



# The coordination chemistry of gold surfaces: Formation and far-infrared spectra of alkanethiolate-capped gold nanoparticles

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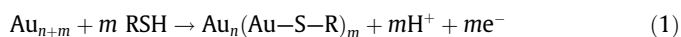
## ABSTRACT

We find that hydrogen is formed (slowly) in the reaction of “naked gold” with thiols in toluene, thereby establishing the fate of a significant fraction of the thiol H when thiols react with gold nanoparticles to yield monolayer-protected clusters. The far-infrared spectra of 2-nm alkane-thiolate-capped Au nanoparticles have been determined in order to probe the binding of alkanethiols (pentane, hexane, decane, dodecane, hexadecane, and octadecane) to the particle surface. Bands due to the Au–S stretch were observed in the range 170–270 cm<sup>-1</sup>, with most samples exhibiting two bands in this region. The Au–S stretch frequencies observed here are similar to those found from HREELS of alkanethiol SAMs on Au(111) (J. Phys. Chem. B 106 (2002) 9655) and are consistent with recent descriptions of the surface as being stabilized by Au(I)-bridged thiolate “staples” (Science 318 (2007) 407).

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## 1. Introduction

Self-assembled monolayers (SAMs) of thiols on gold and other metals are widely used to tailor the surfaces of crystals/electrodes and nanoparticles under a wide range of synthetic conditions [1,2]. Gold nanoparticles capped with alkanethiols have been studied extensively [3,4]. There is now general agreement [3] that this capping material is bound as “thiolate” R–S, although instances are known in which some of the coordination sites are occupied by thiol R–SH [5]. For a 2-nm nanoparticle an Au–S bond length of 2.31 Å has been inferred from X-ray absorption fine structure spectroscopy (EXAFS) studies [6]. A combined EXAFS/transmission electron microscopy (TEM) study indicates thiolate-binding to a threefold site and an Au–S distance of 2.31 Å, with ca. two-thirds of the surface Au atoms bound to RS [7]. However, much confusion has remained as to the nature of the metal–thiolate bond and the nature of the thiol adsorption process in both two-dimensional (SAM) and three-dimensional (nanoparticle assemblies). Denoting the Au SAM or nanoparticle as Au<sub>n</sub>(Au–S–R)<sub>m</sub> where the Au<sub>n</sub> are in the bulk or core and Au<sub>m</sub> are on the surface, an oxidative adsorption mechanism (e.g. Eq. (1))

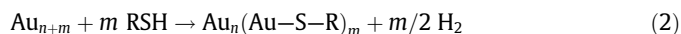


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has been invoked for spontaneous self-assembly [8,9] and for the electrochemically assisted formation of thiol SAMs on Au [10,11] and Pt [12]. (For the former case dioxygen or adventitious impurities serve as oxidant; for the latter, the oxidation is electrochemical). In addition there is evidence for



conversion of thiol H to dihydrogen [1,2]. On the other hand, in HREELS studies of methanethiol on Au(111), the SH stretch was detected, indicating binding of thiol, not thiolate [13]. In temperature-programmed-desorption studies of alkanethiols on Au(111) H<sub>2</sub> was found to desorb below the desorption temperature of the parent thiol for octanethiol (at 280 K), but not for lower thiols [14]. In 2002 Hasan et al. detected bound S–H by proton NMR on 2–5-nm particles and provided the first direct evidence for this bonding mode on nanoparticles [5]. The approach used exploited “place-exchange” of thioether ligands, which, unlike thiols, provide no suitable site for the H of the incoming thiol.

What has remained unclear is whether in the preparation of SAMs or monolayer-protected clusters, the thiol H is lost as H<sup>+</sup>, as H<sup>+</sup> + e<sup>-</sup> by reaction with O<sub>2</sub>, or as H<sub>2</sub>. For self-assembled monolayers, the amount of material – and hydrogen gas that would be evolved – are very small, complicating any determination of the amount of hydrogen produced. In contrast, the availability of high-surface-area nanoparticles in mg-g quantities provides an opportunity for a conventional analytical approach to hydrogen determination. For example, for “naked gold” particles stabilized

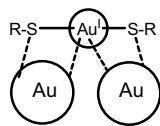


Fig. 1. R-S-Au-S-R "staple" adapted from Ref. [23].

by tetraoctylammonium bromide (TOAB), the fraction of Au atoms on the surface ranges from 25% (5 nm particles of 3800 total with 950 atoms on the surface) to 60% (2-nm particles of 300 total Au atoms with 180 on the surface). In the present work, we report determination of  $H_2$  from the reaction of "naked gold" nanoparticles with octadecanethiol and 4-methylthiophenol by gas chromatography under reaction conditions similar to those of the Brust et al. [15] synthesis, except that no aqueous phase containing sodium borohydride is present.

In the second part of this study we use far-infrared spectroscopy to probe the binding of thiolate to the surface of 2-nm Au nanoparticles. Though many studies have examined the properties of the hydrocarbon portion of the capping material and the self-assembly of the nanoparticles, the Au-S bond itself has received less attention. Previous IR and Raman studies [16–18] of gold nanoparticles and self-assembled monolayers focused on the structural defects of the alkanethiol chain seen in the mid-IR range and not the sulfur binding. Characterization of the Au-S bond by far-IR spectroscopy offers the possibility of elucidating the nature of surface interaction with this ligand and of also probing the nature of the surface of the nanoparticle itself, since information on the environment of the surface gold atoms can be extracted. Such an examination is particularly relevant in the context of recent structural studies that have led to revision of the description of these surfaces. Thus, a model of the clusters and SAMs as a metallic gold core encapsulated by a gold thiolate oligomers -SR-Au-SR- or -SR-AuSR-Au-SR) is emerging [19]. Recent studies of octanethiol [20] and benzenethiol [21] bonding to Au(111), probed by scanning tunneling spectroscopy (STM), implicate PhS-Au-SPh complexes in which one gold is an adatom and the other is a surface Au atom. Crystallographic study of  $Au_{102}(MBA)_{44}$  (MBA = mercaptobenzoic acid) [22] reveals a "staple" R-S-Au-SR motif (Fig. 1) in which the thiol sulfur is bound to a core and to a bridging Au atom [23], as does  $[TOA^+][Au_{25}(SCH_2CH_2Ph)_{18}]$ , where  $TOA^+ = N(C_8H_{17})_4^+$  [24,25].

In the present study, the nanoparticles were prepared using the Brust method, which has very recently been shown to yield mainly  $Au_{38}$  and  $Au_{144}$  species [26]. Six different gold nanoparticle samples were prepared with the capping material ranging from pentane thiol ( $C_5$ ) up to octadecanethiol ( $C_{18}$ ) to observe the effect of the carbon chain on the binding and the samples were studied by far-infrared (far IR) spectroscopy.

## 2. Experimental

"Naked gold" particles stabilized by tetraoctylammonium bromide were prepared by reduction of  $H AuCl_4$  (phase-transferred into toluene) with sodium borohydride [27]. The resulting toluene solution was washed with MilliQ water and dried with  $Na_2SO_4$  and stored until use in a refrigerator. The rate of reaction of the particles with dodecane thiol was surveyed by monitoring the decrease in intensity of the plasmon band in a 1 mM gold solution. The absorbance change appeared biphasic, with a first half-life of ca. 1 h, followed by a ca. three times slower decrease. For the  $H_2$  determinations portions of the "naked gold" solution were deaerated with argon and transferred to an Ar-filled glove box. Typically 0.5 mL gold stock solution was diluted with 2.0 mL 0.01 M TOAB in toluene, then 0.5 mL of 5 mM thiol in toluene containing

0.01 M TOAB was added and the stopcock was closed. The capped assemblies were removed from the glove box to determine  $H_2$ . The  $H_2$  in the head space of the cuvettes was determined by gas chromatography on molecular sieve 5 Å (Ar carrier) [28].

The "naked gold" particles were transferred to  $D_2O$  as described by Gittins and Caruso [29] and their near-infrared-visible spectrum is presented in Fig. 2.

For the far-infrared studies the thiolate-protected gold nanoparticles were synthesized by the method of Brust et al. [15] and "annealed" as described by Murray and co-workers [31]. Solid samples were made for each of the different alkanethiols and the size distribution was calculated based on the TEM images obtained for each. The alkanethiols used (Aldrich, used without further purification) were pentane ( $C_5$ ), hexane ( $C_6$ ), decane ( $C_{10}$ ), dodecane ( $C_{12}$ ), hexadecane ( $C_{16}$ ), and octadecane ( $C_{18}$ ). The nanoparticle samples were stored as dried powders in the refrigerator. UV-Vis spectra of the samples are given in Fig. 3.

For the infrared work, the nanoparticle films were made just before use by applying a concentrated colloidal solution (addition of methylene chloride to the dried powder sample) dropwise onto 1 mil polyethylene film mounted in a standard FTIR sample holder and allowed to dry completely under Ar. The far-IR spectra were collected on a dry-air purged Bruker IFS-66 spectrometer equipped with a T222 mylar beamsplitter and a Far-IR DTGS detector and obtained from 200 scans at  $1\text{ cm}^{-1}$  resolution recorded between 700 and  $70\text{ cm}^{-1}$  at room temperature.

The transmission electron microscopy (TEM) was performed using a JEOL 100CXII instrument. As shown in Fig. 4, the average size of each of the thiolate-capped nanoparticle samples was  $\sim 2\text{ nm}$  in diameter, except that the decanethiol sample had a larger size (up to 20 nm) distribution than the other samples imaged.

## 3. Hydrogen formation in thiolate-nanoparticle assembly

Hydrogen-determination data are given in Table S1 and illustrated in Fig. 5. The reaction of the aromatic thiol, 4-methylthiophenol, was considerably more rapid than that of the  $C_{18}$  alkanethiol. In neither case is the yield quantitative: for 5-nm particles  $2H_2/Au$  (Eq. (2)) should be 0.17 and for 3-nm particles 0.29 is expected, but the highest value we measured was 0.1.

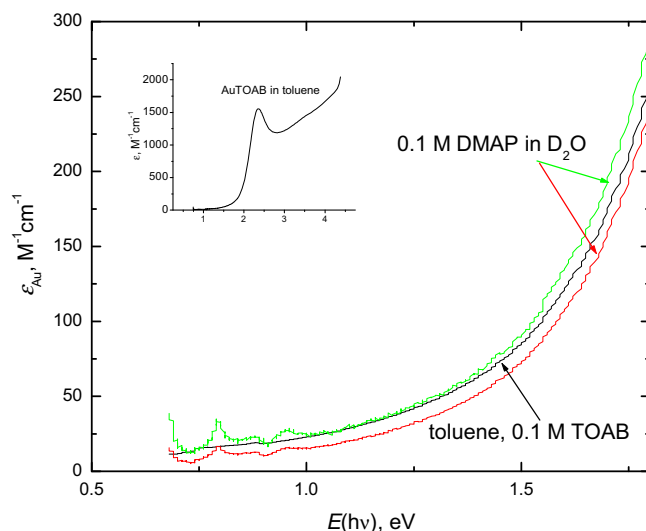


Fig. 2. Comparison of the spectra of 1–3 nm gold particles stabilized by tetraoctylammonium bromide in toluene and by dimethylaminopyridine (DMAP) in deuterium oxide. This provides evidence of only weak electronic interaction between dimethylaminopyridine adsorbate and the surface gold [30].

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