We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900
Open access books available

185,000
International authors and editors

200M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



8

Environmentally-Safe Polymer-Metal Nanocomposites with Most Favorable Distribution of Catalytically Active and Biocide Nanoparticles

A. Alonso[1], J. Macanás[2], G.L. Davies[3], Y.K. Gun'ko[3], M. Muñoz[1] and D.N. Muraviev[1]
[1]*Universitat Autònoma de Barcelona*
[2]*Universitat Politècnica de Catalunya*
[3]*Trinity College Dublin*
[1,2]*Spain*
[3]*Ireland*

1. Introduction

As rule of thumb, nanomaterials (NMs) possess different properties compared to the same material in its coarser or bulk form (Schulenburg, 2008). Once a material is reduced below 100 nm in size, its components begin demonstrating unusual features based on quantum mechanics, rather than macroscopic Newtonian mechanics, which influence a variety of material properties such as conductivity, heat transfer, melting temperature, optical properties, magnetization, etc. (Bhushan, 2007). Taking advantage of these singular properties in order to develop new products (and also new synthetic procedures) is the main purpose of Nanotechnology, and that is why it is frequently regarded as ''the next industrial revolution'' (Lane, 2002; Miley et al., 2005). Although Nanoscience and Nanotechnology are quite recent disciplines, there have already been a high number of publications which discuss these topics (Ajayan et al., 2005; Blackman, 2008; Campelo et al., 2009; Giannazzo et al, 2011; Hassan, 2005; Joo, 2006; Klabunde, 2005; Li et al., 2008; Macanás et al., 2011; Nicolais & Carotenuto, 2005; Rozenberg & Tenne, 2008; Schmid, 2010; Vatta et al., 2006; Zeng, 2004). However, some important concepts are still under debate. The safety of nanomaterials is of high priority, but more fundamental ideas are also quite unclear nowadays. NMs are commonly defined as discrete objects whose size is less than 100 nm in at least one dimension (Haverkamp, 2010). Nanocomposites are known as materials which include in their composition one or more functional materials. Nanotechnology is a multidisciplinary field, as it combines the knowledge from different disciplines: chemistry, physics and biology amongst others (Klabunde, 2005; Schmid, 2006, 2010). Surface chemistry is also of great importance to the properties of NMs and nanoparticles (NPs) in particular. This is thanks to decreasing NPs size which causes their surface effects to become more significant, due to an increase in the volume fraction of surface atoms, which determines in some instances their special properties (Bowker, 2009). NPs have always been present in the

environment and have been used by humans in coincidental way, for example in decorative glasses and ceramics (Macanás et al., 2011; Walter et al., 2006). Some examples are carbon black, lustre pottery, or some catalysts, which were often used without knowing their nanoscale nature (Haverkamp, 2010). More recently, an important source of NPs are diesel engine emissions or dust from road fragmentation (Gramotnev, D. K. & Gramotnev, G. 2005; Haverkamp, 2010; Ristovski, 2006). In any case, engineered NPs are of the most economic importance at present (Hillie & Hlophe, 2007; Ju-Nam & Lead, 2008; Maynard, 2007; Narayan, 2010; Schulenburg, 2008; Schmid, 2010; Theron et al., 2008). Indeed, NPs are already applied in paints, where they serve to break down odour substances, on surgical instruments in order to keep them sterile, in highly effective sun creams, in slow release pharmaceuticals and many others (Schulenburg, 2008).

The development of uniform nanometer sized particles has been intensively pursued and within this broad field, metal NPs (MNPs) have attracted particular interest (Blackman, 2008; Campelo et al., 2009; Hyeon, 2003; Klabunde, 2005; Macanás et al., 2011; Park & Cheon, 2001; Schmid, 2010). The synthesis of MNPs may be carried out through various synthetic routes based either in bottom-up or top-down approaches, which have been summarized in recent publications (Ajayan et al., 2005; Bhushan, 2007; Campelo et al., 2009; Klabunde, 2005; Macanás et al., 2011; Schmid, 2010). One of the most frequently used procedures involves the use of capping stabilizing agents or surfactants, which help to prevent NPs aggregation and Ostwald ripening (Houk, et al., 2009; Imre et al., 2000). In such cases, stabilizers not only preserve NPs size but they also play a crucial role in controlling the shape of the NPs (Haverkamp, 2010; Kidambi & Bruening, 2005; Zeng et al., 2007). More exotic procedures have also been used for NPs synthesis including the use of ultrasound irradiation in the presence of aliphatic alcohols, docecyl sulfate or polyvinyl-2-pyrrolidone (Haverkamp, 2010; Vinodgopal et al., 2006). UV light, thermal treatments, cryochemical methods, pyrolysis or laser ablation have also been used, for instance, for silver or silver-gold NPs synthesis producing either simple or core@shell structures (Haverkamp, 2010; Nicolais & Carotenuto, 2005; Rao et al, 2004).

1.1 Drawbacks of nanoparticles

The main limitation in the wide application of MNPs is their insufficient stability arising from their tendency to self-aggregate (Houk et al., 2009; Imre et al., 2000; Macanás et al., 2011). In many instances, NPs are dispersed after synthesis in a liquid or solid medium by using different mechanochemical approaches (*transfer*) but the success of such approaches for dispersing the NPs is limited by their re-aggregation. This problem is common for many NPs obtained by using *ex-situ* fabrication techniques, i.e. NPs synthesized in a phase different from that of their final application (Campelo et al., 2009; Nicolais & Carotenuto, 2005). A completely opposite strategy that avoids NPs transfer stage is *in-situ* fabrication (Figure 1). In this case, NPs can be grown inside a matrix using different techniques, yielding a material that can be directly used for a foreseen purpose.

Another critical issue concerning NPs is their environmental and health safety risks, sometimes referred as nanotoxicity (Bernard et al., 1990; Borm & Berube, 2008; Chen & Fayerweather, 1988; Li et al., 2008).

NMs safety doubts have been underlined and their use has come under some scrutiny by both private and public institutions, regarding in particular the possible hazards associated with NPs either deliberately or inadvertently produced (Abbott & Maynard, 2010; Hassan, 2005; Ju-Nam & Lead, 2008; Klabunde, 2005;; Maynard, 2007; Theron et al., 2008).

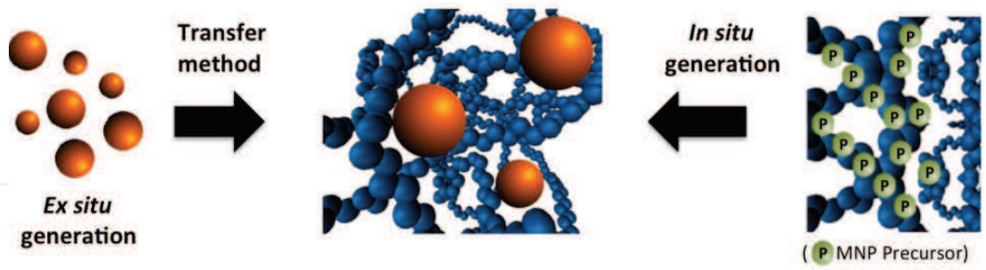


Fig. 1. Schematic comparison of *ex-situ* and *in-situ* nanoparticle generation methods.

Nowadays, there is a claim for more restrictive legislation that could allow a better protection for both human beings (workers and customers) and the global environment. A massive industrial production of NMs 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.

When considering the environmental risks of NMs, a paradox arises when one understands that potentially dangerous NMs also have the potential to produce more environmentally friendly processes, so-called 'green chemistry', and can be used to deal with environmental contaminants (Albrecht et al, 2006; Bell et al., 2006; Bottero et al., 2006; Haverkamp, 2010; Joo, 2006; Schmid, 2010; Schulenburg, 2008; Yuan, 2004).

An example of that is the use of engineered NPs for water treatment and groundwater remediation, which has been proved to be efficient but has also raised concerns for human exposure to NPs contained in the treated water. In order to guarantee the safe use of NMs, some aspects must be taken into account: knowledge, detection and prevention.

A comprehensive knowledge of properties of these materials (both physical and chemical) is important to find standards and control materials to work with as reference models (British Standards Institute: BSI PAS 130 [BSI], 2007; International Standards Organisation: ISO/TS 27687:2000 [ISO], 2000; Maynard, & Howard, 1999). Up to now, some environmental and health aspects of NPs have already been investigated (Abbott & Maynard, 2010; Li et al., 2008). An investigation into whether a substance is dangerous or not involves a determination of the material's inherent toxicity, the manner of its interaction with living cells and the effect of exposure time (Bottero et al., 2006). It should be noted that the doses or exposure concentrations used in *in vitro* and *in vivo* toxicological studies are most often extraordinarily high in comparison with possible accidental human exposure (Borm & Berube, 2008; Abbott & Maynard, 2010). Consequently, more research is needed before generalized statements can be made regarding NPs ecotoxicology. Few initiatives in this direction have been started so far. However, 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 (Schulenburg, 2008). Scientists and technologists in this area have to deal with NPs presence in the environment but do not have the appropriate tools and analytical methods for NPs detection and quantification to guarantee a satisfactory detection (Giannazzo et al., 2011). It is vital that efforts are dedicated towards this direction, as we have not yet invented a so-called "Geiger counter for NPs".

Currently, prevention of the escape of NPs to the environment is the best approach under consideration. If NPs do not reach the environment, we can confidently eliminate the danger for living beings (Zeng, 2004). In this sense, the embedding of NPs into organic or inorganic matrices reduces their mobility and prevents their appearance in the environment (Ajayan et al., 2005; Macanás et al., 2011). The use of nanocomposites such as these might be the simplest way to increase the safety of NMs. A complimentary approach to ensure the safety of NMs is to use magnetic NPs in their design (Vatta et al., 2006). Magnetic NPs are of great interest for researchers from a wide range of disciplines due to their useful properties and reaction to a magnetic field (Belotelov et al., 2005; Hayashi, 2007). In fact, polymeric materials containing magnetic NPs with certain functionalities (e.g., catalytically-active or bactericide) can find numerous technological applications. Their popularity lies in the fact that magnetic NPs can be easily recovered if leakage from the nanocomposite occurs by using simple magnetic traps (Hyeon, 2003; Qiao et al., 2007).
At the same time, immobilization of NPs within a solid matrix may cause potential problems. For example, during a catalytic reaction, if the support has a dense structure, diffusion of reactants to the nanocatalysts may cause diffusion resistance. Therefore, it is necessary to tune the structural properties of nanocomposites to make such functional NPs maximally accessible by the substrates of interest (chemical reagents to be catalyzed or bacteria to be eliminated) and active (Xu & Bhattacharyya, 2005).

1.2 Nanocomposites

The engineering of nanocomposites for different applications has been extensively tackled in the last decade, as demonstrated in the literature analysis depicted in Figure 2. In the words of Ajayan, "the promise of nanocomposites lies in their multifunctionality, the possibility of realizing unique combinations of properties unachievable with traditional materials" (Ajayan et al., 2005).

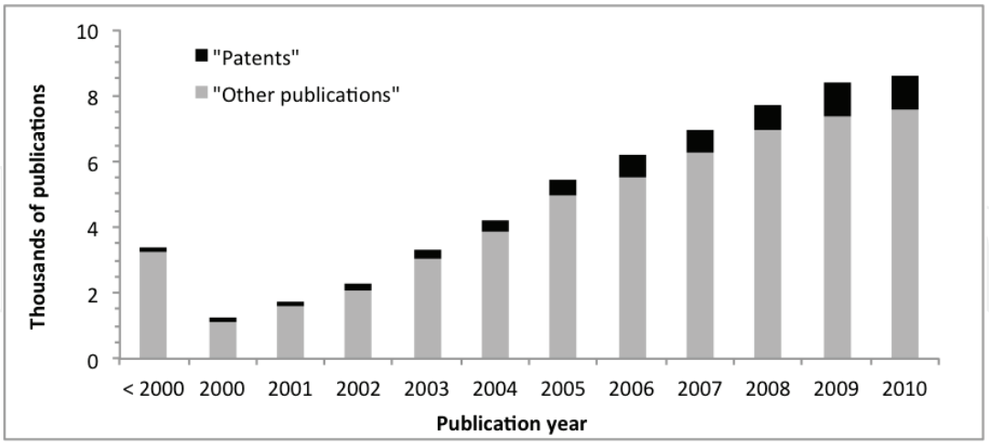


Fig. 2. Bibliographic analysis for the term "nanocomposite" in Scifinder Scholar.

Depending on the nature of the nanophase and the matrix, a wide variety of nanocomposites can be prepared(Kim & Van der Bruggen, 2010). These composite materials can assume a mixture of the beneficial properties of their parent compounds, leading to materials with improved physical properties and unprecedented flexibility (Figure 3). Among them, we will focus our attention on polymer-metal composites.

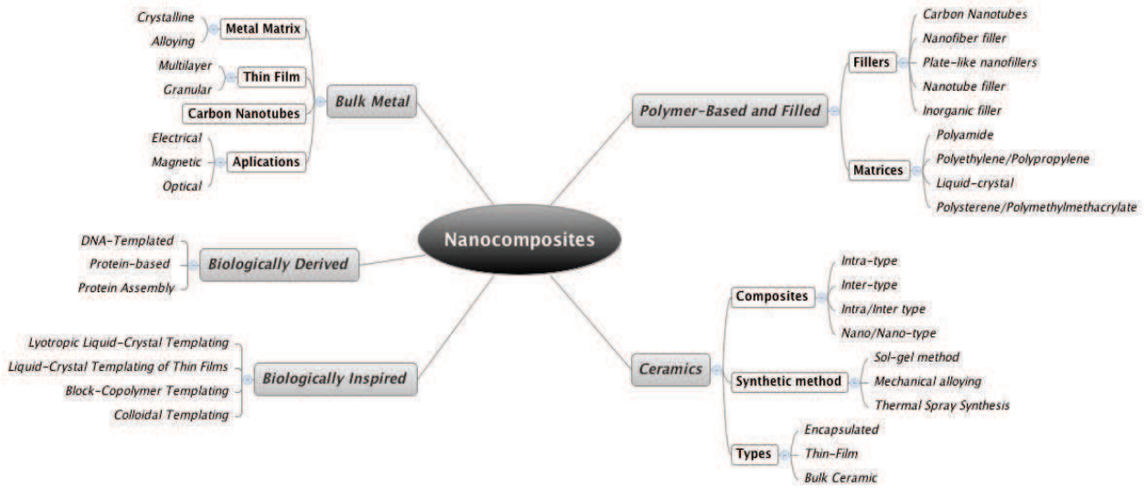


Fig. 3. General overview of nanocomposites.

2. Polymer-metal nanocomposites

The idea of using polymer-metal nanocomposites can be advantageous from two different points of view. Firstly, the development of polymer-stabilized metal NPs is considered to be one of the most promising solutions to the issue of NPs stability, by preventing their self-aggregation. Secondly, the use of immobilized NPs reduces the chances of their appearance in the environment (Klabunde, 2005; Nicolais & Carotenuto, 2005; Pomogailo & Kestelman, 2005; Rozenberg & Tenne, 2008). In addition, the incorporation of MNPs into polymeric matrices can endow the polymer with distinctive properties (Corain & Kralik, 2000; Jin et al., 2007; Pomogailo, 2000; Pomogailo et al. 2003; Muraviev 2005). A non exhaustive list of these advantages include: high permanent selectivity, low electrical resistance, good mechanical stability, high chemical stability, decreased permeability to gases, water and hydrocarbons, thermal stability, surface appearance and electrical conductivity (Nicolais & Carotenuto, 2005). In any case, the properties will highly depend on the type of nanocomposites and the procedures used for their preparation (see Figure 4 below).

The polymer-embedded nanostructures are potentially useful for a number of technological applications, especially as advanced functional materials (e.g., high-energy radiation shielding materials, microwave absorbers, optical limiters, polarisers, sensors, hydrogen storage systems, etc.) (Belotelov et al., 2005; Nicolais & Carotenuto, 2005). This chapter, apart from environmentally friendly nanocomposites materials and their advantages, is also focused on two kinds of applications: catalysis and biocide activity.

Polymer-metal nanocomposites can be prepared by two different approaches, namely, *in situ* and *ex situ* techniques. In the first case MNPs can be generated inside a polymer matrix by decomposition (e.g., thermolysis, photolysis, radiolysis, etc.) or by the chemical reduction of a metallic precursor inside the polymer. In the *ex situ* approach, NPs are first produced by soft-chemistry routes and then dispersed into polymeric matrices (Nicolais & Carotenuto, 2005). Within these categories of technologies, many different methods are used to produce inorganic NPs-based nanocomposites (Pomogailo & Kestelman, 2005). Both chemical and physical techniques can be used for this purpose but chemical processes have several advantages because of their relative simplicity. Inside this group of techniques there are two general types of procedures based on in-situ and ex-situ techniques (Figure 4).

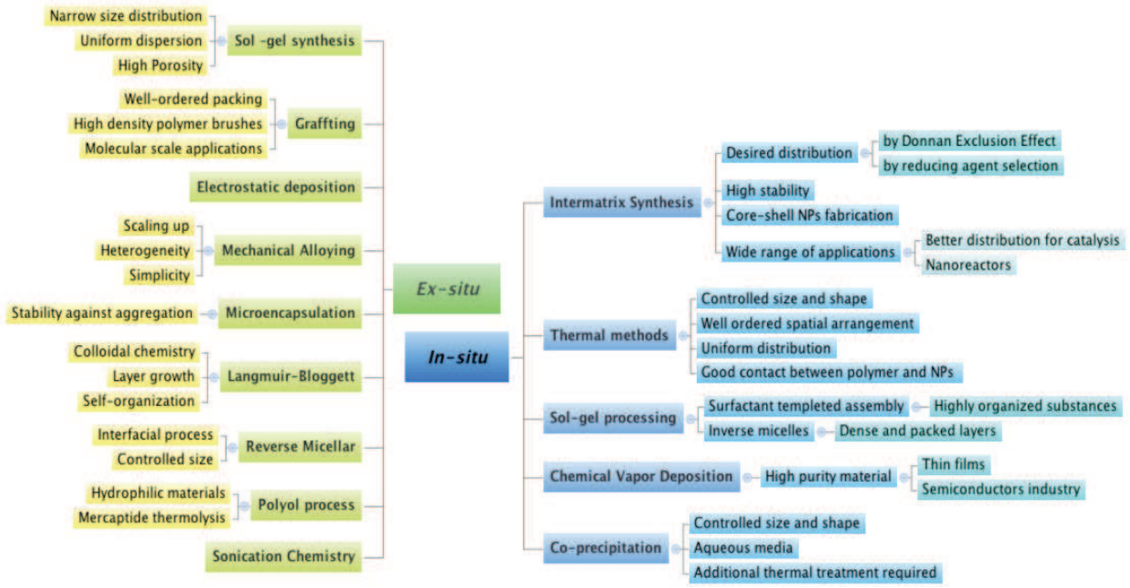


Fig. 4. *Ex situ* and *in situ* methods for polymer-metal nanocomposites synthesis.

Due to their technological advantages, *in situ* approaches are currently the focus of much attention and applications (Christy, 2003). Such approaches allow the preparation of a variety of metal–polymer nanocomposites with highly controllable particle size, material morphology and other properties. One of the most promising routes to produce the Polymer Stabilized/Supported MNPs (PSMNPs) and nanocomposites base on these is Intermatrix Synthesis (IMS), which consists of sequential loading of the functional groups of the polymer with desired metal ions (MNP precursors), followed by their chemical reduction (Alonso, 2010; Muraviev, 2005). The main advantages of this method are explained in detail in the following section.

3. Intermatrix synthesis of polymer-metal nanocomposites

3.1 Advantages

Figure 5 shows the main variables, which can be chosen as working parameters to carry out IMS of MNPs with desired composition and structure via an *in-situ* approach. The synthetic procedure and, consequently, the properties of the final nanocomposite will be determined by the following parameters (see Table 1): polymer matrix type and porosity, type of the functional groups, metal reduction conditions and some others. For example, the functional groups of the polymer, which may be cationic or anionic, determine the type of MNPs precursor and the sequence of IMS stages. PSMNP formation involves two simple consecutives stages: a) the loading of the functional groups of the polymer with metal ions (e.g., Co^{2+}) followed by b) their reduction inside the matrix resulting in the formation of monometallic MNPs. Reduction can be carried out by using $NaBH_4$ or other reducing agents. These two stages may be described by the following equations:

$$\text{a) } 2\text{R-SO}_3^-\text{Na}^+ + \text{Co}^{2+} \rightarrow (\text{R-SO}_3^-)2\text{Co}^{2+} + 2\text{Na}^+ \quad (1)$$

$$\text{b) } (\text{R-SO}_3^-)_2\text{Co}^{2+} + 2\text{NaBH}_4 + 6\text{H}_2\text{O} \rightarrow 2\text{R-SO}_3^-\text{Na}^+ + 7\text{H}_2 + 2\text{B(OH)}_3 + \text{Co}^0 \text{ (Co-MNPs)} \quad (2)$$

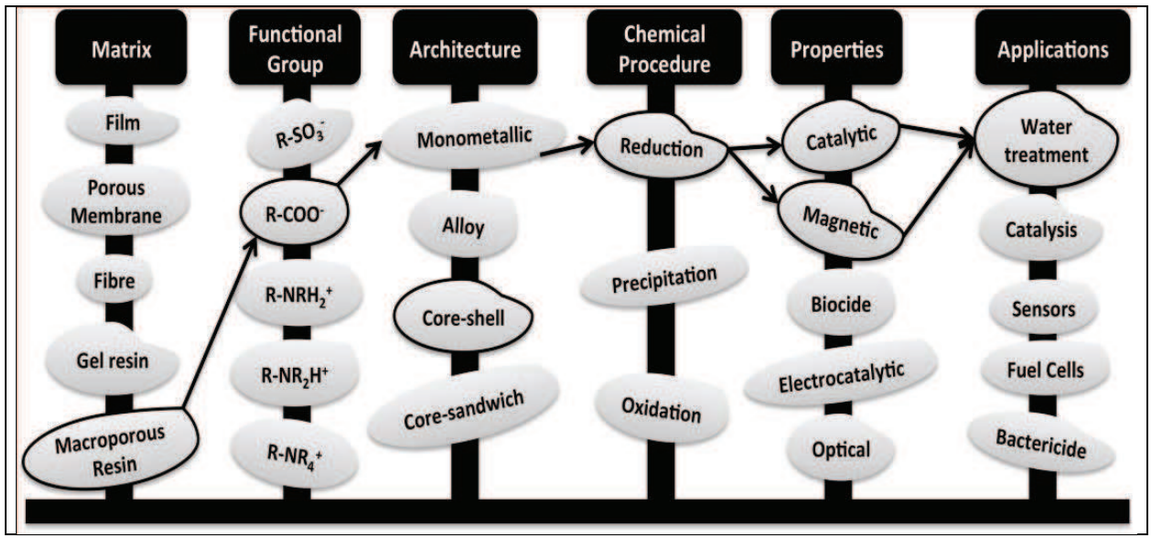


Fig. 5. Synthetic possibilities of IMS of MNPs.

As can be seen from equation (2), the functional groups of the polymer ($R\text{-}SO_3^-$) appear completely regenerated after the second IMS stage (metal reduction), i.e. they are converted back into their initial ionic form. This means that the metal-loading-reduction cycle can be repeated. In other words, the IMS method allows for multiple sequential metal-loading-reduction cycles. For example, this allows the production of core@shell MNPs by coating the monometallic MNPs obtained after the first cycle with a secondary functional metal shell. The properties of the metal shell (e.g. catalytic or bactericide) will determine the properties of the final nanocomposite.

Since the PSMNPs are strongly captured inside the polymer matrix, the hosting polymer prevents MNPs escape into the medium under treatment, providing the first level of the nanocomposite safety. In addition, IMS of bimetallic core@shell MNPs consisting of magnetic (specifically superparamagnetic) cores coated with a functional shell is of particular interest as it can also increase the nanocomposite safety. Indeed, the superparamagnetic nature of MNPs provides an additional level of the material safety as any MNPs leached from the polymer matrix can be easily captured by magnetic traps. This permits either complete prevention of any post-contamination of the treated medium or recycling of MNPs, a particularly important consideration when they contain precious metals. This novel strategy for the synthesis of new nanocomposite materials is based on 1) IMS of a low-cost metal core (e.g. Co, Fe or their oxides) with super-paramagnetic properties and 2) coating of the core with functional metal shell of desired thickness with catalytic or bactericide properties (e.g., Pd, Pt or Ag). Different kinds of functional polymers can be used for this purpose (see Table 1). The use of different polymeric materials for the synthesis of core@shell PSMNPs permits the final polymer-metal nanocomposites in different applications, such as catalysis or water disinfection filters, with the maximum efficiency.

Moreover, it has been shown that IMS of MNPs inside a polymer matrix results in the appearance of additional nanoporosity of the polymer, enhancing the mass transfer characteristics of the nanocomposite in comparison with those of the unmodified polymer.

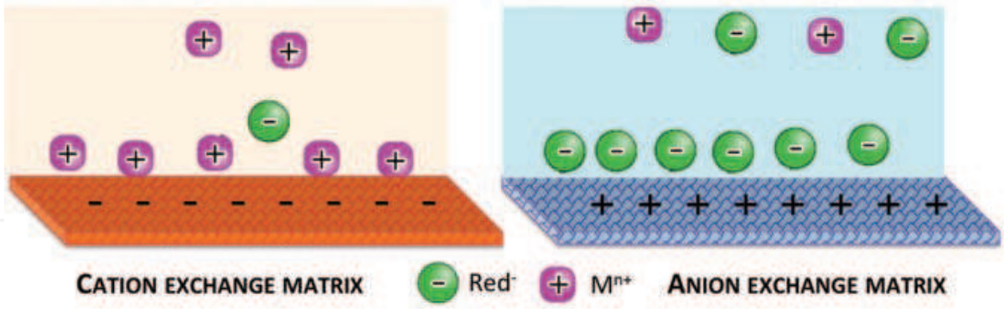


Fig. 6. Donnan exclusion effect.

3.2 Donnan-exclusion-effect as powerful tool for tuning structural properties of polymer-metal nanocomposites

An important property of nanocomposite materials is the accessibility of substrates of interest (chemical reagents or bacteria) to the functional MNPs. In this regard the distribution of MNPs on the surface of polymeric matrices appears to be the most favourable for their practical applications. The Donnan exclusion effect (Figure 6) 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 functional. This effect is observed, for instance, in IMS of MNPs in polymers with negatively charged functional groups when reducing metal ions with borohydride anions to zero-oxidation state. The polymer matrix bears negative charges due to the presence of well dissociated functional groups (see above equation 2). This means that the borohydride anions cannot deeply penetrate inside the matrix due to the action of electrostatic repulsion. The action of this driving force results in the formation of MNPs mainly near the surface of the polymer. Therefore, the desired distribution of MNPs inside stabilizing polymer can be achieved by using the Donnan exclusion driven IMS of MNPs in the functional polymers (e.g., ion-exchangers materials). The use of IMS coupled with Donnan exclusion effect allows the most favourable distribution of MNPs inside respective nanocomposites making them maximally accessible for the bacteria to be eliminated or reactants to be catalyzed (Alonso et al., 2010; Medyak, 2001; Yegiazarov, 2000).

Borohydride is one of the most often selected reducing agents for the synthesis of various MNPs, however in certain cases, e.g. in the case of iron and some other metals, the metal reduction can be accompanied by the appearance of boride impurities in the final material. At the same time, the high rate of the reduction process and some other advantages make it one of the most popular reducing agents. An alternative can be hydrazine hydrate, which has the some advantages such as, its strong reducing capability and low cost amongst others, and which has been used for the synthesis of a variety of metals (Xiaomin et al., 2005). However, its non-ionic nature limits the conditions of its application in the Donnan exclusion driven IMS of MNPs by low pH interval.

The reduction process can also affect the main MNPs parameters such as their shape and size, possible aggregation rate and structure as well as their distribution inside the supporting polymer (Sarkar, 2010). For instance, the use of mild reducing agents like N_2H_4 leads to much larger MNPs than a stronger reducing agent (such as $NaBH_4$) does. The SEM images shown in Figure 7 demonstrate the difference in MNPs distribution as the result of varying of the strength of the reducing agent.

As can be seen in Figure 7, the quantity of reduced metal (see the thickness of white peripheral layer) varies significantly with the strength of reducing agents ($NaBH_4$ >> $Na_2S_2O_4$). At the same time, their anionic nature provides the desired surface distribution of MNPs due to the action of Donnan exclusion effect.

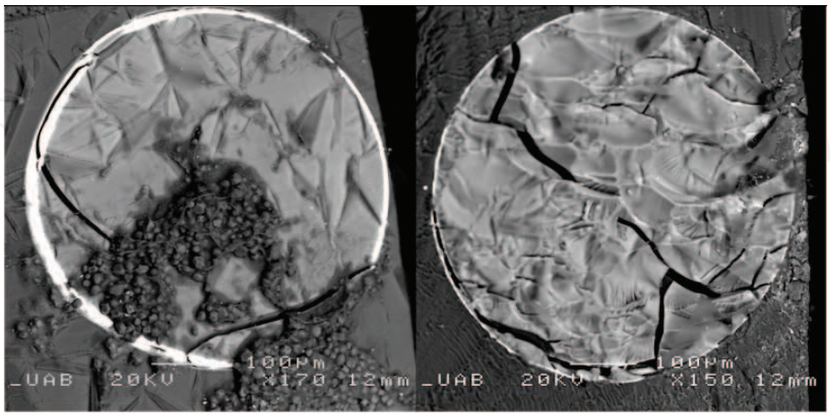


Fig. 7. SEM images of Pd-PSMNPs modified gel-type sulfonic resin reduced by 0.5M solutions of a) $NaBH_4$ and b) $Na_2S_2O_4$.

3.3 Non-crosslinked and crosslinked polymeric matrices

Ion-exchange materials are also known as ion exchange resins, whose matrices bear either cationic or anionic functional groups. The properties of ion exchange resins are determined by the degree of cross-linking of their matrices and the specific amount and type of ion exchange groups (functional groups). The polymer structure and the cross-linking degree determine the main chemical, physical and mechanical properties of these materials such, as their swelling ability and the mobility of exchanging ions inside the matrix (the intermatrix diffusivity), which are also very important for IMS of MNPs. Non-crosslinked gel polyelectrolytes can also be used for this purpose as they have some advantages, such as solubility in some organic solvents. This can be used for preparation of MNPs solutions (or inks), which can be applied for the purposeful modification of the surfaces of some devices, such as, electrochemical sensors (Macanás et al, 2011; Muraviev 2005). Some examples of polymeric matrices, which have been used for IMS of Pd@Co MNPs are listed in Table 1).

The membranes made of non-cross-linked sulfonated polyetherether ketone (SPEEK) have been used as a model polymeric matrix for IMS of various MNPs to optimize the synthetic conditions and to study the structural characteristics of both MNPs and respective nanocomposites. The practical applications of functional MNPs-based nanocomposites (in catalysis or water treatment) require the use of cross-linked polymers in the form of granulated resins or fibers of both gel and macroporous types.

The matrices of macroporous polymers, being highly crosslinked, are generally tougher than their gel analogs and are more resistant to mechanical stresses, osmotic pressure, and chemical degradation due to the action of oxidizing agents. On this basis, the nanocomposites are optimally applicable to catalytic processes (Qiao, 2007).

In summary, the main properties of ion exchange materials which must be taken into account before IMS of MNPs can be carried out are the following: 1) uniform or controlled bead or fiber size, 2) chemical and physical resistance, 3) sufficiently high ion-exchange capacity, 4) fast ion-exchange kinetics and some others.

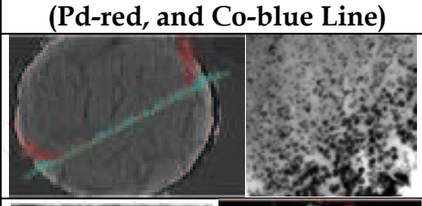
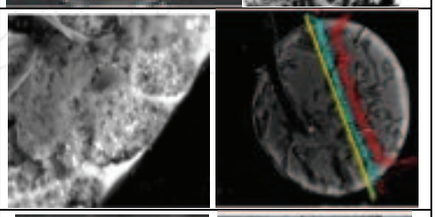
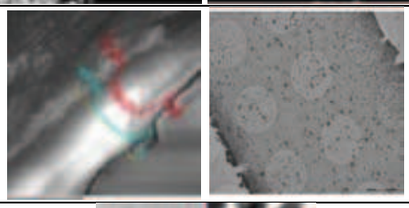
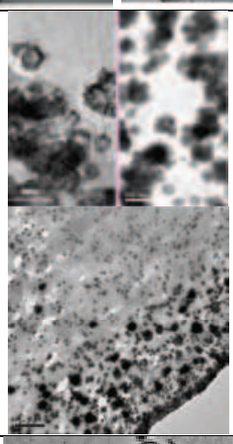
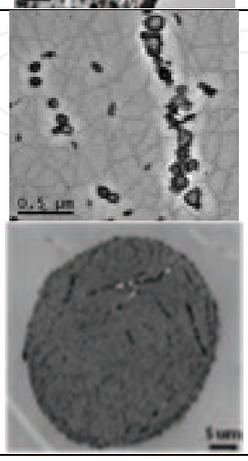
Functional group	Form	Polymeric matrix	SEM, TEM images and EDS spectra of resulting nanocomposites (Pd-red, and Co-blue Line)
$R\text{-}SO_3^-$	Granulated gel resin	PE-PVB	
$R\text{-}COO^-$	Granulated macroporous resin	Acrylic	
$R\text{-}SO_3^-$	Membrane (dense)	SPEEK	
$R\text{-}SO_3^-$	Fiber (non-woven)	PP fiber with graft copolymer of styrene and divinilbenzene	
$R\text{-}COO^-$	Fiber (non-woven)	PP fiber with graft co-polymer of acrylic acid on polypropylene	

Table 1. Examples of polymeric matrices applicable for IMS of MNPs.

4. Magnetic nanoparticles

Magnetic NPs are of great interest for researchers from a wide range of disciplines, including catalysis, biotechnology/biomedicine and environmental science and technology (Hyeon, 2003; Lu et al., 2007; Pankhurst et al., 2003; Vattaet al., 2006). For many practical applications, it is necessary to develop some strategies to chemically stabilize the magnetic NPs against degradation (e.g., oxidation) during (or after) their synthesis and, especially, during their use. Therefore, many efforts have been dedicated to the synthesis of polymeric materials containing magnetic NPs, making them ideal candidates for many technological applications (Qiao, 2007; Suchorski et al., 2008). Systems based on these kinds of nanocomposites are employed in magnetic recording devices, ferrofluids, medical diagnosis, drug delivery, pigments for paintings and ceramics (Bastida et al., 2006).

For example, a new family of potential contrast agents has been recently synthesized based on magnetic nanoparticles stabilized using commercially available polyelectrolytes (such as poly(sodium-4-styrene) sulfonate) that act as both nanocomposite assembly directors and water-stable surfactants, instead of the classical biopolyelectrolyte DNA (Corr et al., 2008; Davies et al., 2011). Hence, using straight-forward one-step procedures, magnetic fluids can be prepared. Similar approaches have also been developed for non-magnetic nanoparticle suspensions (Alonso et al., 2010; Kidambi & Bruening, 2005).

It is also important to note that quite different metals or their compounds show similar magnetic properties. Therefore, a wide variety of magnetic NMs and nanocomposites based on these can be prepared. These NMs can be iron oxides, such as Fe_3O_4, pure metals, such as Fe and Co, spinel-type ferromagnets, such as $MgFe_2O_4$, $MnFe_2O_4$, and $CoFe_2O_4$ and some others (Davies et al., 2011). The main advantages and drawbacks of magnetic NMs are summarized in Figure 8. For instance, regarding the materials safety, it is important to notice that due to their low level of toxicity and their good magnetic properties, the use of ferrites is very convenient for biological applications (Laurent et al., 2008).

However, magnetic NPs do not usually have the desired properties required for their immediate application in catalysis or water desinfection. Therefore, they can serve as a magnetic core in core@shell MNPs, in which the shell consists of the metal with the desired activity (catalytic or bactericide). Core@shell MNPs of this type can be easily prepared by using IMS technique (Macanás et al., 2011) and the resulting nanocomposites can be applied in catalysis or water treatment (Medyak, 2001). In catalysis, for instance, due to the magnetic properties of MNPs, the nanocomposites can be easily recovered and reused in sequential catalytic cycles, which is particularly important for MNPs containing platinum group metals.

In fact, the synthesis of new nanocomposite materials based on the synthesis of polymer-immobilized bi- and poly-metallic NPs with core@shell architecture consisting of a low-cost magnetic (ferromagnetic or super-paramagnetic) core coated with a functional shell (having, for example, catalytic or bactericidal properties) is of particular interest for many advanced applications (Corain & Kralik, 2000; Medyak, 2001; Muraviev et al., 2008a).

It is also important to emphasize that in some cases the performance of such nanocomposite materials in their practical application can be comparable to (or often even better than) that of their monometallic analogs (containing shell-metal NPs). At the same time, the cost of nanocomposites containing core@shell MNPs is far lower due to significantly lower loading with precious metals (e.g., Pt, Pd or Ag). These considerations represent an additional advantage of these NMs.

As it has been previously reported (Muraviev et al., 2006, 2008b) that the IMS technique makes it possible to prepare both mono-component and bi-component NPs (metal- or metal oxide-based) in different cation exchange matrices (Table 1, Figure 9). In all cases, the polymer–metal nanocomposites demonstrate quite strong magnetic properties and are easily attracted by permanent magnets. Some parameters such as NPs size and spatial distribution were studied by examining sample cross-sections by Scanning Electron Microscopy (SEM) (see Figure 9). Similar results were obtained for Ag@Co and Ag@ferrite (such as Fe_3O_4 and $MnFe_2O_4$) PSMNPs synthesized in different types of polymer matrices (sulfonic and carboxylic resins) following modified literature procedures (Corr at al., 2008, Alonso, 2011).

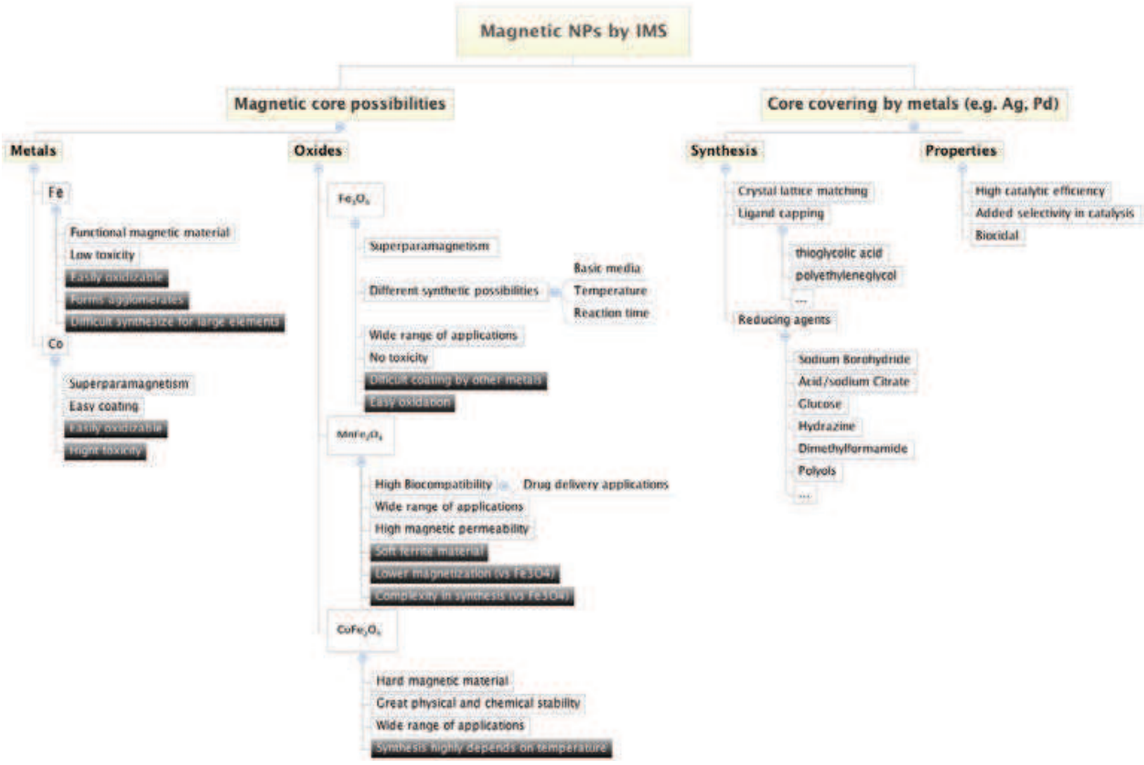


Fig. 8. General overview of preparation of magnetic nanocomposites by IMS technique. Advantages and drawbacks are given in white and black, respectively.

In all cases, NPs were distributed heterogeneously inside polymer matrices and with far higher concentrations on the surfaces of the nanocomposites. This distribution is favorable for both catalytic and water disinfection applications.

The magnetic properties of both bimetallic (Pd@Co and Ag@Co) and metal-metal oxide ($Ag@Fe_3O_4$) core@shell NPs within the different polymer resins were found to be super-paramagnetic at room temperature (Figure 10). Magnetic measurements were carried out using SQUID magnetometer and Vibrating Sample Magnetometer.

The magnetization of polymer-Pd@Co nanocomposites can be seen in Figure 10 (see left hand side), and is higher for the sulfonic resin than for the carboxylic one. This difference can be attributed to a higher Co concentration in the first resin in comparison with the second one (due to the conditions of IMS procedure). The magnetization of the NPs magnetite does not decrease after their coating with silver shell, as shown in Figure 10b.

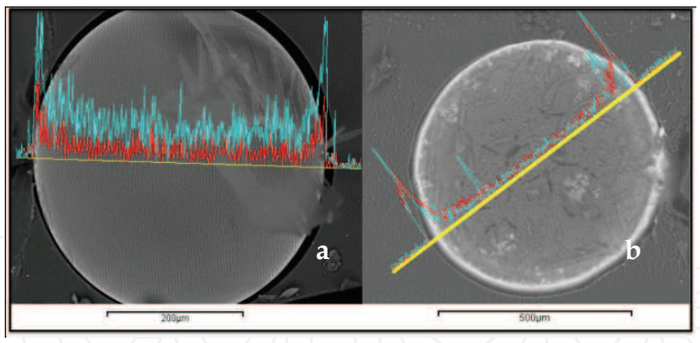


Fig. 9. SEM images of ferric oxide NPs in sulfonic ion exchange polymers: a) $MnFe_2O_4$ gel-type resin where the blue line represents Mn and the red line represents Fe, and b) $Ag@Fe_3O_4$ gel-type resin where blue line represents Ag and the red line represents Fe.

Moreover, as it can be seen the bimetallic $Ag@Fe_3O_4$ NPs demonstrate a sort of a synergistic effect towards magnetization similar to that reported for Pt@Co alloys (Lee et al., 2005) and Pd@Co core@shell MNPs (Durand et al., 2008) however, this point requires further investigation.

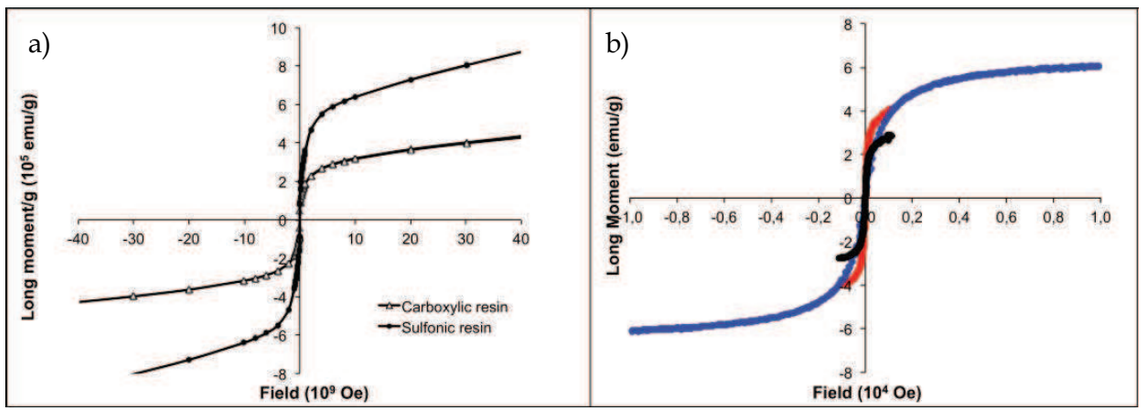


Fig. 10. a) SQUID hysteresis curves of Pd@Co NPs in carboxylic and sulfonic resins and, b) SQUID hysteresis curve of ferrite core NPs synthesized in sulfonic resin: blue) $Ag@Fe_3O_4$, red) Fe_3O_4, black) $Ag@Fe_3O_4$ half concentration compared with blue).

5. Applications of polymer-metal nanocomposites

5.1 Catalysis

As previously mentioned, catalysis is one of the largest areas of MNPs application (Campelo et al., 2009; Zeng, 2004). Platinum Group Metal (PGM) NPs are very well-known as highly selective catalysts and are widely used in organic synthesis, chemical industry and other areas (Durand et al., 2008). Heterogeneous catalytic reactions are known to proceed on the surface of the catalyst. This means that in the case of monometallic MNPs, the central part of the catalyst particle does not take part in the catalytic process and can be substituted by another metal. The synthesis of core@shell catalyst MNPs composed of a low-cost metal core coated with a thin PGM-shell can substantially lower the total cost of the catalyst in comparison with monometallic PGM-MNPs. Incorporating a core metal with magnetic

functionality provides an additional advantage to these nanocatalysts, allowing them to be easily recovered from the reaction mixture and recycled.

Pd@Co MNPs synthesized in different polymeric matrices have been tested as catalysts for various cross-coupling reactions (Table 1, Figure 11) (Son et al, 2004), although they can also be applied as catalysts in other processes like dehalogenation, hydrodechlorination, carbonylation or oxidation (Wilson et al., 2006; Umpierre et al., 2005).

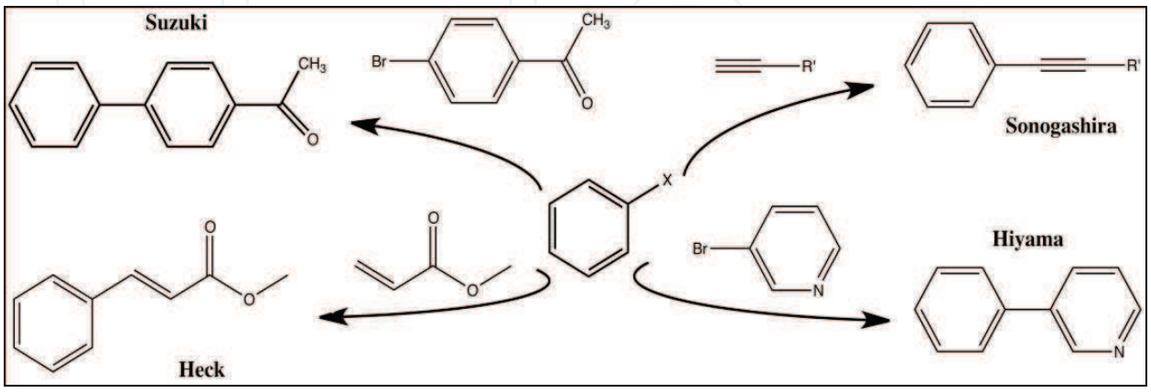


Fig. 11. Typical **c**ross-coupling reactions tested with Pd@Co NPs as catalyst.

Non-supported monometallic palladium MNPs have been efficiently used to study NP effects in catalysis. Supported Pd-MNPs embedded in polyelectrolyte films, beads or fibers can be easily prepared by employing the IMS technique (Alonso et al., 2010; Ouyang et al., 2010). Certain types of Pd-PSMNPs synthesized by IMS have been tested as catalysts for the Suzuki reaction (Medyak, 2001), which is a cross coupling reaction between arylboronic acids and aryl halides leading to the formation of biphenyls (Niembro et al., 2008). However, bimetallic catalysts such as alloy MNPs or core@shell MNPs are of particular interest for several reasons: i) the combination of two metals may provide control over catalytic activity, selectivity and stability, and ii) by controlling the thickness of a catalytically-active shell, one can improve the "catalytic atom economy" (Baranchikov, 2007).

The catalytic activity of various nanocomposite materials in the form of a membrane, fiber or granulated resin (bearing either carboxylic or sulfonic groups, Table 1) with core@shell Pd@Co PSMNPs distributed mainly on the surface part of the polymeric matrix was tested in Suzuki cross-coupling reaction (Figure 12).

As shown in Figure 12, the catalytic activity of fibrous nanocomposites does not depend on the type of fiber functionality and both carboxylic and sulfonic fibers achieve a 100% reaction yield. Due to the higher stability of the carboxylic matrix it was possible to successfully use it in the successive catalytic cycles (up to 3). The insufficient chemical stability of the sulfonic fibers did not allow their complete separation and recovery from the final reaction solution mixture, despite the magnetic properties of the material. When using a sulfonated polyetheretherketone (SPEEK) nanocomposite membrane, the reaction yield in the second catalytic cycle was dramatically reduced due to the partial dissolution of this non-crosslinked polymer in the solvent mixture (DMF:water) under the reaction conditions and substantial loss of the catalyst PSMNPs. The results obtained with granulated ion exchange resin nanocomposites show that their catalytic efficiency is lower than that observed for the fibers what can be attributed to the higher surface area of fibers providing

increased contact between the reagents and catalyst MNPs. Although no dramatic differences have been observed between carboxylic or sulfonic resins, the macroporous structure of the later is known to be more applicable for catalytic reactions (Biffis et al., 2000; D'Archivio et al., 2000; Zagorodni, 2007).

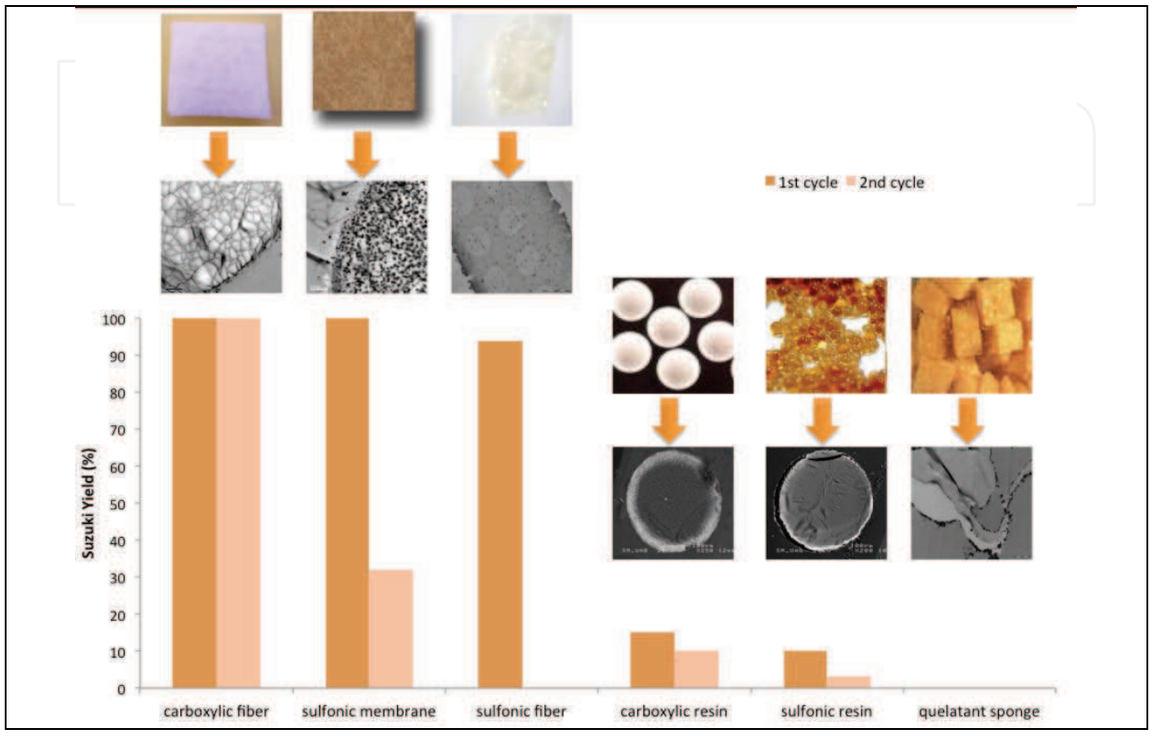


Fig. 12. Comparison of catalytic activity for different kinds of catalytic nanocomposites.

Finally, the nanocomposite sponge demonstrated essentially zero catalytic activity due to difficulties associated with the accessibility of reactants to the catalyst MNPs located mainly in the internal part of the sponge.

Therefore, the properties of the polymeric matrices themselves (distinct from those of MNPs) represent another important parameter, which determines the applicability of the catalytically-active nanocomposite under certain reaction conditions. The chemical stability, the specific surface area and the penetrability of the nanocomposite matrix towards chemical reagents are also important parameters, which has to be taken into account when choosing the polymeric supports for IMS of catalytically-active MNPs.

5.2 Biocide and antibiofouling applications

The presence of microorganisms in water makes disinfection treatment before consumption a necessity. In the majority of cases, the potable water is currently disinfected by using various chemicals such as ozone, chlorine and some of its compounds and others having bactericide properties. The Chemical-free disinfection is considered to be an attractive alternative and it is usually associated with silver metal. While silver has been known to be a bactericide element for at least 1200 years, colloidal silver or silver MNPs have recently been recognized and tested in various applications as excellent antimicrobial agents because of their high biocide activity (Kong & Jang, 2008; Law, 2008; Pal et al., 2007). The

antibacterial action of silver MNPs is still under debate but it has been reported to be similar to that of silver ions, which bind to DNA, block transcription, and therefore interrupt the bacterial respiration and the adenosine triphosphate synthesis. In *in vivo* assays, the majority of Ag-MNPs are often located in the membranes of treated *E. coli* cells and only a few of them penetrate inside the cells. However, the exact biochemical and molecular aspects of the actions of this distinct silver species have never been directly addressed (Sondi & Salopek-Sondi, 2004).

Ag-MNPs purportedly present high antibacterial activity, relatively low toxicity, chemical and thermal stability, and a long-lasting action period (Cubillo et al., 2006).The stabilization and immobilization of Ag-MNPs in different matrices has recently gained great attention from scientists and technologists for two main reasons: i) immobilization in the matrix can improve the safety of the material (due to the reasonable doubt of their human toxicity) and ii) the immobilization improves the handling of MNPs and simplifies their final application. The use of Ag-MNPs containing nanocomposites can also help to solve another important technological problem associated with water treatment, known as biofouling. The Biofouling (or biological fouling) is the undesirable accumulation of microorganisms on the surface of water treatment devices and materials such as, reverse osmosis membranes, cooling water cycles, ion exchange resins, etc. (Kim & Van der Bruggen, 2010).

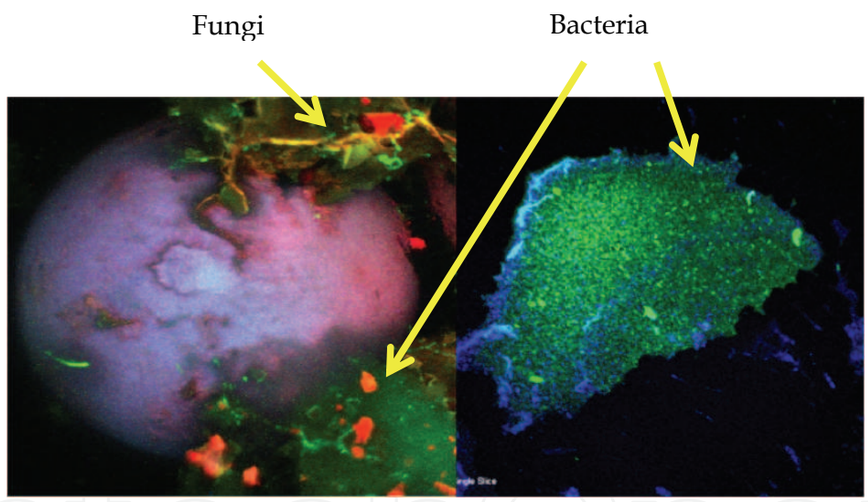


Fig. 13. Confocal microscope image of surface of carboxylic ion exchange resin after being used for the domestic water treatment.

As an example, Figure 13 shows confocal microscope images of the biofouling of ion exchange resin beads taken after their use in a conventional domestic tap water treatment filter usually used for the removal of undesired metal ions (hardness ions, iron, heavy metal ions, etc.). As shown, the surface of the resin beads appears to be strongly contaminated by the accumulated fungi and bacteria. The use of ion exchange resins modified with Ag@Co MNPs for conventional domestic water treatment helps to solve this problem. The surface of the nanocomposite resin beads appears to be far less biocontaminated after the treatment of the same water volume. A similar solution can be used for prevention of biofouling of the membranes used at reverse osmosis water treatment plants (Taurozz, 2008). The surface modification of ion exchange materials used for traditional water treatment (ion exchange resins, membranes, etc.) with ecologically safe MNPs, which have high biocide activity (e.g.,

Ag@Co or Ag@Fe_3O_4) can successfully solve the problems associated with biofouling of their surfaces in the course of water treatment processes.

The authors of this chapter (A. Alonso, M.Muñoz and D.N. Muraviev) have recently developed and patented (Muraviev et al., PCT/ES2010/000323, 23th of July, 2010) a methodology for the surface modification of commercially available ion exchange materials with core@shell MNPs containing silver shell and a magnetic core (Savage & Diallo, 2005). These materials represent the environmentally friendly bactericide nanocomposites suitable for conventional water treatment coupled with reagent-free disinfection. The main advantages of such materials are:

- First, MNPs are strongly captured inside the polymer matrix that prevents their escape into the medium under treatment.
- Second, the surface distribution of MNPs within the material provides their contact with the bacteria to be eliminated and fast water disinfection.
- Third, the super-paramagnetic nature of MNPs provides an additional level of the material safety as the use of a simple magnetic trap prevents any post-contamination of treated water with MNPs leached from the polymer matrix.
- Fourth, the surface location of MNPs does not essentially influence the main characteristics of the ion exchange material such as, the ion exchange capacity and some others, which permits the use of these nanocomposites for complex water treatment, including removal of undesired ionic contaminants and reagent-free disinfection.

The bactericide properties of the nanocomposites were evaluated by using antibacterial kinetics tests, by the determination of the minimum inhibitory concentration, and by the modified Kirby-Bauer test. The antibacterial activity of Ag@Co-PSMNPs towards several types of microorganisms such as *Escherichia coli, Staphylococcus aureus* (Gram-positive bacteria), *Salmonella, Klebsiella, Pseudomonas aeruginosa, Enterobacter* (all Gram-negative bacteria) was tested and confirmed high bactericide activity of the nanocomposites (Alonso et al., Unpublished results).

The antibiofouling activity of nanocomposite materials was evaluated by carrying out the following tests: water with a constant concentration of Psedomonas Putida (103cfu/ml) was passed through the columns loaded with non-modified ion-exchange resin and with the same resin modified with Ag-MNPs. The samples of treated water were collected periodically, seeded, incubated and subjected to Petri dish recounts. Figure 14 shows that the colonies of Pseudomonas were formed on the surface of polymer without Ag-MNPs whereas the surface of Ag-MNPs modified resins appeared to be essentially free from biofouling.

The results presented in this section represent an integration of Nanotechnology and Bacteriology, which may lead to possible important advances in the formulation of new types of bactericides. Moreover, additional studies of the biocide activity of these nanomaterials towards Gram-positive and Gram-negative bacteria of other types have also been carried out in order to fully evaluate their potential use as a new bactericidal material.

5.3 Complex water treatment

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 (**Ruparelia,** 2008). The importance of potable water for the people in some countries dictates the need for the development of innovative technologies and materials for the production of safe potable water.

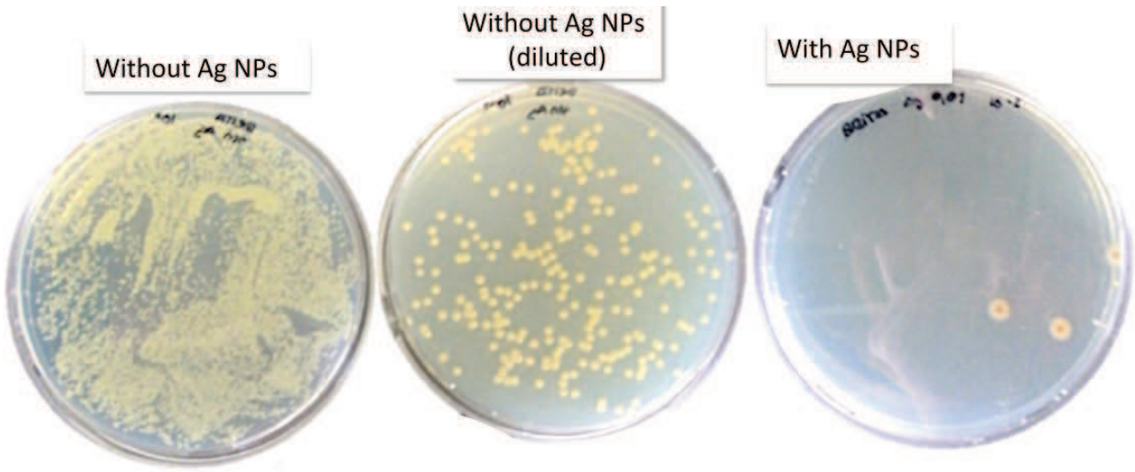


Fig. 14. Petri dishes with cultures from treated and untreated water.

Nowadays the different strategies for water disinfection include (Das, 2005): chemical agents (e.g. chlorine and its compounds, ozone, hydrogen peroxide and some others), physical treatment (e.g. heat, UV-irradiation, etc.) and mechanical means (e.g., ultrafiltration). All these strategies differ from each other by their efficiency, water treatment cost and potential usability. For instance, heat is commonly used in the beverage and dairy industry, but it is not a feasible means of disinfecting large quantities of wastewater because of the high cost. The use of oxidizing chemical substances can cause corrosion in the water treatment and supplying facilities.

Thus, new approaches for the complex water treatment are continually being examined. However, it appears to be quite difficult to fulfill all the necessary requirements such as, lower overall treatment cost, durablility and high efficiency, higher than current options for the removal of contaminants from water. Nanotechnology has been identified as a technology that could play an important role in resolving many of the problems involving water purification and quality (Bottero et al, 2006; Savage & Diallo, 2005; Theron et al., 2008; Weber et al., 2003). As such, the application of MNPs has been extensively studied for reductive dechlorination of halogenated organic compounds in ground water (Xu & Bhattacharyya, 2005). One of the most efficient elements is iron nanoparticles as pure monometallic entities or in combination with platinum (bimetallic particles). However, the long-term stability of these nanoparticles can be enhanced by immobilization in a solid support (Ponder et al., 2000). A variety of nanomaterials are in various stages of research and development, each possessing unique functionalities that are potentially applicable to the remediation of industrial effluents, groundwater, surface water and drinking water.

It is worthy to note that ion exchange materials are widely used for various water treatment processes, mainly to eliminate undesired or toxic ionic impurities such as hardness ions, iron, heavy metals, and others. The modification of such supports with bactericide MNPs enables the combination of traditional water treatment with disinfection to eliminate microbiological contaminants. Using this approach, two complementary water treatment steps could be performed with a single material. Nonetheless, the following important

points have to be taken into account when using silver MNPs as a bactericide agent (Savage& Diallo, 2005):

1. The size of microorganisms to be eliminated from water in the course of its disinfection with polymer-metal nanocomposite does not allow them to deeply penetrate inside solid biocide materials. For this reason, Ag-MNPs have to be located near the surface of the immobilizing matrix to make them maximally accessible to bacteria.
2. Since, free Ag-MNPs have been reported to be far more toxic than bulk silver metal polymer-stabilized silver MNPs and the nanocomposites based on these represent one of the most attractive solutions to this problem since these materials guarantee at least the first level of safety due to the strong retention of MNPs by polymer matrix.
3. Even if the immobilization of Ag-MNPs in the polymer might prevent post-contamination of treated water with MNPs, the surface location of Ag-NPs in the stabilizing polymer increases the probability of their uncontrollable escape from the matrix. This, in turn dictates the necessity providing the nanocomposite material with an additional safety level, which can be based on the use of ferromagnetic (or super-paramagnetic) polymer-stabilized-Ag-MNPs. In such cases, NPs which have escaped from the polymer into the treated water can be easily captured by a simple magnetic trap.

Finally we would like to emphasize that all of the above requirements are fulfilled by the materials developed by our group (Weber et al., 2003). A possible way to apply in complex water treatment is shown in **Figure 15**.

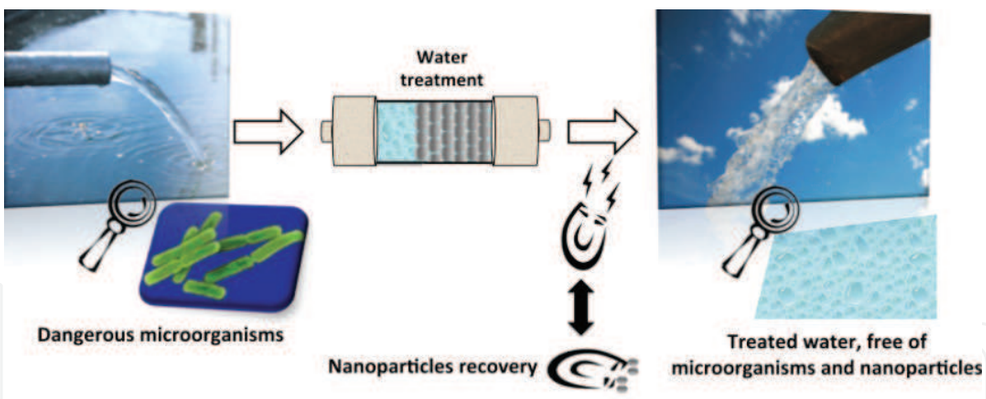


Fig. 15. Use of environmentally friendly nanocomposites for complex water treatment.

6. Conclusions

The following conclusions can be derived from the results summarized in this chapter:

1. The Intermatrix Synthesis (IMS) technique represents a promising technique that allows the production of a wide variety of polymer–metal nanocomposites of practical importance for different fields of modern science and technology. The attractiveness of this technique is determined not only by its relative simplicity but 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 obtain 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 mainly functionalized polymers, i.e. those bearing functional groups, which are capable of binding to metal ions prior to their reduction inside the polymer matrix (IMS of PSMNPs). The dissociated ionogenic functional groups of the polymer bear certain charges, making it it possible to couple the IMS technique with the Donnan exclusion effect when using ionic reducing agents bearing the charge of the same sign as that of the polymer at the metal reduction stage of IMS.
3. We have demonstrated that the nature of the agent used to reduce metal ions to MNPs plays an important part in IMS as it determines the conditions of MNPs formation inside the polymer matrix (metal reduction stage) and their distribution inside the matrix. Thus, the use of anionic reducing agents (e.g., borohydride) for IMS of PSMNPs in cation 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 water disinfection, catalysis and some others.
4. The properties of metal–polymer nanocomposites 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, which enhances the rate of mass transfer inside the nanocomposites as well as some other structural parameters which are of great importance in their practical applications.
5. The IMS of core shell PSMNPs consisting of super-paramagnetic 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 nanocomposites can be easily recovered from the reaction mixture and reused. In water treatment applications, the magnetic nature of MNPs permits prevention of their uncontrollable escape into the treated water by using simple magnetic traps.
6. Finally, the last and the most important cocnclusion, in our opinion, concerns the general strategy in the development of novel nanocomposite materials. This strategy has to be focused not only on the desired properties of the 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.

7. Acknowledgements

We are sincerely grateful to all our associates cited throughout the text for making this publication possible. Part of this work was supported by Research Grant MAT2006-03745, 2006–2009 from the Ministry of Science and Technology of Spain, which is also acknowledged for the financial support of Dmitri N. Muraviev.
We also thank ACC1Ó for VALTEC 09-02-0057 Grant within "Programa Operatiu de Catalunya" (FEDER). AGAUR is also acknowledged for the predoctoral grant supporting A.Alonso.

8. References

Abbott, L.C. & Maynard, D.M. (2010). Exposure Assessment Approaches for Engineered Nanomaterials. *Risk Analysis,* vol. 30, 11, pp. 1634-1644

Ajayan, P.M. et al. (2005). *Nanocomposite science and technology*. pp. 230

Albrecht, M. A., C. W. Evans, & C. L. Raston. (2006). Green chemistry and the health implications of nanoparticles. *Green Chemistry,* 8, 5, pp. 417–432.

Alonso, A. (2011). Unpublished results.

Alonso, A., et al. (2010). Donnan-Exclusion-Driven distribution of catalytic ferromagnetic nanoparticles synthesized in polymeric fibers. *Dalton Transactions*, vol. 39, pp. 2579 – 2586

Baranchikov, A.Y. (2007). Sonochemical synthesis of inorganic materials. *Russian Chemical Reviews*, vol. 76, 2, pp.133–151.

Bastida, M.A. et al. (2006). Magnetic properties of Co/Ag core/shell nanoparticles prepared by successive reactions in microemulsions, *Journal of Magnetism and Magnetic Materials,* vol. 300, 1, pp. 185–191

Bell, C. A. et al. (2006). Surface-functionalized polymer nanoparticles for selective sequestering of heavy metals. *Advanced Material, vol.* 18, 5, pp. 582–586.

Belotelov, V.I., Perlo, P. & Zvezdin, A.K. (2005). Magnetooptics of granular materials and new optical methods of magnetic nanoparticles and nanostructures imaging. In: L. Nicolais and G. Carotenuto (Eds.). *Metal–Polymer nanocomposites,* John Wiley & Sons, pp. 201-240.

Bernard, B.K. et al. (1990). Toxicology and carcinogenesis studies of diatery titanium dioxide-coated mica in male and female Fischer 344 rats. *Journal of Toxicology and Environmental Health*, 29, 4, pp. 417–429.

Bhushan, B. (2007). Springer Handbook of nanotechnology (2nd Ed.). pp. 1916, ISBN: 354029855X

Biffis et al. (2000). The Generation of Size-Controlled Palladium Nanoclusters Inside Gel-Type Functional Resins: Arguments and Preliminary Results. *Advanced Materials,* vol. 12, 24, pp. 1909-1912.

Blackman, J.A. (2008). *Metallic nanoparticles*. pp. 385, ISBN: 9780444512406

Borm, P. & Berube, D. (2008). A tale of opportunities, uncertainties, and risks. *NanoToday,* vol. 3, 1-2, pp. 56-59

Bottero, J.Y., et al. (2006). Nanotechnologies: tools for sustainability in a new wave of water treatment processes. *Integrated Environmental Assessment and Management,* vol. 2, 4, pp. 391-395

Bowker, M. (2009). A prospective: Surface science and catalysis at the nanoscale, *Surface Science*, vol. 603, 16, pp. 2359-2362

British Standards Institute: BSI PAS 130. (2007). *Guidance on the labelling of manufactured nanoparticles and products containing manufactured nanoparticles*

Campelo, J.M. et al. (2009). Sustainable Preparation of Supported Metal Nanoparticles and Their Applications in Catalysis. *ChemSusChem,* vol. 2,1, pp. 18-45

Chen, J.L. & Fayerweather, W.E. (1988). Epidemiologic study of workers exposed to titanium dioxide. *Journal of Occupational Medicine and Toxicology*, 30, 12, pp. 937–942.

Christy, R. (2003). Effects of Surface Coordination Chemistry on the Magnetic Properties of $MnFe_2O_4$ Spinel Ferrite Nanoparticles. *Journal of American Chemistry Society*, vol. 125, pp. 9828-9833

Corain, B. & Kralik, M. (2000). *Journal of Molecular Catalysis A.: Chemical,* vol.159, pp. 153.

Corr, S. A. (2008). Linear Assemblies of Magnetic Nanoparticles as MRI Contrast Agents, *Journal of the American Chemical Society*, vol. 130, pp. 4214-4215

Corr, S. A. (2007). *New Magnetic Nanocomposite materials,* Ph.D Thesis, pp.54, Chemistry from Trinity College Dublin

Cubillo, A.E. et al. (2006). Antibacterial activity of copper monodispersed nanoparticles into sepiolite, *Journal of Materials Science*, vol. 41, 16, pp. 5208-5212.

D'Archivio et al. (2000). Metal palladium dispersed inside macroporous ion-exchange resins: rotational and translational mobility inside the polymer network. *Journal of Molecular Catalysis A: Chemical,* vol. 157, 1-2, pp. 269-273

Das. "Disinfection". In: Kirk-Othmer Encyclopedia of Chemical Technology. Kirk-Othmer Encyclopedia of Chemical Technology (2005) pp. 1-68

Davies, G.-L., et al. (2011). NMR Relaxation of Water in Nanostructures: Analysis of Ferromagnetic Cobalt–Ferrite Polyelectrolyte Nanocomposites, *ChemPhysChem*, vol. 12, pp. 772-776.

Durand, J. et al. (2008). An overview of palladium nanocatalysts: Surface and molecular reactivity. *European Journal of Inorganic Chemistry,* vol. 23, pp. 3577-3586

Giannazzo, F. et al. (2011). Advanced materials nanocharacterization. *Nanoscale Research Letters,* vol. 6,1, pp. 107

Gramotnev, D. K. & Gramotnev, G. (2005). A new mechanism of aerosol evolution near a busy road: Fragmentation of nanoparticles. *Journal of Aerosol Science,* 36, 3, pp. 323–340.

Hassan, M. (2005). Small things and big changes in the developing world. *Science*, vol. 309, 5731, pp. 65-66

Haverkamp, R.G. (2010). A Decade of Nanoparticle Research in Australia and New Zealand. *Particulate Science And Technology,* vol. 28, 1, pp. 1-40

Hillie, T. & Hlophe, M. (2007). Nanotechnology and the challenge of clean water, *Nature Nanotechnology*, vol. 2, 11, pp. 663-664

Houk, L.R., et al. (2009). The Definition of "Critical Radius" for a Collection of Nanoparticles Undergoing Ostwald Ripening. *Langmuir,* vol. 25, 19, pp. 11225-11227

Hyeon, T. (2003). Chemical synthesis of magnetic nanoparticles. *Chemical Communications*, 8, pp. 927-934

Imre, A., et al. (2000). Surface Ostwald ripening of Pd nanoparticles on the MgO (100) surface. *Applied Physics A*, vol. 71, pp. 19-22

International Standards Organisation: ISO/TS 27687:2000. (2000). *Nanotechnologies - Terminology and definitions for nanoobjects - Nanoparticle, nanofiber and nanoplate*

Joo, H. (2006). *Nanotechnology for environmental remediation*. pp. 165, ISBN: 0387288252

Ju-Nam, Y. & Lead, J.R. (2008). Manufactured nanoparticles: An overview of their chemistry, interactions and potential environmental implications. *Science of the Total Environment*, vol. 400, 1-3, pp. 396-414

Kidambi, S., & Bruening, M.L. (2005). Multilayered polyelectrolyte films containing palladium nanoparticles: Synthesis, characterization, and application in selective hydrogenation. *Chemistry of Materials*, 17, pp. 301–307

Kim, J & Van der Bruggen, B. (2010). The use of nanoparticles in polymeric and ceramic membrane structures: Review of manufacturing procedures and performance improvement for water treatment. *Environmental Pollution,* vol. 158, 7, pp. 2335-2349

Klabunde, k.J. (2005). Nanoscale Materials in Chemistry. *Wiley-VCH,* pp. 1-293

Kong, H. & Jang, J. (2008). Antibacterial Properties of Novel Poly(methyl methacrylate) Nanofiber Containing Silver Nanoparticles. *Langmuir*, vol.24, 5, pp. 2051-2056

Lane, N. (2002). Nanotechnologies meet market realities. *Chemical & Engineering News*, pp. 17

Laurent, S. et al. (2008). Magnetic Iron Oxide Nanoparticles: Synthesis, Stabilization, Vectorization, Physicochemical Characterizations, and Biological Applications. *Chemical Reviews*, vol. 108, 6, pp. 2064–2110

Law, N. (2008). Formation of Nanoscale Elemental Silver Particles via Enzymatic Reduction by *Geobacter sulfurreducens*. *Applied And Environmental Microbiology*, vol. 74, 22, pp. 7090–7093

Lee, W.-R. et al. (2005). Redox-Transmetalation Process as a Generalized Synthetic Strategy for Core-Shell Magnetic Nanoparticles. *Journal of the American Chemical Society*, vol. 127, 46, pp. 16090-16097.

Li et al. (2008). Antimicrobial nanomaterials for water disinfection and microbial control: Potential applications and implications. *Water Research,* vol. 42,18, pp. 4591-4602

Lu, A-H. et al. (2007). Magnetic nanoparticles: synthesis, protection, functionalization, and application.*Angewandte Chemie International Edition*, vol.46, 8, pp. 1222 – 1244

Macanás, J. et al. (2011). Ion-exchange assisted synthesis of polymer-stabilized metal nanoparticles. Solvent Extraction and Ion Exchange. *A series of Advances,* Tailor & Francis, vol.20, chapter 1.

Maynard, A.D. (2007). Nanotechnology: The next big thing, or much ado about nothing?. *Annals of Occupational Hygiene,* vol. 51, 1, pp. 1-12

Maynard, R. L. & Howard, C. V. (1999). Particulate Matter: Properties and Effects upon Health. *Bios Scientific Publishers*, Oxford UK.

Medyak, G.V. (2001). *Russian Journal of Applied Chem*istry, vol. 74, 10, 16583.

Miley et al. (2005). Nanotechnology. *Kirk-Othmer Encyclopedia of Chemical Technology,* pp. 1-29

Muraviev, D.N. (2005). *Contribute to Science,* vol. 3, 1, pp. 17.

Muraviev, D.N. et al. (2008). Novel strategies for preparation and characterization of functional polymer-metal nanocomposites for electrochemical applications. *Journal of Pure and Applied Chemistry*, vol. 80, 11, pp. 2425-2437.

Muraviev, D.N. et al. (2008). Synthesis, stability and electrocatalytic activity of polymer-stabilized monometallic Pt and bimetallic Pt/Cu core-shell nanoparticles. *Physica Status Solidi A*, vol. 205, 6, pp. 1460-1464.

Muraviev, D.N. et al. (2006). Novel routes for inter-matrix synthesis and characterization of polymer stabilized metal nanoparticles for molecular recognition devices. *Sensors and Actuators B: Chemical*, vol. B118, 1-2, pp. 408-417.

Muraviev, D.N. et al. *Nanocomposite with bactericide activity*, PCT/ES2010/000323, (23th of July, 2010)

Narayan, R. (2010). Use of nanomaterials in water purification. *Materials Today,* vol. 13, 6, pp. 44-46

Nicolais, L. & Carotenuto, G. (2005). Metal-polymer nanocomposites. *Wiley-VCH*, pp. 300

Niembro, S. et al. (2008). Phosphine-Free Perfluoro-Tagged Palladium Nanoparticles Supported on Fluorous Silica Gel: Application to the Heck Reaction. *Organic Lett*ers, vol. 10, pp. 3215.

Ouyang, L. et al. (2010). Catalytic hollow fiber membranes prepared using layer-by-layer adsorption of polyelectrolytes and metal nanoparticles. *Catalysis Today*, vol. 156, 3-4, pp. 100-106

Pal, S. et al. (2007). Does the Antibacterial Activity of Silver Nanoparticles Depend on the Shape of the Nanoparticle? A Study of the Gram-Negative Bacterium *Escherichia coli. Applied and Environmental Microbiology*, vol. 73, 6, pp. 1712-1720

Pankhurst, Q.A. et al. (2003). Applications of magnetic nanoparticles in biomedicine. *Journal of Physics D: Applied Physics*,vol. 3,6, pp. 1-15

Park, J. & Cheon, J. (2001). *Journal of American Chemical Society*, 123, pp. 5743-5746

Pomogailo, A.D. & Kestelman, V.N. (2005). *Metallopolymer Nanocomposites*, Springer in Materials Science, pp. 553, ISSN: 0933033X

Pomogailo, A.D. (2000). Uspekhi Khimii*, Russian Chemical Reviews,* 69, p. 53.

Pomogailo, A.D., et al. (2003). Polymer Sol–Gel Synthesis of Hybrid Nanocomposites. *Journal of Nanoparticle Research*, vol.5, pp. 497.

Ponder, S.M. et al.(2000). Remediation of Cr(VI) and Pb(II) aqueous solutions using supported, nanoscale zero-valent iron. *Environmental Science Technology,* vol. 34, pp. 2564–2569.

Qiao, R. (2007). Fabrication of Super-paramagnetic Cobalt Nanoparticles-Embedded Block Copolymer Microcapsules. *Journal of Physical Chemistry C,* vol. 111,pp. 2426-2429

Qiao, R. et al. (2007). Fabrication of super-paramagnetic cobalt nanoparticles-embedded block copolymer microcapsules. *Journal of Phyiscal Chemistry C*, vol. 111, pp. 2426-2429

Rao, C.N.R. et al. (2004). *The Chemistry of Nanomaterials*. Wiley-VCH, pp. 1-762

Ristovski, Z. D. (2006). Influence of diesel fuel sulfur on nanoparticle emissions from city buses. *Environmental Science Technology,* 40, 4, pp. 1314–1320.

Rozenberg, B.A. & Tenne, R. (2008). Polymer-assisted fabrication of nanoparticles and nanocomposites. *Progress In Polymer Science*, vol. 33, 1, 40-112, ISSN: 00796700

Ruparelia, J.P. et al. (2008). Strain specificity in antimicrobial activity of silver and copper nanoparticles, *Acta Biomaterialia*, vol. 4, 3, pp. 707–716

Sarkar, S., Sengupta, A.K. & Prakash, P. (2010). *Environmental Science Technology*, vol. 44, pp.1161–1166

Savage, N. & Diallo, M. (2005). Nanomaterials and water purification: opportunities and challenges, *Journal of Nanoparticle Research*, vol. 7, pp. 331-342

Schmid, G. (2010). *Nanoparticles: from theory to application* (2nd Ed.). pp. 533, ISBN: 978-3-527-32589-4

Schmid, G. et al. (2006). *Nanotechnology: Assessment and Perspectives.* Gethmann Springer-Verlag, Berlin

Schulenburg, M. (2008). *Nanoparticles – small things, big effects Opportunities and risks*. Federal Ministry of Education and Research, Berlin, Germany.

Son, S.U et al. (2004). Designed Synthesis of Atom-Economical Pd/Ni Bimetallic Nanoparticle-Based Catalysts for Sonogashira Coupling Reactions, *Journal of American Chemistry Society*, vol. 126, 16, pp. 5026-5027

Sondi, I. & Salopek-Sondi,B. (2004). Silver nanoparticles as antimicrobial agent: a case study on E. coli as a model, *Journal of Colloid and Interface Science,* vol. *275*, 1, pp. 177-182.

Suchorski, Y. et al. (2008). CO Oxidation on a CeOx/Pt(111) Inverse Model Catalyst Surface: Catalytic Promotion and Tuning of Kinetic Phase Diagrams *Journal of Physical Chemistry C*, vol. 12, 50, pp. 20012-20017

Taurozz i, J. S. (2008). Effect of filler incorporation route on the properties of polysulfone-silver nanocomposite membranes of different. *Journal of Membrane Science*, vol. 325, pp. 58–68

Theron, J. et al. (2008). Nanotechnology and water treatment: Applications and emerging opportunities. *Critical Reviews In Microbiology,* vol. 34, 1, pp. 43-69

Umpierre, A.P. et al. (2005). Selective Hydrogenation of 1, 3-Butadiene to 1-Butene by Pd(0)Nanoparticles Embedded in Imidazolium Ionic Liquids. *Advanced Synthesis and Catalysis*, vol. 347, pp. 1404–1412.

Vatta, L.L. et al. (2006). Magnetic nanoparticles: Properties and potential applications. *Pure And Applied Chemistry,* vol. 78, 9, pp. 1793-1801

Vinodgopal, K., Y. H. He, M. Ashokkumar & F. Grieser. (2006). Sonochemically prepared platinum-ruthenium bimetallic nanoparticles. *Journal of Physical Chemistry B, vol.* 110, 9, pp. 3849–3852

Walter, P. et al. (2006). Early Use of PbS Nanotechnology for an Ancient Hair Dyeing Formula, *Nano Letters*, 6, pp. 2215–2219.

Weber, A.P. et al. (2003). Size effects in the catalytic activity of unsupported metallic nanoparticles, *Journal of Nanoparticle Research,* vol. 5, pp.293–298, 2003.

Wen-Ji Jin et al. (2007), Synthetic Metals, 157, pp. 454-459

Wilson, O.M. et al. (2006). The Effect of Pd Nanoparticle Size on the Catalytic Hydrogenation of Allyl Alcohol. *Journal of American Chemistry Society*, vol.128, pp. 4510–4511.

Xiaomin, N., et al. (2005). *Journal of Crystal Growth,* vol. 275, pp. 548–553

Xu, J. & Bhattacharyya, D. (2005). Membrane-based bimetallic nanoparticles for environmental remediation: Synthesis and reactive properties. *Environmental Progress*, vol. 24, 4, pp. 358-366

Yegiazarov, Yu.G. (2000). *Reactive and Functional Polymers*, vol.44, pp.145.

Yuan, G. D. (2004). Natural and modified nanomaterials as sorbents of environmental contaminants. *Journal of Environmental Science Health Part A: Toxic Hazardous. Substances Environmental Engineering, vol.* 39, 10, pp. 2661–2670.

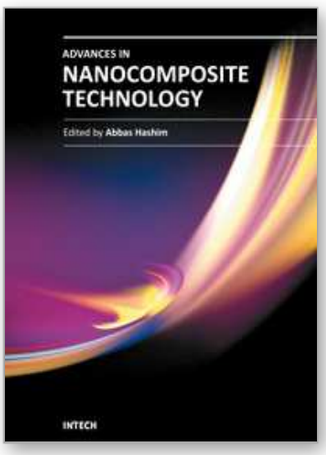
Yujiro Hayashi. (2007). Diphenylprolinol Silyl Ether as a Catalyst in an Enantioselective, Catalytic, Tandem Michael/Henry Reaction for the Control of Four Stereocenters. *Angewandte Chemie International Edition*, vol. 46, pp. 1222 – 1244

Zagorodni, A. (2007). *Ion exchange materials: properties and applications*. Elsevier, pp. 477, ISBN:9780080445526

Zeng, H.C. (2004). *Nanostructured Catalytic Materials: Design and Synthesis,* Tailor & Francis, pp. 1-13

Zeng, Q. H. et al. (2007). Growth mechanisms of silver nanoparticles: A molecular dynamics study. *Nanotechnology*, 18, 3, 035708.

IntechOpen



Advances in Nanocomposite Technology

Edited by Dr. Abbass Hashim

ISBN 978-953-307-347-7
Hard cover, 374 pages
Publisher InTech
Published online 27, July, 2011
Published in print edition July, 2011

The book â€œAdvances in Nanocomposite Technologyâ€ contains 16 chapters divided in three sections. Section one, â€œElectronic Applicationsâ€, deals with the preparation and characterization of nanocomposite materials for electronic applications and studies. In section two, â€œMaterial Nanocompositesâ€, the advanced research of polymer nanocomposite material and polymer-clay, ceramic, silicate glass-based nanocomposite and the functionality of graphene nanocomposites is presented. The â€œHuman and Bioapplicationsâ€ section is describing how nanostructures are synthesized and draw attention on wide variety of nanostructures available for biological research and treatment applications. We believe that this book offers broad examples of existing developments in nanocomposite technology research and an excellent introduction to nanoelectronics, nanomaterial applications and bionanocomposites.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Amanda Alonso, Jorge Macanás, Gemma-Louise Davies, Yuri Gounko, Maria Muñoz and Dmitri Muraviev (2011). Environmentally-Safe Catalytically Active and Biocide Polymer-Metal Nanocomposites with Enhanced Structural Parameters, Advances in Nanocomposite Technology, Dr. Abbass Hashim (Ed.), ISBN: 978-953-307-347-7, InTech, Available from: http://www.intechopen.com/books/advances-in-nanocomposite-technology/environmentally-safe-catalytically-active-and-biocide-polymer-metal-nanocomposites-with-enhanced-str

INTECH
open science | open minds

InTech Europe
University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China
Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

© 2011 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution-NonCommercial-ShareAlike-3.0 License, which permits use, distribution and reproduction for non-commercial purposes, provided the original is properly cited and derivative works building on this content are distributed under the same license.

IntechOpen

IntechOpen