic properties of hybrid material obtained by the combination between conducting polypyrrole (PPY) and Fe_3O_4 magnetic nanoparticles in different synthesis conditions. Our main goal is to gain insight into the effects of several synthesis parameters on the PPy magnetic nanocomposites properties in order to obtain the required characteristic for specific applications.

2. EXPERIMENTAL

2.1. SAMPLES PREPARATION

The magnetic nanocomposites based on polypyrrole were prepared by the oxidative polymerization of pyrrole (Py) in aqueous solution containing an oxidant, ammonium peroxodisulfate (APS) and water based magnetic nanofluid (MF). The ratio of MF/Py was varied in the range 2-20 (v/v). The reaction proceeded at room temperature under magnetic stirring for different time intervals between 6 to 20 h. The resulting black precipitate was separated by centrifugation, washed with water and dried at 60^oC for 24 h.

2.2. CHARACTERIZATION METHODS

The morphology of PPY nanocomposites was investigated by TEM using 1010 JEOL microscope. The electrical conductivity of PPy nanocomposites was determined by the four contacts method on pellets pressed at 400 MPa. The magnetic measurements were performed at room temperature using a Vibrating Sample Magnetometer DMS 880. Structural characterisation of the samples was performed by X-ray diffraction (XRD) using 4B9A beamlines in Beijing Synchrotron Radiation Facilities equipped with a 5-circle diffractometer operating at 50-80 mA and 2.2 GeV at room temperature. Incident X-ray for the experiments was adjusted to 1.54 Å and a NaI(Ta) detector was used. The standard sample for the instrumental function was a silicon powder. X-ray photoelectron spectroscopy (XPS) was carried out on a VG Scientific ESCA-3 Mk-II spectrometer having as X-ray source the Al Kα radiation (1486.6 eV, non-monochromatic) of an anode operating at 14 kV and 20 mA. The photoelectrons were collected at an electron take-off angle of 50°, and analysed by their kinetic energies, with the pass energy of 50 eV. The binding energy (BE) shifts due to the surface charging during the measurements were corrected by using the C1s level (284.8 eV) of the adventitious carbon on the sample surface, as an internal standard. FTIR spectroscopy was carried out on a JASCO FTIR 610 spectrophotometer.

3. RESULTS AND DISCUSSION

Room temperature d.c. conductivity values, σ for PPy magnetic nanocomposites obtained in different synthesis conditions are given in Table 1. The electrical conductivity increase by decreasing the MF/Py ratio (see the samples PPyF2, PPyF3, PPyF4 from Table 1), or by increasing the polymerization time (see the samples PPyF2, PPyF5, PPyF6 from Table 1). These results are in agreement with that reported in the literature for PPy magnetic nanocomposites [4,5], showing that the electrical conductivity can be controlled by the ratio of the starting materials.

Table 1

The synthesis parameters and room temperature d.c. conductivity for PPy-Fe_3O_4 nanocomposites

Sample	MF/Py (v/v)	DBSA/Py (molar ratio)	Polymerization time (h)	σ ($\Omega^{-1}cm^{-1}$)
PPyF1	2	0.5	6	3×10^{-3}
PPyF2	20	-	6	10^{-4}
PPyF3	10	-	6	6×10^{-2}
PPyF4	5	-	6	1
PPyF5	20	-	12	8×10^{-4}
PPyF6	20	-	20	3×10^{-1}

One can observe from Table 1 that the addition of dodecylbenzensulphonic acid (DBSA) in the polymerization solution does not improve the electrical conductivity of the resulted composite (PPyF1).

The nanocomposites PPY-Fe_3O_4 obtained by pyrrole polymerization in the presence of Fe_3O_4 nanofluid, have a core-shell structure, where Fe_3O_4 is the magnetic core and PPY is the conducting shell. The TEM photographs for PPy-Fe_3O_4 nanocomposite, sample PPyF2 from Table 1 is shown in Fig. 1. The nanocomposite morphology shows particles with an average diameter of 15-25 nm, some of them forming aggregates.

Fig. 2 shows the behaviour of the magnetization at room temperature for PPY-Fe_3O_4 nanocomposite (sample PpyF2 from Table 1). The magnetization curves at room temperature for the all the investigated nanocomposites show no hysteresis loop, being typical for fine particles with superparamagnetic behaviour. For such a system, above the blocking temperature the magnetic moment of the particle is free to rotate in response to the applied magnetic field.

The synthesis conditions influence the magnetization of PPY nanocomposites. MF/Py ratio and polymerization time, respectively) are the main synthesis parameters, which influence the electrical and magnetic properties of the nanocomposites. The values of the saturation magnetization, M_S for the investigated PPy-Fe_3O_4 nanocomposites are in the range 53-8.8 Am^2/kg. M_S increases by increasing the magnetic fluid concentration in the synthesis solution see the samples PPyF2, PPyF3 and PPyF4 from Fig. 3. On the contrary, the increase of composites PPy content by increasing the polymerization time results in the decrease of

M_S, see the samples PPyF2, PPyF5 and PPyF6 from Fig. 4. Our results show that MF/Py ratio and polymerisation time represents the main synthesis parameters which allow controlling the nanocomposites electrical and magnetic properties.
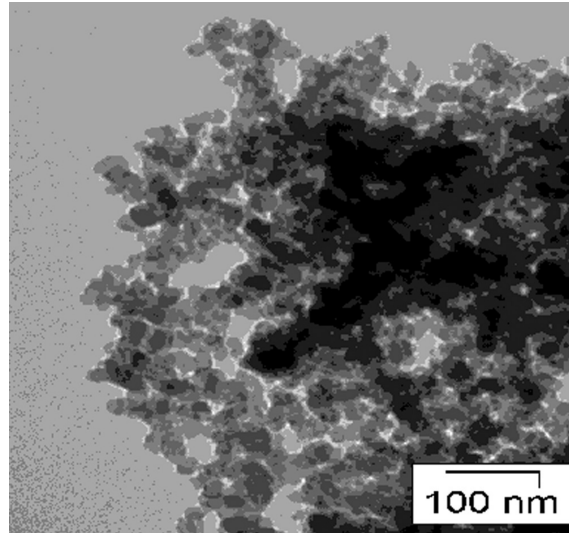

Fig. 1 – TEM photographs of PPy-Fe$_3$O$_4$ nanocomposite, sample PPyF2 from Table 1.
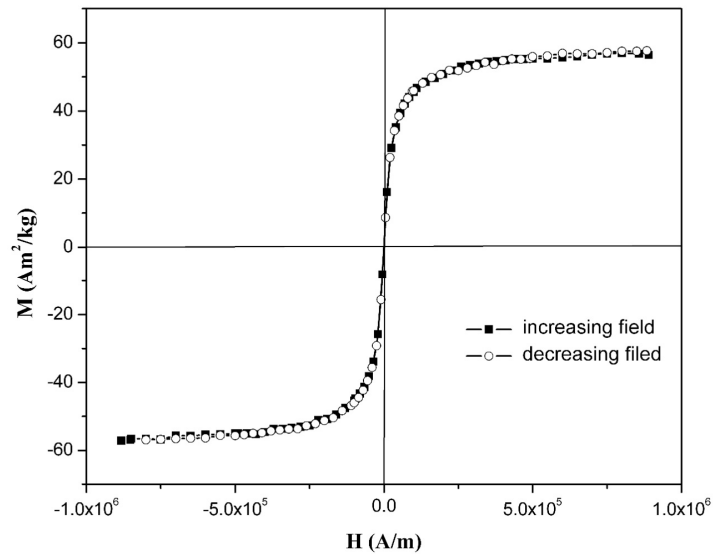

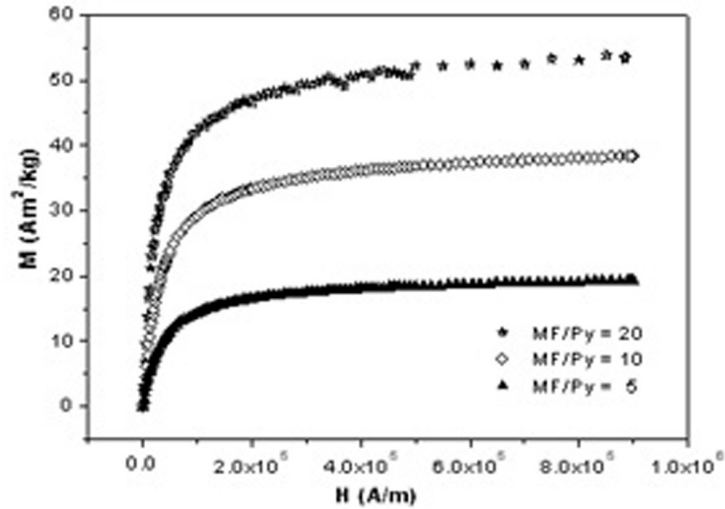Fig. 2 – The magnetisation *vs.* applied magnetic field for nanocomposite PpyF2 from Table 1 at room temperature.

Fig. 3 – The influence of MF/Py ratio on the PPY-Fe$_3$O$_4$ nanocomposites magnetization values.

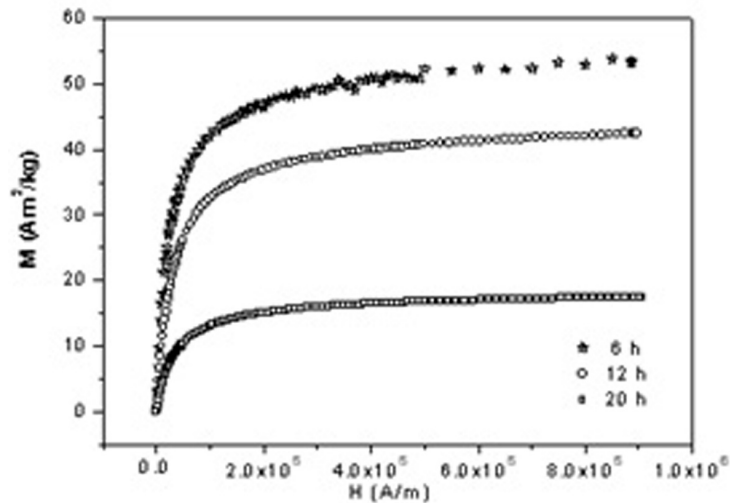Fig. 4 – The influence of polymerization time on the PPY-Fe$_3$O$_4$ nanocomposites magnetization values.

The XRD spectra for PPy-Fe$_3$O$_4$ nanocomposites are given in Fig. 5. The characteristic peaks for Fe$_3$O$_4$ can be clearly observed in the XRD spectra from Fig. 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$_3$O$_4$ characteristic peak (311) and FeO characteristic peak (111).
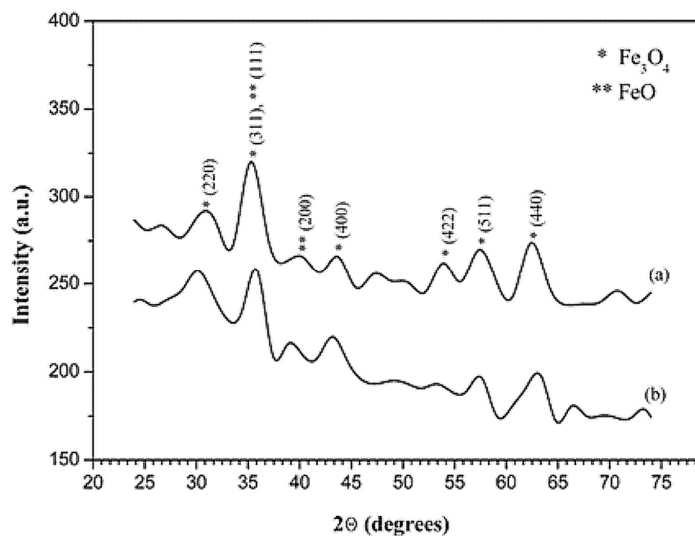
Fig. 5 – XRD spectra for PPY-Fe_3O_4 nanocomposites from Table 1: (a) PPyF2; (b) PPyF6.

The oxidation state of iron was inferred from the XPS core-level spectra of Fe 2p. Although a large number of XPS studies approached the iron oxides, to unambiguously discern between them remains a difficult task. The corresponding binding energy (BE) values of Fe $2p_{3/2}$, previously reported, spread over broad, superposed ranges: between 709.1 and 710.65 eV for FeO, between 707.9 and 710.7 eV for Fe_3O_4, and between 710.6 and 711.5 eV for Fe_2O_3 [6,7]. However, a recent study on iron compounds [8], with various iron environments and oxidation states, revealed significant differences of the charge-transfer (CT) satellites of the Fe 2p peaks. For Fe^{2+} (*e.g.,* in FeO), the CT satellites appear as peak shoulders, with a small satellite-peak separation, while for Fe^{3+} (Fe_2O_3), the satellites are much more distinct, at larger distances to the photoelectron peaks. These spectral features are vanishing for iron in intermediate oxidation states, as in Fe_3O_4. This behaviour enables to detect small amounts of iron oxides different of Fe_3O_4, by the simple presence of the Fe 2p satellites.

The Fe 2p spectra of the PPy-Fe_3O_4 composites, with the specific spin-orbit split in two components ($2p_{3/2,1/2}$), is shown in Fig. 6.

Strong CT satellites are visible as peak shoulders on the spectrum of PPyF1. For the other samples, the satellites are much weaker, but still distinct. The BEs of the Fe $2p_{3/2}$ peak and its satellite were indicated in Table 2, by comparison with the energies specific to the iron oxides, as reported in [8]. As can be seen, the Fe $2p_{3/2}$ position for PPy is close to that characteristic of Fe_3O_4, with deviations of ±0.2 eV. However, the CT satellites point out the presence of additional iron oxides in the

PPy composition. The peak-satellite separation, relatively small, clearly corresponds to FeO (see Table 2). The Fe $2p_{3/2}$ peak is therefore contributed by both Fe_3O_4 and FeO, while its satellite is the fingerprint of FeO. These results are in agreement with the XRD data, showing that besides Fe_3O_4 the nanocomposites contain small amounts of FeO, which could appear, on the magnetic nanoparticles surface due to the charge transfer interaction with the surfactant or PPy. For PPyF1, the FeO fraction is much higher and this fact could explain the lower magnetisation values as compared with the other samples.
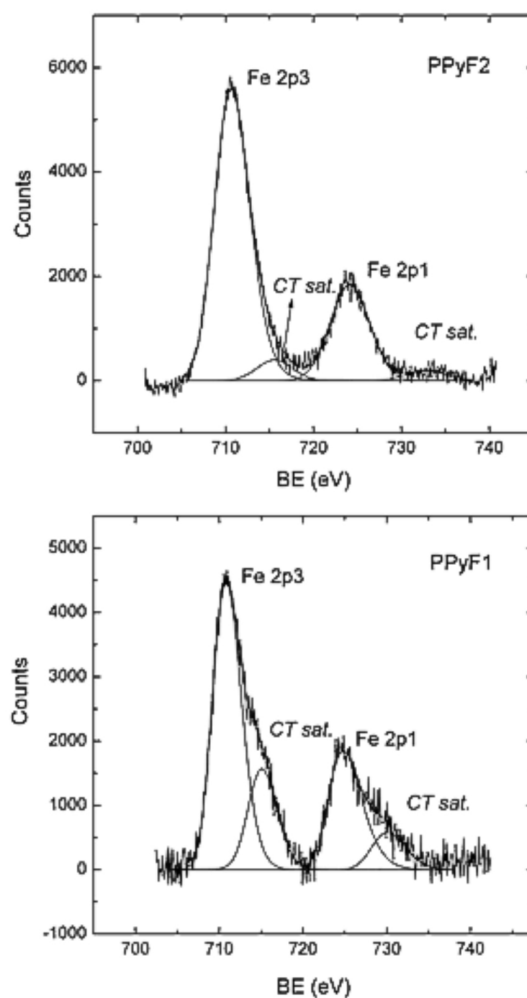

Fig. 6 – Fe 2p core-level spectra for PPy-Fe_3O_4 nanocomposites.

The BEs of the Fe $2p_{3/2}$ photoelectron peak and its satellite, in iron oxides and PPy nanocomposites.
The BEs of the former compounds was taken from ref. [8]

Nr. Crt.	Sample	BE (eV)		peak-satellite separation (eV)
		Fe $2p_{3/2}$	Fe $2p_{3/2}$ satellite	
1	FeO	709.85	715.5	5.65
2	Fe_3O_4	710.6	–	–
3	Fe_2O_3	710.95	719.0	8.05
4	PPyF1	710.8	715.1	4.3
5	PPyF2	710.6	715.6	5.0

FTIR spectra (Fig. 7) shows that the main characteristic absorption bands for PPy into the composites are shifted to higher frequencies as compared to those of pure PPy [9]. The absorption bands ascribed to pyrrole ring vibrations shift to higher frequencies with the increase of Fe_3O_4 content, indicating the existence of an interaction between PPy backbone and magnetic nanoparticles.
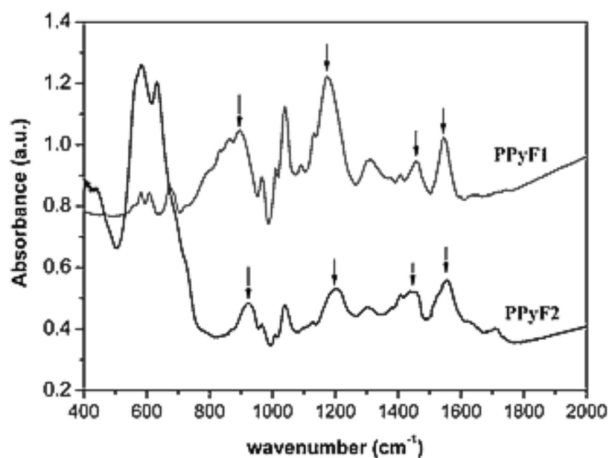

Fig. 7 – FTIR spectra of PPY-Fe_3O_4 nanocomposites.

4. CONCLUSIONS

Nanocomposites PPy-Fe_3O_4 were obtained by the polymerization of pyrrole in the presence of water based magnetic nanofluid. The double layer sterical stabilisation of Fe_3O_4 nanoparticles with myristic acid and DBS avoids their aggregation and allows the pyrrole polymerisation around the magnetic nanoparticles.

The magnetic fluid/pyrrole ratio and the polymerisation time mainly determine the properties of PPy magnetic nanocomposites. The variation of these synthesis parameters allows the tailoring of electrical conductivity and magnetisation values for PPy-Fe_3O_4 nanocomposites. The magnetisation *vs*. applied magnetic field for the reported nanocomposites shows no hysterezis loop, indicating a superparamagnetic behaviour.

XRD and XPS studies show that besides Fe_3O_4 the nanocomposites contain small amounts of FeO, which could appear on the magnetic nanoparticles surface due to the charge transfer interaction with the surfactant or PPy. FTIR spectra of the nanocomposites support the idea of an interaction between PPy and magnetite, because a shift of the characteristic pyrrole ring absorption bands to higher frequencies as compared to those of pure PPy was observed.

Our results show that the polymerization of polypyrrole in stable dispersions of magnetic nanoparticles represents a good strategy to generate nanocomposites with controllable magnetic and electric properties. These nanocomposites have potential applications as electromagnetic shielding. In addition, the nanocomposites polypyrrole/magnetic nanoparticles can be easily provided with biofunctionality by the attachment of specific molecular groups to the polymer chains, offering great promise applications in biotechnology.

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