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Electrochemical analysis of iron-porphyrin-catalyzed CO₂ reduction under photoirradiation

Arisa Fukatsu^{a,b}, Mio Kondo^{a,b,c,d}, Yuki Okabe^{a,b}, Shigeyuki Masaoka^{a,b,c,*}

^a Department of Life and Coordination-Complex Molecular Science, Institute for Molecular Science, 5-1, Higashiyama, Myodaiji, Okazaki, Aichi 444-8787, Japan

Japan ^b SOKENDAI (The Graduate University for Advanced Studies), Shonan Village, Hayama, Kanagawa 240-0193, Japan

^c Research Center of Integrative Molecular Systems (CIMoS), Institute for Molecular Science, 38, Nishigo-naka, Myodaiji, Okazaki, Aichi 444-8585, Japan

^d ACT-C, Japan Science and Technology Agency (JST), 4-1-8, Honcho, Kawaguchi, Saitama 332-0012, Japan

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ABSTRACT

In this study, the photochemical reaction of a metal-complex-based catalyst was analyzed by electrochemical measurements. A well-known catalyst for the CO_2 reduction reaction, *meso*-tetraphenylporphyrin iron(III) chloride (**Fe(tpp)CI**), was selected as the target analyte. Although the analysis of the electrochemical response of **Fe(tpp)CI** under photoirradiation with conventional cyclic voltammetry (CV) was not allowed, the adaptation of thin layer cyclic voltammetry (TLCV) enabled us to detect the photochemical reaction of **Fe(tpp)CI**. The influence of photoirradiation on the electrochemical property of **Fe(tpp)CI** was investigated both under Ar and CO_2 atmospheres. Although the thin layer cyclic voltammograms of **Fe(tpp)CI** upon photoirradiation under an Ar atmosphere were almost the same as those measured in the dark, the measurements under a CO_2 atmosphere clearly indicated the change of the electrochemical response upon photoirradiation. The detailed analysis of this phenomenon revealed that the photoinduced decarbonylation reaction regenerates the original [Fe^{III}(tpp)] complex under photoirradiation.

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1. Introduction

Artificial photosynthesis, which is a representative example of solar-energy conversion systems, has attracted much attention due to its potential application in renewable energy [1]. To construct such artificial photosynthetic systems, the development of efficient catalysts for reactions involving multi-electron transfer, such as CO₂ reduction and water oxidation, is essential. There are two primary approaches to developing such catalysts: homogeneous [2] and heterogeneous systems [3]. Homogeneous catalysts such as metal complexes are advantageous for the analysis of their reaction mechanisms, including the respective photochemical and electrochemical processes, to allow for further modification of the catalyst design at the molecular level. To understand the detailed reaction mechanisms, the electrochemical response of the catalysts should be investigated under photoirradiation because the electrochemical process in solar-

E-mail address: masaoka@ims.ac.jp (S. Masaoka).

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energy conversion reactions. However, in general, the electrochemical and photochemical properties of molecular catalysts are separately evaluated using different experimental setups. To the best of our knowledge, there have been no reports on the electrochemical analysis of molecular catalytic systems in homogeneous solutions under photoirradiation.

Recently, we established a method to perform electrochemical analysis of photoirradiated solutions [4]. In our previous report, we measured cyclic voltammograms of ferrocene ($Fe(C_5H_5)_2$) under photoirradiation in a conventional electrochemical setup and obtained sigmoidal-shaped voltammograms that were unsuitable for the detailed analysis of the electrochemical processes. This result suggested that the photoirradiation may have generated convection due to local increases in temperature, and the mass transfer subsequently induced by this convection affected the electrochemical responses. Based on this result, we aimed to decrease the unfavorable electrochemical response under photoirradiation and found three techniques (measurements with a rotating disk electrode (RDE), fast scanning, and thin layer cyclic voltammetry (TLCV)) that could suppress the aforementioned unfavorable current change. We also succeeded in detecting the electrochemical response of photochemically generated molecules using TLCV techniques.

^{*} Corresponding author at: Department of Life and Coordination-Complex Molecular Science, Institute for Molecular Science, 5-1, Higashiyama, Myodaiji, Okazaki, Aichi 444-8787, Japan.

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As a further extension of our study, in this work, we applied our photo-electrochemical method for the analysis of catalytic systems. As a catalytic system, the CO_2 reduction reaction is an attractive target because molecules that can catalyze CO_2 reduction are longstanding targets for direct electrolytic fuel synthesis. Moreover, the capture and the efficient use of CO_2 is an important issue to resolve not only the shortage of fossil fuels but also global warming caused by increasing atmospheric CO_2 concentrations. In this contribution, the influence of photoirradiation on the electrochemical CO_2 reduction reaction catalyzed by *meso*-tetraphenylporphyrin iron(III) chloride (**Fe(tpp)CI**) [5,6] was analyzed using the electrochemical technique.

2. Results and discussion

A cyclic voltammogram of **Fe(tpp)Cl** measured by the conventional technique is shown in Fig. 1a. The voltammograms were measured in 0.1 M tetra(*n*-butyl) ammonium perchlorate (TBAP)/*N*,*N*-dimethylformamide (DMF). Under an Ar atmosphere in dark conditions, the voltammogram displayed three reversible reduction waves at $E_{1/2}$ (half-wave potentials)= –0.6, –1.5 and –2.1 V vs. ferrocenium/ferrocene (Fc⁺/Fc), which were assigned as Fe(III)/Fe(II), Fe(II)/Fe(I) and Fe(I)/Fe(0) redox couples, respectively

[6]. Under photoirradiation using a Xe lamp with a CM-1 cold mirror (400-800 nm), the shape of the voltammogram dramatically changed, and the current that was attributed to the convection induced by the photoirradiation was observed. These results indicated that the analysis of the photoelectrochemical response of Fe(tpp)Cl was not allowed with the conventional technique. By contrast, the measurements using the TLCV technique with a layer thickness (d.Fig. 1c) of 0.25 mm gave different results. As shown in Fig. 1b. under dark conditions, three reversible redox waves were observed at approximately the same potentials as those obtained in the conventional measurement. Under photoirradiation, the same three reversible reduction waves were observed, maintaining the shape of the voltammogram. Therefore, the convection induced by photoirradiation was suggested to be suppressed in the TLCV measurements, and it was confirmed that the electrochemical measurement of Fe(tpp)Cl under photoirradiation could be performed using the TLCV technique.

TLCV measurements of **Fe(tpp)Cl** were also performed under a CO_2 atmosphere to analyze the catalytic reduction of CO_2 . In the voltammogram of **Fe(tpp)Cl** under dark conditions (Fig. 2), the first and second reduction peaks were observed at the exact same potentials as those observed under Ar conditions.



Fig. 1. (a) Cyclic voltammograms (d = 5 mm) with Fe(III)/Fe(II), Fe(II)/Fe(I) and Fe(I)/Fe(0) redox waves. (b) Thin layer cyclic voltammograms (d = 0.25 mm) with Fe(III)/Fe(II), Fe (II)/Fe(I) and Fe(I)/Fe(0) redox waves. (c) Schematic illustration of the thickness of the solution layer. CV measurements were performed with **Fe(tpp)Cl** (1 mM) in a 0.1 M TBAP / DMF solution with photoirradiation (red, 400 nm $< \lambda < 800 \text{ nm}$) and without photoirradiation (blue) under an Ar atmosphere (WE: GC; CE: Pt wire; RE: Ag⁺/Ag; scan rate: 20 mV s⁻¹). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 2. Thin layer cyclic voltammograms (d = 0.25 mm) of **Fe(tpp)Cl** (1 mM) in a 0.1 M TBAP / DMF solution with photoirradiation (red, 400 nm $< \lambda < 800 \text{ nm}$) and without photoirradiation (blue) under a CO₂ atmosphere (WE: GC; CE: Pt wire; RE: Ag⁺/Ag; scan rate: 20 mV s⁻¹). (a) Voltammograms with a catalytic current. (b) Enlarged voltammograms focusing on Fe(III)/Fe(II) and Fe(II)/Fe(I) redox waves. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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Fig. 3. Thin layer chronoamperograms (E = -2.3 V vs. Fc⁺/Fc, d = 0.25 mm) of **Fe(tpp)Cl** (1 mM) in a 0.1 M TBAP / DMF solution with photoirradiation (red, 400 nm $< \lambda < 800 \text{ nm}$) and without photoirradiation (blue) under a CO₂ atmosphere (WE: GC; CE: Pt wire; RE: Ag⁺/Ag). (a) Time vs. Current, (b) Time vs. Coulombs. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Additionally, large irreversible cathodic currents were observed at the potential corresponding to the Fe(I)/Fe(0) redox couple (-2.1 V vs. Fc⁺/Fc), indicating the electrocatalytic CO₂ reduction to CO. In the subsequent anodic scan in the positive direction, the irreversible wave was observed at approximately $E_{pa} = -1.7 \text{ V}$ vs.

Fc⁺/Fc, and the original re-oxidation waves observed at $E_{\rm pa}$ = -0.6 and -1.5 V under an Ar atmosphere were not detected (Fig. 2, blue line). By contrast, under photoirradiation, the two reversible redox waves at $E_{1/2}$ = -0.6 and -1.5 V and the catalytic currents at approximately -2.1 V were observed (Fig. 2, red line).



Fig. 4. Thin layer cyclic voltammograms (d = 0.25 mm) of **Fe(tpp)Cl** (1 mM) in a 0.1 M TBAP / DMF solution for which the negative edges of the potential sweep were -2.5 V (blue), -2.2 V (green) and -2.1 V (red) (WE: GC; CE: Pt wire; RE: Ag⁺/Ag; scan rate: 20 mV s⁻¹). (a) Voltammograms showing the negative edges of potential sweeping without photoirradiation. (b) Enlarged voltammograms focusing on Fe(III)/Fe(II) and Fe(II)/Fe(I) redox waves without photoirradiation. (c) Voltammograms showing the negative edges of potential sweeping with photoirradiation. (d) Enlarged voltammograms focusing on Fe(III)/Fe(II) and Fe(II)/Fe(II) and Fe(II)/Fe(I) redox waves with photoirradiation. (c) redox waves with photoirradiation. (for interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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Fig. 5. Thin layer cyclic voltammograms (d = 0.25 mm) of **Fe(tpp)Cl** (1 mM) in a 0.1 M TBAP / DMF solution with photoirradiation in various light intensities (red, 150 W; green, 300 W) and without photoirradiation (blue) under a CO₂ atmosphere (WE: GC; CE: Pt wire; RE: Ag⁺/Ag, scan rate: 20 mV s⁻¹). (a) Voltammograms showing a catalytic current. (b) Enlarged voltammograms focusing on Fe(III)/Fe(II) and Fe(II)/Fe(I) redox waves. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

It should be noted that the intensity of the irreversible wave at $E_{pa} = -1.7$ V, which was observed in the measurements under dark conditions, dramatically decreased in the voltammogram under photoirradiation. These results clearly indicated that photoirradiation largely affected the redox properties of **Fe(tpp)Cl** under a CO₂ atmosphere.

To further understand this phenomenon, several electrochemical measurements were performed in thin-layer conditions under a CO₂ atmosphere. First, chronoamperometry was performed both under photoirradiation and in the dark. The solution of **Fe(tpp)Cl** (1 mM) in DMF containing TBAP (0.1 M) was electrolyzed at the GC electrode with a cell operating potential of -2.3 V vs. Fc⁺/Fc while keeping the layer thickness as 0.25 mm. As shown in Fig. 3, constant currents flowed during the 300 s of electrolysis, and the intensities of the currents were almost the same irrespective of the photoirradiation. From these results, it was assumed that the catalytic current of CO₂ reduction catalyzed by **Fe(tpp)Cl** was not affected by photoirradiation.

Second, the origin of the irreversible peak at approximately -1.7 V under the dark conditions was investigated by changing the negative edges of the potential sweep. Fig. 4 shows the voltammograms of Fe(tpp)Cl for which the negative edges of the potential sweep were -2.5 (blue line), -2.2 (green line) and -2.1 V (red line). Although the shapes of the voltammograms were almost the same when the measurements were performed under photoirradiation, a clear difference was observed in the measurement under the dark condition. For the negative edge located at -2.1 V, which was more positive than the CO₂ reduction potential catalyzed by Fe(tpp)Cl, the second redox wave was reversibly observed. By shifting the negative edges to the negative region, the irreversible peak at -1.7 V gradually appeared, and the intensity of the peak at $E_{pa} = -1.5$ V decreased. These observations suggested that the flow of the large catalytic current induced the generation of the irreversible peak at -1.7 V.

Finally, the dependence of the generation of the irreversible peak on the light intensity was investigated. Fig. 5 shows the cyclic voltammogram of **Fe(tpp)Cl** under photoirradiation with different intensities of light (150 and 300 W). When the light intensity was increased, the peak height of the irreversible wave at -1.7 V decreased, and the original re-oxidation wave at $E_{\text{pa}} = -1.5 \text{ V}$ increased. From these results, the generation of the irreversible

peak around -1.7 V was presumed to be effectively suppressed by photoirradiation.

The aforementioned observations enabled us to describe the effect of photoirradiation on the redox properties of Fe(tpp)Cl in combination with the proposed catalytic cycle. The proposed reaction mechanism of electrocatalytic CO₂ reduction by Fe(tpp)Cl was reported by Costentin et al. [6] and is summarized in Scheme 1. Initially, Fe(tpp)Cl is reduced from Fe(III) to Fe(0) by the sequential one-electron reduction processes; these processes were observed in the measurement under an Ar atmosphere (vide supra). The generated Fe(0) species react with CO_2 , and the CO₂-bound complexes forms. Subsequent adduction of acid (in this case, the hydrated water of the catalyst) and the C-O bond cleavage reaction in coordination with proton transfer result in the formation of the CO-bound complex. Further reaction with the Fe(0) species leads to the generation of CO. It was also reported that CO generated by the catalytic reaction could bind to catalysts with the Fe(I) state as the side reaction of the CO_2 reduction reaction by Fe(tpp)Cl (I in Scheme 1), and the electrochemical response corresponding to this side reaction was observed at approximately -1.7 V. Similarly, the irreversible peak, which was attributed to the side reaction, was detected at -1.7 V in our experiments using the TLCV technique in the dark condition. Furthermore, we found that the intensity of the peak decreased upon photoirradiation and, in some conditions, the electrochemical response of the side reaction could be suppressed. A reasonable explanation of this phenomenon is given by considering the photoinduced decarbonylation from carbonyliron tetraphenylporphyrin [7]. The oxidative Fe–CO reassociation $([Fe^{I}(tpp)]^{-} + CO \rightarrow [Fe^{II}(tpp)CO] + e^{-}, I \text{ in Scheme 1})$ occurs at $E \approx -1.7 \text{ V}$ regardless of photoirradiation. Under photoirradiated condition, the photoinduced decarbonylation reaction of [Fe^{II}(tpp) CO] proceeds to afford [Fe^{II}(tpp)] ([Fe^{II}(tpp)CO] + $h\nu \rightarrow$ [Fe^{II}(tpp)] + CO) [7]. The photochemically generated [Fe^{II}(tpp)] is successively reduced ([Fe^{II}(tpp)] + e⁻ \rightarrow [Fe^I(tpp)]⁻, $E_{1/2} \approx -1.5$ V, II in Scheme 1). As a result, the current attributed to the oxidative Fe-CO reassociation (I in Scheme 1) is offset by the current attributed to the reduction of the photochemically generated [Fe^{II}(tpp)] (II in Scheme 1). In total, the electrochemical response of the side reaction in the catalytic system could be hindered by photoirradiation.

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Scheme 1. Proposed mechanism of the catalytic reaction [6]. The coordination of solvent molecules and counter anions is in equilibrium [8] and omitted for clarity.

3. Conclusions

In conclusion, we first demonstrated the electrochemical analysis of a catalytic system under photoirradiation. A wellknown catalyst for CO₂ reduction, Fe(tpp)Cl, was selected as a target analyte, and the electrochemical response of the catalyst was successfully investigated using the TLCV technique. Under a CO₂ atmosphere, the catalytic current originating from CO₂ reduction was observed both under the dark and light conditions. Under the dark conditions, an irreversible re-oxidation wave was observed at -1.7 V vs. Fc⁺/Fc in the voltammogram. Under photoirradiation, on the other hand, the intensity of the irreversible peak dramatically decreased; however, the intensities of the reversible peaks originating from the redox of the catalyst increased. Further electrochemical measurements with various conditions revealed that the generation of the irreversible peak depended on the negative edges of the potential sweep and the intensity of the light used in photoirradiation. Moreover, it was found that the original [Fe^{II}(tpp)] complex is regenerated by the photoinduced CO dissociation from [Fe^{II}(tpp)CO] based on the analysis of these electrochemical responses in combination with the proposed reaction mechanism. These results show that our method presented in this contribution has the possibility of analyzing various catalytic reactions. Further analysis of this reaction and other catalytic reactions by thin layer techniques is currently being investigated.

4. Experimental

4.1. Materials

Pyrrole was purchased from Sigma–Aldrich Co., LLC. Benzaldehyde, propanoic acid, hydrochloric acid and ferrocene (**Fc**) were purchased from Wako Pure Chemical Industries, Ltd. FeCl₂·4H₂O and *N*,*N*-dimethylformamide (DMF) were purchased from Kanto Chemical Co., Inc. Tetra(*n*-butyl) ammonium perchlorate (TBAP) was purchased from Tokyo Chemical Industry Co., Ltd. All of the solvents and reagents were of the highest quality available and

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Fig. 6. Schematic illustration of the custom-made photoelectrochemical cell.

were used as received, except for TBAP and DMF for the electrochemical measurements. TBAP was recrystallized from absolute ethanol and dried in vacuo. DMF was degassed and purified under N_2 atmosphere using a GlassContour solvent system (Nikko Hansen Co., Ltd.).

4.2. Syntheses

4.2.1. Synthesis of meso-tetraphenylporphyrin (H₂(tpp))

H₂(tpp) was prepared as previously described [9]. Pyrrole (1.7 mL, 25 mmol) and benzaldehyde (2.6 mL, 25 mmol) were dissolved in propanoic acid (50 mL), then refluxed for 1 h and cooled to room temperature. The resulting mixture was filtered and washed with methanol. Recrystallization from CH₂Cl₂/ methanol gave a purple solid. ¹H NMR (CDCl₃): δ 2.80 (s, 2H), 7.71–7.78 (m, 12H), 8.19–8.21 (m, 8H), 8.82 (s, 8H).

4.2.2. Synthesis of meso-tetraphenylporphyrin iron(III) chloride (**Fe** (**tpp)CI**)

Fe(tpp)Cl was prepared by the modification of a previous report [10]. To a solution of $H_2(tpp)$ (200 mg, 0.32 mmol) in *N*,*N*-dimethylformamide (DMF) (70 mL), a DMF (60 mL) solution of FeCl₂·4H₂O (388 mg, 1.95 mmol) was added dropwise at room temperature. The mixture was refluxed for 1 h and then cooled to room temperature. Diluted hydrochloric acid (HCl) (6M, 80 mL) was added to the resulting solution. A purple solid was collected by filtration and washed with 3 M HCl. The compound was identified by elemental analysis. Found: C, 73.63; H, 4.21; N, 7.97. Calcd for C₄₄H_{29.4}ClFeN₄O_{0.7} ([**Fe(tpp)Cl**]·0.7H₂O): C, 73.74; H, 4.14; N, 7.82.

4.3. Measurements

All of the electrochemical measurements were conducted under argon unless otherwise mentioned. A three-electrode configuration was employed in conjunction with a Biologic SP-50 potentiostat that interfaced with a computer with Biologic EC- Lab software. The measurements were performed using the system shown in the previous report [4] (Fig. 6) to avoid photoirradiation of the reference electrode and the counter electrode. The photo-irradiation was performed using an ILC Technology CERMAX LX-300 Xe lamp (operated at 150 W unless otherwise mentioned) equipped with a CM-1 cold mirror (400 nm $< \lambda < 800$ nm). In all cases, a platinum wire counter electrode (diameter 0.5 mm, from BAS) and a glassy carbon (GC) disk working electrode (diameter 3 mm, from BAS) were used. The working electrode was treated between scans by means of polishing with 0.05- μ m alumina paste (from BAS) and washing with purified H₂O. For all measurements, an Ag⁺/Ag reference electrode was used. The supporting electrolyte was 0.1 M TBAP. The potentials reported within these measurements were referenced to the Fc⁺/Fc couple at 0 V.

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