Improvement of Photocatalytic Activity and Product Selectivity by Cadmium Metal Deposited *in situ* on Suspended Cadmium(II) Sulfide Particles

Bunsho Ohtani, Satoshi Kusakabe, Sei-ichi Nishimoto, Michio Matsumura,[†] and Yoshihiro Nakato[†]
Division of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-01
[†]*Research Center for Photoenergetics of Organic Materials and Faculty of Engineering Science, Osaka University, Toyonaka 560*

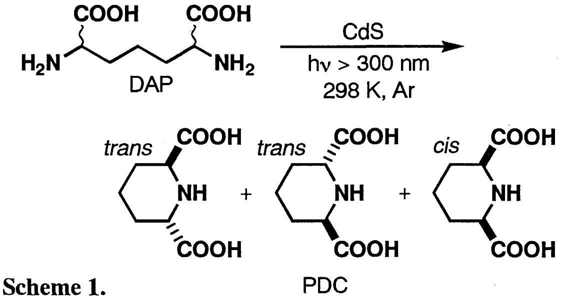
(Received June 12, 1995)

Effect of annealing of commercial crystalline CdS powders on their photocatalytic activity and product selectivity was investigated for stereoselective diamino-N-cyclization of 2,6-diaminopimelic acid operated in a deaerated aqueous solution. Surface analyses revealed the formation of sulfur vacancy, which promotes the photoinduced cadmium metal (Cd^0) deposition. The Cd^0, detected by reduction of methylviologen, may act as a reduction site for photoexcited electrons.

Cadmium(II) sulfide (CdS) is one of the most efficient photocatalysts and has been used in a large number studies. Although several papers have reported that pre-heat-treatment could drastically enhance its photocatalytic activity, the reason is still ambiguous.[1] A recent report by Lee and co-workers[2,3] also claimed that annealing of commercial CdS leads to the efficient photocatalytic production of alanine from aqueous suspension containing lactic acid and ammonia (NH_3) and the annealing accounts for formation of active surface species. A part of the present authors has found that the CdS photocatalysis can be applied to N-cyclization of α,ω-diaminoalkanes, *e.g.*, production of piperidine-2,6-dicarboxylic acid (PDC) from 2,6-diaminopimelic acid (DAP) with release of NH_3.[4] The annealing effect was also seen in this case; photocatalytic activity of a commercial CdS powder for DAP consumption was improved along with the increase in stereoselectivity of the product, *trans*-PDC. This paper describes *in situ* deposition of cadmium metal (Cd^0), acting as a reduction site for the stereoselective reduction of a reaction intermediate on the annealed CdS particles.

CdS powders were purchased from Furuuchi (99.999%) and Mitsuwa (99.999%) and annealed at 823-1023 K for 1 h under deaerated (Ar) or partly aerated conditions. A 50 mg portion of the photocatalyst was suspended in an aqueous DAP (100 μmol, 2:1:1 mixture of meso, DD and LL isomers) solution (5.2 cm^3) containing NaOH (200 μmol). The suspension was irradiated for 24 h with a 400-W mercury arc (Eikosha) under Ar at 298 K with magnetic stirring (1000 rpm). Procedures of work-up and product analyses were reported elsewhere.[4]

For both commercial CdS powders, the annealing effect, especially under partly aerated conditions, can be seen (Table 1); conversion of DAP, as well as the *trans*-PDC yield, was markedly increased (ca. 3 times for both CdS's), while the increase in the yield of *cis*-PDC was not so evident. This resulted in the larger *trans*/*cis* ratio. The highest ratio of 7.8, corresponding to diastereomeric excess of 77%, was obtained by the Mitsuwa CdS annealed under partly aerated conditions. These results are consistent with the previous report.[4]



Scheme 1.

Table 1. Photocatalytic activity of commercial crystalline CdS powders for N-cyclization of DAP

CdS[a]	treat-ment[b]	PDC yield/% *cis*	PDC yield/% *trans*	*trans*/*cis*	DAP conv./%
F	none	1.4	2.2	1.5	11.0
F	A	1.2	2.8	2.3	17.1
F	B	4.9	20.2	4.2	34.9
M	none	2.6	7.2	2.8	13.9
M	C	2.8	22.1	7.8	37.7

[a]F: Furuuchi and M: Mitsuwa. [b]A: annealed at 1023 K for 1 h under Ar (50 cm^3 min^{-1}), B: same as A, but Ar-air (1.7 cm^3 min^{-1}) mixture was used, and C: same as B, but at 823 K.

Careful inspection of the irradiated reaction mixtures revealed that the suspension of active CdS had turned a little brownish and 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 intense blue color owing to its cation radical ($MV^{+\bullet}$). Such behavior has been reported first by Gutiérrez and Henglein[5] for the suspension of a commercial (Fulka) CdS powder, and later by Shiragami and co-workers[6] for CdS colloid; photoinduced formation of Cd^0 and its oxidative dissolution with air or MV^{2+} were suggested in both papers. Being consistent with the latter paper, the untreated CdS powders gave negligible $MV^{+\bullet}$ even after the 24 h irradiation.

The molar amount of Cd^0 deposited on CdS was evaluated from that of $MV^{+\bullet}$(its extinction coefficient at 602 nm has been reported to be 13700 dm^3 mol^{-1} cm^{-1})[7] on the assumption of stoichiometry, $Cd^0 + 2MV^{2+} = Cd^{2+} + 2MV^{+\bullet}$, and plotted in Fig. 1. As clearly seen, the yield of *trans*-PDC increased with increasing Cd^0, while *cis*-PDC seemed to be independent of Cd^0, leading to higher *trans*/*cis* ratio. Thus, the deposited Cd^0 improves the photocatalytic activity of CdS for N-cyclization of DAP into PDC and stereoselectivity for the *trans*-isomers, and the annealing under partly deaerated conditions makes the CdS powders feasible for *in situ* Cd^0 photodeposition.

X-ray diffraction analyses of the CdS powders gave no evidence for the formation of surface layer, while X-ray photoelectron spectroscopy suggested that surface oxide species appeared with the annealing under partly aerated conditions, *i.e.*, on the active CdS. The annealing gave a shoulder in the lower binding energy region (ca. 529.5 eV) of an intense O 1*s* peak assigned to surface hydroxyls (531.2 eV). Comparison with the

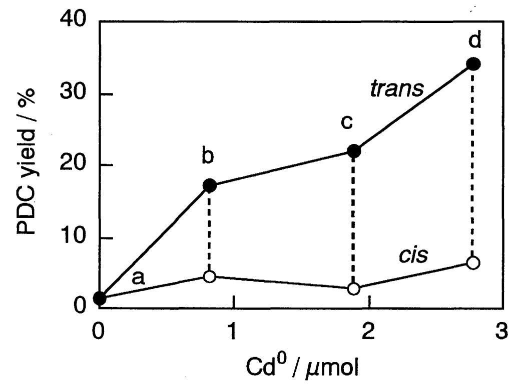


Figure 1. Yield of *trans*- and *cis*-PDC as a function of amount of Cd^0 deposited during photoirradiation. Catalyst a: CdS(F) as received, b: CdS(F) with treatment B (see Table), c: CdS(M)-C, and d: CdS(F) was annealed in air at 1023 K and left for 15 months in air.

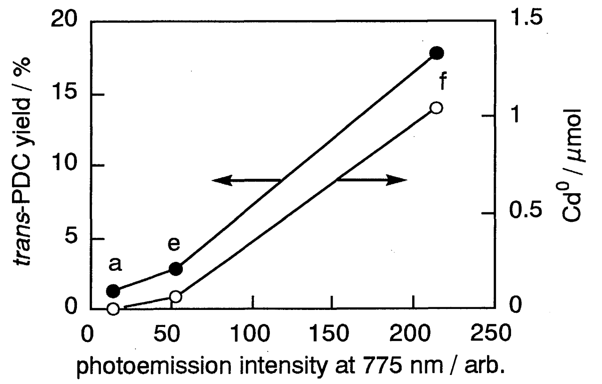
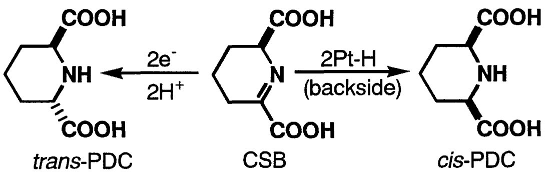


Figure 2. Yields of *trans*-PDC and Cd^0 as a function of photoemission intensity at 775 nm. Catalyst a was same as in Fig. 1, e: CdS(F)-A, and f: CdS(F) was annealed at 1023 K under Ar (50 cm^3 min^{-1}) with continual air pulses (20 cm^3 every 10 min).



Scheme 2. Reduction of the intermediate, cyclic Schiff base (CSB) by consecutive electron transfer and atomic hydrogen adsorbed on platinum to yield, respectively, *trans* and *cis*-PDC. One enantiomeric isomer is shown for convenience.

previous reports[8,9] leads to the idea that O^{2-}(lattice), CO_3^{2-}, or O_2^{2-} species could not account for the shoulder. Since for a commercial cadmium(II) oxide (CdO, Nakarai) powder, the similar peak, as well as peaks of hydroxyls and lattice oxide (O^{2-}), was observed, we concluded that the surface of the active CdS had been partially oxidized to have surface oxide species (e.g., chemisorbed oxygen), but not forming a thick CdO layer.

Further information on the annealing effect was obtained from photoluminescence measurements. As reported previously,[10] excitation of bulk CdS powder at 300-400 nm leads to broad band photoemissions at around 775 and 900 nm which are attributable to sulfur and cadmium vacancies, respectively. The annealing under partly aerated conditions markedly enhanced the 775 nm emission, rather than the 900 nm one, while the CdS annealed under Ar emitted predominantly in the longer wavelength region. The photoemission intensity at 775 nm was measured in the aqueous suspensions under the conditions similar to the photocatalytic reaction, and plotted in Fig. 2 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), promotes the *in situ* deposition of Cd^0, leading to the selective and efficient formation of *trans*-PDC. Henglein[11] proposed the Cd^0 photodeposition through a mechanism that a photoexcited electron (e^-) is trapped at the sulfur vacancy and then reduces an adjacent Cd^{2+} to form Cd^0. The thus produced Cd^0 may act as a reduction site for e^- and enhance the photocatalytic activity of CdS by prohibiting geminate recombination of e^- and a positive hole. Being different from deposited metals such as platinum, the surface of Cd^0 might not produce hydrogen atoms which are added to C=N bond in a cyclic Schiff base (Scheme 2) intermediate to give *cis*-PDC, but reduce the bond, presumably, via consecutive electron transfer along with proton addition. Although a similar product-selectivity switching by Cd^0 has been reported for photocatalytic reduction of a nicotinamide over CdS colloids,[6] this is the first report, to the best of our knowledge, of stereocontrol of photocatalytic reaction products by the surface modification.

Further detailed investigation on the properties of Cd^0 and application of this activated CdS to the other photocatalytic reactions are now in progress.

We thank Messrs. Kunihiro Iwai (Kyoto University) and Yoshihiro Magari (Osaka University) for their help in XPS and photoluminescence measurements, respectively. This work was partly supported by the Grant-in-Aid for Scientific Research on Priority Area of New Development of Organic Electrochemistry (No. 06226236) from Ministry of Education, Science and Culture, Japan.

Reference and Notes

1 For example, M. Matsumura, S. Furukawa, Y. Saho, and H. Tsubomura, *J. Phys. Chem.*, **89**, 1327 (1985).
2 B. Y. Lee, B. G. Kim, C. R. Cho, and T. Sakada, *Bull. Korean Chem. Soc.*, **14**, 700 (1993).
3 B. Y. Lee, S. S. Lee, C. R. Cho, C. K. Lee, and B. G. Kim, *Bull. Korean Chem. Soc.*, **15**, 917 (1994).
4 B. Ohtani, S. Kusakabe, K. Okada, S. Tsuru, K. Izawa, Y. Amino, and S.-i. Nishimoto, *Tetrahedron Lett.*, **36**, 3189 (1995).
5 M. Gutiérrez and A. Henglein, *Ber. Bunsenges. Phys. Chem.*, **87**, 474 (1983).
6 T. Shiragami, H. Ankyu, S. Fukami, C. Pac, S. Yanagida, H. Mori, and H. Fujita, *J. Chem. Soc., Faraday Trans.*, **88**, 1055 (1992).
7 T. Watanabe and K. Honda, *J. Phys. Chem.*, **86**, 2617 (1982).
8 J. S. Hammond, S. W. Gaarenstroom, and N. Winograd, *Anal. Chem.*, **47**, 2193 (1975)
9 Z. Jin, Q. Li, X. Zheng, C. Xi, C. Wang, H. Zhang, L. Feng, H. Wang, Z. Chen, and Z. Jiang, *J. Photochem. Photobiol., A: Chem.*, **71**, 85 (1993).
10 T. Uchihara, M. Matsumura, and H. Tsubomura, *J. Phys. Chem.*, **93**, 3207 (1989).
11 A. Henglein, *Top. Curr. Chem.*, **143**, 113 (1988).