A photoelectrochemical solar cell composed of supramolecular nanoclusters of lithium encapsulated fullerene and zinc sulphonated meso-tetraphenylporphyrin exhibits significant enhancement in the photoelectrochemical performance as compared with the reference system containing only a single component.

Photoelectrochemical cells (PECs) have been widely investigated as a next-generation solar cell because of their simple structure.1–3 The photoinduced charge separation between the excited state of dye and the electrode plays an important role in improvement of PEC performance. In the natural photosynthetic reaction centre, the efficient photoinduced electron transfer occurs to give a long-lived charge separated (CS) state with high quantum yield.4 Extensive efforts have so far been devoted to design and synthesize electron donor–acceptor linked molecules to achieve efficient photoinduced charge separation.6,7 However, the synthetic difficulty of the covalently linked donor–acceptor molecule has precluded the development of simple photovoltaic devices using such model compounds.1,2 The supramolecular approaches for PECs are also investigated, however, there was no report of supramolecules with a strong binding between neutral porphyrins and fullerenes.

We have recently designed and synthesized simple electron donor–acceptor supramolecular complexes composed of lithium ion encapsulated fullerene (Li+@C60) and sulphonated meso-tetraphenylporphyrin (MTPPS4–: M = Zn, H2), which have strong 1:1 supramolecular binding due to the cation–anion and π–π interactions (K = ~105 M–1).8 Photoexcitation of the supramolecule exhibited extremely slow charge-recombination of the CS state (τ = 0.3 ms) in benzonitrile (PhCN).8 Li+@C60 has been reported to act as a more effective electron acceptor than pristine C60.9 The driving force of photoinduced electron transfer from MTPPS4– to the triplet excited state of Li+@C60 is highly positive (–ΔGET = 0.98 eV for ZnTPPS4– and 0.67 eV for H2TPPS4– in polar PhCN),8 which is large enough to afford the CS states even under the non-polar environment in nanoclusters.

We report herein photovoltaic cells using Li+@C60–MTPPS4– nanoclusters, which are assembled on the optically transparent electrode (OTE) of nanostructured SnO2 (OTE/SnO2). The photoelectrochemical behaviour of the nanostructured SnO2 film of supramolecular nanoclusters between Li+@C60 and MTPPS4––Li+@C60 showed significantly higher than the single component films of MTPPS4– or Li+@C60 clusters, denoted OTE/SnO2–(MTPPS4––Li+@C60)n or OTE/SnO2–(Li+@C60)n (Scheme 1).

A solution of Li+@C60–MTPPS4– supramolecule was prepared by mixing Li+@C60PF6 (2.5 × 10–3 M) and (Bu4N+)4 MTPPS4– (2.5 × 10–4 M) in PhCN. The mother PhCN solution of 1 mL was injected to an acetonitrile (MeCN) solution (3 mL) to produce the suspension containing the supramolecular

\[ \text{Li}^+@\text{C}_6\text{O}_3 + \text{MTPPS}^4– \rightarrow \text{Li}^+@\text{C}_6\text{O}_3{\cdot}\text{MTPPS}^4– \]

Scheme 1 Schematic image of a photoelectrochemical cell of OTE/SnO2–Li+@C60–MTPPS4–.
nanoclusters [(MTPPS$^4$-Li$^+@C_{60})_n]. The suspension of (MTPPS$^4$-Li$^+@C_{60})_n$ was transferred into a cuvette, in which the two electrodes OTE and OTE/SnO$_2$ were placed and kept at a distance of 5 mm using a Teflon spacer. Then, application of the DC electric field ($\sim 100$ V cm$^{-1}$) resulted in the deposition of (MTPPS$^4$-Li$^+@C_{60})_n$ from the suspension to the electrode surface and the formation of a robust thin film of OTE/SnO$_2$-{(MTPPS$^4$-Li$^+@C_{60})_n$} as documented by discoloration of the suspension and the simultaneous coloration of the OTE/SnO$_2$ electrode. For reference purposes, a thin film of only Li$^+@C_{60}$ or MTPPS was analogously deposited onto the electrode surface to form OTE/SnO$_2$-(Li$^+@C_{60}$) or OTE/SnO$_2$-(MTPPS)$_n$.

Steady-state UV-vis absorption spectroscopy was used to follow the deposition of the MTPPS$^4$-Li$^+@C_{60}$ supramolecular material onto the electrode surface. The UV-vis absorption spectra of OTE/SnO$_2$-{(MTPPS$^4$-Li$^+@C_{60})_n$} are shown in Fig. 1, exhibiting significant broadening as compared with those in PhCN solutions of MTPPS$^4$. Such broadening behaviour indicates that the molecular environment on the OTE/SnO$_2$ surface is significantly perturbed because of the aggregation of the porphyrin molecules or the supramolecules by $\pi$-stacking. Thus, MTPPS$^4$-Li$^+@C_{60}$ is successfully deposited on OTE/SnO$_2$. The broad absorption band at 725 nm shown in Fig. 1a may be assigned to the charge-transfer band of the OTE/SnO$_2$ electrode. For reference purposes, a thin film of only Li$^+@C_{60}$ or MTPPS was analogously deposited onto the electrode surface to form OTE/SnO$_2$-(Li$^+@C_{60}$) or OTE/SnO$_2$-(MTPPS)$_n$.

TEM was used to evaluate the topography of an OTE/SnO$_2$-{(MTPPS$^4$-Li$^+@C_{60})_n$} film as shown in Fig. 2. The (MTPPS$^4$-Li$^+@C_{60})_n$ films are composed of closely packed MTPPS$^4$ and Li$^+@C_{60}$ composite clusters of about 80 nm in size, which renders a nanoporous morphology to the film. The cluster sizes were also evaluated by the dynamic light scattering (DLS) measurements (see Fig. S1 in the ESI†). The grape bunch morphology of the cluster assembly thus provides a high surface area to the electrophoretically deposited film of Li$^+@C_{60}$ clusters. As indicated earlier, charging of porphyrin and fullerene moieties in the DC electric field plays an important role in the growth and deposition process. These films are quite robust and can be washed with organic solvents to remove any loosely bound MTPPS$^4$ and Li$^+@C_{60}$ nano-assemblies.

Photoelectrochemical measurements were performed using a standard two-electrode system consisting of a working electrode and a Pt wire gauze electrode in air-saturated MeCN containing 0.5 M LiI and 0.01 M I$_2$ (Scheme 1). In order to evaluate the response towards the photocurrent generation, a series of photocurrent action spectra were recorded. The IPCE (incident photon-to-photocurrent efficiency) values were calculated by normalizing the photocurrent values for incident light energy and intensity and using eqn (1),

$$\text{IPCE (\%) = } \frac{100 \times 1240 \times i_{sc} (I_{inc} \times \lambda)}{I_{inc}} \quad (1)$$

where $i_{sc}$ is the short circuit photocurrent (A cm$^{-2}$), $I_{inc}$ is the incident light intensity (W cm$^{-2}$) and $\lambda$ is the wavelength (nm). The maximum IPCE values of OTE/SnO$_2$-(Li$^+@C_{60}$)$_n$ (black spectrum in Fig. 3a) and OTE/SnO$_2$-(ZnTTPPS$^4$)$_n$ (blue spectrum) are only 5% (425 nm) and 22% (445 nm), respectively. In contrast to the reference experiments, the IPCE value of OTE/SnO$_2$-(Li$^+@C_{60}$)$_n$ is much higher than the sum of the two individual IPCE values of the individual systems OTE/SnO$_2$-(ZnTTPPS$^4$)$_n$ and OTE/SnO$_2$-(Li$^+@C_{60}$)$_n$ in the visible region. The maximum IPCE value attained in these experiments was 77% at 450 nm. The high IPCE value at the Q-band region was also observed to be 50% at 570 nm. Such a high IPCE value indicates that photocurrent generation is initiated via photoinduced electron transfer in supramolecules between ZnTTPPS$^4$ and Li$^+@C_{60}$, followed by the charge transport to the collective surface of the OTE/SnO$_2$ electrode (Scheme 1). When ZnTTPPS$^4$ was replaced by H$_2$TTPPS$^4$, a significantly low IPCE value of 7% was observed at 440 nm (Fig. 3b) probably because of the self-aggregation of H$_2$TTPPS$^4$ without binding with Li$^+@C_{60}$.13

Fig. 1 UV-vis absorption spectra of PhCN solutions of MTPPS$^4$ (black) and electrodes of OTE/SnO$_2$-{MTPPS$^4$-Li$^+@C_{60}$}$_n$, (red), M = (a) Zn and (b) H$_2$.

Fig. 2 TEM images of (a) Li$^+@C_{60}$-ZnTTPPS$^4$ and (b) Li$^+@C_{60}$-H$_2$TTPPS$^4$ nanoclusters.

Fig. 3 Photocurrent action spectra of (a) OTE/SnO$_2$-(ZnTTPPS$^4$-Li$^+@C_{60}$)$_n$ (red), OTE/SnO$_2$-{MTPPS$^4$-Li$^+@C_{60}$}$_n$ (blue) and OTE/SnO$_2$-(Li$^+@C_{60}$)$_n$ (black) and (b) OTE/SnO$_2$-(H$_2$TTPPS$^4$-Li$^+@C_{60}$)$_n$. Electrolyte: 0.5 M LiI and 0.01 M I$_2$ in MeCN-PhCN (3 : 1 v/v).
We have also evaluated the power characteristics of the OTE/SnO₂-(H₂TPPS⁴⁺–Li⁺@C₆₀)₀ electrode (Fig. S2 in the ESI†). The power conversion efficiency, η, is calculated using eqn (2):¹²

\[ \eta = \frac{FF \times I_{sc} \times V_{oc}}{W_{in}} \]

in which the fill factor (FF) is defined as \( FF = \frac{[V]_{max}/I_{sc} \cdot V_{oc}}{V_{oc}} \). The fill factor is the short-circuit photocurrent. OTE/SnO₂-(ZnTPPS⁴⁺–Li⁺@C₆₀)₀ has an overall η value of 2.1% at an input power (\( W_{in} \)) of 28 mW cm⁻², whereas FF = 0.37, \( V_{oc} = 460 \) mV and \( I_{sc} = 3.4 \) mA cm⁻² in the OTE/SnO₂-(ZnTPPS⁴⁺–Li⁺@C₆₀)₀. Note that the η value is two orders of magnitude greater than that of the previously reported simple porphyrin and C₆₀ composite system (≈ 0.03%).¹² Such a significant enhancement of the η value demonstrates that the strong ordering in the clusters and the efficient charge separation in (ZnTPPS⁴⁺–Li⁺@C₆₀)ⁿ improved the light energy conversion properties.

In order to clarify the photocurrent generation mechanism, we examined formation of the CS state \([\text{ZnTPPS}^{4+}–\text{Li}⁺@\text{C}_6\text{O}_3]⁻⁻\) by nanosecond laser flash photolysis measurements. Time-resolved transient absorption spectra of (ZnTPPS⁴⁺–Li⁺@C₆₀)₀ dispersed in a deaerated MeCN–PhCN solution (3 : 1 v/v) are shown in Fig. 4a, which clearly exhibit a broad absorption band at around 1035 nm.⁵⁻⁶ This is diagnostic of formation of Li⁺@C₆₀ upon laser irradiation. Thus, photoinduced electron transfer occurs from ZnTPPS⁴⁺ to Li⁺@C₆₀ in the composite cluster to produce the CS state \([\text{ZnTPPS}^{4+}–\text{Li}⁺@\text{C}_6\text{O}_3]⁻⁻\). The absorption profile of \([\text{ZnTPPS}^{4+}–\text{Li}⁺@\text{C}_6\text{O}_3]⁻⁻\) recorded at 1035 nm is shown in Fig. 4b. The first-order decay kinetics (inset of Fig. 4b) corresponds to back electron transfer from Li⁺@C₆₀⁻⁻ to (ZnTPPS⁴⁺⁺⁻¹), affording a rate constant of back electron transfer \( k_{\text{RET}} = 4.6 \times 10^3 \) s⁻¹. The lifetime of the CS state is 220 μs, which is long enough to inject an electron from Li⁺@C₆₀⁻⁻ of the CS state to the SnO₂ electrode before the charge recombination. Such a long-lived CS state was further detected by EPR under photoinirradiation of an MeCN–PhCN solution (1 : 3 v/v) containing \([\text{ZnTPPS}^{3+}–\text{Li}⁺@\text{C}_6\text{O}_3]₀ \) at 77 K. The EPR signal was observed at \( g = 2.0020 \), which is attributable to the mixture of the porphyrin radical cation (\( g = 2.002 \)) and Li⁺@C₆₀⁻⁻ (\( g = 2.0014 \)) (see Fig. S3a in the ESI†).¹⁵ When ZnTPPS⁴⁺ was replaced by H₂TPPS⁺, the transient absorption bands due to the CS state was significantly smaller than the case of ZnTPPS⁴⁺ (Fig. S4, ESI†).

This is the reason why the IPCE value of OTE/SnO₂–(H₂TPPS⁴⁺–Li⁺@C₆₀)₀ was low as shown in Fig. 3b.

Based on the above-mentioned results, the photocurrent generation is initiated by photoinduced electron transfer from ZnTPPS⁴⁺ to Li⁺@C₆₀ in the cluster to produce the CS state, \([\text{ZnTPPS}^{3+}–\text{Li}⁺@\text{C}_6\text{O}_3]⁻⁻\). The reduced Li⁺@C₆₀⁻⁻ (Li⁺@C₆₀⁻⁻) \( \Delta \text{E}(\text{Li}⁺@\text{C}_6\text{O}_3/\text{Li}⁺@\text{C}_6\text{O}_3⁻⁻) = 0.14 \) V vs. SCE⁸⁻⁹ injects electrons into the conduction band of SnO₂ (0.2 V vs. SCE),¹¹ whereas the oxidized ZnTPPS⁺⁺ \( \Delta \text{E}(\text{ZnTPPS}^{2+}/\text{ZnTPPS}^{4+}) = 0.74 \) V vs. SCE undergoes the electron-transfer reduction with the iodide (\( I_1/I^- = 0.7 \) V vs. SCE)¹² in the electrolyte solution.

In conclusion, the photoinduced electron transfer from ZnTPPS⁴⁺ to Li⁺@C₆₀ in the supramolecular cluster makes it possible to enhance the performance of the photoelectrochemical cell. Thus, the use of Li⁺@C₆₀ as an electron acceptor in the supramolecular clusters with ZnTPPS⁺⁺ paves a new way for the design of high performance solar cells.

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