

Photocurrent generation at a fullerene self-assembled monolayer-modified gold electrode cast with a polyurethane membrane

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Two photoelectrochemical cells based on C₆₀-SAM-modified gold electrodes have been fabricated and their photoelectric responses with Ar- or O₂-saturated electrolyte investigated. High quantum yields under visible light illumination and without an external electron sacrifier were observed. A new approach consisting of casting an ion-selective polyurethane membrane on the C₆₀-SAM leads to improved stability of the photocurrent generation.

Exploitation of the rich optical and electrical behaviour of fullerenes has become a field of intensive investigation.^{1–3} In particular, the ability of the carbon sphere to act as a strong electron acceptor⁴ and to participate efficiently in photo-induced electron transfer processes has given rise to increasing development of fullerene-based electronic devices. In this respect, the modification of semiconductor or metal electrodes with fullerene thin films by Langmuir–Blodgett (LB) techniques,^{5–7} sandwich-type conjugated polymer/C₆₀ heterojunctions,^{8–10} or self-assembled monolayers (SAMs)^{11,12} has revealed promising photoelectrochemical properties,¹³ including good solar energy conversion efficiencies. As ordered, stable and processable assemblies, SAMs provide particularly attractive tools for the realisation of fullerene-based photovoltaic devices. Recently, the electrochemical and photoelectrochemical properties of C₆₀-derived SAMs on gold electrodes have been investigated.¹¹ Stable anodic photocurrents and fairly high quantum yields under monochromatic illumination in the presence of a sacrificial electron donor were observed. Here, we report the efficient photoelectrochemical response of a C₆₀-SAM-modified gold electrode, together with a novel approach to increase its stability using a cast solvent–polymeric membrane. We found high quantum yields for photoinduced electron transfer and propose a charge separation mechanism.

We recently reported the preparation and electrochemical properties of a SAM of C₆₀-alkanethiol conjugate **1** (Fig. 1) on gold (referred to as I/Au in the following) and its use as an inner electrode in solid-contacted ion-selective electrodes when cast with a potassium-selective polyurethane membrane (referred to

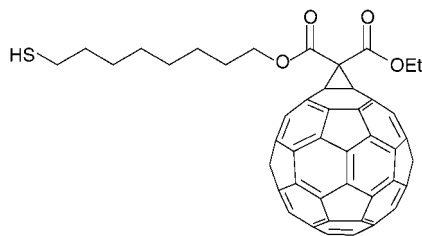


Fig. 1 Molecular structure of **1**.

as Mb/I/Au).¹⁴ I/Au showed a half-wave potential of $E_{1/2} = -680$ mV (all potentials are given vs. Ag/AgCl and measured in a solution of 0.1 M Bu₄NPF₆ in CH₂Cl₂) for the first reduction of the fullerene, with surface-confined behaviour for electron transfer, and a surface coverage of 3.9×10^{-10} mol cm⁻². Additionally, long-term stability measurements under ambient conditions revealed the enhanced stability of Mb/I/Au electrodes, with a long-term drift (over 100 h) of 85 μ V h⁻¹, as compared to 360 μ V h⁻¹ without the polyurethane membrane. In the course of our study, we observed a photoelectrical response to ambient light. As a matter of course, we studied the photoelectrochemical characteristics of two cells composed of I/Au or Mb/I/Au as working electrodes, a platinum counter electrode, and an Ag/AgCl reference electrode in Ar- or O₂-saturated 10⁻³ M aqueous KCl solutions.¹⁵

Both systems showed immediate and reversible anodic short-circuit photocurrent and open-circuit photovoltage upon illumination of the modified gold electrode. In contrast, no photocurrent was observed for a bare gold electrode without the SAM of **1** under the same conditions. As shown in Fig. 2, the action spectra of I/Au and Mb/I/Au between 300 and 700 nm correlate strongly with the solid-state absorption spectrum of a 49 nm thin spin coated film of **1** on sapphire. This demonstrates that a photoinduced electron transfer occurs through the C₆₀-SAM acting as the photoactive species. Moreover, the solid film gives rise to an increased spectral weight in the visible domain as compared to the absorption in solution.¹⁶ From the photocurrent action spectra, we can see that the spectral weight in the visible is increased with respect to

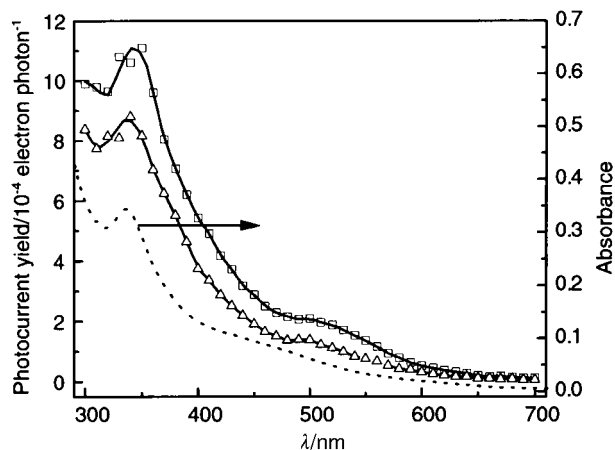


Fig. 2 Photocurrent action spectra for cells with I/Au (Δ) and Mb/I/Au (\square) as working electrodes¹⁵ (Ar-saturated 10⁻³ M aqueous KCl solution, pH 5.6, no applied voltage) and absorption spectrum of a 49 nm thick spin coated film of **1** on sapphire (dotted line).

the disordered film, which is important for solar energy conversion. The typical order of magnitude of the photocurrent ranged from 0.1 to 1 nA with an incident monochromatic light ($\lambda \pm 5$ nm) intensity of 4.3 to $67 \mu\text{W cm}^{-2}$. Moreover, the photocurrent yield for Mb/1/Au is higher than that of 1/Au, indicating that the membrane not only increases the stability of the SAMs, but also has a favourable effect on the light conversion efficiency. The direction of the photocurrent flow was found to be anodic—*i.e.* from the electrolyte to the gold electrodes—by applying a bias voltage (from -0.4 to $+1.2$ V) to 1/Au and Mb/1/Au under monochromatic illumination in Ar-saturated electrolyte (Fig. 3). In both systems, the anodic photocurrent starts to flow at a certain potential (zero-current potential V_0), then increases as the bias voltage becomes more positive, reaching saturation over *ca.* $+1$ V and *ca.* $+1.2$ V bias for 1/Au ($V_0 \approx -0.17$ V) and Mb/1/Au ($V_0 \approx -0.40$ V), respectively. At this point, it should be noted that the photoelectrochemical response of Mb/1/Au is higher than that of 1/Au when no bias is applied (*cf.* Fig. 2), but becomes somewhat lower under positive bias.

Compared to similar photoelectrochemical cells,^{6,7,11,17–19} this is the first time that such saturation behaviour has been observed. The anodic photocurrent increases linearly in the range $+0.2$ to $+1$ V (with a slope of -77 nA V^{-1}) for 1/Au and from $+0.5$ to $+1.1$ V (with a slope of -68 nA V^{-1}) for Mb/1/Au. Besides the generation of an anodic photocurrent, a cathodic photocurrent could also be seen for 1/Au with applied potentials lower than V_0 . With a view to determining the effect of air, and in particular of oxygen, on the photocurrent generation, some atmosphere-controlled experiments were performed. When O_2 was bubbled into the electrolyte solution, the photocurrent at saturation was reduced by *ca.* 4 and 11 times for 1/Au and Mb/1/Au, respectively, but could reversibly recover its initial value on subsequent Ar bubbling. Under O_2 -saturation conditions, the photocurrent saturation occurred at a less positive bias (*ca.* $+0.5$ V) for electrode 1/Au, but followed the same course as in Ar-saturated electrolyte between -0.4 and $+0.5$ V. On the other hand, a strong suppression of the photocurrent was observed for Mb/1/Au in the presence of O_2 with only a slight increase with forward bias. Under optimal conditions—*i.e.* $+1.2$ V bias voltage and Ar-saturated electrolyte—one can estimate the quantum yields based on the number of photons absorbed by the SAMs of **1** in the photoelectrochemical cells without external electron sacrificer. Hence, taking into account the estimated absorbance²⁰ of the modified gold electrodes, the incident light intensity and the photocurrent density generated upon monochromatic illumination at 500 nm (Fig. 3), the quantum yields were calculated

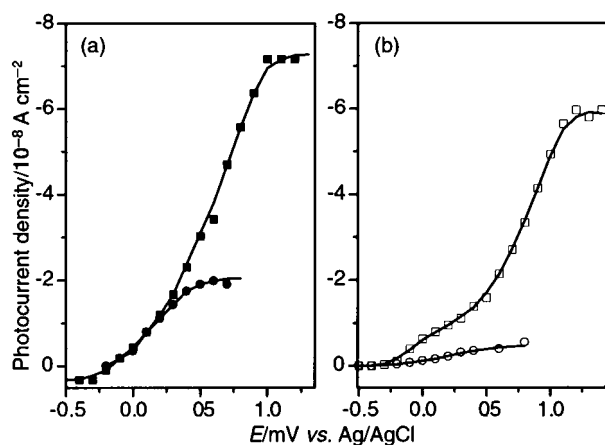


Fig. 3 Photocurrent vs. bias potential applied at 1/Au (a) (■: Ar- and ●: O_2 -saturated 10^{-3} M aqueous KCl solutions, pH 5.6) and Mb/1/Au (b) (□: Ar- and ○: O_2 -saturated 10^{-3} M aqueous KCl solutions, pH 5.6) electrodes under monochromatic illumination ($\lambda = 500 \pm 5$ nm, $6.7 \times 10^{-5} \text{ W cm}^{-2}$).

to be 31% for 1/Au and 25% for Mb/1/Au. Comparatively, both cells present high quantum yields, at least two times higher than previously reported for similar photoelectrochemical cells based on C_{60}^- or porphyrin-based SAMs,^{11,17} LB films,^{6,7} or lipid bilayers,^{21–23} and comparable to the highest value given for artificial photosynthetic systems on gold electrodes.¹⁸ These results confirm that C_{60} conjugate **1** acts as an efficient photosensitiser, owing to its small reorganisation energy in photoinduced electron transfer.^{24,25}

In light of these experimental results and previous reports on C_{60} -based LB films on indium–tin oxide,^{6,7} a mechanism for the anodic photocurrent generation is proposed in Fig. 4. The excited singlet state $^1\text{C}_{60}^*$ of **1**, generated upon illumination, relaxes to the triplet state $^3\text{C}_{60}^*$ in near quantitative yield through a very efficient intersystem crossing.²⁶ The anodic photocurrent is then generated by electron transfer from the C_{60}^- radical anion in **1**, resulting from reductive quenching of the excited triplet state $^3\text{C}_{60}^*$ by water, to the gold electrode. Water is presumed to be the electron donor since it has a suitable redox potential ($E^\circ = +0.69$ V at pH 5.5)²⁷ for oxidation by $^3\text{C}_{60}^*$, and no other electron sacrificer is present in the system. On this assumption, the generation of an anodic photocurrent and photochemically induced O_2 -evolution should be the net result of the photoelectrochemical processes at 1/Au and Mb/1/Au. This hypothesis is currently under investigation.

Based on this mechanistic proposal, further insight into the observed photoelectrochemical properties was obtained. High quantum efficiencies at 500 nm can be explained by an adequate distance (determined by the alkyl chain length in **1**) between the fullerene core and the metal electrode, corresponding to a good compromise between little quenching of the C_{60} excited states by energy transfer to the gold electrode¹⁸ and fast kinetics of electron transfer. The membrane has proved to ensure improved stability of the SAMs and higher photoelectric conversion efficiency without applied bias (Fig. 2). This might express a favourable matrix effect reducing deactivation processes such as triplet–triplet or singlet–singlet annihilation,²⁸ fullerene self-quenching^{29–31} or quenching of C_{60} excited states by the gold electrode. However, it is still unclear why the generated photocurrent is lower for Mb/1/Au than for 1/Au under positive bias, and why the presence of the membrane also renders the photoelectrochemical cell more sensitive towards O_2 . The effect of O_2 in both cells can be rationalised by energy-transfer quenching of $^3\text{C}_{60}^*$ forming singlet oxygen,³² and/or trapping of photogenerated electrons.³³ The levelling behaviour of the photocurrent corresponds to the maximum number of electrons that can be transferred from the SAM to the gold electrode. This limitation is imposed by the illumination intensity and by the competition between charge separation and recombination. In the case of Mb/1/Au, the

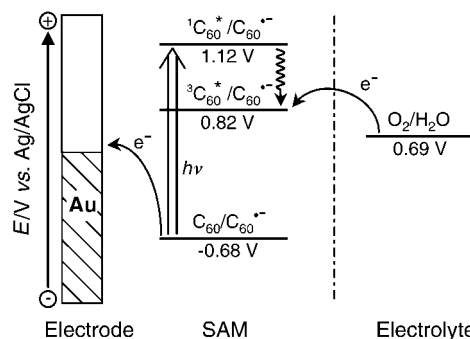


Fig. 4 Schematic representation of the electron transfer mechanism for anodic photocurrent generation in 1/Au and Mb/1/Au cells (redox potentials of excited states are estimated by taking into consideration the redox potential of 1/Au measured in CH_2Cl_2 and the excitation energy²⁵).

photocurrent saturation might additionally be limited by the diffusion of the redox species through the membrane. For O₂-saturated electrolytes, the additional quenching pathways preventing charge separation have been described above.

In summary, we have developed two photoelectrochemical cells based on C₆₀-derived SAMs, exhibiting high quantum efficiencies with respect to the previously observed fast rate of electron transfer. Deposition of a polyurethane membrane on the SAM showed an improved stability and efficiency of the photoelectric response under unbiased conditions. However, the photocurrent was found to be reduced compared to the SAM only system when a positive bias was applied and/or in the presence of oxygen. The fact that water probably acts as the electron sacrifier together with the precise elucidation of the effect of the membrane on the photocurrent generation are under investigation.

Acknowledgements

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- 14 M. Fibbioli, K. Bandyopadhyay, S.-G. Liu, L. Echegoyen, O. Enger, F. Diederich, P. Bühlmann and E. Pretsch, *Chem. Commun.*, 2000, 339; Composition of the membrane: valinomycin (10 mg), potassium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (4.1 mg), tetradodecylammonium tetrakis(4-chlorophenyl)borate (11.5 mg), bis(2-ethylhexyl) sebacate (330.2 mg), Tecoflex[®] (661.7 mg). A membrane of 60 μm thickness was obtained by casting 2.5 mg of these components dissolved in 50 μL THF and fully characterised.
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