Solar Cells

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An Efficient Dye-Sensitized Solar Cell with an Organic Sensitizer Encapsulated in a Cyclodextrin Cavity**

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Heterogeneous electron transfer in functional nanostructured hybrid materials is currently attracting significant attention in technological applications of photovoltaic energy conversion. In particular, dye-sensitized solar cells (DSSCs) that involve the immobilization of a single molecular species to the nanocrystalline titania are of widespread interest as low-cost alternatives to conventional solid-state photovoltaic devices.[1] Our approach to the high power conversion efficiency of organic-dye-sensitized solar cells is based on the interface engineering of a dye-absorbed TiO_2 surface in order to diminish the charge recombination and to prevent the aggregation of dye molecules. Efficient operation of the DSSC devices relies upon the minimization of interfacial recombination losses.[2] The strategy for minimizing such losses in DSSCs involves the coating of inorganic barrier layers,[3] saccharides,[4] and metal-assembling dendrimers,[5] and the introduction of long alkyl chains to the dyes.[6] A second major factor responsible for the low efficiency of an organic dye-sensitized solar cell is the formation of dye aggregates on the semiconductor surface. Several strategies have been considered for controlling the aggregation of dyes through the use of helical-shaped polysaccharide,[7] aerosol-OT (sodium 1,2-bis(2-ethylhexoxycarbonyl)ethanesulfonate) micelles,[8] dendritic side chains,[9] and encapsulation by cyclodextrins (CDs).[10] Both problems can be attenuated by adapting supramolecular encapsulation strategies that accommodate the individual dye molecules and prevent self-aggregation.

Herein, we present an alternative methodology to the immobilization of dyes on nanocrystalline TiO_2 electrodes. Our strategy is based on insulated sensitizer dyes, in which dye molecules are encapsulated in cyclodextrin hosts. Such encapsulation of dyes by the cyclodextrin cavity could provide a means to not only prevent the formation of dye aggregates, but also to retard the interfacial charge recombination dynamics. Although insulated dyes created by threading dyes through cyclodextrins have been reported,[10] our approach to cells with high photovoltaic performance involves anchoring CDs to TiO_2 and the subsequent formation of a pseudorotaxane by encapsulating an organic dye inside the CDs.

The organic dye JK-2[11] was chosen for encapsulation by CDs that were adsorbed onto TiO_2 (Figure 1). We first determined the Langmuir isotherm for the adsorption of various cyclodextrins on the surface of TiO_2.[10d] Adsorption studies were carried out on transparent TiO_2 films of a known weight. After the adsorption of CDs on TiO_2 films in H_2O, the remaining CD concentration was determined by the induced spectral change of methylene blue. The amount of CDs adsorbed as a function of the equilibrium concentration in H_2O is shown in Figure S1 in the Supporting Information. We obtained the adsorption equilibrium constant K_{ads} of 1.50×10^4 for β-CD and the amount of β-CD adsorbed at saturation on TiO_2 n_α of 7.65×10^{-8} mol mg^{-1} of TiO_2 by fitting the data to a Langmuir isotherm. The specific surface area obtained from BET (Brunauer–Emmett–Teller) experiments for transparent films is 130 m^2 g^{-1} of TiO_2. The surface concentration value, which corresponds to an area of 2.82 nm^2 per β-CD, can be estimated from the value of n_α, assuming full coverage of the TiO_2 surface. As the effective surface area of a β-CD is approximately 2.16 nm^2, the coverage of TiO_2 by β-CDs is 76.6 %. We next measured the adsorbed amount of JK-2 encapsulated in the CDs anchored to the TiO_2 film by monitoring the changes in the absorption spectrum of JK-2 upon encapsulation. The adsorbed amount of JK-2 in α-, β-, and γ-CD was 7.98×10^{-8}, 9.78×10^{-8}, and 6.97×10^{-8} mol mg^{-1} of TiO_2, respectively. The adsorbed amounts of JK-2 on TiO_2 in the absence of CDs was measured to be 2.04×10^{-7} of TiO_2

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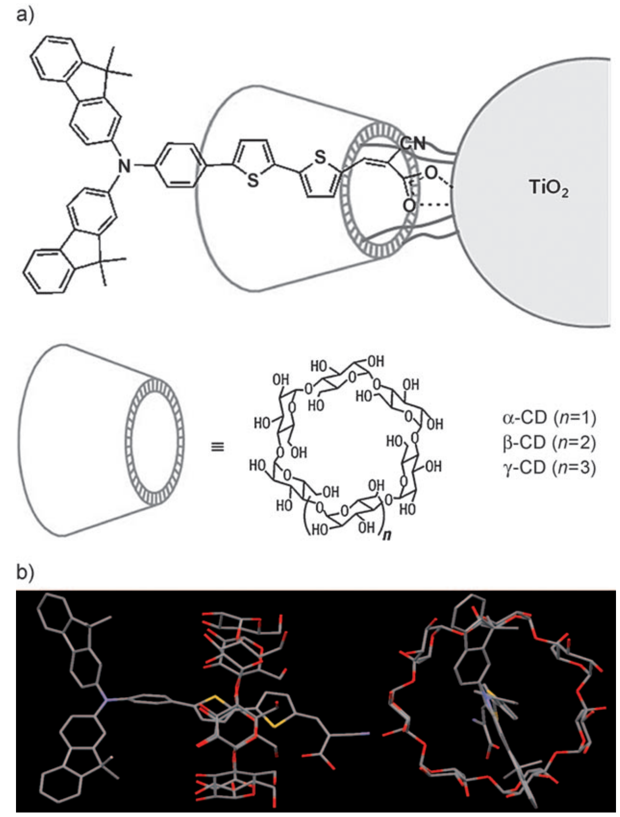

Figure 1. a) The JK-2 sensitizer encapsulated in a cyclodextrin anchored to TiO$_2$. b) Energy-minimized structure of JK-2 inside a β-cyclodextrin.

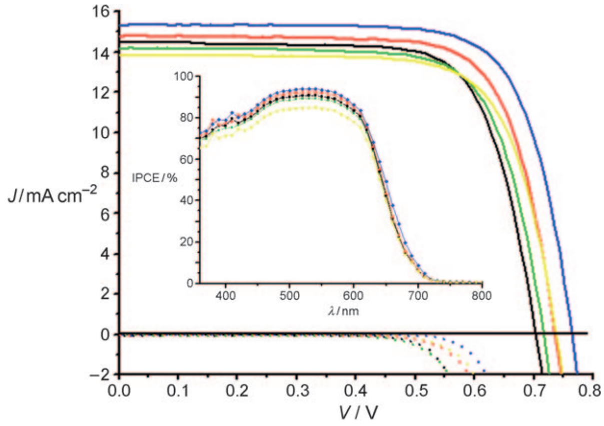

Figure 2. *J*–*V* curve and IPCE spectra (inset) of JK-2 (black line), JK-2/DCA (red line), α-CD/JK-2 (green line), β-CD/JK-2 (blue line), and γ-CD/JK-2 (yellow line). The dark current/bias potential relationship is shown as dotted curves.

Table 1: DSSC performance parameters of dyes.[a]

Dye	J_{sc} [mAcm^{-2}]	V_{oc} [V]	*ff*	*η* [%]
JK-2	14.51	0.70	0.73	7.42
JK-2 + DCA	14.85	0.73	0.74	8.01
α-CD/JK-2	14.26	0.71	0.73	7.41
β-CD/JK-2	15.34	0.76	0.74	8.65
γ-CD/JK-2	13.68	0.74	0.73	7.42

[a] Performances of DSSCs were measured with a working area of 0.18 cm^2. Electrolyte: 0.6 M DMPII, 0.05 M I$_2$, 0.1 M LiI, and 0.5 M *tert*-butylpyridine in acetonitrile.

(see Table S2 in the Supporting Information). The CDs remain strongly adsorbed on the TiO$_2$ surface throughout the process of JK-2 binding to the TiO$_2$ surface (see Figure S7 in the Supporting Information). Comparison of the adsorbed amount of β-CD (7.65×10^{-8} of TiO$_2$) with that of JK-2 indicated that the JK-2 dye molecules were encapsulated inside the cavity of β-CD. The association constants for the formation of CD/JK-2 in H$_2$O/EtOH (v/v, 1:10) were determined to confirm the formation of a complex in solution. We found that the association constant ($K_a = 5.6\times10^3\,\text{M}^{-1}$) of β-CD with JK-2 was larger than those the two other CDs (see Table S3 in the Supporting Information).

Figure 2a shows action spectra of monochromatic incident photon to current conversion efficiencies (IPCEs) for DSSCs based on JK-2, JK-2/DCA (3a,7a-dihydroxy-5b-cholic acid), α-CD/JK-2, β-CD/JK-2, and γ-CD/JK-2 (electrolyte: 0.6 M DMPImI, 0.05 M iodine, 0.1 M LiI, and 0.5 M *tert*-butylpyridine in acetonitrile). The IPCE of β-CD/JK-2 showed a plateau of over 80 % from 400 to 630 nm, reaching a maximum 93 % at 535 nm. Furthermore, the photoresponse of the cell extends up to 750 nm. The cell clearly exhibited an impressive response over the entire region relative to cells comprising JK-2 and JK-2/DCA. The photovoltaic performances of the JK-2 sensitized cells are listed in Table 1.

Under standard global AM 1.5 solar conditions, the β-CD/JK-2 sensitized cell gave a short-circuit photocurrent density (J_{sc}) of 15.34 mA cm^{-2} , an open-circuit voltage (V_{oc}) of 0.76 V and a fill factor (*ff*) of 0.74, which correspond to an overall conversion efficiency (*η*) of 8.65 %. From the overlap integral of the IPCE with the standard AM 1.5G solar emission spectrum, a J_{sc} value of 14.82 mA cm^{-2} was calculated, which is in good agreement with the measured photocurrent density. Under the same conditions, the JK-2 sensitized cell gave J_{sc} = 14.51 mA cm^{-2}, V_{oc} = 0.70 V, and *ff* = 0.73, which correspond to $\eta = 7.42$ %.

From these results (Table 1), we have observed that the *η* value of the β-CD/JK-2 cell was higher than those of the other cells. Neither the α-CD/JK-2 nor γ-CD/JK-2 cells could reach the high value of the β-CD/JK-2 cell. This result arises from the different quantities of JK-2 encapsulated in each CD cavity. Of particular importance is the 30–60 mV increase in the V_{oc} value of the β-CD/JK-2 cell relative to the JK-2 and JK-2/DCA based cells. This result implies that the encapsulation of JK-2 results in the reduction of the electronic coupling between the TiO$_2$ surface and the oxidizing hole to yield a long-lived charge separation. The use of an encapsulated dye can also lead to an effective spatial separation of the charges, which aids retardation of interfacial charge recombination losses in the device, as confirmed by the dark-current data (Figure 2b).

Since long-term stability is a vital parameter for sustained cell operation, we substituted a volatile liquid electrolyte by an ionic-liquid electrolyte or a quasi-solid-state electrolyte. Figure 3 shows the photovoltaic performance during a long-term accelerated aging of β-CD/JK-2 with an ionic-liquid

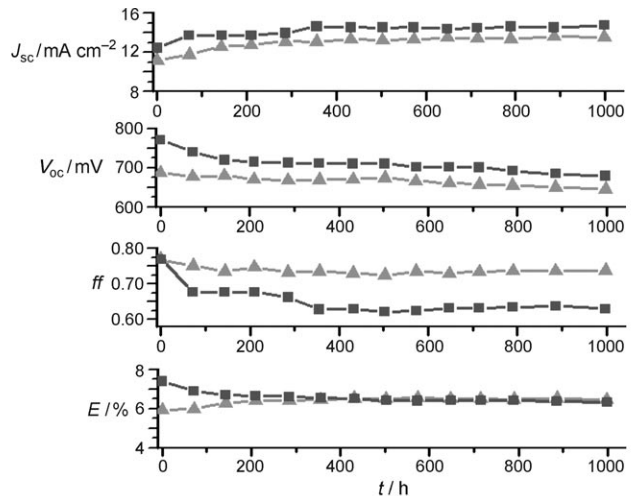

Figure 3. Evolution of solar-cell parameters with β-CD/JK-2 during visible-light soaking (AM 1.5G, 100 mW cm^{-2}) at 60 °C. A 420 nm cut-off filter was placed on the cell surface during illumination. Ionic-liquid electrolyte (▲): 0.2 M iodine, 0.5 M NMBI, 0.1 M guanidinium thiocyanate (GuNCS) in propylmethylimidazolium iodide (PMII)/ ethylmethylimidazolium thiocyanate (EMINCS; 13:7). Quasi-solid-state electrolyte (■): 0.1 M iodine, 0.5 M NMBI, 0.6 M DMPII, 5 wt% PVDF-HFP in MPN.

electrolyte or a polymer-gel electrolyte composed of 0.1 M I_2, 0.5 M *n*-methyl-benzimidazole (NMBI), 0.6 M 1-propyl-2,3-dimethylimidazolium iodide (DMPII), 5 wt% poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) in 3-methoxypropionitrile (MPN). The β-CD/JK-2 sensitized cell with a quasi-solid-state electrolyte gave a remarkably high conversion efficiency of 7.40 %, which is the highest efficiency ever reported for DSSC based on organic sensitizer with a quasi-solid-state electrolyte. After 1000 hours of light soaking at 60 °C, the initial efficiency of 7.40 % in β-CD/JK-2 decreased to 6.31 %. This is the first example of an organic-dye-sensitized solar cell with a quasi-solid-state electrolyte and an efficiency above 6.3 % that has passed the light-soaking test. On the other hand, the efficiency of β-CD/JK-2 with an ionic-liquid electrolyte increased from 5.93 to 6.48 % because of the concomitant increase in the J_{sc} value. The enhanced long-term stability of β-CD/JK-2 can be attributed to the encapsulation of JK-2, which leads to retardation of charge recombination.

The electron diffusion coefficient (D_e) and lifetime (τ_e) of the DSSCs with different dye adsorption conditions (i.e., JK-2, β-CD/JK-2, and JK-2/DCA) as a function of J_{sc} and V_{oc}, respectively are shown in Figure S6 in the Supporting Information. The D_e and τ_e values were determined by the photocurrent and photovoltage transients induced by a stepwise change in the laser light intensity controlled with a function generator.[12] The D_e value was obtained by a time constant (τ_c) determined by fitting a decay of the photocurrent transient with $\exp(-t/\tau_c)$ and the TiO_2 film thickness (ω) using the equation, $D_e = \omega^2/(2.77\,\tau_c)$.[12a] The τ_e value was also determined by fitting a decay of photovoltage transient with $\exp(-t/\tau_e)$.[12a] The D_e values of the photoanodes are shown to be similar under identical short-circuit current conditions, regardless of the dye-adsorption conditions. Meanwhile, a dramatic difference in the cell τ_e values was observed. The increasing order of the τ_e values under identical open-circuit voltage conditions was JK-2 < JK-2/DCA < β-CD/JK-2, which demonstrated that the electron-recombination process was effectively retarded by controlling the dye adsorption, especially by the introduction of CDs onto TiO_2. The results for the charge-separation lifetime are also in good agreement with those of the V_{oc} values shown in Table 1.

The ac impedance spectra of the cells were measured under dark and illuminated conditions (Figure 4). In the dark, under forward bias (−0.67 V), the semicircular curve obtained in the intermediate-frequency regime shows the dark reaction impedance caused by electron transport from the TiO_2 conduction band to the I_3^- ions in the electrolyte.[13] The increased radius of the semicircular curve in the intermediate frequency regime implies a reduced electron recombination rate at the dye-adsorbed TiO_2/electrolyte interface. In the dark, the radius of the intermediate-frequency semicircle showed the increasing order of JK-2 (94.2 Ω) < JK-2/DCA (106.4 Ω) ≪ β-CD/JK-2 (168.3 Ω), which is in agreement with the trends of the V_{oc} and τ_e values. Under illumination (100 mW cm^{-2}, open-circuit voltage (OCV) conditions), the radius of the intermediate-frequency semicircle in the Nyquist plot decreased in the order JK-2 (11.3 Ω) > JK-2/DCA (10.5 Ω) > β-CD/JK-2 (10.1 Ω), which indicates the improved electron generation and transport. This result is also in good agreement with the trend of the overall cell efficiency.

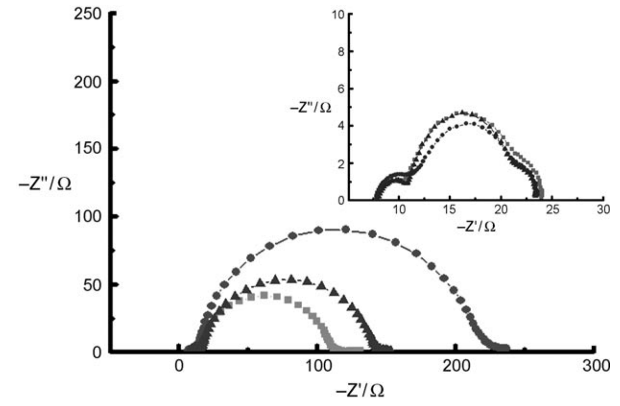

Figure 4. Electrochemical impedance spectra measured in the dark and under illumination (1 sun; inset) for the cells with different dye adsorption conditions (JK-2 (■), JK-2/DCA (▲), and β-CD/JK-2 (●).

In conclusion, encapsulated of the JK-2 dye inside CD cavities retarded charge recombination and prevented dye aggregation. The β-CD/JK-2 device with a polymer gel electrolyte gave an overall conversion efficiency of 7.40 %, which is the highest value for DSSCs based on the organic sensitizers reported to date. Moreover, the β-CD/JK-2 device showed an excellent stability under light soaking at 60 °C for 1000 h. The high efficiency and excellent stability may be attributed to the encapsulation of JK-2 inside the CD cavity. We believe that the development of highly efficient DSSC devices with excellent stabilities is possible through various interfacial modifications; work on these devices is now in progress.

Experimental Section

TiO_2/CD/JK-2: The TiO_2 electrodes were immersed in a solution of CD in H_2O (0.8 mM) and kept at room temperature for 12 h. The film was subsequently washed in absolute ethanol and dried. The TiO_2 electrodes were then immersed in a solution of JK-2 in EtOH (0.3 mM) and kept at room temperature for 4 h.

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