Enhanced Photocatalytic Activity of Porphyrin Nanodisks Prepared by Exfoliation of Metalloporphyrin-Based Covalent Organic Frameworks

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ABSTRACT: Organic polymers derived from covalent organic frameworks (COFs) have various applications, including photocatalysis. The synthesis of organic polymer materials from COFs to obtain higher activity for photocatalysis by changing the unit molecule has been investigated. The choice of the unit molecule is important to characterize the photochemical properties. Among various such unit molecules, porphyrins have attracted much attention as organic chromophores commonly used in photocatalytic reactions with COFs. Although COFs with various organic chromophores have been synthesized and attempts have been made to improve their photocatalytic activity, enhancing the photocatalytic activity by adjusting the layer thickness through exfoliation of COFs has yet to be fully studied. In the present study, the exfoliation of metalloporphyrin-based COFs with pyridine as the axial ligand and adjustment of the layer thickness were found to enhance the photocatalytic activity. Hydrogen generation and 3,3′,5,5′-tetramethylbenzidine oxidation reactions were investigated as representative photocatalytic reactions, with the photocatalytic activity up to 7 times that of the original free-base porphyrin COFs. These results indicate that the different thicknesses synthesized by exfoliating COFs increased the photocatalytic effect of polymers.

INTRODUCTION

Covalent organic frameworks (COFs) are a class of novel organic materials that form two- or three-dimensional structures through covalent bonding between small molecules. COFs have been used in various applications, including gas and molecular separation, sensing, and catalysis. Recently, COFs have been used as organic heterogeneous photocatalysts. The photochemical properties of chromophore molecules as building blocks are important in designing COFs with improved photocatalytic activity. Porphyrins have unique photochemical properties and are important small molecules for photocatalytic COFs. In particular, metalloporphyrins have been employed in various COFs for photocatalytic reactions. Recent studies have shown that the spin state of excited metalloporphyrins in COFs is an important factor in modifying photochemical reactions, including reactive oxygen species generation. In order to improve the photocatalytic activity of COFs and their polymers, structural design of the catalyst itself is an important factor. We have previously shown that porphyrin COFs can be exfoliated into 1 nm thick disks in solution and that using these synthesized disk-shaped polymers as photocatalysts results in 2−5 times higher photocatalytic activity for hydrogen generation than that of the original COFs. However, the generality of the photocatalytic activity enhancement by exfoliation, especially through tuning the polymers thickness, remains to be clarified. For example, whether exfoliation also promotes the generation of reactive oxygen species in photocatalytic reactions needs to be investigated. In this study, nanodisk-like polymers derived from metalloporphyrin COFs were newly synthesized by exfoliation, and the photocatalytic activity of nanodisks with varying thicknesses in the hydrogen evolution reaction (HER) and photocatalytic oxidation reaction was investigated.

RESULTS AND DISCUSSION

Synthesis and Structural Characterization. Porphyrin polymers with nanodisk-like shapes were synthesized by exfoliating metalloporphyrin-based COFs (Figure 1). In a previous study, we synthesized porphyrin polymers by exfoliating free-base porphyrin COFs through simultaneous coordination of the metal center and axial ligand to the porphyrin unit. As a result, we succeeded in synthesizing polymer nanodisks with a thickness of approximately 1 nm. However, as the catalytic activity obtained was only about 2 times that of the original COFs, further understanding of the exfoliation and catalytic processes is needed to develop more...
active photocatalysts. Recently, Wang et al. reported that metalloporphyrin-based COFs showed photocatalytic activity for the hydrogen generation reaction and that the carrier dynamics were affected by the type of the metal center.6b Based on this study, we expected that exfoliated nanodisks consisting of multiple layers with a controlled thickness of the

Figure 1. (a) Synthetic schemes for the exfoliation of porphyrin COFs. (b) Chemical structure of metalloporphyrin-based COFs (DhaMTph) used in this study.

Figure 2. (a) PXRD spectra of DhaCuTph (black) and e-CuCON(epy) (red) (λ = 1.5418 Å). (b) FT-IR spectra of DhaCuTph (black) and e-CuCON(epy), (red). The orange lines are for 1000 cm\(^{-1}\) (the insertion of metal ions into the porphyrin unit) and 1613 cm\(^{-1}\) (the C=N stretching mode). (c) TEM image of e-CuCON(epy). Scale bar is 10 nm. (d) AFM-measured thickness distribution histogram and a representative AFM image of e-CuCON(epy). Scale bar is 250 nm. (e) Deconvoluted high-resolution Cu 2P\(_{3/2}\) XPS spectrum of e-CuCON(epy).
metal center would exhibit higher photocatalytic activity, probably owing to efficient charge separation.\textsuperscript{2b} In the present study, we investigated the exfoliation of metalloporphyrin-based COFs by reaction with epy to further improve the photocatalytic activity (Figure 1a). By introducing the axial ligand with the lateral size of 6 Å, which is larger than the layer distance \(d\) of 4 Å, the metalloporphyrin COFs could be easily exfoliated into porphyrin nano-disk like polymers. Cu was selected as the metal center for comparing the synthetic procedure with our previous studies,\textsuperscript{9b} while Ni was selected to study the impact of the metal center. The Ni and Cu metalloporphyrin [MTph (M = Cu or Ni)] starting materials were synthesized as previously described\textsuperscript{10} and characterized by UV–vis absorption, Fourier transform infrared (FT–IR) spectroscopy, and matrix-assisted laser desorption/ionization-time of flight mass spectrometry (MALDI-TOF MS) (Figure S1). The metalloporphyrin-based COFs were synthesized from Dha and MTph (M = Cu or Ni), as described by Banerjee et al. and our group.\textsuperscript{5b,9} Intralayer hydrogen bonds derived from the hydroxyl groups of Dha locked the torsion of the imine bonding units, resulting in improved crystallinity. In this study, in order to promote crystalline structure formation via hydrogen bonding, DhaMTph was synthesized under acidic conditions, different from that of previous methods. Under these conditions, CHN elemental analysis showed no distinctive demetalation of DhaMTph (Table S1).\textsuperscript{1d} Therefore, the modified synthetic method for DhaMTph was concluded to have little effect on demetalation. In order to exfoliate DhaMTph into nanodisk-like polymers, DhaMTph was reacted in epy at 120 °C for 20 h with magnetic stirring. The exfoliated nanodisks were denoted as e-MCON(epy) (M = Cu or Ni) (Figure 1a).

The crystallinity of e-MCON(epy) (M = Cu or Ni) was evaluated using powder X-ray diffraction (PXRD) (Figures 2a and S2a). After the synthesis of e-MCON(epy) via the reaction with DhaMTph in epy, the strong peak at 3.6° assigned to the (100) facet was reduced by 47 and 45% for DhaTph (M = Cu and Ni), respectively. As we anticipated, the crystallinity loss was not drastic compared with that observed in the previous synthetic method in Figure 1a,\textsuperscript{9b} suggesting that the catalytic activity could be improved by preventing charge recombination through charge migration among several layered porphyrins with a thickness of several nanometers. The FT-IR spectra showed a characteristic peak at 1000 cm\(^{-1}\) attributed to the insertion of metal ions into the porphyrin unit (Figures 2b and S2b).\textsuperscript{9b} The FT-IR spectra also showed no characteristic decrease in the C=N stretching mode at 1613 cm\(^{-1}\), suggesting that no bond dissociation occurred due to reduced crystallinity.\textsuperscript{9b}

Transmission electron microscopy (TEM) and atomic force microscopy (AFM) imaging were used to estimate the size of e-MCON(epy) (Figures 2c,d, S2c,d, S3, and S4). TEM images showed that the synthesized nanodisks were 40 and 50 nm in diameter, averaged over \(n = 100\), for e-MCON(epy) (M = Cu and Ni) (Figures 2c and S2c), respectively. The size and thickness of e-MCON(epy) (M = Cu and Ni) was also measured using AFM (Figures 2d and S2d). The diameter of e-MCON(epy) (M = Cu and Ni) was 30–50 nm, which was consistent with the TEM results. The thickness of e-MCON(epy) (M = Cu and Ni) was 0.5–3 and 0.5–6 nm, respectively, averaged over \(n = 100\). Compared with previous results for free-base porphyrin COFs exfoliated with metal ions and pyridines (simultaneous concerted synthesis of nanodisks, Figure 1a), the thickness of e-MCON(epy) (M = Cu and Ni) was 3–5 times larger than that of e-CON(M, epy), as shown in Figure 1a. Therefore, the successful synthesis of porphyrin nanodisks with varying thickness was clearly achieved by simply reacting DhaMTph with epy for 20 h.

X-ray photoelectron spectroscopy (XPS) was performed to determine the oxidation state of metal ions in the porphyrins of e-MCON(epy) (Figures 2e, S2e, S5, and S6 and Tables S2 and S3). The N 1s and metal 2p XPS spectra of DhaMTph and e-MCON(epy) (M = Cu and Ni) were compared with those of the corresponding metalloporphyrin monomer (MTph). The results suggested that the main oxidation states of metal ions in e-MCON(epy) (M = Cu and Ni) were Cu\textsuperscript{II} and Ni\textsuperscript{II}, respectively. The N\textsubscript{2} adsorption–desorption isotherm further showed that several layers of porphyrin polymers still constituted a partially porous structure (Figure S7). These results indicated that when metalloporphyrin COFs (DhaMTph) were exfoliated with epy, disk-shaped polymers comprising divalent metalloporphyrins with thicknesses of several nanometers were produced. These nanodisks were used in the following photocatalytic reactions.

**Photocatalytic Reactions.** The photocatalytic activity of e-MCON(epy) (M = Cu and Ni) was compared with that of DhaMTph and DhaTph under visible light irradiation (\(\lambda > 420\) nm) from a solar light simulator. In order to study photocatalytic hydrogen evolution, Pt/reduced graphene oxide (RGO) was used as the co-catalyst (Figures 3 and S8).
Hydrogen evolution was investigated in the presence of methanol as a sacrificial reagent (Figure 3 and Table S4). The results showed that the photocatalytic activity of DhaMTph (M = Cu and Ni) was enhanced by a factor of 3.7, compared with that of DhaTph, which was consistent with the recent results of Wang et al.6b Furthermore, the catalytic activity was further increased 2.2-fold by exfoliation and reuse (Figures 3 and S9a). The apparent quantum yields and turnover numbers for hydrogen generation were also estimated (Table S4). These results were consistent with our recent work on nanodisks synthesized by exfoliation in a solvent, showing that nanodisks with a thickness of a few nanometers exhibited relatively enhanced photocatalytic activity.9a

In order to understand the generality of the enhanced photocatalytic activity of e-MCON(epy) (M = Cu and Ni) synthesized by exfoliation, photochemical reactions with 3,3′,5,5′-tetramethylbenzidine (TMB) under visible light irradiation (λ > 420 nm) were conducted under an acidic condition (pH 4) in the presence of molecular oxygen (Figures 4 and S9).11 TMB is an aromatic amine, and the oxidation process of TMB to diimine was monitored by the formation of a charge transfer complex with an absorption maximum at 652 nm (ε = 39,000 M⁻¹ cm⁻¹).12 The apparent oxidation rates of TMB (k_{app}) obtained using e-MCON(epy) (M = Cu and Ni) were 2 times those obtained using DhaMTph (M = Cu and Ni) (Figures 4c and S9e,f and Table S5). Furthermore, the apparent quantum yields for TMB oxidation were estimated, as shown in Table S6. In order to understand the oxidation mechanism of TMB in the presence of e-MCON(epy) (M = Cu and Ni), the oxidation reactions were conducted in the presence of various quenchers of reactive oxygen species (Figures 4d and S10). The results showed that oxidation of TMB was significantly inhibited in the presence of benzoquinone (BQ), a superoxide quencher, but no significant
difference in oxidation was observed with other scavengers. The quenching experiments of DhaMTph (M = Ni) showed a similar tendency to those recently reported by Jiang et al.7b The cytochrome c assay was also performed to directly monitor the involvement of superoxide in the photocatalytic reaction (Figures 4e and S11).15 Cytochrome c is reduced by superoxide to produce ferrocytochrome c, which is detected by an absorption change at 550 nm.13 The increase in absorption at 550 nm was clearly observed, indicating that superoxide was involved in the photocatalytic reaction of TMB (Table S7). The apparent quantum yields for cytochrome c were also measured, as shown in Table S6. These results further indicated that the oxidation reaction was promoted by e-MCON(epy) (M = Cu and Ni) synthesized through exfoliation of DhaMTph and that superoxide was involved in the oxidation reaction of TMB.

In order to understand the photocatalytic reaction in more detail, the redox potentials were estimated using photoelectrochemical yield spectroscopy (EIS) and the absorption spectra (Table S8). The reduction potentials of the nanodisks were sufficient for the reduction of RGO (reduction potential, −0.41 eV) and molecular oxygen (reduction potential, −0.28 eV) to produce hydrogen and superoxide in the above reactions, respectively. The TMB oxidation scavenger experiment suggested that singlet oxygen had limited involvement.9b,14 Although singlet oxygen is a major reactive oxygen species in free-base porphyrin COFs, the energy of the triplet excited state of MTph (Cu and Ni) was not sufficient to form singlet oxygen, which requires 94 kJ/mol (0.98 eV). Therefore, we speculated that singlet oxygen was not involved in the reactions using e-MCON(epy) (M = Cu and Ni), similar to the monomeric metalloporphyrin (singlet oxygen generation quantum yields, <10−3).15

The photocurrent responses and electrochemical impedance spectroscopy (EIS) spectra were also evaluated to study the photoelectric properties (Figure S12). The photocurrent response of e-MCON(epy) (M = Cu and Ni) was 2−3 times higher than that of DhaMTph, indicating that the generated electrons and holes were well-separated and transferred at the interface with Nafion. The Nyquist plots of EIS measurements in Figure S12c,d showed that the resistance of e-MCON(epy) (M = Cu and Ni) was smaller than that of DhaMTph, indicating that the charge separation and charge transfer processes were enhanced at the interface. These results clearly indicated that the exfoliated organic polymer, e-MCON(epy) (M = Cu and Ni), exhibited enhanced photocatalytic activity, which might be attributed to the improved charge separation and charge transfer in the polymer. These results demonstrated that the photocatalytic activity can be enhanced by exfoliating COFs into thinner nanodisk-like polymers with a thickness of several nanometers. Direct measurements, such as transient absorption measurements, are useful for confirming these charge-separated states in polymers but are not the subject of this study. Nonetheless, we believe that we have clearly explained how the synthesis of organic polymers with a nanodisk-like structure of sub-nanometer thickness by exfoliating COFs can promote the photocatalytic activities for hydrogen generation and oxidation reactions.

## CONCLUSIONS

In this study, the photocatalytic activities of e-MCON(epy) (M = Cu and Ni) were investigated. The synthesized organic polymers with nanodisk-like structures had a thickness of 0.5−3 nm, as obtained by AFM, indicating that varying the thickness of organic nanomaterials can improve their photocatalytic properties. Importantly, the exfoliated organic polymers showed up to 6−7 times higher photocatalytic activity compared with the original COFs (DhaTph). These results indicated that structural and photochemical properties are important for designing effective photocatalytic organic polymers. We believe that this study provides an important prerequisite for the development of organic polymer photocatalysts.

## EXPERIMENTAL SECTION

### Materials. 5,10,15,20-Tetrakis(4-aminophenyl)-21H,23H-porphyrin (Tph) and 4-ethylpyridine (epy) were purchased from TCI (Tokyo, Japan). Acetic acid was purchased from Nacalai Tesque (Kyoto, Japan). Cytochrome c from bovine heart, TMB, 1,2-dichlorobenzene (DCB), and 2,5-dimethoxy-1,4-dibenzaldehyde were purchased from Sigma-Aldrich (Missouri, USA). Other reagents were purchased from FUJIFILM Wako (Tokyo, Japan). All chemicals were used without further purification.

### General Synthetic Procedures. Synthesis of Metalloporphyrin-Based COFs. Dihydroxyterephthalaldehyde (Dha, 14 mg) and tetra-aminophenyl-metalloporphyrin (MTph, M = Cu or Ni, 28 mg) in a mixture of DCB/ethanol/acetic acid (6 N) (15 mL, 5:5:1) were added to a 50 mL round-bottom flask, and the mixture was stirred at reflux for 3 days. After cooling down to room temperature, the product was filtered and washed with ethanol. The resulting product was dried under vacuum at 120 °C to afford DhaMTph.

### Synthesis of e-MCON(epy) (M = Cu or Ni). DhaMTph (15 mg) and epy (15 mL) were added to a 50 mL round-bottom flask. The mixture was stirred at 120 °C for 20 h. Upon cooling to room temperature, the product was collected by filtration and dried at room temperature to afford e-MCON(epy).

### General Methods. PXRD data were recorded at a scanning rate of 2°/min with Cu Kα radiation (λ = 1.5406 Å) using a SmartLab diffractometer (RIGAKU, Tokyo, Japan) by placing powder samples on a glass sample holder. UV−vis absorption spectra were recorded using a V-630 or V-770 spectrophotometer (JASCO, Tokyo, Japan). Solid−state FT−IR spectra were recorded using an FT/IR-4100 spectrometer (JASCO, Tokyo, Japan) and collected in the attenuated total reflectance mode after 16 scans operated with a 4.0 cm−1 resolution. AFM images were recorded using a SPI3800 instrument (Seiko Instruments, Chiba, Japan). Samples were prepared by dispersing and sonicating in N,N-dimethylformamide for 10 min and then dropping on newly prepared mica plates (1 cm × 1 cm). Analysis was performed using Gwyddion software. High-resolution TEM images were captured on a JEM-2100 instrument (JEOL, Japan) at an accelerator potential of 200 kV. Samples were prepared by dispersing and sonicating in methanol for 15 min and then dropping onto the Cu grid. PYS was conducted under vacuum with a D2 lamp on a BIPKV202GD instrument (Bunko-keiki, Tokyo, Japan). N2 adsorption−desorption isotherms were obtained using a NOVA 4200e instrument (Quantachrome Instruments Japan G.K., Kanagawa, Japan).

### Photo-Electrochemical Measurements. Photo-electrochemical measurements were conducted using an electrochemical CHI 660B workstation (BAS, Tokyo, Japan) with a three-electrode system comprising a Ag/AgCl-reference
electrode, a Pt counter electrode, and a Au working electrode. The electrolyte selected was 0.2 M NaSO₄ aqueous solution. Samples (1 mg) were sonicated in ethanol containing 2% Nafion (0.25 mL) for 30 min before being dropped on the working electrode and dried for measurement. The working electrode was irradiated by an HAL-320W solar simulator (Asahi-bunko, Tokyo, Japan) through a 420 nm long pass filter. The photocurrent responses were recorded at a bias potential of 0.4 V. EIS was conducted with an amplitude of 5 mV over the range of 0.1 to 10⁵ Hz.

**Hydrogen Evolution Reaction.** The HER was performed as described in our previous report.² Briefly, samples were dispersed in MeOH and sonicated for 10 min to prepare a 0.5 mg/mL suspension. The prepared Pt/RGO aqueous suspension was sonicated for 3 min before use. The sample suspension (5 mL, 0.5 mg/mL) and irradiated by an HAL-320W solar simulator (Asahi-bunko, Tokyo, Japan) with stirring at room temperature. UV light was removed by a 420 nm long pass filter. The generated H₂ amount was measured using a GC-8A gas chromatograph equipped with an MS-5A column (Shimadzu, Kyoto, Japan).

**TMB Reaction.** TMB was dissolved in acetate buffer (pH 4) at a concentration of 0.05 mg/mL. DhaMTph or e-MCON(epy) was dispersed in water at a concentration of 0.5 mg/mL, and DhaMTph or e-MCON(epy) solution (0.2 mL) was added to the TMB solution (2 mL). After visible light irradiation (λ > 420 nm) with O₂ bubbling, a suspension sample (1.0 mL) was taken and centrifuged at 10,000 rpm for 5 min. The resulting supernatant was subjected to UV−vis absorption measurements. For quencher experiments, individual quenchers were added at concentrations of 1 mM for NaN₃, 2-propanol (IPA), and ethylenediaminetetraacetic acid (EDTA) and 0.01 mM for p-BQ.

**Cytochrome c Reaction.** Cytochrome c was dissolved in H₂O at a concentration of 50 µM. The DhaMTph or e-MCON(epy) suspension (0.2 mL, 0.5 mg/mL) was then added to the cytochrome c solution (2 mL). The resulting solution was subjected to visible light irradiation (λ > 420 nm) while bubbling with O₂. A suspension sample (1 mL) was taken and centrifuged at 10,000 rpm for 5 min, and the resulting supernatant was subjected to UV−vis absorption measurements.

**ASSOCIATED CONTENT**

*Supporting Information*

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c06838.

Absorption, FT-IR, and MALDI-TOF mass spectra for the monomer; PXRD patterns, FT-IR spectra, TEM and AFM images, and XPS spectra for DhaCuTph, DhaNiTph, and e-NiCON(epy); nitrogen gas adsorption and desorption isotherms; TEM images for Pt/RGO and their composites; reusability test for H₂ generation and TMB and cytochrome c experiments for DhaCuTph, DhaNiTph, and e-NiCON(epy); photocurrent measurements; CHN elemental analysis; XPS analysis; AFM measurement summary; apparent quantum yields and apparent rate constants for TMB and cytochrome c experiments; and energy level summary (PDF)

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*Notes*

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