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A Photoresponsive Ruthenium Complex-Titanium Oxide-Viologen Film Prepared by the Combination of Self-Assembly and Surface Sol-Gel Processes

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1. Introduction

Fabrication of ultrathin molecular films in which a photoredox pair is elaborately arranged on a conductive support has been promising to achieve highly efficient photoelectric conversion [1]. A tris(2,2'-bipyridine) ruthenium (II)-viologen (Ru^{2+} - V^{2+}) couple is an excellent photoredox pair for generating highly efficient charge-separated states [2]. We previously reported the photocurrent responses from the monolayer assemblies of Ru^{2+} - V^{2+} linked thiols formed on gold electrodes [3,4]. However, synthetic procedures of those linked compounds are complicated and time-consuming.

Quite recently, we preliminarily tried to combine self-assembly [5] and surface sol-gel [6] methods in order to easily fabricate an assembly of a porphyrin-fullerene pair via TiO_2 layers [7]. In this study, we have successfully built-up a Ru^{2+} - V^{2+} superstructure on an indium-tin-oxide (ITO) electrode by the combination of self-assembly and surface sol-gel processes, and have found clear photocurrent responses from the film.

2. Experimental Section

Tris(4,4'-dicarboxy-2,2'-bipyridine)ruthenium(II) **RuTC**, 1-(6-mercaptohexyl)-1'-carboxymethylviologen **CVS**, and thioundecanoic acid $\text{HOOC}(\text{CH}_2)_{10}\text{SH}$ (**CCS**) were prepared in our laboratory. Other chemicals were used as received.

The preparation procedure of the **RuTC**- TiO_2 -**CVS** film on the ITO electrode is shown in Fig. 1. Assembling of **CVS** was carried out under electrochemical reduction of the V^{2+} moiety. The applied potential of the ITO electrode was set at -0.7 V vs. Ag/AgCl for 3 hours in an aqueous solution containing **CVS** (1×10^{-3} M monomer unit) and KCl (0.1 M) [8]. After withdrawal, the electrode was rinsed with ethanol and dried with a stream of nitrogen gas, giving the modified electrode denoted as **CVS**/ITO electrode (step 1). In the case of **CCS**, the ITO electrode was immersed into an ethanol solution of **CCS** (1×10^{-3} M) for 4 days. Next, the **CVS**/ITO electrode was immersed into a toluene/ethanol (1:1 v/v) solution of titanium butoxide $\text{Ti}(\text{O}i\text{Bu})_4$ (0.1 M) for 3 min to achieve coordinative bonding of **CVS** and $\text{Ti}(\text{O}i\text{Bu})_4$, and then was dipped into ethanol for rinsing and then water for hydrolysis, giving the TiO_2 -**CVS** assembly on the electrode

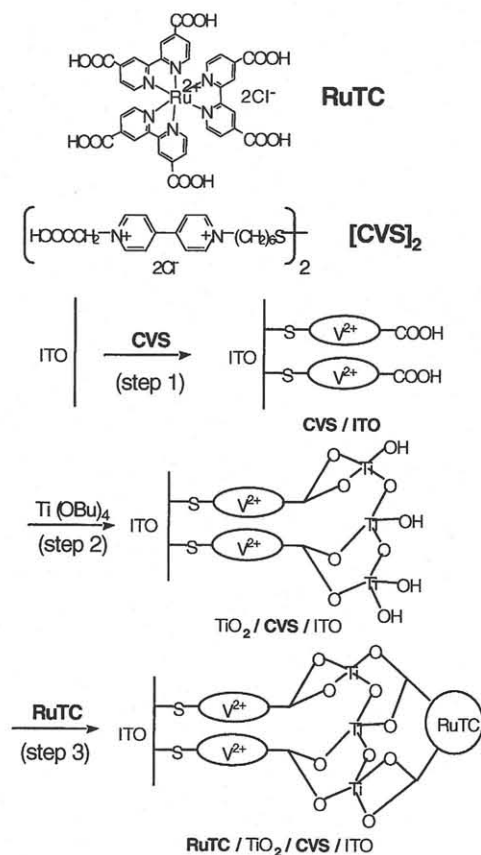


Fig. 1. Preparation procedure of the film.

(TiO_2 /**CVS**/ITO electrode) (step 2). Finally, this electrode was immersed into a methanol solution of **RuTC** (1×10^{-3} M) for 30 min, followed by rinsing with methanol and drying to give the **RuTC**- TiO_2 -**CVS** assembly on the ITO electrode (**RuTC**/ TiO_2 /**CVS**/ITO electrode) (step 3).

Photocurrent measurements were carried out in an aqueous solution containing triethanolamine (TEOA) (0.5 M) as a sacrificial reagent and KCl (0.1 M). The monochromatic light from a Xe lamp (300W) was used [4].

2. Results and Discussion

As shown in Fig. 2, clear redox waves due to the first and the second reduction of the viologen moiety is observed in the $-0.3 \sim -0.6$ V region in the cyclic voltammogram of the **CVS**/ITO electrode. From the analysis of these reduction peaks, the surface coverage of **CVS** was evaluated as $\sim 6 \times 10^{-10}$ mol cm^{-2} by assuming unity of the roughness

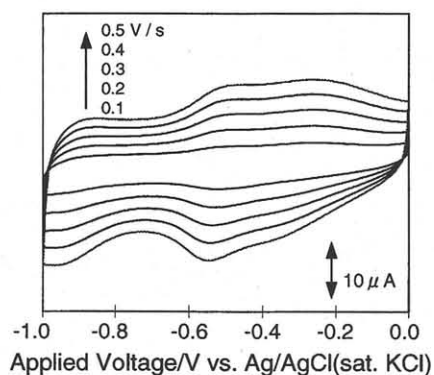


Fig. 2. Cyclic voltammogram of CVS/ITO electrode.

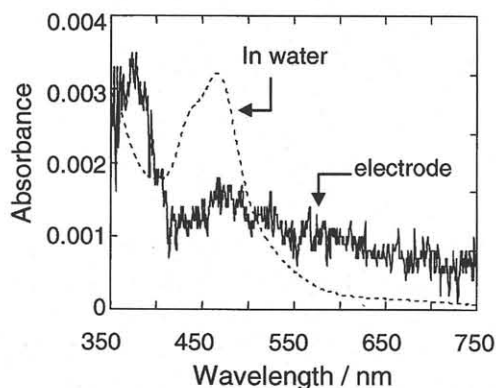


Fig. 3. Absorption spectrum of RuTC/TiO₂/CVS/ITO electrode and RuTC in water.

factor.

Quartz crystal microbalance (QCM) measurements were carried out for evaluating the degree of TiO₂ deposition on the CVS/ITO electrode. The CVS assembly was prepared on the gold surface of the QCM plate by immersing it into the ethanol solution of CVS for 1 day. Then, this plate was immersed into the solution of Ti(OBu)₄ in a similar manner as described above. The frequency decrease (mass increase) was ~170 Hz. Thus, the thickness of the TiO₂ layer is estimated to be ~2 nm [6, 7].

Absorption spectrum of the RuTC/TiO₂/CVS/ITO electrode is shown in Fig. 3. The characteristic absorption band due to the Ru²⁺ moiety is seen in the 400-500 nm region. The coverage of RuTC on the TiO₂ layer was evaluated to the $\sim 5 \times 10^{-11}$ mol cm⁻², by using the molar absorptivity (1.3×10^4 M⁻¹ cm⁻¹ at 460 nm) in water.

Figure 4 shows photocurrent action spectrum of the RuTC/TiO₂/CVS/ITO electrode, together with the absorption spectrum of RuTC in water. Photocurrents were certainly observed in the anodic direction. Although the action spectrum showed no clear peaks around 460 nm corresponding to the absorption band of the Ru²⁺ moiety, the RuTC/TiO₂/CVS/ITO electrode gave about 3 times larger photocurrents than the RuTC/TiO₂/CCS/ITO electrode (without V²⁺ moieties) under the identical coverage of RuTC. The TiO₂/CVS/ITO electrode showed no

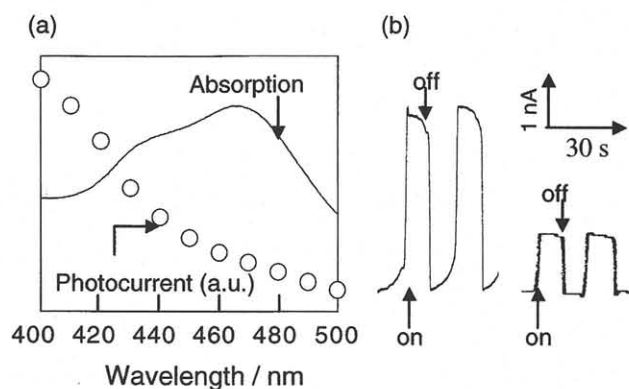


Fig. 4. (a) Photocurrent action spectrum of RuTC/TiO₂/CVS/ITO electrode and the absorption spectrum of RuTC in water (—). (b) Comparison of photocurrents excited at 460 nm (0 V).

appreciable photocurrents. The photocurrent of the RuTC/TiO₂/CVS/ITO electrode decreased with lowering the applied voltage and was negligible below -0.2 V. These observations strongly suggest that the photocurrents are generated via photoinduced electron-transfer from Ru²⁺ to V²⁺ moieties.

In conclusion, we have succeeded in the construction of the photoresponsive Ru²⁺-V²⁺ film. Quantitative and morphological characterization of the assembly is underway.

References and Notes

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- [8] Assembling of CVS on the ITO electrode was carried out in a three-electrode cell with Ag/AgCl (sat. KCl) (reference) and platinum (counter) electrodes containing CVS (1×10^{-3} M) and KCl (0.1 M). As shown in Fig. 2, two-electron reduction of the dicationic V²⁺ moiety is possible at -0.7 V, which must reduce electrostatic repulsion in the assembly and thus must be favorable for dense packing.