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Loss of Hydrogen upon Exposure of Thiol to Gold Clusters at Low Temperature

John E. Matthiesen,[†,‡] Deepa Jose,[†] Christopher M. Sorensen,[§] and Kenneth J. Klabunde*[,†]

[†]Department of Chemistry and [§]Department of Physics, Kansas State University, Manhattan, Kansas 66506, United States
[‡]Wartburg College, Waverly, Iowa 50677, United States

ABSTRACT: Gold−acetone−dodecanethiol and gold−acetone−phenylethanethiol colloids were prepared by the solvated metal atom dispersion method. Hydrogen evolution occurred at fairly low temperature, when the melting acetone−gold solvate encountered the thiol molecules, due to S−H bond scission. The gas inside the reactor was analyzed by gas chromatography, and the moles of H_2 was determined by calibration curves obtained from a series of known concentration samples. The gold-to-thiolate ratio was calculated using thermal gravimetric analysis. The average particle diameter was also calculated using the gold-to-thiolate ratio.

■ INTRODUCTION

In 2002, Brust and co-workers showed that the formation of the gold−thiol bond in nanoparticle gold (2−5 nm) proceeds by first adopting an intact thiol where the hydrogen atom is still present (either bonded to sulfur or directly to gold).[1] However, when thiol was added in smaller amounts, there was a complete uptake of thiol with release of dihydrogen.

Small gold clusters have been shown to possess only surface-bound thiolates, and sulfur-bound hydrogen is not present.[2−4] X-ray crystal structure studies of $[Au_{25}(SCH_2CH_2Ph)_{18}][N(C_8H_{17})_4]$ and $Au_{102}(p\text{-MBA})_{44}$ (p-MBA = $SC_7O_2H_5$) discovered a gold core protected by gold−thiolate staple motifs (-RS-Au-RS- and -RS-Au-RS-Au-Rs-) (R = alkyl chain).[2,3] In more recent work, theoretical calculations for a $Au_{20}(SR)_{16}$ cluster showed a prolate Au_8 core protected by four extended gold−thiolate staple motifs (-RS-Au-RS-Au-RS-Au-RS-).[4]

In the case of gold nanoparticles of about 5 nm size, no X-ray crystal structures have been reported, and the fate of sulfur-bound hydrogen of thiol molecule is controversial. Studies showed that, the sulfur-bound hydrogen could be either intact (RSH) or absent (RS^- or R-S-S-R) during the formation of self-assembled thiol monolayers around the gold nanoparticle.[1,5−14] The adsorption of short-chain thiol molecules (up to five carbon atoms in the hydrocarbon chain) on Au(111) surface is non-dissociative. For example, methanethiol and *n*-propanethiol adsorb without S−H bond cleavage on defect-free Au(111) surface.[9,10] It has also been shown that S−H bond scission takes place even with short-chain alkanethiols when there are defects on the Au(111) surface. Dissociative interaction between thiol molecules and Au surface yields both thiolates and disulfides on Au(111) surface.[11,12] In dissociative adsorption of thiol molecules on gold surface, the released hydrogen could either adsorb on the gold surface or desorb as molecular hydrogen.[1] Kankate et al. demonstrated the formation of atomic hydrogen by the scission of S−H bond during gold−thiol interaction.[13] Petroski et al. also observed the formation of hydrogen when naked gold nanoparticles react with thiols.[14]

By far the most common method of preparation of nanoparticle gold−thiolate is by chemical reduction of gold ions in the presence of surfactants.[15] What happens to the sulfur-bound hydrogen is almost never discussed, presumably because of the complex mixtures involved and the inability to trace its fate. We have developed a somewhat different approach, and we have prepared gold nanoparticles by weakly solvating them with ketone molecules, specifically acetone, and treating these gold−acetone colloidal solutions with thiols. The experiment is carried out by vaporization of bulk gold and trapping the gold atoms in freezing acetone. Upon warming, the solvated gold atoms migrate and nucleate to form stable colloids. Such weakly ligated gold nanoparticles exhibit unusual properties. For example, at reflux temperature of butanone or 2-pentanone, alkylsilanes ($RSiH_3$) in the presence of water undergo polymerization on the surface of the gold particles to form siloxane nanowires, filaments, and tubes.[16]

Herein, we report that exposing these gold−acetone colloids to excess dodecanethiol (or phenylethanethiol) yields thiolate-coated gold nanoparticles with the quantitative evolution of dihydrogen.

■ EXPERIMENTAL SECTION

Materials and Methods. Phenylethanethiol (PET) (98%) and 1-dodecanethiol (DDT) (98%) were purchased from Sigma-Aldrich and used without further purification. Toluene (99.9%) and acetone (99%) were purchased from Fischer Scientific, distilled, and degassed four times by the standard freeze−pump−thaw procedure prior to use in solvated metal atom dispersion (SMAD) experiments.

Preparation of Gold−Acetone−Dodecanethiol and Gold−Acetone−Phenylethanethiol Colloid. Gold−acetone−dodecanethiol and gold−acetone−phenylethanethiol colloid were prepared by

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the SMAD method. The details of SMAD method are given elsewhere.[17] In a typical experiment, a tungsten crucible was loaded with gold shot (~100 mg), and DDT (or PET) was placed at the bottom of the reactor. The metal-to-thiol ratio was kept 1:30. Liquid nitrogen cooling and vacuum were applied. The crucible was heated resistively in vacuo, and the Au vapor was allowed to co-condense on the walls of the reactor with acetone vapors. Once the metal vaporization was completed, the liquid nitrogen dewar was removed, and the gold−acetone matrix was allowed to melt down under Ar atmosphere. The gold−acetone colloid came into contact with the thiol taken at the bottom of the reactor and formed gold−acetone−dodecanethiol or (−phenylethanethiol) colloid. An aliquot of (2 mL) of gas was taken from the reactor at regular intervals of time (2, 45, and 90 min) and put into the gas chromatograph to analyze the formation of dihydrogen.

Sample Preparation for Thermogravimetric Analysis (TGA). Ethanol (150 mL) was added to the as-prepared gold−acetone−dodecanethiol (or −phenylethanethiol) colloid and kept overnight undisturbed. The supernatant was decanted and the precipitate was dissolved in toluene (2 mL). This colloid was again precipitated by addition of ethanol and the precipitate was dried in vacuo. This dried sample was used for TGA.

Instrumentation. H_2 production was monitored during the interaction between gold nanoparticles and thiol molecules using a GC system (GOWMAC model) employing a Supelco 80/100 molecular sieve 5A column with Ar as the carrier gas and a thermal conductivity detector. TGA of the dried thiol-capped gold nanoparticles were recorded using a Shimadzu TGA_50 thermogravimetric analyzer. FT-IR spectra of the gold−thiol sample were recorded using a Nicolet Nexus 670 FT-IR spectrometer.

■ RESULTS AND DISCUSSIONS

In 2002, we prepared DDT-capped gold colloids by the SMAD method and showed the self-assembly and formation of monolayer around gold nanoparticles by DDT.[18] Fewer reactions are involved in the synthesis of such monolayers of thiol molecules around gold nanoparticles by the SMAD method compared to other chemical reduction methods. We tried to use SMAD-prepared gold−thiol monolayers as a standard system to study the fate of sulfur-bound hydrogen. First, gold−acetone−thiol colloids were prepared by the SMAD method. Acetone has a dual role: the initial weak capping agent and the solvent. Two different thiols were used: an alkyl thiol (DDT) and an aryl thiol (PET). Acetone was replaced by thiol molecules when the gold−acetone solvate came into contact with the thiols. The strong interaction between the sulfur atom of the thiol molecule and surface gold atoms of the nanoparticle is due to the soft nature of both sulfur and gold atoms. Thus, thiol molecules form stable self-assembled monolayers around the gold nanoparticles. We wanted to see whether the S−H hydrogen of thiol molecule is still intact or not when the thiols react with these nanoaprticles. We analyzed the gas inside the reactor at regular intervals and characterized the isolated gold−thiol sample using ^{1}H NMR and FT-IR spectroscopy and TGA.

Several studies of gold−thiol interactions in nanoparticles favor thiolate rather than thiol, especially in the case of long-chain thiols.[13,14] If a thiolate is binding the surface cluster atoms, the hydrogen atoms released could either adsorb on gold surface or combine with another hydrogen atom to form hydrogen gas. We took aliquots of gas (2 mL) at regular intervals from the reactor and put it into the GC for hydrogen analysis. When gold−acetone solvate came into contact with DDT, initially (after 2 min the dewar removed from the reactor) there was no indication of hydrogen formation as per our GC data. However, hydrogen gas was detected in the GC as the cold acetone−thiol−gold mixed and warmed toward room temperature. When 230 μmol of gold reacted with DDT, 9 and 15 μmol of hydrogen gas was evolved after 45 and 90 min, respectively (Figure 1). There was no hydrogen formation 2 min after the removal of dewar in the case of PET, too, but 31 μmol of hydrogen evolved when 456 μmol of gold reacted with PET in 90 min. The initial absence of hydrogen could be due to the high melting point of DDT in comparison with the gold−acetone solvate. Hydrogen evolution takes place due to the S−H bond scission of thiol molecule when it reacts with surface atoms of the gold nanoparticle. No other side reactions leading to the formation of hydrogen gas are possible in our SMAD method due to its simplicity. We did some control experiments wherein we prepared gold−acetone colloids and analyzed the gas in the reactor at regular intervals of time. No hydrogen gas was detected in this case. This confirms that the interaction between DDT and gold, indeed, caused the evolution of hydrogen gas by S−H bond scission. In addition, an FT-IR spectrum of the purified gold−thiol sample did not show any S−H stretching bands, corroborating the S−H bond scission during gold−thiol interaction (Figure 2).

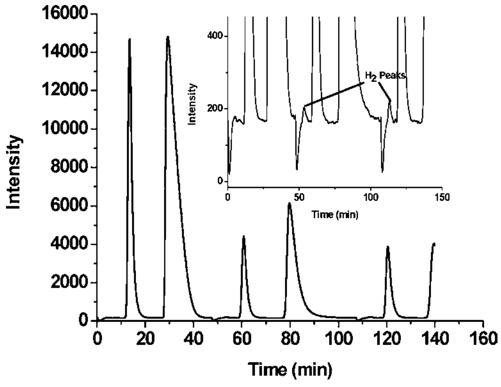

Figure 1. GC analysis of the gas in the reactor containing gold−acetone−dodecanethiol colloid at different intervals of time. The inset shows the less intense peaks corresponding to hydrogen. The intense peaks after hydrogen are oxygen and nitrogen, respectively.

$$\mathrm{Au}_{(\mathrm{surface})} + \mathrm{RS{-}H} \rightarrow \mathrm{Au}_{(\mathrm{surface})}\mathrm{{-}SR} + \frac{1}{2}\mathrm{H}_2$$

In another set of experiments, the $Au_{(surface)}SR$ nanoparticles were subjected to TGA in air (Figure 3). Loss of mass in the temperature range of 200−300 °C corresponds to the thiolate oxidized away leaving only gold. From the TGA data, 0.75

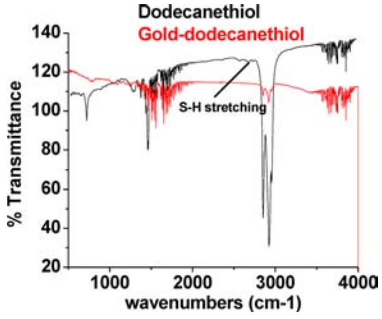

Figure 2. FT-IR spectra of dodecanethiol and purified gold−dodecanethiol.

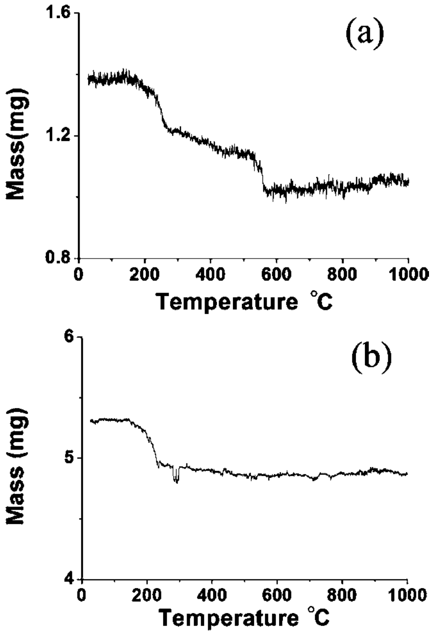

Figure 3. TGA of (a) dodecanethiol-capped and (b) phenylethanethiol-capped gold nanoparticles in air.

μmol of thiolate vs 6.2 μmol of gold in the case of Au-DDT and 3.2 μmol of thiolate vs 25 μmol of gold in the case of Au-PET.

From the GC data, Au/H = 7.6 and from the TGA data, Au/SR = 8.2, when DDT was used as the capping agent. The same experiments with PET gave essentially the same results Au/H = 7.4 (from GC) and Au/SR = 7.7 (TGA). Therefore, the moles of hydrogen gas produced were about equal to the moles of thiolate produced within 7%. Thus, our GC and TGA data confirmed a thiolate binding to the surface cluster atom of the gold nanoparticle rather than a thiol. These data also indicated that there are 8 times as many atoms of gold as thiolate molecules. This Au/SR ratio obtained from our TGA data can also be used to calculate the average particle diameter (d) of the nanoparticle using the formula, d = 0.47 Au/SR.[19] We assumed spherical particles of gold with the bulk density of 19.3 g/cm^3 and the thiol to occupy a surface area of 0.215 nm^2.[20] We found Au/SR = 8, then the d value calculated using the above equation is 3.8 nm, ~4 nm. This is quite consistent with TEM observation of the particles which show the sizes ranging from 2 to 8 nm (Figure 4).

Upon doing similar experiments with alkylamines instead of alkylthiols, no hydrogen gas was evolved, suggesting that gold−amine nanoparticles are best described as $Au_{(surface)}NH_2R$.

■ CONCLUSIONS

These experiments show that the surface atoms of weakly solvated gold nanoparticles in the 2−8 nm size range are oxidized by thiols to yield hydrogen gas and thiolate-stabilized nanostructures. Alternatively, the sulfur−hydrogen bond could be broken in a homolytic fashion to form a RS-Au bond and hydrogen atoms to yield hydrogen gas.[21] An empirical formula of approximately Au_8SR was observed. For a 4 nm gold particle, a molecular formula of about $Au_{2000}(SR)_{235}$ would be indicated. It should be noted that the hydrogen evolution occurs when thiol contacts the gold particles upon matrix melt-down and slow warm-up to room temperature.

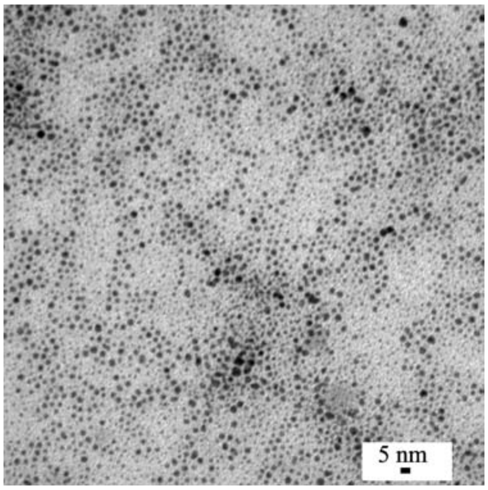

Figure 4. TEM bright-field image of as-prepared gold−acetone−dodecanethiol SMAD colloid.

■ AUTHOR INFORMATION

Corresponding Author

kenjk@ksu.edu

Notes

The authors declare no competing financial interest.

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(19) The total number of gold atoms in the nanoparticle, $N(\mathrm{Au}) = 31d^3$, and the total number of thiol ligands on the surface of the nanoparticles, $N(\mathrm{SR}) = 14.67d^2$, where d = particle diameter in nanometers. The Au/SR ratio is identically equal to $N(\mathrm{Au})/N(\mathrm{SR})$. Then, with the above equation, one finds $d = 0.47$ Au/SR.

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