

On the surface structure of 1,3-dithiol-protected gold nanoparticles interpreted by the size effect of IR absorption properties



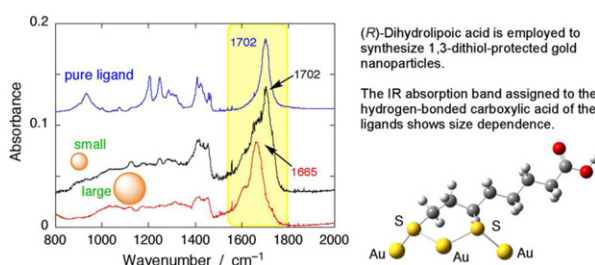
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HIGHLIGHTS

- Dihydrolipoic acid is employed to prepare 1,3-dithiol-protected gold nanoparticles.
- A bidentate ligation is prone to make the nanoparticle size large unexpectedly.
- This is due to thermal lability of dithiolate desorption from the gold surface.
- The IR absorption due to the hydrogen-bonded carboxylic acid shows size dependence.
- The existence of intraparticle coupling indicates that of bent S–Au–S binding modes.

GRAPHICAL ABSTRACT



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ABSTRACT

Inspired by the monothiol-bridging staple structure typically observed for the ligand-protected Au₂₅ or Au₃₈ clusters, a bidentate molecule, (R)-dihydrolipoic acid (R-DHLA), is employed to synthesize dithiol-protected gold nanoparticles. The obtained nanoparticles are separated by gel electrophoresis; the most abundant compound has the mean core diameter of 2.47 nm, but a very small cluster compound with the diameter of 0.83 nm is also produced. We find for the first time that the IR absorption assigned to the hydrogen-bonded carboxylic acid in the surface ligands shows size dependence. This can be explained in terms of a bonding manner whether the hydrogen-bond formation occurs between nanoparticles or within a single nanoparticle. The existence of intraparticle coupling between ligands also implies that the bent S–Au–S is likely to form on the surface structures.

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1. Introduction

Investigations of ligand-protected metal nanoparticles are largely motivated in the past decade due to their intriguing size-dependent physicochemical properties [1,2]. In particular, successful synthesis of extremely small thiolate-protected gold nanoparticles (or clusters) with diameters smaller than ~2 nm

leads to the formation of thermodynamically stable, atomically monodisperse clusters of the formula Au_m(SR)_n [3], which have allowed detailed characterizations of their electronic, chemical and spectral properties such as highly structured (molecule-like) optical absorption and intense fluorescence [4]. These characters can be primarily ascribed to discrete single electron transitions between occupied and unoccupied electronic energy levels rather than by collective many-electron excitations [5]. In addition, a key point in understanding of the surface chemistry of the Au–S interface in the gold nanoparticles has been the elucidation of the Au₁₀₂(p-mercaptobenzoic acid)₄₄ crystal structure by

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X-ray diffraction [6]. In the nanoparticle, a 79-atom gold core is surrounded by two types of bonding motifs; RS–Au–SR (short staple) and RS–Au–RS–Au–SR (long staple or semi-ring), where SR denotes the thiolate [6]. Then, it is now well-established that the Au–S interface in such small nanoparticles consists of staple RS–(Au–SR)_n units, so an explicit way to write the molecular formula of the nanoparticles can be based on the “divide and protect” notation; for example, Au₂₅(SR)₁₈ = Au₁₃[RS–(Au–SR)₂]₆; Au₃₈(SR)₂₄ = Au₂₃[RS–Au–SR]₃[RS–(Au–SR)₂]₆ [7].

In comparison to the above-mentioned thiolate-bridging motifs, multidentate (particularly, bidentate) ligation would have an impact not only on the cluster stability but also on the electronic or structural response of the clusters because of the constraint by linking two thiol groups on the same molecule (Fig. 1a). In addition, the surface Au–S bond formation with bidentate dithiols invites some interesting questions within the context of the well-known semi-ring structures; for example, do dithiols favor intrastaple (=within a staple; refer to as W-type configuration) or interstaple (=between staples; refer to as B-type configuration) binding as in the cartoon of Fig. 1b, under the geometrical constraints that only one bidentate ligand per semi-ring is allowed? How does the bidentate binding influence the electronic structure of the cluster? Previous reports have so far documented the synthesis of gold nanoparticles protected by dithiols or ligand exchange reactions from monothiol protection to dithiol modification [8]. Some results imply that, from a viewpoint of surface chemistry, the interstaple coupling (B-type configuration) would be favored compared to the intrastaple coupling when 1,5- or shorter dithiols are applied [9]; but other infers that 1,4-type dithiol (1,1'-binaphthyl-2,2'-dithiol) would provide a suitable structure only for the incorporation into short staples (that is, W-type configuration) based on mass spectrometry [10].

In the present study, a bidentate 1,3-dithiol, (*R*)-dihydrolipoic acid (*R*-DHHLA) shown in Fig. 1c, is employed to synthesize *R*-DHHLA-protected gold nanoparticles. Upon binding of *R*-DHHLA to the gold surface, the constraint imposed by the linker between the bidentate sites within the individual ligand is expected to result in novel properties compared to the monothiol-protected gold nanoparticles. The use of “optically pure” dithiol ligand is here to prevent stereochemical disorder for the ligation, and thus, the main purpose is to investigate whether the single DHHLA ligand can produce intrastaple linkage (or W-type configuration) on the nanoparticle surface. We then present experimental evidence for the existence of W-type configuration based on the size-dependent IR spectra.

2. Experimental

2.1. Materials

HAuCl₄·4H₂O (99%), sodium borohydride (NaBH₄, >90%), methanol (GR grade), and ethanol (GR grade) were received from Wako Pure Chemical and used as received. (*R*)-α-Lipoic acid (abbreviated as *R*-LA, Fig. 1c) was received from Tokyo Chemical Industry and used as received. Pure water was obtained by a water-distillation supplier (Advantec GS-200).

2.2. Synthesis of *R*-DHHLA-protected gold nanoparticles

In a typical experiment, ice-cooled aqueous solution of NaBH₄ (19.0 mg/1 mL water) was added to the methanolic solution of *R*-LA (206.3 mg/20 mL) at 0 °C under vigorous stirring. After 2 h stirring, the solution was filtered to remove solid impurities. In this step, *R*-LA is reduced to form (*R*)-α-dihydrolipoic acid (*R*-DHHLA) [11]. Then, 80 mL of methanol was added, followed by addition of 0.5 mmol of HAuCl₄ dissolved in water (2.06 mL) under vigorous stirring. Note that the dithiol/Au molar ratio in the synthesis was 4/1. After

further stirring (3 h), a freshly prepared ice-cooled 0.2 M methanolic NaBH₄ solution (25 mL) was added and the mixture was well-stirred for 1.5 h. After overnight storage, the solvent was mostly evaporated under vacuum below 30 °C, followed by addition of ethanol to obtain a reddish-brown precipitate. The precipitate was thoroughly washed with water/ethanol (1/9) and ethanol through redispersion–centrifugation processes. Finally, a cluster powder was obtained by a vacuum-drying procedure.

2.3. Polyacrylamide gel electrophoresis (PAGE)

The *R*-DHHLA-protected gold nanoparticles can be negatively charged in basic solutions, so to separate the particles that differ in size, we applied polyacrylamide gel electrophoresis (PAGE) using a slab gel unit (ATTO, AE-6200) [12]. The gels were comprised of 3% stacking gel (pH 6.8) and 15% separating gel (pH 8.8). It should be noted that three separable regions (**1–3**; **1** for the most mobile species, **3** for the densely colored region with less mobility, and **2** in between the regions) are typically assigned. To extract the gold nanoparticle compound into aqueous solution, a part of the gel containing the fraction was cut out and homogenized, followed by the addition of distilled water. The gels were removed by a centrifuge and using a syringe filter with pore size of 450 nm. Addition of hydrochloric acid (6.0 M) into the extract allowed obtaining precipitates of the product (fractioned) due to the formation of neutral carboxylic acid, followed by washing with a common protocol for purification.

2.4. Instrumentation

UV–vis absorption spectra were recorded with a Hitachi U-4100 spectrophotometer. The mean core diameter of the gold nanoparticle sample was determined by a solution-phase small angle X-ray scattering (SAXS) technique and electron microscopy. The SAXS analyses are based on the assumption that spherical particles are distributed with a simple Γ -distribution function [12]. Field emission scanning transmission electron microscopy (FE-STEM) was conducted with a Hitachi S-4800 electron microscope. FT-IR spectra were recorded with a Horiba FT-720 infrared spectrophotometer by the KBr disk pellet method. ¹H NMR spectra were recorded on a Chemagnetics CMX-400 NMR spectrometer operating at the ¹H resonance frequency of 400.16 MHz under magic angle spinning (MAS) conditions [13]. Elemental analysis was conducted by energy dispersive X-ray (EDX) spectroscopy excited by an electron beam at 6.0 kV with an EDAX Genesis-2000 system attached to the S-4800 electron microscope.

2.5. Computational methods

The geometry optimizations of the related compounds were carried out with the Gaussian 09 program at the density functional theory (DFT) level using B3LYP functional and a LanL2DZ basis set for a gold atom and a 6-31G* basis set for other atoms in gaseous phase, followed by calculations of their harmonic vibrational frequencies to verify their stability and to obtain IR spectra [14]. Calculated frequencies were empirically scaled by a so-called scaling factor (0.9614 in this case) [15].

3. Results and discussion

We used ¹H NMR spectroscopy to confirm that DHHLA ligation onto the gold nanoparticles has been successful. The spectral result with the proton assignments is shown in the Supplementary Material (Fig. S1). The assignment could be done based on that for free DHHLA. In comparison to the free DHHLA ligand study in basic D₂O solution [16], the spectral features for the nanoparticle sample are

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