

Developing nanotechnological strategies for green industrial processes*

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Abstract: Nanotechnology and green chemistry can have much in common from the point of view of processes, considering the possibilities of improving efficiency and quality, achieving a better economy of atoms and energy, promoting catalysis under mild and sustainable conditions, and facilitating online monitoring of production lines and environment. Some of these aspects are dealt with in this paper, focusing on selected examples of application of functionalized nanoparticles and -materials in chemistry and industry.

Keywords: biocatalysis; chemical sensors; environmental chemistry; green chemistry; nano-materials; nanoparticles.

INTRODUCTION

Nowadays, the development and implementation of industrial processes are increasingly dependent upon environmental, economy, and societal factors. As pointed out by Clark [1], serious concerns are being raised by (i) the tendency of diminishing supplies of non-sustainable resources; (ii) the impact of new legislation, forcing testing of all chemicals; (iii) increasing producer responsibility; (iv) increasing costs for storing hazardous substances; (v) increasing costs of waste disposal; (vi) increasing energy costs; and (vii) increasing petrochemical costs.

These critical points, encompassed in many senses by the green chemistry principles, demand new strategies to generate sustainable industrial processes, including new chemistry, new process design, and new equipment [2]. Along these lines, the association between nanotechnology and green chemistry can be highly rewarding. As a matter of fact, many of the green chemistry requirements, such as the economy of atoms, processing steps, materials, solvents, and energy can be fulfilled by the responsible development of nanotechnology. In particular, nanotechnology can provide suitable, high-performance nanomaterials for green applications, including better products and manufacturing. This issue will be dealt with in the first part of this article. Among the nanomaterials, functionalized nanoparticles can be a good choice for developing greener industrial processes. The possibilities in this area are widespread, and for this reason, in this article, the examples will be restricted to a few classes of nanoparticles exhibiting special or relevant properties.

Green chemistry requires the development of sensors for online monitoring of industrial processes, in order to detect problems and prevent accidents and failures. Accordingly, the second part of this article will focus on the possibilities of using nanotechnology for sensor applications in chemical industries.

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Catalysis is another point recognized by green chemistry as a very important way of increasing the efficiency of a process, providing higher benefits in terms of the economy of atoms, energy, and yields. This subject is also quite broad, and for the sake of brevity, only a special topic will be commented on this article, dealing with the question: How can nanotechnology improve biocatalysis?

Finally, remediation and rational exploration of natural resources are one of the issues demanding green chemistry concerns and solutions. Some relevant aspects will be discussed in the last part of this article, focusing on the applications of nanotechnology in environmental problems and on a new, promising green process for metal extraction and production, called *magnetic nanohydrometallurgy* (MNHM) [3].

NANOPARTICLES FOR GREEN CHEMISTRY APPLICATIONS

In recent years, nanoparticles have been successfully employed in many nanotechnological applications, either as structural components of hybrid materials and nanocomposites, or as functional nanomaterials, especially for sensor, catalysis, and biological applications [4,5]. The reasons for the increasing demand of nanoparticles are related to their outstanding properties in relation to the conventional materials, such as

- a very large surface area—in a 1-nm metal particle, about 60 % of atoms are exposed at the surface, enhancing their chemical and physical activity, for instance, in catalysis and light scattering properties;
- the possibility of introducing functional groups, in order to make them compatible with different media, such as solvents, polymers, and biomaterials;
- good mobility in fluids, for application in direct and supported catalysis, and in some cases, as ferrofluids;
- occurrence of local plasmon resonance effects, particularly for copper, silver, and gold nanoparticles (Au-NPs), allowing one to exploit their use as SERS (surface-enhanced Raman scattering) probes;
- occurrence of superparamagnetism in the case of some metal-oxide nanoparticles, leading to very strong magnetization response; and
- the possibility of performing photoinduced charge separation at the nanoscale, particularly in the case of the wide band-gap metal oxides such as titanium dioxide, allowing important applications in photoelectrochemical and photocatalytical devices.

Nanoparticles are being used as additives to improve the performance in conventional materials, yielding nanocomposites displaying better physical and chemical properties [4], such as strong mechanical resistance, flame retarding, and large gas-diffusion barriers.

Carbon nanoparticles are currently employed in the fabrication of tires. About 25 % of a tire is composed of carbon black. The successful use of silicon dioxide or clay nanoparticles replacing carbon black is being announced as the new age of green tires. Such composite materials exhibit superior qualities in relation to conventional tires, in terms of thermal behavior and mechanical resistance. The observed carbon economy is not only related to the replacement of carbon by the inorganic nanoparticles, but it also reflects a better performance, preventing excessive heating and increasing the useful lifetime of the tire. These aspects have inspired the green tire denomination for this product.

Silver nanoparticles (Ag-NPs) can impart effective antibacterial properties to materials, for health applications, food containers, and a clean environment. Their use for antibacterial protection is actually very old. For instance, at the beginning of the last century, Robert Hottinger, a sanitarian and professor at the Polytechnic School in Brazil, introduced the use of colloidal silver coatings in domestic clay pots in order to sterilize drinking water. Such a strategy helped reduce considerably the occurrence of diseases and health problems in the population. In spite of this, nowadays there is a general concern regarding the manipulation of nanoparticles by the workers, and silver is not an exception. On the other hand,

Ag-NPs can be incorporated into composite materials in order to prevent their release to the environment, while keeping their bacteriostatic activity, as a source of silver ions. In this sense, green procedures have already been developed for generating Ag-NPs directly inside the master batch supplies, facilitating their incorporation into plastics and nanocomposite materials without exposing the workers to any possible risk [6].

Another interesting green application of Ag-NPs has been patented by PETROBRÁS [7], for the separation of propylene from propane, using facilitated transport in membranes. Propylene is one of the most important primary petrochemical products, however, its separation from propane mixtures is quite difficult, because of their very similar physical properties. For this reason, gigantic distillation towers, rising up to 100 m high, are usually required, demanding huge quantities of energy. In the alternative green process, polymeric membranes containing Ag-NPs were employed to interact, in a selective way, with propylene/propane mixture. Propylene, in contrast to propane, is able to bind silver atoms using their available π -orbitals, forming labile complexes at the nanoparticles surface. In this way, it can be transported by the nanoparticles, permeating the membrane in order to be collected outside, while propane remains in the original reservoir. Effective separation, proceeding at room temperature and ambient conditions, can be performed using this green strategy, exhibiting separation factors up to 400 times, more than enough to be explored commercially.

NANOTECHNOLOGY-BASED SENSORS FOR ONLINE MONITORING OF PROCESSES

Nanotechnology can greatly improve the performance of sensors, by using nanoparticles and nanostructured materials as probes, including thin-layer molecular materials conveying the functionality of all the chemical components involved. As a matter of fact, many successful electrochemical methods are based on the use of molecularly modified electrodes, because they exhibit enhanced performance, incorporating the chemistry and physics of the immobilized species. The use of modifiers can also improve electron transfer, helping in many cases to prevent electrode poisoning and undesirable electrochemical processes [8–11].

Versatile nanosensors have already been obtained using functional supramolecular materials [8–11] derived from porphyrins and porphyrazines combined with ruthenium polypyridine complexes (Fig. 1). Such materials are really outstanding because of their facility to yield electrochemically conducting thin films, providing specific redox gates for electron transport to the electrode.

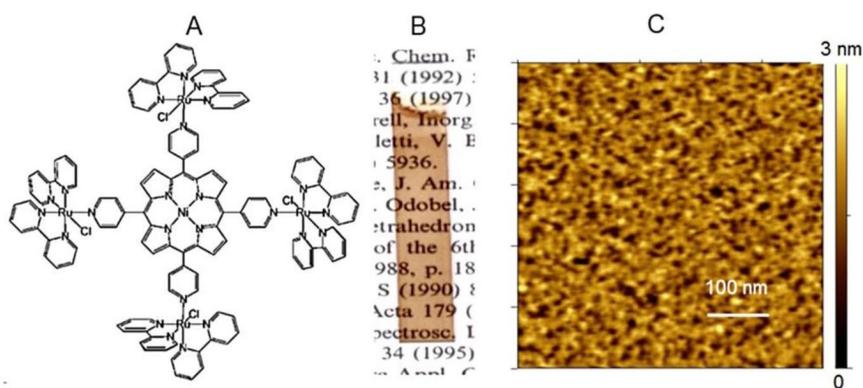


Fig. 1 A typical supramolecular porphyrin containing four peripheral ruthenium polypyridine complexes (A), and its drop casting generated molecular film on glass (B), with the corresponding AFM (MAC mode) imaging (C).

A typical electrochemical gate associated with the presence of the ruthenium complexes is observed around 0.9 V, corresponding to the Ru(III)/(II) redox potential. In the presence of redox analytes such as ferrocyanide, sulfite, vitamin C, nitrite and L-dopa, their conventional electrochemical response is replaced by a very sharp peak, appearing just at the onset of the Ru(III)/(II) gate (Fig. 2). This peak is highly reproducible, and its intensity is proportional to the concentration of the analytes, showing a remarkable sensitivity up to the ppm limit.

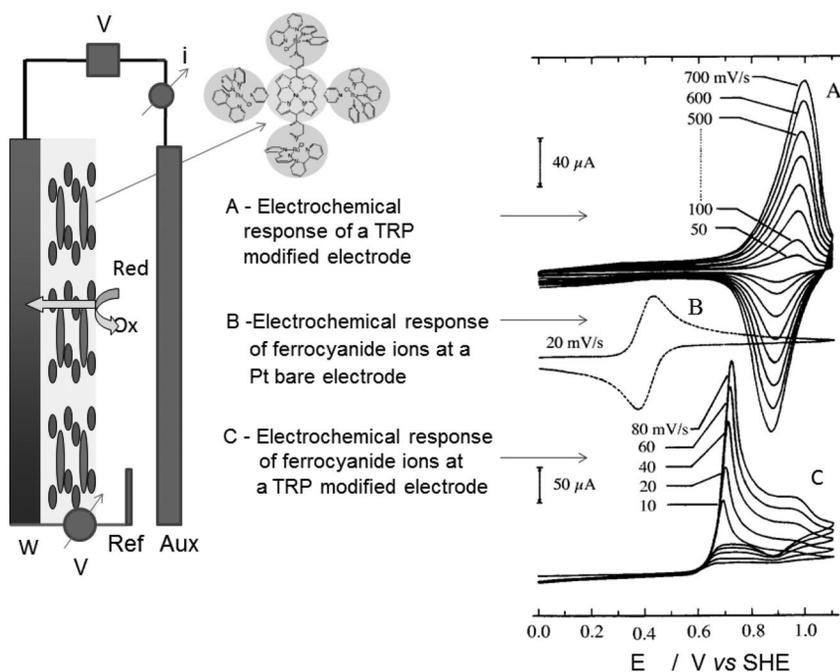


Fig. 2 The molecular film of the tetraruthenated porphyrin (TRP) can be directly employed in the electrochemical device (left), exhibiting a reversible wave at 0.9 V associated with the Ru(III)/(II) redox couple (A). The characteristic $[\text{Fe}(\text{CN})_6]^{3-/4-}$ wave at 0.4 V observed using a bare Pt electrode (B) is replaced by a very sharp peak in the presence of the supramolecular film (C), occurring just at the onset of the redox gate.

In this way, conventional solid electrodes (e.g., platinum, gold, glassy carbon) can be readily converted into selective redox probes by simple drop casting, generating thin films of the supramolecular compounds. Some films are relatively soluble, precluding their long-term use. For this reason, several strategies have been devised to overcome this problem, including the formation of electrostatically self-assembled thin films, in situ electropolymerization, or the generation of hetero-hybrid films combining, for instance, Au-NPs and supramolecular species. Such thin films are suited for application in flow injection analysis, affording rapid, reliable analytical response for online application in food and beverage analysis [8–17].

Another type of application is provided by Au- and Ag-NPs and their thin films, based on the occurrence of the so-called surface plasmon resonance (SPR) effect. Under the influence of oscillating electric fields, the surface electrons of such thin films can enter in resonance, generating periodic waves called plasmons. In principle, an electromagnetic radiation could also excite the surface plasmon waves, however, there are some restrictions imposed by the local dielectric constants, preventing the matching of the exciting and propagating vector waves. This problem has been solved [18] by modulating the excitation waves using an optical prism placed below the gold film. In this arrangement, there is a crit-

ical angle capable of inducing resonance between the exciting wavelength and the plasmon waves. Such an angle is sensitive to picogram amounts of substrates adsorbed onto the gold film, providing a very sensitive analytical tool, commercially available as the SPR technique. It illustrates an interesting application of a nanometric film, which is also suitable for online monitoring the production processes, such as in biotechnology and pharmaceutical industries.

In the case of the metal nanoparticles, the plasmon waves are localized and can interact directly with the exciting radiation, showing a resonance effect at specific wavelengths depending upon the dielectric constants involved and the particle size. Such resonance has already been theoretically modeled by Mie, more than a century ago [19].

Basically, the nanoparticle electrons oscillate simultaneously with the radiation electromagnetic fields, creating oscillating dipoles. The resonant electric field leads to anomalous light scattering and absorption, responsible for the typical reddish colors of the Au-NPs. Such electric fields are strongly enhanced particularly at the conjunction of two or more nanoparticles, because of the occurrence of local "hot spots". One of the consequences of such local electric fields is the strong enhancement of Raman scattering for the molecules adsorbed on the nanoparticles surface, also known as the SERS effect [20–23]. When the exciting wavelength is in resonance with the electronic bands of the adsorbed molecules and/or charge-transfer bands from the molecules to the metal Fermi level (or vice versa), the enhancement can reach more than 10 orders of magnitude. In some cases, even a single-molecule detection has been performed using SERS probes.

An interesting SERS nanoprobe has been obtained by incorporating a multifunctional ligand, such as trimercaptotriazine (TMT), at the Au-NP surface [24]. It has been shown that the localized plasmon resonance band of the 25-nm citrate-stabilized Au-NPs shifts from 522 to 528 nm in the presence of TMT, with no evidence of agglomeration. In order to observe the SERS effect, using the excitation wavelength at 785 nm, a very small amount of NaCl solution has been added, just enough to start agglomeration. This can be monitored by rise of a characteristic plasmon coupling band at 700 nm. Agglomeration was kept only incipient, in order to ensure stationary conditions and prevent precipitation. Under this circumstance, strong, reproducible SERS signals have been recorded for the TMT-Au-NPs (Fig. 3).

The observed SERS peaks are mainly associated with the vibrations involving the C–S and S–H groups at 1259, 897, 872, 485, and 432 cm^{-1} , as well as with the ring vibrations at 1218 and 971 cm^{-1} of TMT. It should be noted that after binding, there are available a third SH and two heterocyclic N atoms of TMT, for interacting with substrates such as heavy metal ions. As a matter of fact, in the presence of Hg^{2+} ions the SERS profile of TMT-Au-NPs is dramatically changed, showing a systematic decrease of the C–S vibrational peaks at 485 and 432 nm, upon the metal ion concentration increase in the range of 2×10^{-7} to 2×10^{-6} mol dm^{-3} , concomitant with the increase of the ring vibrational peak at 971 cm^{-1} . The changes in the vibrational pattern are indicative of the binding of Hg^{2+} ions to the thiol groups, and to the heterocyclic N-atom, presumably in a bidentate coordination mode, as illustrated in Fig. 4.

The simultaneous changes in the intensities of the vibrational peaks at 973, 485, and 432 cm^{-1} allow to use the relative intensities, e.g., at 432/971 and 485/971, to build up calibration curves as a function of the concentration of Hg^{2+} ions, as shown in Fig. 3 inset. In this way, the determination of the concentration of Hg^{2+} at ppb levels, from the SERS spectrum can be carried out directly, with no need of using internal standards as in the conventional Raman experiments. The method has been extended for other heavy metal ions, and in practice, it can be carried out using very small amounts of substrates in association with portable Raman equipment for in situ measurements of hazardous metal ions in water. Recently, the application of this type of SERS probe has been extended to the classical Feigl spot test analysis, which is carried out on a filter paper, by using selective reagents in the presence of Au-NPs, and monitoring the enhanced Raman signals [25]. Such application, extending the detection limit of the analytes, can open interesting possibilities in forensic chemistry.

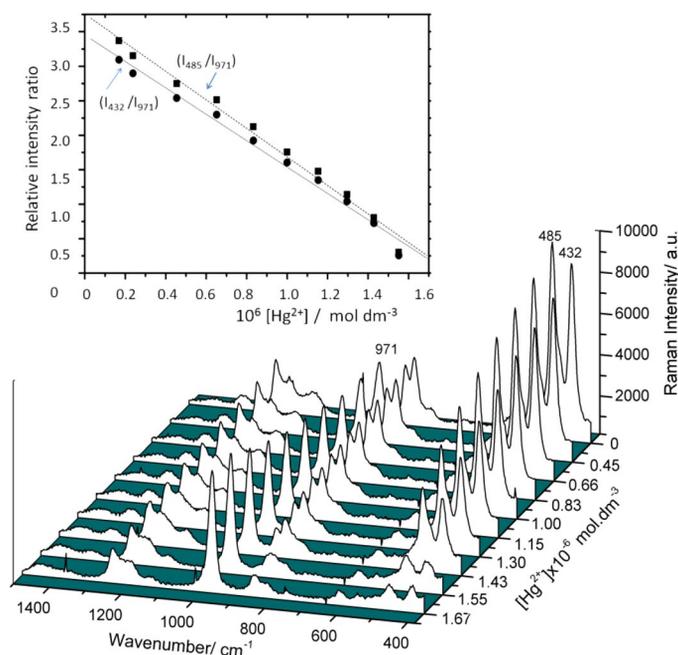


Fig. 3 Changes in the SERS profiles of TMT-AuNPs in the presence of $0\text{--}10^{-6}$ mol dm $^{-3}$ Hg $^{2+}$ ions in aqueous solution, and the linear correlation of the peak intensity ratios at 485 or 432 and 971 cm $^{-1}$ vs. concentration (inset).

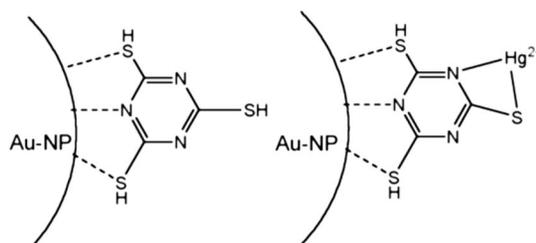


Fig. 4 Binding modes of TMT to AuNP and Hg $^{2+}$ ions.

NANOTECHNOLOGY IMPROVING ENZYMATIC CATALYSIS

Enzymes are important biocatalysts increasingly employed in the production of fine chemicals, particularly when a high enantiomeric purity is required, e.g., for pharmaceutical use. As naturally occurring catalysts, they are of great interest from the point of view of green chemistry; however, they also exhibit some limitations, such as their relatively poor stability for long-term use and their high cost. Their catalytic roles rely on the stabilization of the transition state, while their specificity is related to the particular mode of enzyme–substrate interaction. This can be dealt with in terms of the Emil Fisher key-lock scheme proposed in 1894, or of Koshland's model [26] incorporating discrete and reversible enzyme conformational changes induced by the substrate. As a matter of fact, enzymes can make use of their internal motion to provide an open form for the entrance of the substrate. After this, the presence of substrate induces a closed conformation, preventing the escape and performing more efficient catalysis.

An important strategy to improve the enzyme performance is by carrying out their immobilization on an appropriate support [27–31]. It has been shown that immobilization can effectively influence

the stability and activity of the enzymes, e.g., by inducing structural changes or improving their protection against intramolecular processes, such as autolysis, proteolysis, and aggregation. On the other hand, the use of immobilized enzymes tends to simplify the design of the reactor, allowing the catalysis to be controlled or stopped, by their programmed removal from the reaction media.

The choice of the best or most convenient support depends upon the type of enzyme. The support characteristics should include a large surface area and an extensive functionalization incorporating a high density of reactive groups, with minimal steric hindrances, in order to improve the combination with the enzyme.

Among the many existing immobilization strategies, the use of superparamagnetic nanoparticles is particularly rewarding from the point of view of efficiency and enzyme recovery processes [32]. Nanoparticles, in general, are particularly interesting support materials because they provide large surface areas and high mass transference, associated with a good mobility in solution. The inclusion of magnetic properties is an additional advantage, allowing enzyme transportation, concentration, and recovery using commercially available magnets.

The magnetic properties associated with nanoparticles, such as magnetite and maghemite, are better described as superparamagnetic, because of their characteristic magnetization profiles in the hysteresis loop. In contrast to the bulk magnetic materials, which respond to the applied field through the alignment of the net magnetic domains, magnetic nanoparticles coherently rotate their single vectors, overcoming any possible anisotropy. In this way, the coherent orientation of the collective single magnetic domains turns the nanoparticles strongly superparamagnetic, exhibiting very large magnetic induction response in the presence of an applied field [33–38]. Under appropriate conditions, this property can be transferred to the whole system, generating superparamagnetic fluids or ferrofluids.

The immobilization procedures can involve the direct interaction (or adsorption) of the enzymes with the functionalized superparamagnetic nanoparticles, by means of hydrogen bonding and/or electrostatic interactions, or by forming covalent bonds (chemisorption). The nanoparticles functionalization is a very important requisite in this process, since it allows introducing suitable functional groups at the nanoparticles surface, in order to interact with the enzymes and to help stabilize the nanoparticles in solution. Generally, this is carried out simultaneously with the nanoparticles silanization, using, for instance, triethoxysilane attached to an alkyl amine, as in the case of aminopropyl-triethoxysilane (APTS), $(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_n\text{NH}_2$, or an alkyl thiol species, e.g., $(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_n\text{SH}$. Silanization leads to the formation of a protecting silicate coating around the magnetic core, while allowing the functional groups on the surface to be anchored. Particularly in the case of the redox enzymes, the presence of exposed iron sites can interfere in the catalysis [39], and the silanization procedure has been reinforced by applying an additional treatment of the freshly prepared nanoparticles with tetraethoxysilane.

After the silanization step, the enzymes can be attached to the functionalized superparamagnetic nanoparticles, by electrostatic adsorption or using a convenient linker such as glutaraldehyde, for amine groups, or EDC (1-ethyl-3-(3-dimethylaminopropyl)carbodiimide), for carboxylic groups.

A large number of enzymes have already been combined with superparamagnetic nanoparticles [32], encompassing mainly three typical classes, in addition to some multi-enzyme systems:

- (a) Hydrolases: acetylcholinesterase, aminopeptidase, amylase, amyloglucosidase, cellulase, chitosanase, chymotrypsin, esterase, epoxide hydrolases, β -D-galactosidase, glucosidase, haloalkanedehalogenase, lipase, lysozyme, pectinase, phosphatase, subtilisin, trypsin, urease.
- (b) Oxidoreductases: alcohol dehydrogenase, D-amino acid oxidase, catalase, catechol dioxygenase, cholesterol oxidase, fructosyl amino-acid oxidase, glucose oxidase, lactase, L-lactate dehydrogenase, peroxidase, tyrosinase, xantine oxidase.
- (c) Transferases: pyruvate phosphate dikinase, RNA polymerase.

A typical example can be illustrated by lipase, an enzyme that hydrolyzes esters such as the triglycerides yielding carboxylic acids and alcohols (glycerol). Esterification, which is the reverse reac-

tion, is usually precluded in water; however, in this case, a suspension of lipase in organic solvents can be employed. In this way, chemo-, regio-, and stereoselective esterification or transesterification reactions have been successfully performed [40].

For instance, *Burkholderia cepacia* lipase (BCL) has been immobilized [41–43] on superparamagnetic nanoparticles using three different methodologies (adsorption, chemisorption with carboxybenzaldehyde, and chemisorption with glutaraldehyde) and employed in the kinetic resolution (KR) of a chiral drug precursor, (RS)-2-bromo-1-(phenyl)ethanol, via enantioselective acetylation reaction (Scheme 1).



Scheme 1 KR of a chiral drug precursor, (RS)-2-bromo-1-(phenyl)ethanol, via enantioselective acetylation reaction using BCL immobilized on superparamagnetic nanoparticles.

A great improvement of the lipase catalytical performance has been reported after immobilization [41–43]. The free enzyme yielded the ester with poor enantiomeric ratio $E < 30$, but after its immobilization on magnetic nanoparticles the E -value exceeded 200. The effect of several reaction parameters in the KR has been studied. The best results for KR were obtained using vinyl acetate as acetyl donor and toluene as solvent, yielding the ester in high enantiomeric excess (ee > 99 %) and $E > 200$.

The immobilized lipase showed a good recyclability for at least five cycles, after collecting with a magnet and employing again in successive experiments (Fig. 5). In this case, from the several immo-

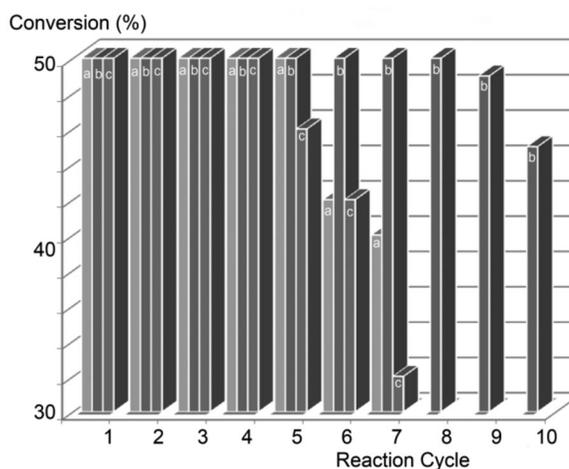


Fig. 5 Comparison on the reusability of the BCL immobilized by different methodologies: (a) carboxybenzaldehyde, (b) glutaraldehyde, (c) adsorption, in the KR of (RS)-2-bromo-1-(phenyl)ethanol (Scheme 1).

bilized forms, the glutaraldehyde method was the best one in terms of temperature stability and reusability, exceeding eight cycles keeping the same conversion efficiency and enantioselectivity.

This case exemplifies the possibilities to be explored in enzymatic catalysis and biotechnology, using superparamagnetic nanoparticles. By improving the performance and allowing the recycling of the very expensive enzymes, the expectations concerning the green chemistry strategies have been fulfilled. It should be noticed that in addition to the biosynthetic catalysis, interesting bioelectroanalytical applications have also been reported using magnetically modified enzymes and substrates [44–48].

NANOTECHNOLOGY APPLIED TO ENVIRONMENTAL AND HYDROMETALLURGY PROBLEMS

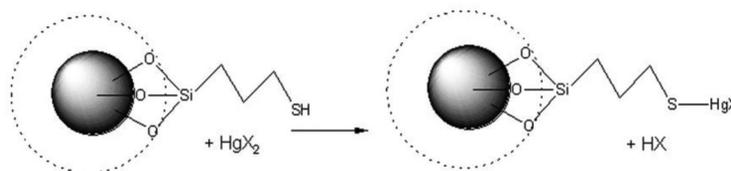
Another potential green application of superparamagnetic nanoparticles is in the environmental and mineral processing area. It should be noted that in the past two decades the global production of strategic metals, such as copper, has trended away from pyrometallurgical processes, in part because of the rich ores depletion and global warming concerns. New initiatives have been directed by legislation towards the supposedly greener hydrometallurgical technologies.

The hydrometallurgical method for copper comprises typically the heap leaching of oxide copper ores with acids (or microorganisms), and metal processing by complexation with a selective organic reagent, followed by solvent extraction (SX), and electrowinning (EW), after the decomposition of the complexes with acids and transference to the aqueous phase [49–54]. Presently, more than 20 % of the world production of copper is being achieved through this route.

In addition to the metalliferous mineral industry, SX-EW hydrometallurgy has also been used in the recovery of copper from electric/electronic wastes, including printed circuit boards [55–59]. Considering the increasing world demand of copper, any improvement in the production process becomes highly relevant in terms of economy and sustainability.

Recently, we have employed an external commercial miniature magnet (e.g., $\text{Nd}_2\text{Fe}_{14}\text{B}$) to concentrate the superparamagnetic nanoparticles at the electrode surface and perform electrolysis directly. Normally, the electrochemical response is blocked by the local film formed by the nanoparticles. However, we have shown that when the superparamagnetic nanoparticles incorporate electroactive species, such as copper and mercury ions, the films become rather strongly conducting, exhibiting, in contrast, an enhanced electrochemical response due to the pre-concentration effect [60–62].

This discovery has been successfully applied for monitoring mercury contamination. Mercury and its common chemical forms are toxic, persistent species in the environment [63,64]. In aqueous solution it is usually present as mercury chloride and soluble aqueous complexes, and its determination has been performed by spectroscopic methods, as well as by stripping analysis, using standard electrochemical methods [65,66]. However, the use of magnetite (Fe_3O_4) superparamagnetic nanoparticles (MagNPs) previously modified with mercaptopropyltriethoxysilane (MPTS, Scheme 2) allowed not only the capture of mercury ions from aqueous solution and in crude oil samples, but also concentration of them at the electrode surface with the aid of an external magnet. In this way, it is possible to perform electroanalysis directly with great sensitivity (Fig. 6), or to apply any of the existing spectroscopic methods on the concentrated nanoparticle samples.



Scheme 2 Capturing and transporting Hg^{2+} ions with superparamagnetic nanoparticles functionalized with MPTS.

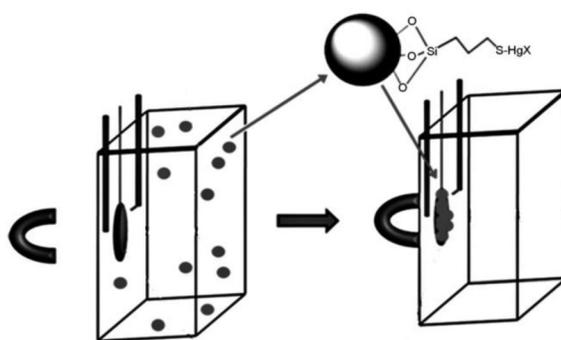


Fig. 6 Concentrating the superparamagnetic nanoparticles on the working electrode, using an external magnet (reproduced from ref. [61])

Their excellent electrochemical response has allowed electrochemical analysis to be performed *in situ* (Fig. 7), with no need to dissolve then in order to release the mercury ions, as commonly performed in most analytical methods.

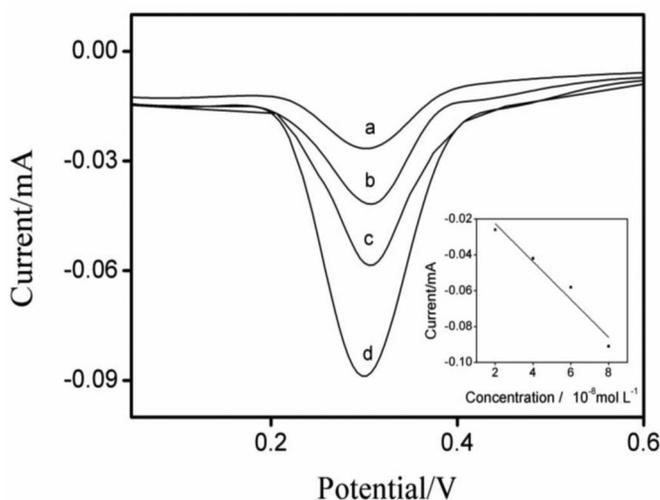


Fig. 7 Square-wave voltammograms of magnetically confined nanoparticles previously treated with 10 ml of (a) 2×10^{-8} ; (b) 4×10^{-8} ; (c) 6×10^{-8} ; (d) $8 \times 10^{-8} \text{ mol L}^{-1} \text{ Hg}^{2+}$ ions, $F = 30 \text{ Hz}$, $E_{\text{step}} = 0.005 \text{ V}$, $E_{\text{Time}} = 10 \text{ s}$ scan rate = $150 \text{ mV} \cdot \text{s}^{-1}$, $0.6 \text{ V} \rightarrow -0.4 \text{ V}$, $\text{KNO}_3 \text{ } 1.0 \cdot 10^{-1} \text{ mol L}^{-1}$, pH 7 (reproduced from ref. [61]).

Inspired by the successful electroanalytical applications of the superparamagnetic nanoparticles, their up-scaling has been pursued in our laboratory, aiming the metal capture, transport, and electrodeposition under experimental conditions close to the hydrometallurgical ones. The possibility of concentrating and confining the metal ions magnetically at the electrode surface eliminates the use of extracting solvents and of any additional chemical treatments to release the metal ions from the complexing agents, into the aqueous media. More than this, the metal-containing superparamagnetic nanoparticles can undergo efficient electrochemical deposition, facilitated by their previous concentration at the electrodes, using an external magnetic field. After electrodeposition, the magnetic nanoparticles can be released just by removing the magnet, and a new process can proceed in the same reactor after replenishing the mineral solution, as illustrated in Fig. 8. The great economy of steps, chemicals,

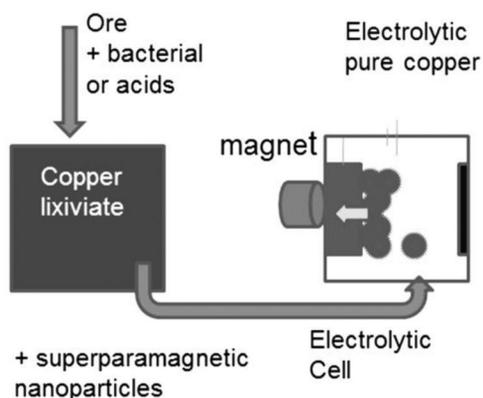
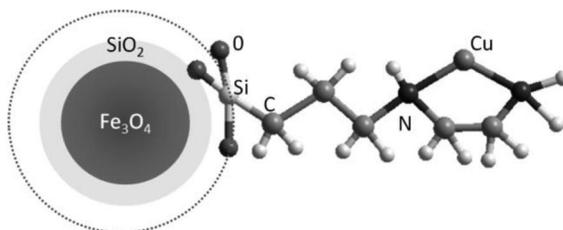


Fig. 8 Simplified scheme of the MNHM process, involving the direct capture, confinement, and electrodeposition of the metal ions.

energy, and solvents is an important green feature of this new promising technology, denoted as *magnetic nanohydrometallurgy* (MNHM) [3].

In a recent publication [3], MNHM has been successfully applied to the capture and electrodeposition of copper from aqueous solution, using superparamagnetic nanoparticles, previously silanized with a silica coating, and functionalized with ethylenediaminepropyltriethoxysilane, MagNP/EAPS, (Scheme 3).



Scheme 3 Capturing Cu^{2+} ions with superparamagnetic nanoparticles functionalized with ethylenediaminepropyltriethoxysilane (MagNP/EAPS).

The experiments, performed under analytical conditions, are illustrated in Fig. 9. The capture of copper proceeds very rapidly and is essentially quantitative in the presence of an excess of MagNP/EAPS. By using an external miniature magnet, the nanoparticles were concentrated on the electrode and the electrodeposition performed directly, as monitored by the square-wave voltammogram. The presence of electrodeposited copper metal was confirmed by the reverse stripping analysis. In addition, the quantitative recovery of the metal element was validated by parallel energy dispersive X-ray fluorescence (EDXRF) measurements from the superparamagnetic nanoparticles collected at the electrode surface.

After the successful analytical experiments, the MNHM process was applied on a larger scale, involving more concentrated solutions and volumes. The MagNP/EAPS became rapidly saturated with copper(II) ions (encompassing about 7 % of the nanoparticles initial mass), and could be easily confined with a magnet forming a compact magnetic coating on the copper electrode. The best experimental conditions depend upon the electrochemical cell design and dimensions. In the reported example, the electrodes were connected to a source power, and 1.2 V potential and 0.5 A current were applied for about 3 min. After this step, the magnet was removed and the nanoparticles released from the elec-

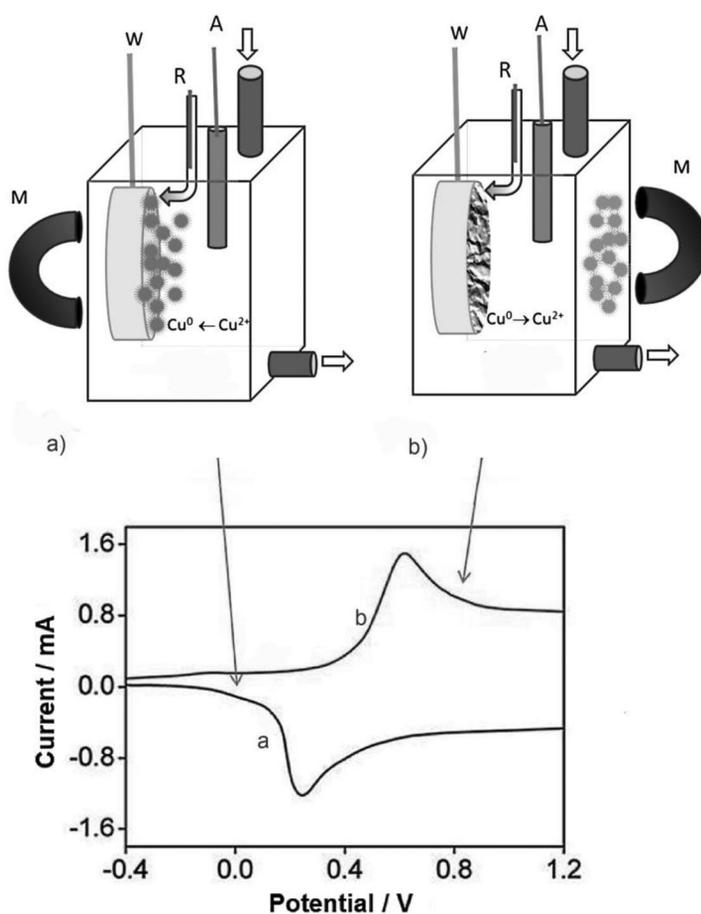


Fig. 9 Square-wave voltammograms (150 mV s^{-1}) of MagNP/EAPS (a) magnetically confined at the gold disc electrode after their interaction with Cu^{2+} ions ($2.0 \times 10^{-3} \text{ mol dm}^{-3}$) and (b) the corresponding reverse stripping analysis, confirming the electrodeposition of the metal (reproduced from ref. [3]).

trodes, leaving a characteristic copper metallic coating. When the copper(II) ions are present in excess in relation to the magnetic nanoparticles, the nanoparticles can be released and process repeated until the complete depletion of the metal ions from the solution.

It should be noted that in the absence of the preconcentration promoted by the superparamagnetic nanoparticles, metal electrodeposition can be very tedious because of the large volumes involved. Typically, in copper hydrometallurgy plants the electrodeposition time is measured in days, even by using extremely concentrated solutions of copper(II) ions and very large electrodes.

Therefore, the great advantages of the MNHM process are associated with the fact that the nanoparticles: (i) are very effective carriers, (ii) can be magnetically concentrated at the electrode, and (iii) are good electrochemical mediators, allowing rapid electrodeposition of the metal. In addition, (iv) they can be recycled, and (v) are effective even under diluted conditions, normally found in industrial effluents, where the use of conventional hydrometallurgy is no longer commercially viable.

CONCLUDING REMARKS

The reported examples illustrate just some of the possibilities of exploring nanotechnology in green chemistry applications. The large surface areas of nanoparticles and nanomaterials allow the reduction of their effective amounts, as additives or catalysts in chemical processes, while their outstanding properties, such as plasmon resonance and superparamagnetism, can be explored in numerous innovative applications in chemistry, engineering, and medicine, including online sensing devices. Recovery is another important point to be mentioned, particularly in enzymatic catalysis and hydrometallurgy. There is a green appeal associated with possibility of metal production under competitive and sustainable conditions, provided by the elimination of solvents, chemicals, and extracting steps, thanks to the facility of recovering and recycling the superparamagnetic nanoparticles. The preconcentration effect is another important highlight, for allowing the commercial exploitation of diluted solutions, and for carrying out selective metal removal for environmental remediation purposes. Therefore, responsible nanotechnology and green chemistry can be really good partners for promoting better, sustainable industrial processes.

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