

# Structural Change of Metal Ion Ligated by Carboxyphenylporphyrin Anchored to TiO<sub>2</sub> for Efficient Photocatalytic CO<sub>2</sub> Reduction into CO

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## 1. Introduction

Photocatalytic conversion of CO<sub>2</sub> into renewable energy sources completes a new C-neutral cycle in sustainable society. Among various catalysts, semiconductors especially TiO<sub>2</sub> have been studied extensively due to its inexpensive price, stability, and superior photo-oxidation activity. Metal complexes are usually employed as homogeneous catalysts for CO<sub>2</sub> photoreduction allowing precise control of catalytic properties. However, they require a sacrificial reductant, and suffer from quick deactivation within few hours. Accurate molecular design of metal complexes and further combination with semiconductors enable higher catalytic activity over stable photocatalyst. In this study, a photocatalyst consisting of Co-tetrakis(4-carboxyphenyl)porphyrin (TCPP) metal complex and TiO<sub>2</sub> semiconductor was designed. The site coordination and electronic structure of active Co sites were monitored by extended X-ray absorption fine structure (EXAFS).

## 2. Experimental section

H-TCPP (0.24 g, 0.3 mmol) and CoCl<sub>2</sub>·6H<sub>2</sub>O (0.36 g, 1.5 mmol) were dissolved into dimethylformamide (15 mL), followed by ultrasonication for 10 min. Then, the mixed solution was refluxed at 433 K for 5 h. The red precipitate was washed with deionized water by three times (each 60 mL), and dried in vacuum at 333 K for 5 h to obtain Co-TCPP.

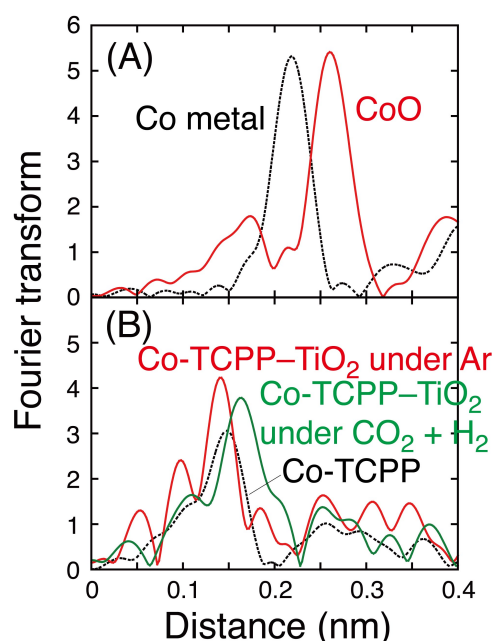
TiO<sub>2</sub> was suspended into ethanol (60 mL) with stirring at 700 rpm for 10 min. Then, Co-TCPP was added into the suspension and kept stirred at 700 rpm for 4 h. The precipitate was filtered, washed with ethanol (20 mL), and dried in vacuum at 298 K for 3 h.

## 2. Results and Discussion

Using <sup>13</sup>CO<sub>2</sub>, H<sub>2</sub>, and UV-visible light, and Co-TCPP (2.5 wt %)-TiO<sub>2</sub> composites, CO formation rate reached the maximum: 7.9 μmol h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>. Among the rate, <sup>13</sup>CO formation rate was 5.6 μmol h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>. No sacrificial reducing agent was added except for H<sub>2</sub>.

In the Fourier transform of angular wavenumber  $k^3$ -weighted EXAFS  $\chi$ -oscillation for Co-TCPP-TiO<sub>2</sub> under argon (Figure 1B), the peak at 0.142 nm (phase shift uncorrected) was attributed to Co-N interatomic pair, based on the comparison to the peak owing to Co-N interatomic pair extracted from the data for Co-TCPP crystals (Figure 1B). This peak was fitted using the parameters of Co-N pair. The best-fit result suggested

preferable J-aggregation with interatomic distance ( $R$ ) value of 0.192 nm. The Co atoms within J-aggregation were coordinated with four N atoms at equatorial position and two N atoms at the axial position, while the monomer and H-aggregation accompanied by four Co-N coordination and the Co centers were loosely combined in sequence. The result compared to the  $R$  value of 0.196 nm for Co-TCPP crystals suggested that Co-TCPP units were partially contracted.



**Figure 1.** Fourier transform EXAFS spectra for (A) standard Co metal and CoO and (B) Co-TCPP, Co-TCPP (25 wt %)/TiO<sub>2</sub> under argon and Co-TCPP (25 wt %)/TiO<sub>2</sub> under CO<sub>2</sub> and H<sub>2</sub>.

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