

# Anchoring and reactivation of single-site Co–porphyrin over TiO<sub>2</sub> for the efficient photocatalytic CO<sub>2</sub> reduction

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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. Semiconductors have been extensively studied for the catalysts. Metal complexes are usually employed for CO<sub>2</sub> photoreduction allowing precise control of catalytic properties. 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> was designed. The site coordination and electronic structure of active Co sites were monitored by EXAFS.

**2. Experimental section** H–TCPP and CoCl<sub>2</sub>·6H<sub>2</sub>O were dissolved into dimethylformamide and refluxed at 433 K. The red precipitate was washed with deionized water, and dried in vacuum at 333 K. Co–TCPP was added into suspended TiO<sub>2</sub> in ethanol and stirred. The precipitate was filtered, washed, and dried in vacuum at 298 K.

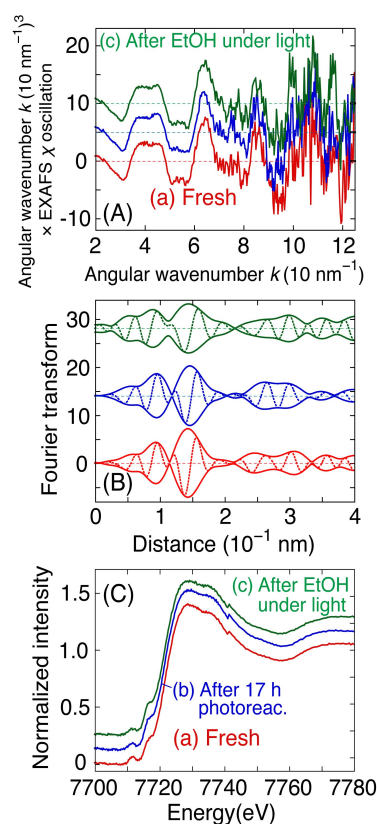
The photocatalysts Co–TCPP–TiO<sub>2</sub> that was used for a photocatalytic test was reactivated under ethanol (2.7 kPa) and the irradiation of UV–visible light [1].

**3. Results and Discussion** Using <sup>13</sup>CO<sub>2</sub>, H<sub>2</sub>, UV–visible light, and Co–TCPP–TiO<sub>2</sub> composites, <sup>13</sup>CO formation rate reached a maximum: 5.6 μmol h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>. When reactivated with ethanol, <sup>13</sup>CO formation rate was 63.0 μmol h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>.

The reason of reactivation was investigated using Co K-edge EXAFS (Figure 1A). The coordination at Co site retained during the reactivation using ethanol and UV–visible light. Co–N coordination number (*N*; the value was 4) for fresh catalyst decreased to 3.5 after the photocatalytic test (a peak at 0.14 nm, phase shift uncorrected, Figure 1B-b) mostly due to the deformation and/or partial/reductive decomposition of Co–TCPP. The *N* value further decreased to 3.1 after the reactivation using ethanol and UV–visible light (a peak at 0.14 nm, phase shift uncorrected, Figure 1B-c) due to the formation of unsaturated Co site by the removal of hydroxy group by ethanol enabling the highest <sup>13</sup>CO formation rate: 63 μmol h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>.

The Co K-edge XANES spectra were also compared for fresh Co–TCPP–TiO<sub>2</sub> (Figure 1C-a), the catalyst under CO<sub>2</sub> and H<sub>2</sub> before, and after UV–visible light irradiation (Figure 1C-b), and the catalyst of Figure 1C-b reactivated under ethanol and UV–visible light (Figure 1C-c). These XANES pattern retained very similar pattern, demonstrating the intact single Co site

coordinated by TCPP ligand. The intensity of pre-edge peak at 7712 eV progressively decreased by CO<sub>2</sub> photoreduction test (Figure 1C-b), then reactivation under ethanol and UV–visible light (Figure 1C-c), suggesting gradual reduction of Co ion site. The reductive decomposition of TCPP was still minor under CO<sub>2</sub>, H<sub>2</sub>, and light and/or under ethanol and light.



**Figure 1.** (A)  $k^3\chi$  and (B) its associated Fourier transform of Co K-edge EXAFS of Co–TCPP (2.5 wt %)-TiO<sub>2</sub> as fresh, evacuated (a), after photoreduction test using CO<sub>2</sub> (2.7 kPa), H<sub>2</sub> (20.7 kPa), and UV–visible light (b), and after subsequent treatment using C<sub>2</sub>H<sub>5</sub>OH (2.7 kPa) and UV–visible light (c).

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**Reference** [1] C. Zhang, J. Yang, K. Hara, R. Ishii, H. Zhang, T. Itoi, and Y. Izumi, *J. Catal.*, in final review process.

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