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Photocurrent responses at dye sensitised ultrathin polyelectrolyte multilayers supported on gold electrodes

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The photoelectrochemical behaviour of ionic conducting ultrathin multilayers formed by sequential deposition of poly-L-lysine and poly-L-glutamic acid on modified gold electrodes is investigated upon sensitisation by zinc meso-tetrakis(*p*-sulfonatophenyl)porphyrin.

The development of photoactive materials exhibiting low-dimensionality is expected to heavily rely on self-assembling processes of organic materials.[1] This new path requires the design of molecular components with the appropriate architecture and functionality for efficient light harvesting, charge separation and collection. Indeed, a distinctive aspect of molecular photovoltaics with respect to semiconductor technology is that these three fundamental processes can take place in different physical domains. A fine example is given by dye sensitised nanocrystalline solar cells, in which the photon capture is performed by the adsorbed dyes and the subsequent ultrafast injection into the mesoporous film leads to efficient charge separation.[2,3] However, a major drawback of this approach is the convoluted path for the photogenerated charge carriers, often featuring a high density of electrically isolated segments acting as recombination centres. Recently, efficient carrier mobility has been observed in self-assembled discotic liquid crystal hexa-*per*-hexabezocoronene.[4] This material forms rod like structures perpendicular to the substrate, showing excellent intracolumnar charge transport.

In this report, we shall describe the photoelectrochemical responses of a new class of dye sensitised system based on ultrathin polypeptide multilayers in which charge transport is performed by mobile redox species. The rationale behind this approach is that ionic transport in molecular system provides an efficient trap-free mean for collection of photogenerated charges. Stable multilayer systems can be developed on gold surfaces by sequential deposition of poly-L-lysine (p-Lys) and poly-L-glutamic acid (p-Glu).[5,6] The Au surface is initially modified by a self-assembled monolayer of 11-mercaptoundecanoic acid (11-MUA), while the alternate cationic p-Lys and anionic p-Glu polyelectrolyte layers are held together by electrostatic forces. Previous reports show that the average thickness increases by approximately 2 nm per layer.[6] This multilayer system effectively blocks the Au surface and no electron transfer can be observed to redox couples present in organic electrolyte solution. However, by introducing hydrophilic redox couples such as hexacyanoferrate into the multilayers, the system exhibits a metallic-like behaviour in which the corresponding Fermi level is fixed by the redox potential of the confined couple.[7] The results described here show that photoreduction of fullerene (C_{60}) in chlorobenzene by ultrathin porphyrin sensitised polypeptide multilayers ionically assembled on Au electrodes manifest itself as photocurrent responses.

The preparation of the polypeptide multilayers were based on the method described by Corn and co-workers.[5,6] Gold slides (1 cm^2) were introduced in 10^{-3} mol dm^{-3} ethanolic solution of 11-MUA for over 12 h. The 9 layer ionic assembly was fabricated by sequentially dipping the modified Au electrode in 1 g dm^{-3} aqueous solutions of p-Lys and p-Glu pH 8.5 (phosphate buffer) for 15 min, starting and ending with a p-Lys layer. Subsequently, the multilayer assembly was introduced into an equimolar solution of hexacyanoferrate-(II) and -(III) (10^{-3} mol dm^{-3}) pH 5.6 (phosphate buffer) for 15 min. The sensitisation was performed by dipping the film in a 10^{-3} mol dm^{-3} aqueous solution of the sodium salt of zinc meso-tetrakis(sulfonatophenyl)porphyrin (ZnTPPS). After each individual step of the film preparation, the films were copiously rinsed with water (Milli-Q system) and dried over an Ar stream. The ZnTPPS sensitisation of the film was verified by the absorption spectrum obtained on transparent glass slides. The Soret and Q-bands of the adsorbed ZnTPPS appeared *ca.* 20 nm red shifted with respect to the absorption spectra of a diluted aqueous solution of the porphyrin, indicating a certain degree of aggregation in the film.

The supporting electrolyte in the chlorobenzene phase was 5 mol dm^{-3} bis(triphenylphosphoanylidene)ammonium tetrakis(pentafluorophenyl)borate.[8] The reference electrode employed for all measurements was Ag/AgCl. The junction between the reference electrode and the organic electrolyte was established by an aqueous electrolyte containing 10^{-2} mol dm^{-3} LiCl and 10^{-3} mol dm^{-3} bis(triphenylphosphoranylidene)ammonium chloride. Photocurrent measurements were performed with a homemade potentiostat. The illumination was provided by the 442 nm line of a CW He–Cd laser.

Photocurrent transient measurements in the presence of 10^{-3} mol dm^{-3} C_{60} at various potentials are shown in Fig. 1. The magnitude of the negative photocurrent increases with decreasing potentials. No photoresponses are observed in the absence of C_{60} or ZnTPPS. Furthermore, no faradaic responses are developed in the dark within the entire polarisable window. This is consistent with the difference of redox potential between hexacyanoferrate and the first reduction state of C_{60} *i.e.* 0.36 and −0.64 V *vs.* SHE, respectively. It should also be indicated that no photocurrent responses were observed in the absence of the hexacyanoferrate couple. This result confirms the role of the

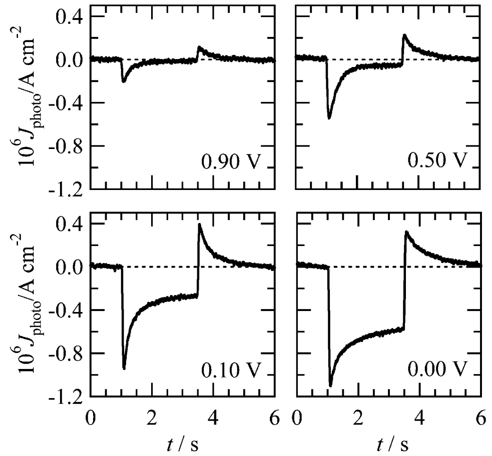

Fig. 1 Photocurrent transient responses at various potentials in the presence of 10^{-3} mol dm^{-3} of C_{60} in chlorobenzene. The photon flux was 3.5×10^{16} cm^{-2} s^{-1} at 442 nm.

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confined redox couple as the carrier of photogenerated charges across the film.

The transients in Fig. 1 exhibit a decay after the initial photocurrent as well as a positive overshoot upon switching off the illumination. These features are similar to those associated with back electron transfer commonly observed at porphyrin sensitised liquid|liquid interfaces.[8–12] In this case, the reduced C_{60} can inject an electron into the oxidised porphyrin or hexacyanoferrate(III) in the polypeptide layer. This short-circuit process generates a positive current which decreases the overall efficiency of the photoreaction.

The dependence of the initial photocurrent on the photon flux at various potentials is illustrated in Fig. 2. The linear dependence observed at all potentials confirms that the mechanism involves a competition between quenching of the porphyrin dye and relaxation of the excited state. No depletion of the ground state porphyrin or self-quenching effects appears to take place at these illumination intensities. Taking the initial photoresponses at 0 V, it can be estimated an incident photon to current efficiency (IPCE) of 0.02%, corresponding to a quantum efficiency of approximately 0.15%.[13] This rather low quantum efficiency indicates that the heterogeneous electron injection to C_{60} in solution is in competition with various interfacial processes.

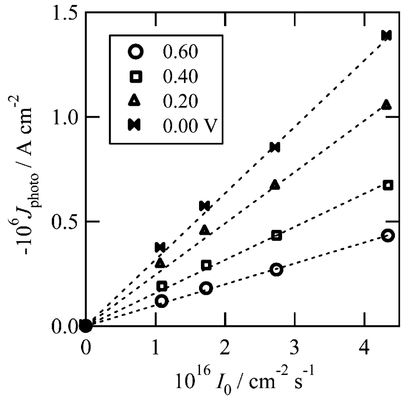

Fig. 2 Initial photocurrent responses as a function of the photon flux at various applied potentials.

Considering that the redox potentials of triplet state and the reduced ground state of the porphyrin are similar,[14] the photocurrent responses can be rationalised by two alternative mechanisms depending on which redox couple act as quencher. For instance, in mechanism I [eqns. (1)–(3)]:

$$\mathrm{ZnTPPS_{film}} + h\nu \rightarrow \mathrm{ZnTPPS^*_{film}} \qquad (1)$$

$$\mathrm{ZnTPPS^*_{film}} + [\mathrm{Fe(CN)_6}^{4-}]_{\mathrm{film}} \rightarrow \mathrm{ZnTPPS^-_{film}} + [\mathrm{Fe(CN)_6}^{3-}]_{\mathrm{film}} \qquad (2)$$

$$\mathrm{ZnTPPS^-_{film}} + [\mathrm{C_{60}}]_{\mathrm{org}} \rightarrow \mathrm{ZnTPPS_{film}} + [\mathrm{C_{60}}^-]_{\mathrm{org}} \qquad (3)$$

hexacyanoferrate acts as quencher of the excited ZnTPPS [eqn. (2)] and the heterogeneous electron transfer associated with the photocurrent responses involves the reduced porphyrin and C_{60} [eqn. (3)]. In this case, the photocurrent efficiency is determined by the competition between step (3) and electron transfer from $\mathrm{ZnTPPS^-}$ to hexacyanoferrate(III) in the film [eqn. (4)]:

$$\mathrm{ZnTPPS^-_{film}} + [\mathrm{Fe(CN)_6}^{3-}]_{\mathrm{film}} \rightarrow \mathrm{ZnTPPS_{film}} + [\mathrm{Fe(CN)_6}^{4-}]_{\mathrm{film}} \qquad (4)$$

Furthermore, the photocurrent relaxation in the millisecond time scale is associated with eqn. (5):

$$[\mathrm{C_{60}}^-]_{\mathrm{org}} + [\mathrm{Fe(CN)_6}^{3-}]_{\mathrm{film}} \rightarrow [\mathrm{C_{60}}]_{\mathrm{org}} + [\mathrm{Fe(CN)_6}^{4-}]_{\mathrm{film}} \qquad (5)$$

Mechanism II is based on heterogeneous electron transfer from the excited porphyrin to the acceptor in the organic phase followed by reduction of the oxidised dye by hexacyanoferrate(II) [eqns. (6) and (7)]:

$$\mathrm{ZnTPPS^*_{film}} + [\mathrm{C_{60}}]_{\mathrm{org}} \rightarrow \mathrm{ZnTPPS^+_{film}} + [\mathrm{C_{60}}^-]_{\mathrm{org}} \qquad (6)$$

$$\mathrm{ZnTPPS^+_{film}} + [\mathrm{Fe(CN)_6}^{4-}]_{\mathrm{film}} \rightarrow \mathrm{ZnTPPS_{film}} + [\mathrm{Fe(CN)_6}^{3-}]_{\mathrm{film}} \qquad (7)$$

In this scheme, the photocurrent magnitude is determined by the ratio of heterogeneous quenching and decay of the excited state. In addition to step (5), back electron transfer in mechanism II can also take place [eqn. (8)]:

$$\mathrm{ZnTPPS^+_{film}} + [\mathrm{C_{60}}^-]_{\mathrm{org}} \rightarrow \mathrm{ZnTPPS_{film}} + [\mathrm{C_{60}}]_{\mathrm{org}} \qquad (8)$$

In summary, we believe that the photocurrent responses described here open new alternatives for developing ultrathin photoelectrodes featuring ionic transport of photogenerated charges. A major challenge to be addressed is the enhancement of the efficiency and rectification of the electron injection across the multilayer|electrolyte boundary. Future strategies involve the incorporation of supramolecular components such as porphyrin triads,[15,16] featuring a substantial electronic overlap between the redox components and the sensitiser unit.

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