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Solvent Diversity in the Preparation of Alkanethiol-capped Gold Nanoparticles. An Approach with a Gold(I) Thiolate Complex

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The reaction of highly soluble gold(I) thiolate complex of tributylphosphine or 2-aminoethanol with a reducing agent gives gold nanoparticles. The complex is soluble in various solvents such as hexane, toluene, THF, Et_2O, and water.

Preparative methodology for gold nanoparticles (AuNPs) has become important in extensive fields of materials science, catalyst design, etc.[1] We have recently shown that alkanethiol-capped gold nanoparticle can be synthesized with triethylsilane as a new class of reducing agent in a single-phase system of an organic solvent to afford spherical and monodisperse gold nanoparticles.[2] The synthesis was performed in several ethereal solvents such as tetrahydrofuran, di-*n*-butyl ether, and cyclopentyl methyl ether, while other organic solvents were found to be ineffective. Such a limitation concerning the available solvent, which is due to the insufficient solubility of starting $HAuCl_4$, lacks preparative versatility, for example, directed to structural design of capping organic molecules bearing functionalities. Formation of gold nanoparticles with $HAuCl_4$ is generally considered to occur through the in situ formed intermediate gold(I) thiolate by the reaction of an alkanethiol and following reduction of thus formed thiolate leads to the nanoparticles.[3] It is thus necessary for the gold nanoparticle synthesis to find a solvent to dissolve both $HAuCl_4$ and intermediate thiolate as well as the produced gold nanoparticle. We envisaged that synthesis of gold nanoparticles starting from gold(I) thiolate would simplify the reaction pathway leading to a solution for the difficulties on the solvent limitation. However, gold(I) thiolate is well known to be hardly soluble in many solvents.[4] Thus, it is intriguing to find an appropriate additive to make insoluble gold(I) thiolate homogeneous, which would enable following reduction to gold nanoparticle to proceed in a variety of solvents.[5] Herein, we report that addition of a coordinative phosphine or amine forms soluble gold(I) thiolate and reduction of thus formed thiolate complex leads to gold nanoparticle in diverse solvents.

Synthesis of gold(I) thiolate of dodecanethiol was performed by the reaction of equimolar amounts of $HAuCl_4{\cdot}4H_2O$ and $n\text{-}C_{12}H_{25}SH$ in the presence of 2,2′-thiodiethanol as shown in eq 1 to afford $n\text{-}C_{12}H_{25}SAu(I)$ (**1**) in a quantitative yield.[4]

$$\mathrm{HAuCl_4{\cdot}4H_2O} \xrightarrow[\mathrm{H_2O}]{\substack{\mathrm{HS{-}{}^{n}C_{12}H_{25}} \\ \mathrm{S(CH_2CH_2OH)_2}}} \underset{\mathbf{1}}{\mathrm{Au(I){-}S^{n}C_{12}H_{25}}} \qquad (1)$$

However, we learned that the thiolate formed was hardly soluble in most of organic solvents and water. Further reduction of the thiolate did not occur, accordingly, to recover the gold(I) thiolate. Several additives such as pyridine, triethylamine, triphenylphosphine, and tri(*o*-tolyl)phosphine were then examined to dissolve **1** in several organic solvents being unsuccessful. Among additives, treatment of gold(I) thiolate **1** with tri-*n*-butylphosphine, which would form phosphine complex of thiolate **2**, was the only soluble choice (eq 2). In contrast to uncomplexed gold thiolate, **2** was found to be dissolved in THF, chloroform, diethyl ether, toluene, etc. It should be pointed out that the complex of gold(I) dodecanethiolate with $^{n}Bu_3P$ was soluble in hexane.

$$\underset{\mathbf{1}}{\mathrm{Au(I){-}S{-}{}^{n}C_{12}H_{25}}} + {}^{n}\mathrm{Bu_3P} \longrightarrow \underset{\mathbf{2}}{\left({}^{n}\mathrm{Bu_3P{-}Au(I){-}S{-}{}^{n}C_{12}H_{25}}\right)} \qquad (2)$$

The thiolate complex **2** was first subjected to the reduction with triethylsilane.[2] Treatment of a hexane solution of **2** with Et_3SiH at room temperature resulted in little color change of the solution, suggesting that reduction of **2** leading to a purple color of AuNP derived from surface plasmon resonance[6] did not take place. The findings show insufficient reactivity of the tertiary alkylsilane reagent toward the thiolate that is stabilized by the formation of Au–phosphine complex. Accordingly, other silane reagents showing higher activity as a reducing agent were examined and we found that a primary silane reagent $PhSiH_3$ reduced the thiolate phosphine complex smoothly to result in immediate color change to dark purple at room temperature.

It was also found that a solution obtained by the addition of $^{n}Bu_3P$ to a suspension of gold(I) thiolate in hexane similarly afforded gold nanoparticles. A representative preparation protocol follows: To a suspension of **1** (0.1 mmol) in hexane (5 mL) was added $^{n}Bu_3P$ (0.15 mmol) to form a clear solution by stirring at room temperature for 0.5 h. $PhSiH_3$ (0.04 mmol) was then added dropwise to the resulting solution. The colorless solution of **2** turned to dark purple immediately. After stirring at room temperature for 2 h, the solution was concentrated under reduced pressure. Following addition of ethanol formed precipitate, which was separated by continuous centrifugation and decantation to afford 16.0 mg of gold nanoparticle as a dark brown solid.[7] The isolated solid was found soluble again in chloroform, toluene, and THF.

UV–vis spectrum of the chloroform solution exhibited the plasmon band at 520 nm as shown in Figure 1a. TEM analysis, whose electron diffraction pattern was assigned as face-centered cubic (fcc) structure of bulk gold supported formation of the gold particles, indicated that spherical particles (5.0 ± 0.66 nm) was formed. (Figure 1b) The size of gold nanoparticle was found to be smaller than that formed by the reaction of $HAuCl_4$ and $^{n}C_{12}H_{25}SH$ with triethylsilane as a reducing agent in THF suggesting that faster reduction took place with $PhSiH_3$. TG

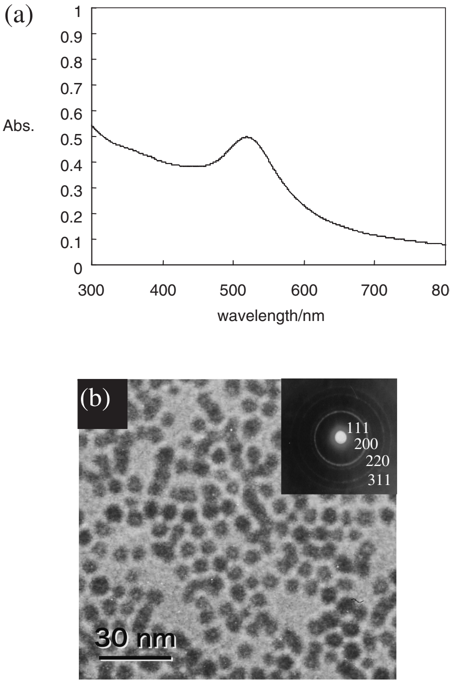


Figure 1. AuNP prepared from gold(I) thiolate: (a) UV–vis spectrum and (b) TEM image with electron diffraction pattern (top-right).

Table 1. Preparation of the AuNP under various conditions[a]

Hexane/mL	Temp/°C	Yield/mg	Size/nm
5	25	16.0	5.0 ± 0.66
5	0	11.9	2.7 ± 0.38
5	50	27.2	—[b]
1	25	12.7	6.4 ± 0.66
10	25	19.6	6.6 ± 0.49

[a]Unless specified, the reaction was carried out with 0.1 mmol of **1**, 0.15 mmol of ^{n}Bu$_3$P, and 0.04 mmol of PhSiH$_3$ in hexane for 2 h. [b]Aggregation of the nanoparticle.

Table 2. Synthesis of the AuNP in various organic solvents[a]

Solvent	PhSiH$_3$/**1** (mol/mol)	Temp/°C	Time/h	Yield/mg	Size/nm
Hexane	0.4	25	2	16.0	5.0 ± 0.66
THF	0.4	25	1	10.8	6.8 ± 0.70
Toluene	1.0	25	2	16.6	—[b]
		0	2	8.5	5.4 ± 0.57
Et$_2$O	0.4	25	2	—	—[b]
		0	5	7.9	4.6 ± 0.26

[a]Unless specified, the reaction was carried out with 0.1 mmol of **1**, 0.15 mmol of ^{n}Bu$_3$P, and PhSiH$_3$ in 10 mL of organic solvent. [b]Aggregation of nanoparticles was observed.

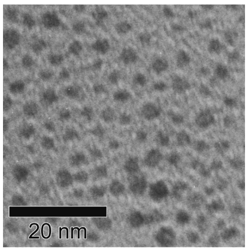


Figure 2. TEM image of AuNP prepared by superhydride.

analysis showed 8.26% mass loss at 800 °C suggesting that 4.3/nm^2 thiol molecules are adsorbed on the gold surface. Measurement of ^{31}P NMR spectrum of the nanoparticle showed no signals indicating that tri-*n*-butylphosphine was not incorporated on the surface of the gold nanoparticle.

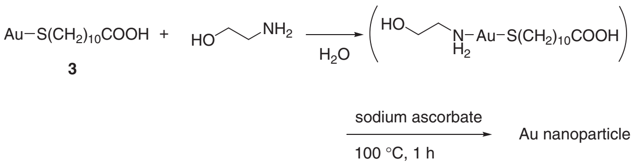
Preparation of AuNP was carried out under several conditions as shown in Table 1. It was found that the reaction temperature significantly affected the formation of AuNP. The addition of PhSiH$_3$ at 0 °C afforded the nanoparticle of 2.7 ± 0.38 nm,[8] while aggregation of the nanoparticles was observed when PhSiH$_3$ was added at 50 °C. The effect of gold(I) thiolate concentration toward the formation of AuNP was then examined. The reaction was carried out with 1 mL of hexane to afford 12.7 mg of the nanoparticle (6.4 ± 0.66 nm). Slight improvement of yield and narrow dispersity were observed when the reaction was carried out in 10 mL of hexane (19.6 mg, 6.6 ± 0.49 nm).

Synthesis of AuNP with several kinds of organic solvents was then carried out in a similar manner. Table 2 summarizes the results. The reaction in THF afforded the corresponding nanoparticle of 6.8 ± 0.70 nm.[8] The use of toluene, in which HAuCl$_4$ was insoluble, at 25 °C also exhibited purple color although the isolated solid did not disperse in organic solvents. Formation of redispersible nanoparticles with toluene was achieved when the reaction was carried out at 0 °C to obtain 8.5 mg of the product (5.4 ± 0.57 nm). Et$_2$O and toluene were also found to be suitable solvents to perform the reaction of **2** in contrast to the synthesis of AuNP from HAuCl$_4$ and triethylsilane being ineffective.[2] Worthy of note is that the nanoparticle synthesis in toluene occurred in a single phase system without phase transfer catalyst, which was shown to cause contamination of the produced AuNP. In addition, the established method for AuNP synthesis with HAuCl$_4$ and NaBH$_4$ under biphasic system in the presence of a quaternary ammonium salt has been performed in only limited solvents and the result that the reaction in hexane was completely unsuccessful under similar conditions is particularly remarkable.[1c]

Tri-*n*-butylphosphine complex of gold(I) thiolate was also subjected to the reduction by another reducing agent. The addition of 20 equiv of superhydride (Et$_3$BHLi/THF)[1d] to a THF solution of **1** (0.1 mmol) and tri-*n*-butylphosphine afforded 15.0 mg of spherical gold nanoparticle with an average diameter of 3.4 ± 1.5 nm. (eq 3) TEM image of the AuNP is shown in Figure 2.

$$\mathrm{Au{-}S^{\mathit{n}}C_{12}H_{25}} + \mathrm{PBu_3} \xrightarrow[\text{THF}]{\text{superhydride}} \text{Au nanoparticle} \qquad (3)$$

Encouraged by remarkable organic solvent diversity for the preparation of AuNP with **2**, we envisaged the synthesis of AuNP in water by employing a long-chained thiolate bearing a carboxy group at the end. Gold thiolate **3** bearing a carboxy



Scheme 1.

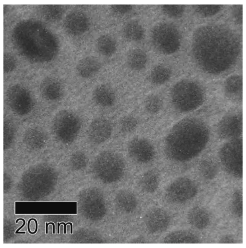


Figure 3. TEM image of AuNP prepared in water.

group was synthesized similarly by the reaction of $HAuCl_4 \cdot 4H_2O$ and 11-sulfanylundecanoic acid in 70% yield. Although the obtained gold(I) thiolate was hardly soluble in water as well as various organic solvents, addition of 2-aminoethanol, which is a water-soluble amine reagent, to the suspension of the thiolate resulted in clear aqueous solution (Scheme 1). Reduction of the thiolate was carried out by the addition of sodium ascorbate[1b] and stirring the solution at 100 °C for 1 h gave a red-purple solution. On the other hand, formation of AuNP with reducing agents such as Et_3SiH, $PhSiH_3$, $NaBH_4$,[1c] and sodium citrate[1a] was totally unsuccessful. TEM analysis also supported formation of AuNP (9.6 ± 2.4 nm), as shown in Figure 3, which was found to be larger than that prepared in organic solvents. Although amine itself was shown to serve as a reducing agent,[9] addition of ascorbate as a reducing agent was necessary to yield AuNP efficiently. Worthy of note is finding of a water-soluble gold(I) thiolate complex and that reduction of the complex proceeded in water to afford water-soluble AuNP. Further studies on optimization of the reaction conditions would be necessary to achieve efficient preparative methodology.

In summary, gold nanoparticles were obtained in various organic solvents and water when soluble tributylphosphine or 2-aminoethanol complex of gold(I) thiolate was subjected to the reduction. Extension of the available organic solvent significantly enhances synthetic versatility of gold nanoparticles, which would also allow design and synthesis of the particle bearing functionalities.

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8 See Supporting Information. Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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