Preparation of stable suspensions of gold nanoparticles in water by sonoelectrochemistry

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Abstract

Stable suspensions of gold nanoparticles in water were prepared with high yield by a novel one-step ultrasound assisted electrochemical process. Various strategies based on the addition of either tailor-made polymers or mixtures of commercially available polymers, in the electrochemical bath have been found successful to avoid nanoparticles aggregation commonly observed by sonoelectrochemistry. α-Methoxy-ω-mercapto-poly(ethylene oxide) or poly(vinyl pyrrolidone)/polyethylene oxide mixtures were able to build up a coalescence barrier around the gold nanoparticles. The results showed that the size of the gold nanoparticles could be easily tuned between 5 nm and 35 nm by simple control of the electrochemical parameters, i.e. the deposition time (T_{ON}) from 10 ms to 20 ms. The properties of as-prepared gold nanoparticles were compared to the ones of gold colloids prepared by the more conventional wet nanoprecipitation method using chemical reductive agents.

Keywords: Sonoelectrochemistry; Nanoparticles

1. Introduction

Nanotechnology is now expanding very rapidly, as result of the unique physical and/or chemical properties that nanoparticles (NPs) exhibit compared to bulk materials. Stabilization of the nanoparticles against coalescence into large aggregates is however a prerequisite for their remarkable optical, electrical, catalytic and magnetic properties to be exploited in a variety of applications. As a rule, the presence of an at least 2 nm thick steric coalescence barrier (which corresponds approximately to a C_{18} chain) can offset the Van der Waals interactions, allowing particles smaller than 10 nm to be stabilized [1].

Nowadays, special attention is paid to organic monolayer-protected clusters (MPC) of metals and especially of gold, because of very specific electronic, biological, and catalytic properties [2-4]. Nevertheless, many applications require the production of large quantities of particles with a controlled and uniform size. Although many synthetic methods have been reported to prepare gold nanoparticles [5-8], only few of them are versatile enough to tune the nanoparticle size in a range of several tens of nanometers while preserving monodispersity of the particles size distribution. The most popular method was developed by Brust et al. It relies on the borohydride reduction of a gold salt in the presence of an alkyl thiol capping agent leading to particles with very narrow size distribution [8]. In this case, varying the size of the nanoparticles requires however, the adjustment of either the reducing agent, the protective substance, the gold concentration the solvent, the temperature or several of these experimental conditions [9a]. Most of the methods used to prepare small gold clusters (1-5 nm), take advantage of the strong capping ability of thiol molecules. Because of a very strong affinity for gold, the alkyl thiols cover the particles with a dense monolayer [9]. Other capping agents mentioned in the literature include organic sulfides, disulfides and carboxylates [10]. Recently, thiolated polymers were also used as macroligands to protect gold nanoparticles more efficiently than alkyl thiols [11-14].

Even if these production techniques are perfectly well-suited for laboratory-scale production and testing, their scaling-up to industrial production might be difficult and expensive. A general method to produce nanoparticles of adjustable size without altering the experimental conditions such as medium concentration, temperature, ligands is the sonoelectrochemical technique. The electrodeposition process combined with high intensity ultrasound pulses was proposed for the synthesis of large amounts of nanoclusters with a narrow size distribution [15]. This technique allows an extensive control of the size and composition of the particles (pure metallic or alloyed nanoclusters) over a quite wide range (few nanometers up to few hundreds of nanomaters) [16,17]. The starting material is an aqueous solution of metal salts which is electrochemically reduced on a titanium electrode for a very short time (~10-30 ms). Then the current is stopped and an ultrasonic wave is applied to the titanium electrode dislodging the metallic nuclei in the liquid medium. By this sonoelectrochemical process,

nanoparticles with a naked surface are however formed, which is a major drawback because of the aggregation of these particles, which settle down as shown in Fig. la. Moreover, the aggregates resist redispersion into individual particles and are thus useless.

The purpose of the study reported here was to synthesize and to use water-soluble macroligands, α-methoxy-ω-mercaptopoly(ethylene oxide) (MPEO-SH) and α,ω-dihydroxy poly(ethylene oxide) disulfide (PEO disulfide), that could be added to the electrochemical bath in which the metal particles are formed under ultrasound irradiation to get stable suspensions of gold colloids prepared by sonoelectrochemistry. Optical properties and sizes of such gold colloids were compared to gold suspensions prepared by conventional reduction of a gold salt by borohydride. MPEO-SH was prepared as a macroligand able to stabilize gold nanoparticles in organic solvents and in water, as well [18,19].

2. Experimental section

2.1. Materials

Toluene was dried by reflux over sodium/benzophenone complex and distilled under nitrogen before use. α-Methoxy, ω-hydroxy poly(ethylene oxide) (MPEO-OH; M_n = 2000 g/mol) was purchased from SIGMA and dried by three azeotropic distillations of toluene before use. All the other reagents were used as received: poly(vinyl pyrrolidone) (PVPr; M_n = 30,000 g/mol) and mercaptoacetic acid were purchased from Aldrich, $HAuCl_4 \cdot nH_2O$ (99.9%) from Strem and $NaBH_4$ (98%) from Janssen.

2.2. Synthesis of α-methoxy-ω-mercapto-poly(ethylene oxide) (MPEO-SH)

α-Methoxy-ω-mercapto-poly(ethylene oxide) (MPEO-SH) was synthesized by esterification of the hydroxyl end-group of the monomethoxy poly(ethylene oxide) (MPEO-OH) (M_n = 2000 g/ mol) with mercaptoacetic acid [18]. A typical reaction was carried out as follows. MPEO-OH (10 g; 5 mmol) was added into a 100 ml two-necked flask equipped with a stirrer and a Dean-Stark device. The MPEO-OH was dried by three azeotropic distillations with toluene and finally dissolved in 50 ml of toluene. Mercaptoacetic acid (3.5 ml, 50 mmol) and concentrated sulfuric acid (two drops) were then added. The flask was heated in an oil bath at 110 °C overnight. MPEO-SH was collected by precipitation in ether at 0 °C and then dried at 40 °C under vacuum for 24 h.

^{1}H NMR (CDC1$_3$) (TMS): δ = 2.01 (t, 1H, SH), δ = 3.26 (d, 2H, S-CH$_2$), δ = 3.36 (s, 3H, CH$_3$), δ = 3.62 (270H,CH$_2$CH$_2$O), δ = 4.28 (t, 2H, CH$_2$OCO). A mixture of MPEO-SH and MPEO disulfide was obtained resulting from the coupling reaction of thiol (Fig. 2). This mixture is abbreviated MPEO in the following.

2.3. Synthesis of α,ω-dihydroxypoly(ethylene oxide) disulfide (PEO disulfide)

Poly(ethylene oxide) disulfide end-capped by hydroxyl groups, (S-PEO-OH)$_2$ (PEO disulfide) was synthesized by anionic polymerization of ethylene oxide from bis(2-hydroxyethyl)disulfide. The starting disulfide (9 g, 0.058 mol) was dried by three azeotropic distillations with toluene. Some of the hydroxyl groups were converted to alkoxide by adding a naphthalene potassium solution in toluene until a light green coloration persisted. The mixture was charged to a 1 1 Engineers Europe Autoclave, and the temperature and pressure were increased to 50 °C and 0.75 bar, respectively. Finally, 60 g of ethylene oxide were added. After 6 h, the polymer was recovered by addition of the solution to ether. The solid product was dried under vacuum until to a constant weight was obtained. M_n was determined by H NMR in CDCl$_3$ (M_n = 1500g/ mol), and polydispersity (IP = 1.09) was determined by size exclusion chromatography (SEC) in THF.

2.4. Chemical synthesis of gold nanoparticles stabilized by MPEO

In a 100 ml flask equipped with a stirrer, 30 ml of twice-distilled water was purged with nitrogen gas for 15 min to deaerate the system. $HAuCl_4 \cdot nH_2O$ (10 mg) and MPEO (3 eq.) were added under nitrogen, and the solution was cooled in an ice bath. After a few minutes, 2 ml of a freshly prepared aqueous solution of $NaBH_4$ (5 eq./Au^{3+}) were rapidly added under vigorous stirring. The yellow mixture immediately turned dark red brown, and the mixture was kept under stirring for five extra hours. The solution was filtered through a 0.45 µm Millipore filter in order to separate the insoluble material and the filtrate that was stored at room temperature.

Fig. 1. *Gold NPs electrochemically prepared by applying repeatedly, (i) a potential of -1300 mV/NHE during T_{ON} = 50 ms, (ii) an ultrasonic wave of 27 kHz during T_{US} = 100 ms and (iii) a rest time, T_{OFF} of 200 ms during 5 h (a) without ligands (b) in the presence of MPEO and PVPr mixture.*
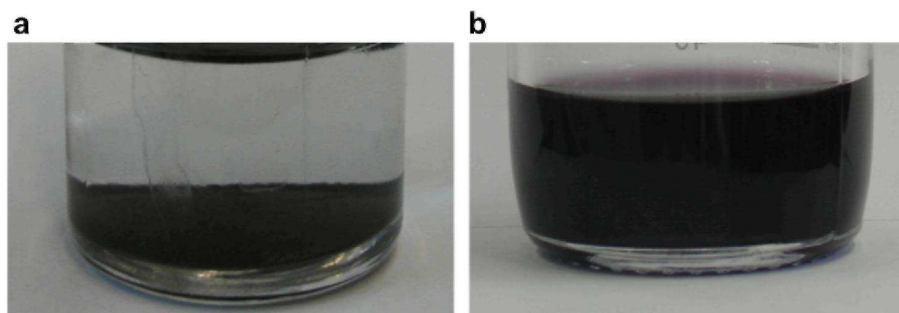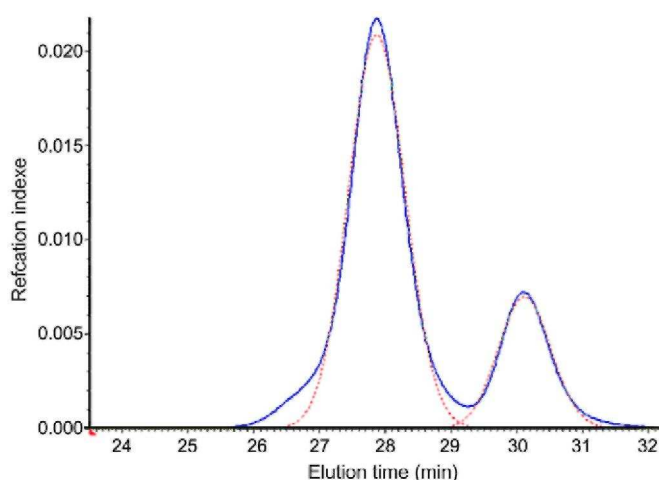

Fig. 2. *SEC chromatogram of the reaction product between α-methoxy, ω-hydroxy poly(ethylene oxide) and mercaptoacetic acid. The dotted curves are the deconvoluted elution peaks.*

2.5. Sonoelectrochemical synthesis of gold nanoparticles stabilized by MPEO

In a typical experiment using MPEO as stabilizing ligand, the concentration of $HAuCl_4 \cdot nH_2O$ was 2.8 x 10^{-4} M in the aqueous electrochemical bath. The pH was adjusted to 1 with HCl followed by the addition of MPEO (1 g/l). The sonoelectrochemical experimental set-up is shown in Scheme 1. A titanium horn is used as cathode completed by a gold anode and a SCE (saturated calomel electrode) reference electrode. All the measured potentials were corrected and reported versus NHE (normal hydrogen electrode). Pulsed electrodeposition was triggered by potential pulses imposed to the cathode (Tacussel PRT 10-20X with a Tacussel GSTP wave generator) and controlled by the cathodic potential, the potential pulse duration (T_{ON}) and the off duration (T_{OFF}) during which the cathodic potential is equal to the rest potential of the electrodes in the electrolyte. Ultrasounds were generated during T_{US} by two piezoelectric crystals (Sinaptec SA; resonance frequency of 27 kHz) and maximized at the end surface of the titanium horn. The surface of the horn was electrically isolated except for the end surface, which acts as cathode. The electrical signal that excited the piezoelectric crystals (Nexus 288) was synchronized with the electrochemical pulse. The ultrasounds were generated during the T_{OFF} period, starting at the end of the potential pulse (after T_{ON}) and lasting for a T_{US} period ($T_{US} < T_{OFF}$). The metallic clusters were formed at the titanium surface during the T_{ON} period and they were expelled into the electrolyte by cavitation during the T_{US} period [15].

The cathodic potential was in the range of -850 mV/NHE to -1300 mV/NHE. T_{ON} ranged from 10 to 50 ms, while T_{OFF} and T_{US} was comprised between 200 and 300 ms. At the end of the sonoelectrochemical process, the electrolytic bath was neutralized by the addition of sodium hydroxide pellets. The excess of salt was dialysed

against water, through a Spectra/Por dialysis membrane with a threshold of 100 kD. A violet suspension of gold nanoparticles was finally recovered from the dialysis membrane.

2.6. Characterization methods

MPEO and PEO disulfide were characterized by (i) ^{1}H NMR spectroscopy with a Bruker AM 400 MHz apparatus at 25 °C, in deuterated chloroform added with tetramethylsilane as an internal reference and by (ii) size exclusion chromatography (SEC) in THF with a HP 1090 liquid chromatography, equipped with a HP 1037 A refractive index detector and four PL GEL columns (10^5, 10^4, 500 and 100 Å) calibrated with poly(ethylene glycol) standards.

Transmission electron micrographs (TEM) were recorded with a Philips CM-100 microscope. Samples were prepared by spreading a drop of a dilute dispersion of nanoparticles on a copper grid coated with formvar. The grid was placed on a filter paper for drying.

The size and size distribution of the particles were determined with a "Disc Centrifuge CPS" device. The centrifugal sedimentation during disc rotation was stabilized by setting up a density gradient within the fluid by the sequential addition of sucrose solutions of increasing/decreasing concentration. The granulometric distribution curve was determined by continuously recording the turbidity of the fluid near the outside edge of the rotating disc. The turbidity measurements were converted into a weight distribution curve on the basis of the Mie's theory for light scattering and the particles density. The particles diameter was probed in the 1 nm and 40 μm range.

The optical absorption spectra of aqueous suspensions of gold nanoparticles were recorded with a UV-vis U-3300 spectrophotometer at room temperature.

Scheme 1. *Electrochemical set-up for the production of nanoparticles by sonoelectrochemistry.*
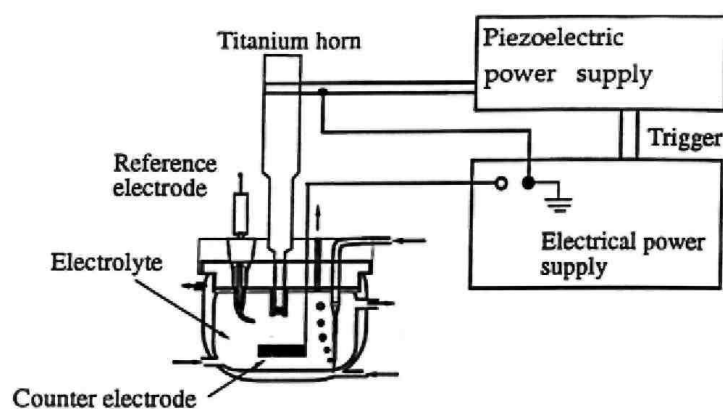
Scheme 2.
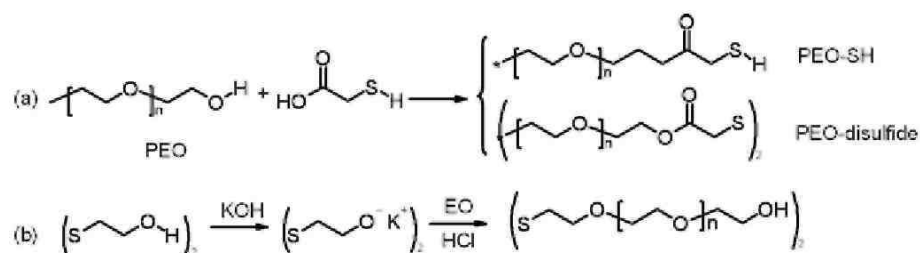
3. Results and discussion

Because of a high solubility in polar and apolar media, poly(ethylene oxide) (PEO) was already previously used as a stabilizing agent of nanoparticles in water [20] and inorganic solvents [21]. Moreover, solid surfaces exhibit biocompatibility and proteins repellence when they are covered by PEO, which is usually explained by the constitutive uncharged hydrophilic residues of PEO and a very high surface mobility responsible for effective steric exclusion [21]. Today, PEO is one of the most attractive synthetic polymers for biomedical applications. In this work, thiol end-capped PEO was prepared for being used as chains prone to be adsorbed at the surface of gold nanoparticles produced by sonoelectrochemistry to form of a steric coalescence barrier.

In order to end-capped commercially available α-methoxy, ω-hydroxy PEO with a thiol group, a first strategy was tested starting from the preformed monomethoxy PEO polymer. The hydroxyl end-group of MPEO-OH was derivatized to get a thiol, by esterification with mercapto acetic acid (Scheme 2a). The yield of this reaction was higher than 90%, as determined by ^{1}H NMR on the basis of the relative resonance intensity of the CH_2 protons adjacent to the ester ω-end-group ($-O-CO-CH_2-SH$; $\delta = 4.2$ ppm) and the CH_3 protons of the α-end-group ($\delta = 3.36$ ppm). SEC analysis of the reaction product showed a bimodal molecular weight distribution (Fig. 2). The small peak at the higher elution volume was characteristic of the original MPEO-OH, whereas a polymer with a twofold higher molecular weight was eluted at the lower volume, resulting from the coupling reaction of thiols in disulfides occurring easily in the used reaction conditions (high temperature). However, since disulfide compounds are as efficient as thiols to chemisorb to gold surfaces [22], the mixture of MPEO-SH and MPEO disulfide was used as such for the preparation of gold colloids.

In order to test the efficiency of this MPEO mixture for stabilizing nanoparticles suspensions by chemisorbing onto gold, nanoparticles were first prepared by conventional $NaBH_4$ reduction of $HAuCl_4$ in the presence of the MPEO stabilizer in water [23].

For the chemical reduction of gold, a classical 1:3 molar ratio of gold salt to stabilizers (a disulfide being considered as equivalent to two thiols) has been dissolved in water. Upon addition of an excess of $NaBH_4$ as reducing agent, gold nanoparticles were formed very rapidly, in agreement with the scientific literature that reports time as short as 20s for a conventional nucleation and growth mechanism [24]. These nanoparticles have been observed by TEM. Fig. 3a shows spherical nanoparticles with a small average size diameter of 5 ± 2 nm and no particles aggregation was observed.

The efficiency of this mixture of MPEO to stabilize gold nanoparticles being checked, this polymer mixture has been added to the electrochemical bath (ratio Au^{3+}:MPEO = 1:~2) for the sonoelectrochemical preparation of gold nanoparticles. Polarisation curves, showing the dependence of the intensity of the reduction current as a function of the imposed potential for the gold/polymer solution, were first recorded in order to determine the value of the cathodic potential pulses to be used for sonoelectrochemical preparation of nanogold. In the absence of macroligands, gold deposition started at +100 mV/NHE and increased drastically at potentials more cathodic than -500 mV/NHE (Fig. 4 ■). In the presence of the MPEO mixture, the curve overlaid the one recorded without ligand meaning that the addition of the polymer to the solution does not modify the reduction potential of the gold salt and that commonly used conditions for the deposition of gold can be applied.

By applying repeatedly, (i) a potential in the range of -850 mV/ NHE to -1300 mV/NHE during T_{ON} ranging from 10 to 50 ms, (ii) an ultrasonic wave of 27 kHz during $T_{US} = 100$ ms and (iii) a rest time, T_{OFF} ranging from 100 ms to 200 ms during 5 h to the MPEO/Au salt solution, gold nanoparticles are formed. However, the nanoparticles aggregate and sediment in the electrochemical bath similarly as presented in Fig. 1a. In contrast to the chemical synthesis, the MPEO mixture (thiol and disulfide) appears to be not efficient for the stabilization of the gold particles produced by the sonoelectrochemical way. One possible explanation for this observation is the significant hydrolysis of the ester bond that links the thiol to the PEO chain during the 5 h of experiment. Indeed, the solution pH is very acidic in the electrochemical bath and the temperature increases significantly upon sonication. As a consequence, MPEO becomes unable to bind to the gold surface and only the mercaptoacetic acid, resulting of the hydrolysis remains available for adsorption to gold surface. As far as the carboxylic acid is kept in strong acidic conditions, it is not ionized and becomes a poor stabilizer.

This problem has been overcome by using two different strategies. In a first approach, a second, commercially available polymer highly prone for chemisorption with gold has been added to the medium. In the second approach, a novel more stable PEO disulfide has been prepared by anionic polymerization (Scheme 2b).

Fig. 3. *Transmission electron micrographs of prepared gold nanoparticles (NPs) by: (a) chemical route stabilized by MPEO (gold diameter 5 ± 2 nm), (b) sonoelectrochemical route stabilized by MPEO/PVPr mixture (E_{0N} = -1300 mV, T_{ON} = 20 ms) (gold diameter 20 ± 4 nm), (c) chemical route stabilized by PEO disulfide (gold diameter 5 ± 0.5 nm), (d) sonoelectrochemical route stabilized by PEO disulfide (E_{ON} = -1300mV, T_{ON} = 20 ms) (gold diameter 35 ± 4 nm) and (e) sonoelectrochemical route stabilized by PEO disulfide (E_{ON} = -1300 mV, T_{ON} = 10 ms) (gold diameter 5 ± 1 nm).*
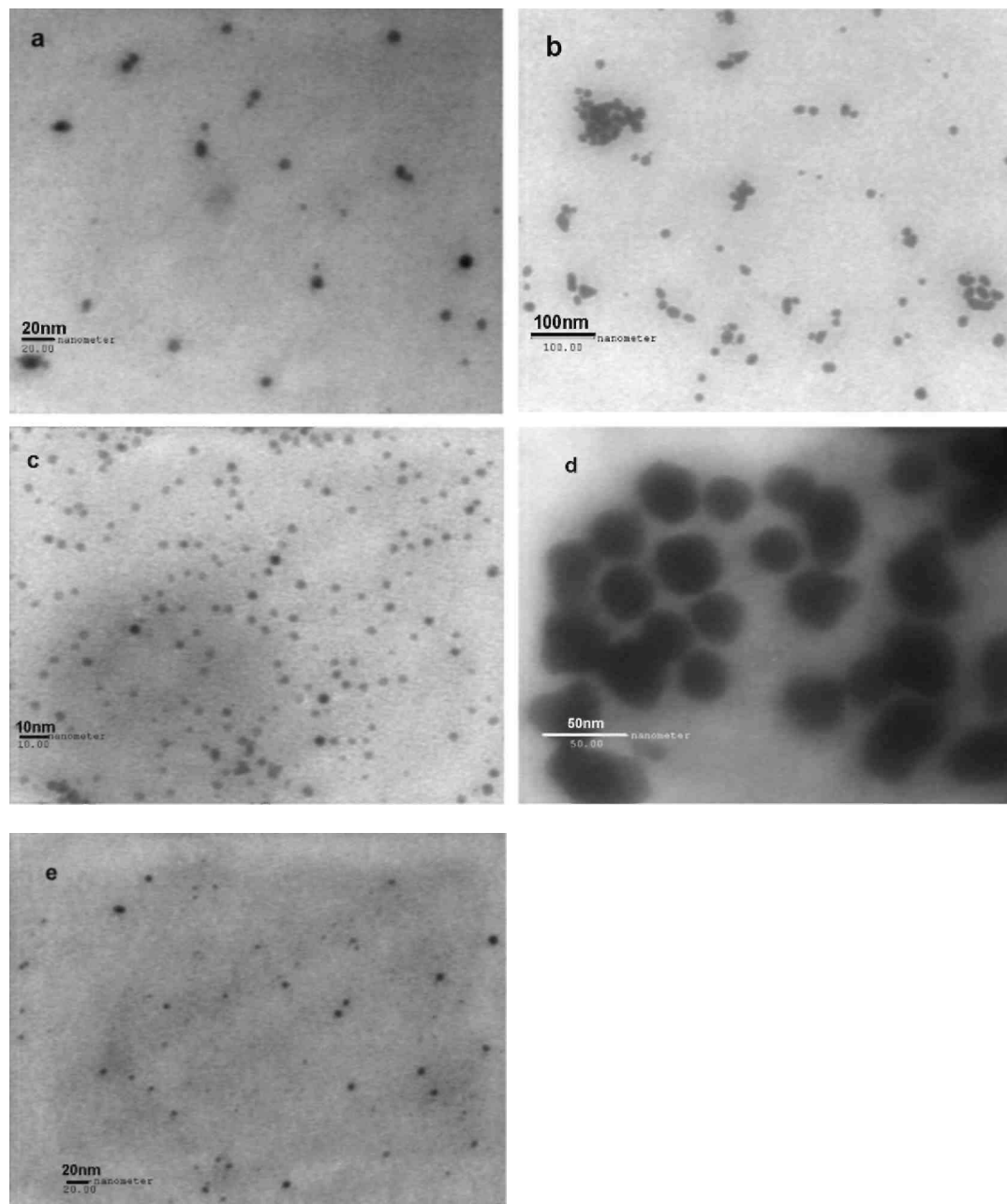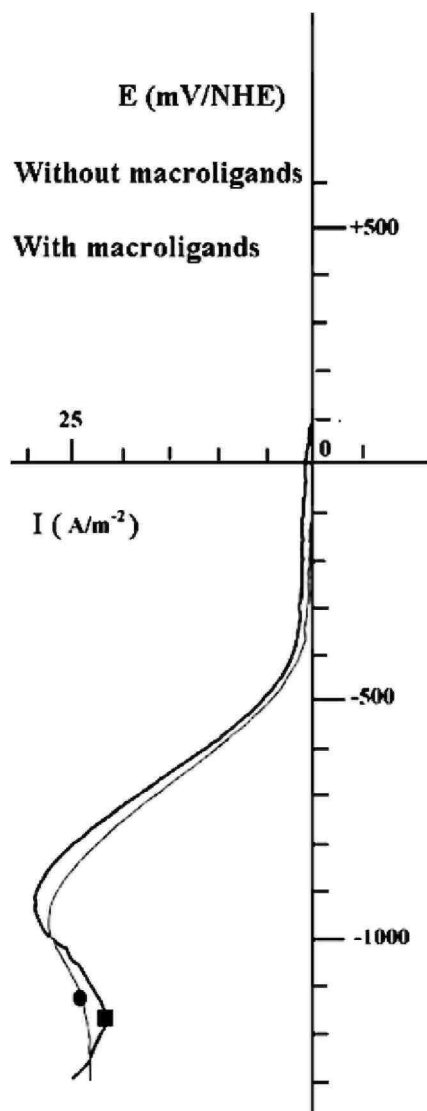
Fig. 4. *Polarization curves recorded on Ti in HAuCl₄ solution. (■): without macroligand; (●): with a mixture of PEO-SH and PVPr.*

## 3.1. First strategy: stabilization of gold by a MPEO/PVPr polymer mixture

PVPr has been extensively used to stabilize colloidal particles of different materials in water and many non-aqueous solvents [25]. Specifically, PVPr protects effectively the surface of gold nanoparticles improving their stability [26]. This commercially available polymer (M_n = 30,000 g/mol) was thus added to the electrochemical bath together with MPEO mixture in a molar ratio Au^{3+}:M-PEO:PVPr = 1:~2:0.2.

Polarization curve was recorded for the aqueous solution of the MPEO/PVPr and gold salt. In this case, the nucleation was slightly delayed, about 100 mV/NHE (Fig. 4 ●). Again, the addition of polymer does not affect too much the gold deposition conditions, the slight shift towards lower potential being in line with stronger interaction of Au with PVPr able to complex already the gold salt. Nevertheless, the deposition potential could still be selected in the -850 to -1300 mV/NHE range.

Applying the sonoelectrochemical conditions in the range described above (particularly E_{ON} = -850 mV/ENH with T_{ON} = 50 ms potential pulses) in the presence of MPEO/PVPr mixture, a stable violet suspension was obtained at the end of the process without sedimentation (Fig. 1b). Disc Centrifuge CPS allowed to determine the size and size distribution of the sample and showed a narrow size distribution centered on 12 nm together with a few larger particles (~30 nm) (Fig. 5a). By using sonoelectrochemistry, it is not rare to get a small population of

nanoparticles of higher size (about double size) which corresponds to nuclei that remained attached to the electrode after the first sonication. Then during the next application of the potential, these nuclei are growing again to reach approximately the double size as before. This can be avoided by increasing the intensity of the ultrasonic wave. As far as size distribution is concerned, comparable results are obtained for the chemical and sonoelectrochemical strategies respectively in the presence of MPEO and a mixture of MPEO and PVPr as evidenced by Fig. 5a and b.

Fig. 5. *Size distribution determined by Disc Centrifuge CPS for (a) electrochemically prepared gold nanoparticles stabilized by a MPEO/PVPr mixture (E_{ON} = -850 mV/ NHE, T_{ON} = 50 ms, T_{OFF}= 100 ms) (b) chemically prepared gold nanoparticles stabilized by MPEO.*
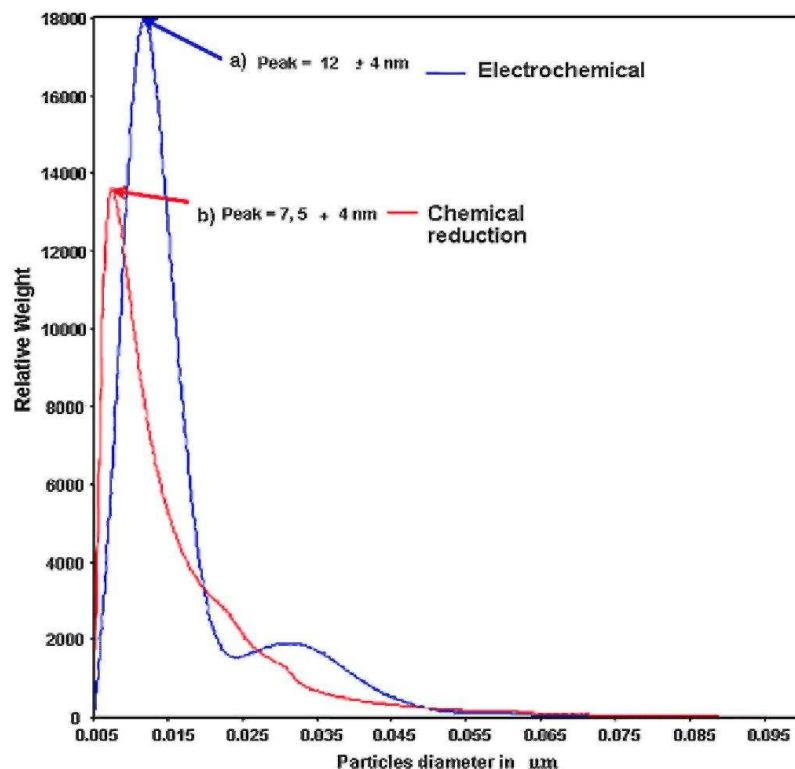
By using the MPEO/PVPr mixture, i.e. commercially available or easily transformed polymers, good quality suspensions were thus successfully obtained for the first time by the sonoelectrochemical process, which makes now the method highly competitive with the more conventional ones.

One advantage of the sonoelectrochemistry is the variety of parameters that are controllable in order to tune the nanoparticles characteristics. By tuning the value of the applied potential (E_{ON}) or its duration (T_{ON}). the amount of reduced gold ions should be controlled and so the size of the grown nuclei on the cathode and consequently, the nanoparticle size of the colloid.

For T_{ON} = 50 ms and E_{ON} = -850 mV (Table 1, entry 1), the particles are small (12 nm) due to low cathodic potential. A more cathodic potential (E_{ON} = -1300 mV/ENH) of shorter potential pulse duration (T_{ON} = 20 ms) (Table 1, entry 2) was then applied in order to modulate the particles size. Gold nanoparticles of increased size (20 nm) are observed by TEM (Fig. 3b). In this case, using a more cathodic deposition potential leads to a faster gold deposition on the surface of the working electrode and thus to the formation of bigger gold nuclei. Let's mention that for this example a shorter deposition time (T_{ON} = 20 ms) was used which opens the possibility to increase further the nanoparticles size by increasing the T_{ON}.

In the presence of the MPEO and PVPr mixture, stable suspensions of gold nanoparticles with a diameter up to 50 nm have been successfully prepared (Fig. lb).

3.2. Second strategy: stabilization of gold by PEO disulfide stable to hydrolysis

In order to avoid the use of PVPr, PEO disulfide - which does not contain hydrolyzable ester bond, obtained by anionic polymerization [27] - was used as a stabilizing ligand in the electrochemical bath (Scheme 2b).

Fig. 3a and c shows that using this PEO disulfide polymer instead of MPEO for the chemical way of preparation in the same conditions as described above leads to similar gold colloids: 5 nm gold nanoparticles are formed by $NaBH_4$ reduction.

By using this PEO disulfide for the sonoelectrochemical way, and applying the same conditions as described above (i.e. Au^{3+}:PEO disulfide = 1:1.5, E_{ON} = -1300 mV/ENH, T_{ON} = 20 ms), a very stable suspension of particles with a mean diameter of 35 nm (Fig. 3d) is obtained. The lower complexation ability of PEO as compared to PVPr (as observed in Fig. 4) could explain the increase in the nanoparticles size (from 20 to 35 nm) when MPEO/PVPr mixture is replaced by PEO disulfide. Sonoelectrochemistry allowed the average diameter to be tuned from 5 to 35 nm when T_{ON} is increased from 10 (Table 1, entry 3; Fig. 3e) when to 20 ms (Table 1, entry 4; Fig. 3d). However, precipitation of the nanoparticles was observed after few days when T_{ON} was 30 ms or higher (Table 1, entry 5). This might be due to the low molecular weight of the ligand.

Although the chemical approach allows very small particles to be formed (less than 10 nm of diameter), it is not effective in producing larger particles. In contrast, the diameter of the particles formed by sonoelectrochemistry can be easily tuned in a large range (5-50 nm at least) by adjusting e.g. the deposition time T_{ON}. Sonoelectrochemistry is thus a flexible and well-suited technique for the production of gold nanoparticles, because size and shape may be also controlled by other experimental parameters including pulsed electrical current density, concentration of the electrolyte, pulsed ultrasonic vibration frequency and amplitude, and duration of T_{ON} and T_{OFF} as already reported elsewhere [28].

3.3. Properties of the PEO-coated gold nanoparticles

The optical properties of the aqueous gold nanosuspensions were analyzed by UV-vis spectroscopy. Fig. 6 compares the absorption spectra for the nanoparticles prepared by the chemical and sonoelectrochemical techniques. A typical strong absorption was observed in the visible region for both samples, which results from the interaction of light with the electrons plasmon of the nanosized gold particles. Moreover, the size of the nanoparticles and the quality of the stabilization by the ligands at their surface play a critical role in the optical properties. The maximum absorption (surface plasmon) was observed at approximately 520 nm (Fig. 6a) for the chemically prepared nanoparticles (5 nm diameter). It was shifted to higher wavelength (550 nm) for the larger nanoparticles (12 nm diameter) prepared by sonoelectrochemistry (Fig. 6b). The maximum absorption was slightly broadened probably due to the bimodal size distribution of the sample (Fig. 5b).

Fig. 6. *UV-visible spectrum of gold nanosuspensions, (a) chemically prepared Au NPs stabilized by MPEO, (b) electrochemically prepared Au NPs stabilized by MPEO/PVPr mixture (E_{ON} = -850 mV/NHE, T_{ON} = 50 ms, T_{OFF} = 100 ms).*
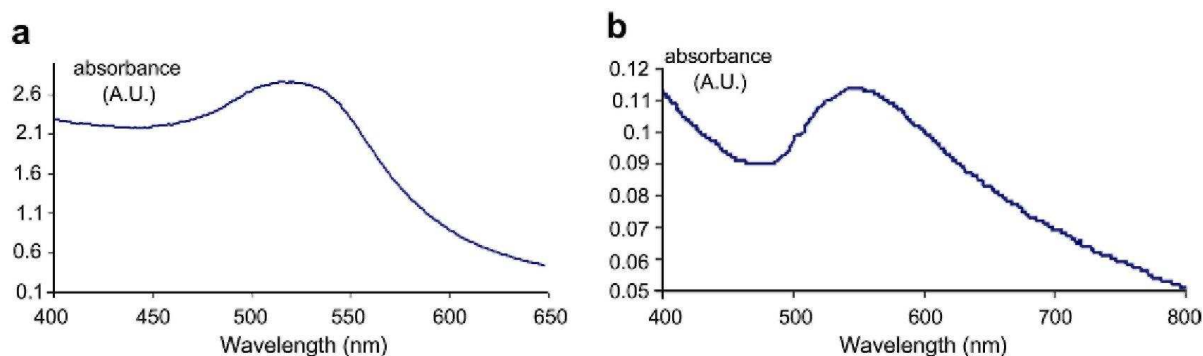
Table 1. *Summary of synthetic conditions and gold nanoparticles size obtained by both strategies*

Entry	Ligand	E (mV/ENH)	T_{ON} (ms)	Size (nm)
1	MPEO/PVPr	-850	50	12 (30)[c,a]
2	MPEO/PVPr	-1300	20	20[b]
3	PEO disulfide	-1300	10	5[b]
4	PEO disulfide	-1300	20	35[b]
5	PEO disulfide	-1300	30	Precipitation

[a] Determined by CPS. [b] Determined by TEM. [c] Bimodal size distribution.

4. Conclusions

Two strategies have been found successful to prepare stable suspensions of gold nanoparticles by sonoelectrochemistry in water. The first one, based on a mixture of the commercially available and easily functionalized products, poly(vinylpyrrolidone) and α-methoxy-ω-mercapto-poly(ethylene oxide) proved to be effective stabilizers of gold nanoparticles in a 10-50 nm diameter range. The second strategy uses a unique PEO disulfide polymer that has to be synthesized by anionic polymerization. This unique ligand has been found efficient to stabilize particles up to 35 nm. The optical properties of these electrochemically prepared colloids are comparable to the one of similar colloids prepared by the traditional chemical method using $NaBH_4$. It thus appears that electrochemical reduction of a metal salt in water complements very well the chemical method. Actually it bridges the gap between the chemical techniques producing very small nanoparticles (diameter smaller than 10 nm) and the classical techniques for the production of micro and sub-micro powders. Last but not least this technique is inexpensive (no need of high cost reducing agent) and flexible being well-suited to be extended to a large variety of metals (including non noble metals) and alloys.

Acknowledgements

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