Photoelectrochemical Responses of Gold Electrodes Co-modified with Sulfur-Containing Ruthenium Tris(2,2'-bipyridine) and Viologen Derivatives

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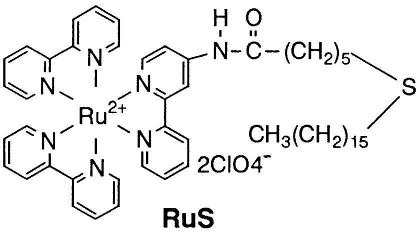
(Received April 10, 1995)

Gold electrodes co-modified with a sulfur-containing ruthenium tris(2,2'-bipyridine) homologue (RuS) and/or a viologen derivative (SC3V), and hexadecylmercaptane (C16SH) were prepared. In the presence of triethanolamine, the RuS-SC3V-C16SH modified electrode gave a larger anodic photocurrent than the RuS-C16SH modified one. The photocurrent was ascribed to RuS-sensitized redox cycles with SC3V as the mediator.

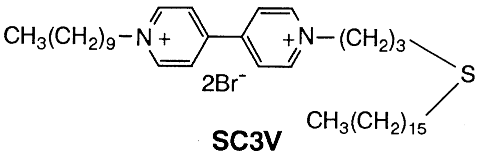
A ruthenium tris(2,2'-bipyridine) - viologen (D - A) couple is a typical redox pair for photogenerating charge-separated states in artificial photosynthesis. As a prerequisite for designing artificial photosynthetic systems with highly-efficient charge separation, one has to fabricate very-thin molecular assemblies in which D and A are elaborately arranged in molecular levels. For this purpose, a number of attempts have been made to use heterogeneous phase boundary between organized molecules (micelles, bilayer membranes) and bulk water.[1]

The electrode surface is a more promising boundary for fabricating photoelectric conversion systems. Modification of gold surface with organosulfur compounds is expected to serve as an efficient method of spatially arranging D and A at the electrode surface. In fact, the tris(2,2'-bipyridine) [2] or the viologen[3] moieties have been successfully incorporated in the monolayer assemblies on gold electrodes. In the present study, the gold electrodes were co-modified with sulfur-containing ruthenium tris(2,2'-bipyridine) homologue (RuS as D) and viologen derivative (SC3V as A), and their photocurrent responses were investigated to elucidate cooperation between the D - A pair.

Sulfide-type ruthenium tris(2,2'-bipyridine) homologue (RuS)[4] and viologen derivative (SC3V)[3] were prepared. Other reagents, hexadecylmercaptane (C16SH), triethanolamine (TEOA), and Na_2SO_4 as supporting electrolyte, were used as received. A semitransparent gold electrode was prepared by vacuum deposition of gold onto a quartz substrate (38×13 mm). The gold electrode was immersed into a chloroform-methanol (2:1) solution containing equimolar concentrations (1×10^{-3} mol dm^{-3} = M) of RuS, SC3V, and/or C16SH, for 24 hrs; the electrode was co-modified with C16SH to attain densely packed structure of monolayer assembly.[5] The electrode was then removed from the solution, rinsed with chloroform, and dried in air.



RuS



SC3V

$CH_3(CH_2)_{15}$-SH

C16SH

Photocurrent measurements were carried out under nitrogen using a three electrode cell consisting of the modified electrode, an Ag/AgCl (3M NaCl) electrode for reference, and a counter platinum electrode. The light from a Xenon lamp (300 W) was passed through a monochromator and irradiated the modified electrode. The photocurrent observed at 0 V was measured with a potentiostat (Fuso HECS-321B); it was too small to be detectable below -0.2 V.

The photocurrents induced by irradiation of the gold electrode with different microenvironments (470 nm) are shown in Figure 1. In the presence of TEOA, the RuS-SC3V-

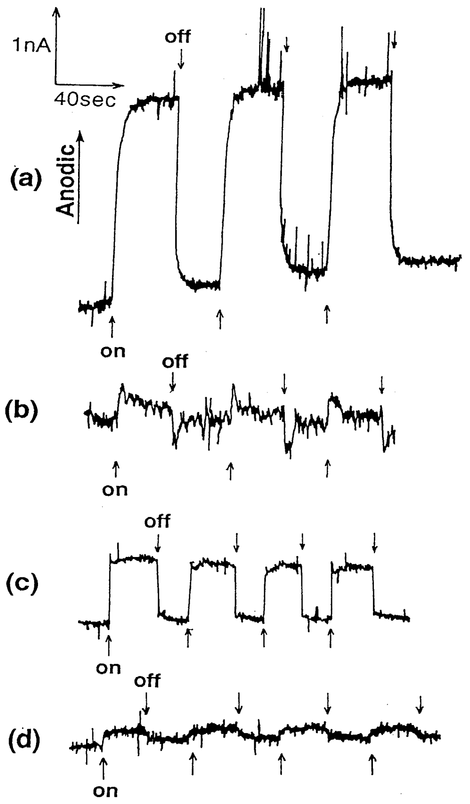


Figure 1. Comparison of photocurrents induced by irradiation of modified electrodes at 470 nm (±40 nm): RuS-SC3V-C16SH/Au in the presence (a) and absence (b) of TEOA (0.01 M), RuS-C16SH/Au (c) and SC3V-C16SH/Au (d) in the presence of TEOA (0.01 M). 0 V vs Ag/AgCl, $[Na_2SO_4]$ = 0.1 M.

C16SH/Au electrode gave a considerably larger photocurrent (a) than the RuS-C16SH/Au electrode (c) in the anodic direction. These two modified electrodes were prepared in the solutions containing equimolar concentrations (1×10^{-3} M) of the solutes. Preliminary studies indicated that the amount adsorbed RuS on RuS-SC3V-C16SH/Au was not more than one third of that on RuS-C16SH/Au.[6] Likewise, the amount of SC3V on RuS-SC3V-C16SH/Au was found only one third of that on SC3V-C16SH/Au on the basis of cyclic voltammetric measurements.[6] In spite of this handicap in chemical composition of the molecular monolayer on the electrodes, the largest photocurrent was observed with the RuS-SC3V-C16SH/Au electrode. No appreciable photocurrents were observed in the SC3V-C16SH/Au electrode (d).

Anodic photocurrent action spectra of RuS-SC3V-C16SH/Au and SC3V-C16SH/Au electrodes in the presence of 0.01 M TEOA as sacrificial reductant are shown in Figure 2. The RuS-SC3V-C16SH/Au electrode showed a broad band at 400 - 500 nm region which was correlated with the electronic absorption band of RuS in methanol. In the case of SC3V-C16SH/Au electrode, the photocurrent decreased monotonically at longer wavelengths lasting up to ~500 nm, probably due to the existence of charge-transfer interactions between the viologen moiety and Br^{-}.[7] The results show that the photocurrent is caused by photoexcitation of RuS.

The most likely mechanism for generating photocurrent is shown in Scheme 1. A redox pair (Ru^{3+}- $V^{+}\cdot$) will be generated on photoirradiation of the modified electrode. The oxidized ruthenium complex (Ru^{3+}) will be reduced to Ru^{2+} by TEOA. The reverse electron-transfer from $V^{+}\cdot$ to Ru^{3+} should be suppressed so that concomitant increase of anodic currents will be observed.

Cooperative photoresponse of the Ru - V pair was thus verified by the monolayer assembly in which D and A were spatially arranged on the gold surface. At present, the photocurrent signal is very small, mainly due to low surface coverage of RuS and SC3V. The efficiency of charge separation must depend on the adsorption ratio of D to A, as well as their spatial alignment, as has been extensively studied in the Langmuir-Blodgett films by Fujihira et al.[8] The work is in progress to improve photocurrent efficiency.

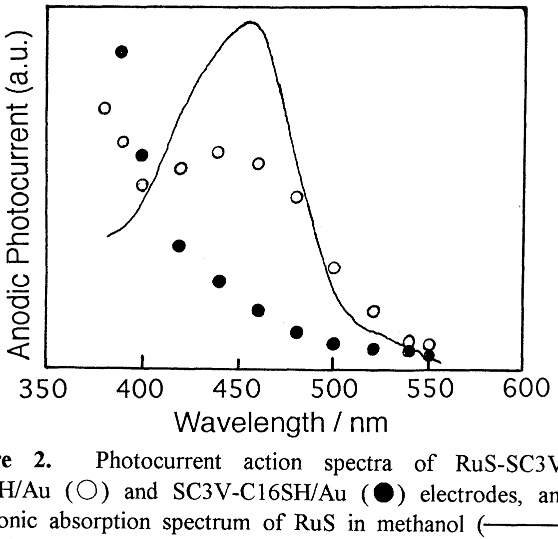
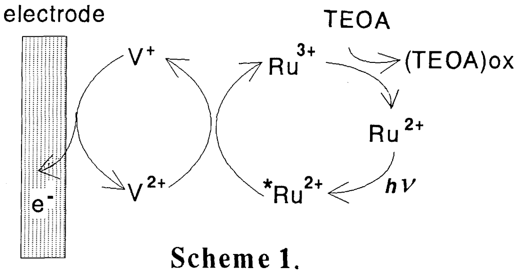


Figure 2. Photocurrent action spectra of RuS-SC3V-C16SH/Au (○) and SC3V-C16SH/Au (●) electrodes, and electronic absorption spectrum of RuS in methanol (———). Condition for photocurrent measurements: 0 V vs Ag/AgCl, [Na_2SO_4] = 0.1 M, [TEOA] = 0.01 M.

The present study was partially supported by the Grant-in-Aid for Scientific Research on Priority Area (No. 06226263).



Scheme 1.

References and Notes

1 See for example: T. Matsuo, *J. Photochem.*, **29**, 41 (1985).

2 a) Y. S. Obeng and A. J. Bard, *Langmuir*, **7**, 195 (1991); b) Y. Sato and K. Uosaki, *Denki Kagaku*, **61**, 816 (1993).

3 a) K. A. B. Lee, *Langmuir*, **6**, 709 (1990); b) H. C. De Long and D. A. Buttry, *Langmuir*, **8**, 2491 (1992); c) E. Katz, N. Itzhak, and I. Willner, *Langmuir*, **9**, 1392 (1993).

4 A 2,2'-bipyridine ligand attached with an alkylsulfide group via an amido bond was prepared by the reaction of 4-amino-2,2'-bipyridine and (hexadecylthio)hexanoic acid. RuS was prepared by the reaction with the 2,2'-bipyridine derivative and ruthenium bis(2,2'-bipyridine) dichloride.

5 The cyclic voltammogram of N,N'-bis(3-sulfonatopropyl)-4,4'-bipyridinium (4ZV) was measured by using the modified electrode. The RuS/Au electrode showed large redox peaks of 4ZV, but the electrode co-modified with C16SH showed no clear redox peaks.

6 From cyclic voltammetric measurements, the surface coverage of SC3V was evaluated to be $\sim 4 \times 10^{-12}$ or $\sim 1.3 \times 10^{-11}$ mol/cm^2 for RuS-SC3V-C16SH/Au or SC3V-C16SH/Au electrode, but the corresponding value for RuS could not be obtained. Relative quantities of RuS in the RuS-SC3V-C16SH and the RuS-C16SH monolayer assemblies were estimated as follows. Gold dust (Ishifuku, type S, average size: 3 μm, weight: 0.1 g) was put into the chloroform-methanol solution (3 ml) containing equimolar concentrations (2×10^{-6} M) of the solutes in the quartz cell for absorption measurements, and the mixture was stirred for 24 hrs. Then the absorption spectrum of the supernatant solution was measured. The absorption band of RuS at the 400 - 500-nm region was reduced due to adsorption of RuS onto the gold dust; SC3V and C16SH have no absorption bands in this wavelength region, so that the absorption decrease is caused only from the adsorption of RuS. The absorption decrease in the RuS-C16SH mixed solution was three- to four-times as large as that in the RuS-SC3V-C16SH mixed solution. This suggests that the concentration of RuS in the RuS-SC3V-C16SH monolayer assembly is three- to four-times lower than that in the RuS-C16SH monolayer assembly.

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8 M. Fujihira, Photo-electric Conversion with Langmuir-Blodgett Films, in K. Honda Ed., *Photochemical Processes in Organized Molecular Systems*, Elsevier Science Publishers, **1991**, 463.