Relationship between diffusion of Co3+/Co2+ redox species in nanopores of porous titania stained with dye molecules, dye molecular structures, and photovoltaic performances

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Diffusion of Co^{2+} and Co^{3+} in nanopores of porous titania stained with various dyes were evaluated and were compared with those of I^-, and I_3^-. Diffusion of Co^{3+} in the bare nanopore was slower than that of I_3^-. Dyes adsorbed on the wall of nanopores affected these diffusion coefficients remarkably. The Co^{3+} diffusion in nanopores became faster when the nanopore wall was covered with dyes with long alkyl groups, probably because the long alkyl groups suppress the interaction between TiO_2 surface and Co^{3+}. Higher open circuit voltage (Voc) was obtained for the DSSC with fast Co^{3+} diffusion in nanopores because the fast diffusion suppresses the charge recombination between electrons in titania and Co^{3+} remaining in the nanopores. The fast diffusion in nanopores was applied to thin nanoparticle spacer (th: 5 μm) of DSSCs. After nanoparticle spacer was stained with dyes with long alkyl groups, the efficiency drastically increased from 2.8% to 5.3%.

1. Introduction

Dye sensitized solar cells (DSSC) consisting of Co^{3+}/Co^{2+} redox shuttle (DSSC-Co) have attract attention because of the high open circuit voltage (Voc).[1-8] The Co^{3+}/Co^{2+} redox potential is deeper (-5.2 eV) than that of I^-/I_3^- redox shuttle (-4.9).[1-8] Because of this, Voc for DSSC-Co has been reported to reach 0.91 V, which is higher than that of DSSC consisting of I^-/I_3^- redox shuttle (DSSC-I) by around 0.1-0.2 V. In addition, since electron transfer from Co redox to the oxidized dye is one step reaction, the voltage loss needed for the dye-generation is about 0.2 V which is lower than 0.4 V needed for dye-regeneration by I^-, where electron transfers from I^- to the oxidized dyes occurs in two steps via I_2^-. From this point of view, DSSC-Co has lower voltage loss and expected to have higher efficiency than DSSC-I. Recently, 13% efficiency for DSSC-Co has been reported.[9]

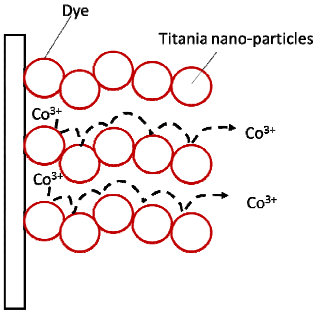

Fig. 1 Conceptual figure for diffusion of Co^{3+} in nanopores prepared with dye-stained nanoparticles

$$I_{lim} = (D \times (2n \times F \times Co))/d \text{ ------ Equation 1}$$

D: diffusion coefficient (cm^2/sec)
d: distance between two electrodes (cm)
I_{lim}: limiting current (mA/cm^2)
F: Faraday constant (C/mol)
C_0: Iodide concentration

One of the problems to be solved for DSSC-Co cell is the slow diffusion of Co ions, resulting in increasing series resistances.[7] One of the approach for solving the diffusion is to use titania fibers.[10-12] Larger titania nanoparticles with thin layer thicknesses has been employed for making the diffusion of Co cation easer in these titania nanopores.[7,9,13] We focused on the diffusion of Co cations in nanopores. Since Co cations diffuse in nanopores of anode, interacting with these nanopore walls as shown in Fig. 1, these nanopore surfaces must affect Co cation diffusions in these nanopores. We have already reported that I^-/I_3^- ion diffusion in titania nanopores were affected by the nanopore walls whose surface was covered with various dyes.[14] This prompted us to study the Co cation diffusions in nanopores whose walls were modified with various dye molecules.The findings were applied to decrease the series resistance of the electrolyte layer. Since limiting current (I_{lim}) is diversely proportional to cell gaps as shown in Equation 1,[15,16] high limiting current is obtained by

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decreasing the electrolyte layer thickness. The electrolyte thickness of DSSC is determined by the thickness (25 to 50 μm) of plastic film spacers. In order to make the electrolyte thickness thinner, nanoparticle spacers have been reported.[17-19] When these nanoparticle spacers were applied to DSSC-Co, contrary to expectations, the Co ion diffusion decreased probably because of the interaction of Co cation and anions presenting on the surface of inorganic nanoparticles. We found that the efficiency of DSSC-Co increased after the surface of nanoparticle spacer was covered with a certain dye.

We now report the relationship between Co cation diffusion in nanopores of the anode modified with dyes and solar cell efficiency. In addition, enhancing efficiency of DSSC-Co consisting of nanoparticles spaces is discussed from the view point of Co ion diffusion in nano-pores of nanoparticle spacer.

2. Experimental

Dyes employed in this experiment are listed in Fig. 2. Fig. 2a shows Ru dyes with various chain length (N3, N719, Z907, and K19). Indoline dyes (D77, D102, D133, D149, D205, and D358) are summarized in Fig .2b. Dyes with oligothiophene structures (MK-1, MK-2, and MK-75) are linsted in Fig. 2c. Ru dyes, Indoline dyes and MK dyes were purchase from Solaronix, Mitsubishi Paper Mills Limited, and Soken Chemical & Engineering respectively and used without further purification. Porphyrin dye (YD-o-C8) was purchased from Yingkou OPV Tech New Energy and used without further purification. $Co(bpy)_3(PF_6)_2$ (bpy:bipyridyl) and $Co(bpy)_3(PF_6)_3$ were prepared in the method reported previously.[20]

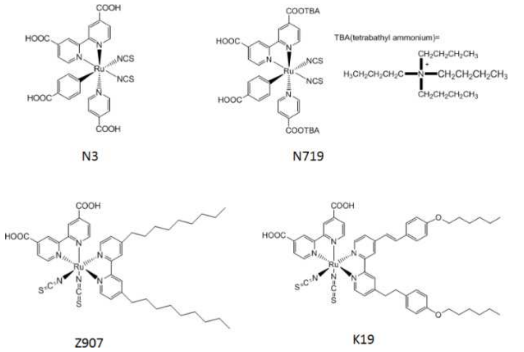

Fig. 2a Dye structures and abbreviations consisting Ru metals

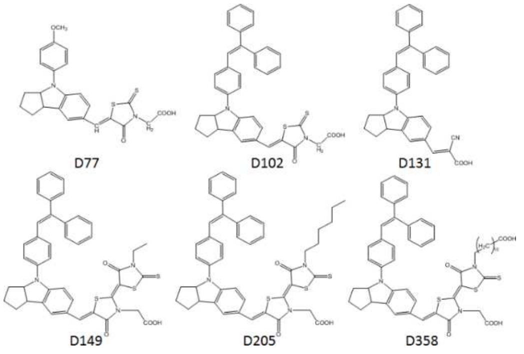

Fig. 2b Dye structures and abbreviations consisting of indoline moiety

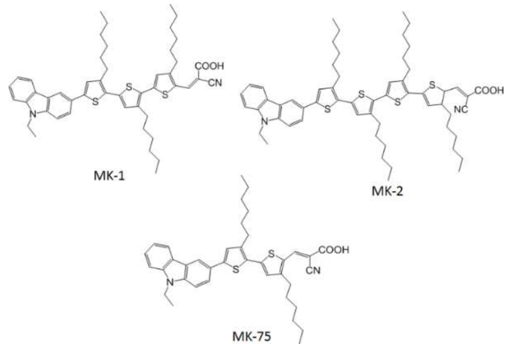

Fig. 2c Dye structures and abbreviations consisting oligo-thiophene moiety

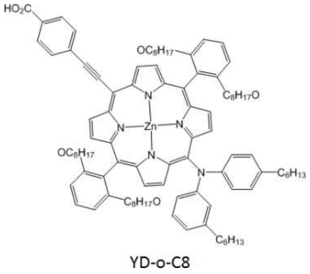

Fig. 2d Porphiline dye structure and the abbreviation

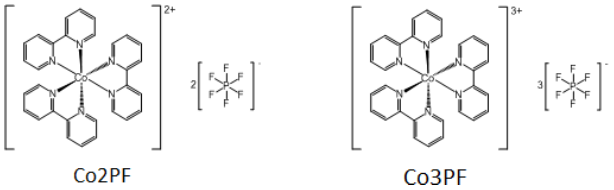

Fig. 2e Co redox shuttle structure

Measurement of ion diffusion in nanopores

Fig. 3 shows a custom made apparatus for measuring ionic diffusion rates. A 50 mM solution of cation (Fig. 2e, Co2PF, Co3PF, Li^+I^-, or LiI_3^-) in acetonitrile was poured in compartment A. Compartment B was filled with acetonitrile and each compartment was stirred. Cations diffuse from the compartment A to the compartment B through a porous titania sheet (Ti-P). The concentrations of these ions in A and B compartments were monitored spectroscopically at 360 nm or 318 nm absorption, respectively. A sheet Ti-P is a nanoporous titania sheet supported by a stainless steel mesh[14] and the porous titania sheet was stained with dyes. A titania paste (Solaronix, Ti-Nanoxide D/SP) was coated on a stainless steel mesh sheet (Asada Mesh, SUS-304 SV-16/16tw) and the composite sheet was baked at 500°C for 30 minutes to prepare 29 μm thickness of porous titania sheet. The sheet was dipped in a dye solution for dye staining. The space of a stainless metal mesh was completely buried with nanoporous titania.[14]

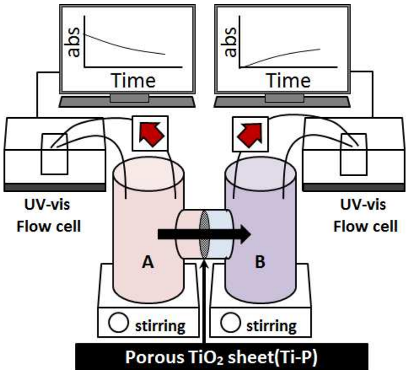

Fig. 3 Apparatus measuring diffusion of Co^{3+}, Co^{2+}, I^- and I_3^-

Conventional DSSC (Con-DSSC) in Fig. 4A was prepared in the method reported previously.[20] A titania paste (Solaronix, Ti-Nanoxide D/SP) was coated on a F-doped SnO_2 glass substrate (FTO glass, Nippon Sheet Glass) followed by baking at 450 °C. The substrate was then dipped in a dye solution. An FTO glass with sputtered Pt layer was employed as the counter electrode. The cell was sealed with Himilan films (Mitsui-DuPont Polychemical, 25 µm thickness). The electrolyte (E-1) consists of $Co(bpy)_3(PF_6)_2$ (0.22 M), $Co(bpy)_3(PF_6)_3$ (0.033 M), $LiClO_4$ (0.1 M), and 4-tert-Butylpyridine (0.2 M) in acetonitrile.

DSSCs with nano-spacer (DSSC-NS) shown in Fig. 4B were fabricated in the following method. The anode was prepared in the same way as that of Con-DSSC. On the Pt layer of FTO glasses working as the counter electrode, PST-30NRD (JGC Catalysts and Chemicals, diameter:30 µm) paste was coated and the sample was baked at 450 °C for 30 min to give nanoporous spacer with 5 µm thickness (TiO_2-2). The cathode was coupled with the anode and the space was filled with electrolyte (E1). Finally the side was sealed with UV curable resin.

DSSCs with surface-modified nano-spacer (DSSC-NS-S) were prepared as follows. The anode was prepared in the same way as that of Con-DSSC. On the Pt layer of FTO glasses working as the counter electrode, PST-30NRD paste was coated and the sample was baked at 450 °C for 30 min to give nanoporous spacer with 5 µm thickness. The sample was dipped in dye solutions to giveDSSC- a counter electrode with surface-modified nano-spacer. (TiO_2-3 in Fig. 4) The counter electrode was coupled with the anode and the space between then was filled with electrolyte (E1). Finally the side was sealed with UV curable resin.

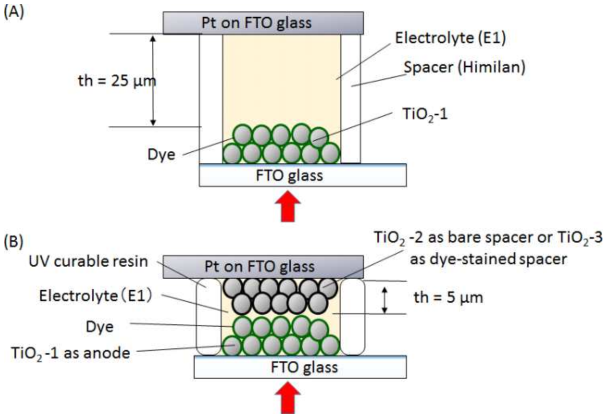

Fig. 4(A) Con-DSSC, (B) DSSC- NS or DSSC-NS-S

Diffusion coefficient (D) of redox species was calculated using equation 2.[14]

$$\ln\frac{C_{A0}-C_{B0}}{C_A-C_B}=\frac{2\varepsilon S}{\tau\delta V}Dt \quad \text{-------- Equation 2}$$

Where, C_{A0} and C_{B0} : initial concentrations of Co2PF or Co3PF (Li^+I^-, or LiI_3^-) in chambers A and B, C_A and C_B : their concentrations in chambers A and B at time t, ε: aperture ratio of nanoporous titania sheet, S: titania film surface area, τ: ratio on actual diffusion length in a nanoporous titania film/titania film thickness, δ: titania film thickness, V: volumes in chambers A and B.

Table 1 Photovoltaic performances for con-DSSC

	Voc[V]	**Jsc[mA/cm^2]**	**FF**	**Efficiency[%]**
N3	0.55	6.57	0.54	1.98
N719	0.59	6.08	0.47	1.68
Z907	0.68	11.93	0.54	4.39
K19	0.60	7.51	0.58	2.59
D77	0.64	4.42	0.53	1.49
D102	0.67	6.92	0.48	2.24
D131	0.65	4.38	0.55	1.57
D149	0.69	8.44	0.61	3.54
D205	0.76	9.94	0.69	5.17
D358	0.72	7.81	0.66	3.68
MK-1	0.69	10.28	0.70	4.99
MK-2	0.70	11.82	0.65	5.34
MK-75	0.70	10.25	0.70	4.98
YD-o-C8	0.75	11.40	0.57	4.92

Table 2 Diffusion coefficent of Co^{3+},Co^{2+},I^-,I_3^- in nanopours stained with various dyes.

	Bare	N3	N719	Z907	K19	D77	D102	D133	D149	D205	D358	MK-1	MK-2	MK-75	YD-o-C8
Co^{3+}	1.74	1.51	1.03	1.49	1.08	1.32	-	-	1.38	2.18	0.80	1.58	1.84	1.21	2.48
Co^{2+}	2.62	4.69	3.07	4.51	3.59	2.10	-	-	1.65	1.74	2.18	2.54	1.47	1.74	3.51
I^-	3.70	4.06	2.68	3.37	3.55	4.59	4.33	3.78	3.66	4.32	4.57	-	-	-	2.91
I_3^-	3.11	1.96	1.75	1.63	2.29	3.86	4.98	3.97	4.20	3.44	3.27	-	-	-	2.43

3. Results and discussion

Table 1 summarizes photovoltaic performances of Con-DSSC whose anode was stained with various dyes. We focused on the variation of open circuit voltage (Voc) for deducing the relationship between the solar cell efficiency and diffusions of Co ions in nanopores of the porous titania layer. Since short circuit current (Jsc) is varied by dyes covering the solar light spectrum range, these changes are not directly associated with the Co ion diffusion. Fill factor (FF) was also varied from 0.47 to 0.70. However, these FFs are affected by charge recombination (Parallel resistance) as well as by series resistance in the solar cells. Therefore, we discussed the solar cell performances by the variation of open circuit voltage (Voc). Voc was varied from 0.55 to 0.76 V, depending on the dyes employed.

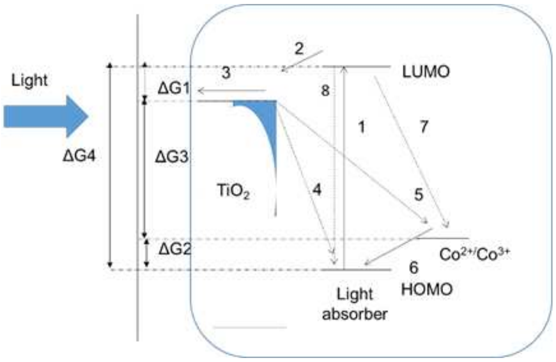

Fig. 5 Working principle for DSSC-Co (DSSC consisting of Co^{3+}/Co^{2+} redox shuttle)

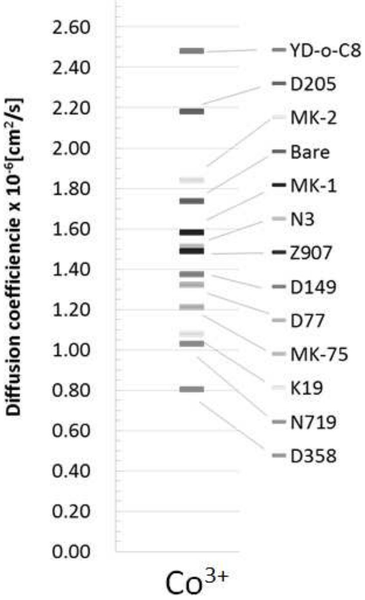

Fig. 6 Summary of diffusion coefficient of Co^{3+} in nanopores stained with various dyes.

Fig. 5 shows the working principle for con-DSSC with Co redox shuttle. The valence band of anatase titania is deeper than HOMO of light absorber. Therefore, we considered the conduction band only in Fig. 5. After light absorber is excited, electrons are injected into titania (2 in Fig. 5), followed by electron injection from Co redox (6 in Fig. 5). Voc is determined by the energy gap (ΔG3 in Fig. 5) between conduction band of titania and redox potential of Co^{2+}/Co^{3+}. The Voc is also affected by charge recombination between electrons in titania and Co^{3+} (5 in Fig. 5). Therefore, route 5 in Fig. 5 is important for determining Voc of the DSSC-Co. Co^{3+} redox species have to travel the long and narrow channels of porous titania from the FTO glass side to the electrolyte layer side. Co cations diffuse, interacting with the surface of the nano-channels as shown in Fig. 1, which is similar to phenomena for material separation by column chromatography.

Table 2 summarizes the diffusion rate of Co^{2+} and Co^{3+} in dye-stained nanopores in porous titania layer. In the nanopores, in almost all cases, the diffusion of Co^{2+} was faster than that of Co^{3+}. For example, in the nanopores without dye-staining (bare porous titania layer), Co^{3+} and Co^{2+} diffusion coefficients were 1.74 x 10^{-6} cm^2/s and 2.62 x 10^{-6} cm^2/s respectively. The exception was D205 and MK-2, where Co^{3+} moved faster than that of Co^{2+}. Since Voc is affected by charge recombination between electrons in titania and Co^{3+} or I_3^-, we want to focus on the diffusion of Co^{3+}or I_3^-. For the comparison, diffusion coefficient for I^- and I^{3-} in nanopores are also summarized on Table 2. The diffusion of larger Co^{3+} bearing three bpy (bipyridyl) group (1.74 x 10^{-6} cm^2/s) was much slower than that of I_3^- (3.11 x 10^{-6} cm^2/s) in the nanopores of the bare porous titania layer, which is expected by the following Stokes-Einstein relation

$$D=RT/6\pi N_a R_a M_a \eta$$

D: Diffusion coefficient
T: Temperature
R_a: Ion radius
M_a: Microviscosity factor
η: Viscosity

After the nanopore walls were stained by dye molecules, the same trend was observed. Diffusion of smaller I^- is faster than that of I_3^-, which has been reported previously. [14] For example, in nanopores fabricated with bare TiO_2 nanoparticles, I^- and I_3^- diffusion coefficients were 3.70 x 10^{-6} and 3.11 x 10^{-6} cm^2/s, respectively. After the nanopore wall was modified with dye molecules, I_3^- diffusion in nanopores stained with D77, D102, D133, D149 and D205 became faster than that of bare TiO_2 nanoparticles. The trend for the relationship between the diffusion of I_3^- and dye structures was not the same as that of Co^{3+} diffusion. The difference may be explained by the opposite charges of Co^{3+} and I_3^-, where interaction site of dyes with these redox ions may be different each other. Since the charge recombination between electrons in porous titania and Co^{3+} occurs in titania nanopores, the diffusion rate of Co^{3+} in nanopores should be associated with Voc. Diffusion coefficients of Co^{3+} species in dye-stained nanopores are summarized in Fig. 6. Among these Ru dyes, Co^{3+} diffusion rate increased as the following order: K19 ≒ N719 < Z907 ≒ N3, however, the variation was not large. Among indoline dyes, Co^{3+} diffusions varied as follows: D359 < D149 < D205. Co^{3+} diffusion in MK2-stained nanopores was faster than those in MK-1 and MK-75-stained nanopores. These results imply that Co^{3+} ions diffuse faster in nanopores stained with dyes consisting of long alkyl chains such as MK-2 and D205. In almost all cases, the Co^{3+} diffusions in nanopores stained with dyes were slower than those of bare-nanopores (nanopores without dye-staying), with the exception of D205 and YD-o-C8. Much faster Co^{3+} diffusions were observed in nanopores stained with D205 and YD-o-C8. Especially, the diffusion rate of the ions in YD-o-C8-stained nanopores was 2.48 x 10^{-6} cm^2/s, which was the fastest among them. Since YD-o- C8 has long C8 alkyl chains, longer alkyl chains suppress the interaction of negatively charged TiO_2 surface with Co^{3+}.

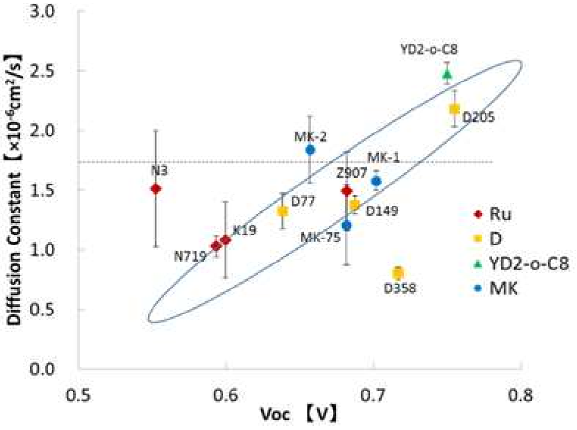

Fig. 7 The relationship between Voc and diffusion coefficient

Fig. 7 shows the relationship between open circuit voltage (Voc) and Co^{3+} diffusion rate in nanopores stained with various dyes. Roughly speaking, Voc increased with an increase in the diffusion coefficient of Co^{3+}. The slow diffusion of Co^{3+} in nanopores increases the opportunities for charge recombination between Co^{3+} and electrons in porous titania layer. D358 and N3 were deviated from the relationship. The Co^{3+} diffuses slowly in the nanopores stained by D358 (0.80 x 10^{-6} cm^2/s) but the Voc was rather high (0.72 V). D358 has two anchoring groups. The two anchoring groups may passivate well the surface state of the porous titaniamore effectively than single anchoring group. We have already reported that the surface states (traps) in porous titania become the center for the charge recombination. The Voc was increased after the surface traps were passivated with organic anchoring groups.[21-23] In addition, large deviation from the line (Fig. 7) was observed for N3. Co^{3+} diffusion coefficient was (1.51 x 10^{-6} cm^2/s) in nanopores stained with N3. From the line shown in Fig. 7, 0.65-0.7 V of Voc was expected. However, the Voc was 0.55 V which was lower than that expected. It has been reported that N3 has four COOH groups and some are used for anchoring to porous titania and the others remain as free COOH groups.

The protons shift the conduction band of porous titania to deeper level, which causes the decrease in the Voc.[24, 25]

It was concluded that Voc of the DSSC is correlated with diffusion rate of Co^{3+} in nanopores stained by dyes. High Co^{3+} diffusion was

Table 3 Photovoltaic parameters for DSSC-NS and DSSC-NS-S consisting of Co^{3+}/Co^{2+} redox shuttle

	Jsc [mA/cm^2]	Voc[V]	FF	Efficiency[%]
Bare spacer	7.23	0.6	0.67	2.92
Dye-stained spacer	9.24	0.7	0.66	4.26

obtained in nanopores stained with dyes consisting of long alkyl chains and gave high Voc. In nanopores stained by YD2-o-C8, Co^{3+} had the highest diffusion coefficient. This corresponds to the high voltage reaching 1 V for DSSC stained with YD2-o-C8.

One of disadvantages for DSSC-Co is the slow diffusion of Co^{3+} in electrolyte solvents, leading to increasing the series resistance. One of approaches for decreasing the series resistance is to make the electrolyte layer thickness thinner. Thickness of conventional polymer film employed as the spacer is 25-50 µm. To make the electrolyte thickness thinner, nanoparticle spacers have been employed.[17-19] However, as was described before, Co ions interact with the surface of inorganic nanoparticles, which suppresses the swift diffusion of Co $^{3+}$ in the nanopores of the nanoparticle spacer layer.

In order to solve the problems, we applied the results obtained above. Namely, nanoparticle spacers covered with dye molecules were employed. The device structure is shown in Fig. 4 B. The devise was composed of TiO$_2$-1 stained with dye working as anode/electrolyte (E-1)/bare TiO$_2$-2 or TiO$_2$-3 stained with dye working as nanoparticle spacer/Pt counter electrode. The thickness of the gap was decreased from 25 µm (Fig. 4A) to 5 µm (Fig. 4B). From the Table 2, Co^{3+} diffusion in the bare nanopores is 1.74 x 10^{-6} cm^2/s and the diffusion increased to 2.48 x 10^{-6} cm^2/s as the nanoparticles were stained with YD-o-C8. Diffusion rate of Co^{2+} in the nanopores also increased from 2.62 x 10^{-6} cm^2/s to 3.51 x 10^{-6} cm^2/s after YD-o-C8 was adsorbed on the nanoparticle spacer. Fig. 8 shows the photovoltaic performances of DSSC-NS consisting of bare nanoparticle spacer and DSSC-NS-S consisting of YD-o-C8-stained nanoparticle spacer. The Jsc, Voc, FF, and efficiency increased from 7.23 to 9.24 mA/cm^2, 0.6 to 0.7V, 0.66 to 0.67, and 2.92 to 4.26% after the nanoparticle spacer was stained with YD-o-C8.

Conclusions

It was found that Co^{3+} diffusion coefficient in nanopores varied when the nanopore surface was stained with various dyes. Among them, Co^{3+} diffusion coefficient in nanopores stained with YD-o-C8 was best. This was applied to surface modification of nanoparticle spacers. The nanoparticle spacers coated with YD-o-C8 gave the better photovoltaic performance than bare nanoparticle spacers, which was explained by swift diffusion of Co^{3+} in the nanopores in nanoparticle spacers stained by YD-o-C8.

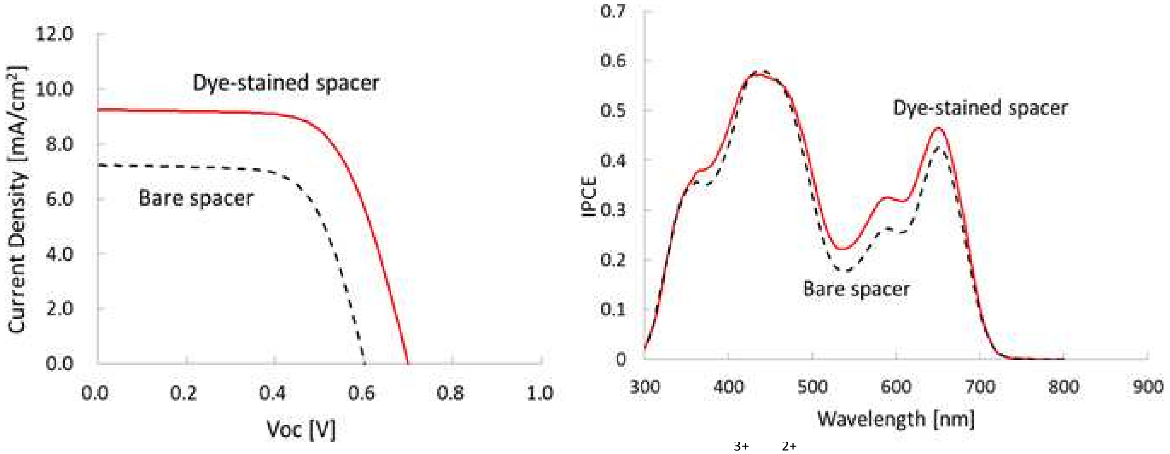

Fig. 8 Photovoltaic performances for DSSC-NS and DSSC-NS-S consisting of Co^{3+}/Co^{2+} redox shuttle. DSSC-NS: DSSC consisting of bare nanoparticle space, DSSC-NS-S: DSSC consisting of nanoparticle spacer stained with YD-o-C8

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