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# Oxidation of alkanethiol monolayers on gold cluster surfaces

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## Abstract

Reaction of ozone with alkanethiol monolayers on gold cluster surfaces is reported. Ozone diffuses through the monolayer and reacts with the head group forming oxidized sulfur on the cluster surface, increasing disorder in the monolayer assembly. During the reaction conducted in toluene, some of the thiols undergo desorption from the surface resulting in increased inter-cluster interaction leading to aggregation and consequent precipitation of the clusters. © 2001 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Monolayer-protected metal clusters (MPCs) is a very active area of research due to the potential applications of these materials in sensors, optical switches and nanoelectronic devices [1]. The central area of investigation is concerned with their structure [2] and to a smaller extent, their reactivity [3]. Understanding the reactivity of monolayers in MPCs directed towards appropriate functionalization is a key aspect in the application of these materials. Reports on the reactivity suggest that the physical and chemical properties of the monolayers on three-dimensional surfaces (3D-SAM) can be changed drastically by means of appropriate functionalization. Although various studies on the structure of monolayers on cluster surfaces exist, information on their stability and reactivity is inadequate.

It is shown that alkanethiol monolayers on planar Au surfaces undergo oxidation and form sulfates or sulfonates upon prolonged exposure to air [4]. IR studies suggest that upon ageing the monolayer over a period of six months, it undergoes tilting, away from the surface normal, suggesting oxidation of the sulfur head group [5]. Photooxidation of SAMs has attracted considerable attention due to its applications in patterning the surfaces [6,7]. A comprehensive study on the air stability of 2D-SAMs has been reported by Schoenfish and Pemberton [8] and their experiments suggest that ozone is the primary oxidant in ambient air, which oxidizes alkanethiol monolayers on both Au and Ag surfaces.

## 2. Experimental

Octadecanethiol-protected gold clusters (Au-ODT) have been synthesized using a modified literature procedure [9]. Passing oxygen (at a flow rate of  $20 \text{ cm}^3 \text{ min}^{-1}$ ) under a silent electric discharge generates ozone, which was passed through

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a toluene solution of Au-ODT for 1 h<sup>1</sup>. In a typical experiment, 0.01 g of the cluster was dissolved in 20 ml of toluene. Temperature of the solution was maintained at 298 K throughout the experiment. After exposure of ozone the cluster becomes insoluble in toluene. The deposited material was collected by centrifuging and was air-dried. These powdery materials have been analyzed with X-ray diffraction (XRD), infrared spectroscopy (IR) and X-ray photoelectron spectroscopy (XPS).

### 3. Results and discussion

Fig. 1 shows the XRD patterns of the reacted and unreacted samples. Whereas the (111) reflection is broad in the unreacted sample, it is significantly narrow for the reacted sample. Narrowing of the peak is indicative of the larger size of the clusters [11]. Particle sizes were calculated from the Scherrer formula [12]. It is found that the size of the unreacted cluster is about 2 nm and that of reacted one is about 12 nm. This suggests aggregation of clusters during reaction. In order to see the nature of the alkyl chain, we measured the IR spectra<sup>2</sup> of both the compounds (Fig. 2). The strong peaks at 1463 and 720 cm<sup>-1</sup> in spectrum 'a' are characteristic of solid-like hydrocarbon assembly and have been discussed in detail earlier [9]. In the reacted sample, there is a peak emerging at around 1030 cm<sup>-1</sup>, which indicates the formation of sulfonates, consistent with the oxidation of 2D-SAMs with ozone [13]. The broad band at 1000–1200 cm<sup>-1</sup> has been assigned to sulfonate stretching mode in correlation to sulfonic acid salts

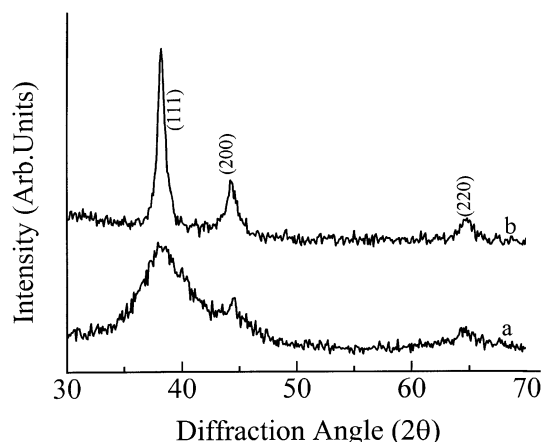


Fig. 1. X-ray diffraction patterns of Au-ODT: (a) unreacted and (b) reacted with ozone. The narrowing of the (111) and other reflections is indicative of aggregation of clusters. Reflections are marked in the figure. X-ray diffractometer with CuK $\alpha$  radiation was used for the measurements. The samples were spread on anti-reflection glass slides to give uniform films.

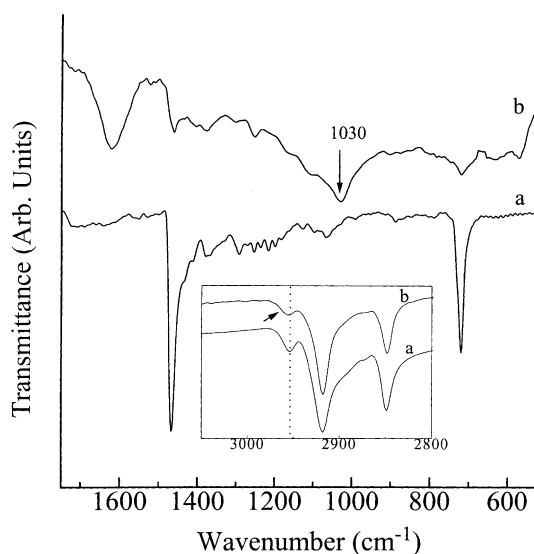


Fig. 2. Low-frequency region of the infrared spectrum of Au-ODT samples: (a) unreacted and (b) reacted with ozone. Presence of 1030 cm<sup>-1</sup> band shows the formation of sulfonate. Inset shows the C-H stretching region of both the samples. Shift of the methyl antisymmetric mode in the reacted sample (b) is marked in the figure.

<sup>1</sup> Ozone was produced by a silent electric discharge of oxygen in a modified apparatus originally described by Brauer [10]. Ozone was prepared by passing zero grade oxygen of 99.8% purity through the ozone tube under silent electric discharge at room temperature. The ozone concentration was about 10% at a flow rate of 20 cm<sup>3</sup> min<sup>-1</sup>.

<sup>2</sup> Infrared spectra were measured with a Perkin Elmer FT-IR spectrometer. Samples were prepared in the form of KBr pellets. All spectra were measured with a resolution of 4 cm<sup>-1</sup> and were averaged over 50 scans. The infrared spectrum of Au-ODT is discussed in [9].

[14]. The bands at 631 and 565 cm<sup>-1</sup> are in the sulfate region, which suggests a minor fraction of sulfate to be present in the product. The spectrum

does not correspond with those of sulfinate and sulfite, both of which show distinct bands at different positions [14]. The band at  $907\text{ cm}^{-1}$  is attributed to S–O stretch in the sulfonate [14]. Decrease in intensity of the methylene rocking and scissoring bands is indicative of a partial desorption of monolayer from the surface. The band at  $1613\text{ cm}^{-1}$  is due to adsorbed water. This shows the free space available on the cluster surface due to the partial desorption of the alkyl chains. The IR intensity ratio  $I_{2920}/I_{2850}$  can be taken as a measure of disorder [15], and with increase in conformational disorder, this ratio increases. Inset of Fig. 2 shows the C–H stretching region of both the compounds. It is clear from the figure that the ratio is larger in the reacted sample, suggesting greater disorder. The C–H stretching region also got shifted; this is especially visible in the methyl antisymmetric band. These changes indicate the increase in disorder as a result of oxidation of the sulfur head group. Increased disorder in the reacted sample may be due to the free volume available as a result of the partial desorption of the monolayer from the surface. This is consistent with the report of Horn et al. [5] who showed the tilting of alkyl chain upon ageing the monolayer on planar Au surface. The bands present at  $1518$  and  $3002\text{ cm}^{-1}$  in the reacted sample indicate inclusion of toluene.

Mass spectral analysis shows a peak at  $333$  amu, which confirms the presence of octadecane sulfonate. We did not see any features corresponding to sulfonates and sulfites. All other peaks in the mass spectrum correspond to the thiolate.

Chemical nature of the reaction products was examined using X-ray photoelectron spectroscopy. In order to avoid beam-induced damage [16], X-ray flux was kept low. All regions were measured with  $20\text{ eV}$  pass energy. Fig. 3 shows the C1s, S2p, Au4f and O1s regions of the reacted and unreacted samples. After the reaction, the S2p peak was shifted to a higher binding energy of  $170\text{ eV}$ , which is due to the presence of oxidized sulfur. Oxidation of the monolayer is almost complete as evident from the poor intensity of the thiolate peak at  $162\text{ eV}$ , which is different from the 2D-SAMs where only partial oxidation is seen [8]. This difference might be attributed to (a) availability of greater

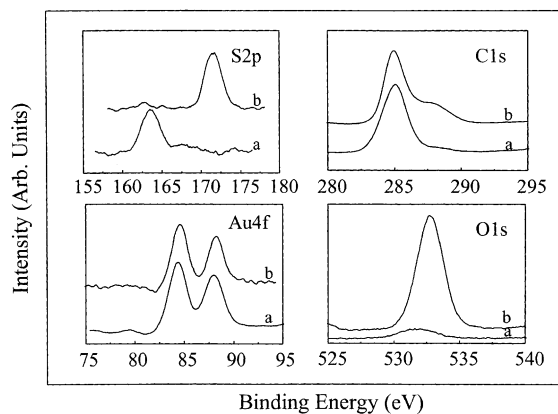


Fig. 3. X-ray photoelectron spectra of the C1s, S2p, Au4f and O1s regions of the (a) unreacted and (b) reacted samples of Au-ODT. Quantitative analysis of the data was not attempted due to differences in the nature of the samples.

free space at the surface due to the curved substrate, and (b) due to partial desorption of monolayers during the reaction providing space for the bulky sulfonate groups at the surface. Since the latter aspect is common for the 2D-SAMs as well, the former seems to be important in helping complete conversion. In the unreacted Au-ODT sample, C1s is present at  $285\text{ eV}$  as in the case of alkanethiol 2D-SAMs. For the reacted sample, there appears a shoulder in the higher binding energy side of the C1s peak. This may be due to a contamination from the toluene solution in the course of this experiment. Note that toluene can be converted to glyoxal by ozone [17]. Au4f shifted slightly, to higher BE indicative of oxidation of Au. Oxidation of surface Au on 2D-SAMs in presence of ozone is reported in the literature [18]. Whereas the intensity of oxygen is less in the unreacted sample, it is much larger in the case of the reacted sample. All these observations suggest that ozone reacted with the head group of the monolayer.

Earlier reports by Schoenfish and Pemberton [8] suggested the oxidation of alkanethiol monolayers on planar surfaces. Using Raman and XPS, they established the oxidation of the sulfur head group. Emergence of new peaks in the Raman spectra at ca.  $615, 850, 917, 980$  and  $1010\text{ cm}^{-1}$  was attributed due to the formation of sulfonate, sulfonite, sulfate and sulfite species. These oxidized sulfur forms shows the S2p peak at  $167\text{ eV}$  in XPS.

UV irradiation of alkanethiolate SAM on Au in air has been shown to form sulfonates [13]. UV irradiation or ozone exposure resulted in the appearance of a new band at  $1017\text{ cm}^{-1}$  in the IR spectrum [13], which has been assigned to the sulfonate stretching mode. In all these experiments, penetration of ozone through the monolayer is suggested to be the reason for the formation of sulfonates. This is in accordance with the results reported here, where monolayers on cluster surfaces are shown to undergo oxidation in presence of ozone, during which part of the monolayers desorb from the surface. As a result of this, inter-cluster interaction between the cluster cores increases leading to aggregation. This is evident from the narrowing of the reflections in XRD. We note that the solubility of the sample decreases, as we store the cluster samples in a laboratory having higher ozone concentration.

In conclusion, monolayer-protected gold clusters react with ozone and form cluster aggregates. The head group of the monolayer undergoes oxidation and as a result disorder in the monolayer increases. The reaction with ozone principally results in sulfonates.

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