Synthesis and Photocatalytic Hydrogen Peroxide Production on Zr-MOF with Missing-Linker Defects

([1]*Graduate School of Engineering, Osaka University*, [2]*Elements Strategy Initiative for Catalysts & Batteries (ESICB), Kyoto University,* [3]*JST PRESTO*)
○Yoshifumi Kondo,[1] Yasutaka Kuwahara,[1,2,3] Kohsuke Mori,[1,2] Hiromi Yamashita[1,2]
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Metal-organic frameworks (MOFs) are a class of coordination compounds composed of metal clusters and organic linkers. Their porosity, high surface area, and modularity have a great potential for catalyst materials. Some amine-functionalized MOFs were reported to be active toward photocatalytic hydrogen peroxide (H_2O_2) production via O_2 reduction.[1] An amine-functionalized Zr-based MOF (UiO-66-NH_2) is expected to be effective for photocatalytic H_2O_2 production due to high stability and large surface area. However, it shows limited photocatalytic activity despite the visible-light absorption property. Previous theoretical and experimental studies have showed the introduction of missing-linker sites in UiO-66-NH_2 is an effective approach to enhance the photocatalytic activity due to increasing charge transfer capability.[2,3] In this work, we synthesized defective UiO-66-NH_2 and applied it to photocatalytic H_2O_2 production.[4]

Defective UiO-66-NH_2 (UiO-66-NH_2-X; X is the amount of the acetic acid added during the synthesis) was synthesized via solvothermal method with acetic acid. Based on ^{1}H-NMR and TG-DTA analysis, the amount of missing-linker defects in UiO-66-NH_2-X increased by increasing concentration of acetic acid added. UiO-66-NH_2-X was dispersed in an O_2-saturated acetonitrile solution containing benzyl alcohol as an electron donor. H_2O_2 was produced over all samples with light ($\lambda >$ 350 nm) irradiation. The produced amount of H_2O_2 utilizing defective UiO-66-NH_2-X was higher than that of the pristine UiO-66-NH_2 (Fig. 1). The improved amount of H_2O_2 obtained by UiO-66-NH_2-X was attributed to not only the promotion of reaction rate but also the suppression of H_2O_2 decomposition by introducing missing-linker defects.

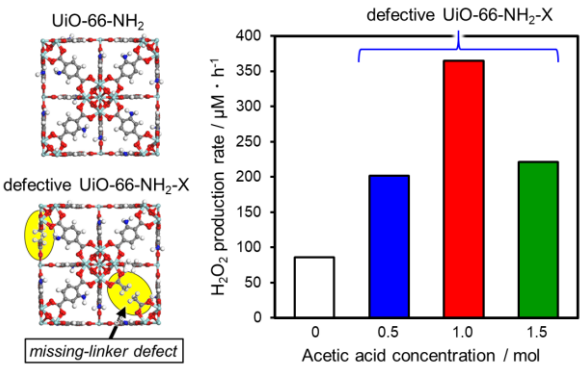

Fig. 1 Photocatalytic H_2O_2 production under light irradiation using UiO-66-NH_2 and defective UiO-66-NH_2-X (X = 0.5, 1.0, 1.5).

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