

Barrier effect of dendrons on TiO₂ particles in dye sensitized solar cells†‡

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The short circuit current of dye sensitised solar cells increased significantly by the simple addition of polyester hydroxyl acetylene bis(hydroxymethyl)propanoic acid dendrons on TiO₂ nanoparticles, resulting in a very high overall energy conversion efficiency.

Ever since the first successful report in 1991,¹ dye sensitised solar cells (DSSCs) have been studied as a promising, low-cost alternative to conventional inorganic solar devices. The energy conversion of DSSCs is based on the electron injection from a photoexcited state of the sensitiser (*i.e.*, dye) attached to TiO₂ semiconductor nanoparticles into the conduction band of the TiO₂. The oxidised sensitisers can be reduced by a redox couple (usually I[−]/I₃[−]) present in the electrolyte and a redox couple renewed in the counter-electrode, making the photoelectrochemical cell regenerative. While an 11.1% power conversion efficiency was reported for a DSSC,² the conversion efficiency still lags behind that of the inorganic solar cell. One of the main reasons for the low performance is the disappearance of the photoelectron density due to the recombination of injected electrons with oxidised species of the redox couple present in the electrolyte (*e.g.*, I₃[−]) at the surface of bare TiO₂ particles.

Much effort has been devoted to the surface modification of TiO₂ to improve the performance by using an inorganic insulating layer³ and chemical co-adsorbents⁴ to manipulate the recombination reaction. It is believed that this insulating molecular layer effectively shields the back electron transfer from the TiO₂ conduction band to I₃[−]. If the effect caused by blocking the bare TiO₂ nanoparticle surface is dominant in retarding the recombination, the surface coverage of TiO₂ nanoparticles has to be optimised. Therefore, a well-defined structural material, dendrons, was used in this research to determine the optimisation coverage of the recombination centre of TiO₂ nanoparticles.

Different generations of polyester hydroxyl acetylene bis(hydroxymethyl)propanoic acid dendrons (dendron)⁵ having carboxylic acid group at the center were chosen as co-adsorbents for TiO₂ nanoparticles in order to understand the coverage effect on the overall conversion efficiency (Fig. S1, ESI†). The fabrication and the characterization are presented in ESI.†

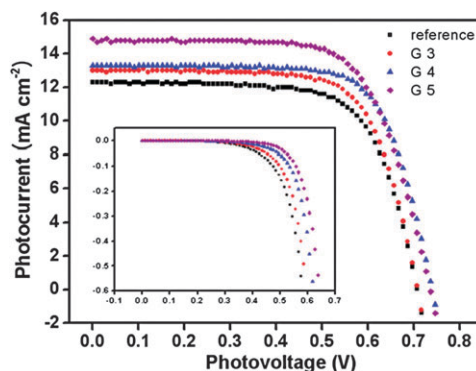


Fig. 1 Photocurrent density–potential characteristics of DSSCs having different generations of dendrons in the dark (inset) and under simulated illumination (AM 1.5, 100 mW cm^{−2}) with masking. The redox electrolyte comprised 0.6 M 1-methyl-3-propyl imidazolium iodide (PMII) and 0.025 M I₂ in acetonitrile. The TiO₂ layer was *ca.* 12 μm.

The photovoltaic performances of DSSCs with different generations of dendrons are shown in Fig. 1. The mole number of dendrons was fixed at 9.03×10^{18} mole per gram(TiO₂) to determine the effect of the dendron size on coverage. The characteristic photovoltaic parameters of short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF) and photovoltaic conversion efficiency (η) are listed in Table 1.

The inset figure presents the current–voltage (J – V) characteristics of the cells under dark conditions. Although the dark current is not a good simulation of the recombination current under illumination due to the localised variation in the electrolyte medium and potential distribution through the TiO₂ electrode, it can be used as an estimation of the extent of the reduction of I₃[−] recombination with the conduction band electrons. The onset voltage of the cells increases in all cases upon the addition of different generations of dendrons, suggesting that the addition of dendrons reduces the electron recombination between the TiO₂ surface and I₃[−],^{4,6} and it is significant for the high generation of dendrons.

The electrolyte we chose for this research was PMII/I₂ dissolved in acetonitrile. The minimisation of the electrolyte-composition was done deliberately, as we intended to have

Table 1 Photovoltaic performance of DSSCs with different generations of dendrons

	$J_{sc}/$ mA cm ^{−2}	$V_{oc}/$ V	FF	$\eta/\%$	Work function	R_2/Ω	CPE_2/Ω	τ/ms
Reference	12.30	0.71	69.2	6.02	5.38	187	0.16	29.9
G3	13.28	0.70	70.4	6.52	5.44	186	0.16	29.7
G4	13.45	0.73	71.0	6.98	5.38	261	0.17	44.4
G5	14.97	0.73	68.5	7.46	5.48	592	0.15	88.8

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distinct insight into the effect of the dendron co-adsorbent in DSSCs. Under standard global AM 1.5 solar conditions with a mask, the reference cell without dendron co-adsorbent gave a J_{sc} of 12.30 mA cm^{-2} , an V_{oc} of 0.71 V and a FF of 0.69 , corresponding to an overall conversion efficiency of 6.02% , these results are reasonable for cells containing the N719 dye without any additives.⁷ Co-adsorption with dendrons leads to an increase in the J_{sc} values with an increasing size of dendron; the J_{sc} reached 14.97 mA cm^{-2} for the cell containing the generation 5 (G5) dendron, and the energy conversion efficiency reached 7.46% while V_{oc} was not changed significantly.

It is known that carboxylic acid adsorption occurs at metal oxide surfaces, generally through coordination *via* the carboxyl group,⁸ which can alter the energy of the TiO_2 /sensitiser interface. This phenomenon can push the band-edge potentials,^{4c,9} which can be measured by a photon electron spectrometer. The Fermi level shift (ϕ)¹⁰ in the FTO- TiO_2 interface is estimated to be $\phi = 5.38 \text{ eV}$ for the reference, and it was not changed significantly for all DSSCs using different generations of dendrons, as presented in Table 1. We found that the observed Fermi level shifted hardly with the addition of dendron co-adsorbents, which is consistent with the value of V_{oc} within the error range. Because J_{sc} is strongly dependent on both the rate of recombination and the band-edge position of TiO_2 , the constant transfer from the band-edge position of TiO_2 and the retarded recombination due to the addition of dendrons provide a significantly increased charge collection yield. This result is consistent with the effect of the addition of carboxylic acids on DSSCs.¹¹

The electrochemical impedance spectroscopy (EIS) spectra were measured to observe the electron transport kinetics of the FTO collector coated with TiO_2 nanoparticles.¹² In the dark, electrons are transported through the mesoporous TiO_2 network and react with I_3^- . At the same time, I^- is oxidised to I_3^- at the counter electrode. The impedance due to the electron transfer from the conduction band of the mesoscopic TiO_2 film to the I_3^- ions in the electrolyte is represented by the semi-circle shown in Fig. S2(a) (ESI†). Analysing EIS measured in the dark yields parameters of charge-transfer resistance R_2 corresponding to the recombination current across the TiO_2 /electrolyte interface. The values of R_2 increased with the increasing size of the dendrons added. The significantly high R_2 values suggest that charge recombination between the injected electrons and the electron acceptors in the redox electrolyte, I_3^- , was remarkably retarded. We found that the charge transfer resistance and the electron lifetime (τ), which is determined by the product of R_2 and CPE_2 , increased when the generation of dendrons increased, due to the retardation of the recombination with I_3^- on the TiO_2 surface. The characteristic frequency peaks in the Bode phase shown in Fig. S2(b) (ESI†) shifted to a lower frequency when the generation of dendrons increased. The characteristic frequency can also be described as the inverse of the recombination lifetime in the TiO_2 film.¹³ The increase in the recombination lifetime in the TiO_2 film is associated with a pronounced rise in the charge transfer resistance, indicating that the addition of dendrons decreases the interfacial rate constant for electron capture by the I_3^- ions. That is, the larger

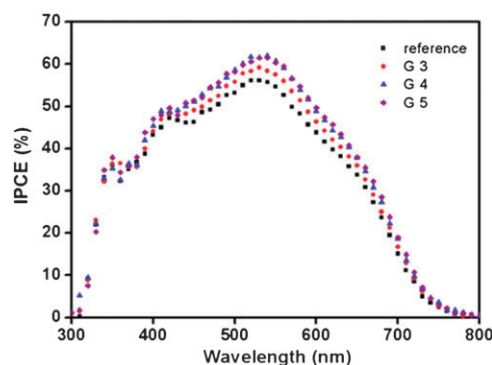


Fig. 2 IPCE spectra of DSSCs having different generations of dendrons.

size (or the higher generation) of dendrons would effectively form a barrier layer that blocks the recapture of the photo-injected electrons by the I_3^- , resulting in a higher charge collection efficiency.

To see the effect on the performance of DSSCs of the co-adsorbent on the TiO_2 -dye film for the different generations of dendrons, IPCEs were measured and a maximum of 61% at 530 nm was observed after the addition of G5 dendron, as shown in Fig. 2.

One interesting observation in this study was the significant increase of J_{sc} with the increase in size of the dendron, which, in turn, increased the coverage of the TiO_2 particles. As the carboxylic acid moieties of the dendrons were bound to oxide surfaces,⁸ the added dendrons producing a more compact monolayer than one formed when the sensitiser is adsorbed alone. The attached dendron would also eliminate most of the hydrophilic surface sites that are available for water absorptions which would reduce the cell efficiency. As the concentration of the sensitiser in the reaction was fixed, the increase in the J_{sc} would be due to both the retarded interfacial charge recombination dynamics and the optimised sensitiser conformation by the prevention of the multi-layer adsorption of dyes.¹⁴

The penetration of the dendrons would depend on their size and the pore size of the mesoporous TiO_2 layer. The average pore diameter and the surface area are 34.17 nm and $55.62 \text{ m}^2 \text{ g}^{-1}$, respectively, as determined by the Brunauer-Emmett-Teller (BET) method from the Ar desorption isotherm.¹⁵ The end-to-end distance of a dendron was estimated to be 1.4 , 2.1 and 2.9 nm , for the third, fourth, and fifth generations of dendrons, respectively, by full optimization without any geometrical constraints using the density functional theory method with Gaussian 03 software, using density functional theory of the B3LYP hybrid exchange functional with a 3-21G basis set¹⁶ (Fig. S3, ESI†). Therefore, dendrons would preferentially penetrate into the mesopores of the TiO_2 layers, resulting in an increased interfacial coverage of the surface of the TiO_2 film.

We prepared DSSCs with different amounts of G5 dendrons and measured $J-V$ characteristics of the DSSCs, the results are shown in Fig. 3 and Table 2. It is clear that the addition of dendrons for the barrier layer retards the electron recombination rate and improves the J_{sc} , thus increasing the cell performance. The main effect due to the addition of dendrons is the blocking of the electron recapture by the

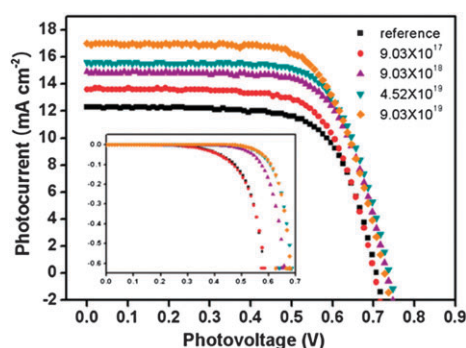


Fig. 3 Photocurrent density–potential characteristics of DSSCs having different amounts of the generation 5 dendrons in the dark (inset) and under simulated illumination.

Table 2 Photovoltaic performance of DSSCs with different amounts of the generation 5 dendrons

Moles per gram of TiO ₂	$J_{sc}/\text{mA cm}^{-2}$	V_{oc}/V	FF	$\eta/\%$	R_2/Ω	CPE_2/Ω	τ/ms
Reference	12.30	0.71	69.2	6.02	187	0.16	29.9
9.03×10^{17}	13.63	0.70	69.5	6.65	230	0.10	23.0
9.03×10^{18}	14.88	0.73	69.8	7.61	732	0.10	73.2
4.52×10^{19}	15.57	0.74	69.5	8.00	1032	0.11	113.5
9.03×10^{19}	16.99	0.73	68.1	8.41	409	0.21	86.0

redox couple in the electrolyte, allowing a higher electron concentration in the mesoscopic TiO₂ films. Hence, a higher J_{sc} is reached under illumination, which can be observed by EIS analysis (Fig. S4, ESI†).

The surface coverage of the TiO₂ particle was roughly estimated under the homogeneous adsorption of dendrons in TiO₂ without N719, and the cell efficiency was plotted with the dendron coverage in Fig. 4. Although the actual coverage value of a TiO₂ nanoparticle could not be determined exactly due to the rough estimation of the size of the dendron and the ignorance of the presence of the sensitizers, it is clear that the cell efficiency increased with an increase in the surface coverage and reached the maximum value when the surface of the TiO₂ particles was covered completely.

The barrier effect of dendrons was tested in the solid-state electrolyte prepared according to the oligomer approach.¹⁷ Composite polymer electrolytes consisting of poly(ethylene glycol)dimethyl ether (PEGDME)/PMII/I₂ with and without fumed silica were prepared and DSSCs were fabricated.¹⁷ Fig. S5 (ESI†) shows the J – V characteristics of the DSSCs

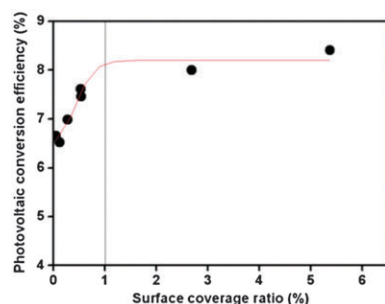


Fig. 4 Dependence of cell efficiency on the surface coverage of TiO₂ particles with dendrons.

both with and without G5 dendron co-adsorbent, and further information is shown in Table S1 in ESI.† With the simple changing of the matrix from liquid acetonitrile into viscous PEGDME, J_{sc} and η decreased *ca.* 2 mA cm^{−2} and 1.5%, respectively. With the addition of G5 dendron co-adsorbents, both DSSCs showed improvement in J_{sc} and η upon addition of co-adsorbents, although the improved numerical amount was lower than that of the liquid acetonitrile matrix. The stability test is under investigation in this laboratory.

In summary, a series of dendrons were employed as co-adsorbents, and their effects on DSSCs were investigated. The addition of dendrons increased the J_{sc} of the DSSC and had no adverse effect on the V_{oc} of the DSSCs. Up to a 40% increase in the total power conversion efficiency was achieved by using the G5 dendron as the co-adsorbent and its efficiency reached 8.41%. EIS and IPCE measurements showed that the increase in J_{sc} is due to the suppression of surface recombination and the surface coverage of the TiO₂ particles. This effect was also observed in the solid-state PEGDME/fumed silica electrolyte, and the value of J_{sc} and the efficiency increased to 11.34 mA cm^{−2} and 5.26%, respectively.

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