

## Photocatalytic Hydrogen Evolution Using Jingle-Bell-shaped Cadmium Sulfide Core-Silica Shell Nanoparticles

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Significant progress has been achieved in the preparation techniques of core-shell nanoparticles for the purpose of the development of novel catalysts and optoelectronic devices, because physicochemical properties of core materials could be modified dependent on the kind of materials used for making the shell structure. Recently, we reported<sup>(1,2)</sup> novel core-shell structure of silica (SiO<sub>2</sub>)-coated cadmium sulfide (CdS) (SiO<sub>2</sub>/CdS) nanocomposites with void space having a jingle-bell structure, where the size of CdS core particles could be adjusted from 3.7 to 2.8 nm by changing the wavelength of monochromatic light used in the size selective photoetching from 514 to 458 nm, respectively. Even if CdS nanoparticles are incorporated in hollow SiO<sub>2</sub> shell structure, they are expected to act as photocatalysts whose properties are different from the nanoparticles prepared by the conventional synthetic methods. However, to the best of our knowledge, the photocatalytic activities of core-shell nanoparticles containing semiconductor cores have never been investigated. Here we report the photocatalytic reaction of methanol dehydrogenation by using SiO<sub>2</sub>/CdS particles having different core size. The decrease in the CdS size and the rhodium (Rh) photodeposition could enhance the photocatalytic activity.

The syntheses of SiO<sub>2</sub>/CdS nanoparticles was carried out in Aerosol OT-reversed micelle method, and the obtained SiO<sub>2</sub>/CdS powders were subjected to the size selective photoetching using Ar ion-laser at 515, 488 and 458 nm light as reported earlier.<sup>(1)</sup> Photodeposition of Rh (0.2 wt%) onto SiO<sub>2</sub>/CdS was carried out by the irradiation ( $\lambda > 300$  nm) to an aqueous solution (5 cm<sup>3</sup>) containing rhodium chloride and methanol (50 vol%) under argon atmosphere. Methanol dehydrogenation reaction was performed by the irradiation (436 nm, intensity, 24 mW/cm<sup>2</sup>) to 5 cm<sup>3</sup> aqueous methanol (50 vol%) suspension containing 10 mg SiO<sub>2</sub>/CdS powders under argon atmosphere.

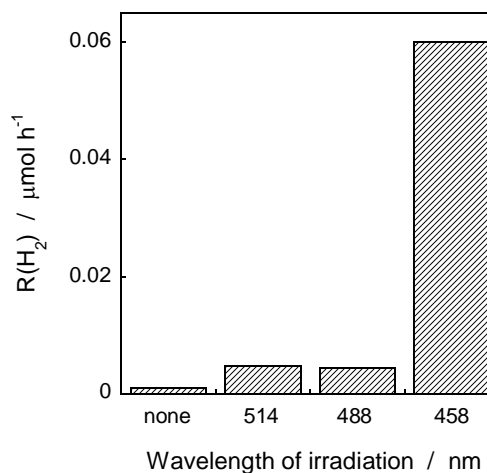
The linear relations were observed in any cases of reactions using SiO<sub>2</sub>/CdS between the amount of H<sub>2</sub> evolution and the irradiation time. Though original SiO<sub>2</sub>/CdS exhibited a little activity for H<sub>2</sub> evolution, the size-selective photoetching at 458 nm irradiation increased the photocatalytic activities of SiO<sub>2</sub>/CdS. Furthermore 0.2 wt% Rh loading enhanced the H<sub>2</sub>

production rate roughly 10 times. These results suggested that the methanol dehydrogenation reaction proceeded photocatalytically and Rh particles effectively acted as co-catalyst for the effective reduction of H<sup>+</sup> with photogenerated electrons in CdS. Furthermore the diffuse reflectance spectra of the 458-nm photoetched SiO<sub>2</sub>/CdS particles were almost unchanged when compared before and after the methanol dehydrogenation reaction, indicating that SiO<sub>2</sub> shell surrounding CdS core was stable and prevented the coalescence of CdS nanoparticles during the photocatalytic reactions.

From the slope of linear relation of amount of H<sub>2</sub> evolved with irradiation time, the rate of H<sub>2</sub> evolution, R(H<sub>2</sub>), was calculated. As shown in Fig. 1, the photocatalytic activities of SiO<sub>2</sub>/CdS without Rh loading greatly increased with a decrease in the wavelength of the irradiation, that is, with a decrease in the size of CdS core. These results could be explained by the change in the energy structure of CdS particles due to the size quantization effect: the decrease in CdS size caused the negative shift of the potential of the conduction band edge and the positive shift of that of the valence band edge, resulting in the increase in overpotentials both of reduction reaction of H<sup>+</sup> with photogenerated electrons and of oxidation reaction of methanol with positive holes.

### References

1. T. Torimoto, J. P. Reyes, K. Iwasaki, B. Pal, T. Shibayama, K. Sugawara, H. Takahashi, and B. Ohtani, *J. Am. Chem. Soc.*, **125**, 316 (2003).
2. T. Torimoto, J. P. Reyes, S.-y. Murakami, B. Pal, B. Ohtani, *J. Photochem. Photobiol. A Chem.*, **160**, 69 (2003).



**Fig. 1.** Effect of wavelength of monochromatic light used for the size-selective photoetching of SiO<sub>2</sub>/CdS on the H<sub>2</sub> evolution rate.