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## Communications

### Highly Selective Photocatalytic Alanine Synthesis by Surface Oxidated CdS Particles

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Photocatalytic reactions of particulate semiconductors have been applied to various organic reactions<sup>1</sup> such as photo-Kolbe reaction<sup>2</sup>, amino acid production<sup>3-5</sup> and carbon-carbon bond formation<sup>6,7</sup>. In photocatalytic organic reaction, the control of reaction paths is a subject of considerable interest to achieve a selective reaction. However, the controlling factors of the reaction selectivity are not well understood and the studies in such a direction are few. Sakata *et al.*<sup>5</sup> have reported the effects of semiconductor on the selectivity of photocatalytic reaction of  $\alpha$ -hydroxycarboxylic acid. This selectivity is related with remarkable semiconductor dependence observed in the photocatalytic amino acid synthesis from  $\alpha$ -hydroxycarboxylic acid and ammonia.

Recently, Yanagida *et al.*<sup>8</sup> reported that the two-electron reduction of aromatic ketones or related compounds takes places efficiently on nanoscale CdS particles prepared under cooled condition, and that photogenerated Cd<sup>0</sup> on the lattice acts as the catalytic site for this two-electron reduction.

In our previous work<sup>9</sup>, we have reported that the effects of heat treatment and platinum loading on CdS particles in the photocatalytic alanine production. From these experimental results, it was found that the rate of alanine production depended strongly on the temperature in heat treatment of CdS powder from lactic acid-ammonia-water system. In particular, the rate of alanine production, which was observed using Pt/CdS(A)-(CdS from Mitsuwa), was increased about six times than that of using Pt/CdS(B)-(CdS from Furruchi) under the same heat treatment condition in 760 mmHg of He atmosphere at 500 °C. From the photoluminescence data,

we concluded that this increase of the photocatalytic activity for alanine production observed with annealed CdS(A) than that of CdS(B) powder might be attributed to the existence of sub-band gap states due to impurities, especially the state located on the surface or near the surface defects of CdS(A).

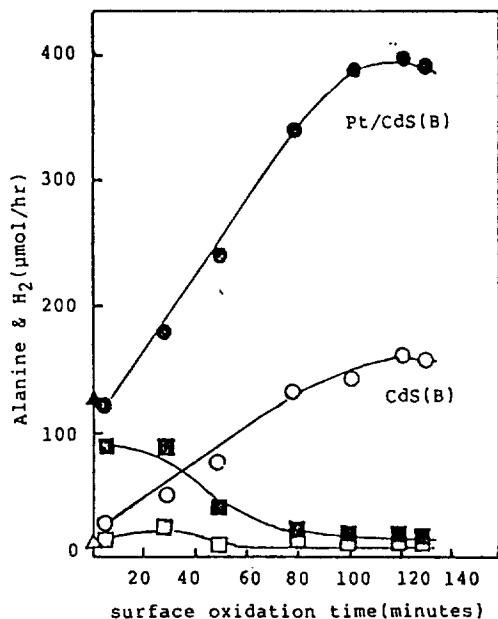
In this communication, we would like to report that selectivity and photocatalytic activity of alanine depend strongly on the surface oxidation of the CdS(B), which was treated by heat in 760 mmHg of the air, not He atmosphere at 500 °C. We also report herein the effect of surface oxidation treatment time and Pt deposition on oxidated CdS(B) as photocatalysts for alanine synthesis, respectively. CdS(B) was purchased from Furruchi Chem. Co (purity: 99.999%, 300 M, deep yellow color). Other chemical used in this experimental, CdSO<sub>4</sub>·8/3H<sub>2</sub>O (Aldrich Chemical Co.), Cd(OH)<sub>2</sub> (Wako Chemical Industries LTD.) and CdO (Aldrich Chemical Co.), were all of reagent grade. Plantinized CdS photocatalysts were prepared by shaking CdS(B) powder with Pt black (3 w/w%) in a glass bottle for 1 hour. CdS(B) as photocatalyst was oxidized in 760 mmHg of air in heating vessel for range of 5-130 minute at 500 °C before use.

The photocatalysts (about 200 mg) were suspended in deaerated ammonia-water solution of lactic acid (Wako Chem. Co.) (lactic acid 10 ml, distilled water 40 ml, and ammonia water (Wako Chem. Co.) 10 ml) in a 200 ml Pyrex glass bulb. The reaction bottle was illuminated from the side direction by a 450 W Xe lamp (Ushio-Xenon Arc Co.). After the irradiation for one min, hydrogen was analyzed by gas-Chromatography (Shimadzu GC-6AM: molecular sieve 13X was packed 2 m stainless steel column).

Alanine was analyzed by an amino acid analyser (Hitachi 835). X-ray diffraction (XRD) data were obtained by a Rigaku Gab-A2 type diffractometer using Cu-K $\alpha$  radiation.

In the presence of lactic acid, distilled water and ammonia water, alanine and hydrogen gas is selectively produced by using CdS(B) or Pt/CdS(B). The photocatalytic reactions are considered as same as previously.<sup>9</sup>

It was found that the surface oxidation treatment of CdS (B) enhanced dramatically the reaction of alanine synthesis. Figure 1 shows the dependence of the production rates of alanine and hydrogen on the oxidation treatment time of bare CdS(B) at 500 °C. Surprisingly, the rate of alanine pro-



**Figure 1.** Effect of surface oxidation time on the rate of hydrogen and alanine production on bare CdS(B) and Pt/CdS(B) as photocatalysts in Lactic Acid-Ammonia-Water solution. (●) alanine production on Pt/CdS(B); (○) alanine production on bare CdS(B); (■) hydrogen production on Pt/CdS(B); (□) hydrogen production on bare CdS(B); (▲) alanine production on non-oxidated Pt/CdS(B); (△) alanine production on non-oxidated CdS(B).

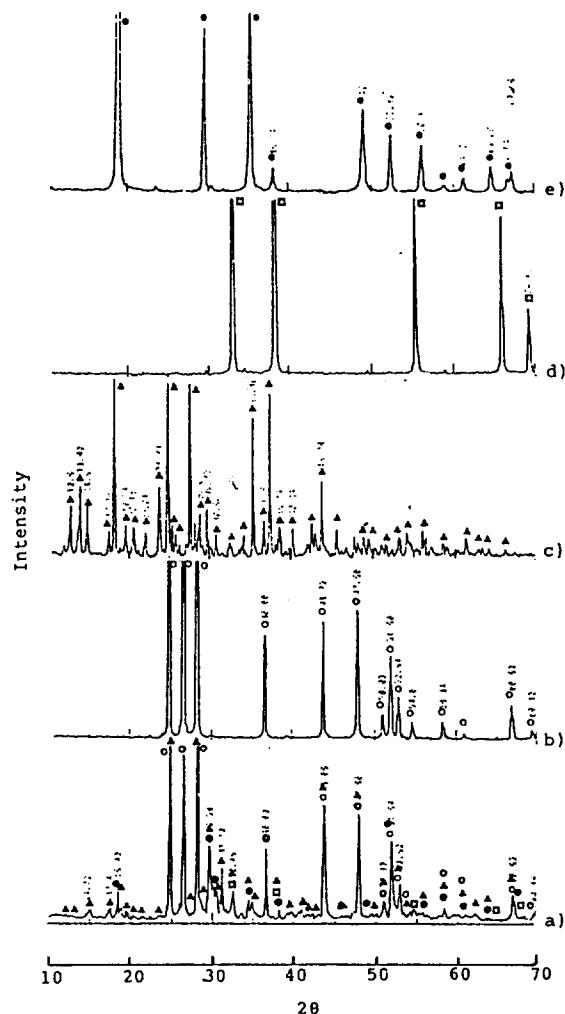
duction linearly increased with increasing oxidation treatment time of CdS(B), while hydrogen production was completely suppressed. In the same figure, the effect of Pt loading is also shown. In this case, Pt black was loaded on CdS(B) after oxidation treatment at 500 °C for 5-130 minutes, respectively.

As expected, Pt loading significantly influenced the rate of alanine production with increasing oxidation treatment time, but hydrogen production was also suppressed. As shown in Figure 1, surface oxidation treatment at 500 °C for about 130 minutes decreased alanine production rates both on Pt/CdS(B) and/or bare CdS(B).

In particular, the rate of alanine production which was observed on oxidated Pt/CdS(B) was increased about three times than that of non-oxidated Pt/CdS(B) under the same heat treatment for 120 minute at 500 °C. This means that the selectivity and photocatalytic activity of CdS(B) can be transformed into that of CdS(A)<sup>9</sup> by this surface oxidation treatment.

In order to investigate the reason of the remarkable effect of surface oxidation treatment of CdS(B) in the air, X-ray diffraction (XRD) spectra were measured for the CdS(B) after surface oxidation treatment at 500 °C for 120 minutes. On the other hand, the CdS(B), whose crystal structure was hexagonal form both before and after heat treatment in 760 mmHg of He gas at 500 °C, did not seem to decompose by heat treatment<sup>9</sup> even at 700 °C.

In Figure 2, the original hexagonal peaks of CdS(B) (Figure 2b) was revealed to change to different diffraction patterns superposed by several new small and weak broad diffraction peaks on its by surface oxidation treatment (Figure



**Figure 2.** X-ray diffraction (XRD) spectra of surface oxidated CdS(B), non-oxidated CdS(B), CdSO<sub>4</sub>, CdO and Cd(OH)<sub>2</sub>. (a) CdS(B) by surface oxidation treatment in 760 mmHg of air at 500 °C for 120 min. (b) CdS(B) by heat treatment in 760 mmHg of He atmosphere at 500 °C for 120 min (○). (c) CdSO<sub>4</sub> (▲). (d) CdO (□). (e) Cd(OH)<sub>2</sub> (●).

2a). After this surface oxidation, the deep yellow color of CdS(B) became more pale yellow. Furthermore, these new small and weak broad diffraction peaks appeared at  $2\theta = 14.72, 17.40, 18.42, 24.25, 25.05, 29.58, 31.12, 32.48, 55.00$  and  $63.00^\circ$  in case of oxidated CdS(B), respectively. As compared with (a)-(e) in Figure 2, we probably assume that these peaks due to CdSO<sub>4</sub>, Cd(OH)<sub>2</sub> or/and CdO by the surface oxidation of CdS(B), respectively. Recently, Jin *et al.*<sup>10</sup> investigated that a CdSO<sub>4</sub>-CdO-Cd(OH)<sub>2</sub> composite layer was formed on CdS in processes of high temperature air treatment at 520 °C for 5 min. Their results are in good agreement with the present study.

Therefore, our X-ray diffraction (XRD) patterns of oxidated CdS(B)-(a) and non-oxidated CdS(B)-(b) in Figure 2 are different each other. These difference suggests that a large number of the surface oxidation states in CdS(B) play an important role to control reaction pathway, likewise impurities<sup>9</sup>, resulting the higher selectivity and photocatalytic activity in alanine production.

To our knowledge, it is for the first time to have shown that the reaction selectivity in photocatalysis can be controlled clearly by this kind of surface modification.

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### A New Type of Stabilized Carbonucleophiles with A Carboranyl Group(I)

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One area of interests concerns the carboranes or boron-carbon cage molecules, upon which a large part of the recent research in the boron field has centered. A significant aspect of carborane chemistry is its considerable overlap with orga-

nic, organometallic and transition metal coordination chemistry.<sup>1</sup>

Recently, the selective synthesis of monosubstituted icosahedral 1,2-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> carborane derivatives is currently of great synthetic importance. Noteworthiness is their use in the boron-neutron capture reaction as the basis of a method for cancer therapy.

Hawthorne,<sup>2</sup> Yamamoto,<sup>3</sup> and Gabel<sup>4</sup> reported on the synthetic methods of 1,2-dicarba-*closo*-dodecaborane (*o*-carborane) derivatives.

Meanwhile, we investigated a new type of stabilized carbonucleophiles based on the strong electron-withdrawing effect of carboranyl group.<sup>5</sup> Especially in order to test the ability of carboranylacetic esters to form stabilized carbanions, the palladium catalyzed C-allylation of carbonucleophiles was carried out under neutral conditions using allylic carbonates.<sup>6</sup>

In this article, the palladium catalyzed reaction of carbonucleophiles containing a carboranyl group was studied.

### Experimental

**Reagent and instruments.** Melting points were checked by using a Yamato Model MP-21 and were uncorrected. FT-IR spectra were recorded on a Mattson Galaxy 6030E FT-IR Spectrophotometer using a thin film of the sample sandwiched between NaCl plates or KBr pellets. Mass spectra were determined on a Shimadzu-QP 1000 spectrometer at 70 eV by the electron impact (EI) method. <sup>1</sup>H NMR spectra were obtained at 60 MHz on a Varian EM 360 or at 300 MHz on a Bruker AM 300 spectrometer. All chemical shifts were measured relative to TMS ( $\delta=0.00$ ). <sup>13</sup>C NMR spectra were obtained at 75.5 MHz on a Bruker AM 300 spectrometer with CDCl<sub>3</sub> as solvent and internal standard ( $\delta=77.0$ ). Analytical thin layer chromatography (TLC) was performed using Merck silica gel 60 F<sub>254</sub>. Preparative thin layer chromatography was prepared using Merck silica gel 60 HF<sub>254</sub>, calcium sulfate and water (weight ratio=10 : 1 : 30) on 20×20 cm<sup>2</sup> glass plate. Column chromatography was performed using Merck silica gel 60 (70-230 mesh). Elemental analyses were performed by a Carlo Erba 1108 Elemental analyzer.

Employed 1,2-dicarba-*closo*-dodecaboranes were received from the Institute of Organoelement Compounds in Russia and identified by <sup>1</sup>H NMR, FT-IR, and GC-MS spectrometer before use.

Dibenzylideneacetone<sup>7</sup>, ethylcinnamyl carbonate<sup>8</sup>, ethyl allyl carbonate<sup>8</sup>, and bis(dibenzylidene-acetone)palladium(O)<sup>9</sup> were prepared according to the method described in previous papers.

**Preparation of Methyl 2-(2-phenyl-*o*-carboran-1-yl) acetate.** To a solution of sodium metal (0.46 g, 20 mmol) and iron nitrate nonahydrate (0.20 g, 0.5 mmol) in a liq. NH<sub>3</sub> (200 mL) at -45 °C was added 1-phenyl-*o*-carborane (4.4 g, 20 mmol) in dry diethyl ether (10 mL) dropwise over 10 minutes. The reaction mixture was allowed to stir for 15 minutes, and then added sodium bromoacetate (3.3 g, 20 mmol). The reaction mixture was allowed to stir for 15 minutes, and then added sodium bromoacetate (3.3 g, 20 mmol). The mixture was allowed to stir 10 minutes in an ice bath. After the ice bath was removed, the reaction mixture was allowed to stir for 1 hour, and then quenched with