Kinetics and Modeling of Gold Nanoparticle Formation

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Abstract

The utilization of monodisperse [COV < 10%] nanoparticles in the fields of catalysis, medicine, biology and electronics is expected to grow rapidly in the coming decade. Many methods are available for synthesis of nanoparticles of desired size and polydispersity. But, all these methods are batch type and quantity of nanoparticles produced by these methods is order of milligrams. To meet the demand for nanoparticles in coming years, it is necessary to scale up theses batch protocols or to develop continuous flow synthesis methods. To perform these tasks, it is required to understand kinetics of nanoparticle formation in batch reactors. In the present work, kinetics of gold nanoparticle formation by tannic acid reduction method was studied using in-situ fast mixing stopped flow device. Kinetics was studied by monitoring variation of the absorbance at spectroscopic surface plasmon resonance (SPR) absorbance peak of gold nanoparticles. Effect of parameters such as concentration of precursors and temperature on kinetics was analysed. Results show that the rate of formation of nanoparticles increases with increase in concentration and temperature. The mean nanoparticle size is independent of concentration at all temperatures. A simplified organizer based model was used to model dynamics of nanoparticle formation. Model predicts nanoparticle formation kinetics over a wide concentration and temperature range.

1 Introduction

Synthesis of gold nanoparticles has achieved great interest in recent years because of the growing applications of these nanoparticles[1]. Most of the reactions for gold nanoparticle synthesis are quite reactive; so, nanoparticle formation occurs on time scale of milliseconds. Therefore, to study kinetics, a fast mixing device that can mix reagents over order milliseconds is needed. To perform this task, we used a stopped flow module (SFM) coupled with UV-Vis spectrophotometer.

Chakraborty reported that simple classical nucleation and growth model doesn't explain nanoparticle formation over a range of precursor concentrations[2]. Organizer based model was proposed by considering the chemistry of tannic acid along with reduction, nucleation, and growth steps. Based on experimental data on final particle size, the reaction network was further simplified. This simplified model forms the basis for modeling of the data obtained during kinetics of gold nanoparticles formation.

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2 Experimental

2.1 Materials: Chloroauric acid and tannic acid supplied from Acros, potassium carbonate supplied from Merck and Millipore water were used as supplied.

2.2 Synthesis of gold nanoparticles: pH of the Chloroauric acid and tannic acid solutions were maintained at 3.1 and 7.7 respectively. The kinetics was studied at 25^0C and 50^0C and concentration of chloroauric acid was varied from 0.38 mM to 0.06 mM while maintained molar ratio of tannic acid to gold chloride at 2.1.

3 Results and Discussion

Evolution curves, at various concentrations of chloroauric acid and reaction temperature of 25^0C, obtained by monitoring variation of the absorbance at 530 nm are shown in figure 1. As the concentration of chloroauric acid increases, rate of formation of nanoparticles increases. Kinetic experiments were also conducted at 50^0C. Evolution curves reached saturation limit faster at 50^0C compared to 25^0C. So, rate of nanoparticle formation is faster at higher temperatures.

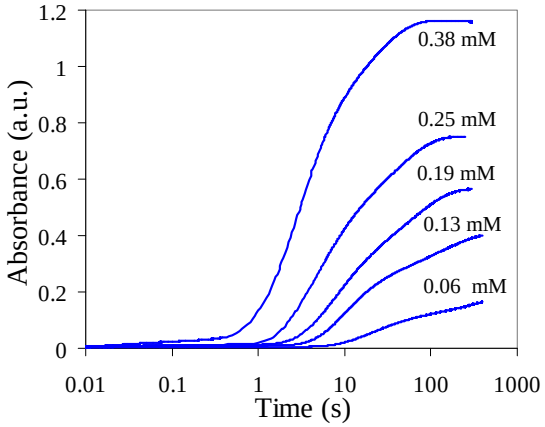

Figure 1 Evolution curves obtained at 25^0C

Mean DLS particle diameter obtained at all concentrations for both 25^0C and 50^0C are shown in table 1. The particle diameter at both temperatures shows that the diameter is independent of concentration of $HAuCl_4$ and variation is with in experimental error. Mean

particle diameter at 50^0C for all concentrations is lower than the diameter obtained at 25^0C.

Concentration of $HAuCl_4$ (mM)	Mean particle diameter at 25^0C (nm)	Mean Particle diameter at 50^0C (nm)
0.38	7.5 ± 1.3	5.5 ± 1.2
0.25	7.1 ± 1.8	5.7 ± 1.5
0.19	8.3 ± 1.2	5.1 ± 2.3
0.13	8.6 ± 1.5	6.1 ± 1.0
0.06	8.2 ± 1.0	9.0 ± 4.2

Table 1 Mean particle diameter obtained at 25^0C and 50^0C

Simplified organizer based model was used to model kinetics of nanoparticle formation. In the model tannic acid is considered as a molecule of two arms and each arm can reduce three gold ions. Order of the reaction with respect to chloroauric acid and tannic acid was taken to be 1.5 and 1 respectively[3]. Overall reaction network by considering all possible interactions is shown in figure 2.

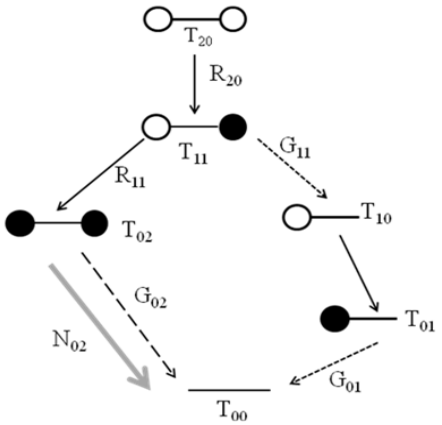

Figure 2 Overall reaction network[2].

Best model parameter values were obtained by fitting model predictions to experimental observations for one concentration. The optimum parameter values are shown in table 2. The same parameter values were used to obtain model predictions at other concentrations. Evolution curves obtained from model and experiment are shown in figure 3, indicating reasonable agreement of the model with experimental evolution curves.

Parameter	value	Units
k_r	0.101	$(mol/m^3)^{-1.5}\ s^{-1}$
k_g	$3.53*10^{-4}$	$mol/m^2\ s$
k_d	0.0104	mol/m^3
k_n	5	s^{-1}

Table 2 Best fit parameter values

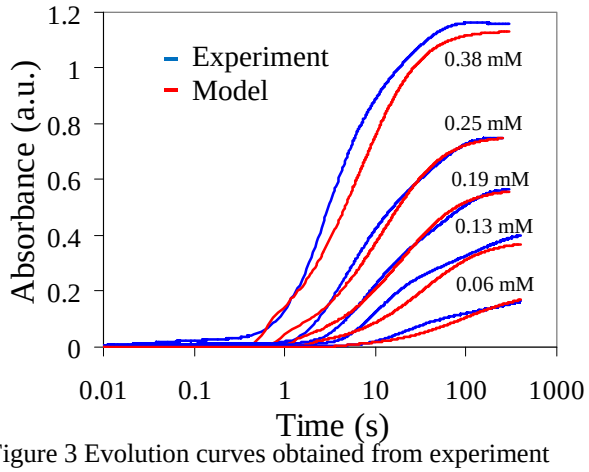

Figure 3 Evolution curves obtained from experiment and model at 25^0C.

The particle diameters obtained from experiment and predicted by model are shown in table 3. The size variation predicted by model is well within experimental error, indicating that model predictions of mean particle size are accurate.

Concentration of $HAuCl_4$ (mM)	Mean particle diameter (nm)	Mean Particle diameter from model (nm)
0.38	7.5 ± 1.3	7.1
0.25	7.1 ± 1.8	7.3
0.19	8.3 ± 1.2	7.5
0.13	8.6 ± 1.5	7.6
0.06	8.2 ± 1.0	7.6

Table 3 Mean particle diameter obtained from experiment and model at 25^0C.

By only changing the reaction rate constant by a factor of three the model predicts experimental observations at 50^0C also.

4 Conclusions

- Rate of formation of nanoparticles increases with increase in precursor concentration and temperature.
- Simplified organiser based model predicts kinetics of nanoparticle formation.

5 References

[1] Moores, A. and Goettmann, F., The Plasmon Band in Noble Metal Nanoparticles: An Introduction to Theory and Applications, *New Journal of Chemistry*, 30, 2006, 1121–1132.

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[3] Anusha M. Investigation of Gold Nanoparticle Formation Kinetics Using Stopped Flow Module, *M.E. Report*, 2008, IISc.