PERKIN 2

Photocatalytic stereoselective N-cyclization of 2,6-diaminopimelic acid into piperidine-2,6-dicarboxylic acid by an aqueous suspension of activated cadmium(II) sulfide particles

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Photoirradiation at a wavelength of >300 nm of a deaerated suspension of cadmium(II) sulfide (CdS) particles in an aqueous solution of a mixture of stereoisomers of 2,6-diaminopimelic acid (DAP; (*S*,*S*) : (*R*,*S*) : (*R*,*R*) = 1 : 2 : 1) produced piperidine-2,6-dicarboxylic acid (PDC) *via* a redox-combined mechanism including oxidation and reduction by positive holes and photoexcited electrons, respectively. Both the yield and *trans* : *cis* ratio of PDC markedly depended on the kinds of CdS photocatalysts, their pre-treatment, and the loading of fine platinum (or its oxide) particles. A CdS photocatalyst prepared by heat treatment of a commercial powder in hexagonal (wurtzite) structure at 1023 K in the presence of a small amount of air gave the highest yield and *trans* : *cis* ratio. Analyses of the activated CdS powder by powder X-ray diffraction (XRD), photoluminescence (PL), X-ray photoelectron spectroscopy (XPS), electron paramagnetic resonance (EPR), and BET surface area measurements revealed the formation of sulfur vacancies due to heat treatment, which promote the photoinduced cadmium metal (Cd^0) deposition. The Cd^0, deposited *in situ* on the CdS surface and detected by reduction of methylviologen, may act as a reduction site for photoexcited electrons toward a cyclic Schiff base intermediate produced by oxidation of DAP with positive holes followed by deamination and intramolecular condensation. Optically pure (*R*,*R*)- or (*S*,*S*)-PDCs were prepared successfully by photocatalytic reaction with the activated CdS particles using (*R*,*R*)- or (*S*,*S*)-DAPs, indicating that stereoselective conversion of organic compounds can be achieved *via* photocatalytic reaction under controlled conditions.

Introduction

One of the most attractive targets of semiconductor photocatalytic reaction is its practical application to organic syntheses,[1–4] as well as solar-energy conversion and storage,[5,6] reductive fixation of carbon dioxide,[7–10] and mineralization and/or detoxification of organic compounds.[11–14] Since both oxidation and reduction occur, in principle, on the photoirradiated semiconductor particles by positive holes (h^+) and photoexcited electrons (e^-), reactions similar to electroorganic synthesis are expected to proceed efficiently on each particle without the use of an electrolyte(s), which is an indispensable element in conventional electrolyses. Furthermore, these redox reactions leave no by-product originating from the reductant and oxidant; this is in contrast to conventional redox reagents such as permanganate or lithium aluminium hydride, which give manganese ion or aluminium hydroxide, respectively, as reaction by-products. These features make the photocatalytic reaction simple and possible to apply to organic synthesis, *e.g.*, the photocatalytic products may be isolated simply by centrifugation or filtering to separate the photocatalysts followed by evaporation of the solvent without tedious work-up procedures. Another characteristic of photocatalytic reactions that makes them superior to general synthetic processes is that they proceed smoothly even in aqueous suspensions at ambient temperature. Therefore, hydrophilic and thermally unstable organic compounds, especially those with biological origins, can be used as a starting material without derivatization of functional group(s); *e.g.*, (*S*)-lysine (Lys) can be dissolved only in water and undergoes deaminocyclization in the aqueous solution to form pipecolinic acid (piperidine-2-carboxylic acid, PCA) by the photocatalytic reaction.[15,16]

Among semiconductors, cadmium(II) sulfide (CdS), as well as titanium(IV) oxide (TiO_2), has been used as a material for a potential and promising photocatalyst. For the CdS photocatalyst, several papers have reported the structural factors that affect the photocatalytic activities.[17–25] Among them, a few studies have shown that annealing, *i.e.*, heat treatment, generally under an inert atmosphere, of the powder at a high temperature enhances the photocatalytic activity of deaerated aqueous CdS suspensions, and this effect was attributed to crystal transformation from sphalerite (cubic) to wurtzite (hexagonal).[17] More recently, Lee *et al.*[26] have claimed that heat treatment under air improves the CdS photocatalytic activity, especially for reduction of intermediate organic compounds, due to an oxidized surface moiety.

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In our previous study, we found that photoirradiation of an aqueous CdS suspension containing 2,6-diaminopimelic acid (DAP) leads to deaminocyclization into piperidine-2,6-dicarboxylic acid (PDC) and that the use of pre-treated CdS particles as a photocatalyst gives *trans*-rich PDC.[27] Although one of the stereoisomers of the product, *trans*-(*S*,*S*)-PDC, is a naturally occurring isomer and can be used as the starting material for syntheses of various types of piperidine alkaloids (*e.g.*, Solenopsin A[28–38]), its stereoselective chemical synthesis is known to be very difficult,[39,40] and there seem to be no established pathways for the synthesis. One-step synthesis of *trans*-PDC through a semiconductor photocatalytic reaction is of great importance. This paper deals with the stereoselective production of PDC from DAP by, in most cases, activated CdS particles in an aqueous suspension, emphasizing the mechanism of activation by pre-treatment of CdS and that producing *trans*-PDC.[41]

Experimental

Photocatalysts

CdS powders were obtained commercially and used as received or after heat treatment. Heat treatment was performed by using a laboratory-made miniaturized rotary kiln consisting of a tubular quartz cell (*ca.* 40 mm diameter and 250 mm length), an airtight motor-driven cell holder with an inlet and outlet for the gas stream, an electric furnace, and a time-programmable temperature controller. The angle between the rotating axis and horizontal level is *ca.* 20°. Four baffle plates on the inside bottom wall of the cell ensured thorough mixing to avoid heterogeneity in the heating of a sample powder. A 2.0 g portion of CdS powder was placed in the cell and rotated at 78 rpm. In almost all cases, a mixture of argon (Ar; 99.99%, 40 $cm^3 min^{-1}$) with air (1.7 $cm^3 min^{-1}$) was passed through the cell during the heat treatment. The temperature of the furnace was raised linearly to 1023 K, unless otherwise stated, over a period of 50 min, maintained at 1023 K for 1 h, and then allowed to cool to room temperature (over a period of about 2.5 h). Loading of platinum(IV) oxide (PtO_2) was achieved by simply shaking CdS and PtO_2 (Wako Pure Chemical) powders in an Erlenmeyer flask using an electric vibrator.[17,18]

Materials

DAP was purchased from Wako as an optically inactive mixture of stereoisomers of (*S*,*S*), (*R*,*S*), and (*R*,*R*) in the ratio of 1 : 2 : 1. In most experiments, this mixture was used as a substrate. Optical resolution of this mixture was achieved following the previously reported procedure.[42] The only exception was that the *N*,*N′*-bis(benzyloxycarbonyl) derivative of DAP was obtained using the reagent, 4-(benzyloxycarbonyloxy)phenyldimethylsulfonium methylsulfate (Z-ODSP, Sanceler). Finally, 145 mg of (*S*,*S*)-DAP and 100 mg of (*R*,*R*)-DAP were obtained from 5 g of racemate. Optical purity of >99% for both isomers was confirmed by HPLC as described below.

Authentic samples of a product, PDC, were prepared as follows. A sample of *cis*-PDC in the form of the monohydrate was prepared by hydrogenation of pyridine-2,6-dicarboxylic acid over platinum black (Wako) suspended in aqueous acetic acid at ambient temperature and crystallized from aqueous ethanol: 71%, mp 250–258 °C (lit.[43] 258 °C). The elemental analysis and NMR spectrum showed >99% purity. For the quantitative analysis of *trans*-PDC, a photocatalytic reaction product, from suspensions of Furuuchi CdS heat-treated at 1023 K under an Ar stream (50 $cm^3 min^{-1}$) with continual air pulses (20 cm^3 every 10 min) for 1 h (CdS (c)), was used after determination of the content of the *trans* isomer by ^1H NMR. The procedure of the photocatalytic reaction is described in the following section. After the irradiation, supernatant solutions of 48 samples were collected and analyzed by HPLC (DAP conversion: 39%, PDC yield based on DAP in feed: 12%). This solution was loaded on an anion-exchange resin (Dowex 1-X8, acetate form) and washed with water to remove the remaining DAP. PDC was eluted with aqueous acetic acid solution and then treated with cation-exchange resin (Dowex 50W-X4, H^+ form) to separate the acetic acid. The eluent (aqueous ammonia) was dried to give 64.4 mg of yellow powder (8% based on DAP in feed). FAB MS (JEOL JMS-HX110 with DA500, Xe; water–glycerin). Calcd for $C_7H_{12}O_4N$ (MH^+): 174.0766. Found: 174.0756. ^1H NMR (D_2O, 400 MHz) *trans*: 4.0, 2.0, 1.9 and 1.6 ppm; *cis*: 3.6, 2.2, 2.0, and 1.6 ppm (2H each) downfield from TPS (3-trimethylsilylpropanesulfonic acid-d_5). These peaks were assigned by comparison of the spectra of the authentic *cis*-PDC and natural product, *trans*-(*S*,*S*)-PDC (teneraic acid).[44] The integrated peak area ratio of H_α (4.0 and 3.6 ppm for *trans* and *cis*, respectively) of the *trans* and *cis* isomers was 3.7. This mixture was used as an HPLC standard of *trans* isomers in equimolar amount. The retention time of one of the *trans*-PDCs coincided with that of the natural (*S*,*S*)-PDC sample in HPLC (see Fig. 2).

The other chemicals used in this study were purchased from Wako Pure Chemical or Nacarai Tesque and were of the highest available grades. Ion-exchanged water prepared with a Corning Mega-Pure System MP-190 (>16 MΩ cm) was used to make the aqueous solutions throughout this study.

Characterization of CdS powders

Measurements of X-ray diffraction (XRD) patterns,[45] photoluminescence spectra of aqueous CdS suspensions,[17,19] and electron paramagnetic resonance (EPR) spectra[25] were performed following the previous reports.

X-Ray photoelectron spectroscopic (XPS) measurements were carried out using an ULVAC PHI 5500 Multi Technique System with a dual anode X-ray source (Mg-K_α 15 kV, 400 W). The photocatalyst powder was pressed in a die (*ca.* 1000 kg) into a self-supporting disk of 2 cm in diameter and introduced in the instrument. The angle between the sample surface and electron beam was 45°. During the measurements, the analyzer chamber was kept at a pressure of <133 nPa (=10^{-9} Torr). Spectra in the Cd1s, S2p, and O1s regions were recorded, and the binding energy was corrected with reference to a contaminated C1s core line (284.6 eV).

The specific surface area of TiO_2 samples was determined from N_2 adsorption at 77 K on the basis of the BET equation by using a glass apparatus for constant-volume adsorption measurement equipped with an oil diffusion pump and an MKS Baratron type 122A capacitance manometer. To minimize the change in physical properties of samples, the drying process prior to surface-area measurement was carried out at 383 K under reduced pressure.

Photoirradiation and product analyses

Commercial CdS and TiO_2 powders were used with and without pre-treatment. An aqueous solution of DAP (Wako Pure Chemical; mixture of (*S*,*S*), (*R*,*R*), and (*R*,*S*) isomers (1 : 1 : 2), total 100 μmol) and catalyst (50 mg) was placed in a glass tube (transparent to >300 nm). An aqueous solution of NaOH (1 mol dm^{-3}, 0–200 μmol) was then added. The suspension was irradiated with a 400 W mercury arc (Eiko-sha) under argon at 298 K (±1 K) with magnetic stirring (1000 rpm) for 24 h. Products in gas and liquid phases were analyzed by GC and HPLC, respectively. Details of the GC measurements have been reported elsewhere.[46] For HPLC analyses using Shimadzu LC-6A high-performance liquid chromatographs, a Mitsubishi Chemicals MCI gel CRS10W or a Daicel Chemicals Chiralpak MA(+) column (4.6 mm inner diameter and 50 mm length) was eluted with 0.5 or 1.0 mmol dm^{-3} copper(II) sulfate solution (10% methanol) at 313 K. Detection of eluted samples was performed at 254 nm.

Table 1 Photocatalytic deaminocyclization of DAP by suspended CdS particles[a]

Catalyst supplier	Purity (%)	Additive	*cis*-PDC/ μmol	*trans*-PDC/ μmol	Yield[c] (%)	*trans*:*cis*	Conv.[d] (%)	*meso*[e] (%)
Diapigment	Unknown	None	5	15	25	3.1	78	50
Furuuchi	99.999	None	3	4	10	1.2	76	49
Kojundo	99.99	None	3	4	9	1.3	74	51
Katayama	96	None	2	2	5	0.7	74	51
Furuuchi[b]	99.999	None	6	26	39	4.1	84	48
Furuuchi	99.999	5 wt% PtO_2	25	7	37	0.3	86	51
Katayama	96	5 wt% PtO_2	3	<1	5	0.2	77	51
Furuuchi[b]	99.999	5 wt% PtO_2	24	7	33	0.3	93	50

[a] Catalyst (50 mg) was suspended in an aqueous solution (5.0 cm^3) of DAP (100 μmol with 50 μmol of NaOH) and irradiated under Ar at 298 K for 24 h. [b] Denotes heat-treated (1023 K under nitrogen with small amount of air) CdS. [c] HPLC yield based on DAP consumption. [d] Conversion of DAP. [e] *meso* isomer in remaining DAP.

An example of isolation and identification of a *cis*-rich product is given below. Furuuchi CdS (as received) loaded with 5 wt% of platinum(IV) oxide (PtO_2) (50 mg) was suspended in an aqueous DAP (105 μmol; 5.0 cm^3) solution containing 50 μmol of NaOH and irradiated under Ar for 20 h to convert DAP almost completely. The catalyst was removed from the reaction mixture, and the resulting solution was treated with cation-exchange resin (Organo IR-120B (H^+ form)) and washed with water. Products were eluted with 5% aqueous ammonia, and ninhydrin-positive fractions were dried to yield a water-soluble pale-yellow solid. GC-MS (Hewlett-Packard 5890 GC with a 5970 mass selective detector) analysis after trimethylsilylation with trimethylsilyl chloride (at 343 K for 10 min) revealed the formation of *cis* and *trans* isomers of PDC in the ratio of *ca.* 4:1. FAB MS (JEOL JMS-HX110 with DA500, Xe; water–glycerin) MH^+: 174.

Analysis of *in situ* deposited metallic cadmium (Cd^0)

Cadmium metal deposited during the photocatalytic reaction, Cd^0, was measured quantitatively with methylviologen (MV^{2+}; Wako) as follows. To the photoirradiated reaction mixture was added a deaerated aqueous solution of MV^{2+} (0.5 mmol, 0.5 cm^3). The resulting pale-blue-colored suspension containing a reduced form of MV^{2+}, $MV^{+\bullet}$, was filtered, and the supernatant solution was loaded in a sealable quartz cell (light path length, 1 mm) in an N_2-purged vacuum glove box. From the absorbance of the solution at 602 nm (using a Shimadzu MP-1000 spectrophotometer) and reported extinction coefficient of $MV^{+\bullet}$ (13700 mol^{-1} dm^3 cm^{-1} at 602 nm),[47] the molar amount of Cd^0 was estimated on the assumption that two-fold higher molar amount of MV^{2+} reacts with Cd^0 to produce $MV^{+\bullet}$.

Results and discussion

Photocatalytic production of PDCs from DAP with aqueous suspension of CdS

Table 1 shows representative results of the photocatalytic reaction of aqueous DAP solutions with various types of CdS powders.

Although the photocatalytic reaction by TiO_2 (Degussa P-25)–Pt[48] (50 mg) gave *cis*-PDC as well as racemic PCA (a decarboxylated product) negligible (<0.1 μmol) formation of *trans*-PDC could be observed (data not shown). On the other hand, bare CdS photocatalyzed the conversion of DAP into PDC as a mixture of *cis* and *trans* isomers, without appreciable formation of PCA. The reaction has been proved to be photocatalytic by the fact that it proceeds only with photoirradiation and in the presence of a catalyst. As clearly seen in Table 1, the *trans*:*cis* ratios of PDC depended on the nature of the CdS photocatalysts. Bare CdS particles tended to produce *trans*-PDC predominantly, except for the case of Katayama CdS of poor photocatalytic activity. In particular, a pigment-grade CdS (Diapigment from Mitsubishi Material) and heat-treated Furuuchi CdS show relatively higher activity for *trans*-PDC production. On the other hand, in all cases of platinum(IV) oxide (PtO_2)-loaded CdS, the *cis* isomer was produced selectively (*trans*:*cis* ratio of <0.3). In this study, one of the best photocatalysts for the *trans*-PDC production was found to be the heat-treated Furuuchi CdS.

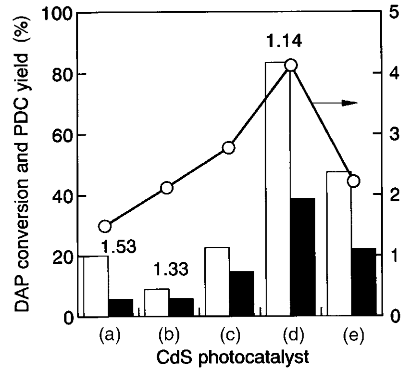
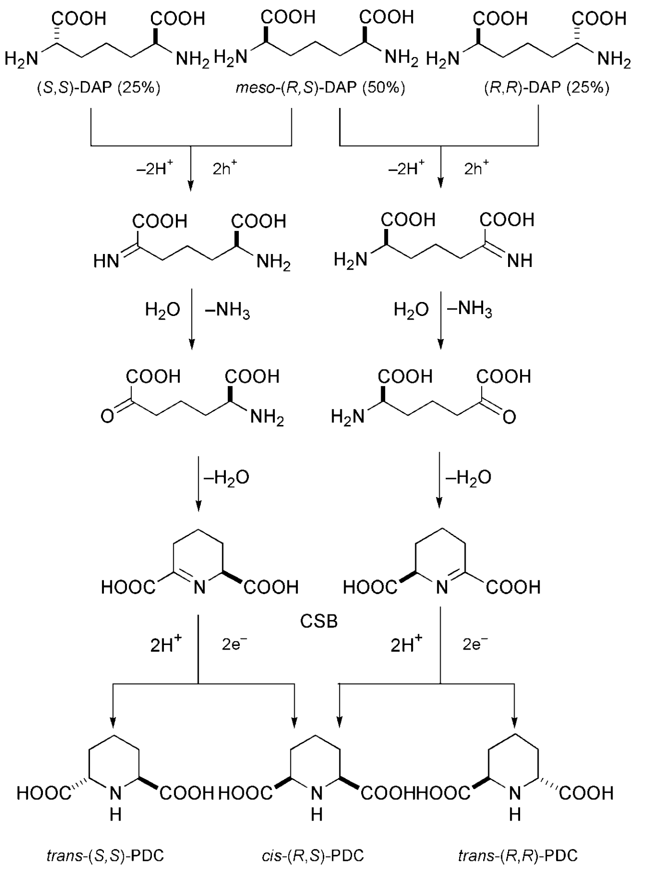


Fig. 1 Representative photocatalytic activities of CdS photocatalysts. White and black bars indicate DAP conversion and PDC yield after 24 h irradiation, respectively. An open circle shows the molar ratio of *trans*- to *cis*-PDC. (a) Furuuchi CdS (99.999%) as received; (b) (a) was annealed at 1023 K under Ar; (c) (a) was annealed in a manner similar to that of (b) but with continual air pulses (20 cm^3 every 10 min); (d) (a) was annealed at 1023 K under Ar (40 cm^3 min^{-1})–air (1.7 cm^3 min^{-1}); and (e) under air. Figures show the BET surface area in units of m^2 g^{-1}.

Fig. 1 shows the effects of pre-treatment of Furuuchi CdS on the rate of DAP consumption, total PDC yield, and *trans*:*cis* ratio. Annealing at 1023 K under completely deaerated conditions decreased the DAP conversion and the PDC yield but improved the *trans*:*cis* ratio a little. On the other hand, treatment with a small amount of air was markedly effective for both the enhancement of photocatalytic activity and the *trans*:*cis* ratio of PDC. Similar treatment under air caused the formation of a CdO layer (as proved by X-ray diffraction (XRD) analysis) resulting in a relatively low rate of DAP consumption and a low *trans*:*cis* ratio compared to those in the case of CdS treated under partially aerated conditions. The change in physical properties of CdS particles due to heat treatment under aerated conditions will be discussed later.

The proposed reaction mechanism is depicted in Scheme 1. By analogy with the photocatalytic reaction of Lys,[15] an amino group in DAP may be oxidized first by a positive hole (h^+), which is generated as a result of photoexcitation of a valence-band electron into the conduction band of semiconducting materials. In the presence of molecular oxygen (O_2), no PDC could be obtained, while DAP was consumed at a faster rate (data not shown), supporting the redox-combined reaction mechanism. For the photocatalytic reaction system yielding pipecolinic acid (PCA) from lysine through a similar redox-combined mechanism on TiO_2–Pt, it has been proved that



Scheme 1 Expected photocatalytic reaction mechanism producing *trans*- and *cis*-PDC from a mixture of stereoisomers of DAP.

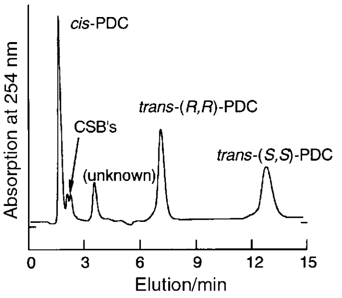
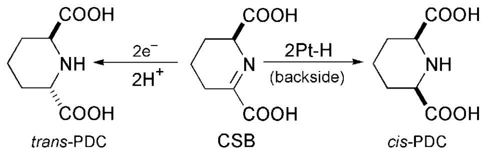


Fig. 2 A representative HPLC chart of *cis*- and *trans*-PDCs with cyclic Schiff base intermediate(s). Column: Daicel Chiralpak MA(+). We could not determine the structure of the "unknown" component, which appeared after photoirradiation.



Scheme 2 Proposed intermediacy of a cyclic Schiff Base (CSB) producing respectively *trans*- and *cis*-PDC through two-step electron transfer and *syn*-addition of hydrogen atoms at the platinum surface.

higher selectivity for PCA is achieved when the reduction sites, Pt deposits, are distributed on the TiO_2 surface in a highly dispersed state.[48] This indicates that the redox-combined reaction does proceed and that the efficiency for reduction of an oxidized intermediate (Schiff base) depends strongly on the distance between oxidation and reduction sites. However, we have no experimental evidence to show how and for how long the two photoexcited electrons survive before the reduction of the cyclic Schiff base intermediate. As reported previously, the cyclic Schiff base was detected under the selected reaction conditions and underwent hydrogenation to give *cis*-PDC in the presence of Pt under an H_2 atmosphere.[27]

In the present experiments, the addition of NaOH was necessary to convert DAP, indicating that the deprotonated amino group, but not the ammonium form, undergoes oxidation.[16] It should be noted that the (*R*,*S*) isomer constituted half of the remaining DAP unchanged by the photocatalytic reaction, irrespective of the CdS catalyst used (Table 1). This means that the DAP isomers are consumed almost equally during the course of the photocatalytic reaction. The stereo selection for *trans*-PDC production is, therefore, attributable to the step involving reduction of a cyclic Schiff base (CSB) intermediate by the photoexcited electrons (e^-). Under conditions of higher pH, formation of the CSB (or α-keto acid in equilibrium with CSB, see Scheme 2) intermediate was observed by enantiomer-separation HPLC analyses (Fig. 2); two peaks with almost the same intensities and widths appeared. It has been reported that CSB is stable only under alkaline conditions.[49] These split peaks in the HPLC chart are attributable to enantiomers of CSBs, since they disappeared on subsequent treatment in the dark with platinum black under an H_2 atmosphere, with a concomitant increase for *cis*-PDC. (We attempted to synthesize the CSBs to show their intermediacy for PDCs but failed due to their instability, as has been reported previously.[50]) These facts suggest both that the present photocatalytic reaction proceeds *via* the CSB intermediate, as shown in Scheme 1, and that its hydrogenation on the Pt surface leads to *cis*-PDC, maybe *via syn*-addition of hydrogen atoms to the C=N bond in CSB (Scheme 2).

In the presence of loaded PtO_2 on CdS particles, the photoexcited electrons could move to the PtO_2 (or Pt formed *via* photodeposition[46]) surface and produce hydrogen atoms, resulting in the selective formation of *cis*-PDC. Almost similar results were obtained with CdS–Pt photocatalysts (data not shown). On the other hand, the bare CdS surface also reduces CSB not by hydrogen atom addition but, presumably, by electron transfer, because CdS particles themselves showed no catalytic activity for hydrogenation of CSB under an H_2 atmosphere in the dark; it seems that the CdS surface does not produce hydrogen atoms. Surface modification of CdS enhances the electron transfer and, furthermore, induces higher selectivity for *trans* isomers, maybe due to interaction with the intermediate species, CSB and/or its one-electron reduced form. Excessive modification to a higher extent, *e.g.*, annealing in air, may cause a decrease in its reduction ability for producing PDC.

Cd^0 formation during the photocatalytic reaction by activated CdS

Careful inspection of the irradiated reaction mixtures revealed that the suspension of active CdS had turned a little brownish and had darkened, and the original bright yellow color was recovered by introduction of air. Furthermore, addition of a deaerated aqueous solution of methylviologen (MV^{2+}) to the irradiated suspension caused the appearance of intense blue color owing to its cation radical ($MV^{+\bullet}$). Such behavior was first reported by Gutiérrez and Henglein[51] for a suspension of a commercial (Fluka) CdS powder and later by Shiragami *et al.*[52] and Rajh *et al.*[53] for CdS colloid; photoinduced formation of Cd^0 and its oxidative dissolution with air or MV^{2+} were suggested in these papers. Consistent with previously reported results,[52] the untreated CdS powders gave negligible $MV^{+\bullet}$ even after 24 h irradiation. The molar amount of Cd^0 deposited on CdS was evaluated from that of $MV^{+\bullet}$ on the assumption of the stoichiometry, $Cd^0 + 2MV^{2+} = Cd^{2+} + 2MV^{+\bullet}$, and is plotted in Fig. 3. As can be clearly seen, the yield of *trans*-PDC grew with increases in Cd^0, while that of *cis*-PDC seemed to be independent of Cd^0, leading to a higher *trans*:*cis* ratio. Thus, the deposited Cd^0 improves both the photocatalytic activity of CdS for N-cyclization of DAP into PDC and the stereoselec-

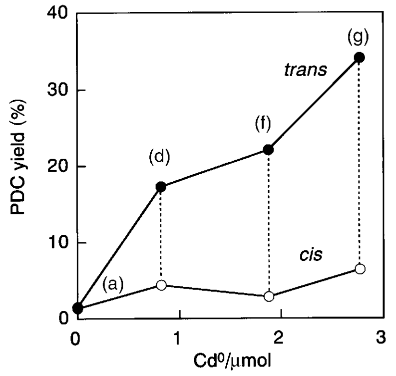


Fig. 3 *trans*- and *cis*-PDC yields as a function of the molar amount of Cd^0 deposited during the photocatalytic reaction over a period of 24 h. (a) and (d) (same as those in Fig. 1), (f) Mitsuwa CdS was annealed at 823 K under an Ar–air stream, and (g) (a) was annealed in air at 1023 K and left for 15 months in air.

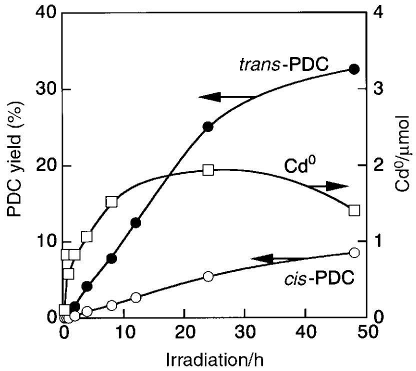


Fig. 4 Time course of photocatalytic Cd^0 and PDC formation by CdS (c) suspension.

tivity for the *trans*-isomers; annealing under partially deaerated conditions makes *in situ* Cd^0 photodeposition of the CdS powders possible.

Fig. 4 shows the time course of Cd^0 formation as well as of the PDC isomers.

The amount of Cd^0 was increased drastically within 2 h irradiation and became almost constant after 5 h. The photocatalytic PDC formation seemed to start at the time when Cd^0 had accumulated on the CdS surface. On the other hand, efficient DAP consumption was observed (data not shown) during the first stage and might correspond to the complementary oxidation reaction to produce Cd^0. In any case, the amount of Cd^0 was sufficiently small and the change in the CdS photocatalyst was negligible.

Physical properties of active CdS particles pre-treated under partially aerated conditions

X-Ray diffraction analyses of the CdS powders gave no evidence for the formation of a surface layer on the active photocatalyst, while annealing under aerated conditions led to the formation of a CdO layer[54] (data not shown). The results of X-ray photoelectron spectroscopic analyses suggested that surface oxide species appeared with annealing under partially aerated conditions, *i.e.*, on the active CdS. The annealing gave a shoulder in the lower binding energy region (*ca.* 529.5 eV in Fig. 5(A), peak iii in Fig. 5(B)) of an intense O1s peak assigned to surface hydroxy groups (531.2 eV, peak ii) as shown in Fig. 5(B). A comparison with the results of previous studies[55,56] suggests that O^{2-}(lattice), CO_3^{2-}, or O_2^{2-} species could not account for the shoulder (Fig. 5(B)). Since for a commercial cadmium(II) oxide (CdO, Nacarai) powder, a similar peak (iii in Fig. 5(C)) as well as peaks of hydroxy groups (531.2 eV, peak ii) and lattice oxide (O^{2-}; 528.2 eV, peak iv), were observed in Fig. 5(C), we concluded that the surface of the active CdS had been partially oxidized to have surface oxide species (*e.g.*, chemisorbed oxygen) but with no formation of a thick CdO layer.

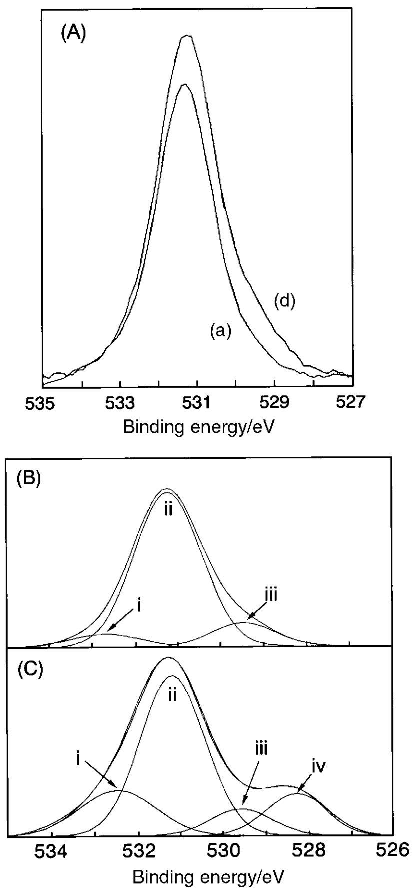


Fig. 5 (A) X-Ray photoelectron spectra in the region of the O 1s of CdS (a) and (d) (same as those in Fig. 1). Deconvoluted spectra of (B) partially oxidized CdS (b) (same as that in Fig. 1) and (C) commercial CdO. Proposed peak assignment is (i) unknown, (ii) surface hydroxy groups, (iii) surface oxygen species, and (iv) lattice oxide (O^{2-}).

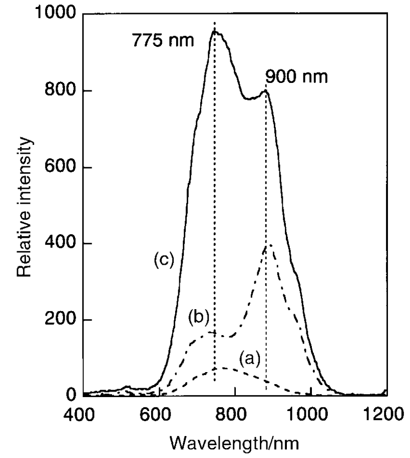


Fig. 6 Photoluminescence spectra of (a) and (b) (same as those in Fig. 1).

Further information on the annealing effect was obtained from photoluminescence measurements. The representative spectra are shown in Fig. 6. As reported previously,[19,57] excitation of bulk CdS powder at 300–400 nm at room temperature leads to broad-band photoemissions at around 775 and 900 nm, which are attributable to sulfur and cadmium vacancies, respectively. Annealing under partially aerated conditions markedly enhanced the 775 nm emission, rather than the 900 nm one, while the CdS annealed under Ar emitted predom-

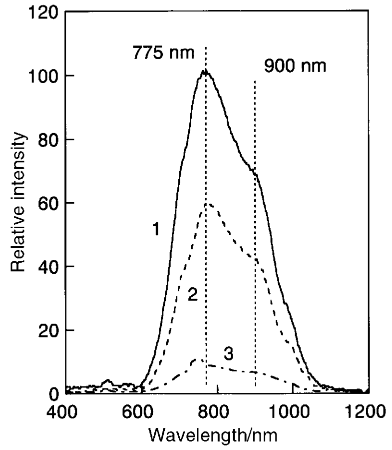


Fig. 7 Photoluminescence spectra of (1) CdS (d) (same as that in Fig. 1) in aqueous suspension, (2) in the presence of methylviologen, and (3) Pt loaded from a colloid solution.

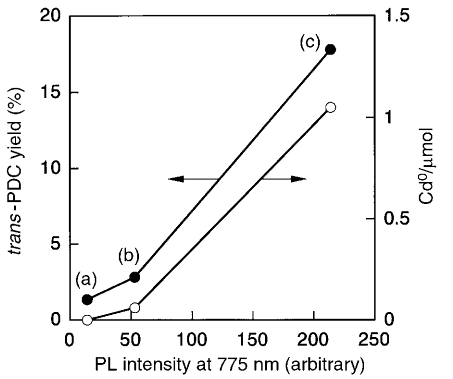


Fig. 8 *trans*-PDC and Cd^0 yields on CdS (a), (b), and (c) (same as those in Fig. 1) as a function of photoluminescence intensity at 775 nm.

inantly in a longer wavelength region, suggesting that the active CdS particles possess sulfur vacancies but not cadmium vacancies. Fig. 7 shows the effect of additives on the photoemission at 775 nm of active CdS suspension. The presence of MV^{2+} as a strong electron acceptor reduced the emission to an appreciable extent, and the loading of Pt from a colloid solution onto the CdS quenched the emission almost completely, while the addition of electron donors such as alcohols or amino acids (DAP) had a negligible influence on the PL spectra (data not shown). Similar behavior has also been reported for CdS particles deposited on porous Vycor glass.[58] These findings suggest that the emission arises from the trapping of photoexcited electrons by sulfur vacancies followed by their deactivation; electron acceptors and Pt deposits, which reduce the steady state concentration, decrease the emission intensity. Furthermore, the emission remaining even in the presence of a large number of electron acceptors suggests that the sulfur vacancies are located not only on the surface but also in the bulk of the CdS particles.

The photoemission intensity at 775 nm was measured in aqueous suspensions under conditions similar to those in the photocatalytic reaction, and the intensity is plotted in Fig. 8 as a common variable for *trans*-PDC and Cd^0 yields. These almost parallel relations suggest that sulfur vacancies, produced by the oxidation of sulfur on the surface (as well as the formation of surface-oxide species as indicated by XPS analyses), promote the *in situ* deposition of Cd^0, leading to the selective and efficient formation of *trans*-PDC. Henglein[59] proposed that Cd^0 photodeposition occurs through a mechanism in which a photoexcited electron (e^-) is trapped at the sulfur vacancy and then reduces an adjacent Cd^{2+} to form Cd^0.

The results of EPR measurement gave little information on the CdS structure related to the photocatalytic activity or on the product selectivity improved by the partial oxidation *via* annealing. Before the treatment, negligible peaks could be seen in the dark at 77 K under deaerated conditions. Photoirradiation caused the appearance of characteristic peaks ($g = 2.035$ and 2.005), which resemble those observed for a commercial CdS powder (Nacarai Tesque) and are attributable to the trapped holes.[60] After the heat treatment, a set of six intense EPR peaks of almost equal intensity separated from each other by a distance of 7.0 mT was observed in the dark and also under the photoirradiation conditions (data not shown). Each peak consisted of eleven fine peaks of intensity ratio of *ca.* 2:5:15:35:58:74:58:35:15:5:2 separated by a distance of 0.14 mT. They were assigned to species having a 5/2 nuclear spin, presumably $^{55}Mn(\textsc{ii})$ in the lattice; a similar EPR spectrum has been reported for zinc sulfide with Mn^{2+}.[61–63] These Mn^{2+} peaks were seen when the Furuuchi CdS was heat-treated, but the other CdS powders did not show any peaks after similar heat treatment. Therefore, Mn^{2+}, possibly included in the original CdS crystallites, might migrate to give the EPR peak during the heat treatment. On the basis of considerations that such behavior should reflect the property of the bulk CdS crystal and that the corresponding EPR signal may be very intense even at lower concentrations, we concluded that the EPR peaks do not account for the improvement in photocatalytic activity and product selectivity by annealing in the presence of a small amount of O_2.

Upon irradiation, the intensity of the Mn^{2+} peaks was slightly reduced and recovered after photoirradiation was ceased, though the reason for this photoinduced change is not clear at present. A small peak appeared at $g = ca.$ 2.00 upon irradiation. Due to its smaller intensity, it was impossible to determine whether the peak was the same as those observed for the powder before annealing. The light intensity during these EPR measurements should be much higher than that during the photocatalytic reaction; the CdS sample powder turned black during the EPR measurement. This might be metallic cadmium and might have an appreciable influence on the behavior of the photoexcited electrons and positive holes. At least for the photoexcited electrons, if they are trapped by this Cd^0, they might not be EPR-active as discussed before.[60]

The results described in this section are summarized and schematically illustrated in Scheme 3.

The surface of untreated CdS is covered with hydroxy groups. Annealing under partially aerated conditions produces sulfur vacancies by the oxidation of a sulfur anion to a sulfite or sulfate anion. The oxide moiety observed in the XP spectrum might be a surface O^{2-} located in the sulfur position on the surface. Photoirradiation of the activated surface in the presence of an electron donor (substrate DAP) causes the reduction of the cadmium cation by photoexcited electrons trapped in the sulfur vacancy to give Cd^0.

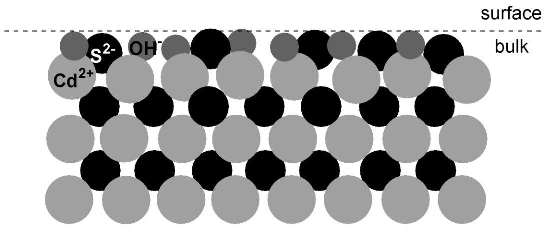
Cd^0 as a reduction site for a Schiff base intermediate

The Cd^0 produced as described above may act as a reduction site for e^- and enhance the photocatalytic activity of CdS by prohibiting geminate recombination of e^- and h^+. Being different from deposited metals such as platinum, the surface of Cd^0 might produce fewer hydrogen atoms that are added to the C=N bond in a cyclic Schiff base intermediate to give *cis*-PDC (Scheme 2) but reduce the bond, presumably, *via* consecutive electron transfer followed by proton addition. Although a similar product-selectivity switching by photodeposited Cd^0 has been reported for photocatalytic reduction of a nicotinamide over CdS colloids,[52] this is the first report, to the best of our knowledge, of stereocontrol of photocatalytic reaction products by surface modification.

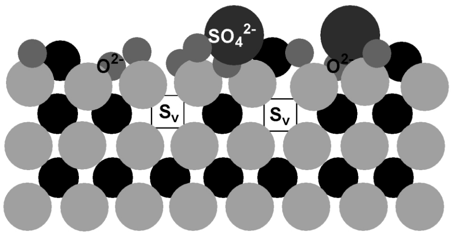
Table 2 Photocatalytic deaminocyclization of optically active DAPs[a]

Substrate	PDC yield (%)			*trans*:*cis*	Ee-(*S*) (%)	Ee-(*R*) (%)	Remaining DAP		
	(*R*,*S*)	(*S*,*S*)	(*R*,*R*)				(*R*,*S*)	(*S*,*S*)	(*R*,*R*)
(*S*,*S*)-DAP	5	22	2	4.8	93	—	9	44	<1
(*R*,*R*)-DAP	5	2	21	4.6	—	92	9	<1	54

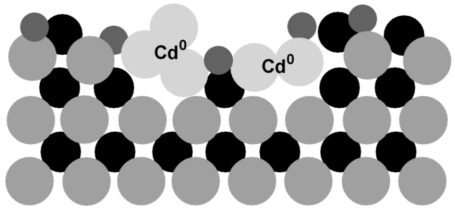
[a] Catalyst: CdS (Furuuchi) was annealed at 1023 K for 1 h under a stream of Ar (50 $cm^3 min^{-1}$) with air (1.7 $cm^3 min^{-1}$).



(A) Untreated CdS with surface hydroxy groups



(B) Annealed in the presence of air



(C) During photoirradiation in the presence of donors

Scheme 3 Schematic representation of the surfaces of CdS photocatalysts. (A) The untreated surface is covered with hydroxy groups as detected by XPS. (B) Annealing in the presence of air induces oxidation of sulfide ions to produce surface-adsorbed surface ions and sulfur vacancies in the lattice, as proved by XPS and photoluminescence measurements. (C) Photoirradiation in the presence of electron donors, such as amines, produces Cd^0 species through trapping of photoexcited electrons at the sulfur vacancies.

At present, we have no direct evidence that Cd^0 receives photoexcited electrons and transfers them to the reaction substrate. Based on the past results of electrochemical measurements of overpotentials for molecular hydrogen evolution, however, it is expected that metallic cadmium favors the mechanism of electron transfer followed by proton transfer rather than atomic hydrogen addition. In order to prove that this is also the case for Cd^0 produced photocatalytically, measurement of the separation factor was carried out. This technique, measuring an isotopic ratio in product molecular hydrogen liberated by the reduction of a mixture of light water and heavy water (D_2O), has been established to analyze the mechanism of hydrogen evolution at metal electrodes and has been applied to clarify the site for H_2 evolution in particulate semiconductor photocatalytic reaction systems.[64] In the photocatalytic reaction system involving platinized TiO_2 powders, it has been shown that H_2 is liberated by photoexcited electrons at the Pt deposits. We tried to measure the separation factor in the photocatalytic systems containing a deaerated aqueous suspension of PtO_2-loaded CdS (Furuuchi) and the heat-treated CdS in the presence of propan-2-ol (500 μmol) under deaerated conditions, in which H_2 evolution is expected to proceed at Pt (or PtO_2) and Cd^0 sites, respectively. However, in both systems, the amount of H_2 liberated was not sufficient to enable precise determination of the separation factor.

Preparation of optically active *trans*-PDC from (*S*,*S*)- or (*R*,*R*)-DAP

On the basis of the results mentioned above, we can expect that an active CdS photocatalyst, giving a large *trans*:*cis* ratio, may induce the formation of optically active (*S*,*S*)- or (*R*,*R*)-PDC from an optically active substrate, (*S*,*S*)- or (*R*,*R*)-DAP. Since the optical resolution of DAP is feasibly achieved through stereoselective enzymatic hydrolysis of an amide derivative, the CdS-induced photocatalytic N-cyclization of DAP should be a potent synthetic procedure for enantiomers of *trans*-PDC. Table 2 shows the results. As expected, (*S*,*S*)- and (*R*,*R*)-DAPs were converted mainly into (*S*,*S*)- or (*R*,*R*)-PDC, *i.e.*, >92% optical purity was obtained for both enantiomers. That the configuration of PDC is almost retained shows consistency with the expected reaction mechanism and, furthermore, no (or negligible) racemization of enantiomeric cyclic Schiff base intermediates *via* imine–enamine tautomerism.

According to the reaction mechanism (Scheme 1), no formation of racemic PDC could be expected; if the photocatalytic reaction only consists of the reaction shown in Scheme 1, the liberated *trans*-PDC should be of 100% optical purity. However, in practice, the purity was at most 92%, suggesting the existence of a reaction pathway(s) other than that shown in Scheme 1. One of the most plausible processes producing a racemic product is the photocatalytic racemization of DAP. As shown in Table 2, the remaining DAP was partly racemized. Since photoirradiation in the absence of CdS or stirring of the suspension in the dark led to no racemization of DAP, the formation of racemic DAP was attributable to the photocatalytic process, as observed in Lys–CdS systems;[65] certain kinds of CdS powders induced photocatalytic racemization of Lys. It has been proved that in the Lys system, Pt (or PtO_2) loading is effective in preventing unexpected racemization, but it cannot be applied to the present system because of contradistinctive stereoselectivity of platinized catalysts. The photocatalytic racemization of Lys, along with PCA production, from aqueous Lys solution and the effect of CdS pre-treatment were examined. Fig. 9 shows the effect of Cd^0 on the ratio of the rate of racemization of Lys and of N-cyclization to PCA. By using a CdS photocatalyst that gives a larger amount of Cd^0, a higher yield of PCA and less racemization product, the best CdS powder showed a racemization : PCA ratio of *ca.* 0.2, while the ratio was more than unity in the absence of photogenerated Cd^0. Thus, similar to the effect of platinization,[65] Cd^0 was also able to prohibit the racemization, resulting in a higher PCA yield. However, complete inhibition could not be achieved even with a larger amount of Cd^0. As shown in Table 3, the increase in Cd^0 could not improve, but rather reduced, the optical purity of *trans*-PDC from the optically pure DAP isomer. This

Table 3 Photocatalytic deaminocyclization of (*R*,*R*)-DAP by CdS suspensions

	PDC yield (%)					Racemization	
Cd^0/μmol	(*R*,*S*)	(*S*,*S*)	(*R*,*R*)	*trans*:*cis*	Ee-(*R*) (%)	PDC	(*R*,*R*)-DAP Conv. (%)
0.88	5	21	2	4.6	92	0.36	46
2.77	9	38	5	4.8	88	0.05	89

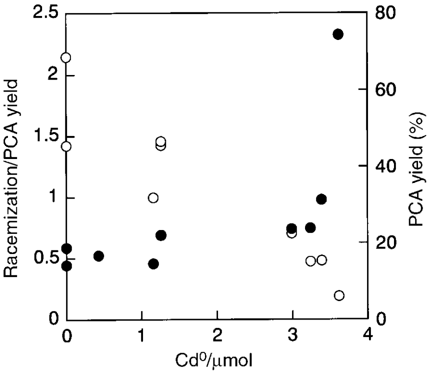


Fig. 9 Ratio of rate of racemization and PCA formation from Lys (open circles) and PCA yield (closed circles) as a function of Cd^0 yield. An aqueous suspension of CdS with Lys (100 μmol) was irradiated under deaerated conditions for 24 h.

is partly attributed to the increased rate of PDC formation, leading to consumption of the racemized DAP (conversion of DAP > 88%).

Conclusion

It has been proved that one-step stereoselective (diastereoselective) preparation of 2,6-disubstituted piperidines can be achieved at room temperature by activated CdS particles in aqueous suspensions. The stereoselectivity giving mainly *trans* isomers was complementary to that of a platinized catalyst that produces the *cis* isomer. This arose from the *in situ* formation of a Cd^0 species on the surface *via* sulfur vacancies formed by annealing under partially aerated conditions and trapping of photoexcited electrons to yield Cd^0. The deposited Cd^0 also enhances the efficiency of utilization of photogenerated electron-positive hole pairs. The previously reported improvement in the rate and selectivity of the CdS-induced photocatalytic reactions by heat treatment must be caused by a similar mechanism. Thus, the Cd^0 species play an important role in the CdS-photocatalyzed reactions including the reduction step by photoexcited electrons.

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