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Electrochemical analysis of iron-porphyrin-catalyzed CO_2 reduction under photoirradiation

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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)Cl**), was selected as the target analyte. Although the analysis of the electrochemical response of **Fe(tpp)Cl** 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)Cl**. The influence of photoirradiation on the electrochemical property of **Fe(tpp)Cl** was investigated both under Ar and CO_2 atmospheres. Although the thin layer cyclic voltammograms of **Fe(tpp)Cl** 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^{II}(tpp)] complex under photoirradiation.

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 CO_2 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 proceeds subsequent to the photochemical process in solar-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.

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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)Cl**) [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.

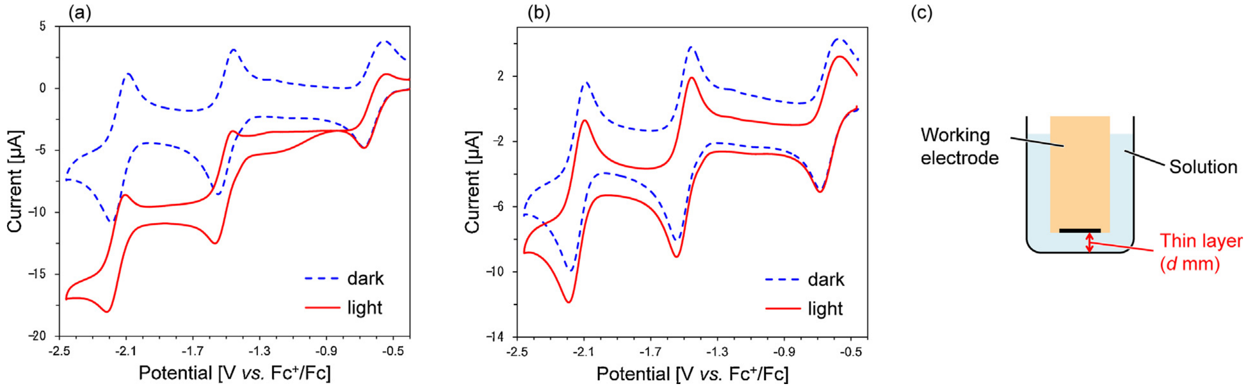

Fig. 1. (a) Cyclic voltammograms (d = 5 mm) with Fe(III)/Fe(II), Fe(II)/Fe(I) and Fe(I)/Fe(0) redox waves. (b) Thin layer cyclic voltammograms (d = 0.25 mm) with Fe(III)/Fe(II), Fe (II)/Fe(I) and Fe(I)/Fe(0) redox waves. (c) Schematic illustration of the thickness of the solution layer. CV measurements were performed with **Fe(tpp)Cl** (1 mM) in a 0.1 M TBAP / DMF solution with photoirradiation (red, 400 nm < λ < 800 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.)

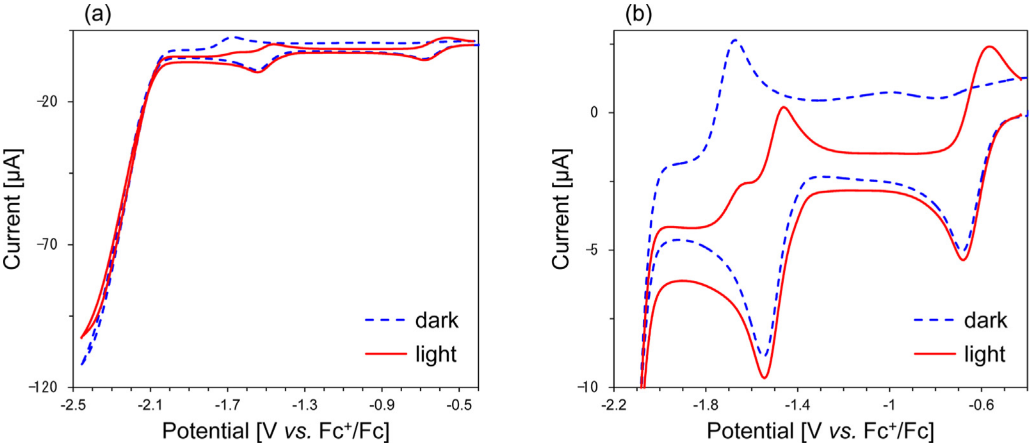

Fig. 2. Thin layer cyclic voltammograms (d = 0.25 mm) of **Fe(tpp)Cl** (1 mM) in a 0.1 M TBAP / DMF solution with photoirradiation (red, 400 nm < λ < 800 nm) and without photoirradiation (blue) under a CO_2 atmosphere (WE: GC; CE: Pt wire; RE: Ag^+/Ag; scan rate: 20 mV s^{-1}). (a) Voltammograms with 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.)