

A Catalytic 2-Aminoethanethiol Reduction on a Gold Electrode through a Sulfur-Gold Bond Formation

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In this note, we report a newly found catalytic reduction of a thiol compound on a gold electrode, which consequently catalyzes the reduction of protons. In a 2-aminoethanethiol solution, no reduction wave was measured with a glassy carbon electrode but a large cathodic wave was observed with a gold electrode indicating a catalytic reduction of a thiol compound at a gold surface. The chemistry involves the adsorption of a self-assembled monolayer (SAM) of 2-aminoethanethiol and its reductive desorption reaction. It was reported that an adsorbed self assembled monolayer (SAM) of a thiol compound on the gold electrode surface was reductively desorbed from the surface in alkaline solutions when an appropriate potential was applied.¹⁻³ The desorbed thiolate anions were electro-deposited again on the gold surface, which is another route to form a thiol monolayer.⁴ In other studies by Morin and coworkers, the amount oxidatively re-deposited was affected by the pH of the solution.^{5,6} It was suggested that the amount of the re-deposition by the oxidation decreases with the increasing solubility of the thiols because of the diffusion into the bulk of the solution.

For this study, 2-aminoethanethiol ($\text{HSCH}_2\text{CH}_2\text{NH}_3^+$) in a pH 6 aqueous solution, which has not been studied for the reductive desorption reaction, was used as a thiol compound. It has a short chain length with an ionic amino group and is easily dissolved in an aqueous solution. Compared to long chain alkanethiols, it gives less ordered monolayer.^{7,8} It is widely employed to give base sites for enzyme layer formations⁹⁻¹¹ and its adsorption was characterized by XPS and electrochemical studies.¹² According to the electrochemical and quartz crystal microbalance measurements of the present study, a catalytic reduction mechanism of a thiol compound is presented here.

Figure 1A shows a comparison of the voltammograms with a bare gold plate electrode in a pH 6.0 phosphate buffer in the absence (the dashed line) and presence (the solid line) of 5.0 mM 2-aminoethanethiol. A reduction wave was observed at about -0.7 V in the solution of the 2-aminoethanethiol. In Figure 1B, when a glassy carbon electrode polished with $0.3 \mu\text{m}$ alumina powder was employed, almost the same two voltammograms in a pure supporting electrolyte (the dashed line) and in a 5.0 mM 2-aminoethanethiol solution (the solid line) were shown. No reduction of the thiol compound was observed with the glassy carbon electrode. The reduction of the 2-aminoethanethiol

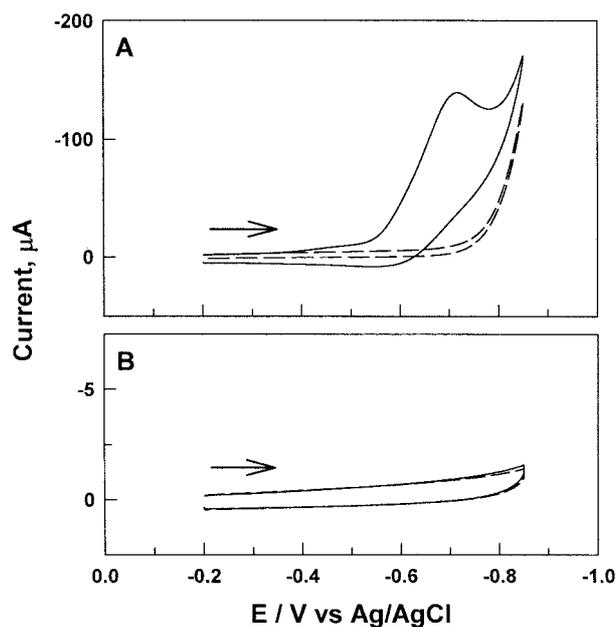


Figure 1. Cyclic voltammograms in a 5.0 mM 2-aminoethanethiol solution with (A) a gold plate electrode (0.32 cm^2) and (B) a glassy carbon electrode (0.071 cm^2). The voltammograms of the dashed lines were obtained in a pure supporting electrolyte. Supporting electrolyte: 0.1 M phosphate buffer (pH 6.0, under Ar). Scan rate: 100 mV/s.

seems to be catalyzed on the gold electrode surface.

Figure 2 is an electrochemical quartz crystal microbalance (EQCM) measurement in a pure supporting electrolyte with a gold electrode on a quartz crystal resonator. A SAM was previously formed on the gold surface by immersing in a 5.0 mM 2-aminoethanethiol solution for three hours. Figure 2A is a cyclic voltammogram as the potential scanning proceeded. In the first negative potential scan, a cathodic wave was shown at -0.63 V and a small anodic wave was shown at -0.58 V with the backward potential scan. After one cycle of the potential scanning, the second cathodic wave, with higher currents than those in the previous anodic wave, was shown. More cathodic waves were measured with further repeated cyclic scans and the wave almost disappeared in about 15 cycles of the scans.

The cathodic wave at -0.63 V in Figure 2A can be assigned to the reductive desorption of the adsorbed 2-aminoethanethiol SAM (Eq. 1) as other thiol compounds were

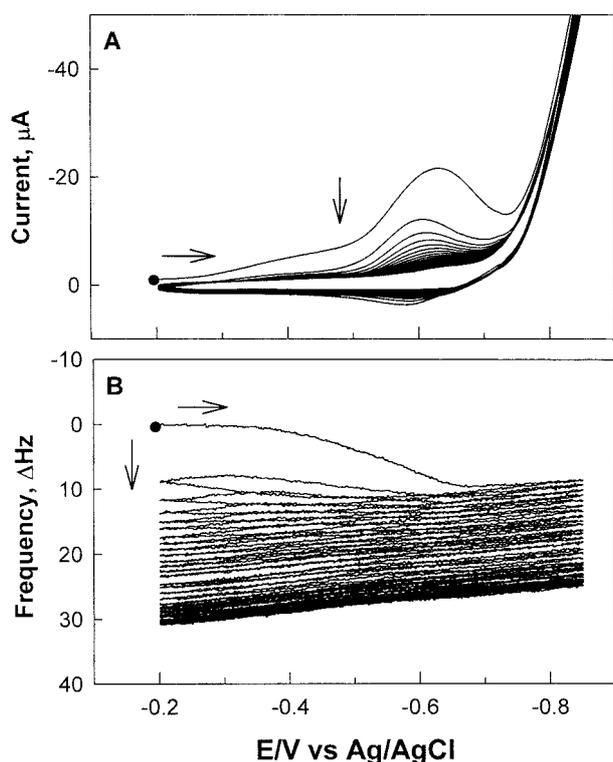


Figure 2. An EQCM measurement in a pure supporting electrolyte. The quartz crystal resonator (9 MHz) with a gold surface (0.20 cm²) was previously immersed in a 5.0 mM 2-aminoethanethiol solution for 3 hours to form its SAM. Each arrow indicates the direction of current or frequency change. The dot points indicate starting points. Supporting electrolyte: 0.1 M phosphate buffer (pH 6.0, under argon). Scan rate: 100 mV/s.

reductively desorbed similarly.¹⁻³



The peak was relatively broad probably because polycrystalline gold with a relatively rough surface was employed as the working electrode.^{1,13,14} In other previous studies, the produced thiolate anions were oxidatively deposited again in the alkaline solutions.⁴⁻⁶ However, in the present study, the reversible oxidative deposition of the R-S⁻ ion on the gold electrode, which is the backward reaction of Eq. 1, appeared to occur with little anodic currents indicating some fraction of the desorbed species proceeding into another pathway. With the pK_a of 8.21 of the thiol group of HSCH₂CH₂-NH₃⁺,¹⁵ the ratio of [R-S-H]/[R-S⁻] was calculated to be 1.6 × 10² at pH 6.0 and most R-S⁻ ions formed during the reduction were protonated by the reaction of Eq. 2 and not oxidatively deposited giving a relatively small anodic wave. The protonated thiols (R-S-H) would be then adsorbed by the oxidative addition to the gold surface, which is a widely accepted reaction (Eq. 3).¹⁶ The adsorption of some thiol compounds by electrochemical oxidation was reported,^{17,18} but, at the present low overpotentials, the thiols seems to be adsorbed by the non-electrochemical oxidation process.

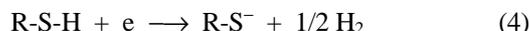


During the cathodic potential scanning, it is thought that the continuous sulfur-gold bond formations occurred with the sequential reactions of Eqs. 1, 2, and 3, which made the electrochemical reaction partially irreversible. It was reported that some alkanethiols of 1 mM concentrations formed monolayers within a few seconds.¹⁹ As the adsorption rate depends on both the fraction of the surface exposed and the thiol concentration,²⁰ with a much higher local concentration of the aminoethanethiol at the surface after the reductive desorption, its re-adsorption by Eq. 3 would occur rapidly within a time for the potential scanning with the scan rate of 100 mV/s. The surface coverage did not go to zero when the first cathodic potential scanning finished. Hence the second cathodic wave shown after one cycle of the potential scanning gave higher currents than those in the previous anodic wave by the reduction of the additionally adsorbed species by Eq. 3. The redox waves gradually decreased with further repeated cyclic scans as some fraction of the desorbed species was diffused out into the bulk of the solution. They almost disappeared in about 15 cycles of the scans.

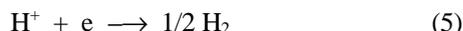
This suggested explanation was further confirmed with the QCM frequency change measurements.²¹ The frequency increase of 9 Hz in Figure 2B in the first cathodic potential scan was observed and, as more scanning proceeded, gradual increase of the frequency was observed. In about 18 cycles, the frequency change reached a limit with a total frequency change of about 28 Hz and the surface coverage was considered to be zero at this stage. In Figure 2A, the charge under the first cathodic wave was estimated as 220 μC/cm² which is equivalent to the reduction of 180 ng/cm² of the 2-aminoethanethiol. In Figure 2B, the 9 Hz frequency change after the first cathodic scan is equivalent to only 49 ng/cm² mass change,^{22,23} which indicates incomplete desorption of the monolayer due to Eqs. 2 and 3. The 28 Hz frequency change, which was the limited value after the repeated 18 cyclic potential scans, is equivalent to a 150 ng/cm² mass change,^{22,23} which is considered to be the actual total amount of adsorbed thiol monolayer after the complete desorption. The value of the mass change of 150 ng/cm² is a little less than the estimated value of 180 ng/cm² from the voltammetric wave. The cathodic wave would include some additional currents due to the cyclic re-adsorptions and reductive desorptions of the produced thiols during the negative potential scanning. The estimations of the mass changes from the cathodic charge and frequency change have several uncertainties. The double layer capacitance change and the adsorption of cationic species occurred during the thiol desorption, and the associated anions to the terminal ammonium groups of the aminoethanethiol were thought to be involved in the mass change.²⁴ Even with these unresolved uncertainties, the QCM experiment was qualitatively consistent with the voltammetric result.

Hence the reaction pathway for the reduction wave at -0.7 V in the solution of 0.5 mM aminoethanethiol in Figure

1A is as follows: the adsorption of the dissolved 2-aminoethanethiol (Eq. 3) and the reductive desorption of the adsorbed species (Eq. 1). The net reaction is the reduction of the dissolved R-S-H to R-S⁻ (Eq. 4).



If the protonation to the produced R-S⁻ anions after the reductive desorption reaction indeed occurred to give R-S-H, which was thought to be adsorbed on the surface by the reaction of Eq. 3 and reduced to give the thiolate anions again, the net reaction is the reduction of protons to yield molecular hydrogen (Eq. 5) by the sequence of the Eqs. 2, 3, and 1.



In the potential range where the cathodic wave was observed in Figure 1A, the 2-aminoethanethiol or proton was not directly reduced through an outer-sphere electron transfer as observed with the glassy carbon electrode in Figure 1B.²⁵ The origin of the catalytic process can now be explained by the sulfur-gold bond formation and relatively easier reduction of the R-S-Au than the R-S-H. Further studies are being carried out to estimate more quantitative data on the kinetics and thermodynamics regarding to the related reactions.

Experimental Section

Materials. Commercial reagent grade chemicals were used as received. A 0.1 M phosphate buffer solution (pH 7.0) was prepared for electrochemical measurements. Deionized water was further purified by a purification train (Milli-Q, Millipore Co.) and used to prepare solutions. A gold plate of a square shape (0.4 mm × 0.4 mm, geometric surface area of 0.32 cm²) connected to a platinum wire for the electric contact or a commercially available GC electrode (0.071 cm², Kosentech Co.) was used as a working electrode.

Apparatus and procedures. Electrochemical experiments were performed in a two-compartment cell closed with a Teflon cap. A working electrode, platinum auxiliary electrode, and gas bubbling tube were fitted through the cap, and a reference electrode was immersed in another compartment separated by glass frit. A CH Instruments electrochemical analyzer (model 630A) controlled through a personal computer was employed for the electrochemical measurements. Potentials were measured and quoted with respect to a Ag/AgCl (3 M NaCl) reference electrode with a potential of 0.22 V vs NHE.

A quartz crystal microbalance (QCM) EQCN 1000 system (SHIn Co., Korea) was employed to measure frequency changes according to minute mass changes on the gold surface during the enzyme immobilization. A 9 MHz quartz crystal resonator with a gold surface (0.2 cm²) was used. All experiments were carried out at the ambient temperature (22 ± 1 °C).

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