

"Confined Molecular Catalyst" for Photoelectrochemical Hydrogen Evolution and CO₂ Reduction

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Hydrogen is the most important clean fuels in the future and production of hydrogen from water by solar energy is required. Photoelectrochemical (PEC) and photocatalytic decomposition of water has been studied for long time. Most serious problem of PEC production of hydrogen from water is that while semiconductor electrodes with small energy gap can absorb large fraction of solar energy but unstable, those with large energy gap are stable but can absorb only small fraction of solar energy. This can be solved by using semiconductor of small gap and separating the reaction site from the surface as schematically shown in Figure 1.

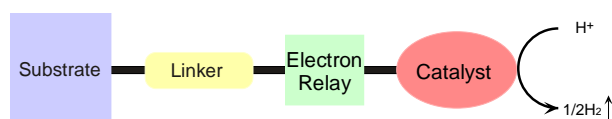


Figure 1. Scheme for photoelectrochemical hydrogen evolution at catalytic site separated from semiconductor surface by molecular layer with electron relay function.

We have realized this concept by constructing viologen molecular layer on hydrogen terminated Si(111) surface followed by incorporation Pt complex within the molecular layer by ion-exchange reaction as schematically shown in Fig. 2 [1, 2].

Figure 2. Photoelectrochemical hydrogen evolution at Si electrode modified by molecular layer with viologen moiety as electron transfer mediator and Pt as a catalyst.

Significant decrease of overpotential for hydrogen evolution reaction (HER) at Si electrode was observed by this modification. Further improvement was achieved by constructing multi-viologen-Pt -layers. Viologen acts as molecular wire and Pt acts as HER catalyst. Figure 3 shows photocurrent-voltage relations of hydrogen terminated p-Si(111) electrode and that modified with 1, 3, and 5 viologen-Pt layers. Hydrogen evolution current flowed at more positive potentials than the reversible potential at p-Si(111) electrodes modified with multi-viologen (molecular wire)-Pt (HER catalyst)-layers under illumination [1, 2].

In situ XAFS study carried out under operation shows that Pt particles were not formed even when HER took place and the Pt complexes acted as HER catalysts, i.e., confined molecular catalysts, as schematically shown in Fig.3 [3]. The decrease of white line intensity suggests the formation of a hydride complex as an intermediate of HER, although more detailed experimental and theoretical examinations are required to clarify the mechanism. The formation of Pt particles may have been inhibited since the complexes are separated by molecular layers.

Similar results were obtained for photoelectrochemical reduction of CO₂ [4].

References:

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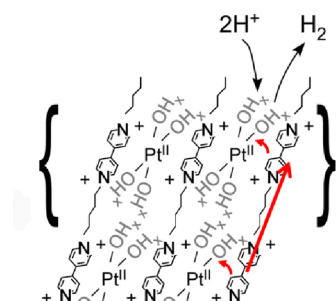


Figure 3. Schematic illustration for electron transfer pathway for HER at Si(111) modified with viologen layer and Pt complex.