

Enhanced H₂ evolution on ZnIn₂S₄ Photocatalyst under Visible Light by Surface Modification with Metal Cyanoferrates

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Abstract: The surface modification with zinc or indium cyanoferrate species was revealed to significantly increase the rate of H₂ evolution on Pt-loaded ZnIn₂S₄ photocatalyst under visible light in the presence of [Fe(CN)₆]⁴⁻ as an electron donor basically due to the stable redox behavior, in addition to the previously reported cadmium cyanoferrate species. A stepwise modification was found to enable the formation of thin layers of such cyanoferrate on the photocatalyst surface and thereby improve further the rate of H₂ evolution.

Keywords: Photocatalyst, Water splitting, Metal sulfide, Visible light.

1. Introduction

Various metal sulfides such as CdS have been extensively studied as the candidate of such photocatalysts due to their narrow bandgaps for visible light absorption and appropriate band levels both for water oxidation and reduction.¹ However, the biggest drawback of metal sulfide photocatalysts is the lack of water oxidation (i.e., O₂ evolution) ability basically due to occurrence of corrosion by photogenerated holes.⁶ We have recently revealed that the surface modification of CdS with a cadmium hexacyanoferrate, K₂Cd[Fe(CN)₆], enables CdS to function as stable H₂-evolving photocatalyst in Z-scheme system water splitting with [Fe(CN)₆]^{4-/3-} redox.² The K₂Cd[Fe(CN)₆] layers formed on the surface efficiently scavenged photogenerated holes in CdS and also facilitated the oxidation of [Fe(CN)₆]⁴⁻ to [Fe(CN)₆]³⁻. In other words, the K₂Cd[Fe(CN)₆] layers function as a hole-transport agent via stable redox cycle of Fe³⁺/Fe²⁺ in the component. In this system, one serious problem to be solved is the content of toxic Cd species in both the layer and photocatalyst. We also demonstrated that the loading of preliminarily-prepared K₂Cd[Fe(CN)₆] particles on the surface of sulfides is also effective to stabilize the H₂ evolution, which is a possible way to modify Cd-free metal sulfide photocatalyst such as ZnIn₂S₄. However, the effect was limited probably due to the difficulty in homogeneous loading of solid K₂Cd[Fe(CN)₆] particles. Thus, it is strongly desired to develop more effective methods to modify non-toxic metal hexacyanoferrates that can function in a same manner as K₂Cd[Fe(CN)₆]. In the present study, we evaluate the redox property of various metal hexacyanoferrate (i.e., K_xM[Fe(CN)₆]_y, M = Zn, In, Ag, Cu, along with Cd) as well as their performance as promoter for [Fe(CN)₆]⁴⁻ oxidation when loaded on the surface of ZnIn₂S₄ photocatalyst to achieve stable and efficient H₂ evolution based on cadmium-free photocatalyst system.

2. Experimental

Particulate ZnIn₂S₄ (ZIS) sample was prepared by a previously reported hydrothermal method. Pt species (1.0 wt%) was deposited onto ZIS as a cocatalyst by impregnation from aqueous solution of H₂PtCl₆. The surface modification of Pt/ZIS by each metal hexacyanoferrate (MHCF) was carried out via two different methods. One is based on the method reported in our previous study.² The MHCF particles were preliminarily prepared by a precipitation method. The obtained MHCF was mixed with Pt/ZIS in a small amount of Milli-Q water, dried up by hot-water bath, and finally heated at 473 K for 30 min under Ar flow (denoted as MHCF(d)/Pt/ZIS). In the present study, we newly developed a stepwise modification, in which the Pt/ZIS particles were firstly loaded with metal species via impregnation of aqueous solution of the metal salts (e.g., CdBr₂), dried and heated at 473 K for 30 min under Ar flow. Then, the obtained sample was dispersed in a borate buffer (BB) solution (0.1 M, pH 8.0) containing K₄[Fe(CN)₆] (5 mM). The samples obtained via this subsequent method will be denoted as MHCF(s)/Pt/ZIS.

3. Results and discussion

Cyclic voltammetry (CV) profiles were measured for MHCF-loaded FTO in a BB solution (pH 8.0). It was revealed that both the ZnHCF and InHCF exhibit stable redox cycles. These redox cycles are assigned to the valence change between Fe^{3+} and Fe^{2+} contained in the MHCFs. On the other hand, the AgHCF showed irreversible behavior. As for the CuHCF, a reversible redox wave for $\text{Fe}^{3+}/\text{Fe}^{2+}$ was observed at $E_{1/2}$ of ca. $0.94 \text{ V}_{\text{SHE}}$ at pH8, whereas an irreversible peak, which is probably corresponding to the reduction of Cu^{2+} included in CuHCF, was also appeared at $E_p = -0.2 \text{ V}$. TEM observation revealed that the direct method resulted in aggregated MHCF particles on the surface of ZIS with relatively large size (20-50 nm). In stark contrast, the surfaces of Pt/ZIS were homogeneously coated by thin layers ($\sim 20 \text{ nm}$) of MHCF. The formation of MHCF species was confirmed by an ATR-FTIR.

Figure 2 shows the time courses of H_2 evolution on these Pt/ZIS photocatalysts in the presence of $[\text{Fe}(\text{CN})_6]^{4-}$ under visible light irradiation. The modification with these MHCF species provided higher rate of H_2 evolution compared to the unmodified one. Importantly, the loading of ZnHCF species is revealed to enhance the H_2 evolution on Pt/ZIS photocatalyst, in addition to the previously-reported CdHCF. Another important finding is that the modification via the stepwise method provided much higher rates compared to those via direct impregnation. The higher activity observed can be reasonably explained by the highly dispersed and/or thinner layers of MHCFs. The newly-developed stepwise method was also applied to the modification of Pt/ZIS by other MHCFs ($M = \text{In}, \text{Ag}, \text{Cu}$). Initial rate of H_2 evolution over these MHCF/Pt/ZIS ($M = \text{Zn}, \text{Cd}, \text{In}, \text{Ag}, \text{Cu}$) are shown in Figure 2. The modification with InHCF was also found to increase the rate of H_2 evolution on Pt/ZIS. This can be understood by the stable redox cycle of $\text{Fe}^{3+}/\text{Fe}^{2+}$ in the components. On the other hand, the modification with AgHCF or CuHCF completely suppressed the H_2 evolution on Pt/ZIS. The CuHCF/FTO exhibited an irreversible peak probably corresponding to the reduction of Cu^{2+} . Therefore, the most plausible reason is that the photoexcited electrons generated in ZIS are preferentially consumed for the unfavorable reduction of the Cu^{2+} in CuHCF. As for the AgHCF, one can expect the oxidative decomposition (or deactivation) of AgHCF species by holes as suggested by the CV.

4. Conclusions

We successfully developed a stepwise modification method as an effective and probably versatile procedure to form various metal cyanoferrate thin layer on the surface of metal sulfide photocatalysts such as ZnIn_2S_4 . Non-toxic, cadmium-free ZnHCF or InHCF can function as hole transporter, thereby improving the H_2 evolution efficiency on ZnIn_2S_4 accompanied by the oxidation of $[\text{Fe}(\text{CN})_6]^{4-}$.

References

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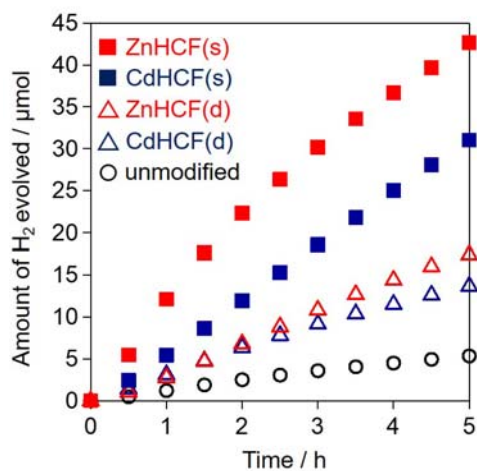


Figure 1. Time courses of H_2 evolution over Pt/ZIS or CdHCF/Pt/ZIS or ZnHCF/Pt/ZIS prepared by the different modification methods in BB solution containing $\text{K}_4[\text{Fe}(\text{CN})_6]$ under visible light irradiation.

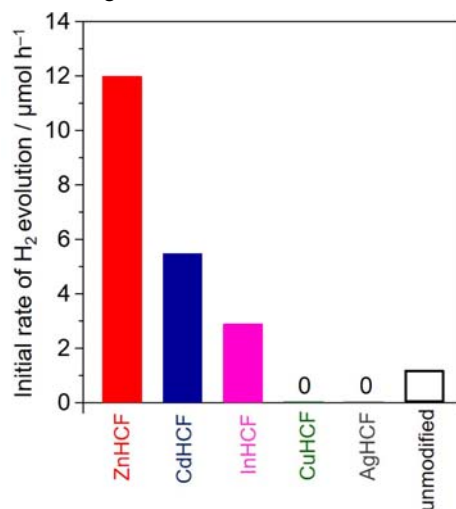


Figure 2. Initial rate of H_2 evolution rate over Pt/ZIS or MHCF/Pt/ZIS ($M = \text{Zn}, \text{Cd}, \text{In}, \text{Cu}, \text{Ag}$) in BB solution containing $\text{K}_4[\text{Fe}(\text{CN})_6]$ under visible light irradiation