Improved Photocatalytic H_2 Evolution Using Novel UiO67-bpy-RuPt MOFs under Visible Light

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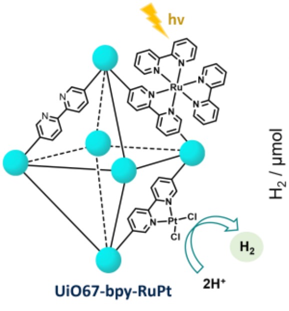
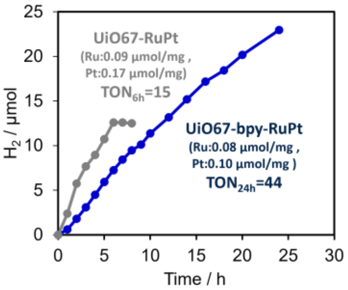
Metal-organic frameworks (MOFs), known as porous crystalline materials, represent a novel class of hybrid materials consisting of metal clusters as secondary building units (SBUs) and organic linkers. Some reports demonstrated the UiO67-derived MOFs modified with $[Ru(dcbpy)(bpy)_2]^{2+}$ (dcbpy=2,2'-bipyridyl-5,5'-dicarboxylic acid) (PS) and $Pt(dcbpy)Cl_2$ (Cat.) can serve as photocatalytic materials for visible-light driven hydrogen evolution reaction (HER). [1,2] However, the reported UiO67-RuPt has relatively low photocatalytic activity. In our investigation, UiO67-RuPt (Ru: 0.09 μmol/mg, Pt: 0.17 μmol/mg) can achieve TON_{6h} =15 for HER in the DMF: H_2O=4:1 (v/v) solution with Dimethylaniline (DMA) as sacrificial donor (SED) under light irradiation (λ>420 nm). After 6 hours of photocatalysis, Ru PS and Pt Cat. detached from the framework, with only 81 % of Ru and 42 % of Pt remaining in the sample.

In this study, we attempt to further optimize the photocatalytic performances of the UiO67-RuPt MOFs by incorporating different linkers that can positively influence HER. A novel UiO67-bpy-RuPt MOFs successfully synthesized by changing the linker from the DCBP (2,2'-biphenyl-4,4'-dicarboxylic acid) to DCBPY (2,2'-bipyridyl-5,5'-dicarboxylic acid). In this bpy-MOF system, the diimine sites is expected to facilitate re-bonding of broken metal–diimine bonds during photocatalysis, which can significantly improve the durability of photocatalyst. [3] To our surprised, under the same photocatalytic performance condition as UiO67-RuPt MOFs, UiO67-bpy-RuPt MOFs show 3 times higher HER activity (TON_{24h}=44) compared with UiO67-RuPt MOF (TON_{6h} = 14), despite the lower loading in both Ru (0.08 μmol/mg) and Pt (0.10 μmol/mg). After 24 hours of photocatalysis, 99% of Ru and 75 % of Pt were confirmed to be retained in the framework.





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