# Redox site separation effects for photocatalytic activity using ZnS stratified photocatalysts

Akihiro Kobayashi, Shun Yokoyama, Hideyuki Takahashi, Kazuyuki Tohji Graduated school of Environmental Studies, Tohoku University, Sendai, 980-8579, Japan e-mail: hideyuki@mail.kankyo.tohoku.ac.jp

## 1. Introduction

Many researchers have been vigorously investigated to increasing the photocatalytic activity for hydrogen production, since it is effective for harvesting solar energy.

We also reported the synthesis of sulfide type photocatalysts with specific morphology which has nano-sized and capsule-like form, called as stratified photocatalysts<sup>[1]</sup>. These materials show the extremely high catalytic activity, because of specific morphological characteristics such as nano-hetero junction between oxide and sulfide within the wall. These natures induce the effective separation of the photo-excited electron hole pairs, consequently photocatalytic activity become extremely improved<sup>[1]</sup>.

For further enhancement of the photocatalytic activity, it can be considered that the separation of the redox reaction site, reduction site (Pt) and oxidation site  $(RuO_2)^{[2-4]}$ , is effective, since it can prevent the re-combination of photo excited electron hole pair.

Therefore, we tried to develop the of redox site separation method utilizing the nano sized capsule like morphology of stratified photocatalysts. In this study, the relationship between the photocatalytic activity and condition of co-catalysts at the surface of ZnS stratified photocatalysts (s-ZnS) was evaluated.

# 2. Experiment

s-ZnS was prepared obeying to the previous report<sup>[5]</sup>. To be deposited Pt at outside of the wall, 100 mg of s-ZnS was added into purified water containing  $2.07 \times 10^{-4}$  M K<sub>2</sub>PtCl<sub>4</sub> (pH6, 9 and 12) and stirred for 24 h. Then, Pt was photo-deposited by using 500 W Hg lamp irradiation. Samples were analyzed by ICP-OES. The photocatalytic activity was evaluated from the amount of hydrogen produced when the particles were immersed in 0.1 M Na<sub>2</sub>S solution at pH 13.5 and exposed to 500 W Hg lamp.

#### 3. Result and discussion

Table 1 shows the rate of Zn dissolution after Pt photo-deposited at each pH. In the case of pH 6 and 9, Zn dissolution due to the photo-dissolution from s-ZnS was observed. On the other hand, in the case of pH 12, Zn was not dissolved. Moreover, stratified morphology was not deconstructed by photo-dissolution.

Table 1 Rate of Zn dissolution after Pt photodeposition at each pH

рН	Rate of Zn dissolution (%)
6	17.6
9	12.7
12	0.2

The effect of photo-dissolution against to the photocatalytic activity was evaluated by using Pt (0.6at.%)/ s-ZnS photocatalysts at pH 9 and 12 (Fig.1). The sample photo-deposited at pH 12 showed the higher activity than that of pH9. These results indicated that photocatalytic activity was higher in the case of that stratified morphology was maintained (pH12).

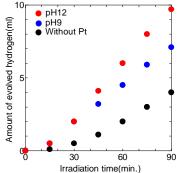


Fig. 1 Time course of  $H_2$  evolution over s-ZnS which deposited 0.6 at. % Pt at outside wall at pH 9 and 12.

#### 4. Conclusion

The pH12 condition is suitable for Pt deposition at outside wall of s-ZnS. Other results will be presented in our presentation.

## Acknowledgement

This work has been supported by the Grant-in-Aid for Scientific Research (A) (No. 23241026).

#### References

- [1] T. Arai, et al. IAPA Conference Series, 3, 75-78 (2001)
- [2] J. Disdier, et al. J. Chem. Soc., Faraday Trans. 1, 79, 651-660 (1983)
- [3] E. Borgarello, et al. Helv. Chim. Acta. 65, 243-248 (1982)
  [4] S. S. K. Ma, et al. Energy Environ. Sci., 5,
- [4] S. S. K. Ma, et al. Energy Environ. Sci., 5 8390-8397(2012)
- [5] T. Arai, et al. Chem. Mater. 20, 1997–2000 (2008)