

Surface-modified metal sulfides as stable H₂ evolving photocatalyst in Z-scheme water splitting system with [Fe(CN)₆]^{3-/4-} redox mediator under visible light irradiation

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Most of metal sulfide semiconductors, such as CdS, possess appropriate band levels for water reduction and oxidation as well as a narrow band gap allowing visible light absorption because the valence bands of them are mainly formed by S 3p orbital. However, the most of sulfides have no capability of O₂ evolution from water due to the occurrence of self-oxidative deactivation by photogenerated holes. Even for the sacrificial H₂ evolution, they require particular electron donor such as S²⁻ and SO₃²⁻ to generate H₂ stably. In the present study, we introduce a new and versatile way that can stabilize metal sulfides, not only CdS but also others such as ZnIn₂S₄ and CdIn₂S₄, as H₂-evolving photocatalyst in Z-scheme water splitting with [Fe(CN)₆]^{3-/4-} redox.

Pt/CdS was found to generate considerable amount of H₂ from water in the presence of [Fe(CN)₆]⁴⁻ under visible light, while the H₂ evolution was soon terminated at ca. 28 μmol in the unbuffered aqueous solution (Fig. 1). However, the production of nearly the twice amount (ca. 53.6 μmol) of oxidant, i.e., [Fe(CN)₆]³⁻, was confirmed in the solution after the reaction. This result indicated that photocatalytic H₂ evolution over Pt/CdS proceeded under visible light, accompanied by the oxidation of [Fe(CN)₆]⁴⁻ to [Fe(CN)₆]³⁻. The cease of H₂ evolution was due to increased pH value (6.7 → 10.7). Then, it was found that the use of borate buffer (BB) was effective to suppress such decrease in H₂ evolution rate. Photocatalytic H₂ evolutions over other metal sulfides (ZnIn₂S₄ and CdIn₂S₄) were also examined in the presence of [Fe(CN)₆]⁴⁻. Pt/ZnIn₂S₄ showed appreciable

H₂ evolution rate (4.8 μmol/h). On the other hand, Pt/CdIn₂S₄ showed quite low activity (0.8 μmol/h). ATR-FTIR analysis revealed that hexacyanometallates, such as K₂[CdFe(CN)₆] [1] and K₂[ZnFe(CN)₆] [2] were formed on Pt/CdS and Pt/ZnIn₂S₄, respectively, after each reaction, both of which showed appreciable H₂ evolution. These hexacyanometallates would be generated from the reaction of [Fe(CN)₆]⁴⁻ and Cd²⁺ or Zn²⁺ ion derived from photocorrosion during photocatalytic reaction. Rubin et al. have reported that such hexacyanometallate formed on CdS electrode efficiently scavenged photogenerated holes, leading to increased rate of oxidation of [Fe(CN)₆]⁴⁻ and also suppression of photocorrosion of CdS. To improve the activity for H₂ evolution, the hexacyanometallate K₂[CdFe(CN)₆] prepared in advance, was loaded onto ZnIn₂S₄ and CdIn₂S₄ particles. The loading indeed improved the H₂ evolution rate in both cases (ZnIn₂S₄: 4.8 → 15 μmol/h, CdIn₂S₄: 0.8 → 6 μmol/h). Finally, we demonstrated that combination of metal sulfides as H₂-evolving photocatalyst and O₂ evolution system (TaON photoanode [3]) could split water stably into H₂ and O₂ under visible light irradiation (Fig.1 inset).

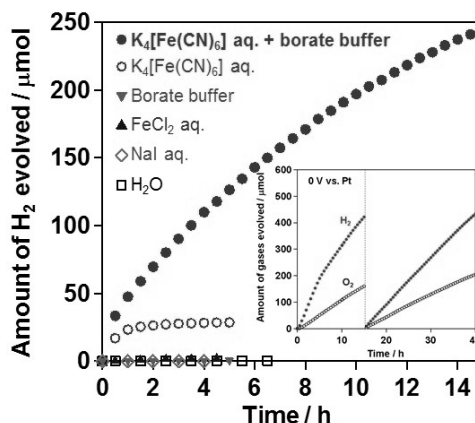


Fig. 1 Time course of H₂ evolution over Pt/CdS in various reaction solutions under visible light. Inset: Z-scheme water splitting using Pt/CdS and CoO_x/TaON photoanode.

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