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SHORT COMMUNICATION

pH-Triggered ionization of self-assembled monolayers investigated by *in-situ* surface plasmon resonance measurements

Surin Hong*, Taewook Kang*, Jungwoo Moon, Seogil Oh and Jongheop Yi†

School of Chemical and Biological Engineering, Institute of Chemical Processes, Seoul National University,
San 56-1, Shinlim-dong, Kwanak-gu, Seoul 151-742, Korea

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Abstract−Self-assembled monolayers (SAMs) of 2-aminoethanethiolhydrochloride (AET) or 2-aminoethanethiolhydrochloride (AHT) were formed on gold substrate. Deprotonation and reprotonation of SAMs of AET and AHT on gold substrate were investigated by using time-resolved surface plasmon resonance (SPR) measurements. The changes of the terminal functional groups from $-NH_3^+Cl^-$ to $-NH_2$ (vice versa) via the HCl and NaOH treatment were successfully detected, based on the fact that the initially formed AET and AHT SAMs were assumed to be a zwitterion-like species, $-NH_3^+Cl^-$.

Key words: Ionization, Surface Plasmon Resonance, Self-assembled Monolayers

INTRODUCTION

Self-assembled monolayers (SAMs) of functionalized alkanethiols on gold substrates are the most often employed templates for the chemical construction of advanced electronic devices and sensors [Fendler, 2001]. The self-assembly of functionalized alkanethiols is governed by the formation of strong S-Au bonds, the hydrophobic interactions between the alkyl chains of the alkanethiol, and group-specific interaction (e.g., H-bond, dipolar) [Ulman, 1996; Fendler, 1996]. SAMs formed from alkanethiols with long chain mediate the charge transfer by electron tunnelling between molecules (or clusters or nanoparticles) attached onto their functionalized end and the gold substrate. In contrast, functionalized alkanethiols with short chain form loosely packed SAMs, which permits the attached charge carriers to transfer electrons directly to the gold substrate. In particular, the SAMs of amino-functionalized alkanethiols have been advantageously utilized for attaching biomaterials [Hong et al., 2003], such as proteins and DNA, and a variety of other electron-transfer agents onto substrates. Hutter and coworkers [2004] reported that amino-terminated alkanethiol (2-aminoethanethiolhydrochloride, AET) could be used as a linker between gold nanoparticles and gold nanoislands for the purpose of the sensitivity enhancement of surface plasmon resonance imaging.

Therefore, understanding and controlling of the self-assembly of amino-terminated alkanethiols and of the factors which determine the surface charge and charge density of amino-terminated SAMs is of fundamental importance and practical utility for the design of devices and sensors. For this purpose, we report here the first SPR observation of pH-triggered ionization of amino-terminated SAMs on a gold substrate.

In this communication, deprotonation and reprotonation of self-assembled monolayers (SAMs) of 2-aminoethanethiolhydrochloride (AET) and 2-aminoethanethiolhydrochloride (AHT) on gold substrate were investigated by using angle and time-resolved surface plasmon resonance (SPR) measurements.

EXPERIMENTAL

2-Aminoethanethiolhydrochloride (AET, Sigma-Aldrich) and 6-amino-1-hexanethiolhydrochloride (AHT, Dojindo Laboratories) were used as received. Sulfuric acid (H_2SO_4, Fisher Scientific) and hydrogen peroxide (H_2O_2, Fisher Scientific) were used to clean the glass slides on which chromium and gold films were subsequently evaporated. Hydrogen chloride (HCl, Fisher Scientific) and sodium hydroxide (NaOH, Mallinckrodt Chemicals) were used to control the pH of the solution. H_2O was purified to more 18 MΩ using a Milli-Q water system (Millipore).

SPR measurements were performed by using an in-house constructed instrument (see Fig. 1A). Briefly, the setup was based on the Kretschmann configuration, in which a *p*-polarized laser beam (λ=635 nm) is focused through a prism onto a metal film placed on the prism. The Au substrate with amino-functionalized alkanethiol monolayer (AHT or AET) was attached to an SF10 prism with index matching oil (Cargille Laboratories Inc., certified refractive index liquids, n=1.730±0.0005). The 635-nm He-Ne diode laser (Power Technology Inc.) was *p*-polarized and focused with a lens through the prism onto the Au substrate. Both the prism and the Au substrate were mounted on a rotating plate to control the angle of the incident light. The reflectance was measured with a photo-power meter (Oriel). A Teflon cell was attached to the Au substrate to hold the solution. The cell had an O-ring (ID=0.8 cm) in the middle through which the laser light contacted the solution.

Glass microscope slides (1-inch×1-inch SF10) were immersed in a piranha solution ($H_2SO_4 : H_2O_2$=7 : 3 v/v) for purification (*caution*: piranha solution should be handled with extreme care). The glass substrate was rinsed several times with copious amounts of deionized water and ethanol and then dried. The 50-nm Au thin film was prepared by a thermal evaporation with a 5-nm Cr adhesion layer. The SAMs of AHT (AET) on the Au thin film was formed

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[†] To whom correspondence should be addressed.
E-mail: jyi@snu.ac.kr

*The authors (Surin Hong and Taewook Kang) contributed equally to this work.

by treatment with a 1 mM AHT (AET) ethanolic solution for 18 hrs. The formation of an AHT (AET) monolayer was investigated by SPR measurements and auger electron spectroscopy (AES).

The initially formed AHT or AET SAM on the Au surface was treated with an NaOH (pH 11) solution for 2 min, in order to remove H^+ on "nitrogen" atoms. To investigate the ionization behavior of AHT (AET) SAM on the Au thin film, the time resolved SPR angle shift was measured by using the fixed angle method which enabled the reflectance change, ΔR, to be linearly correlated with the SPR angle shift, $\Delta\Theta_{SPR}$. The fixed incident angle for measuring the reflectance was adjusted before the ionization of AHT (AET) SAM. The reflectance data at a fixed incident angle were acquired by a computer in real time. Based on the previous results for the pH-dependent SPR response of carboxylic acid-terminated SAM, we found that changing the buffer solution had a significant effect on the SPR data (by significantly affecting the refractive index of medium 4), irrespective of the presence of the SAM layer in the multilayer structure [Chah et al., 2002]. Therefore, instead of using a buffer solution, HCl and NaOH were used to control the pH of the ambient medium. Intrinsic optical effects of these latter solutions were also examined by SPR measurements.

RESULTS AND DISCUSSION

We utilized a five-phase, denoted as (01234), SPR system in the Kretschmann configuration using attenuated total reflection (ATR) as shown in Fig. 1B. The different phases were labelled as follows: 0, a glass slide (SF10), optically coupled to a 90° ATR prism; 1, a thin binder layer of Cr (5 nm); 2, a layer of Au thin film (50 nm); 3, amino-terminated self-assembled monolayers (SAM) of AHT or AET; 4, an ambient dielectric medium of air (for the determination of parameters such as thickness and dielectric constant) or water (*in-situ* analysis of ionization). In order to convert $\Delta\Theta_{SPR}$ to surface changes induced by pH alteration for the *in-situ* analysis, the theory of Maxwell Garnett was employed here on the basis of neglecting the possible anisotropy [Kang et al., 2005].

$$\frac{(\varepsilon_{eff}-\varepsilon_4)}{(\varepsilon_{eff}+2\varepsilon_4)} = \beta f \text{ where } \beta = \frac{(\varepsilon_3-\varepsilon_4)}{(\varepsilon_3+2\varepsilon_4)} \qquad (1)$$

Here f is the volume fraction occupied by $-NH_2$ and ε_3 and ε_4 are the dielectric constants of the fully neutralized status (*i.e.*, $-NH_2$) and a zwitterion-like species, $-NH_3^+Cl^-$, respectively. From the fact that the optical response is proportional to the average layer thickness (when adlayer thickness is very small), in this sense, it might be convenient to assume that change in reflectance is equivalent to variation in charge density of AHT (AET). To test this assumption, changes in $\Delta\Theta_{SPR}$ as a function of surface coverage (charge density) for a fixed refractive index were calculated (data not shown here). The result suggests that it is also reasonable to correlate changes in $\Delta\Theta_{SPR}$ with charge density of AHT (AET). Fig. 2 shows the angle-dependent SPR contour plots for the AHT-free Au thin film and the AHT-SAM (Fig. 2A) and AET-SAM (Fig. 2B) on Au thin film using an ambient dielectric of air. For a five-layered (approximated as a stacked Fresnel system) architecture as defined in Fig. 1B, the angle change in the SPR response can be approximated as [Chen et al., 1980; Sarkar et al., 2004].

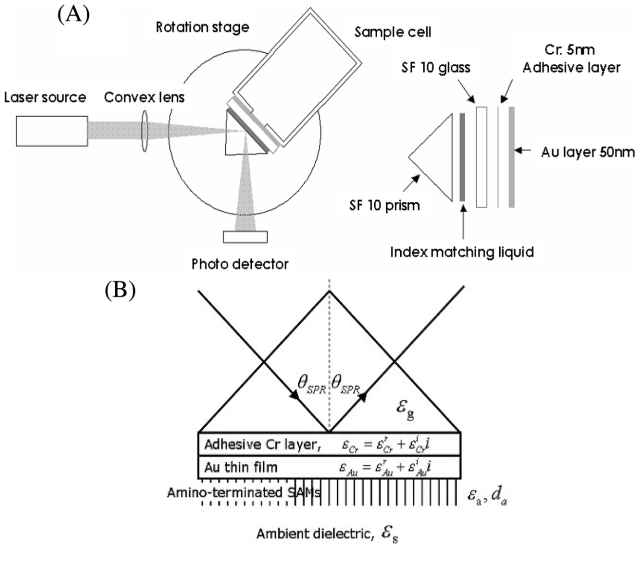

Fig. 1. (A) The schematic configuration of surface plasmon resonance (SPR) measurements in the present study. (B) Stratified structure of an SPR system.

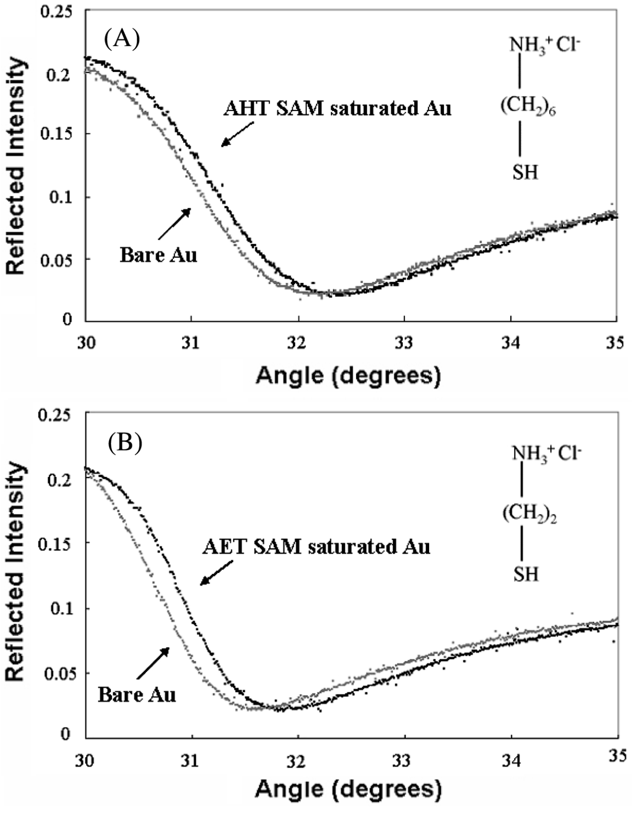

Fig. 2. Incident angle dependent SPR reflectivity of (A) AHT and (B) AET SAM for four-phase (grey) and five-phase multilayer systems (black), using the ambient dielectrics of air. For each graph, every fourth point from the collected raw data is plotted to preserve the clarity of the contour plot. The four-phase system corresponds to an AHT (AET)-free Au SPP substrate. In the five-phase case, the Au thin film is coated with a SAM of AHT (AET) by immersing the Au thin film in a 1.0 mM ethanolic solution of AHT (AET).

$$\Delta\theta_{SPR} \propto \mathrm{k}_o\left(\frac{\varepsilon_a-\varepsilon_s}{\varepsilon_a}\right)\left(\frac{\varepsilon_m^r\varepsilon_s}{\varepsilon_m^r+\varepsilon_s}\right)^2\left(\frac{\varepsilon_a-\varepsilon_m^r}{\varepsilon_s-\varepsilon_m^r}\right)(-\varepsilon_m^r\varepsilon_s)^{-1/2}\left(\frac{2\pi\mathrm{d}_a}{\lambda}\right) \tag{2}$$

As can be seen in the above Eq. (2), the SPR resonance angle (θ_{SPR}) increases as a function of both the thickness (d_a) and the dielectric constant (ε_a) of layer 4 (amino-terminated alkanethiol layer). Therefore, the formation of a new amino-terminated alkanethiol layer (AHT or AET) with a dielectric constant of *ca.* 2.0 larger than that of air (~1.0) on the surface of the Au thin film is responsible for the increase in θ_{SPR} in Fig. 2.

The initially formed amino-terminated SAM was assumed to be a zwitterion-like species, $-NH_3^+Cl^-$ for both AHT and AET. Therefore, through the NaOH treatment, we were able to change the terminal functional group from $-NH_3^+Cl^-$ to $-NH_2$ by the removal of H^+. can be protonated (below the pK_a) or deprotonated (above the pK_a) according to the following equation:

$$\mathrm{RNH}_{3\,surface}^{+} \xrightleftharpoons{pK_a} \mathrm{RNH}_{2\,surface} + \mathrm{H}^{+}_{solution} \tag{3}$$

We focused our attention on the detection of changes in the optical properties of the SAM layer as a result of the deprotonation and reprotonation of the AHT (AET) SAM layer. It would be expected that (irrespective of the location of H^+ generated in the forward reaction of Eq. (3)) these changes in surface charges would affect both the electronic configuration and the orientation of the AHT (AET) SAM layer. This would result in a change in the dielectric function ε_a and, hence the refractive index, $n_a=(\varepsilon_a)^{1/2}$ under visible light, of the AHT (AET) SAM. For *in situ* SPR measurements of the AHT (AET) SAM ionization, it was necessary to induce deprotonation in the same experimental cell where the SAM was formed on the Au thin film. We proceeded to examine the pH-dependent ionization behavior of formed SAM using time-resolved SPR measurements. The Au thin film modified with an AET SAM layer was introduced in the aqueous solution (pH=3) and the ΔR(t) behavior of this system was monitored in real time (as in Fig. 3). At a sufficient time after the immersion (the moment that ΔR was considered to settle at its time-independent value), at time t_o, we changed the pH of the solution to 11. Following the subsequent stabilization of the SPR angle, the pH of the solution was again changed to 3. The results for two such cycles of pH alterations are presented in Fig. 3. The arrows indicate the instants when the solution pH is changed by the injection of HCl or NaOH into the experimental cell. A definite trend in variation, above the experimental noise level and following the sequence of pH changes, was observed for the ΔR(t) data (symbols) of Fig. 3A for AHT SAM and Fig. 3B for AET SAM. The line through the data represents this trend. Interestingly, it was also found that exactly the opposite trend in the variations in ΔR(t) seen in Fig. 3C were observed when the pH-dependent SPR measurements of Fig. 3A and 3B were repeated by using the SAM-free Au thin film (blank test), with all other experimental conditions being unchanged. Therefore, it is obvious that the observed pH-dependent changes in SPR reflectance in Fig. 3A and 3B are due to morphological changes in amino-terminated SAMs (AHT and AET) caused by deprotonation and reprotonation. The SPR angle increases when AHT (AET) is protonated in an acid environment, and the reverse situation is observed in the case where a base solution is used. For AHT SAM on the gold substrate variation in the reflectance along with pH alteration is not as pronounced as that for AET SAM. This result implies that the chain length of the SAM plays a role in determining the ionization constant, pK_a, of amino-terminated alkanethiol on the gold substrate [Kakiuchi et al., 2000]. The accurate measurement of these parameters is currently underway to focus, in particular, on the careful determination of the SAM

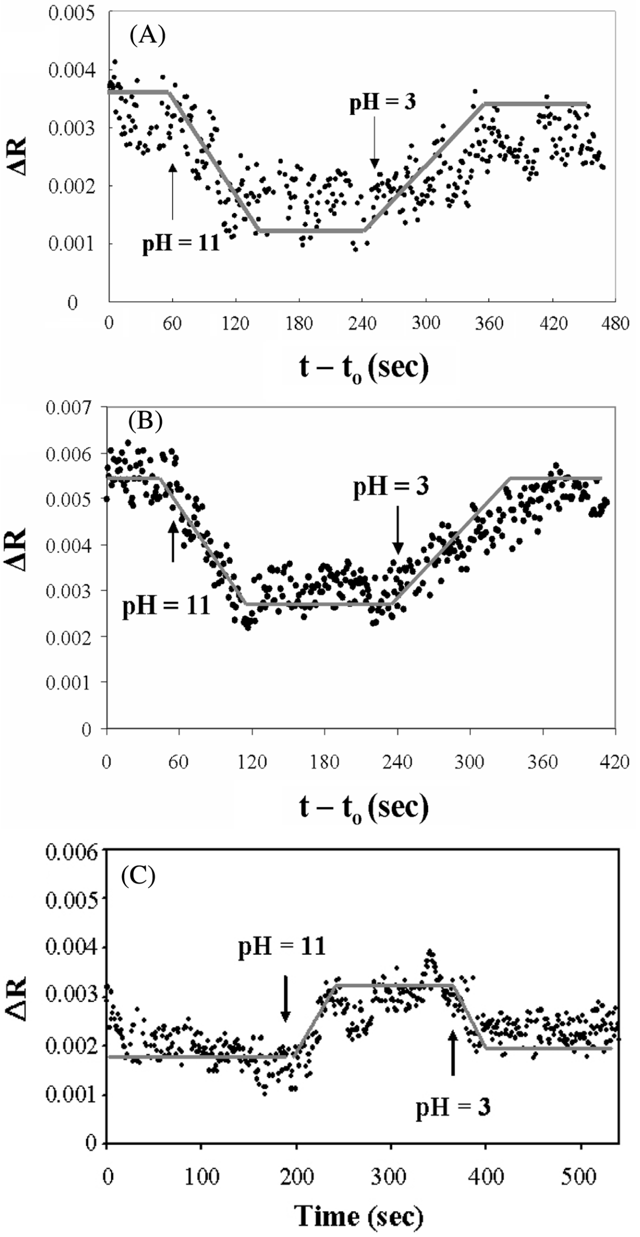

Fig. 3. Effects of changing the solution pH on the SPR angle for a five-phase multilayer structure including (A) a completely formed SAM of (A) AHT or (B) AET on Au film and (C) SAM-free Au film. After the AHT (AET) SAM is formed in an ethanolic solution of 1 mM AHT, the AHT-Au surface is dried with N_2 and allowed to stabilize in an aqueous solution at pH 3 for t_o (~10 min). At $t>t_o$, the solution pH is again changed to between 11 and 3. The symbols represent experimental data, and the arrows indicate the points in time when NaOH (at $t-t_o=60$) or HCl ($t-t_o=240$) is introduced in the cell to change the solution pH. The line through the symbols shows the general trend for the variations in ΔR.

packing density. Nevertheless, the above-estimated values permit an overall description of the optical response of an AET modified surface to deprotonation-reprotonation and also provide convincing evidence for the reversible change of $-NH_3^+Cl^-$ to $-NH_2$ as the result of the NaOH and HCl treatment.

In conclusion, the findings herein suggest that deprotonation and reprotonation of self-assembled monolayers (SAMs) of 2-aminoethanethiolhydrochloride (AET) and 2-aminoethanethiolhydrochloride (AHT) on gold substrate are able to be observed by *in-situ* SPR measurements. The reflectance (SPR angle) increases when amino-terminated SAM is protonated in an acid environment, while the reverse situation is observed in the case that a base solution is used.

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