An *in situ* FT-IR Study on Photocatalytic Reaction at Semiconductor-Aqueous Solution Interface — Mechanism of Photocatalytic *N*-Cyclization of (S)-Lysine

Bunsho Ohtani,*# Takayuki Yako, Yoriaki Samukawa, Sei-ichi Nishimoto, and Kiyoshi Kanamura
Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-01

(Received September 18, 1996)

Photoinduced reaction occurring at an aqueous solution-semiconductor interface was analyzed *in situ* by reflection FT-IR spectroscopy. The photoinduced reflection spectral change, ΔR (= $(R-R_0)/R_0$), was recorded by using an IR cell consisting of a semiconductor (TiO_2 or CdS) thin film electrode, a thin layer of aqueous (S)-lysine solution, and a calcium fluoride window. Structure of adsorbed substrate and mechanism of photoinduced reaction were discussed.

Although many reports claimed that various reactions proceed on photoirradiated particulate semiconductors, such as titanium(IV) oxide (TiO_2) or cadmium(II) sulfide (CdS), suspended in aqueous solutions,[1,2] few *in situ* spectroscopic investigations on these photocatalytic reactions have been performed. This is due to some problems, e.g., probe light is scattered at the surface of suspended powders, and water as a dispersion medium strongly absorbs the light of infrared region. One of the methods overcoming such problems is reflection spectroscopy at a flat thin-film semiconductor electrode in contact with a thin layer of an aqueous solution[3-6] as a model system of particulate photocatalytic reactions.

Among the photocatalytic reactions, several systems have shown dependence of reaction pathway on semiconductors used as photocatalyst, e.g., acetaldehyde and pyruvic acid were produced from lactic acid by TiO_2 and CdS, respectively.[7] We have also found the difference in optical purity of pipecolinic acid (PCA) from (S)-lysine (Lys) by these semiconductors.[8] The reason for such differences, especially in the latter case, is ambiguous at present. The aim of this paper is to clarify the cause of dependence by reflection IR spectroscopy at the thin semiconductor film-aqueous solution interface.

A Shimadzu FTIR-8200PC spectrophotometer equipped with a reflection measurement apparatus (RAS-8000; incident angle of the IR beam was 70 °) was used. A thin film electrode of TiO_2 (anatase) and CdS (hexagonal) was prepared on a mirror-finished (0.1 μm silica) stainless steel rod (2 cm in diameter) by pyrosol method with titanium(IV) tetra-2-propoxide at 703-743 K and electrodeposition following the reported procedure,[9] respectively. The IR cell configuration has been reported recently[10] and modified for the photoirradiation. The semiconductor electrode was pressed onto a calcium fluoride window interposing an aqueous Lys solution (0.1 mol dm^{-3}, pH 10.1) with sodium sulfate (0.1 mol dm^{-3}). Thickness of the aqueous solution was not measured but was thin enough to record in the wavenumber region of 1100-4000 cm^{-1} without interference by strong absorption of water at around 1600 and 3000 cm^{-1}. An ultraviolet light beam (300-400 nm, ca. 28 μW cm^{-2}) was introduced through the window from a 300-W xenon arc (Eagle LX-300UV) equipped with glass filters, a cold mirror, and an optical fiber.

Figure 1 shows representative photoinduced reflection spectral change, ΔR (= $(R-R_0)/R_0$), where R_0 and R are reflection intensities before and after commencement of photoirradiation. The R_0 spectrum was recorded after > 1 h duration in the dark under Ar atmosphere. The measurement was carried out under open circuit conditions and the irradiation

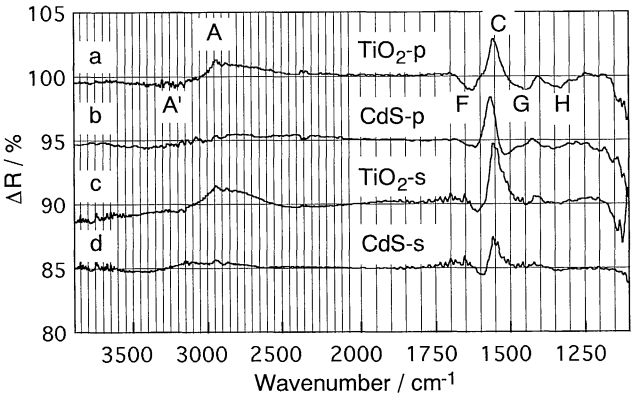


Figure 1. Representative photoinduced reflection spectral change of p and s-polarized IR beam on TiO_2 and CdS thin films in contact with an aqueous Lys solution. Irradiation: 1 h. Spectra b-d were translated along the vertical axis to be separated by 5 %.

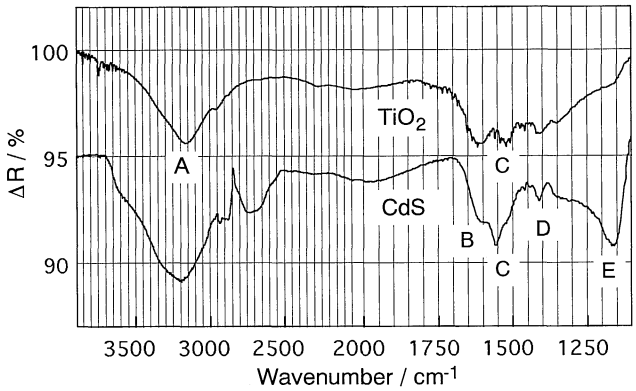
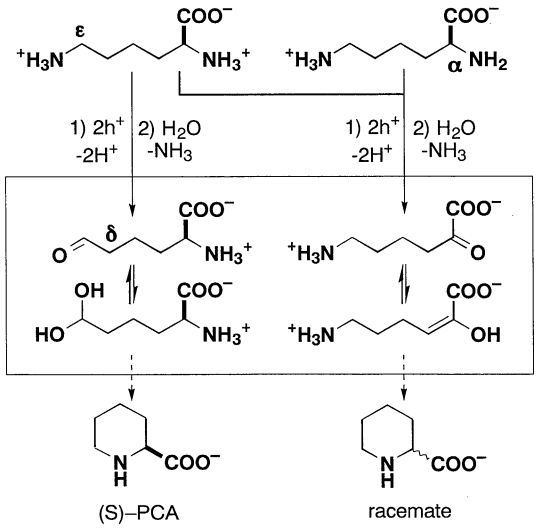


Figure 2. Subtractively normalized spectra of Lys in aqueous solution in contact with TiO_2 and CdS thin films (pH of the bulk solution was adjusted to 10.1).

induced negative shift of electrode potential (ca. 150 and 300 mV for TiO_2 and CdS, respectively). Upward and downward peaks in Figure 1 refer to consumption of Lys and formation of product(s). The intensity of peaks in both sides increased monotonously with irradiation. First, to assign the consumption peaks, reflection spectral change by addition of Lys to an aqueous layer was obtained in the dark (Figure 2) from spectra (R_0 and R) recorded without and with Lys (R was recorded 12 h after the addition of Lys to allow the thorough diffusion into the thin aqueous layer). For these ΔR spectra, a little difference was seen by using s and p-polarized light. As reported recently,[5] reflection IR spectrum at semiconductor-solution interface is less selective for surface-adsorbed species toward bulk ones than at metal-solution interface. Moreover, the thin semiconductor films used in this study consist of small particles,



Scheme. Mechanism of photocatalytic reaction of Lys in aqueous solution to yield (S)-excess and racemic PCA by TiO_2 and CdS.

i.e., porous structure, and therefore comparison of effect of the polarization is difficult. However, the spectra of Lys in Figure 2 depends strongly on the semiconductor film; some differences were found, indicating that the reflection spectral change arises mainly from the surface-bound species.

It was rather difficult to discuss the difference in broad peak of $-NH_3^+$ at 2500-3500 cm^{-1} (**A**). A slight shift toward lower wavenumber and broadening of peak at 1550 cm^{-1} (**C**) were observed in TiO_2 spectrum compared with that for CdS. Since similar shift was observed for the spectra of alanine (having only α-amino group) on both films; reducing pH of the bulk solution afforded the shift toward lower wavenumber (data not shown), the above-mentioned facts suggest that both amino groups in Lys are protonated on TiO_2 while one (ε-) amino group is protonated (as in the aqueous solution of same pH) on CdS (Scheme). Appearance of broad peak at ca. 1150 cm^{-1} (**E**), assignable to $-NH_2$, only for CdS,[12] was consistent with this interpretation. The reason for such difference in the structure of adsorbed Lys has not yet been confirmed, but acidic hydroxyls on TiO_2, which has been reported,[11] may induce the adsorption of Lys in its protonated form. On the other hand, two characteristic peaks at 1400 (**D**) and 1600 cm^{-1} (**B**) were observed on both films, showing that carboxyl moiety in Lys was deprotonated as seen generally in non acidic aqueous solutions.

On the basis of these results, the photoinduced spectral change (Figure 1) could be interpreted as follows. The upward consumption peaks **A** and **C** are assigned to disappearance of $-NH_3^+$ and amino group ($-NH_3^+$ and/or $-NH_2$), respectively. The latter peak coincided with that in Figure 2, reflecting the difference between CdS and TiO_2. The former peak, mainly attributable to $-NH_3^+$ (intensity of $-NH_2$ peak in this region has been reported to be rather smaller[13]), was deformed compared with that in Figure 2; the reason for this shift might be the downward peak at higher wavenumber region (**A'**) due to NH_4^+ formation; a downward peak at 1450-1500 cm^{-1} (**G**) was also assigned to NH_4^+. It is clear by comparison of spectra for TiO_2 and CdS, only TiO_2 made the photoinduced consumption of $-NH_3^+$, while CdS also induced the decrease in N-H (**C**). These facts indicate that only the deprotonated α-amino group was oxidized[14] on the CdS surface, while both α and ε-NH_3^+ might be consumed on TiO_2.

The reaction mechanism being consistent with the above-mentioned results is shown in Scheme. An initial product via oxidation at α-position is expected to be a keto acid in equilibrium with an enol acid. Downward peaks are assignable as, 1640 cm^{-1} (**F**): C=O and/or C=C, 1615 cm^{-1} (**F**): C=C, and 1350 cm^{-1} (**H**): C=C-O in these proposed intermediates.[15] Reduced intensities of these product peaks by s-polarized IR beam suggest the oriented adsorption on the surface. On the other hand, we have no clear evidence of oxidation of ε-amino group of Lys to give δ-aldehyde.[16]

As reported previously,[8] the keto acid or δ-aldehyde intermediate is proposed to undergo intramolecular cyclization into Schiff bases to be reduced into final product, PCA, in particulate photocatalytic reaction systems. The results shown above strongly support the fact that CdS tends to produce racemic PCA via keto-acid and TiO_2 to give (S)-excess PCA via δ-aldehyde, though the present model system can not reproduce and detect the reduction step by photoexcited electrons.

Thus, the reflection IR spectroscopy on semiconductor-solution interface could be successfully applied to mechanistic investigation of photocatalytic reaction occurring in the aqueous suspension systems. Extended study, e.g., on the mechanism of photocatalytic decarboxylation, is now under way.

We are indebted to Professor Akira Fujishima, Professor Kazuhito Hashimoto, and Dr. Shigemichi Fukayama (Kanagawa Academy of Science and Technology) for the preparation of TiO_2 thin films.

References and Notes

Present Address: Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060.

1 M. A. Fox and M. T. Dulay, *Chem. Rev.*, **93**, 341 (1993).

2 B. Ohtani, in "Trends in Photochemistry and Photobiology," ed by Council of Scientific Information, Research Trends, Trivandrum (India), (1994) p 531.

3 L. M. Peter, D. J. Blackwood, and S. Pons, *Phys. Rev. Lett.*, **62**, 308 (1989).

4 L. M. Peter, D. J. Blackwood, and S. Pons, *J. Electroanal. Chem.*, **294**, 111 (1990).

5 K. Uosaki, Y. Shigematsu, H. Kita, and K. Kunimatsu, *J. Phys. Chem.*, **94**, 4623 (1990).

6 L. Kavan, K. Kratochvilova, and M. Grätzel, *J. Electroanal. Chem.*, **394**, 93 (1995).

7 H. Harada, T. Sakata, and T. Ueda, *J. Am. Chem. Soc.*, **107**, 1773 (1985).

8 B. Ohtani, S. Tsuru, S.-i. Nishimoto, T. Kagiya, and K. Izawa, *J. Org. Chem.*, **55**, 5551 (1990).

9 H. Minoura, T. Kajita, K. Yamaguchi, Y. Takahashi, and D. P. Amalnerkar, *Chem. Lett.*, **1994**, 339.

10 K. Kanamura, S. Toriyama, S. Shiraishi, and Z.-i. Takehara, *J. Electrochem. Soc.*, **142**, 1383 (1995).

11 H. P. Boehm, *Disc. Faraday Soc.*, **52**, 264 (1971).

12 The control experiment with alanine in its aqueous solution revealed that deprotonation of the α-NH_3^+ with alkali caused the appearance of an intense but broad peak at 1150 cm^{-1}, indicating that peak **E** is assignable to -NH_2.

13 R. M. Silverstein, G. C. Bassler, and T. C. Morrill, Spectrometric Identification of Organic Compounds, John Wiley & Sons, New York (1991).

14 Decrease in the characteristic $-NH_2$ peak (**E**) could not be observed for both films, maybe due to appearance of certain product peak. However, relatively small decrease at 1150 cm^{-1} in ΔR spectra of CdS possibly accounts for the selective oxidation of α–NH_2 as shown in Fig. 1.

15 Presumably enol-acid form is predominant, judging from the IR observation of similar keto acid, pyruvic acid.

16 It was clear that no free aldehyde was detected because of the absence of characteristic peak at around 1720 cm^{-1}. At present, we have no authentic sample and IR spectrum of such aldehyde in aqueous solution. The aldehyde might undergo hydration. A relating compound, chloral hydrate (2,2,2-trichloro-1,1-ethanediol)[13] gives peaks at 1300 and 1400 cm^{-1}, maybe corresponding to **H** and **G**.