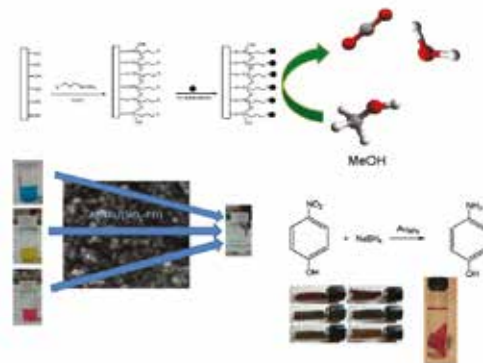


SUPPORTED METAL NANOPARTICLES FOR CATALYTIC AND ENVIRONMENTAL APPLICATIONS



THE FABRICATION OF STABLE SUPPORTED METAL NANOPARTICLES (M_{NPs}) SUITABLE FOR HETEROGENEOUS CATALYSIS OR ENVIRONMENTAL APPLICATIONS, TO PREVENT NANOPARTICLES AGGREGATION AND TO FACILITATE CATALYST RECYCLING, IS THE GOAL OF OUR RESEARCH GROUP OF THIS LAST DECADE. THIS PAPER PRESENTS CONVENIENT, STRAIGHTFORWARD, EASY METHODS TO OBTAIN POLYETHYLENIMINE FUNCTIONALIZED SILICA BEADS, ORGANOSILANE-COATED INDIUM TIN OXIDES OR HYDROPHILIC NUCLEOPORE TRACK-ETCHED POLYCARBONATE MEMBRANES (PC) FUNCTIONALIZED WITH GOLD OR SILVER NANOPARTICLES

Introduction

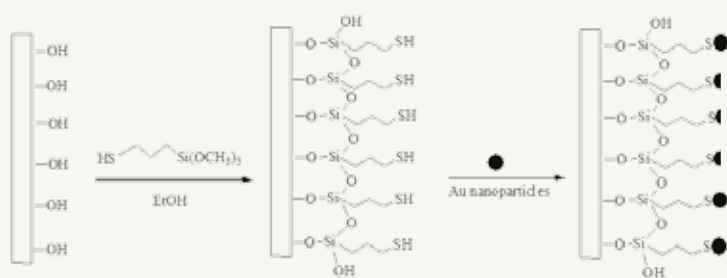
Metal nanoparticles (M_{NPs}), which have a high specific surface area and a high surface-to-volume ratio, have been extensively studied because of their unique physicochemical characteristics. Owing to their extreme small size which makes them different from macroscopic solids they hold important applications in catalytic, medical, electronic and environmental areas [1-7]. Gold nanoparticles (Au_{NPs}) have attracted increasing attention due to some unique properties such as high biocompatibility, distinctive size-related electronic and optical behaviour, good conductivity and high catalytic activity, that make them key materials and building blocks for the 21st century [8-10]. Similarly, even silver nanoparticles ($AgNPs$) display a variety of potential applications, including catalysis, optics, nanotechnology and bioengineering [11, 12]. In particular, their well known antimicrobial properties against a broad spectrum of pathogens stimulate their use in several biomedical applications, such as wound dressing, catheters, bone cemen-

ts and implant coatings [13-17]. These properties are dependent from a combination of factors, including preparative route, size, support and assembling methods; therefore, it is not surprising that several studies have been dedicated to analyse the role played by each factor [18, 19].

In general, although M_{NPs} with smaller size show greater activity (i.e. catalytic, antibacterial, antimicrobial) they tend to be less stable and prone to aggregation, and, in order to overcome this problem, M_{NPs} are usually immobilized on a suitable support material which also facilitates their re-cycling or applications [6, 20-25]. A large amount of supports have been investigated in the recent years. For example, taking advantage of the conducting and transparent properties of the ITO glasses [26], these substrates have been largely employed for optical devices and electrocatalytic purpose. Silica beads provide high surface area, give excellent mechanical strength and offer thermal stability. Moreover, silica with different size and surface functionalizations are commercially

available. Porous membranes represent an attractive alternative to powders as catalyst supports for several reasons, just to name a few: high surface area provided by the internal pores, high rapidity in the contact between reactants and the active catalyst surface, no need to separate the catalyst from the reaction mixture, and the possibility to run the catalytic reaction continuously [27, 28].

A variety of methods are reported in the literature to obtain M_{NPs} linked on suitable functionalized surfaces, and among these the self-assembling (SAM) approach represents a simple, fast, and versatile method to obtain 2D or 3D nanoparticles arrays in which coverage and spatial distribution can be easily controlled [19, 29-33]. The bifunctional crosslinkers 3-(mercaptopropyl)-trimethoxy silane (MPTMS) and 3-(aminopropyl)-triethoxysilane (APTES) are among the most common organosilanes used for colloidal immobilization [18, 34-39]. Alternatively Layer by Layer (LBL) self assembled polyelectrolyte of different charge can be used. It was reported [40] that LBL of M_{NPs}



Scheme 1

Procedure for the preparation of $\text{Au}_{\text{NPs}}/\text{MPTMS}/\text{ITO}$ ($X=\text{SH}$, $R=\text{Me}$) and $\text{Au}_{\text{NPs}}/\text{APTES}/\text{ITO}$ ($X=\text{NH}_2$, $R=\text{Et}$) electrodes

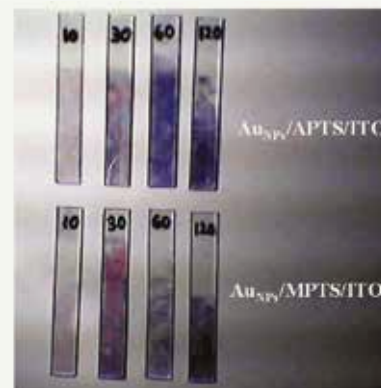


Fig. 1

$\text{Au}_{\text{NPs}}/\text{MPTS}/\text{ITO}$ and $\text{Au}_{\text{NPs}}/\text{APTS}/\text{ITO}$ obtained with different dip times in the Au_{NPs} colloidal solution

could occur via two modes of deposition:

- (1) sequential adsorption of densely packed adsorption layers (normal growth mode);
- (2) in-plane growth of isolated particle domains (lateral expansion mode).

In this paper we present an overview of low cost, easy and straightforward methods, optimized during these last years, to obtain supported gold or silver nanoparticles (Au_{NPs} or Ag_{NPs}) on different substrates and some examples of their applications [41-44].

Preparation of supported M_{NPs}

Preparation of $\text{Au}_{\text{NPs}}/\text{MPTMS}$ and $\text{Au}_{\text{NPs}}/\text{APTES}$ ITO electrodes

In this case ITO glass slides were used (exposed geometry area 1.96 cm^2) [41]. To obtain the functionalised ITO surfaces, after deep cleaning with sonication, the slides were immersed in 5% (v:v) MPTMS/ethanol or 10% (v:v) APTES/ethanol solutions overnight. After exhaustive rinsing with ethanol, the derivatized ITO substrates were heated at 100°C for 10 min. to remove loosely bound organosilane molecules and then placed in sealed

vessels containing 5 mL of $(14 \pm 4) \text{ nm}$ Au_{NPs} colloidal solution prepared by reduction of aqueous HAuCl_4 by citrate [34, 45, 46] for a fixed time (see Scheme 1 and Fig. 1).

PC membrane modification

Hydrophilic Nuclepore track-etched polycarbonate membranes (PC) ($0.05 \mu\text{m}$ pore size, 47 mm disk-shaped), obtained from Whatman, were modified using layer-by-layer (LBL) adsorption of a polyelectrolyte (PEI)/ Au_{NPs} system [PE = poly(ethylenimine), PEI, and poly(acrylic acid) sodium salt, PAA] in which the Au_{NPs} formation occurs via the *in situ* post-deposition reduction of the incorporated Au precursor, in this case a gold (III)-aminoethylimidazolium aurate salt $[\text{Cl}_3\text{AuNH}_2(\text{CH}_2)_2\text{MIM}][\text{AuCl}_4]$, (1), [42].

Both PEI and PAA are interesting material for reducing and stabilizing M_{NPs} . PEI is a cationic polymer with a high charge density. PEI fragments containing amino groups can easily chelate with metal ions, and they can also act as both reducing agents and stabilizers in preparation of M_{NPs} without the additional step of introducing other reducing and/or protective agents. On the contrary of PEI, PAA has milder reducing properties. The LBL depositions of the two polyelectrolytes were carried out at room temperature following scheme in Fig. 2A; after each step the membranes were thoroughly rinsed and stored in Milli-Q water. Because of the mild reducing properties of PAA,

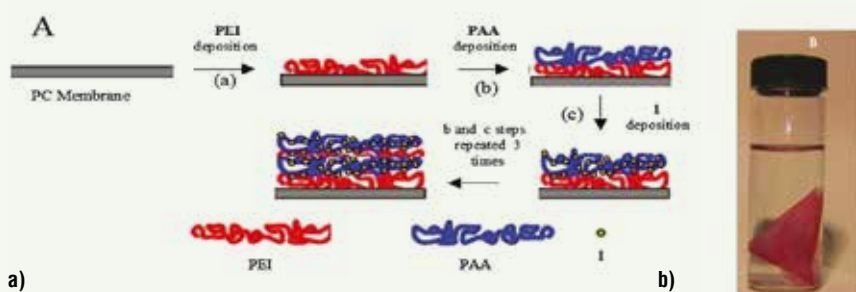


Fig. 2

A) Procedure for preparing (PEI/PAA)/(ILNH₂-Au_{NPs}/PAA) membranes (ILNH₂ = functionalized ionic liquid (IL) with terminal primary amine group on the pendant side chain); B) (PEI/PAA)/(ILNH₂-Au_{NPs}/PAA) membranes after 2 cycles

when the PEI/PAA/1 first layer was immersed in the former, the membrane colour turned to red, with the colour intensity proportional to the number of deposited layers (Fig. 2).

Commercial silica-polyethyleneimine beads modification

Here we obtained stable silica-supported M_{NPs} , suitable for catalysis applications and

environmental remediation, by using commercial polyethyleneimine-functionalized silica beads (SiO_2 -PEI) as the only reactants, with the need of neither external reducing agents nor conventional stabilizing moieties and the metal nanoparticles precursor salt (i.e. $HAuCl_4$ or $AgNO_3$) [43, 44].

In a typical procedure SiO_2 -PEI was added to an aqueous solution of nanoparticles precursors (i.e. 1, 5, and 10 mM $HAuCl_4 \cdot 3H_2O$ or 41.2 mM $AgNO_3$). The resulting suspension was stirred at 25 °C with an orbital shaker for 1 or 24 h. In a few minutes, for chloroauric acid, the yellow solution turned colourless due to its adsorption and subsequent reduction on SiO_2 -PEI. Whereas, in the case of silver, the orange SiO_2 -PEI beads turned brown due to the adsorption of silver on SiO_2 -PEI; with no subsequently changes observed after the silver reduction. The $AuNPs/SiO_2$ -PEI or $AgNPs/SiO_2$ -PEI beads were obtained after filtration, washing with water, and drying under a vacuum (Fig. 3). Only in the case of $AgNPs$, the commercial SiO_2 -PEI beads were preliminary treated with 1.3 M KNO_3 for 6 h under stirring to eliminate chlorides (present as impurity) via anionic exchange; their presence should in fact cause problems during the $AgNPs/SiO_2$ -PEI preparation, giving rise to silver chloride precipitation.

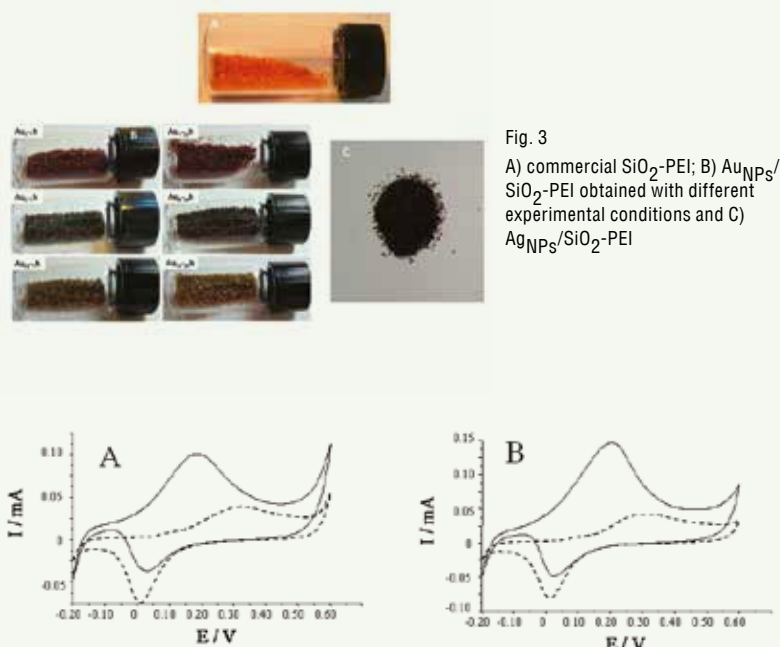


Fig. 3
A) commercial SiO_2 -PEI; B) $AuNPs/SiO_2$ -PEI obtained with different experimental conditions and C) $AgNPs/SiO_2$ -PEI

Fig. 4
Cyclic voltammograms for A) $AuNPs/MPTMS/ITO$ and B) $AuNPs/APTES/ITO$ in an electrolyte solution of 0.5 M KOH with (solid curve) and without (dash curve) 2.75 M methanol addition. Scan rate: 50 mV s^{-1} ; Ref: SCE

Tab. 1

Methanol electro-oxidation activity for Au catalyst; for comparison all the potential are referred to NHE (Normal Hydrogen Electrode)

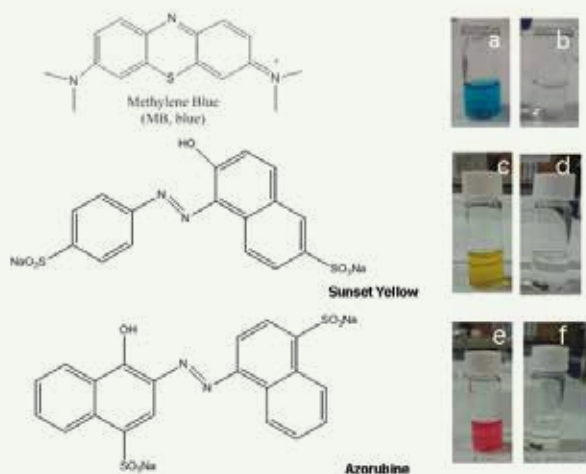
| Electrode | Electrolyte | Methanol oxidation potential (V vs NHE) | Ref. |
|-------------------|-------------|---|------|
| $AuNPs/MPTMS/ITO$ | KOH 0.5 M | 0.434 | 41 |
| $AuNPs/APTES/ITO$ | KOH 0.5 M | 0.447 | 41 |
| $AuNPs/NDT/GC$ | KOH 0.5 M | 0.544 | 7 |
| $AuNPs/NDT/EQCN$ | KOH 0.5 M | 0.459 | 55 |
| $AuNPs/$ | KOH 0.5 M | 0.499 | 47 |
| $AuNPs/GC$ | NaOH 0.1 M | 0.820 | 56 |
| $AuNPs/GC$ | NaOH 1.0 M | 0.800 | 56 |

NDT=1,9-nonanedithiol; MPTMS=(3-mercaptopropyl)trimethoxysilane; APTES=3-aminopropyltriethoxysilane; GC=Glassy carbon; EQCN=electrochemical quartz-crystal nanobalance; C=carbon black

Supported metal nanoparticles applications

Electrocatalytic methanol oxidation

The development of an highly efficient non-Pt catalyst in methanol oxidation, which can overcome the problem of poisoning, is a challenging task in fuel cell technology. Borkowska *et al.* [47, 48] have reported that methanol can be oxidized at low potentials in alkaline solution at very rough golden surface and electrodes does not undergo poisoning during the electro-oxidation. An unusual electrocatalytic activity towards the methanol oxidation was observed even for gold nanoparticles coverage [49]. Taking advantage of the conductivity of ITO glass we have explored the electrocatalytic activity of $AuNPs/MPTMS$ and $AuNPs/APTES$ ITO following the oxidation of methanol in an alkaline media [41]. As shown in Fig. 4, for $AuNPs/MPTMS$ -ITO the addition of methanol in 0.5 M KOH solution causes a progressive change in the registered cyclic voltammetric path. Analogous behaviour occurs on $AuNPs/APTES$ -ITO. A large anodic wave around $E=+0.190 \text{ V}$ and $+0.207$



Scheme 2

Methylene Blue, Sunset Yellow and Azorubine. Inset: photographs of vials with MB, SY and AZ (a, c, e) before and (b, d, f) after decoloration in presence of $\text{Ag}_{\text{NPs}}/(\text{SiO}_2\text{-PEI})$ and NaBH_4

Tab. 2

Kinetic parameters of dye reduction for all the catalytic tests

| Dye | Dye/Ag/NaBH ₄ (moles/moles/moles) | Reaction time (s) | k ^a (10 ⁻² s ⁻¹) | R ² |
|-----|---|-------------------|--|----------------|
| MB | 1/4.4/1700 | 500 | 0.80±0.05 | 0.95 |
| MB | 1/5.4/1700 | 500 | 0.90±0.12 | 0.97 |
| MB | 1/8/1700 | 150 | 1.03±0.07 | 0.98 |
| MB | 1/9/1700 | 150 | 2.11±0.15 | 0.98 |
| MB | 1/10.5/1700 | 30 | 7.67±0.09 | 0.99 |
| MB | 1/12/1700 | 30 | 7.65±0.11 | 0.99 |
| SY | 1/4/1700 | 1-2 | n.d | n.d |
| SY | 1/4/21 | 200 | 1.40±0.3 | 0.99 |
| AZ | 1/4/1700 | 1-2 | n.d | n.d |

^a Average (3 measures) ±S.D., n.d = not detectable because the reaction result too fast

V was observed with the disappear of the oxidation wave between +0.320 V and +0.400 V attributable to Au oxide formation [49-53]. This confirms that the electrogenerated Au oxide species are involved in the electrocatalytic oxidation of methanol and the surface oxides act as an electron-transfer mediator in the oxidation process, as suggested in literature [54]. Moreover the electrocatalytic current increases with the rising of the Au_{NPs} coverage, that can be tuneable during the synthesis procedure.

Stable voltammograms have been obtained after 10 and 20 cycles, respectively. The methanol oxidation occurs at E = +0.186 V ($\text{Au}_{\text{NPs}}/\text{MPTMS}/\text{ITO}$) and +0.203 V ($\text{Au}_{\text{NPs}}/\text{APTES}/\text{ITO}$) with an onset of c.a. 0.00 V (vs SCE). These potentials are much less positive than those reported in the literature for other gold nanocrystals (see Tab. 1) [41].

Decoloration treatment for environmental remediation

Dyes containing heterocyclic aromatic are normally present in the wastewater of textile, paper, cosmetics and leather factories. These compounds are very dangerous for the environment and for human health, particularly to respiratory and gastro-intestinal tracts. Furthermore, most of these compounds (in particular azo dyes) are highly resistant to conventional wastewater biological treatments and therefore require pre-treatment processes to achieve an efficient degradation.

For this purpose, the processes normally available, such as oxidation with ozone or peroxides, or electrochemical treatments, are for the most part expensive, do not operate in mild conditions and can often generate a large volume of sludge for disposal. The use of photocatalytic materials such as titania has been

even reported [57, 58] but the degradation of these compounds requires in such case the use of a light radiation, generally ultraviolet. The development of catalytic materials which can be prepared by simple methods and low cost has therefore become a challenge. Metal nanoparticles supported on solid matrices, have recently attracted considerable attention due to their high catalytic activity in the treatment of discoloration and easiness of use in heterogeneous catalysis [59, 60].

Taking advantage to the simple, low cost and one step way to obtain $\text{Ag}_{\text{NPs}}/\text{SiO}_2\text{-PEI}$ catalyst, we have explored its catalytic activity in presence of NaBH_4 , towards the reduction of Methylene Blue (MB) to Leuco Methylene Blue (LMB) and towards the decoloration of some azo dyes such as Sunset Yellow (SY) and Azorubine (AZ), note as E110 and E122 in food applications (see Scheme 2) [44]. Different Dye/Ag/NaBH₄ molar ratio have been investigated, as reported in Tab. 2; the catalytic reaction, followed by UV-Vis measurement, occurred very fast, from a minimum of 1-2 s until a maximum of 1,000 s.

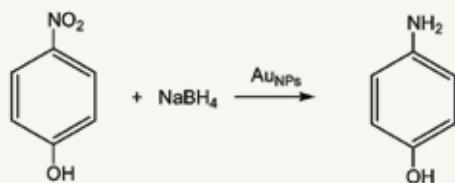
The resulting materials can behave like heterogeneous catalysts towards the degradation of Methylene Blue in presence of NaBH_4 , and show kinetic constants (Tab. 2) comparable or higher than those reported in the literature for similar applications [61, 62]. Finally, $\text{Ag}_{\text{NPs}}/(\text{SiO}_2\text{-PEI})$ can be also successfully employed for discoloration of some azo dyes, such as Sunset Yellow and Azorubine, largely used in food industry.

Catalytic hydrogenation of 4-nitrophenol

Manufacturing of many analgesic and antipyretic drugs, such as acetaminophen, phenacetin, and so on needs 4-aminophenol (4-AP) as intermediate. It is also used enormously as a photographic developer, corrosion inhibitor, anticorrosion-lubricant, and hair-dyeing agent [63-65].

Thus, being a common precursor material for 4-AP, a newer and cheaper method for catalytic hydrogenation of 4-nitrophenol (4-NP) is always in demand. The conventional methods for hydrogenation of 4-NP involve iron/acid as a reducing agent [66].

However, the use of metallic reagents has limitations. Metal oxides in huge amounts are produced as sludge out of these reactions. Therefore, there is a need for an alternative effective and eco-friendly method for nitrophenol reduction.



Scheme 3
Reduction reaction of
4-NP to 4-AP

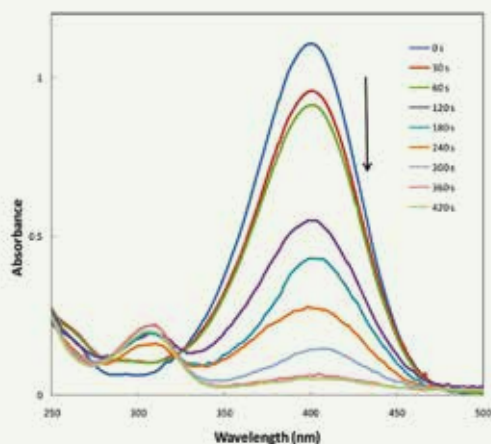


Fig. 5
UV-vis spectra of 4-NP reduction in the presence of excess NaBH_4 over (PEI/PAA)/(ILNH₂-Au_{NPs}/PAA) membranes. Reaction conditions: aqueous media at 295 K, 4-NP=5.19x10⁻² mM, NaBH_4 =83 mM, Au=3.52x10⁻¹ μmol

Tab. 3

Kinetic constants (k) of 4-NP reduction using different Au_{NPs}/SiO₂-PEI catalysts

| Sample ^a | wt Au (%) | Au/4-NP/ NaBH_4 (moles/moles/moles) | k ^a (s ⁻¹) | R ² |
|---------------------|-----------|---|-----------------------------------|----------------|
| Au1-1h | 0.5 | 1/0.44/711 | 6.84x10 ⁻⁴ | 0.999 |
| Au1-24h | 0.5 | 1/0.44/711 | 5.98x10 ⁻⁴ | 0.997 |
| Au5-1h | 2.4 | 1/0.44/711 | 1.33x10 ⁻⁴ | 0.998 |
| Au5-24h | 2.4 | 1/0.44/711 | 1.02x10 ⁻⁴ | 0.988 |
| Au10-1h | 4.9 | 1/0.44/711 | 3.39x10 ⁻⁴ | 0.986 |
| Au10-24h | 4.9 | 1/0.44/711 | 1.06x10 ⁻⁴ | 0.987 |

^aThe Au_{NPs}/SiO₂-PEI beads have been termed Au_x-y^h, where x is the initial HAuCl_4 concentration (1, 5, or 10 mM) and y is the reaction time (1 or 24 h)

Recently, many applications of metal nanosized as catalysts have been reported [65, 67, 68]. Moreover the reduction of 4-NP to 4-AP by sodium borohydride (NaBH_4) can be easily monitored by a simple and fast technique as UV-Vis spectroscopy by the decrease of the strong adsorption of 4-nitrophenolate anion at 400 nm, leading directly to the rate constant. For this reason this reaction has been used as a model reaction to investigate the catalytic activity of the (PEI/PAA)/(ILNH₂-Au_{NPs}/PAA) membrane and the Au_{NPs}/SiO₂-PEI

(see Scheme 3 and Fig. 5) [42, 43]. (PEI/PAA)/(ILNH₂-Au_{NPs}/PAA) membranes exhibited a pseudo-first-order rate constant in the reduction of 4-NP to 4-AP with a kinetic constant $k = (7.0 \pm 0.3) \times 10^{-3} \text{ s}^{-1}$, comparable to the best values reported so far in the literature for Au_{NPs} polymer supported catalysts. Moreover, these nanoparticles-based heterogeneous catalysts can be easily used in flow through systems. As regards Au_{NPs}/SiO₂-PEI, their catalytic activity is strongly influenced by the experimental conditions of the sample preparation. Sam-

ples Au1-1h and Au1-24h gave the best catalytic performances (see Tab. 3) with rate constants in the range of reported literature data [69].

Conclusions

Stable supported metal nanoparticles were successfully synthesized using convenient, cheap substrates and reagents for their fabrication, in a very straightforward way. All studied processes lead to systems capable of both reducing the metal precursor and stabilizing the resulting M_{NPs} without the need of any additional agent and preventing aggregation. The resulting materials can behave like heterogeneous catalysts and show kinetic constants comparable or higher than those reported in the literature for similar applications.

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Nanoparticelle metalliche supportate per applicazioni catalitiche ed ambientali

La preparazione di nanoparticelle metalliche (M_{NPS}) stabili e supportate allo scopo di prevenirne l'aggregazione e facilitare il riciclo del catalizzatore per l'impiego sia in catalisi eterogenea che in applicazioni ambientali è stato l'obiettivo del nostro gruppo di ricerca di questi ultimi dieci anni. Questo articolo presenta metodi semplici e convenienti per ottenere silice funzionalizzata con polietilenimina (SiO_2 -PEI), materiali trasparenti conduttivi (ITO) modificati con organosilani MPTMS/ITO e APTES/ITO (MPTMS=3-(mercaptopropil)-trimetossisilano, APTES=3-(amminopropil)-trietossisilano, ITO ossido di stagno drogato con indio) e membrane idrofile in policarbonato (PC, Nuclepore Track-Etched) funzionalizzate con nanoparticelle d'oro o d'argento (Au_{NPS} o Ag_{NPS}). Le sintesi proposte possono essere effettuate mediante un unico step o in due step. Nel primo caso, il supporto (generalmente commerciale) viene fatto reagire con una soluzione acquosa del precursore metallico (tipicamente $HAuCl_4$ o $AgNO_3$) in assenza di alcun agente riducente esterno e/o stabilizzante. Nel caso della procedura in due step, il substrato viene prima modificato con gruppi funzionali (generalmente contenenti -SH o -NH₂) e poi viene fatto reagire con una soluzione acquosa colloidale di M_{NPS} . L'attività catalitica delle M_{NPS} supportate è stata valutata studiando: i) la riduzione di 4-nitrofenolo a 4-amminofenolo in presenza di $NaBH_4$; ii) l'elettrossidazione di metanolo in condizioni alcaline oppure iii) la riduzione di coloranti.

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