Porphyrin-Dye Sensitized Solar Cell Utilizing Nitroxide Radical Mediator

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1. Introduction

Dye-sensitized solar cells (DSSCs) are attractive energy source in academic and industrial field. The most effective DSSC was reported by Grätzel et al. in 1991, the total conversion efficiency was over 11 % in standard global AM 1.5 solar light in standard condition.[1] It was composed dye-sensitized nanocrystalline porous semiconductor metal oxide and I/I_3^- electrolyte. The dye-sensitizer is excited by Sun light absorption, and its excited electron inject to semiconductor's conduction band. The dye is regenerated by I in electrolyte. The redox couple of I/I_3^- propagates charge to counter electrode. The I/I_3^- is known good redox mediator for DSSCs. However the redox potential of I/I_3^- (0.4 V vs SHE) is different from that of dye-sensitizer. The large potential gap results energy loss during dye regeneration, and makes DSSC properties,

especially open circuit voltage (V_{oc}) lower.

To improve this mismatch, a new redox mediator having appropriate potential is necessary material. In order to achieve the higher photovoltaic performance, a lot of dye sensitizers such as ruthenium complex, indoline derivatives and so on have been synthesized and modified to exhibit much wider and stronger absorption by changing of their ligands or substituent groups. Porphyrin derivatives are the attractive candidates for novel dye sensitizer due to their strong absorbance in visible region. Then, the antenna dye molecules were also examined to achieve the effective light-harvest.

2,2,6,6-Tetramethylpiperidine-1-oxyl(TEMPO) is widely known as an oxidation catalyst for alcohol. And some nitroxide radical molecules have been applied to organic secondary battery, organic radical memory, and hole-transporting material because of its rapid and reversible redox property. Nitroxide radical molecules have great potential as DSSC's redox mediator. Here, we report the application of nitroxide radical mediator and porphyrin dye to DSSC. In the

Figure 1. Schematic image of DSSC utilizing nitroxide mediator and hetero-dye sensitizer.

Figure 2. Chemical structure of TEMPO, ZnTCCP, and 1-pyrene carboxylic acid.

Present paper, we use a typical porphyrin 5,10,15,20-*tetra*(4-carboxyl-phenyl)porphyrin-Zn(II) (ZnTCCP) as a dye sensitizer and 1-pyrene carbonate as light-harvesting antenna dye.

2. Experimental

TEMPO, *N*-methylbenzimidazole (NMB), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), 1-pyrene carbonate and ZnTCCP were purchased by Tokyo Kasei Inc.. The acetonitrile electrolytes contained 1 M nitroxide radical molecule, 1.6 M NMB, and 0.5 M LiTFSI. In electrolyte, 0.1 M NOBF₄ was also added to make radical cation as redox couple. UV-vis spectra and cyclic voltammetry(CV) were recorded by using JASCO V-550 UV/vis spectrophotometer and BAS 100B/W electro-chemical analyzer, respectively.

Test cells were fabricated as follows. A TiO₂ nanoparticle layer (1.5 μm) and a light scattering layer were fabricated on a fluorine-doped tin oxide-coated glass substrate.¹¹ The resulting layer was heated at 450°C for 2 h in air. Dye adsorption was carried out by immersing the TiO₂ electrode into two solutions for 20 h at room temperature. The dye solution A was a 0.3 mM ZnTCCP and 3 mM deoxychoalic acid in *tert*-butyl alcohol/CH₃CN (1/1 v/v), and the dye solution B was a 0.3 mM ZnTCCP and 3 mM deoxychoalic acid, and 0.3 mM 1-pyrene carbonate in *tert*-butyl alcohol/CH₃CN (1/1 v/v). To add excess deoxychoalic acid, the porphyrin dye absorbed on TiO₂ could avoid the excimer quenching to inhibit π-π stacking state of the dyes. 1-Pyrene carbonate, which achieves effective energy transfer to porphyrin dye, was added as an antenna molecule to emphasize the photovoltaic performance. The counter electrode consisted of a platinum-coated glass plate. Into the fabricated cell assembly was then introduced a solution of the nitroxide mediator which was a CH₃CN solution of 0.25 M TEMPO, 0.05 M NOBF₄, 1.6 M lithium bis(trifluoromethanesulfonyl)imide, and 0.25 M *N*-methyl-benzimidazole. The photovoltaic performances were measured using a Keithley 2400 source meter and an AM 1.5 solar simulator (YSS-40S, Yamashita Denso Co.) as the light source.

3. Results and Discussion

Cyclic voltammetry of TEMPO exhibited reversible redox waves at 0.66 V vs. Ag/AgCl. The oxidation potential was suitable to regenerate the porphyrin dye cation. The diffusion coefficient was 7.5×10^{-5} cm²/s, and the rate constant of electrode reaction was 3.3×10^{-2} cm/s. These values were same order of I/I_3^- . UV-vis absorption of these radical molecules was negligible and avoided the loss induced by light absorption of electrolyte. These results suggest that radical molecules have possibility of an effective dye regeneration and charge propagation.

Though the absorption of ZnTCCP didn't overlap to that of 1-pyrene carbonate, the emission spectra of them was existed very close region. The UV-vis spectrum of these dyes on TiO₂ exhibited a stronger and broaden peak. These results implied that the energy transfer pyrene to ZnTCCP might be effective system, and 1-pyrene was novel antenna dye for ZnTCCP to use UV reagon light. The fluorescence lifetime of ZnTCCP in THF was decreased by addition of the 1-pyrene carbonate. The rapid energy transfer was occurred between ZnTCCP and pyrene, and the energy transfer rate constant was 1.5×10^{12} M⁻¹s⁻¹ estimated by the Stern-Volmer plots.

Figure 3. Absorption spectra of (a) 1-pyrene carbonate, (b) ZnTCCP in methanol and (c) 1-pyrene and ZnTCCP absorbed on TiO₂ electrode commonly from acetonitrile/*t*-butanol solution with a molar ratio of 1/1. Inset: Fluorescence spectrum of 1-pyrene carbonate (solid) and absorption spectrum of ZnTCCP (dotted) in methanol.

Figure 4. Time-resolved emission decays for 1-pyrene carbonate with ZnTCCP in THF. Inset; Stern-Volmer plots for the 1-pyrene fluorescence quenching by ZnTCCP.

Current density-voltage characteristics were shown in Figure. 5. DSSC using TEMPO and ZnTCCP with deoxychoal acid gave maximum properties; V_{oc} was 0.65 V, current density was 2.3 mA/cm², fill factor was 0.74, and conversion efficiency was 1.1 %. The DSSC which is common absorption of ZnTCCP and pyrene was decrease of photovoltaic performance. This decrease gave less absorption of ZnTCCP due to excess pyrene dye.

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Figure 5. Current density-voltage (J - V) characteristics for the ZnTCCP-sensitized solar cells using 0.1 M TEMPO as the redox mediators and a 1.5 mm thick TiO₂ layer on the FTO as the electron transport layer, measured under an AM1.5 full sunlight (100 mWcm⁻²) irradiation.

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