

Efficient Hydrogen Evolution Sites of Photocatalysts for Water Splitting

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Introduction

From the view points of environmental and energy problems, huge scale utilization of solar energy is probably the most attractive solution in future. In addition to solar energy conversion to electricity by solar cells, its conversion to chemical energy, which is similar to the photosynthetic reaction, is a big challenge for human beings. Among such energy conversion reactions, overall water splitting into hydrogen and oxygen has been considered as one of the most ideal reactions to generate clean and recyclable energy carrier, i.e. H_2 , without being accompanied by CO_2 emission.

Although there are several different types of approaches to achieve the reaction, overall water splitting on heterogeneous photocatalysts is one of the potential candidates especially from the view point of large scale application. Key issues to establish an efficient photocatalytic reaction system using solar energy is to find suitable photocatalytic materials under visible light and proper modification methods for efficient hydrogen and oxygen formation.

Many photocatalysts for overall water splitting under UV light have already been established. To efficiently utilize solar energy, of course, visible light driven photocatalysts have to be developed. At present, however, such photocatalytic systems are still very limited and various kinds of attempts are being pursued by many researchers.

Visible Light Responsive Photocatalysts

Recently, we have found that some typical elements containing oxynitride photocatalysts such as $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ actually work under visible light irradiation to accomplish overall water splitting [1,2]. This is the first example that accomplished overall water splitting reaction under visible light irradiation on a photocatalyst with a band gap less than 3 eV. $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ is a solid solution of GaN and ZnO and has been proved to be stable materials during overall water splitting reaction with proper modification.

Hydrogen Evolution Sites with Core/Shell Structure

To obtain effective photocatalytic activity of overall water splitting reaction, however, it is indispensable to construct hydrogen evolution sites on the particles of $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$. There have been known several materials as hydrogen evolution sites such as NiO, RuO_2 and Rh-Cr mixed oxide. Among them, Rh/ Cr_2O_3 core /shell nano-structure has also been established as active sites [3]. This structure has been proved to efficiently reduce protons into H_2 molecules and simultaneously prevent the reverse reaction to form H_2O from H_2 and O_2 . It is also possible to replace Rh metal with other noble metals such as Pt. The unique structure has attracted our attention to study the detailed reaction mechanism on the photocatalysts.

Model Electrode Study of Core/Shell Structure

Cr_2O_3 /Rh and Cr_2O_3 /Pt electrodes were prepared as model surfaces of core/shell cocatalysts. Cr oxide was electrochemically deposited on Rh and Pt plates from 0.5 M K_2CrO_4 aqueous solution with the thickness of 2-3 nm. The thickness was estimated by angle resolved XPS. The electrodes were examined in 0.5 M Na_2SO_4 adjusted with H_2SO_4 to pH 3.6. The protons adsorption/desorption and the hydrogen evolution currents were observed at the same voltage for the both electrodes with and without covering of Cr_2O_3 . These results suggested that protons were reduced on the Rh/Pt surfaces even for the Cr_2O_3 -covered electrodes. The cathodic current due to oxygen reduction reaction (ORR) was clearly observed at 0.6 V vs. NHE only for the bare Rh/Pt electrodes but not for the Cr_2O_3 -covered ones. This indicates that the Cr_2O_3 -covered Rh electrode selectively reduces H^+ but not oxygen molecules. Spectroscopic measurements were performed by FTIR spectrometer with subtractively normalized interfacial Fourier transform infrared reflectance spectroscopy (SNIFTIRS) method. The absorption peaks due to the Pt-H stretching mode was observed at 2050 cm^{-1} for both bare and Cr_2O_3 -covered Pt electrodes, which was the direct evidence of H^+ reduction on the core noble metals.

Based on these results, we propose the reaction mechanism of H_2 evolution on the core/shell structure as shown in Figure 1.

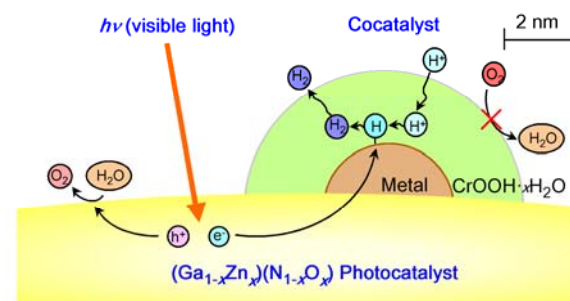


Figure 1. Schematic model of H_2 evolution at core/shell metal/ Cr_2O_3 co-catalyst on $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$.

References

1. Maeda, K., Teramura, K., Lu, D., Takata, T., Saito, N., Inoue, Y., and Domen, K. *Nature* 440, 295 (2006).
2. Maeda, K., and Domen, K. *J. Phys. Chem. C* 111, 7851 (2007).
3. Maeda, K., Teramura, K., Lu, D., Saito, N., Inoue, Y., and Domen, K. *Angew. Chem., Int. Ed.* 45, 7806 (2006).