Figure 7. ICP mass spetrum of Th and U.

and three gold wire samples, together with the best ranges detemined with the integrated counts.

Conclusion

A new analytical method has been successfully employed for pure gold samples. The analytical method takes advantage of the clean and simple matrix separation technique of the controlled potential deposition followed by the highly

accurate and precise isotope dilution mass spetrometry. However, the blank contamination has to be minimized in order to get more precise results. Sensitivity enhancement was found necessary to improve precision and accuracy for ultratrace elements (Ni, Zn, Th and U). Thus more efficient sample introduction methods such as ultrasonic nebulizer and electrothermal vaporizer could give better results.

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Effects of Heat Treatment and Platinum Loading on CdS Particles in the Photocatalytic Alanine Synthesis

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The photocatalytic alanine and hydrogen production reaction were studied by using CdS as a semiconductor photocatalysts. The rate of alanine and hydrogen production depends strongly on the temperature in heat treatment of CdS powder. 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 at 500°C. And the photocatalytic activity for alanine production using bare CdS(A) or Pt/CdS(A) was almost same with increasing temperature in heat treatment in the range of 100-600°C. From X-ray diffraction data and photoluminescence spectrum, we conclude that the crystal structure changes of CdS(A) or strong interaction at interface of Pt and CdS contribute to increasing the rate of alanine and hydrogen production reaction.

Introduction

The control of photocatalytic organic reactions is one of the very interesting subjects. Bard *et al.*[1] have examined that amino acid including alanine can be formed from methane-ammonia water in aqueous solution with Pt/TiO_2 as photocatalyst under near UV irradiation.

Sakada[2,3] have reported that various amino acids such as alanine were produced efficiently with visible light from ketocaboxylic acids in ammonia water through photocatalytic reaction with dyes, for example, zinc tetraphenylphosphine *p*-tetrasulfonate, acridine yellow and fluorescein derivatives, etc.

In the previous result[3], It was found that the photocatalytic

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organic reaction was selective and the selectivity of the photocatalytic reaction strongly depended on the kinds of dyes.

In order to understand more clearly the photocatalytic organic reactions, we extended to examine the photocatalytic alanine production reaction using semiconductors, such as CdS powder as photocatalysts. We also report here the effects of heat treatment and platinum deposition on different kinds of CdS (one is CdS from Mitsuwa, other is CdS from Furruchi) as photocatalysts for alanine or/and hydrogen production reaction, respectively.

Experimental

Semiconductor powders such as, bare CdS (A: purity 99.900%) from Mitsuwa Chem. Co. (size 300 M), Pt/CdS(A) made from CdS(A), bare CdS (B: purity 99.999%) from Furruchi Chem. Co., and Pt/CdS(B) made from CdS(B) were used as photocatalysts. The photocatalysts Pt/CdS(A) and Pt/CdS(B) were prepared by loading 3% Pt black (Rare Metallic Co.) mixture after heat treatment of CdS. The platinum loading of CdS powder was carried out by shaking CdS powder with platinum powder in a 100 ml glass vessel for 1 hr.[4]

All photocatalysts including bare CdS (or Pt/CdS) were heated to the range of 100-600℃ in 760 mmHg of He atmosphere in the heating vessel for 1 hr. before the use.

All CdS powders were treated by the heat without the purification.

X-ray diffraction data were obtained by a RIGAKU GAB-A2 type diffractometer using Cu-Kα radiation.

The photocatalytic reaction were performed in 200 ml reaction bottle with jointing stopper for connecting it into vacuum line, which approximatly 200 mg of CdS as the photocatalysts, 40 ml of distilled water, 10 ml of lactic acid (Wako Chem. Co.), and 10 ml of ammonia water (Wako Chem. Co.) were added for alanine production reaction. The pH of this mixture solution was 9.6. For the hydrogen production reaction only, the same amount of catalyst, lactic acid and water were added, and the pH of this solution was found to be 2.6.

In order to adjust a constant pH of solution, 20 ml of 8 M NaOH was added to the latter solution. After the air in the reaction bottle was removed by repeated vacuum degassing method, the reaction bottle was illuminated from the side direction by a 450 W Xe-Lamp (USHIO-XENON ARC., Co.). After the irradiation, the gaseous and liquid reaction products were analyzed as the same as reported previously.[2] The photoluminescene spectra for bare CdS untreated and treated by heat were obtained by monitoring the intensity of light emitted at 750 nm for emission spectra or excitation at 440 nm through a Xe lamp with a SPEXFLUOLOG-2 luminescence spectrometer in IMS (Institute for Molecular Science, Japan). The luminescence spectrum of CdS powder was pressed a flat plate by 200 kgf/cm² were measured in air.

Results and Discussion

In the presence of lactic acid and ammonia water, alanine is selectively produced by using CdS or Pt/CdS. The reactions are considered as follows.
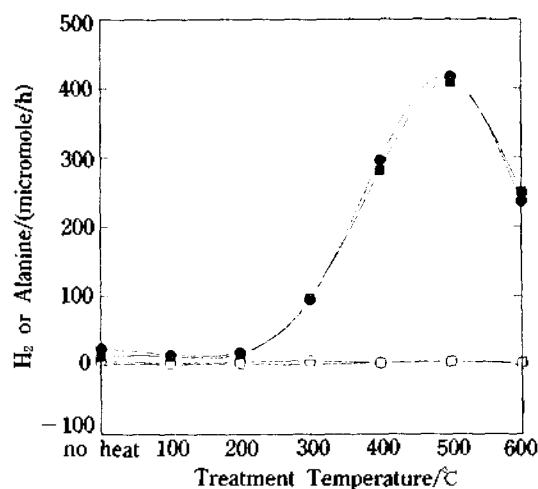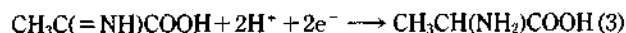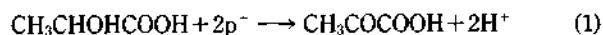

Figure 1. Effect of the heat treatment on the rate of hydrogen and alanine production on bare CdS(A) and Pt/CdS(A) as photocatalysts in lactic acid-ammonia water solution. 1) -●-; alanine production on Pt/CdS(A), 2) -■-; alanine Production on bare CdS (A), 3) -○-; Hydrogen production on Pt/CdS(A), 4) -□-; Hydrogen production on bare CdS(A).

$$CH_3CHOHCOOH + 2p^- \longrightarrow CH_3COCOOH + 2H^+ \qquad (1)$$

$$CH_3COCOOH + NH_3 \longrightarrow CH_3C(=NH)COOH + H_2O \qquad (2)$$

$$CH_3C(=NH)COOH + 2H^+ + 2e^- \longrightarrow CH_3CH(NH_2)COOH \,(3)$$

Besides alanine, a small amount of Hydrogen is produced due to the reduction of water, competing with reaction (3).

$$2H^+ + 2e^- \longrightarrow H_2 \qquad (4)$$

It was found that the heat treatment of CdS enhances dramatically the reaction rate of alanine synthesis. Figure 1 shows the dependence of the production rates of alanine and hydrogen on the heat treatment temperature on CdS (A).

As shown Figure 1, the rate of alanine decreases until 100℃ and increase remarkably with increasing the treatment temperature. It has a maximum at about 500℃ and then the products are decreased above 500℃. In the same figure the effect of Pt loading is not shown. In this case Pt black was loaded on CdS (A) after heat treatment at each temperature. Beyond expectation, Pt loading hardly gives influence on the rate of alanine Figure 1, while the rate of hydrogen production is enhanced Figure 2. Figure 2 shows the dependence of the hydrogen production rate on the temperature of heat treatment of CdS (A) in the photocatalytic reaction of lactic acid. The reaction in this case is expressed by eqs. (1) and (4). As shown in Figure 2, the heat treatment gives an effect similar to the case of alanine synthesis. However, Pt loading on CdS increases remarkably the hydrogen production rate. These results seem to have an important implication to the reaction mechanism: In the reduction of imino acids, Eq. (3), reduction by absorbed hydrogen atom does not take place but electron transfers to reduce the imino acid. If the former mechanism were correct, Pt loading should enhance the rate of alanine production.

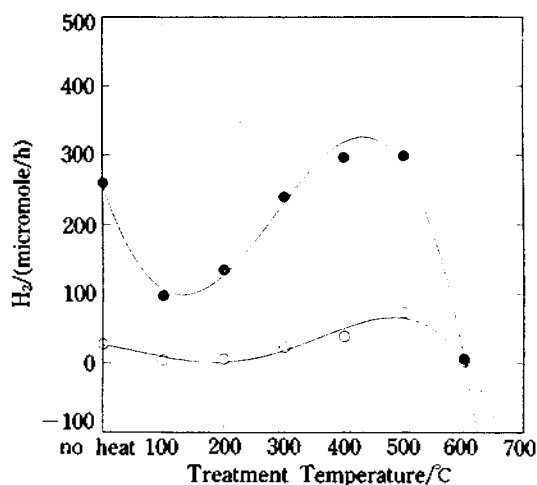In order to investigate the reason of the remarkable effect

Figure 2. Effect of the heat treatment on the rate of hydrogen production on Pt/CdS(A) as amorphous type photocatalysts in lactic acid-water solution. 1) -●-; Hydrogen production on Pt/CdS (A), 2) -O-; Hydrogen production on bare CdS(A).
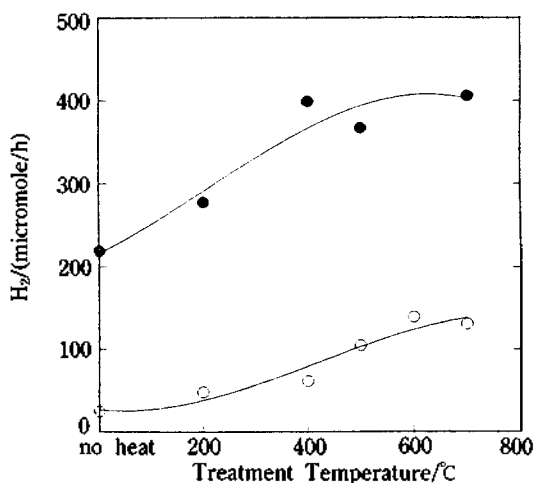

Figure 3. Effect of the heat treatment on the rate of hydrogen production on Pt/CdS(B) as hexagonal type photocatalysts in lactic acid-water solution. 1) -●-; Hydrogen production on Pt/CdS (B), 2) -O-; Hydrogen production on bare CdS(B).

Figure 4. Effect of the heat treatment on the rate of hydrogen and alanine production on bare CdS(B) and Pt/CdS(B) as photocatalysts in lactic acid-ammonia water solution. 1) -●-; alanine production on Pt/CdS(B), 2) -■-; alanine Production on bare CdS (B), 3) -O-; Hydrogen production on Pt/CdS(B), 4) -□-; Hydrogen production on bare CdS(B).

of heat treatment, the X-ray diffraction was measured for powdered CdS samples treated at various temperatures. CdS (A) was found to be amorphous (or might be cubic), because of the lack of any diffraction peaks. The color is reddish yellow before heat treatment. After heat treatment at 100℃, the color becomes more reddish. When the temperature of heat treatment exceed a 200℃, this reddish color is being lost. The higher the temperature, the color becomes more pale yellow, corresponding to this color change, the crystal structure was revealed to change to hexagonal at the temperature higher than 300℃.[5,6] As shown in Figure 1 and 2, heat treatment at 600℃ decreases both the alanine and hydrogen production rates. After the heat treatment, the color of CdS became greyish yellow and metal was deposited on the inner surface of the quartz tube for heat treatment. After dissolving this metal in a diluted hydrochloric acid electrochemical analysis was carried out. The result showed that
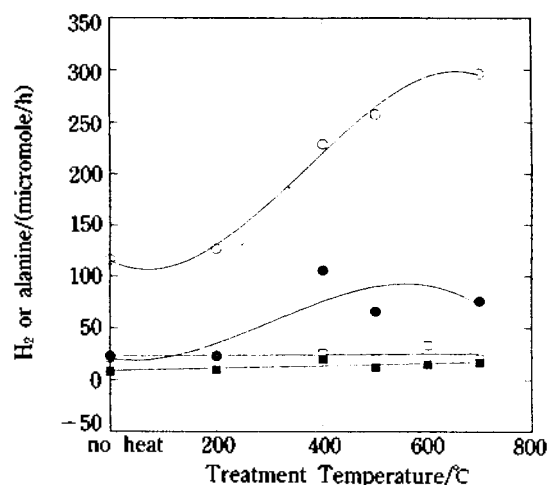
it is cadmium metal. This indicates that CdS(A) is decomposed partially by the heat treatment at 600℃.

Since the crystal structure of CdS is considered to be one of the important factors to control the photocatalytic reactions, the powder CdS(B), whose crystal structure is mostly hexagonal before heat treatment, was used for the experiment. The result for hydrogen production from lactic acid solution is shown in Figure 3.

As compared with that in Figure 2, the hydrogen evolution rate is a little larger in this case than in the case of CdS(A). Moreover, the dependence of treatment temperature for CdS (B) is different from that for CdS(A). The alanine and hydrogen production in lactic acid-ammonia water solution is shown in Figure 4. The result is quite different from that for the photocatalysts based on CdS(A). Hydrogen is produced much more than alanine both for CdS(B) and Pt/CdS(B) and alanine production is suppressed. These results indicate that photoexcited electrons are not used to reduce imino acid (reaction (3)) but to reduce water on the surface of photocatalysts based on CdS(B). These results can be explained that the bare CdS(B) is much more efficiently for hydrogen production than that of the bare CdS(A). Tsubomura *et al.*[7] investigated the effect of heat treatment of CdS (Kojundo Chem. Co., cubic structure) and found that the abundance of hexagonal CdS is increased by heat treatment and the efficiency of hydrogen evolution is enhanced. They concluded that hexagonal CdS is more advantageous to hydrogen evolution. Their results are good agreement with the present results, However, as shown in Figure 1, alanine is produced selectively by CdS(A) even after the heat treatment at 500℃. This fact cannot be explained by the crystal structure, since most part of CdS(A) is transformed into hexagonal structure at 500℃.

In order to find the difference of CdS(A) and CdS(B) after the heat treatment, the emission spectra are measured. The luminescence intensity of both CdS(A) and CdS(B) was increased by heat treatment at 400-600℃. In particular, the
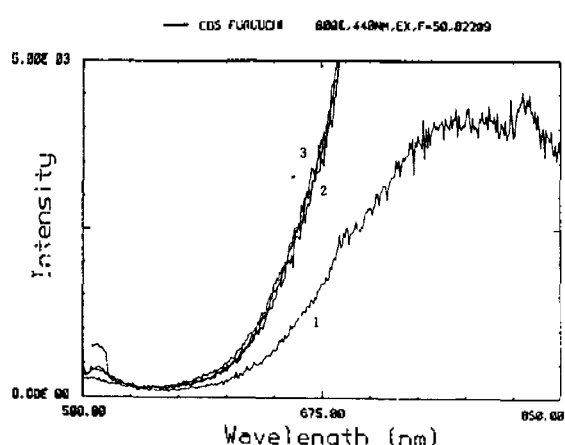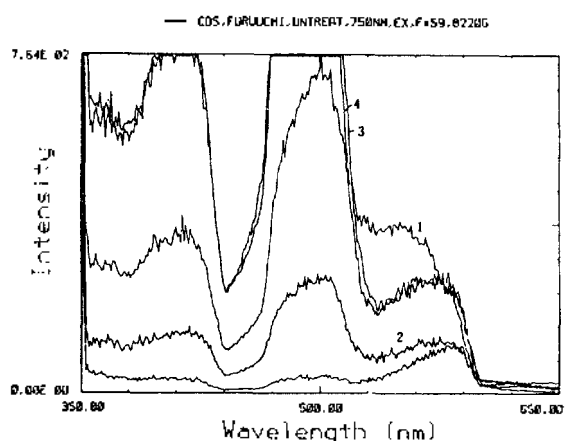
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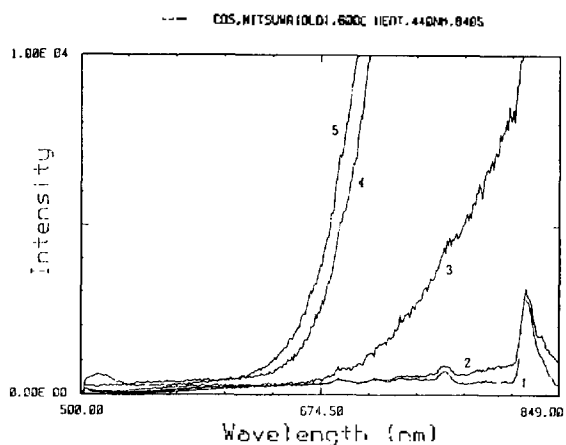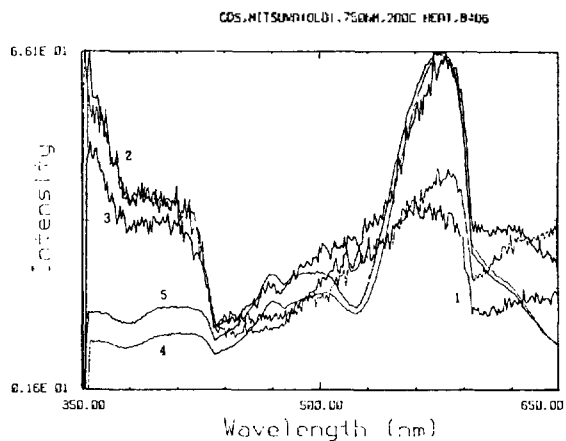
Figure 5. (a) Emission spectrum of bare CdS(A) as photocatalyst by heat treatment. 1) no heat 2) 300℃ heat 3) 400℃ heat 4) 500℃ heat 5) 600℃ heat. (b) Excitation spectrum of bare CdS(A) as photocatalyst by heat treatment. 1) no heat 2) 200℃ heat 3) 300℃ heat 4) 400℃ heat 5) 500℃ heat 6) 600℃ heat.

Figure 6. (a) The variation of emission spectrum for bare CdS (B) as photocatalyst by heat treatment. 1) no heat 2) 500℃ heat 3) 600℃ heat, (b) The variation of emission spectrum for bare CdS(B) as photocatalyst by heat treatment. 1) no heat 2) 200℃ heat 3) 500℃ heat 4) 600℃ heat.

intensity of emission spectra of CdS(A) in Figure 5a is strengthened about two times comparing with CdS(B) as shown in Figure 6a under the same heat treatment.

The excitation spectra of CdS(A) and CdS(B) are shown in Figure 5b and 6b, respectively. The excitation spectra of CdS(A) show a pronounced peak at about 600 nm and the existence low energy states extending up to 650 nm and the existence low energy states extending up to 650 nm range, which might be ascribed to sub-band gap states due to impurities or defects of surface states.[9] The high selectivity for alanine production observed with annealed CdS(A) powder might be attributed to the existence of these sub-band gap states, especially the states located on the surface or near the surface defects.[9a,b]

Consequently, the results coming out from photocatalytic reaction for alanine and hydrogen production using CdS or Pt/CdS as photocatalyst are as follows; (1) The rate of alanine production for Pt/CdS(A) used as photocatalyst increased about six times in comparison with Pt/CdS(B) under the same experimental condition. (2) The rate of alanine production observed in bare CdS(A) or Pt/CdS(A) treated by heat was nearly same. (3) Increasing of temperature in heat
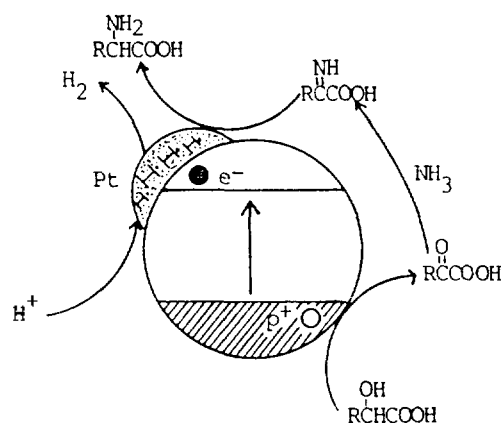

Figure 7. Scheme of reaction path way for photocatalytic alanine production reaction on CdS.

treatment for bare CdS(A) formed amorphous, crystal structure of CdS(A) was changed to hexagonal. This hexagonal structure of CdS(A) attributes to increase efficiency of charge separation. Although the discussion of reaction mechanism

for alanine production is very difficult from this simple experimental results. However, we can propose the reaction scheme as in Figure 7.

The imino acid, which is produced from thermal equilibrium between lactic acid and ammonia, is reduced by excited electrons on the conduction band of CdS or on Pt to produce alanine. These exicted electrons are also consumed to reduced water, *i.e.* for hydrogen production. The difference in the selectivity of alanine production would be explained as follows. In the case of CdS(B), the electron energy must be lost to some extent by the trapping in the surface sub-band gap levels. If we assume that these surface trapped electrons can reduce the imino acid but not water, the high selectivity of alanine production of CdS(A) would be explained. On the other hand, in the case of CdS(A), the energy of excited electrons are not lost and they are used promptly to reduced water. Therefore in this case, electrons would be consumed much more to reduce water than to reduce the imino acid. Although this assumption can explain the difference in the selectivity between CdS(A) and CdS(B) in the same hexagonal form, the further investigation would be needed to clarify the mechanism. These studies are now in progress by using single crystal electrode of CdS.

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Micellar Effects on Intramolecular Charge Transfer Emission from Biphenylcarboxylic Acids

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The intramolecular charge transfer (ICT) phenomena of the photoexcited 2-biphenylcarboxylic acid (2BPCA) and 4-biphenylcarboxylic acid (4BPCA) have been investigated in some surfactant micellar solutions. The ICT emission of 4BPCA and 2BPCA in aqueous solution at sufficiently low pH (1-3) has been observed to be markedly quenched and blue-shifted upon addition of a cationic surfactant, cetyltrimethylammonium chloride (CTAC) in contrast to little change in anionic sodium dodecyl sulfate (SDS) and neutral Brij 35. An anionic emission band has been observed to be enhanced at expense of the ICT emission as a function of the concentration of CTAC. These results with the micellar effects on the fluorescence decay kinetics of 4BPCA suggest that formation of the ICT state of the excited acids is inhibited by CTAC-induced proton transfer as well as the decrease in the polarity and/or hydrogen-bonding ability of the micellar microenvironment entrapping the acids.

Introduction

The intramolecular charge transfer (ICT) emission is currently the most attractive topics in the investigation of solvation dynamics.[1-3] It has been observed that the excited-state ICT processes in many molecules are accompanied by solvent relaxation and their rates are controlled exclusively by polarity of the medium.[4-6] The rate of the excited-state ICT process is also controlled by the molecular geometry both

in the ground and the excited states, which is greatly affected by the specific solvent-solute interaction.[2,7-9] Because of these characteristics, the ICT emission is commonly used to probe the microenvironments, including microscopic polarity of complex biological systems.[10,11] However, there have not been systematic investigations of the ICT emission in the simple biomimetic systems such as surfactant micelles or cyclodextrins, although preliminary reports are available for the effects of cyclodextrins on the ICT emission from dimethylamino benzonitrile.[12,13]

The surfactant micelles, one of microheterogeneous structures, have been attracting much attention as good membrane mimetic media.[14] The micelles provide such a wide va-

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