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Bifunctional Polymer-Metal Nanocomposite Ion Exchange Materials

Berta Domènech, Julio Bastos-Arrieta, Amanda Alonso, Jorge Macanás, Maria Muñoz and Dmitri N. Muraviev

Additional information is available at the end of the chapter

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1. Introduction

The unusual electrical, optical, magnetic, and chemical properties of metal colloids (better known nowadays as metal nanoparticles, MNPs) have attracted increasing interest of scientists and technologists during the last decade. In fact, although Nanoscience and Nanotechnology are quite recent disciplines, there have already been a high number of publications that discuss these topics. [1-11] What is more, there are quite new high impact peer-reviewed journals especially devoted to these research fields and there is also a particular subject category “Nanoscience & Nanotechnology” in the Journal Citation Reports from Thomson Reuters.

MNPs can be obtained by various synthetic routes, such as electrochemical methods, decomposition of organometallic precursors, reduction of metal salts in the presence of suitable (monomeric or polymeric) stabilizers, or vapour deposition methods. Sometimes, the presence of stabilizers is required to prevent the agglomeration of nanoclusters by providing a steric and/or electrostatic barrier between particles and, in addition, the stabilizers play a crucial role in controlling both the size and shape of nanoparticles.

In this sense, the development of polymer-stabilized MNPs (PSMNPs) is considered to be one of the most promising solutions to the MNPs stability problem. For this reason, the incorporation of MNPs into polymeric matrices has drawn a great deal of attention within the last decade as polymer-metal nanocomposites have already demonstrated unusual and valuable properties in many practical applications.

The modification of commercially available ion exchange resins and the development of suitable polymeric membranes with metal nanoparticles (MNPs) having certain functionality, such as for example, biocide or catalytic activity has proved to be a theme of

great interest. The main advantage of the nanocomposite ion exchange materials is the location of metal nanoparticles near the surface of the polymer what substantially enhances the efficiency of their biocide and catalytic application.

1.1. Metal nanoparticles

The most commonly accepted definition for a nanomaterial is “a material that has a structure in which at least one of its phases has a nanometer size in at least one dimension.” [12] Regarding this definition, it is possible to classify nanoobjects in three groups:

- i. 1D nanometer-size objects (e.g., thin films)
- ii. 2D nanometer-size objects (e.g., nanowires, nanorods and nanotubes)
- iii. 3D nanometer-size objects (e.g. nanoparticles and/or nanoclusters)

Such materials include porous materials (with porous sizes in the nanometer range), polycrystalline materials (with nanometer-sized crystallites), materials with surface protrusions separated by nanometric distances, or nanometer-sized metallic clusters. Among all of these materials, metal nanoparticles (MNPs) have attracted increasing interest of scientists and technologists during the last decade, due to their unique electrical, optical, magnetic, and chemical properties.

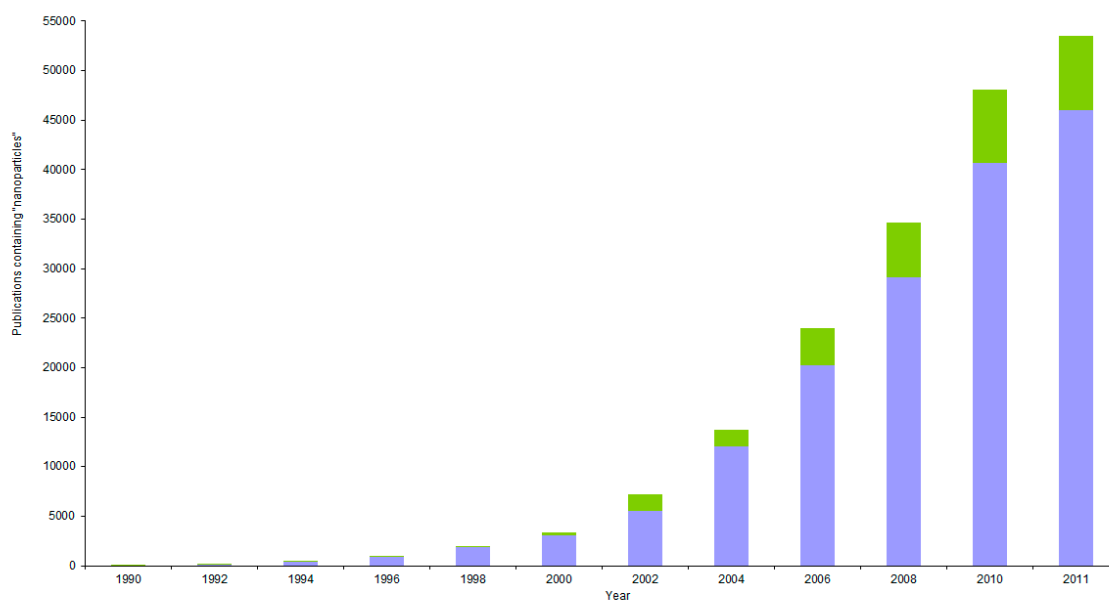


Figure 1. Bibliographic analysis based on the search of “nanoparticles” in Scifinder Scholar. Blue represents scientific publications (e.g. books, articles, reviews) and green represents patents.

Within the last two decades a new focus has been initiated to control and to better understand the nanometer-size objects due to the appearance of a new interdisciplinary field, which is known now as Nanoscience and Nanotechnology. This has stimulated a new wave of intensive and more detailed studies of MNPs and various nanocomposites on their base. Figure 1 shows the tendency in publication about this issue, where it is shown that the

number of publications has increased exponentially due to their wide applications in different fields such as Medicine, Chemistry, and Physics and so on. Moreover, not only scientific publications have been growing in the last decades but also a huge number of patents have been issued in the last decade.

The main goal of Nanoscience and Nanotechnology is the creation of useful/functional materials, devices and systems through the control of matter on the nanometer length scale and exploitation of novel phenomena and properties (physical, chemical and biological) at that scale. To achieve such goal it is necessary to use a multidisciplinary approach: inputs from physicists, biologists, chemists and engineers are required for the advancement of the understanding in the preparation, application and impact of new nanotechnologies.

1.2. General properties

Because of the decrease in the scale of the materials, their behaviour changes in a remarkable form. In fact, the reduction of the bulk materials to a nanometric size induces size-dependant effects resultant from:

- i. An increase of the ratio surface-volume, what gives to an increase in the total surface area and in the fraction of the entities (e.g. atoms) in the surface of the material, as shown Figure 2.
- ii. Changes in the electronic structure of the entities forming the nanoparticles and in the nanoparticles as whole.
- iii. Changes in the associations (e.g. interatomic distances) of the entities forming the nanoparticle and presence of defects.
- iv. Confinement and quantic effects (due to the confinement of the charge carriers in a particle of size comparable to the wavelength of the electron).

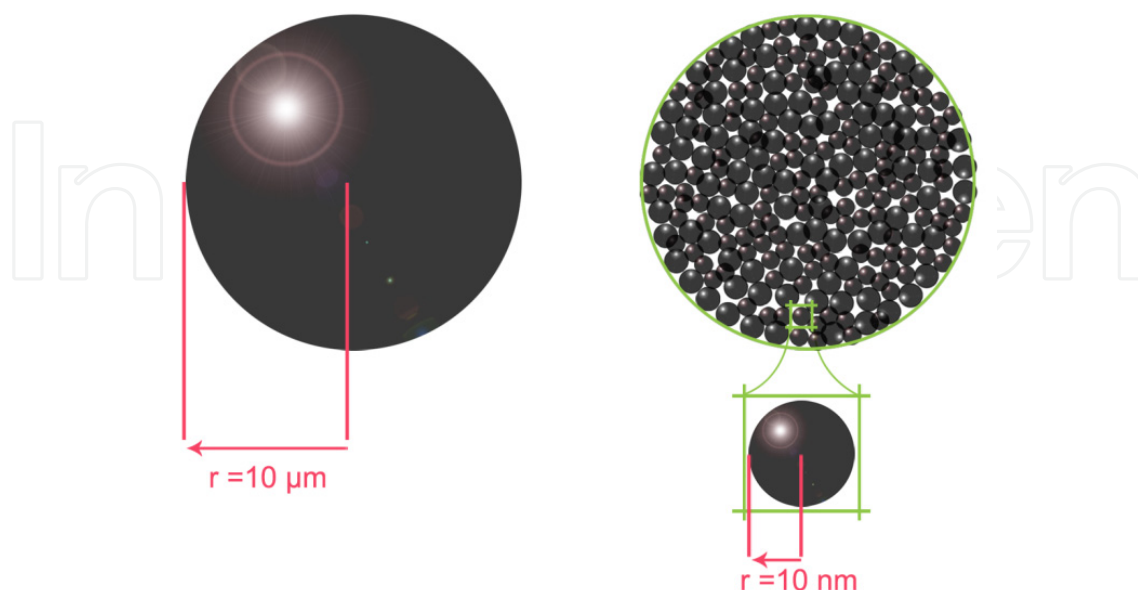


Figure 2. Schematic representation of the change in the ratio surface/volume between a bulk microsphere and the same microsphere composed by NPs.

This can be illustrated, for example, by the dependence of gold melting point on the size of gold nanoparticles, or by suspensions of Ag nanoparticles with sizes ranging from 40 to 100 nm which show different colours. [13] In addition, there are physical phenomena that do not exist in materials with larger grain sizes, as the general quantum-size effect for optical transitions in semiconductor nanocrystals which occurs in very small nanoparticles (<10 nm) due to the quantum confinement effects inherent in particles of that size.

Is due to all of these new properties that, indeed, research centred on nanoscopic materials have a large field of application which extends from the semiconductor industry, where the ability to produce nanometer-scale features leads to faster and less expensive transistors [6], to biotechnology, where luminescent nanoparticles are extremely interesting as bioprobes. [14] Some other particular examples are catalyst for fuel cells [15] or electrocatalysts used in sensing devices with enhanced properties. But, as a rule of thumb, nanoparticles, due to the large percentage of surface atoms [12, 16], have already made a major impact on the field of surface science, as Catalysis or Biocide treatment.

1.3. MNPs Preparation: Stability challenges and stabilization mechanisms

In general there are two routes for the preparation of MNPs (see Figure 3):-Down and Bottom-Up. The top-down methods are those that reduce the macroscopic particles to the nanoscale. This route is not very suitable to prepare uniform particles of very small sizes. In contrast, with the bottom-up methods it is possible to obtain uniform particles (usually of different shapes and structures). These routes start from atoms that can be added (either in solution or gas phase) to form larger particles.

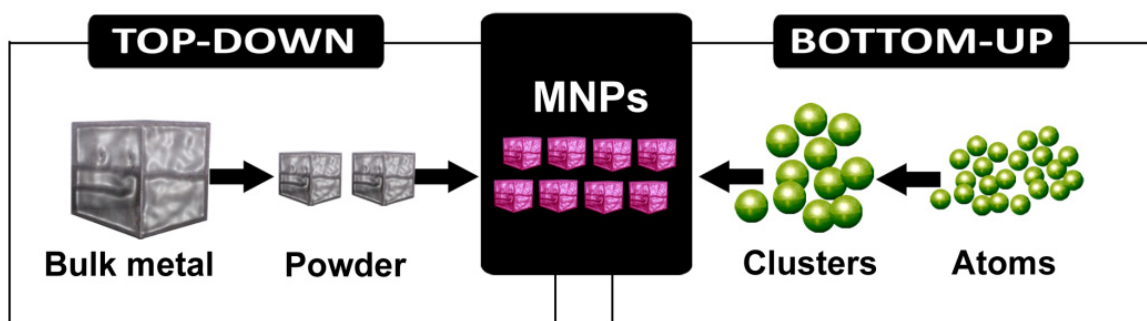


Figure 3. Scheme of Top-Down and Bottom-Up approaches to the synthesis of MNPs.

Overall, a good method to classify the different methods of synthesis of MNPs is by Physical, Physicochemical and Chemical routes (See Figure 4). [13] Many synthetic pathways can be used but the chemical ones are generally cheaper and do not require equipment or instruments as specific as in the case of physical methods the physical methods.

However, the main drawback which still limits the wide application of MNPs is their insufficient stability dealing with their high tendency to self-aggregate. [17] MNPs are so reactive that when they touch each other, they surfaces fuse, what results in a loss of the nanometric size and in their special properties. These features of nanoparticles, in part

determined by the conditions of synthesis, create enormous difficulties in their fabrication and application. [18]

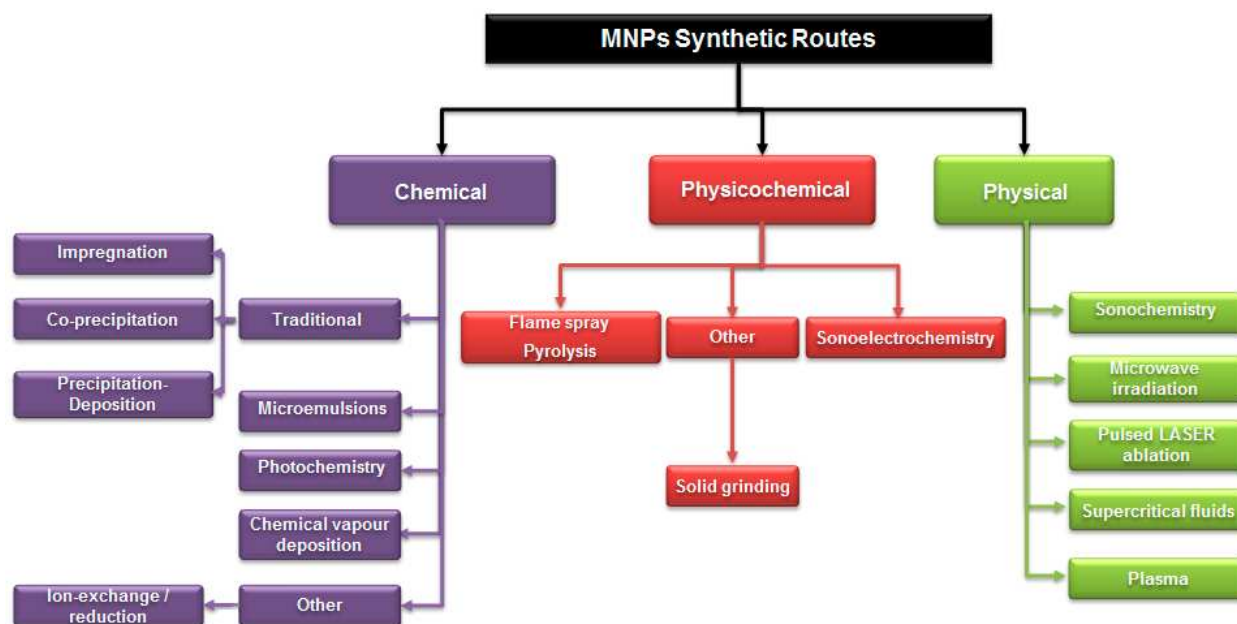


Figure 4. Physical, Physicochemical and Chemical routes for the preparation of MNPs.

It is noteworthy that NPs can aggregate not only as a result of a further manipulation but also during their growth. A typical mechanism of aggregation is the Ostwald ripening which is a growth mechanism where small particles dissolve, and are consumed by larger particles. [19] So, the average nanoparticle size increases with time, the particle concentration decreases and their solubility diminishes.

Therefore, the stabilization of MNPs is specifically required to:

- i. prevent their uncontrollable growth
- ii. prevent particle aggregation
- iii. control their final shape and size
- iv. allow particle solubility in various solvents
- v. terminate the particle growth reaction

The successful synthesis of nanoparticles usually involves three steps: nucleation, growth, and termination by a capping agent or ligand (or stabilizing agent) through colloidal forces.[20] These colloidal forces can be classified in three main types as follows: Van der Waals interactions, electrical double-layer interactions, and steric interactions. In addition, hydrophobic and solvation forces may be important. [21]

Some of the mechanisms regarding the stabilization forces have been thoroughly revised in the literature.[13, 22]

Specially the use polymer-assisted fabrication of inorganic nanoparticles is probably one of the most efficient and universal ways to overcome the stability problem of MNPs and to save their properties. Metal nanoparticles synthesized by this approach exhibit long-time

stability against aggregation and oxidation while nanoparticles prepared in the absence of polymers are prone to quick aggregation and oxidation.[18, 23]

In this sense, stabilization of MNPs can be done by different strategies. In the ex-situ synthesis, NPs are dispersed after their synthesis in a solid or liquid medium by using different mechanochemical approaches. The problem is that in these cases, the success of the stabilization is limited by the possibility of re-aggregation of the MNPs along the time. On the opposite hand, by the in-situ synthesis, MNPs are grown directly in the stabilizer medium yielding a material that can be directly used for a foreseen purpose. For this reason, in-situ approaches are getting much attention, because of their technological advantages (Figure 5).

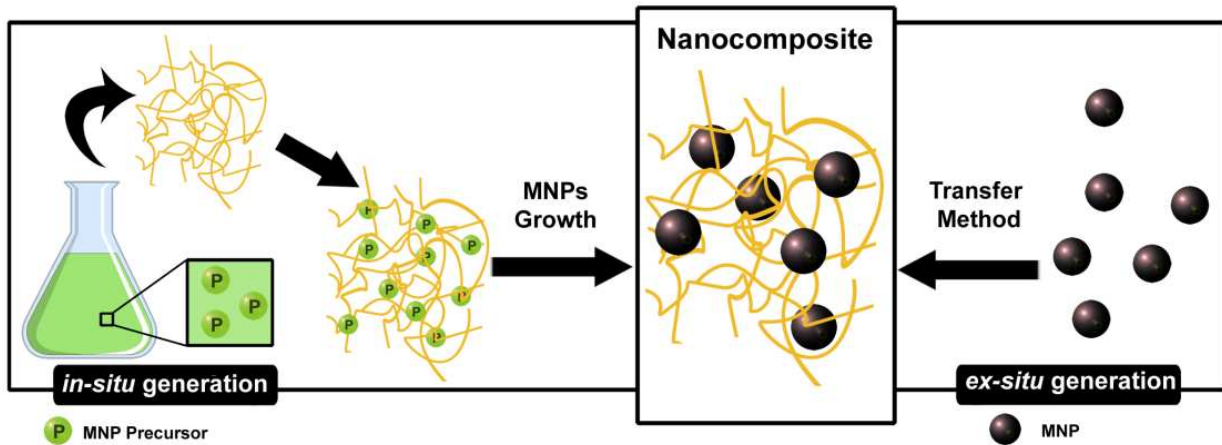


Figure 5. Schematic comparison between in-situ and ex-situ methodologies.

Despite the methodology employed, it is of crucial importance to understand the processes occurring in polymer interactions with nanoparticles. In this regard, the mechanism of MNP stabilization with polymers can be explained by two approaches which run simultaneously in the system and influence one another: the substantial increase of viscosity of the immobilizing media (the polymer matrix), and the decrease of the energy of particle-particle interaction in PSMNP systems versus non-stabilized MNP dispersions. [24]

In the first approach, the substantial increase of viscosity of the immobilizing media (the polymer matrix), the Coagulation velocity depends on factors as the range of attraction forces, Brownian motion velocity, concentration of colloidal solution, presence of electrolytes... As follows from the Smoluchowsky equation [25], the rate constant of particle coagulation, k_c , is inversely proportional to the viscosity of the media, η , (here k stands for the Boltzman constant, and T is the temperature):

$$k_c = \frac{8kT}{\eta} \quad (1)$$

The second approach is the decrease of the energy of particle-particle interaction in PSMNP systems versus non-stabilized MNP dispersions. The potential energy of attraction U_r between two spherical particles of radius r and minimum distance l_0 between their surfaces can be given by the following equation:

$$U_r \approx \frac{Ar}{12 l_o} \text{ at } r \gg l_o \quad (2)$$

where A is the effective Hamaker's constant with dimensions of energy. The value of A is known to be close to kT for polymer particles (e.g. $6.3 \times 10^{-20} \text{ J}$ for polystyrene), while for the metal dispersions it is far higher ($40 \times 10^{-20} \text{ J}$ for silver). [24]

2. Inter-Matrix synthesis in ion exchange matrices

The ion-exchange synthesis of Metal Nanoparticles (MNPs) refers to a group of methods which can be generally classified as Inter-Matrix Synthesis (IMS) technique. The main feature of IMS is the dual function of the matrix, which allows the stabilization of the MNPs to prevent their uncontrollable growth and aggregation and provides a medium for the synthesis.

It is noteworthy that IMS was essentially the first method employed by the humans to incorporate nanoparticles inside inorganic materials. In this sense, one of the oldest nanocomposite materials found is the "Lycurgus cup" which dates back to the late 4th century B.C.[26] and it is made of a sort of glass that changes its colours depending on the incident light: in reflected light the glass turns green, but when the light is shone directly through it, it turns red due to the presence of small amount of Ag-Au-MNPs with the diameter of approximately 70 nm. It is remarkable that Greco-Roman techniques have been used up to modern times: related recipes were described by Arabian authors during the medieval period [27], during the Renaissance as practical application of alchemical knowledge[28], and by modern chemists, from the Encyclopedie of Diderot and d'Alembert [29] through to the present day.

Another example is the "lustre pottery"[30] employed at the same time in Asian and European countries by a simple two-step procedure:

1. the immobilization of metal cations (MNP precursors) inside the ceramic matrix.
2. the reduction of metal ions to the zero-valent state with carbon monoxide leading to the formation of MNPs.

Examples of this ceramics are showed in Figure 6.

Although, as it has been shown above, humanity had used the properties of the nanoscale materials for a long time, the fundamentals of the scientific Nanoscience and Nanotechnology studies did not appear since the middle of the XIXth. As an example, in 1949 the first communication of the IMS is published by Mills and Dickinson.[31] In this pioneered publication it is described the preparation of the anionic resin containing Cu-MNP ("colloid copper") and the use of this nanocomposite material for the removal of oxygen from water due to its interaction with copper MNPs. Since that, a great number of researchers focused their efforts to the development of a new class of ion-exchange materials, combining ion-exchange and redox properties (known also as "redoxites" or "electron-ion exchangers").

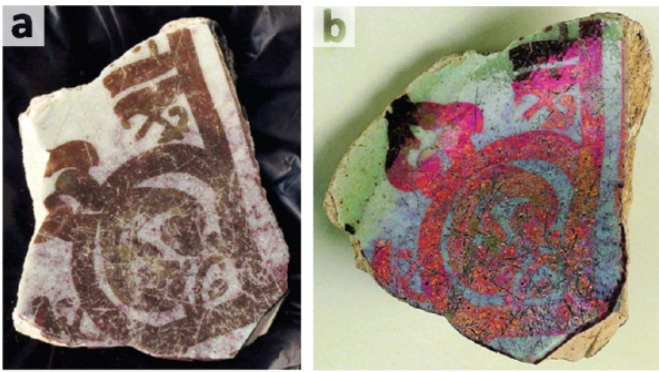


Figure 6. Lustre Pottery. Fatimid-sherds excavated from Fustât; (a) the sample and (b) sample with an orientation that corresponds to the diffraction angle and lustre shining is observed.

2.1. General principles

This section describes the principles of the IMS in ionic exchange matrices. This technique takes advantage of the in-situ approach (above mentioned), and has a wide range of application because of the multiple metal-polymer existing possibilities. In this sense, even if the number of polymers is reduced to those with ion exchange capacities, the multiple possibilities remain and a different number of polymer-nanocomposites can be obtained. Figure 7 shows the multiple possibilities of the IMS methodology.

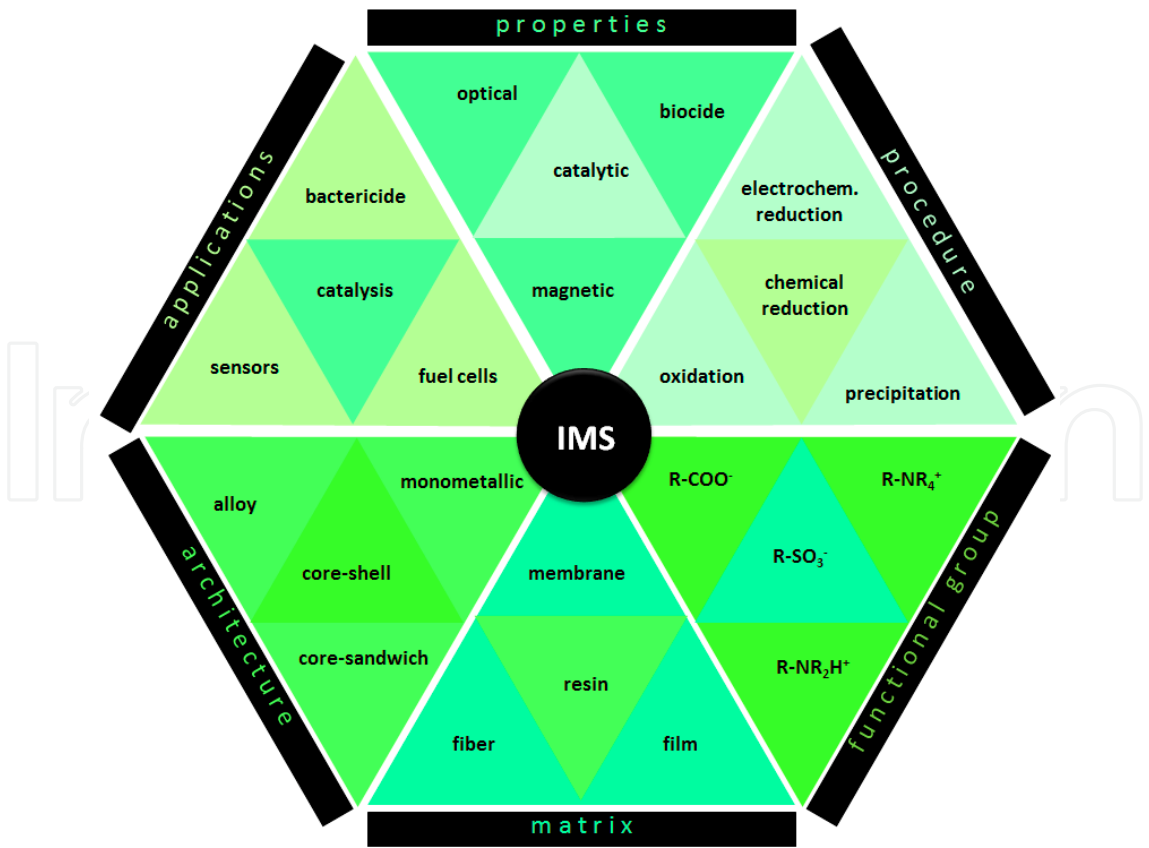


Figure 7. Scheme of the multiple possibilities of Ion-Matrix Synthesis.

The general principles of IMS, valid for any kind of polymer matrix and type of nanoparticle, are based on:

1. The nanoreactor effect: the confinement of the particles by the polymer molecules which allows limiting the size and the particle size distribution; and,
2. The barrier effect: the polymer molecules locally isolate the formation of each single NP preventing the contact between their surfaces and therefore their aggregation.

These guidelines are only achievable if NPs precursors can properly be immobilized in the polymeric matrix. In this sense, Ion Exchange matrices are the perfect template to retain the ionic species, either metal cations, anions or any kind of coordination compound.

To illustrate this approach, two anion charged groups as sulfonic group (SO_3^-) can efficiently interact with the metal cation (M_1^{2+}) which afterwards can undergo a chemical reaction (precipitation, reduction, etc.) which finally will yield to the formation of the MNP.

The same can be done for an anion exchange matrix bearing a functional group such as a quaternary ammonium ($-\text{NR}_4^+$), capable to immobilize metal complexes (i.e. $[\text{CoCl}_4]^{2-}$) or other anions (i.e. BH_4^-).

Figure 8 illustrate the two main consecutive stages which rule the IMS technique: (i) the immobilization of the metal ion or complex (in a Cation Exchange Matrix, CEM) or immobilization of the reductant (in an Anion Exchange Matrix, AEM) and (ii) the reduction of the metal ion inside the matrix.

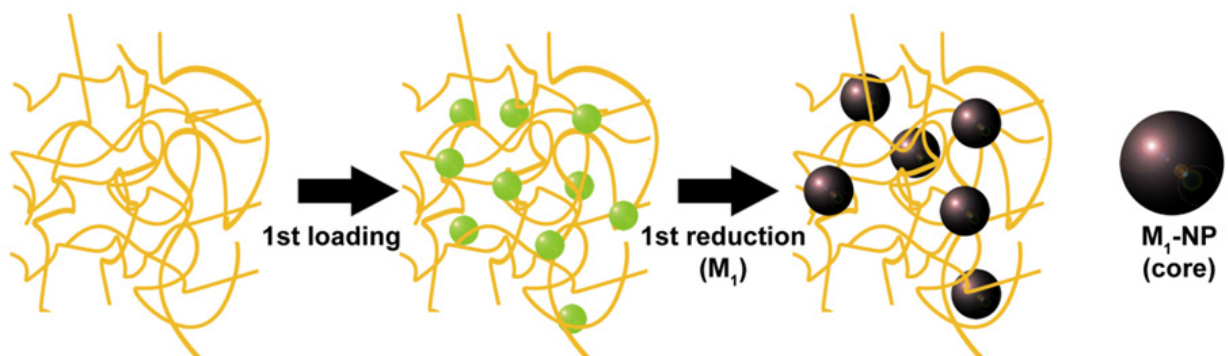
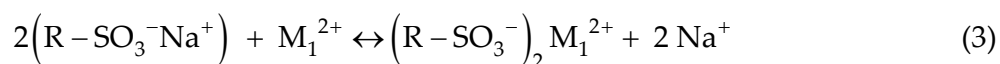
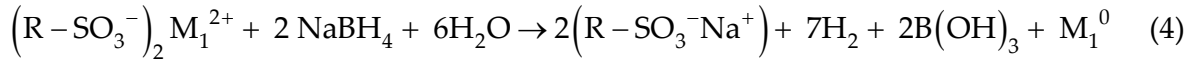


Figure 8. Monometallic MNPs preparation inside a polymeric ion-exchange matrix by IMS. Green spheres represent the M_1^{2+} cation, and the black ones the MNPs obtained after the reduction.

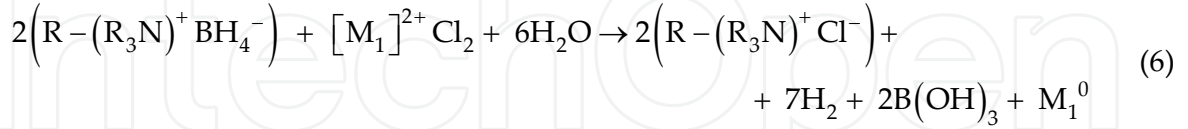
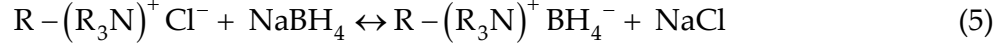
These two stages may be described by the following equations (equations 3-4 and 5-6) considering the presence of strong acid groups (2R-SO_3^-) in the CEMs and the presence of strong basic groups ($\text{R-R}_3\text{N}^+$) in the AEMs. M_1 represents a divalent metal and R the organic radical.

For CEMs:



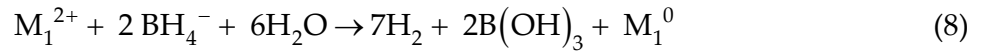
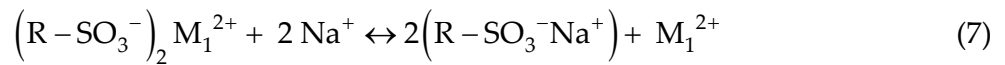


For AEMs:

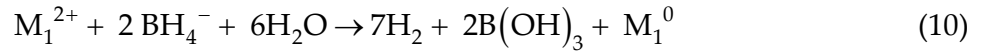
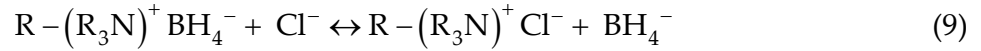


A deeper look in the second stage reveals that the MNPs formation (equations 4 and 6) is, indeed, a combination of an ion-exchange reaction and a reduction reaction, accordingly the reduction of the metal ions to the zero-valent metal takes place in the solution boundary, close to the ion exchange groups:

For CEMs:



For AEMs:



Additionally, as it can be seen from equations 7 and 9 in both cases the matrix is regenerated after the second stage of the IMS, so it is possible to apply consecutive IMS cycles to increase the total loaded metal [32] or to obtain bimetallic nanoparticles (core-shell, alloys or core-sandwich).

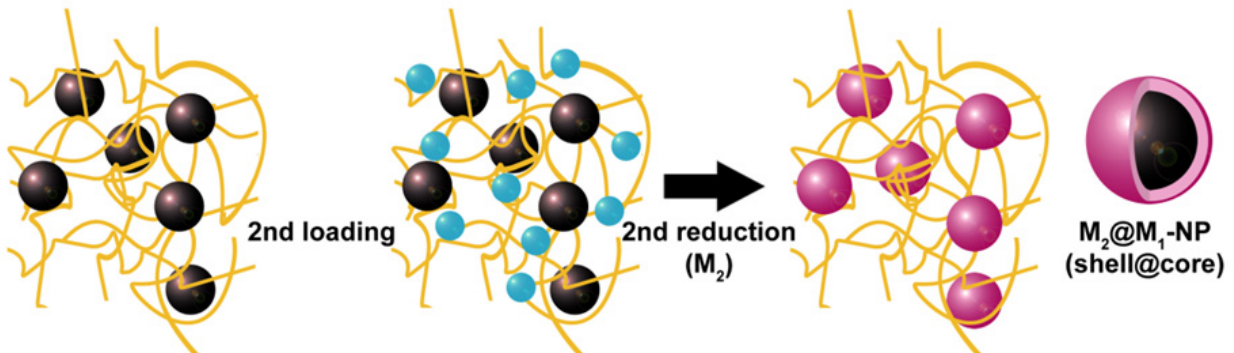
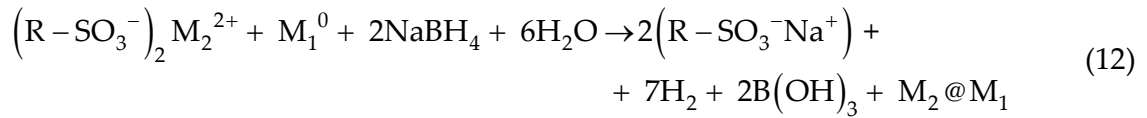


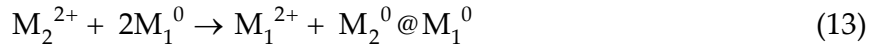
Figure 9. Bimetallic core-shell MNPs preparation. Black spheres represent the MNPs obtained after the first loading-reduction cycle, blue spheres the M_2^{2+} cations and the pink ones are the final core-shell MNPs.

In Figure 9, there is a schematic representation for the preparation of core-shell NPs by coating the monometallic MNPs obtained after the first cycle with a secondary functional metal shell. As follows, the formation of core-shell MNPs (M_1 - M_2 , represented as $M_2@M_1$ where M_2 is the coating and M_1 is the core) allows modification of charge and functionality, improves the stability or combines the properties of both metals to make their future applications more efficient. The final activity of the nanocomposite is determined by the properties of the shell metal, although in some cases the properties of the metal core may add an additional advantage to the final nanocomposite (e.g. magnetic core).

To better understand the procedure shown in Figure 9, let us consider the reactions corresponding to the IMS of PSMNPs inside the parent polymeric matrix after the first loading-reduction cycle for example in the CEM:



According to some authors [33], the second metal ion can act as an oxidizing agent towards the core-metal (M_1^0) resulting in the oxidation of the first metal by the following transmetallation reaction:



As it can be seen, in the general IMS procedure described before, there are always two species bearing the same charge: the matrix and the reducing agent (in CEMs) or the metal ion (in AEMs). This means that there is an electrostatic repulsion between the matrix and one of the species mentioned that impede the penetration inside the polymeric matrix, referred to as Donnan-exclusion effect [34, 35].

The Donnan-exclusion effect is based on the exclusion (inability to deeply penetrate inside the polymer) of co-ions when the sign of their charge coincides with that of the polymer

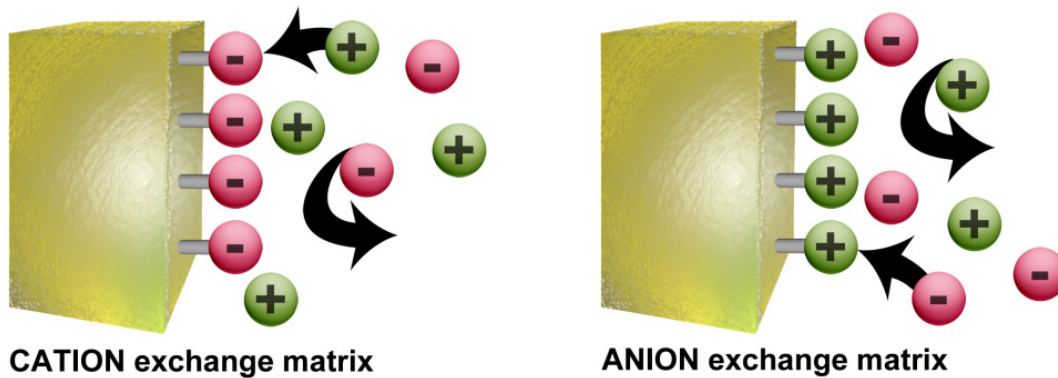


Figure 10. Donnan Exclusion Effect.

functional groups. Consequently, ion penetration inside the matrix is balanced by the sum of two driving forces acting in opposite directions: the gradient of the ion concentration and the Donnan-effect itself. The result of these two driving forces is the formation of the MNPs mainly near the surface of the polymer matrix (see Figure 10).

Regarding the final application of the nanocomposite, this is a really suitable distribution, since MNPs remain maximally accessible for substrates of interest such as chemical reagents or bacteria.

2.2. Requirements for parent polymers

Many materials which contain functional groups can be used as supports for the IMS disregarding their form or shape: granulated form, fibrous or membranes. In all cases, when using the IMS technique it is important to take into account both the polymer properties and the final application of the nanocomposite since as both points dictate certain necessary requirements to the parent matrix (inside which the MNPs must be synthesized).

For example, when using a nanocomposite for making a sensor or a biosensor to be applied in aqueous solutions, the polymer must be insoluble in water. But, at the same time, the polymer has to provide sufficient permeability towards the analyte under study (ions or molecules). Besides, the polymer must either slightly swell in water or at least be hydrophilic to enhance both the sensor and the response rate.

Similarly, the solubility of the nanocomposite in some organic solvents allows for the preparation of homogeneous Polymer Stabilized MNPs solutions (PSMNPs “inks”) that can be deposited onto the desired surfaces (e.g. electrodes) to modify their properties. This solubility would also allow the characterization via microscopic analysis, electrochemical techniques and others.[36]

The main requirements for a polymer to be used as a matrix for the IMS technique are the following:

- The polymer must be chemically compatible with the MNPs surface.
- The polymer must bear functional groups which would act as nanoreactors.
- Appropriate distances between the coordinating centers to insure the hopping of charge carriers.
- Sufficient flexibility of the polymer chain segments to facilitate movements of ionic carriers.
- Appropriate swelling ratio of the matrix.
- Adequate hydrophilicity.

In polymer functional matrices, ionic transport occurs in a highly amorphous, viscoelastic (solid) state. In this sense, the most intensively studied polymers are based on poly(oxa alkanes), poly(aza alkanes), or poly(thia alkanes).

In general, it is possible to state that functional groups define the chemical properties of the polymer matrix, by bearing on the surface a negative or positive charge. Due to this fact

different dissociation properties of group lead to strong and weak exchangers (which are named similar to that of strong and weak electrolytes). Based on these functional groups, classification of Ion Exchange matrices involves four main groups:

1. Cation exchangers (with anionic functionalities and positively charged mobile ions)
 - a. strong acid exchangers (e.g., containing sulfonic acid groups or the corresponding salts)
 - b. weak acid exchangers (e.g., containing carboxylic acid groups or the corresponding salts)
2. Anion exchangers (with cationic functionalities)
 - a. strong base exchangers (e.g., containing quaternary ammonium groups)
 - b. weak base exchangers (e.g., containing amine groups)

The Ion exchange capacity (IEC) is the main feature of ion exchange materials. Taking into account that an ion exchanger can be considered as a “reservoir” containing exchangeable counterions, the counterion content in a given amount of material is defined essentially by the amount of fixed charges which must be compensated by the counterions, and thus is essentially constant.

Above all mentioned polymer matrices, this chapter is mainly focused in the use of cross-linked polymers in the form of resins and in commercial or tailored polymeric membranes.

2.2.1. Resin beads

As IMS is based on the feasibility of the polymeric support used, which must contain ionic functional groups, one of the typical matrices that accomplish this requirement are Ion-exchange resins, also known as granulated polymers.[34, 37]

Ion-exchange resins are commercial products commonly available and their shape and size allow these materials to be easily and quantitatively recovered by simple filtration or decantation. Ion exchange resins are usually used in water treatment processes (e.g. water softening) but have many other applications in chemical production. For instance, several common applications include immobilization of biological and inorganic catalysts, extraction procedures, metal recovery and separation and acid-base catalysis.[38, 39]

The first effort to obtain more stable synthetic resins for ion exchange reactions is attributed to B.A. Adams and E.L. Holmes, who in 1935 published the condensation polymerization of methanal (formaldehyde) with phenol or polysubstituted benzene compounds to give reversible exchange resins. [40] Based on the same concept Adams and Holmes quickly developed anion exchange resins, obtained by the condensation between methanal and phenylamines giving directly a copolymer matrix bearing weak basic secondary amine groups, that in presence of strong acid solutions result in acid amine salts (anion exchangers). Although nowadays the polymerization mechanism is entirely different, based on the so called addition or vinyl polymerization (first applied by D'Alelio in 1944) commercial ion exchange resins production uses the same principles as their predecessors, and the two kind of resin explained before are still the most commonly used resins.[41]

Regarding their chemical composition, most ion-exchange resins are based on cross-linked polystyrene- divinylbenzene (DVB) copolymers bearing ion-exchanging functional groups. Besides, from the morphological point of view, the following types can be considered:

- Gel type: resins with a macroscopic homogeneous and elastic framework which contains the solvent employed in its synthesis. What characterizes the resin is the presence of channels (instead of pores) in the matrix, with a size depending on the proportion of DVB employed in the synthesis. Is the size of these channels what determines the size of the specie, ion or molecule allowed to pass though it and the velocity and diffusion.
- Macroporous type: resins with a higher cross-linking level than gel type. Inside their structure macropores and micropores coexist as a result of the elimination of the solvent, what gives to these kinds of resins a high inner surface area. In this sense, it is necessary a high amount of DVB to maintain the resin structure. The high level of porosity affect to the swelling properties, making the inner structure heterogeneous, thus their behaviour in to polar solvents or to nonpolar solvents solvents is really different. As advantages it is important to say that they are easily sulfonated and they are really resistant.
- Isoporous type: Their structure is modified during their synthesis, thus polymers with a relative uniform pore size are obtained. These resins present a low sensibility to the fouling, have a higher capacity, high regenerating effectiveness and low production costs.
- Film type resins: They are an special type of ion exchangers that consist in an exchange material in a film shape deposited above an inert support. These resins present quick kinetics and allow working in high pressure conditions (i.e. chromatography).

Considering the feasibility of this matrix type for the synthesis of MNPs, it is noteworthy to mention that they lead to obtain a stable support for the embedded MNPs, are insoluble in water and offer different types of functionalities (e.g. sulfonic, carboxylic, quaternary ammonium), as well as different distributions of functional groups. Some common important parameters, from chemical and physical points of view, are listed in the following table (Table 1).

Chemical Parameters	Physical Parameters
Polymer structure, Ion conductivity	Grading
Functional group type	Particle Size
Ion Exchange Capacity	Pore size and morphology
pH working range	Form
Chemical stability	Density
Water absorption (swelling)	Shipping weight

Table 1. Common important parameters in Ion Exchange Resins.

From those parameters listed in Table 1, the functional groups nature is one of the key ones since it defines the chemical properties and applicability of ion-exchange resins and, what is crucial for IMS, the sign of the matrix charge (either positive or negative). Moreover, the

different dissociation properties of the functional groups leads to the distinction between strong and weak exchangers, which have to be considered separately since they have a remarkably different chemical behaviour. In this sense, in Figure 11 are shown some typical resin beads with their polymeric structure formula.

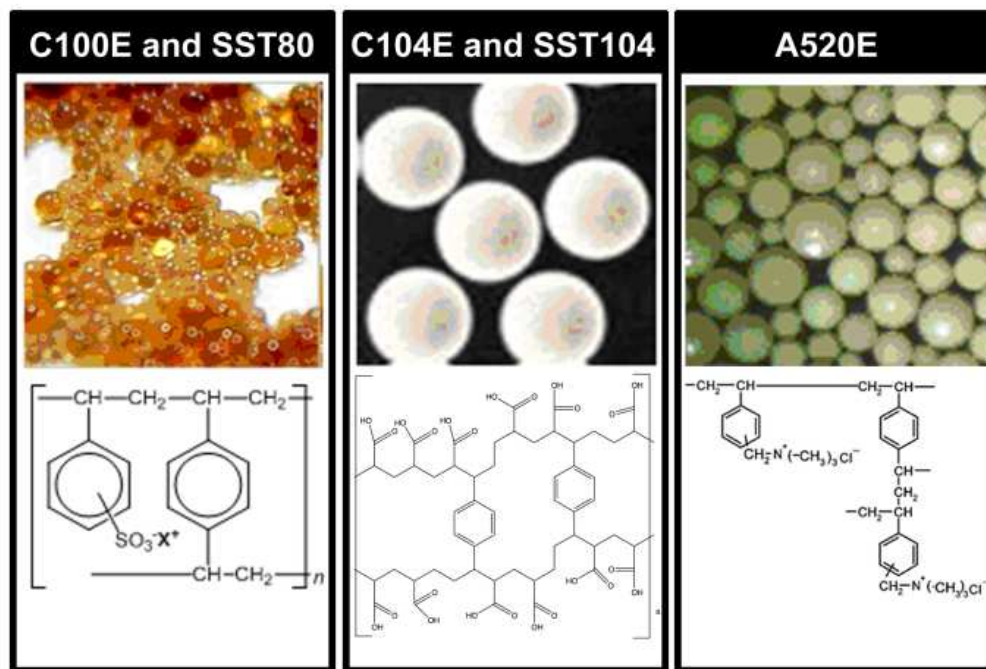


Figure 11. Physical and chemical features of some ion exchange resins.

Another very important parameter to be taken into account is porosity, which affects some bulk properties of the resins, and which have important consequences on their catalytic applications through direct influence on swelling capacity, equilibration rate, and selectivity. In this sense, swelling is an important to be taken account on resin behaviour, because depending on the nature of the ion-exchange resin, this interaction with the solvent may lead to a volume increase (swelling volume) up to 800% and a decrease around 90% of the cross-linking percentage. Hence, gel-type resins are generally preferred over macroporous ones due to enhanced mass transfer inside the polymer beads, resulting in good active-sites accessibility to all soluble reactants.

2.2.2. Membranes

The separation of substances by membranes has been (and still is) essential in the industry development and in the human life. Among various separation membranes, the ion exchange membranes, membranes with ionic groups permeable to electrolytes in an aqueous solution, are widely used in different fields: dialysis, solid polymer electrolyte of batteries, analytical chemistry, etc.

In its origins, the ion exchange membrane was developed from two different sources: the finding of ion exchange phenomena in soil and biological phenomena in cell membranes. In 1939 many researchers focused to the establishment of the basis of the studies on

electrochemical ion exchange membrane. For example, in 1939 K.H. Meyer, J.F. Sievers and T. Teorell obtained the first artificial charged membrane with the aim of developing a theory of membrane potential; in 1949 Sollner published a paper concerning bi-ionic potential (a measure of permselectivity between ions with the same charge through the membrane); etc. But it is not until 1950, with the work of M.R.J. Wyllie, W. Juda and M.R.C. McRae, when the first ion exchange membranes synthesis is published.

After these works, studies on ion exchange membranes, their synthetic methods, modifications, theoretical explanations and applications in industry became very active. But what really made the researchers focus in the development of this kind of membrane is that the charged groups of the membrane act as a fixed carrier for various ionic materials and provide new applications of the membrane.[42, 43] (See Table 2).

Characteristics	Application	Example
Ion conductivity	Electrodialysis	Separation between electrolyte and non-electrolyte
	Separator for electrolysis	Synthesis of H ₂ O ₂
	Diffusion Dialysis	Acid or alkali recovery from waste
	Neutralization Dialysis	Desalination of water
	Donnan Dialysis	Recovery of precious metals
	Up-hill transport	Separation and recovery of ions
	Piezodialysis	Desalination
	Thermo-dialysis	Desalination
	Battery	Concentration cell
	Fuel cell	H ₂ -O ₂
	Actuator	Catheter for medical use
Hydrophilicity	Pervaporation	Dehydration of water miscible organic solvents
	Dehumidification	Dehumidification of air
	Sensors	Gas sensor
Fixed Carrier (Ion exchange groups)	Facilitated transport	Separation of sugars
	Modified Electrodes	-

Table 2. Principal applications of Ion Exchange membranes

Though ion exchange membranes can be used in many fields, most are used in electrochemical processes such as electrodialysis, separation of electrolytes and solid polymer electrolytes for fuel cells (which really boosted the development of these membranes).

The properties required basically depend on their final application, but generally they can be summarized as:

1. low electrical resistance,
2. high transport number of counterions,
3. low diffusion coefficient of salt,
4. low osmotic water and low electroosmotic water,
5. permselectivity for specific ions with the same charge,
6. antiorganic properties,
7. mechanical strength,
8. dimensional stability,
9. high chemical stability and durability,
10. low cost.

Ion Exchange membranes can be classified in various ways: by their structure and microstructure, by their functionality, materials, etc. But maybe one of the simplest classifications is the morphology which, in first instance, will determine their preparation methodology. In this sense, it is possible to classify ion exchange membranes in two main types: Heterogeneous and Homogeneous membranes.[43]

In an initial stage of membrane development, heterogeneous ion exchange membranes were actively developed by blending finely powdered ion-exchange materials and a binder. In a general procedure, cation or anion exchange resins are homogeneously blended and heated with a thermoplastic polymer (i.e. polyethylene, polypropylene, etc.) and the mixture is formed as a membrane by pressing or heating.

Although these types of membranes are easily prepared and have a great mechanical strength, their electrochemical properties are lower than the ones of homogeneous ones in which the fixed charged groups are evenly distributed over the entire membrane polymer matrix. This homogeneity in the homogeneous membranes structure is due to the fact that they can be produced, e.g. by polymerization or polycondensation of functional monomers such as phenylsulfonic acid with formaldehyde, or by functionalizing a polymer such as polysulfone dissolved in an appropriate solvent.

But the completely homogeneous and the macroscopically heterogeneous ion-exchange membranes are extreme structures. Most ion-exchange membranes show a certain degree of heterogeneity on the microscopic scale. Thus, other properties may be considered to classify them. In this regard, according to the distribution and species of the fixed charge (ion exchange groups) it is possible to difference between:

- i. cation exchange membranes (with anionic charged groups)

- ii. anion exchange membranes (with cationic charged groups)
- iii. amphoteric ion exchange membranes (with both cation and anion exchange groups at random throughout the membrane)
- iv. bipolar exchange membranes (bilayer membranes composed by a cation exchange membrane layer and an anion exchange membrane layer)
- v. mosaic ion exchange membranes (which have certain domains that may be separated with an isolator of cation-exchange groups and also domains with anion-exchange groups).

On the other hand, a classification based on the constituent materials allows grouping such membranes as:

1. membranes composed of hydrocarbons or partially halogenated hydrocarbons
2. perfluorocarbon membranes
3. inorganic membranes
4. composite membranes of inorganic ion exchanger and organic polymer (e.g., hybrids).

Nowadays, one of the most employed commercial ion exchange membranes is Nafion, a cation exchange homogenous perfluorinated membrane. It is an excellent proton conductor: it has excellent chemical stability, high ionic conductivity, good mechanical strength, good thermal stability, etc. ideal for performance in fuel cells. The main drawback of these membranes and of those containing Fluor in their structure (i.e. Selemion) are their high cost and, specially, the absence of pores that limits their application to the transport of ions in solution or vapour (pervaporation). Thus, the search of new homogeneous cation exchange membranes has been focussing much of efforts. In these sense, sulfonated polymers open a new window to the ion exchange membranes field. Some typical sulfonated polymers are shown in Figure 12.

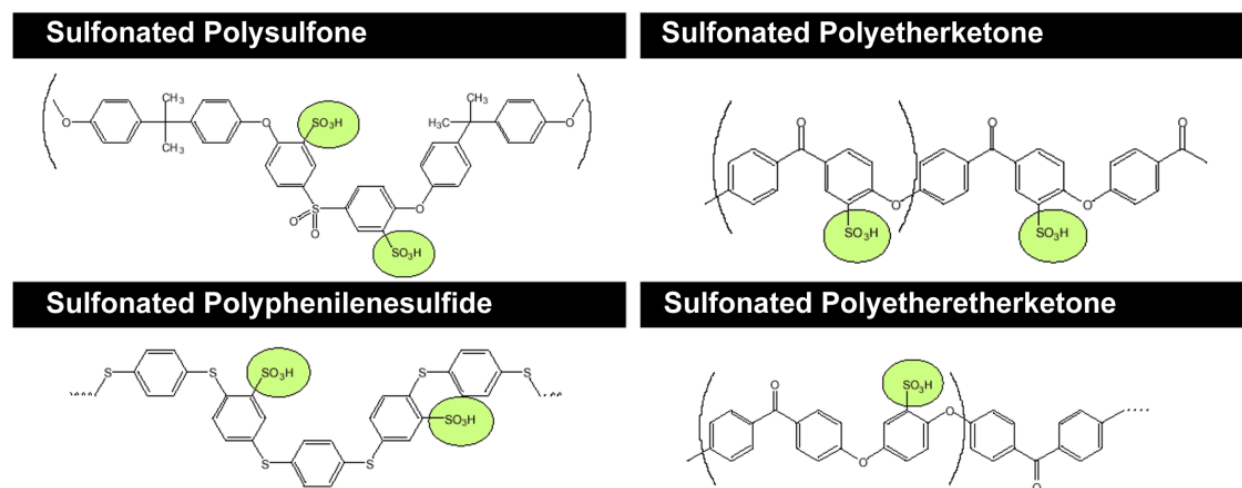


Figure 12. Typical Sulfonated polymers.

One of the polymers that fulfils the properties to be casted as an ion exchange membrane is sulfonated poly(ether-ether ketone) (SPEEK) which is nowadays attracting great interest regarding the fabrication of membranes for fuel cells, due to its thermoplastic properties, its high chemical strength, its high stability towards oxidation and its low cost.[44, 45]

However, regarding this last option it is important to take into account that an excess of ionic groups (in this case, sulfonic groups) could cause the dissolution of the polymeric material in water since an increase of the ionic groups in the polymer directly increases the hydrophilicity of the material.

To cope with this limitation, one good option is the sulfonation of a polymer with a very hydrophobic group so as to reduce the hydrophilicity of the final polymer, the polyethersulphone with Cardo group (PES-C) [46-48] which bears a five-member lactone ring and whose sulfonation can be done in a simple way. Among all the stability properties mentioned, this polymer can be casted by wet phase inversion methodology to obtain porous membranes be applied in filtration. By controlling the ratio of sulfonic groups in the polymer, different porosity can be obtained.

3. Environmental and safety concerns

Perception and knowledge are important parts of public understanding of nanotechnology. They can be influential, for an achievable benefit obtained and the possible risks and hazard which it could imply.

The use of engineered nanoparticles (ENPs) in the environment, as a consequence of the development of nanotechnology, is a serious case of worldwide concern. However, a few studies have already demonstrated the toxic effects of nanoparticles on various organisms, including mammals. Nanotechnology is still in a discovery phase in which novel materials are first synthesized in small scale in order to identify new properties and further applications.

Therefore, detail understanding of their sources, release interaction with environment, and possible risk assessment would provide a basis for safer use of ENPs with minimal or no hazardous impact on environment

In order to do that, future directions such as the inclusion of regulatory and knowledge gaps within the risk identification framework should be designed and applied.

Thus, the evaluation of potential health impact as well as an enhanced design of the production of higher performance nanomaterials is mandatory; as well as defining criteria that distinguish between technologies and products more or less likely to present a health risk to avoid inappropriate and possibly deleterious sweeping conclusions regarding potential impact.

It is required to study their release, uptake, and mode of toxicity in the organisms. Furthermore, to understand the long-term effect of ENPs on the ecosystem, substantial information is required regarding their persistence and bioaccumulation.

3.1. Safe polymer-metal nanocomposites

A massive industrial production of nanomaterials in the near future may result in the appearance of both NPs and the waste generated during their production in various

environments, yielding the possibility that humans could be exposed to these NPs through inhalation, dermal contact or ingestion and absorption through the digestive tract. Nowadays, there is claim for more restrictive legislation that would allow a better protection for both human beings and the global environment.

In this sense, for a comprehensive knowledge of properties of these materials (both physical and chemical), it is important to find standards and control materials to work with as reference models (such those from the British Standards Institute and International Standards Organisation).[49]

An investigation into nanomaterials toxicity involves: a determination of the inherent toxicity of the material, their interaction with living cells and the effect of exposure time.[50] It should be noted that the doses or exposure concentrations used for in vitro and in vivo toxicological studies are most often extraordinarily high in comparison with possible accidental human exposure.[51, 52]

Consequently, more research is needed before generalized statements can be made regarding NPs ecotoxicology.

Unfortunately, only few initiatives in this direction have been started so far. For instance, the German Federal Ministry for Education and Research, together with industry, has established the research programme NanoCare. This programme has a budget of €7.6 million and aims to assess and communicate new scientific knowledge of the effects of NPs on health and the environment.[53]

Scientists and technologists in this area have to deal with NPs presence in the environment but very often they do not have the appropriate tools and analytical methods for NPs detection and quantification to guarantee a satisfactory detection.[4]

Thus, it is of vital relevance to dedicate those efforts towards this direction, as we have not yet invented a so-called “Geiger counter” for NPs.

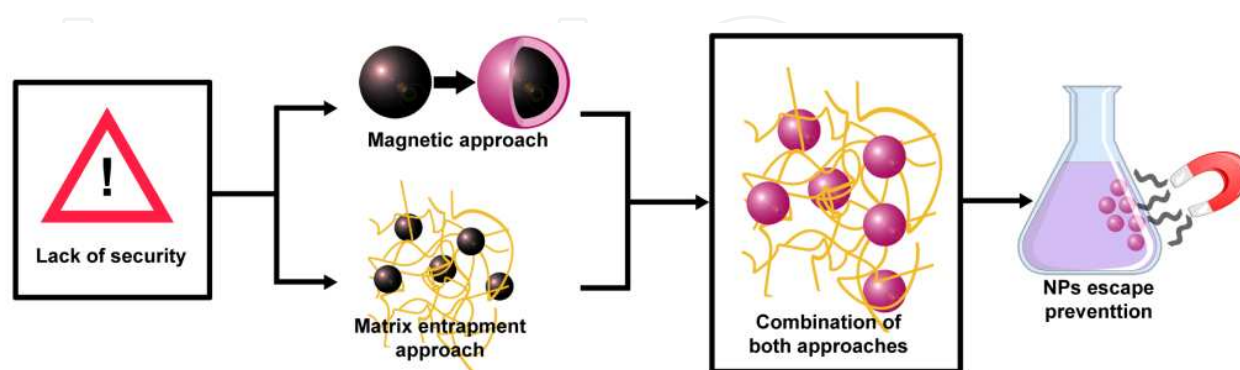


Figure 13. Schema describing the concepts involved in the design of safe polymer-metal nanocomposites.

As a consequence, the prevention of NPs escape into the environment is currently most likely the best approach that can be considered. In this regard, a possible solution appeared

through the development of this project, which describes the results obtained by developing environmentally safe polymer-metal nanocomposite materials exhibiting magnetic properties. These materials prevent NPs escape by profiting of the embedding of NPs into organic matrices and the use of magnetism. [54] As a result, NPs reduce their mobility and, in case of leakage, NPs could be easily recovered by using simple magnetic traps.[13, 55-57]

4. Characterization of Polymer-Stabilized Nanoparticles (PSMNPs)

One of the main features for the development of polymer stabilized metal nanoparticles (PSMNPs) and nanocomposites is their detailed characterization. Specific techniques have to be applied in order to better understand the parameters affecting their synthesis, explain their properties and to adequate them to their final application.

In this sense, several techniques can be used, involving techniques for the chemical characterization and the typical techniques applied in Material Science to determine the MNPs composition, size and shape and their distribution into the matrix as well as the nanocomposite morphology and their special properties (such as magnetism, biocidal, electrocatalytic and catalytic activity among others). These parameters can be studied by using some of the techniques explained in this chapter (or by a combination of some) which include:

- Scanning Electron Microscopy (SEM)
- Transmission Electron Microscopy (TEM)
- Atomic Force Microscopy (AFM)
- Nuclear Magnetic Resonance (NMR)
- X-Rays Diffraction (XRD)
- Impedance Spectroscopy (IS)
- X-rays Photoelectron Spectroscopy (XPS)
- X-Rays Energy Dispersion Spectroscopy (EDS)
- Infrared-Attenuated Total Refraction (IR-ATR)
- Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)
- and many others.

4.1. Characterization of MNPs

When synthesizing PSMNPs the first parameter to determine is the metal content of the polymer-metal nanocomposite.

The composition of MNPs (even that of a single nanoparticle) can be determined by High Resolution TEM or SEM analysis coupled with EDS techniques. The microscopic techniques allow for the selection of the nanoobject(s) whereas the EDS provides the composition analysis. These methods usually gives qualitative or semi-quantitative results which can be useful to have an estimation of the composition differences in a sole sample. An example of this analysis is showed in in Figure 14, where a crossed-section resin bead sample is shown, prepared as described afterwards.

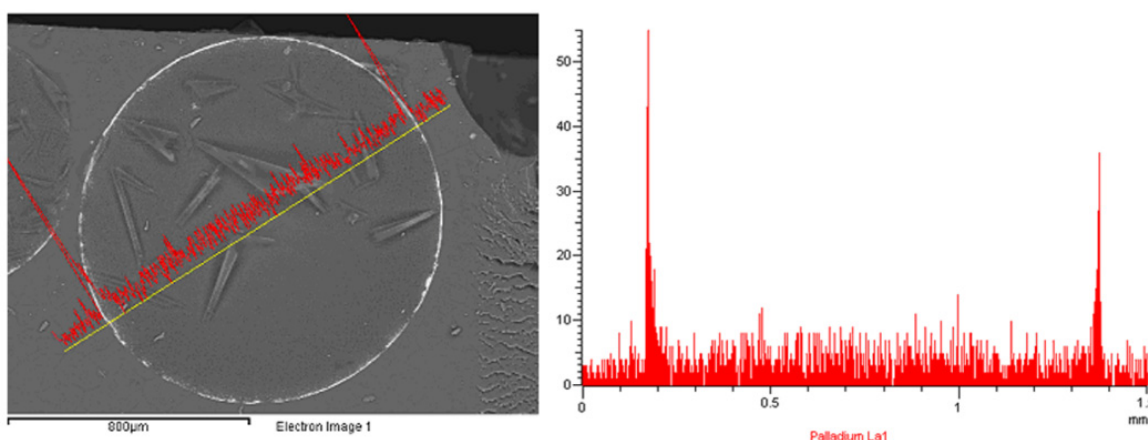


Figure 14. SEM image of an Ion Exchange resin with PdNPs and the corresponding EDS analysis.

If a quantitative analysis is required, the total metal content in the matrix can be determined by using and ICP coupled to an Atomic Emission Spectrometer (for metal concentrations between 0.1 to 500 ppb, depending on the metal) or coupled to a Mass Spectrometer (for metal concentrations between 0.1 to 10 ppb, depending on the metal)[58] to analyse the solution obtained after the treatment of a known amount of the nanocomposite with aqua regia to completely dissolve the MNPs and degrade the polymeric matrix.

The size and the shape of the MNPs obtained are important parameters allowing determining the nanocomposite characteristics. Further development of Nanotechnology needs a better understanding of nanomaterial properties and implies a better characterization of the above parameters, which are evaluated as a rule by using TEM technique.

In this sense, depending on the solubility properties of the polymeric matrices different sample preparation methodologies have to be considered. If the polymeric matrix is soluble in a volatile organic solvent (e.g. DMF, CHCl_3 , THF) it is possible to prepare MNPs suspensions or “inks” (5% mass solutions) in adequate organic solvents which can be deposited onto a TEM grid to perform the microscopic characterization. On the contrary, if the MNPs are stabilized in a non-soluble matrix (e.g. Nafion), the preparation of the sample is more difficult (although allows us to determine the distribution of the MNPs in the matrix), since it requires to cut thin or ultrathin slices (thickness about $1\mu\text{m}$ or less) of the nanocomposite material and deposit them onto a TEM grid. An example of this procedure and the final image obtained is showed in Figure 15.

Unfortunately, in practice, in many instances the quality of TEM images appear to be quite low due to the high noise and low contrast, making their processing a challenging task to accomplish. Also, the quantitative treatment of TEM images is often carried out by manual measurements of high number of nanoparticles, a task that is highly subjective and time consuming. During the last years, several computer imaging particle analysis software tools have been conceived to achieve a more accurate assessment of the size and frequency (size distribution) of nanoparticles.

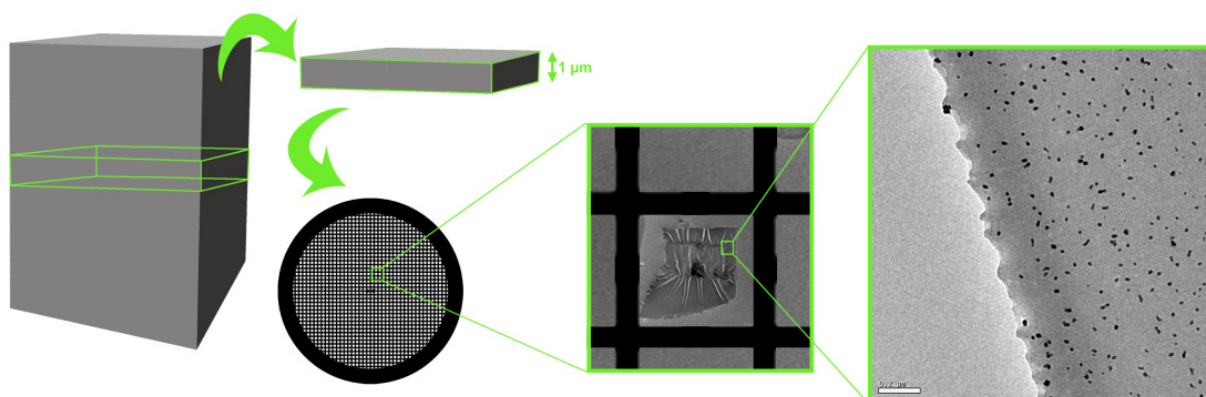


Figure 15. Sample preparation of cross-sectioned with microtome of a sulfonated polyethersulphone (SPES-C) membrane with AgNPs and the corresponding TEM image obtained.

Through the image analysis of TEM micrographs (either manually or automatically) it is possible to make size distribution histograms from the sample data as the one shown in Figure 16. The obtained data can be used fitted to a 3-parameter Gaussian curve (14) where a is the height of Gaussian peak, d_m is the position of the center of the peak (corresponding to the most frequent diameter), and σ is the standard deviation.

$$y = a \cdot \exp \left[-0.5 \cdot \left(\frac{d - d_m}{\sigma} \right)^2 \right] \quad (14)$$

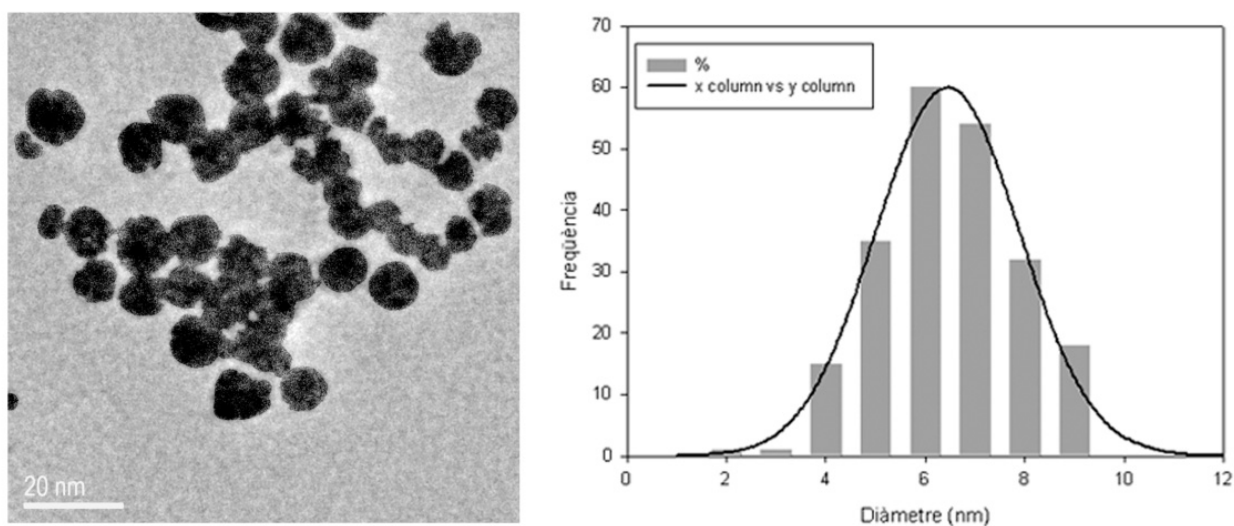


Figure 16. TEM image of an ink of PdNPs obtained in a SPES-C membrane with the corresponding histogram adjusted by a 3 parameter Gaussian curve.

4.2. Metal–polymer nanocomposite morphology

The loading of MNPs in the polymeric matrix may cause important changes in the polymer morphology. For this reason, a characterization of the matrix previous and after the stabilization of the MNPs on it is required.

In this sense and among other techniques, SEM has been established as a referent in the field of the surface characterization. Because polymeric matrices usually are not conductive, in some cases (in matrices without MNPs or with a low content of MNPs) it is imperative to prepare the sample for the study, by a sputter coating with gold, carbon or palladium layers of about 50Å of thickness.

For membranes and films, cross-section images can be obtained by cutting the samples under liquid N₂. For resin nanocomposites, it is necessary to embed the material in an epoxy resin to cut it transversally with a microtome, as shown in Figure 17.

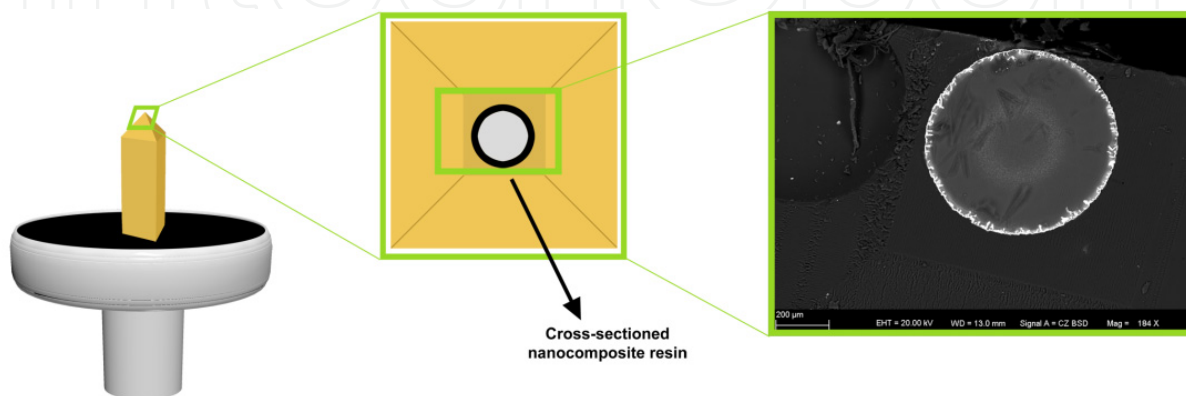


Figure 17. Sample preparation of a resin bead for SEM characterization.

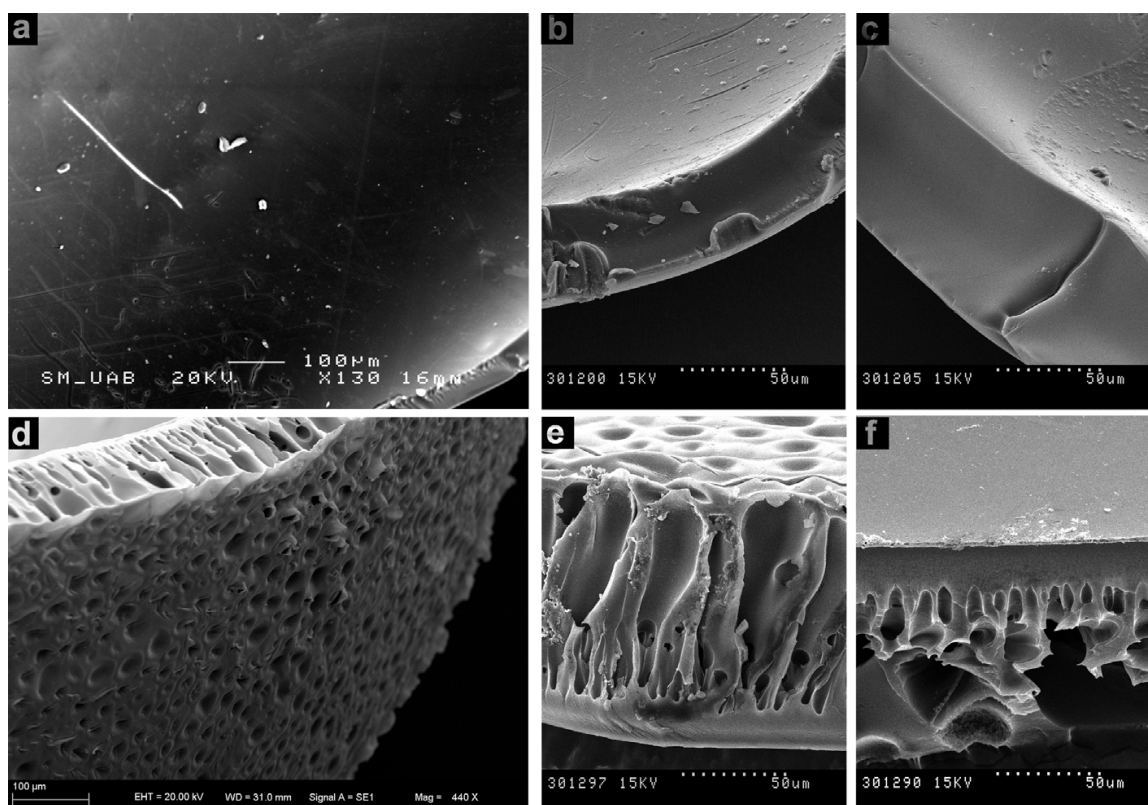


Figure 18. SEM images of (a) SPES-C membrane surface, (b) bare SPES-C membrane, (c) SPES-C membrane with PdNPs, (d) Blend membrane surface, (e) bare Blend membrane and (f) Blend membrane with PdNPs.[32]

Figure 18 shows SEM images of bare and coated SPES-C and Blend membranes (prepared with sulfonated and non sulfonated Polyethersulphone). Whereas in the case of SPES-C membranes there is an absence of porosity and surface defects in the case of Blend membranes it can be observed a finger structure porosity, and the existence of defects on the surface. In both cases, the load with PdNPs do not affect the final structure of the membrane.

The difference in porosity between the two types of membranes can be explained by an increase in the hydrofobicity of the final polymer: adding PES-C polymer increases the capacity of repulsion of H₂O molecules thus, when preparing the membranes by wet phase inversion method by immersion in a non-solvent such as water, pores are generated during the precipitation of the membrane.

In this way, changing the ratio of PES-C / SPES-C in the final polymer blend membranes with different morphology and, therefore, different final application can be obtained.

4.3. Magnetic properties

The metallic nanoparticles have larger magnetization compared to metal oxides, which is interesting for many applications. But metallic magnetic nanoparticles are not air stable, and are easily oxidized, resulting in changes or loss in their magnetization properties.

Thus, IMS of magnetic NPs open a new range of research. Lack of stability of this kind of nanoparticles finds a counterpart by their stabilization on a polymeric matrix.

Magnetic properties of metallic nanoparticles are dependent on the oxidative state of the NPs components. Therefore, the true knowledge of the degree of nanoparticle oxidation is necessary for the forecasting of magnetic characteristics of the obtained samples. This is not easy, but techniques such as XANES (X-Ray Absorption Near Edge Structure) may do it achievable by interaction of the atom core with the source of energy. By comparison with previously placed and analyzed patterns, information about chemical bonding and oxidative states is obtained. Figure 19 shows XANES analysis of nanocomposites containing either Ag or Ag@Co MNPs (with a superparamagnetic Co⁰-core) on sulfonic resin. Standard elements spectra were linearly combined and fitted with the sample in order to determine the oxidative state of each element in the sample. The linear combination results are also included (normalized) inset. Ag@Co NPs in sulfonated matrices showed an average Co spectrum similar to that recorded by the Co⁰ standard. In fact, linear combination fitting results confirmed that all the Co present in that sample was Co⁰.

Furthermore, to characterize magnetic behavior SQUID (Superconducting Quantum Interference Device) magnetization curves are obtained. In order to do that, sample is placed in a changing magnetic field over at room temperature. Magnetization loops are registered through the overall process.

In general, ferromagnetic species have normally evident hysteresis curves. However, superparamagnetic materials (frequently, ferromagnetic materials at nanometer scale) shows a lack of hysteresis but high magnetic saturation. Figure 20 presents SQUID

magnetization curves for Pd@Co MNPs supported on a sulfonic (C100E) and carboxylic(C104E) cation exchange resin.

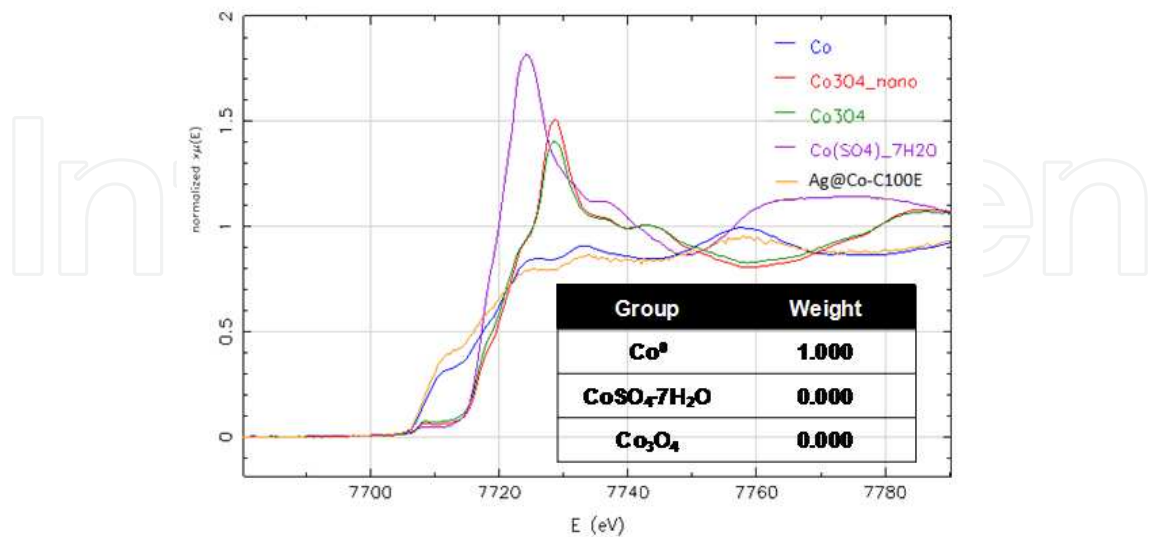


Figure 19. XANES spectra of Ag in comparison with Ag standards for Ag@Co-C100E sample (blue line in the graphic) and the linear combination fitting among all of the compounds analyzed is also shown in a fitting range from -20 to 30 eV. Ag⁰ (red) and AgNO₃ (green) are standards.

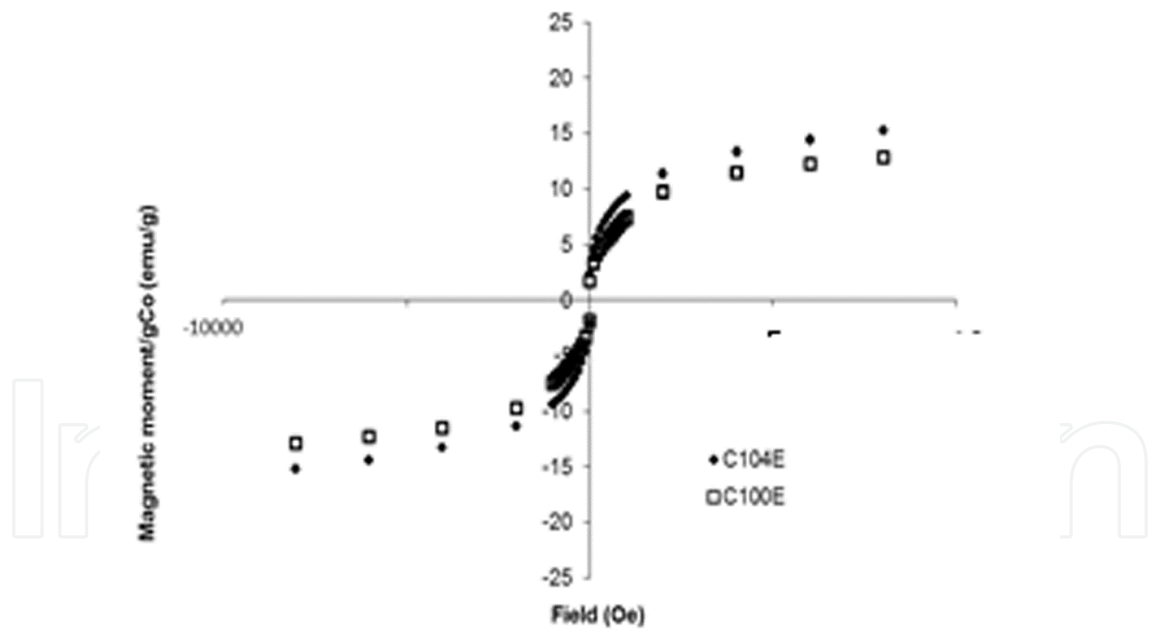


Figure 20. SQUID Magnetic curves obtained of Pd@Co-NPs stabilized in C100E and C104E supports

5. Applications

The use of nanomaterials to assemble architectures of defined size, composition and orientation allows researchers to utilize the particular electrical, optical, catalytic and magnetic properties of those materials for:

- the creation of functional materials, devices, and systems through control the matter on the nanometer scale and,
- the exploitation of novel phenomena and properties at that scale.

To achieve these goals, it is necessary to use multidisciplinary approaches; inputs from physicists, biologists, chemists, and engineers[59-61] are required to advance our understanding of nanomaterials.[62] In fact, NPs properties are already used for developing new products[63, 64] such as paints, where they serve to break down odour substances, on surgical instruments in order to keep them sterile, in highly effective sun creams, slow release pharmaceuticals and many others.[50, 65-67] Bench-marketing studies on main current industries[53, 68] revealed that market opportunities that are illustrated in Figure 21.

As it is clearly shown, most of these market opportunities are involved in the development of new materials. Moreover, among the applied NPs, metal nanoparticles and metal oxide nanoparticles are of the most importance. However, because of the aforementioned toxicity and stability concerns have driven the research to develop nanomaterials with higher levels of safety. In this sense, here two different examples of safe and stable nanocomposites applications are discussed: their use for organic catalysis or for water disinfection.

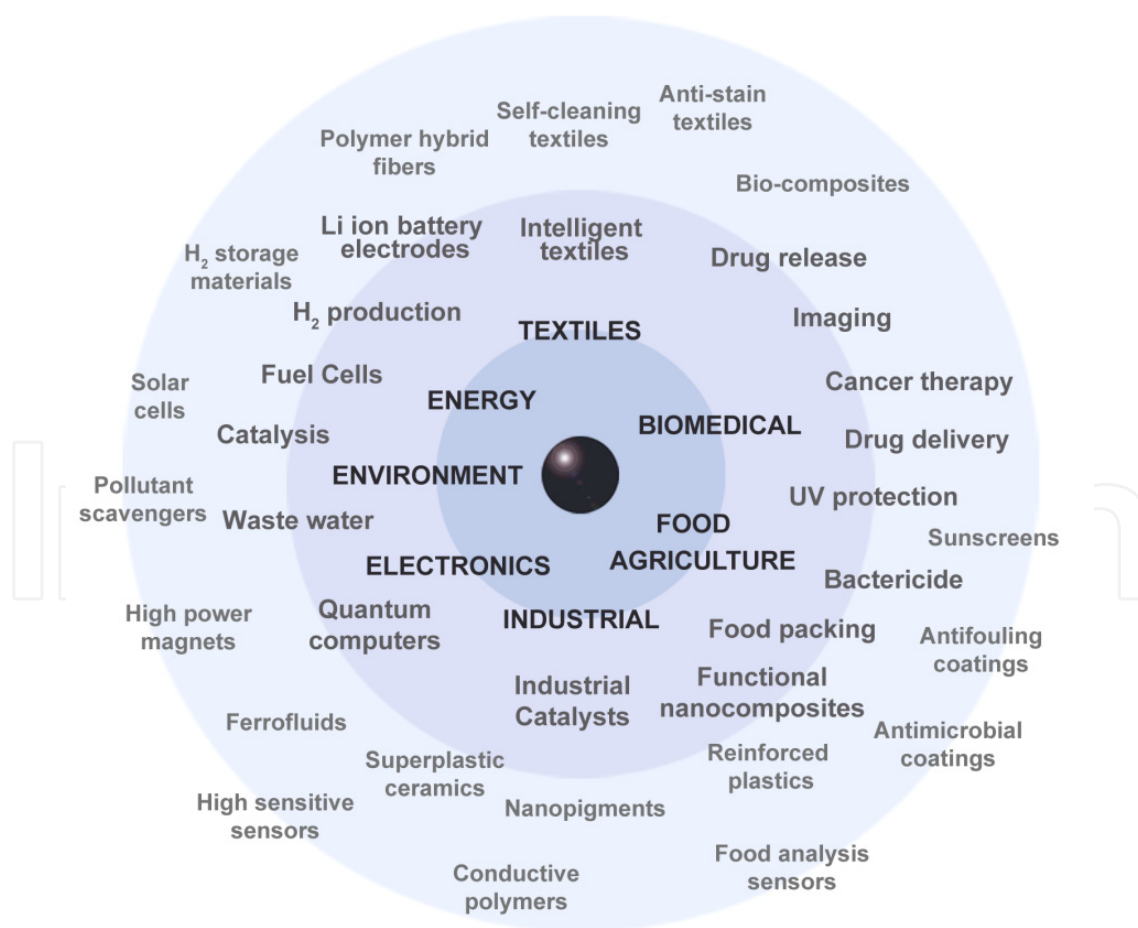


Figure 21. Possible marketable applications of nanocomposites in different fields.

5.1. Bactericidal activity of MNPs

Among the currently known nanomaterials, it is well-known that AgNPs have unique antimicrobial properties.[69] Textiles, keyboards, wound dressings, and biomedical devices now contain AgNPs that continuously release a low level of Ag ions to provide protection against bacteria. Even if Ag has been known to be a bactericidal element for at least 1200 years, considering the unusual properties of nanometric scale materials, largely different from those of their bulk counterparts[70], it is not surprising that AgNPs have been found significantly more efficient than Ag⁺ ions in mediating their antimicrobial activities.[71-75] All in all, the exact antibacterial action of AgNPs is still under debate.

Conversely, in many countries the microbial contamination of potable water sources poses a major threat to public health and the emergence of microorganisms resistant to multiple antimicrobial agents increases the demand for improved disinfection methods.[76] The importance of potable water for people in some countries dictates the need for the development of innovative technologies and materials for the production of safe potable water. This type of application can be a perfect niche for nanomaterials containing AgNPs. However, it is necessary to develop ecologically-safe nanomaterials that prevent the post-contamination of the used samples.[77] In this sense and as it has been already stated, functionalized polymers are currently acquiring a prominent role as NPs stabilizers for their excellent performance.[78, 79]

It is worthy to note here that ion-exchange materials are already widely used for various water treatment processes, mainly to eliminate undesired or toxic ionic impurities including hardness ions, iron, heavy metals, and others. The stabilization and immobilization of AgNPs in such matrices is very promising since using this approach, two complementary water treatment steps could be performed with a single material and the safety of the nanocomposites could be increased.

In our research group, the surface modification of ion-exchange materials used for traditional water treatment has been undertaken and promising results have been patented.[80] Such modification included the incorporation of either Ag or Ag@Co NPs.

As an example of the obtained results, Table 3 shows the synthetic conditions and the corresponding compositions of some nanocomposites of this family, probing the feasibility of the synthesis of both pure and core-shell nanoparticles.

To evaluate the efficiency of these nanocomposites for disinfection procedures, an increasing amount of nanocomposites beads was added to individual wells containing 10⁵ CFU/mL of *E. coli* suspension in LB medium. After overnight incubation, bacterial proliferation was evaluated by measuring the optical density of each well at 550 nm (this wavelength is indicative of bacterial proliferation). The bactericidal activity of the Ag, Co and Ag@Co nanocomposites (in all the polymeric granulated matrices studied) was determined and raw materials were used as control (results are shown in Figure 22).

As it was expected, Ag and Ag@Co NPs containing sulfonated granulated materials increased their activity due to the presence NPs, but the enhancement was slightly higher for modified Ag@Co NPs. Anyhow, this proof of concept demonstrates the rightness of the approach.

Matrix	IEC / meq·g ⁻¹	NPs	[Ag ⁺]/M	[Co ²⁺]/M	mmol _{Ag} /meq	mmol _{Co} /meq
C100E (-SO ₃ ⁻)	2.3	Ag	0.01	--	0.064	--
		Ag@Co	0.01	0.01	0.069	0.061
C104E (-COO ⁻)	6.0	Ag	0.01	--	0.010	--
		Ag@Co	0.01	0.01	0.010	0.017

Table 3. Metal content in granulated nanocomposites containing Ag- or Ag@Co-NPs and, analyzed by ICP-MS.

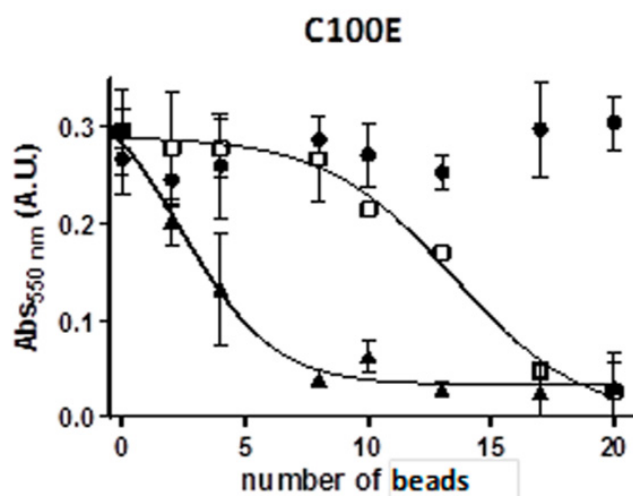


Figure 22. Variation of the absorbance at 550 nm with the number of polymer beads for (●) the raw material, (□) Ag- and, (▲) Ag@Co-nanocomposites (3 replicates).

5.2. Nanocatalysts for organic synthesis

Nanoparticles are increasingly used in catalysis, where the large surface area per unit volume of the catalyst may enhance reactions. This enhanced reactivity significantly reduces the quantity of catalytic materials required to carry out the reactions. Particular industries, including the oil and the automobile ones, are interested in this area for the use of NPs in catalytic converters.[81] As a prove of their industrial potentiality, many big companies, including BASF, Johnson Matthey and 3M, have interests in developing commercial applications for AuNPs catalysts.

In the last decade, heterogeneous catalysts have attracted much interest because of their general advantages that have been boosted thanks to the use of nanomaterials.[82, 83] One crucial property for catalysts is their recovery and, in this sense, magnetic nanocatalysts present some outstanding advantages because they can be conveniently recovered by using an external magnetic field.[84]

On the one hand, Platinum Group Metals (PGMs) are well-known as highly selective catalysts and are widely used in organic synthesis, chemical industry and other areas like dehalogenation, hydrodechlorination, carbonylation or oxidation.[85-87] Concerning the potential applications, Pd, Pt, Rh, and Au-NPs have proven to be very versatile as they are

efficient and selective catalysts for several types of catalytic reactions, including olefin hydrogenation and C-C coupling such as Heck, Suzuki and Sonogashira reactions.[88-90] Among them, Pd-catalyzed cross-coupling has emerged as an effective synthetic methodology that is employed in both academic and industrial sectors.[91] Despite such progress, a number of challenges still remain unknown, including the dilucidation of highly efficient and selective catalysts able to react with multiple reactive C-H or N-H bonds.

On the other hand, several types of magnetic materials have been used, including magnetite, hematite, maghemite, wüstite.[92] Magnetic aggregation and their need for functionalization do still hinder the application of magnetic NPs in industry. Thus, searching for more suitable magnetic materials to overcome these restrictions is still a challenge for realizing practical catalytic applications. Yet, for catalytic purposes, magnetic NPs surface is often chemically functionalized with molecular catalytic complexes because of the poor catalytic properties of the bare Fe oxides or other catalytic materials (*e.g.*, Co).[93, 94]

Therefore, and taking into account, the demonstrated efficiency of PGMs and the advantages of magnetic nanoparticles, it has been possible to apply develop Pd@Co-based nanocomposites for a typical C-C coupling reaction: the Suzuki reaction.[95] The preparation of such catalyses has only been possible thanks to the characteristics of IMS procedure, which allows the combination of a magnetic nanocore (made of Co) with the catalytic activity of a shell (Pd). The resulting material can be separated by simple filtration methods and, moreover, NPs can be re-covered and re-used by their retention under a magnetic field (Figure 23).[96]



Figure 23. Suzuki reaction by using Pd or Pd@Co nanocomposites with optimized conditions.

Previous results with Pd@Co-NPs incorporated to fibrous materials showed the feasibility of this approach.[37] Differently, as it can be seen in Table 4, the catalytic efficiency of granulated polymers (containing either sulfonic or carboxylic groups) was very scarce, very likely due to the low metal immobilization achieved. However, two interesting results can be withdrawn: a substantial increase of the reaction yield was obtained when using the nanocomposite samples with higher Pd-content and the reaction yield could increase for consecutive runs.

Even if low conversions were achieved, these results are not discouraging since granulated polymeric matrices are still interesting for industrial applications because of their mechanical properties. Their high mechanical resistance leads to obtain higher reproducibility in synthesis as well as easier manipulation. Moreover, granulated polymer

industry is big enough to pay attention on it. Further research is needed to successfully increase the amount of immobilised metals what, very probably will provide better catalytic nanocomposites.

Samples		Metal Content		Yield (%)		
Matrix	MNPS	Pd (mg/gNC)	Co (mg/gNC)	#0	#1	#2
C100E	Pd	57	-	44	-	-
	Pd	30	50	8.6	-	-
C104E	Pd@Co	47	48	9.8	8.4	-
	Pd@Co	30	7,6	4	26	28

Table 4. Suzuki reaction yields (in %) for the Pd- and Pd@Co-nanocomposites

6. Conclusions

The conclusions derived from the results presented in this chapter can be briefly formulated as follows:

1. The ion-exchange assisted Intermatrix Synthesis (IMS) technique represents one of the most promising techniques that allows for the production of a large variety of polymer-metal nanocomposites of practical importance for different fields of modern science and technology.

The attractiveness of this technique is basically determined by its relative simplicity in comparison with other methods used for production of nanocomposite materials and also by its flexibility and the possibility of tuning the specific properties of the final nanocomposites to meet the requirements of their final applications. IMS technique gives a unique possibility of production of nanocomposites containing MNPs of various composition and structure (for example, monometallic, bimetallic or polymetallic MNPs with core-shell, core-sandwich and even more complex structures) for the applications of interest.

2. The spectrum of polymers applicable for IMS of PSMNPs is quite wide and includes various functionalized polymers, i.e. those bearing functional groups in the form of granules, fibers or membranes, which are capable to bind either metal or reducer ions prior to the metal reduction inside the polymer matrix (IMS of PSMNPs).

The dissociated ionogenic functional groups of the polymer bearing positive or negative charges provide a possibility to couple IMS technique with Donnan exclusion effect. In case of polymers with negatively charged groups the IMS technique consists of the metal loading stage followed by metal reduction inside the polymer. When polymer bears positively charged groups the IMS procedure starts with the reducer loading followed by the simultaneous metal loading-reduction stage.

3. It has been shown that the use of, for example, anionic reducing agents (e.g., borohydride) for the synthesis of PSMNPs by using IMS coupled with Donnan effect in both cation exchange and anion exchange matrices results in their formation mainly near the surface of the polymer. This type of MNP distribution is favorable for many practical applications of polymer-metal nanocomposites such as reagent-free water disinfection, catalysis and some others.
4. The general properties of polymer-metal nanocomposite are not determined only by the properties of the MNPs. The formation of MNPs within the polymer matrices may strongly modify the polymer morphology, for example due to the appearance of nanoporosity in gel-type polymers, which enhances the rate of mass transfer inside the nanocomposites as well as some other structural parameters of great importance in their practical applications.
The polymer matrix also serves as the MNPs stabilizing media preventing their aggregation and release to the medium under treatment. The functional properties of the nanocomposites (e.g., catalytic or bactericide) are mainly determined by the properties of MNPs immobilized inside the matrix.
5. The repetitive metal-loading-reduction (in case of cation exchangers) or reducer-loading-metal-reduction (in case of anion exchangers) permits to synthesize MNPs of core-shell or even more complex structure provided with additional functional properties.
For example, the IMS of core shell PSMNPs consisting of superparamagnetic cores coated with functional shells having for example, catalytic or bactericide properties provides the polymer-metal nanocomposites with additional advantages. In the case of catalytic applications, the nanocomposite can be easily recovered from the reaction mixture and reused. In water treatment applications, the magnetic nature of MNPs permits for preventing their uncontrollable escape into the treated water by using simple magnetic traps.
6. Finally, the last and the most important in our opinion conclusion concern the general strategy in the development of novel nanocomposite materials. This strategy has to be focused not only on the desired properties of material, which is dictated by its further practical applications, but also on the material safety in both environmental and human health senses. The last point seems to be of particular importance for the further development of Nanoscience and Nanotechnology.

Author details

Berta Domènech, Julio Bastos-Arrieta, Amanda Alonso, Maria Muñoz
and Dmitri N. Muraviev

*Analytical Chemistry Division, Chemistry Department, Autonomous University of Barcelona,
Barcelona, Spain*

Jorge Macanás

Department of Chemical Engineering, Universitat Politècnica de Catalunya, Barcelona, Spain

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