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Photocatalytic hydrogenation of azobenzene to hydrazobenzene on cadmium sulfide under visible light irradiation

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Visible light irradiation (λ <600 nm) of commercially-available CdS in alcohol successfully promotes hydrogenation of azobenzene to hydrazobenzene with more than 95% selectivity. This is promoted by strong adsorption of azobenzene to the photoformed zerovalent Cd species adjacent to the surface S vacancies on CdS, leading to efficient reduction to hydrazobenzene.

Hydrazobenzenes is one important chemical for synthesis of pharmaceuticals and dyes.¹ It is usually manufactured by hydrogenation of azobenzene using stoichiometric amounts of metal reducing reagents such as Zn, Fe, and Mg, along with concomitant formation of large amounts of inorganic wastes.² Catalytic hydrogenation on Pd catalysts with H₂ has also been proposed.³ This, however, subsequently reduces the formed hydrazobenzenes to anilines (Scheme 1), and optimization of reaction conditions such as temperature and H₂ pressure is necessary. Creating a new method for selective azobenzene-to-hydrazobenzene reduction under mild conditions is desired for green hydrazobenzene synthesis.



Photocatalysis is one ideal system for this purpose because it promotes reduction reactions using inexpensive and safe reducing reagents such as alcohols at room temperature and atmospheric pressure. Some systems have been employed for azobenzene reduction. TiO₂ loaded with Pt particles (Pt/TiO₂)⁴ and CeO₂ loaded with Au particles (Au/CeO₂)^{5,6} promote photocatalytic azobenzene reduction with alcohol as a sacrificial electron and proton donor. Both systems, however, promote subsequent reduction of the formed hydrazobenzene to aniline (Scheme 1). In addition, the former system needs UV light for catalyst photoexcitation, and the latter needs a base (NaOH). Exploring a new catalyst that promotes selective azobenzene-to-hydrazobenzene photoreduction driven by visible light without noble metal or base is therefore desired.

Here we report that cadmium sulfide (CdS), a common and inexpensive semiconductor photocatalyst driven by visible light irradiation (λ <600 nm),^{7,8} promotes azobenzene-to-hydrazobenzene reduction with >95% selectivity. UV-vis and X-ray photoelectron spectroscopy (XPS) analysis revealed that S vacancies on the CdS surface act as the reduction sites. The Cd atoms adjacent to the S vacancies are photoreduced, producing zerovalent Cd species. Azobenzenes are strongly adsorbed onto the Cd⁰ species and successfully reduced to hydrazobenzene, whereas the formed hydrazobenzenes are inactive. This thus suppresses further reduction of hydrazobenzene.

Photoreactions were performed by visible light irradiation (λ >420 nm, Xe lamp) of a 2-PrOH/water mixture (9/1 v/v, 5 mL) containing catalyst (50 mg) and azobenzene (50 µmol) under Ar atmosphere (1 atm) at 303 K with magnetic stirring. Commercially-available CdS (Sigma-Aldrich; average diameter, 40 nm, BET surface area, 49 m² g⁻¹) was used. Scanning electron microscopy (SEM) images of the sample are shown in Fig. S1 (ESI⁺). Table 1 summarizes the results obtained by 5 h photoirradiation with respective catalysts. Absence of catalyst does not promote the reaction (entry 1). However, as shown by entry 2, use of CdS promotes almost complete azobenzeneto-hydrazobenzene transformation with 97% selectivity, where aniline, a further hydrogenation product of hydrazobenzene, is produced at only a minor level (3%). Note that other common visible-light-responsive semiconductors such as Fe₂O₃,⁹ $BiVO_4$, ¹⁰ WO_3 , ¹¹ Ag_3PO_4 , ¹² and $g-C_3N_4$ ¹³ (entries 3–7) are inactive; almost no azobenzene reacts even in 5 h reaction. In contrast, TiO₂ (rutile),¹⁴ which absorbs visible light only weakly, promotes selective azobenzene-to-hydrazobenzene conversion (entry 8), although the azobenzene conversion is

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⁺ Electronic Supplementary Information (ESI) available: Experimental details and supplementary data (Figs. S1–S3). See DOI: 10.1039/x0xx00000x

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only 20%. The TiO₂, when photoexcited at $\lambda >$ 300 nm (entry 9), promotes almost complete transformation. These indicate that bare CdS and TiO₂ promote selective azobenzene-tohydrazobenzene conversion; only CdS is effective under visible light. As shown by entry 2, the CdS recovered after the reaction, when reused for further reaction, shows almost the same activity and selectivity to those obtained by the fresh one. In addition, inductively-coupled plasma (ICP) analysis of the solution recovered after the reaction scarcely detected Cd or S component. These suggest that CdS activated by visible light promotes selective azobenzene-to-hydrazobenzene conversion and is reusable at least two times without loss of activity and selectivity.

Table 1 Results of photocatalytic reduction of azobenzene on the respective catalysts."					
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Entry	Catalyst	Light ^b	Azobenzene	Selectiv	vity / % 2 ^c
1	none	UV + vis	<0.1	-	-
2	CdS	vis	99	97	3
	1st reuse ^d	vis	94	95	5
	2nd reuse ^d	vis	96	97	3
3	Fe ₂ O ₃	vis	<0.1		
4	BiVO ₄	vis	<0.1		
5	WO ₃	vis	<0.1		
6	Ag ₃ PO ₄	vis	<0.1		
7	g-C ₃ N ₄	vis	<0.1		
8	TiO ₂ ^e	vis	20	96	4
9	TiO ₂ ^e	UV + vis	99	97	3
10	Pt (0.5 wt %)/CdS	vis	37	84	16
11	Pt (1 wt %)/CdS	vis	0.3		

^{*a*} Reaction conditions: catalyst (50 mg), 2-PrOH/water mixture (9/1 v/v, 5 mL), Ar (1 atm), time (5 h), temperature (298 K). ^{*b*} UV + vis (λ >300 nm), vis (λ >420 nm). ^{*c*} Amounts of substrate and products were determined by GC-FID. ^{*d*} Catalysts were recovered by centrifugation, washed with water, and used for further reactions. ^{*e*} Japan Reference catalyst (JRC-TIO-6) supplied from the Catalyst Society of Japan. Average diameter (20 nm), BET surface area (49 m² g⁻¹).

Fig. 1 shows time-dependent change in the amounts of azobenzene and products during photoreaction on CdS. Almost all of azobenzene is transformed to hydrazobenzene selectively and quantitatively with only a minor amount of aniline. The amounts of hydrazobenzene and aniline scarcely change even after prolonged photoirradiation, indicating that further reduction of hydrazobenzene scarcely occurs (Scheme 1). As shown in Fig. S2 (ESI⁺), photoirradiation of a 2-PrOH solution with CdS and hydrazobenzene gives only a minor amount of aniline, again indicating that subsequent reduction of hydrazobenzene scarcely occurs. During the reaction of azobenzene, formation of H_2 was not detected by GC analysis. In addition, as shown by green symbols in Fig. 1, amount of acetone formed is similar to the sum of the amounts of hydrazobenzene (blue) and aniline (black). These data indicate that H atoms of 2-PrOH are used quantitatively for hydrogenation of azobenzene.



Fig. 1 Change in the amounts of azobenzene and products during photoreaction with CdS under visible light. Reaction conditions are identical to those in Table 1.



Fig. 2 (a) Structure of S vacancies on Wurtzite CdS surface, and proposed mechanism for the formation of Cd⁰ species by the photoformed CB electrons. (b) Electronic band structure of CdS and reduction potential of azobenzene.

As shown in Fig. 2b, valence band (VB) and conduction band (CB) of CdS lie at 1.88 V and -0.52 V (vs. NHE), respectively, with the band gap energy 2.4 eV (514 nm).⁷ It is, however, reported that reduction potential of azobenzene lies at -1.1 V (vs. NHE),⁵ more negative than the CdS CB. This suggests that reduction of azobenzene by the CB electrons on CdS is thermodynamically unfavourable. As shown in Fig. 2a, CdS has a hexagonal wurtzite structure and usually contain a large number of surface S vacancies.^{15,16} These S vacancies play a crucial role in the photocatalytic azobenzene reduction. On the S vacancies, low-coordinated Cd atoms are exposed on the surface. The donor levels of these Cd atoms lie at ca. 0.1–0.4 eV below the CB bottom.^{17,18} They, thus, act as the trapping sites for the CB electrons. As shown in Fig. 2a, the trapped

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electrons reduce these Cd atoms and produce Cd⁰ species via aggregation, although structure of the species has not been clarified.^{19,20} As shown in Fig. 2b, electron-deficient N=N bond of azobenzene is adsorbed onto the Cd⁰ via the electron transfer. This decreases the reduction potential of azobenzene and successfully promotes the reduction to hydrazobenzene.

The S vacancies as the reduction sites for azobenzene are confirmed by loading of metal particles onto CdS. Pt particles were loaded by the photodeposition method with $H_2PtCl_6.6H_2O$ as a precursor, where Pt particles are created on the surface vacancies.^{21,22} As shown in Table 1 (entries 10, 11), CdS loaded with 0.5 or 1 wt % Pt show decreased azobenzene conversion, and the decrease becomes more apparent with the amount of Pt. This indicates that the surface S vacancies indeed act as the active sites for azobenzene reduction.



Fig. 3 XPS chart (Cd 3d region) of (a) CdS, (b) CdS obtained after visible light irradiation in a 2-PrOH/water mixture, and (c) the sample obtained after adsorption of azobenzene onto the photoirradiated CdS (b).

Azobenzene adsorption onto the Cd⁰ species photoformed on the S vacancies is confirmed by XPS analysis. CdS powders, when photoirradiated by visible light in a 2-PrOH/water mixture (9/1 v/v) under Ar, turns brownish, indicative of a formation of Cd⁰. Exposure of the solution to air immediately recovers the original bright yellow color. This indicates that, as shown in Fig. 2a, the Cd⁰ species formation occurs reversibly.^{23,24} Azobenzene, when added to the photoirradiated brownish CdS suspension under Ar, leads to a formation of bright orange powders. This color does not change even after exposure to air. Fig. 3 shows XPS (Cd 3d level) of CdS during the course of these sequence. CdS itself (Fig. 3a) shows a single component assigned to Cd^{2+} (red). The

CdS, when photoirradiated by visible light in a 2-PrOH solution under Ar (Fig. 3b), shows a new component assigned to Cd⁰ (blue).²⁵ This indicates that the Cd⁰ species are indeed produced by the photoformed CB electrons (Fig. 2a). In contrast, as shown in Fig. 3c, azobenzene, when adsorbed onto the photoirradiated CdS, creates additional component at higher binding energy (green), together with a decrease in the Cd⁰. This indicates that the surface Cd⁰ are oxidized via electron donation to the adsorbed azobenzene. As shown in Fig. S3 (ESI⁺), XPS (S 2p) of CdS reveals that photoirradiation creates an S component charged more negatively at lower binding energy. This is due to the formation of adjacent Cd^0 by photoreduction. Addition of azobenzene to this sample recovers the S component at higher binding energy due to the electron donation from Cd⁰ to the adsorbed azobenzene. These are consistent with the Cd XPS data.



Fig. 4 (Solid lines) Absorption spectra of CdS and the sample obtained after visible light irradiation in a 2-PrOH/water (9/1 v/v) mixture under Ar for 6 h followed by adsorption of azobenzene or hydrazobenzene. The spectra for azobenzene or hydrazobenzene in a 2-PrOH/water mixture (1 mM) are also shown. (Dashed line) difference spectra obtained by subtraction of CdS (black) from azobenzene-adsorbed CdS (red). (Circles) Action spectrum for hydrazobenzene formation obtained by the photoreactions of azobenzene on CdS. The apparent quantum yields for hydrazobenzene formation was determined with the equation: Φ_{AQY} (%) = ([hydrazobenzene formed (µmol)] ×2) / [photon number entering into the reaction vessel (µmol)]) × 100.

As shown in Fig. 4 (red), the obtained azobenzeneadsorbed CdS shows red-shifted absorption at λ >600 nm as compared to bare CdS (black), although azobenzene itself absorbs light at λ <570 nm (orange). This new band originates form the interfacial charge transfer (IFCT)²⁶ from the CdS VB to the adsorbed azobenzene, as is also observed for nitrobenzene-adsorbed TiO2.²² The absorption maximum of this band, determined by subtraction of the spectrum for bare CdS, is ca. 620 nm (2.0 eV). The donor level of this transition calculated from the CdS VB is therefore -0.12 V (vs NHE). As shown in Fig. 2b, this donor level is similar to that of surface S vacancies (-0.42 to -0.02 V vs NHE). This suggests that the red-shifted absorption is indeed due to the IFCT transition from CdS VB to the adsorbed azobenzene. Electron donation from the Cd⁰ species to the electron-deficient N=N bond of azobenzene may lead to strong adsorption and facilitate the IFCT transition. Similar strong interaction with the Cd⁰ species is observed for electron-deficient C=O, C=C,^{19,27} or C=N groups.²⁰ As shown in Fig. 2b, the donor level of this IFCT transition (-0.12 V) is more positive than the reduction potential of azobenzene (-1.1 V). The strong Cd⁰-azobenzene

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interaction may lead to a decrease in its reduction potential and, hence, facilitates efficient reduction of azobenzene.

As shown in Table 1 (entries 8, 9), TiO_2 is also active for azobenzene reduction. As shown in Fig. S4 (ESI⁺), azobenzene, when adsorbed onto the TiO₂ obtained after UV irradiation in a 2-PrOH/water mixture under Ar, shows red-shifted absorption, as observed for CdS (Fig. 4), although other semiconductors do not. It is well known that TiO₂ contains a large number of surface oxygen vacancies, where neighboring Ti⁴⁺ act as trapping sites for the CB electrons and produce Ti³⁺.^{28,29} The observed red-shifted absorption may thus be due to the IFCT transition from TiO₂ VB to the azobenzene adsorbed onto the Ti³⁺. This allows efficient azobenzene reduction on TiO₂.

It is noted that, in the CdS system, subsequent reduction of the formed hydrazobenzene to anilines scarcely occurs. This is because hydrazobenzene has a saturated N–N bond and does not interact with the Cd^0 species. As shown in Fig. 4 (blue), hydrazobenzene adsorbed onto the photoirradiated CdS does not show red-shifted absorption. This clearly indicates that hydrazobenzene does not associate with the Cd^0 species, thus suppressing its subsequent reduction.

Fig. 4 (plot) shows the action spectrum for the formation of hydrazobenzene during photoreaction of azobenzene on CdS measured by monochromated light irradiation. The apparent quantum yields (Φ_{AQY}) agree well with the absorption spectrum of CdS (black). This suggests that, as shown in Fig. 2b, band gap photoexcitation of CdS and transfer of CB electrons to the S vacancy promotes azobenzene reduction.

It is also noted that activity for azobenzene reduction on CdS is enhanced by the addition of small amount of water. Fig. S5 (ESI⁺) shows the effect of the amount of water added (0-50 vol%) to 2-PrOH on the azobenzene reduction. Selectivity for the hydrazobenzene formation scarcely change (97-98%) by water addition. Azobenzene conversion by 5 h reaction in pure 2-PrOH is 79%, but increases with the amount of water. Almost complete conversion is achieved with 10% water, but further addition decreases the conversion due to the decrease in the amount of 2-PrOH as an electron donor. Fig. S5 (ESI†) also shows the amount of azobenzene adsorbed onto CdS during stirring in the dark. The adsorbed amount of azobenzene in pure 2-PrOH is 1.6 µmol, but increases with water addition; \geq 10% water shows the highest adsorption amount (8.5 μ mol). This indicates that addition of small amount of water decreases the solubility of azobenzene and leads to its strong adsorption onto CdS, resulting in enhanced activity.

In summary, we found that CdS promotes selective azobenzene-to-hydrazobenzene conversion under visible light. The surface Cd adjacent to the S vacancies act as the trapping sites for photoformed CB electrons and are transformed to the Cd⁰ species. Azobenzenes are adsorbed onto the species and their reduction potentials decrease significantly. This allows efficient reduction to hydrazobenzenes. The results presented here based on surface S vacancy as the reduction sites may contribute to the development of photocatalytic organic synthesis driven by visible light.

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Graphical Abstract



Visible light irradiation of commercially-available CdS in alcohol successfully promotes selective azobenzene-to-hydrazobenzene reduction, where surface S vacancies play a crucial role for activity and selectivity.