Journal of
Nanoscience and Nanotechnology
Vol. 7, 1911–1915, 2007

Synthesis of Au Nanoparticles at "all" pH by H_2O_2 Reduction of $HAuCl_4$

Biswa Ranjan Panda[1] and Arun Chattopadhyay[1,2,*]

[1]Department of Chemistry and [2]Centre for Nanotechnology
Indian Institute of Technology Guwahati, Guwahati 781039, India

In this article we report the synthesis of Au nanoparticles (NPs), from $HAuCl_4$, in the pH range of 2.9 to 11.2 using H_2O_2 as the reducing agent. Ultraviolet-visible (UV-Vis) spectroscopy, transmission electron microscopy (TEM), and X-ray diffraction techniques have been used to characterize the Au NPs. UV-Vis spectral observation showed that the Au NPs synthesized in acidic conditions tend to generate particles with absorption maximum around 540 nm. On the other hand the NPs generated at a pH higher than 8.0 generally have broad absorption with maxima occurring beyond 600 nm. Interestingly, TEM analysis showed that the NPs generated at pH lower than 7.0 tend to be smaller and spherical in shape, whereas the particles generated at a pH beyond 7.0 tend to be non-spherical and larger in sizes or agglomeration of small particles. Also, we speculate on the mechanisms of reduction of $HAuCl_4$ by H_2O_2 under different pH conditions.

Keywords: Nanoparticles, Redox Reactions, pH, Hydrogen Peroxide, Surface Plasmon Resonance.

1. INTRODUCTION

In the currently dominant field of nanoscale science and technology chemical synthesis of various inorganic, organic, polymer, and composite nanoparticles (NPs) have special importance because of their ease of generation under different experiment conditions required for their use in appropriate applications.[1] In this regard, the synthesis of metal and semiconductor NPs under a variety of experimental conditions such as different solvents, acidic, alkaline pH as well as electrochemical generation of them have received added attention as these particles have wide application potential such as in photonics,[2] optoelectronics,[3] information storage,[4] catalysis,[5] bio-labeling,[6] and magnetic ferrofluids.[7] Understandably, a large number of methods have been developed for their size, shape, and capping-agent selective syntheses.[8]

Among all the inorganic NPs of interests Au has received the maximum attention because of its optical, catalytic, electrical properties that are not only size-dependent but also shape-dependent.[9] In addition, Au NPs have been functionalised with alkane thiols, proteins, DNA, RNA, and a host of other substrates depending on the application purpose such as in electronics, bio-labelling, and drug-delivery.[10–12] Further, because of the need for structure generation in two and three-dimensional[13] surfaces Au NPs have either been generated or immobilized on various substrate surfaces using primarily chemical, physical, and electrochemical methods.[14]

It is interesting to note that even though there are a large number of methods for the generation of Au NPs under different experimental conditions, there is no single or simple scheme to generate Au NPs at various pH, especially with the use of a single reducing agent. This is important considering the application potential of Au NPs with respect to their functionalization or composite formation under various pH conditions.

Herein we report the generation of Au NPs in the pH range of 2.9 through 11.2 by the reduction of $HAuCl_4$ using H_2O_2 as the reducing agent. Even though it is a common belief that H_2O_2 is a typical oxidizing agent and it can reduce $HAuCl_4$ only under alkaline condition, we found that Au NPs could be generated in the pH range mentioned above. Our study is based on an earlier observation that even under acidic pH condition H_2O_2 could reduce $HAuCl_4$.[15] We decided to find a general method of synthesis of Au NPs in aqueous solution from $HAuCl_4$ precursor using H_2O_2 as the reducing agent. We have been successful in obtaining such Au NPs in the above pH range. The method is primarily based on addition of H_2O_2 to an aqueous $HAuCl_4$ solution where the pH of the starting solution was adjusted by using either HCl or NaOH as per the requirement. In all the cases the solution turned coloured in a matter of about 2 min. UV-Vis spectra

*Author to whom correspondence should be addressed.

 1533-4880/2007/7/1911/005 doi:10.1166/jnn.2007.740

of the product solution in acidic pH consisted of peaks characteristic of that of Au NPs occurring around 540 nm. On the other hand the spectra of Au NPs solution above pH 8.0 results a broad peak having maximum absorption above 600 nm, which increases in wavelength with the increase of pH. Transmission electron microscopic (TEM) observations indicated the formation of primarily spherical NPs with typical average size of about 5–10 nm when the initial pH was in the acidic range. On the other hand the Au NPs generated under alkaline condition were of large sizes and of non-spherical shapes. X-ray diffraction measurements showed the growth of lattices in all three planes, namely, (111), (200), and (220) under all pH conditions.

2. EXPERIMENTAL DETAILS

In a typical experiment, 8.5 mM sodium dodecyl sulphate (SDS, from Merck) was prepared in 10 ml Milli-Q filtered water. 50 μl of 1.7×10^{-2} M of $HAuCl_4$ (diluted from original 17% w/v in dilute HCl solution as purchased from Aldrich) was added to the above solution such that final $HAuCl_4$ concentration was 8.5×10^{-5} M. This resulted a solution of pH around 3.5. To the above solution 200 μl of H_2O_2 [38% w/v, Merck] was added at a time. This resulted in an intense pink coloured solution and the resultant solution had a pH of 3.3.

In order to perform the reaction at different pH, the initial SDS containing $HAuCl_4$ solution was treated either with HCl (taken from stock solution) or with NaOH (taken from stock solution), as appropriate, to obtain a particular pH of the resulting solution. 200 μl of H_2O_2 (38% w/v, Merck) was then added to each of the solution prepared at different initial pH values. In all the cases the solution turned coloured in about 2 min of the addition of H_2O_2. We also observed that in all the reactions the pH of the final product solution reduced in comparison to the initial solution (solution before the addition of H_2O_2) and the pH change varied from solution to solution depending on the initial pH such that at higher initial pH (alkaline) the change was much more than that at lower pH (acidic).

UV-Visible spectra of the resulting solutions were recorded as such in a cuvette by using a Perkin-Elmer Lambda 25 spectrophotometer.

Transmission electron microscopic pictures were recorded after evaporation of a drop of the solution in carbon-coated copper grid using a JEOL electron microscope (Model 1200EX) operated at 120 kV accelerating voltage. X-ray diffraction measurements was performed by evaporating a part of the solution on a microscope glass slide and then recording in a Seifert powder X-ray diffractometer (Model 3003TT).

3. RESULTS AND DISCUSSION

When H_2O_2 was added to a solution containing $HAuCl_4$ and SDS with pH of the solution adjusted to a predetermined value the colouration occurred typically within about 2 min of addition. The colour of the solution was stable for more than a month without any observable change. It may also be mentioned here that the colour was stable even in the absence of SDS at least for a few days. An important question that arises out of the use of commercial H_2O_2 is whether the stabilizer used can also reduce $HAuCl_4$ or not. In order to find out the answer, we first dried 200 μl of H_2O_2, used as above, by simple air evaporation after keeping the solution in a beaker. We then added the other solution ($HAuCl_4$ and SDS in water) to the beaker and gently shook the beaker for mixing. We found no colouration of the solution under an arbitrary pH condition. This means that in the main reaction H_2O_2 reacted with $HAuCl_4$ and not the stabilizing agent(s) to produce the NPs. Commercial H_2O_2 stabilizing agents generally contains either of boric acid, glycerol, or salicylic acid. We tested with each of these reagents independently by individually treating them with $HAuCl_4$ plus SDS solution. For example, we had prepared three different 20 ml solutions each containing either of 5.3×10^{-2} M salicylic acid, or 9.5×10^{-3} M of boric acid or 2.6×10^{-2} M glycerol. We then added $HAuCl_4$ to each of the solutions such that the final concentration of $HAuCl_4$ in each of them was 8.5×10^{-5} M. We did not observe any immediate colouration; however there was a faint pink colour in the case of glycerol after two days of keeping the solution and in other two reagents the colour was brown also after two days. Thus it is safe to assume that H_2O_2 is the primary reagent that leads to the NPs upon treatment with $HAuCl_4$. Figure 1(A) shows the photographs of five resultant solutions of $HAuCl_4$ (in SDS) when treated with H_2O_2 at five different initial pH values such that the final pH values of the solutions were 3.7, 4.9, 6.3, 7.6, and 10.0, respectively. We had observed that the change in the pH of the solution before and after addition of H_2O_2 (and after colouration) in

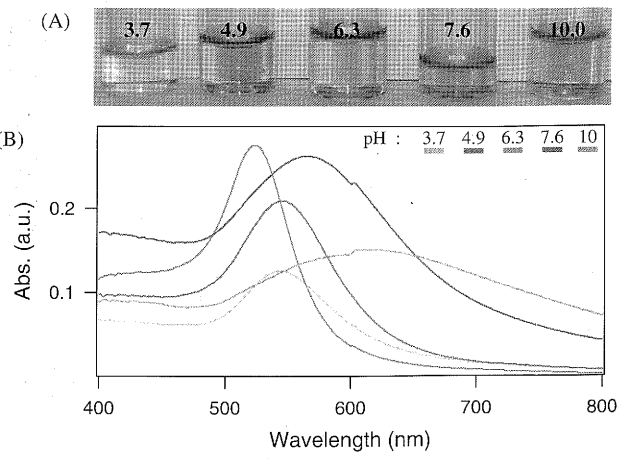

Fig. 1. (A) Photographs of Au colloids synthesized using the present method at different pH. The number on the vial indicates the final pH of the solution in which the colloids were generated. (B) UV-Visible spectra of Au colloids synthesized at different pH of the solutions.

a way that the final solution always had a lower pH value than that of the solution before addition of H_2O_2. As can be seen from the pictures, different initial pH resulted in different coloured solution with lower pH generating more pinkish colour, whereas at higher pH the solution is violet or blue.

UV-Vis absorption spectra of the corresponding solutions shown in Figure 1(B) indicate that the colour of the solutions might be due to formation of Au NPs as the spectra are that of characteristic surface plasmon resonance of Au NPs. However, it is interesting to note that the absorption maximum is dependent on the pH of the solution. Colloidal solutions of spherical Au NPs typically give rise to a single surface plasmon resonance peak at around 535 nm, which depends on their sizes. On the other hand when asymmetric particles are formed in the solution typically two peaks are observed, one of which occur at lower wavelength (535 nm or so) due to transverse plasmon excitation and a second one at a higher wavelength due to the longitudinal surface plasmon resonance. Additionally, in one of our previous work we have observed that shape-specific NPs can also give rise to two peaks instead of one.[9b] For example, triangular Au NPs have been shown to have two peaks one occurring at around 535 nm while the other one typically occurring at a relatively higher wavelength of about 750 nm. On the other hand, hexagonal Au NPs have their longitudinal plasmon resonance peak at a much higher wavelength of around 900–1000 nm. In the present set of experiments, we did not observe any second peak in the absorption spectra of Au NPs in the region of our studies (up to 1100 nm, but not shown here). Thus in our cases only spherical or nearly spherical particles are probably formed.

Further investigations of the product solutions by TEM reveal that at a lower pH typically uniform small sized NPs are formed. This is shown in Figure 2. The particle formed at a pH 2.9 have sizes that are typically in the range of 5–10 nm. On the other hand with the increase in pH there is an apparent increase in particle size. For example, as shown in the panels of Figure 2, the NPs generated at pH 7.2, and 7.6, respectively have typical particle diameters of 60–80 nm. It is also interesting to note that the NPs formed at higher pH are not exactly spherically symmetrical as can be seen in Figure 2 for pH values of 7.2 and 7.6. On the other hand their shapes cannot be assigned any specific geometric form although they are close to being spherical. Also shown in Figure 2 is the TEM of Au NPs prepared at a pH of 11.2. It is interesting to note that these particles seem to be an agglomeration of smaller particles that having individual diameter in the range of 25–30 nm. We would like to mention here that there have been reports of the role of ions in the formation of non-spherical NPs[16] as well as the role of hydroxide[17] ions in the formation of irregularly shaped particles and their corresponding assembly. In our case a host of factors like pH at which the

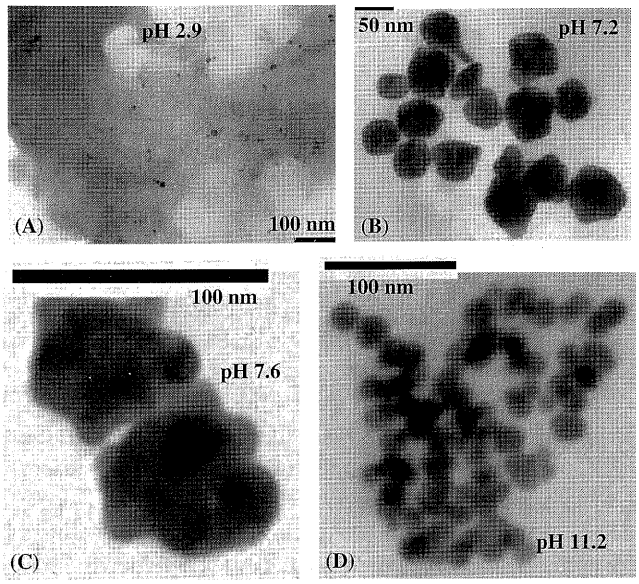

Fig. 2. TEM of the Au NPs generated at various pH values. The pH label in each panel is the pH at which the Au NPs were generated and the corresponding TEMs are due to Au NPs formed at that pH.

particles are formed, the presence of ions such as Na^+, OH^-, Cl^- and the stabilizing agents probably contribute towards the sizes and shapes of particles formed.

Figure 3 shows the powder XRD patterns of some of these NPs generated at two different pH values and recorded after evaporation of drops of NPs solution on glass slides. Figure 3(A) is the XRD patterns obtained from the Au NP solution prepared at pH 3.1. On the other hand the XRD patterns in Figure 3(B) is due to Au

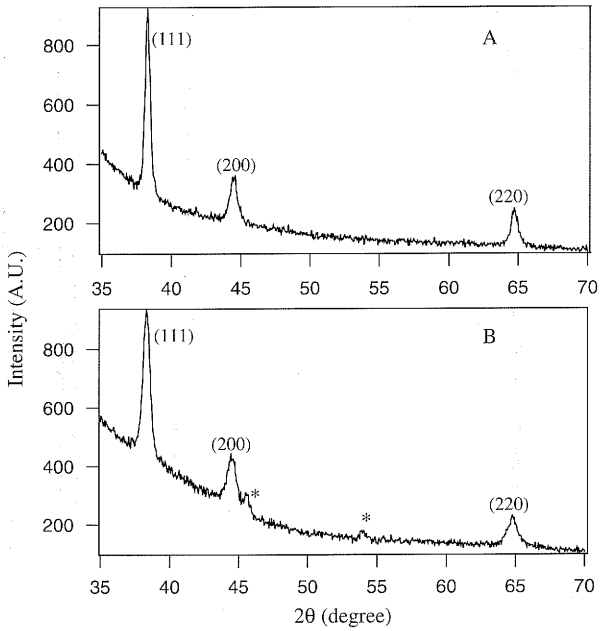

Fig. 3. XRD patterns of Au NPs generated at two different pH values; one at pH 3.1 (panel A) and the other is at pH 9.8 (panel B). The asterisk marks (*) are due to the peaks of NaCl with lattices of (220) and (311).

NPs prepared at pH 9.8. Both the figures clearly show that the particles formed have growth in all three lattice planes namely (111), (200), and (220) of Au nanocrystals as the XRD patterns have peaks at 38.5°, 44.5°, and 64.5° characteristic of growth of all the above three planes of Au respectively. This also support that the particles generated under the present conditions are three dimensional in nature and no disc or such shapes were obtained. We would like to make an observation here with respect to the XRD patterns in Figure 3(B), which is due to the Au NPs generated under alkaline pH. In addition to three prominent peaks due to the three planes of Au NPs there are two more small peaks occurring at 45.5° and 54°. These are not due to Au NPs in the film rather due to the NaCl formed by the reaction of NaOH with HCl present in the medium. The peaks are due to the lattices (220) and (311) of NaCl. This is especially the case as we have observed that in acidic condition the Au NPs generated had peaks only due to Au and no other impurity. On the other hand we have used NaOH to change the pH of the solution, the presence of NaCl contributed to the extra XRD peaks of the Au NPs generated under alkaline pH.

A fascinating and often intriguing question comes when H_2O_2 is used as the reducing agent especially while reducing such a species as Au^{3+} to Au. One would normally be quick to dismiss the possibility of reduction of Au^{3+} to Au under acidic condition as the standard reduction potential of $Au^{3+} \rightarrow Au$ is 1.498 V, while that of H_2O_2 to H_2O under acidic condition is 1.776 V. This makes it apparently improbable to reduce Au^{3+} to Au by H_2O_2. In the present set of experiments $HAuCl_4$ was used as the precursor for Au generation. Consideration of the standard electrochemical potentials of the following reactions would help understand the possibility of reductions of $HAuCl_4$ by H_2O_2 under all pH conditions.[18]

Reaction	E^0(V)	
$AuCl_4^- + 3e = Au + 4Cl^-$	+1.002	(1)
$H_2O_2 = O_2 + 2H^+ + 2e$	−0.695	(2)
$H_2O_2 + 2OH^- = O_2 + 2H_2O + 2e$	+0.146	(3)
$H_2O_2 + 2H^+ + 2e = 2H_2O$	+1.776	(4)

As evident from the above, reaction (1) and reaction (2) can combine resulting into the reduction of $AuCl_4^-$ to Au by H_2O_2. In other words, the following reaction is thermodynamically favourable

$$2AuCl_4^- + 3H_2O_2 = 2Au + 8Cl^- + 3O_2 + 6H^+ \quad (5)$$

The standard redox potential of the net reaction is +0.307 V. The same reaction would occur even in neural pH. On the other hand, under alkaline condition the reduction is even more favored as the net standard redox potential is +1.148 V. This is a combination of reactions (1) and (3). The overall reaction under alkaline condition would be as follows.

$$2AuCl_4^- + 3H_2O_2 + 6OH^- = 2Au + 8Cl^- + 3O_2 + 6H_2O \quad (6)$$

Thus reduction of $HAuCl_4$ under all pH conditions is possible although the exact mechanism of reduction may vary depending on the pH of reaction medium.

In brief, herein we have reported the generation of Au NPs from $HAuCl_4$ by reduction using H_2O_2 in aqueous solution. The UV-Vis absorption spectra of the NPs generated at various pH consisted of single peaks characteristic of plasmon resonance and were different depending on pH with peak shifting towards higher wavelength as the pH was increased. TEM pictures indicated that at lower pH the particles were generally spherical and small in sizes. The particles generated at higher pH tend to be larger and sometimes agglomerated to form large structures. We are working on the coupling of this reaction with other reactions using either the product NPs or H_2O_2 or both as the precursor for subsequent reactions.

Acknowledgments: We thank DST (SR/S5/NM-68/2002, 2/2/2005-S.F, and No. DST/TSG/ME/2003/83) and, New Delhi for grants, Dr. Renu Pasricha (NCL, Pune) and Mr. S. Sarma and Mr. M. Kar (IITG), Central Instruments Facility (IITG) for help with various measurements.

References and Notes

1. P. V. Kamat, *J. Phys. Chem. B* 106, 7729 (**2002**).
2. S. A. Maier, M. L. Brongersma, P. G. Kik, S. Meltzer, A. A. G. Requicha, and H. A. Atwater, *Adv. Mater.* 13, 1501 (**2001**).
3. T. Miyasaka and T. N. Murakami, *Appl. Phys. Lett.* 85, 3932 (**2004**).
4. S. Kolliopoulou, P. Dimitrakis, P. Normand, Hao-Li Zhang, N. Cant, S. D. Evans, S. Paul, C. Pearson, A. Molloy, M. C. Petty, and D. Tsoukalas, *J. Appl. Phys.* 94, 5234 (**2003**).
5. J. Liu, Y. Chi, H. Lin, C. Mou, and B. Wan, *Catalysis Today* 93–95, 141 (**2004**); (b) B. L. V. Prasad, S. I. Stoeva, C. M. Sorensen, V. Zaikovski, and K. J. Klabunde, *J. Am. Chem. Soc.* 125, 10488 (**2003**).
6. M. Bruchez, Jr., M. Moronne, P. Gin, S. Weiss, and A. P. Alivisatos, *Science* 281, 2013 (**1998**).
7. K. S. Suslick, M. Fang, and T. Hyeon, *J. Am. Chem. Soc.* 118, 11960 (**1996**).
8. (a) U. Schlotterbeck, C. Aymonier, R. Thomann, H. Hofmeister, M. Tromp, W. Richtering, and S. Mecking, *Adv. Funct. Mater.* 14, 999 (**2004**); (b) B. Pal, T. Torimoto, K. Iwasaki, T. Shibayama, H. Takahashi, and B. Ohtani, *J. Phys. Chem. B* 108, 18670 (**2004**); (c) M. J. Hosteler, J. E. Wingate, C.-J. Zhong, J. E. Harris, R. W. Vachet, M. R. Clark, J. D. Londono, S. J. Green, J. J. Stokes, G. D. Wignall, G. L. Glish, M. D. Porter, N. D. Evance, and R. W. Murray, *Langmuir* 14, 17 (**1998**).
9. T. R. Tshikhudo, Z. Wang, and M. Brust, *Mater. Sci. Technol.* 20, 980 (**2004**); (b) T. K. Sarma and A. Chattopadhyay, *Langmuir* 20, 3520 (**2004**); (c) S. Kan, T. Mokari, E. Rothenberg, and U. Banin, *Nature Mater.* 2, 155 (**2003**).

10. (a) K. I. Bolotin, F. Kuemmeth, A. N. Pasupathy, and D. C. Ralph, *Appl. Phys. Lett.* 84, 3154 (**2004**); (b) S. I. Khondaker and Z. Yao, *Appl. Phys. Lett.* 81, 4613 (**2002**).
11. (a) J. J. Storhoff and C. A. Mirkin, *Chem. Rev.* 99, 1849 (**1999**); (b) R. Elghanian, J. J. Storhoff, R. C. Mucic, R. L. Letsinger, and C. A. Mirkin, *Science* 277, 1078 (**1997**); (c) T. A. Taton, R. L. Letsinger, and C. A. Mirkin, *Science* 289, 1757 (**2000**).
12. G. F. Paciotti, L. Myer, D. Weinreich, D. Goia, N. Pavel, R. E. McLaughlin, and L. Tamarkin, *Drug Delivery* 11, 169 (**2004**).
13. (a) L. Motte, F. Billoudet, E. Lacaze, J. Douin, and M. P. Pileni, *J. Phys. Chem. B* 101, 138 (**1997**); (b) S. Chen, *Adv. Mater.* 12, 186 (**2000**).
14. (a) S. Paul, C. Pearson, A. Molloy, M. A. Cousins, M. Green, S. Kolliopoulou, P. Dimitrakis, P. Normand, D. Tsoukalas, and M. C. Petty, *Nano Lett.* 3, 533 (**2003**); (b) S. Shih, W. Su, Y. Lin, C. Wu, and C. Chen, *Langmuir* 18, 3332 (**2002**).
15. T. K. Sarma, D. Chowdhury, A. Paul, and A. Chattopadhyay, *Chem. Commun.* 1048 (**2002**).
16. A. Filankembo and M. P. Pileni, *J. Phys. Chem. B* 104, 5865 (**2000**).
17. K. K. Caswell, C. M. Bender, and C. J. Murphy, *Nano Lett.* 3, 667 (**2003**).
18. R. C. Weast, D. R. Lide, M. J. Astle, and W. H. Beyer, in CRC Handbook of Chemistry and Physics, 70th edn., CRC Press, Boca Raton, Florida (**1989–1990**), p. D-151–D-153.

Received: 17 March 2006. Accepted: 21 September 2006.