

Water-soluble Au nanoparticles: from catalytic selective nitroarene reduction in water to refractive index sensing

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Full Papers

Abstract: Water-soluble gold nanoparticles (Au NPs) stabilized by a nitrogen-rich PEG-tagged substrate have been prepared by reduction of HAuCl₄ with NaBH₄ in water at room temperature. The morphology and size of the nanoparticles can be controlled by simply varying the gold/stabilizer ratio. The nanoparticles have been fully characterized by TEM, HRTEM, ED, EDS, UV-vis, *p*-XRD and elemental analysis. The material is efficient as a recyclable catalyst for the selective reduction of nitroarenes with NaBH₄ to yield the corresponding anilines in water at room temperature. Furthermore, the potential ability of the Au NPs as a refractive index sensor due to their localized surface plasmon resonance (LSPR) effect has also been assessed.

Introduction

Within the ever-growing field of the application of metal nanomaterials, the scientific community has dedicated a large amount of effort to studying the properties and potential applications of gold nanoparticles (Au NPs). This rising interest is due, in large part, to the remarkable Au NPs stability, biocompatibility, as well as their size-related electronic and optical properties (quantum-size effect). Thus, Au NPs have found applications in areas as diverse as chemical and biological sensing,^[1,2] catalysis,^[3] and biomedicine.^[4] Various methods have been developed for the preparation of gold NPs, including both the "top-down" (mainly physical manipulation) and "bottom-up" procedures,^[5,6] the latter consisting mainly of chemical methods, with the reduction of gold salts being the most common. For the use in catalytic applications, it is often desirable to obtain small-size Au NPs, thus maximizing the fraction of gold atoms on the surface, given that these atoms are generally responsible for the catalytic activity. Unfortunately, metal NPs in solution are subjected to facile agglomeration towards the thermodynamically favored bulk metal, with the consequent loss of their catalytic activities. The most popular strategies for chemists to overcome this problem consists in supporting Au NPs on an inorganic matrix^[5] or preventing the aggregation of soluble Au NPs with effective stabilizing agents,^[7] including those based on polymers.^[8] The nature of the protecting agent, in turn, determines the solubility properties of the metal nanoparticles. Thus, a suitable choice of the stabilizer may render the nanomaterial soluble in organic or aqueous medium and may even facilitate the recycling potential for

NP solubility in aqueous media is highly attractive, given that water is a low cost environmentally benign medium, non-toxic and safe, which is of particular interest not only as a laboratory but also for industrial processes. However, many of the stabilized Au NPs reported in the literature are not water soluble, which, for a catalytic application, greatly decreases the chances of the substrate to contact the catalyst in aqueous medium, resulting in long reaction times or low activities.

Besides its effect on solubility, the nature and protection of the stabilizer employed is also a tool to control the size of the NPs formed, which, as already mentioned, is often the key to a high catalytic activity. In addition, the size of a NP also translates into its electronic properties, which, for Au NPs, includes the Localized Surface Plasmon Resonance (LSPR) effects, making them excellent scaffolds in various sensing applications.^[1,2] For instance, recent reports showed the potential of Au NPs as sensors of heavy metal ions in aqueous solutions.^[10] Thus, to prepare water-soluble Au NPs is of great significance, especially when considering their catalytic uses in aqueous medium, as well as their sensing and biological applications.

Scheme 1. Au NPs stabilized by **L** for catalysis and as refractive index sensors.

As a consequence, a sustained effort^[11,12] has gone into the development of protocols to prepare Au NPs that are stable and easily dispersible in water. The most common method is the growth of Au NPs in the presence of hydrophilic thiols containing short ethylene oxide oligomers or long poly(ethylene glycol) (PEG) chains.^[13,14]

Our group previously described^[15] water-soluble Pd NPs, stabilized by two different star-shaped PEG-tagged substrates, as recyclable catalysts for cross-coupling reactions. However, these ligands fell short for the formation of other metal nanocatalysts, including Au and Rh, in terms of yields in the nanoparticles synthesis and/or reproducibility of the procedures. This led us to design a new nitrogen-rich polyoxyethylenated stabilizer **L** with a triazine core and triazole moieties in the branches (Scheme 1). Thus, we recently reported^[16] the synthesis of this PEG-tagged substrate **L** via copper-catalysed alkyne-azide cycloaddition (CuAAC, *click* chemistry), and the use of this molecule as stabilizer for the formation of size and morphology controllable Rh NPs. The materials proved to be excellent recyclable catalysts in the hydrosilylation of internal alkynes (Scheme 1).

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Table 1. Preparation of Au NPs stabilized by **L** from the reduction of tetrachloroauric acid with sodium borohydride^[a].

Entry ^[a]	L : Au ^[b]	Diameter / nm ^[c]	% Au		Yield ^[e] / %	Name of material
			Theoretical	Experimental ^[d]		
1	2.00 : 1	1.1±0.2	1.54	1.26	68	M1
2	1.00 : 1	1.3±0.3	2.33	1.91	76	M2
3	0.70 : 1	1.5±0.3	4.27	3.66	83	M3
4	0.50 : 1	1.7±0.4	6.23	5.21	84	M4
5	0.30 : 1	2.1±0.3	9.43	8.21	85	M5
6	0.20 : 1	2.4±0.5	13.60	10.86	-	-
7	0.10 : 1	3.0±0.5	24.10	17.41	71	M7
8	0.07 : 1	3.3±0.8	31.12	19.40	61	M8
9	0.04 : 1	4.4±1.6 ^[f]	44.17	37.30	76	M9
10	0.01 : 1	tadpole morphol. ^[g]	75.98	56.80	75	M10
11	0 : 1	bulk gold	100.0	-	-	-

[a] [Au] = 0.6 mM, 6 mmol of NaBH₄ per 1 mmol of Au. [b] Molar ratio. [c] Mean \pm SD, TEM. [d] Determined by ICP. [e] Based on HAuCl₄ used. [f] It is a mixture of spherical Au NPs and tadpole-like NPs, herein only the spheric NPs were considered. [g] Irregular tadpole-like Au NPs were observed.

This three-fold symmetric molecular architecture was initially proposed taking into account the potential benefits of both the nitrogen-rich structure and the PEG moieties on the nanoparticle stabilization and also the operational convenience of bonding *via* triazole linkages built by a click reaction.^[17,18] Encouraged by these results with Rh NPs, herein we report our latest results on using the stabilizer **L** for the efficient preparation of size and morphology controllable Au NPs, and their subsequent use as recyclable catalysts in the selective nitroarene reduction in water.

Results and Discussion

Preparation and characterization of Au NPs

A chemical reduction method was applied to test the stabilizing ability of **L** for the formation of Au NPs, whereby HAuCl₄·3H₂O was used as the source of gold and NaBH₄ as a reducing reagent, with reactions run in water at room temperature.

We initially examined the formation of Au NPs with a L/Au ratio of = 2.00/1 (Table 1, entry 1). It was found that, upon addition of an excess of the NaBH₄ solution (6 mmol per mmol Au), the reaction mixture immediately underwent a color change from light yellow to black, but with no presence of bulk metal after stirring overnight. The reaction mixture was then filtered through a Millipore filter and the filtrate was extracted with dichloromethane. In this manner, M₁ was obtained as a black solid upon removal of solvent. The ¹H NMR spectrum of M₁ was identical to that of stabilizer **L** (see supporting information). TEM analysis confirms the presence of spherical and well dispersed nanoparticles with a mean size of 1.1 nm (based on 150 particles measured, Table 1, entry 1). The yield with respect to the Au used was calculated as 68% on the basis of the material's elemental analysis (1.26% Au). Although

the size of the NPs obtained appeared adequate for catalytic applications, we were interested in probing the influence of the stabilizer-to-metal ratio on the nanoparticle size, morphology and reactivity. Indeed, the size and morphology of metal nanomaterials have been reported to play a key role in the activity and selectivity for some catalytic systems.^[19] Thus a careful screening of the L/Au ratio under the present reaction conditions was performed (Table 1, entries 1-10).

As summarized in Table 1 (entries 1-8), although spherical well dispersed nanoparticles (M₁-M₈) were formed over a wide L/Au ratio, as the L/Au ratio was gradually decreased from 2.00 to 0.07/1, the particle size rose from 1.1±0.2 to 3.3±0.8 nm in a manner somewhat analogous to what had been observed with Rh NPs.^[16]

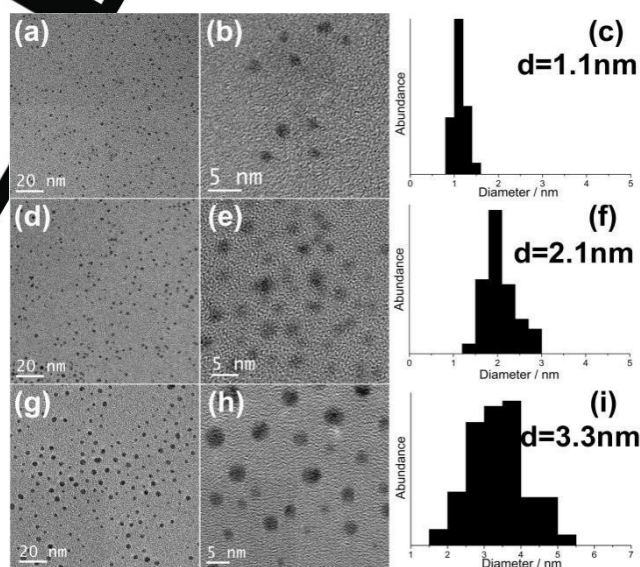


Figure 1. TEM and HRTEM images, and the corresponding size distributions of the materials **M1** (a-c), **M5** (d-f) and **M8** (g-i).

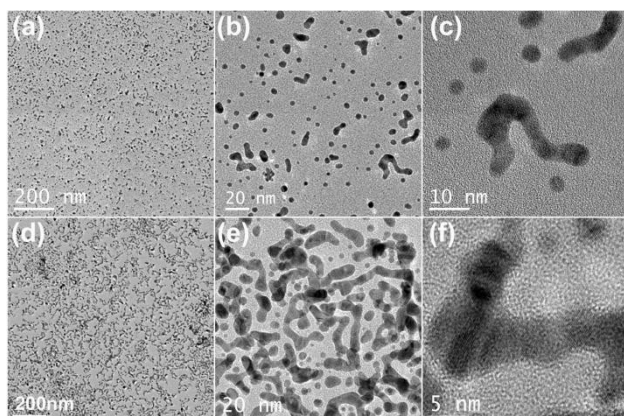


Figure 2. TEM images under different magnifications and the corresponding HRTEM images: **M9** (a-c) and **M10** (d-f).

Selected TEM and HRTEM images, and the corresponding size distributions of the materials **M1**, **M5** and **M8** are shown in Figure 1. Since the size of the Au NPs (and of the metal nanoparticles, in general) should, in principle, be determined by the relative rates of nucleation and particle growth, the formation of smaller nanoparticles with a higher amount of stabilizer can be ascribed to the more efficient suppression of the nanoparticle growth at higher stabilizer-to-metal ratios.

Table 2. Electron Diffraction pattern of **M10**.

h k l	d_{hkl} (nm)	
	Exper.	Theor.
(111)	0.2327	0.2319
(200)	0.2040	0.2071
(220)	0.1426	0.1400
(311)	0.1209	0.1211

Interestingly, when the L/Au ratio was further decreased to 0.04/1 (Table 1, entry 9), a mixture of spherical and tadpole-like Au NPs structures was observed (**M9**, Figure 2a-c). Even at a stabilizer loading as low as 0.01 equiv, no bulk metal was detected, with the Au NPs formed predominantly as a tadpole-like morphology (**M10**, Table 1, entry 10 and Figure 2d-f). For the latter material, a 56.8% gold content was determined by elemental analysis (ICP) (Table 1). As a reference, the reduction of HAuCl₄ with NaBH₄ in the absence of **L** did produce bulk gold precipitate (Table 1, entry 11). As shown in Table 2, the experimental interplanar distances measured by electron diffraction (ED) for **M10** were found to be close to those expected for the face-centered cubic (fcc) gold lattice.

The water solubility of the Au NPs was tested by adding 2 mg of the selected catalyst into 1 mL of water. Upon stirring

thoroughly, the materials were found to be completely soluble in water as depicted in Figure 3a.

Further structural investigation was conducted by registering the UV-vis spectra of the materials **M1-M10** in THF (Figure 3b). For particles larger than 2 nm (**M5-M10**), the appearance of a broad shoulder at 450-600 nm could be discerned representing the localized surface plasmon resonance (LSPR). This absorption shows an appreciable red shift with the decreasing L/Au ratio (0.30/1 to 0.01/1), consistent with the known^[20] dependence between the LSPR band and the particle size. Nevertheless, for materials **M1-M4** containing particles smaller than 2 nm, the LSPR band was not clearly observed, in good agreement with previous research.^[11]

The *p*-XRD patterns (Figure 3c) of **M5**, **M6** and **M7** showed two intense peaks located in the range of $2\theta = 15^\circ$ attributed to the crystalline (120) and (111) planes of the PEG-tagged stabilizer.^[16,21] Four additional weak diffraction bands in the range $2\theta = 40^\circ$ to 80° were assigned to the (111), (200), (220) and (311) planes of fcc gold lattice, respectively.^[22] These data fit well with the ED analysis. The Energy-Dispersive X-ray Spectroscopy (EDS) spectrum of **M10** is given in the supporting information as a representative example, confirming the presence of gold.

Reduction of nitroarenes in water under catalysis by gold nanoparticles

Among the many potential catalytic applications of gold nanoparticles,^[3] the reduction of nitroarenes in water was chosen as a model process. This reaction has been widely studied, not only because the corresponding anilines are very important industrial raw materials, but also because the nitroaryl compounds are common organic pollutants in industrial and agricultural wastewaters due to their use as building blocks in many areas such as dyes, pesticides, explosives and as organic solvents. Sodium borohydride is one of the most employed reducing agents for nitroarenes under metal nanoparticles catalysis.^[23,24,25] However, in many cases the reactivity studies have been limited to the model reduction of *p*-nitrophenol to *p*-nitroaniline. We were interested in broadening the scope of this reaction by performing the selective reduction of the nitro group even in the presence of other sensitive functional groups under mild reaction conditions in aqueous medium.

A first reaction was carried out with nitrobenzene as model compound (at 0.5 mol% of Au loading using **M5**) employing 50 mmol of NaBH₄ per mmol of substrate^[23] (Table 3, entry 1). To our delight, monitoring the reaction by TLC showed a spot-to-spot conversion of the starting material to a new product after just 1 h at room temperature. Taking into account that the stabilized Au NPs are soluble in water but not in diethyl ether, the reaction mixture was extracted with diethyl ether, affording the pure aniline in a quantitative yield after solvent removal. Lowering the amount of the sodium borohydride to 35 mmol/mmol of nitrobenzene (Table 3, entry 2), still allowed for an efficient, although somewhat slower, reaction.

Keeping the amount of sodium borohydride constant at a 35:1 molar ratio, the reaction time did not change significantly on lowering the loading of catalyst to 0.3 mol% (Table 3, entry 3), although at this catalyst loading an attempt to further decrease the NaBH₄ equivalents led to a lower product yield and a considerable more sluggish reaction (Table 3, entry 4). As a reference experiment, no conversion took place in the absence of the Au catalyst (Table 3, entry 5). Similarly, no

reaction occurred in the absence of sodium borohydride (Table 3, entry 6). It is worth noting that all the reactions mentioned

above were performed without any special precaution in water under air at room temperature.

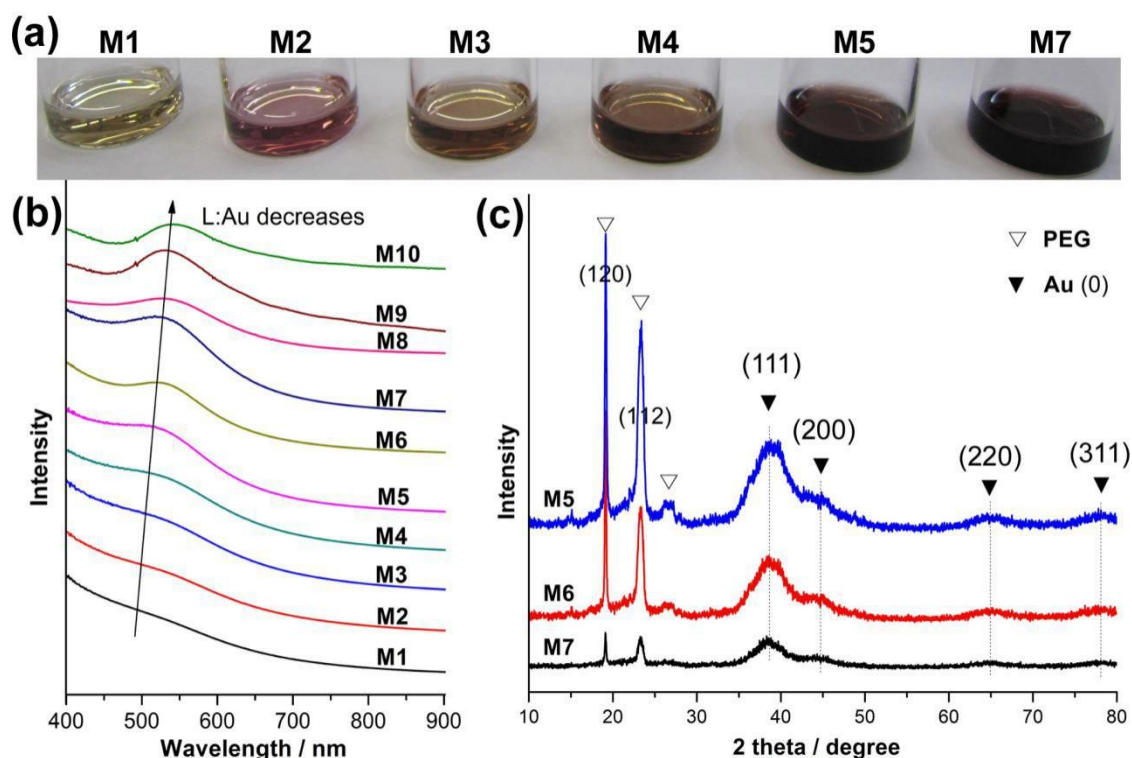


Figure 3. (a) Optical photographs of Au NPs (2 mg) in H₂O (1 mL); (b) Absorption spectra of Au NPs in NaBF₄ (0.2 mM of Au); (c) *p*-XRD patterns of select. Au NPs.

Table 3. Optimization of the reaction conditions^[a].

Entry	Cat. /mol % ^[b]	NaBH ₄ ^[c]	Time /h ^[d]	Yield /% ^[e]
1	M5/0.5	50	1.0	99 ^[e]
2	M5/0.5	35	1.5	99 ^[e]
3	M5/0.3	35	1.5	99 ^[e]
4	M5/0.3	20	6.0	78 ^[f]
5	L/0.3	50	3.0	-
6	M5/0.3	-	3.0	-

[a] **M5** added to a well-stirred mixture of PhNO₂ (1.0 mmol) and NaBH₄ in H₂O (10 mL). [b] mol % Au vs PhNO₂, based on Au ICP analysis for **M5**. [c] mmol of NaBH₄ per mmol of PhNO₂. [d] Time by TLC. [e] % isolated by extraction with diethyl ether, further purification was unnecessary. [f] Corrected GC yield.

Under the optimized conditions (0.3 mol% Au, 35 mmol of sodium borohydride/mmol of substrate), we first investigated the reusability of **M5** in the reduction of nitrobenzene, taking advantage of its solubility properties (soluble in water, insoluble in diethyl ether). Thus, once the reaction was deemed complete by GC, the product was extracted with diethyl ether leaving the Au NPs in the aqueous phase ready to be reused. Four consecutive cycles were performed (Table 4, entries 1-4) with a slight decrease of the

activity, probably due to some loss of catalyst, but giving a respectable isolated yield of 78% in the fourth run.^[26] The reaction scope was then extended to several additional nitroarenes using **M5** as a representative catalyst (Table 4). The protocol was found to be tolerant of the presence of electron-withdrawing and electron-donating substituents on the aromatic ring. Thus, the catalyst was very effective for the reduction of 3-nitroaniline and 4-nitrobenzenesulfonamide to the corresponding products in quantitative yields in less than an hour (Table 4, entries 5-6). The *p*-nitroanisole gave an excellent yield of *p*-methoxyaniline albeit at a longer reaction time (Table 4, entry 7). The reduction of *p*-bromonitrobenzene furnished *p*-bromoaniline in 72% isolated yield with only trace of dehalogenated product detected (Table 4, entry 8). The catalytic system was also able to reduce the *p*-nitrobenzonitrile and methyl *p*-nitrobenzoate, yielding the corresponding anilines in 89% and 82% isolated yields, respectively (Table 4, entries 9-10); the -CN and -COOMe remained unaltered under the reaction conditions.

Last, the catalytic activity of **M5** was tested on *p*-nitrophenol, an environmentally hazardous substance included by the U. S. Environmental Protection Agency on its "Priority Pollutant List".^[24] Remarkably, the reduction of *p*-nitrophenol was completed in only 11 min affording *p*-aminophenol in quantitative yield (Table 4, entry 11). The faster reaction with this substrate compared with the reduction of *p*-methoxyaniline (compare entries 7 and 11) must be due to its higher hydrophilicity derived from the presence of the hydroxyl group. This reaction was also used as a model to investigate the catalytic activities of other Au NPs systems (**M1** and **M9**) featuring nanoparticle sizes and morphologies different from those of **M5** (Table 4, entries 12-13). As expected, **M9** showed lower activity when compared with **M5**, which should be ascribed to the higher particle size and, consequently, lower number of active sites on the surface. However, the catalysis using **M1** needed the longest reaction time (22 min) which might be rationalized by the excess of stabilizer blocking the particle surface and causing a drop in catalytic activity.

Table 4. Reduction of nitroarenes catalyzed by Au NPs^[a].

Entry	Product	Cat.	Conv. /%	Time ^[b]	Yield /% ^[c]
1		M5	> 99	1 h	99 ^[d]
2		M5	> 99	1.5 h	88 ^[e]
3		M5	94	2 h	86 ^[f]
4		M5	87	5 h	78 ^[g]
5		M5	> 99	35 min	99
6		M5	> 99	48 min	99
7		M5	> 99	3 h	98
8		M5	> 99		72
9		M5	> 99	1.5 h	89
10		M5	> 99	1 h	82
11		M5	> 99	11 min	99 ^[h]
12		M9	> 99	16 min	99
13		M1	> 99	22 min	99

[a] To a well stirred mixture of nitroarene (1.0 mmol) and NaBH₄ (35 mmol) in water (10 mL) at room temperature was added the catalyst (0.3 mol%). [b] TL (Total Loss) time. [c] Isolated

yield. [d-g] Consecutive cycles with the same batch of catalyst. [h] TON (mol product/mol catalyst) = 330, TOF (TON/time) = 30 min⁻¹.

It is worth noting that the scope of the present catalytic system is broader than in most of other reports, where only *p*-cresophenol was used to test to catalytic activity. In this context, an interesting comparison can be made with a recent report from the Kantam laboratory, describing a supported gold nanocatalyst for the reduction of a wide range of nitroarenes in water,^[23] and providing the catalytic TON's of up to 207 when employing a 50-fold excess of the reducing agent. As seen in Table 1, our new Au NP catalyst reaches a TON of 330 (TOF = 30 min⁻¹) while requiring less NaBH₄ loading.

Evaluation of the gold nanoparticles as refractive index sensor

One of the simplest applications of the nanoparticle LSPR phenomenon is the detection of changes in the bulk refractive index of their environment through shifts in the LSPR peak wavelength.^[1] In order to investigate the ability of the Au NPs as refractive index sensors, **M7** (mean size of 3.0±0.5 nm) was chosen as representative nanomaterial. The nanoparticles were dissolved (Au concentration of 0.2 mmol/L) in a series of solvents covering a range of refractive index values. Specifically, the experiments were conducted in carbon disulfide (n = 1.627), toluene (n = 1.496), chloroform (n = 1.447), *t*-butanol (n = 1.399) and water (n = 1.333).

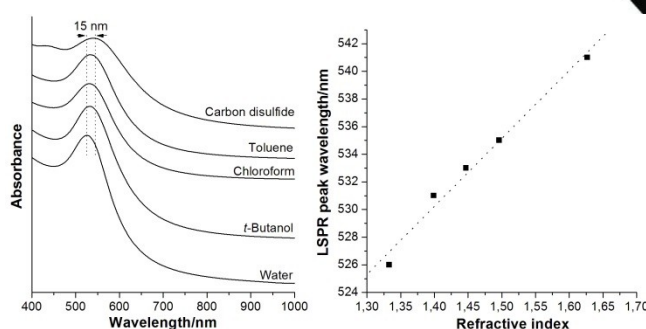


Figure 4. Optical absorbance of **M7** with gold concentration of 0.2 mM in carbon disulfide, toluene, chloroform, *t*-butanol and water (a); plotting of the peak wavelength versus refractive index indicating the linear correlation (b).

The absorbance spectra of these five samples (Figure 4a) showed that as the refractive index increased from 1.333 to 1.627, the maximum absorbance of the samples experienced a notable redshift from 526 nm to 541 nm, indicating that Au NPs could, indeed, be used as refractive index sensors. As can be seen in Figure 4b, there is an approximately linear correlation between the LSPR peak wavelength and the medium refractive index, in good agreement with the reported theory.^[1,2,27]

Conclusions

A nitrogen-rich polyoxyethylenated substrate was used for the formation of water soluble Au NPs upon NaBH₄ reduction of hydrogen tetrachloroaurate(III) in water at room temperature. The size and morphology of the nanoparticles can be controlled by simply varying the gold-to-stabilizer ratio. The newly prepared nanomaterials were fully characterized by TEM, HRTEM, ED, EDS, *p*-XRD, UV-vis and elemental analysis. Further investigation showed that the Au NPs displayed excellent activity as catalyst for the mild and selective reduction of differently substituted nitroarenes to the corresponding anilines using NaBH₄ as reducing agent in water at room temperature. The new nanocatalyst could be easily recycled (four runs) taking advantage of its solubility properties. Thus, the product was directly extracted from the reaction medium with diethyl ether, leaving the Au NPs-containing water phase ready for the next run. The Au NPs were also successfully tested as refractive index sensors.

Experimental Section

The stabilizer **L** was prepared according to our previous report.^[16] All NMR spectra were recorded with Bruker Avance360 (360 MHz for ¹H) and AvanceII 400 MHz (400 MHz for ¹H) spectrometers. ICP measurements of gold content were carried out at the *Serveis Científico-Tècnics* of the *Universitat de Barcelona* with a multichannel Perkin-Elmer instrument, model Optima 3200 RL. TEM and ED analyses were performed at the *Servei de Microscòpia* of the *Universitat de Barcelona*, with a JEOL JEM-2010 model instrument operating at 200 kV. The nanoparticle sizes were determined by measuring 150 particles with Digital Micrograph software (Gatan, Inc.) and were subsequently averaged to produce the mean NP

diameter. UV-vis spectra were acquired at room temperature using a HP8453 spectrophotometer (Agilent) running a ChemStation software. The powder X-ray diffraction (*p*-XRD) patterns were collected using a conventional powder X-ray diffractometer (Siemens D5000) at the *Institut de Ciència dels Materials de Barcelona*.

General procedure for the preparation of Au NPs (**M5** as an example): To a solution of the stabilizer **L** (112 mg, 0.018 mmol) and hydrogen chloroaurate(III) trihydrate (24 mg, 0.06 mmol) in water (100 mL) under nitrogen atmosphere, was added dropwise via a syringe (over 2 minutes) a solution of 0.1 M sodium borohydride (3.6 mL, 0.36 mmol of NaBH₄). The mixture was stirred at room temperature overnight, and then it was filtered through a Milli-Pore filter. The filtrate was extracted with dichloromethane (6 × 20 mL) and the organic phase was dried over anhydrous sodium sulfate. After the removal of the solvent, Au NPs were obtained as a black powder (122 mg, Au % = 8.21%, 85% yield with respect to the Au used).

General procedure for the reduction of nitroarenes (reduction of *p*-nitrophenol as example): To a well stirred mixture of *p*-nitrophenol (1.0 g, 1.0 mmol) and sodium borohydride (1.324 g, 35 mmol) in water (10 mL), **M5** was added (0.3 mol% Au catalyst loading, 0.007 g) and the mixture was stirred at room temperature. Upon the completion of the reaction (TLC monitoring), the mixture was extracted with diethyl ether. The organic fraction was dried over anhydrous Na₂SO₄ and then the solvent was evaporated under reduced pressure, affording pure *p*-aminophenol (white solid, 0.108 g, 99% yield).

Acknowledgements

Financial support from Ministerio de Ciencia e Innovación (MICINN) of Spain (Projects CTQ2009-07881, CTQ2011-22649), Consolider Ingenio 2010 (CSD2007-00006), Ministerio de Economía y Competitividad (MINECO) of Spain (Projects CTQ2013-46705-R; CTQ2014-51912-REDC), a Ramón y Cajal scholarship to A. S. (MEC, Spain, RYC2006-00110), DURSI-Generalitat de Catalunya (SGR2009-1441; SGR2014-1105, SGR2014-1192) and China Scholarship Council (CSC) scholarship to W. G. are gratefully acknowledged.

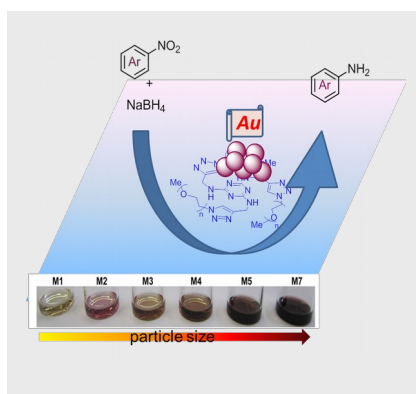
Keywords: Water-soluble Au NPs • Reduction • Nitroarenes • Anilines

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FULL PAPER

Water-soluble gold nanoparticles were synthesized using a PEG-tagged N-rich stabilizer, **L**. The particle size can be fine-tuned via the **L**/Au ratio. The new Au NPs are highly efficient and reusable in the selective reduction of ArNO₂ in water. The particles also act as refractive index sensors via the shift in the UV absorption.



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