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Catalytic Materials Based on Surface Coating with PEI-Stabilized Gold Nanoparticles

Mariano Ortega-Muñoz, Victor Blanco, Fernando Hernandez-Mateo, F. Javier Lopez-Jaramillo,* and Francisco Santoyo-Gonzalez*[a]

Abstract: Gold nanoparticles (AuNPs) can be obtained from $HAuCl_4$ by using polyethyleneimine (PEI) as both reductant and stabilizing agent. However, the known affinity of PEI for different materials has not been exploited to coat them and turn their surface into catalytic. We demonstrate that the irradiation of a solution of $HAuCl_4$ and branched PEI 1800 (bPEI2K) with microwave (MW) yields PEI-stabilized AuNPs (MW-PEI@AuNPs) with an average size of 7.6 nm that are catalytically active in the reduction with $NaBH_4$ of different nitroarenes functionalized with a variety of functional groups. Moreover, the as-prepared MW-PE@-AuNPs show affinity for different materials such as polystyrene (standard spectrophotometry disposal cuvettes), polypropylene (falcon-type tubes) and silica (Silica gel 60), turning their surface into catalytic without any additional synthetic step. This feature is exploited to transform standard tubings (Tygon, PEEK and stainless steel) into flow reactors by simple passage of a solution of MW-PEI@AuNPs. This straightforward functionalization is especially appealing in the case of the stainless steel tubing, one of the materials more widely used in HPLC, being of interest in the context of flow nanocatalysis.

Introduction

Nanocatalysis is a domain at the interface between homogeneous and heterogeneous catalysis and it is based on the use of nanomaterials and nanoparticles (NPs). The catalytic activity of the NPs is influenced by multiple variables, among them the number of surface atoms, especially those located at the corners and edges, and the size of the NPs.[1-3] Hence, NPs need to be stabilized to prevent aggregation. Alloying, encapsulation or the use of stabilizing agents (i.e. capping agents) such as polymers, surfactants or ligands in colloidal chemistry are common stabilization strategies.[4-5] However, stabilization may exert an influence on the reactivity, morphology or surface chemistry and, in this context, the advent of nanotechnology has facilitated not only the study of NPs at atomic resolution but also the techniques to control the overall shape, composition, morphology and uniform size.[6-7]

Despite metallic gold was historically identified as a noble metal chemically inert toward chemisorption and discarded for catalysis, the pioneering works by Haruta *et al.* changed this vision.[8-10] Nowadays, catalytically active gold nanoparticles (AuNPs) are prepared either by loading a gold precursor (usually a gold salt or complex) onto a solid support followed by chemical reduction or calcination to promote the reduction of the gold cations into elemental gold that forms NPs, or via traditional colloidal chemistry by the reduction and stabilization of $AuCl_4^-$ with reductants and stabilizing agents that prevent aggregation, such as polymers, surfactants or ligands.[11-12] Colloidal AuNPs can be used either directly as catalysts in liquid phase or deposited onto solid supports (i.e. colloidal deposition).[1-3] AuNPs have been supported on materials such as TiO_2, ZnO, Al_2O_3, SiO_2, CeO_2, Fe_2O_3, metal-phosphonates, carbonaceous supports and stainless steel (SS).[14-16] However, neither the stabilizing ligands nor the support may be passive elements and they can block the reactive surface sites or influence the characteristic of the NPs by tuning the oxidation state of the gold or by adsorbing the reactants or intermediates/products, provoking the activation of the reaction or the deactivation of the catalyst.[17-19]

In some cases, both reduction and stabilization can be achieved by the use of a single specific polymer such as polyvinylpyrrolidone (PVP), polyethylene glycol (PEG), polyamidoamine (PAMAM), poly(propyleneimine) (PPI) or polyethylenimine (PEI), among others.[20-24] In particular, linear PEI was the first polyelectrolyte reported with this dual role by Sun *et al.* in 2004[21] but it is branched PEI (bPEI) with a molecular weight of 25 kDa the most widely used.[21-24] It has been demonstrated that PEI acts as an efficient reductant of $HAuCl_4$ at both 60-80 ºC and room temperature, the size of the resulting NPs being dependent on the bPEI:$HAuCl_4$ ratio.[21-24] Additionally, PEI, as a polymeric amine with a high density of charge, has been used to improve the adhesion of different compounds onto surfaces as diverse as clay, polystyrene, silica, glass, graphite and metal oxides such as SnO_2, ZrO_2 or TiO_2.[25-30] However, to the best of our knowledge the affinity of PEI has not been fully exploited to extend its role and synthesize stabilized AuNPs with the capability of coating different surfaces.[25-30] Recently we have reported the one-pot synthesis of PEI coated AuNPs that combines the reductant/stabilizer properties of PEI and the use of use of microwave irradiation to yield DNA delivery nanocarriers.[31] In this work we explore the ability of these AuNPs to coat surfaces and turn them into catalytic materials.

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Results and Discussion

Synthesis and Characterization of MW-PEI@AuNPs

PEI was the first polyelectrolyte reported as both reducing and stabilization agent in the synthesis of AuNPs[21-24] and we have recently demonstrated[31] that a short microwave (MW) irradiation of a solution of PEI and $HAuCl_4$ yields PEI-stabilized AuNPs (PEI@AuNPs) that can be used as DNA delivery nanocarriers. However, to the best of our knowledge the known affinity of PEI for different materials has not been exploited to coat surfaces with PEI@AuNPs and turn them into catalytic.[25-30] We focused on branched PEI with molecular weight of 1800 (bPEI2K) as a key compound for the triple purpose of reducing, stabilizing and coating. First we analyzed the influence of both the PEI (repeating units):Au ratio and the MW irradiation. As expected from literature,[21] our preliminary experiments at room temperature showed that a PEI(repeating units):Au ratio of 9.3 yielded PEI@AuNPs that aggregated but that were stable when the amount of $HAuCl_4$ was reduced to increase the ratio to 18.7. The synthesis was monitored by UV-Vis spectroscopy and after 30 h the surface plasmon resonance (SPR) peak was detected while the colour of the reaction medium evolved from yellow to dark red, supporting the formation of dispersed PEI@AuNPs. However, as the synthesis progressed the reaction medium darkened and the SPR peak showed a red shift from 530 nm to 548 nm, suggesting the formation of larger PEI@AuNPs (Figure S1). Since the optical properties of AuNPs are dependent on the size and the wavelength, the size of AuNPs was estimated with an expected error of ~11% from the ratio between the absorbance of the SPR peak and that at 450 nm by applying the expression (1), that is applicable in a 4 to 100 nm range.[32]

$$d = e^{(3.0*(Aspr/A450)-2.2)} \quad (1)$$

A closer analysis of the spectra using expression (1) revealed a clear trend with the size increasing as the synthesis progressed to reach a plateau at 12 nm after 60 h of reaction in agreement with the red shift of the SPR peak and the observed darkening of the reaction medium (Figure 1).

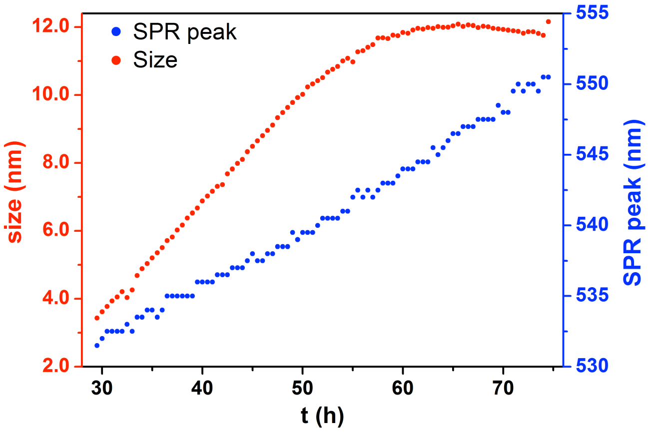


Figure 1. Red-shift of the SPR peak during the synthesis of PEI@AuNPs (PEI(repeating unit):Au ratio=18.7, room temperature) and estimation of the size of the NPs according to expression (1).[32]

It is well established that the size of the NPs is a critical parameter in nanocatalysis and that in the particular case of AuNPs, diameters of ~5 nm are catalytically active under mild conditions for a variety of reactions.[1,33] This size dependence has been found to be related with the fraction of low coordinated Au atoms that decreases as the size of the NPs increases, suggesting that the atoms on the corners and edges are the active site.[1] Among the different approaches to reduce the size of the AuNPs, two are straightforward: i) increasing the PEI:Au ratio, and ii) increasing the temperature of reaction. The former leads to a significant suppression of the primary nucleation whereas the latter yields a higher activity of the amino groups in reducing Au^{3+}.[34] Since the assayed PEI:Au ratio of 18.7 yielded a suitable NP size, close to the optimum values, we decided to focus on the temperature and used MW irradiation. Unlike conventional thermal techniques, MW is characterized by a more homogeneous heating that provides rapid initial heating and rapid consumption of the starting material which yields smaller NPs with a narrow particle size distribution in shorter reaction times.[35-37] Thus, based on our previous experience, MW irradiation of a mixture of $HAuCl_4$and bPEI2K using the optimal 18.7 PEI(repeating units):Au ratio at 300 W and 100 ºC for 3 min turned the solution into dark red, the colour being stable for weeks.[31] The UV-Vis spectrum revealed a SPR peak at 521 nm (Figure 2) and the average size of these NPs, named MW-PEI@AuNPs, was estimated from expression (1) as 7.2 nm.

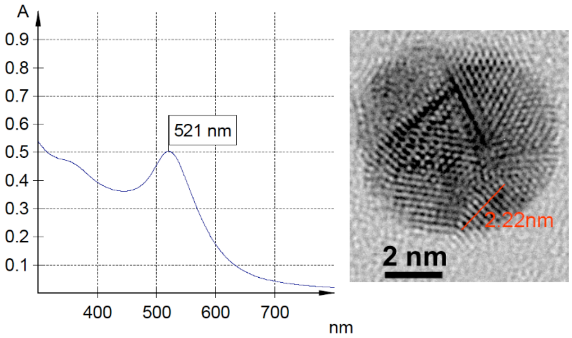


Figure 2. SPR peak (left) and HRTEM image (right) from a MW-PEI@AuNP.

The characterization of MW-PEI@AuNPs by transmission electron microscopy (TEM) demonstrated that they are homogeneous, with an average size of 7.6±1.5 nm, being 0.20 the coefficient of variance (Figure S2), in good agreement with the size estimated from the UV-Vis spectrum. HR-TEM images also suggest that these NPs are nanocrystals with high crystallinity (Figure 2 right). Considering the ratio between the NP volume and the volume per atom in the bulk metal (assuming the same packing) the number of atoms per NP was estimated as 14122-14165, which is very close to the magic number 14993 for an icosahedron or cuboctahedron with 17 shells and 2562 surface atoms.[38,39]

Fourier transform Infrared spectroscopy (FTIR) provides additional insight into the transformations that PEI suffers during the synthesis of the MW-PEI@AuNPs (Figure 3). Similarly to our PEI@AuNPs reported as efficient DNA delivery nanocarriers,[31] the most characteristic feature of the FTIR spectrum of MW-PEI@AuNPs are the bands at 1631 cm^{-1} and 1557 cm^{-1} absent in bPEI2K and that were tentatively assigned to the C=O stretching and the N-H bending of amide groups respectively. Additionally, the shape of the peak at 3280 cm^{-1} assigned to the N-H stretching of amino groups changes and shifts to 3343 cm^{-1} whereas the signal at 1598 cm^{-1}, corresponding to N-H bending

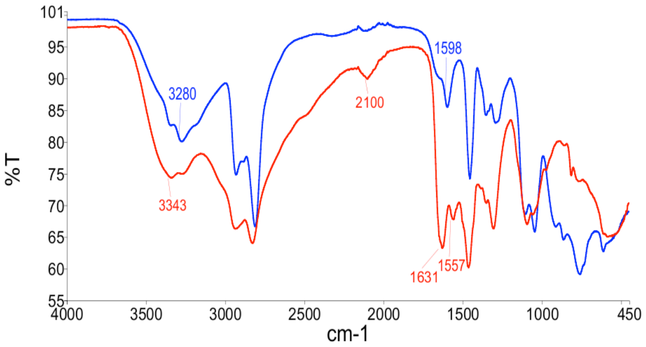


Figure 3. IR spectra of MW-PEI@AuNPs (red) and bPE2K (blue) depicting representative peaks.

of amino groups shifts to 1557 cm^{-1} as expected from the formation of amides. Moreover, the spectrum of MW-PEI@AuNPs shows a signal at 2100 cm^{-1} that may be tentatively attributed to CO linearly bonded to AuNPs.[40, 41] These findings support the transformation of amino groups into amides and the role of amines as reductants to convert Au^{3+} into Au^{0}.[42]

Catalytic activity of MW-PEI@AuNPs

Among the different reactions that AuNPs catalyze, the reduction of nitroarenes by NaBH$_4$ is relevant because nitro-aromatics are an important class of environmentally toxic compounds widely employed in the production of explosives, pesticides, plastics and pharmaceuticals and the resulting amines can find application in many fields, underlying the opportunity to carry on new studies to continuously improve the reduction efficiency.[43,44] Additionally, the transformation of 4-nitrophenol (4-NP) in 4-aminophenol (4-AP) is a model reaction widely used to study the efficiency of metallic NPs.[45-47] On this basis, the reduction of 4-NP, 4-nitroaniline (4-NA) and 4-nitroacetanilide (4-NAc) were assayed as model reactions to test the catalytic activity of the MW-PEI@-AuNPs. In these experiments the decrease of the strong absorption at 400 nm, 380 nm and 319 nm characteristic of each of these starting materials was observed. In the presence of a large excess of NaBH$_4$ and an adequate amount of MW-PEI@AuNP the reaction can be described by a pseudo-first-order kinetics and analyzed using the Langmuir-Hinshelwood model. The catalytic property can be quantified by the apparent rate constant (k_{app}) obtained from the slope of the linear correlation of ln(At/Ao) with time. This model involves the adsorption of both the reducing agent and the nitroarene on the surface of the NPs and it assumes that the diffusion of the reactants to the NPs and all the adsorption-desorption steps are fast, being the reduction of the adsorbed nitroarene the rate-limiting step.[45-47] MW-PEI@AuNPs are catalytically active in the reduction of 4-NP, 4-NA and 4-NAc, with an induction time of 1-1.5 min (Figure S3). Many authors have attributed the observation of an induction time to a slow surface reconstruction of the NPs, usually ascribed to the diffusion/adsorption time for 4-NP previous to the start of the reaction.[45-47] The kinetic parameters are summarized in Table 1.

It is important to recall that TON is defined as the number of moles of substrate that a mol of catalyst can convert before becoming inactivated and its estimation has to deal with two sources of uncertainty: i) the definition of the time when thecatalyst is considered inactivated and ii) the challenge of defining *mol of catalyst* with NPs due to the importance of atoms placed at specific positions, specially those located at the corners and edges.[1-3,38] An additional difficulty is the fact that soluble metal NPs are surrounded by agents/ligands that may limit the accessibility of the reactant to the surface atoms.[38] Bearing in mind all these limitations we have estimated the total turnover number (tTON) defined as the sum of TON obtained in each run of catalyst recycling until the catalytic activity dropped below 20% and we have assumed that only surface atoms are responsible for the catalysis and that all of them are equivalent. Our data show that the reduction of 4-NP is faster than that of 4-NAc and slower than that of 4-NA but the catalyst becomes deactivated sooner (Table 1).

Table 1. Catalytic efficiency of MW-PEI@AuNPs in the reduction of 4-nitrophenol (4-NP) 4-nitroaniline (4-NA), 4-nitroacetanilide (4-NAc) by NaBH$_4$.

Nitroarene	**tTON**[a] (%activity)	**TOF (min^{-1})**
4-NP	1.33×10^{-14} (18.2%)	4.84×10^{-16}
4-NA	5.35×10^{-15} (19.2%)	5.35×10^{-16}
4-NAc	4.17×10^{-15} (17.8%)	3.09×10^{-16}

[a] Total turnover number (moles of substrate per mol of surface atom) calculated as the sum of TON obtained in each run of catalyst recycling until the catalytic activity dropped to the value in brackets

As already discussed, NPs aggregation is a major concern that it is circumvented by alloying, encapsulation or by the use of capping agents.[4,5] The as-prepared MW-PEI@AuNPs are stable in solution, which has an alkaline pH, and catalytically active for weeks. It has been suggested that the degree of protonation of PEI has a strong influence on its conformation, being more elongated at strong acidic conditions as a consequence of a steady increase in the electrostatic interactions that cause repulsions of the repeating units.[48] On the basis of this hypothesis the effect of acidic pH was evaluated. The incubation of MW-PEI@AuNPs at different concentrations of HCl yields a red-shift and a broadening of the SPR that was dependent on the time of incubation. Moreover, pH values lower that 3 (i.e. 30 mM HCl) provoked the precipitation of the MW-PEI@AuNPs (Figure S4). The evaluation of the catalytic activity after incubation with 30 mM or 60 mM HCl for 60 min reveals that, although this short incubation has not a significant influence on the size or the induction time, k_{app} diminishes significantly (Table 2). These results led us to conclude that MW-PEI@AuNPs are not stable at strong acidic pH and, although the aggregation is not instantaneous, the effect on the catalytic performance is relatively fast.

Table 2. Influence of the incubation during 60 min with different concentrations of HCl on the size, k_{app} and induction time (t_o) in the reduction of 4NP to 4AP by NaBH$_4$ catalyzed by MW-PEI@AuNPs

[HCl] mM	**Estimated Size (nm)**[a]	**k_{app}**	**t_o(min)**
0	7.2	0.405	1.5
30	6.9	0.210	1.5
60	7.5	0.177	1.0

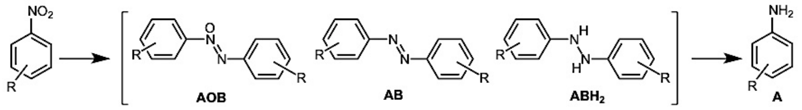
[a] Estimated from the UV-Vis spectra according to expression (1).[32]

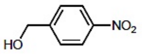
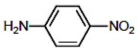
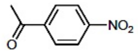
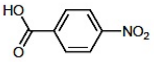
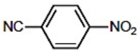
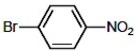
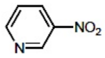
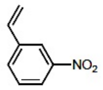
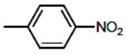
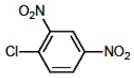
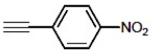
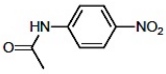
To further assess the performance of the MW-PEI@NPs, the reduction of a series of nitroarenes with structurally diverse functional groups was evaluated. The reaction was allowed to proceed for 1 h at room temperature and an aliquot was quenched by addition of formic acid and analyzed by HPLC-MS. Results are summarized in Table 3. In all cases except for 4-nitrobenzonitrile and 4-NAc (Table 3, entries 5 and 12) more than 95% of the starting material was transformed within 1 h. In order to evaluate whether these substrates were less reactive the reaction was studied as a function of time. The percentage of 4-NAc consumed after 1, 2.5, 5.5 and 8 h of reaction was 72%, 83%, 93% and 95%, respectively, confirming the kinetic parameters previously estimated that demonstrate the lower reactivity of 4-NAc when compared to 4-NP and 4-NA. However, for 4-nitrobenzonitrile the fact that the transformation was affected neither by the reaction time nor by the addition of extra $NaBH_4$ at 2.5 and 5.5 h of reaction led us to conclude that the catalyst was inactivated.

An attempt to identify the products resulting from the reduction was carried out by searching the mass of all the intermediates of the general mechanism of the reduction of nitrobenzene proposed by Haber and accepted by the scientific community.[49] Haber´s mechanism is a multistep pathway where nitroso and hydroxylamine intermediates are formed to yield the direct reduction to the amino group (i.e. direct route) or a condensation to yield azoxy and azo derivatives (i.e. condensation route). The intermediates identified among the different species formed for the different nitroarenes assayed are depicted in Table 3.

For 4-nitroaniline, 4-nitrobenzoic acid, 4-nitrobenzonitrile, 4-nitrobromobenzene, 1-chloro-2,4-dinitrobenzene and 4-NAc (Table 3, entries 2, 4-6, 10 and 12) only the amino derivatives

Table 3. Reduction of nitroarenes by $NaBH_4$ catalyzed by MW-PEI@AuNPs and intermediates identified[a].



Entry	Substrate	Conversion[b]	AOB[c]	AB[c]	ABH_2[c]	A[c]	Comments
1		99%		✔			Chemoselectivity
2		99%				✔	
3		96%			✔	✔	Chemoselectivity
4		95%				✔	Chemoselectivity
5		28%				✔	Inactivation of the catalyst
6		97%				✔	
7		99%					Identification of products failed
8		99%	✔	✔	✔	✔	Chemoselectivity
9		99%	✔	✔		✔	
10		99%				✔	No regioselectivity
11		99%		✔	✔	✔	No chemoselectivity.1-ethyl-4-nitrobenzene, 4-ethyl-aniline and 4-ethenyl-aniline identified
12		72%				✔	Chemoselectivity. Slow reaction: 95% after 8 h

[a]Reaction conditions: nitroarene (5×10^{-4} M), $NaBH_4$ (5×10^{-2} M), MW-PEI@-AuNPs (20 µL), H_2O (20 mL), rt; [b]Percentage of substrate transformed within 1 h of reaction determined by integration of the HPLC peak; [c]Intermediates identified by HPCL-MS.

were detected whereas adducts resulting from the condensation route were distinguished for 4-nitrobenzyl alcohol, 4-nitroacetophenone, 3-nitrostyrene, 4-nitrotoluene, 1-ethynyl-4-nitrobenzene (Table 3, entries 1, 3, 8, 9, and 11). 4-nitropyridine (Table 3 entry 7) was transformed but we did not find any match between the mass spectra and the mass of the intermediates proposed by Haber.[49] These results support that the reduction catalyzed by MW-PEI@AuNPs proceeds by both mechanisms, in full agreement with previous reports for nitrobenzene. Thus, Corma *et al.* [50,51] have demonstrated that the reaction proceeds through the direct route when it is catalyzed by Au-TiO_2 while Noschese *et al.* [52] showed that the condensation route seems to prevail when the AuNPs are supported onto a nanoporous polymeric matrix. Regardless of the reaction route, the reduction is chemoselective except for 1-ethynyl-4-nitrobenzene (Table 3, entry 11) that yields not only the expected amine and the intermediates, but also the reduction of the alkyne group to alkene and alkane (Figure S5). The interpretation of these data is not straightforward but they seem to point to the importance of the position of the substituents, the alkenyl moiety being reduced when it is placed in *para* position while remaining unaltered when placed in *meta-* (Table 3, entry 8).

Preparation of catalytic MW-PEI@AuNPs coated materials

Having assessed the catalytic properties, we focused on exploring whether the affinity of PEI for different materials was retained by MW-PE@-AuNPs and whether they can coat surfaces without any additional synthetic step. Our first candidate was silica, that has been previously used to prepare supported metal catalysts.[53-57] Since the impregnation of SiO_2 with a gold precursor yields relative large NPs, different approaches have been successfully assayed to prepare catalytic composites.[53-57] In addition, commercial silica-PEI beads have been previously used to synthesize supported AuNPs and the interaction between PAMAM and SiO_2 has been already exploited to prepare silica-supported gold nanocomposites.[55[Considering the fact that PEI efficiently coats the surface of metal oxides such as TiO_2, ZrO_2, or SnO_2 to yield stable amino functionalized particles that withstand pH 10, we decided to evaluate the suitability of MW-PEI@AuNPs to functionalize silica.[25-30] Simple addition of commercial silica to MW-PEI@AuNPs turned the solution transparent and the silica reddish almost instantly (Figure S6). Washing with abundant water and different ionic strengths did not yield any appreciable leaching and the resulting composite was catalytically active. In order to put to test the feasibility of using commercial silica coated with MW-PEI@AuNPs for the large-scale reduction of 4-NP, 7.5 g of the nanocomposite were packed in a chromatographic column and different volumes of 35-45 mL of 4-NP were passed. The column efficiently reduced up to 920 mL of solution along 23 cycles with an average conversion rate of 98%. However, when the lag time between two cycles was long (i.e. hours) the first milliliters eluted from the column (i.e. the dead volume) showed a faint reddish colour and a weak signal of the SPR peak at 527 nm was detected confirming the presence of MW-PEI@AuNPs. This limited leaching was not observed when there was no stop between cycles and it may be consequence of the poor long-term stability of silica at alkaline pH. In order to rule out a desorption event the performance of 0.5 g of silica coated with MW-PEI@AuNPs was evaluated along 5 cycles of the catalytic reduction of 4-NP. In full agreement with the results reported for AuNPs supported on commercial silica-PEI beads,[53] the catalytic efficiency diminishes as the material is reutilized, k_{app} being 0.55 and 0.16 for cycle 1 and 5 respectively (Figure S7). However, ICP-OES analyses revealed that the content of gold was 12.1μg/g for the silica coated with MW-PEI@AuNPs with no significant change after cycle 5. These results suggest that the decrease of the catalytic activity is more directly related to the leaching due to the poor stability of the silica at the alkaline pH of the reaction rather than to the weakness of the coating.

Standard disposable cuvettes made of polystyrene (PS) and used in UV-Vis spectroscopy were next considered as a good model material to gain additional insight into the effect of the coating on the SPR and the catalytic performance of MW-PEI@AuNPs since they can be determined *in situ*. The adsorption of the MW-PEI@AuNPs turned the surface of the cuvette reddish (Figure S8) and catalytically active. It is noteworthy that the reaction proceeds without a detectable induction time and, although k_{app} decreases as the cuvette is reutilized and the reaction proceeds slower, complete reduction of 4-NP is reached (Figure 4). The analysis of SPR peak reveals that the adsorption and the reutilization is accompanied by a red-shift and broadening of the SPR peak. However, changes in the size of the adsorbed PEI@AuNPs estimated from the

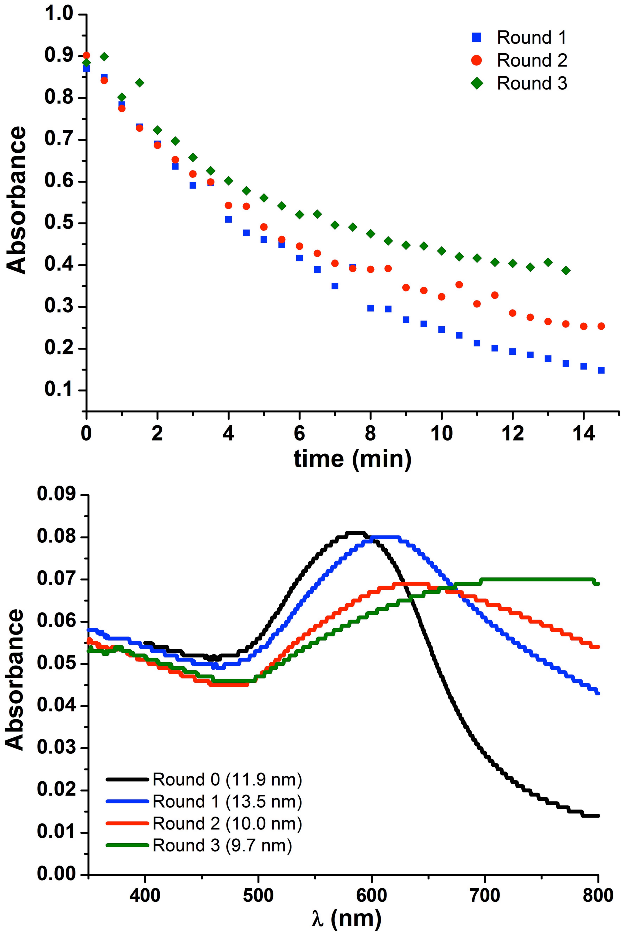


Figure 4. Kinetics of three rounds of reduction of 4NP to 4AP by $NaBH_4$ catalyzed in situ by the MW-PEI@AuNPs immobilized on the surface of a disposable cuvette (left) and evolution of the SPR peak after each round (right). Size of the NPs estimated according to expression (1)[32] are shown in brackets.

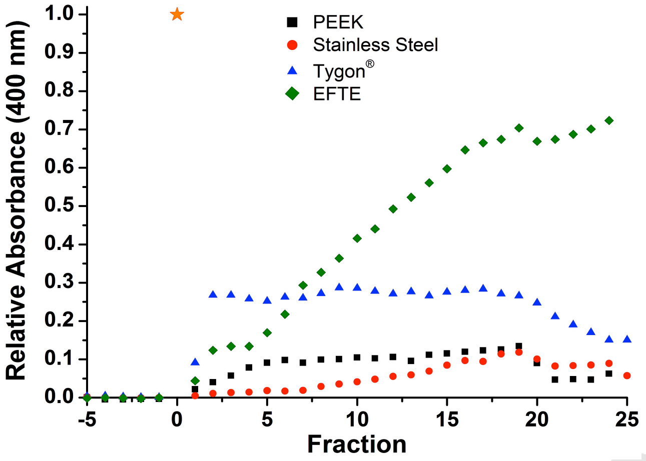


Figure 5. Catalytic performance of different tubing systems (1.5 m) coated with MW-PEI@AuNP. The tubing was pre-equilibrated with 5 mL of $NaBH_4$ (2.5×10^{-2} M) (fractions with negative numbering) and then 40 mL of aqueous an aqueous solution of 4-NP (5×10^{-5}) and $NaBH_4$ (2.5×10^{-2} M) were passed. After fraction 19, the reaction mix was supplemented with fresh $NaBH_4$. Absorbance (400 nm) is normalized by that of the 4-NP solution assayed (fraction 0)

spectra are not significantly since they are within the ~11% error expected from the use of expression (1) (Figure 4).[32]

Polypropylene (PP), a multipurpose polymer used to produce plasticware and Falcon®-type and Eppendorf®-type tubes, was the next material considered. MW-PEI@AuNPs are also easily adsorbed by this material, being 10 µg/cm^2 the amount of gold attached to the surface. Its catalytic performance in the reduction of 4-NP was assayed along 11 cycles of reuse. Although a decrease in k_{app} is observed during the first cycle, this parameter is constant from the fourth cycle, demonstrating that MW-PEI@AuNPs coated PP can be reused a number of times (Figure S9).

MW-PEI@AuNPs-coated chromatography tubings.

Nanocatalysis has found application in continuous flow technology in the so-called flow nanocatalysis.[58] The stability of both NPs and their anchoring to the micro reactor is a critical issue that has been addressed by three classical approaches: i) packed beads with the catalyst being tethered onto the bead, ii) monolithic columns with the catalyst in porous channels resulting from the copolymerization of the catalyst with other monomers inside the reactor and iii) wall-coated where the catalyst is immobilized onto the inner walls of the reactor.[59] In this context, chromatography tubings are interesting materials since their functionalization with MW-PEI@AuNPs yields systems that combine the catalytic activity of the NPs with the high surface area-to-volume ratio of the tubing. A length of 1.5 m of Tygon® lab tubing with internal diameter of 0.8 mm and standard ethylene-tetrafluoroethylene (ETFE), fluorinated ethylene propylene (FEP), polyetheretherketone (PEEK) and stainless steel (SS) tubings with internal diameter of 0.5 mm were selected because they are used in peristaltic pumps and as tubing systems in liquid chromatography. The immobilization of the MW-PE@-AuNPs onto the inner surface of the tubing systems was approached by recirculating the as-prepared MW-PEI@AuNPs overnight at room temperature. Although no apparent colour change demonstrating the adsorption of AuNPs on the inner wall of the tubings was observed, the circulation of 20 mL of a solution of 4-NP and $NaBH_4$ (Figure S10) revealed that the tubings were catalytically active, although to at different extent depending on the composition of the tubing (Figure 5). FEP was discarded due to its poor performance, that was not unexpected since as a Teflon®-like polymer this material is used as anti-adherent coating. After washing thoroughly with distilled water, the tubings were further tested with 40 mL of a solution of 4-NP and $NaBH_4$ to evaluate the stability of the coating and the reusability of the tubing. As shown in Figure 5 PEEK, SS and Tygon® tubings were turned into stable catalysts, the latter being less efficient, whereas the performance of ETFE was compromised and it was discarded as a suitable material.

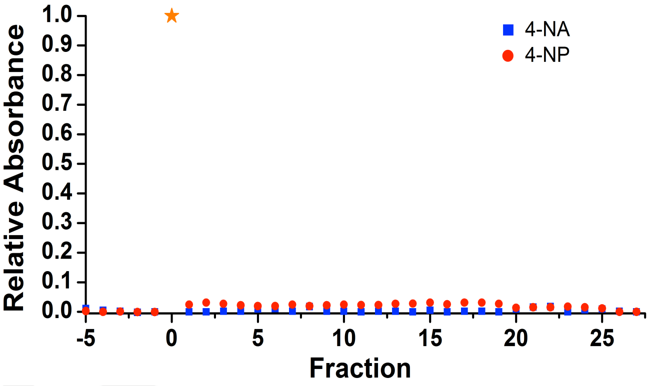


Figure 6. Conversion rate in the reduction of 4-NA (blue squares) and 4-NP (red circles) after a Stain Steel tubing flowing along (1.5 m) coated with MW-PEI@AuNP

It is well established that $NaBH_4$ decomposes in water[60, 61] and a closer analysis of Figure 5 shows that performance dropped as the experiment proceeded and it is improved when the 4-NP solution was supplemented with fresh $NaBH_4$ after collecting fraction 19. In order to improve the catalytic efficiency, the starting solution of 4-NP and $NaBH_4$ was maintained in a water-ice bath and a new experiment with the PEEK tubing coated with MW-PEI@AuNPs demonstrated that low temperature reduces the decomposition of $NaBH_4$, further supporting the stability and reusability of the coated tubings as catalysts (Figure S11).

The good performance of the SS tubing and its widespread use in HPLC encouraged us to further put to test its application. A new experiment showed that the MW-PEI@AuNPs-coated SS tubing displayed good catalytic efficiency when assayed with 40 mL of an aqueous solution of $NaBH_4$ and either 4-NA or 4NP, the average conversion rate being 98% and 97% respectively (Figure 6) whereas blank experiments with the tubing as purchased did not show catalytic activity (Figure S12). This experiment also supports the stability and reusability of the SS tubing, for which an overall of ca. 340 tubing volumes were passed through the system without any appreciable loss of catalytic activity.

Characterization of the MW-PEI@AuNPs-coated materials

Although the catalytic activity of the coated materials demonstrated the presence of accessible MW-PEI@AuNPs on their surface, the samples were further characterized to gain an additional insight into the coating. Different attempts to prepare

Table 4. Au 4f binding energies (BE) and FWHM (in parenthesis) of the gold nanoparticles coating different materials

support	BE Au $4f_{5/2}$ (eV)	BE Au $4f_{7/2}$ (eV)
Silica	85.5 (2.0)	82.0 (2.0)
Falcon®-type tube	86.1 (0.8)	82.5 (0.8)
PEEK tubing	85.6 (1.5)	82.0 (1.5)

thin slices for TEM failed and although the nanoparticles were not visualized by SEM, EDX analysis revealed the presence of Au in both large aggregates and along the surface of the Falcon®-type tube (Figure S13). XPS spectra of the silica, the Falcon®-type tube and the inner side of the PEEK tubing showed the Au $4f_{7/2}$ and Au $4f_{5/2}$ peaks (Figure S14), the binding energies (BE) differences between Au 4f7/2 and Au 4f5/2 being close to the standard value of 3.67 eV, indicating the presence of metallic AuNPs on the surface[62]. The observed Au $4f_{7/2}$ BE, 82.0 – 82.5 eV (Table 4), are lower than the expected bulk value of 84.0 eV but in the range of those reported for supported bimetallic AuPd nanoparticles.[63] This BE shift of the core levels of supported AuNPs is well known and it has been related to the influence of the oxidation (electronic) state of the AuNPs, the particle size effect or different structural arrangement in the surface of the nanoparticle.[64] A map of the distribution of Au on the surface of the Falcon®-type tube was determined by searching the energy of the Au $4f_{7/2}$ a surface of 200 x 200 μm and further confirmed the coating of the surface (Figure S15).

Conclusions

bPEI2K is a polyamine suitable for the synthesis of PEI@AuNPs at room temperature. However their synthesis was optimized by using a short microwave irradiation that reduces the time of reaction and yields stabilized AuNPs of suitable size for their use as a chemoselective catalyst in the $NaBH_4$-mediated reduction of nitroarenes bearing different functionalities. The role of PEI is not limited to a reductant and a stabilizer but its known affinity for different materials has been exploited to coat the surface of different materials with AuNPs. The anchoring of MW-PEI@NPs to PS, PP, silica and Tygon®, PEEK and SS tubings yields novel, effective and stable catalytic materials that can be reused a number of times. This feature may be of interest in the field of flow nanocatalysis since PEEK and SS tubings are readily transformed into very efficient flow reactors by passage of a solution of MW-PEI@AuNPs without any further synthetic step. This straightforward functionalization is especially appealing in the case of the SS tubing due to the widespread application of this material in HPLC.

Experimental Section

Materials and Methods

Unless stated otherwise, commercially available compounds where used without further purification. Masterflex Tygon® lab (formula R-3603, i.d. 0.8 mm), IDEX Health and Science EFTE (Ref. WO 832930, i.d. 0.5 mm), FEP (Ref. WO 828932, i.d. 0.5 mm), PEEK (Ref. WO 721383, i.d. 0.5 mm) and VICI Jour SS (Ref. JR-T-625-20, i.d. 0.5 mm) tubings were used. Microwave (MW) synthesis was carried out on a Milestone Star Microwave Labstation. UV-Vis spectra were recorded on a Specord Plus 200 spectrophotometer (Analytik Jena AG). IR spectra were recorded in the range 4000-450 cm-1 on a Spectrum Two (Perkin-Elmer). Transmission electron microscopy images were obtained from a FEI TITAN G2 60-300 field emission instrument, equipped with a HAADF detector at “Centro de Instrumentación Científica”, Universidad de Granada. Samples were prepared by drying a drop of solution on carbon coated grid. ICP-OES measurements were carried out on a PERKIN-ELMER OPTIMA 8300 HPLC-MS. Scanning electron microscopy study was performed with an Auriga (FIB-FESEM) equipped different detectors (SE, Se-inLens, BSE, EsB, STEM (Bf/DF) and system for chemical (EDX) and crystallographic (EBSD) at “Centro de Instrumentación Científica”, Universidad de Granada. XPS measurements was carried on a Katros AXIS Ultra-DLD at “Centro de Instrumentación Científica”, Universidad de Granada. Monochromatic AlKα radiation was used for the analysis of a surface of 300 x 700 μm of the coated silica and Falcon-type tube materials and spot with diameter of 110 μm of the functionalized PEEK tubing, conveniently cut to access to the interior. A map of the distribution of gold on the surface of the Falcon-type tube, the intensity of the Au $4f_{7/2}$ peak was scanned over a surface of 200 x 200 μm.

Synthesis of the PEI@AuNPs at Room Temperature

$HAuCl_4\cdot 3.5H_2O$ (25 mg, 62.1 μmol) and bPEI2K (50 mg, 100 mg of a commercial solution) were added to distilled water (50 mL) (PEI repeating unit:Au ratio =18.7). The synthesis was allowed to proceed for 70 h at room temperature. The process was monitored by UV-Visible spectrophotometry, recording a spectrum in the range 400-700 nm every 30 min.

Synthesis of the MW-PEI@AuNPs

$HAuC_{l4}\cdot 3.5H_2O$ (25 mg, 62.1 μmol) and bPEI2K (50 mg, 100 mg of a commercial solution at 50% w/w) were added to distilled water (50 mL) (PEI repeating unit:Au ratio =18.7). After homogenization, the solution was MW irradiated at 300 W and 100 ºC for 3 min. The solution was allowed to cool to room temperature and the obtained MW-PEI@AuNPs were used as-prepared without further purification.

Adsorption of MW-PEI@AuNPs onto Silica

Silica Gel 60 (0.063-0.200 mm, 12.5 g) was incubated with the as-prepared MW-PEI@AuNP solution (25 mL) for 5 min. After this time, the solution turns colourless and the silica reddish. The solution was filtered under vacuum and the resulting solid was thoroughly washed with distilled water and dried under vacuum (1 mm Hg).

Coating of Polystyrene and Polypropylene Surfaces

Standard disposable cuvettes (polystyrene) and Falcon®-type tubes (polypropylene) were incubated at room temperature overnight with a solution of as-prepared MW-PEI@-AuNPs. After removing the MW-PEI@AuNPs solution, the coated materials were thoroughly rinsed with distilled water and dried at room temperature.

Coating of Tubing with MW-PEI@AuNPs

The inner wall of 1.5 m of Tygon®, FEP, ETFE, PEEK, and SS tubings was functionalized by recirculation of the as-prepared MW-PEI@AuNPs solution at room temperature overnight. After this time each tubing was washed by circulating distilled water (ca.100 mL).

Kinetic Studies of the Reduction of 4-NP, 4-NA and 4-NAc in Solution

To a solution of the corresponding nitroarene (5×10^{-5} M) and $NaBH_4$ (2.5×10^{-2} M) in distilled water (20 mL), a solution of MW-PEI@AuNPs (20 µL, 1:25 dilution from the as-prepared solution) was added. The reaction was carried out at room temperature and monitorized by the decrease of the absorbance at 400 nm, 380 nm and 319 nm resulting from the reduction of 4-NP, 4-NA and 4-NAc respectively. Between consecutive measurements the reaction was shaken to favour the elimination of bubbles. The apparent rate constant was determined from the slope of the linear correlation of $\ln(A_t/A_o)$ versus time, being A_t and A_o the absorbance at the beginning or the reaction (i.e. t=0) and at a given time (t=t).

Scope of the MW-PEI@AuNPs-catalyzed Reduction

A solution of the corresponding nitroarene (1.0 mL, 10 mM) in MeOH or MeOH/THF (19:1) was added to a solution of $NaBH_4$ (38 mg, 1.0 mmol) in distilled water (19 mL) to obtain a solution of nitroarene (5×10^{-4} M) and $NaBH_4$ (5×10^{-2} M) to which the as-prepared solution of MW-PEI@AuNPs (40 µL) was added. The reaction mixture was kept at room temperature with occasional mixing. Aliquots (500 µL) were taken at different times (0 h and 1 h for all compounds and 0 h, 1 h, 2.5 h, 5.5 h and 8 h in the case of 4-benzontrile and 4-NAc) and the reaction quenched by addition of formic acid (500 µL, 1 % v/v). The reaction mixtures were analyzed by HPLC-MS.

Assessment of the Activity of the Catalytic Materials

The catalytic activity of the MW-PEI@AuNPs-coated materials was evaluated with a solution of 4-NP (5×10^{-5} M) and $NaBH_4$ (2.5×10^{-2} M) in distilled water. Typically, the volume of reaction mixture assayed for the MW-PEI@AuNPs was 1 mL for cuvettes and 20 mL for Falcon®-type tubes and for batch experiments with silica (0.5 g). For silica column experiments, silica (7.5 g) was packed into a glass column and the reaction mixture, maintained in a water-ice bath, was passed under gravity. The eluted fractions (35-45 mL) were collected, sonicated and the conversion determined by measuring the absorbance at 400 nm.

Flow Nanocatalysis

For the flow nanocatalysis the MW-PEI@AuNPs coated tubing was connected to a Masterflex peristaltic pump and a volume (20-40 mL) of a solution of the corresponding nitroarene (5×10^{-5} M) and $NaBH_4$ (2.5×10^{-2} M) in distilled water was passed at a flow rate of 0.155 mL/min. The solution eluted was collected in fractions (ca. 1.5 mL), which were sonicated and the absorbance at 400 nm (4-NP) or 380 nm (4-NA) was monitorized. Higher conversion was achieved when the reaction mixture was cooled in a water-ice bath to prevent $NaBH_4$ decomposition.

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Keywords: gold nanoparticles • PEI • surface coating • supported catalysts • nanocatalysis

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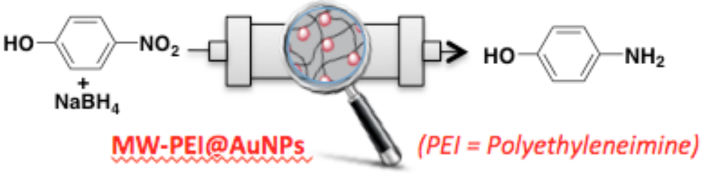

Getting Catalytic Gold Surfaces: bPEI2K is a reductant and stabilizer suitable for the easy preparation of PEI@AuNPs under MW irradiation. The affinity of these hybrid NPs forthe surface of PS, PP, silica and Tygon®, PEEK and SS tubings has been exploited for their anchoring yielding effective and stable catalytic materials

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Catalytic Materials Based on Surface Coating by PEI-Stabilized Gold Nanoparticles