Supporting Information

Studies on the effect of electrode pretreatment on the coverage of self-assembled monolayers of dodecanethiol on gold by electrochemical reductive desorption determination

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Contents

1. The characteristics of various methods for determination of the surface coverage Γ_m of Au-SAMs

Table S1. The characteristics of various methods for determination of the surface coverage Γ_m of Au-SAMs

Techniques	Characteristics	Ref.
(1)RD (Reductive desorption)	Electrochemical desorption of alkanethiolates (RS$^-$) from a gold surface are preformed in an alkaline solution, by the following one electron reduction process Au-SR + e- → Au(0) + -SR. The area, shape, and position of the cathodic peak for the reductive desorption can provide useful information on the SAM such as the adsorbed amount, stability, adsorption energy, orientation, and substrate morphology.	[1-20]
(2)OD (Oxidative desorption)	Integrated charge for oxide reduction is subtraction from the total anodic charge in the first positive scan, we can get the charge for oxidation of the surface alkanethiolates. Oxidative desorption is restricted by degree of desorption of organic layer and thiol desorption species, has not been widely used.	[2, 21. 22]
(3) UPD (Underpotentially deposited)	Foreign metal atoms can be electrodeposited between SAMs and gold substrates through electrochemical and high-quality monolayers formed on the deposition of the metal layer.	[23-27]
(4) EQCM (Electrochemical quartz crystal microbalance)	From the frequency curve, the frequency and mass changes can be obtained by Sauerbrey equation. EOCM is covenient and efficient, which can used in-depth to study the dynamic process of self-assembly through different assembling time.	[28-33]
(5) SPR (Surface plasmon resonance)	Surface plasmon resonance (SPR) is sensitive to the thickness and refraction index of material at the intereface between a thin metal film (gold) and a bulk medium (air), can obtain the character of the measured alkanethiols. But most are used to study the character of biological molecules self-assembled on metal surfaces.	[34-39]
(6) IR (Infrared spectra)	Orderly arrangement of alkyl thiols can be characterized by FTIR microspectroscopy, which is the best technology to provide detailed structural and conformation information of SAMs, combined with Fourier transform can well detect the tightness and ordered arrangement of alkyl thiol monolayer.	[40-42]
(7) AFM (Atomic force microscopy)	Atomic force microscope (AFM) can observe directly the structure each phase and quantitative information of self-assembly kinetics, it revealed the lattice of one of the thiols on Au(111) with molecular (lattice) resolution showing a reduced area per molecule which is consistent with a reduced tilt angle.	[43, 44]
(8) XPS (X-ray photoelectron spectroscopy)	XPS is employed to gain information on the electronic structure and chemical bonding of the molecules. The incident X-ray photons are absorbed by various atoms in the surface layer leading to the ionization and the emission of an inner shell electron. Photoelectrons from each element will have a characteristic binding energy and relative intensity associated with each core atomic orbital providing an extremely powerful tool for quantitative analysis of the surface composition. But XPS was often used to study the information on the structure and electronic properties of M-DNA adsorpted on the metal surface.	[45-48]

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2. Major groups for determining the coverage Γ_m of C_nSH-SAMs-Au using reduction desorption

Table S2. Major groups for determining the coverage Γ_m of C_nSH-SAMs-Au using reduction desorption

Research groups	Pretreatment	Research features	Ref.
(1) M. D. Porter	Annealed pretreatment, γ=1.1±0.1.	They reported oxidative- and reductive-desorption of the adsorbed n-alkanethiol monolayer for the first time. Alkanethiolates were electrochemically desorbed from a gold surface by one electron reduction process in an alkaline solution, and reductive-desorption charge was independent of alkyl chain length n. In addition, they proposed the result of double peaks appeared in reductive desorption experiment: (a) The short chain systems exhibited a single voltammetric wave for the resorption and re-deposition processes. In contrast, multiple voltammetric waves were found for the long chain systems. The key difference between the short chain and long chain monolayers was the difference in cohesive interactions between alkyl chains because of differences in the adlayer domain structures and the binding modes between sulfur and gold. (b) The difference between substrates was the key reason of difference cohesive interactions between alkyl chains and different adlayer domain on Au.	[1-8]
(2) M. Morin	Mechanically polished – flame-annealed.	They thought that coverage Γ_m was independent of alkaline solution with different pH, and proposed the method to remove the double layer capacitance effect on reductive desorption charge. According to the formula: $\Delta Q=C_2(E_2-E_{2,PZC})-C_1(E_1-E_{1,PZC})$. Where C_1 was the coated electrode capacitance at a potential E_1, $E_{1,pzc}$ was the potential of zero charge of the coated electrode; C_2 was the uncoated electrode capacitance at a potential E_2, $E_{2,pzc}$ was the potential of zero charge of the uncoated electrode. In the later research reductive desorption ΔQ of different C_nSH could be handled as a constant.	[9-13]
(3) T. Kakiuchi	550 °C annealed for 6 h, γ=1.0～1.1.	They adopted Porter's reductive desorption method and proposed coverage Γ_m was independent of alkyl chain length n. In addition they supposed that the total contribution from surface roughness and the nonfaradaic current was assumed to be constant at ca. 30% of the total reductive charge, so reductive desorption coverage Γ_m could be corrected.	[14, 15]
(4) J. J. Gooding	Different gold substrates (piranha reagents, polishing and annealed pretreatment).	They used six different gold substrates((A) bulk gold, (B) Au-mica, (C) Au-mica annealed, (D) flat gold, (E) Au-Ti-glass and (F) Au-MPS-glass) for assembly experimental in solution. The results of surface methods (STM) and electrochemical measurements showed that different position and peak shape for the reductive desorption of the SAMs on the different surfaces, the potential required to remove the SAM becomes progressively more negative with the smoother surfaces, which all indicated the SAMs formed on smooth electrode was more stable.	[16]

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3. Summary of Au electrode roughness factor γ by different pretreatment from literature

Table S3. Summary of Au electrode roughness factor γ by different pretreatment from literature

No.	Type	Method	Roughness γ	Ref.
		(I) Aqua regia pretreatment		
1	Poly Au	Al_2O_3(down to 0.06 μm), sonicated for 10 min in water, etched for 3 min in a 1: 3: 4 (in volume) mixture of concentrated HNO_3/ concentrated HCl/water and sonicated in deionized water for 30 min, CV (0.5 M H_2SO_4, -0.2～1.5 V, v=0.1 V s^{-1}, 20 min).	1.2	[1]
2	Poly Au	Al_2O_3(1.0, 0.3, 0.05 μm), sonicated in ultrapure water, the gold surface was then cleaned with freshly prepared aqua regia solution (60% v/v water, 30% hydrochloric acid, and 10% nitric acid), CV (N_2-purged 1 M $HClO_4$, 0～1.7 V, v=0.08 V s^{-1}).	1.0～1.1	[2]
3	Poly Au	(d=1.5 mm), etched in aqua regia (3: 1 HCl/HNO_3), CV (0.05 M $KClO_4$, -0.8～1.3 V, v=0.02 V s^{-1}).	1.2	[3]
4	Poly Au	Al_2O_3(1.0, 0.3, 0.05 μm), sonicated in ultrapure water for 2 min, cleaned with freshly prepared aqua regia solution (60% v/v water, 30% hydrochloric acid and 10% nitric acid), CV (1 M $HClO_4$, 0～1.7 V, v=0.08 V s^{-1}).	1.0	[4]
5	Poly Au	(d=2.0 mm), Al_2O_3(1.0, 0.3, 0.05 μm), sonicated in twice-distilled water for 15 min, cleaned with freshly prepared aqua regia solution (HCl: HNO_3: H_2O=3: 1: 6, v/v) for 5 min, CV (0.5 M H_2SO_4, -0.4～1.5 V, v=0.1 V s^{-1}).	1.1	[5]
6	Poly Au	(d=2.0 mm), Al_2O_3(1.0, 0.3, 0.05 μm), sonicated in twice-distilled water for 15 min, cleaned with freshly prepared aqua regia solution (HCl: HNO_3: H_2O=3: 1: 6, v/v) for 5 min, CV (0.5 M H_2SO_4, -0.4～1.5 V, v=0.1 V s^{-1}).	1.1	[6]
7	Poly Au	(d=2.0 mm), Al_2O_3(1.0, 0.3, 0.05 μm), sonicated in twice-distilled water for 15 min, cleaned with freshly prepared aqua regia solution (HCl: HNO_3: H_2O=3: 1: 6, v/v) for 5 min, CV (0.5 M H_2SO_4, -0.4～1.5 V, v=0.1 V s^{-1}).	1.1	[7]
8	Poly Au	(d=2.0 mm), Al_2O_3(1.0, 0.3, 0.05 μm), sonicated in twice-distilled water for 15 min, cleaned with freshly prepared aqua regia solution (HCl: HNO_3: H_2O=3: 1: 6, v/v) for 5 min, CV (0.5 M H_2SO_4, -0.4～1.5 V, v=0.1 V s^{-1}).	1.1	[8]
9	Poly Au	(d=2.0 mm), Al_2O_3(1.0, 0.3, 0.05 μm), sonicated in twice-distilled water for 15 min, cleaned with freshly prepared aqua regia solution (HCl: HNO_3: H_2O=3: 1: 6, v/v) for 5 min, CV (0.5 M H_2SO_4, -0.4～1.5 V, v=0.1 V s^{-1}).	1.1	[9]
10	Poly Au	(d=1.5 mm), etched in aqua regia (3: 1 HCl/HNO_3), CV (0.05 M $KClO_4$, -0.8～1.3 V, v=0.02 V s^{-1}).	1.2	[10]
	Average and RSD (n=10)		1.1±0.1	

Table S3. Summary of Au electrode roughness factor γ by different pretreatment from literature (continued)

No.	Type	Method	Roughness γ	Ref.
		(II) Reductive annealed pretreatment		
11	Au/mica	Annealed at 200~300 □	1.1±0.1	[11]
12	Au(111)	Annealed at 300°C in a muffle furnace.	1.1±0.1	[12]
13	Au/mica	Annealed at 300°C for 5 h in a muffle furnace.	1.1±0.1	[13]
14	TSG	Template-stripped gold(TSG) mica/gold/epoxy/glass sandwich.	1.3±0.1	[13]
15	Au(111)	(A_G=0.57 cm^2), cleaned in piranha solution for few minutes and flame-annealed in an oxygen-gas flame, confirmed by STM before each experiment and by cyclic voltammetry in 0.1 M H_2SO_4.	1.2	[14]
16	Au(111)	(d=2.2 mm,A=0.152 cm^2), annealed at 580°C for 6 h.	1.1～1.2	[15]
17	Au/mica	Substrates of mica with an epitaxial (111) gold layer.	1.1	[16]
18	Au/mica	Annealed at 550°C for 8 h, CV(0.01 M $HClO_4$).	1.1	[17]
19	Au/mica	(A=0.67 cm^2), annealed in the laboratory ambient at 300 °C for 3 h.	1.2	[18]
20	Poly Au	Annealed in a muffle furnace at 300°C for 3 h.	1.1±0.1	[19]
21	Au	Polished Au with annealing, 800℃, 30 min.	1.2±0.1	[20]
22	Au	Polished Au with annealing, 400℃, 30 min.	1.3±0.1	[20]
23	Au	Evaporated Au on mica with annealing.	1.2±0.1	[20]
24	Au/mica	Annealed at 300°C for 4 h.	1.1±0.1	[21]
25	Flat Gold	Annealed.	1.1	[21]
26	Au-Ti-Glass	Annealed at150-200°C.	1.4±0.1	[21]
27	Au-MPS-Glass	Annealed at 150°C for 3 h.	1.3±0.1	[21]
28	Au(111)	Cleaned in “piranha” solution for few minutes, rinsed with ethanol and water and flame-annealed in an oxygen-gas flame.	1.2	[22]
29	Au(111)	Flame-annealed for approximately 2 min in a Bunsen burner.	1.2	[23]
30	Au(111)	Hydrogen flame annealed.	1.1	[24]
31	Au/mica	Hydrogen flame annealed.	1.0	[24]
	Average and RSD (n=21)		1.2±0.1	
		(III) UV/O_3 pretreatment		
32	Au	Treated in a UV/ozone reactor for 15 min.	1.7	[25]
33	Au	3 h annealing at 250°C in air, UV-ozone treated for 20 min.	1.2	[26]
34	Au	3 h annealing at 250°C in air, UV-ozone treated for 20 min.	1.2	[27]
35	Au	Placed in a UV-ozone cleaner for 20 min and immersion in neat ethanol for 30 min to reduce gold oxide.	1.4	[28]
36	Au	Treated in a UV/ozone reactor for 15 min.	1.7	[29]
37	Au	UV-ozone treatment for 5 min and immersion for 20 min in ethanol.	1.1	[30]
	Average and RSD (n=6)		1.4±0.3	
		(IV) Piranha reagents pretreatment		
38	Poly Au	Cleaned with piranha solution (1:3 H_2O_2 and concentrated H_2SO_4).	1.5	[31]
39	Poly Au	Al_2O_3(0.05 μm) mechanical polishing for 3-4 min, ultrasonicated (in deionised water) for 1-2 min, hot piranha solution (3 + 1 conc. H_2SO_4 and H_2O_2) for 15 min, ultrasonicated for 1 min, CV (0.1 M H_2SO_4, -0.2～1.5 V, v=0.1 V s^{-1}, 25 successive CV scans).	1.4	[32]
40	Poly Au	Al_2O_3(1.0, 0.3, 0.05 μm), dipped into piranha solution (conc. H_2SO_4:30% H_2O_2 = 3:1, v:v) for 2 min, sonicated in twice-distilled water for 15 min, CV (0.5 M H_2SO_4, -0.4～1.5 V, v=0.1 V s^{-1}).	1.5±0.2	[33]

Table S3. Summary of Au electrode roughness factor γ by different pretreatment from literature (continued)

No.	Type	Method	Roughness γ	Ref.
41	Au	Treated in piranha solution (1:4 30% H_2O_2 in concentrated H_2SO_4) for 1 min to oxidize any impurities, CV (10 mM KCl/0.1 M H_2SO_4, 1.5～0 V, 30 min).	1.1～1.3	[34]
42	Au foil	Treated with fresh piranha (7/3 v/v concentrated H_2SO_4/H_2O_2), polished successively with 5, 1, 0.3, and 0.05 μm Buehler alumina polish, ultrasonicated in water; retreated with piranha for amaximum of 10 min, ultrasonicated in water.	1.7	[35]
43	Au(111)	Kept in Piranha solution (1:3 v/v, 30% H_2O_2 and concentrated H_2SO_4) for 3 min and polished with 0.05 μm alumina slurry, rinsed with water and sonicated in water/chloroform/water each step 5 min, CV (0.1 M H_2SO_4, v=0.05 V/s, 40 min).	1.6±0.2	[36]
44	Bulk Gold	Polished using 1, 0.3, and 0.05 μm alumina/water slurry, ultrasonic cleaner and cleaned with "piranha" solution comprising 1:3 (v/v) 30% H_2O_2 and concentrated H_2SO_4 for 2 min, CV (0.5 M H_2SO_4, -0.5～1.5 V vs Ag/AgCl, v=0.1 V s^{-1}, 30 min).	1.5	[21]
45	Poly Au	Al_2O_3(1.0, 0.3, 0.05 μm), dipped into piranha solution (conc. H_2SO_4:30% H_2O_2 = 3:1, v:v) for 2 min, sonicated in twice-distilled water for 15 min, CV (0.5 M H_2SO_4, -0.4～1.5 V, v=0.1 V s^{-1}).	1.5±0.2	[37]
46	Poly Au	Al_2O_3(1.0, 0.3, 0.05 μm), dipped into piranha solution (conc. H_2SO_4:30% H_2O_2 = 3:1, v:v) for 2 min, sonicated in twice-distilled water for 15 min, CV (0.5 M H_2SO_4, -0.4～1.5 V, v=0.1 V s^{-1}).	1.3±0.2	[38]
47	Poly Au	(A_G=0.0314 cm^2), polished carefully with Al_2O_3(1.0, 0.3, 0.05 μm) and ultrasonic vibration in ethanol, etched for 2 min in a hot Piranha solution (1 : 3 (v/v) 30% H_2O_2 and concentrated H_2SO_4), CV (0.1 M H_2SO_4, v=0.05 V s^{-1}, -0.2～1.6 V).	1.3	[39]
	Average and RSD (n=10)		1.5±0.1	
		(V) Simple polishing pretreatment		
48	Au	After mechanically polished, CV (0.1 M PBS(pH 7.0), -0.1～1.2 V, v=0.05 V s^{-1}).	2.8±0.3	[40]
49	Poly Au	Polished sequentially in a slurry of Al_2O_3(1.0, 0.3, 0.05 μm), sonicated for 5 min and rinsed thoroughly with Milli-Q water. The electrodes were placed in hot (~60 ºC) concentrated H_2SO_4 for 5 min and in aqua regia for 30 s, followed by a further 30 s polishing in the 0.05 μm alumina slurry. The electrodes were sonicated again for 2 min, CV (0.5 M H_2SO_4, -0.2～1.6 V, v=0.5 V s^{-1}).	1.7	[41]
50	Poly Au	(A_G=0.25 cm^2, A_R=0.4～0.6 cm^2), polished with alumina powder (0.1 μm), sonicated for a few minuters.	1.6～2.4	[42]
51	Poly Au	(d=1.6 mm, A_G=2.01×10^{-2} cm^2), polished no. 2000 emery paper, then with aqueous slurries of successively finer alumina powder (down to 0.06 μm) and were sonicated for 10 min in Milli-Q water. CV (0.05 M H_2SO_4, -0.2～1.5 V， v=0.1 V s^{-1}).	3.1	[43]
52	Poly Au	Polished sequentially in a slurry of Al_2O_3(0.3, 0.05 μm), then sequentially sonicated for 5 min with twice-distilled water, chloroform and twice-distilled water. A_G=0.0314	1.8	[44]
53	Au	Polished Au.	1.4±0.1	[20]

Table S3. Summary of Au electrode roughness factor γ by different pretreatment from literature (continued)

No.	Type	Method	Roughness γ	Ref.
54	Au	Evaporated Au on mica.	1.7±0.1	[20]
55	Au	Sputtered Au on glasss.	2.0±0.1	[20]
56	Au	Sputtered Au on plastic.	2.0±0.1	[20]
57	Poly Au	(A_G=0.07 cm^2, d=3.04 cm), the electrode is polished with0.3 μm Al_2O_3, and then the electrode is ultrasonicated in absolute ethanol and in pure water for 10 min each. (CV (0.5 M H_2SO_4, v=0.1 V s^{-1}, 30 scans).	1.4	[45]
58	Au film	CV (0.1 M H_2SO_4 and 0.01 M KCl).	2.1	[24]
59	Poly Au	Etched for 10 min in dilute aqua regia ($HCl/HNO_3/H_2O$ = 3:1:6) and subsequently polished using Al_2O_3 (5, 1.0, 0.3, 0.05 μm), then sonicated, CV (0.1 M H_2SO_4 and 0.01 M KCl).	1.5	[24]
60	Au/mica	Mechanically polished.	1.6	[21]
	Average and RSD (n=13)		1.9±0.5	

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4. Summary of coverage Γ_m of long-chain alkyl thiol (≥24 h) from the literature reports

Table S4. Summary of coverage Γ_m of long-chain alkyl thiol (⩾24 h) from the literature reports

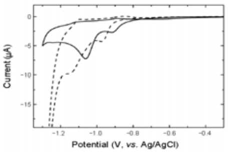
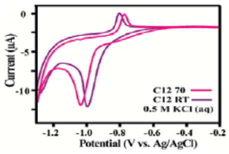
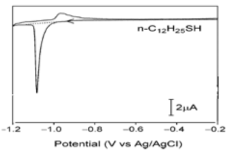
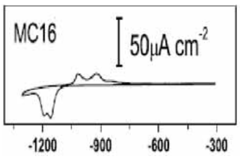
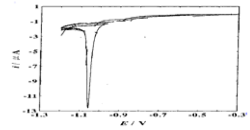
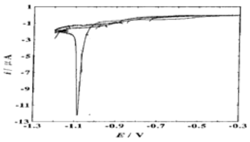
NO.	n	Pretreatment	Assembled conditions	Experimental conditions	Reductive desorption CV grams [(c)]	Γ_m / mol cm^{-2} [(c)]		
						Original value	Literature correction	Correction by us [(f,g)]
				(I) Aqua regia pretreatment				
1 [1]	16	Au-Ti-Si-glass, A=0.02 cm^2, polishing-aqua regia 60 s, CV(0.2 M $HClO_4$, 0-1.5 V).	**10 mM $C_{16}SH$ in 1-butanol 10 h.[(a)]	0.5 M KOH.	—	9.2×10^{-10}	8.4×10^{-10}[(b)]	—
					Average and RSD (n=1)		*8.4×10^{-10}*	
				(II) Reductive annealed pretreatment				
2 [2]	12	Au, γ, A_G and A_R unknown.	1 mM $C_{12}SH$ in EtOH 24 h.	0.1 M KOH, v=0.05 V s^{-1}, -0.3～-1.3 V.	 Cyclic voltammograms for the reductive desorption of dodecanethiols (solid line).	1.1×10^{-9}	8.0×10^{-10}[(d)]	—
3 [3]	12	Au(111), A_R=0.5 cm^2, hydrogen-flame annealed.	70℃ or room temperature(RT), 1 mM $C_{12}SH$ in EtOH 24 h.	0.5 M KCl, v=0.02 V s^{-1}, -0.2～-1.3 V.		6.6×10^{-10} (70℃) 7.6×10^{-10} (RT)	6.6×10^{-10} (70℃) 7.6×10^{-10} (RT)	6.6×10^{-10} (70℃) 7.6×10^{-10} (RT)
4 [4]	12	Au(111), d=2.2 mm, A_G=0.152 cm^2, γ=1.05-1.15, annealed at 580□ for 6 h.	0.1 mM $C_{12}SH$ in CH_2Cl_2 24 h.	0.5 M KOH, v=0.02 V s^{-1}, -0.2～-1.2 V.		1.0×10^{-9}	7.3×10^{-10}[(d)]	8.8×10^{-10}
5 [5]	12	Poly Au, annealed at 300□ for 3 h.	2-4 mM $C_{12}SH$ in EtOH 24 h.	0.1 M KOH (pH 13); 0.0539 M KOH (pH 12.7); v=0.1 V s^{-1}.	—	8.1×10^{-10} (pH 13) 7.8×10^{-10} (pH 12.7)	8.1×10^{-10} (pH 13) 7.8×10^{-10} (pH 12.7)	8.1×10^{-10} (pH 13) 7.8×10^{-10} (pH 12.7)
6 [6]	16	Au/mica, γ=1.07, A_G, A_R unknown, Annealed.	1 mM $C_{12}SH$ in EtOH 24 h.	0.5M KOH, v= 0.02 V s^{-1}, -0.3～-1.3 V.		1.1×10^{-9}	7.3×10^{-10}[(e)]	7.0×10^{-10}
7 [7]	12 14	Au/mica, γ=1.05, annealed at 550□ for 8 h, CV(0.01 M $HClO_4$).	1 mM $C_{12}SH$/ $C_{14}SH$ in EtOH 24 h.	0.5 M KOH, v=0.02 V s^{-1}, -1.2～-0.2 V.	 	1.1±1.6×10^{-9}	7.0×10^{-10}[(e)]	8.3×10^{-10} 8.9×10^{-10}

Table S4. Summary of coverage Γ_m of long-chain alkyl thiol (⩾24 h) from the literature reports (continued)

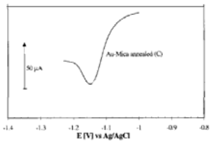
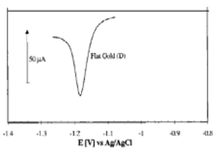
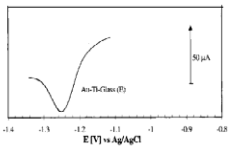
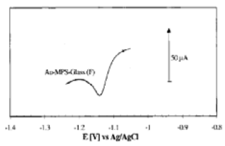
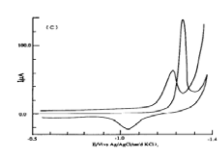
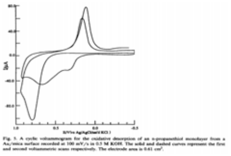
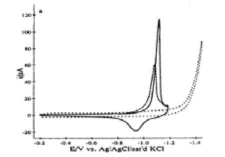
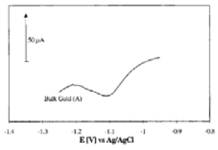
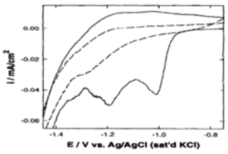
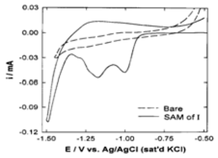
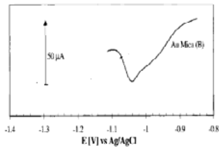
NO.	n	Pretreatment	Assembled conditions	Experimental conditions	Reductive desorption CV grams [(c)]	Γ_m / mol cm^{-2} [(c)]		
						Original value	Literature correction	Correction by us [(f,g)]
8 [8]	16	Au-mica, γ=1.11±0.05, annealed at 300℃ for 4 h.	10 mM $C_{16}SH$ in EtOH 24 h.	0.5 M KOH, v= 0.1 V s^{-1}.		8.2×10^{-10}	7.4×10$^{-10(b)}$	—
9 [8]	16	Flat Gold, γ=1.05±0.04.	10 mM $C_{16}SH$ in EtOH 24 h.	0.5 M KOH, v= 0.1 V s^{-1}.		8.1×10^{-10}	7.7×10$^{-10\ (b)}$	—
10 [8]	16	Au-Ti-Glass, γ=1.37±0.06, annealed at 150-200℃.	10 mM $C_{16}SH$ in EtOH 24 h.	0.5 M KOH, v= 0.1 V s^{-1}.		7.9×10^{-10}	5.8×10$^{-10\ (b)}$	—
11 [8]	16	Au-MPS-Glass, γ=1.26±0.05, annealed at 200～250℃ for 2～4 h.	10 mM $C_{16}SH$ in EtOH 24 h.	0.5 M KOH, v= 5 mV s^{-1}.		7.5×10^{-10}	6.0×10$^{-10\ (b)}$	—
12 [9]	10 12 16 18	Au/mica, A=0.67 cm^2, γ=1.2, annealed at 300℃ for 3 h.	1 mM C_nSH(n= 10, 12, 16, 18) in EtOH 24 h.	0.5 M KOH， v=0.1 V s^{-1}, -0.55～-1.35 V.	 n-octadecanethiol monolayers from Au/mica surfaces. the solid and dashed curves represent the first and second voltammetric	9.3×10^{-10}	7.6×10$^{-10\ (b)}$	8.0×10^{-10}
13 [9]	10 12 16 18	Au/mica, A=0.61 cm^2, γ=1.2.	1 mM C_nSH(n= 10, 12, 16, 18) in EtOH 24 h.	Oxidative desorption 0.5 M KOH， v=0.1 V s^{-1}， -0.5～0.9 V.		9.7×10^{-10}	8.1×10$^{-10\ (b)}$	—
14 [10]	12	Au(111), γ=1.1±0.1, annealed at 300℃ for 3 h.	0.5-1 Mm $C_{12}SH$ in EtOH 24 h.	0.5 M KOH， v=0.1 V s^{-1}, -0.2～-1.2 V.	 The solid and dashed lines are the first and second voltammetric scans; the dotted line in part a is for uncoated gold.	8.7±0.5×10^{-10}	7.9×10$^{-10\ (b)}$	7.5×10^{-10}
					Average and RSD (n=15)		*7.3±0.7×10^{-10}*	

Table S4. Summary of coverage Γ_m of long-chain alkyl thiol (⩾24 h) from the literature reports (continued)

NO.	n	Pretreatment	Assembled conditions	Experimental conditions	Reductive desorption CV grams [c]	Γ_m /mol cm^{-2} [c] Original value	Literature correction	Correction by us [f,g]
					(III) UV/O$_3$ pretreatment			
15 [11]	18	Au-Ti-Si, A_G=6.25×10^{-6} cm^2, cleaned with oxygen plasma.	100 µM $C_{18}SH$ in EtOH 24 h.	infrared spectra	—	5.3×10^{-10}	5.3×10^{-10}	5.3×10^{-10}
					Average and RSD (n=1)		*5.3×10^{-10}*	
					(IV) Piranha reagents pretreatment			
16 [8]	16	Bulk Gold, γ=1.54±0.01, polishing-"piranha" reagents, CV(0.5 M H_2SO_4, -0.5～1.5 V, v=0.1 V s^{-1}).	10 mM $C_{16}SH$ in EtOH 24 h.	0.5 M KOH, v= 0.1 V s^{-1},		7.3×10^{-10}	4.7×10^{-10} [b]	—
17 [12]	12	Au-Cr-glass, A=1.4 cm^2, Piranha reagents.	1 mM $C_{12}SH$ in EtOH 24-36 h.	0.5 M KOH/ethanol, v=0.1 V s^{-1}.		7.8±0.1×10^{-10}	5.2×10^{-10} [b]	5.9×10^{-10}
18 [12]	12	Au-MPS-glass, A=1.4 cm^2, Piranha reagents.	1 mM $C_{12}SH$ in EtOH 24-36 h.	0.5 M KOH/ethanol, v=0.1 V s^{-1}.	—	7.1±0.2×10^{-10}	4.7×10^{-10} [b]	—
19 [12]	12	Au foil, A=1.44 cm^2, Piranha reagents.	1 mM $C_{12}SH$ in EtOH 24-36 h.	0.5 M KOH/ethanol, v=0.1 V s^{-1}.	—	7.4±0.5×10^{-10}	4.9×10^{-10} [b]	—
20 [13]	12	Au-Cr-glass, γ, A_G and A_R unknown.	1 mM $C_{12}SH$ in EtOH 24 h.	0.5 M KOH/ethanol, v=0.5 V s^{-1}.		8.1±2.9×10^{-10}	5.4×10^{-10} [b]	—
					Average and RSD (n=5)		*5.0±0.3×10^{-10}*	
					(V) Simple polishing pretreatment			
21 [8]	16	Au-Mica, γ=1.62±0.02.	10 mM $C_{16}SH$ in EtOH 24 h.	0.5 M KOH, v= 0.1 V s^{-1},		7.4×10^{-10}	4.6×10^{-10} [b]	—
					Average and RSD (n=1)		*4.6×10^{-10}*	

(a) “**” showed 10 h modification time. No other report about coverage of C_nSH-SAMs-Au($n \geq 12$) on this pretreamnet.

(b) Right column for γ correction showed calculation values according literature.

(c) Right column for “—” showed no report for this content.

(d) Right column for 30% correction was based on the total contribution from surface roughness and double-layer capacitance was assumed to be constant at ca. 30% of the total reductive charge.((1) Y. Chu, B. Seo and J. Kim, Electrochemical properties of alkanethiol monolayers adsorbed on nanoporous Au surfaces. *Bull. Kor. Chem. Soc.,* 2010, 31, 3407-3410. (2) D. Qu, B. C. Kim, C. W. J. Lee and K. Uosaki, 1,n-Alkanedithiol (n = 2, 4, 6, 8, 10) self-assembled monolayers on Au(111): electrochemical and theoretical approach. *Bull. Korean Chem. Soc.,* 2009, 30, 2549-2553. (3) D. Qu and M. Morin, An EQCM study of the oxidative deposition of alkylthiolates on gold. *J. Electroanal. Chem.,* 2001, 517, 45-53. (4) T. Sumi, H. Wano and K. Uosaki, Electrochemical oxidative adsorption and reductive desorption of a self-assembled monolayer of decanethiol on the Au(111) surface in KOH+ethanol solution. *J. Electroanal. Chem.,* 2003, 550-551, 321-325.)

(e) Right column for the reductive desorption charge Q values under the peak area were not all derived from the Faraday charge, which contains contribution of non-Faraday charge (mainly double-layer capacitance), then reductive desorption $\triangle Q$ of different C_nSH can be handled as a constant. ((5) D. F. Yang, C. P. Wilde and M. Morin, Electrochemical desorption and adsorption of nonyl mercaptan at gold single crystal electrode surfaces. *Langmuir,* 1996, 12, 6570-6577. (6) D. F. Yang, C. P. Wilde and M. Morin, Studies of the electrochemical removal and efficient re-formation of a monolayer of hexadecanethiol self-assembled at an Au(111) single crystal in Aqueous Solutions. *Langmuir,* 1997, 13, 243-249. (7) T. Sumi and K. Uosaki, Electrochemical oxidative formation and reductive desorption of a self-assembled monolayer of decanethiol on a Au(111) surface in KOH ethanol solution. *J. Phys. Chem. B,* 2004, 108, 6422-6428. (8) F. Loglio, M. Schweizer and D. M. Kolb, In situ characterization of self-assembled butanethiol monolayers on Au(100) electrodes. *Langmuir,* 2003, 19, 830-834.)

(f) Our correction: selected manual-lineation the first lap of reductive desorption directly as the determination results.

(g) Other notes: Unless otherwise specified, all above were reported for carring out at room temperature, and the determination was reductive desorption CV gram; Average and RSD are obtained from the column of the literature correction.

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5. Effects of different measurement methods on the accuracy of the reductive desorption charge Q_m determination

5.1. Effects of different measurement methods on the determination of the reductive desorption charge Q_m

In general, the reductive desorption charge Q values under the peak area were not all derived from the Faraday charge, which contains contribution of non-Faraday charge (mainly double-layer capacitance). Previous studies have pointed out this background correction. Different pretreatment methods caused the difference of Au surface roughness factors, thus leading to the difference of density of SAMs, ultimately coverage Γ_m could be different. There were four measurement methods for the charge Q_m corresponding to reductive desorption peak area：(A) computer reading of manual-lineation the first lap of reductive desorption; (B) computer reading of manual-lineation of reductive desorption by subtracting the bare gold background; (C) computer reading of manual-lineation of reductive desorption by subtracting the 40th scan of reductive desorption background; (D) computer reading of the first lap of reductive desorption directly (Fig. S2-7).

The experimential results in Fig. 4 showed that: method A and method B achieved the best Γ_m values under aqua regia and reductive annealed pretreatments, which were closest to the theoretical value Q^0_m. The value was larger when put the 40th CV lap as the background (method C). In contrast, computer reading value of the first lap of reductive desorption directly was too large (method D), which was not suitable for selection for the determination of the coverage. Thus, we selected the method A for more convenience than method B as for the determination of Γ_m.

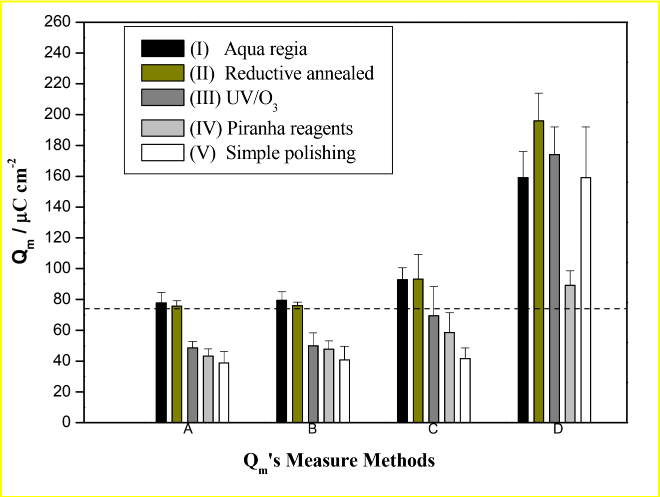

Fig. S1. Reductive desorption charge Q_m of C_{12}SH-SAMs-Au electrode treated by five pretreatments. Four kinds of measurement methods are following: (A) computer reading of manual-lineation the first lap of reductive desorption; (B) computer reading of manual-lineation of reductive desorption by subtracting the bare gold background; (C) computer reading of manual-lineation of reductive desorption by subtracting the 40th scan of reductive desorption background; (D) computer reading of the first lap of reductive desorption directly. (Table S5, ESI†) Dotted line showed Q^0_m=73.3 μC cm^{-2}(obtained from Γ_m~8.0×10^{-10} mol cm^{-2}).

5.2 Summary of the experimental data for Q_m determination results by four measurement methods corresponding to different pretreatments

There were four measurement methods for the charge Q_m corresponding to reductive desorption peak area：

(A) computer reading of manual-lineation the first lap of reductive desorption;

(B) computer reading of manual-lineation of reductive desorption by subtracting the bare gold background;

(C) computer reading of manual-lineation of reductive desorption by subtracting the 40th scan of reductive desorption background;

(D) computer reading of the first lap of reductive desorption directly.

The experimental results of four measurement methods of the reductive desorption charge Q_m under different pretreatment (Fig. S2-7 and Table S5) showed that: method A and method B achieved the best Γ_m values under aqua regia pretreatments and reductive annealed pretreatments, which were closest to the theoretical value Q_m^0 (73.3 μC cm^{-2}).[1] The value was larger when put the 40th CV lap as the background (method C). In contrast, computer reading value of the first lap of reductive desorption directly was too larger (method D), which was not suitable for selection for the determination of the coverage. Therefore, we selected the method A for more convenience than method B as for the determination of Γ_m.

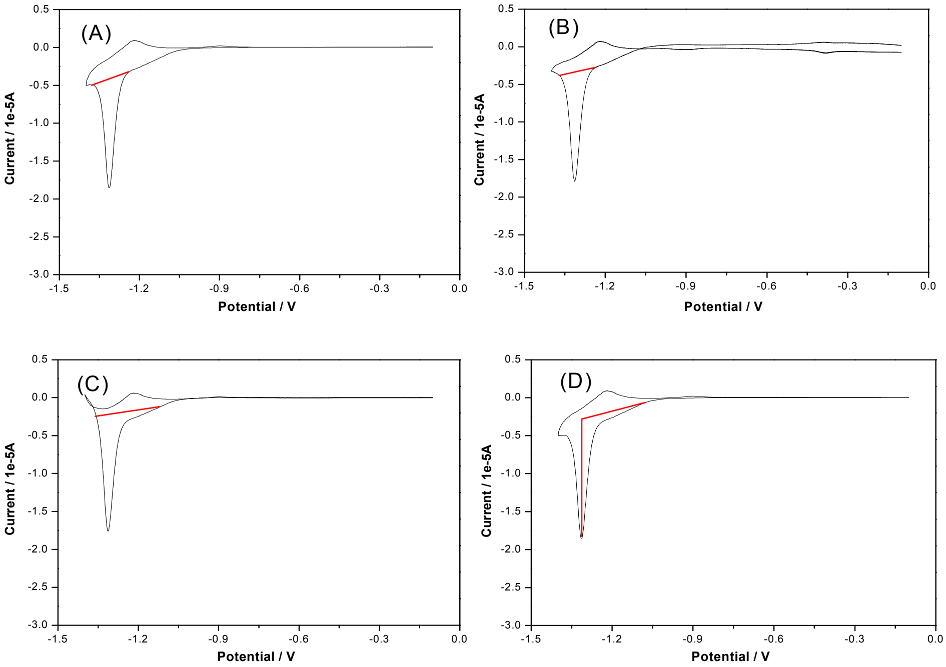

Fig. S2. Comparison of coverage of $C_{12}SH$-SAMs-Au electrode treated by aqua regia. Four kinds of measurement methods are following: (A) computer reading of manual-lineation the first lap of reductive desorption; (B) computer reading of manual-lineation of reductive desorption by subtracting the bare gold background; (C) computer reading of manual-lineation of reductive desorption by subtracting the 40th scan of reductive desorption background; (D) computer reading of the first lap of reductive desorption directly.

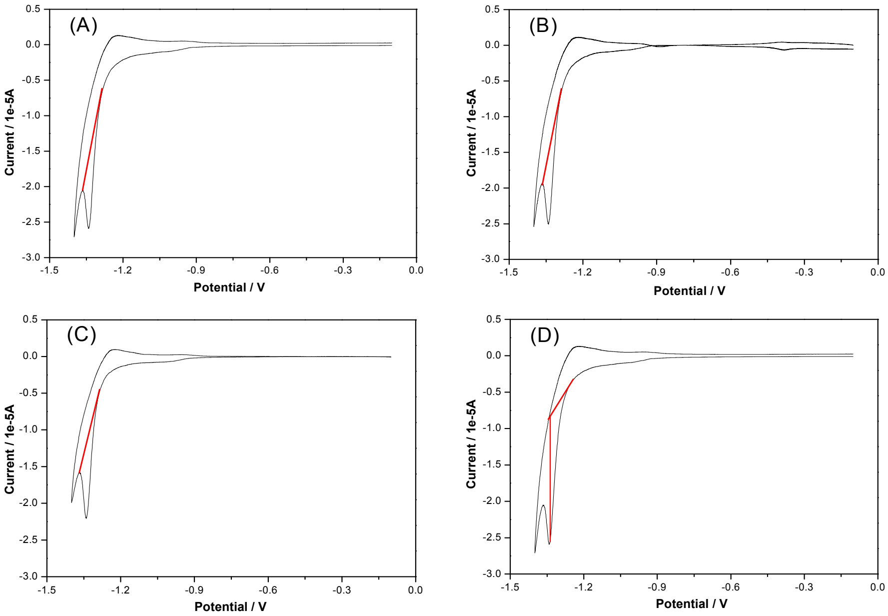

Fig. S3. Comparison of coverage of C_{12}SH-SAMs-Au electrode treated by reductive annealed. (A～B are the same as showed in Fig. S2.).

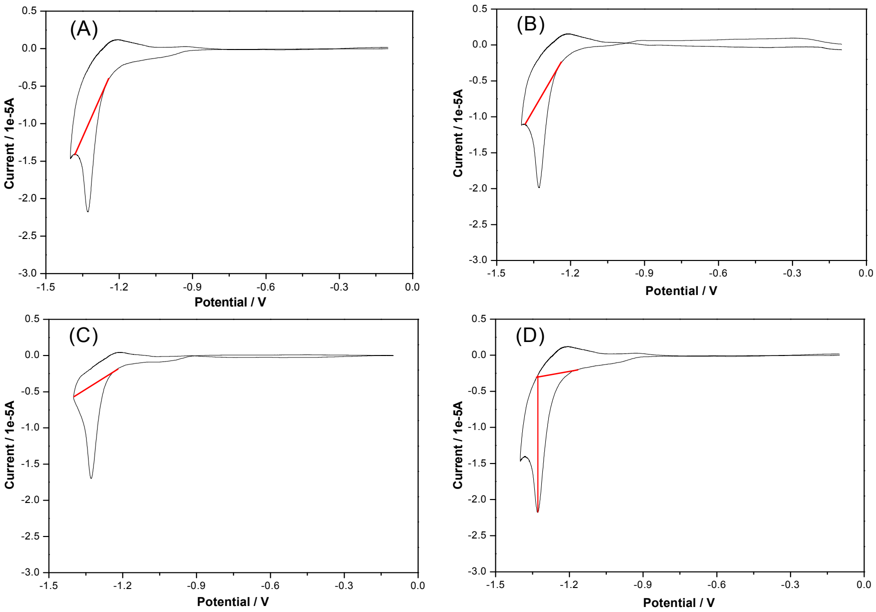

Fig. S4. Comparison of coverage of C_{12}SH-SAMs-Au electrode treated by UV/O_3. (A～B are the same as showed in Fig. S2.).

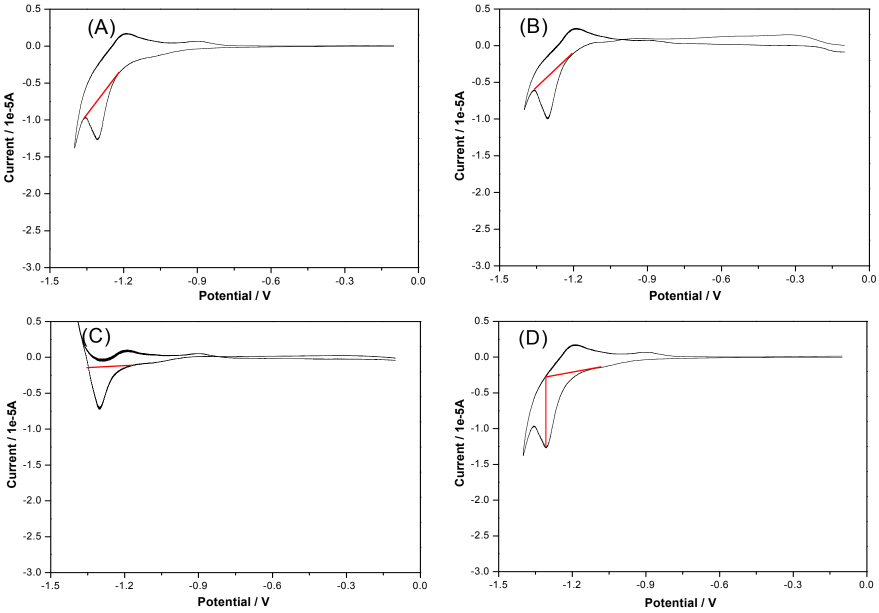

Fig. S5. Comparison of coverage of C_{12}SH-SAMs-Au electrode treated by Piranha reagents. (A～B are the same as showed in Fig. S2.).

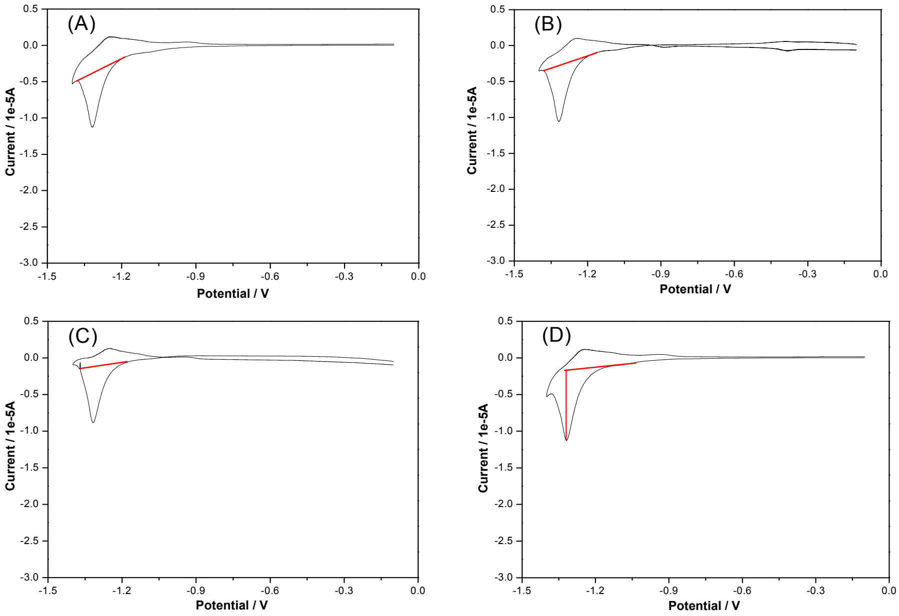

Fig. S6. Comparison of coverage of C_{12}SH-SAMs-Au electrode treated by Simple polishing. (A～B are the same as showed in Fig. S2.).

Table S5. Q_m (μC cm^{-2}) obtained from four different measurement methods under five different pretreatment

Mothods	A	B	C	D
(I) Aqua regia pretreatment	77.8±6.8	79.5±5.6	92.7±7.9	159±17
(II) Reductive annealed pretreatment	75.7±3.5	75.9±2.3	116±36	312±54
(III) UV/O_3 pretreatment	48.2±3.4	50.0±8.3	69.4±19.5	173±18
(IV) Piranha reagents pretreatment	43.3±4.6	47.6±5.5	58.5±13	89.2±9.5
(V) Simple polishing pretreatment	38.7±7.6	40.7±8.9	41.6±7.0	159±33

* Four kinds of measurement methods A～B are the same as showed in Fig. S1.

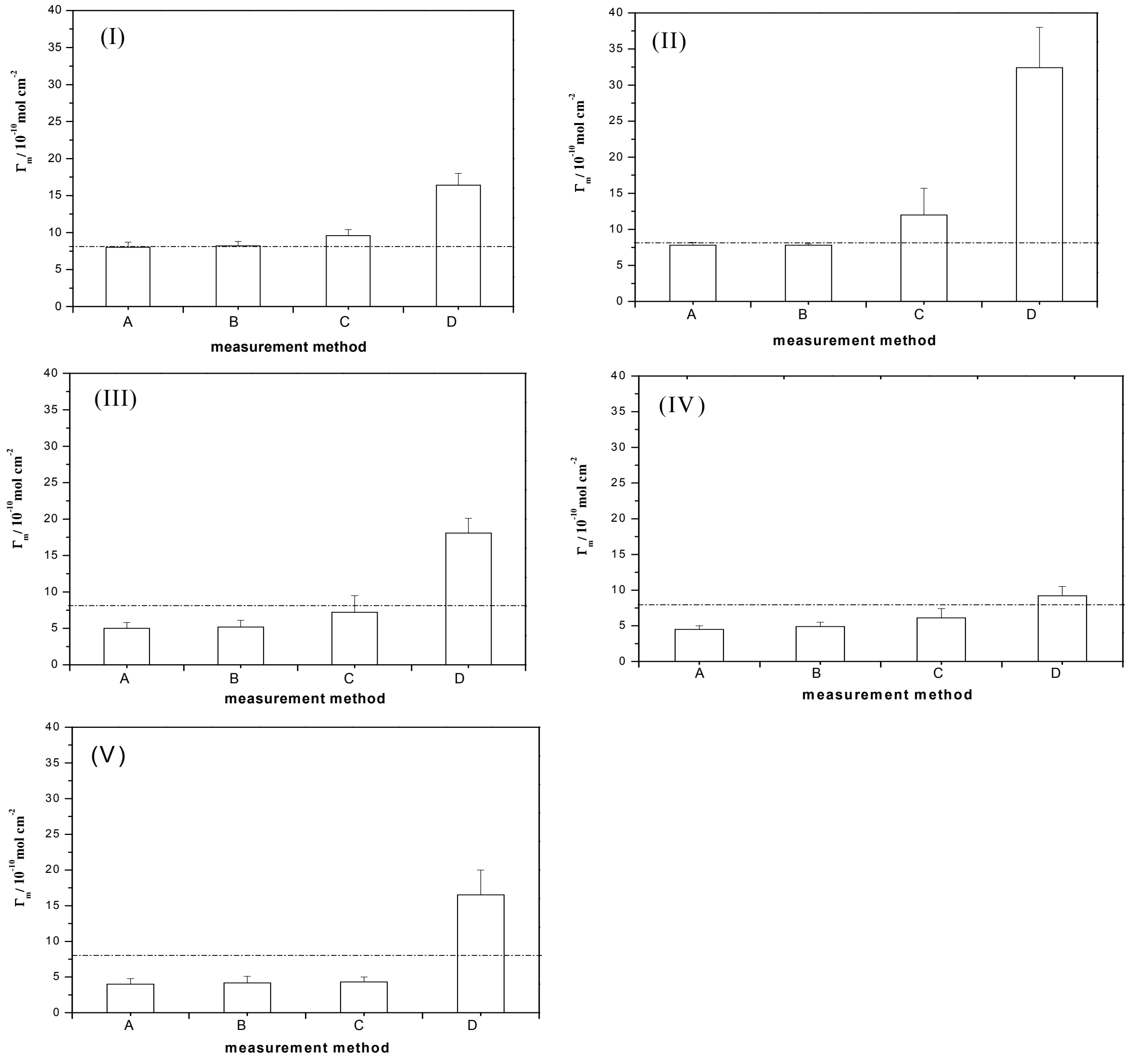

Fig. S7. Histogram of coverage Γ_m obtained by four kinds of ways about $C_{12}SH$-SAMs-Au treated by five different pretreatment. Ordinate values shown here were coverage Γ_m of $C_{12}SH$, Abscissa represented different measurement methods. Dotted line showed: 8.0×10^{-10} mol cm^{-2} (average of Au(111) 7.6×10^{-10} mol cm^{-2}, Au(110) 7.0×10^{-10} mol cm^{-2} and Au(100) 9.3×10^{-10} mol cm^{-2})[1]. Five different pretreatment methods: (I) Aqua regia; (II) Reductive annealed; (III) UV/O_3; (IV) Piranha reagents; (V) Simple polishing. Four kinds of measurement methods A～B are the same as showed in Fig. S2.

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6. Discussion about double-peak

(1) The case of double-peak in our reductive desorption experiments.

Fig. S8 showed the cases of double-peak in our reductive desorption experiments. There were double-peaks appeared in Aqua regia pretreatment, Reductive annealed pretreatment, Piranha reagents pretreatment and Simple polishing pretreatment. In contrast, there was no double-peak phenomenon pretreated by UV/O$_3$. In general, the appearance probabilities of double-peak were less and the coverage Γ_m was generally based on the summation of the charge of double-peak ($Q_m = Q_1 + Q_2$), which was consistent with the value of the single peak.

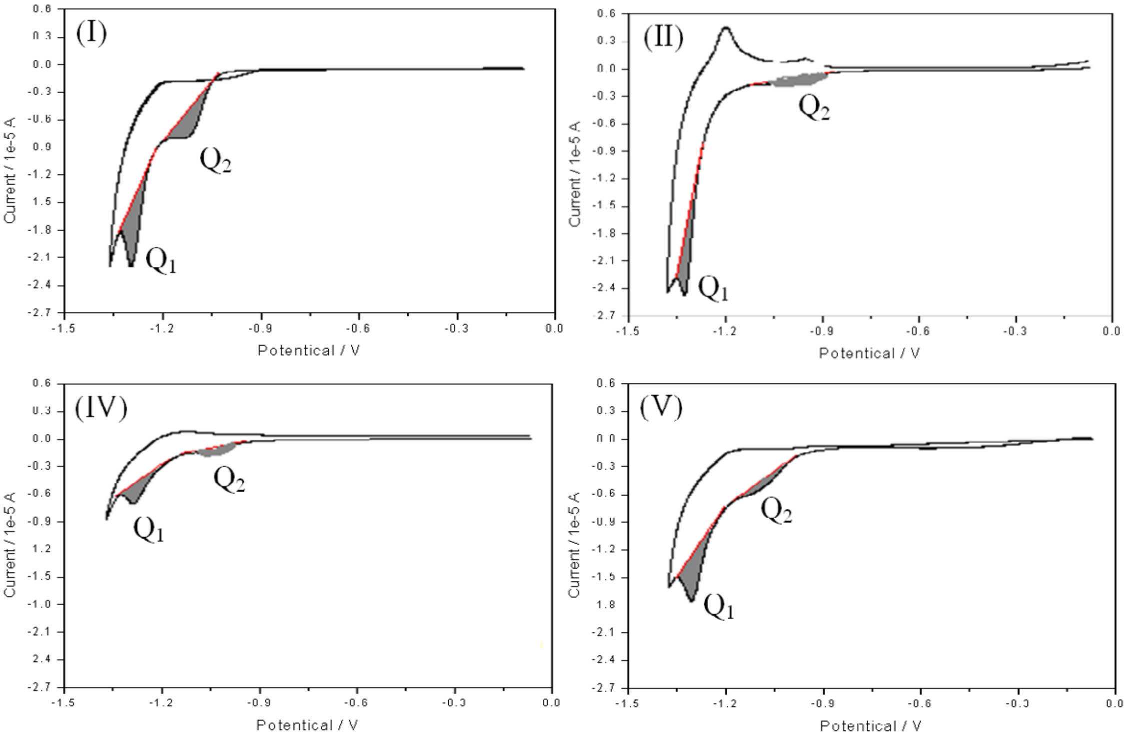


Fig. S8. Cyclic voltammetry image of reductive desorption under different pretreatment for C$_{12}$SH-SAMs-Au. The potential window was from -0.1 to -1.4 V at 0.1 V s^{-1} in 0.5 M NaOH solution; Pretreatment methods were as following: (I) Aqua regia pretreatment; (II) Reductive annealed pretreatment; (IV) Piranha reagents pretreatment; (V) Simple polishing pretreatment.

(2) The case of double-peak in the literature.

The mechanism of double-peak was unclear and need further study. From the summary of the literature, there were three main reasons (literature spectrum showed in Table S6).

(a) Porter et al. proposed that the short chain systems exhibited a single voltammetric wave for the resorption and re-deposition processes. In contrast, multiple voltammetric waves were found for both the desorption and the re-deposition of the long chain systems. The key difference between the short chain and long chain monolayers was the difference in cohesive interactions between alkyl chains because of differences in the adlayer domain structures and binding modes between sulfur and gold.[1]

(b) Morin et al. suggested that the presence of two reductive current peaks was due to thiol domains having different ionic permeabilities. Mainly for long-chain alkyl thiols, which were relatively compact and orderly assemblied on the gold electrode surface. While reductive desorption was performed in the higher pH (eg 0.5 M KOH) alkaline solution, pH> pK$_a$ (RSH~10). The different of ions penetration between orderly arrangement sites and defective arrangement sites caused the significantly different of desorption peak.[2]

(c) Different gold electrode substrate morphology caused different RS- adsorbed sites on gold surface and adsorption energy between the thiols chain were also different. All of these made adsorption morphology (physical adsorption or chemical adsorption) different, and in reductive desorption double-peak may occur.$^{3-6}$

Table S6. Double-peaks of reductive desorption from literature

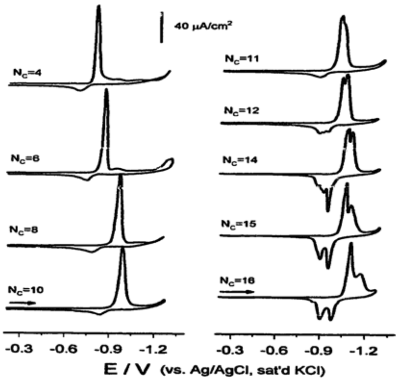
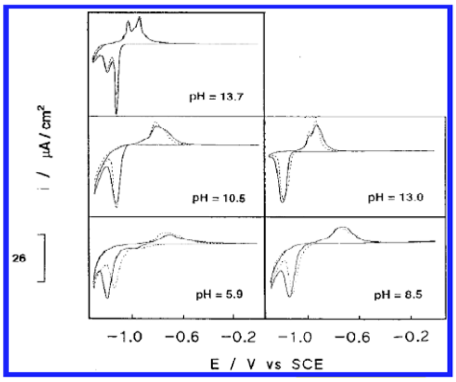
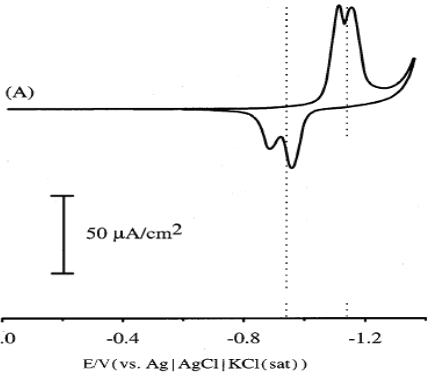
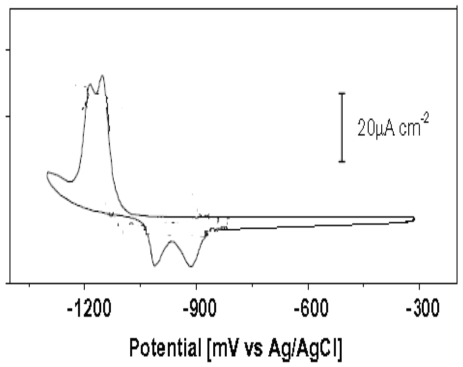
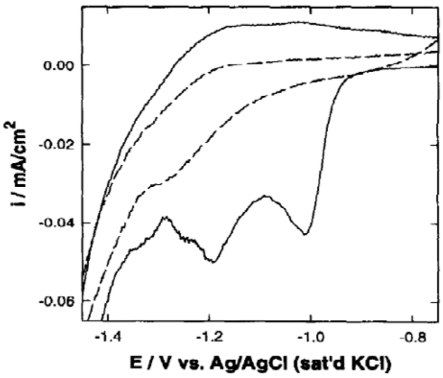
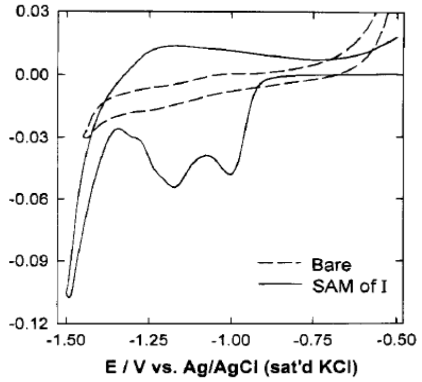
No.	Experimental conditions	Typical CV diagrams
1 [1]	annealed at 300°C, γ=1.1±0.1; 1～5 mM C_nSH(n=4～16) in EtOH for 12 h; 0.5 M KOH, v=0.05 V s^{-1}, -1.3～-0.2 V.	 Figure (a) Cyclic voltammograms of alkanethiolate monolayers of various chain lengths (N_c=number of carbons in the alkyl chain) at annealed Au(111) films in 0.5 M KOH. Scan rate 50 mV s^{-1}.
2 [2]	Au(111), CV (0.1 M $HClO_4$), annealed in a natural gas/air flame and quenched with Milli-Q water; 1 mM $C_{16}SH$ in EtOH for 30 min; KOH(different pH), v=0.1 V s^{-1}, -1.4～-0.1 V.	 Figure (b) Cyclic voltammograms of a hexadecanethiol layer deposited on a Au(111) single crystal electrode at different pH values of an aqueous electrolyte solution (see Experimental Section for the composition of the solution): solid line, first cycle; dashed line, third cycle.
3 [3]	Au/mica, annealed at 300°C for 5 h (γ=1.01～1.1); 1 mM $C_{16}SH$ in EtOH for 2 h; 0.5 M KOH, v=0.05 V s^{-1}, -1.35～0.0 V.	 Figure (c) Current–potential curves for the reductive desorption and oxidative redeposition of monolayers formed from HDT on annealed Au:mica Electrolyte: 0.5 M KOH, Scan rate: 50 mV s^{-1}.

Table S6. Double-peaks of reductive desorption from literature (continued)

No.	Experimental conditions	Typical CV diagrams
4 [4]	Substrates of mica with an epitaxial (111) gold layer 300 nm thick (Au/mica) (γ=1.07); 1 mM $C_{16}SH$ in EtOH for 24 h; 0.5 M KOH, v= 0.02 V s^{-1}, -0.3～-1.3 V.	 Figure (d) Cyclic voltammograms for a SAM of MC16 adsorbed on Au/mica. Samples were prepared at 295 K. Scan rate was 20 mV/s. Electrolyte was deaerated 0.5 M KOH(aq).
5 [5]	Au foil electrodes (A=1.44 cm^2), sanded with vely fine silicon carbide (3M), cleaned in a solution of 5 mL 30% H_2O_2, 1 mL concentrated NH_4OH, and deionized H,O for 15 min at 80 □. 1 mM $C_{12}SH$ in EtOH for 24-36 h; 0.5 M KOH-EtOH, v=0.1 V s^{-1}.	 Figure (e) Reductive desorption at 100 mV s^{-1} in 0.5 M KOH -ethanol of a non-conditioned electrode with SAM of $C_{12}SH$ (solid line) and same electrode after complete desorption of SAM, i.e. bare (dashed line).
6 [6]	Gold evaporation and deposition on the mica: Au/mica; 1 mM $C_{12}SH$ in EtOH for 24 h; 0.5 M KOH-EtOH, v=0.5 V s^{-1}.	 Figure (f) Reductive desorption at 500 mV/s in 0.5 M KOH /ethanol vs Ag/AgCl (saturated KCl) of a bare gold electrode and gold electrode coated with a SAM of $C_{12}SH$.

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