A facile synthesis of aliphatic thiol surfactant with tunable length as a stabilizer of gold nanoparticles in organic solvents

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Abstract

Three new aliphatic thiol surfactants were synthesized by reacting alkyl bromide with hexamethyldisilathiane under a mild condition. This approach provides an easy access for the direct synthesis of various different length thiol surfactants which play a crucial role in tuning the properties of gold nanoparticles. Gold nanoparticles encapsulated with one of our synthetic thiols were prepared and well characterized by H NMR, UV–vis, FT-IR, and TEM. The hybrid nanoparticles are very stable in both organic solvents and the solid state.

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1. Introduction

Metal nanoparticles have attracted tremendous attention due to their unusual behaviors compared with corresponding bulk materials [1], and hold a great promise in the area of ferrofluids [2], catalysis [3], optoelectronics [4], and biomedical applications [5]. One of the major challenges is to control the size and monodispersity of metal nanoparticles, and to organize them into nanostructured devices and composite materials. Dispersing metal particles in organic solvents is appealing since the low interfacial energies should allow for a high degree of control during solution and surface processing. Thiols have been used to stabilize dispersions of metal nanoparticles in organic solvents, however studies on the spontaneous assemblies of organic thiols on the surface of gold nanoparticle to date have mainly relied on the availability of a relatively few commercially available unbranched alkanethiols. Recently Zhong et al. [6] demonstrated that the size of gold nanoparticles can be tuned molecularly by manipulating different length alkanethiols. By using the commercially available alkanethiols C_NH_2N+1SH with N = 5 to 17, gold nanoparticle sizes ranging from 5 to 8 nm with good monodispersity were obtained. An increase in the alkanethiol chain length leads to a gain in stabilization energy due to additional interchain cohesive interactions. In addition, gold nanoparticles below 5 nm are thought to be of great practical value for numerous applications [7]. In order to obtain stable and monodispersed gold nanoparticles with a desired particle size, it is important to synthesize thiol surfactants with tunable length. For this purpose, a logical way is to connect two length-controllable linear chains via an ester group as a linker. The length of the resultant surfactant will be controlled by the combination of different length aliphatic alcohols and aliphatic acids.

In the synthesis of thiols, a protecting group is often employed since organic thiol has the propensity to be oxidized into corresponding disulfide. The most common protecting group is acetyl which can be deprotected by using harsh reaction conditions such as the strong acids or bases (e.g., sulfuric acid, hydrochloride, potassium hydroxide, potassium carbonate, and lithium aluminum hydride) [8]. However, the strong acidic or basic condition results in the formation of by-products or the decomposition of the target thiols containing the group (e.g., ester and amide) sensitive to acid or base. An ideal synthetic procedure to prepare thiol surfactant should involve an efficient construction of thiol molecule.
Here we report a facile synthesis of aliphatic thiol surfactants with a tunable length to stabilize gold nanoparticles in organic solvents. Gold nanoparticles encapsulated with one of our synthetic thiols were prepared. As expected, the hybrid nanoparticles are very stable in both organic solvents and the solid state.

2. Experimental

2.1. Materials and measurements

All chemicals and solvents were purchased from commercial suppliers and used without further purification. Deionized water was used in the preparation of the gold nanoparticles. HAuCl4 is a 30 wt% in diluted HCl solution. 1H and 13C NMR spectra were recorded in CDCl3. Chemical shifts are in δ units (ppm) with the residual solvent peak as the internal standard. The coupling constant (J) is reported in hertz (Hz). NMR splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; and m, multiplet. Column chromatography was carried out on silica gel (60–200 mesh). Infrared FT-IR spectra were recorded with a KBr pellet. UV–vis spectra were measured on silica gel (60–200 mesh). Infrared FT-IR spectra were recorded in CDCl3. Chemical shifts are in δ units (ppm) with the residual solvent peak as the internal standard. The coupling constant (J) is reported in hertz (Hz). NMR splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; and m, multiplet. Column chromatography was carried out on silica gel (60–200 mesh). Infrared FT-IR spectra were recorded with a KBr pellet. UV–vis spectra were measured in CH2Cl2. TEM images were taken on a Hitachi H-7600 transmission electron microscope.

2.2. Synthesis of thiols

The thiol was introduced by a convenient (trimethylsilyl)thioly-dehalogenation reaction [9]. The target thiols 4a–4c were synthesized starting from aliphatic acid 1 which was reacted with aliphatic alcohol 2 under N,N′-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) at room temperature to get aliphatic bromide 3. The intermediate 3 was reacted with hexamethyldisilathiane in the presence of tetra-n-butyl ammonium fluoride (Bu4NF) to get thiol 4 (Scheme 1). The structures of thiols 4a–4c were well identified by 1H NMR, 13C NMR, FT-IR, MS, and elemental analysis.

Data for thiol 4a (m = 3, n = 1): white solid; IR (KBr) νmax (cm⁻¹): 2920, 2851, 1736, 1177; 1H NMR (CDCl3): δ = 0.88 (t, 3H), 1.33 (m, 30H), 1.63 (m, 6H), 2.28 (t, 2H, J = 7.6 Hz), 2.52 (q, 2H), 4.04 (t, 2H, J = 6.6 Hz); 13C NMR (CDCl3): δ = 14.07, 22.66, 24.60, 25.03, 25.92, 28.35, 28.67, 29.04, 29.16, 29.21, 29.26, 29.31, 29.46, 29.59, 31.90, 34.03, 34.41, 64.32, 173.87; MALDI-TOF MS calcd for C29H58O2SNa (M + Na): 409.3116, found: 409.3108. Anal. calcd for C29H58O2S: C, 73.98; H, 12.42; S, 6.91.

Data for thiol 4b (m = 3, n = 3): white solid; IR (KBr) νmax (cm⁻¹): 2918, 2850, 1736, 1182; 1H NMR (CDCl3): δ = 0.88 (t, 3H), 1.31 (m, 38H), 1.60 (m, 6H), 2.27 (t, 2H, J = 7.6 Hz), 2.51 (q, 2H), 4.04 (t, 2H, J = 6.8 Hz); 13C NMR (CDCl3): δ = 14.05, 22.65, 24.58, 25.02, 25.92, 28.35, 28.66, 29.04, 29.15, 29.21, 29.24, 29.32, 29.45, 29.62, 31.90, 34.01, 34.39, 64.30, 173.84; MALDI-TOF MS calcd for C33H60O2SNa (M + Na): 437.3429, found: 437.3426. Anal. calcd for C33H60O2S: C, 71.44; H, 11.99; S, 8.29. Found: C, 71.19; H, 12.01; S, 8.08.

Data for thiol 4c (m = 3, n = 7): white solid; IR (KBr) νmax (cm⁻¹): 2918, 2850, 1737, 1464, 1193, 1175; 1H NMR (CDCl3): δ = 0.87 (t, 3H), 1.31 (m, 42H), 1.60 (m, 6H), 2.28 (t, 2H, J = 7.6 Hz), 2.52 (q, 2H), 4.04 (t, 2H, J = 6.8 Hz); 13C NMR (CDCl3): δ = 14.05, 22.70, 24.64, 25.04, 25.93, 28.38, 28.66, 28.89, 29.07, 29.17, 29.24, 29.28, 29.38, 29.49, 29.62, 29.67, 29.71, 31.94, 34.06, 34.41, 64.36, 173.98; MALDI-TOF MS calcd for C29H58O2SNa (M + Na): 493.4055, found: 493.4048. Anal. calcd for C29H58O2S: C, 73.98; H, 12.42; S, 6.81. Found: C, 74.03; H, 12.55; S, 6.91.

2.3. Synthesis of the gold nanoparticles encapsulated with the thiol 4c

Gold nanoparticle solutions were prepared following the procedure described by Brust et al. [10] with slight modification. The thiol 4c was used as a stabilizer to synthesize the gold nanoparticles in a ratio of 2:1 for Au:S. In a typical procedure, 15 ml of 0.015 M aqueous solution of HAuCl4 was mixed with 10 ml of 0.05 M solution of tetraoctylammonium bromide (TOAB) in toluene. The mixture was vigorously stirred for 0.5 h until the gold solution was extracted into the organic layer completely. The top orange red toluene layer was separated from the aqueous layer, and washed twice with water. The solution of thiol 4c (0.09 mmol) in toluene was quickly added to the above mixture with stirring. Freshly prepared aqueous NaBH4 solution (12 ml, 0.2 M) was added slowly. The resulting mixture was continued to stir for 3 h at room temperature. The toluene layer was separated and concentrated with a rotary evaporator under reduced pressure. The thiol monolayered gold particles were precipitated in ethanol and kept overnight in the refrigerator, then filtered with Millipore filter paper (0.5 µm pore size) and washed with ethanol. The precipitation procedure was done twice in order to get rid of free thiol and TOAB impurities. The black precipitate was collected for IR, UV–vis, 1H NMR, and TEM studies.

3. Results and discussion

Three new thiols were prepared with this facile synthetic procedure. The ester group as a linker is stable under the aforementioned mild reaction condition. The method is also generally applicable to other thiols with aliphatic or aromatic structural moieties. We can use this approach to synthesize different length thiols or functional thiols by introducing some functional.

![Scheme 1. Synthesis of aliphatic thiols.](image-url)
Fig. 1. TEM images (left, middle, and right) of gold nanoparticles encapsulated with the thiol 4b under different magnification.

Scheme 2. Synthesis of aliphatic thioacetates.


Using the thiol 4c as the stabilizer, gold nanoparticles in organic solvents were prepared by reducing HAuCl₄ in the presence of TOAB as a capping ligand in an organic/aqueous two phase solution [10,12]. As expected, the resulting hybrid gold nanoparticles encapsulated with the thiol 4c were stable in both organic solvent (e.g., CH₂Cl₂, THF, toluene or ether) and the solid state. These nanoparticles did not show any sign of aggregation or precipitation with time, and they could be redispersed in organic solvent after complete removal of solvent [13]. Size distribution and particle size can be obtained from the TEM which shows almost uniform size and shape of the nanoparticles which is consistent with the literature. Their sizes were 2–4 nm, and TEM images in Fig. 1 also clearly show isolated nanoparticles without aggregation. A unique property of the gold nanoparticles encapsulated with thiol surfactants is that they can be handled and characterized as a simple chemical compound. Therefore, NMR, UV–vis, and FT-IR are useful tools to characterize them. The ¹H NMR spectra of the gold nanoparticle samples in CDCl₃ were similar to the free thiols spectra, but with broadened peaks and the disappearance of the methyl group of the thiols. The presence of the methyl group in the TEM images suggests that the nanoparticles are not fully dispersed, even after extensive sonication. This is in contrast to the TEM images of the nanoparticles prepared with the thiol 4b, which show well-defined and isolated nanoparticles without aggregation.

Data for thioacetate 6a (m = 3, n = 1): white solid; yield: 91%; IR (KBr) νmax (cm⁻¹): 2914, 2849, 1725, 1653; ¹H NMR (CDCl₃): δ = 0.88 (t, 3H), 1.29 (m, 30H), 1.58 (m, 6H), 2.28 (t, 2H), 2.32 (s, 3H), 2.86 (t, 2H, J = 7.2 Hz), 4.05 (t, 2H, J = 6.6 Hz); ¹³C NMR (CDCl₃): δ = 14.09, 22.66, 25.01, 25.91, 28.64, 28.78, 29.08, 29.10, 29.14, 29.21, 29.26, 29.32, 29.41, 29.45, 29.49, 29.59, 30.57, 31.89, 34.37, 64.32, 173.90, 195.86; MALDI-TOF MS calcd for C₂₅H₄₈O₃SNa (M + Na): 451.3222, found: 451.3222.

Data for thioacetate 6b (m = 3, n = 3): white solid; yield: 84%; IR (KBr) νmax (cm⁻¹): 2917, 2849, 1736, 1725, 1694, 1202, 1183; ¹H NMR (CDCl₃): δ = 0.87 (t, 3H), 1.25 (m, 34H), 1.59 (m, 6H), 2.28 (t, 2H), 2.31 (s, 3H), 2.85 (t, 2H, J = 7.4 Hz), 4.05 (t, 2H, J = 6.8 Hz); ¹³C NMR (CDCl₃): δ = 14.10, 22.70, 25.04, 25.94, 28.66, 28.82, 29.11, 29.16, 29.24, 29.28, 29.36, 29.44, 29.48, 29.61, 29.66, 29.68, 30.64, 31.93, 34.43, 64.39, 174.04, 196.07; MALDI-TOF MS calcd for C₂₇H₅₂O₃SNa (M + Na): 479.3535, found: 479.3537.

Data for thioacetate 6c (m = 3, n = 7): white solid; yield: 90%; IR (KBr) νmax (cm⁻¹): 2918, 2850, 1721, 1697, 1471, 1179; ¹H NMR (CDCl₃): δ = 0.87 (t, 3H), 1.24 (m, 42H), 1.60 (m, 6H), 2.28 (t, 2H), 2.31 (s, 3H), 2.85 (t, 2H, J = 7.4 Hz), 4.04 (t, 2H, J = 6.8 Hz); ¹³C NMR (CDCl₃): δ = 14.10, 22.70, 25.03, 25.93, 28.66, 28.82, 29.10, 29.14, 29.17, 29.24, 29.29, 29.37, 29.44, 29.48, 29.62, 29.67, 29.70, 30.63, 31.93, 34.41, 64.37, 174.00, 196.00; MALDI-TOF MS calcd for C₃₁H₆₀O₃SNa (M + Na): 535.4161, found: 535.4160. Anal. calcd for C₃₁H₆₀O₃S: C, 72.60; H, 11.79; S, 6.25. Found: C, 72.50; H, 11.94; S, 6.14.
Fig. 2. Partial $^1$H NMR spectra of the hybrid gold nanoparticles encapsulated with thiol 4c (above) and the free thiol 4c (bottom).

The $^1$H NMR spectra showed the disappearance of any TOAB residual after the precipitation and washing with ethanol for two times. The FT-IR spectra of the free thiol ligands and of the Au-thiol nanoparticles are similar which indicates that the thiol is part of the composite and the gold nanoparticles are effectively stabilized with these ligands. The ester peak at 1736 cm$^{-1}$ indicates that there is no reduction of the ester group in the thiols ligands during the preparation of the gold nanoparticles. The UV–vis spectrum of the gold nanoparticles encapsulated with thiols 4c in CH$_2$Cl$_2$ (Fig. 3) shows a broad plasmon band around 517 nm which originates from the formation of the gold colloids [15].

4. Conclusion

We have demonstrated a facile synthesis of the three new aliphatic thiols by reacting alkyl bromide with hexamethyldilathiane under a mild condition. The ester group as a linker in the thiol-functionalized aliphatic esters is stable under the mild reaction condition. The synthetic method is very versatile and effective for constructing many other different length thiol surfactants with aliphatic or aromatic structural moieties, which play a crucial role in tuning the properties of gold nanoparticles for various technological applications. Gold nanoparticles encapsulated with one of our synthetic thiols are stable in both organic solvent and the solid state. These hybrid gold nanoparticles did not show any sign of aggregation or precipitation with time, and they could be redispersed in organic solvent after complete removal of solvent.

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