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Photoelectric response of ITO electrode sensitized by single-layer C_{60}-aminodicarboxylate derivative $C_{60}(C_7H_{13}NO_4)$

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A single layer of an amphiphilic C_{60}-aminodicarboxylate ($C_{60}AC$) derivative has been fabricated on semiconducting transparent ITO electrodes with transfer ratios of about 0.90 ± 0.05 at 25 mN m^{-1} by the Langmuir–Blodgett (LB) technique. The photoelectric response of the modified electrodes has been investigated under a nitrogen atmosphere. The photocurrent action spectrum shows that the excited $C_{60}AC$ acts as a photoactive species in the photoinduced electron transfer process. Factors such as the intensity of the irradiation, concentration of reducing agent in the electrolyte solution and bias voltage have been studied. The results indicate that electrons flow from the electrolyte through LB film to the ITO electrode. The quantum yield is 3.0% under favorable conditions.

C_{60} and its derivatives are good electron acceptors.[1–3] Electron transfer from various amines[2] and semiconductor colloids[3] to photoexcited singlet and triplet C_{60} has been reported. Cast films of C_{60} on metal electrode surfaces have been found to act as n-type semiconductors.[4] C_{60} and C_{70} embedded within a lipid membrane can act both as photosensitizers for efficient electron transfer from a donor and mediators for electron transport across the membrane.[5] However, photoelectric investigations on fullerene LB films are still rare. Monolayer films of C_{60} are very sensitive to vibration, aggregate easily and are difficult to transfer onto solid substrates due to the very high hydrophobicity of the rigid ball-shaped molecules. The introduction of hydrophilic groups into the close-caged molecule can enhance the stability of these Langmuir films. Some monolayers of C_{60} derivatives were obtained and transferred onto hydrophilically pretreated substrates by carefully controlling the experimental conditions.[6] When amphiphilic C_{60} derivatives are deposited onto conducting or semiconducting electrodes by LB techniques to form organized assemblies, effective electron transfer between the materials and the electrode may be expected. It has been reported that aggregates formed in Langmuir–Blodgett films at the air–water interface possess photophysical properties that are significantly different from the monomers.[7] Previous work in our laboratory has shown that C_{60}-pyrrolidine derivatives can generate anodic photocurrents, the magnitude of which depends on the structure of the introduced groups.[8] Here we report the film formation properties of a new C_{60}-aminodicarboxylate derivative ($C_{60}AC$) and the photoelectric response of its single-layer modified ITO electrodes. The dependence of the photocurrent on some factors that may enhance or decrease the observed photocurrent was investigated. A possible mechanism for electron transfer is proposed.

Experimental

Materials and sample preparation

Ascorbic acid (AA) was reagent grade and recrystallized from water before use. Chloroform was purified by distillation. Deionized water was purified by passing through an EASY pure RF compact ultrapure water system (Barnstead Co. US).

$C_{60}AC$ was prepared by the process shown in Scheme 1. To a solution of iminodiacetic acid (5.32 g, 40 mmol) in methanol (250 ml) was added anhydrous sodium carbonate (8.48 g, 80 mmol) and methyl chloroacetate (8.68 g, 80 mmol). The mixture was stirred at room temperature for 12 h, then refluxed for another 12 h. The pH of the solution was adjusted with sodium carbonate to 8.5, then filtered. One eighth of the filtrate was taken and diluted with methanol to 50 ml. This solution, containing about 5 mmol of nitrilotriacetate, was added to a C_{60} solution (72 mg, 0.1 mmol) in toluene (250 ml). To make the solution homogeneous, more methanol was added (*ca.* 30–50 ml). The reaction flask was fitted with a condenser. The mixture was irradiated for 2.5 h with two 150 W high pressure fluorescent bulbs (of the type used in Beijing street lights). The solution began to reflux after 1 h of photolysis. The solution was treated with water twice (20 ml each time) to remove some water soluble components. The organic solvents were evaporated. The residue was chromotographed on silica gel using toluene as eluent. Unreacted C_{60} (40 mg, 0.055 mmol) and $C_{60}AC$ (6.7 mg, 0.007 mmol) were eluted as well-separated bands. δ_H(400 MHz, $CDCl_3$–CS_2) 3.76 (s, 6H), 4.15 (s, 4H), 4.72 (s, 2H), 7.11 (s, 1H); δ_C(100.6 MHz, $CDCl_3$–CS_2) 170.16 ($2CO_2Me$), 154.36, 154.19, 147.07 (1C), 146.95, 146.88 (1C), 146.44, 146.12, 146.04, 145.91, 145.86, 145.50, 145.28, 145.11, 145.07, 145.05, 144.46, 144.18, 142.96, 142.31, 142.27, 142.07, 141.81, 141.68, 141.42, 141.40, 141.36, 140.08, 139.84, 135.92, 135.63 (all signals represent 2C except those indicated), 68.13 (CH), 67.10, 57.35 (CH_2), 56.09 (CH_3), 51.17 (CH_2) (DEPT spectra located the H containing carbons); ν_{max}/cm^{-1} 527, 574, 998, 1012, 1144, 1169, 1203, 1261, 1384, 1411, 1429, 1742; *m/z* (FDMS) 895 ($M^+ + 1$); λ_{max}($CHCl_3$)/nm 257 (with shoulder centered at 328), 434 [Found (Calc.) for $C_{67}H_{13}O_4N$: C, 90.20 (89.83); H, 1.30 (1.46); N 1.38% (1.56%)].

LB film preparation

Single layers of $C_{60}AC$ were obtained using a NIMA 622 computer-controlled Langmuir trough (UK). The subphase was deionized water (20 ± 1 °C, pH 5.6, $> 18\ \Omega$). A solution of $C_{60}AC$ (6 ml, 1.5×10^{-5} mol dm^{-3} in chloroform) was carefully added dropwise to the subphase over 1 h. After evaporation of the solvent (*ca.* 30 min) the monolayer was compressed. The monolayer was deposited onto a hydrophilically pretreated transparent indium-tin oxide (ITO) glass substrate at a rate of 5 mm min^{-1} (vertical dipping) under a constant surface pressure 25 mN m^{-1}. The transfer ratio was 0.90 ± 0.05.

Photoelectrochemical and electrochemical measurements

The photocurrent measurements were carried out using a model 600 voltammetric analyzer (CH Instruments Inc., US)

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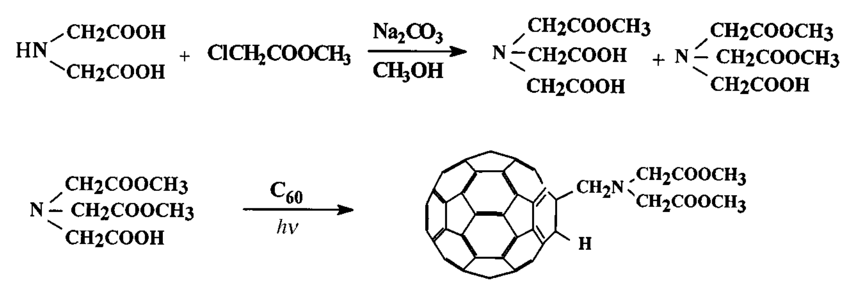

Scheme 1

and a 500 W xenon lamp (Ushio Electric, Japan). A series of filters (Toshiba, Japan) with certain band passes were used to obtain different wavelengths of incident light. The intensity of incident light was measured by a power and energy meter (Scientech 372, boulder Co., US). The IR light was filtered throughout the experiment with a Toshiba IRA-25s filter (Japan). A three-electrode cell having a flat window for illumination of the working electrode was used. The counter-electrode was Pt wire and the reference was a saturated calomel electrode. The $C_{60}AC$ LB film modified ITO electrode was used as the working electrode. KCl solution (0.1 mol dm^{-3}) was used as the electrolyte solution. Because oxygen could suppress the photocurrent, all experiments were carried out under a nitrogen atmosphere. At least eight independent monolayer-modified electrodes were used for each experiment to test the reproducibility of the photocurrent data.

Cyclic voltammograms were measured on a PAR-270 Electrochemical Analysis System (US). A three-electrode configuration was used throughout. A polished platinum electrode (0.5 mm diameter) was used as the working electrode. The counter and reference electrodes were platinum wire and Ag/AgCl, respectively. The concentration of $C_{60}AC$ was 1.0×10^{-4} mol dm^{-3}. In the cyclic voltammetry experiment, a ferrocene/ferrocenium couple ($F_C/F_C{}^+$) was used as the internal standard. All measurements were performed at ambient temperature under a nitrogen atmosphere in a 0.1 mol dm^{-3} chloroform solution of $Bu^n{}_4NPF_6$.

Results and Discussions

Modification of ITO electrodes

The π–A isotherm of $C_{60}AC$ (Fig. 1) shows that it can form stable films on an aqueous subphase due to the two hydrophilic ester groups and the nitrogen atom in the molecule. The limiting area per molecule, obtained by extrapolation of the rising portion of the isotherm to $\pi = 0$, was 95 Å^2 molecule^{-1}. This value is in good agreement with that of $C_{60}O$,[6b] indicating that the substituted group does not affect the distances between the molecule at the air–water interface and that a monolayer is probably formed. This is reasonable if the hydrophilic group is arranged under the water surface and only the hydrophobic fullerene ball stands on the surface. The film could be easily transferred on to a hydrophilic ITO plate.

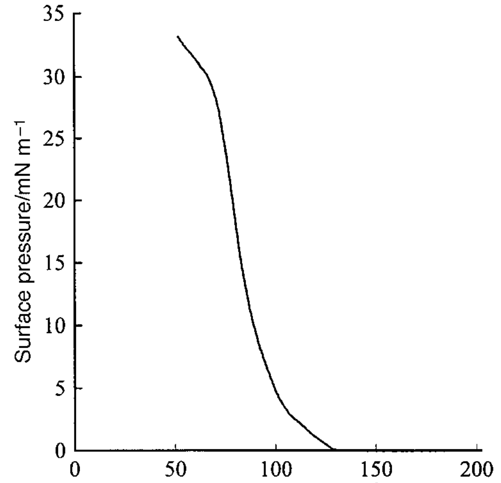

Fig. 1 Surface pressure–area (π–A) isotherm of $C_{60}AC$ at the air–water interface (293 ± 1 K, pH 5.6)

Photoelectric response of the LB films

A typical photocurrent response of a single-layer $C_{60}AC$ film as a function of excitation wavelengths is shown in Fig. 2. The absorption spectrum is also shown. Owing to a large forbidden gap (3.8 eV[9]), the background anodic photocurrent due to ITO excitation was negligibly small in the visible region. Since the absorbencies of C_{60}-pyrrolidine films on a quartz substrate in the near-ultraviolet region are several times higher than those in the visible region,[10,6a] 404 nm was chosen as the exciting source throughout the experiment. At this wavelength the anodic photocurrent of bare ITO is below 4 nA.

The photocurrent was measured under nitrogen atmosphere. If oxygen was bubbled through the electrolyte, *ca.* 40% of the photocurrent could be suppressed. However, this process is reversible in the case of $C_{60}AC$. When nitrogen was bubbled again to remove oxygen, the photocurrent rose gradually to the value before addition of oxygen. Under a nitrogen atmosphere, an anodic photocurrent ranging from 38–52 nA was observed when the $C_{60}AC$-modified electrodes were illuminated by 404 nm light of 2.10 mW cm^{-2} intensity (after transmitting the ITO electrode) for a series of eight independent samples (Table 1). The quantum yield is *ca.* 0.76%. The action spectrum resembles the absorption spectrum, which indicates that $C_{60}AC$ is the photoactive species.

The photocurrent ranges of $C_{60}AC$ without a bias voltage or electron donor overlap to quite an extent (Table 1). This

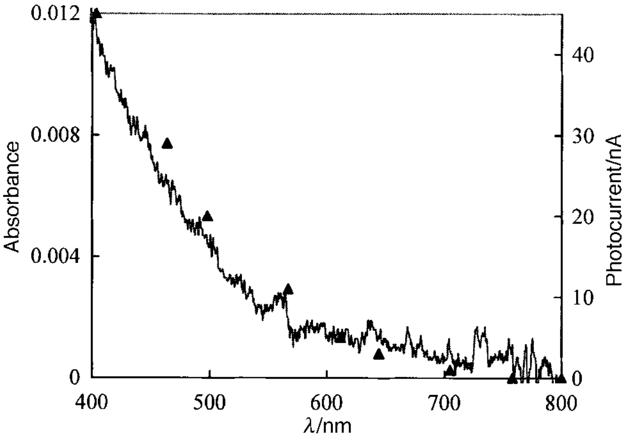

Fig. 2 (▲) Photocurrent (0.1 mol dm^{-3} KCl, pH 5.6, no bias voltage, light intensity = 2.10 mW cm^{-2}, $\lambda = 404$ nm) and (full line) absorption spectrum for a monolayer of $C_{60}AC$ on ITO

Table 1 Three sets of data from eight independent modified electrodes

Samples	photocurrent^a/nA KCl, no bias, no AA	KCl, no bias, AA	KCl, bias, AA
1	49	86	180
2	47	80	182
3	52	92	180
4	50	84	181
5	46	86	179
6	39	90	180
7	44	94	183
8	35	92	183
av.	45	88	181

^{a}[KCl] = 0.1 mol dm^{-3}, bias = 0.2 V, [AA] = 38 mmol dm^{-3}.

may be due to the influence of the produced oxygen, the release rate of oxygen from the electrolyte solution and the different adsorption abilities of oxygen on the surface of the modified electrodes.

Characteristics of photocurrent *versus* voltage and light intensity

In order to determine the direction of the current flow, the effect of bias voltage was investigated. A linear relationship with a slope of 0.10 nA mV^{-1} between the observed photocurrent and the bias voltage in the range −0.35 to 0.4V *vs.* SCE was observed (Fig. 3). The photocurrent increases as the positive bias of the electrode increases. This is a result of the applied positive voltage having the same polarity to the photocurrent. A linear relationship between the photocurrent and light intensity (from 0.28 to 2.10 mW cm^{-2}) is also observed. The photocurrent increases as the light intensity increases. Photocurrent saturation was not observed. It may be that the intensities used cannot supply enough photons to make all molecules active and contribute to photocurrent.

Effect of an electron donor in the electrolyte solution

The effect of the electron donor (AA) also gives evidence for the direction of electron transfer. The photocurrent increases with the concentration increase of AA in the electrolyte, and a limiting value at high concentration (beginning at *ca.* 38 mmol dm^{-3}, Fig. 4) is reached. This indicates that the quantum yield for effective electron transfer is higher in the presence of the reducing agent. Under the favorable conditions determined above, *e.g.* 0.2 V bias and 38 mmol dm^{-3} AA, the photocurrent at 404 nm was four times higher than in pure 0.1 mol dm^{-3} KCl electrolyte solution. The quantum yield of single-layer C_{60}AC can be increased to 3.0%. The photocurrent is stable in the presence of AA and on/off switching of the light can be repeated tens of times with very little attenuation (Fig. 5).

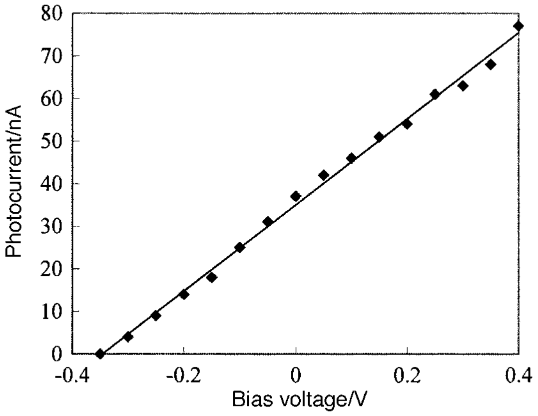

Fig. 3 Photocurrent *vs.* electrode potential for LB film of C_{60}AC on ITO (0.1 mol dm^{-3} KCl, pH 5.6, light intensity = 2.10 mW cm^{-2}, λ = 404 nm)

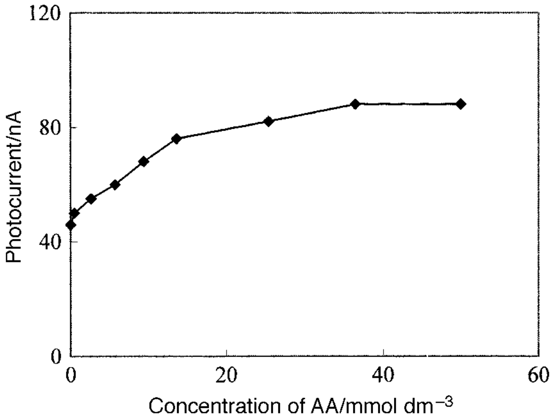

Fig. 4 Photocurrent as a function of ascorbic acid concentration for LB film of C_{60}AC on ITO (0.1 mol dm^{-3} KCl, no bias voltage, light intensity = 2.10 mW cm^{-2}, λ = 404 nm)

Mechanism of photocurrent generation from the C_{60}AC–ITO electrode

In order to examine the electron transfer process for the anodic photocurrent, the energies of the relevant electronic states must be estimated. The redox energy level for the excited state of C_{60}AC, E° ($^*C_{60}AC/C_{60}AC^{\cdot -}$), is situated above the E° ($C_{60}AC/C_{60}AC^{\cdot -}$) level by the excitation energy Δ^*E.[11]

$$E^{\circ}({}^*C_{60}AC/C_{60}AC^{\cdot -}) = E^{\circ}(C_{60}AC/C_{60}AC^{\cdot -}) + \Delta^*E$$

Since the functionalization of C_{60} leads only to a minor change in the excitation energy,[12] and the reduction potential of the

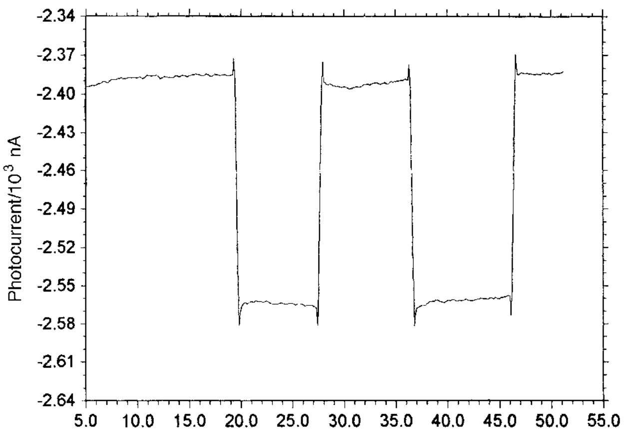

Fig. 5 Representative photocurrent obtained from a C_{60}AC monolayer-modified electrode (0.2 V bias voltage, 38 mmol dm^{-3} AA, 0.1 mol dm^{-3} KCl electrolyte solution, light intensity = 2.10 mW cm^{-2}, λ = 404 nm)

Table 2 Half-wave potentials^a of C_{60} and its derivatives by cyclic voltammetry

Compound	potential/V $E^{0/-1}$	$E^{-1/-2}$	$E^{-2/-3}$	ref.
C_{60}	−1.13	−1.50	−1.95	13
$C_{60}(C_3H_4O)$	−1.23	−1.58	−2.11	13
$C_{60}(C_4H_8O_2)$	−1.21	−1.57	−2.11	13
C_{60}AC	−1.26	−1.76	−2.22	this work

^{a}V *vs.* ferrocene/ferrocenium couple. Bu$^n{}_4$NPF$_6$ (0.1 mol dm^{-3}) in chloroform. Scan rate = 0.1 V s^{-1}.

ground state of $C_{60}AC$ is only negatively shifted 0.13 V compared with C_{60} (Table 2),[13] the reduction potential of $^*C_{60}AC$ is expected to be slightly lower than that of $^*C_{60}$ (*ca.* 1.01 V for $^3C_{60}/C_{60}^{\cdot -}$; 1.44 V *vs.* SCE for $^1C_{60}/C_{60}^{\cdot -}$).[12] Note that these data are based on solution values rather than aggregates in a closely packed film, for which the appropriate parameters are unknown.

It should be emphasized that the photocurrent of the LB films were measured in aqueous KCl (except for the experiments on the effect of AA) without any additional reducing agent. The excited state of $C_{60}AC$ must have been reduced by H_2O. The possible reaction scheme is then given by:

$$C_{60}AC \xrightarrow{h\nu} {}^*C_{60}AC$$

$$^*C_{60}AC + H_2O \longrightarrow (C_{60}AC)^{\cdot -} + O_2$$

or

$$^*C_{60}AC + AA \longrightarrow (C_{60}AC)^{\cdot -} + AA^{\cdot +}$$

$$(C_{60}AC)^{\cdot -} \longrightarrow C_{60}AC + e^-$$

When irradiated the $C_{60}AC$ molecules are excited to the excited state, $^*C_{60}AC$ is reduced to the anion by water because the reduction potential of $^*C_{60}AC$ is higher than the reduction potential of H_2O ($E_{O_2/H_2O} = 0.66$ V *vs.* SCE at pH 5.6). The electron transfer from $C_{60}AC^{\cdot -}$ to the electrode completes the circuit for the observed photocurrent. When an electron donor (AA) is added to the electrolyte, it gives electrons to the $C_{60}AC$ more readily than water because the reduction potential of AA (−0.21 V *vs.* SCE) is lower than E_{O_2/H_2O}.

The suppression of the photocurrent in the presence of oxygen may be due to two processes: (i) the quenching of $^3C_{60}AC$[14] or (ii) the trapping of photogenerated conduction electrons.[11] It is well-known that in solution the excited singlet state of fullerenes is efficiently converted to the excited triplet state by rapid and quantitative intersystem crossing.[12] However, in a closely packed assembly singlet–singlet annihilation may predominate. The detailed mechanism is still being investigated.

Conclusion

A new amphiphilic C_{60}-aminodicarboxylate derivative was shown to readily form stable films at the air–water interface which can be deposited onto an ITO substrate to form a photoactive electrode. The photocurrent spectrum clearly indicates that $C_{60}AC$ acts as the photoactive species. The anodic photocurrent increases when AA is added or a positive bias voltage is applied, indicating that electrons flow from the electrolyte through the LB film to the ITO. These results show that single-layer sensitized semiconductor electrodes made from fullerene derivatives can initiate effective photoinduced electron transfer.

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