

Photocurrent properties of *cis*-di(thiocyanato)-bis(4,4'-dicarboxy-2,2'-bipyridine) ruthenium(II) monolayers on the gold surfaces

Nao Terasaki¹, Satoshi Nitahara, Tsuyoshi Akiyama and Sunao Yamada

Department of Applied Chemistry, Kyushu University, 6-10-1 Hakozaki, Fukuoka 812-8581, Japan

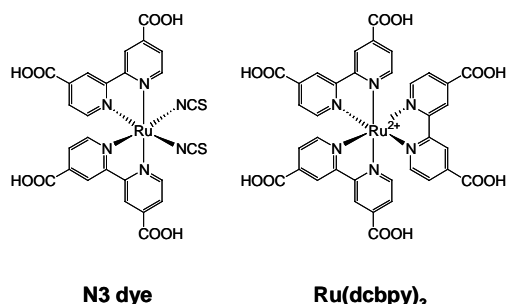
¹Present address: National Institute of Advanced Industrial Science and Technology (AIST),
1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

Phone : +81-0727-51-9655, Fax : +81-0727-51-9637, E-mail : nao-terasaki@aist.go.jp

1. Introduction

A pre-requisite for constructing an organic photoelectric conversion system is to fabricate very thin regular assemblies of organic dyes. A self-assembling method using organosulfur dyes has attracted much attention as a useful method for fabricating well-ordered monolayer assemblies on the surface of gold electrode, and has been successful for photocurrent generation [1-7].

In the meantime, a dye-sensitized solar cell consisting of a ruthenium complex and a nanocrystalline TiO₂ film has received significant attention because of its high efficiency and low cost as compared with silicon-based solar cells [8]. Especially, *cis*-di(thiocyanato)-bis(4,4'-dicarboxy-2,2'-bipyridine)ruthenium(II) (denoted as N3) and its derivatives have given outstanding performance as the sensitizer [9-12]. They have isothiocyanate (SCN⁻) group as the ligands of complex, which results in great advantages for harvesting a larger fraction of light and for achieving relatively long excited-state lifetime [9]. Early studies indicated that some isothiocyanate complexes of metals showed strong adsorption on the mercury electrode surface via the NCS ligand [13]. Quite recently, a (SCN)₂⁻ radical was found to bind strongly to the gold surface [14]. From these viewpoints, we have tried in this study to prepare monolayer assemblies of the N3 dye on the gold surfaces via NCS ligand(s) and have evaluated their photocurrent properties. In addition, effects of gold nanoparticles on the photocurrent responses were investigated.



2. Experimental

The N3 dye was purchased from Kojima Chemicals (Japan) and used as received. 4,4'-Dimethylviologen (MV) was prepared in our laboratory. Tris(4,4'-dicarboxy-2,2'-bipyridine)ruthenium(II), Ru(dcbpy)₃, was synthesized by the reaction of RuCl₂ and 4,4'-dicarboxy-2,2'-bipyridine. A gold electrode was prepared by vacuum deposition of titanium followed by gold onto a glass plate (1.5×0.9×0.1 cm) at 300°C

(roughness factor 1.4) [3]. The nanostructured gold electrode was prepared as ascribed previously [4]. The electrode was immersed into an ethanol solution of N3 (3×10⁻⁴ M) for seven days. After soaking with ethanol and then methanol, the N3-modified electrode was dried with a stream of nitrogen gas.

Cyclic voltammetric (CV) and differential pulse voltammetric (DPV) measurements of a modified electrode (working) were carried out using a platinum counter electrode and a Ag wire as a reference electrode in a dichloromethane solution containing 0.1M tetra(n-butylammonium)perchlorate (TBAP). Photocurrent measurements were carried out in the acetonitrile solution of 0.1M TBAP and dimethyl viologen (MV) di(perchlorate) (5×10⁻³ M) under an aerobic condition. The light from a Halogen lamp (150 W) was passed through a monochromator and irradiated the modified electrode (irradiation area 0.2 cm²). All measurements were carried out at room temperature.

3. Results and discussion

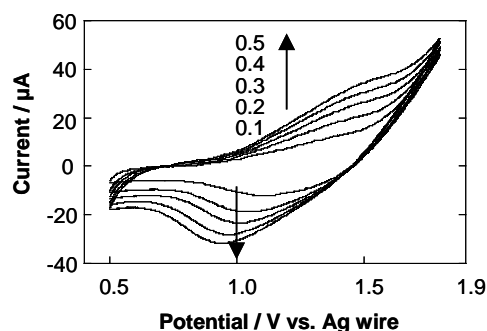


Figure 1. Cyclic voltammogram of N3-modified gold electrode. Scan rate: 0.1-0.5 V/s. [TBAP] = 0.1 M in CH₂Cl₂.

In order to evaluate the fractional coverage of N3 on the gold electrode, CV and DPV measurements were carried out. CV data of the N3-modified electrode after soaking are shown in Fig. 1. Although the peaks were not clear, one-electron redox waves due to Ru^{3+/2+} are certainly observed with the half-wave potential of +1.3 V vs. Ag wire. Redox waves due to one electron oxidation of N3 in the acetonitrile solution were observed at +0.85 V vs SCE [9]. From the cathodic peak of CV, the fractional coverage of N3 was evaluated to be ~5×10⁻¹⁰ mol cm⁻², close to monolayer level.

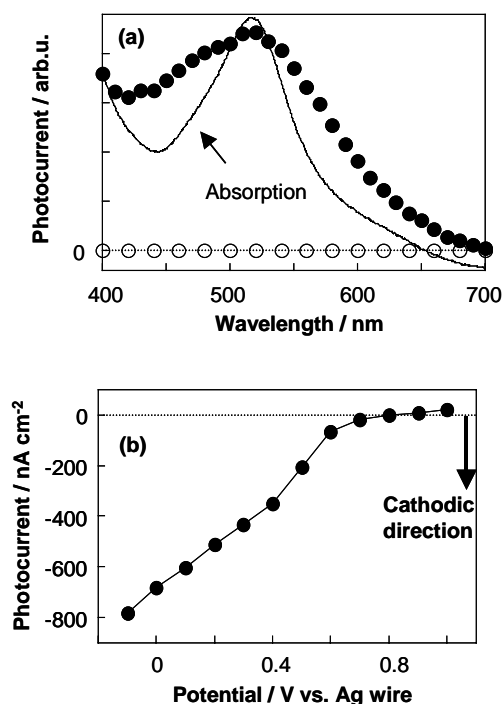


Figure 2. (a) Photocurrent action spectra of N3-modified electrode (●), the bare electrode (○) and electronic absorption spectrum (solid line) of N3 in ethanol under aerobic condition. Conditions for photocurrent measurements: $E=0$ V vs. Ag wire. (b) Applied potential dependence on the photocurrents from N3-modified electrode under aerobic condition. Conditions: $\lambda_{\text{ex}}=500$ nm; $[\text{MV}]=5\times 10^{-3}$ M; $[\text{TBAP}]=0.1$ M.

The gold electrode was also immersed into a methanol solution of $\text{Ru}(\text{dcbpy})_3$ (1×10^{-3} M) for seven days, followed by soaking with ethanol and methanol, as in the same procedure for the preparation of the N3-modified electrode. DPV measurements of the above treated gold electrode showed no appreciable redox waves due to $\text{Ru}(\text{dcbpy})_3$. Thus, $\text{Ru}(\text{dcbpy})_3$ is not immobilized on the gold surface, because $\text{Ru}(\text{dcbpy})_3$ has no NCS ligands. This indicate that immobilization of N3 on the gold surface is achieved not via the carboxyl groups but via the NCS ligands, in different with the case of N3 molecules bound to the nanoporous TiO_2 film.

In most potential region studied, the photocurrent was measured in aerobic condition in the presence of MV (5mM), and was observed in the cathodic direction. As shown in Fig.2(a), the peak position of the photocurrent action spectrum with the N3-modified electrode at 0 V is well correlated with the absorption spectrum of N3 in ethanol. Thus, the photocurrent is induced by photoexcitation of N3. Fig. 2(b) shows the applied potential dependence of the N3-modified gold electrode. The photocurrent decreased as the applied potential became positively larger and the direction of the photocurrent changed to the anodic direction above $+0.8$ V, due to increased electron-transfer from the photoexcited N3 to the

electrode. The electron-transfer from the photoexcited N3 to oxygen is much more favorable than that to MV. In fact, deaeration induced substantial reduction of the photocurrent ($\sim 1/20$) but the current was still observed in the cathodic direction at $E = 0$ V. Thus, the electron-transfer from the photoexcited N3 to the acceptor (oxygen and/or MV) is superior to the electron-transfer to the gold electrode contributing to the anodic photocurrent.

In order to evaluate the effects of surface plasmon oscillation on the photocurrent responses, we have prepared the nanostructured electrodes consisting of gold nanoparticle precipitates. Interestingly, relative enhancement of photocurrents as compared with those from the planar electrode was larger for longer wavelengths, corresponding with the plasmon band of the nanostructured electrode.

4. Conclusions

In conclusion, we have demonstrated, for the first time, the self-assembled monolayer of the N3 dye on the gold electrode. Photocurrent responses were superior in the nanostructured electrode, especially in the longer wavelength region.

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