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Improved Tri-iodide Reduction Reaction of Co-TMPP/C as a Non-Pt Counter Electrode in Dye-Sensitized Solar Cells

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ABSTRACT :

We report Co-tetramethoxyphenylporphyrin on carbon particles (Co-TMPP/C) as a non-Pt catalyst for tri-iodide reduction in dye-sensitized solar cells (DSSCs). The presence of well-dispersed carbon and cobalt source in the catalyst surface is confirmed by transmission electron microscopy, scanning electron microscopy, and energy dispersive X-ray analysis. In the C 1s, Co 2p, and N 1s peaks measured by X-ray photoelectron spectroscopy, the C-N, Co-N_4, and N-C are assigned to the component at 285.7, 781.8, and 401 eV, respectively. Especially, the Co-TMPP/C shows improved current density, diffusion coefficient, and charge-transfer resistance in the I_3^-/I^- redox reaction compared to conventional catalysts. Furthermore, in the DSSCs performance, the Co-TMPP/C shows increased short circuit current density, higher open circuit voltage, and improved cell efficieny in comparison with Pt/C.

Keywords : Tri-iodide reduction, Co-TMPP, Non-Pt, Counter electrode, Dye-sensitized solar cells

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1. Introduction

Dye-sensitized solar cells (DSSCs) have been intensively studied because of high energy conversion efficiency and low cost for production.[1-7] Generally, DSSCs consist of TiO_2 electrode as an anode, dye for light harvesting, Pt electrode as a cathode, and electrolyte for an electron transfer mediator. An electron is photoexcited and injected from dye to the TiO_2 under an illumination. The dye is reduced by electron transfer mediator, I^-/I_3^-. The generated electrons flow through the external circuit, arrive at Pt counter electrode, and reduce the oxidized electrolyte as the mediator. The electrons that flow through an external circuit arrive at the counter electrode and participate in the regeneration of tri-iodide, according to reaction of $I_3^- + 2e^- = 3I^-$.[8-11]

For practical applications of DSSCs, many efforts have been made to improve efficiency and long-term

stability in the anode,[12-16] whereas only few studies of the cathode for the tri-iodide reduction in DSSCs have been reported.[17-20] The best candidate for use as a reduction cathode catalyst is Pt metal due to its excellent electrocatalytic activity. Especially, the sputtered Pt showed the best cathode performance due to its low charge transfer resistance, moderate porosity, and good adhesion of the Pt layer onto the transparent conducting oxide (TCO) substrate.[21] In addition, to replace expensive Pt catalysts, Saito *et al*. and Suzuki *et al*. suggested the utilization of a conducting polymer and carbon nanotube as the counter electrode, respectively.[22-25] However, still, few studies of the cathode for the tri-iodide reduction in the DSSCs have been reported.

In this paper, we prepared Co-tetramethoxyphenylporphyrin (Co-TMPP) supported by carbon as a non-Pt catalyst for tri-iodide reduction in dye-sensitized solar cells (DSSCs). The catalyst was characterized using transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), and X-ray photoelectron

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spectroscopy (XPS). To characterize the photoelectrochemical properties and cell performance in DSSCs, cyclic voltammograms (CVs) and current-voltage curves were obtained using carbon supported Co-TMPP as a counter electrode compared to conventional catalysts.

2. Experimental

Carbon-supported Co-TMPP catalysts (Co-TMPP/C) were prepared with precursors in organic solvent. Cobalt(II) acetate (0.08 g, Aldrich) and 5, 10, 15, 20-tetrakis(4-methoxyphenyl)-21H,23H-porphyrin (H$_2$TMPP, 0.1 g, Aldrich) were dissolved in 99.7% acetic acid (Aldrich) solution for 1 h. After completely dissolving, carbon powder (Vulcan XC-72R) was added slowly into the solution to form a homogeneous blended solution by adsorbing the Co-TMPP on carbon. After an adequate stirring, the solution was completely evaporated the solvent and then dried at 60°C overnight. The obtained powder was placed in a quartz boat and heat-treated at 700°C for 3 h in a horizontal quartz furnace under N$_2$ atmosphere.

The catalyst was characterized by transmission electron microscopy (TEM) using a Philips CM20T/STEM Electron Microscope system at 200 kV. The TEM sample was prepared by placing a drop of the catalyst suspension with ethanol on a carbon-coated copper grid. Scanning electron microscopy (SEM, JSM-6700F) and energy dispersive X-ray (EDX, EX-23000BUB) analyzer were used to identify the Co-TMPP in the catalyst. X-ray photoelectron spectrometry (XPS, Thermo Scientific) study was carried out with the Al K$_\alpha$ X-ray source of 1486.6 eV at the chamber pressure below 5×10^{-9} Pa. The C 1s electron binding energy was referenced at 284.6 eV and a nonlinear least-squares curve-fitting program was employed with a Gausian-Lorentzian production function.

In order to evaluate an electrocatalytic activity towards tri-iodide reduction, cyclic voltammetry was carried out in the solution consisting of 0.1 M LiClO$_4$ as supporting electrolyte and 10 mM LiI and 1 mM I$_2$ as redox couple in acetonitrile solvent. A Pt (20 wt%)/C (E-TEK), Co-TMPP/C or carbon (Vulcan XC-72R) was used as a working electrode. The catalyst paste for the counter electrode was prepared using 0.5 g catalyst mixed with acetic acid (0.09 mL), distilled ion water (0.54 mL), ethanol (9.62 mL), ethyl cellulose (0.25 g) and terpineol (1.79 mL), and then evaporated at 80°C for 20 min. The prepared catalyst paste was coa-

ted on the FTO glass (F-doped tin oxide, 12 ohm/sq) using doctor blade method and annealed at 400°C for 30 min in N$_2$ atmosphere.

To characterize cathodic tri-iodide reduction of the catalysts, cyclic voltammograms (CVs) were obtained using a potentiostat (CH Instruments Inc. 700C Series) in a three-electrode electrochemical cell. The catalysts, Pt wire, and Ag/AgCl were used as a working, counter, and reference electrode, respectively. The CVs of the catalysts were obtained from −0.2 to +1.3 V in the solution consisting of 0.1 M LiClO$_4$ as supporting electrolyte and 10 mM LiI and 1 mM I$_2$ as redox couple in acetonitrile solvent.[24]

Nanocrystalline TiO$_2$ powder (Degussa, P25) of 0.5 g was ground in a bowl for a few minutes with acetic acid (0.09 ml), deionized water (0.54 mL), ethanol (9.62 mL), ethyl cellulose (0.25 g), and terpineol (1.79 mL). The paste was deposited on a transparent conducting glass (SnO$_2$: F, 12 ohm/sq) by using doctor blade technique. The films were annealed at 500°C for 1 h in air. For photosensitization studies, the TiO$_2$ films were soaked in an anhydrous ethanol solution containing 5×10^{-4} M Ru535 (Solaronix, N3 dye) for 24 h. The dye-absorbed TiO$_2$ film used as working electrodes in two-electrode sandwich cells with effective areas of 0.16 cm^2 and the inner space was filled with a liquid electrolyte containing 0.5 M LiI and 0.05 M I$_2$ as a redox mediator. Photocurrent measurements were carried out using a 500 W Xe lamp (XIL model 05A50KS) simulated AM 1.5 solar irradiance with the intensity of 100 mW cm^{-2}, which was adjusted using a NREL fabricated Si reference solar cell.[25] Electrochemical impedance spectroscopy (EIS) was carried out to identify charge-transfer resistance of counter electrodes in DSSCs. The EIS spectra were obtained at open circuit potential with 10 mV amplitude over the frequency range of 0.01-10^5 Hz.

3. Results and discussion

Fig. 1 shows transmission electron microscopy (TEM) images of the Co-TMPP supported by carbon (Co-TMPP/C) as a reduction catalyst. The Co-TMPP/C seems to be the carbon particles mixed with tetramethoxyphenylporphyrin (TMPP) exchanged by cobalt metal. In other words, the Co-TMPP is well dispersed on the carbon particles without any precipitates such as cobalt oxides or nitrides. However, to identify the Co-TMPP in the catalyst, as shown in
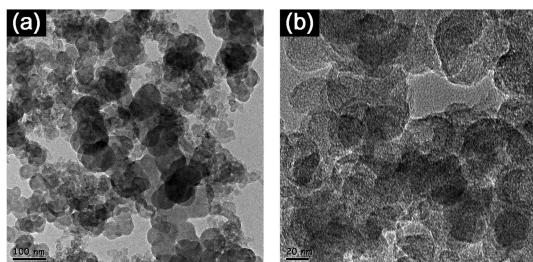
Fig. 1. (a) Transmission electron microscopy and (b) high-resolution transmission electron microscopy images of Co-TMPP/C.
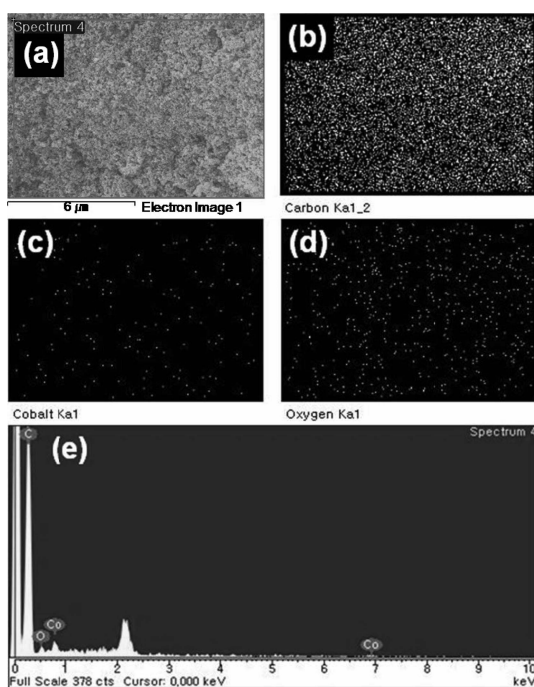

Fig. 2. Scanning electron microscopy (a), mapping images ((b) carbon, (c) cobalt, and (d) oxygen), and energy dispersive X-ray spectrum (e) of Co-TMPP/C.

Fig. 3. X-ray photoelectron spectra of (a) C 1s, (b) Co 2p, and (c) N 1s of the Co-TMPP/C.

Fig. 2, the SEM, mapping images, and EDX spectrum of the catalyst were obtained. The presence of carbon and cobalt source homogeneously dispersed in the catalyst surface is confirmed by X-ray mapping images (Fig. 2(b),(c)) and EDX result (Fig. 2(e)). As shown in Fig. 3(a), C 1s spectrum consists of four peaks at 284.3, 285.7, 287.2, and 290.4 eV corresponding to C-C, C-N, C-O(ethers), and C-O(carbonates), respectively. Fig. 3(b) shows that Co 2p spectrum consists of four symmetrical peaks at 780.5, 781.8, 783, and 785 eV for curve fitting of the Co-TMPP catalyst.
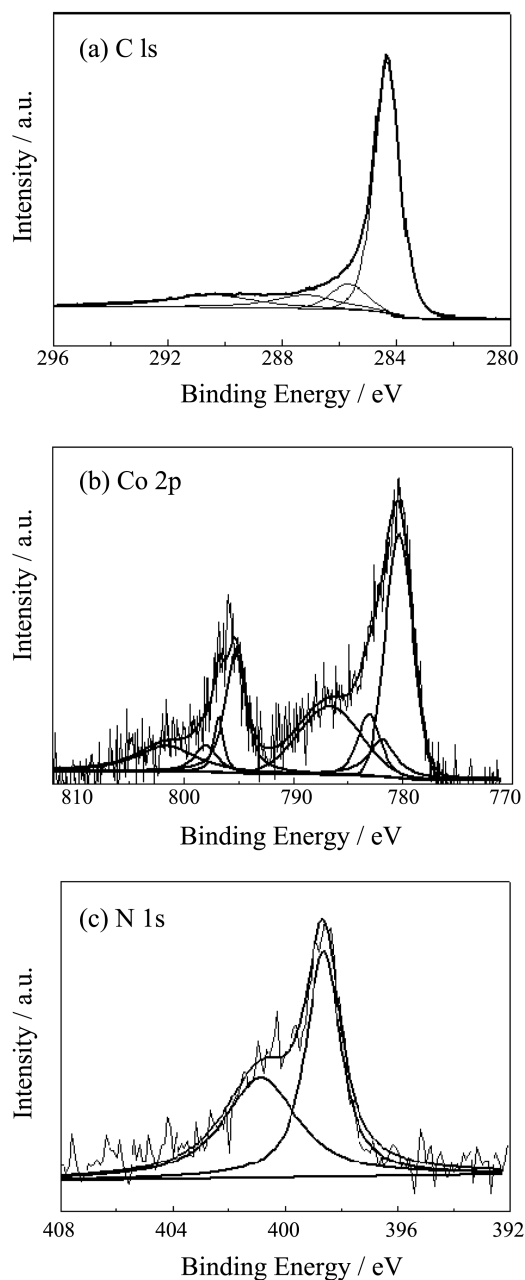
Based on the theoretical stoichiometry of the TMPP precursor, all of the cobalt should be present in a Co-N_4 environment. In the Co 2p spectrum, however, two main oxidation states are present at 780.5 and 781.8 eV. The Co-N_4 is assigned to the component at 781.8 eV, while there are several possible assignments for the

peak at 780.5 eV. This component may be due to cobalt oxides, cobalt carbide, or cobalt within an incomplete N_4 environment with some Co-C bonds. As shown in Fig. 3(c), two main binding energy peaks of nitrogen exhibit at 398.8 and 401 eV required to curve fit in the N 1s spectrum. The pyridinic N is assigned to the component at 398.8 eV and quaternary N is presented for the peak at 401.5 eV.

Fig. 4 shows SEM images of C, Co-TMPP/C, and Pt/C electrodes with ~10 μm in thickness for tri-iodide reduction prepared by coating on the FTO substrates using doctor blade method followed by annealing at

400°C for 30 min in N_2 atmosphere. The counter electrodes seem to be identically homogeneous structure for electrochemical reduction in DSSCs. This suggests that the mesoporous structure of the electrodes can facilitate the diffusion of I_3^- ions. Fig. 5(a) shows cylic voltammograms (CVs) of I_3^-/I^- system for the C, Co-TMPP/C, and Pt/C electrodes at a scan rate of 50 mV s^{-1}. In the CVs, two pairs of redox peaks were observed in all the cases. The more positive pair between 0.4 and 0.8 V is assigned to the redox reaction Eq. (1) and the more negative one is assigned to redox reaction Eq. (2).

$$3I_2 + 2e^- = 2I_3^- \qquad (1)$$

$$I_3^- + 2e^- = 3I^- \qquad (2)$$

In the DSSC, electrons are injected to photo-oxidized dye from I^- ions in the electrolyte (Eq. (1)), and the
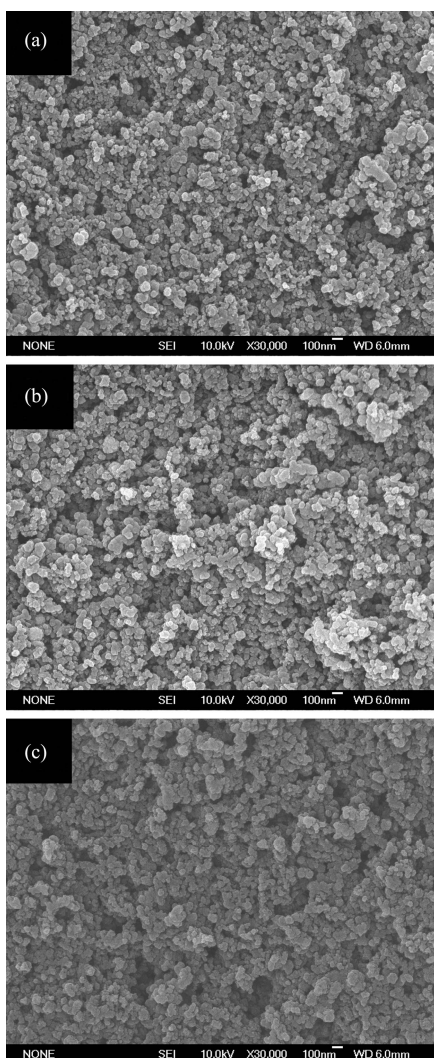
Fig. 4. Scanning electron microscopy images of (a) C, (b) Co-TMPP/C, and (c) Pt/C electrodes for tri-iodide reduction.
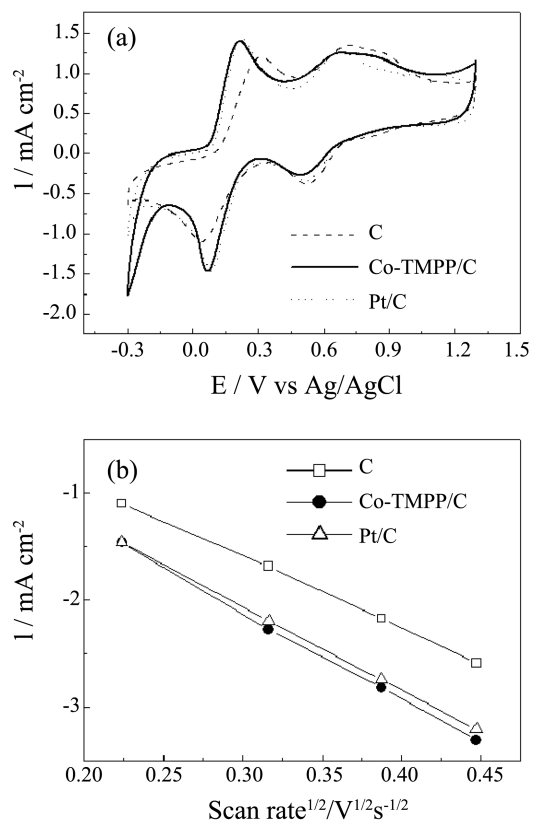
Fig. 5. (a) Cyclic voltammograms for electrodes in 10 mM LiI and 1 mM I_2 acetonitrile solution containig 0.1 M LiClO$_4$ at a scan rate of 50 mV s^{-1}. (b) Redox peak currents at reduction potential of I_3 as a function of different scan rates.

produced I_3^- ions are reduced on the counter electrode (Eq. (2)). As shown in the Fig 5(a), two significant reduction peaks appear at −0.1 and 0.5 V which probably correspond to the two-step reaction process. The Co-TMPP/C electrode shows much larger current density than C and comparable catalytic reduction to Pt/C. This indicates an improved reaction rate on the Co-TMPP/C, i.e. the lower charge-transfer resistance of the I_3^-/I^- redox reaction for the Co-TMPP/C. Fig. 5(b) illustrates a relation between all the peak currents at reduction potential of I_3^- as a function of a square root of scan rate. The linear relationship with various scan rates means the diffusion limitation of the redox reaction, which can be related with the transport of tri-iodide species.[26] The reduction rate of I_3^- on the counter electorde should be explained by the diffusion coefficient (D_a).[27-28] The diffusion coefficient was calculated from the slope of plots of redox peak currents according to different scan rates using Randles-Sevcik equation : $I_P = (2.69 \times 10^5) \cdot n^{3/2} \cdot A \cdot D_a^{1/2} \cdot C_o^* \cdot v^{1/2}$, where I_P is current density, n is the number of electrons, A is the area of the electrode, C_o^* is the concentration in bulk solution, and v is the scan rate involved in the reaction. The slopes of the C, Co-TMPP/C, and Pt/C were −0.00653, −0.00824, and −0.00782, respectively. The calculated diffusion coefficients for slopes are 3.828×10^{-6}, 6.095×10^{-6}, and 5.489×10^{-6} $cm^2 s^{-1}$ for C, Co-TMPP/C, and Pt/C, respectively. This means that the Co-TMPP/C shows such an improved reduction rate of I_3^- as a counter electrode in dye-sensitized solar cells.

To evaluate the performance of dye-sensitized solar cells using the C, Co-TMPP/C, and Pt/C electrodes, as shown in Fig. 6 and Table 1, photocurrent-voltage curves were obtained. The short circuit current density (J_{sc}) of C, Co-TMPP/C, and Pt/C is 6.29, 9.37, and 8.54 mA cm^{-2}, respectively. The open circuit voltage (V_{oc}) of C, Co-TMPP/C, and Pt/C is 0.69, 0.73, and 0.72 V, respectively. Furthermore, the cell efficiency (η) of C, Co-TMPP/C, and Pt/C is 2.96, 4.59, and 4.17%, respectively. Compared to C and Pt/C, the Co-TMPP/C shows improved photoelectrochemical properties such as higher values of J_{sc}, V_{oc}, and h. Furthermore, to investigate the charge transfer resistance of the electrodes for I_3^- reduction in the DSSCs, the electrochemical impedance spectra were obtained as shown in Fig. 7. The charge transfer resistance (R_{ct}) of C, Co-TMPP/C, and Pt/C is 18.48, 9.02, and 9.67 Ω, respectively, which means the lower charge-transfer
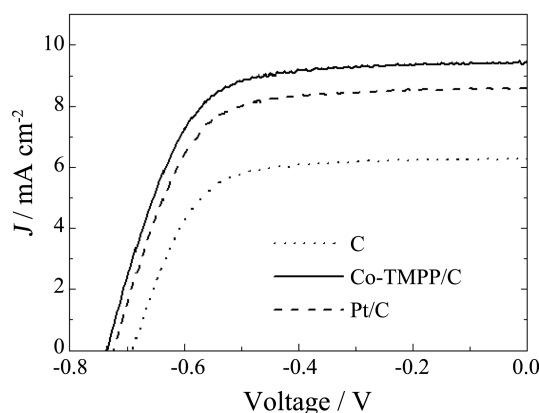

Fig. 6. Photocurrent-voltage curves in DSSCs using C, Co-TMPP/C, and Pt/C as counter electrodes under AM 1.5 light irradiation (100 mW cm^{-2}).
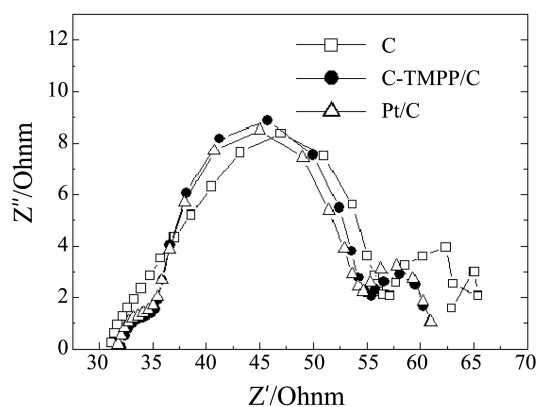

Fig. 7. Electrochemical impedance spectrum in DSSCs using C, Co-TMPP/C, and Pt/C as counter electrodes.

Table 1. Comparison of cell performance of dye-sensitized solar cells using C, Co-TMPP, and Pt/C electrodes. The J_{sc}, V_{oc}, *FF*, and *h* are short circuit current density, open circuit voltage, fill factor, and efficiency in the DSSCs, respectively

Counter electrodes	J_{sc} (mA cm^{-2})	V_{oc} (V)	*FF*	η (%)
C	6.29	0.69	0.68	2.96
Co TMPP/C	9.37	0.73	0.67	4.59
Pt	8.54	0.72	0.68	4.17

resistance of the I_3^-/I^- redox reaction for the Co-TMPP/C.[29-30] Thus, it is likely that such an excellent performance in the DSSC using the Co-TMPP/C as a non-Pt catalyst could result from an improved current density, diffusion coefficient, and charge-transfer resistance for the I_3^-/I^- redox reaction.

4. Conclusions

The Co-TMPP/C as a non-Pt catalyst for tri-iodide reduction in DSSCs was well dispersed on the carbon particles without precipitates such as oxides or nitrides. The XPS spectra of the C, Co, and N in the Co-TMPP/C contained possible assignments of C-N, Co-N, and N-C, respectively. Due to the well defined configuration and structure of the Co-TMPP on carbon, the Co-TMPP/C showed improved current density, diffusion coefficient, and charge-transfer resistance in the I_3^-/I^- redox reaction thus resulting in an excellent cell performance such as increased short circuit current density, higher open circuit voltage, and improved efficieny in the DSSCs.

Acknowledgment

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