Process Engineering Studies on Synthesis of Gold Nanoparticles by Turkevitch Method

Anirban Chakraborty[a], Tausif Ahmad[b], Bawadi B. Abdullah[b], Sekhar Bhattacharjee*[b]

[a]Department of Chemical Engineering, University of Calcutta,92, A.P.C. Road, Kolkata-700 009, India
[b]Department of Chemical Engineering, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 31750 Tronoh, Perak, Malaysia
sekharbhatta@gmail.com

Process design of a reactor for gold nanoparticle (AuNP) synthesis requires reaction rate data and an appropriate kinetic model. In the present work, rate parameters for AuNP synthesis by Turkevitch method were investigated. Influences of process conditions- molar ratio of reactants (chloroauric acid to trisodium citrate: 0.33 - 5.32) and temperature (333 -373 K) of reaction medium on kinetic parameters were studied. From an Arrhenius plot activation energy for AuNP synthesis reaction was estimated to be 21.69 ±2.3 kJ/mol suggesting that precursor reduction occurred in aqueous phase followed by diffusion controlled nucleation and aggregation of reduced metals ions forming larger nanoparticles. Increase or decrease of molar ratio beyond the optimal range (M = 0.75 - 1.35) led to slower reaction rate, larger particle diameter and formation of AuNPs, which were unsuitable for biological applications.

1. Introduction

Gold nanoparticles are extensively used for bioimaging, protein conjugation and drug delivery due to their distinct optical, spectroscopic and catalytic properties. Extensive research data were published in the last decade on gold nanoparticles and their various preparative methods, mechanisms of reaction, characterization, growth kinetics and stability (Basu et al., 2004).

There are several physical, chemical and biological approaches for gold nanoparticle synthesis. Physical methods, such as, ultraviolet irradiation, lithography, laser ablation, ultrasound and photochemical reduction of gold have been used successfully to produce gold nanoparticles (Daniel and Astruc, 2004). Simplest procedure for AuNP preparation is reduction of chloroauric acid ($HAuCl_4$) using trisodium citrate. This method was introduced by Turkevitch in 1953 and later modified by Frens (Frens, 1973). In Brust-Schiffrin method sodium borohydride is the main reducing agent where alkane thiol provides long term stability (Zhou et al., 2009). Other preparative methods of AuNPs include reduction of chloroauric acid or sodium tetrachloroaurate using aromatic amines, tryptophan and bioactive molecules (Subramanian et al., 2005). Chow and Zukoski (1994) have reported formation of clusters of large particles, followed by reduction of these clusters to smaller particles during the formation and maturing stages of AuNP. Kimling et al., (2006) proposed a multistep mechanism for AuNP formation - appearance and collapse of larger primary particles which is followed by growth of smaller particles by the residual amount of reduced gold in the solution. Kumar et al. (2007) developed a kinetic model which was combined with a population balance model to predict particle-size distribution during AuNP synthesis. The model predicted that the balance between rate of nucleation and degradation of dicarboxyacetone determines AuNP particle size distribution. Pong et al. (2007) reported experimental procedure for formation of nonlinear Au nanowires. Diameters of the nanowires progressively increase in size while the connected network is fragmented into smaller segments before the final spherical AuNP particles are formed. They proved experimentally that initial molar ratios of citrate to gold (III) salts have a profound influence on formation of either monodispersed or polydispersed gold nanoparticles. Based on experimental findings, they proposed a pH-dependent reaction mechanism for particle formation, proceeding either in two steps- rapid nucleation and

slow diffusion-controlled growth (pH > 6.5) or in three steps- rapid nucleation, random attachment, and intra-particle ripening (pH < 6.5). Polte et al., (2010) reported multistep formation of nanoparticles via in situ SAXS and XANES using synchrotron radiation. Bastus et al. (2011) reported experimental results on formation of gold nanoparticles under different pH conditions of the reaction medium and conclusively demonstrated that pH has a profound influence on synthesis mechanism and morphology of nanoparticles. Sivaraman (2011) reported that size distribution of the gold nanoparticles can be altered by manipulating the order of addition of the reactants (gold salt or citrate). Under similar process conditions, addition of precursor to the citrate resulted in lower particle diameter and better sphericity of the gold nanoparticles.

During the Turkevitch-Fren's method of AuNP synthesis, the reaction medium exhibits sharp single absorption peaks in the visible range between 510 and 550 nm due its Surface Plasmon Resonance (SPR). SPR peak is indicative of particle size and origin of SPR is attributed to collective oscillation of free conduction electrons induced by interacting electromagnetic fields. Wavelength of peak absorption depends on various factors like process conditions, particle size distribution and dielectric constant of the reaction medium. With increasing particle size absorption maximum shifts to a longer wavelength and the width of the absorption spectra relates to size of the particles.

Particle shape, size, stability and dispersity are important factors for application of AuNPs (Kumar et al., 2007). Zabetakis et al. (2012) studied an extension of the Turkevitch-Frens method wherein they have established the fact that gold (III) salt solutions having concentrations lower than 0.8mM lead to formation of monodispersed gold nanoparticles for citrate to gold molar ratio larger than 4:1. Paclawski et al., (2012) used the modified Finke-Watzky model to derive rate parameters for AuNP formation using hydrazine sulfate as reductant. Patakfalvi et al. (2007) used the same model to evaluate kinetic rate constants for formation of silver nanoparticles.

Although Turkevitch method is a well-established and popular method of AuNP synthesis, not many investigation have been reported on process engineering- influence of reaction parameters on reaction order and kinetics. Proper understanding of reaction kinetics and growth mechanism is of great importance for controlling size, shape, dispersity and stability of gold nanoparticles. It is also essential for scaling up production of gold nanoparticles for biomedical applications. In this paper AuNP formation by the standard Turkevitch method has been chosen as a model reaction and experimental investigations on reaction kinetics and time-dependent spectroscopic and morphological characterizations of AuNPs are reported. Time-concentration profiles of chloroauric acid reduction reaction and formation of AuNPs were determined using iodometric and UV-Vis spectroscopic methods and the data were analyzed to determine the pseudo-first order reaction rate constants. Using DLS and Atomic Force Microscopy (AFM) time-particle diameter history and surface morphology were studied to investigate Turkevitch-Fren's method of AuNP synthesis.

Process conditions play an important role in synthesis mechanism, size, shape and dispersity of AuNP particles (Chow and Zukoski, 1994). To study the effects of reaction conditions on AuNP formation kinetics, experiments were first carried out at a fixed baseline condition: M = 1.33 ± 0.053 (50 mL of 0.254 mM chloroauric acid and 0.5 mL of 0.34 mM sodium citrate solutions) and T = 373 ± 1 K. Later, AuNP synthesis experiments were performed by changing molar ratio of reactants (M = 0.33-5.32) and temperature (333 - 373 K) of the reaction medium. Stirrer speed in all experiments was always maintained at 600 rpm.

2. Experimental Methods

2.1 Material
Crystalline chloroauric Acid (HAuCl$_4$,3H2O, purity ≥99.997 %; s.d. fine-Chem Ltd.), trisodium citrate dihydrate (C$_6$H$_5$Na$_3$O$_7$.2H$_2$O; purity ≥99.98 %; Merck Specialties Pvt. Ltd) and triple distilled water obtained from laboratory distillation plant were used for AuNP synthesis,

2.2 Preparation of AuNP
Gold nanoparticles were prepared by the standard Turkevitch method (Kumar et al., 2007). 50 mL of 0.254 mm solution of chloroauric acid was heated and stirred continuously on a hot plate magnetic stirrer and 0.5 mL of 34 mM trisodium citrate solution was added to boiling chloroauric acid solution. After addition of citrate color of the colloidal solution changed from colorless to deep wine red colour in about 200-250 s. Temperature and pH of the reaction medium were recorded continuously using a digital thermometer and a digital pH meter. pH of 0.254 mmol/L choloroauric acid solution is 3.18 while that of 34 mmol/L trisodium citrate is 8.44. During reaction pH of the reaction medium remained nearly constant at 3.6. Aliquot samples of the reaction medium (from colourless to wine red) were collected at definite time intervals for further analysis.

A UV-Vis spectrophotometer (Hitachi U-4100) was used to record absorbance corresponding to maximum wavelength during spectrophotometric scanning for each sample collected during reaction. At first a blank test was performed using triple distilled water. Then each of the collected solutions was taken in a quartz cuvette (after proper rinsing) and then placed inside the spectrophotometer and its absorbance corresponding to maximum wavelength (λ_{max}) was recorded. The spectrophotometer was also used to measure directly the concentration of chloroauric acid in the reaction medium. Tapping mode AFM (Veeco, Multimode, Nanoscope IIIa) measurements were performed under ambient conditions for samples collected during reaction. One drop of the collected samples was taken on a freshly cleaved mica sheet and dried and RTESP (Si nitride) tip of resonant frequency of 358.14 kHz was used for AFM imaging. DLS instrument (Malvern, Zetasizer Nano ZS) was used to analyze particle size distribution of AuNPs in the samples collected during the reduction reaction. At first a blank test was performed using water. Then each of the collected solutions was taken in a disposable, plastic cuvette (after proper rinsing) and placed inside the DLS instrument and size distributions of AuNPs in the reaction medium were noted.

3. Results and Discussions

3.1 Kinetics and particle formation

Concentration of chloroauric acid in samples collected during reaction was measured directly by monitoring spectroscopic absorbance at 212.5 nm and cross-checked by iodometric titration method (Chakraborty et al., 2012). During baseline reaction conditions, concentration of chloroauric acid decreased exponentially with time suggesting a pseudo-first order reaction kinetics [$C=C_o exp(-kt)$] for the reduction reaction. Mean diameters of particles in samples were recorded with DLS instrument (Figure 1). During initial stages (<50 s) the AuNP particles were irregular and non-spherical with about 24.5 ± 2.9 nm mean diameter. These particles formed the nuclei for further growth of matured gold nanoparticles. With time (between 50 and 200 s) these non-spherical nuclei became larger and more spherical in shape. After about 250 s, the AuNP particles were matured to nearly perfect spherical shape with about 44.31 ± 5.2 nm mean diameter. Similar observations were also reported by Kimling et al. (2006).

AuNP formation and optical behavior of reaction medium is a subject of intensive research. Several in-depth reviews on particle formation mechanism have been published (Daniel and Astruc, 2004). Nucleation-growth mechanism suggests that AuNP formation in an aqueous medium proceeds in several stages- precursor is reduced to form a supersaturated solution leading to formation of asymmetric primary particles, which with time grow to form mature, spherical secondary particles. The entire process of formation of primary particles and their subsequent maturing to secondary nanoparticles is strongly influenced by process conditions of the reacting medium. DLS and AFM studies of samples collected from reaction medium under baseline condition show that gold particles gradually build up during the course of reaction. No primary particles could be detected, either by DLS or AFM, within the first 20-30 s after addition of citrate to the boiling chloroauric acid solution. This lag period may be attributed to the time required for formation of the Au^{3+}-dicarboxyacetone complex, supersaturation of the reaction medium and formation of an aggregate of critical size before a nucleus of the gold atom is formed. Primary particles, which were found to be irregular, asymmetric and non-spherical with about 24.5 ± 2.9 nm mean hydrodynamic diameter, could be detected 25 - 30 s after addition of citrate to the reaction medium. These particles formed the nuclei for further growth to form secondary AuNPs. With time (30 - 150 s) these non-spherical nuclei became larger and more spherical in shape. After about 200 - 250 s, the particles were found to be symmetrical and nearly spherical with about 44.31 ± 5.2 nm mean diameter, although at times, significant polydispersity of AuNPs in the reaction medium was observed. Our experimental data seem to support the nucleation-growth mechanism of AuNP formation (Kimling et al., 2006) where each nucleus increases its size progressively until the final colloidal particle is formed. Chow and Zukoski (1994) described formation of large AuNP entities of 100 nm or more in size and reduction of these clusters to smaller particles through a stabilization mechanism. Kimling et al. (2006) proposed a multistep mechanism of particle formation - particle appearance, collapse to form larger particles and growth of particles by the residual amount of reduced gold in solution.

3.2 Initial concentration of reactants

Frens (1973) first pointed out that citrate concentration in the reaction medium has a profound influence on size and shape of the AuNP particles. To investigate the effects of changing initial concentrations of chloroauric acid and trisodium citrate on reaction kinetics, experiments were performed at different initial molar ratios of reactants (M = 0.33 to 5.32).

Curve A represents experiments where initial concentration of chloroauric acid was increased from 0.0318 mM to 1.016 mM in several stages keeping concentration of citrate (34.3 mM) constant. Curve B

represents experiments where concentration of citrate was decreased from 136 mM to 8.5 mM in several stages keeping concentration of $HAuCl_4$ constant (0.254 mM). Appropriate volumes of these reactants were mixed to maintain the desired molar ratio. Final solutions obtained after 300 s reaction were analyzed using UV-Vis spectroscopy, DLS and AFM. Plots of mean particle diameter (Curves A and B) versus molar ratio are shown in Figure 2. As the molar ratio was increased from 0.35 to 2.5, a steep drop in AuNP diameter was observed. At molar ratio higher than 2.5, both the SPR wavelength and AuNP diameter increased. At higher molar ratio of the reactants, significant polydispersity of the aqueous medium was observed, which might have contributed to the observed changes in SPR wavelength.
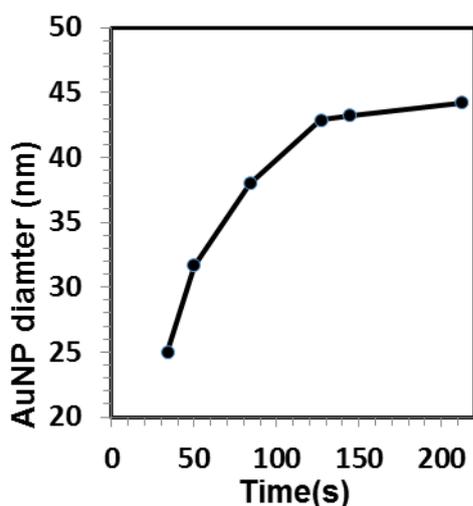
Figure1: Particle diameter vs time plot during reaction
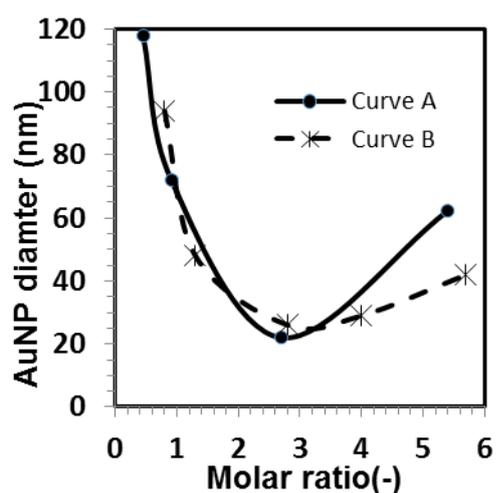
Figure 2: Variation of mean particle diameter with initial molar ratio of reactants (M)

In Figure 2, as the two curves, A and B, almost overlap on each other it may be concluded that final diameters of AuNP colloids depend only on initial molar ratio of reactants and are independent of precursor concentrations. Investigations by other researchers (Chow and Zukoski, 1994) on mean particle diameter substantiate these experimental findings and conclusions. Vacca et al.(2014) have conclusively demonstrated that molar concentrations of the precursor on the surface of the nanoparticle do not determine the degree or nature of the surface coverage. Pseudo-first order rate constants (k) were calculated for these two sets of experiments. Maximum value of rate constant was observed for baseline molar ratio M = 1.33 ± 0.08. When the molar ratio was increased or decreased by changing concentration of either chloroauric acid or trisodium citrate, values of rate constant (k) always decreased from the maximum value (0.0075 s^{-1}) indicating that the reduction reaction was fastest under baseline process conditions (Kimling et al., 2006).

3.3 Temperature of reaction medium

Temperature of the reaction medium has a significant effect on the pseudo-homogenous reaction kinetics during the formation of gold nanoparticles. Experiments were conducted at baseline molar ratio (1.33 ± 0.053) while temperature of the reaction medium was varied between 333 K and 373 K. For all temperatures studied, exponential decrease in concentration of chloroauric acid with time was observed. From an Arrhenius plot of computed rate constants and temperatures, activation energy for liquid phase AuNP synthesis reaction was estimated to be 21.69 ±2.3 kJ/mol. The estimated values of activation energy suggests that reduction of chloroauric acid in aqueous phase is a pseudo-homogenous reaction which is followed by diffusion controlled nucleation and aggregation of reduced metals ions to form larger nanoparticles(Paramaconi et al., 2014). Mechanistic explanations relating reaction kinetics and growth kinetics have been discussed in detail by Zhao and Astruc (2013). Delavani et al. (2014) has recently published mechanistic explanations on role of noble metal catalysis during photocatalytic conversion of CO_2 on semiconductor nanotubes

3.4 pH of reaction medium

In baseline experiments, pH of 0.254 mM chloroauric acid solution was 3.18 while that of 0.34 mM trisodium citrate was 8.44. During reaction pH of the reaction medium remained nearly constant at 3.6. To investigate the effect of pH on reduction kinetics, experiments were conducted at baseline molar ratio while pH of reaction medium was adjusted between 3.6 and 6.5 by adding 75 - 500 µL of 0.1 M NaOH. At pH lower than 3.6 an additional peak at 314 nm appeared in the UV-Vis spectrum and estimation of chloroauric acid concentration became difficult; results of these experiments are not reported here. We could not carry out experiments at pH higher than 6.5 because even after 300 s no substantial change in colour, SPR wavelength or concentration of chloroauric acid in the reaction medium could be detected.

In the pH range 3.6 - 5.2, exponential decay of time-concentration profile, indicative of pseudo-first order kinetics, was observed. At pH higher than 5.2, the time-concentration profile showed distinct deviation suggesting an onset of shift in the reduction–particle formation mechanism. Near neutral pH (6.5), after an initial lag phase (no color change or significant concentration change of chloroauric acid till about 80 - 100 s) a steep fall in concentration of chloroauric acid was observed. This could be due to slow diffusion controlled growth followed by a rapid nucleation step (Subramanian et al., 2005). Molecular forces between citrate protection groups and gold surfaces and zeta-potential of AuNPs are strongly pH dependent (Daniel and Astruc, 2004). At lower pH (3.6-5.2), the well-defined kinetics could be attributed to the presence of the highly reactive $[AuCl_3(OH)]^-$ as the sole oxidant. At pH > 6.5 the very reactive $[AuCl_3(OH)]^-$ is converted to less reactive $[AuCl_2(OH)_2]^-$ and $[AuCl(OH)_3]^-$ following a substantially different mechanistic pathways of AuNP formation.

4. Conclusions

AuNP synthesis experiments were conducted using the standard Turkevitch method. Time-variant precursor concentrations in reaction medium were measured directly by recording absorbance of reaction medium at 212.5 nm and cross-checked by iodometric estimation method. During reaction, chloroauric acid concentration in the reaction medium decreased exponentially with time suggesting an apparent pseudo-first order reaction kinetics ($k=0.0075 \pm 0.0016$ s^{-1}). During nucleation stage (< 35 s) non-spherical particles with mean hydrodynamic diameter of 24.5 nm were detected which formed the nuclei for further growth and maturing to spherical AuNPs after about 300 s. Mole ratio of reactants (Citrate: Chloroauric acid) in the baseline experiment was maintained at 1.33 ± 0.053 because, AuNP size and spherical symmetry obtained under this condition are suitable for biological applications. Influences of process parameters- temperature and molar ratio of the reactants on kinetic rate constants were investigated. It may be emphasized that the chemistry of AuNP synthesis is quite complex and an attempt has been made in this paper to fit a simplistic pseudo-first reaction kinetic order model using experimental data collected over a limited rang of experimental conditions. Development and validation of a more rigorous kinetic model based experimental data collected over a wider range of process conditions are required.

Nomenclature

C: Concentration of chloroauric acid at time t (mM)
C_0:   Initial concentration of chloroauric acid (mM)
k: Pseudo-first order reaction rate constant (s^{-1})
M: Molar Ratio (Citrate/ $HAuCl_4$)
t: time (s)

References

Bastus N.G., Comenge J., Puntes V., 2011, Kinetically controlled seeded growth synthesis of citrate-stabilized gold nanoparticles of up to 200nm: size focussing versus ostwald ripening, Langmuir, 27, 11098-11105.

Chow M.K., Zukoski C.F., 1994, Gold Sol Formation Mechanisms: Role of Colloidal Stability, J. Colloid Interf. Sci., 165, 97−109.

Daniel M.C., Astruc D., 2004, Gold Nanoparticles: assembly,supramolecular chemistry,quantum-size-related properties, and applications toward biology, catalysis, and nanotechnology, Chem. Rev., 104, 293−346.

Delavari S., Nor Aishah S.A., 2014, Response surface methodology analysis of CO_2 photocatalytic conversion in presence of CH_4 over nitrogen-doped titania nanotube arrays, Chemical Engineering Transactions, 39, 235-240

Frens G., 1973, Controlled nucleation for the regulation of the particle size in monodisperse gold suspensions, Nature Phys. Sc., 241, 20-22.

Kimling J., Maier M., Okenve B., Kotaidis V., Ballot H.,Plech A., 2006, Turkevitch method for gold nanoparticle synthesis revisited, J. Phys. Chem., B 110 , 15700–15707.

Kumar S., Gandhi K.S., Kumar R., 2007, Modeling of formation of gold nanoparticles by citrate method, Ind. Eng.Chem.Res., 46, 3128–3136.

Pacławski K., Streszewski B., Jaworski V., Luty-Błocho M., Fitzneret K., 2012, Gold nanoparticles formation via gold(Iii) chloride complex ions reduction with glucose in the batch and in the flow microreactor systems, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 413, 208-215.

Paramaconi R.D.P., Fermin D.J., Marc T., Koper T.M., 2014, New insights into the catalytic activity of gold nanoparticles for co-oxidation in electrochemical media, J. Catal., 311,182-189.

Patakfalvi R., Papp S., Dekany I., 2007, The kinetics of homogeneous nucleation of silver nanoparticles stabilized by polyme, J. Nanopart Res., 9, 353-364.

Polte J., Ahner T.T., Delissen F., Sokolov S., Emmerling F., Thunemann A.F., Kraehnert R., 2010, Mechanism of gold nanoparticle formation in the classical citrate synthesis method derived from coupled in situ XANES and SAXS evaluation, J.Am.Chem.Soc., 132, 1296-1301.

Pong B.K., Hendry I.E., Chong J.X., Ji W., Trout B.L., Lee J.Y., 2007, New insights on the nanoparticle growth mechanism in the citrate reduction of gold(III) salt: formation of the Au nanowire intermediate and Its nonlinear optical propertie, J. Phys. Chem. C, 111, 6281-6287.

Sivaraman S.K., Kumar S., Santhanam V., 2010, Room temperature synthesis of gold nanoparticles-size control by slow addition, Gold Bull., 43(4), 275–286.

Sivaraman S.K., Kumar S., Santhanam V., 2011, Monodisperse sub-10 nm gold nanoparticles by reversing the order of addition in Turkevitch method-The Role of Chloroauric Acid, Gold Bull., 43(4), 275–286.

Subramaniam C., Tom R.T., Pradeep T., 2005, On the formation of protected gold nanoparticles from $AuCl_4$ by the reduction using aromatic amine, J. Nanopart. Res., 7, 209-217.

Turkevitch J., Hillier J., Stevenson P.C., 1951, A study of the nucleation and growth processes in the synthesis of colloidal gold, Trans. Faraday Soc., 11, 55-75.

Vacca A.,Mascia M.,Rizzardini S.,Palmas S.,Lai S, Napoli C.,Barbaro M.,2014, Functionalization of polycrystalline gold through the electroreduction of aryldiazonium salts in ionic liquids, Chemical Engineering Transactions,41,79-84

Zabetakis K., Ghann W.E., Kumar S., Daniel M.C., 2012, Effect of high gold salt concentrations on the size and polydispersity of gold nanoparticles prepared by an extended Turkevitch-Frens method, Gold Bull., 45, 203-211.

Zhou J., Ralston J.R., Sedev J.,David A.B., 2009, Functionalized gold nanoparticles: Synthesis, structure and colloid stability, J. Colloid and Interface Sc., 331, 251-262.

Zhao P., Li N., Jing S., Astruc D., 2013, State of the art in gold nanoparticle synthesis, Coord. Chem Rev., 257, 638–685.