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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.

Keywords: Synthesis; Thiol; Surfactant; Gold nanoparticles

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 nanopartilce 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 $C_NH_{2N+1}SH$ 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 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 aluminium 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.

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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. $HAuCl_4$ is a 30 wt% in diluted HCl solution. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$. 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 CH_2Cl_2. TEM images were taken on a Hitachi H-7600 transmission electron microscope.

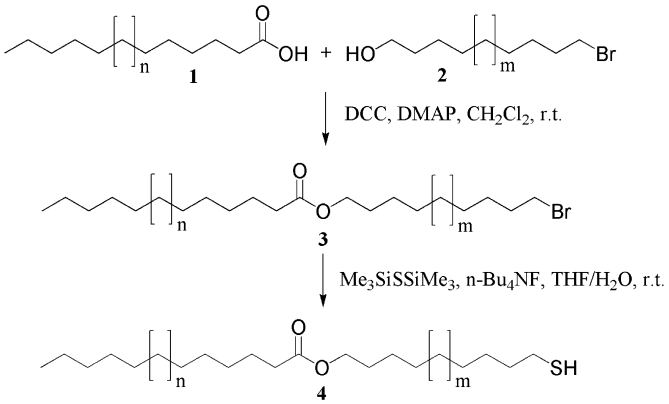
2.2. Synthesis of thiols

The thiol was introduced by a convenient (trimethylsilyl)thioxy-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 tetrabutyl ammonium fluoride (Bu_4NF) to get thiol **4** (Scheme 1). The structures of thiols **4a**–**4c** were well identified by ^1H NMR, ^{13}C NMR, FT-IR, MS, and elemental analysis.

Data for thiol **4a** ($m = 3$, $n = 1$): white solid; IR (KBr) ν_{max} (cm^{-1}): 2920, 2851, 1736, 1177; ^1H NMR ($CDCl_3$): $\delta = 0.88$ (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); ^{13}C NMR ($CDCl_3$): $\delta =$ 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 $C_{23}H_{46}O_2SNa$ (M + Na): 409.3116, found: 409.3108. Anal. calcd for $C_{23}H_{46}O_2S$: C, 71.44; H, 11.99; S, 8.29. Found: C, 71.19; H, 12.01; S, 8.08.

Data for thiol **4b** ($m = 3$, $n = 3$): white solid; IR (KBr) ν_{max} (cm^{-1}): 2918, 2850, 1736, 1182; ^1H NMR ($CDCl_3$): $\delta = 0.88$ (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); ^{13}C NMR ($CDCl_3$): $\delta =$ 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 $C_{25}H_{50}O_2SNa$ (M + Na): 437.3429, found: 437.3426. Anal. calcd for $C_{25}H_{50}O_2S$: C, 72.40; H, 12.15; S, 7.73. Found: C, 71.19; H, 12.01; S, 8.08.

Data for thiol **4c** ($m = 3$, $n = 7$): white solid; IR (KBr) ν_{max} (cm^{-1}): 2918, 2850, 1737, 1464, 1193, 1175; ^1H NMR ($CDCl_3$): $\delta = 0.87$ (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); ^{13}C NMR ($CDCl_3$): $\delta = 14.05$, 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 $C_{29}H_{58}O_2SNa$ (M + Na): 493.4055, found: 493.4048. Anal. calcd for $C_{29}H_{58}O_2S$: C, 73.98; H, 12.42; S, 6.81. Found: C, 74.03; H, 12.55; S, 6.91.



Scheme 1. Synthesis of aliphatic thiols.

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 $HAuCl_4$ 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 $NaBH_4$ 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

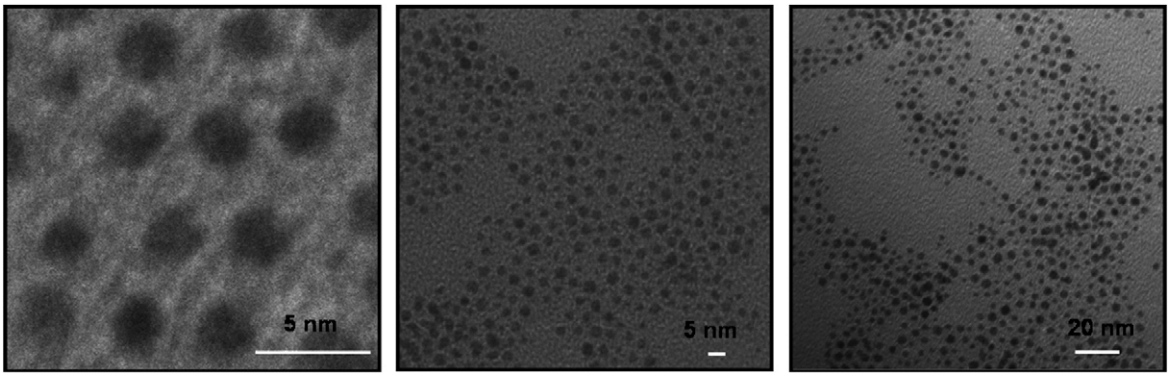
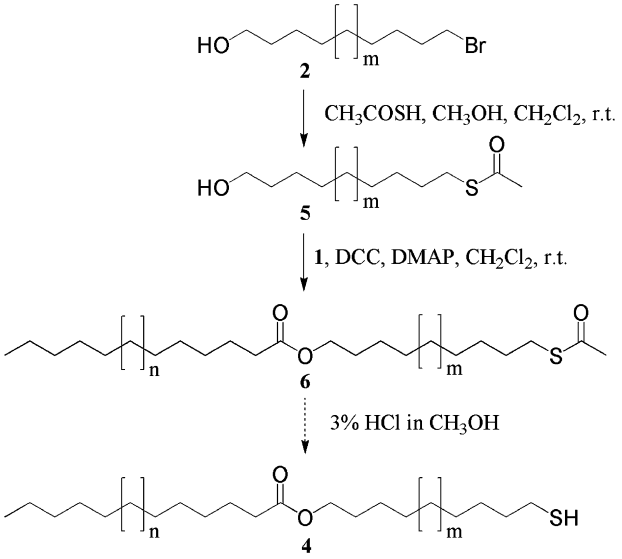


Fig. 1. TEM images (left, middle, and right) of gold nanoparticles encapsulated with the thiol **4b** under different magnification.



Scheme 2. Synthesis of aliphatic thioacetates.

group into the molecular structure. Interestingly, our synthetic thiols are not easily oxidized into disulfides, as evidenced by the proton–proton coupling between $-CH_2-$ and –SH in the NMR spectra recorded from samples even after having been kept for a long time under ambient condition. So the thiols can be purified by flash chromatography on silica gel with 1% ethyl acetate in hexane as the eluent. Another synthetic method to prepare the thiols was also attempted (Scheme 2). 11-Bromo-undecan-1-ol **2** was reacted with thioacetic acid to give **5** followed by treatment with different length aliphatic acid to get the ester **6** in a high yield. However, conversion of thioacetate **6** to free thiol using 3% HCl/CH_3OH [11] was not successful, and its hydrolyzed products were obtained. This is not surprising since the ester group as the linker might be easily hydrolyzed under the acidic reaction condition. The structures of the thioacetates (**6a**–**6c**) were well identified by ^{1}H NMR, ^{13}C NMR, FT-IR, MS, and elemental analysis.

Data for thioacetate **6a** ($m = 3$, $n = 1$): white solid; yield: 91%; IR (KBr) ν_{max} (cm^{-1}): 2914, 2849, 1725, 1691, 1653; ^{1}H NMR ($CDCl_3$): $\delta = 0.88$ (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); ^{13}C NMR ($CDCl_3$): $\delta = 14.09$, 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 $C_{25}H_{48}O_3SNa$ (M + Na): 451.3222, found: 451.3222.

Data for thioacetate **6b** ($m = 3$, $n = 3$): white solid; yield: 84%; IR (KBr) ν_{max} (cm^{-1}): 2917, 2849, 1736, 1725, 1694, 1202, 1183; ^{1}H NMR ($CDCl_3$): $\delta = 0.87$ (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); ^{13}C NMR ($CDCl_3$): $\delta = 14.10$, 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 $C_{27}H_{52}O_3SNa$ (M + Na): 479.3535, found: 479.3537.

Data for thioacetate **6c** ($m = 3$, $n = 7$): white solid; yield: 90%; IR (KBr) ν_{max} (cm^{-1}): 2918, 2850, 1721, 1697, 1471, 1179; ^{1}H NMR ($CDCl_3$): $\delta = 0.87$ (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); ^{13}C NMR ($CDCl_3$): $\delta =$ 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 $C_{31}H_{60}O_3SNa$ (M + Na): 535.4161, found: 535.4160. Anal. calcd for $C_{31}H_{60}O_3S$: C, 72.60; H, 11.79; S, 6.25. Found: C, 72.50; H, 11.94; S, 6.14.

Using the thiol **4c** as the stabilizer, gold nanoparticles in organic solvents were prepared by reducing $HAuCl_4$ 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., CH_2Cl_2, 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 ^{1}H NMR spectra of the gold nanoparticle samples in $CDCl_3$ were similar to the free thiols spectra, but with broadened peaks and the disappearance

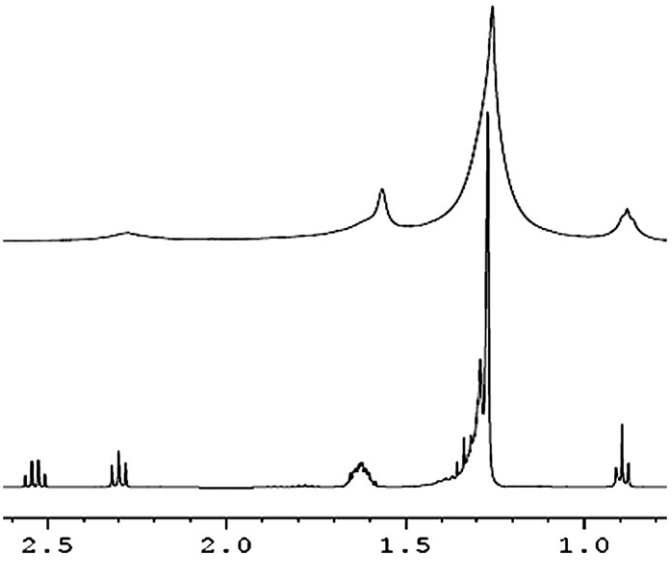


Fig. 2. Partial ^{1}H NMR spectra of the hybrid gold nanoparticles encapsulated with thiol **4c** (above) and the free thiol **4c** (bottom).

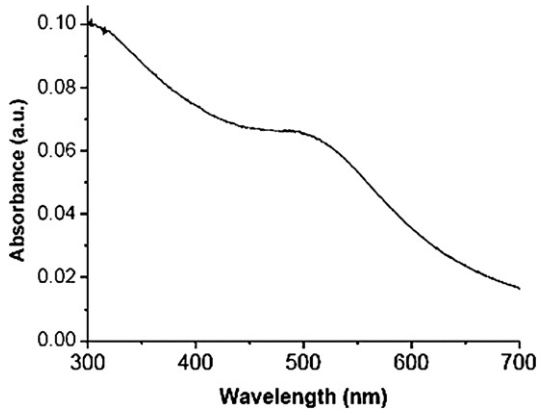


Fig. 3. UV–vis spectrum of the gold nanoparticles encapsulated with thiol **4c**.

of the α-methylene quartet at 2.55 ppm close to the thiol group (Fig. 2) [14]. Also 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_2Cl_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 hexamethyldisilathiane 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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