

Experimental and Theoretical Investigation of Hydrogen and Oxygen Production Reactions on Visible-light Responsive MOF Photocatalysts

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Abstract: The hydrogen production reaction proceeded on the amine-functionalized Ti-based MOF (MIL-125(Ti)-NH₂) from water in the presence of triethanolamine (TEOA) as a sacrificial agent, and the oxygen production reaction proceeded on the Fe-based MOF (MIL-101(Fe)) in the presence of AgNO₃ as a sacrificial agent. Electronic structure calculations based on DFT and various spectroscopies revealed that the charge transfer from the organic linker to the metal-oxo cluster and the charge separation in the sub-nanoscale metal-oxo cluster played important roles in the hydrogen and oxygen production systems, respectively.

Keywords: Metal–organic framework (MOF), Hydrogen and oxygen production system, DFT calculation.

1. Introduction

The applications of metal–organic frameworks (MOFs), a group of substances generated from various combinations of metal nodes and organic ligands, for photocatalysts have attracted increasing attention. In this context, our group reported so far that visible-light-driven H₂ production reactions can be promoted by on MIL-125(Ti)-NH₂¹ and O₂ production reaction on MIL-101(Fe)², respectively, from water in the presence of sacrificial agent, however, their reaction mechanisms have not been fully elucidated.

Recently, in the field of heterogeneous catalysts, the use of first–principles calculation to understand their reactivity is also spreading thanks to the high precision and popularization of the density functional theory (DFT). In electronic structure calculations, it is possible to obtain information that is difficult to experimentally verify, such as the band structure and electron density distribution. Therefore, it can be an effective approach for revealing the reaction mechanism of photocatalytic reactions.

Herein, H₂ and O₂ production reactions promoted by various visible-light responsive MOF photocatalysts including MIL-125(Ti)-NH₂ and MIL-101(Fe) have been investigated from both experimental and theoretical aspects. In particular, reaction mechanisms revealed by electronic structure calculation based on DFT are discussed in detail.

2. Experimental and theoretical methods

H₂ and O₂ production reactions were carried out in the presence of triethanolamine (TEOA) and AgNO₃ as respective sacrificial agents. As for the H₂ production reaction, MIL-125(Ti)-NH₂, UiO-66(Zr)-NH₂ and bulk anatase (TiO₂) were selected as photocatalysts. On the other hand, MIL-101(Fe) and bulk hematite (α -Fe₂O₃) were employed for the O₂ production reaction.

Electronic structures of MOFs and bulk metal oxides were calculated using the plane-wave based projector augmented wave (PAW) method as implemented in the VASP code. Lattice constants and atomic positions in crystalline MOFs and bulk metal oxides were optimized using the semi-local PBEsol functional. Then, the single-point calculations were performed using the non-local screened HSE06 hybrid functional to evaluate density of states (DOS) and work functions. Kohn-Sham orbital energies were aligned to the vacuum level using a procedure developed by Butler, Hendon and Walsh³.

3. Results and discussion

H₂ production from aqueous TEOA solution under visible–light irradiation was observed only for MIL-125(Ti)-NH₂ among explored photocatalysts in this study. In order to elucidate the reason of these different photocatalytic reactivity, Partial density of states (PDOS) and band alignments of MIL-125(Ti)-NH₂, UiO-66(Zr)-NH₂ and bulk TiO₂ (Anatase) were evaluated by DFT calculation as shown in Figure 1. LUCO (Lowest unoccupied crystalline orbital) levels of MIL-125(Ti)-NH₂ and UiO-66(Zr)-NH₂ were sufficiently higher than the proton reduction level. Results also showed that HOCO–LUCO transition of MIL-125(Ti)-NH₂ involves the electron transfer from organic linker (HOCO) to the Ti-oxo cluster (LUCO), resulting in the charge separation and possible increase in the lifetime of the photo-excited state. On the other hand, the electron densities on HOCO and LUCO of UiO-66(Zr)-NH₂ were both localized on the organic linker, leading to the possible decrease in the lifetime of excited state and the enhanced charge recombination. These differences in the mode of electron transitions were considered one of the crucial factors to control the H₂ evolution rate on MOF photocatalysts.

The O₂ production reaction proceeded on MIL-101(Fe) from aqueous AgNO₃ solution under visible–light irradiation, and the activity per weight was more than 6 times higher than that of bulk hematite (α -Fe₂O₃). PDOS and band alignments of MIL-101(Fe) and α -Fe₂O₃ are shown in Figure 2. The valence band of MIL-101(Fe) was mainly consisted C 2*p* and O 2*p* orbitals. HOCO level of MIL-101(Fe) and the upper end of the valence band of α -Fe₂O₃ were sufficiently deeper than water oxidation level. Therefore, photo-excitation of MIL-101(Fe) is thought to occur mainly in the Fe-oxo cluster. The size of Fe-oxo cluster of MIL-101(Fe) was sub-nanoscale and much smaller than the primary particle size of α -Fe₂O₃. As a result, the generated electrons and holes could quickly reach the surface and react with the substrate, and thus recombination was suppressed and the activity was considered to be improved.

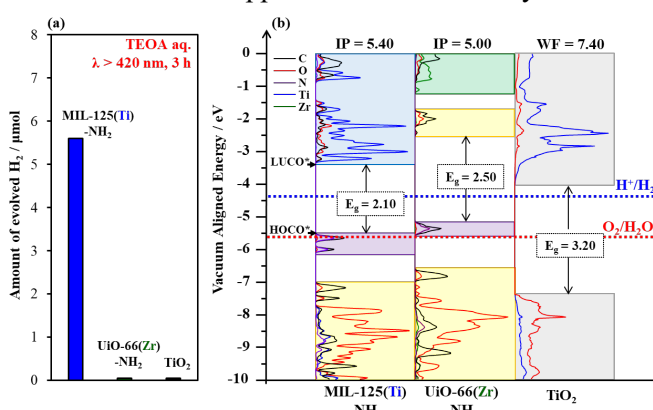


Figure 1. (a) The amount of H₂ formed after visible–light irradiation for 3 h. (b) Partial DOS and electronic band alignment relative to the vacuum level of the MIL-125(Ti)-NH₂, UiO-66(Zr)-NH₂ and bulk anatase (TiO₂).

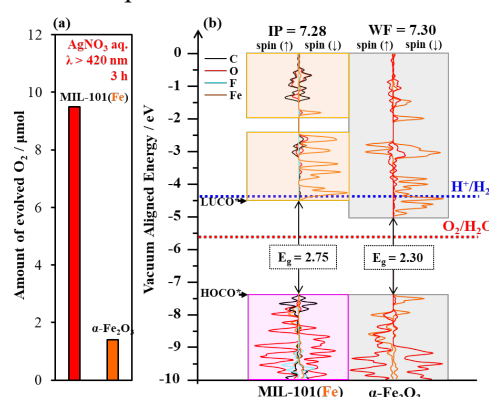


Figure 2. (a) The amount of O₂ formed after visible–light irradiation for 3 h. (b) Partial DOS and electronic band alignment relative to the vacuum level of the MIL-101(Fe) and bulk hematite (α -Fe₂O₃).

4. Conclusions

In summary, visible-light responsive MOF photocatalysts that promote hydrogen and oxygen production reactions from water in the presence of sacrificial agents were developed and their photocatalytic reactivity was investigated. By electronic structure calculation based on DFT, we revealed that hydrogen production reaction on MIL-125(Ti)-NH₂ was promoted by Linker–to–Cluster Charge Transfer (LCCT). On the other hand, oxygen production reaction on MIL-101(Fe) was thought to proceed by charge separation in sub-nanoscale Fe-oxo cluster with higher oxidation ability than bulk α -Fe₂O₃.

References

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