

pH-Dependent Stability of Self-Assembled Monolayers on Gold

Bokyoung Kong, Yongseong Kim,^{†,*} and Insung S. Choi^{*}

*Department of Chemistry, KAIST, Daejeon 305-701, Korea. *E-mail: ischoi@kaist.ac.kr*

*†Department of Chemistry, Kyungnam University, Masan 631-701, Korea. *E-mail: kimys@kyungnam.ac.kr*

Received June 10, 2008

Key Words : Self-assembled monolayers, Alkanthiols, Stability, Gold, pH

Self-assembled monolayers (SAMs) have attracted considerable attention because of their wide applications to biosensors, optoelectronic devices, control of wettability and biocompatibility, corrosion resistance, etc.¹ Among various types of SAMs formed on numerous kinds of substrates, the SAMs of alkanethiols on gold have extensively been studied, primarily because it is relatively easy and simple to form well-organized monolayers on gold compared with the methods used for other substrates. In addition, the gold surface enables us to effortlessly use analytical techniques, including surface plasmon resonance spectroscopy, quartz crystal microbalance, reflection absorption infrared spectroscopy and ellipsometry, in the mechanistic studies and potential applications of SAMs.^{1b,c,g} Especially, the SAMs of long-chain alkanethiols with ω -functional groups, such as OH, COOH, and NH₂, have attracted a great deal of interest, because the use of these alkanethiols would yield more interesting properties of surfaces through post-modification reactions, such as nucleophilic substitution,^{2a-i} nucleophilic addition,^{2e,h} esterification,^{2a} and acylation,^{2j,m} in addition to their own chemical properties. For example, the surface modifications of OH-, COOH-, and NH₂-terminated SAMs have been used for the attachment of biopolymers, such as oligonucleotides and peptides, onto gold surfaces, which is the essential step for the application to biotechnology.³

Since the post-modifications and applications of SAMs are performed under various conditions of temperature, pH and solvents,⁴ studies on the stability of SAMs against potentially destructive conditions of monolayers are important for wider applications of SAMs as well as design of post-modification reactions. The air-stability of alkanethiol-based monolayers on gold was studied with long-chain alkanethiols for one week to several months.⁵ Their long-term stability was also investigated in biological media, because biomaterials and biological devices, which use SAMs as a platform, necessitate prolonged exposure to the biological media.⁶ Recently, the effect of storage conditions, such as air, N₂, ethanol, phosphate buffer and H₂O, on the stability of mixed poly(ethylene oxide)-thiol SAMs was studied to ensure the long-term preservation of biosensing property.⁷ In addition to these studies on the stability of SAMs, the pH dependency of the stability of SAMs in aqueous solutions is to be established, since the numerous surface modification reactions and applications of SAMs are performed at various pH values. As a related work, the dissociation phenomena of thiolate ligands from the surface

of cadmium chalcogenide nanocrystals have been examined by varying the pH values.⁸ In this work, we investigated pH-dependent stability of alkanethiol SAMs with various functional groups at their terminals, in order to give a basic but crucial information for post-modifications and other SAM-based reactions. The SAMs of long-chain alkanethiols with CH₃, OH, COOH, or NH₂ group were prepared on gold, and their stability was studied for one week at pH values from 1 to 14 by measuring the changes in the ellipsometric thickness.

For the preparation of the SAMs on gold, a clean gold substrate was immersed for 20 h in each alkanethiol solution of HS-(CH₂)₁₅-CH₃, HS-(CH₂)₁₆-OH, HS-(CH₂)₁₅-COOH, or HS-(CH₂)₁₆-NH₂. The SAMs were characterized by FT-IR spectroscopy (Figure 1). Figure 1a shows the IR peaks

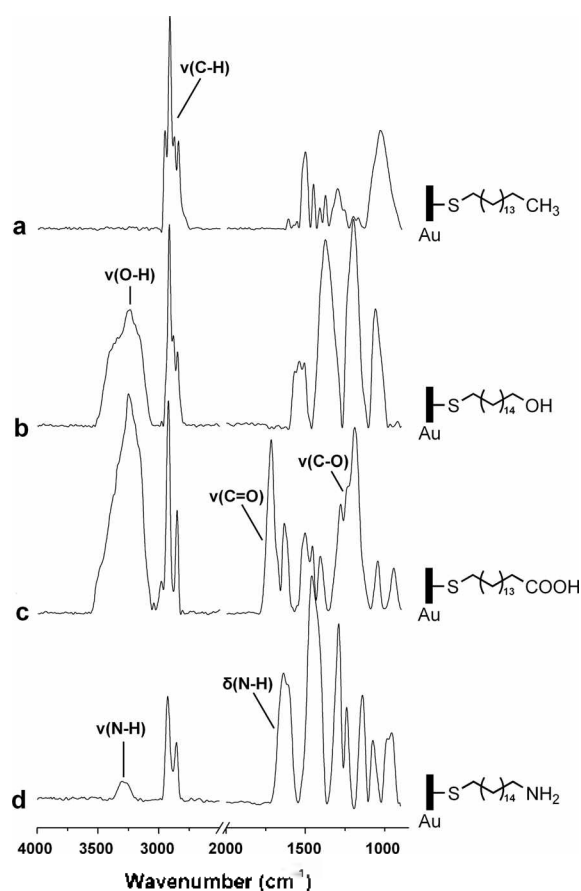


Figure 1. IR spectra of SAMs: (a) HS-(CH₂)₁₅-CH₃, (b) HS-(CH₂)₁₆-OH, (c) HS-(CH₂)₁₅-COOH, and (d) HS-(CH₂)₁₆-NH₂.

associated with normal alkyl chain and terminal methyl group of **HS-(CH₂)₁₅-CH₃** SAMs: 2957 and 2946 (symmetric C-H stretching), 2917 (asymmetric C-H stretching), 1507 (CH₂ bending), and 1460 cm⁻¹ (CH₃ bending). For the SAMs of **HS-(CH₂)₁₆-OH**, peaks from the hydroxyl group additionally appeared at 3528-3239 (O-H stretching) and 1062 cm⁻¹ (C-O stretching) (Figure 1b). The formation of the SAMs of **HS-(CH₂)₁₅-COOH** and **HS-(CH₂)₁₆-NH₂** was also confirmed by the presence of the characteristic IR peaks: for the SAMs of **HS-(CH₂)₁₅-COOH**, peaks at 3564-3062 (O-H stretching), 1721 (C=O stretching), and 1194 cm⁻¹ (C-O stretching) (Figure 1c); for the SAMs of **HS-(CH₂)₁₆-NH₂**, peaks at 3303 (N-H stretching), 1638 (N-H bending), and 1291 cm⁻¹ (C-N stretching) (Figure 1d).

We first investigated the stability of simplest alkanethiol, **HS-(CH₂)₁₅-CH₃**, in the whole range of pH values, 1 to 14. The pH of acidic and basic aqueous solutions was adjusted with NaOH and HCl for pH 1, 2, 10, 11, 12, 13, 13.5, and 14. For the rest of pH values (pH 3, 4, 5, 6, 7, 8, and 9), the pH-solutions were prepared by dissolving buffer powders in distilled water, as pH values were fickle in these ranges depending upon the concentration of CO₂ in atmosphere. The pH of the pH-solutions was checked by a pH meter and adjusted everyday during the one-week-long experiments. The immersed samples were taken out from the solutions, and the ellipsometric thickness of the SAMs was measured everyday. We used fifteen plates for the measurements, and the averaged thickness was calculated. Figure 2a shows the pH-dependent change in the thickness of the SAMs of **HS-(CH₂)₁₅-CH₃**. The SAMs were found to be stable for the pH range of 1 to 12; no significant thickness decrease was

observed in this pH range. In other words, the methyl-terminated SAMs were quite stable under acidic conditions. However, the SAMs were labile in basic solutions, and the thickness decreased rapidly at pH values of 13, 13.5, and 14. The thickness was measured to be 10.3 Å from 16 Å after 3 days and 5.6 Å after six days for pH 13; the thicknesses of the SAMs at pH 13.5 and 14 rapidly decreased to 2.2 Å and 4.5 Å after 2 days, respectively. In the case of pH 13, we observed a gradual decrease in the thickness, and the decrease rate was calculated to be approximately 2.0 Å/day. In contrast, the SAMs were desorbed quickly from gold at pH 13.5 and above. The thickness of 5 Å indicates that about two-third of the alkanethiols were desorbed in one day (see Figure 2a). These results suggest that it should be avoided to use highly basic solutions for post-modifications of SAMs, but the pH values up to 12 were tolerable.

The stability test for the SAMs of **HS-(CH₂)₁₆-OH** was performed by following the same procedures (Figure 2b). The SAMs of **HS-(CH₂)₁₆-OH** were found to be a little bit more stable than those of **HS-(CH₂)₁₅-CH₃**. The initial thickness was 22.2 Å, and the thickness did not decrease at pH 13 (we observed a slight increase in the thickness as time went, but the reasons remain to be seen). The thickness decrease was 19.8% (from 22.2 to 17.8 Å) after 2 days at pH 13.5; in contrast, we observed almost complete desorption of **HS-(CH₂)₁₅-CH₃** after 2 days at pH 13.5. It is noteworthy that the thickness did not change after the initial, 3-day decrease at pH 14 (and 13.5). The thickness decreased gradually to 12.9 Å for the first 3 days but was unchanged afterwards, which indicates that about 40% of the **HS-(CH₂)₁₆-OH** compounds still existed on gold. This obser-

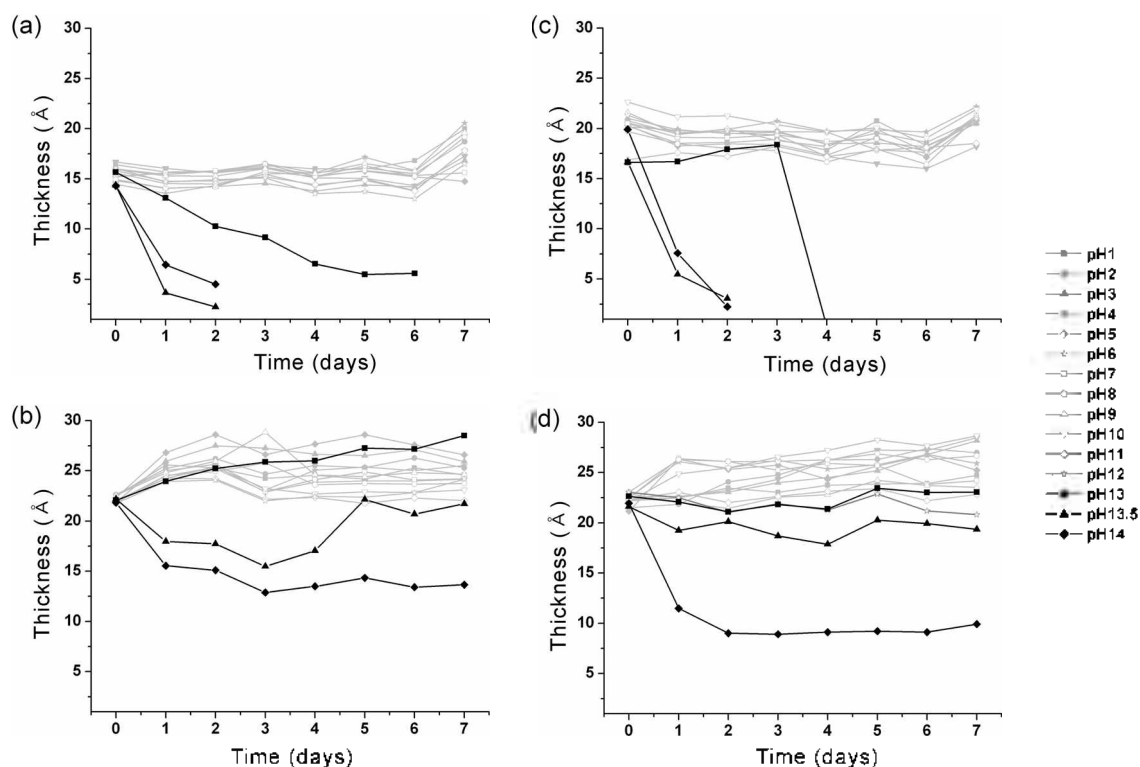


Figure 2. Ellipsometric thickness of SAMs: (a) **HS-(CH₂)₁₅-CH₃**, (b) **HS-(CH₂)₁₆-OH**, (c) **HS-(CH₂)₁₅-COOH**, and (d) **HS-(CH₂)₁₆-NH₂**.

vation was rather unexpected, because relatively more hydrophilic SAMs would have had more permeability for hydroxide ions or other polar species than the SAMs of **HS-(CH₂)₁₅-CH₃** with well-packed/ordered structures.

The surface $pK_{1,2}$ values of the SAMs of **HS-(CH₂)₁₅-COOH** were reported to be 8.0 and 6.4,⁹ which means that the SAMs would be negatively charged under basic conditions by the deprotonation of the carboxylic acid groups to carboxylates. However, the stability of the SAMs was not dictated by the charge development of the surface, but followed a similar trend to that of the SAMs of **HS-(CH₂)₁₅-CH₃** (Figure 2c). At pH 13.5 and 4, the thiols were desorbed rapidly from gold, and the desorption was almost completed in 2 days. However, the desorption characteristic of the SAMs of **HS-(CH₂)₁₅-COOH** at pH 13 was peculiar compared with the other SAMs. At pH 13, the SAMs were stable for the first 3 days, but after 3 days most of the thiols were desorbed abruptly. The SAMs of **HS-(CH₂)₁₆-NH₂** showed highest stability against basic conditions: the SAMs were stable at pH 13 and 13.5 (Figure 2d). In addition, although there was an initial desorption in 2 days (about 58.9%) at pH 14, the SAMs became stable after the initial desorption.

The results with OH- and COOH-terminated alkanethiol SAMs indicate that these SAMs were quite stable at pH 12 and below: these were stable even under highly acidic conditions, such as pH 1 and 2. This stability characteristic seemed contradictory to the previous report, where OH- and COOH-containing thiolate ligands (3-mercaptopropionic acid and 3-mercapto-1-propanol) were dissociated from the surface of cadmium chalcogenide semiconductor nanocrystals by lowering the pH of solutions.⁸ In the paper, they concluded that the desorption (or detachment) of the ligands resulted from protonation of the ligands by H⁺; re-adsorption of the ligands onto the nanocrystals was observed when the pH value reached about the pK_a of the free thiols. We thought that these seemingly contradictory results might be explained by the differences between the two systems, such as characteristics of metal-thiol (or thiolate) interactions, chain length of thiols, packing density of SAMs, substrate identity (nanocrystals vs. flat surfaces), etc. Our results might imply that the desorption of the thiols in our system did not involve the protonation of thiolates: the desorption might have been caused by direct attack of hydroxide ions or other anions to gold and corrosion of gold.

In summary, all the SAMs of alkanethiols studied were found to be stable at pH 12 or below in aqueous solutions, regardless of functionality at their terminal. The SAMs of **HS-(CH₂)₁₆-NH₂** showed exceptional stability at pH 13 and 13.5. Many reactions on SAMs have been performed under acidic or basic conditions. Especially, hydrolysis involved highly basic conditions (pH 12 and above), although the reaction time was relatively short (typically less than 1 hour).¹⁰ However, our results imply that the desorption of alkanethiols from gold should be considered seriously when SAM-based reactions are conducted under basic conditions, because the desorption of thiols would interfere with the desired reactions. In this respect, we believe that the results

of this work will give fundamental but useful information for designing and performing SAM-based organic reactions, although no mechanistic studies were attempted to elucidate the pH-dependent desorption phenomena.

Experimental Section

Gold-coated substrates were prepared by a thermal deposition of gold (100 nm) onto silicon wafers that had been primed with titanium (5 nm) as an adhesive layer. 1-Hexadecanethiol (**HS-(CH₂)₁₅-CH₃**, $\geq 95\%$, Fluka), 16-mercaptohexadecanol (**HS-(CH₂)₁₆-OH**, Cos Biotech), 16-mercaptohexadecanoic acid (**HS-(CH₂)₁₅-COOH**, 90%, Aldrich), 16-amino-1-hexadecanethiol (**HS-(CH₂)₁₆-NH₂**, Cos Biotech), sulfuric acid (H₂SO₄, 95.0+%, Junsei), acetic acid (CH₃COOH, 99.0+%, Junsei), hydrogen peroxide (H₂O₂, 30-35%, Junsei), buffer (hydriion™, Aldrich), sodium hydroxide (NaOH, 96%, Junsei), hydrochloric acid (HCl, 35.0%, Junsei), and absolute ethanol (EtOH, 99.8+%, Merck) were used as received without purification.

For the preparation of SAMs, The gold substrates were cut into pieces (1 × 1 cm²) and then cleaned for 1 min in piranha solution (v/v 70% H₂SO₄/30% H₂O₂, *Caution: piranha solution reacts violently with organic materials and must be handled with extreme care utilizing the use of acid resistant gloves and adequate shielding*) to remove organic contaminants. After 1 min, the gold substrates were taken out, rapidly rinsed with deionized water and EtOH, and then dried with a flow of argon. The SAMs of **HS-(CH₂)₁₅-CH₃**, **HS-(CH₂)₁₆-OH**, **HS-(CH₂)₁₅-COOH** and **HS-(CH₂)₁₆-NH₂** were prepared by immersing thoroughly washed gold substrates for 20 h in the 1-mM solutions of the thiols, respectively. The solutions of **HS-(CH₂)₁₅-CH₃**, **HS-(CH₂)₁₆-OH**, and **HS-(CH₂)₁₆-NH₂** were simply prepared by dissolving each thiol compound in EtOH, while the solution of **HS-(CH₂)₁₅-COOH** was prepared by dissolving the thiol compound in EtOH/water/CH₃COOH (85/10/5, v/v/v).

The thicknesses of the SAMs were measured with a Gaertner L116s ellipsometer (Gaertner Scientific Corp., IL) equipped with a He-Ne laser (632.8 nm) at a 70° angle of incidence after the formation of SAMs. Polarized infrared external reflectance spectroscopy (PIERS) spectra of each SAMs were obtained in a single reflection mode using a dry N₂-purged Thermo Nicolet Nexus FT-IR spectrophotometer equipped with the smart SAGA (smart apertured grazing angle) accessory. The *p*-polarized light was incident at 80° relative to the surface normal of the substrate. The spectra were taken by adding approximately 8000 scans for background and 800-2000 scans for the samples at a resolution of 4 cm⁻¹, and all spectra were reported in the absorption mode relative to a clean gold surface. The pH values of the prepared pH-solutions and buffer solutions were checked with a pH meter purchased from Iotec.

Acknowledgments. This work was supported by Kyungnam University Foundation Fund, 2008. The FT-IR spectrophotometer and ellipsometer were purchased with research funds from the Center for Molecular Design and Synthesis.

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