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Polymer-supported metals and metal oxide nanoparticles: synthesis, characterization, and applications

Sudipta Sarkar · E. Guibal · F. Quignard ·
A. K. SenGupta

Abstract Metal and metal oxide nanoparticles exhibit unique properties in regard to sorption behaviors, magnetic activity, chemical reduction, ligand sequestration among others. To this end, attempts are being continuously made to take advantage of them in multitude of applications including separation, catalysis, environmental remediation, sensing, biomedical applications and others. However, metal and metal oxide nanoparticles lack chemical stability and mechanical strength. They exhibit extremely high pressure drop or head loss in fixed-bed column operation and are not suitable for any flow-through systems. Also,

nanoparticles tend to aggregate; this phenomenon reduces their high surface area to volume ratio and subsequently reduces effectiveness. By appropriately dispersing metal and metal oxide nanoparticles into synthetic and naturally occurring polymers, many of the shortcomings can be overcome without compromising the parent properties of the nanoparticles. Furthermore, the appropriate choice of the polymer host with specific functional groups may even lead to the enhancement of the properties of nanoparticles. The synthesis of hybrid materials involves two broad pathways: dispersing the nanoparticles (i) within pre-formed or commercially available polymers; and (ii) during the polymerization process. This review presents a broad coverage of nanoparticles and polymeric/biopolymeric host materials and the resulting properties of the hybrid composites. In addition, the review discusses the role of the Donnan membrane effect exerted by the host functionalized polymer in harnessing the desirable properties of metal and metal oxide nanoparticles for intended applications.

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Synthetic polymers · Entrapment · Sorbents ·
Supported catalysts

Introduction

Many metal and metal oxide nanoparticles offer unique properties as sorbents, catalysts, sensors, reducing

agents, and bactericides (Pradeep and Anshup 2009; Sharma et al. 2009a; Astruc et al. 2005; Rao et al. 2004; Luo et al. 2006; Miehr et al. 2004; Wang and Zhang 1997; Sharma et al. 2009a, b). They offer very fast kinetics and enhanced sorption capacity due to their high surface to volume ratio. However, their propensity to aggregate, extremely high pressure drop in flow-through systems, lack of specificity for reactions in complex systems and weak mechanical strength often pose major obstacles against frequent real-life applications. Functionalized polymers and biopolymers are a completely different class of organic materials that are robust, chemically stable and amenable to chemical modifications depending on the intended application needs. These synthetic and semi-synthetic functionalized materials, often referred to as reactive polymers or ion exchangers, have seen explosive growth during the last five decades and created myriad scientific endeavors—from mining to microelectronics, deionization to decontamination, synthesis to sensing, drug delivery to desalination, to name just a few (Zagorodni 2007; SenGupta 1995; Sarkar et al. 2009; Greig 2000). In this context, polymer-supported metal or metal oxide nanoparticles are a new class of hybrid polymeric/inorganic materials that offer properties and application opportunities not exhibited separately by the polymeric host materials or inorganic nanoparticles alone. For convenience, these specific classes of hybrid materials are referred to as polymer-supported nano particles (PSNPs) in this communication. In PSNPs, the metal and metal oxide nanoparticles are dispersed within the polymer phase in accordance with in-situ and ex-situ processes. While the metal and metal oxide are always present as nanoparticles in PSNPs, the morphology or the physical configuration of the polymeric materials may vary widely, from spherical beads to granules, to membranes, fibers and others. In PSNPs, the polymer and metal/metal oxide nanoparticles retain their intrinsic properties even at nano-scale level but they can be easily tailored to complement the overall properties of PSNPs in various ways.

Figure 1a depicts the diverse properties of several metal and metal oxide nanoparticles as sorbents, oxidizing/reducing agents, nanomagnets etc. Figure 1b helps illustrate how individual shortcomings of nanoparticles and polymeric host materials can be overcome in PSNPs or hybrid nanocomposites, thus offering multitude of new application opportunities.

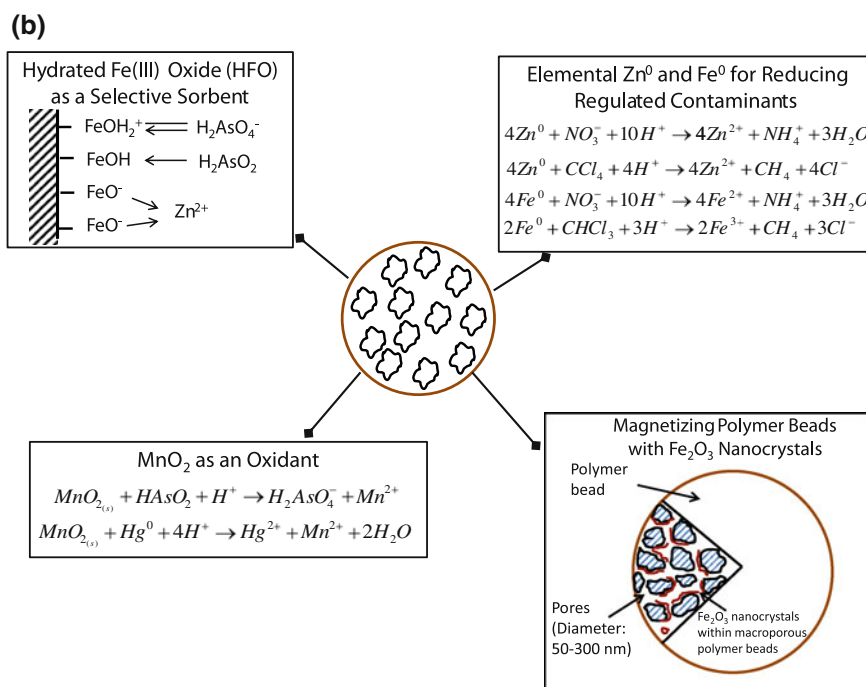
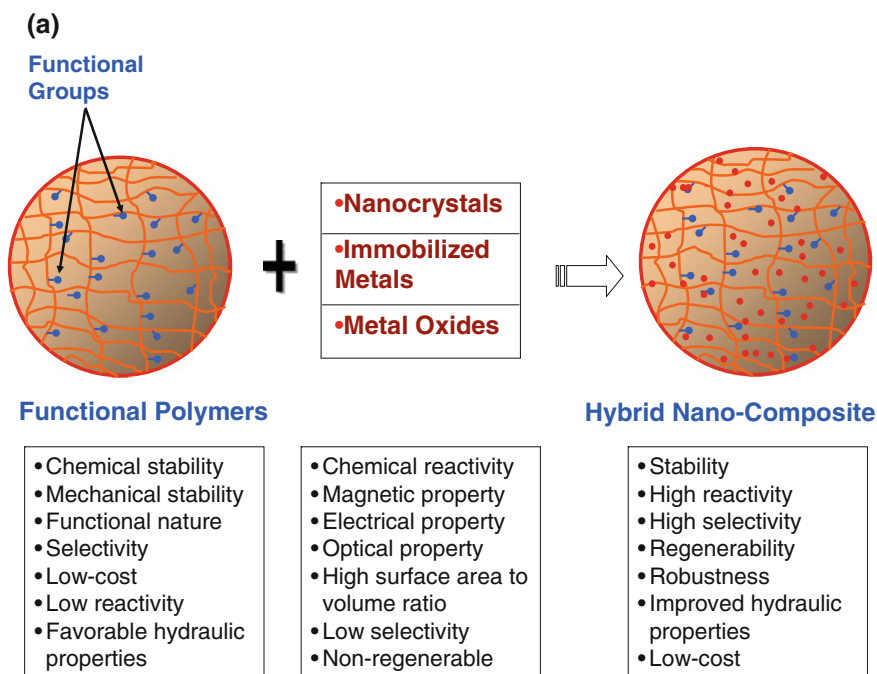
The nature and characteristics of the hybrid materials depend on various factors including the

morphology of the polymeric host materials, type and concentration of the functional groups, the method for immobilization on the properties of the final products, etc. The physical and functional characteristics of the host materials play important role in determining the overall characteristics of the PSNPs. The nature of the functional groups such as amine, sulfonic, carboxylic, iminodiacetate, etc. determine the host material's capacity to bind the metal ions, metal complexes or other precursor ions containing the target metal. The nature of the dispersed nanoparticles also depends on the method of dispersal. The dispersion of metal or metal oxides inside the host material can take place through a combination of different mechanisms such as complexation/chelation, electrostatic interactions, precipitation or reduction reactions, etc. Also, the physical characteristics of the host material such as morphology, size, surface area, porosity, and shape of the micropores, etc. determine the size and nature of the nanoparticles of metal and metal oxides dispersed within the host material (Rozenberg and Tenne 2008). The diverse nature of the functional groups and the different factors controlling the sizes of the dispersed nanoparticles often make it a challenging task to synthesize and impart desired properties in the hybrid material. This review reports synthesis and characterization of various types of PSNPs consisting of combinations of different synthetic polymers and biopolymers with metal and metal oxides nanoparticles.

Synthesis

The two main routes of synthesis of the polymer-supported nanoparticles are ex-situ and in-situ. Ex-situ method of synthesis can be obtained by first synthesizing the inorganic nanoparticles and then dispersing them in a polymer solution or three-dimensional matrix. This method of synthesis is a popular one because it does not set a limitation on the nature of nanoparticles and host polymer to be used. However, blending polymers and nanoparticles to afford homogeneous and well dispersed inorganic material in the polymer pose significant challenges. To address these difficulties, a different method, the in-situ process of synthesis, is utilized. In this process, the preformed polymer phase acts as a micro-reactor and metal and metal oxide nanoparticles are generated inside the polymer phase from a precursor that are transformed into the desired nanoparticles by a series of appropriate

Fig. 1 **a** Diverse properties of metal and metal oxide nanoparticles used for different environmental applications and **b** attributes of polymer-supported nanoparticles compared to those of parent nanoparticles and functional polymers



reactions. The process is gaining popularity for their technological advantages over the ex-situ methods because particle size and morphology can be controlled with relative ease. A wide variety of HNCs can be prepared using the in-situ process.

Ex-situ synthesis

The ex-situ process consists of physical entrapment of the metal or metal oxides nanoparticles in the polymer or biopolymer network. This physical entrapment may

proceed through casting and solvent evaporation, chemical polymerization, or co-precipitation. Such encapsulation of nanoparticles also helps in the stabilization of nanoparticles by preventing them to agglomerate and form larger particles. This is a problem always encountered in the traditional method of nanoparticle formation, where nanoparticles are synthesized in a bulk solution. In general, the procedure of ex-situ synthesis consists of mixing of the metal salt or pre-formed nanoparticles with the polymer solution followed by the casting of the suspension in the form of a membrane or crosslinking the suspension to create a three-dimensional framework. The film or the framework is later subjected to an oxidation/reduction step wherein the nanoparticles are formed from the precursor salt or complexes, followed by solvent evaporation.

Solvent mediated synthesis process has been used in the preparation of several types of PSNPs for various uses. In this process, the nanoparticles are pre-formed, and mixed with a solvent and a polymer solution. After the solvent is cast either in a form of membrane or coating on another surface, low grade heat is utilized to evaporate the solvent, leaving behind

a hybrid nano-composite material. Table 1 provides a few example of the different methods used for solvent mediated synthesis. Polymerization or co-polymerization procedure was also used for the entrapment of metal or metal oxide nanoparticles. Table 2 summarizes some of the techniques used for polymerization for ex-situ synthesis of the PSNPs. In addition to the synthetic polymers, biopolymers such as chitosan, alginate, etc. have been widely used for ex-situ synthesis of the PSNPs. Many of the bio-polymers are soluble in acidified aqueous solution. The preparation of PSNP containing bio-polymer generally involves conditioning of the bio-polymer in different physical shapes and entrapment of the nanoparticles within the various shapes (Guibal et al. 2009). The process consists of two steps, namely (i) polymer dissolution, and (ii) polymer neutralization, coagulation or ionotropic gelation. Table 3 lists some of the encapsulation processes. This technique has been widely used for the preparation of spherical hydrogels. However, manufacturing of films, membranes, fibers, hollow fibers can be done using specific extrusion equipment. Figure 2 shows some different physical forms obtained with chitosan.

Table 1 Solvent mediated ex-situ preparation of PSNP

Nanoparticle (NP)	Synthesis of NP	Polymer used	Solvent used	Brief process of synthesis of PSNP	Reference
Fe/Fe-oxide	Precipitation from FeCl ₃ or reduction from Fe-salt	Poly(methylmethacrylate) (PMMA)	Acetone	Suspension of NP and PMMA and acetone spin casted and dried to form magnetically active films	Baker et al. (2004)
Au–Ag alloy	Reduction of a mixture of Au and Ag salts by NaBH ₄ solution	Amphiphilic block co-polymers of PDMA-b-PMMA-b-PDMA	Tetrahydrofuran (THF)	The suspension of Au–Ag NPs with the block copolymer and THF cast on glass surface and air-dried	Chatterjee and Jewrajka (2007)
Fe ₃ O ₄ (magnetite)	Precipitation from Fe-salts	Block polymers (styrene- <i>b</i> -ethylene/butylene- <i>b</i> -styrene)/ Gum Arabic		Metal oxide mixed with block polymers/bio-polymer, separated by magnetization, rinsed and dried at low-heat condition	Yang et al. (2008) and Banerjee and Chen (2007)
Gold	From tetrachloroauric acid (TCA)	Chitosan		Chitosan, TCA and acetic acid are mixed intimately, acetic acid reduces the gold salt to produce NP	dos Santos et al. (2004) and He et al. (2008)
Fe ₃ O ₄	Precipitation from Fe-salts	Chitosan in acetic acid solution		NP, Chitosan in acetate buffer and another enzyme (tyrosinase, glucose oxidase) mixed together and applied on to glass electrodes to prepare biosensors	Wang et al. (2008) and Kaushik et al. (2008)

Table 2 Polymerization/Co-polymerization method of synthesis of PSNP

Nanoparticle (NP)	Synthesis of NP	Name of the polymeric host	Brief process of synthesis	Reference
Hydrated tin oxide	Reaction of SnCl ₄ with ammonia in aqueous phase	Carboxylated polyacrylamide	Synthesized NP was mixed with <i>N,N'</i> -methylenebisacrylamide and potassium peroxydisulphate before adding acrylamide monomers. After polymerization, the PSNP was functionalized by succinic anhydride dissolved in dioxane at pH 4	Shubha et al. (2001)
Fe ₃ O ₄ (magnetite)	Precipitation from Fe-salts	Carboxylated polyacrylamide	Similar to the above	Manju et al. (2002)
Silver	Reduction of silver salt with citrate	Mercaptomethylstyrene/PVA	PVA (polyvinyl alcohol) and benzoyl peroxide were added to a suspension of silver NP in a solution of 4-mercaptomethylstyrene in toluene. Polymerization took place under nitrogen atmosphere and at 80 °C	Farah et al. (2008)
Fe ₃ O ₄	Precipitation from Fe-salts	Poly(3,4-ethylene-dioxythiophene)	Magnetite NP in PVA was mixed with 3,4-ethylene-dioxythiophene followed by addition of HCl. Acid exposes some Fe ³⁺ ions that initiate polymerization and catalyze the formation of PSNP	Shin et al. (2008)
Magnetite, Barium titanate	Various methods	Poly(urethane)	Catalyst-accelerator dissolved in THF before the addition of NP; resultant solution sonicated before addition of urethane monomers	Guo et al. (2009)

In-situ synthesis

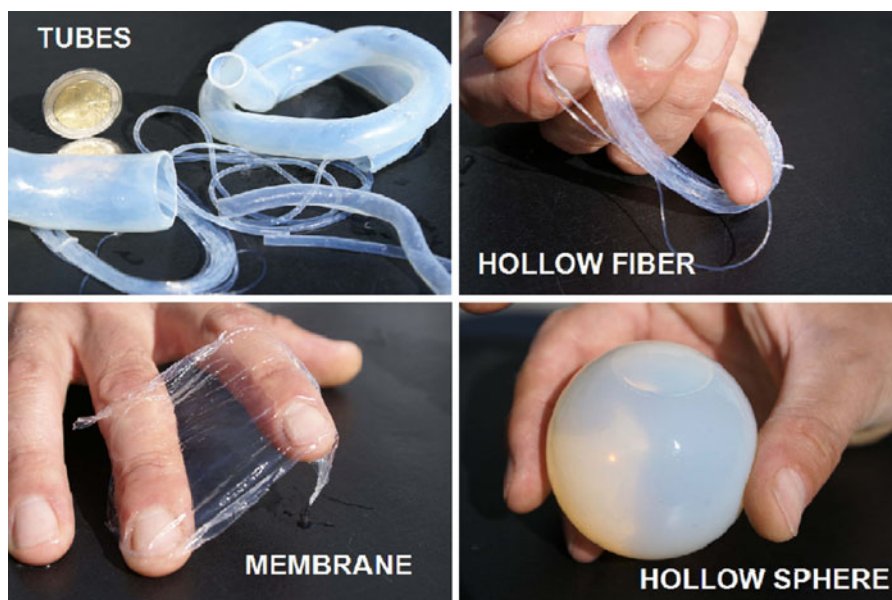
In contrast with the ex-situ method of synthesis, in this method the nanoparticles of metal and metal oxides are synthesized within a pre-formed polymer framework or matrix. Considering the in-situ approach the combination of the wide number of functionalized polymers available and different types of nanoparticles that can be prepared gives rise to huge number of different PSNPs possible to be synthesized. The parameters that control the nature of the PSNPs are (i) nature of the functional polymer, (ii) the type of nanoparticle pre-cursor, (iii) the reaction that forms the nanoparticles, and (iv) the composition of the metal and metal oxide nanoparticles. In this process, the polymers serve as nano-reactors and provide confined medium for synthesis; also, they stabilize and isolate the synthesized nanoparticles preventing their aggregation. Although boundaries between the different processes of synthesis are very tight, the in-situ process can be subdivided into two groups, namely, (i) sorption followed by redox and/or precipitation reaction, and (ii) impregnation followed by precipitation and/or redox reaction.

Sorption followed by in-situ redox and/or precipitation reaction

In this process, the metal ion or the metal-precursor is first adsorbed on the polymeric host, followed by either a change in the valence state of the metal ion (reduction/oxidation) or an in-situ precipitation. Table 4 summarizes some of the examples of such synthesis process. The synthesis of magnetically active hybrid nano-composites involves desorption of already adsorbed Fe²⁺ ion by Na⁺ ions followed by oxidation and precipitation at elevated pH. Precise control over the oxidation is required, because the formation of magnetite nanoparticles take place only in a narrow band of Pe–pH condition. Synthesis of hybrid cation exchange resin (HCIX) is straightforward and does not involve any tight control of the conditions as such. Cation exchange resin is contacted with a solution containing Fe³⁺ ions which are readily adsorbed by the cation exchangers due to their high affinity. The Fe³⁺ ions are replaced by Na⁺ ions when the resin is contacted with a concentrated solution of NaCl and NaOH. As soon as Fe³⁺ ions are released from the ion exchange site, it precipitates as Fe(OH)₃

Table 3 Bio-polymers for ex-situ synthesis of PSNPs

Nanoparticle (NP)	Synthesis of NP	Bio-polymer used	Brief process of synthesis of PSNP	Reference
Fe(III)/Ni(II)-oxides and hydroxides	Precipitation from metal salts	Alginate	NPs are mixed with acidified alginate solution followed by addition in calcium chloride solution	Escudero et al. (2009)
Fe ⁰ metal	Reduction of Fe(II) salts by sodium borohydride	Alginate	NPs are mixed with a solution of sodium alginate and the suspension is added in drops in a solution of CaCl ₂ when Ca-alginate crosslinking occurs to produce beads of alginates with nanoparticles of zero-valent iron dispersed within	Krajangpan et al. (2008)
Magnetite	Precipitation from metal salts	Chitosan and alginate	Chitosan with CaCl ₂ was mixed with NPs before introduction of alginate solution to form hydrogels which were dried before use as adsorbent	Ma et al. (2007, 2008)

**Fig. 2** Different physical forms in which chitosan can be fabricated

nanoparticles inside the ion-exchanger matrix due to the high pH condition remaining within the micropores of the ion exchanger. Dispersal of hydrated ferric oxide (HFO) nanoparticles within the anion exchanger phase was challenging due to the fact that the positively charged functional groups of the resin tends to exclude the cations from entering the ion-exchanger phase due to Donnan potential (Helfferich 1962; Donnan 1995; Sarkar et al. 2010a). The Donnan barrier is overcome or reduced by various methods to disperse HFO nanoparticles within the anion exchangers as described in Table 4. Immobilization of

nanoparticles of metal involved two steps: first, sorption of the metal ion or a metal-precursor inside the ion exchange resin, functionalized membrane, etc. and second, reduction of the metal ion or a metal-precursor by a suitable reducing agent. For metal and metal oxide nanoparticle dispersion in the functionalized matrix of an ion exchanger or a membrane using in-situ method, the process can be repeated many times to disperse more NPs within the micropores of the host material, an advantage only available in the in-situ method of synthesis (Sarkar et al. 2011a, b).

Table 4 In-situ synthesis of PSNP using sorption followed by redox and/or precipitation reaction

Type of nanoparticle (NP) dispersed	Type of polymeric support	Brief process of synthesis of PSNP	Reference
Magnetite (Fe ₃ O ₄)	Cation exchange resins with styrene-divinyl benzene matrix and functional groups like carboxylate, sulfonic acid	<ol style="list-style-type: none"> 1. Cation exchange resins (gel or macroporous type) were loaded with Fe²⁺ ions by using solution of Fe(II) salts at acidic pH under nitrogen at 60 °C 2. Slow oxidation at pH 10 by addition of 5% NaCl and 0.5% NaOH solution with bubbling of air with volume concentration of O₂ in 0.1–1% range 3. Rinsing and drying of iron-loaded resin after washing with alcohol or solvent with low-dielectric constant 	Leun and SenGupta (2000) and Cumbal et al. (2003)
Hydrated Ferric oxide (HFO)	Cation exchange resin with sulfonic acid functional group	<ol style="list-style-type: none"> 1. cation exchanger was loaded with Fe(III) ions by contacting with a solution of ferric salt 2. Desorption of Fe³⁺ ions and simultaneous precipitation of Fe(OH)₃ by a solution of 5% NaCl +NaOH 3. Rinsing and drying followed by a wash with alcohol 	DeMarco et al. (2003) and Cumbal and SenGupta (2005a)
Hydrated Ferric oxide (HFO)	Anion exchange resin with quaternary amine functional group (gel type and macroporous)	<ol style="list-style-type: none"> 1. Loading of an oxidizing anion such as MnO₄⁻ or ClO₄⁻ on the anion exchanger by contacting with a solution containing the salt of such ions 2. Contacting the anion exchanger with a solution of FeSO₄ when Fe(II) is oxidized to Fe(III) by the oxidizing anion that desorbs from the anion exchanger 3. A passage of 5%NaOH solution precipitates Fe(III) ions as Fe(OH)₃ nanoparticles within the ion exchanger 	Cumbal and SenGupta (2005a), SenGupta and Cumbal (2005), Sarkar et al. (2007), Möller and Sylvester (2008), Hristovski et al. (2008), Putamraju and SenGupta (2006) and Blaney et al. (2007)
Hydrated Ferric oxide (HFO)	Anion exchange resin with quaternary amine functional group	<ol style="list-style-type: none"> 1. Loading of a precursor complex anion of Fe(III) such as FeCl₄⁻ on the anion exchange resin 2. Contacting the anion exchanger with a solution of NaOH causes the precipitation of Fe(OH)₃ nanoparticles within the anion exchange resin <p>The polyimide films were hydrolyzed with KOH solution so that imide cycles open up to reveal carboxylic acid functional groups. Ag⁺/Ni²⁺ ions were adsorbed onto carboxylic acid groups, and the film is annealed at 250 °C or reduced with hydrogen gas at elevated temperature. Same process is followed for resins with divinyl benzene matrix also</p>	Zhang et al. (2008a, b)
Zero-valent Ag and Ni	Polyimide films; resins with divinyl benzene matrix		Li et al. (2004), Shinkai et al. (2004) and Akamatsu et al. (2008)

Table 4 continued

Type of nanoparticle (NP) dispersed	Type of polymeric support	Brief process of synthesis of PSNP	Reference
Zero-valent Fe, Cu, Pd, Pt, Rh, Ag	Poly(vinylidene fluoride) PVDF membrane, Polyamide blends, PEEK (poly(etherether Ketone)), PEM (polyelectrolyte membrane), etc.	PVDF microfiltration membranes were functionalized by deposition of polyacrylic acid followed by loading of Na ⁺ ions at higher pH by contacting with NaOH. Na ⁺ ions are exchanged for Fe ²⁺ ions in the next step followed by treatment with NaBH ₄ to reduce Fe(II) to Fe ⁰ NPs. Similar methods used for immobilizing Cu ⁰ NPs within a sulfonated PEEK membrane. In a similar fashion, Pd ⁰ NPs were immobilized in various polyamide blends starting from PdCl ₂ in acetic acid solution. Different other reducing agents such as hydrazinehydrate, UV-irradiation, H ₂ gas etc. have also been used	Xu and Bhattacharyya (2006), Monticelli et al. (2005), Muraviev et al. (2007), Bronstein et al. (1998, 2000) and Wang et al. (2002)
Zero-valent Ag, Pd, Pt, Au, Cu	Chitosan	The chitosan polymers were crosslinked to different degrees in the first step to maintain stability when the metal ions are adsorbed at acidic pH in the next step. Further reduction of the metal by a host of reducing agents such as sodium formate, hydrazine, sodium borohydride, hydrogen gas, etc.	Guibal (2004), Murugadoss and Chattopadhyay (2008), Guibal and Vincent (2004), Guibal et al. (2005), Pierno et al. (2008, 2009), Vincent and Guibal (2002, 2003, 2004), Vincent et al. (2003, 2004), Laudenslager et al. (2008), Guibal et al. (2005), Guibal et al. (2007) and Wu et al. (2009a, b)

Chitosan, an aminopolysaccharide, obtained by the deacetylation of chitin (a major component of the cuticle of insects, the membrane of fungi, and the exoskeleton of arthropods), has also been used as a host material. As the metal ion loading process involves subjecting to a solution at low pH where the chitosan tend to become soluble, it is important to control the cross-linking to the desired degree before such step. However, the degree of cross-linking depends on the physical nature of the end-product targeted; for example, an excess of cross-linking increases the brittleness of a chitosan PSNP fiber, a property not suitable for application purposes. Common reducing agents used for reduction are sodium formate, hydrazine, sodium borohydride, hydrogen gas, as reported by Guibal et al. (2005) and Guibal et al. (2007) .

Impregnation followed by precipitation and/or redox reaction

This process is similar to the previous one with a difference that incorporation of the metal ion or the metal precursor does not involve any chemical interaction between the functional groups of the functional polymer, the metal ions, or a metal precursor. The first of the two-step process can have two major variations before a common final step in which the metal or metal oxide is immobilized by redox reaction or chemical precipitation. These are: (a) soaking of support polymer with metal or metal oxide precursor, without chemical reaction between the support and the metal, and (b) mixing of the polymer (support) in liquid state (dissolved) with the metal precursor.

In many cases, biopolymer beads were impregnated with solutions containing precursor chemical and dried to produce PSNPs. Molvinger et al. (2004) and Di Renzo et al. (2005) mixed chitosan beads with tetraethoxysilane (SiO_2 precursor) and initiated hydrolysis and silica condensation by addition of sodium fluoride. The microspheres were finally dried under supercritical CO_2 conditions. Synthesis of carrageenan–silica hybrid followed a similar process (Boissiere et al. 2006). El Kadib et al. (2008), impregnated chitosan beads with a titania precursor (either $\text{Ti}(\text{aca})_2(\text{iOPr})_2$ or $\text{Ti}(\text{iOPr})_4$) in isopropanol solvent; after reaction, the hybrid materials were rinsed with the same solvent and finally dried under supercritical CO_2 conditions. These PSNPs find extensive

use as catalysts. Djelad et al. (2008) compared the encapsulation procedure and the impregnation procedure for the immobilization of zeolite in chitosan. Quignard et al. (2006) prepared hybrid alginate–Cu particles by a two-step procedure: (a) sodium alginate solution was dropped into a copper nitrate solution causing ionotropic gelation of alginate followed by (b) mineralization by contact with an alkaline solution (NaOH or KOH) at pH 9. Tsoi et al. (2004, 2005), Brown and Rehse (2007) used a similar procedure for the preparation of a magnetic PSNP of alginate using FeCl_2 as the metal oxide precursor. Similarly, in order to synthesize HFO-dispersed PSNP, De et al. (2009) used ferric nitrate as metal precursor with PVA mixed with sucrose as support and finally, firing the gel in air at 300 °C to obtain granulated iron oxide NPs.

Using a method termed as redox polymerization, Mallick et al. (2006, 2008) synthesized composite Cu and Pd catalysts where a monomer (*o*-toluidine or 5-ammo-ortho-cresol) in alcohol is mixed with Cu or Pd salts which were reduced to the zero valent metal with simultaneous polymerization of the monomer. Ponder et al. (2000) impregnated a hydrophobic resin with ferrous sulfate in a water/ethanol solution followed by reaction with NaOH to precipitate HFO was reduced by NaBH_4 to get Fe^0 NPs within the polymer phase. He and Zhao (2005) used starch to synthesize bi-metallic catalyst of Fe–Pd in a multi-step process in which Fe^0 /starch composite was prepared first using reduction of Fe(III) salts in starch followed by loading of Pd in a second step by cementation using potassium tetrachloropalladate as the precursor. Xiong et al. (2007) followed a similar procedure for synthesis of bimetallic NPs containing Fe^0 and other metals such as Al, Cu, Co, Ni or Pd. Chitosan-supported magnetic Fe_3O_4 particles were synthesized by Wu et al. (2009a, b) when chitosan was cross-linked with tripolyphosphate was contacted with a Fe(II) precursor solution containing ferrous ammonium under controlled atmosphere (99.5% nitrogen, 0.5% oxygen) to carefully manage the formation of magnetic Fe_3O_4 nanoparticles within the polymer.

Characterization of the hybrid nano-composite materials

The hybrid nano-composites can have three physical forms: granular, membrane, and fibrous. The physical

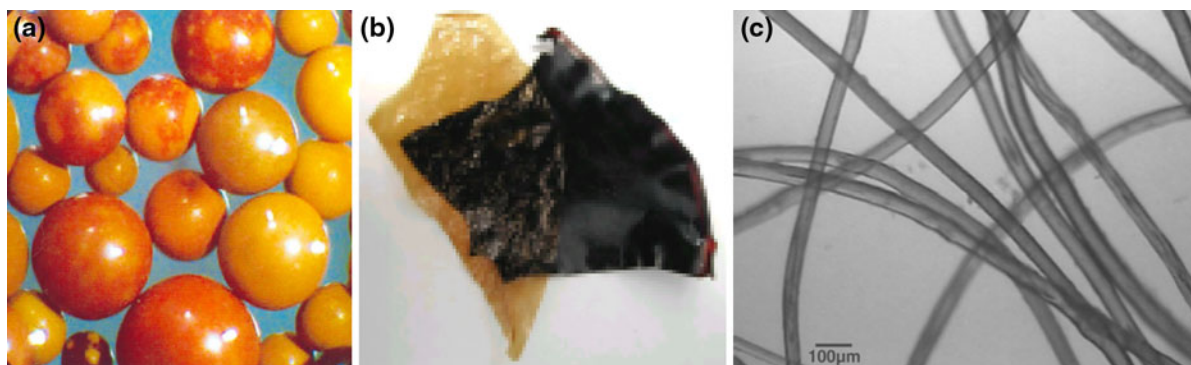


Fig. 3 Physical shapes of some of the PSNPs. **a** Hybrid anion exchange resin dispersed with hydrated ferric oxide nanoparticles; **b** chitosan membranes dispersed with: Pd(II) [yellow

membrane at the back] and Pd⁰ nanoparticles [black membrane at the front]; and **c** hybrid anion exchange fiber dispersed with hydrated ferric oxide nanoparticles. (Color figure online)

form of the PSNPs that are prepared using the in-situ process depends on the physical nature of the parent host material in which the nanoparticles are dispersed. Figure 3 shows the different forms in which the PSNPs have been synthesized and used for different applications.

The detailed characterization of PSNPs plays important role in the development of the nanocomposite materials. Several widely used material science techniques are applicable for the characterization of the PSNP. They include scanning electron microscopy (SEM), environmental SEMs (ESEMs) (for PSNPs at the wet state), transmission electron microscopy (TEM), atomic force microscopy (AFM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), energy-dispersive X-ray analysis (EDAX), and many others.

Microscopic analysis

Figure 4a shows scanning electron micrograph (SEM) of freshly precipitated HFO whereas, Fig. 4b–c show SEM of sliced beads of parent macroporous type anion exchanger and hybrid anion exchanger (HAIX) beads, respectively. It is observed that the HFO particulates deposited throughout the bead including both gel phase and macropores. It can be readily observed that the nanoscale deposits of amorphous and crystalline HFO particles were accessible to the dissolved species through a network of macropores that originally had sizes in the range 20–300 nm. Figure 5 shows the transmission electron micrograph (TEM) image of a HAIX nanosorbent which suggests that the apparent

amorphous coatings of HFO particles as observed in the SEM images are composed of agglomerates of discrete nanoparticles of individual sizes of 5–10 nm. Figure 6a (Peirano Blondet et al. 2008) shows SEM micrograph of a parent chitosan hollow fiber (100× magnification) whereas, Fig. 6b, c show the SEMs at different range of magnifications. Figure 7 shows SEM–EDAX analysis of PSNP of chitosan hollow fiber–Pd⁰ NP, the cross-section is through the wall of the hollow fiber.

Figure 8 shows the SEM and EDAX study of a hybrid anion exchanger dispersed with hydrated titanium oxide nanoparticles. Figure 9 shows SEM of a cross-section of hybrid anion exchange fiber dispersed with nanoparticles of HFO. The EDAX analysis shows the distribution of HFO NPs along the cross-section, showing that most of the NPs lie at the surface.

Figure 10 shows the TEM analysis of chitosan particles loaded with Pd(II) which was later reduced by hydrogen gas generated by the reaction of sulfuric acid on zinc powder. The nanoparticles (around 5 nm) are found to be homogeneously distributed over the support. However, at high metal loading, the nanoparticles agglomerated to form large clusters (60–120 nm). As size of the nanocrystals impact the efficiency of the composite material for its intended catalytic reactions, a strict control over the size of the nanocrystals is required (Vincent and Guibal 2002, 2003). Atomic force microscopy (AFM) is another tool that is used for the examination of the surface of these materials; dos Santos et al. (2004) used AFM to show that gold nanoparticles were fully embedded into chitosan films.

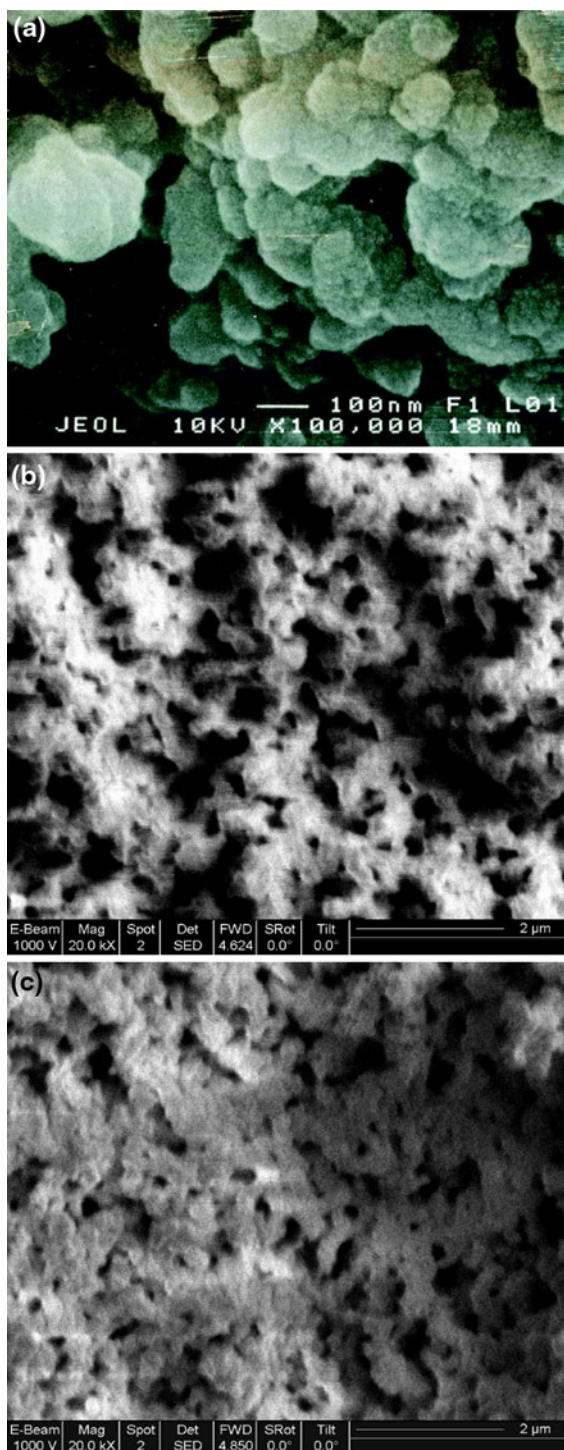


Fig. 4 Scanning electron micrograph (SEM) of **a** freshly precipitated hydrated ferric oxide (HFO) ($\times 100,000$ magnification), **b** parent macroporous anion exchanger ($\times 20,000$ magnification) and **c** hybrid anion exchanger dispersed with HFO ($\times 20,000$ magnification)

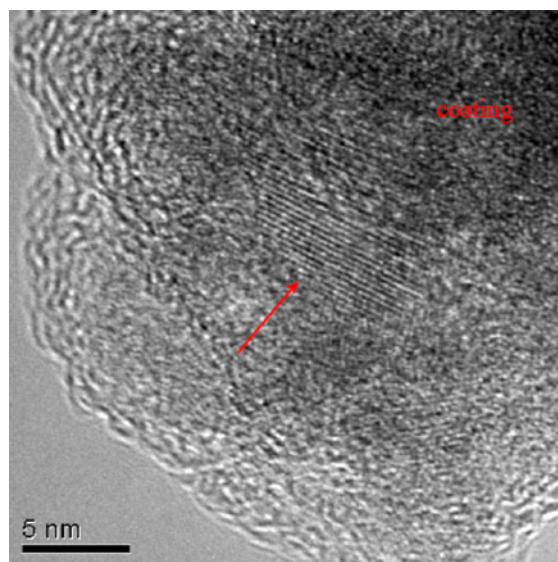


Fig. 5 Tunneling electron micrograph (TEM) image of a macroporous hybrid anion exchanger

XPS analysis

X-ray photoelectron spectroscopy (XPS) is capable of determining the valence state of metals dispersed within the PSNPs. It is important to determine the oxidation state of the metal dispersed within the PSNPs because the properties of many of the PSNPs depend on this property, such as in magnetite and zero valent metal NPs. In many cases, the synthesis procedure involves redox reactions taking place inside the matrix of the host material. The evaluation of the oxidation state of the metals incorporated inside the matrix of the host is therefore a critical parameter. Figure 11 shows an example of XPS analysis of chitosan hollow fiber loaded with Pd(II) and partially reduced (Peirano Blondet et al. 2008). The synthesis of the PSNP involved loading Pd²⁺ ions on the chitosan hollow fibers by circulating a solution of metal salt through the lumen of the fiber. The metal ion was reduced to the metal NP by circulating a solution of a reducing agent through the lumen.

The analysis shows that the metal was not completely reduced. Also, the difference between the ratio of Pd(II) to Pd⁰ before and after grinding and mixing indicates that the reduction was not homogeneous across the wall of the hollow tube. XPS analysis was also used for understanding the interactions including alloy formation between different metals when

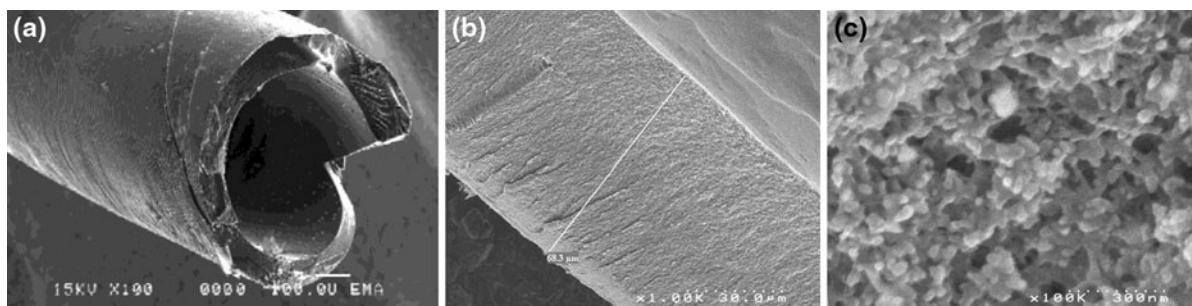


Fig. 6 SEM micrograph of **a** raw hollow fiber ($\times 100$ magnification); **b, c** hollow fiber loaded with Pd^0 (at $\times 1000$ and $\times 100,000$ magnifications, respectively)

Fig. 7 SEM-EDAX analysis (Pd) of a cross-section of chitosan hollow fiber loaded with Pd^0 at **a** high and **b** low metal content (*top* cross-section distribution, *bottom* element cartography)

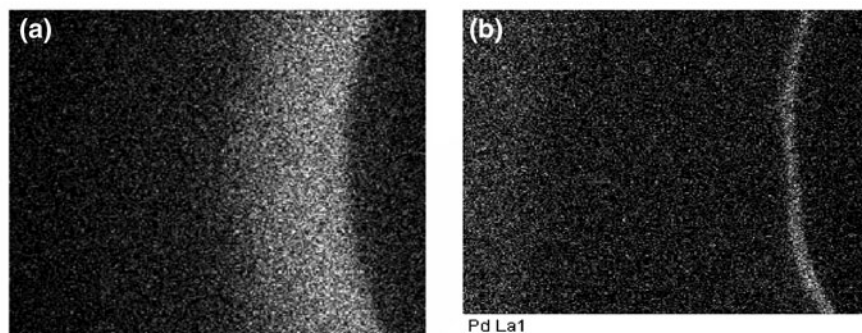
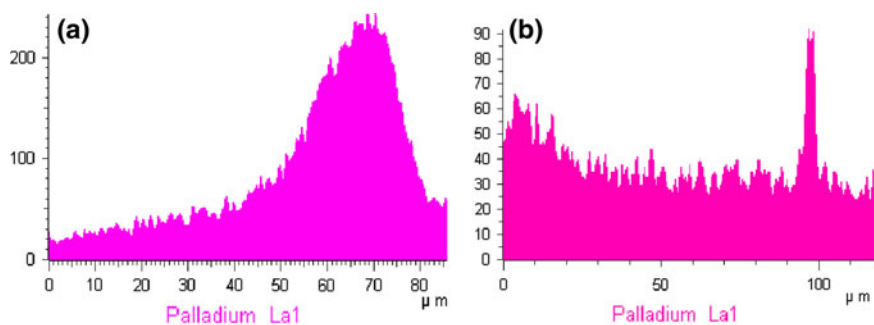
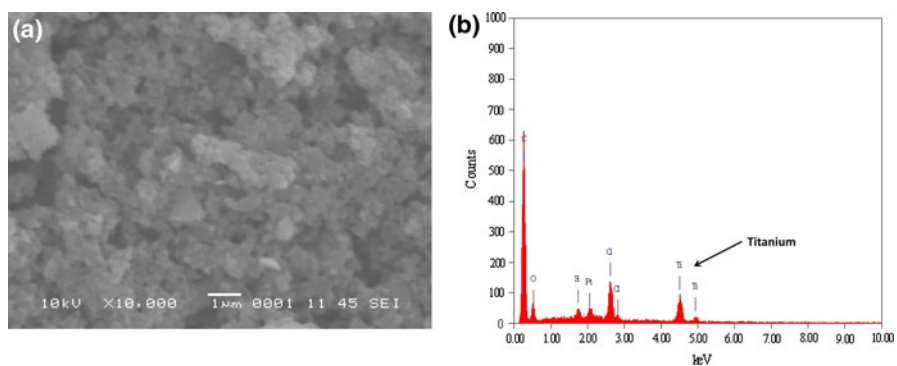


Fig. 8 **a** SEM at $\times 10,000$ magnification and **b** energy-dispersive X-ray (EDAX) spectra showing titanium for a hybrid anion exchange resin dispersed with nanoparticle of titanium dioxide



simultaneously or sequentially immobilized in synthetic polymers (Ozkaraoglu et al. 2009). XPS can be also used for identifying the metal oxide phases: for

example, Üzüim et al. (2008) used XPS to characterize the evolution of iron oxides during the sorption of Co(II) ; Wu et al. (2009a, b) characterized the

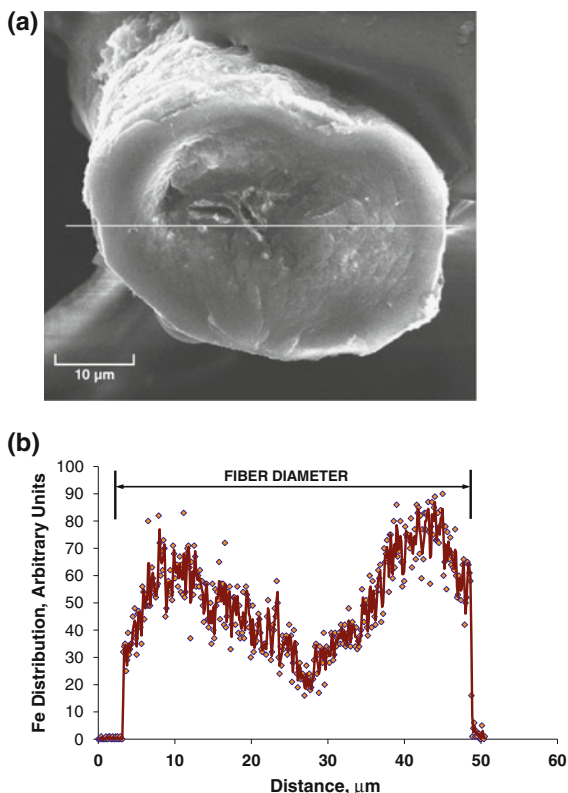


Fig. 9 **a** SEM image of cross-section of a hybrid anion exchange fiber at $\times 2,000$ magnification and **b** energy-dispersive X-ray (EDX) mapping of iron along the diameter of the cross-section of the hybrid fiber

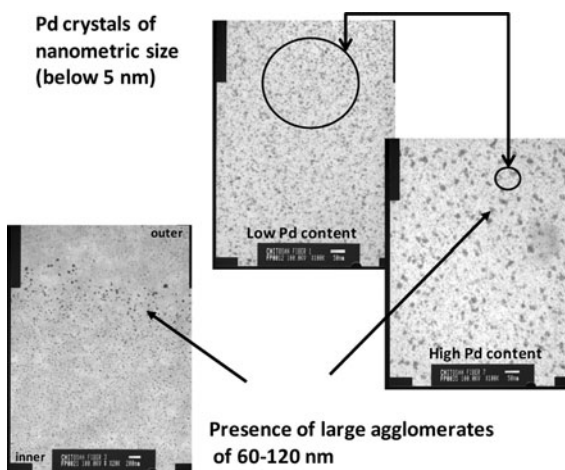


Fig. 10 TEM analysis of chitosan-Pd catalyst

reduction of the target metal from Cr(VI) to Cr(III)) when adsorbed on chitosan-Cu⁰ PSNP. Akcora et al. (2005) showed that both γ -Fe₂O₃ and Fe₃O₄ phases

were present after immobilization of iron oxides into a di-block polymer.

X-ray diffraction analysis (XRD)

XRD is used for the evaluation of the crystalline structure of the dispersed nanoparticle within the PSNPs, a property that determines accessibility to reactive groups. This technique can contribute to identify the physical and chemical form of the nanoparticles such as different forms of iron oxides (De et al. 2009), structure of the nano particles (Liu et al. 2009; Zhi et al. 2002), or to identify the mechanisms involved in metal binding on nanoparticles (Hu et al. 2006). This technique can be also used for the evaluation of the size of the nanocrystallites (Wenger et al. 2008). Figure 12 shows an example of X-ray diffraction analysis of chitosan hollow fibers loaded with Pd which is actually only partially reduced to Pd⁰ (Guibal et al. 2007). The graph in the inset shows the size of Pd⁰ nanocrystals as calculated by the Scherrer equation. Increasing the amount of Pd causes an increase in the size of the crystallites.

Surface analysis

The analysis of surface properties such as specific surface area, pore size can be approximated by BET-measurements. This parameter is strongly controlled by the structure of the parent material (macroporous or gel-type resin), the procedure followed for the dispersion of nanoparticles, or by the type of polymer (synthetic or biopolymers). For example, the process of dispersal of metal particles, their oxides, and hydroxides inside biopolymers consists of biopolymer dissolving, mixing with the metal or metal oxide, followed by coagulation, neutralization, or ionotropic gelation of the biopolymer in an appropriate cross-linking bath. The procedure results in the manufacturing of hydrogels containing huge amounts of water. The uncontrolled drying of these materials leads to the formation of xerogels with diminished pore properties whereas employment of solvent exchange (alcogels) followed by drying under supercritical CO₂ conditions (aerogels) insures enhanced porosity and better diffusion properties (Di Renzo et al. 2005; Valentin et al. 2003; Quignard et al. 2008; Robitzter et al. 2004). The drying under supercritical conditions allows

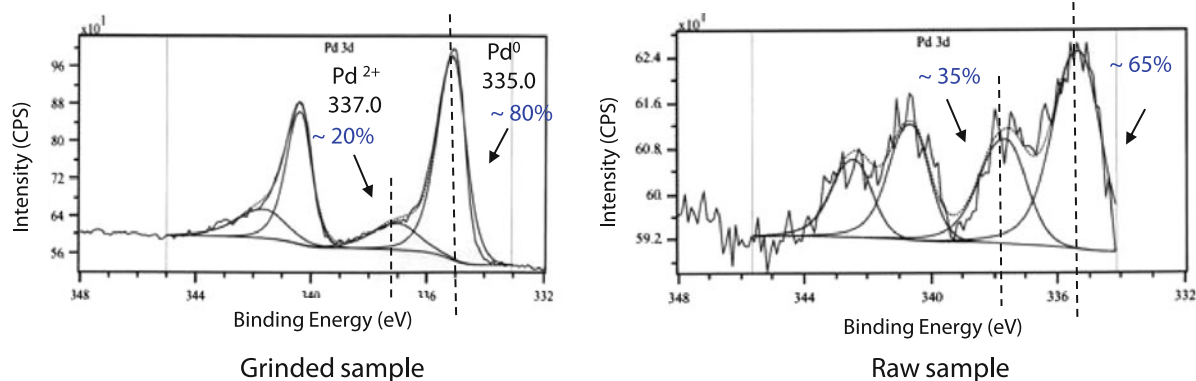


Fig. 11 XPS analysis of chitosan hollow fibers, before and after grinding

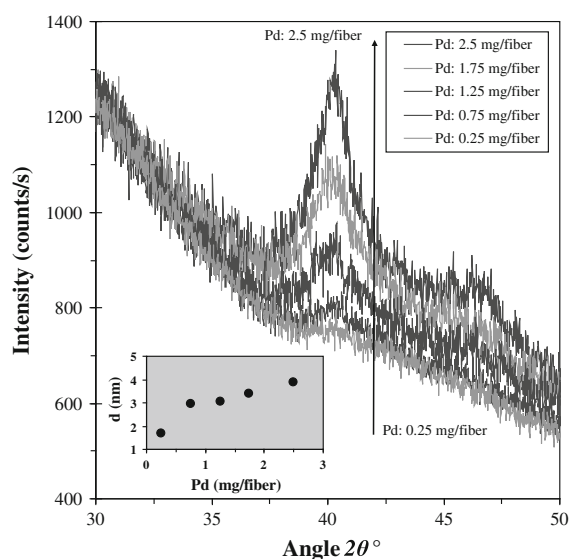


Fig. 12 X-ray diffraction pattern of chitosan hollow fibers loaded with different amounts of Pd

maintaining specific surface areas as high as 200–300 m² g⁻¹ for polysaccharides aerogels, while the uncontrolled drying irreversibly destroy the initial porosity (a few m² g⁻¹ in case of xerogels). This drying method is a promising way to synthesize new biopolymer-based materials with high mass transfer performance which is the result of fibrillar structure of these materials (Luong et al. 2008).

Other analytical techniques are available including UV–Vis spectrophotometry or FT-IR spectrometry, for the characterization of the polymers, especially for identifying the modifications brought by metal binding (Guo et al. 2009; Akamatsu et al. 2008; White et al. 2009; Zhao et al. 2006).

Applications

Most of the PSNPs containing metal oxide NPs have been developed primarily for various applications related to selective sorption of target contaminants from the background of other ions. The practical applications of metal/metal oxide-polymer PSNPs cover wide fields because the composites combine the properties of the nanoparticles and polymers. Examples of such wide range of applications in various fields include supported catalysis, sensors and biosensors, biomedical devices, electro-conductive pastes and glues, special coatings, paints and varnishes, rheomagnetic fluids, antifriction polymeric coatings among various others. The following provides an account of different applications of PSNPs to date.

Sorption applications

Different types of metal oxides have been dispersed within polymeric, porous host materials to develop a PSNP with improved durability, robust mechanical strength, and excellent sorption characteristics. Table 5 summarizes various examples of PSNP prepared and applied for sorption of different target species from the contaminated water and wastewater.

Encapsulating the metal oxide nanoparticles in a polymeric host material is necessary from the point of view of applications; however, it is also important to find out whether the functionality of the host material plays any role in the overall sorption behavior of the PSNP. Theoretically, if metal oxide nanoparticles are dispersed within a cation or anion exchanger, the

Table 5 Composite metal/metal oxide nanoparticles-polymer for sorption applications

Metal/Metal oxide phase	Support	Target sorbate	Reference
Fe(III)	Alginate	As(V)	Min and Hering (1998)
Fe ₃ O ₄	Synthetic resins	Cu(II)	Leun and Sengupta (2000)
Fe(III) oxide	Synthetic –COOH resin	Cd(II) Pb(II)	Manju and Anirudhan (2000)
SnO(OH) ₂ 1.96 H ₂ O	Carboxylated polyacrylamide	Pb(II), Hg(II), Cd(II)	Shubha et al. (2001) and Manju et al. (2002)
Fe(III) oxide	Alginate	As(III), As(V)	Zouboulis and Katsoyiannis (2002)
FeOOH	Sulfonic resin	As(III), As(V)	DeMarco et al. (2003)
FeOOH + amorphous HFO particles	Sulfonic resin, quaternary ammonium resin	As(III), As(V)	Cumbal and SenGupta (2005a)
HFO + magnetite	Amberlite XAD-2	As(V), Cu(II) 2,6-dichlorophenol	Cumbal and Sengupta (2005b)
HFO	Ion exchange fibers	As(III), As(V)	Greenleaf et al. (2006)
HFO	Sulfonic resin, quaternary ammonium resin	Cu(II), As(III), As(V)	Puttamraju and SenGupta (2006)
ZrO ₂	Quaternary ammonium resin	Cu(II), As(III), As(V)	
Fe ₃ O ₄	Gum arabic	Cu(II)	Banerjee and Chen (2007)
HFO	Quaternary ammonium resin	Phosphate	Blaney et al. (2007)
Fe ₃ O ₄	Chitosan	Fluoride	Ma et al. (2007)
HFO	Purolite A-500	As(III),As(V)	Sarkar et al. (2007, 2010b)
HFO	FIBAN (fibrous ion exchanger)	As(III),As(V)	Vatutsina et al. (2007)
Fe ₃ O ₄	Alginate	Cu(II)	Lim et al. (2008)
HFO	Polystyrene anion exchanger	As(V)	Zhang et al. (2008a, b)
Fe ₃ O ₄	Alginate	As(III),As(V)	Escudero et al. (2009)

presence of the functional groups in the ion exchanger will influence the sorption behavior of the hybrid ion exchanger. The fixed nature of the functional groups covalently attached to the polymeric matrix of the ion exchanger makes it act like a virtual semi-permeable membrane which restricts the movement of one particular type of ion across the phase boundary in an effort to conserve the electroneutrality. This gives rise to the development of Donnan potential (Helfferich 1962; Donnan 1995; Sarkar et al. 2010a). Under the influence of this potential, groups of ions with charge similar to the functional groups (co-ions) are excluded from entering in the exchanger phase while the ions with charge opposite to the functional groups (counter-ions) tend to concentrate inside the exchanger phase. Therefore, the ion-exchanger host material for nanoparticles of metal oxides can be made to completely reject the transition-metal cations while allowing enhanced selective sorption of anionic ligands and vice versa (Puttamraju and SenGupta 2006). This phenomenon offers a unique opportunity to enhance the sorption properties of metal oxide

nanoparticles through wise selection of the type of functional groups associated with the polymeric host. Figure 13a shows schematically the Donnan membrane phenomenon as applied to hybrid anion exchange resin. The concentration of anions inside the anion exchanger is much higher compared to that in the bulk. Therefore, the iron oxide nanoparticles dispersed within the bead get exposed to much higher concentrations of anions and, being selective for ligands such as arsenate anions, ends up adsorbing more arsenic than iron oxide nanoparticles alone. The data shown in Fig. 13b from a field trial at Sahuarita, Arizona supports this fact. Here, granular ferric oxide (GFO), an iron-oxide based adsorbent, was outperformed by a hybrid anion exchanger dispersed with Fe nanoparticles (Layne^{RT}) (Sarkar et al. 2011b). It proves that the anion exchanger support played a critical role in enhancing the activity of the HFO nanoparticles. It is the same principle which explains the lack of arsenic removal capacity of the hybrid cation exchange resin dispersed with Fe nanoparticles as shown in Fig. 14. A common cation exchanger bead

Fig. 13 **a** Schematic description of Donnan membrane principle explaining the enhanced capacity of the hybrid anion exchangers and **b** comparative arsenic breakthrough profiles of arsenic for field trials of hybrid anion exchanger (Layne^{RT}) and granulated ferric oxide (GFO) media

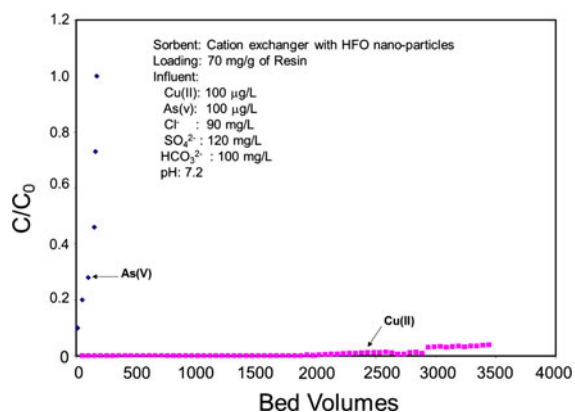
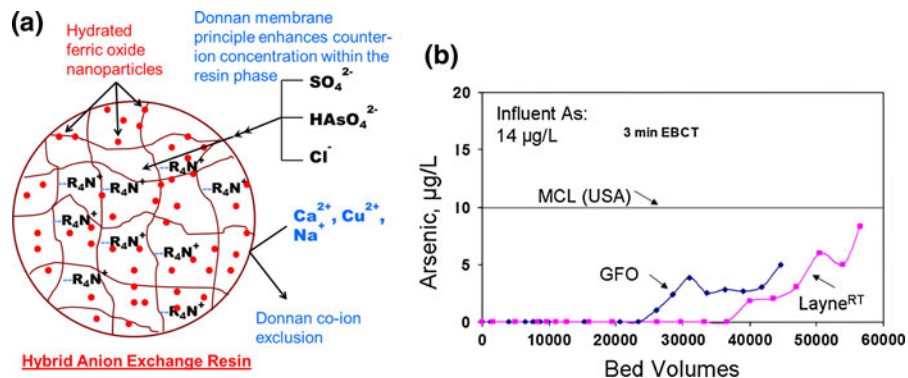


Fig. 14 Concentration profiles of Cu(II) and As(V) during the column run for hybrid cation exchanger dispersed with nanoparticles of hydrated ferric oxide

contains huge number of covalently attached anionic sulfonic acid groups (on the order of 10^{17}) (Cumbal and SenGupta 2005a). The negatively charged functional groups largely excluded negatively charged arsenate ions from entering the ion exchanger phase while attracting a high concentration of cations inside the resin bead. HFO nanoparticles are capable of showing amphoteric sorption behaviors at near-neutral pH adsorbing both Lewis acids and bases. The hybrid cation exchangers therefore showed high copper removal capacity while arsenic removal was absent, as demonstrated in Fig. 14.

Encapsulation of ferric oxide nanoparticles allow the PSNP to be regenerated. In many cases, regeneration and reuse of the PSNPs help improve the economics of the process, as well as in the overall ecological sustainability when the spent regenerants are transformed to innocuous end products and a small mass of contaminants that is stored in such a way not to leach any contaminant back into the environment

(Sarkar et al. 2005, 2008, 2010b). The adsorption capacity of the PSNP was not found to deteriorate due to regeneration. It is evident from Fig. 15 which shows that hybrid anion exchange resins dispersed with Fe removed phosphorus with the same efficiency over a number of cycles of operation (Blaney et al. 2007).

Heterogeneous catalysis

Bio- and synthetic polymer–nanoparticle composites have been extensively studied during the last decades as support for heterogeneous catalysis. A wide range of reactions have been investigated, including oxidation, hydrogenation, cyclic polymerization, Suzuki cross-coupling reaction, Tsuji–Trost reaction and so on. A review on chitosan as support for heterogeneous catalysis has been published by Guibal (2005). Table 6 summarizes various uses of the PSNPs in the field of heterogeneous catalysis.

Apart from the functionality of the polymer matrix, it is also important to consider the physical properties and the final application of the PSNP. The parent polymer as well as the synthesized PSNP must provide sufficient permeability for the target ions or molecules or reactants to gain access to the nanoparticles which actually is the site where the catalysis reaction takes place. Thus, for the reactions taking place in aqueous phase or in polar solvents, the polymer must be hydrophilic or swell slightly in water to enhance the desired properties.

Sensors and biosensors

Chemical sensors are widely used to detect and quantify both organic and inorganic substances in clinical (Lin and Leu 2005), biomedical (Endoa et al.

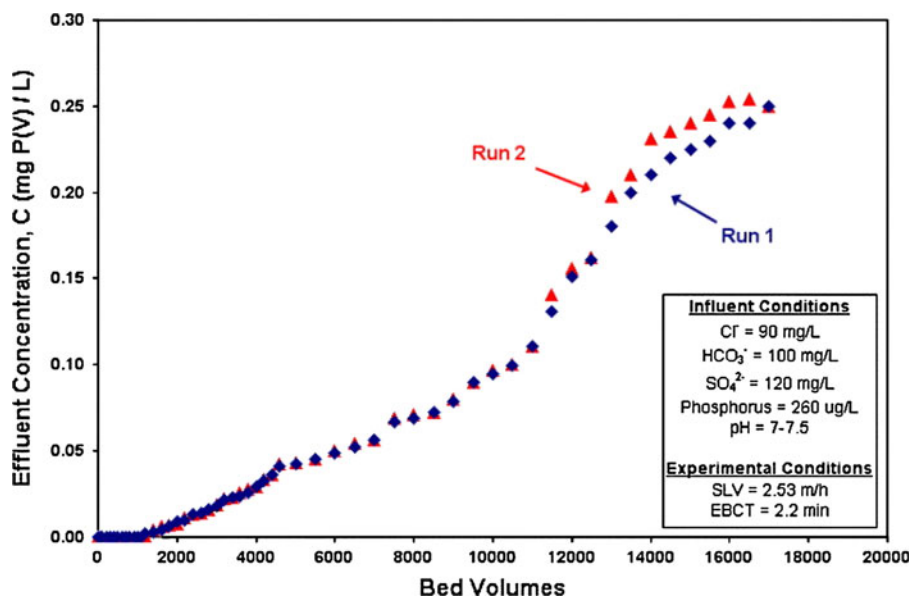


Fig. 15 Phosphate effluent histories during two consecutive runs with secondary wastewater from a wastewater treatment plant using “virgin” HAIX (Run 1) and “regenerated” HAIX (Run 2)

Table 6 A few examples of metal- and metal oxide nanoparticles immobilized on polymers

Metal/Metal oxide phase	Support	Reaction	Reference
Cu ⁰	Synthetic polymer matrix	C–Cl metathesis	Trakhtenberg et al. (2000)
Pd ⁰	Chitosan	Hydrogenation of nitro compounds	Guibal (2004, 2005) and Vincent et al. (2003, 2004)
Pd ⁰	Chitosan	Dehalogenation of chlorophenol	Vincent et al. (2003)
SiO ₂	Chitosan ^a	Monoglyceride synthesis	Molvinger et al. (2004)
TiO ₂	Chitosan ^a	Monoglyceride synthesis	El Kadib et al. (2008)
Pd ⁰	Synthetic polymer	Styrene hydrogenation	Li et al. (2008)
Fe ⁰	Carboxymethylcellulose, Starch	Perchlorate destruction	Xiong et al. (2007)
Cu ₂ ⁰	Chitosan	Dye photo-degradation	Li et al. (2008)
Pd ⁰	Synthetic polymer	Ethylene hydrogenation	Mallick et al. (2008)
Ag ⁰	Chitosan	Nitrophenol hydrogenation	Murugadoss and Chattopadhyay, (2008)
Fe ₃ O ₄	Synthetic polymer	Fenton’s reaction	Shin et al. (2008)
Pd–Co	Synthetic polymer	Suzuki cross-coupling	Niembro et al. (2008)

^a In these reactions most of the catalytic activity was provided by chitosan, the metal oxide contributed to enhancing diffusion properties by the control of polymer architecture

2007), environmental (Shenhar et al. 2005), and other fields. The main requirements for a sensor include selectivity, high response speed, sensitivity, and low cost. Amperometric sensing devices work based on measuring the current passing through an electrochemical cell when an external potential is applied; the

proportionality between the concentration of the electro-active analyte and the amount of current allows for the quantitative determination of analytes (organic and inorganic) present at trace concentrations. The disadvantages of conventional amperometric sensors, such as limited selectivity and relatively

Table 7 Applications of metal/metal oxide-polymer PSNPs in sensors and biosensors

Metal/Metal oxide phase	Support	System	Reference
Au ⁰	Synthetic polymer	Vapor sensing	Grate et al. (2003)
Au ⁰	Dextran + Synth. polymer	Biomolecule detection	Lee and Perez-Luna (2005)
Au ⁰	Chitosan	Metal sensor	Sugunan et al. (2005)
Au ⁰	Synthetic polymer	Dopamine sensor	Mathiyarasu et al. (2006)
Pd ⁰	Synthetic polymer	Glucose biosensor	Foxx and Kalu (2007)
Au ⁰	Synthetic polymer	DNA biosensor	Yang et al. (2007)
Au ⁰	Chitosan	Antigen biosensor	He et al. (2008)
Iron oxide	Chitosan	Glucose biosensor	Kaushik et al. (2008)
Fe ₃ O ₄	Chitosan	Herbicide biosensor	Loh et al. (2008)
SiO ₂	Alginate/Ionic liquid/hemoglobin	Electrocatalytic system/sensor	Sun et al. (2008)
Fe ₃ O ₄	Chitosan	Tyrosinase biosensor	Wang et al. (2008)
Pt ⁰	Synthetic polymer	H ₂ O ₂ biosensor	Chakraborty and Retna Raj (2009)
Au ⁰	Alginate/Cysteamine	H ₂ O ₂ biosensor	Chico et al. (2009)
Au ⁰	Chitosan	Glucose sensor	Feng et al. (2009)
Au ⁰	Chitosan	Metal sensor	Praig et al. (2009)

long response times, can be overcome by the use of PSNPs specially designed for the purpose. A polymer-metal PSNP yields a number of advantages based on the enhancement of both the rate of mass transfer inside the nanocomposite membrane (sensing element), and the electrocatalytic activity arising from the great specific surface area of the nanocatalyst in comparison with that of the bulk material (Welch and Compton 2006). For example, Pt and Pd nanoparticles are widely used despite their relatively high cost because of their good stability both in acidic and alkaline media, resistance to oxidation (Hrapovic et al. 2004) and high catalytic activity in various types of chemical reactions (Céspedes et al. 1996). PSNPs can be also used to enhance biosensor performance. Adhikari and Majumdar (2004) reviewed the contribution of polymers in sensor applications: these polymers contribute by intrinsically conducting properties or through the immobilization of components responsible for sensing the analyte. Decreasing the size of these conducting components (i.e., nanoparticles) contributed to the enhanced efficiency of the sensor/biosensor. Most of these systems involve the use of noble metals (gold, and platinum) (Guo and Wang 2007). The introduction of PSNPs into an enzyme immobilizing matrix can substantially improve the electron conductivity of the matrix and, therefore, enhance electron transfer from the enzyme molecule to the surface of the electrode of the sensor

(Macanas et al. 2011). Table 7 indicates a few examples of the use of PSNPs for sensing purposes.

Biomedical applications

Khlebtsov et al. (2006) described the recent advances in the use of biopolymer-gold PSNPs for the optical amplification of photothermal therapy (laser-induced therapy). They show the importance of the control of nanoparticle size (which depend on the synthetic route and conditions) on the absorption efficiency. Brown and Rehse (2007) described the encapsulation of γ -Fe₂O₃ in alginate matrix for the drug delivery of magnetic-resonance imaging contrast agent and for hyperthermic treatment of malignant tumors. Ma et al. (2008) reported a series of applications of superparamagnetic iron oxide nanoparticles immobilized in alginate in the field of health: among these applications the most relevant were the study of pharmacokinetics and tissue distribution, drug release, magnetic resonance imaging contrast agent, and specific organ delivery. The system was also very efficient for the detection of liver cancers. Gold-chitosan PSNPs have been used for the delivery of plasmid DNA (Zhou et al. 2008). Compared to conventional free DNA vaccine, the PSNPs were revealed to be ten times more efficient; the gold-chitosan conjugate was also efficient against cytotoxic T lymphocytes while the free DNA vaccine was not active.

Bactericide

Polymer–metal PSNPs can also find application for disinfection in water treatment. Ion exchange materials modified with nanoparticles that display antimicrobial activity, for example, silver nanoparticles (Schmid 1994; Nowack 2007; Kong and Jang 2008) are of particular interest. Modification of ion exchange materials such as resins, membranes or fibers with nanoparticles with bactericidal properties can enable water utilities to achieve ability to eliminate microbiological contaminants without the production of harmful by-products such as chlorinated organics that are produced during disinfection by chlorine, the widely used disinfection process. Environmental safety of nanoparticles is currently a concern; therefore encapsulation of the nanoparticles within a polymeric host offers a viable alternative. One material is a fibrous functional polymer (e.g., FIBAN-K1 or FIBAN-K4) with immobilized core shell Ag–Co nanoparticles distributed mainly at the surfaces of the fibers so that they are maximally accessible for the elimination of bacteria. MNPs consist of superparamagnetic cores coated with silver metal shells of minimal thickness that provide maximal bactericidal activity. The nanoparticles are captured inside a polymer matrix that prevents their escape into the water under treatment. The superparamagnetic nature of nanoparticles provides additional material safety, as any nanoparticle leached from a polymer matrix can be easily captured by magnetic traps to completely prevent post-contamination of the treated water (Macanas et al. 2011).

Conclusion

PSNPs or polymer-supported nanoparticles are a new class of materials that are permeable with two distinctly different phases, namely, a functionalized polymeric phase that primarily acts as a host and an inorganic metal or metal oxide phase that is finely dispersed within the host material. The properties of the hybrid material depend on the nature of functional groups on the polymeric phase as well as on the size and nature of the nanoparticle dispersed within. Diverse nature of the functional groups and the different factors controlling the sizes of the dispersed nanoparticles often make it a challenging task to effectively disperse and control the properties of the

hybrid material. The hybrid material retains the properties of each of the phases it consists of; yet, it offers a synergy that is not otherwise attainable individually in absence to the other. Synthesis of the PSNPs can follow several routes; however, the in-situ method of synthesis is the most promising techniques, because it can produce a variety of polymer–metal/metal oxide PSNPs that offer practical applications in different fields. The attractiveness of this technique lies not only in its relative simplicity but also in its flexibility and the possibility to tune the properties of the final product to the requirements of its final application. This is especially true for biopolymers such as alginate and chitosan, PSNP composed of which can have various morphologies depending upon simple variations in the synthesis process such as the process of drying. It is also possible to run repetitive loading cycles either with the same or different metal (or metal oxides), which results, in the first case, in the increase of the density of NPs population inside the polymer matrix and in the variation of the sizes of the NPs dispersed. In the second case, it is possible to have more than one metal or metal-oxides dispersed within the polymer giving rise to core–shell or core-sandwich structures. There is still a need for standardization of the synthesis of these PSNP products to make them attractive at the industrial scales for both production as well as synthesis. Through a combination of the diverse chemical nature, physical properties, and morphology of both the constituting phases, namely the functional polymeric and inorganic nanoparticle phases, it is possible to prepare numerous types of PSNPs with varied properties and applications. To date, only a few of the available combinations have been attempted. Nevertheless, the hybrid ion exchangers have already found numerous applications in practical fields including environmental remediation. Ample opportunities exist for the development of new types of hybrid ion exchangers for applications in areas such as heterogeneous catalysis, sensors, health and medicine and drug-delivery.

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