

Magnetic Nanoparticles-Based Conducting Polymer Nanocomposites

A. Muñoz-Bonilla, J. Sánchez-Marcos and P. Herrasti

Abstract This chapter reviews the state of art of nanocomposites based on conducting polymers and magnetic nanoparticles. The preparation of hybrid nanocomposites with both magnetic and electrical properties has emerging as attractive alternative in a wide number of applications especially as microwave absorbing material and electromagnetic shielding. An overview of the different synthetic routes of the hybrid nanocomposites is presented, which outlines the most development techniques to prepare homogenous matrix, core-shell nanoparticles, and thin films. This chapter also covers the discussion of both the magnetic and electrical properties of the nanocomposites that significantly vary from the individual components. Finally varies of the most relevant applications of the magnetic nanoparticles-based conducting polymer nanocomposites are highlighted.

Keywords Magnetic nanoparticles · Conducting polymers · Nanocomposites · Magnetic properties · Electrical properties

1 Introduction

Conducting polymers were first produced in the mid-1970s as a novel generation of organic materials that have both electrical and optical properties similar to those of metals and inorganic semiconductors, combined with attractive properties associated with conventional polymers, such as ease of synthesis and flexibility in processing.

Magnetic nanoparticles (NPs), in particular iron oxide magnetic nanoparticles exhibit remarkable magnetic properties particularly in radiofrequency region, physical flexibility, high electrical resistivity, mechanical hardness and chemical stability. They have found widespread applications in many fields covering

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catalysis, data storage, environmental remediation separation, purification, and biomedical uses [1–4]. For many of these applications, the synthesis of uniformly sized nanoparticles is of key importance, because their electrical, optical, and magnetic properties depend strongly on their dimensions.

In recent years the preparation of hybrid nanocomposites with both magnetic and electrical properties has received a great attention in industrial and academic fields. For instance, nanocomposites based on conducting polymers and magnetic nanoparticles are one of the most widely studied materials for microwave absorbing and electromagnetic shielding. The extensive development of electronic devices and the intensive usage of electromagnetic waves have created several problems of electromagnetic interferences (EMI) and the demand of adequate shielding is continuously growing. Besides, magnetoelectric polymeric nanocomposites find applications in many other fields such as in solar cells, sensors, memory devices, catalysis, among others. In general, the hybrid nanocomposites can be prepared, depending on their final use, by incorporating the magnetic nanoparticles in a conducting polymer matrix or by encapsulation of the nanoparticles leading to core–shell systems. Besides, the final properties of the hybrid materials depend not only on the properties of the individual components thus on the composition but also on the dispersibility of the nanoparticles, homogeneity of the nanocomposite and on the interfacial interactions between the components. Indeed, many attempts and synthetic strategies have been carried out with multiple nanocomposite systems to achieve highly uniform materials in order to attain the desirable electric and magnetic properties. Table 1 summarizes some of the most relevant magnetic nanoparticles-based conducting polymer nanocomposites reported in literature, with their respective properties and applications.

Table 1 Some of the most relevant examples of magnetic nanoparticles-based conducting polymer nanocomposites

Polymer	Magnetic Nps	Properties/applications	Refs
PPy	CoZnFe ₂ O ₃	Ferrimagnetic behavior	[5, 6]
PPy	Fe ₂ O ₃	Ferromagnetic/superparamagnetic	[7–14]
PPy	Fe ₃ O ₄	Superparamagnetic/conductivity decreases with the NPs content	[15–18]
PPy	Fe ₃ O ₄	Superparamagnetic/conductivity increases with the NPs content	[19]
PPy	Co	Induced resistive switching and magnetism (memory device application)	[20]
PANI	Fe ₃ O ₄	Ferromagnetic/conductivity decreases with NPs content	[21–26]
PANI	Fe ₃ O ₄	Superparamagnetic/conductivity decreases with the NPs content	[27–31]

(continued)

Table 1 (continued)

Polymer	Magnetic Nps	Properties/applications	Refs
PANI	CoFe ₂ O ₄	Ferromagnetic/magnetization increases and coercivity decreases with NPs content	[32, 33]
PANI	ZnFe ₂ O ₄	The conductivity decreases with the NPs content higher magnetoresistance	[34]
PANI	NiFe ₂ O ₄	Ferromagnetic/conductivity decreases with NPs content	[35]
PANI	BaFe ₁₂ O ₁₉ Ba _x LaFe ₁₂ - _x O ₁₉	Ferromagnetic/conductivity decreases with the NPs content	[36, 37]
PANI PAOABSA	γFe ₂ O ₃	Superparamagnetic/conductivity decreases with the Nps content	[38–40]
PANI	Fe ₂ O ₃ NiO	Superparamagnetic/conductivity decreases with the Nps content	[41]
PANI	NiCrFe _x O ₄	Ferromagnetic/magnetization decreases with the NPs content	[42]
POEA	γFe ₂ O ₃	Conductivity does not change with the content of NPs	[43]
SPAN	γFe ₂ O ₃	Conductivity increases in the nanocomposite	[44]
PEDOT	Fe ₃ O ₄ CoFe ₂ O ₄ NiFe ₂ O ₄	Superparamagnetic	[45–48]
PEDOT	Co ₃ O ₄ /GO	Electromagnetic absorption properties	[49]
PAN	Ni, Co, Ni–Co	Superparamagnetic/microwave absorption application	[50]

PPy polypyrrole, *PANI* polyaniline, *PAOABSA* poly(aniline-*co*-aminobenzenesulfonic acid), *POEA* poly(*o*-ethoxyaniline), *SPAN* sulfonated polyaniline, *PEDOT* poly(3,4-ethylenedioxythiophene), *PAN* polyacrylonitrile

As shown, a large number of investigations are focused on typical conducting polymers such as polypyrrole, polyaniline, polythiophene and their derivatives due to its good electrical properties and ease of synthesis. Relative to the magnetic component, iron oxide nanoparticles, i.e., magnetite and maghemite, are by far, the most preferred nanomaterials as a consequence of their strong magnetic and semiconducting properties together with their low cost. In addition, these ferromagnetic iron oxide nanoparticles can become superparamagnetic when they behave as single magnetic domains typically with small diameter. In general, the magnetic properties of the nanocomposites differ from the pure magnetic nanoparticle as a result of the nonmagnetic polymeric component, decreasing the magnetization saturation values and also affecting the anisotropy and the coercivity values [51, 52]. Regarding the electrical properties of the nanocomposites, the conductivity usually decreases with the content of magnetic nanoparticles due to the reduction of the electronic density of the polymer chains as a result of their interactions with the metal cations of the nanoparticles, among other factors. As commented the incorporation of magnetic

nanoparticles into a conducting polymer matrix introduces magnetic character, modifies the electrical behavior but also can vary other properties such as the processability, mechanical, and thermal properties, all of them highly important for the applicability of the materials. Hence, several aspects have to be taken into account and controlled to tune the desirable magneto-electrical behavior of the nanocomposites and suitable properties depending on their final application.

This chapter gives a brief overview of the hybrid magnetic nanoparticles-based conducting polymer nanocomposites and of their recent advances in the last decade. Also, it pretends to provide a complete background in the area, given a wide and insightful understanding of these kinds of materials, which have received a great attention in the last years due to the very promising potential in several applications. This chapter includes several sections that cover general topics, preparation methods, properties, and applications. The synthetic strategies employed to incorporate nanoparticles in the polymer matrix and to obtain core-shell materials and films will be addressed in detail. The magnetic and electrical properties of the hybrid nanocomposites will be presented second and compared with the pure components. The final section will be focused on the most important practical applications of the conductive and magnetic nanocomposites to end with the conclusion remarks and possible future research directions.

2 Synthetic Strategies

As described along the different chapters, most of the conducting polymers are typically synthesized by oxidative polymerization method induced chemically or electrochemically. Chemical oxidation (i.e., oxidation of aniline or pyrrole by iron salts [53] or peroxydisulfate [52]) is preferred when large amount of polymer is needed while the electrochemical oxidation [54] is more suitable to fabricate polymer films for electronic devices.

The polymerisation mechanism of conducting polymers is complex and number of explanations have been suggested by different researchers [54, 55].

Next, it is briefly described the accepted polymerisation mechanism of polypyrrole, probably the most used conducting polymers, in the electrochemical synthesis, although this mechanism can be extended to the chemical polymerisation.

Typically the monomer is oxidized losing an electron and forming different radical cation resonances (R^+) as shown in Scheme 1 of Fig. 1. If the oxidation of the monomer at the electrode surface is faster than the diffusion of the oxidized radicals from the electrode surface to the electrolyte solution the concentration of the radical cation increases and they can be involved in different coupling reactions. The monomer can react and generate nonconducting oligomers, which may deposit on the electrode, or diffuse into the solution and produce a soluble brown cloud if the radical cation is extremely active (unstable) or extremely inactive (stable). The stable radical cation can also undergo further coupling reactions to form dimers that lead to a proton release, as shown in Scheme 2 of Fig. 1.

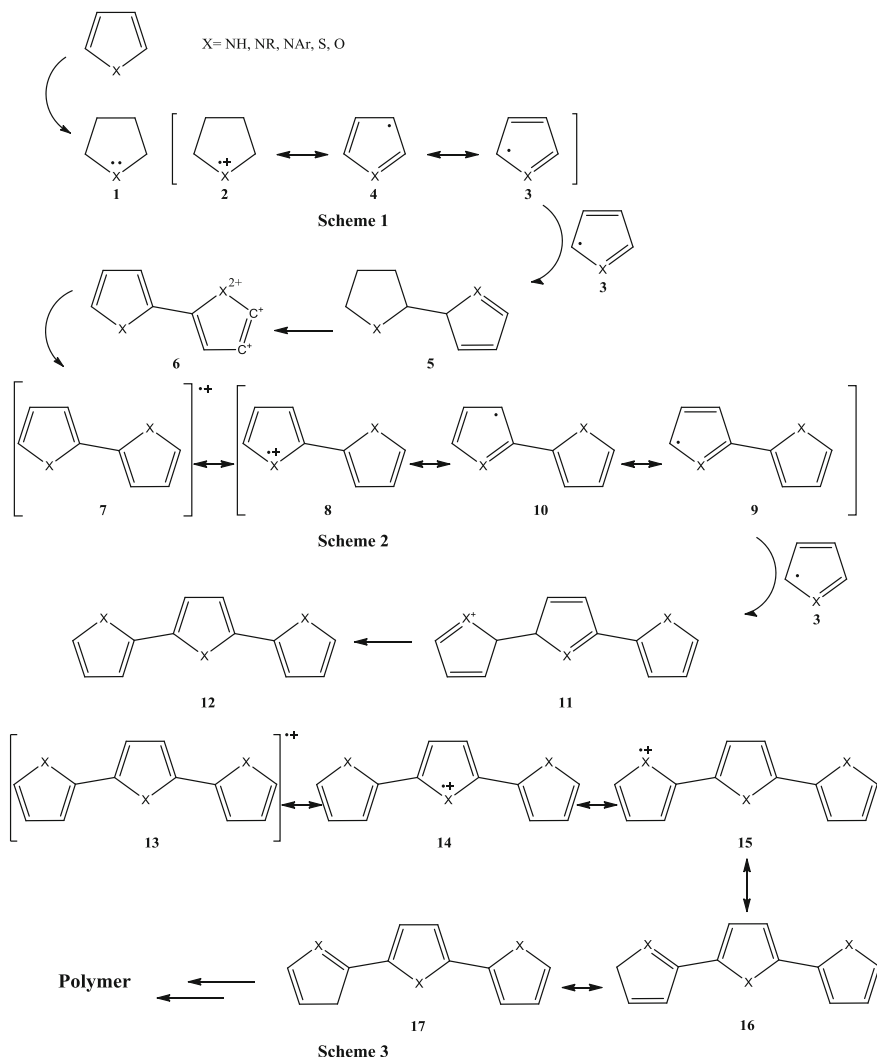


Fig. 1 Proposed mechanism for obtaining conducting polymers by polymerization of aromatic heterocyclic monomers [54]

The resonance form (3) with the α - α' (2, 5) position having greatest density of unpaired electrons is predominant. The propagation of the polymer chain begins with the reaction between two stable radical cations at the α position to form a dication. This species loses two protons becoming neutral and stable (see Scheme 2). According to Genies et al. [55] the reaction coupling is between two π -radical cation monomers that leads to the formation of a dimer precursor which then deprotonates eliminating two protons to form a dimer radical, Scheme 2 of Fig. 1.

The dimer radical cation oxidizes easier than the monomer at the existing anode applied potential because of the delocalized unpaired electron over the heterocyclic rings. The predominant resonance form (9) is oxidized into a cation radical and undergoes further coupling reactions at β or β' with monomer radical cation 3 at α or α' positions, producing a trimer dication (11) (see Scheme 3, Fig. 1). The trimer dication then loses two protons to form the neutral trimer (12).

The neutral trimer (12) is oxidized to a trimer radical cation (13) (see Scheme 3 of Fig. 1), which reacts with the monomer to form a tetramer. The polymer chain continues growing via the same oxidation sequence, coupling and deprotonating until the chain growth terminates and the final polymer is obtained. Reaction with water could be one of the steps that end the polymerisation. Although, α position is the most active and predominant, the β position also reacts and increases the chain length and also the disorder. This disorder that forms the β coupling is responsible for the poor crystallinity of the conducting polymer but the crystallinity can be improved by blocking the two β positions with methyl groups or Cl atoms in order to form poly (β - β' -dimethylpyrrole) and the poly (β - β' -dichloropyrrole), respectively.

In relation with the magnetic nanoparticles component, a wide variety of magnetic nanoparticles with controlled size and shape have been synthesized including pure metal, such as Fe, Co, and Ni; iron oxides, such as Fe_3O_4 and Fe_2O_3 ; mixed ferrites as MnFe_2O_4 and CoFe_2O_4 ; as well as alloys, i.e., FePt. The magnetic properties of the nanoparticles are principally dominated by the chemical composition, phase, size effect, and surface effect and all of these aspects will be determined by the synthetic route. A large number of suitable methods have been developed to obtain magnetic nanoparticles which are mainly based on chemical approaches. The most popular and used methods include coprecipitation, thermal decomposition, microemulsion, hydrothermal synthesis, electrochemical route, and laser pyrolysis among other techniques [56]. The chemical coprecipitation is the preferred method to synthesize magnetic nanoparticles, especially iron oxides [57]. This general method consists in a solution containing Fe^{2+} and Fe^{3+} ions in water, to this solution is added NH_4OH and the system is stirred for a period of time. The precipitate is separated by magnetic decantation and washed with deionized water and ethanol to obtain the final magnetic nanoparticle iron oxide powder. Although, this is the most common method, some others have been used to generate magnetic nanoparticles to produce nanocomposites, for example, the electrochemical synthesis of magnetite and other ferrites nanoparticles [58–60]. The advantage of this method against conventional methods is the better nanoparticle size control by changing experimental parameters, such as oxidative potential or current. The control of size and the dispersion of the magnetic nanoparticles is a key parameter to obtain nanocomposites with homogeneous properties.

Therefore, the preparation of magnetic nanoparticles-based conducting polymer nanocomposites may successfully combine the strategies to synthesize both the magnetic nanoparticles and the conducting polymer in order to obtain a homogenous and appropriated material. The preparation method strongly affects the final properties of the nanocomposites and many investigations have been published regarding

the suitable incorporation of the nanoparticles into the conducting polymer matrix. As commented one of the major challenge is related to achieve a homogeneous dispersion because the aggregation of the nanoparticles generally demerits the properties of the materials and could limit the applications. In particular, the magnetic nanoparticles tend to the agglomeration due to magnetostatic interactions and this makes them difficult to be well dispersed into the polymer matrix. In the same way there are several synthetic methods to develop nanocomposites in stable colloidal form. A number of magnetic nanoparticles have been encapsulated by conducting polymer shells using a variety of strategies to overcome agglomeration problems and maintain the nanocomposite colloidally stable in the medium. Related to the preparation of thin film, much effort is dedicated to build homogeneous monolayer or multilayer usually by previously covering the nanoparticles with organic ligands to gain dispersibility in the used solvent [61].

In brief, the preparation methods of these nanocomposites can be classified in four main routes proposed in the literature that are graphically represented in Fig. 2 for the preparation of composites based on PPy. In the first strategy, both components, the polymer and the magnetic nanoparticles are synthesized separately and then mixed to produce the nanocomposite. This route presents as the main inconveniences that the conducting polymers, i.e., PPy, are not soluble in common solvent and also this method normally conducts to heterogeneous composites with

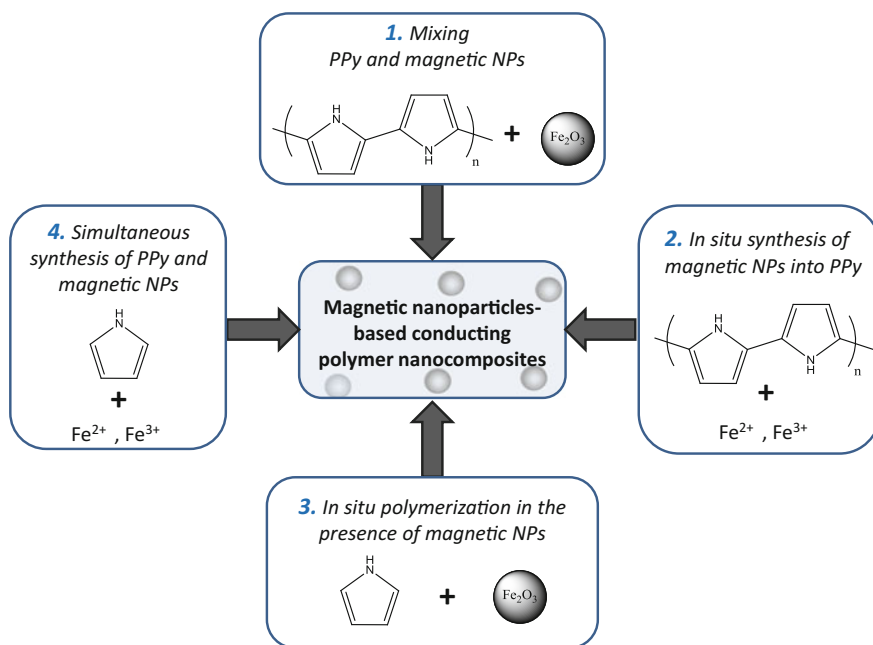


Fig. 2 Scheme of the different preparation methods of magnetic nanoparticles-based conducting nanocomposites

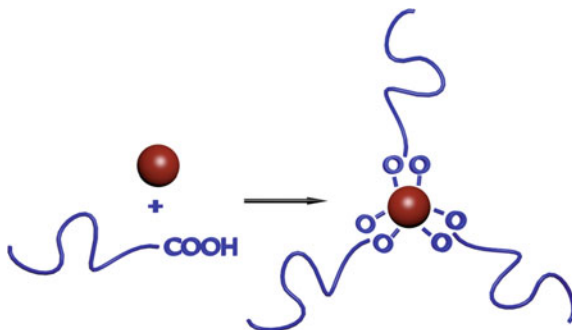
large aggregates of particles, and consequently it is not commonly used. Second route consists in the synthesis of the nanoparticles within the PPy previously synthesized, which provides nanocomposites more homogeneous. However, the control of the nanoparticle size is difficult and the solubilization of the polymer implies again an inconvenience. The third route is probably the most employed for the formation of magnetic nanoparticles-based conducting polymer nanocomposites. In this method, the nanoparticles are generated at first and then the polymerization is carried out in situ in the presence of the nanoparticles. Therefore, it is possible to synthesize nanoparticles in a controlled manner and at the same time, to produce homogeneous composites. At last the preparation of the nanocomposites by the in situ preparation of both the polymer and the nanoparticles is not yet very commonly used despite its simplicity and rapidity, as a result of its poor control over the polymer and the nanoparticles.

Next, the different strategies used to prepare magnetic nanoparticles-based conducting polymer nanocomposites employing both chemical and electrochemical routes are further discussed.

2.1 *Mixing or Blending Pre-synthesized Conducting Polymers and Magnetic NPs*

Hybrid nanoparticles–polymer nanocomposites are typically prepared by blending or mixing the different components in solution or in a melting process. However, these conventional strategies are not feasible in case of most of conjugated conducting polymers because they are generally insoluble in common solvents and present a very-high melting temperature. Only few examples are reported related to the preparation of nanocomposites based on conducting polymers using a solution method. In those cases the polymer has to be soluble or dispersible in the solvent and also the magnetic nanoparticles need to be colloidal stable in order to avoid the aggregation in the final nanocomposite (Fig. 3). For instance, water-soluble

Fig. 3 Illustrative representation of the conducting nanocomposites prepared from pre-synthesized conducting polymers and magnetic NPs



polymers such as poly(1-vinyl-1,2,4-triazole) [62], as well as a polypyrrole derivative, poly(*N*-pyrrole phosphonic acid) [16, 17], were mixed with Fe_3O_4 nanoparticles in aqueous solution leading conducting and magnetic nanocomposites.

Other strategies employ polymer aqueous dispersion instead of solution, that is the case of the PEDOT:PSS (polystyrene sulfonate) system which is commercially available in aqueous dispersion and was blended with anionic coated iron oxide nanoparticles to prepare composite thin films [48]. Besides, layer by layer technique has been used to prepare several nanocomposite thin films from conducting polymer solution and ferrofluids for different applications [5, 43]. In these approaches layers of positively charged conducting polymer, such as PPy and poly(*o*-ethoxyaniline), in combination with positively charged magnetic nanoparticles were deposited alternatively with layers of negatively charged polymers such as polystyrene sulfonate.

On the other hand, cryomilling technique has been proposed as interesting alternative to the solvent method in order to obtain nanocomposites with magnetic nanoparticles homogenously dispersed in the polymer. This solid state method blends the components by milling under cryogenic temperature reducing the viscoelasticity of the polymer thus improving the compatibility between the polymer and the nanoparticles. Nanocomposites of PANI and iron nanoparticles were prepared by this technique using both micrometer and nanometer Fe particles as starting material [63, 64].

2.2 In Situ Synthesis of Magnetic Nanoparticles into Conducting Polymers

With the purpose of improving the nanoparticles dispersion into the conducting polymer, some investigations attempt to carry out the in situ synthesis of the magnetic nanoparticles into the polymer which again needs to be soluble in the used solvent. In a reported example, magnetite nanoparticles were synthesized by coprecipitation method in an aqueous solution containing a pre-synthesized poly(3-pyrrol-1-ylpropanoic acid) [16]. The incorporation of sulfonated groups into polyaniline also conducts to water-soluble conducting polymers and allows the preparation of the nanocomposites in aqueous solution by the in situ synthesis of iron oxide nanoparticles in the polymer solution [38]. Besides, the polymer chains can be chemically attached to the surface of the nanoparticles towards these functional groups enhancing the final properties of the nanocomposites. These particular kind of polymers with sulfonated groups, such as poly(pyrrole-*N*-propylsulfonate), when are prepared by reaction with FeCl_3 produce polymers with pendant SO_3^- and Fe^{2+} ions that provide overall charge neutrality in the material (Fig. 4). Further treatment with NH_4OH allows the synthesis of iron oxide

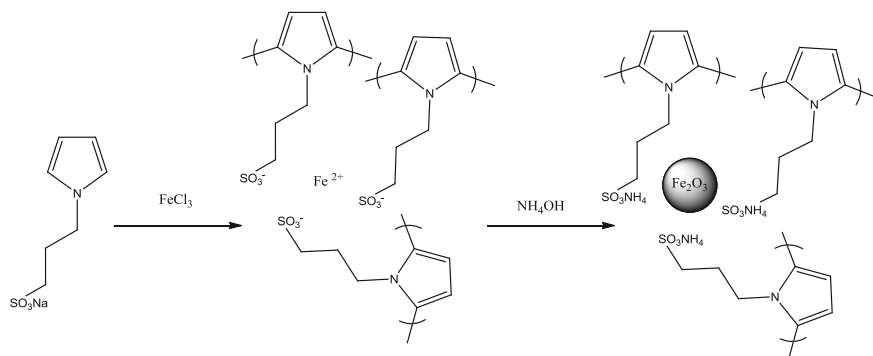


Fig. 4 Scheme of the synthetic procedure to obtain magnetic nanoparticles-based conducting polymer nanocomposites by in situ synthesis of Fe₂O₃ nanoparticles

nanoparticles in the polymer solution thus the in situ preparation of the magnetic polymer nanocomposite in aqueous solution [65].

A mixture of solvent can be also used to prepare the nanocomposite by in situ synthesis of the magnetic nanoparticles into the previously prepared polymer. A composite of PANI and Fe₃O₄ nanoparticles were prepared from *N*-methyl pyrrolidone polymeric solution by addition of an aqueous solution of iron(II) sulfate [66]. The magnetic properties of the final composites strongly depend on the preparation conditions, such as the reaction temperature and the FeSO₄ concentration.

Alternatively, the conducting polymers can be suspended in aqueous solution instead of be solubilized, and the magnetic nanoparticles created in the same medium, as reported for a nanocomposite consisting of PANI and magnetite [67].

Moreover, magnetic nanoparticles of Ni and Co have been also synthesized and directly incorporated into PANI fibers by electroless metal deposition [50]. However, by using this strategy only the surface of the fibers is functionalized with the magnetic nanoparticles.

2.3 *In Situ Polymerization in the Presence of Magnetic Nanoparticles*

However, and without any doubt, the in situ monomer polymerization in the presence of pre-prepared magnetic nanoparticles is the most common strategy to prepare nanocomposites based on conducting polymers. In this sense the polymerization can be carried out in either homogeneous medium or heterogeneous medium, i.e., in emulsion using surfactants, providing different types of nanocomposites, from films to core-shell particles.

The easiest strategy consists in the in situ polymerization of monomers, such as pyrrole or aniline, in solution and in the presence of magnetic nanoparticles. In this approach the selection of the solvent is of great importance to obtain a proper nanocomposite with the nanoparticles well dispersed into the polymeric matrix. The solvent should dissolve the monomer and the magnetic nanoparticles have to be colloiddally stable in it to avoid their agglomeration. Nevertheless, vigorous stirring of the solution and/or sonication are normally required to suspend the nanoparticles and prevent their aggregation during the polymerization. Once the polymer is formed, thus the nanocomposite, a black precipitate is normally obtained in the reaction medium.

For instance, polyaniline is usually prepared by oxidative polymerization of aniline in acidic aqueous solution using oxidants such as ammonium persulfate. Under those conditions a wide number of magnetic nanocomposites based on PANI have been prepared by incorporation of magnetic nanoparticle into the polymerization mixture, Fe_3O_4 [44], NiFe_2O_4 [35], CoFe_2O_4 [32, 68], and ZnFe_2O_4 [34]. Similarly magnetic nanoparticles/polypyrrole nanocomposites are typically synthesized by in situ oxidative polymerization of pyrrole in a dispersion of magnetic nanoparticles [13, 69]. In this case, the pyrrole is directly soluble in distilled water and does not require the use of acidic conditions.

On the other hand, a wide number of core-shell particles nanocomposites have been obtained by in situ oxidative polymerization but using emulsion or microemulsion polymerization method instead. Surfactants are added to the aqueous solution forming micellar aggregates and stabilizing the magnetic nanoparticles in the medium to obtain a ferrofluid. Then, the monomer molecules are adsorbed at the surface of the magnetic nanoparticles and the polymerization takes place to generate core-shell structures (see Fig. 5). Presence of the surfactant enhances the dispersibility of nanoparticles, increases the polymerization rate and also acts as dopant improving the conductivity of the final nanocomposite. The use of surfactants offers other advantages to the nanocomposite such as better adhesion to the substrate and smoothness.

A large number of surfactants have been used in the preparation of conducting and magnetic composites principally based on PANI and PPy, such as dodecyl benzene sulphonic acid (DBSA) [39, 40, 45, 70, 71], sodium dodecylbenzene sulfonate (NaDS) [24, 72], sodium dodecyl sulfate (SDS) [18, 31, 73–75],

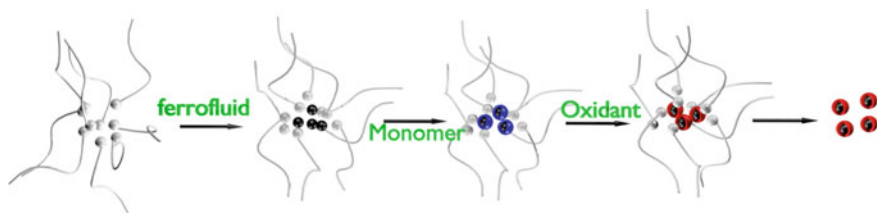


Fig. 5 Schematic representation of the formation of particle nanocomposites via in situ oxidative emulsion polymerization

p-toluenesulfonic (TSA) [8, 14, 21], cetyltrimethylammonium bromide (CTAB) [42], tetramethylammonium hydroxide [76], tetramethylammonium chloride [53], lignosulfonic acid (LSA) [46] sodium bis(2-ethylhexyl) sulfosuccinate (AOT) [19], polyvinyl alcohol [77], and so on. The addition of a cosurfactant, typically alkyl alcohols, is sometime required, especially in microemulsion polymerization.

In order to avoid the agglomeration of the nanoparticles and prepare composite core-shell particles an alternative process has been introduced in addition to the use of surfactant, the so-called common ion effects. This approach is based on the use of FeCl_3 as oxidant agent in the polymerization. Briefly, iron oxide nanoparticles are placed in a FeCl_3 solution and the Fe^{3+} ions are adsorbed onto the surface of the nanoparticles induced by the common ion effect principle forming a positively charged shell that prevents the aggregation. Besides, this shell became an active site to polymerize the monomer (see Fig. 6). This methodology has been employed for the polymerization of pyrrole [15, 78] and aniline [25] among others.

In addition to spherical particle nanocomposites, the preparation of nanotubes and nanowires composites with both magnetic and electrical properties is of great interest due to the enhancement of the conductivity. In general, the room temperature conductivity increases when the diameter decreases [79]. Conducting polymer nanotubes can be chemically or electrochemically synthesized by “hard” and “soft” template or template-free method in the presence of magnetic nanoparticles [8, 23, 27].

On the other hand, the in situ electropolymerization with magnetic nanoparticles in the medium generally conducts to the deposition of composite films. In this sense, the synthesis of conducting polymer layer containing magnetic nanoparticles on the surface of electrodes provides advanced properties interesting for instance, in electrocatalysis. For example, poly(3-thiophene-acetic-acid)/magnetite nanoparticles composite thin films were deposited onto a gold-covered quartz crystal electrode galvanostatically employing a current density of 3 mA/cm^2 and Bu_4NBF_4

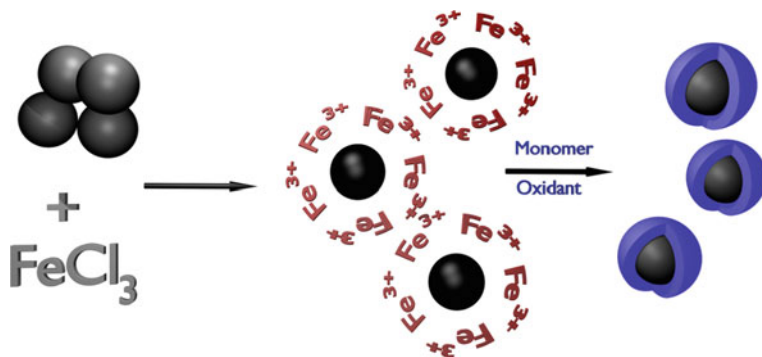


Fig. 6 Scheme of the mechanism for the synthesis of core-shell particle composites on the basis of the common ion effect

nitrobenzene solution [80]. In a previous step, the magnetic nanoparticles were stabilized in the medium by chemisorption of the 3-thiophene-acetic-acid monomer. In a similar way polypyrrole-magnetite composite films were electrodeposited via galvanostatic approach onto platinum electrodes and platinum-covered quartz crystal electrodes at a 3 mA/cm^2 current density in an aqueous solution containing potassium tetroxalate [9]. In this particular case, the nanoparticles were functionalized with B12 biomolecules prior the polymerization. Potentiostatic electropolymerization has been also performed to deposit nanocomposite films. In particular PEDOT and PANI layers with embedded magnetite nanoparticles were formed onto a platinum electrode in presence of magnetite nanoparticles at a potential of 1.1 V and a charge density of 120 mC/cm^2 [81]. Smoother and more compact continuous films can be obtained by cyclic voltammetry (potential between 0.5 and 1.0 V at 250 mV/s) in comparison with the deposition under constant potentials [20]. In effect, high-quality electromagnetic composite films of PPy with different content of Co nanoparticles have been prepared onto Si/SiO₂/Ti/Pt substrates from aqueous solution containing sodium sulfate and DBSA as electrolytes.

2.4 Simultaneous Polymerization and Synthesis of Magnetic Nanoparticles

In this methodology the synthesis of the nanoparticles and the monomer polymerization is carried out simultaneously in order to produce a homogenous nanocomposite. PANI/Fe₃O₄ nanocomposites have been obtained in one single step in aqueous solution as common solvent [26]. Typically, aniline monomer is added to a mixed solution of FeCl₂ and FeCl₃, which works as oxidant. The pH is controlled with NH₃ and after a certain time a black precipitate of PANI/Fe₃O₄ is formed.

Poly(*p*-phenylenediamine)(PpPD)/Fe₃O₄ composites were prepared by chemical oxidation polymerization of pPD monomer with APS and Fe(NO₃)₃ as oxidizing agents [82]. The Fe³⁺ was partly reduced to Fe²⁺ allowing the formation of the magnetite nanoparticles.

3 Magneto-Electrical Properties

3.1 Magnetic Nanoparticles

The magnetic nanoparticles are of great interest for numerous applications including separation systems, data storage, catalysis, and biomedical uses such as magnetic resonance imaging [83]. Each potential application requires different and

specific properties. While data storage applications need particles with switchable magnetic state being at the same time stable to temperature fluctuations, biomedical uses in general require superparamagnetic behavior, colloidal stability, and biocompatibility.

As described above a number of suitable methods have been developed for the synthesis of magnetic nanoparticles of various compositions, sizes, crystalline structures, shapes, and surfaces functionalities that will determine the magnetic properties of the nanoparticles and thus the final applications. In this sense the chemical composition is crucial for the magnetic behavior. There are a number of materials that exhibit magnetism, among other Fe, Co Ni, some rare earth, their oxides and alloys. The bulk ferromagnetic materials reduce its magnetostatic energy, created at the magnetic order, generating domains with random magnetic moments and making zero the net magnetic moment. In the presence of an external magnetic field the domain walls tend to move in order to the domains with the magnetic moment oriented in the direction of the field grow, at the expense of the rest domains. In other words, the magnetic moment of the domains tends to align with the field destroying the domain walls. When all the moments are aligned with field the materials reach the magnetic saturation (M_S), (Fig. 7a). Materials that retain the magnetization, remanence magnetization (M_r), in the absence of magnetic field are defined as hard magnet or permanent magnets and show a high coercivity field (H_C), the field required to bring the magnetization to zero, (Fig. 7a). Nevertheless, the materials that are easy to magnetize and demagnetize are known as soft magnetic materials and show a small remanence magnetization and coercivity field. In fact, not only the composition changes the magnetic behavior, the cation distribution is also important for the magnetic saturation. As an example, one of the most studied compounds is the ferrites, in which the iron cations are substituted by other 3d metals. Depending on the inverse degree of the ferrite, the relation between cations in the octahedral and tetrahedral sites of the spinel structure, the magnetic saturation moment could change drastically. The chemical composition also determines the magnetic transition temperature.

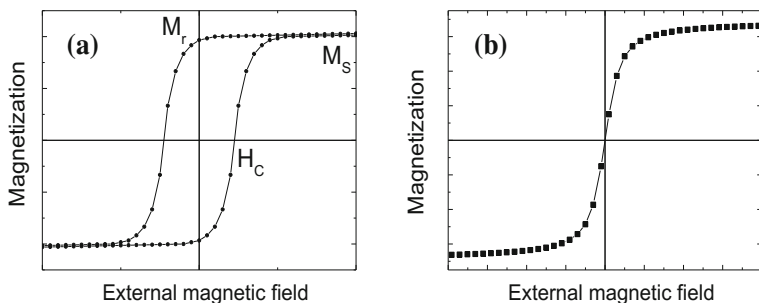


Fig. 7 Magnetic hysteresis loops of ferromagnetic material (a) and superparamagnetic material (b)

Besides, the size is crucial in all applications and its reduction induces new and exotic magnetic behaviors. In fact, the surface to volume ratio is the origin of these behaviors. The bulk ferromagnetic materials reduce its magnetostatic energy creating domain walls and regions with random magnetic moments, as it is described above. The magnetostatic energy is proportional to the volume, if volume increases the magnetostatic energy increases. On the other hand, the energy necessary to create the domain wall is proportional to the surface. Nevertheless, when the particle size decreases the volume decreases faster than surface area, thereby the magnetostatic energy decreases faster than domain wall energy. At certain size, the magnetostatic energy is less than domain wall energy and domains are not created, appearing nanoparticles with only one domain. It means that all atomic moments in the nanoparticles are aligned in one direction, showing a permanent magnetic in each nanoparticle. This critical size depends on the magnetic anisotropy of the material but is typically around 10–100 nm. Then, each nanoparticle becomes a single magnetic domain and shows supermagnetism [84]. In fact, the supermagnetism could be understood as a magnetism of super-magnetic-moments, one moment per nanoparticle. The different behaviors included in the supermagnetism are related with the interparticle interactions. For example, when the interaction is high, so the particle concentration is high, the superferromagnetism (SFM) appears as a ferromagnetism of super-magnetic-moments [85]. On the other side, when particle interactions are negligible the nanoparticle magnetic moments move randomly, as paramagnetic atoms, and superparamagnetic (SPM) behavior is expected. Undoubtedly, superparamagnetism depends on the temperature. There is a temperature called blocking temperature, below which the magnetic moments are frozen but above which the thermal energy is high enough to overcome the magnetic anisotropy. In this region the nanoparticle magnetic moments show a fast response to applied magnetic fields with negligible remanence magnetization (M_r) and coercivity field (H_c), Fig. 7b.

Due to the small surface to volume ratio, the surface plays an important role in the magnetic behavior. Usually the disorder in the surface reduces the magnetic saturation moment because the magnetic atoms at the surface do not contribute to the total magnetic moment. This surface is normally called dead layer. In other case, the surface could show another magnetic behavior creating a core-shell magnetic nanoparticle. In this sense the more interesting effect appears when the shell shows a high temperature antiferromagnetic order and the core a ferromagnetic one. The coupling each other produces the exchange bias effect which is a promising effect for storage data. The interaction between the AFM shell and FM core induces a shift in the magnetic hysteresis loop (exchange bias field; H_{eb}), Fig. 8, and an increase in the coercivity [56, 86].

In most of the applications the surface functionality of the magnetic nanoparticles needs to be controlled. The covering of the nanoparticles for instance with polymers protects the nanoparticles of degradation and oxidation that usually conduct to a loss of properties. The modification of the surface by the attachment of stabilizing molecules or compatibilizers is typically carried out to avoid the undesirable agglomeration of the particles and also favoring the stabilization and

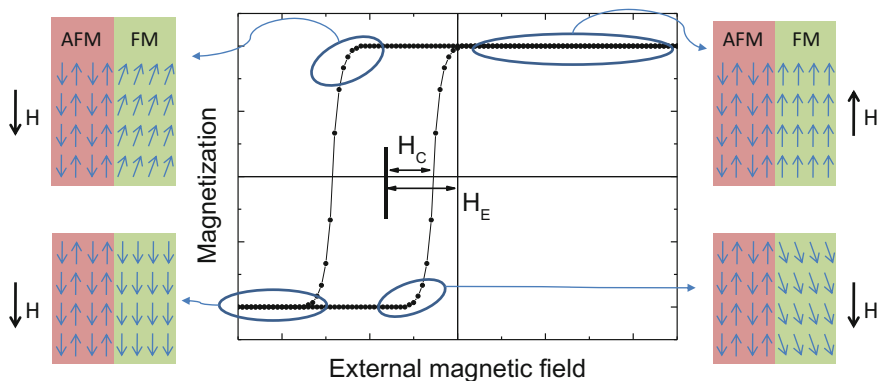


Fig. 8 Magnetic hysteresis loop showing the exchange bias effect with a schematic picture of magnetic moment behavior

dispersibility of the particles. In particular, coating the nanoparticles with a shell of conducting polymers not only stabilize the nanoparticles and enhance the dispersibility, but also confers to this system electrical conductivity.

3.2 Conducting Polymers

In the last decade, the discovery that is possible to control the electrical conductivity of polymers over the range from insulating to metallic had led to substantial efforts to prepare conducting polymers for technological applications.

The first major breakthrough in the field of electrically conducting polymers took place around 1978 when it was demonstrated by Shirakawa et al. [87, 88] that polyacetylene (PA) and intrinsically insulating organic conjugated polymer, exhibits a dramatic increase in electrical conductivity on treatment with oxidizing (electron-accepting) or reducing (electron-donating) agents. These processes are termed as p-doping, and n-doping, respectively.

The nature of the process responsible of inducing high conductivity in conducting polymers is different than that for inorganic semiconductors. In the doping of inorganic semiconductors the dopant species occupies positions within the lattice of the host materials thereby resulting in the presence of either electron-rich or electron-deficient sites with no charge transfer reaction occurring between the two sites. The doping reaction in organic conjugated polymers, on the other hand, is a charge transfer reaction, resulting in the partial oxidation, or reduction of the polymer.

The semiconductor properties of conjugated polymers are provided by the delocalised electrons of the aromatic or aliphatic carbon structures [89]. The conductivity can be improved by a doping process that in simple terms consists on

injecting charged species into the conjugated polymer backbone by chemical, electrochemical, or interfacial method [90]. The doping process is reversible and polymers can return to their original state with little or no degradation.

The increase in conductivity observed upon doping organic conjugated polymers are associated with formation of self-localized excitations such as solitons, polaron, and bipolarons [91]. These quasiparticles which arise from a strong interaction between the charge on the chain (electron or hole) acquired as a result of doping. In polymers such as polypyrrole, polythiophene, or poly(*p*-phenylene), initially polarons (positively charged, or negatively charged) are formed on doping. These polarons then combine to form spinless bipolarons which acts as the charge carriers.

The increase in the electrical conductivity is not without accompanying problems. The process of doping is often the source of chemical instability and poor processibility. In this sense the preparation of conducting polymer-based-hybrid composites is nowadays an interesting alternative and has been the focus of an intensive investigation. A variety of conjugated polymers has been combined with different nanoparticles leading nanocomposites with high electrical conductivity, in particular those including metal nanoparticles such as Ag, Au [92] and carbon nanotubes [93]. Related to the formation of hybrid nanocomposites the dispersion of the nanoparticles into the polymer matrix and the organic–inorganic interface are important issues in the achievement of the desirable electrical conductivity. Reddy et al. [93] reported the synthesis and the electrical conductivity studies of nanocomposites consisting in polyaniline functionalized multiwalled carbon nanotubes (MWCNTs) containing Au and Ag nanoparticles. It was demonstrated that the conductivity increases with the incorporation of MWCNTs, from 2.5×10^{-3} S/cm to 9.3×10^{-3} S/cm, for pristine PANI and after the incorporation of MWCNTs, respectively. The augment in the conductivity is, however, more significant when the MWCNTs are previously functionalized to improve the compatibility with the polymer matrix up to 0.18 S/cm. The additional incorporation of metal nanoparticles provokes a further increase in the conductivity, 5.04 S/cm in the case of the nanocomposites containing silver nanoparticles and functionalized MWCNTs.

3.2.1 Characteristics of the Most Common Conducting Polymers

Polyaniline

Discovered in 1862 during the oxidation of aniline, polyaniline (PANI) can be synthesized chemically and electrochemically in aqueous solutions [94]. PANI exists in the following species depending on its oxidation state: leucoemeraldine, emeraldine and pernigraniline but only protonated emeraldine is electrically conductive, while doped leucoemeraldine and pernigraniline have poor conductivity. PANI is thermally, electrochemically and environmentally stable in solution and air [95] and presents interesting electrochemical, electronic, optical and electro-optical properties resulting from the flexible—NH group in its backbone. PANI has been

used in different applications such as in corrosion protection, in OLED devices, electrochromic displays, electro-optic and smart windows for energy storage in secondary batteries [96, 97], and due to its biocompatibility PANI has extensively been used for biosensor [98, 99].

Polythiophene

This polymer has excellent environmental and thermal stability in their neutral and doped states [100, 101] exhibiting optical properties and conductivity values up to 600 S cm^{-1} in the doped form [102]. Polythiophene presents poor solubility in most organic solvents, except in mixtures such of arsenic trifluoride/pentafluoride which limits its applications. However, it has been reported that the incorporation of a long flexible alkyl side chain on the 3-position of the thiophene ring produces a soluble polymer in common organic solvents without altering the chemical and physical properties of the polymer [103].

In particular poly(3,4-ethylenedioxythiophene) (PEDOT) widely used can be synthesized by oxidative chemical or electrochemical polymerisation producing thin films that are optically transparent in the reduction state and light blue color in the oxidized state with high stability and conductivity. The most common dopant for PEDOT is polystyrene sulfonate (PSS) rendering a water-soluble compound [102].

Polypyrrole

Polypyrrole is probably the most common conducting polymer used due to its excellent properties. Pyrrole monomer is commercially available, easily oxidized, water-soluble that conducts to polymers with high electrical conductivity, redox properties and good environmental stability. Over the past three decades polypyrrole has attracted interest for a number of applications including supercapacitor for energy storage and secondary batteries [104], in dye-sensitized solar cells [105]. This polymer has been also used for metal protection [106] and to manufacture patterned arrays of nanoparticles for data storage or biosensors [107].

3.3 *Magneto-Electrical Properties of the Composites*

The formation of nanocomposites of conducting polymers and magnetic nanoparticles will lead to the combination of the electrical and magnetic properties from the individual components, described in the previous subsections, in one nanomaterial. The composites with both responses are of great interest because are suitable materials for a wide range of applications as will be exposed in following sections, especially as electromagnetic interference shielding and microwave absorbing,

actuators, solar cells, or sensors. The final properties of the nanocomposites will depend not only on the individual components but also on the proportion of both materials and on the microstructure, factors that are controlled by the preparation method. The electrical and the magnetic behavior in the nanocomposites will differ, in principle, from those in the polymer and in the magnetic nanoparticles, and, in general, both properties are deteriorated. Typically, magnetic parameters such as magnetization saturation and coercivity field values decrease with the content of the nonmagnetic polymeric component. Similarly, the electrical conductivity of the nanocomposites is normally reduced with the incorporation of magnetic nanoparticles. Nevertheless, this reduction in the properties is not progressive as a function of the percentage because the homogeneity and also the interface polymer-particle surface play an important role.

Typically the magnetization saturation (M_S) decreases with the content of the nonmagnetic polymer in the nanocomposites following the well-known equation $M_S = \phi \times m_S$, where ϕ is the mass fraction of the magnetic component and m_S is the saturation moment of a single nanoparticle. It is clear that M_S of the nanocomposite depends on the mass fraction of the magnetic nanoparticles and consequently on the mass fraction of the conducting polymers. This means that the total magnetic behavior of the nanocomposite can be tailored as a function of the percentage of both components (see Fig. 9) [23, 27, 51, 52].

However, in several described nanocomposites the magnetization saturation does not decrease progressively with the polymer content appearing some discrepancies. A series of nanocomposites based on PANI and $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_{1.5}\text{Cr}_{0.5}\text{O}_4$ (NZFCO) were prepared varying the proportion of PANI [108]. Although the incorporation of PANI reduces the M_S (referred to the nanocomposite mass) in comparison with the nanoparticles, the sample with the lower content of PANI exhibits an anomaly low value of M_S , the lowest of the series. This was attributed to

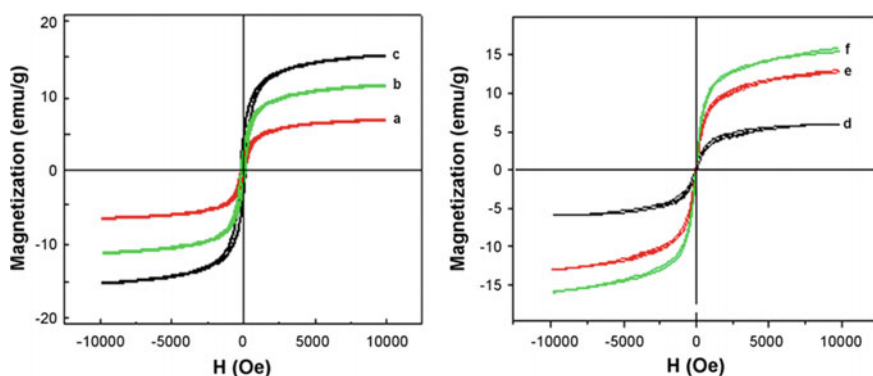


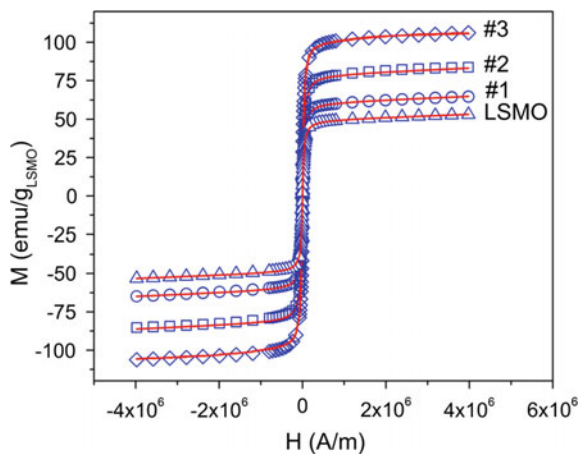
Fig. 9 Hysteresis loop of PANI/ $\text{Zn}_{0.6}\text{Cu}_{0.4}\text{Cr}_{0.5}\text{Fe}_{1.46}\text{Sm}_{0.04}\text{O}_4$ nanocomposite at a nanoparticle content of **a** 20 wt%, **b** 40 wt% and **c** 60 wt%; and PPY/ $\text{Zn}_{0.6}\text{Cu}_{0.4}\text{Cr}_{0.5}\text{Fe}_{1.46}\text{Sm}_{0.04}\text{O}_4$ at a nanoparticle content of **d** 20 wt%, **e** 40 wt% and **f** 60 wt%. Reprinted with the permission from Ref. [51]. Copyright (2010) Elsevier

the influence of the amorphous polymer–nanoparticles interactions. Concretely the polymeric molecules strongly interact electrostatically with the Fe^{3+} ions of the ferrite at the surface, leading to the creation of a dipole moment toward the PANI/nanoparticles interfaces. This reduces the free Fe^{3+} ions, which are the responsible of the magnetization. The surface modification effect of magnetite by conducting polymer, in the saturation magnetization was also observed in other studies. It was demonstrated that polypyrrole coating increases the saturation magnetization of magnetite nanoparticles, as a result of a charge transfer process from the polymers to the iron ions of the magnetite surface (Fig. 10) [70, 109]. Besides, the presence of the nanoparticle–polymer interactions can also explained the unexpected increase in the remanence magnetization and coercivity field with the polymer content that was recently observed in composites of PANI with ferromagnetic nanoparticles of cobalt ferrite [110].

Concerning the use of superparamagnetic nanoparticles, generally this superparamagnetism is retained in the nanocomposites [46, 74]. However, very different trend is observed in other systems. For instance, superparamagnetic $\text{Mn}_{0.68}\text{Zn}_{0.25}\text{Fe}_{2.07}\text{O}_3$ nanoparticles (with a blocking temperature of around 50 K) in the polypyrrole matrix present a significant increment in the blocking temperature and large hysteresis at 300 K, probably due to the clustering of the nanoparticles [6].

In contrast, it is reported in certain nanocomposites that the coercivity field and remanence magnetization decrease with increasing polymer concentration, becoming even negligible (Fig. 11) [111]. At low polymer content (PANI/ $\text{Fe}_2\text{O}_3 = 0.1/1$) the nanocomposites show low values, 155–160 Oe of coercivity field and remanence magnetization of $\sim 6\text{--}8$ emu/g, while at composition of 2/1 H_c and M_r decrease down to 1.2 Oe and 0.03 emu/g, respectively. Therefore, the nanocomposite system changes from ferromagnetic to superparamagnetic for high polymer percentage. In addition, the systems became paramagnetic with higher content of polymer, fact that was confirmed through zero field cooled–field cooled magnetization measurements. This behavior can be explained as the interparticle distances increases as the polymer

Fig. 10 Magnetic hysteresis loops of hybrid nanocomposites based on $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ (LSMO) nanoparticles covered with different quantities of PPy: 14.3 wt% (#1), 56.3 wt% (#2) and 68.3 wt% (#3). Reprinted with the permission from Ref. [109]. Copyright (2012) AIP publishing



content augments and consequently the exchange and dipolar distances become weaker, diminishes the long range order in the nanocomposite and transforms the superferromagnetic material into a superparamagnetic one, as had been explained in the previous section. Similar results were obtained for composites formed by PPy and Fe_2O_3 in the same polymer concentration range [112].

Regarding the electrical properties of the nanocomposites, the electrical conductivity remarkably differs from the conducting polymers with the incorporation of magnetic nanoparticles as can be expected. The inherent conductivity of the conducting polymers arises from the presence of a conjugated electron system in their chain structures and the addition of nonconductive nanoparticles can disturb this conjugation and reduce the conductivity [21, 22, 40, 72]. Therefore the main reason of this decrease in conductivity lies in the partial blockage of conductivity path by the nanoparticles. Also the bonds between the particles and the polymers decrease the conjugated electron density in the polymer structure. In general, the total conductivity is the summation of the band and hopping parts that is the dc conductivity and the ac conductivity, respectively. Both terms have been studied more in detail in various publications related to magnetic nanoparticles-based conducting polymer nanocomposites. For instance, the ac conductivity of nanocomposites composed of PANI and ferrite nanoparticles, $\text{Zn}_{0.2}\text{Mn}_{0.8}\text{Fe}_2\text{O}_4$ [113] and CoFe_2O_4 nanoparticles [114] increases sharply at high frequency whereas in the neat PANI slowly increases with frequency even at high values. The augment in the frequency

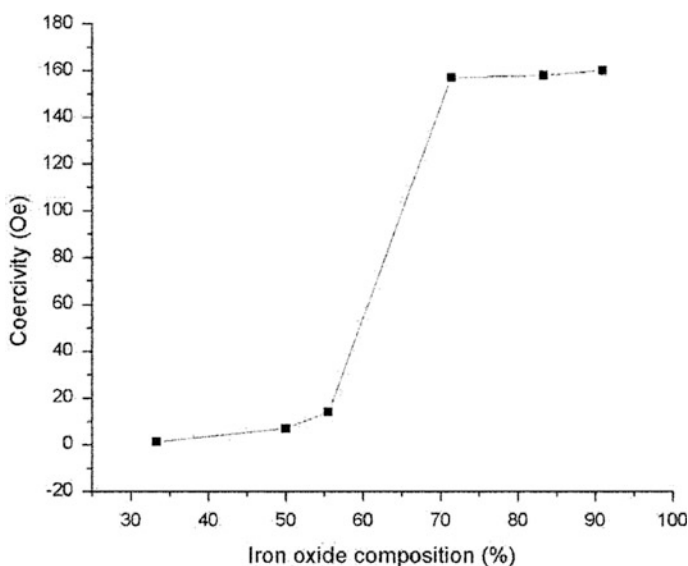


Fig. 11 Coercivity as a function of iron oxide composition in nanocomposites based on PANI. Reproduced with the permission from Ref. [111]. Copyright (2008) Springer

enhances electronic exchange occurring among the cations in the ferrite thus resulting in more ac conductivity. The ac conductivity usually increases with the content of ferrite nanoparticles in the nanocomposite probably due to the electron hopping processes. Other studies however, show nearly the same frequency dependent behavior in nanocomposites and in the pristine conducting polymer [16]. On the other hand, the direct current (dc) conductivity is strongly temperature dependent, decreasing with decrease in temperature following a semiconductor behavior. The incorporation of magnetic nanoparticles can modify this dependence. It is reported in PPy/Fe₃O₄ nanocomposites a first step at low temperatures where the conductivity decreases as the temperature rises [16]. As shown the nanoparticles modify the electrical conductivity processes, in general the conductivity in nanocomposites is usually lower than the pristine conducting polymers because the nanoparticles increase the charge carrier scattering and also the carrier charge trapping.

On the other hand it is reported a contrary effect, increasing the conductivity in the nanocomposites with the content of magnetic nanoparticles up to certain portion and then decreasing with further content of nanoparticles as displayed in Fig. 12. For instance in nanocomposites of PPy prepared by ultrasonication the maximum conductivity (11.3 S/cm) was reached with 40 wt% of Fe₃O₄ nanoparticles, 9 times higher than that of neat PPy [115]. Further content of nanoparticles conducts, however, to a decrease of conductivity. This behavior can be attributed to the doping level of the samples, which augments in the ultrasonication process thus becoming higher in the nanocomposites.

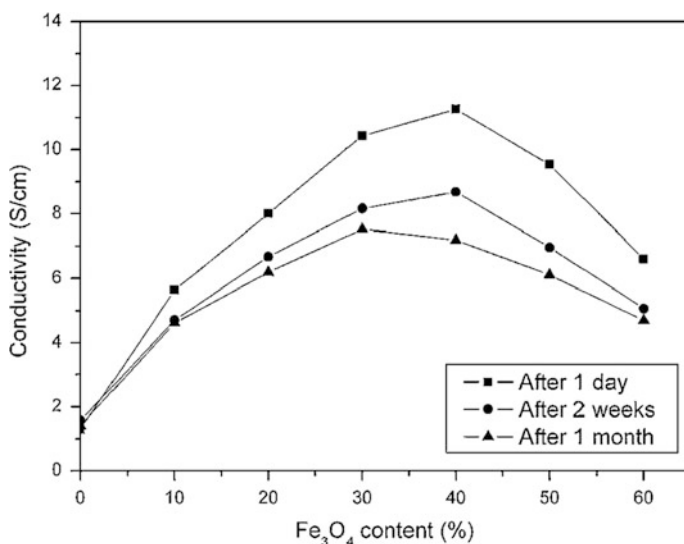


Fig. 12 Conductivity of PPy/Fe₃O₄ nanocomposites at different magnetite content and at after different period of time. Reprinted with the permission from Ref. [115]. Copyright (2006) Wiley

In addition to the influence of dopant in the nanocomposites, the increase of conductivity associated with the incorporation of nanoparticles can be due to other factors. Core-shell structures were fabricated with Fe_3O_4 nanoparticles of 4 nm as core and PPy as shell [19]. The augment of the polymer content up to 36 % provokes a change of morphology from spherical to tubular, that could be the reason of the conductivity enhancement in comparison with the PPy without nanoparticles, from 10.1 to 59.4 S/cm. In the same way, nanocomposites of PPy functionalized with *p*-TSA and Fe_2O_3 nanoneedles show very high conductivity, ~ 65 S/cm [8].

4 Applications

The majority of conducting polymers offers several advantages over other polymeric systems in addition to their conductive properties, such as the ease of preparation and low cost, good environmental, and thermal stability. Therefore, they are extensively investigated as the polymeric component of many magnetic nanoparticles-based nanocomposites for a wide number of applications including remediation [31], catalysis [28], memory devices [20], magnetic resonance imaging [18], hyperthermia [77], photothermal therapy [116], etc. [117]. Nevertheless, the following section will be focused on the most important applications of magnetic nanoparticles-based conducting polymer nanocomposites derived from the conducting properties of the polymer in combination with the magnetic behavior provided by the magnetic nanoparticles component.

4.1 *Electromagnetic Shielding and Microwave Absorbing Materials*

Currently, there is a great interest in the development of microwave absorbing materials and electromagnetic shielding to avoid the interferences induced by electromagnetic signals in all the electronic devices and radiation sources. With the intensive growth of the telecommunication devices and electronic products, the development of these materials is necessary as the electromagnetic interferences (EMI) reduce the lifetime and efficiency of the equipment and affect the safety coexistence of all those instruments. The electromagnetic wave has essentially two components a magnetic field and an electric field perpendicular to each other. Therefore, these absorber materials should cancel both components for an effective absorption, by transforming the electromagnetic energy into other kinds of energy or simply dissipating the electromagnetic waves. The absorption basically relies on three main factors, dielectric loss, magnetic loss, and impedance matching, thus the combination of magnetic nanoparticles and polymers in a nanocomposite is

considered a proper strategy for this application with a reduced weight and cost, enhanced flexibility and corrosion resistance. Therefore, the electromagnetic interference can be diminished by positioning this kind of shielding material between the source and the component to be protected. The shielding can be defined as the reduction of the magnetic and electric fields and the effectiveness of a shield (SE), that is, its resulting attenuation can be expressed as

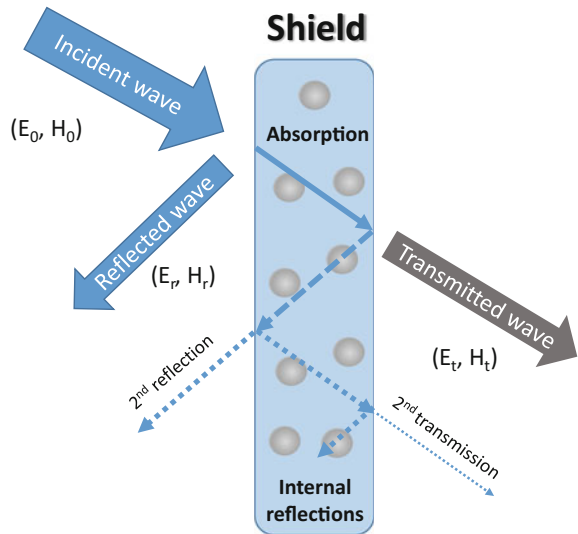
$$SE = -10 \log \frac{P_t}{P_o} = SE_R + SE_A + SE_M \quad (1)$$

where P_t and P_o are the transmitted and incident electromagnetic power, respectively, and SE_R , SE_A and SE_M are the shielding effectiveness due to reflection, absorption and multiple reflections, respectively [118]. As described in the Eq. 1 there are three main mechanisms that contribute to the shielding effectiveness. On one hand, the incident wave is reflected from the surface of the shield, on second hand, the shield material absorbs part of the radiation and the third mechanism is based in multiple reflections which can either, support, or hinder the effectiveness as shown in Fig. 13.

All the terms in the Eq. 1, SE_R , SE_A , and SE_M , are expressed in decibels (dB). The multiple reflection factor SE_M is normally neglected in practical calculation due to the high value of SE_A (typically higher than 10 dB) [119]. The absorption loss is a function of the physical properties of the shield material then is expressed by the following equation:

$$SE_A = 131t\sqrt{f\sigma\mu} \quad (2)$$

Fig. 13 Schematic representation of the EMI shielding



where t is the thickness, f is the frequency, σ is the electrical conductivity and μ is the magnetic permeability of the shield material. Related the SE_R component, this can be expressed as

$$SE_R = -10 \log \left(\frac{\sigma_T}{16\omega\epsilon_0\mu} \right). \quad (3)$$

where σ_T is the total electrical conductivity, ω is the angular frequency, μ is the magnetic permeability of the shield material and ϵ_0 is the vacuum permittivity.

Experimentally, the shielding effectiveness of the nanocomposites is typically measured using network analyzer instruments. Scalar network analyzer (SNA) only measures the amplitude of signals whereas vector network analyzer (VNA) measures both amplitude and phase properties.

Several studies reported the preparation of nanocomposites composed on conducting polymers and iron oxide nanoparticles as magnetic components and their abilities as electromagnetic shielding. In all those investigations, the absorption properties of the nanocomposites also depend on their micro/nanostructure which is controlled by the synthesis method. A core-shell nanocomposite consisting of barium ferrite nanoparticles covered with a PEDOT polymeric layer was synthesized by in situ emulsion polymerization [120]. The barium ferrite contributes to the absorption properties due to its high magnetic losses and high resistivity whereas the PEDOT provides conductivity and dielectric properties. The EMI shielding effectiveness (SE) of the material was significantly higher as compared with that obtained by the PEDOT containing only the surfactant as control experiment, and the value increased with the content of ferrite nanoparticles in the measured frequency range between 12 and 18 GHz.

It was demonstrated that the main contribution to the SE comes from the absorption, 22.5 dB, as a result of the dielectric and magnetic losses. Similar study was carried out with a nanocomposite based on PANI also obtained by emulsion polymerization, with a SE_A value of 28.9 dB (99.9 %) in the same frequency range [121]. The same group prepared a PPy/ Fe_3O_4 nanocomposite by in situ oxidative polymerization which likewise demonstrates a strong microwave absorption properties in 12.4–18 GHz exhibiting a SE_A value of 20.4 dB [76]. Slightly higher values were obtained for polypyrrole nanocomposites decorated with Fe_2O_3 showing a total shielding effective of 28.4 dB and a SE_A of around 22.6 dB [122].

A recent study shows that electromagnetic wave absorbing properties can be controlled by tuning the proportion of both components in the composites based on PPy and Co nanoparticles [123]. It was demonstrated that reducing the Co NPs content could make the wave absorption performance of the nanocomposite moves to a lower wave absorbing frequency range, whereas a higher amount of Co could conducts to a higher frequency of wave absorption performance.

However, many investigations indicate that a shielding effectiveness value of 30 dB is required to protect electronic equipment in most of the cases [118]. In this regard, multicomponent nanocomposites containing also titanium dioxide nanoparticles have been evaluated as microwave absorbing material because the TiO_2 has

high dielectric constant and may contribute to the absorbing properties. PANI composites with γ -Fe₂O₃ and TiO₂ nanoparticles were synthesized via emulsion polymerization showing a SE_A value ~ 45 dB, in effect much higher than that obtained for PANI/ γ -Fe₂O₃ and PANI/TiO₂ composites [124]. In a same way, PANI nanocomposites with TiO₂ and Fe₃O₄ show excellent microwave absorption, 99.950–99.999 %, when the magnetic nanoparticles are well dispersed in the polymer [25].

Besides, multifunctional nanocomposites consisting of conducting polymers, magnetic nanoparticles and graphene can be also applied as EMI shielding materials. Graphene mostly contributes to the electromagnetic absorption properties due to the dielectric loss. It has been described the development of nanocomposites by the incorporation of Fe₃O₄ NPs decorated-graphene oxide into PEDOT polymeric matrix. The loading of only 1 wt% of the Fe₃O₄ NPs decorated-graphene conducts to an EMI SE value of 22 dB and a surface resistivity of 80 Ω sq⁻¹ [47]. Hybrid materials consisting of PEDOT and graphene but with Co₃O₄ [49] or CoFe₂O₄ [125] nanoparticles instead also show interesting shielding properties.

4.2 Polymer Solar Cells

In recent years, bulk heterojunction (BHJ) polymer solar cells (PSCs) have attracted a growing interest as a possible substitute to the inorganic-based cells due to their several advantages such as its light weight, flexibility, ease of fabrication, and promising capability for low-cost and large-scale production. Briefly, BHJ-PSCs consist on an active layer of conjugated polymer donor blended with fullerene derivative acceptor. In a typical design, both the donor and acceptor are sandwiched by a metal cathode, such as aluminum and an indium tin oxide (ITO) anode previously coated with a thin film of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Fig. 14). This layer smooths the ITO surface reducing the contact resistance with the BHJ layer, however, at the same time tends to degrade the BHJ component due to its acidic nature. In this sense magnetic nanoparticles, in particular magnetite, were incorporated into the PEDOT:PSS layer to improve the stability and enhance the efficiency as the nanoparticles may reduce the acidity of the PEDOT:PSS layer and also generate iron ions resulting in high conductivity [126]. Even the PEDOT:PSS layer was completely substituted by a magnetite nanoparticle layer in a success manner [127].

Magnetic nanoparticles have been also incorporated into the BHJ layer [128]. The composite was formed by mixing in a solution process poly(3-hexylthiophene-2,5-diyl) (P3HT) as conjugated polymer donor and [6,6]-phenyl-C61-butyricacidmethyl ester (PCBM) as acceptor, both soluble in chloroform. The addition of the nanoparticles significantly enhances the power conversion efficiency mainly attributed to the increase of short circuit currents as a consequence of the magnetic field effect from the superparamagnetic nanoparticles that increase the population of triplet excitons.

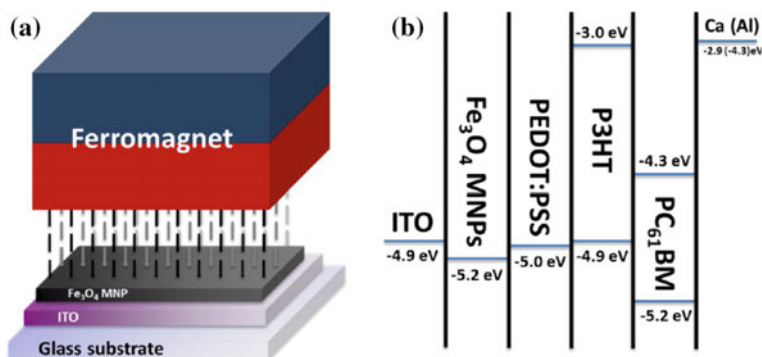


Fig. 14 **a** Schematic illustration of the fabrication procedure of a solution-processed Fe₃O₄ NP, followed by external magnetostatic field alignment, as a HEL for PSCs and **b** the LUMO and HOMO energy levels of P3HT and PCBM and work functions of PEDOT:PSS, Fe₃O₄, ITO, and Ca (Al). Reprinted with the permission from Ref. [127]. Copyright (2013) ACS

4.3 Sensors

Conducting polymer films and colloids have been widely investigated for sensor applications. Especially polypyrrole, which is one the most employed for the fabrication of biosensor because in addition to its good physical and electrical properties, this polymer is highly biocompatible. The association with magnetic nanoparticles to form a nanocomposite presents considerable progresses for their use as sensor. On one hand the nanostructuration created by the nanoparticles augments the surface area and provides new active sites. Second, they exhibit the capacity to promote faster electron transfer kinetics between electrodes. Moreover, their magnetic properties provide to the nanocomposites enhanced recovery ability and also the capacity of being oriented by external magnetic field. In this regard, the immobilization of magnetic nanoparticles on the surface of magnetic glassy carbon electrode (MGCE) is considered very promising approach for the fabrication of biosensors due to its high specific surface area and stability. Polypyrrole-ZnFe₂O₄ core-shell nanoparticles supported on the surface of MGCE were evaluated as enzymeless glucose sensor [129]. In the proposed electro-oxidation mechanism the glucose loses one proton in alkaline solution and forms the enediol structure that is able to complex with the Zn²⁺ ions of the nanoparticles to finally be oxidized. The presence of polypyrrole in the nanocomposites facilitates the electron transfer rate due to its good electrical conductivity. Other core-shell nanocomposites based on polypyrrole and magnetite nanoparticles were also employed for the detection of glucose by immobilization, in this case, of the enzyme glucose oxidase [130]. The modified electrode presented significant sensibility and selectivity and short response time.

A biosensor based on magnetic Fe₂O₃-polypyrrole core-shell particles has been also prepared by immobilization of other biomolecules on their surface, such as

biotin with a strong affinity toward the protein avidin [11]. These core-shell particles were synthesized using a certain amount of pyrrole derivative containing *n*-carboxyl groups and through them were attached the biotin biomolecules.

Alternatively biotin molecules have been anchored directly to the magnetic nanoparticles component to create the biosensor [10]. Concretely, a nanocomposite was first obtained by immobilization of streptavidin labeled magnetic particles onto a thin PPy film. The covering of the nanoparticles was carried out by applying a magnetic field that conducts to a uniform assembly. Second, the nanoparticles were further functionalized with biotin-Fab fragment K47 antibody. This designed biosensor was successfully applied to measure very low concentration of atrazine.

Moreover, a photoelectrochemical bilirubin biosensor was fabricated by anchoring core-shell nanoparticles to the surface of MGCE [131]. Magnetite nanoparticles were first covered with a hydroxyapatite layer that exhibits photocatalyst activity and subsequently with polypyrrole in the presence of bilirubin molecules, thus employing the molecular imprinting approach (Fig. 15). Finally the nanocomposite particles were attached to the MGCE with the purpose of developing the biosensor which was highly sensitive to bilirubin in solutions and selective against very similar biomolecules such as biliverdin, cholesterol and testosterone. It was demonstrated that the PPy layer plays an important role in the transfer of the charges and thus enhancing the photoelectric conversion efficiency.

A biosensor based on hemoglobin (Hb) for hydrogen peroxide determination has been prepared by immobilization of hemoglobin into poly(*p*-phenylenediamine)/Fe₃O₄ nanocomposite previously deposited on the glassy carbon electrode [132]. This sensor works as an electrocatalytic process due to the reaction of HbFe(II) with H₂O₂. The cyclic voltammograms of the modified electrode in the presence of H₂O₂ shows an increase in the reduction peak current accompanied by a decrease of

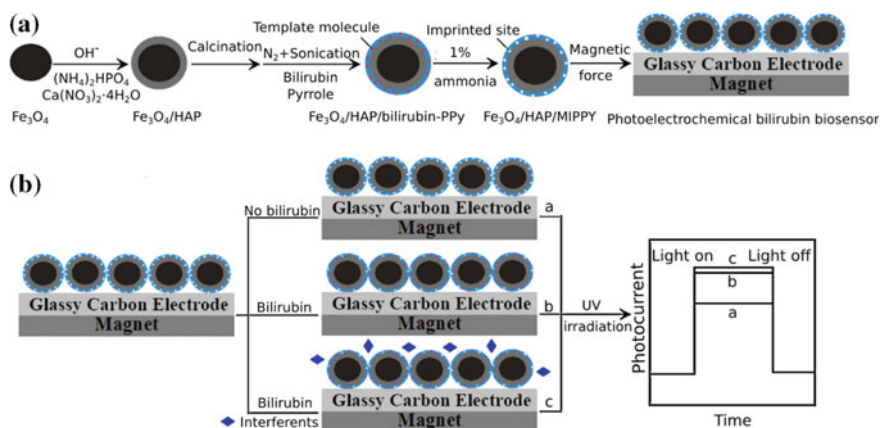


Fig. 15 Schematic illustration for **a** fabrication and **b** detection mechanism of the photoelectrochemical bilirubin biosensor. Reprinted with the permission from Ref. [131]. Copyright (2014) Elsevier

oxidation peak current. The nanocomposite acts in this case as an adequate platform.

Besides, nanocomposites of conducting polymers with iron oxide nanoparticles have been extensively used directly as sensor system. For example, core-shell particles of Fe_2O_3 covered with PANI were prepared by oxidative polymerization. In this case the sensing properties were investigated towards uric acid and those were attributed to the presence of both PANI and Fe_2O_3 electrocatalytic center [133].

The conducting polymer-based nanocomposites have also presented a great potential as humidity sensor and to monitor other gases. These sensors are based on changes in the resistance and capacitance when exposure to water vapor or other gases and, thus the microstructure of the nanocomposites is a crucial factor. Besides, the incorporation of semiconducting inorganic nanoparticles, e.g., Fe_3O_4 , generally improves the stability of the sensor in those atmospheres. Tandon et al. [134, 135] have prepared different PPy/iron oxide nanocomposites with PPy contents up to 27 %. Then, they further studied their sensitivity to humidity as well as their gas sensing properties to CO_2 , N_2 , O_2 , and CH_4 .

An interesting system based on PEDOT:PSS with embedded iron oxide nanoparticles has been proposed as resistive humidity sensor due to the water adsorbing properties of this conducting polymer [48]. In particular a free standing nanocomposite films were prepared to be easily transferred onto different substrates which favor its applicability. Remarkably, the sensitivity to humidity increased with the nanoparticle concentration probably due to the augment of the surface roughness of the film that enlarges the exposed area to interact with water vapor.

5 Concluding Remarks and Future Perspectives

In the last decades, conducting polymers have evidenced much interest as they combine the properties of metal with the advantages of polymers. The preparation of magnetic nanoparticles-based conducting polymer nanocomposites goes one-step further with the addition of magnetic properties to the material. This emerging technology has attracted a great attention in many applications, especially as microwave absorbing materials and electromagnetic shielding. As commented, nowadays there is a great demand in the development of materials able to absorb or disperse electromagnetic radiation coming from telecommunication and electronic devices, and these magnetic and conductive materials seem to be appropriated for such a purpose. An intensive effort has been carried out in the preparation methods, many different nanocomposites have been prepared varying the type of polymers and magnetic nanoparticles, the percentage of each component and also using a large number of synthetic strategies. It is well known that the final properties of the nanocomposite depend on the type of polymer and magnetic nanoparticles but also on the dispersibility and homogeneity of the nanocomposites. Therefore, it is important to optimize the synthetic procedure to achieve more effective methods

and materials with enhanced properties. In general, the aim of all the investigations is the development of materials with high electrical conductivity and high magnetic properties, i.e., high magnetization saturation. However, these properties are typically diminished in the nanocomposite in comparison with the pristine component. Nevertheless, opposite results are also obtained in several works, in which the electrical conductivity increases with the incorporation of magnetic nanoparticles and magnetic parameters are enhanced in a particular concentration range. Most of these investigations seem to indicate that the interface polymer-magnetic nanoparticles plays a key role on the final properties and these interactions are probably the responsible of such contradictory results. However, these aspects and the complete mechanism of the process are still not well understood. The current directions in this field of research are mainly focused in addressing these features, establishing a clear relation between properties and structure, which is necessary for the development of materials with enhanced properties, especially for applications that will require a great improvement because of the more demand for new technologies and advancement of current technologies. This is the case of renewable energy, particularly solar energy, or the development of EMI shielding systems. Precisely in this last application, by the growth of the electronic industry in which the systems are getting lighter and faster, it is expected an important progress and the magnetic nanoparticles-based conducting polymer nanocomposites are a very promising candidate to fulfill these expectations. EMI shielding design should be optimized to meet the required efficiency while maintaining low cost and lightness, and presumable in the future flexibility and thinness will be also essential properties.

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