Effect of Surface Morphology of a Gold Substrate on Photocurrent Efficiency at a Gold Electrode Modified with a Self-Assembled Monolayer of a Porphyrin–Ferrocene–Thiol Linked Molecule

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The effect of the surface roughness on the characteristics of self-assembled monolayers (SAMs) was quantitatively examined by measuring the photocurrent efficiency at a gold electrode modified with a SAM of a porphyrin–ferrocene–thiol linked molecule as a function of the surface roughness. The photocurrent efficiency was higher for the flatter substrate. This result confirms the importance of the substrate's surface roughness to achieve the ordered arrangement of the functional moieties of the SAM, i.e., effective control of the electron/energy transfer.

Ordered molecular layers on solid surfaces have been the subject of intensive studies due to its fundamental importance in interfacial science and possible applications for the construction of functional materials.[1,2] Although it is obvious that the structure and characteristics of the molecular layers should be critically affected by the surface flatness in atomic/molecular dimensions, the quantitative investigations concerning the effects of surface roughness on the properties of molecular layers have been limited.[3]

Recently, we achieved a very efficient visible light induced electron transfer at a gold electrode modified with a self-assembled monolayer (SAM) of a molecule, which has porphyrin, ferrocene, and thiol as the photo-sensitizer, electron relay, and surface binding groups, respectively, separated from each other by alkylchains, (5-(4-(8-(10-mercaptoundecanoyl)-ferrocenyloctane)oxy-phenyl)-10,15,20-triphenylporphyrin, $PC_8FcC_{11}SH$).[4,5] We have proposed that one of the most important reasons for the very high efficiency of this system is the effective inhibiting of the backward electron and energy transfer from the excited porphyrin to a gold electrode because of the relatively longer distance between the porphyrin and gold with a highly ordered SAM structure. Actually, we found that the SAM was very highly oriented in order and the distance between the center of the porphyrin ring and gold surface was ca. 35 Å based on angle-resolved X-ray photoelectron spectroscopy (ARXPS) combined with electrochemical measurements.[6] Furthermore, it was found that the longer the alkyl chain separating the ferrocene and porphyrin, the higher the efficiency.[5] These results show that the order of the molecular layer and the distance between the porphyrin ring and gold surface have critical effects on the efficiency. Thus, this should be the ideal system to clarify the effect of the surface roughness on the characteristics of the molecular layers.

In this letter, we report the effect of the gold substrate surface roughness on the photocurrent efficiency for a gold electrode modified with the SAM of $PC_8FcC_{11}SH$ measured in an electrolyte solution containing methylviologen (MV^{2+}) as an electron acceptor.

$PC_8FcC_{11}SH$ was synthesized by a previously reported procedure.[4] Gold was vacuum deposited (1500 Å) onto a mechanically polished gold disk[7] at 300 °C in a vacuum evaporation apparatus (Ulvac, EBH-6) under 2×10^{-6} Torr at a deposition rate of 0.1–1.0 Å s^{-1}. The gold substrate was then annealed at 850 °C for 1–10 h under an N_2 atmosphere and stored in conc. H_2SO_4. The surface roughness of the gold substrate was controlled by the deposition rate and the annealing period. The slower the deposition rate and the longer the annealing time, the lower the roughness factor of the gold surface. The roughness factor was determined by dividing the real area, which was obtained from the charge needed for the reduction of the gold oxide, by the apparent area (0.785 cm^{-2}).[8] The gold substrates with surface roughness factors between 1.1 and 2.5 were obtained. Before the surface modification, these gold substrates were washed with pure water, annealed by a hydrogen flame for several seconds, and quenched with pure water. The surface modification of gold was carried out by dipping the substrate in dichloromethane solution containing 1.0 mM $PC_8FcC_{11}SH$ at 20 °C for 15 h under an Ar atmosphere. After the modification, the samples were sequentially washed with dichloromethane, ethanol, and pure water. Surface coverage of $PC_8FcC_{11}SH$ on gold was determined from the charge due to the redox of the ferrocene (Fc)/ferricenium cation (Fc^+) divided by the real gold surface area. Photocurrent measurements were carried out in 0.1 M $NaClO_4$ containing 5.0 mM MV^{2+} when the irradiation to the $PC_8FcC_{11}SH$ SAM modified gold electrode held at –200 mV (vs Ag/AgCl) was switched on and off. The photocurrent density was determined from the obtained photocurrent by dividing by the real surface area of gold. The intensity and wavelength of the irradiation were 40 $\mu W\ cm^{-2}$ and 430 nm, respectively.

Cyclic voltammograms (CVs) of the $PC_8FcC_{11}SH$ SAM modified gold electrodes prepared from the gold substrates with various surface roughnesses showed that the redox potential of Fc/Fc^+ (+610 mV) and the number of molecules per real area (1.4×10^{14} molecules cm^{-2}) were roughly independent of the surface roughness of the gold substrates.

The photoelectrochemical characteristics, on the other hand, significantly depended on the surface roughness. Figure 1 shows the time course of the current of the modified gold electrodes of various surface roughnesses when the electrodes were irradiated with 430 nm pulsed light under the conditions mentioned above. When the roughness factor of the gold substrate was less than 1.2, a stable cathodic photocurrent flowed as soon as the electrodes were irradiated and fell instantly when the irradiation was switched off. When the roughness factor was greater than 1.3, a spike-like transient photocurrent flowed as soon as the irradiation was started and then the photocurrent gradually decreased with time. After several tens of seconds, the decrease in the photocurrent stopped and then photocurrent became constant. When the irradiation was switched off, a

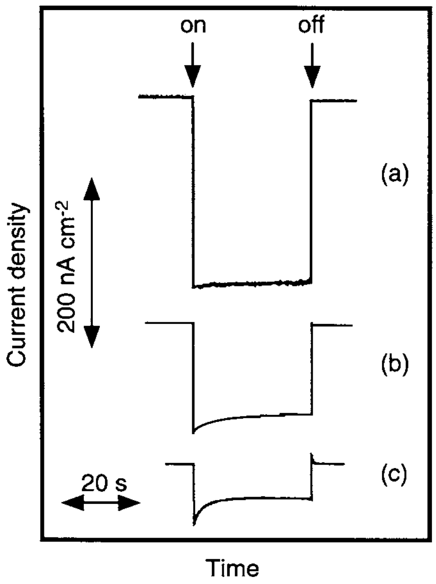

Figure 1. Time course of the current at the $PC_8FcC_{11}SH$ SAM modified gold held at -200 mV in 0.1 M $NaClO_4$ + 5.0 mM MV^{2+} when the electrodes were irradiated with pulsed light. The surface roughness factor of the gold substrate was (a) 1.2, (b) 1.5, and (c) 2.1.

spike-like anodic transient current flowed and it gradually returned with time to the original value in the dark.

The effect of the gold electrode's surface roughness factor on the steady state photocurrent density is summarized in Figure 2. The steady state photocurrent was independent of the surface roughness, ca. 250 nA cm^{-2}, as long as the roughness factor was less than 1.2, but decreased steeply as the roughness factor increased from 1.3 to 1.7, and became constant at ca. 40 nA cm^{-2} when the roughness factor was greater than 1.7.

Independence of the surface coverage of $PC_8FcC_{11}SH$ with respect to the real area on the surface roughness of the gold substrate means that the adsorbed molecules are close-packed on the gold surface in all cases and they adsorb not only on the flat domain but also on the domain boundary and step sites.

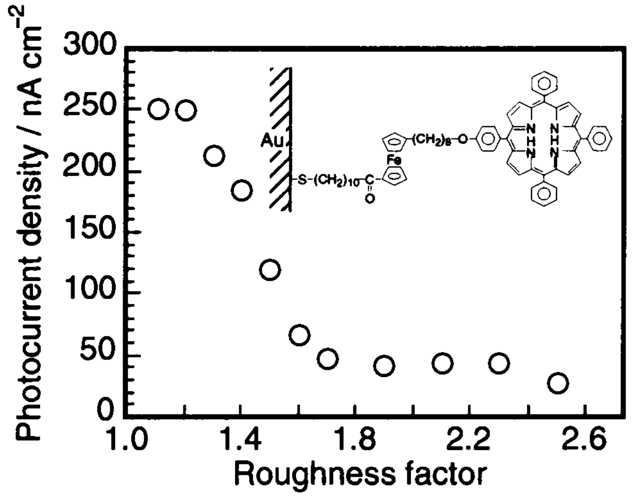

Figure 2. Photocurrent density per real area as a function of the surface roughness factor of the gold electrode. Inset: Schematic view of $PC_8FcC_{11}SH$ absorbed on gold.

When the surface roughness was higher, the number of the domains and the size of each domain were larger and smaller, respectively, resulting in the larger number of domain boundaries and step sites. Actually, STM measurements of the gold substrates show that the surface with the roughness factor of less than 1.2 consisted of the 100 nm × 100 nm domains with a (111) phase and the steps with a monoatomic height.[7] When the roughness factor was more than 2.0, the domain size decreased to less than 10 nm × 10 nm and the step height increased to ca. 10 nm. At the domain boundaries and step sites, a more disordered SAM structure is expected than on the flat terraces. The back electron transfer and energy transfer from the excited porphyrin to ferrocene and/or gold should be easier to occur for $PC_8FcC_{11}SH$ adsorbed on these sites due to the closer distance between the porphyrin and ferrocene and/or gold. Thus, the higher the surface roughness factor, the more effective the back electron transfer and energy transfer. In the present system, the photocurrent should be determined by the competitive reactions between the forward electron transfer process from the excited porphyrin to MV^{2+} and the backward electron and energy transfer processes from the excited porphyrin to the ferrocene and/or gold. Thus, the higher the surface roughness, the lower the photocurrent efficiency.

In conclusion, we have demonstrated the importance of the surface flatness of the substrate to achieve the ordered arrangement of the functional moieties of the SAMs, i.e., better characteristics, by showing that the photocurrent efficiency at the SAM modified gold electrodes is higher on the flatter substrate as a result of the effective inhibiting of the backward electron and energy transfer from the excited porphyrin to the gold due to the formation of highly ordered SAM.

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