

Plasmon-enhanced Photocatalytic Hydrogen Evolution Using ZnS-AgInS₂ Solid Solution Nanoparticles

Tsukasa Torimoto¹, Takuya Takahashi,¹ Akihiko Kudo,² Susumu Kuwabata,^{3,4} and Tatsuya Kameyama¹

¹Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan

²Faculty of Science, Tokyo University of Science, Shinjuku-ku, Tokyo 162-8601, Japan

³Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

⁴Japan Science and Technology Agency, CREST, Saitama 332-0012, Japan

Photoexcitation of a localized surface plasmon resonance (LSPR) peak of metal nanoparticles, such as Au and Ag, produces an intensified electric field near the metal particles. The physicochemical properties of chromophores, such as organic dyes and semiconductor nanoparticles, are modulated if they are located in the LSPR-induced electric field. Recently, we have reported that photocatalytic activity of CdS particles was enhanced by the immobilization on the surface of SiO₂-coated Au particles.⁽¹⁾ Though the overlapping between optical properties of semiconductor and metal nanoparticles seems to be necessary for the effective utilization of LSPR-induced electric fields, the details have not been clarified, especially for the enhancement of the photocatalytic reaction.

In this study, we prepared nanocomposite photocatalysts composed of ZnS-AgInS₂ solid solution (ZAIS) nanoparticles and Au particles, where the overlapping of the optical properties of Au and ZAIS particle could be tuned by changing the chemical composition of ZAIS, and then investigated their photocatalytic property for the hydrogen evolution.

Solid solution nanoparticles of (AgIn)_xZn_{2(1-x)}S₂ (ZAIS(x)) nanoparticles (size: 4.4 nm) were prepared by thermal decomposition of a precursor powder (50 mg) of (AgIn)_xZn_{2(1-x)}(S₂CN(C₂H₅)₂)₄ in oleylamine (3.0 cm³) at 180 °C by the same procedure as that reported in our previous paper.⁽²⁾ The surface of ZAIS(x) were modified with 3-mercaptopropyl trimethoxysilane and then the resulting particles were immobilized on SiO₂-coated Au particle (Au size: 15 nm, SiO₂ shell thickness: 18 nm) (Au@SiO₂) to prepare nanocomposite photocatalysts (Au@SiO₂/ZAIS(x)). Photocatalytic hydrogen (H₂) evolution was performed by irradiation of light from a Xe lamp ($\lambda > 350$ nm). Each photocatalyst containing 5 nmol(particle) of ZAIS particles was suspended in an aqueous solution (5 cm³) containing 2-propanol (50 vol%) and irradiated under an argon atmosphere at a room temperature with vigorous magnetic stirring.

TEM measurements revealed that the nanoparticles of ZAIS(x) were densely immobilized on the surface of Au@SiO₂. The irradiation to the photocatalyst suspensions induced the linear increase of the amount of the H₂ evolved, regardless of the kind of photocatalysts, indicating that ZAIS particles worked as a stable photocatalyst under the experimental conditions. However, the H₂ evolution rate (R(H₂)), calculated from the slope of the linear portion in time-course curves, became larger in the case of using Au@SiO₂/ZAIS(x) than that of the corresponding ZAIS(x) nanoparticles only. Since the simple particle mixture of ZAIS(x) and Au@SiO₂ did not cause any enhancement or retardation of H₂ evolution rate, we concluded that the enhancement of photocatalytic

activity required the immobilization of ZAIS photocatalysts at an appropriate distance from Au particles. The enhancement factor (f_{enhance}) was calculated as the ratio of R(H₂) of Au@SiO₂/ZAIS(x) to that of ZAIS(x). Figure 1 shows the wavelength-dependent f_{enhance} for the case of Au@SiO₂/ZAIS(0.8). The spectral profile of f_{enhance} roughly corresponded to the LSPR peak observed in the extinction spectrum of Au@SiO₂ used in the preparation. This indicated that the photocatalytic activity enhancement of ZAIS(x) particles on the Au@SiO₂ layer originated from the increase in photoexcitation probability of ZAIS due to the LSPR-induced local electric field around Au particles.

Figure 2 shows the dependence of f_{enhance} for photocatalytic H₂ evolution on the chemical composition, x , of ZAIS(x) particles used. The f_{enhance} was monotonously enlarged with an increase in the value of x . Optimum f_{enhance} was ca. 2.0 with use of ZAIS(x) particles having $x=1.0$. Considering the red shift of absorption onset (λ_{onset}) of ZAIS(x) with an increase in x , it was indicated that the absorption properties of ZAIS(x) particles needed to effectively overlap with the LSPR peak of Au particles to obtain a larger value of f_{enhance} . The LSPR peak appeared at ca. 550-560 nm for Au@SiO₂, so it was reasonable that the ZAIS(x) particles with x larger than 0.8, of which λ_{onset} was longer than ca. 570 nm, were effectively photoexcited with the LSPR-induced electric field, the degree being enlarged with an increase in the value of x .

In summary, we have successfully demonstrated that the photochemical properties of nanoparticles of a ZnS-AgInS₂ solid solution (ZAIS) could be modulated by combination with Au nanoparticles, the degree being dependent on the overlapping between optical properties of ZAIS(x) and Au nanoparticles.

References

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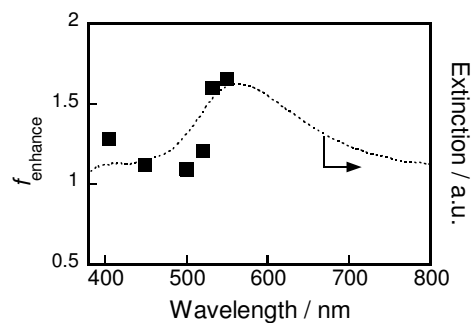


Fig. 1 Wavelength dependence of f_{enhance} for R(H₂) with Au@SiO₂/ZAIS(0.8).

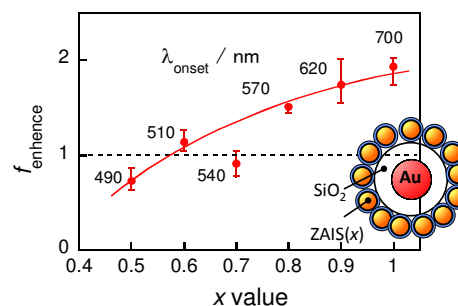


Fig. 2 Relationship between f_{enhance} for photocatalytic activity of Au@SiO₂/ZAIS(x) particles and the chemical composition (x) of the ZAIS(x) particles used.