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Fabrication and Photoelectrochemical Properties of Porphyrin-Fullerene Assemblies by Self-assembly and Surface Sol-Gel Processes

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1. Introduction

Photoenergy conversion is basically important from a viewpoint of clean energy generation systems as well as various photoelectric devices. Ultrathin organic molecular films in which a photoredox pair is elaborately arranged on a conductive support has been promising to realize efficient photoelectric conversion systems.¹ Especially, photoelectric conversion using the self-assembled monolayer of thiol derivatives of a photoredox pair on a gold electrode via S-Au bonding has been promising.²⁻⁵ However, synthetic procedures of these derivatives are generally complicated and time-consuming. From these viewpoints, we preliminarily tried the combined use of self-assembly and surface sol-gel methods^{6,7} in order to readily fabricate assemblies of several photoredox pairs via titanium oxide (Ti(O)) layers without sophisticated synthetic procedures.^{8,9}

Here we report, fabrication and photoelectrochemical properties of porphyrin-fullerene multilayered assemblies via Ti(O) layer constructed on an indium-tin-oxide (ITO) electrode.

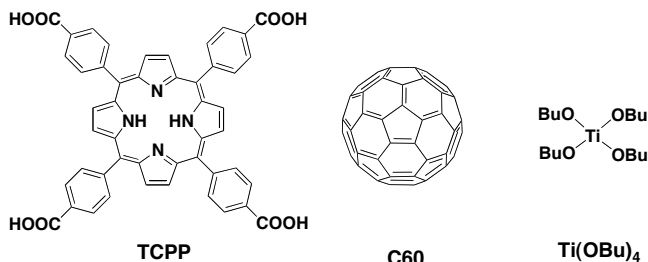
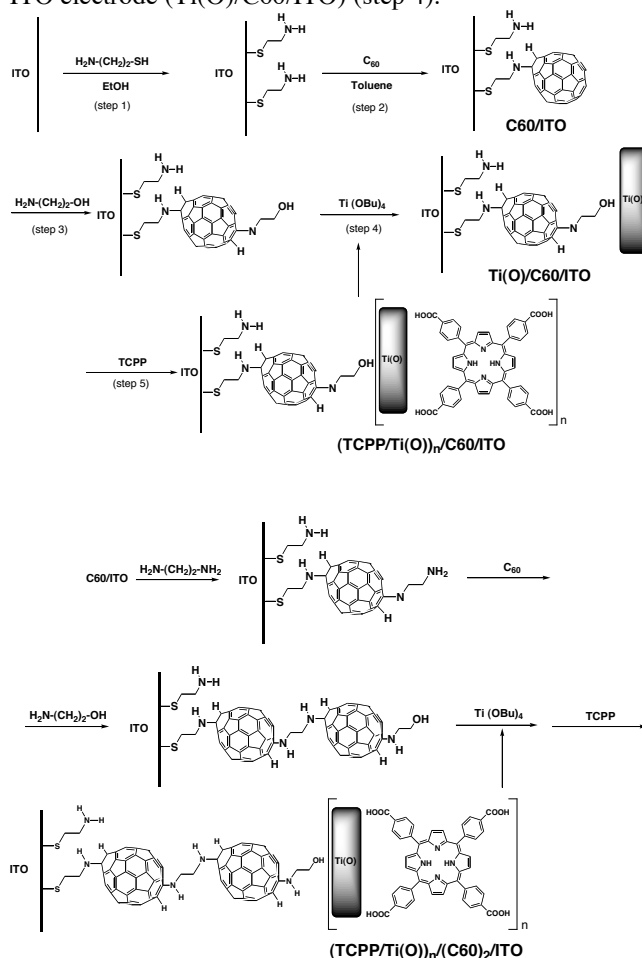


Figure 1. Structures of molecules

2. Experimental

5, 10, 15, 20-Tetracarboxyphenyl porphyrin (TCPP), C60 fullerene (C60) and other chemicals were used as received. Preparation procedures of photofunctional electrode modified with porphyrin-fullerene assemblies are shown in Scheme 1. First, the bare ITO electrode was immersed into an EtOH solution of cysteamine (1.0×10^{-3} mol dm⁻³) for 2 days to immobilize cysteamine on the ITO surface (step 1). The cysteamine-modified electrode was then immersed into a toluene solution of C60 (1.0×10^{-3} mol dm⁻³) for 1 day, to give C60-modified electrode denoted as: C60/ITO (step 2).¹⁰ Then, C60/ITO was soaked in an EtOH solution of 2-ethanolamine (1.0×10^{-3} mol dm⁻³) for implanting a hydroxy group to the immobilized C60 (step 3).¹¹ Then, this electrode was immersed into a tolu-

ene/EtOH solution of Ti(OBu)₄ (0.1 mol dm^{-3}) for 3 min. After withdrawal, the electrode was subsequently dipped into water and dried, giving Ti(O)-C60 assembly on the ITO electrode (Ti(O)/C60/ITO) (step 4).



Scheme 1. Preparation procedures of modified electrodes

Finally, Ti(O)/C60/ITO was immersed into an EtOH solution of tetracarboxyphenylporphyrin (TCPP) (1.0×10^{-3} mol dm⁻³) for 10 min, followed by rinsing with EtOH and drying, to give a TCPP-Ti(O)-C60 assembly on the ITO electrode denoted as: (TCPP-Ti(O))_n-(C60)₂/ITO (step 5). The multilayer of TCPP was prepared on the surface of C60 by repeating alternate assembling of Ti(O) and TCPP layers. The (TCPP-Ti(O))_n-(C60)₂ assembly was also obtained by a similar manner using ethylenediamine as the binder between C60s (see the bottom scheme).

Photocurrent measurements were carried out in an aqueous solution containing $0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$, by using a three-electrode photoelectrochemical cell, where an Ag/AgCl (sat. KCl) electrode for reference, and a platinum-counter electrode were used. In all measurements, triethanolamine (TEOA) was added as a sacrificial reductant, and methylviologen (MV) was also added to the electrolyte solution. The monochromatic light from a Xe lamp irradiated the modified electrode. All measurements were carried out at room temperature.

3. Results and Discussion

The absorption spectra of $(\text{TCPP}/\text{Ti}(\text{O}))_n/\text{C60}/\text{Ti}(\text{O})/\text{ITO}$ ($n = 1, 2$), are shown in Figure 2. In both electrodes, Soret bands of TCPP were clearly observed at around 420 nm, which indicate no obvious interactions between TCPP and C60 at the ground states. The absorption intensity of $(\text{TCPP}/\text{Ti}(\text{O}))_2/\text{C60}/\text{ITO}$ was larger than that of $\text{TCPP}/\text{Ti}(\text{O})/\text{C60}/\text{ITO}$. This indicates that the adsorbed amount of TCPP also increases by repeating the sol-gel process. Similar results were observed in other modified

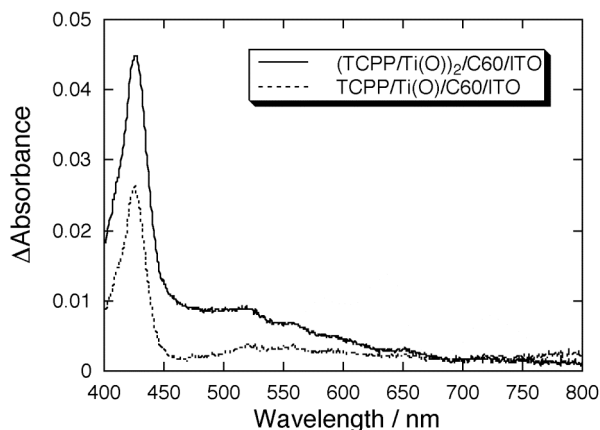


Figure 2. Absorption spectra of $(\text{TCPP}/\text{Ti}(\text{O}))_n/\text{C60}/\text{ITO}$

electrodes. Meanwhile, the emission spectra of modified electrodes show that the wavelength of emission peaks was essentially identical with that of TCPP in solution. This indicates that the photoexcitation of TCPP is possible even in the sol-gel film. The photocurrent action spectrum of $\text{TCPP}/\text{Ti}(\text{O})/\text{C60}/\text{ITO}$ at 0V vs. Ag/AgCl(sat. KCl) is shown in Figure 3. The photocurrents were observed in the anodic direction. The broad peak around 420 nm corresponded well to the Soret band of TCPP in solution. The photocurrent increase with lowering the wavelength ($< \sim 450 \text{ nm}$) may be attributable to direct photoexcitation of the ITO substrate. The possible mechanism for generating anodic photocurrents in the present modified electrodes is as follows: (1) photoinduced electron transfer from the photoexcited TCPP to the C60 moiety generates a charge separated states, (2) the oxidized TCPP is reduced to the neutral form by the reduction with TEOA, and (3) the electron is transferred from the anion radical of C60 to the electrode. The photocurrent efficiencies varied with the number of TCPP layers and C60 layers. Optimization of experimental conditions and a detailed structural characterization of the electrode system are now in progress.

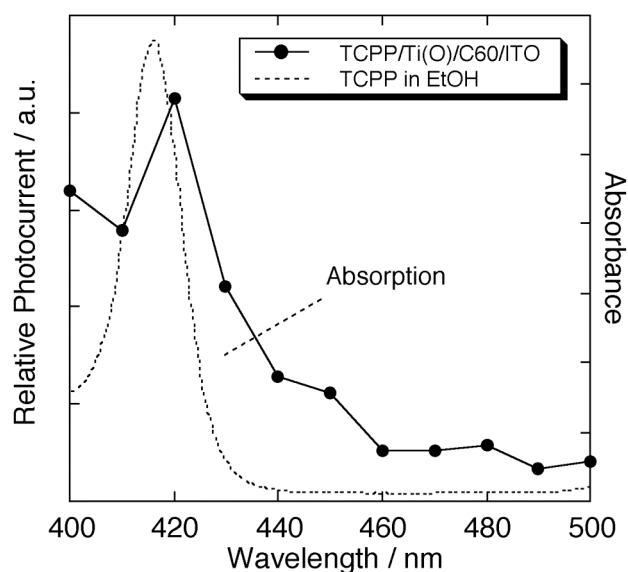


Figure 3. Photocurrent action spectrum of $\text{TCPP}/\text{Ti}(\text{O})/\text{C60}/\text{ITO}$ at 0V vs. Ag/AgCl (sat. KCl)

4. Conclusion

We preliminary demonstrated novel multilayer assemblies of porphyrin and fullerene by self-assembly and surface sol-gel processes. The photocurrent efficiencies varied with the number of TCPP layers.

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