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ARTICLE

Gold Nucleation Inhibition by Halide Ions: a Basis for a Seed-Mediated Approach[†]

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In the present work we examine the effect on gold nucleation of halide ions, a typical synthetic variable in the wet-chemical production of gold nanostructures. It was found that the gold homogeneous nucleation by chemical reduction of aqueous gold ions is kinetically quenched by the rise in the halide ions concentration and this effect is stronger as the Au-halide complex stability increases. The nucleation quenching is not exclusively related to a specific reducing agent but appears to be a more general behavior and is affected by the pH of the media. While no nucleation is observed, Au(I) metastable species coexist together with the reducer constituting metastable solutions. It is demonstrated that the nucleation inhibition by halide ions can be employed as a basis for a seed-mediated approach to produce gold nanostructures. The metastable solutions are proved to function as growth baths where Au(I) reduction is triggered on the surface of previously synthesized gold nanoparticles driving their growth in absence of secondary nucleation. It is also shown how, with this approach, the synthesis conditions can be rationally designed in order to obtain gold nanoparticles with the desired properties in a controlled and reproducible fashion.

Introduction

Synthesis of noble metal nanoparticles (NPs) is an active research area; thousands of new synthetic protocols are reported every year. There have been great advances in producing metal NPs with several morphological and compositional features with novel properties and applications.[1-4] Nevertheless, the physicochemical processes so as the mechanisms involved in NPs formation are still scarcely known. Upon nowadays is consensual that two main processes in NPs formation can be differentiated: nucleation and growth. In the LaMer´s mechanism, proposed for sulphur sols formation,[5] self-nucleation (homogeneous nucleation) is claimed to be very fast and the growth, diffusion-controlled. Beyond this often quoted mechanism, in metallic systems, nucleation has been shown to be continuous[6-13] and growth, autocatalytic[6-13] and aggregative.[14] Furthermore, other processes have been identified such as Ostwald ripening,[15,16] digestive ripening[17] and oxidative etching.[18] All these factors may contribute to the size, shape and stability of the NPs. In

a typical synthesis, nevertheless, since many of these processes take place simultaneously, it is difficult to unravel the influence of each one. Likewise, there is not clear how the diverse synthetic variables contribute to each one of these processes. In order to planify a synthesis, however, it is consensual that one of the keys in controlling the size dispersion is to "separate" in time the nucleation and growth stages.[19] The search for synthetic conditions to accomplish such separation is not trivial and, in addition, other requirements may have to be consider, *e.g.*, suspension media, long-term stability, functionalization, etc. In the synthesis of very small NPs, for example, the use of strong reducing agents such as borohydride ion and the use of stabilizing agents that are tightly bind to the NPs, as the case of thiols over gold surfaces has been proved to be effective to favour nucleation over growth.[20] Nevertheless, for many applications such as catalysis or sensing, the presence strongly bind stabilizing agents represents a serious disadvantage. Another example where separation of nucleation and growth by has been successfully achieved by applying temperature ramps is the Hot-

injection method.[21] Much more extensively employed, seed-mediated approaches have accomplished this separation by using different chemical environments.[22-24] Particularly, the quaternary ammonium-based seed-mediated growth method first reported by Murphy's group[25-27] has been successfully used to synthesize anisotropic gold NPs (AuNPs) of various shapes such as nanorods,[26-28] nanocubes,[29] nanostars,[29] bypiramids,[30] nanoprisms,[31] dumbbell-like,[32] jack-shaped,[33] etc. This synthesis consists in the seeding of small AuNPs (seeds) into reactive solutions, where AuNPs grow in absence of homogeneous nucleation. These reactive solutions, usually called growth baths, contain the Au(III) precursor, a quaternary ammonium, typically hexadecyltrimethylammonium bromide (CTAB), and ascorbic acid (AA) as the reducing agent. For this case the absence of homogeneous nucleation during the AuNPs growth is attributed to the weak nature of the reducing agent employed (ascorbic acid).[34] In this synthesis, as in many other synthetic procedures to obtain gold nanostructures, halide ions are present. Generally, the investigations about the effect of the halide ions are mainly focused on determining their role in the anisotropic growth.[35-37]
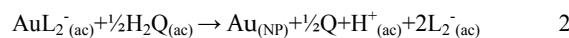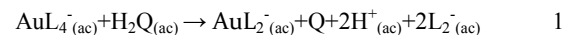
In the present work, we study the chemistry of aqueous halide-gold systems and its consequences in gold nucleation by chemical reduction of gold ions. The effect of experimental variables such as, the reducing agent nature and the pH of the media are explored. Owing to the rich spectroscopic features that Au(III) and Au(0) species display, the studies were carried out mainly by employing UV-Vis spectroscopy. The implications of the present investigations in the quaternary ammonium-based seed-mediated growth method are discussed. Additionally, it is shown how the knowledge developed in this work constitutes a basis for a seed-mediated approach for gold nanostructures. It is exemplified how, with the basic recipe of Au(III) precursor, halide ions and a mild reducing agent, many seed-mediated methods can be build up by, for example, varying the reducing agent nature or the seed nature or by adding other co-reactants such as polymers or amphiphilic molecules.

Results and discussion

Halide ions effect

When bromide ions are added in to a solution of HAuCl$_4$, an increase in the yellow colour intensity is observed. This phenomena is the result of the exchange of the hydroxyl and chloride ions by bromide ions in the coordination sphere of Au(III). The spectra sequence for increasing concentration of bromide ions is displayed in Figure 1-a. As the bromide ion concentration rises up, the absorption increases in the 350 to 650 nm region as the ligand exchange process takes place.[38] The absorption growth above 400 nm is the responsible for the increase in the yellow colour intensity observed. No mayor differences are noticed in the spectroscopic behaviour for bromide ions concentrations higher than 5 mM (spectra are overlap), indicating that the ligand exchange reaction to give AuBr$_4^-$ is complete. This complex exhibits a strong absorption peak at 382 nm, followed by a shoulder and a tail that quickly decreases up to 600 nm to reach very small values along the rest of the spectral range. When hydroquinone (H$_2$Q) is added into these solutions drastic spectroscopic changes are observed (Figure 1-b). The absence of the characteristic Au(III) complexes spectral features for all concentrations, indicates that the reduction reaction took place. However, the resulting spectral profiles show a strong dependence on the bromide ion content. At low bromide ions concentrations (Figure 1 black and red lines) the reactive solutions

have extinction peaks in between 700 nm and 800 nm. These features are associated with the surface plasmon resonance (SPR) of large AuNPs (diameter ~ 150 nm)[39] produced by the reduction of Au(III) according to reactions 1, 2 and/or 3:

$$AuL_4^-{}_{(ac)}+H_2Q_{(ac)} \rightarrow AuL_2^-{}_{(ac)}+Q+2H^+{}_{(ac)}+2L_2^-{}_{(ac)} \qquad 1$$

$$AuL_2^-{}_{(ac)}+\tfrac{1}{2}H_2Q_{(ac)} \rightarrow Au_{(NP)}+\tfrac{1}{2}Q+H^+{}_{(ac)}+2L_2^-{}_{(ac)} \qquad 2$$

$$3AuL_2^-{}_{(ac)} \rightarrow AuL_4^-{}_{(ac)}+2Au_{(NP)}+2L_2^-{}_{(ac)} \qquad 3$$

where L$^-$ represents the complexing agent of Au(III) and Au(I) species, Br$^-$ or OH$^-$. At intermediate bromide ions concentrations (blue line), although no surface plasmon resonance (SPR) peak is observed, a non-zero extinction value is obtained along the whole visible range due to the dispersion of large AuNPs (diameter > 500 nm). It should be pointed out that although AuNPs are also formed in this case, they are larger than those produced at lower bromide ions content. The presence of larger AuNPs is an indication that whether the growth reaction goes faster or that nucleation is quenched under these conditions. For bromide concentrations equal or higher than 5 mM (orange, green and pink lines), very small extinction values are observed above 500 nm (extinction being lower than 0.01). These low extinction values indicate that if Au(0) is produced, in the form of AuNPs or as microparticles, it is generated in very small amounts despite that the concentration of H$_2$Q in enough to completely reduce all the Au(III) to Au(0). As previously mentioned, the absence of the AuBr$_4^-$ main peak (382 nm) indicates that the Au(III) has been reduced, hence if is not reduced to Au(0) then is principally reduced to Au(I). This is consistent with the spectroscopic evidence since Au(I) species have a d^{10} electronic configuration and, consequently, they do not absorb in the visible region.
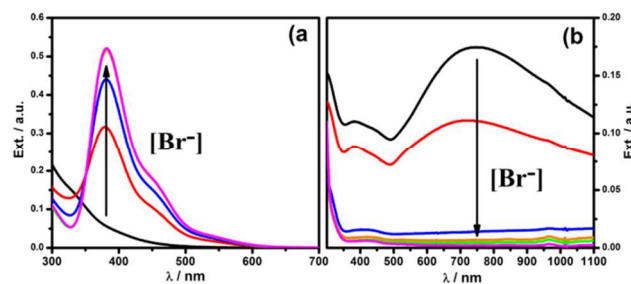

Figure 1. Extinction spectra of 0.1 mM HAuCl$_4$ reactive solutions with increasing bromide ion concentration: (black) 0.01 mM, (red) 0.05 mM, (blue) 1 mM, (orange) 5 mM, (green) 7.5 mM, (pink) 50 mM; (a) before and (b) 15 min after H$_2$Q addition ([H$_2$Q]final=0.15 mM, pH=6.5).

The presence of Au(I) in the reactive solutions with high concentrations of bromide ions was further confirmed by Raman analysis. In Figure 2 are displayed the Raman spectrum of a AuBr$_4^-$ solution (red line) and the Raman spectrum from a reactive solution with high bromide ion concentration (black line). The AuBr$_4^-$ is identified by two peaks located at 197 cm^{-1} and 212 cm^{-1}.[40-43] In the reactive solution, the AuBr$_4^-$ peaks are not present, as expected from UV-Vis spectroscopic analysis, but a peak at 210 cm^{-1} is observed which is associated to the presence of AuBr$_2^-$.[43,44] The formation of Au(I) and the absence of Au(0) species for high bromide ions concentrations indicates that while reaction 1 takes place, the nucleation of AuNPs by reactions 2 and/or 3 is somehow inhibited under this conditions. The overall trend indicates that as the bromide

ion concentration grows, the Au(0) nucleation is quenched leading to the formation of larger AuNPs for intermediate concentrations and to the formation of Au(I) for high concentrations.
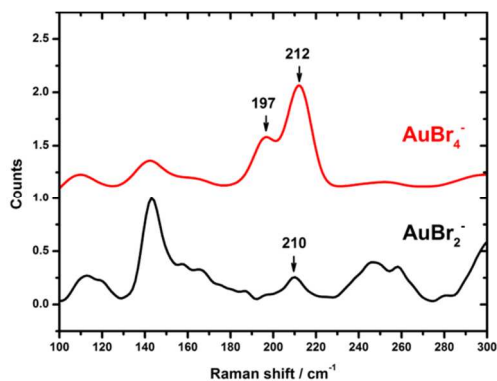

Figure 2. Raman spectra of $AuBr_4^-$ solution (red line) and of the $AuBr_2^-$ extracted from a reactive solution formed by 0.1 mM $HAuCl_4$, 50 mM KBr and 0.15 mM H_2Q (black line).

The 50 mM KBr reactive solution does not show spectral evidence of Au(0) nucleation over a period of 165 days but, a year after, the reactive solution exhibit gold macroscopic crystals (data not shown). Furthermore, the Nernst potential calculated for the Au(I) to Au(0) reduction reaction 2, in the conditions of the reactive solution, predicts spontaneous Au(0) formation ($\Delta E = 0.52$ V). It is clear that, Au(0) formation in such conditions is thermodynamically favored, so the absence of AuNPs at relatively short times is due to the kinetic inhibition of the nucleation process. In this context the solutions are called metastables.

A similar behavior to that observed with bromide ions is obtained for reactive solutions with variable concentrations of chloride ions and iodide ions (see Figures S1 and S2, Supporting Information). Furthermore, the halide concentration necessary to obtain metastability, in similar conditions ($HAuCl_4$ 0.1 mM and H_2Q 0.15 mM), follows the order $[I^-]<[Br^-]<[Cl^-]$ with values of 0,5 mM, 5 mM and 50 mM respectively. Interestingly, the more stable the AuX_2^- complex is (X= Cl, Br, I), the lower the halide ion concentration needed to attain metastability is. The formation of Au(I) metastable species in presence of iodide ions has also been proposed in similar conditions to the ones studied here.[45] It should be mentioned that when iodide ions are added to the Au(III) solution, along with the ligand exchange reaction, triiodide ion is also formed by iodide ion oxidation caused by the Au(III) species; this reaction is observed in our experiments and has already been reported.[38,45] Nevertheless with the hydroquinone addition, the triiodide ion return to the reduced iodide ion form, and thus, the reactive solutions composed by different halide ions are comparable.

Temperature effect

As nucleation inhibition is kinetically controlled, is interesting to explore how temperature affects the metastability in a reactive solution. For this, a reactive solution containing 50 mM of KBr was prepared at 98 °C. Under these conditions nucleation inhibition is not observed (see Figure S3, supporting information) since gold microparticles are formed. Reactive solutions of identical composition prepared at room temperature display metastability for months (see previous section). This indicates that the temperature accelerates the nucleation diminishing the metastability period and further confirms that nucleation inhibition by halide ions is a kinetically controlled phenomenon.

Solution pH effect

Since hydroxyl ion is also a ligand for Au(III), the effect of halide ions cannot be regarded separately from solution pH. Figure 3 exhibits the spectral profiles of Au(III) complexes formed in 50 mM KBr solutions at different pH values (solid lines). $AuBr_4^-$ spectral profile at pH 6.5 (Figure 3, solid black line) presents the characteristic features already described for Figure 1-a. As the pH increases, extinction profiles with decreasing intensity in the 300-500 nm interval are observed (red and green solid lines), where the peak in 382 is absent. This unlike spectroscopic behavior corresponds to the presence of different relative concentrations of Au(III) complexes: $AuBr_4^-$, $AuBr_3(OH)^-$, $AuBr_2(OH)_2^-$, $AuBr(OH)_3^-$ and $Au(OH)_4^-$.[38] At low pH values (pH = 6.5 or lower) $AuBr_4^-$ predominates, however, as pH increases, bromide ions are partially replaced by hydroxyl ions in the coordination sphere of gold giving as a result the vanishing of the 382 peak. When hydroquinone is added into these solutions, notorious differences are observed in the spectroscopic behavior (Figure 3 dashed lines). At low pH values, where $AuBr_4^-$ predominates (black line), partial reduction of Au(III) to Au(I) is observed and thus metastability is obtained as was already discussed for Figure 1. At pH values higher than 6.5, irrespective of the high bromide ions concentration, the solutions show a non-cero extinction value in the whole visible range associated to the dispersion of large AuNPs.
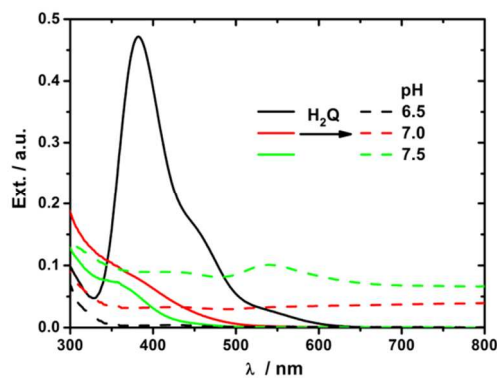

Figure 3. Extinction profiles for 0.1 mM $HAuCl_4$, 50 mM KBr solutions at different pH values: (black) 6.5, (red) 7, and (green) 7.5, before (solid lines) and 15 min after (dashed lines) H_2Q addition. Final H_2Q concentration: 0.15 mM.

Although the Gibbs free energy is negative for Au(0) formation in the three cases evaluated here, the rise of hydroxyl concentration in the media clearly accelerates the nucleation process diminishing the metastability. It is important to notice that the effect of raising the pH is similar to the effect of lowering the halide ions concentration; in both cases the metastability period is shortened. It would appear that, the presence of hydroxyl ions in the coordination sphere of Au(I) accelerates the nucleation process, although in order to prove such hypothesis a deeper insight in nucleation mechanisms beyond the classical theory is needed.

Reducing agent effect

In order to assess if the AuNPs nucleation quenching with increasing halide concentration is exclusive to H_2Q, experiments under similar conditions were performed with ascorbic acid (AA). This reducing agent was chosen because it is the most employed in the seed-mediated growth method developed by Murphy´s group,[25-]

[27] where the growth baths have similar conditions of the explored in this work (high halide concentrations), although, hydroquinone has been recently used to produce gold nanorods by this method.[46] Figure 4 shows the extinction spectra of reactive solutions prepared with AA and different halide ions content. In absence of halide ions (black line) the characteristic SPR peak around 520 nm of AuNPs is observed, indicating that AA is a reducer strong enough to nucleate AuNPs. When reactive solutions contain high concentrations of halide ions (green and red lines), the absence of spectral features associated with Au(III) and Au(0) species, indicates the nucleation inhibition of AuNPs and the formation of Au(I) species. Therefore, the nucleation quenching by halide ions is a more general behaviour instead of a particular feature associated with a specific reducing agent. In this context, nucleation quenching should be considered always when AuNPs are formed by chemical reduction in presence of halide ions.
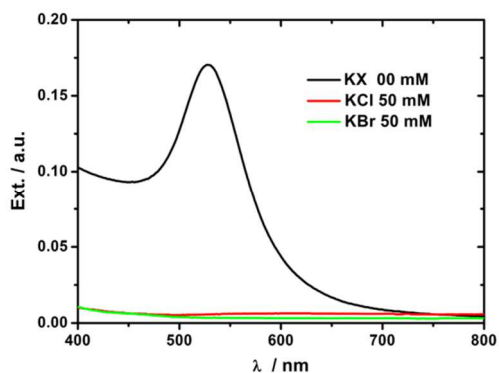

Figure 4. UV-Vis spectra for reactive solutions of 0.1 mM HAuCl$_4$ and 1 mM AA after 15 min of prepared in absence of halide ions (black line) and in the presence of: 50 mM NaCl (red line), and 50 mM KBr (green line).

In the particular case of the quaternary ammonium-based seed-mediated method, the growth baths have high halide ions concentrations (typically around 0.1 M) coming from the quaternary ammonium salt employed (CTAB, CTAC, etc.). Hence, is most likely that, the absence of self-nucleation during AuNPs growth in this method is a result of the nucleation inhibition by halide ions. In order to prove this point, a simple test was performed where the halide ions in the hexadecytrimethylammonium salt are replaced by nitrate ions (see Figure S4, Supporting Information). In this test, the reactive solution was identical in composition to a typical growth bath in the quaternary ammonium-based seed-mediated method with the exception that halide ions were not present. In this reactive solution, no nucleation inhibition was obtained whatsoever, unraveling that halide ions are essential to attain self-nucleation inhibition in this method. From these experiments a new role of the halide ions is identified in the quaternary ammonium-based seed-mediated growth method. As stated in the introduction, there are plenty of studies that show that halide ions play an important role in the anisotropic growth of AuNPs.[36] We have now also identified that halide ions are responsible for preventing self-nucleation during AuNPs growth in this method.

Seed-mediated approach

The kinetic inhibition of the nucleation in reactive solutions with high halide concentrations constitutes the basis for a seed-mediated approach. In these metastable solutions, AuNPs homogeneous

nucleation does not occur, but the Au(I) to Au(0) reduction (reactions 2 and/or 3) may be activated by applying a perturbation. This perturbation may be the surface of previously synthesized AuNPs (seeds) which catalyze Au(0) formation giving as a result AuNPs growth as represented in the scheme of Figure 5-a. When used to grow AuNPs, the metastable solutions are referred as growth baths. This section has the objective to illustrate this last point on how this basic recipe for metastability, can be applied to grow AuNPs.
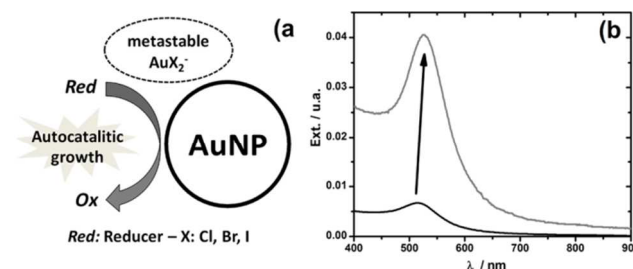

Figure 5. (a) Scheme of AuNP growth form metastable Au(I) solutions. (b) Final extinction spectra of: Black line: dilution 1/100 of the seed solution. Gray line: AuNPs produced in the first step of the seeding procedure in a bath composed by 0.01 mM HAuCl$_4$, 0.1 mM KI and 0.03 mM H$_2$Q.

The AuNPs employed as initial seeds have spherical shape with a mean diameter of 7 nm and a narrow size distribution (14 % S.D.). The synthesis of these gold seeds is highly reproducible and the AuNPs are stable for months. Figure 5-b shows, in black line, the spectrum of the seeds' solution with the same dilution as they have after their addition in a growth bath; this can be taken as a reference spectrum at zero-time reaction after seeding. In gray line it is shown the final spectrum after the first step seeding into a growth bath formed by iodide ions; no spectral changes are detected whatsoever after three minutes of the seeding. There are two main features observed in the spectral evolution: (i) the increase in the extinction values and (ii) the red-shift in the SPR maximum from 514 nm to c.a. 525 nm. Both characteristics are consistent with AuNPs growth, the only process capable of occurring given that the nucleation is inhibited. Similar spectroscopic characteristics are observed after every seeding process indicating that growth process took place in each step. The corresponding TEM images for the seeds and the AuNPs grown in the first and second steps of the seeding procedure with iodide ion growth baths are shown in Figure 6 a to c. TEM images reveal that the AuNPs increase in size after each seeding step; this feature is more clearly shown in the size distributions represented in Figure 6-d. The AuNPs grown have a nearly spherical shape with sizes of (16 ± 3) nm and (37 ± 4) nm in diameter for the first and second steps of the seeding procedure respectively. The absence of much smaller AuNPs confirms that the continuous nucleation process is absent. TEM results are in complete agreement with the main conclusions drawn from the spectroscopic analysis. It is noticeable that the size dispersion does not show a trend to increase with the size of the grown AuNPs; values of 14 %, 18 % and 11% were obtained for the seeds and the 16 nm and 36 nm AuNPs respectively. This indicates a control over the growth process and, it is also evidence that nucleation reaction is inhibited. As shown in Figure 6, the control over AuNPs size can be achieved by setting the [Au(I)]/[seeds] ratio used in the seeding as well as the seed size. These experiments demonstrate that either reactions 2 and/or 3 are catalyzed in the AuNPs' surface and constitute one of the many evidences that autocatalytic growth is present in metal NPs formation. Although no appreciable amount of Au(III) were detected

during AuNPs growth, Au(I) disproportionation by reaction 3 is considered since has been informed to occur in conditions similar to those explored here.[45] Furthermore, other reactions may be also taking place during AuNPs growth such as oxidative etching of the AuNPs by the Au(III) coming from the disproportionation reaction and the reduction of Au(I) by the iodide ions.
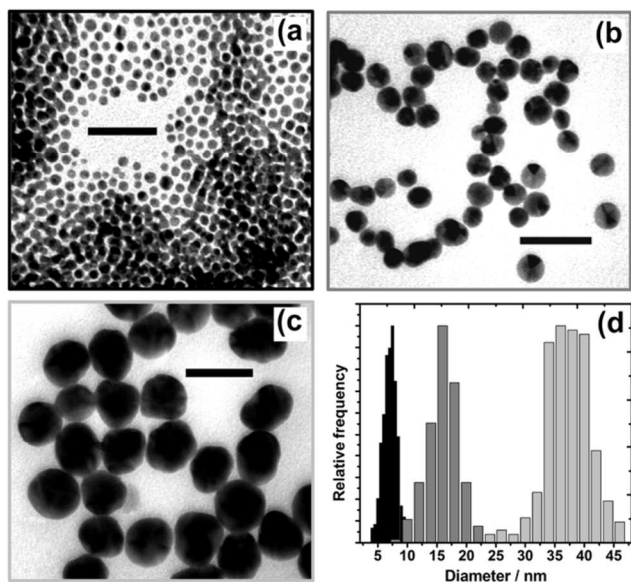

Figure 6. (a), (b) and (c) TEM images of the Au seeds and the AuNPs produced in the first and in the second steps of the seeding procedure respectively, in a bath composed by 0.01 mM HAuCl$_4$, 0.1 mM KI and 0.03 mM H$_2$Q. (d) Size distributions obtained from TEM analysis where the color of the bars is the same as the corresponding AuNPs TEM image frame. Scale bars: 50 nm.

The AuNPs synthesized here offer the great advantage of being only stabilized by halide ions and, consequently, they can be used in many applications without the need of further purification. Also they can be easily functionalized with a broad variety of chemical compounds of interest. This synthetic procedure is also simple, of low cost and environmentally friendly. This basic synthetic scheme of gold precursor (Au(III)), high halide ion concentration and a mild reducing agent can be modified according to the needs: shape inductors such as silver can be added in order to obtain anisotropic AuNPs, as in the case of the quaternary ammonium-based seed-mediated growth;[27,28,30] the reducing agent can be varied altering the Au(I) reduction rate; organic molecules such as polymers or amphiphilic compounds can be added to increase NPs´ stability among others. For example, although with a different approach than the presented here, the suppression of AuNPs nucleation by iodide ions and its use to grow AuNPs with AA and poly(vinyl pirrolidone) (PVP) had been informed.[47]

In order to stress about the versatility of the seed-mediated approach presented, Figure 7 shows TEM results of AuNPs synthesized using bromide ions growth baths in presence of PVP, a biocompatible polymer which improves AuNPs stabilization. The AuNPs grown in this case have spherical shape with sizes of (21 ± 2) nm and (49 ± 4) nm for the first and second steps of the seeding procedure respectively. Similar to the AuNPs produced with iodide ion growth baths, the size dispersion in both cases does not exceed the 10%, a feature indicative of a remarkable growth control. Furthermore, some of the AuNPs grown in presence of PVP exhibit a considerable lower contrast than the spherical ones of similar size in the TEM photographs. The lower contrast indicates that a small portion of the

AuNPs have plate-like shape. The origin of such anisotropic NPs is hard to identify due to the ongoing discussion about the anisotropic growth, however, it is worth to mention that such plate-like AuNPs have been already identified in aqueous environments in presence of PVP.[48] The obtained anisotropic NPs are predominantly triangles in the first step and hexagons in the second step of the seeding procedure. In both cases they represent approximately 6% of the total. This is a strong suggestion that the AuNPs produced in the second step have grown from the anisotropic AuNPs formed in the first step of the seeding and that no new anisotropic particles are formed in the last step. Along similar lines of thoughts, it would appear that the triangles formed in the first step of the seeding evolved into the hexagons in the second step. A deeper inside into the effect of PVP and other species over the AuNPs anisotropic growth constitute a topic to be developed in the future.
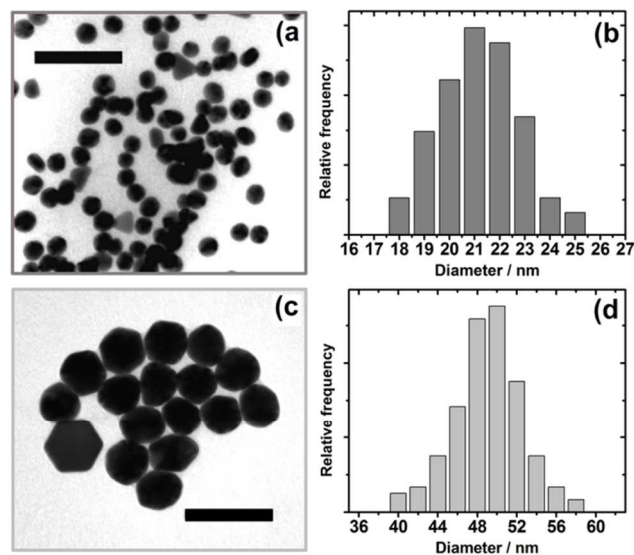

Figure 7. (a) and (c) TEM images of the AuNPs produced in the first and second steps of the seeding procedure respectively, in a bath composed by 0.05 mM HAuCl$_4$, 20 mM KBr, 0.0145% PVP and 0.2 mM H$_2$Q. (b) and (d) Size distributions obtained from TEM analysis where color of the bars is the same as the corresponding AuNPs TEM image frame. Scale bars: 100 nm.

At last, in Figure 8 is shown a comparison between the experimental diameter of the AuNPs with its corresponding dispersion vs. the predicted diameter after AuNPs growth for the four seeding procedures discussed above. The final diameter after the seeding was calculated from (see derivation in the Supporting Information):

$$d_{final} = \sqrt[3]{\frac{6V_m N_A [Au(I)]}{\pi [seeds]} + d_{seed}^3}$$

where V_m is the molar volume of gold, N_A is the Avogadro number and d_{seed} is the seed diameter. The [Au(I)]/[seeds] ratios were calculated from experimental data and seeds diameters extracted from TEM analysis. For this calculation some assumptions have been made: (i) Samples are monodisperse in size, (ii) the AuNPs are perfect spheres, (iii) all gold species are completely reduced to Au(0) in all the synthetic stages and (iv) the AuNPs have the same molar volume as the bulk. Noticeably, the predicted diameters are contained within the size dispersion and the slope between experimental and predicted AuNPs size is near 1. This is a remarkable result considering that the two seeding procedures were

carried out under different conditions, using seeds synthesized in separated events and with different aging time. Furthermore, the excellent accordance between experimental and predicted diameters suggests that the approximations used in the calculation correspond to a good interpretation of the real system. These results demonstrate that the method is highly reproducible and controlled. In addition, they show that the experimental conditions can be rationally planified in order to obtain the desire product which is one of the main goals in Nanosynthesis. It is noteworthy that, although the growth of the AuNPs was performed in steps this is not a mandatory condition; for example, 50 nm AuNPs can be grown in one step from the 7 nm seeds by simply adjusting the [Au(I)]/[seeds] ratio.
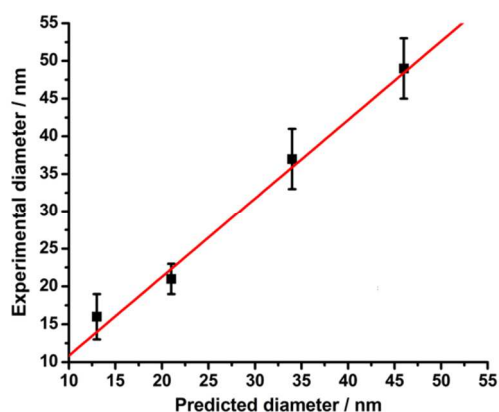

Figure 8. Experimental AuNPs diameter determined by TEM with its corresponding dispersion bars vs. calculated diameter by using as inputs the seed size and the [Au(I)]/[seeds] ratio.

Experimental

Materials
All stock solutions were prepared from AR chemicals and purified water (Milli Ro, Milli Q system). $HAuCl_4$ solutions were kept in the dark in order to prevent their photochemical decomposition. $NaBH_4$ solutions were prepared in ice-cooled water and were kept refrigerated no more than one hour before their use.

Reactive solutions
Aqueous solutions of 0.1 mM $HAuCl_4$ in presence of a reducing agent and variable concentration of halide ions or hexadecytrimethylammonium nitrate (CTAN) are referred as reactive solutions. As reducers 0.15 mM H_2Q (hydroquinone, equinormal to Au(III)) and, 0.15-1 mM Ascorbic Acid (AA, in excess to Au(III)) were employed. The concentrations of KCl, KBr and KI were varied between 0 and 50 mM. The pH was adjusted by employing NaOH. In all cases, the reducing agent was added at the end. For the experiment performed at 98 °C, the solution was thermalized in bath previous to the addition of the reducer. Then, the heating was suspended and the reactive solution was cooled with water to room temperature.

Seeds AuNPs
The 7 nm seed AuNPs were synthesized as follows: 1 mL of 0.1 M $NaBH_4$ ice-cold solution is added under vigorous stirring into 50 mL of 0.2 mM $HAuCl_4$ and 2 mM HAc aqueous solution heated up to 90 °C. The heating was kept for 30 min until reaction was complete.

Seed-mediated approach
Reactive solutions which are used to grow NPs are call "growth baths". Two different compositional growth baths were employed: 1)

Organic molecules-free iodide ions growth baths: 0.01 mM $HAuCl_4$, 0.1 mM KI and 0.03 mM H_2Q; 2) Poly(vinyl pirrolidone) (PVP) bromide ion growth baths: 0.05 mM $HAuCl_4$, 20 mM KBr, 0.0145% PVP and 0.2 mM H_2Q. For the seeding, a two-step protocol was employed where the volume ratio between seeds and the growth bath solutions was kept in 0.1 and the growth bath composition constant. In the first step, an aliquot of a previously prepared 1/10 dilution of the 7 nm seeds solution is added into a growth bath under vigorous stirring; the agitation is suspended after homogenization. Following the same procedure, in the second step, the AuNPs grown in the first step are used as seeds in a second seeding.

Characterization
A Shimadzu UV-1200 spectrometer with a 1 cm quartz cell was used to characterize the solutions at room temperature. Transmission Electron Microscopy (TEM) characterization was carried out in a JEM-JEOL 1120 microscope. The samples were prepared, without any purification treatment, by seeding many drops of the colloidal solutions onto a Formvar-covered cooper grid and evaporating the water in air at room temperature.

Raman measurements
Raman spectra were recorded on a Horiba Jobin Yvon LabRAM HR Raman spectrometer by using a He-Ne laser (632.82 nm) as excitement source. The Raman of $AuBr_4^-$ was performed using a quartz cell containing an $AuBr_4^-$ solution. To measure the $AuBr_2^-$ spectrum, a reactive solution composed by 0.1 mM $HAuCl_4$, 50 mM KBr and 0.15 mM H_2Q was employed. Since the solution was to dilute to detect any Raman signals is was necessary to concentrate the $AuBr_2^-$. To prevent that the $AuBr_2^-$ reacted during its concentration, the $AuBr_2^-$ was extracted to $CHCl_3$ by employing CTAB as extraction agent. Then the $CHCl_3$ was evaporated over a glass slide in order to produce thin layer deposits for Raman analysis.The conclusions section should come at the end of article, before the acknowledgements.

Conclusions

In the present work it has been demonstrated that gold homogeneous nucleation by chemical reduction of aqueous gold ions is kinetically quenched by the increase in the concentration of halide ions. The nucleation quenching is stronger as the AuX_4^- complex stability increases, where the halide ion concentration needed to attain nucleation inhibition follows the order: $[Cl^-]>[Br^-]>[I^-]$. It has been also determined that the nucleation quenching by halide ions decreases while increasing the pH likely due to changes in the gold ions speciation. Moreover, this halide ions effect on gold nucleation appears to be a general feature since it has been proven to be present with different reducing agents. Hence, gold nucleation quenching should always be considered when halide ions are present. For example, this halide ions effect has been found to be responsible for the absence of self-nucleation in the quaternary ammonium-based seed-mediated growth method. Furthermore, halide ions can be used to manipulate and control the gold homogeneous nucleation. We have shown that, by setting suitable conditions of pH and halide ions concentration, gold nucleation can be inhibited generating Au(I) metastable species which coexist together with the reducer. We have also proved how these metastable solutions constitute a basis for a seed-mediated approach. In order to achieve this, several metastable solutions were used as growth baths where Au(I) reduction was activated over the surface of seed AuNPs driving

their growth. Adjusting the synthesis parameters, spherical shaped 7 nm AuNPs seeds have been grown to different sizes in a controlled and reproducible manner up to 49 nm. The AuNPs were synthesized under different conditions, free of organic molecules and in presence of PVP, a biocompatible polymer. Hence, the seed-mediated approach proposed has been shown to be highly reliable where the synthesis conditions can be rationally designed in order to obtain the desired AuNPs size and surface properties among others.

Notes and references

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† Electronic Supplementary Information (ESI) available: UV-Vis characterization of reactive solutions formed with chloride and iodide ions and with CTAN. Derivation of the equation used to predict the diameter of the AuNPs after seeding. See DOI: 10.1039/b000000x/

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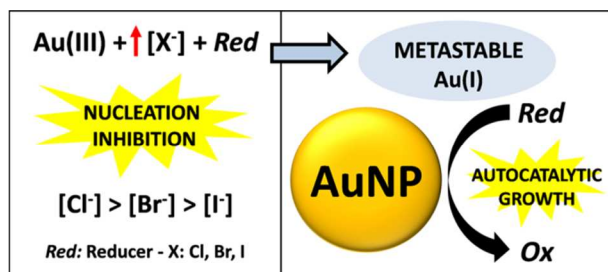
Halide ions kinetically quench the gold homogeneous nucleation by chemical reduction of aqueous gold salts. Under suitable conditions, gold nucleation is inhibited and Au(I) metastable species coexist with the reducer. Hence, this metastable solutions constitute a basis for a seed-mediated approach since the Au(I) reduction can be activated on the surface of seed AuNPs driving their growth.