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Synthesis of thiol-capped gold nanoparticle with a flow system using organosilane as a reducing agent

Atsushi Sugie,[a] Hansoo Song,[a] Takafumi Horie,[a] Naoto Ohmura,[a] Kiyoshi Kanie,[b] Atsushi Muramatsu,[b] and Atsunori Mori [a]*

[a] *Department of Chemical Science and Engineering, Kobe University, 1-1 Rokkodai, Nada, Kobe, 657-8501 Japan*
[b] *Tohoku University, Institute of Multidisciplinary Research for Advanced Materials, Katahira 2-1-1, Aoba-ku, Sendai 980-8577*

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ABSTRACT

Synthesis of thiol-capped gold nanoparticle is carried out by mixing of a THF solution of $HAuCl_4•4H_2O$ and ${}^nC_{12}H_{25}SH$ with a THF solution of triethylsilane in a flow system consists of polytetrafluoroethylene tubing. The effect of residence time and reaction temperature on the particle size is examined.

Gold nanoparticle (AuNP) consists of gold cluster and a capping agent of an organic molecule which is adsorbed onto the gold surface to introduce stability and functionality.[1] Since application of AuNP attracts considerable attention in various fields such as materials science, catalysis, and biology, development of preparative methodology for AuNP has become an important issue. Synthesis of AuNP has been generally carried out by the addition of a reducing agent to a mixture of a gold salt and a capping agent in a batch system. A variety of reagents such as $NaBH_4$,[2] superhydride ($LiBHEt_3$),[3] borane-amine complex,[4] and ascorbic acid[5] have been reported as an effective reducing agent for the synthesis of AuNP. We have previously shown that spherical and monodisperse alkanethiol-capped AuNP can be synthesized with triethylsilane as a new class of reducing agent in a single-phase system of an organic solvent.[6]

Recently, intense research interest has been focused on organic synthesis in a flow reactor.[7] It is known that large surface area of the flow reactor in comparison to the conventional batch reactor offers rapid mass and heat transfers to give various advantages such as control over the selectivity of fast reactions involving highly reactive species. Application of the flow reactor can also give the alternative methodology to the synthesis of metal nanoparticles. The enhanced mass and heat transfers would provide improved control over the nanoparticle's size and morphology, which influence the properties of the nanoparticles significantly.[8] Although there are a few reports on AuNP synthesis, these are mostly performed in an aqueous system to afford hydrophilic AuNPs.[9] Only a limited example to give hydrophobic alkanethiol-capped AuNP has been shown with $NaBH_4$ as a reducing agent.[10] However, the reaction requires an organic/aqueous biphasic system in the presence of a surfactant to proceed. If it is possible to undergo flow synthesis of the AuNP in a single-phase system of an organic solvent, the reaction can be a straightforward method. The use of triethylsilane, which we have shown to be available as a mild reducing agent for the synthesis of the AuNP in a batch system, would be intriguing for the promising nanoparticle synthesis in a flow system (eq. 1). Herein, we report that synthesis of hydrophobic thiol-capped AuNP is successfully achieved in a flow system using organosilane as a reducing agent.

$$HAuCl_4·4H_2O + {}^nC_{12}H_{25}SH \xrightarrow[\text{THF}]{Et_3SiH} \text{thiol-capped AuNP} \qquad (1)$$

flow system

The flow system was designed as depicted in Figure 1. Synthesis of AuNP in a flow system was carried out by the following procedure. A solution of $HAuCl_4•4H_2O$ and 1-dodecanethiol in THF, which was prepared by vigorous stirring for 3 h to form a yellow solution, and a THF solution of triethylsilane were mixed with a syringe pump (flow rate: 2.5 $mL·h^{-1}$) at the Y-shaped mixer **M**. The mixed solution was directed into tubing **R** (5 m, internal diameter of 1 mm)

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* Corresponding author. Tel.: +81 788036181; fax: +81 788036181; e-mail: amori@kobe-u.ac.jp

immersed in a thermostatic bath (25 °C) for generation and growth of AuNP. After 23 minutes of residence time, the resulting purple solution discharged from the tubing was poured into EtOH to precipitate the AuNP. After eduction of all the solution, the precipitate was centrifuged to isolate the thiol-capped AuNP. When 10 mL of THF solution of $HAuCl_4$ (0.15 mmol) and 1-dodecanethiol (0.15 mmol) and 10 mL of THF solution of triethylsilane (0.15 mmol) were injected in polytetrafluoroethylene (PTFE) tubing and mixed, AuNP (**1**, 11.1 mg) was obtained as dark-brown powder. The isolated nanoparticle was dispersible to chloroform and THF. In contrast that formation of gas bubbles was shown to be observed in the flow reaction with $NaBH_4$ under biphasic conditions,[10,11] no bubbles were observed in the reaction of triethylsilane and thus continuous flow was maintained during the reaction.

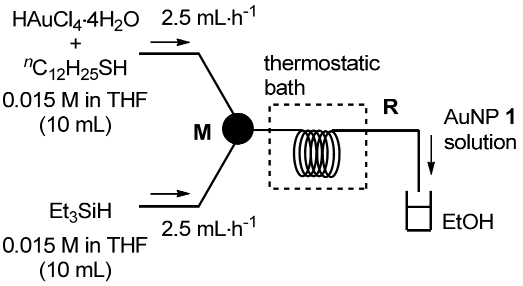


Figure 1. Synthesis of thiol-capped AuNP in a flow system. **M**: Y-shaped mixer, **R**: PTFE tubing (diameter = 1 mm, length = 5 m)

The obtained AuNP **1** was characterized by UV-vis spectroscopic analysis and TEM observation. The results are summarized in Table 1 comparing with characteristics of AuNP **1'**, which was prepared in a conventional test tube batch reactor with magnetic stirring by the reduction of $HAuCl_4$ and 1-dodecanethiol with triethylsilane for 23 minutes.[6a] The UV-vis spectrum of **1** exhibited λ_{max} of 527 nm, which is assigned to the surface plasmon resonance absorption of the AuNP.[1] TEM observation of **1** indicated formation of spherical nanoparticle, whose average diameter is 7.0±0.82 nm (Figure 2). Though the yield and λ_{max} of **1** were similar to those of **1'**, the particle size was found to be larger than that of **1'**.

Table 1. Comparison of characteristics of AuNPs

AuNP	reactor	yield/ mg	particle size/nm	UV-vis absorption λ_{max}/nm[a]
1	flow	11.1	7.0±0.82	526
1'[b]	batch	12.6	5.8±0.62	529

[a] UV-vis spectra were measured as a $CHCl_3$ solution.

[b] The reaction was carried out with $HAuCl_4 \cdot 4H_2O$ (0.15 mmol), 1-dodecanethiol (0.15 mmol), and triethylsilane (0.15 mml) in THF (10 mL)

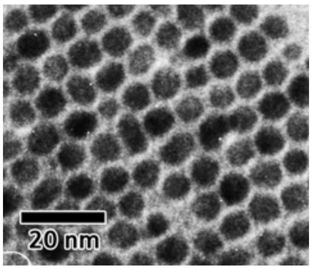


Figure 2. TEM image of AuNP **1**

Synthesis of AuNP by the flow system was carried out with several residence times and reaction temperatures. Table 2 shows the average particle size and the size distribution of the AuNP obtained under the corresponding conditions. It was found that a higher reaction temperature and a longer residence time led to formation of larger AuNPs. The AuNP with the largest size of 8.7 nm was obtained when the reaction was carried out at 60 °C for 94 min of residence time, while the smallest AuNP (4.3 nm) was prepared by the reaction at 25 °C for 12 min. Increase of both the reaction temperature and the residence time also showed a trend toward improved monodispersity of the AuNP. The size was controllable between ca. 4.3 to 8.7 nm in the flow system at 25 to 60 °C.[12] It should be pointed out that AuNP was successfully obtained at 60 ºC, while the reaction in the batch system at the same temperature resulted in the formation of insoluble precipitates.[6a] It is considered that the flow reactor inhibits excess growth of the AuNP core, which may result in the precipitation.

Table 2. Effect of residence time and temperature on the average particle size and the size distribution of the AuNPs[a]

residence time/min.	particle size/nm (25 °C)	(40 °C)	(50 °C)	(60 °C)
12	4.3±0.57	5.9±0.82	7.2±0.79	7.9±1.05
23	4.8±0.66	5.8±0.64	7.7±0.89	8.0±1.22
47	7.0±0.82	7.2±0.69	7.9±0.82	8.6±0.69
94	7.8±1.2	8.3±1.2	8.7±0.80	8.7±0.66

[a] The reaction was carried out with mixing of 10 mL THF solution of 0.15 mmol of $HAuCl_4 \bullet 4H_2O$ and 0.15 mmol of 1-dodecanethiol and 10 mL THF solution of 0.15 mmol of Et_3SiH.

We next carried out synthesis of AuNP with other organosilanes as a reducing agent in the flow reactor in a similar manner. Table 3 shows the results of flow and batch reactions.[6a] The flow reactions using diethoxy(methyl)silane proceeded smoothly to afford AuNP of 6.1 ± 0.65 nm. Siloxane was also found to be effective to perform the flow reaction. AuNPs with narrow dispersity were obtained when the reaction was carried out with pentamethyldisiloxane (6.5 ± 0.57 nm) and tetramethyldisiloxane (6.3 ± 0.60 nm). Worthy of note is that a variety of silanes can be employed as a reducing agent. By contrast, when the reaction was carried out in a batch system, those reducing agents only gave nonspherical nanoparticle ranging in the size from 6-60 nm or insoluble precipitates. Mild mixing of the reducing agent with gold would occur in the tube reactor to result in the formation of spherical and dispersible AuNPs.

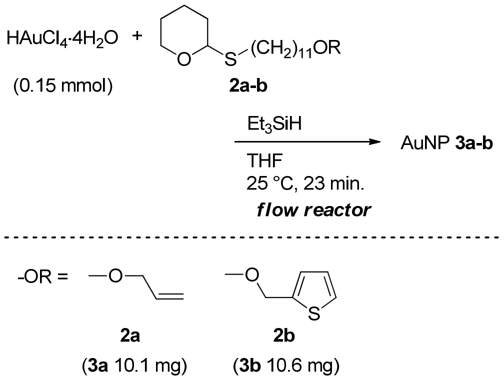
Table 3. Synthesis thiol-capped AuNP with organosilane reagents

reducing agent(eq.)	flow system[a]		batch system[b]
	yield/mg	particle size/nm	particle size/nm
$HSiMe(OEt)_2$ (1.0)	3.2	6.1±0.65	-[c]
$HMe_2SiOSiMe_3$ (1.0)	12.2	6.5±0.57	-[c]
$(HMe_2Si)_2O$ (0.5)	7.6	6.3±0.60	-[d]

[a] The reaction was carried out with mixing of 10 mL THF solution of 0.15 mmol of $HAuCl_4 \cdot 4H_2O$ and 0.15 mmol of 1-dodecanethiol and 10 mL THF solution of reducing agent for 23 minutes of residence time. [b] The reaction

was carried out with 0.1 mmol of $HAuCl_4 \cdot 4H_2O$, 0.1 mmol of 1-dodecanethiol, and reducing agent in THF for 6 h (See ref. 6). [c] Nonspherical nanoparticles ranging in size from 6-60 nm are formed. [d] Formation of insoluble precipitate.

The reaction in the flow reactor was then applied to the preparation of AuNP bearing a functional group at the end of a capping reagent. Tetrahydropyranyl (THP) thioether was used as a capping reagent instead of unprotected thiol.[6c] The flow reaction of a mixture of $HAuCl_4$ and THP thioether **2a** bearing an allyloxy group with triethylsilane proceeded smoothly to afford functionalized AuNP **3a** (Scheme 1). The similar reaction employing THP thioether **2b** bearing a (2-thienyl)methoxy group also furnished functionalized AuNP **3b**. Introduction of the functional group was confirmed by measurement of the ^1H NMR spectrum after treatment of the functionalized AuNP with excess iodine to isolate the organic residue.[13]



Scheme 1. Preparation of functionalized AuNP with THP thioethers bearing functional groups.

In summary, synthesis of thiol-capped gold nanoparticle was accomplished in the flow system using organosilane as a reducing agent. Since organosilane is a mild reducing agent, continuous flow was maintained during the synthesis of thiol-capped AuNP. It was found that the size of AuNP was dependent on the residence time and the reaction temperature. Comparing with the conventional batch system, application of the flow system led to increased diversity of available organosilane compounds as reducing agents. In addition, introduction of alkanethiol bearing a functional group onto AuNP was also successful by the flow reaction. Accordingly, the method would be a potentially useful tool of choice for the preparation of size-controlled thiol-capped gold nanoparticles.

Acknowledgments

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11. The Attempted single-phase flow reaction with $NaBH_4$ was unsuccessful due to the little solubility of the reducing agent in an ethereal organic solvent, which was both likely to the reduction of $HAuCl_4$ and the formation of the well-dispersed AuNP.
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Supplementary Material

Supplementary material that may be helpful in the review process should be prepared and provided as a separate electronic file. That file can then be transformed into PDF format and submitted along with the manuscript and graphic files to the appropriate editorial office.

Graphical Abstract

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