Role of Coagulation in the Synthesis of Gold Nanoparticles by Citrate Reduction

Sankar Kalidas Sivaraman*, Mohana Rao*, Sanjeev Kumar* and Venugopal Santhanam*

We investigate the kinetics of reduction of chloroauric acid during the synthesis of gold nanoparticles by citrate reduction protocol, to understand the effect of molar ratio of citrate to chloroauric acid on the mean particle size (d_p). Unlike the expected trend, the rate of reduction is higher at lower molar ratio (large d_p) than that at higher ratio (small d_p). The variation of pH as a function of molar ratio is found to be the main cause of the observed trend. At lower molar ratio (lower pH), the electrostatic stabilization is poor, whereas at higher molar ratio (pH ~7) it is good. A combination of fast reaction and good stabilization that can lead to small monodisperse particles never occurs together in the standard citrate reduction protocol. By avoiding coagulation using additional stabilizer, we show that the minimum size of nanoparticles synthesized in citrate reduction protocol, presently at 16 nm, can be lowered by a significant factor to 6 nm.

INTRODUCTION

Nanomaterials possess fascinating size tunable properties and their properties vary from that of bulk. Gold nanoparticles are one of the widely used nanomaterials and have potential applications in a variety of fields like photonics, nanoelectronics, energy conversion, biological engineering, sensors etc (Daniel and Astruc, 2004; Shipway et al., 2000). Synthesis of nanoparticles of a desired monodisperse size and shape is a challenging task and this is important due to their size and shape dependent properties. Variety of methods are exploited to synthesize gold nanoparticles, like two phase method, reverse micelle, ultraviolet irradiation, sonochemical process and reduction in aqueous phase (Cushing et al., 2004). Amongst these, citrate reduction pioneered by Turkevich et al. (Turkevich et al. 1951) is a widely used protocol. Eventhough the citrate reduction is widely used, it fails to synthesize nanoparticles of size less than 10 nm that have more interesting applications in nanoelectronics, surface enhanced raman spectroscopy (Dieringer et al., 2006), drug delivery (Ghosh et al., 2008), catalysis (Somorjai et al., 2008) etc. Currently, hazardous chemicals like hydrazine, sodium borohydride etc.(Cushing et al., 2004) are employed to synthesize smaller nanoparticles (< 10nm). Hence, it is essential to find an alternate facile, green route to synthesize nanoparticles of size less than 10 nm.

Investigation of the various processes involved in the citrate protocol, like rate of reduction of metal salt, nucleation, growth and coagulation, is necessary to understand, model and improve the protocol. Pong et al. (Pong et al., 2007) studied the formation of intermediates during the synthesis and found the presence of nanowire intermediates. Ji et al. (Ji et al., 2007) investigated the role of citrate in altering the pH of solution, its effect on the synthesis and showed that the change in pH causes variation in the particle size. Gonzalez et al. (Gonzalez et al., 2007) proposed an electrochemical model for formation of intermediates and breakdown into smaller nanoparticles. Here, we study the kinetics of reduction of chloroauric acid and analyze it with respect to the size of nanoparticles formed. We show that the coagulation of nanoparticles during the synthesis plays a major role in determining the size of nanoparticles at lower molar ratio. As an outcome of the detailed analysis, we propose a new route to synthesis nanoparticles of size smaller than 10 nm and validate it experimentally.

EXPERIMENTAL DETAILS

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*Department of Chemical Engineering, Indian Institute of Science, Bangalore 560012;
Email:venu@chemeng.iisc.ernet.in

Synthesis of gold nanoparticles by citrate reduction was performed as described by Frens et al.(Frens et al., 1973) except that the temperature was changed to 60°C. The molar ratio (MR) of citrate to chloroauric acid was varied from 0.6 to 50. If necessary, the pH of citrate solution was changed to desired value using hydrochloric acid. Kinetic studies were performed either by removing an aliquot of sample from reaction mixture in a beaker or by monitoring time evolution of UV visible spectra at millisecond time scale in a Stop Flow Module. The absorbance value of chloroauric acid at a wavelength of 315 nm (after adjusting the pH to 2) and nanoparticle at 520 nm were monitored with time. In the case of Stop Flow Module, Multivariate Curve Resolution – Alternating Least Squares (MCL-ALS) method was used to extract kinetic information (Mohana Rao, 2009). To study the effect of stabilizers, a desired concentration of the stabilizer was added to chloroauric acid.

UV visible spectrometer from Systronics instruments was used to measure absorbance. Stop Flow Module from Biologic, S. A, was used to obtain kinetic data. Carl Zeiss FESEM was used to take images of drop coated sample on silicon wafer. For TEM characterization, nanoparticle solution was drop coated on carbon film coated copper grid and Tecnai F30 operating at 200KV was used for imaging.

RESULTS AND DISCUSSION

The synthesis of nanoparticles in liquid phase involves reduction of the metal salt and is commonly explained through LaMer model (LaMer, 1952). The reduction of metal salt results in an increase of the concentration of gold atoms. As their concentration crosses a critical supersaturation, rapid nucleation begins. The sudden burst of nucleation results in a drop of the concentration of gold below the threshold and nucleation ceases. This is followed by the growth of nanoparticles. Unavailability of stabilizer on the surface of nanoparticles during the nucleation and growth phase can result in coagulation of nanoparticles. The size of the nanoparticles synthesized is generally tailored by varying the rate of nucleation or by varying the concentration of stabilizer. The change in concentration of reactant alters the rate of reduction which in turn controls the rate of nucleation. Fast reduction of the salt should result in higher rate of nucleation, leading to more nuclei and smaller particles; whereas slow reduction of salt lead to bigger nanoparticles. The change in the concentration of stabilizer can cause variation in the extent of coagulation during the synthesis and results in change of particle size. In the case of citrate reduction protocol, citrate acts as both the reducing agent as well as stabilizer. Here, the size of nanoparticles is tuned by varying the molar ratio of citrate to chloroauric acid and larger particles are formed at the lower values of molar ratio (Kumar et al., 2007)

Characterization of Intermediates

During the synthesis of nanoparticles by citrate method the colour of solution, which is colourless initially, turns blue and then wine red. The UV visible spectra of the reaction mixture at different stages of synthesis are shown in figure 1. The characteristic colour of nanoparticles arises due to size dependent surface plasmon resonance. Smaller particles have higher resonance frequency than bigger particles. The presence of blue colour during the synthesis indicates the presence of bigger particles. The observation of bigger intermediates is a deviation from LaMer model which suggests that the particle size grows monotonically.
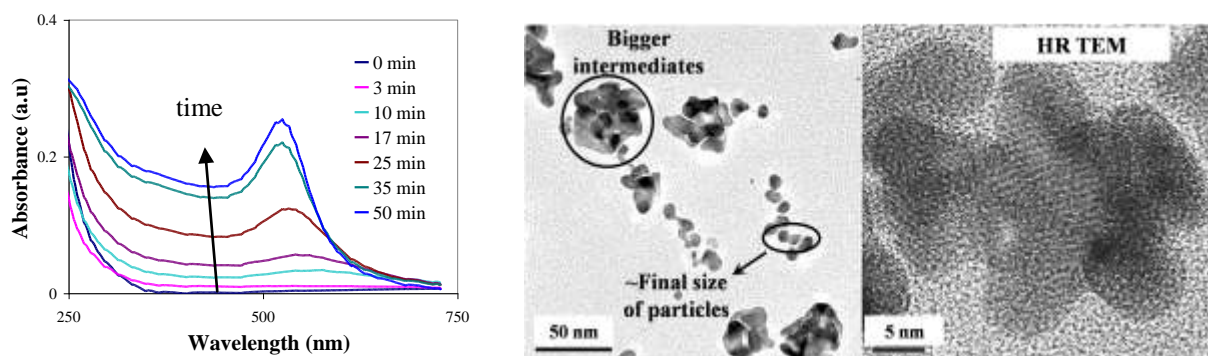

Figure 1: UV visible spectra obtained at various stages of nanoparticle formation and TEM images of intermediate sampled at 17 minutes.

Chow et al. (Chow et al., 1994) investigated the intermediate formation during the synthesis in a modified citrate reduction protocol at 50°C and reported that the bigger intermediates are "reversible aggregates" formed due to the preferential adsorption of auric ions that do not hinder the growth. Their explanation was in accordance with LaMer model. We investigated the presence of the intermediate in the protocol described by Frens et al. at 60°C and at a molar ratio of 1.5. The TEM image of intermediate shows a completely different image from that expected from that expected based on the mechanism proposed by Chow et al. The intermediates are single crystalline large particle with multiple lobes. These intermediates break down into small particles. The process of peptization is not clearly understood yet. During the synthesis of nanoparticles at lower molar ratio, the solution turns blue but remains blue till the end. To understand the underlying process determining the nanoparticle size in the synthesis, we investigated the kinetics of chloroauric acid reduction and dynamics of nanoparticle formation at different molar ratios.

Kinetics of Chloroauric Acid Reduction at Different Molar Ratio

Initial experiments were carried out following the Frens protocol without adjusting pH. The absorbance of chloroauric acid and nanoparticles was determined at different time intervals. Figure 2 shows the changes in the absorbance of chloroauric acid with time at different molar ratio. A higher concentration of citrate should increase the rate of reduction. But the results clearly show that as the molar ratio increases from 0.6 to 20, the rate of reduction decreases and then increases again for molar ratios greater than 20. Given the reduction rates, one would expect that the faster reduction will yield smaller nanoparticles. But contrary to the expectation, faster reaction results in nanoparticles with larger mean size than those formed under the condition of slower reduction.
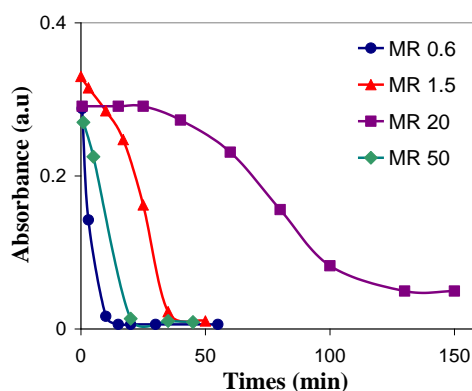

Figure 2: Kinetics of chloroauric acid reduction at different molar ratio

Ji et al. (Ji et al., 2007) investigated the synthesis of citrate reduction and reported that the pH of reaction mixture controls the rate of reduction. Sodium citrate is a buffering agent and hence at higher molar ratio the pH of the reaction mixture turns basic and at lower ratio, the pH remains acidic. Chloroauric acid possesses pH dependent reactivity (Ji et. al, 2007). At lower molar ratio, the pH remains acidic and the active form of chloroauric acid results in faster reaction while at higher molar ratio, pH is basic and the inactive form of chloroauric acid leads to slow reaction. Even though this mechanism explains the fast reduction at lower molar ratio, it does not account for the variation of the mean size of nanoparticles with molar ratio.

To compare rate of reduction at different molar ratios and decouple its effect on mean particle size from that produced by poor stabilization, the reactions must be carried at same pH. Figure 3 shows the rate of reduction of chloroauric acid at different molar ratio but at same pH. These experiments were carried out in a SFR and analyzed using MCR-ALS method. Because of the constant pH conditions, it is feasible to obtain the kinetics of reduction of chloroauric acid as well as that of nanoparticle formation. As expected, the rate of reduction is slow at lower molar ratio and the mean size of nanoparticles synthesized is higher than that synthesized at higher molar ratio. For an increase in the value of molar ratio from 0.6 to 5.2, the mean size of the particles decreased from 400 nm to 40 nm. It is also interesting to note that the experiments conducted with molar ratio of 1.5 at pH 3.2 yielded particles of larger mean

size than that conducted at pH 7.0. These results clearly indicate that pH dependent stabilization plays a critical role in determining the mean size of nanoparticles formed by the citrate reduction protocol.
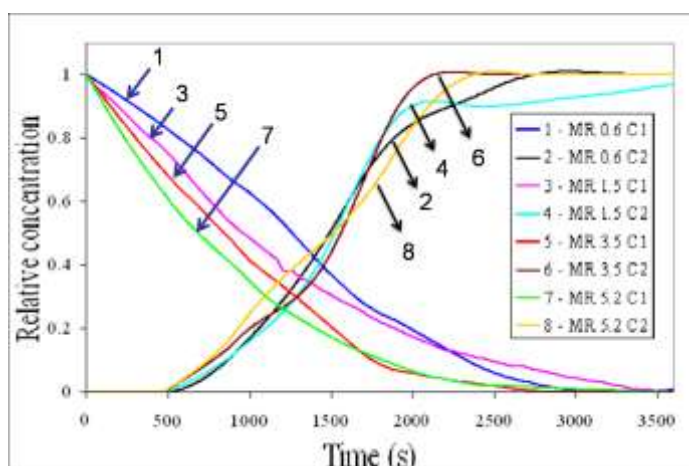

Figure 3: Kinetics of chloroauric acid reduction and nanoparticle formation at different MR and pH 3.2. (C1: Chloroauric acid and C2: Nanoparticles)

pH Dependent Coagulation During Synthesis

During the growth phase of nanoparticles, the surface area increases with time. The new surface area generated must be covered at faster rate by the stabilizers than the collision rate of nanoparticles to avoid coagulation between two nanoparticles. In the case of citrate reduction, citrate anions provide electrostatic stabilization stabilization by specific adsorption onto the gold surface. As there are three ionisable carboxylic groups in citrate, with each having different pKa values, the overall charge on gold nanoparticles in solution is highly sensitive to pH of the solution. For a given condition of growth, the electrostatic stabilization provided by citrate at acidic pH is lower than the stabilization provided by citrate at basic pH. Thus, nanoparticles synthesized at basic pH are less prone to coagulation than those synthesized at acidic pH. The reduction of chloroauric acid is fast at acidic pH, but higher extent of coagulation leads to bigger particles. A combination of fast reduction and good stabilization of particles during the growth phase never occurs together in the standard citrate reduction protocol. In order to minimize the extent of coagulation during a fast reaction, an additional stabilizer must be added during the synthesis.

Effect of the Presence of Stabilizer

The presence of additional stabilizer can decrease the extent of coagulation and result in particles having smaller size. Different stabilizers, like polyvinylpyrrolidone (0.003 mM), sodium dodecyl sulphate (3 mM), Triton X100 (0.11 mM), Tween 40 (0.02 mM), chitosan (0.01% w/v) and aspargine (0.8 mM), were used and the effect on final nanoparticle size was explored.
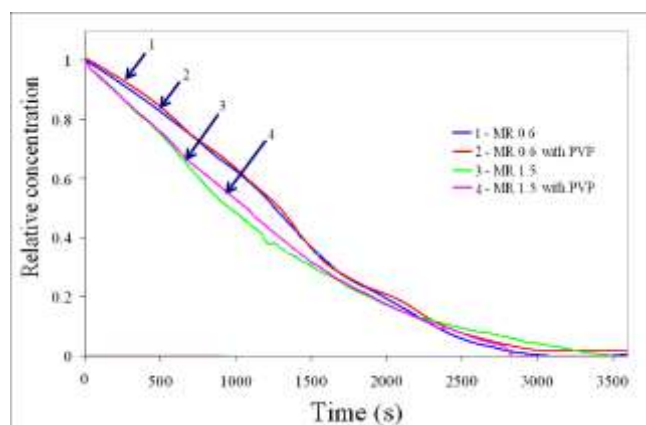

Figure 4: Kinetics of chloroauric acid reduction and formation of nanoparticles with and without PVP.

The stabilizers were selected such that they do not interact with chloroauric acid and citrate during the reaction time scale (~ 600s). Figure 4 shows the change in concentration of chloroauric acid in the presence and absence of PVP at two different molar ratios, obtained by using MCR-ALS analysis of SFR data. These results show that the reduction rate remains unaffected by the presence of PVP at these reaction conditions.

In case of ionic stabilizers, the concentration of stabilizer was lesser than the amount needed to cause coagulation by double layer compression. It is expected that the diffusion of stabilizers to the growing surface area of nanoparticles would be the limiting step for stabilization. Hence, the stabilizer of higher molecular weight should be ineffective when compared to the lower molecular weight stabilizers. But experimental results show that higher molecular weight stabilizers, PVP and chitosan, yield smaller nanoparticles than other stabilizers. Figure 5 shows scanning electron microscopy image of nanoparticles synthesized using different stabilizers.
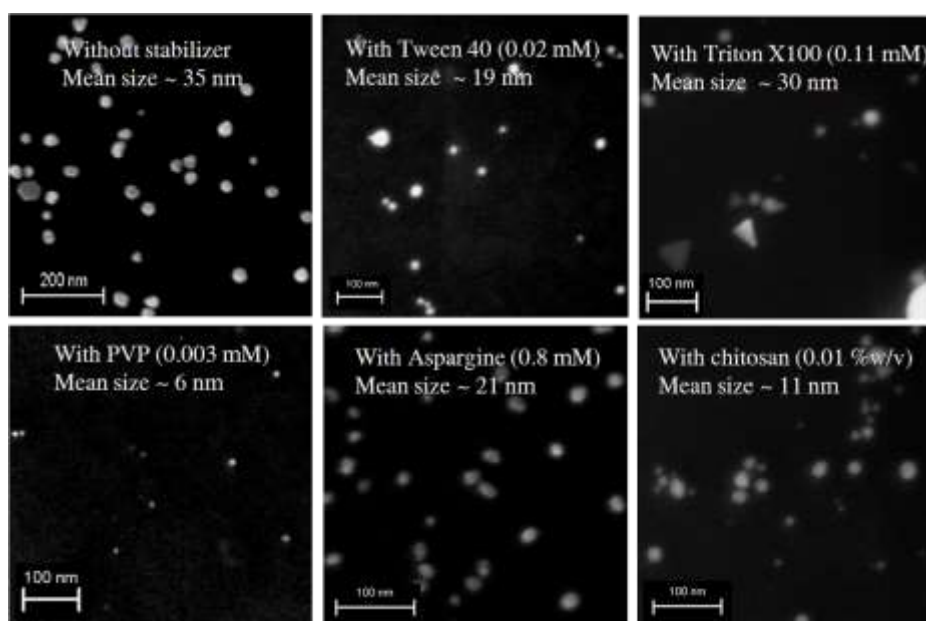

Figure 5: Scanning Electron Microscopy images of nanoparticles synthesized without and with different types of stabilizers. Reaction temperature = 60°C, pH = 3.8, Molar ratio [citrate]/[chloroauric acid]=1.5

Preliminary experiments conducted with mixture of stabilizers, consisting of low molecular and high molecular weight compounds, proved to be more effective in producing monodisperse nanoparticles (Coefficient of Variance ~ 10%).

CONCLUSIONS

We investigated the rate of reduction of chloroauric acid in the standard citrate reduction protocol at different molar ratios. We showed through kinetic analysis that the opposing trend of rate of reduction and strength of stabilization with pH variation caused by changing the molar ratio of citrate to chloroauric acid limits the minimum size of nanoparticles that can be synthesized. Based on this insight, we have modified the protocol by adding various stabilizers to form smaller and more monodisperse particles. PVP and chitosan proved to be good stabilizers resulting in nanoparticles of mean size 6 nm and 11 nm respectively.

ACKNOWLEDGEMENT

REFERENCES

Chow, M. K. and Zukoski, C. F; 1994, Gold sol formation: Role of Colloidal Stability. *J. Colloid Interf. Sci.*, 165, 97- 109.

Cushing, B. L.; Kolesnichenko, V. L. and O'Connor, C. J.; 2004, Recent Advances in the Liquid-Phase Syntheses of Inorganic Nanoparticles. *Chem. Rev.* 104, 3893 – 3946.

Daniel, M. C. and Astruc, D.; 2004, Gold nanoparticles: Assembly Supramolecular Chemistry, Quantum-Size-Related Properties, Applications toward Biology, Catalysis, and Nanotechnology. *Chem. Rev..* 104, 293-346.

Dieringer, J. A.; McFarland, A. D.; Shah, N. C.; Stuart, D. A.; Whitney, A. V.; Yonzon, C. R.; Young, M. A.; Zhang, X. and Van Duyne, R. P.; 2006, Surface Enhanced Raman Spectroscopy: New materials, Concepts, Characterization Tools, and Applications. *Faraday Disc., 132*, 9-26.

Frens, G.; 1973, Controlled Nucleation for the Regulation of the Particle Size in Monodisperse Gold Suspensions. *Nature*, 241, 20-24.

Ghosh, P.; Han, G.; De, M.; Kim, C. K.and Rotello, V. M.; 2008, Gold Nanoparticles in Delivery Applications. *Adv. Drug Del. Rev., 60*, 1307-1315.

Gonzalez, B. R.; Mulvaney, P. and Liz-Marzan, L. M.; 2007. An Electrochemical Model for Gold Colloid Formation via Citrate Reduction. *Z. Phys. Chem*., 221, 415-42

Ji, X.; Song, X.; Li, J.Bai, Y.; Yang, W. and Peng, X.; 2007, Size Control of Gold Nanocrystals in Citrate Reduction: The Third Role of Citrate, *J. Am. Chem. Soc.*, 129, 13939 – 13948

LaMer V.K.; 1952, Nucleation in phase transtition. *Ind. Eng. Chem.* 44, 1270-1277.

Mohan Rao; 2009, Kinetics, Data Analysis and Modeling of Gold Nanoparticle Formation. ME thesis, IISc

Kumar, S.; Gandhi, K. S. and Kumar, R.; 2007, Modeling of Formation of Gold Nanoparticles by Citrate Method. *Ind. Eng.Chem. Res*., 46, 3128-3136

Pong, B. K.; Elim, H. I.; Chong, J. X.; Ji, W and Trout, B. L ; 2007, New Insights on the Nanoparticle Growth Mechanism in the Citrate Reduction of Gold III Salt: Formation of Au Nanowire Intermediates and its Optical Non Linear Properties, *J. Phys. Chem. C* ., 111, 6281-6287.

Shipway, A. N.; Katz, E. and Willner, I.; 2000, Nanoparticle Arrays on Surface for Electronic, Optical and Sensor Application. *ChemPhyChem*., 1, 18-52.

Somorjai, G. A. and Park, J. Y.; 2008, Colloid Science of Metal Nanoparticle Catalyst in 2D and 3D Structures. Challenges of Nucleation, Growth, Composition, Particle Shape, Size Control and Their Influence on Activity and Selectivity. *Top. Catal.*, *49*, 126-135.

Turkevich, J.; Stevenson, P.C. and Hiller, J.; 1951, A Study of the Nucleation and Growth Processes in the Synthesis of Colloidal Gold. *Discuss. Faraday Soc*., 11, 55-75.