

Fabrication of a Photoelectrochemical Cell Using a Self-Assembled Monolayer of Tris(2,2'-bipyridine)ruthenium(II)-Viologen Linked Thiol on Multistructured Gold Nanoparticles

Nao Terasaki¹, Keisuke Otsuka, 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),

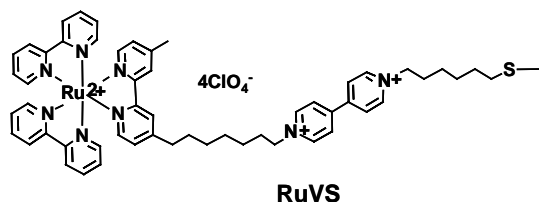
1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

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

1. Introduction

Due to potential advantages of organic compounds such as light absorptivity and easiness for film preparation, the development of organic photoelectric conversion devices has been attractive. A prerequisite for fabricating organic photoelectric conversion devices is to prepare very thin molecular assemblies on conductive supports. Well organized assemblies of electron donor(D)-acceptor(A) pairs on the electrode have achieved high efficiencies of photoelectric conversion based on photoinduced intermolecular electron-transfer reactions [1]. Particularly, the gold (or indium-tin-oxide: ITO)-sulfur self-assembled monolayers (SAMs) of D-A pairs have been successful for photocurrent generation [2-6]. However, early photocurrent studies on SAMs were limited to planar electrodes, so that the number of immobilized molecules had been restricted.

Recently, we first reported multistructured assemblies consisting of thiol dyes and gold nanoparticles on the planar electrode and their photocurrent responses [7,8]. This method simply gives substantial increase in the number of immobilized dyes per projective surface area. In the present study, We have fabricated a photoelectrochemical cell using the multistructure consisting of the SAM of a D-A linked compound (**RuVS**) on gold nanoparticles deposited on the planar gold electrode. Photocurrents as well as photovoltages increased with increasing the number of gold particles (that is, the number of immobilized **RuVS**).



2. Experimental

The preparation procedure of **RuVS** has been described previously [9]. An aqueous solution of gold particle was prepared by the reduction of HAuCl_4 with sodium citrate as before [10]. The mean diameter was 18 ± 5 nm, analyzed by a transmission electron micrograph (TEM). The planar gold electrode (A_{flat}) was prepared by vacuum deposition of titanium followed by gold onto a glass plate ($1.0 \times 1.0 \times 0.1$ cm) at 300°C . The

nanosubstructured gold electrodes (**B**_{10ml}, **C**_{20ml} and **D**_{40ml}) were prepared by precipitation of the gold nanoparticles on the planar gold substrates from the colloidal solution (10, 20 and 40 ml, respectively). Then, the electrodes were immersed into a CH_3CN solution of **RuVS** (1×10^{-3} M) for three days to self-assemble **RuVS** on the gold surface.

Figure 1 shows schematic illustration of a photoelectrochemical cell, which is similar to the previous one [11]. The modified (WE) and the counter ITO (CE) electrode was fixed snugly in a concave-shaped silicon rubber plate (SR; ~ 0.5 mm thickness). A polyimide film (PF; ~ 12.5 μm thickness) was inserted between the two electrodes to keep electrical insulation. The film has a hole of 5-mm diameter for filling an electrolyte solution between the electrodes and for irradiation of the modified electrode. The electrolyte solution is a mixture of hydroxymethylferrocene (FcOH: 0.02 M) and NaClO_4 (0.1 M) in water. A small amount of the electrolyte solution was dropped between the electrodes, and the whole cell parts were fixed tightly by viton rubber plates (VR; having 5-mm hole for the top plate for light illumination) and champs. The light from a Xenon lamp (150 W) irradiated the modified electrode through the counter electrode (irradiation area: 0.2 cm^2) using an optical fiber (OF). Resultant photocurrents were measured with the electrometer, while the photovoltages with the potentiostat using external load resistors.

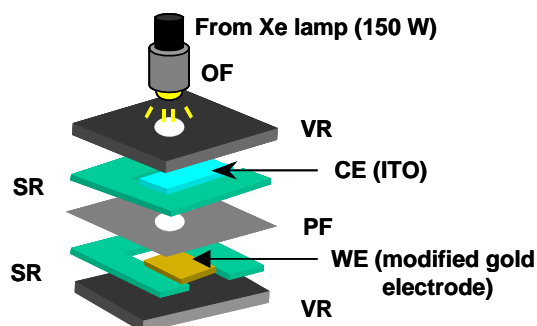


Figure 1. Schematic illustration of a photocell

3. Results and discussion

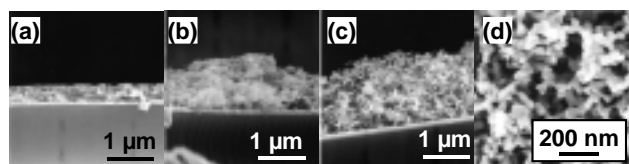


Figure 2. SEM images of nanosubstructured gold electrodes **B**_{10ml} (a), **C**_{20ml} (b), **D**_{40ml} (c), magnification of deposited gold nanoparticles layer (d).

As is recognized from the SEM images (Figure 2), most of the gold particles are agglomerated with each other. It is also clear that the bare part (dark sites) of the planar gold electrode decreases and the thickness of the deposited past becomes larger (~ 0.5 to ~ 2 μm) with increasing the volume of colloidal solution used. Through the degree of agglomeration is microscopically uniform, the deposited structure becomes macroscopically homogenous.

CV (and DPV) and photocurrent measurements with triethanolamine (TEOA) as a sacrificial reagent in the three-electrode mode show the amounts of adsorbed **RuVS** and anodic photocurrents induced by photoexcitation of the tris(2,2'-bipyridine). They increased with the increase of deposited gold nanoparticles.

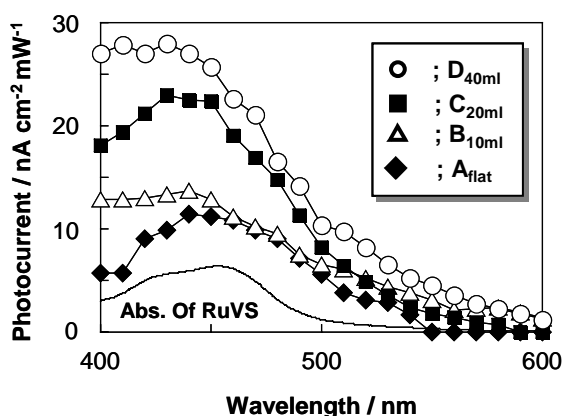


Figure 3. Photocurrent action spectra of photocells at short circuit current (I_{sc}). WE: the modified gold electrode (**A**_{flat}-**D**_{40ml}); CE: ITO electrode.

The performance of the photoelectrochemical cell as described Figure 1 was investigated by measuring the photocurrent action spectra and photocurrent (I)-photovoltage (V) curves. Figure 3 shows photocurrent action spectra of the photoelectrochemical cell at short circuit current (I_{sc}). The photocurrent (I_{sc}) tended to be larger for higher number of immobilized **RuVS** (that is, higher number of deposited gold particles).

The I-V curves showed that both I_{sc} and V_{oc} values tended to be large for higher number of deposited gold particles. Larger I_{sc} values must be due to higher numbers of immobilized **RuVS**. Thus, the increase in the V_{oc} value at higher number of deposited gold particles

(immobilized **RuVS**) may be due to the change in the rate-determining process of electron-transfer in the overall electron flow in the cell system. However, the V_{oc} value (WE; **A**_{flat}: 1.3 mV; **B**_{10ml}: 4.1 mV; **C**_{20ml}: 9.3 mV; **D**_{40ml}: 38 mV) is still very low as compared with the previous photocell using the **RuVS**-modified ITO electrode (420 mV), where the electrolyte solution was a mixture of LiI(0.03 M) and I_2 (1×10^{-3} M) in acetonitrile [12]. In the case of the gold electrode, the electrolyte solution containing I^- (I_2) caused dissolution of gold, and thus it could not be useful in the present cell. Thus, a smart choice of an electrolyte (electron mediator) must be a key for improving the performance of the present photoelectrochemical cell.

4. Conclusions

In conclusion, the gold-sulfur self-assembled monolayer can be applicable to the organic photoelectrochemical cell. The use of gold particle multistructures has enabled the increase in the number of immobilized **RuVS**, resulting the increase in the photocurrent and the photovoltage. A smart choice of an electron mediator (electrolyte) is a key to improve the performance of the present photocell and the work is in progress along this line.

Acknowledgements

N. T. is grateful for financial support by the Kyushu Univ. Foundation.

References

- [1] M. Fujihira, Mol.Cryst. Liq. Cryst. 183, 59 (1990).
- [2] S. Yamada, H. Kohrog, T. Matsuo, Chem. Lett. 639 (1995).
- [3] N. Terasaki, T. Akiyama, S. Yamada, Langmuir, 18, 8666 (2002).
- [4] H. Yamada, H. Imahori, Y. Nishimura, I. Yamazaki, S. Fukuzumi, Adv. Mater. 14, 892 (2002).
- [5] T. Kondo, T. Ito, S. Nomura, K. Uosaki, Thin Solid Films 284/285, 652 (1996).
- [6] D. Hirayama, K. Takimiya, Y. Aso, T. Otsubo, T. Hasebe, H. Yamada, H. Imahori, S. Fukuzumi, Y. Sakata, J. Am. Chem. Soc. 124, 532 (2002).
- [7] Y. Kuwahara, T. Akiyama, S. Yamada, Thin Solid Films 393, 273 (2001).
- [8] Y. Kuwahara, T. Akiyama, S. Yamada, Langmuir 17, 5714 (1991).
- [9] S. Yamada, Y. Koide, T. Matsuo, J. Electroanal. Chem. 426, 23 (1997).
- [10] J. Turkevich, P. C. Stevenson, J. Hiller, Discuss. Faraday Soc. 11, 55 (1951).
- [11] N. Terasaki, K. Kakutani, T. Akiyama, S. Yamada, in press.
- [12] T. Akiyama, M. Inoue, Y. Kuwahara, S. Yamada, Jpn. J. Appl. Phys. 43, 4737 (2002).