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Activation of Thiols at a Silver Nanoparticle Surface**

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Adsorption of organosulfur (thiol) molecules on noble metal surfaces has been widely used to fabricate self-assembled monolayers or modify surface properties in a broad range of novel technological applications.[1–3] Adsorption of thiols on the surface of noble metals, such as gold or silver, has been intensively studied[1–16] to gain fundamental understandings on the adsorption process, including its mechanism and rates. It is generally accepted that thiol adsorption onto the gold/silver surfaces consists of many steps, starting with physical adsorption, followed by the sulfur–metal bonding reaction, the reorientation of the adsorbed thiol molecules, and the formation of a compact self-assembled layer.[5,14–16] On the other hand, both diffusion-limited and non-diffusion-limited adsorptions have been reported, though the conditions for the two scenarios have not been consistently defined.[6,8,9,13–16]

Thiol adsorption has been widely used to influence the properties of metallic nanoparticles, such as controlling their biomedical functions,[17,18] tuning optical properties,[19] changing the attached chromophores,[20] and the synthesis of nanoparticles/nanocages of different shapes and size.[21,22] The adsorption of thiol molecules on metallic nanoparticles have been studied mostly using optical techniques.[19,20,23–25] For example, a sum frequency vibrational spectroscopy study has revealed that long-chain thiol molecules on gold nanoparticles of varying sizes have different conformations.[24] The adsorption free energies of several thiol molecules on gold and silver nanoparticles have been determined using fluorescence or second harmonic generation (SHG) measurements.[19,25]

More than a decade ago, hyper Rayleigh scattering from gold nanoparticles was pursued and first reported as an incoherent second harmonic method for examining nanoparticles,[26] as it was thought that there is an inherent size restriction in SHG such that the method could not be detected from particles with diameters much smaller than the optical wavelength. We have subsequently demonstrated that SHG from the surface of nanometer size particles can be detected at specific scattering angles where phase matching conditions are satisfied.[27–29] This advancement has led to the detection of SHG from silver nanoparticles (AgNPs).[19] In principle, the SHG signal may arise from the surface and/or bulk of the nanoparticles. In the case of AgNPs, the surface contribution is identified by the response in the SHG signal to the formation of surface bonding that would diminish the polarizability of the free electrons at the surface. The surface portion of the SHG signal can then be used for probing processes occurring at the surface.

It was illustrated in our work[19] that the adsorption of thiols onto the AgNP surface can be directly monitored with time using SHG. The SHG intensity generated at the surface layer of the silver particle is sensitive to the formation of the S−Ag bonds at the nanoparticle surface.[19] It was found that the majority of the SHG signal from AgNPs of 80 nm diameter can be quenched by the adsorption of thiol molecules as the formation of the S−Ag bonds localizes the Ag electrons that are responsible for the nonlinear susceptibility. The change of the SHG intensity can be quantitatively related to the thiol coverage on the surface, and used for the determination of the adsorption and desorption rates as well as the free energy change of the adsorptive reaction process.[19] If there is a barrier associated with the rate-limiting process in the adsorption, temperature dependence of the adsorption rate should enable the determination of the activation energy and reveal which is the activation process. Herein we present experimental observations indicating that the thiol reactions at the silver nanoparticle surface is an activated process and that temperature can be used to control the reaction rates. For the case of 1,2-benzenedithiol adsorption onto a silver nanoparticle, the activation energy was determined as 8.4 kcal mol^{-1}. This energy barrier is likely associated with the formation of the transition state during the formation of sulfur–silver bond and not from the diffusion-limited process.

Figure 1 shows that as 1,2-benzenedithiol at different concentrations was added into Ag colloids at 293 K, the intensity of the SHG light scattered from silver nanoparticles decreased. The decrease is resulted from the reduction of the nonlinear susceptibility of the Ag surface atoms as S−Ag bonds form.[13,19] As indicated by the rate of the SHG intensity decay, which is proportional to the square of the thiol coverage on the surface, the rate of adsorption of thiol molecules is faster when thiol concentration is higher. Figure 1 shows three of the five experimental measurements conducted with added thiol concentrations varying from 0.1 to 0.5 μM.

The Langmuir model can be used to describe the adsorption kinetics with adsorption and desorption rate constants k_a and k_d:

$$\mathrm{T} + \mathrm{ES} \underset{k_d}{\overset{k_a}{\rightleftharpoons}} \mathrm{TS} \qquad (1)$$

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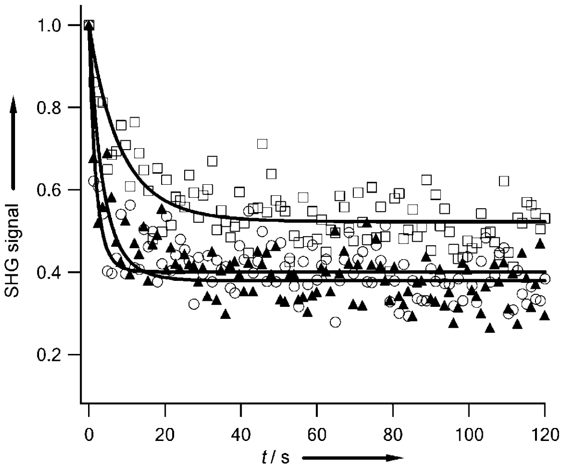

Figure 1. The second harmonic generator (SHG) intensity detected from Ag NPs at room temperature as a function of time after addition of 1,2-benzenedithiol at different concentrations (□ 0.1 μM, ▲ 0.3 μM, ○ 0.5 μM). Solid lines are the results of fitting using the Langmuir adsorption model.

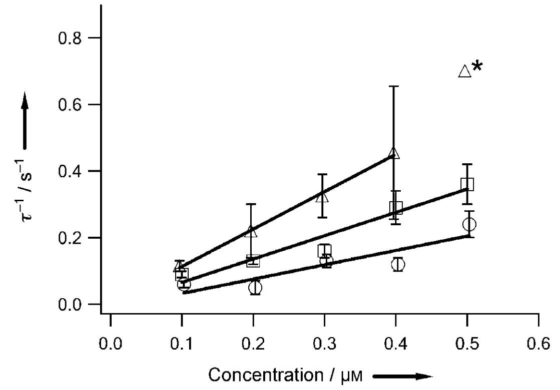

Figure 2. $1/\tau$ values plotted as a function of thiol concentration at three temperatures (○ 284 K, □ 293 K, ▲ 303 K). The large size of the error bars associated with the high concentration measurements at 303 K is because SHG intensity decays are at a fast rate that is close to the experimental time resolution of one second. The point marked with $*$ is not included in the analysis because of its very large error bar of 0.6. At 303 K, the points from 0.1 to 0.4 μM are results from the average of two sets of experiments. Solid lines are fits for the extraction of the adsorption rate constants.

In Equation (1), thiol (T) adsorbs onto a surface site (ES) of the silver nanoparticle, resulting in a thiol-occupied site (TS). The number of thiol molecules on the surface N, under the condition that the total number of molecules C in the colloid (including those in solution and on surface) is much larger than N, can be described as:[19]

$$\frac{\partial N}{\partial t} = k_\mathrm{a} C(N_\mathrm{max} - N) - k_\mathrm{d} N \tag{2}$$

with N_max being the maximum number of thiol molecules that can adsorb onto the surface. The surface coverage of thiol as a function of time is then:

$$\theta = N/N_\mathrm{max} = g\left(1 - e^{-(k_\mathrm{a}C + k_\mathrm{d})t}\right) \tag{3}$$

with g being the saturation surface coverage at the particular concentration C. The change of the surface nonlinear susceptibility is proportional to the surface coverage,[13,19,30–32] and the SHG intensity can be expressed as:

$$I_\mathrm{SHG} \propto \left|B - Q\theta e^{i\phi}\right|^2 \tag{4}$$

with B being the total susceptibility of the nanoparticle before thiol adsorption, Q the overall portion which can be quenched by thiol adsorption, and ϕ the phase difference between these two parts. By combining Equations (3) and (4), the SHG intensity during thiol modification of the surface can be expressed as:

$$I_\mathrm{SHG} = \left|b - q^*\left(1 - e^{-t/\tau}\right)e^{i\phi}\right|^2 \tag{5}$$

with b and q as fitting parameters and the time constant τ being related to k_a and k_d by the relation $1/\tau = k_\mathrm{a}C + k_\mathrm{d}$.

Equation (5) was used to fit the decay of the SHG intensities from silver colloids after the addition of 1,2-benzenedithiol (Figure 1). The $1/\tau$ values obtained through the fitting are shown in Figure 2 (the squares).

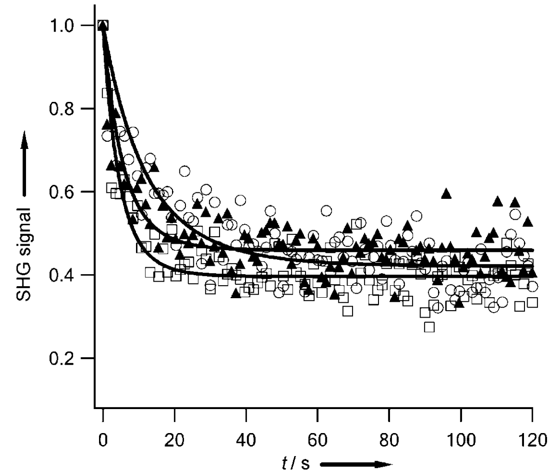

Figure 3. The decay of the SHG signal from Ag NP colloids following addition of 1,2-benzeneditiol (0.2 μM) at different temperatures (○ 284 K, ▲ 293 K, □ 303 K). Solid curves are fits with the Langmuir model.

Similar concentration-dependent measurements with samples kept at 284 K and 303 K were conducted and analyzed. Figure 3 shows the SHG decay curves following the addition of 0.2 μM 1,2-benzenedithiol into Ag colloids at three temperatures. The decay is noticeably faster at higher temperature. The rate constants obtained from all three temperatures are plotted in Figure 2. The data points at the same temperature display the linear relationship of $1/\tau = k_\mathrm{a}C + k_\mathrm{d}$. The k_a values can be obtained by a nonlinear least-squares fit (Figure 2): $(4.3 \pm 1.2) \times 10^5\,\mathrm{L\,mol^{-1}\,s^{-1}}$ for 284 K, $(7.0 \pm 1.0) \times 10^5\,\mathrm{L\,mol^{-1}\,s^{-1}}$ for 293 K, and

$(1.1 \pm 0.1) \times 10^6\ \mathrm{L\,mol^{-1}\,s^{-1}}$ for 303 K. The k_d values obtained are smaller than the uncertainty. This result indicates that the desorption of the adsorbed 1,2-benzendithiol from a silver surface is too slow to be detected, which is consistent with the previous understanding that thiols adsorbed on a noble-metal surface do not desorbed easily.[9,13]

The temperature-dependent adsorption rate constant can be modeled by the Arrhenius equation for the extraction of the activation energy E_a. For the adsorption of 1,2-benzenedithiol onto AgNPs, E_a was determined to be (8.4 ± 0.3) kcal mol^{-1} (Figure 4).

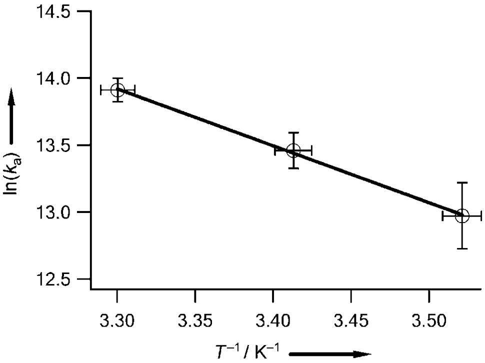

Figure 4. An Arrhenius plot of the adsorption rate constants. The solid line is an nonlinear least-squares fit.

The adsorption of decanethiol on Au(111) in ethanol have been reported with an energy barrier of 7.1 kcal mol^{-1},[16] which is close to the value of 6.9 kJ mol^{-1} for the adsorption of several alkanethiol groups on Au(111) obtained from ultrahigh-vacuum studies.[12] These results obtained with different environments and surfaces have been consistent in terms of the magnitude of the activation energy. In comparison, the activation energy of 8.4 kcal mol^{-1} for 1,2-benzenedithiol on AgNPs appears to be relatively large. It is most likely that this value is due to the two thiol groups in the molecule. A previous report showed that both sulfur atoms are bonded on the silver surface.[10] The larger activation energy in relation to the formation of more bonds indicates that the barrier is likely associated with the bonding process.

The effect of the stronger bond is also reflected in the adsorption free energy of 1,2-benzendithiol on the AgNP surface, which has been determined to be at least −8.8 kcal mol^{-1},[19] and is relatively larger in magnitude than the adsorption free energy of −6.0 kcal mol^{-1} for ethanethiol on silver nanoparticles (see the Supporting Information).

The proposed mechanism for thiol adsorption on noble-metal surfaces starts with a physical adsorption process before chemical reactions.[5,14–16] Several previous studies of thiol adsorption onto flat gold surfaces reported that the adsorption rate was diffusion-limited, particularly when the thiol concentration in the solution is at the micromolar scale.[9,15,16] The average diffusion distance for thiol molecules traveling to the surface can be as long as 1.9 mm for a 2 μM solution.[15] Here, in the environment of a colloid, the average distance between thiol molecules and silver nanoparticles is on the order of 10 μm, since the average distance between two nearby particles is about 30 μm at the particle density we have used. Adsorption on the small surface area of the nanoparticle does not deplete the nearby thiols in the solution so that diffusion is not the rate-determining step and not the source of the activation energy.

The particles are stabilized with citrate ions (Cit) in the colloid (Figure 5). Their presence at the surface, established through the charge–charge interaction with the silver surface, may present a barrier for the thiols to physically approach the surface. The activation barrier of 8.4 kcal mol^{-1} is too high to be associated with diffusion, but it may arise either from the physical adsorption or the chemical bonding process. Based on the correlation with the number of bonds, we attribute this activation energy to the formation of the transition state during the chemical reaction. A possible transition-state structure is shown in Figure 5. A previous IR spectroscopic study has determined the adsorption structure of 1,2-benzenedithiol on a flat silver surface.[10] Accordingly, we propose the steps of the thiol reaction on AgNPs as illustrated in Figure 5.

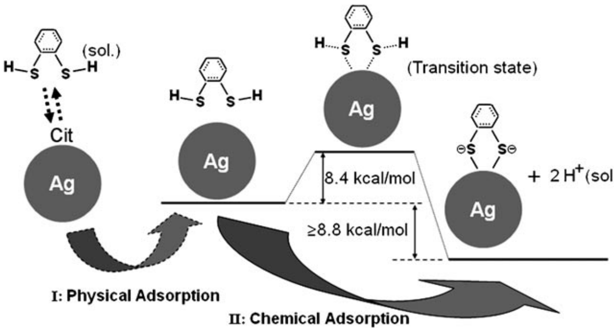

Figure 5. Illustration of the mechanism and the energy change associated with the reaction of 1,2-benzenedithiol on a AgNP surface.

In summary, the second harmonic light generated from the surface of the AgNPs upon laser irradiation, detected with time resolution, enabled the determination of the rate constant of adsorption of thiol on AgNPs. From the temperature dependence of the adsorption rate, the activation energy barrier of (8.4 ± 0.3) kcal mol^{-1} was determined for the adsorption of 1,2-benzenedithiol onto the surface of silver nanoparticles in aqueous colloids. This energy barrier is attributed to the formation of the transition state during the bonding reaction, and not the physical adsorption or diffusion processes.

Experimental Section

Silver colloids (British Cellbio International) with an average particle diameter of 80 nm and aq density of 1.1×10^9 particles mL^{-1} were diluted 36 times in volume with deionized water (Millipore, 18.2 MΩ). 1,2-benzenedithiol (Sigma–Aldrich, 96%) was used after being dissolved in water. Sodium citrate (Sigma–Aldrich, 99%) was added at a concentration of 5 μM in all of the samples to stabilize the colloids. A hot water bath was used to increase the temperature of samples from room temperature, (293 ± 1) K, to (303 ± 1) K, and a coolant bath was used to lower the temperature to (284 ± 1) K.

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