Research Article

High Efficiency of Dye-Sensitized Solar Cells Based on Ruthenium and Metal-Free Dyes

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The influence of using different concentrations of triazoloisoquinoline based small molecule as coadsorbent to modify the monolayer of a TiO_2 semiconductor on the performance of a dye-sensitized solar cell is studied. The co-adsorbent significantly enhances the open-circuit photovoltage (V_{oc}), the short circuit photocurrent density (J_{sc}) the solar energy conversion efficiency ($> \eta$). The co-adsorbent 4L is applied successfully to prepare an insulating molecular layer with N719 and achieve high energy conversion efficiency as high as 8.83% at 100 mW cm^{-2} and AM 1.5 at 1 to 0.25 (N719 : co-adsorbent) molar ratio. The resulting efficiency is about 6% higher than that of a nonadditive device. The result shows that the organic small molecule 4L (2-cyano-3-(5-(4-(3-oxo-[1,2,4]triazolo[3,4-a]isoquinoline-2(3H)-yl)phenyl)thiophene-2-yl)acrylic acid) is the promising candidates for improvement of the performance of dye-sensitized solar cell.

1. Introduction

Dye-sensitized solar cells have attracted considerable academic and industrial research interest since Regan and Grätzel's report in 1991 [1]. Usually these cells consist of a working electrode which is coated with a dye-sensitized mesoporous film of nanocrystalline particles of TiO_2, a Pt-coated counterelectrode, and an electrolyte containing a suitable redox couple. The function of such devices is based on the electron injection from the photoexcited state of the dye molecule into the conduction band of the TiO_2, followed by regeneration of the dye by an iodide/triiodide redox couple. Typically, high power conversion efficiencies (η) of more than 11% have been achieved by using ruthenium complex and acetonitrile based electrolytes [2]. However, organic additives play a key role in the characteristics of both electrolytes and devices and have been explored extensively with regard to improving the efficiency of DSSC [3–5].

A few reports have described the use of organic additives for a compact layer, comprised of the dye and coadsorbent

[6, 7]. Chenodeoxycholic acid (DCA) is frequently added to the dye solution to enhance the open-circuit photovoltage (V_{oc}), the short circuit photocurrent density (J_{sc}), and the efficiency (η) of DSSC [8, 9]. The V_{oc}, J_{sc}, and FF of the DSSC are affected by DCA due to the suppression of dark current at the semiconductor/electrolyte junction, since DCA blocks the surface states Ti(IV) ions that are active in the charge transfer [10]. Due to the insulating molecular layer, the charge recombination process can be shielded, and this increases the V_{oc}, J_{sc}, and η. Several approaches have been developed for this purpose, such as the use of pyridinium additives [11], pyrimidine additives [12], dipolar carboxylic acid derivatives [13], zwitterionic coadsorbents [14], and guanidinium cations [4]. In this paper, we synthesize a new triazoloisoquinoline-based organic small molecule used as co-adsorbents to modify the monolayer of a TiO_2 semiconductor. We discuss the concentration effect of co-adsorbents and investigate the possibility of using triazoloisoquinoline-based organic small molecule as co-adsorbents in DSSC.

2. Experimental

2.1. General Procedure for Preparation of Solar Cells.
Fluorine-doped tin oxide (FTO, $10\,\Omega\,\text{square}^{-1}$) glass plates were cleaned using detergent solution, water, and ethanol in an ultrasonic bath overnight. The screen-printing procedure was repeated with TiO_2 paste (~15–20 nm colloidal particles, Ti-Nanoxide T series, Solaronix SA) to obtain a transparent nanocrystalline film of thickness around $12\,\mu\text{m}$. The 100 nm colloidal particles were prepared in a basic environment according to the literature [15] and dispersed in α-terpineol with ethyl cellulose for scattering TiO_2 paste. A scattering layer around $4\,\mu\text{m}$ was deposited by using this scattering TiO_2 paste and a final thickness of $16\,\mu\text{m}$ was attained. The TiO_2 electrodes were gradually annealed at $450°C$ for 30 min in an oven in an air atmosphere. After sintering, the electrodes were further treated with $0.2\,M$ $TiCl_4$ aqueous solution at room temperature for 12 h, then washed with water and ethanol, and annealed at $450°C$ for 30 min. When the temperature decreased to $70°C$ after sintering, the electrodes were immersed into dye solution, which included $0.5\,mM$ N719 and different concentrations of co-adsorbent in tert-butanol/acetonitrile (AN) (1 : 1 in volume). The dye solutions were kept at $25°C$ for more than 18 h to allow the dye to adsorb to the TiO_2 surface. After the adsorption of the dyes, the electrode was rinsed with the same solvent. The dye-loaded TiO_2 film as the working electrode and Pt-coated TCO as the counterelectrode (about 20 nm) were separated by a hot-melt Surlyn sheet ($25\,\mu\text{m}$) and sealed together by pressing them under heat. The electrolytes were introduced into the gap between the working and counterelectrodes from two holes predrilled on the back of the counterelectrode. Finally, the two holes were sealed with a Surlyn film covering a thin glass slide under heat. The cells were evaluated by using $0.6\,M$ [BMI][I], $0.1\,M$ GuNCS, $0.3\,M$ I_2, and $0.5\,M$ TBP in a AN/VN (85/15, v/v) solvent as the redox electrolyte.

2.2. Photovoltaic Measurement.
The current-voltage (I-V) characteristics in the dark and under illumination were measured with a Keithley 2400 sourcemeter. The photocurrent was measured in a nitrogen-filled glove box under a solar simulator (Oriel 96000 150 W) with AM 1.5 G-filtered illumination ($100\,\text{mW}\,\text{cm}^{-2}$). The spectra-mismatch factor of the simulated solar irradiation was corrected using a Schott visible-color glass-filtered (KG5 color filter) Si diode (Hamamatsu S1133). The active area of the device was $0.25\,\text{cm}^2$.

2.3. Dye Loading Measurement.
The TiO_2 films were put into the dye solution (N719, $3 \times 10^{-4}\,M$ in tert-butanol and acetonitrile, 1 : 1, v/v) for 24 h. Subsequently, the TiO_2 films were washed with acetonitrile after the adsorption process and then dried in N_2 flow. Dye loading measurements were conducted by desorbing the dye molecules from the dye-anchored films in NaOH ethanolic solution. The loading amount was calculated from the absorbance of the completely desorbed dye solutions by the spectrophotometer.

2.4. Synthesis

2.4.1. Synthesis of 2-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaboro-lane-2-yl)phenyl)-[1,2,4]triazolo[3,4-a]isoquinoline-3(2H)-one (2).
In a round-bottom flask, compound 1 (5.6 g, 16.3 mmol), 4,4,5,5-tetramethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-1,3,2-dioxaborolane (4.4 g, 17.1 mmol), and potassium acetate (4.8 g, 49.0 mmol) were dissolved in dimethyl sulfoxide (DMSO) under nitrogen atmosphere. After adding a catalyst of dichloro-[1,1′-bis(diphenylphos-phino)ferrocenyl]palladium(II) (Pd(dppf)Cl$_2$), the mixed solution was heated at $80°C$ for 6 hours with vigorous stirring. It was then poured into EtOAc-water for extraction. The organic phase was concentrated and adsorbed on silica gel and purified by column chromatography using hexane/EtOAc mixture (5 : 1) as the eluant: white powder; yield 5.32 g (84.2%); ^{1}H NMR (300 MHz, d$_6$-DMSO): δ 8.31 (d, 1H, $J = 7.53$ Hz), 8.17 (d, 2H, $J = 8.23$ Hz), 7.84 (d, 3H, $J = 8.57$ Hz), 7.77~7.66 (m, 3H), 7.02 (d, 1H, $J = 7.44$ Hz), 1.32 (s, 12H).

2.4.2. Synthesis of 5-(4-(3-Oxo-[1,2,4]triazolo[3,4-a]isoquino-line-2(3H)-yl)phenyl)thiophene-2-carbaldehyde (3).
In a three-necked round-bottomed flask (25 mL) equipped with a reflux condenser, compound 2 (1.71 g, 4.4 mmol), 5-bromothiophene-2-carbaldehyde (1.0 g, 5.2 mmol), and 2 M potassium carbonate solution were added to a suspension of Pd(PPh$_3$)$_4$ (3.0 mol%) in tetrahydrofuran (30 mL) at ambient temperature under nitrogen. The reaction mixture was heated to $80°C$ with rapid stirring for 16 hours. After cooling, the resulting solution was poured into water. The separated solid was filtered and thoroughly washed with water-acetone and dried: pale yellow powder; yield 1.0 g (61.6%); ^{1}H NMR (300 MHz, d$_6$-DMSO): δ 9.23 (s, 1H), 8.32 (d, 1H, $J = 7.56$ Hz), 8.24 (d, 2H, $J = 8.53$ Hz), 8.07 (d, 1H, $J = 3.81$ Hz), 8.01 (d, 2H, $J = 8.60$ Hz), 7.86~7.67 (m, 5H), 7.04 (d, 1H, $J = 7.39$ Hz).

2.4.3. Synthesis of 2-Cyano-3-(5-(4-(3-oxo-[1,2,4]triazolo[3,4-a]isoquinoline-2(3H)-yl)phenyl)thiophene-2-yl)acrylic Acid (4L).
In a three-neck bottle, compound 3 (1.2 g, 3.3 mmol), 2-cyanoacetic acid (0.6 g, 6.5 mmol), and piperidine (0.08 g, 0.98 mmol) were dissolved in chloroform. The mixed solution was refluxed for 16 hours with rapid stirring. After cooling, the resulting solution was poured into EtOAc-MeOH. The separated solid was filtered and thoroughly washed with EtOAc and MeOH and dried: pale orange powder; yield 1.2 g (85.0%); ^{1}H NMR (300 MHz, d$_6$-DMSO): δ 8.32 (d, 1H, $J = 7.50$ Hz), 8.23 (s, 1H), 8.20 (d, 2H, $J = 3.20$ Hz), 7.93 (d, 2H, $J = 8.72$ Hz), 7.89~7.67 (m, 6H), 7.03 (d, 1H, $J = 7.46$ Hz); ESI-MS m/z 437 (M-H$^+$); Anal. Calcd for $C_{24}H_{14}N_4O_3S$: C, 65.74; H, 3.22; N, 12.78. Found: C, 65.96; H, 3.28; N, 12.60.

3. Results and Discussion

3.1. Synthesis.
The synthetic route of the co-adsorbent is shown in Figure 1. 2-(4-bromophenyl)-[1, 2, 4]triazolo[3,4-a]isoquinoline-3(2H)-one (1) was obtained as reported earlier
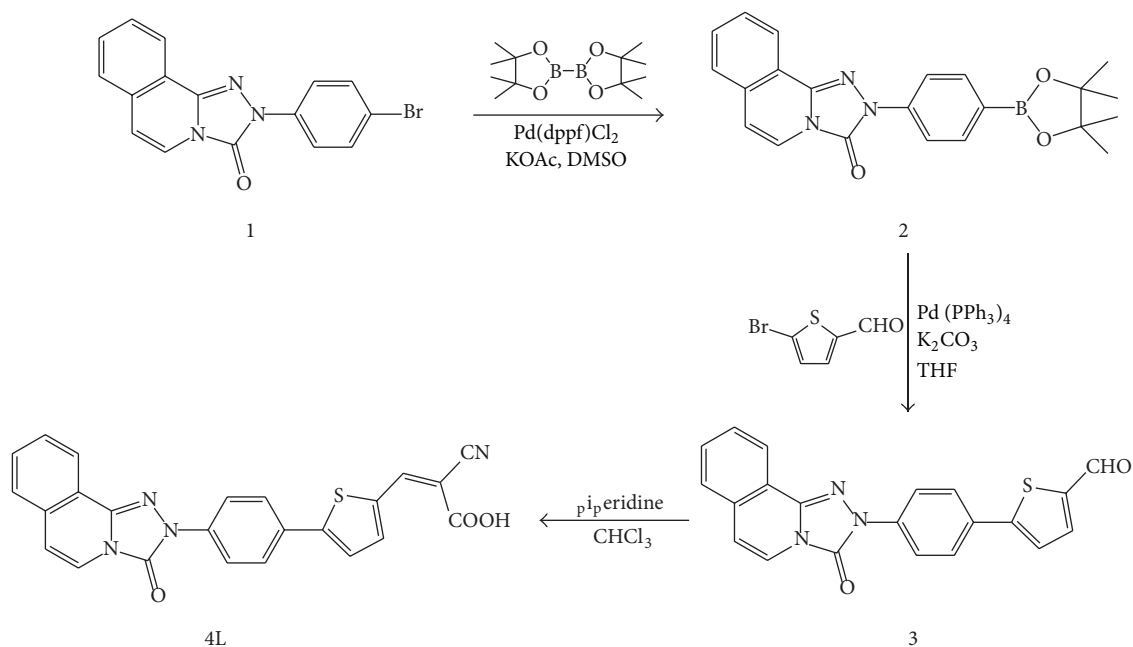
FIGURE 1: Synthetic route of co-adsorbent 4L.

[16]. 4L was synthesized by Suzuki coupling of compound 2 with 5-formylthiophene-2-ylboronic acid, followed by Knoevenagel condensation reaction with cyanoacrylic acid in the presence of piperidine. This product was well characterized by spectroscopic analyses.

3.2. The Double-Layer TiO$_2$ Film.

Recently, an enhancement in light absorption via application of light scattering has been studied for DSSCs [17, 18]. To take advantage of the light-scattering effect of TiO$_2$ particles, light absorption can be enhanced in TiO$_2$ films by increasing the absorption path length of photons, which can effectively improve the photocurrent output of cells. In order to obtain a high photoelectric conversion efficiency in DSSCs, a double-layer TiO$_2$ film was fabricated, composed of a light-scattering layer and a transparent layer. The transparent layer was prepared by commercial TiO$_2$ paste and the light-scattering layer was deposited by home-made scattering TiO$_2$ paste. First, TiCl$_4$ solution was converted to Ti(OH)$_4$ gel after ammonia neutralization and H$_2$O$_2$ was used to hydrolyze Ti(OH)$_4$ to form TiO$_2$ sol. Subsequently, the result solution was refluxed 35–40 hours for crystallization, and the anatase type TiO$_2$ organic sol was obtained. This solution was concentrated by rotary evaporator and dispersed in α-terpineol with ethyl cellulose for scattering TiO$_2$ paste. After screen-printing, the thickness of the double-layer film was about 16 μm. Figure 2(a) shows the surface morphology of the light-scattering layer, revealing their well-connected network and the porous nature of TiO$_2$ film. The average sizes of the nanostructures were about 100 nm in diameter. This results in a good scattering effect because of the elongated optical path length. Figure 2(b) shows the surface morphology of light-scattering layer after TiCl$_4$ posttreatment. From the SEM image, one can see that

TABLE 1: The amount of adsorbed N719 dye for different TiO$_2$ structures.

TiO$_2$ structure	Dye adsorption (10^{-7} mol cm^{-2})
Film 1	FTO/transparent layer	5.23
Film 2	FTO/transparent layer/light-scattering layer	5.35
Film 3	FTO/transparent layer/light-scattering layer/TiCl$_4$ posttreatment	7.02

the necking of the TiO$_2$ particles and the surface roughness are enhanced and resulting in higher dye adsorption amount. As summarized in Table 1, it was found that the dye amount on a film of Film 3-TiCl$_4$ posttreatment is higher than those of Films 1 and 2. It is well known that the short-circuit current density is mainly determined by the initial number of photogenerated electrons, and the initial number of photogenerated electrons could be significantly affected by the dye amount on the TiO$_2$ films. This result agrees well with recent experiments [19, 20]. In order to maximize the light harvesting efficiency, we fabricate the structure of Film 3 for the follow-up discussion of co-adsorbent effect.

3.3. The Concentration Effect of Coadsorbents.

After optimization of the devices, the photovoltaic characteristics of the small molecule as co-adsorbent for DSSCs were evaluated with a sandwich DSSC cell (as shown in Figure 3) using 0.6 M [BMI][I], 0.1 M GuNCS, 0.3 M I$_2$, and 0.5 M TBP in a AN/VN (85/15, v/v) solvent as the redox electrolyte. Details of the device preparation and characterization are described in the experimental section, and all the essential properties of these cells are listed in Figure 3 and Table 2.
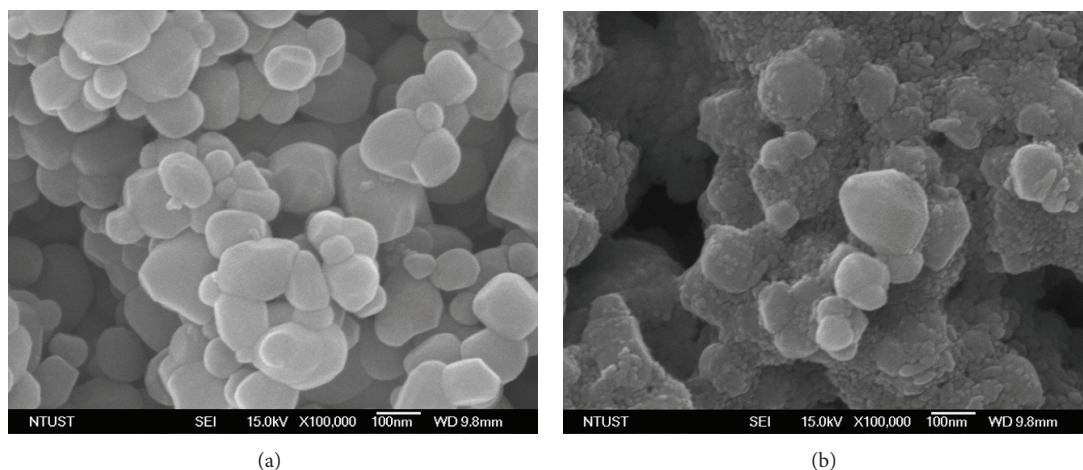
(a)

(b)

Figure 2: SEM images of (a) light-scattering layer of double layer TiO_2 films and (b) $TiCl_4$ posttreatment of light-scattering layer.

Table 2: Photovoltaic parameters of the DSSCs with N719 : 4L in different molar ratios under AM 1.5 G sunlight[a].

	Dyestuff coadsorbent molar ratio	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	η (%)
Device A	N719	15.65	0.76	0.70	8.36
Device B	N719-4L 1 : 0.25	16.39	0.77	0.70	8.83
Device C	N719-4L 1 : 0.50	15.27	0.76	0.71	8.21
Device D	N719-4L 1 : 1	15.72	0.75	0.69	8.10

[a]Performances of DSSCs were measured with 0.25 cm^2 working area.

Under the standard AM 1.5 G irradiation, the maximum efficiency (η) for the N719-sensitized solar cell-device B with an active area of 0.25 cm^2 was calculated to be 8.36%, with a J_{sc} of 15.65 mA cm^{-2}, a V_{oc} of 0.76 V, and a fill factor (FF) of 0.70. However, the solar cells based on the 12 + 4 μm transparent layer which was sensitized by N719-4L with 1 to 0.25 molar ratio yielded a remarkably high photocurrent density of 16.39 mA cm^{-2}, an open circuit voltage of 0.77 V, and a fill factor of 0.70, corresponding to an overall power conversion efficiency of 8.83%. This result is also in agreement with the observation of the incident photon-to-electron conversion efficiency (IPCE) action spectra of DSSCs presented in Figure 4. With the increase in 4L concentration, the overall power conversion efficiency shows a downward trend. Compared to device A with a single dyestuff-N719, devices C and D based on a high 4L molar ratio exhibit lower η values of 8.21% and 8.10%. It is well known that co-adsorbents will compete with N719 for adsorption on the TiO_2 surface. This result shows that N719 and co-adsorbent 4L are in balance at a 1 to 0.25 molar ratio. In this concentration of cosensitizers, N719 may occupy positions on the TiO_2 surface, and coadsorbent 4L then anchors to the blank to create a perfect insulating molecular layer. Because of this layer, the charge recombination process can be shielded, and the incident photo-to-electron conversion efficiency can be enhanced, and this increases V_{oc}, J_{sc}, and η. On the other

hand, devices C and D show downward trend at V_{oc} and FF values in comparison with device A. This indicates that co-adsorbent 4L has considerable superiority at 1 to 0.50 and 1 to 1 molar ratios, with some N719 molecules having lost their positions on TiO_2 and being replaced by co-adsorbent 4L. This increases the opportunities for π-π stacking of small organic molecule-4L and decreases the contribution of N719 to the incident photon-to-electron conversion efficiency [20–22]. These photovoltaic performance results indicate that coadsorption with 4L and N719 in an appropriate concentration is effective in improving solar cell performance.

4. Conclusions

A new triazoloisoquinoline-based co-adsorbent has been prepared and applied in DSSC. This study demonstrates that coadsorption of N719 sensitizer with triazoloisoquinoline-based organic small molecule onto nanocrystalline TiO_2 films significantly increases the photovoltage and photocurrent, thus enhancing the total conversion efficiency. After optimization of the structure of the TiO_2 layer, the cell produced in this work achieved an energy conversion efficiency as high as 8.83% at 100 mW cm^{-2} and AM 1.5 G at 1 to 0.25 (N719 : co-adsorbent) molar ratio. This improved conversion efficiency is attributed to the insulating molecular layer, which was composed of small molecule 4L and N719,
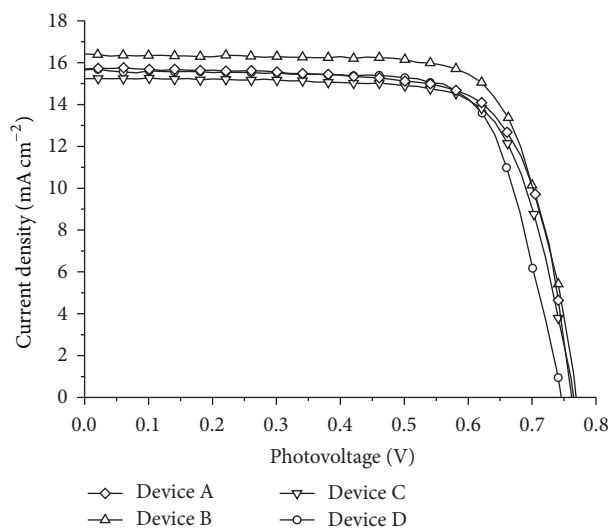
FIGURE 3: Photocurrent density-voltage characteristics of solar cells sensitized by N719 (Device A), N719 : 4L (1 : 0.25) (Device B), N719 : 4L (1 : 0.5) (Device C), and N719 : 4L (1 : 1) (Device D) with $12.0 + 4.0\,\mu m$ double layers nanocrystalline TiO_2 electrodes.
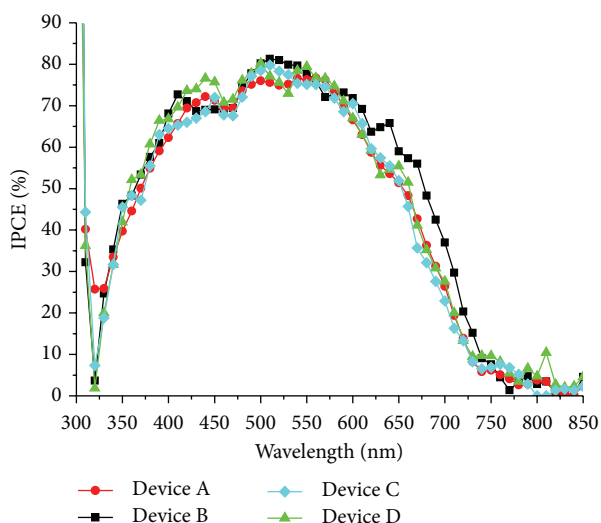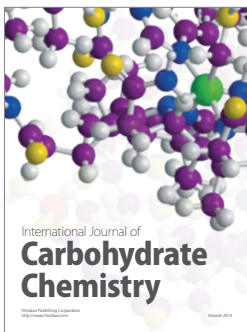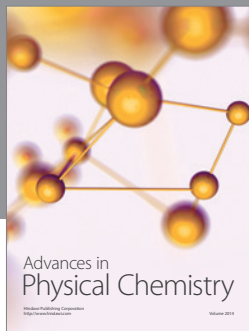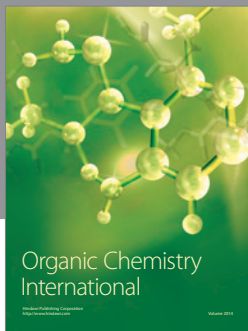

FIGURE 4: IPCE action spectra of solar cells sensitized by N719 (Device A), N719 : 4L (1 : 0.25) (Device B), N719 : 4L (1 : 0.5) (Device C), and N719 : 4L (1 : 1) (Device D) with $12.0 + 4.0\,\mu m$ double layers nanocrystalline TiO_2 electrodes.

and the charge recombination process can be shielded. This breakthrough will contribute to promoting organic small molecule as co-adsorbents in DSSC.

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