

Photosensitization of Nanocrystalline TiO₂ Electrode Modified with C₆₀ Carboxylic Acid Derivatives

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C₆₀ carboxylic acid derivatives can be readily adsorbed on the surface of nanocrystalline TiO₂ film. The C₆₀ carboxylic acids adsorbed on nanocrystalline TiO₂ films act as charge-transfer sensitizer. The electron transport from TiO₂ to the C₆₀ derivatives results in the generation of the cathodic photocurrent. The short-circuit photocurrent of a C₆₀ tetracarboxylic acid is 0.45 $\mu\text{A}/\text{cm}^2$ under 464 nm light illumination. The photoelectric behaviour of ITO electrodes modified by the same C₆₀ carboxylic acids is different from that of the modified TiO₂ electrodes, and shows anodic photocurrent.

Keywords C₆₀, photocurrent, titanium dioxide

Introduction

Fullerenes and their derivatives exhibit remarkable photochemical,^{1,2} photophysical,³⁻⁶ and charge transfer properties.^{7,8} Photodriven electron transfer from various electron donors such as amine,⁴ semiconductor colloids,⁹ and conjugated polymers⁸ to C₆₀ has been reported. Most of the photophysical studies of fullerenes involved solution system or thin polymer films. The investigation of fullerenes and their derivatives as a monolayer on a solid surface such as metal oxide is limited.^{9,10} Previous work in our laboratory has shown that the modified semiconductor ITO electrodes by amphiphilic C₆₀ derivatives exhibit effective photoinduced electron transfer at the electrode/electrolyte interface.^{11,12} The observed anodic photocurrent corresponds to the electrons transfer from electrolyte through fullerene derivatives to the electrode.

Photosensitization of thin semiconductor films with inorganic^{13,14} and organic dyes^{15,16} regained a considerable interest after the pioneering work of Gratzel and co-workers.¹⁴ The large surface area and high porosity of the nanocrystalline TiO₂ films enhance the light-harvesting capability of the adsorbed pigment and also allow the penetration of the electrolyte right up to the supporting electrode that aids in charge separation process, thus leading to a high power conversion efficiency of the cell.^{17,18} In such a model, excited dye molecules injected electrons to the conduction band of TiO₂ and an anodic photocurrent was observed.

Here we report the modification of nanocrystalline TiO₂ electrodes with C₆₀ carboxylic acids and their photocurrent generation. A different electron transfer pathway from the most dye sensitized TiO₂ electrodes is observed.

Experimental

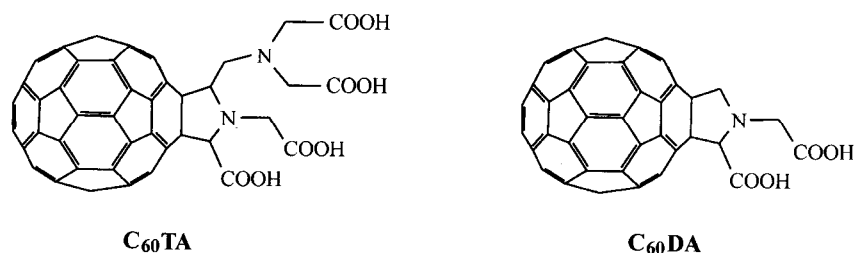
Materials

C₆₀ dicarboxylic acid (C₆₀DA) and C₆₀ tetracarboxylic acid (C₆₀TA), Scheme 1, were prepared by the hydrolysis of their ester precursors² using a procedure similar to Hirsch's.¹⁹ Under nitrogen atmosphere, 70 mL of toluene was added to a reaction flask containing 100 mg of C₆₀TA tetramethyl ester or C₆₀DA dimethyl ester and 160 mg of NaH. The mixture was stirred for 3.5

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Scheme 1 Chemical structures of **C₆₀DA** and **C₆₀TA**

h at 60°C, then 3 mL of methanol was added. After stirring for 10 min the precipitate was separated and treated with 20 mL of H₂SO₄ (2 mol/L). The product was filtered, washed with water and dried under vacuum. **C₆₀TA**: Yield: ~ 90%. ¹H NMR (400 MHz, C₆D₆/DMSO-*d*₆) δ: 6.55 (s, 1H), 6.24–6.37 (m, 1H), 5.62 (d, *J* = 16 Hz, 1H), 5.02 (d, *J* = 16 Hz, 1H), 4.76 (dd, *J* = 4, 12 Hz, 1H), 4.38–4.49 (m, 1H), 3.84 (s, 4H); IR ν: 1732, 1635, 1630, 1430, 1396, 1359, 1219, 1190, 527 cm⁻¹; Electrospray MS: 1010 (M⁺); MALDI-TOF MS: 1033 (M⁺ + Na), 1010 (M⁺). Anal. Calcd for C₆₀C₁₀H₁₄N₂O₈·H₂SO₄·CH₃C₆H₅: C 77.00; H 2.00; N 2.33; Found: C 77.57; H 1.77; N 2.35. **C₆₀DA**: Yield: ~ 90%. ¹H NMR (400 MHz, C₆D₆/DMSO-*d*₆) δ: 4.08 (d, *J* = 17 Hz, 1H), 4.28 (d, *J* = 17 Hz, 1H), 4.53 (d, *J* = 9 Hz, 1H), 5.02 (d, *J* = 9 Hz, 1H), 5.44 (s, 1H). ¹³C NMR (100.6 MHz, C₆D₆/DMSO-*d*₆) δ: 171.59, 171.0, 155.34, 154.22, 153.56, 151.66, 147.84, 147.74, 147.38, 146.97, 146.84, 146.76, 146.74, 146.72, 146.54, 146.51, 146.49, 146.47, 146.32, 146.14, 146.11, 146.05, 146.02, 145.95, 145.91, 145.85, 145.77, 145.73, 145.68, 145.12, 144.94 (2C), 144.86, 143.50, 143.48, 143.13, 143.07 (2C), 142.68, 142.65, 142.61, 142.54 (4C), 142.42, 142.27 (2C), 142.23, 142.22, 140.78, 140.73, 140.13, 139.89, 138.44, 137.07, 136.64, 136.19, 76.63, 73.04, 69.90, 65.87, 52.69; IR ν: 1598, 1402, 1140, 1121, 1107, 1067, 1051, 1022, 527 cm⁻¹. MALDI-TOF MS: 865 (M⁺); Anal. Calcd for C₆₀C₅H₇NO₄·2H₂SO₄: C 73.24; H 1.03; N 1.31. Found: C 73.53; H 1.16; N 1.27.

Chloroform and DMSO were purified by distillation. Deionized water purified by passing through an EASY pure RF compact ultrapure water system was used in all experiments.

The substrates for the monolayer deposition of **C₆₀DA** and for the preparation of nanocrystalline TiO₂ film were transparent indium-tin oxide (ITO) coated glass. The sheet resistance was ~ 30 Ω/sq. TiO₂ colloidal solution and TiO₂ films were prepared by following the procedure developed by Graetzel and co-workers.¹⁴ The thickness of the resulting films was about 0.4–0.6 μm. The prepared nanocrystalline electrodes were modified with **C₆₀DA** or **C₆₀TA** by dipping them directly in an 6 × 10⁻³ mol/L DMSO solution of **C₆₀DA** or **C₆₀TA**. To minimize rehydration of the TiO₂ surface from moisture in ambient air, the electrodes, while still warm (80–100°C) from annealing, were soaked to the **C₆₀DA** or **C₆₀TA** solution. After dipping for about 12–15 h at room temperature, the electrodes were then thoroughly washed with DMSO and dried in a stream of N₂.

LB film preparation

Monolayer LB film of **C₆₀DA** was obtained on a NIMA 622 computer-controlled Langmuir trough (UK). The subphase was deionized water (20 ± 1°C, pH 5.6, > 18 MΩ·cm). Spreading solution was prepared by dissolving **C₆₀DA** in minimum DMSO and then diluted with chloroform to a concentration of 1.82 × 10⁻⁵ mol/L. 5 mL of the above solution was carefully deposited on the clean subphase in about 1 h. After the evaporation of the solvent over 30 min the floating film was compressed at a rate of 40 cm²/min and the surface pressure-area (π-A) isotherm was recorded. The limiting area per molecule, obtained by extrapolation of the rising portion of the isotherms to π = 0, was 0.92 nm²/molecule (Fig. 1) which is in agreement with the typical monolayer area of other amphiphilic C₆₀ derivatives.^{20–22} The monolayer was deposited onto the hydrophilic pretreated transparent ITO glass substrate at a rate of 5 mm/min (vertical dipping) under a constant

surface pressure of 20 mN/m. The transfer ratios were 0.90 ± 0.05 .

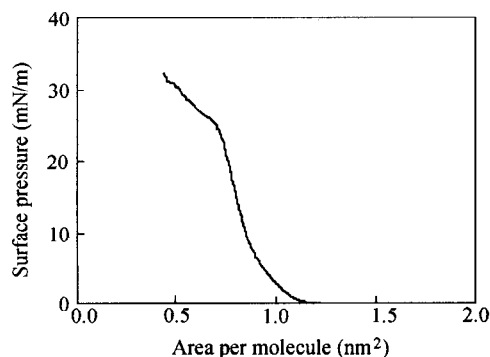


Fig. 1 Surface pressure-area isotherm of $C_{60}DA$ at the air/water interface, 293 ± 1 K, pH 5.6.

Electrochemical and photoelectrochemical measurements

Cyclic voltammetry was measured on an EG/G PAR-273 potentiostat/galvanostat with model 270 electrochemical software. A three-electrode configuration was used throughout. The measurements were carried out in DMSO solution by using a platinum electrode (0.5 mm diameter) as working electrode. The counter and reference electrodes were a platinum wire and a Ag/AgCl, respectively. The concentration of $C_{60}DA$ or $C_{60}TA$ was 1×10^{-3} mol/L. The potentials were referenced to the internal standard ferrocene/ferrocenium couple (F_c^+/F_c). The measurements were performed at ambient temperature under nitrogen atmosphere in a 0.1 mol/L solution of $(n-Bu)_4NClO_4$.

The photocurrent measurements were carried out on a model 600 voltammetric analyzer (CH Instruments Inc. USA) and a 500 W xenon lamp (Ushio Electric, Japan) as a light source. 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 (Sciencetech 372, boulder Co. USA). 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. KCl solution (0.1 mol/L) was used as the electrolyte solution. All experiments were carried out under a nitrogen atmosphere.

Results and discussion

Photoelectrochemical behavior of $C_{60}DA$ LB film modified ITO electrode

An ITO/ $C_{60}DA$ electrode could generate an anodic photocurrent when it is used as working electrode in a photoelectrochemical cell. Fig. 2 shows the dependence of the photocurrent on illumination wavelengths (400–800 nm) and the absorption spectrum of an ITO/ $C_{60}DA$

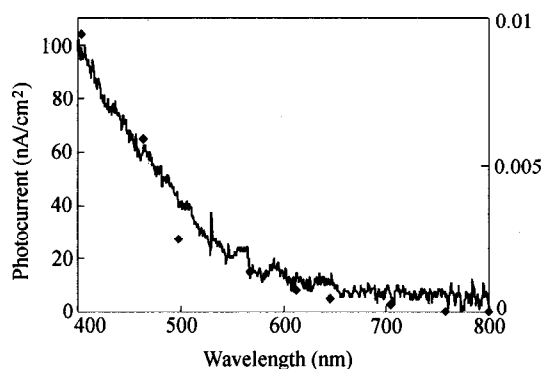


Fig. 2 Photocurrent action spectrum (\blacklozenge) (0.1 mol/L KCl, pH 5.6) and absorption spectrum (—) of a monolayer LB film of $C_{60}DA$ on ITO.

electrode. The resemblance of the two spectra indicates that $C_{60}DA$ is photoactive species in the electron transfer process. Under the illumination of 404 nm light, the measured short-circuit photocurrent was *ca.* 104 nA/cm². The observed anodic photocurrents increase as the positive bias of the electrode increase and are always anodic under potential range from -0.1 – 0.4 vs. SCE

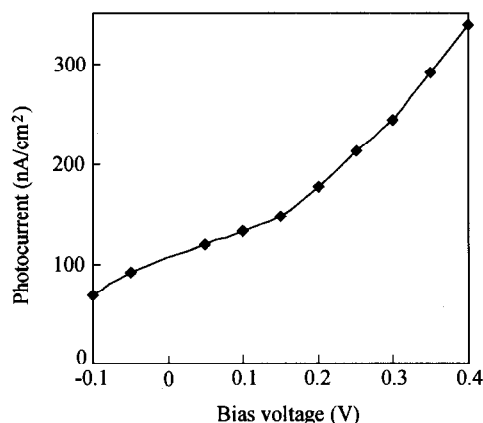


Fig. 3 Photocurrents vs. bias voltages for the monolayers of $C_{60}DA$ on ITO (0.1 mol/L KCl, $\lambda = 404$ nm).

(Fig. 3). This indicates that the applied positive voltage has the same polarity as the photocurrent. These phenomena are similar to the photoelectric response of other $C_{60}DA$ derivatives modified ITO electrodes and the same electron transfer pathway is expected.^{11,12} Table 1 gives the photocurrent densities of $C_{60}DA$ and $C_{60}TA$.²³

Photoelectrochemical behavior of $TiO_2/C_{60}DA$ and $TiO_2/C_{60}TA$ electrodes

Photocurrent generation

To avoid direct excitation of the semiconductor supporter ($E_g = 3.2$ eV), above 450 nm light was used as excitation source. Fig. 4 shows the wavelength depen-

dence of the photocurrent of $TiO_2/C_{60}DA$ and $TiO_2/C_{60}TA$ along with their absorption spectra. Compared with the absorption of $C_{60}DA$ on ITO (Fig. 2), surface complexation of TiO_2 by $C_{60}DA$ produces an enhanced intensity in its absorption. This is due to the large surface area of nanocrystalline TiO_2 film, and the quantity of the molecules absorbed on its surface is much larger than that on the smooth surface of ITO. A charge-transfer transition between $C_{60}DA$ and TiO_2 is also possible.²⁴ The resemblance of the two spectra implies that $C_{60}DA$ is responsible for the generation of the photocurrent. Similar spectra were obtained for $TiO_2/C_{60}TA$ electrode (Fig. 4B). Under the illumination of the 464 nm light, the short circuit photocurrent of $TiO_2/C_{60}DA$ and $TiO_2/C_{60}TA$ were 312 and 447 nA/cm², respectively. The

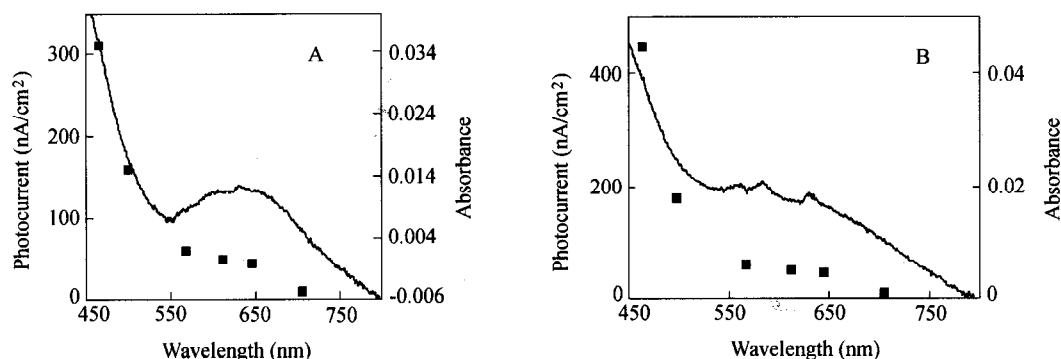


Fig. 4 Photocurrent action spectra (0.1 mol/L KCl, pH 5.6) and absorption spectra (—) of a $TiO_2/C_{60}DA$ electrode (A) and a $TiO_2/C_{60}TA$ electrode (B).

cathodic photocurrent corresponds to the electron transfer from TiO_2 to the excited state of fullerene derivatives. It has been reported that fullerene derivatives can be reduced on TiO_2 surface under illumination.²⁵ This electron transfer pathway is contrary to the ITO/ $C_{60}DA$ and ITO/ $C_{60}TA$ systems in which anodic photocurrents are observed (Table 1).

Table 1 Photocurrent densities (nA/cm²) of $C_{60}DA$ and $C_{60}TA$ on ITO and TiO_2

Compd.	TiO_2 ($\lambda = 464$ nm)	ITO ($\lambda = 404$ nm)
$C_{60}DA$	312	-104*
$C_{60}TA$	447	-83

* (—) is a indication of anodic photocurrent.

The difference for these two systems results from the different position of the conduction bands of ITO (-0.24 V *vs.* SCE) and TiO_2 (-0.74 V *vs.* SCE).

From the first reduction potentials of $C_{60}DA$ (Table 2, -0.94 V *vs.* F_c^+/F_c or -0.48 V *vs.* SCE) and $C_{60}TA$ (-0.92 V *vs.* F_c^+/F_c or -0.46 V *vs.* SCE) and their excitation energy (~ 1.77 eV),³ their reduction potentials of excited state can be estimated to be 1.29 and 1.31 V *vs.* SCE, respectively.

Table 2 Half-wave potentials of $C_{60}DA$ and $C_{60}TA$ by cyclic voltammetry

Compd.	$E^{0/1}$	$E^{-1/2}$	$E^{-2/-3}$
$C_{60}TA$	-0.92	-1.43	-2.13
$C_{60}DA$	-0.94	-1.23	-1.82

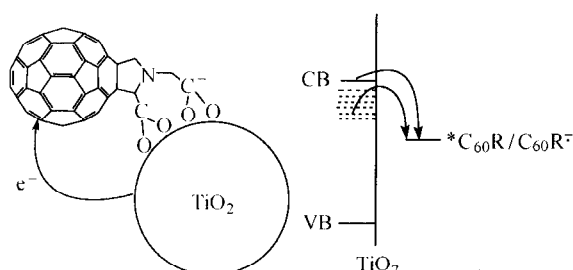
V *vs.* F_c^+/F_c . ($n-Bu$)₄NPF₆ (0.1 mol/L) in DMSO.

Scan rate = 0.1 V/s.

With these data a possible electron transfer process for the generation of sensitized photocurrent in $TiO_2/C_{60}DA$ or $TiO_2/C_{60}TA$ system can be considered as follow:

upon photoexcitation of fullerene derivative, electron transfer from the conduction band or surface states of TiO_2 to the excited state of C_{60}DA or C_{60}TA leads to the formation of C_{60}DA^- or C_{60}TA^- , and then electron transfer to the electrolyte results in the generation of the observed cathodic photocurrent. Scheme 2 shows the possible electron transfer for this system.

Scheme 2 Schematic diagram showing electron transfer process



The above electron transfer mechanism is different from many dye-sensitized nanocrystalline TiO_2 electrodes in which excited dye molecules inject electrons to the conduction band of TiO_2 . However, as shown recently by Maggini and coworkers,²⁶ it is impossible that C_{60} derivatives inject electrons to the conduction band of TiO_2 under the conditions. The irreversible oxidation of C_{60} on TiO_2 can only be achieved by a biphotonic electron ejection from C_{60} under laser irradiation.¹⁰ Unlike a conventional Schetty photoelectrochemical system in which the charge carrier being separated in the semiconductor space charge layer, a space charge layer and a band bending is not likely to be formed in nanoporous semiconductor electrodes due to the small particle size.²⁷ Hodes *et al.*²⁸ has reported that the photocurrent at the same nanocrystalline CdS electrode could switch direction behaving as *p*- or *n*-doped semiconductors, depending on the electrolyte and on the semiconductor surface. C_{60} carboxylic acid acted as a strong electron acceptor when it was adsorbed on the TiO_2 surface. The electron transport from the conduction band or surface states in the band gap region to the excited state of C_{60} derivatives may be highly favored. The exact state of the donor orbital is unclear. It is not known whether the donor is the conducting electrons or the electrons in the surface states associated with Ti^{4+} atoms, which may be strongly coupled to the conduction band.²⁹ The existence,

of trapping states with different energies has been observed.^{30,31}

The larger photocurrent of $\text{TiO}_2/\text{C}_{60}\text{TA}$ compared with $\text{TiO}_2/\text{C}_{60}\text{DA}$ system may result from its polycarboxyl structure. The carboxylates serve as a link group between C_{60}DA and C_{60}TA and the surface of oxide to establish good electronic coupling between their excited state and TiO_2 film. Laser photolysis experiments have shown that the surface complexation of TiO_2 by benzoic acid derivatives drastically accelerates the electron transfer from the conduction band of the colloidal oxide to acceptors in solution.²⁴

Photocurrent-Voltage characteristics

The current-voltage curves for $\text{TiO}_2/\text{C}_{60}\text{DA}$ and $\text{TiO}_2/\text{C}_{60}\text{TA}$ systems are shown in Fig. 5. Aqueous 0.1 mol/L KCl and 464 nm monochromatic light were used. The maximum cathodic photocurrent was observed around 0.1 V *vs.* SCE for both compounds. When the positive bias was increased further or negative bias voltage was applied, a decrease of photocurrents was observed. We do not have a good explanation for this phenomenon at present. Since electron transfer rate depends on the overlap of the donor states in the semiconductor with acceptor states of the excited sensitizer, an optimal overlap between these states must be reached when 0.1 V bias is applied. It has been reported that applied potential can influence the energy level of colloidal TiO_2 electrode³² and the mechanism of electron transfer in a

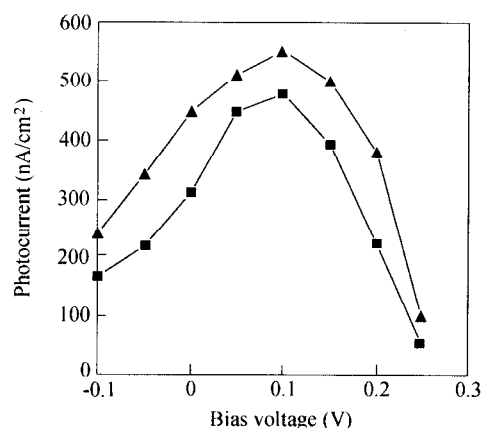


Fig. 5 Photocurrents *vs.* bias voltages (0.1 mol/L KCl, $\lambda = 464$ nm) for $\text{TiO}_2/\text{C}_{60}\text{DA}$ (■) and $\text{TiO}_2/\text{C}_{60}\text{TA}$ (▲).

TiO₂, ruthenium complex and viologen electrode is altered upon application of sufficiently negative potential.³³ Further work is needed to clarify the present observation.

Conclusion

The photoelectric behavior of nanocrystalline TiO₂ film can be modulated by the surface modification with C₆₀ carboxylic acid derivatives. When C₆₀ carboxylic acids were adsorbed on the surface of TiO₂ electrode, the direction of electron transfer at the electrode-electrolyte interface was drastically influenced. The experimental results show that C₆₀ carboxylic acids act as strong electron acceptors and TiO₂ electrode exhibits the behavior of a p-doped semiconductor. The electron transfer from TiO₂ to C₆₀ moiety results in the generation of the cathodic photocurrent.

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