

Research Article

Donor- π -Conjugated Spacer-Acceptor Dye-Sensitized Solid-State Solar Cell Using CuI as the Hole Collector

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Dye-sensitized solid-state solar cells (DSSCs) replacing the liquid electrolyte with a p-type semiconductor have been extensively examined to solve the practical problems associated with wet-type solar cells. Here, we report the fabrication of a solid-state solar cell using copper iodide (CuI) as the hole conductor and alkyl-functionalized carbazole dye (MK-2) as the sensitizer. A DSSC sensitized with MK-2 showed a solar-to-electrical power conversion efficiency of 3.33% with a V_{oc} of 496 mV and a J_{sc} of 16.14 mA cm⁻² under AM 1.5 simulated sunlight. The long alkyl chains act as a barrier for charge recombination, and the strong accepting and donating abilities of the cyanoacrylic and carbazole groups, respectively, enhance the absorption of light at a longer wavelength, increasing the short-circuit current density. The efficiency recorded in this work is higher than similar DSSCs based on other hole collectors.

1. Introduction

Since the mid-nineteen nineties, considerable attention has been focused on dye-sensitized solid-state solar cells (DSSCs) due to their attractive features over the wet-type solar cells. Replacing the liquid electrolyte with a p-type hole conductor eliminates liquid leakage and evaporation [1, 2]. However, efficiency remained lower than the wet-type dye-sensitized solar cells (DSCs) and many attempts have been made to enhance the efficiency of DSSCs. The solid-state cell configuration (n-type semiconductor/dye/p-type semiconductor) has the potential of increasing the recombination rate, which reduces efficiency [3, 4]. In order to achieve this, the charge recombination reactions must be slower than the charge injection into the conduction band of the semiconductor. The recombination rate mainly depends on the nature of the dye molecules and the morphology of the semiconductor

[5–7]. The metal-free organic dye with a donor- π spacer-acceptor (D- π -A) configuration is an ideal system for suppressing recombination [8–10]. In addition, metal-free organic dyes are environmentally friendly, easily synthesized, and modifiable to increase the molar absorption coefficient. Recently, an organic dye named MK-2 with a D- π -A configuration has been synthesized and the DSSC application was examined. MK-2 is an alkyl-functionalized carbazole dye, where the carbazole donor group is linked to the acceptor cyanoacrylic acid via an oligothiophene linkage (Figure 1). The long alkyl chain is expected to increase the electron lifetime, facilitating a long distance for charge separation. It is reported that the MK-2 dye has achieved efficiencies of 8.3% and 2.8%, respectively, for wet-type DSC and spiro-OMeTAD-based solid-state versions [11–15]. However, the MK-2 dye has not been used as a sensitizer with an inorganic hole conductor, to the best of our knowledge. The present

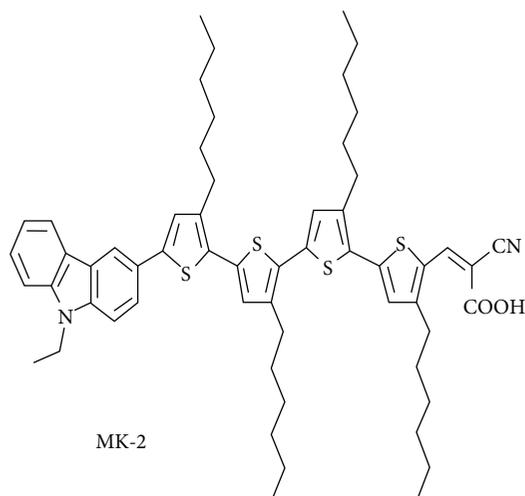


FIGURE 1: Molecular structure of MK-2 dye.

work describes a solid-state DSSC sensitized with MK-2, using CuI as the hole collector.

TiO₂ films required for DSSCs (i.e., largely free of pin-hole contacts exposing the FTO surface) were deposited by the procedure described in the Section 2, which is the simplest and helps to create a mesoporous film of the TiO₂ semiconductor.

2. Materials and Methods

2.1. Deposition of TiO₂ Film on FTO Glass Plate. Titanium tetraisopropoxide (5.0 ml) was mixed with glacial acetic acid (5.5 ml), and 2-propanol (20.0 ml) was added and mixed well. Subsequently, distilled water (5.0 ml) was added to the mixture to hydrolyse isopropoxide during the process of stirring. Subsequently, P25 Degussa TiO₂ powder (0.65 g) was added and the mixture was ground for 10 minutes. A small amount of the resultant hydrolysed suspension was evenly spread on preheated (200°C) FTO plates, solvents were allowed to evaporate, and the loosely bound TiO₂ crust was blown away. During high-temperature deposition, solvents tend to evaporate spontaneously producing bubbles and creating a porous structure within the film. This porous structure has a favourable effect in increasing the film surface area. Finally, films are sintered at 500°C for 20 minutes and the procedure was repeated to obtain a thickness of 15-17 μm.

2.2. Dye Adsorption on TiO₂ Film. The dye 2-cyano-3-[5'''-(9-ethyl-9H-carbazol-3-yl)-3',3'',3''',4-tetra-*n*-hexyl-[2,2',5',2'',5'',2''']-quater thiophen-5-yl] acrylic acid (MK-2) was used as the sensitizer. The TiO₂ electrode, preheated at 80°C, was immersed either in a mixture of acetonitrile/*tert*-butyl alcohol (1:1 volume ratio) or in toluene at a concentration of 3 × 10⁻⁴M for 12 h. The adsorbed dye amount was determined by spectrophotometry. Dye was desorbed from the TiO₂ surface using a triethylamine solution.

2.3. Deposition of CuI on Working Electrode. A saturated CuI solution was prepared by dissolving CuI in acetonitrile. Fifty

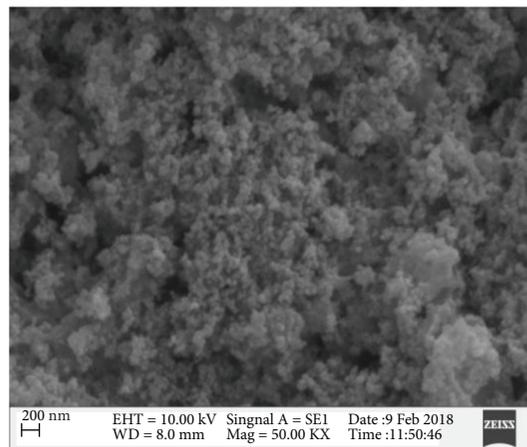


FIGURE 2: SEM micrograph shows the surface morphology of a nanoporous TiO₂ film.

milligrams of triethylamine thiocyanate (TAT) was added to 10 ml of the saturated CuI solution. The dyed TiO₂ plates were kept at 80°C and CuI was deposited dropwise until the surface was fully covered. The CuI-deposited working electrode was sandwiched with the counter electrode to form the cell. The active area of cells used to obtain *I-V* characteristics was 0.25 cm².

2.4. Characterization. The current-voltage characteristics were recorded by using a solar simulator under AM 1.5 illumination. The absorption spectra of the dye solution and the dye-coated TiO₂ films were measured using a UV spectrophotometer (UV-1800, Shimadzu). The TiO₂ photoanode was characterized by using a powder X-ray diffractometer (XRD) (D5000, Siemens) and a scanning electron microscope (LS 15, EVO). To identify the effect of TAT, SEM images were recorded for samples deposited with and without TAT. Incident Photon-to-current Conversion Efficiency (IPCE) was recorded for the best DSSCs which were shown to have a higher photovoltaic efficiency using a photovoltaic characterization machine (PVC300, Bentham).

3. Results and Discussion

The cyanoacrylic moiety of the MK-2 dye possesses a good ability to anchor onto the TiO₂ surface. The molecular structure of MK-2 is shown in Figure 1 [11]. The MK-2 dye is adsorbed onto the semiconductor via a carboxylic group by forming a strong covalent bond with the hydroxyl group on the TiO₂ surface [7, 11]. Figure 2 shows the SEM image of TiO₂ photoanode revealed nearly 96 nm sized particles which were deposited in a uniform manner forming a highly porous structure on the FTO glass substrate.

SEM micrographs show the surface morphology of CuI deposited with and without TAT on a nanocrystalline TiO₂ layer (Figure 3). It is clearly seen that CuI consists of large crystals nearly 7-10 μm in size which would form large vents in the film interfering with the electron transport process. The next SEM image reveals the effect of TAT on CuI. It has been shown that TAT inhibits crystal growth.

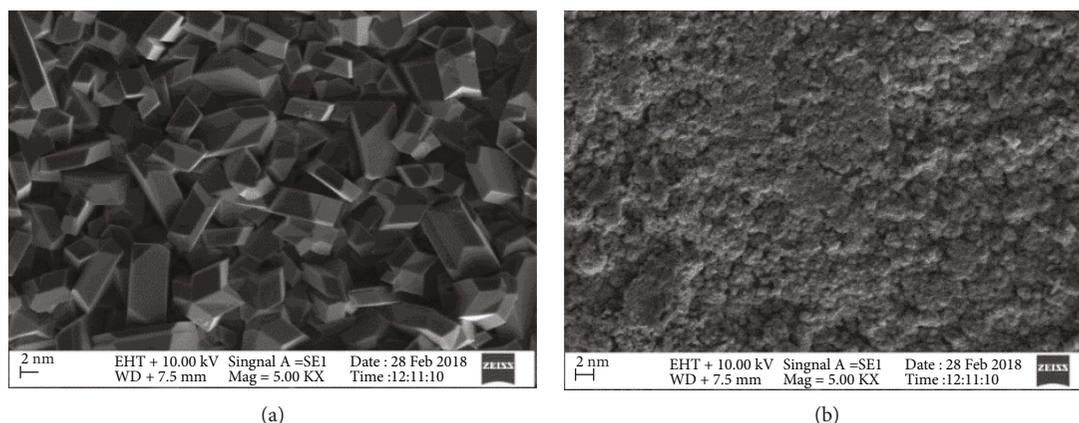


FIGURE 3: SEM micrographs of CuI deposited on the TiO_2 surface with (a) and without (b) triethylamine thiocyanate (TAT).

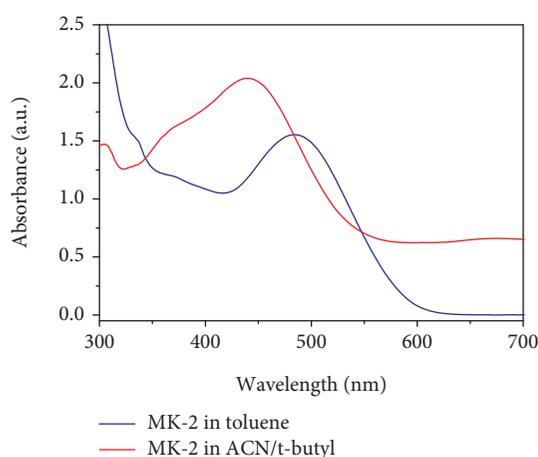


FIGURE 4: UV-visible absorption spectra of the MK-2 dye dissolved in acetonitrile/*tert*-butyl (1 : 1 v/v ratio) and in toluene are indicated by the red line and the blue line, respectively.

Two different solvents (i.e., acetonitrile/*tert*-butyl alcohol (1 : 1 volume ratio) and toluene) are used to prepare the dye solutions of MK-2 because the same solvents were used in the previous study with spiro-OMeTAD. The absorption spectra of the MK-2 dye dissolved in acetonitrile/*tert*-butyl (1 : 1 v/v ratio) and in toluene are shown in Figure 4. The spectra show that both dye solutions have a maximum absorption range of 300 nm-550 nm at the visible region with the maxima at 439 nm and 484 nm. The strong accepting and donating abilities of the cyanoacrylic and carbazole moieties are the causes for the larger given wavelength absorption values. The values for the molar absorption coefficient (ϵ) at λ_{max} 439 nm and 484 nm are $20,392 \text{ M}^{-1} \text{ cm}^{-1}$ and $15,594 \text{ M}^{-1} \text{ cm}^{-1}$, respectively. A clear distinction in the absorption peaks in the two cases indicate a difference in the aggregation blue shift in toluene due to J-aggregation and the red shift in CAN due to H-aggregation. The higher affinity of the hydrophobic moiety to toluene seems to account for the observed difference.

Figure 5 shows the current-voltage characteristics for the MK-2 dye dissolved in acetonitrile/*tert*-butyl alcohol (1 : 1

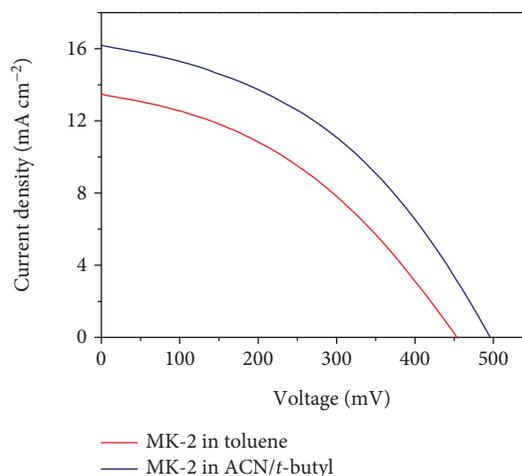


FIGURE 5: Red and blue lines correspond to the I - V characteristics of the DSSCs with $15 \mu\text{m}$ thick TiO_2 films dyed using 0.3 mM of MK-2 in acetonitrile/*t*-butyl (1 : 1 v/v ratio) and 0.3 mM of MK-2 in toluene, respectively (active cell area 0.25 cm^2 and measured under simulated 100 mW cm^{-2} AM 1.5 illumination).

volume ratio) and in toluene. The photovoltaic performances of the DSSCs were measured under 100 mW cm^{-2} AM 1.5 irradiation over an area of 0.25 cm^2 . The performances of the cells are summarized in Table 1. As is observed, DSSCs sensitized with the MK-2 dye and dissolved in acetonitrile/*tert*-butyl alcohol show the best performance with a 0.496 V open-circuit voltage, 16.14 mA cm^{-2} current density, and 0.42 fill factor, with an overall efficiency of 3.33% . The MK-2 dye has been used with the organic hole conductor (spiro-OMeTAD) previously [15].

They have achieved 0.7 V open-circuit voltage, 6.89 mA cm^{-2} current density, and 0.58 fill factor, with an overall efficiency of 2.8% . In terms of photovoltaic performance, the MK-2 dye achieved the highest efficiency with the CuI hole conductor compared to that of the spiro-OMeTAD for DSSCs. The most significant difference can be seen in current density. MK-2 with CuI showed the highest current density of 16.14 mA cm^{-2} , which is more than two times larger than that of spiro-OMeTAD. It is supposed that

TABLE 1: I - V characteristics of DSSCs sensitized with MK-2 dissolved in different solvents.

Solvent type	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	η (%)
Acetonitrile/ <i>tert</i> -butyl alcohol solution	0.496	16.14	0.42	3.33
Toluene	0.453	13.42	0.39	2.40

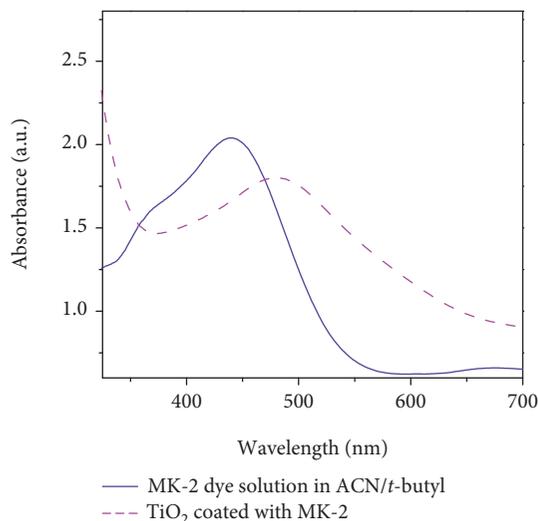


FIGURE 6: Absorption spectra of the MK-2 dye in acetonitrile/*tert*-butyl alcohol (solid line) and dye absorbed in TiO_2 film (dash line).

the MK-2 dye is able to generate suitable electronic communication with CuI. Also, the current density observed for $\text{TiO}_2/\text{MK-2}/\text{CuI}$ is the highest value when compared with a similar type of DSSC with D149 and it is the highest efficiency level recorded for a DSSC so far [16, 17].

The UV-visible absorption levels of the MK-2 dye solution in acetonitrile/*tert*-butyl (1:1 v/v ratio) and the dye-coated nanocrystalline TiO_2 electrode are shown in Figure 6. The dye-coated TiO_2 anode also absorbs visible light at the range from 350 nm to 600 nm. The UV-visible spectrum of the MK-2 dye absorbed on the TiO_2 electrode shows a more remarkable broadening peak than the UV-visible spectrum of the MK-2 dye solution. The MK-2 dye absorbed on the TiO_2 electrode has an absorption maxima λ_{max} at 480 nm. A red shift in the peak, with respect to the solution, is clearly noticeable. This could be due to the π - π stacking interaction between MK-2 dye molecules and the strong interaction between the anchoring group and the TiO_2 surface.

The action spectrum (IPCE vs wavelength) is shown in Figure 7 for the film dyed using acetonitrile/*tert*-butyl alcohol. It reveals that the maximum IPCE of 55% is attained in the wavelength range from 430 nm to 545 nm.

4. Conclusion

In this work, we have fabricated a TiO_2 -based solid-state solar cell with the alkyl-functionalized carbazole dye MK-2. Acetonitrile/*tert*-butyl (1:1 v/v ratio) is found to be a

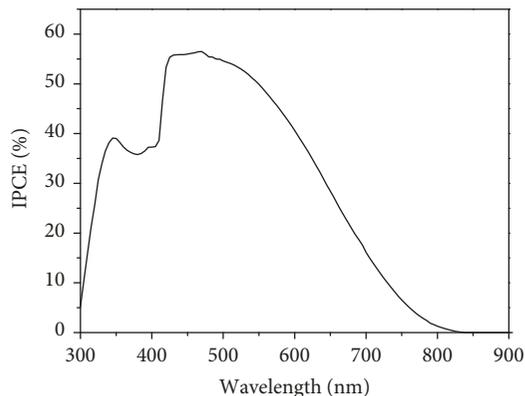


FIGURE 7: IPCE of the DSSC sensitized with MK-2 in acetonitrile/*tert*-butyl alcohol (1 : 1 by volume).

superior toluene as a solvent for dye deposition, giving a higher efficiency. The efficiency obtained for our cell $\text{TiO}_2/\text{MK-2}/\text{CuI}$ is higher than that of the cell $\text{TiO}_2/\text{MK-2}/\text{spiro-OMeTAD}$, implying that MK-2 adapts better to CuI than spiro-OMeTAD. The higher efficiency obtained with MK-2 could be attributed to this effect, as the dye is able to establish strong electronic coupling with CuI. This naturally originates from a difference in the nature of bonding of the dye in two cases. Unfortunately, we could not elucidate the details related to the bond formation via FTIR. This cell gives an overall 3.33% efficiency with a V_{oc} of 496 mV, J_{sc} of 16.14 mA cm^{-2} , and FF of 0.42 under 100 mW cm^{-2} AM 1.5 illumination. The present study suggests that the MK-2 structure can be further modified to suit solid-state cells, especially those based on the hole collector CuI.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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