Triethylsilane as a mild and efficient reducing agent for the preparation of alkanethiol-capped gold nanoparticles†

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The reaction of $HAuCl_4{\cdot}4H_2O$ and n-$C_{12}H_{25}SH$ with 1 equiv. of Et_3SiH in an organic solvent affords spherical gold nanoparticles (AuNPs) with narrow dispersity.

The gold nanoparticle (AuNP) has attracted considerable attention for applications to catalysis, nonlinear optical materials and biological sensing due to its characteristic magnetic, electronic and optical properties.[1] Since the size of the nanoparticle has a significant effect on its properties, the development of synthetic methodologies for the preparation of AuNPs with narrow dispersity becomes highly important. AuNPs have generally been synthesized under biphasic conditions in a mixed aqueous and organic solvent system with sodium borohydride as a reducing agent in the presence of quaternary ammonium salt as a phase transfer catalyst.[2] On the other hand, synthesis of AuNPs in a single-phase system has been performed with stronger hydride ions such as $LiBH_4$,[3] amine–borane complex,[4] and superhydride ($LiBHEt_3$).[5,6] These reactions are carried out under anhydrous conditions since the hydride reacts vigorously with water and protocols generally employ a large excess of the reducing agent. Organosilanes react with a variety of carbon–carbon and carbon–heteroatom unsaturated bonds through the addition of hydrogen and silicon atoms, namely hydrosilylation, and have been widely utilized in organic synthesis.[7] As the silicon–hydrogen bond is less ionic and stable to water, hydrosilylation reactions have been carried out by transition metal catalysis.[8] Several other functional groups are tolerable for the reaction with silane reagents, accordingly. In addition, organosilanes are less toxic and their use is thereby a potentially environmentally benign process. If successful, preparation of AuNPs with an organosilane as a reducing agent, a protocol that is performed in an organic solvent under mild conditions, would be intriguing. We herein report that triethylsilane is a highly effective reducing agent for the single-phase preparation of thiol-capped AuNPs.

Synthesis of AuNP was carried out by the following procedure. A solution of $HAuCl_4{\cdot}4H_2O$ (0.1 mmol) and dodecanethiol (0.1 mmol) in 10 mL of THF was vigorously stirred for 3 h at 25 °C. To the resulting yellow solution triethylsilane was added dropwise at 25 °C to form a purple solution immediately. After stirring for 6 h at 25 °C, ethanol was added to the solution to precipitate AuNP, which was centrifuged to isolate the thiol-capped AuNP (**1**, 15.1 mg) as dark brown powder.

The obtained **1** was found to be dispersible with organic solvents such as THF or $CHCl_3$, suggesting that aggregation did not occur during the isolation procedure.

It should be pointed out that the preparation of AuNP performed with 1 molar amount of triethylsilane with respect to $HAuCl_4$ and alkanethiol represents high synthetic efficiency. An advantage would be provided by the characteristics of Et_3SiH which is unreactive towards water in $HAuCl_4$ and hydrogen chloride formed by the reduction of the gold species. Indeed, the reaction with an increased amount of Et_3SiH did not improve the yield of **1**.[9] Since synthesis of AuNPs has been generally carried out with excess amounts of reducing agent, it is remarkable that the use of 1 equiv. of Et_3SiH can result in the formation of AuNP. Worthy of note, in addition, is the AuNP preparation in an organic solvent as a single phase medium. According to Blackmond,[10] a process which causes contamination of water by organic compounds, like a reaction with a water–organic solvent system, is *environmentally unfriendly*. Therefore, the preparation in THF with 1 equiv. of less toxic Et_3SiH under mild conditions is an *environmentally benign* protocol.

$$HAuCl_4 \cdot 4H_2O \ + HS - nC_{12}H_{25} \xrightarrow[\text{THF}]{Et_3SiH} \underset{\mathbf{1}}{\text{gold nanoparticle}} \qquad (1)$$

Characterization of obtained AuNP **1** was carried out by measurements of TEM images, UV–Vis spectra, and ^1H NMR analyses. Fig. 1 shows the TEM image of the AuNP, which is spherical and exhibits an average diameter of 8.6 ± 0.65 nm, indicating the formation of unaggregated and highly

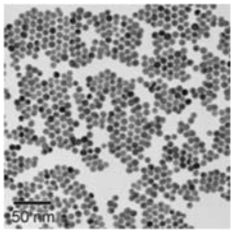

Fig. 1 TEM image of thiol-capped AuNP **1**.

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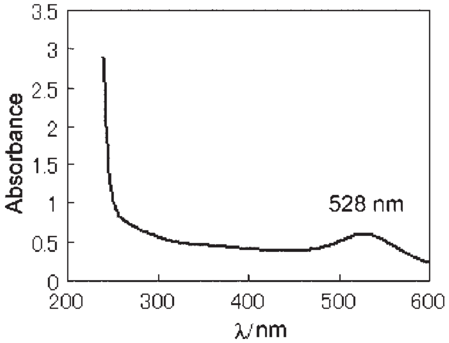

Fig. 2 UV–Vis spectrum of thiol-capped AuNP **1**.

monodispersed AuNP. The UV–Vis spectrum of the AuNP is shown in Fig. 2. The λ_{max} value of the UV–Vis spectrum was observed at 528 nm, which is attributed to the characteristic plasmon resonance absorption of AuNP.[1] The ^1H NMR spectrum of AuNP as a solution in $CDCl_3$ exhibited a triplet signal at δ 0.88 and a broad signal at δ 1.26, respectively, which are assigned to CH_3– and CH_2– of dodecanethiol adsorbed on the surface of AuNP.

Table 1 summarizes the results on the scope and limitations of the preparation of AuNP with Et_3SiH. It is highly important to stir the mixture of dodecanethiol and $HAuCl_4$ for longer than 3 h before addition of the reducing agent to prepare monodisperse AuNP. Stirring for a shorter period resulted in agglomeration of the nanoparticles, which was confirmed by TEM analyses. Although other organosilanes, diethoxy(methyl)silane and pentamethyldisiloxane, were found to form a purple solution immediately similar to Et_3SiH, nonspherical nanoparticles ranging in size from 6–60 nm were obtained. Treatment of tetramethyldisiloxane, $(HMe_2Si)_2O$, and poly(methylhydrosiloxane) [PMHS: $(HMeSiO)_n$] was found to be ineffective to observe precipitation of insoluble flocculated product.[11] Among several solvents examined, di-*n*-butyl ether (9.3 ± 0.91 nm), cyclopentyl methyl ether (8.8 ± 0.58 nm), and *tert*-butyl methyl ether (9.5 ± 0.84 nm) were found to form monodisperse nanoparticles, while other solvents such as diethyl ether, 1,4-dioxane, 1,2-dimethoxyethane (DME) and methoxybenzene did not afford monodisperse nanoparticles. The key to success in forming monodisperse gold nanoparticles is probably the formation of a homogeneous solution of the intermediate gold thiolate in THF, di-*n*-butyl ether, cyclopentyl methyl ether and *tert*-butyl methyl ether, while the use of solvents such as diethyl ether, 1,4-dioxane, *etc.* resulted in precipitation in the reaction of $HAuCl_4 \cdot 4H_2O$ and dodecanethiol. Other organic solvents such as dichloromethane and toluene were found to be ineffective since $HAuCl_4$ was not dissolved at all.

Table 1 Formation of AuNP with a silane reagent[a]

Entry	Silane	Solvent	Yield/mg	Size/nm
1	Et_3SiH	THF	15.1	8.6 ± 0.65
2	Et_3SiH[b]		15.7	8.4 ± 0.64
3	$HSiMe(OEt)_2$	THF	8.9	—[c]
4	$HMe_2SiOSiMe_3$		18.0	—[c]
5	$(HMe_2Si)_2O$		—[d]	—
6	$(HMeSiO)_n$		—[d]	—
7	Et_3SiH	$^nBu_2O$	13.2	9.3 ± 0.91
8		CPME[e]	14.6	8.8 ± 0.58
9		$^tBuOCH_3$	8.9	9.5 ± 0.84
10		Et_2O	—[f]	—
11		1,4-Dioxane	—[f]	—
12		DME	—[f]	—
13		$PhOCH_3$	—[f]	—

[a] Unless noted, the reaction was performed with dodecanethiol (0.1 mmol), $HAuCl_4 \cdot 4H_2O$ (0.1 mmol) and Et_3SiH (0.1 mmol) with 10 mL of the solvent at 25 °C. [b] 10.0 mmol of Et_3SiH was employed. [c] Nonspherical nanoparticles ranging in size from 6–60 nm formed. [d] Insoluble precipitate formed. [e] Cyclopentyl methyl ether. [f] Precipitation occurred during the reaction of $HAuCl_4$ with thiol.

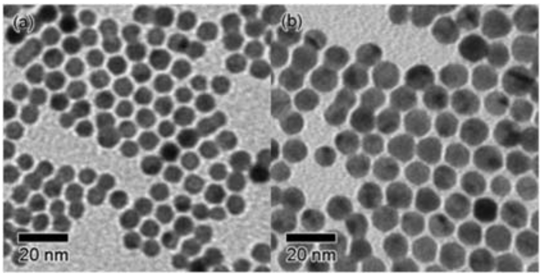

Fig. 3 (a) TEM image of AuNP synthesized at 0 °C (7.5 ± 0.57 nm). (b) TEM image of AuNP synthesized at 50 °C (10 ± 0.9 nm).

The size of AuNP was found to be dependent on the reaction temperature. The addition of triethylsilane to a THF solution of $HAuCl_4 \cdot 4H_2O$ and dodecanethiol at 0 °C afforded 9.3 mg of 7.5 ± 0.57 nm nanoparticles after stirring for 24 h. On the other hand, the reaction at 50 °C furnished 17.3 mg of 10.0 ± 0.90 nm nanoparticles within 3 h (Fig. 3a, b). In contrast to the single-phase method using superhydride or $LiBH_4$, a stronger reducing agent, which afforded AuNP in the range of 2–4 nm,[5] the use of triethylsilane produced AuNP of larger size, 7–10 nm. Accordingly, the size of the gold nanoparticle would be dependent on the reduction rate of gold thiolate, which is rapidly reduced by a strong metal hydride to afford smaller nanoparticles or by the use of not a large excess amount of the mild reducing agent, Et_3SiH to bring about the reduction of the thiolate at a reasonable rate leading to the size of 7.5–10.0 nm.

In summary, gold nanoparticles were found to be generated by the reaction of dodecanethiol and $HAuCl_4$ in the presence of triethylsilane as a new class of reducing agent. The AuNPs obtained were in the form of 7–10 nm spherical particles and exhibited high monodispersity. Since the nanoparticles were prepared with 1 equiv. of organosilane in an organic solvent as a single phase, the protocol is a highly efficient and environmentally benign process.

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11 See Supplementary Information.

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