Problems in Evaluation of Surface Coverage of Self-assembled Monolayers on Gold Crystal Electrode by Electrochemical Reductive Desorption.

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Surface coverages evaluated by electrochemical reductive desorption are always bigger than those calculated from STM images, because of the charge for double layer capacitance. In this study, we will describe the precise evaluation of surface coverage of the modified molecules on gold single crystal electrodes.

Au single crystal electrodes were prepared by the flame-annealing method. Au(111) or Au(100) electrode was immersed into thiol solution of interest, to obtain modified electrodes. Cyclic voltammogram (CV) was used for evaluation of surface excess, and A.C impedance technique was used for determining the double layer capacitance (C_{dl}).

Fig. 1 shows CVs of reductive desorption of a) 4-pyridinethiol (4-PySH) and b) 1-dodecanthiol, respectively, in a 0.01 M KOH solution. The total charge (Q_{total}), shown as the hatched portion, contains background faradaic charge, desorption of thiolate (Q_{des}), and double-layer charge (Q_{dl}). In order to evaluate Q_{des} precisely, The Q_{dl} and point of zero charge (pzc) should be determined. In Table 1, pzc evaluated by impedance measurements, C_{dl} calculated by eq.(2), and Q_{total} obtained are summarized, and calculated values of Q_{dl}, Q_{des}, Q_{des}/Q_{total}, and Γ_{des} were shown in Table 2. C_{dl} and pzc was obtained by the impedance method, and surface excess (Γ_{des}) of the SAM on the gold single crystal electrode was calculated to be 5.13 x 10^{-10} mol cm^{-2} for 1-dodecanthiol and 6.84 x 10^{-10} mol cm^{-2} for 4-PySH (Table 2).

On the other hand, the Γ_{STM} calculated based on the structure obtained from STM images were 7.6 x 10^{-10} mol cm^{-2} for 1-dodecanthiol and 4.6 x 10^{-10} mol cm^{-2} for 4-PySH. The reason for this difference between Γ_{des} and Γ_{STM} is now under investigation.

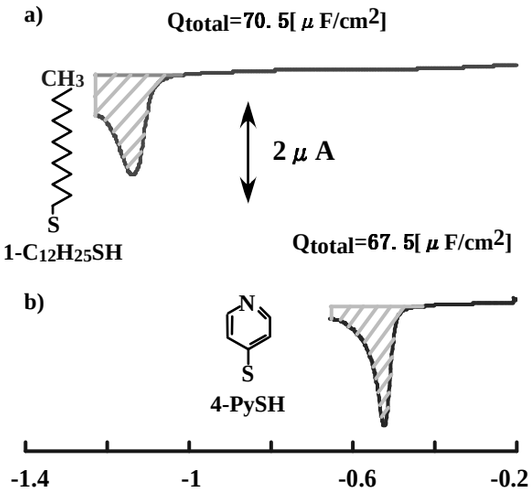

Fig. 1 Cyclic voltammograms for the reductive desorption of a) 1-dodecanthiol and b) 4-PySH SAM on Au(111) in 0.01 M KOH solution. Scan rate : 50 mV/s

$$Q_{total} \fallingdotseq Q_{des}+Q_{dl} \quad (1)$$

$$Q_{dl}=[(E2-pzc_{Au})C_{Au}]-[(E1-pzc_{SAM})C_{SAM}] \quad (2)$$

$$\Gamma=Q_{des}/F \quad [mol/cm^2] \quad (3)$$

Table 1. Measurement result of pzc, C_{dl} and Q_{total}

SAM	pzc[V]	C_{dl} [μ F/cm^2]	Q_{total} [μ c/cm^2]
1-$C_{12}H_{25}$SH	-0.5	2.4	70.0
4-PySH	0.03	14.1	67.5
Bare	-0.49	31.0	

Table 2. Calculated values of Q_{dl}, Q_{des}, Q_{des}/Q_{total} and Γ_{des}

SAM	Q_{dl} [μc/cm^2]	Q_{des} [μc/cm^2]	$\frac{Q_{des}}{Q_{total}}$	Γ_{des} [mol/cm^2]
1-$C_{12}H_{25}$SH	20.54	49.50	0.707	5.13×10^{-10}
4-PySH	1.34	66.07	0.979	6.84×10^{-10}