Preparation and Photoelectrochemical Properties of Fullerene Modified ITO Electrodes Using Self-Assembled Monolayer

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Fullerene (C₆₀) immobilized indium-tin-oxide (ITO) electrodes were prepared by a technique of self-assembled monolayers (SAMs) using five compounds of alkyldiamine (NH₂(CH₂)ₙNH₂; n=4, 6, 8, 10 and 12). These C₆₀/diamine-SAMs modified ITO (C₆₀/n/ITO; n=4, 6, 8, 10 and 12) electrodes were examined in terms of properties of electrochemical and photoelectrochemical responses. The C₆₀ surface coverage of C₆₀/n/ITOs estimated was ca. 3×10⁻¹⁰ to 4×10⁻¹⁰ mol cm⁻². The stable anodic photocurrent appeared immediately after the irradiation of the C₆₀/n/ITO electrode in 0.1 M Na₂SO₄ containing 50 mM ascorbic acid (AA) as an electron sacrificer with λ = 400～600 nm, light power of 4.0～6.5 mW cm⁻² and electrode potential of −0.15 V to +0.15 V vs. Ag/AgCl (saturated KCl). The photocurrents generated by C₆₀/n/ITOs increased with the number of the methylene unit (n) except for n=12. These results have shown that increasing the length of the methylene contributes to only immobilization of C₆₀, because of highly ordered structure of diamine-SAMs.

1. Introduction

Recently, many researchers have studied on fullerene (C₆₀) thin films formed using a variety of methods as Langmuir-Blodgett (LB) techniques and evaporation.¹ These C₆₀ thin films have exhibited interesting electrochemical, photochemical and optical properties. However, the instability and the defect have disadvantaged practical application of these systems to molecular devices. Similarly, these physisorbed fullerene thin films lack the stability and uniformity at the nano-scale level. Several studies have previously reported C₆₀-containing self-assembled monolayers (SAMs) immobilized onto the surfaces of gold,²～⁴ indium-tin-oxide (ITO)⁵ and silicon dioxide.⁶ SAMs are an interesting method for constructing highly ordered and densely packed structures on substrates. But, synthesis and preparation of self-assembling compounds linkage with the C₆₀ moiety was very arduous. Therefore, another approach for immobilization of C₆₀ onto the ITO surface has been presented using prelayer of diamine SAMs.⁷ The spontaneous adsorptions of amine moiety onto ITO,⁸ gold⁹ surfaces have been reported previously. Because diamine show pronounced reactivity to both C₆₀ and ITO, they have been employed as prelayer of immobilized C₆₀.

Organic-based photovoltaic cells,¹⁰,¹¹ which mimic photoinduced multistep electron transfer processes in photosynthesis,¹²～¹⁴ have been developed in recent years. Photosynthesis is among the most characteristic examples of complicated molecular assemblies in nature. In the photosynthesis system, following multistep electron transfer takes place from the di- mer of chlorophyll to the quinines along the well-arranged pigments fixed in the protein matrix, leading to the generation of a long-lived, charge-separated state with nearly 100 % quantum yield. The importance of molecular aggregates in nature has encouraged us to assemble function molecules in artificial manner without the assist of protein. Covalent attachment of functional molecules to the terminal of SAMs has been pursed to construct well-organized molecular assemblies containing photoactive and/or electroactive molecules using fullerenes,¹⁵ ferrocenes,¹⁶ azobenzenes,¹⁷ porphylins¹⁸ and others¹⁹ onto gold electrodes.

In this work, we examine to one attempt of photovoltaic cell mimicking photosynthesis to arrange C₆₀
using SAM technique take place for protein complex of photosynthesis. And we report here the preparation, electrochemistry, and photoelectrochemistry of $C_{60}$/diamine-SAMs modified ITO electrodes.

2. Experimental Section

Figure 1 shows a schematic representation of the formation of $C_{60}$ SAMs using diamine linkages. ITO glass electrode (1 cm × 2 cm) was sonicated and rinsed with acetone, and dried by a blowing argon stream over the surface. Monolayer-modified ITO surfaces were formed by immersion in a solution of each diamine. Adsorption of the diamines (NH$_2$(CH$_2$)$_n$NH$_2$; $n$ = 4, 6, 8, 10 and 12) was carried out from absolute ethanol solution of 5 mM at 25 °C for 4 days. After soaking, the diamine/ITO electrode (hereafter n/ITO; n = 4, 6, 8, 10 and 12) was washed well by sonication in absolute ethanol, and dried with a stream of argon. The surface densities of diamine onto n/ITO were determined using imine formation between 4-nitrobenzaldehyde and amine group.20) All n/ITOs were immersed into the solution of 1250 : 1 absolute ethanol/acetic acid containing 1.6 µM 4-nitrobenzaldehyde under argon atmosphere at 50 °C for 3 h. The labeling n/ITOs were washed in absolute ethanol and sonicated in absolute ethanol for 2 min, and dried with a stream of argon. The imine-formed n/ITOs were hydrolyzed at 30 for 1 h into 500 : 1 milli-Q water/acetic acid. The recovered 4-nitrobenzaldehyde was quantified by UV-vis spectroscopy.

To immobilize of $C_{60}$ onto diamine-monolayers, the n/ITO electrodes were immersed in a 30 mM chlorobenzene solution of $C_{60}$ at 25 °C for 3 days under argon atmosphere. The $C_{60}$-immobilized ITO electrodes (hereafter, $C_{60}$/n/ITO; n = 4, 6, 8, 10 and 12) were rinsed and sonicated in chlorobenzene for 2 min, and washed with chlorobenzene and dichloromethane twice to remove physisorbed $C_{60}$ and dried with a stream of argon.

Cyclic voltammetry was performed on automatic polarization system (HSV-100, HOKUTO DENKO Co.) using a standard three-electrode cell with a modified ITO working electrode (0.283 cm$^2$), platinum wire counter electrode, and an Ag/AgCl (saturated KCl) reference electrode. Photochemical measurements were carried out automatic polarization system (HZ-3000, HOKUTO DENKO Co.) using one-compartment quartz cell (3 mL) under argon atmosphere. The cell was illuminated with monochromatic excitation light generated by irradiation system by a 500 W xenon lamp (XE-150, RITU OUYOU KOUGAKU) on a modified ITO working electrode. The photocurrent was measured in a three-electrode arrangement; a modified ITO working electrode (0.126 cm$^2$), platinum wire counter electrode, and an Ag/AgCl (saturated KCl) reference electrode. The light intensity was measured using an optical power meter (AQ-2101, ANDO).

3. Result and Discussion

The diamine monolayer formation on to the surface of ITO electrode was confirmed by the method as previously used.20) The terminal amine group of diamine prelayer was labeled by 4-nitrobenzaldehyde formed an imine. After procedure of labeling, the imine was hydrolysis incubating CH$_3$COOH/H$_2$O solution for 3 h. The amount of recovered 4-nitrobenzaldehyde was quantified with UV-vis absorption spectroscopy. Figure 2 shows the relationship of the surface densities of diamine onto n/ITO (n = 4, 6, 8, 10 and 12) electrodes and the number of methylene unit (n). The surface density of diamine was increased with increasing the number of
methylene unit. These estimated surface densities by all n/ITO were ca. 2 × 10^{-10} to 3.5 × 10^{-10} mol cm^{-2}, and these were smaller values on ITO previously reported.7, 8) These difference values of surface density might be due either to the activation treatment of ITO surface or to the hostile properties of solvent for the adsorption process.21) Figure 3 shows typical cyclic voltammograms of C_{60} in CH_{2}Cl_{2} and C_{60}/10/ITO, respectively. Cyclic voltammetry of C_{60} in CH_{2}Cl_{2} containing 0.1 M n-Bu_{4}NPF_{6} as an electrolyte with a scan rate of 100 mV s^{-1} exhibited reversible redox waves. The formal potentials of the three-redox waves were −1.071, −1.489 and −1.930 V (vs. Fc/Fc^{+}), respectively. Cyclic voltammogram of C_{60}/10/ITO showed only broad reduction waves at E_{pc} = −1.617, −2.155 V (vs. Fc/Fc^{+}), which correspond to the second and the third reductions of C_{60}. The disappearance of the oxidation waves might be due to desorption of C_{60} during negative potential sweep. The first redox wave of C_{60} did not appear on cyclic voltammograms using the C_{60}/n/ITO electrodes (n = 4, 6, 8, 10 and 12). The peak potential values of the second and third reduction were shifted by −0.077 and −0.159 V compared to that of unmodified C_{60}. This cathodic shift reflects not only the modification of C_{60} but also the special environment in the C_{60}/n/ITO electrodes.2) Indeed, similar anodic shifts of the monolayer formed ferrocenylalkanethiol were reported previously.22) From these results, there is no significant difference among the five types of C_{60}/n/ITO electrodes. Assuming that each second reduction wave on cyclic voltammograms of C_{60}/n/ITO (n = 4, 6, 8, 10 and 12) corresponds to a one-electron reduction of immobilized C_{60}, integration of the current associated with these waves corresponds to a C_{60} surface coverage of ca. 6.5 × 10^{-10} to 8.5 × 10^{-10} mol cm^{-2}. These values of C_{60} surface coverage were more larger than that previously reported.2, 7, 23) Considering the first redox wave of C_{60} was not appeared (Fig. 3), the second reduction wave on cyclic voltammograms of C_{60}/n/ITO electrodes might be due either to a two-electron one-step reduction or to a broad mixed peak area of the first and the second reduction steps of immobilized C_{60} in this cases. If the observed second reduction wave is assigned to two electrons, the values of a C_{60} surface coverage were estimated to ca. 3 × 10^{-10} to 4 × 10^{-10} mol cm^{-2}, as shown in Fig. 4. These results were slightly larger compared with the surface density (Fig. 2) that is calculated for compact monolayers of C_{60}, assuming fcc packing and an area of 100 Å^{2} molecule^{-1} : 1.9 × 10^{-10} mol cm^{-2}.23) It is considered that a physisorption of C_{60} on n/ITO electrodes remains during preparation procedure in this study.

The photochemical measurements were carried out for bare ITO, n/ITO and C_{60}/n/ITO (n = 4, 6, 8, 10 and 12) electrodes in an argon-saturated 0.1 M Na_{2}SO_{4} solution containing 50 mM ascorbic acid (AA) as an electron sacrificer. The photocurrent was measured in a three-electrode arrangement; a modified ITO working electrode (0.126 cm^{2}), platinum wire counter electrode, and an Ag/AgCl (saturated

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**Fig. 2.** Relation between surface density of alkyldiamine onto ITO and number of methylene unit (n) of alkyldiamine.

**Fig. 3.** Cyclic voltammograms of (a) C_{60} in CH_{2}Cl_{2} and (b) C_{60}/10/ITO electrode at 0.1 V s^{-1}.
Fig. 4. Relation of surface coverage of immobilized C60 and number of methylene unit (n) of alkyldiamine.

Fig. 5. Photoelectrochemical responses of (a) C60/10/ITO, (b) 10/ITO and (c) bare ITO electrode irradiated with $\lambda$=400 nm light of 4.0 mW cm$^{-2}$, AA concentration of 50 mM and applied potential $+0.1$ V.

Fig. 6. Dependence of ascorbic acid (AA) concentration to photocurrent of C60/10/ITO electrode.

KCl) reference electrode. Figure 5 shows a stable anodic photocurrent from electrolyte to the ITO electrode appeared immediately after the irradiation of the C60/10/ITO electrode with $\lambda$=400 nm, light power of 4.0 mW cm$^{-2}$ and electrode potential of $+0.1$ V vs. Ag/AgCl (saturated KCl). When the irradiation to the ITO electrode was terminated, the photocurrent fell down instantaneously to a base line current before the irradiation. The intensities of the photocurrent for C60/10/ITO were larger than those of the bare ITO or 10/ITO, indicating the involvement of C60 and AA for the photocurrent generation. Similarly, photocurrent for C60/n/ITO (n=4, 6, 8 and 12) electrodes was observed. The photochemical responses were not attenuated with the cycle of the irradiation (a period of light on was 10 s) for ten times. The intensity of photocurrent was maintained constantly during the irradiation of at least 1 h. The photocurrent increases linearly with an increasing of the concentration of AA at low concentration ($<5$ mM), and then deviates gradually from the slope, and finally becomes constant at around 50 mM, as shown in Fig. 6. The anodic photocurrent increases with an increase of positive potential applied to the C60/10/ITO electrode as a working electrode (between $-0.15$ V and $+0.15$ V) in the electrochemical cell, whereas a slight of the photocurrent was observed in the bare ITO electrode (Fig. 7). This demonstrates that the photocurrent flow from the electrolyte to the ITO electrode by way of the excited state of C60. However, when a further increase of positive potential (more than $+0.15$ V) applied to C60/10/ITO electrode, the measurement of photocurrent could not be carried out, because of significant increase of the anodic current as the dark current. And when a further decrease of negative potential (lower than $-0.15$ V) applied to C60/10/ITO electrode, because little cathodic photocurrent was observed in cell of a bare ITO, the photocurrents could not be calculated by this competition between anodic and cathodic photocurrent. The action spectrum calculated by pho-
Fig. 7. Anodic photocurrent vs. applied potential curves used by C$_{60}$/10/ITO (open circles) and bare ITO electrode (triangles).

Fig. 8. Action spectrum (open circles with solid line) and transmittance absorption spectrum (dotted line) of C$_{60}$/10/ITO. Standardized input light power was 1 mW cm$^{-2}$ at each wavelength.

Fig. 9. The dependence of the photocurrents against the number of methylene unit in C$_{60}$/n/ITO (n=4, 6, 8, 10 and 12) electrodes irradiated with $\lambda=400$ nm light of 4.0 mW cm$^{-2}$.

tocurrents of C$_{60}$/10/ITO electrode to use 1 mW cm$^{-2}$ of input irradiation power at each wavelength (400–600 nm) was compared with the transmittance absorption spectrum of C$_{60}$/10/ITO. Standardized input light power was 1 mW cm$^{-2}$ at each wavelength.

The dependence of the photocurrents against the number of methylene unit in C$_{60}$/n/ITO (n=4, 6, 8, 10 and 12) electrodes irradiated with $\lambda=400$ nm light of 4.0 mW cm$^{-2}$ is shown in Fig. 9. The photocurrents of C$_{60}$/n/ITO increase with an increasing of the number of methylene unit (n=4 to 10), the value of C$_{60}$/12/ITO decreases significantly to although a similar level of C$_{60}$/4/ITO. This relationship of the photocurrents measured using C$_{60}$/n/ITO electrodes agrees with that between the surface coverage and the number of methylene unit (Fig. 4). But, many C$_{60}$/12/ITO electrodes measured the very small photocurrent usually. The photocurrents of porphyrin SAM system, where the porphyrin assembled with different methylene unit, were reported previously.24 Those results showed that as the length of the methylene unit increases, the SAMs tend to form highly ordered structure and then to increase the photocurrents of generated by the SAM-modified gold electrodes. The phenomenon of decreasing photocurrent by C$_{60}$/12/ITO electrode was not understood, because the structural measurements (AFM, XPS, Raman spectroscopy) of these C$_{60}$/n/ITOs (n=4, 6, 8, 10 and 12) were not examined. Preliminary measurement of FTIR-RAS showed that the absorption of C-H stretching assignment region (2926 and 2860
on C60/12/ITO was diminished than that on C60/10/ITO (not data shown). Therefore, generated photocurrent of C60/12/ITO in this work might be under influence of the unusual structures for C60-immobilized SAMs onto 12/ITO with consideration of surface coverage data.

4. Conclusion

In summary, photoelectrochemical responses of C60-modified SAM/ITO electrodes using prelayer of alkyldiamine (NH2(CH2)nNH2; n = 4, 6, 8, 10 and 12) have been investigated systematically. The structural information of the C60/diamine-SAMs ITO electrodes are currently in progress. The simple preparation procedure of the C60-modified electrode implies that C60 SAMs exhibit potential for applications of material science. These results give basic information for the generation of homogeneous surface and for the progress of photovoltaic cells and sensors in addition to electron transfer in molecular assemblies.

References