Accepted Article

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: *ChemSusChem* 10.1002/cssc.201901488

Link to VoR: http://dx.doi.org/10.1002/cssc.201901488

Gold recycling at laboratory scale: from nanowaste to nanospheres

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Abstract

The market for products based on nanotechnology increases day by day, and with it the use of nanomaterials and the generation of waste that contain *nanowaste*. Among the vast variety of nanomaterials available, gold nanoparticles (AuNPs) are within the most studied and applied ones in commercial products. This current situation requires both, the development of recovery methods to reduce the amount of produced nanowaste and new synthetic methods that allow the reuse of recovered gold for new nanomaterial production; in both cases keeping in mind economical and ecological reasons. In this work, a methodology to recover gold from aqueous laboratory nanowaste and to transform it into an aqueous $HAuCl_4$ solution was developed, using extremely simple procedures and easily available chemical reagents (NaCl, HCl, H_2O_2), allowing the recovery of more than 99% of the original gold. The experiments were performed using both simulated and real laboratory nanowastes obtaining practically the same results. Moreover, the subsequent use of the obtained aqueous $HAuCl_4$ solution, from the recovered gold, to produce spherical AuNPs through a seed-mediated approach was demonstrated. Thus, this work presents, for the first time to the best of our knowledge, a complete recycling cycle from nanowaste, to the reagent and back to the nanomaterial.

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Introduction

In the last years, nanoscience and nanotechnology have received plenty of attention, including not only a large number of scientific and technological publications, but also a large number of products containing nanomaterials in the hands of consumers. In fact, the number of such products has increased by more than 100% every year during the last decade.[1] This rapid progress can also be measured by the amount of international patent applications in the nanotechnology area, that is constantly growing,[2–4] guaranteeing the use of more nanoentities in future products. This constant demand for nanomaterials brings two issues that must be pointed out: the use of non-renewable resources and expensive raw materials and the generation of waste that contains nanoentieties, i.e. *nanowaste*. At industrial level, some protocols are employed to carry out nanowaste management but those remain far away from the Green Chemistry's renewables revolution.[5] In addition, it is usual for products containing nanomaterials to be recycled along with their analogous not containing nanomaterials. A specific practice for nanomaterial waste treatment is still demanded.[6] The recovery and recycling of these critical materials is important nowadays and will be crucial in the future; in fact, this topic is among the highlights of the G20 agenda,[7] and. This is driven by the importance of recycling in waste minimisation and waste prevention strategies,[8] as well as the key role of sustainable materials management when non-renewable resources are involved[9]. Moreover, the potential risks of nanomaterials and their impact to human beings and the environment are currently insufficiently understood and could become a key point in the future.[1]

Gold nanoparticles (AuNPs) are currently one of the most studied nanomaterials,[10, 11]. AuNPs and play not only an important role in fundamental and applied science and but are also present in several commercial products. These applications include electronics and photonic devices, catalysts and sensors, with a particular emphasis in lateral flow immunoassays.[12, 13] The last application, related to medical and veterinary industries, is expected to increase more than four-times in the next five years.[14]

In many research and industrial laboratories, AuNPs are produced by chemical methods that allow obtaining them with different morphologies (spheres, rods, triangles, bipyramids, among others) and sizes.[15] The common approach for the design of these synthetic procedures involves trial and error, and after obtaining the AuNPs, their physicochemical characteristics are tested, and functionalization and/or attachment to substrates is performed, by means of a wide variety of methodologies. All these processes and tests produce a huge production or consumption of AuNPs with the consequent generation of nanowaste. Since Au(III) salts (the precursor used to produce AuNPs) are expensive resources and their price depends on the world's gold market, a simple methodology which allows laboratory scale gold recovery and its transformation into new AuNPs, would present a significant profit in terms of laboratory's resources. Moreover, it would help to diminish the amount of nanowastes that are produced and must be treated. Additionally, this procedure could pave the way towards the recovery of other wastes that contain gold, at both laboratory and industrial scale.

The recovery of gold from bulk solid wastes, either as Au(0) or Au(III), is well established at both industrial and laboratory scales. The most widespread strategies are based on pyrometallurgical and hydrometallurgical methods, that involve the use of high temperature furnaces or aggressive and/or toxic leaching solutions (including cyanide, halides, thiosulfate, thiourea, thiocyanate, etc.), respectively.[16–23] A mechanochemical approach has also been presented, that require the use of specific equipment.[24] Thus, these approaches are not adequate for the

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treatment of laboratory scale nanowastes, due to the toxicity of the involved materials and/or the complexity of the methodology. In the case of gold nanoparticles, their separation from aqueous suspensions, mediated by surfactants, zwitterionic molecules and pH responsive microgels has been explored.[25–31] Similarly, Praharaj *et al.*[32] presented: the use of an anion exchange resin to immobilise and subsequently recover Au nanoparticles from aqueous suspensions. Other strategies that involve magnetic separation and organic solvent extraction have also been presented.[31] However, most of these approaches were specifically dedicated to a particular kind of AuNPs; besides, in the majority of the reports no further use of the recovered material was envisioned. In addition, several laboratory approaches to recover Au(III) from aqueous wastes are available nowadays. Cementation, adsorption, solvent extraction, ion exchange, chemical and electrochemical reduction and coagulation strategies have been developed.[17, 33, 34] Even bio-remediation methodologies based on immobilization and/or reduction by bacteria and other biological species were developed.[35–37] Recent works include the Au(III) recovering taking advantage of the coordination of $AuCl_4^-$ with α-cyclodextrin,[6, 38, 39] with ionic liquids[40–42] or with amides[43]. Another study howed the possibility of Au(III) extraction by reduction and formation of a floating Au(0)/polyvinylpyrrolidone film.[44] However, although the different chemical aspects discussed and the good recovery percentages obtained, all these works were focused on recovery of soluble gold and no information was presented about its further use.

To the best of our knowledge, the only work focused on nanowaste recovery and recycling is so far from Pati *et al.*[6] In this work, α-cyclodextrin was used for Au(III) extraction after oxidation, employing a mixture $HBr : HNO_3 = 3 : 1$, of a simulated aqueous nanowaste containing gold nanoparticles capped with citrate. Afterwards, several steps of reduction, precipitation and oxidation were carried out, allowing to obtain a gold solution that was employed to synthesize AuNPs. However, the obtained AuNPs, which contained unidentified impurities, were unstable and coalesced.

Herein a simple methodology to recover and reuse Au(III) from aqueous laboratory nanowaste is presented, using commonly available reagents. The recovery process involves three-steps: (1) gold nanoparticles separation from real or simulated nanowaste by salting-out; (2) aqueous $HAuCl_4$ solution preparation and quantification through ICP-OES and UV-Vis; and (3) Au nanospheres synthesis employing a seeded growth approach. The following aspects are highlighted in the proposed methodology: insignificant use of water, use of cheap and commonly available reagents, high degree of Au (III) recovery and quantitative AuNPs synthesis with a well defined shapes and optical properties.

To the best of our knowledge, this work is the first one to present a complete recycling circle from real nanowaste, to the reagent and back to the nanomaterial in perfect agreement with Green Chemistry guidelines towards a more circular economy approach in resource utilization.[5]

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Experimental

Materials

Gold (III) chloride trihydrate (HAuCl$_4$ · 3 H$_2$O), trisodium citrate dihydrate (Na$_3$Cit · 2 H$_2$O), ascorbic acid (H$_2$Asc), cetyltrimethylammonium bromide (CTAB), polyvinylpyrrolidone MW = 10000 g/mol (PVP), hydrogen peroxide solution 30% (H$_2$O$_2$), hydrochloric acid 37% (HCl) and sodium chloride (NaCl) were supplied by Sigma-Aldrich. All reagents were used without further purification. Deionized water (18 MΩ.cm) was used for all preparations.

Separation of gold from laboratory nanowaste: Au(s)

The AuNPs suspension volume was measured with a graduated test tube and solid NaCl was added until a final concentration of ∼ 1 M was reached (58 g of NaCl per liter of nanowaste solution). The mixture was stirred manually in order to ensure NaCl dissolution. After $12 - 24$ hours, a AuNPs sediment forms spontaneously, resulting in a black solid and a supernatant. To reduce the volume, the resulting supernatant was manually discarded in the adequate waste container. More than 90% of supernatant volume was removed in this step. Then the black solid suspension was transferred to centrifugation tubes and was centrifugated for 10 min at 1000 RPM. The supernatant was discarded and the solid was resuspended with water; the same procedure was repeated three times. Alternatively, due to the coalescense of the AuNPs into microparticles by the addition of NaCl, the black solid suspension can be filtered and washed. The final black solid represents the recovered gold, which was employed in the next step, as an aqueous suspension.

Preparation of gold solution from a recovered gold: HAuCl$_4$ (aq)

Aqueous HAuCl$_4$ solution from recovered gold was prepared employing a mixture of hydrogen peroxide and hydrochloric acid. Typically, 500 μL of recovered gold suspension was added to 25 mL of a solution of H$_2$O$_2$ (6 M) and HCl (1 M). The solid dissolves almost immediately and the solution becomes light yellow. Then, the solution was heated under reflux for 15 min to decompose the excess of H$_2$O$_2$.

Synthesis of Gold nanoparticles

AuNPs synthesis: Turkevich method

AuNPs of *ca.* 15 nm (AuNPs$_{15nm}$) were prepared based on the approach of Turkevich *et al.*[45] A $0.25 - 0.50$ mM aqueous solution of HAuCl$_4$ was heated until boiling point and left at that temperature for 5 min. Afterwards, Na$_3$Cit solution was quickly added to rise a final concentration of 2.5 mM. The reaction mixture was refluxed for 15 min, obtaining a ruby red coloured solution. The same procedure was carried out using a gold recovered solution instead of commercial HAuCl$_4$. Additionally, control experiments with increasing concentration of Na$_3$Cit (from 2.5 mM to 25 mM), addition of NaCl (from 5 to 25 mM) and/or addition of PVP (50 μM) were carried out.

AuNPs synthesis: seeded growth approach

Gold nanospheres were prepared by seeded growth approach, according to the work by Rodríguez-Fernández *et al.*[46] $AuNPs_{15nm}$ capped with CTAB were used as seeds. The seed solution was prepared mixing aqueous solutions of $AuNPs_{15nm}$ and CTAB until final concentrations of $[AuNP] = 0.25$ mM ($Abs_{400nm} = 0.6$) and $[CTAB] = 15$ mM, respectively. The growth solution was prepared by mixing $HAuCl_4$, CTAB and H_2Asc until a final concentration of: $[HAuCl_4] = 0.25$ mM, $[CTAB] = 15$ mM and $[H_2Asc] = 0.50$ mM. The growth solution was kept at 35 °C and the seed solution was added. After mixing, the solution was held at 35 °C for 1 hour. The seed solution volume was fixed according to the desired final AuNPs diameter (for more details see SI), whereas final diameters of 30 nm, 45 nm and 60 nm were chosen.

Besides these control experiments, two other sets of experiments were carried out. In the first, HCl was added to the growth solutions, prepared with commercial $HAuCl_4$ to get a final concentration of 100 mM. In the second, a growth solution was prepared using recovered gold instead of commercial $HAuCl_4$. The concentrations of CTAB and H_2Asc were maintained.

Characterization

Gold concentration was determined using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES PerKin Elmer, serie Optima 8000. Autosampler AS10 PerkinElmer). ICP-OES instrumentation and operational conditions are described in Table S1, SI. Working solution for ICP-OES were prepared from 1000 mg/L monoelement standard solution (Au, Cetripur, Merck) with deionized water MilliQ quality. Sc standard solution, 1000 mg/L (Cetripur, Merck), was added and used as internal standard. All samples were prepared with a final concentration of 0.6 M HCl (Carlo Erba Regeants 37%, for analysis).

UV-Vis spectra were collected by a Shimadzu or Agilent 8453 spectrophotometers.

SEM inspection was performed in a Carl Zeiss NTS - SUPRA 40 equipment operating at 3 kV (CMA-UBA). To perform such measurements, the samples were centrifuged at 5000 RPM for 15 minutes and resuspended in water, the procedure was repeated twice. Ten microliters of the washed sample were drop onto a silicon wafer and let to dry. Nanoparticles' average diameters and their distribution were determined by measuring at least 100 particles in SEM images, using ImageJ software.

Results and Discussion

Gold recovery from simulated nanowaste: *proof of concept*

Having in mind the idea of recovering Au from gold nanowaste, a suspension of $AuNPs_{15nm}$ prepared following Turkevich's protocol[45] was used. The choice of this kind of sample lies in the fact that it represent one of the simplest nanowastes available: the particles size is small enough and the matrix is quite simple (AuNPs, remaining Na_3Cit and its oxidized products and water). Moreover, the Au concentration can be easily estimated by UV-Vis spectroscopy using the absorbance at 400 nm.[47, 48]

The first step to recover Au is to separate the $AuNPs_{15nm}$ from the solvent. For that purpose, solid NaCl was added to as-synthesized Turkevich AuNPs suspension, until reaching a *ca.* 55 g/L concentration. After the addition, the typical ruby red colour suspension (Figure 1-A) turns firstly violet-blue and then black, with a sedimentation of the NPs.[6, 49] This process involves the coalescence of nanoparticles to form microparticles, a process that can be explained by the decrease in the double layer thickness due to the increase of ionic strength. As a consequence, the AuNPs stability is disrupted by the increasing importance of the attractive interactions. An alternative separation approach for the AuNPs is centrifugation. Noteworthly, the addition of NaCl significantly increases the gold recovery, since the centrifugation of AuP_{15nm} results in only a 90% recovery after one hour at 7000 RPM (see Figure S1, SI). After the sedimentation process, a colourless solution with a black Au pellet is observed (Figure 1-B) and no traces of AuNPs are detected by UV-Vis spectra of the supernatant. After the sedimentation process, the supernatant was discarded and the black solid suspension was transferred to centrifugation tubes. Three centrifugation-resuspension steps were carried out using water as solvent, in order to clean the excess of NaCl. Afterwards, Au must be oxidized to Au(III). *Aqua regia* (a 3:1 mixture of HCl(c) and HNO_3(c)) is typically employed to dissolve Au,[18, 21] and is usually used for glassware cleaning at laboratory scale. However, although this mixture's efficiency, the resultant Au(III) solution presents a high ionic strength, making it incompatible for its further use in AuNPs synthesis. In a recent report,[6] the use of a $HBr:HNO_3$ 3:1 mixture to dissolve AuNPs was proposed. This mixture is very effective but adds Br^- to the final solution, an ion that has influence on Au (III) reduction.[50] Moreover, this mixture and *aqua regia* produce toxic NO_X gases. In order to develop a greener and cleaner approach, the use of a mixture of diluted H_2O_2 and HCl was tested. This mixture generates small amounts of chlorine, which works as an oxidizing agent for the metallic gold. The excess of Cl^- anions (whose concentration is fixed with the initial [HCl]) allows the formation of the $AuCl_4^-$ complex, stable in aqueous solution. Moreover, the excess of H_2O_2 is decomposed to H_2O by boiling. Thus, a mixture of H_2O_2-HCl was added to the black Au pellet. After its addition, the mixture reacts with the solid, dissolving it. A very light yellow solution is observed after some minutes (see Figure 1-C). UV-Vis spectrum confirms the effectiveness of the reaction, since the sharp absorption band around 313 nm, related to the metal to ligand charge transfer[51] of $HAuCl_4$ is clearly observed.

Au(III) concentration in the obtained solution was determined by ICP-OES and UV-Vis. Both techniques were used simultaneously, in order to generate a simple Au(III) determination procedure by spectrophotometry, correlated with a more sensitive analytical technique. Figure 2 depicts a perfect correlation between both techniques in the $0.010 - 0.250$ mM range for commercial $HAuCl_4$. For UV-Vis measurements, the solutions must be prepared using more
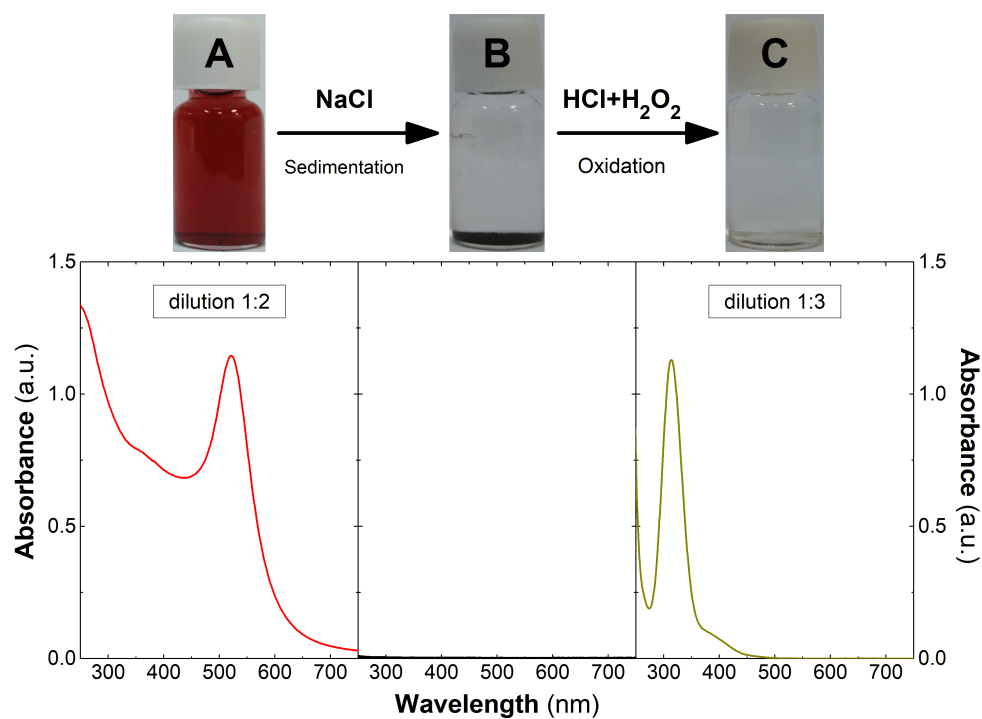
Figure 1: Images and UV-Vis spectra of representative states during gold recovery. From left to right, AuNPs$_{15nm}$ Turkevich's suspension (A), AuNPs sedimentation by NaCl addition (B), HAuCl$_4$ solution after oxidation with HCl + H$_2$O$_2$ of gold sediment (C).
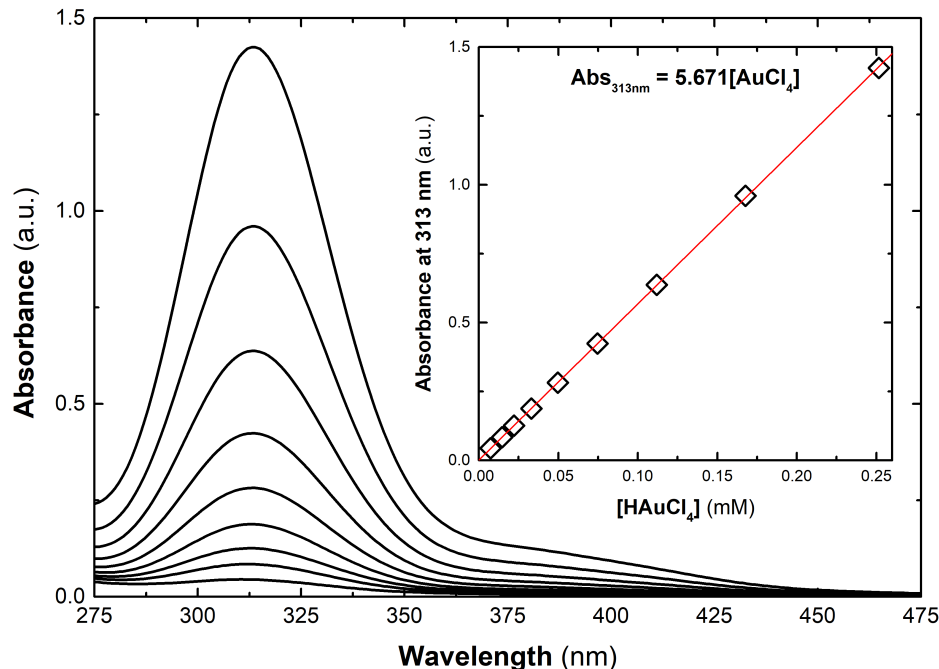
Figure 2: UV-Vis spectra of $HAuCl_4$ aqueous solution in HCl 250 mM as a function of its concentration. Inset: absorbance maximum at 313 nm as a function of $HAuCl_4$ concentration measured by ICP-OES.

than 100 mM of HCl, in order to ensure the presence of the $AuCl_4^-$ complex over the hydroxylated ones ($Au(OH)_xCl_{4-x}^-$ with $0 \leq x \leq 4$), since dilution in water increases the pH and thus promotes the exchange of chloride by hydroxyl (see Figure S2 and S3, SI). After analyzing the obtained Au (III) solution, both techniques confirm a Au recovery higher than 99.5%. This is the largest recovery reported so far for gold nanowaste[6], and among the highest for mimicked Au(III) waste in acidic solution.[38–40, 42, 44] In addition, this approach is simpler than other methodologies proposed before, since only three steps are required (precipitation, separation and dissolution) and not specific complexing agents were added.[6, 19, 34, 38, 43, 52, 53]

Gold recovery from a real nanowaste

Once the highly quantitative recovery process for $AuNPs_{15nm}$ was confirmed, a typical aqueous gold laboratory waste solution was employed to test the proposed methodology. The chosen gold nanowaste contains mainly: AuNPs of different sizes and morphologies (spheres, rods, triangles, stars), stabilizing agents (CTAC, CTAB, BDAC, different molecular weights of PVP) reducing agents ($NaBH_4$, H_3Cit, Na_3Cit, H_2Asc), and their oxidation products. This nanowaste (a brownish suspension, that can be seen in Figure 3-A) derives from a series of several different AuNPs syntheses, in which the initial concentration of $HAuCl_4$ was below 1 mM and an excess of reducing agent was always employed. These facts allow to confirm that
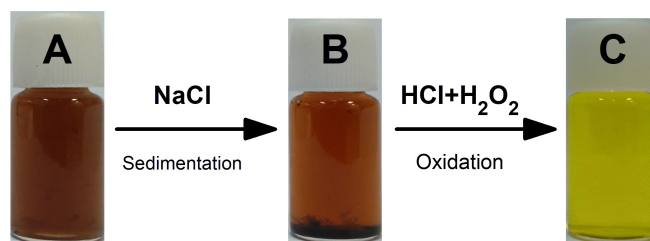
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Figure 3: Images of representative states during gold recovery from nanowaste. From left to right, $AuNPs_{nanowaste}$ waste suspension (A), AuNPs sedimentation by NaCl addition (B), $HAuCl_4$ solution after oxidation with $HCl + H_2O_2$ of gold sediment (C).

gold is mainly ($> 99.9\%$) as metallic gold in this nanowaste.

For a first test, 5 mL of the described brown suspension were taken directly from the laboratory nanowaste container. As described before, the addition of NaCl promotes the destabilization of the AuNPs, that coalesce into microparticles that finally precipitate as a black solid (Figure 3-B). This solid is composed of a wide variety of AuNPs, as seen in SEM images (see Figure S4, SI). After gold precipitation, the resulting supernatant remains coloured, due to the presence of decomposition products of the organic reducing and stabilizing agents. UV-Vis inspection does not allow to detect the presence of AuNPs, only a very intense band in the UV region was observed after diluting the original solution 50 times (see Figure S5, SI). Moreover, ICP-OES measurements indicate that the Au(III) concentration in the supernatant is below the detection limit of the technique (3.4×10^{-5} mM). The solid was washed with water and finally, the oxidizing mixture of $H_2O_2 : HCl$ (6M:1M) was added, resulting in the reaction of the solid gold to produce a yellow $HAuCl_4$ solution (Figure 3-C).

After this first successful step, a scale-up procedure was carried out with two litres of nanowaste. As before, after 12 hours the AuNPs coalesce and precipitate as a black solid by the addition on NaCl. In this case, this solid was separated by filtration and the supernatant was discarded. At this point, it is important to note that the supernatant volume is almost the same as the original nanowaste and contains NaCl and decomposition products of reducing and stabilizing agents but no nanomaterials. Thus, the potential toxicity of this solution is reduced, and it can be discarded as any other aqueous solution of organic compounds, according to the health and safety regulations of each country.

The resulting solid, *i.e.* the recovered gold, was washed and oxidized as described before. In this case, the solution turned yellow and the release of bubbles was observed. The mixture was refluxed during 15 minutes, to ensure the complete H_2O_2 decomposition. Finally, HCl 1 M was added until a final volume of 25 mL. UV-Vis measurements indicate that a concentration of $HAuCl_4$ 37.5 mM in 1 M HCl was reached. This solution, named Au_{REC}, was stored in a refrigerator and was used to obtain AuNPs, as presented below.

Synthesis of AuNPs from a Au(III) solution derived from nanowaste

To synthesize AuNPs from Au_{REC} solution, different approaches were explored. In a first approach the Au_{REC} solution was used for the 15 nm spheres Turkevich's synthesis. This approach involves the reduction of $HAuCl_4$ with Na_3Cit at boiling temperature,[45] and it is the

most cited work of AuNPs synthesis in aqueous media.[54] Thus, the Au_{REC} solution was used as Au(III) source for this synthetic procedure. As expected, a change in the solution colour was observed after the Na_3Cit addition, indicating the formation of AuNPs. However, instead of the typical red ruby suspension obtained in the case of commercial $HAuCl_4$ ($AuNPs_{15nm}$ - Figure 1-A), a violet suspension with a plasmonic band maximum at around 535 nm was obtained (see Figure S6, SI). Moreover, a shoulder at higher wavelengths is also noticeable, suggesting either the presence of other morphologies and/or the aggregation of the AuNPs. Moreover, the suspension was not stable, and a precipitate appeared after one week.

This change in the characteristics of the AuNPs synthesized with Au_{REC} can be assigned to both the pH decrease (that affects chemical speciation of Au(III) complexes and citrate moieties) and the ionic strength increase, probably responsible for NP precipitation. In order to rationalize the difference between the expected and the obtained results, several control experiments were carried out using commercial $HAuCl_4$. Experiments with increasing concentration of Na_3Cit (from 2.5 mM to 25 mM) and NaCl (from 5 mM to 25 mM) were performed. At higher concentration of NaCl or Na_3Cit, AuNPs tend to agglomerate immediately due to the high ionic strength (see Figure S7, SI). But, for intermediate NaCl concentration, the Localized Surface Plasmon Resonance (LSPR) bands' position and shape are similar if Au_{REC} is employed. Noting that Cl^- concentration is around 7 mM in the experiment (Au_{REC} is diluted 150 times from $HAuCl_4$ 37.5 mM to 0.25 mM, hence HCl from 1000 mM to 7 mM) this in-between behaviour could be explained in terms of Cl^- concentration. The addition of a polymeric stabilizing agent (polyvinilpirrolidone, MW 10000 g/mol) was also tested, in order to prevent coalescence of AuNPs. But even when no NaCl was added, the obtained AuNPs were different than the expected in Turkevich conditions (see Figure S8, SI). These results confirm that it is not possible to employ the Turkevich condition employing Au_{REC} as Au(III) source, something that is not surprising taking into account the strict conditions required by this synthesis.[45, 54] Besides, similar unstable AuNPs were obtained in a previous paper that dealt with Au recovery and recycling from simulated nanowaste.[6]

Thus, a new approach was selected: Au_{REC} was used as a part of an overgrowth solution in a seed mediated synthesis. The synthetic approach reported by Rodríguez-Fernández et al.[46] was chosen. This method allows obtaining spherical AuNPs with controlled diameters, using Turkevich's $AuNPs_{15nm}$ as seeds and a mixture of Au(III), CTAB and H_2Asc as growth solution.

A set of experiments was carried out using Au_{REC} solution as gold source. In all cases, the expected colour changes were observed in the reaction mixture: the formation of an orange solution after mixing Au_{REC} and CTAB, the disappearance of colour after H_2Asc addition (due to the reduction of Au(III) to Au(I)) and, after the seeds incorporation, the appearance of a redish colour whose intensity increased as the reaction proceeded. Moreover, in all cases the seeded growth reactions was completed in terms of Au(0) production, calculated from absorbance at 400 nm, i.e. all the Au_{REC} was transformed to metallic AuNPs. Figure 4 presents the UV-Vis spectra and the SEM inspection of the spherically shaped AuNPs obtained using Au_{REC} solution. As it is possible to see, the AuNPs presented the expected spherical shape. In addition, as lower seed solution volume was added, the diameter and the LSPR band maximum position increased (see Equation 1, SI). Control experiments with $HAuCl_4$ and $HAuCl_4 + HCl$ solutions were carried out in parallel. Noting that final concentration of HCl will depend on the concentration of $HAuCl_4$ in Au_{REC} solution (dilution rate, see above), in the present control, a higher final HCl concentration of 100 mM was selected, to test the effect of acid media and
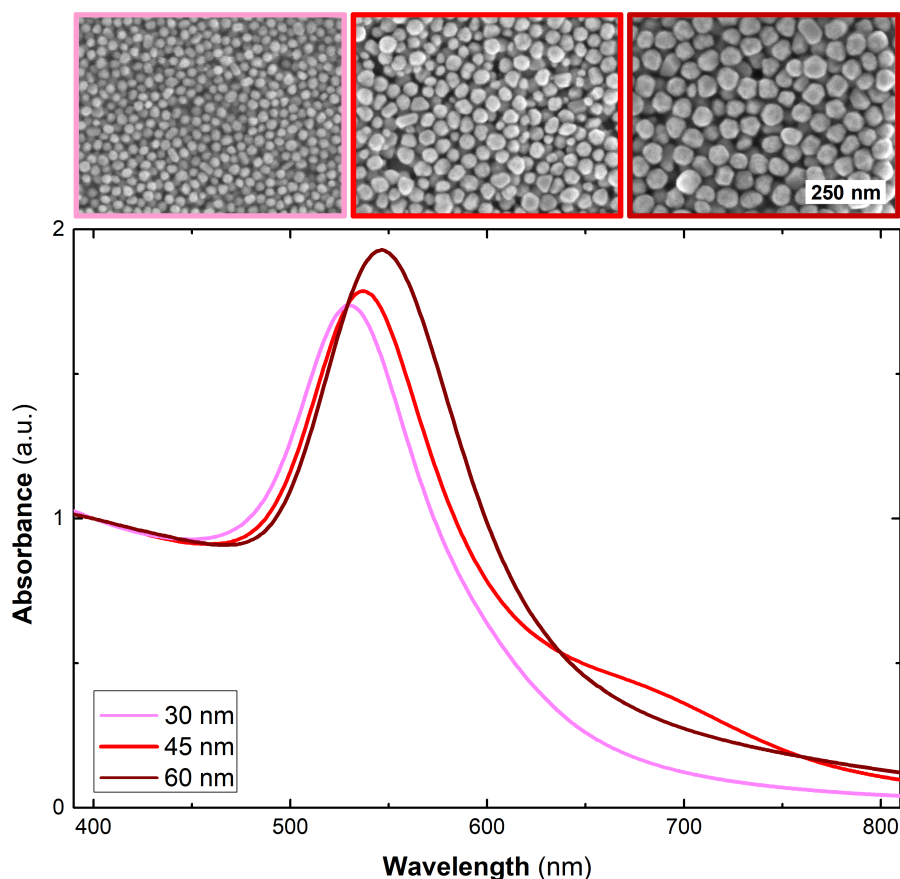
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Figure 4: SEM images and UV-Vis spectra of the different gold nanospheres obtained using a Au$_{\text{REC}}$ solution.

chloride concentration over the reaction. In the three sets of experiments, the results of the UV-Vis spectra were equivalent (see Figure S9, SI) and the obtained AuNPs diameters and particle size distributions were similar (see SEM images in Figure S10 and size distributions in Figure S11 and Table S2, SI). These results confirm that the AuNPs, obtained from Au$_{\text{REC}}$ solution are equivalent to the ones obtained from commercial HAuCl$_4$. Moreover, the obtained AuNPs remain stable in solution for several months, a clear difference to the previously presented Turkevich synthesis results. Interestingly, as the amount of seeds is small, the 30 nm, 45 nm and 60 nm diameter AuNPs obtained from Au$_{\text{REC}}$ solution are composed of 87.5%, 96.3%, 98.4% of gold recovered from nanowaste, respectively.

In order to rationalize the success of the proposed methodology, a physicochemical analysis is needed. In a solution containing CTAB and AuCl$_4{}^-$ the exchange of chloride by bromide resulted in the formation of a AuBr$_4{}^-$ complex. This fact is noticeable by a change in the solution's colour, from light yellow to orange. UV-Vis spectra confirm such exchange by the maximum in absorbance shift from 313 nm to $\sim$ 390 nm.[51] According to exchange constant to AuCl$_4{}^- \longleftrightarrow$ AuBr$_4{}^-$ of 3.2 x 10^7[55], both complexes, AuCl$_4{}^-$ and AuBr$_4{}^-$, would have the same concentration if the ratio between [Cl−] : [Br−] is higher than 75. Figure S12

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presents the speciation diagram, obtained from tabulated data[55], of Au(III) in presence of both chloride and bromide in acid aqueous media. At the explored condition: $[Cl^-] = 100$ mM and $[Br^-] = 15$ mM (black line), $AuBr_4^-$ is the main species present. Thus, the presence of Cl^- excess in the Au_{REC} solution, or in the control where $HAuCl_4 + HCl$ solution is employed, does not change the chemical characteristics of the growth solution. Furthermore, under these experimental conditions the reactive gold moieties remains unchanged, fixing the reduction potential of Au(III)/Au(I) and Au(I)/Au(0). As a consequence, the obtained particles present the same characteristics of the particles prepared employing commercial $HAuCl_4$. It should be mentioned that the more acidic condition given by HCl affects the H_2Asc speciation, from a dissociation degree of less than 30% to a 1%, but this effect does not seem to produce a major effect over the reaction.

Finally, the possible applications of the obtained AuNPs should be considered. Spherical AuNPs have been used for the production of optical[56, 57] and Surface Enhanced Raman Spectroscopy based sensors[58, 59] and for other medical[60] and biological applications.[61] All these uses require AuNPs with certain sizes, shapes and LSPR band positions. As stated before, these characteristics are equivalent in particles obtained from Au_{REC} and $HAuCl_4$ solutions and thus, equivalent uses for such particles can be envisioned. A simple experiment was performed in order to test the sensitivity of the LSPR band towards changes in the local refractive index[56] in 60 nm diameter AuNPs obtained from Au_{REC} and $HAuCl_4$ solutions (see SI for details). The results indicate that the LSPR band shift upon a solvent change is equivalent for both cases (see Figure S13, SI). These results demonstrate equivalent sensitivity of the optical properties for both kinds of AuNPs to a change in environment, proving that the reported method is suitable for widespread optical applications of AuNPs obtained from recovered gold sources.

Conclusion

In this report, a methodology to recover gold from laboratory aqueous nanowaste and to transform it into a $HAuCl_4$ solution was developed, using extremely simple procedures and easily available chemical reagents (NaCl, HCl, H_2O_2). As a first step, the feasibility of the proposed method was demonstrated by using a solution of 15 nm diameter Au nanospheres as simulated nanowaste. For such solution, 99.5% of the Au could be recovered, as demonstrated by ICP-OES and UV-Vis spectrometry.

In a second step, the method was extended to recover Au from a mixture of aqueous nanowaste that contained AuNPs of several shapes and sizes and a wide variety of organic reductive and stabilizing agents. The obtained $HAuCl_4$ solution presents an excess of HCl, in comparison with the commercial reagent and thus, can not be used to obtain stable AuNPs using the one-pot Turkevich's method. Nevertheless, it was demonstrated that the recovered Au(III) solution can be used as a part of a growth solution to obtain uniform spherical AuNPs with diameters from 30 nm to 60 nm, using a seed mediated approach. The success of this approach, explained by the chemical characteristics of the reaction, invites to broaded this methodology to obtain other morphologies beyond spheres. Thus, this work represents, to the best of our knowledge, the first example in which a recovered Au(III) solution from real aqueous nanowaste is employed to obtain new and stable Au nanospheres. Finally, it is important to highlight that the methodology presented here demonstrates the feasibility of Au recovery and reuse of aqueous nanowaste at laboratory scale but, due to its simplicity, it may find applications at industrial level. Besides, it can also be expanded for nanowaste that contain volatile organic solvents, by resorting to a distillation step, and/or other noble metals, by controlling the reduction potential of the reducing agents.
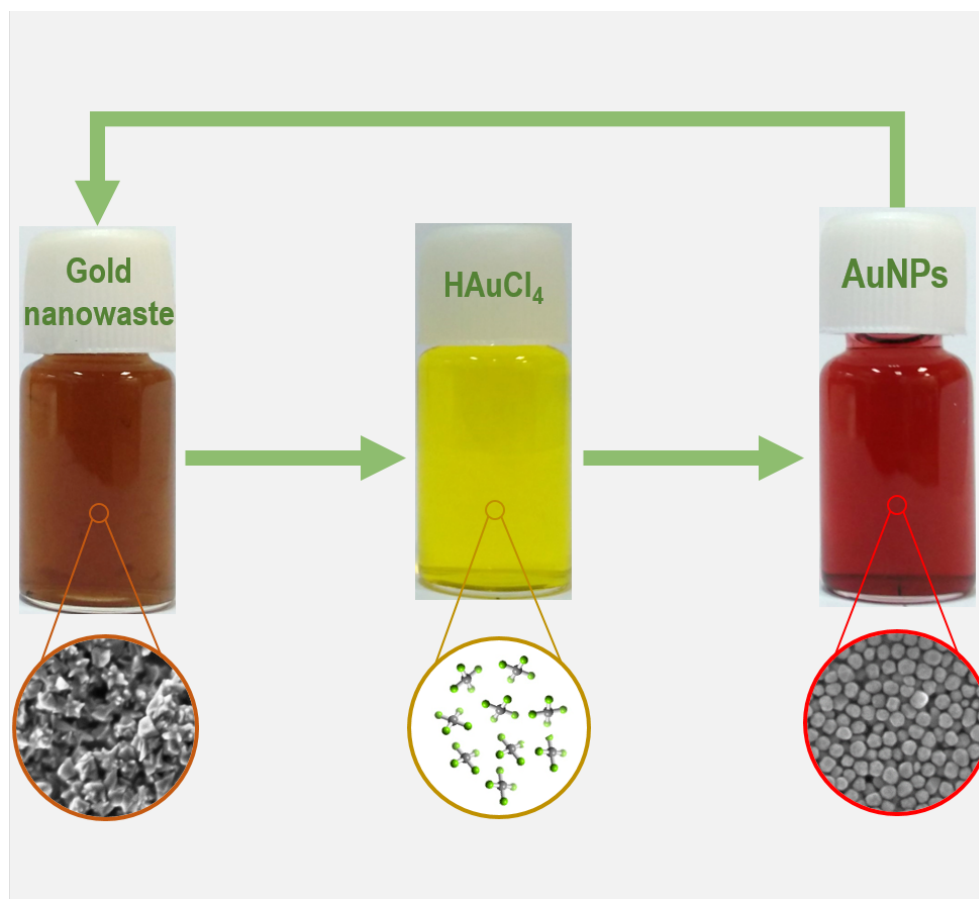
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