Photocatalytic syntheses of azoxybenzene by visible light irradiation of silica-coated cadmium sulfide nanocomposites

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Photoirradiation (λ = 436 nm) of a deaerated 2-propanol aqueous solution containing nitrobenzene and rhodium-loaded silica-coated cadmium sulfide nanoparticles produced azoxybenzene with relatively high selectivity (68%), the photocatalytic activity being enhanced with a decrease in the size of the semiconductor particle core.

Size-quantized semiconductor nanoparticles (less than *ca.* 10 nm in size) have attracted much attention because of their unique size-dependent physicochemical properties; the positions of the conduction band and the valence band become shifted toward negative and positive potentials, respectively, with a decrease in particle size.[1–8] One of the promising applications of such small particles seems to be photocatalysts for the development of new synthetic routes to organic compounds in environmentally benign processes. However, although there have been many studies aiming at organic syntheses using bulk semiconductor particles as photocatalysts,[9–15] little attention has been paid to the utilization of nanoparticles because these particles are generally not stable and easily coalesce into larger particles owing to their extremely large surface-to-volume ratio.

Recently, we reported a novel synthesis of silica (SiO_2)-coated cadmium sulfide (CdS) nanoparticles with a void space, in which a CdS core was incorporated in hollow SiO_2 shell particles to form a "jingle-bell"-shaped nanocomposite, using a size-selective photoetching technique.[16–19] The size of the CdS core can be adjusted from 3.7 to 2.8 nm with a relatively narrow size distribution by changing the wavelength of the monochromatic light used for the size-selective photoetching (λ_{etch}) from 514 to 458 nm. It has also been demonstrated in methanol dehydrogenation that CdS core particles did not coalesce with each other owing to the surrounding SiO_2 shell but acted as more efficient photocatalysts than did bulk CdS, the photocatalytic activity being enhanced with a decrease in the size of the CdS core.[18] The high stability of SiO_2/CdS enables application to the development of novel photocatalytic reactions. Here we report photocatalytic reduction of nitrobenzene (NB) using SiO_2/CdS nanoparticles with visible-light irradiation. The nanostructure of SiO_2/CdS particles can be controlled to obtain the optimum yield and selectivity of azoxybenzene (AZYB) as a reduction product, which has been utilized in dyes, analytical reagents, reducing agents and polymerisation inhibitors. As a related subject to the present study, it has been reported that aniline (AN) was preferentially produced by the photocatalytic reduction of NB with irradiation of deaerated alcoholic suspensions containing bulk semiconductor particles,[20–23] though NB was photochemically reduced to AZYB by the direct photoexcitation of NB with UV irradiation in the presence of cyclohexene and semiconductor particles.[24]

The jingle-bell-shaped SiO_2/CdS particles were prepared by the same procedure as that reported previously.[18] The surface of CdS nanoparticles (diameter: *ca.* 5.0 nm) was modified with 3-mercaptopropyltrimethoxysilane (MPTS), followed by hydrolysis of its trimethoxysilyl group to make a thin silica shell layer (*ca.* 0.3 nm). The obtained particles were subjected to size-selective photoetching to form the jingle-bell structure and then rhodium (Rh) nanoparticles were photodeposited as cocatalysts onto SiO_2/CdS. The amount of Rh loading was 0.37 atom% based on that of Cd atoms in the powders. Photocatalytic reduction of nitrobenzene (NB) was performed by irradiation at 436 nm with monochromatic light that was extracted from a high-pressure mercury lamp using glass filters (Asahi Techno Glass V-42 and Y-43). The irradiation intensity was 7.3 mW cm^{-2}. Photocatalyst powder containing 6 mg CdS was suspended in an aqueous solution (5.0 cm^3) containing NB (100 μmol) and 2-propanol (50 vol%) as a hole scavenger, followed by irradiation under an argon atmosphere at 298 K. Bulk CdS particles (Furuuchi) having a bare surface were used for comparison. Platinum (Pt) particles with a size of *ca.* 60 nm were added to the reaction suspension to give 0.24 atom% when necessary. The products were characterised by HPLC and GC-MS analyses. The apparent quantum yield (Φ_{app}) was defined as the ratio of the rate of consumption of photogenerated electrons to the flux of incident photons.

Fig. 1 shows the time course of product formation and NB consumption by irradiation of the 458 nm-photoetched SiO_2/CdS with Rh loading. The irradiation produced four kinds of reduction products, that is, nitrosobenzene (NSB), aniline (AN), azoxybenzene (AZYB) and azobenzene (AZB), the amount of each being increased with increase in irradiation time. No other reduction product, such as hydrogen, was detected. Irradiation of the solution without the addition of CdS particles did not cause the formation of these reduction products. The amount of NB consumption was in agreement with the total amount of nitrogen atoms detected in reduction products, regardless of the irradiation time. These facts indicated that NB was photocatalytically reduced to NSB, AN, AZYB, or AZB without formation of detectable amounts of any other reduction products. The formation of AZYB molecules by the reduction of NB requires 6 electrons per AZYB molecule, though the detailed mechanism has been

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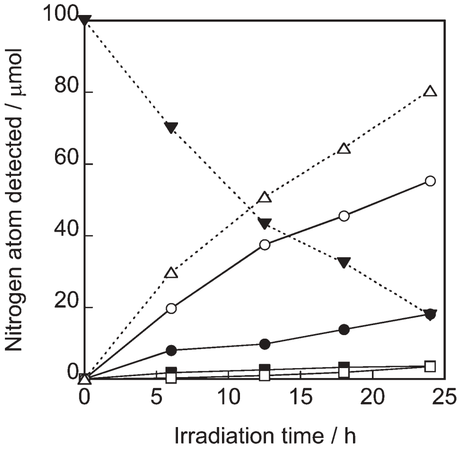


Fig. 1 Time course of the photocatalytic reduction of NB (▼) by irradiation of 458 nm-photoetched SiO_2/CdS with Rh loading. Reduction products NSB (●), AN (■), AZYB (○), and AZB (□) were detected. The total amount of nitrogen atoms detected in reduction products is also shown (△).

reported to be complicated.[25] From the slope of linear increase in the amount of AZYB with increase in irradiation time (< 13 h), Φ_{app} was estimated to be 2.4%. The selectivity of AZYB after 24 h of irradiation was calculated to be *ca.* 68% based on the amount of nitrogen atoms detected in reduction products, which was remarkably higher than that reported by direct photoexcitation of NB with UV irradiation in the presence of cyclohexene and bulk WO_3 particles, 41%.[24]

The photoreduction of NB with CdS photocatalysts gave NSB, AN, AZYB and AZB as products in all cases but their yields were greatly dependent on the kind of photocatalyst used, as summarized in Fig. 2. Though the reaction conditions used for the present study were not optimized for any kinds of CdS particles used, the observed difference in the photocatalytic activities was large enough to be discussed. Without Rh loading, NSB was formed as the main product except for the case of original SiO_2/CdS. It was reported in our previous papers[16,18] that the surface of the CdS core in the original particles was completely covered with a SiO_2 shell layer but that size-selective photoetching decreased the core size, resulting in exposure of the bare CdS surface within the SiO_2 hollow shell. These facts suggested that the bare CdS surface had a strong tendency to form NSB by the reduction of NB with photogenerated electrons in the CdS core (Scheme 1a), which was weakened by the covering of the bare surface with a SiO_2 shell layer. On the other hand, the Rh deposition induced the AZYB production, indicating that deposited Rh particles effectively captured the photogenerated electrons in CdS particles to produce AZYB and then the reaction on the bare CdS surface, that is, NSB formation, was attenuated (Scheme 1b), except for the case of SiO_2/CdS photoetched at 458 nm in which a similar amount of NSB was formed regardless of Rh loading. This exception may have been caused by the inhomogeneity of Rh deposition; that is, Rh particles were deposited on some part of the particles because of the larger specific surface area of the 458 nm-photoetched CdS core, resulting in a mixture of SiO_2/CdS photocatalyst particles with and without Rh loading.

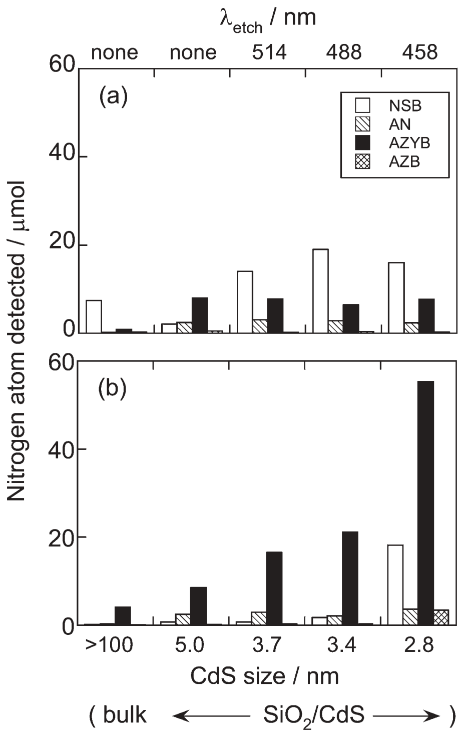
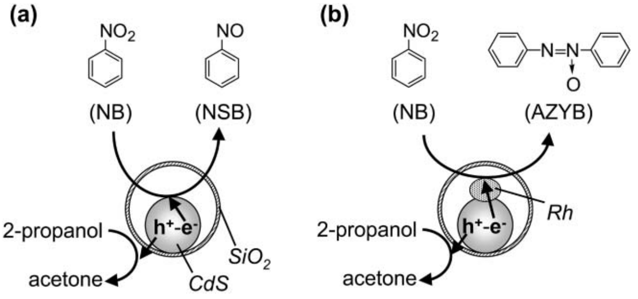


Fig. 2 Distribution of NB reduction products by irradiation of CdS photocatalysts without (a) and with Rh loading (b) for 24 h.



Scheme 1 Proposed reaction models for the photocatalytic reduction of NB by SiO_2/CdS without (a) and with Rh loading (b).

The above interpretation is also supported by the photocatalytic reduction of NB in the presence of a Pt colloid. The addition of a Pt colloid to bare bulk CdS attenuated the NSB production and increased by 4–5 times the yield of AZYB as observed for bulk CdS with Rh loading. On the other hand, in the case of SiO_2/CdS particles photoetched at 458 nm, the yield and selectivity of reduction products were almost the same as those without Rh loading; that is, NSB was mainly produced regardless of the addition of Pt particles. It has been reported for photocatalytic methanol dehydrogenation with jingle-bell-shaped SiO_2/CdS particles that the SiO_2 shell layer surrounding the photoetched CdS core prevented direct contact between CdS cores and Pt particles because the shell had no pore large enough for Pt particles (*ca.* 60 nm in size) to enter, resulting in little probability of electron transfer from the photoexcited CdS core to Pt particles.[18] Therefore, these results indicated that noble metal particles could act as cocatalysts for AZYB production only when photoexcited electrons in CdS were effectively transferred to them.

It should be noted that the photocatalytic activity of CdS cores tended to increase with a decrease in the size, especially in the case of Rh loading, though bulk CdS particles exhibited only very low activity. We previously reported similar behaviour for photocatalytic methanol dehydrogenation with the use of SiO_2/CdS.[18] The size quantization effect is remarkable if the size of the CdS particle becomes smaller than the exciton Bohr diameter, *ca.* 6 nm, and then the electronic energy structure of CdS greatly varies depending on the particle size.[26,27] This fact explains the enhancement of photocatalytic activities of CdS. The decrease in particle size caused a negative shift of the potential of the conduction band edge (E_{CB}) and then enhanced the potential difference between E_{CB} and the reduction potential of NB, resulting in acceleration of the rate of electron transfer from photoexcited CdS nanoparticles to NB.

In conclusion, we have demonstrated for the first time the potential capability of jingle-bell-shaped SiO_2/CdS photocatalysts for efficient synthesis of AZYB from NB reduction, in contrast to conventional bulk semiconductor photocatalysts. Furthermore, the yield and selectivity of products can be tuned by changing the size of the CdS core and noble metal loading. Since it has been reported in our recent paper that a SiO_2 shell has pores whose sizes determine the mass transfer of target molecules,[19] the jingle-bell-shaped semiconductor core-SiO_2 shell particles are promising materials for the development of novel molecular-size-dependent photocatalytic reactions with precise control of the pore size on a SiO_2 shell to sieve molecules. Work in this direction is in progress.

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