

A synthesis route of gold nanoparticles without using a reducing agent

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(Received 8 February 2010; accepted 6 May 2010; published online 28 May 2010)

In the present work we show that synthesis of gold nanoparticles (NPs) could be performed by microwave-assisted technique without the need of adding any reducing agent. Only water and the gold salt precursor are necessary to generate the NPs under the influence of microwaves. The produced NPs have been characterized by state-of-art microscopy techniques, like high resolution transmission electron microscopy, scanning electron microscopy, and energy-dispersive x-ray. Theoretical calculations have been performed to support the experimental findings. It is expected that the present work opens routes for synthesis of NPs using green, fast, and safe methods. © 2010 American Institute of Physics. [doi:10.1063/1.3442479]

Since Faraday,¹ who first elucidated the preparative method for aqueous dispersions of colloidal metal particles, metallic NPs have often been produced by chemical reduction of the corresponding metal salts in solution in the presence of suitable reducing agents and stabilizers organic molecules. Although chemical methods are capable of producing a large amount of material, the reducing agent stays in the solution and is very difficult to remove. In many cases the reducing agent might have toxic characteristics, this further complicates the application of NPs to biomedicine.²⁻⁴ However, very recently,⁵ microwave (MW) radiation has been used to accelerate the reduction reaction. The interaction between the MW radiation and the solution containing the precursor salt, produce a fast heating. Basically, two absorption mechanisms are present: dipole rotation and ion migration, which increase the temperature of the solution. Therefore the heating of the solution is of the order of magnitude faster than conventional plates or oil baths. When the MW radiation penetrates the solution, its power dissipation is fairly uniform throughout the solvent. Water has a very high dipole moment which makes it one of the best solvents for MW assisted reactions. For high values of MW power and long periods of exposure to radiation, there is a superheating of solvents above their boiling point and a power dissipation in the entire volume of the liquid.⁶ Concerning to water as solvent, it has been shown to have a high value of dielectric loss ($\epsilon=12.3$) and some authors have reported to have a small ability with respect to the reducing metal salts. Tsuji *et al.*⁵ have reported that they did not observe reduction of HAuCl₄ without adding polyvinyl pyrrolidone to the solution. The importance of the solvent is crucial for practical applications of gold or silver NPs for biomedical use. Therefore, the synthesis of NPs without the use of reducing agents is necessary to prevent contamination from external agents.

Preparation of samples. Solutions of HAuCl₄·3H₂O. (Sigma-Aldrich, 99.9+) in deionized water (15 ml) were prepared at 1.2×10^{-3} M concentration. All chemicals were of analytical grade used without further purification. The Au

NPs were prepared as follows: the auric solution were stirred for 10 min and then placed inside the MW high-pressure tetrafluoromethaxil vessel to proceed with the reaction. Two kinds of samples were sintered, the first sample was obtained using only water and HAuCl₄, and in the second one with water, HAuCl₄, and 1-dodecanethiol [CH₃(CH₂)₁₁SH, Aldrich]. For the synthesis the ETHOS EZ Digestion System MicroWave (Milestone, 2.5 GHz, sensor ATC400) was used and the samples were irradiated in a continuous wave mode during 30 s at a power of 800 W and then during 9 min at a power 1000 W. All samples were heating in a fast temperature program until it reaches 200 °C. Subsequently the samples were cooled at room temperature in a standard way, without the use of any cooler system. The particles were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy-dispersive x-ray (EDX). SEM was performed in a FEG Hitachi S-5500 ultrahigh resolution electron microscope (0.4 nm at 30 kV) with BF/DF Duo-STEM detector. TEM, high resolution transmission electron microscopy (HRTEM), and EDX were carried out in the JEOL JEM-2010, field emission electron microscope operating at 200 kV and a resolution 0.19 nm point-to-point. Filtering of the images was done by the Richardson-Lucy method as implemented in the HRTEM Inc. software.^{7,8}

Gold NPs formation using HAuCl₄ and water. At difference of all previous syntheses reported in the literature using the MWAT,^{3,9} in this work we have prepared gold NPs without the use of any external reducing agent. In the MW synthesis large particles produced in the *in situ* process have been obtained, due to the absence of protective agent and the power dissipation (PD) in the entire volume of the liquid. The PD increases the temperature of the solution and produces a secondary nucleation on the initial gold seeds. Figures 1(a)–1(c) show typical SEM images of large Au NPs obtained by the MW-assisted method after centrifugation of the samples at 3000 rpm during 10 min. The EDX analysis revealed only the existence of Au on the particle [see Fig. 1(b)]. Closer inspection of the samples were made by means of extraction of small quantities of the colloidal suspension from the center of the MW-vessel without the subsequent

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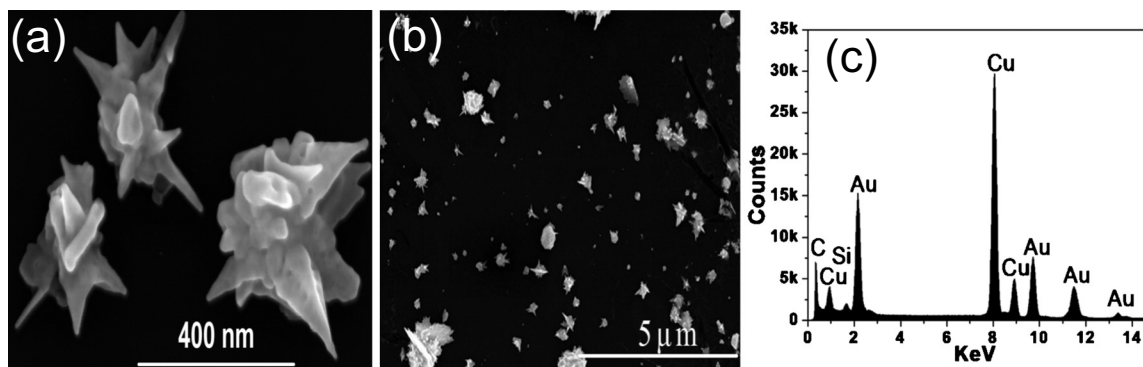


FIG. 1. [(a) and (b)] SEM images of large gold NPs produced by reduction of HAuCl_4 salt assisted by water and MW radiation. (c) EDX spectrum of the Au NP. Carbon, silicon, and copper peaks correspond to the grids used to deposit the colloidal suspension.

centrifugation step in order to avoid extraction of large particles that have precipitated (like those obtained by centrifugation at 3000 rpm during 10 min, as shown in Figs. 1(a) and 1(b)). TEM micrographs of Au NPs taken from the center of the MW-vessel without the subsequent centrifugation step are shown in Fig. 2. A typical low-magnification image is shown in Fig. 2(a) in order to demonstrate that a large distribution nonhomogeneous in shape particles was obtained. The averages size of the NPs is smaller than 5 nm. Of course, due to the resolution limit of the SEM, these small Au seeds were not observed, therefore TEM measurements were performed. As stated above, several NP shapes were observed, however it must be mentioned that all NPs present well defined crystalline structure. Typical HRTEM images of two selected nanocrystals are shown in Figs. 2(b) and 2(c), from which Au decahedra (b), characterized by pentagonal projections with slightly rounded apexes (see fast Fourier transform inset) and a fcc-like NP oriented along the [111] direction can be observed, respectively [see also the atomic models in Figs. 2(b) and 2(c)]. Besides the HRTEM images is shown the atomic models of the NPs. These results are quite surprising because of the absence of protecting agent which commonly is expected to control the crystal growth and the morphology of the NPs.

Gold NPs formation using HAuCl_4 +water +1-dodecanethiol. The same synthesis procedure described above was performed but now a protecting agent is added in order to avoid coalescence of the Au NPs to make it practically usable. Figure 3 shows typically TEM images of the

obtained NPs. As expected, when capping agents are added to the synthesis procedure, well-defined shapes and sizes are obtained. In Fig. 3(a), a low-magnification TEM image is shown, where a self-ensemble of Au NPs capped with 1-dodecanethiol molecules is evident. It should be noted that a very good size distribution is obtained using the present synthesis route. In Fig. 3(b), a HRTEM image of Au NPs, is shown. As can be appreciated in the image, the Au NPs present very well defined crystalline planes, and not amorphous structures due the fast heating procedure. A HRTEM image of an fcc-like NP oriented along the [011] direction is shown in Fig. 3(c). The lattice distances are approximately 0.235 and 0.209 nm, which corresponds to the $d_{111}=0.2355$ and $d_{200}=0.2039$, respectively, (JPDF 04-0784). This result, strongly indicates that the interaction between 1-dodecanethiol with the surface of Au NPs induce a morphological growth different to that observed without protecting agents.

Formation mechanisms of Au NPs using water as reducing agent. It is expected that with the use of MW, in addition to the dipole rotation,¹⁰ some normal modes of vibration will produce privileged directions of growth in the NPs, and in highly polar solvent such as water can induce formation of complex structures with antennas or tips as shown in Fig. 1. Moreover, due to the presence of planarlike ions (AuCl_4)⁻ in the solution the heating rate is expected to increases because

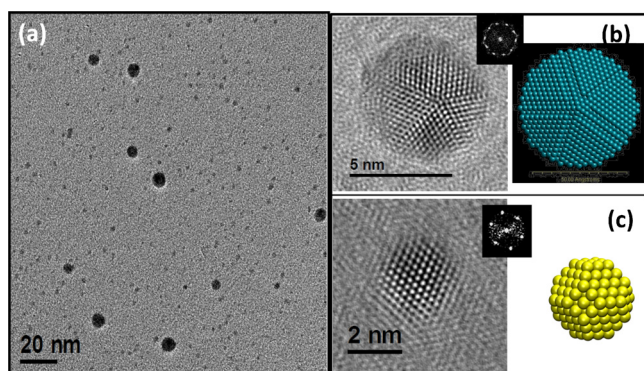


FIG. 2. (Color online) (a) A typical low-magnification TEM image of gold NPs obtained by the MWAT in presence of HAuCl_4 and water without the centrifugation step. [(b) and (c)] HRTEM images of a typical gold decahedral NP of 6 nm and fcc-like NP of 2 nm with their atomic model, respectively.

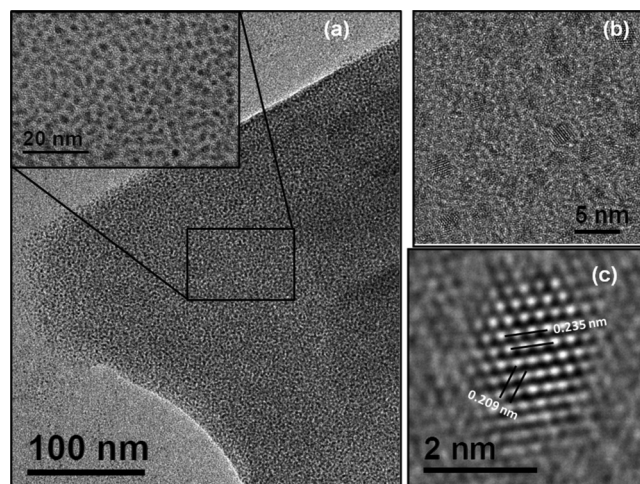


FIG. 3. (a) TEM images of gold NPs obtained by the MWAT in presence of HAuCl_4 , water, and 1-dodecanethiol. (b) HRTEM image of a portion of the self-ordered Au NPs and (c) a HRTEM image of a typical fcc-like gold NP showing the interplanar distances.

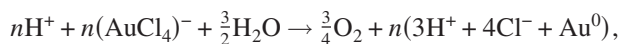
of the ion-migration mechanism. In the following, two possible formation mechanisms are proposed to explain the experimental finding:

Mechanism 1: Au reduction assisted by superheated water. The action of an electromagnetic field on liquid water, owing to partial absorption, heating, and the generation of intense motion of the water (vortices in local regions). Vaks *et al.*¹¹ have proposed the following dissociation reactions of water under the influence of a MW electromagnetic radiation at 2.5–10 GHz.



The first one represents a chemical dissociation with the formation of solvated hydrogen atoms and hydroxyl groups. While the second reaction represent the so-called self-ionization of water. From where the ion product of water for the self-ionization reaction $\text{p}K_w$ could be defined. It should be mentioned that varies from 14 (at 25 °C) to 11 (at 200 °C). Several recombination reactions have been proposed by Valks *et al.*¹¹ however of particular interest is the following: $\text{H}_{\text{aq}}^{\bullet} + \text{OH}_{\text{aq}}^- \rightleftharpoons (\text{H}_2\text{O})_{\text{liq}} + e_{\text{aq}}^-$, where a solvated (highly instable) electron is produced, which finally can reduce the Au^{3+} ions present in the salt, according to the following reaction: $n[\text{AuCl}_4]_{\text{aq}}^- + 3e^- \rightarrow \text{Au}_n^0 + \text{HCl}_{\text{aq}}$. In the spirit of the reactions presented above, we propose that metallic Au NPs could be generated by superheated water produced by electromagnetic irradiation in the MW range.

Mechanism 2: Electrochemical formation of Au nanoparticles. It is well-established that formation of nanoparticles (NPs) from liquid or gas phase must be determined by the change in Gibbs free energy of the redox reaction (ΔG_r). In this context, a $\Delta G_r < 0$ means that the reaction will evolve spontaneously. We will consider the following overall redox reactions for the formation of Au particles:



where the global standard redox potential is $\Delta E^\circ = -0.227$ V.¹² The equilibrium reduction potential of the overall reaction can be estimated using the Nernst equation, $\Delta E = \Delta E^\circ - \left(\frac{RT}{nF}\right) \ln K_{\text{eq}}$, where R is the universal gas constant, T is the absolute temperature, n is the number of electrons involved in the reaction, F is the Faraday's constant, and K_{eq} is the equilibrium constant of the overall reaction. The change in Gibbs free energy of the overall redox reaction (ΔG_r) can be calculated as follow: $\Delta G_r = -nF\Delta E$. Finally, replacing the values of $\log[\text{H}^+]$ by the pH and the concentration of HAuCl_4 used in the experiment, we obtain an expression to compute the equilibrium reduction potential as a function of the pH, the temperature, and the concentration of the metal salt, which are of course three relevant parameters in the synthesis of NPs. In Fig. 4 the Gibbs free energy as a function of the temperature is plotted for different pHs. As can be observed for low temperatures, $T < 78$ °C, $\Delta G_r > 0$ indicating that the reduction reaction is energetically unfavorable. However, at $T = 200$ °C (the experimental temperature) clearly the Gibbs free energy is negative, which indicates the spontaneous reduction of the salt, by means of oxidation of water. The reaction depends also on the $[\text{H}^+]$ (i.e., pH) and therefore switching the pH to higher or lower values at the same final temperature can be used to control the overall reduction reaction. The pH before and after the

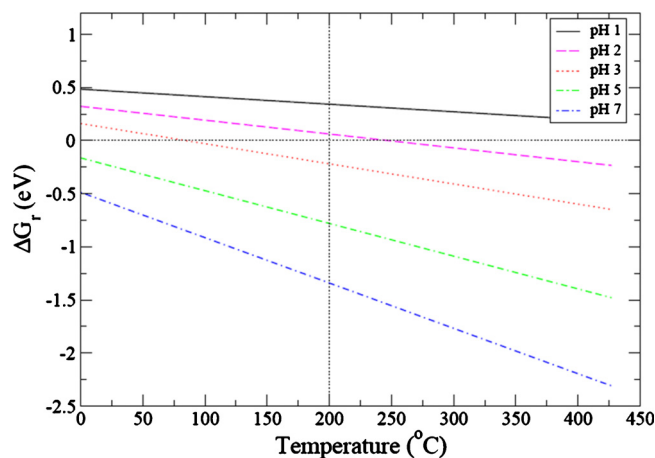


FIG. 4. (Color online) Gibbs free energy change as a function of temperature for different pH during the reduction reaction.

synthesis as been measured and a value of 3.1 has been found, results that are in good agreement with the theoretical predictions using the Nernst equation.

In conclusions, using HAuCl_4 as the metal precursor, water, and a MW oven, we were able to produce Au NPs, in a fast, safe, economic, and simple method. The obtained NPs have been characterized using SEM, HRTEM, and EDX. In general, small seeds of Au are observed, with diameter $d < 3$ nm, however due to the absence of any protecting agent, particles coalescence and rapid growth is also observed. In order to prevent this effect dodecanethiols molecules have been added to prevent aggregation. Two mechanism has been proposed to explain the reducing ability of water, in first place the effect of superheated water has been considered, and second, a purely electrochemical reaction was considered to calculate the Gibbs free energy for the overall redox reaction. The theoretical predictions are in good agreement with the experimental evidence and some interesting points emerge from thermodynamics considerations. Using a simple analysis, we found that for $\text{pH} \sim 3$ (the experimental value) the Gibbs free energy goes from positive to negative values at temperatures higher than 100 °C. Our method opens up the possibility of producing NPs free of toxic agents such as NaBH_4 , sodium citrate or sugars that are frequently used for metal reduction. This might allow reducing toxicity in NPs.

Authors wish to thank for financial support from Welch Foundation Agency under Project No. AX-1615 to the ICNAM of the University of Texas. We also thank Dave Olmos from UTSA for technical support. M. M. M. thanks CONICET.

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