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PHOTOCATALYSIS OF IRRADIATED SEMICONDUCTOR SURFACES: ITS APPLICATION TO WATER SPLITTING AND SOME ORGANIC REACTIONS*

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Summary

Hydrogen production from organic compounds and water was investigated using powdered semiconductor photocatalysts. The complete decomposition observed for several organic compounds demonstrated that water is involved in the reactions as an oxidizing agent. Photocatalyses of dyes and semiconductors were found to be applicable to amino acid synthesis. The quantum yields of photocatalytic amino acid synthesis using visible light are about 20% - 40% in the absence of a metal catalyst such as platinum. Moreover the reactions are highly selective and depend strongly on the type of semiconductor. This method was applied to the asymmetric synthesis of amino acids using asymmetric catalysts. Rather high optical yields of 50% were achieved for the synthesis of L-phenylalanine.

1. Introduction

The photocatalytic effects of semiconductors and dyes have been under investigation because of their potential applicability to the direct conversion of solar energy to chemical energy [1]. Rapid progress is now being made in research in this field. During recent years surface modification of powdered semiconductors such as TiO_2, $SrTiO_3$ and CdS by the addition of platinum, palladium or RuO_2 has been found to increase the photocatalytic activity of the semiconductor by a factor of $10 - 10^3$ [2]. By using these surface-modified photocatalysts, water can be split into oxygen and hydrogen [2]. Other photocatalytic reactions such as the oxidation of cyanide [3, 4], sulphite [4], acetate [5], hydrocarbons [6 - 9] and other substances [10] have been investigated. We have demonstrated photocatalytic hydrogen production from the reactions of water with various organic compounds such as alcohols [11, 12], carbohydrates [13], hydrocarbons [14, 15], artificial high polymers [14, 16] and biomasses [16, 17] using powdered semiconductor photocatalysts. In these reactions, organic

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molecules are oxidized and water is reduced to produce hydrogen. In several cases hydrogen production is very efficient. With TiO_2 photocatalysts organic compounds are finally oxidized to CO_2 owing to the strong oxidation power of the holes generated in the valence band of TiO_2. These photocatalytic reactions can also be applied to organic synthesis. Here we report some of the results of their application to the reactions of organic acids and amino acid synthesis.

2. Photocatalytic hydrogen production from organic compounds and water

Several examples of photocatalytic reactions which have been investigated in this laboratory are shown in Table 1. The evidence that H_2O is involved in these reactions and is reduced photoelectrochemically was obtained by using D_2O instead of H_2O. For the decomposition of ethanol in D_2O 88% of the evolved gas was D_2, 10% was DH and 2% was H_2 [12]. In order to confirm whether the reactions proceed quantitatively, the complete decomposition was carried out for methanol, ethanol, sugar [13] and *n*-hexadecane [15]. The amount of H_2 and CO_2 produced agreed well with the theoretical value calculated from the quantity of the starting material and the equations shown in Table 1. These results indicate clearly that water is involved in the reactions as an oxidizing agent. Oxygen is not evolved, but is captured by the carbon in the organic compounds, and water is split with the aid of the reducing power of the organic compounds. In many cases light energy is stored through the reactions, although the increase in free energy per transferred electron is rather small as shown in Table 1. Interestingly, methane is formed in addition to hydrogen in the case of ethanol; this can be explained by the photocatalytic decomposition of acetic acid accumulated as a reaction intermediate [12]. This reaction is described in Table 1, eqn. (4). The ratio of hydrogen to methane expected from this equation is 2.0. However, the experimental value is about 14, which is much larger than the expected value. This can be explained well by assuming that reactions (5) and (4) both take place. The result of the complete decomposition of ethanol indicated that the photogenerated electrons and holes were consumed four times as fast for reaction (5) as for reaction (4).

The above result for the photocatalytic reaction of ethanol shows that the flow of photogenerated electrons and holes is controlled on the photocatalyst. In order to clarify this type of phenomenon the photocatalytic reaction of organic acids was investigated [18]. Krauetler and Bard [19] found that in the presence of Pt–TiO_2 the hydrocarbon was formed by the following reaction which they denoted the photo-Kolbe reaction:

$$RCOOH \longrightarrow RH + CO_2 \qquad (I)$$

Sato [20] has recently reported photocatalytic synthesis of ethane from acetic acid in the vapour phase. Yoneyama *et al.* [21] investigated

TABLE 1

Examples of photocatalytic hydrogen production from organic compounds and water

Reactant	*Photocatalytic reaction*	ΔG° (kJ mol^{-1})	$\Delta\epsilon^\circ$ [a] (eV)
Carbon	(1) $C + 2H_2O \longrightarrow 2H_2 + CO_2$	63	+0.16
	(2) $C + H_2O \longrightarrow H_2 + CO$	92	+0.48
Alcohols	(3) $CH_3OH + H_2O \longrightarrow 3H_2 + CO_2$	9.0	+0.02
	(4) $C_2H_5OH + H_2O \longrightarrow 2H_2 + CH_4 + CO_2$	−34	−0.07
	(5) $C_2H_5OH + 3H_2O \longrightarrow 2CO_2 + 6H_2$	97	+0.08
Carbohydrate (glucose)	(6) $C_6H_{12}O_6 + 6H_2O \longrightarrow 6CO_2 + 12H_2$	−32	−0.01
Hydrocarbons	(7) $C_6H_6 + 12H_2O \longrightarrow 6CO_2 + 15H_2$	356	+0.12
	(8) $C_{16}H_{34} + 32H_2O \longrightarrow 16CO_2 + 49H_2$	1232	+0.14
Amino acid	(9) $H_2NCH_2COOH + 2H_2O \longrightarrow 3H_2 + NH_3 + 2CO_2$	47	+0.06
Polymers	(10) $\text{-}(CH_2CHCl)\text{-} + 4H_2O \longrightarrow 5H_2 + 2CO_2 + HCl$		
	(11) $\text{-}(CH_2NHCONH)\text{-} + 3H_2O \longrightarrow H_2 + 2NH_3 + 2CO_2$		

[a] Change in free energy per transferred electron.

the factors influencing product distribution in the photocatalytic decomposition of aqueous acetic acid on Pt–TiO_2. We measured the rates of production of hydrogen, RH and CO_2 during the decomposition of several organic acids on Pt–TiO_2 and found that the rate of production of hydrogen is large even compared with that of the hydrocarbon. This result suggests that reactions other than reaction (I) take place. Further evidence supporting this proposal is the pH dependence of the rates of production of hydrogen and methane from acetic acid as shown in Fig. 1. The ratio of hydrogen to methane depends strongly on the pH, and increases with increasing pH. Above pH 8.8 for TiO_2(anatase)–Pt (pH 7.1 for TiO_2(rutile)–Pt) only hydrogen is evolved and almost no methane is produced. The formation of methanol (CH_3OH) and glycol acid ($HOCH_2COOH$) in the aqueous medium suggests that a new reaction path in which water is involved as an oxidizing agent exists since they react with water to produce hydrogen and CO_2 [11, 12, 18]. This new reaction is written as

$$CH_3COOH + 2H_2O \longrightarrow 2CO_2 + 4H_2 \quad \Delta G^\circ = 78.5 \text{ kJ mol}^{-1} \qquad \text{(II)}$$

Reaction (II) has two characteristic features. The first is that water is involved in the reaction as an oxidizing agent, and the second is that a substantial amount of free energy is stored ($\Delta G^\circ = -52.3$ kJ mol^{-1} for the photo-Kolbe reaction of acetic acid (reaction (I)) [18]). The non-Kolbe-type electrode reaction of organic acids in which olefins and alcohols are produced is known as the Hofer–Moest reaction [22]. Since methanol and glycol acid are produced as reaction intermediates, reaction (II) has a close similarity to the Hofer–Moest reaction.

TiO_2 has been used as the catalyst in most of the above reactions. However, because of its large band gap ($E_g = 3.0$ eV) only 6% of the solar energy can be utilized to excite the photocatalyst. We have investigated photocatalytic hydrogen production from various organic compounds and water using visible light and many kinds of powdered semiconductor [14].

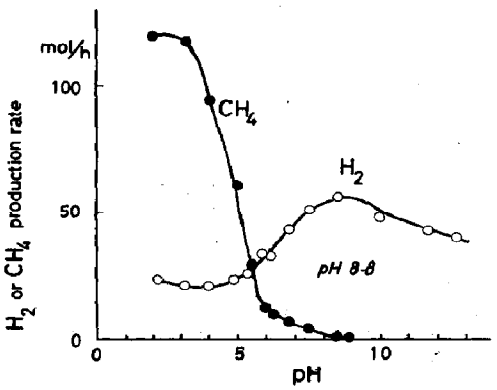


Fig. 1. Dependence of the rates of production of hydrogen and methane on pH for the photocatalytic decomposition of acetic acid. (30 ml of a water–acetic acid mixture (6:1 by volume) containing 300 mg of TiO_2(anatase)–Pt was irradiated using a 500 W xenon lamp.)

To date we have only been able to obtain efficient and stable hydrogen production with visible light by using CdS. Although CdS is a cheap material, it is not ideal because of its toxicity. Therefore it is very important to identify new stable semiconductors which work efficiently with visible light. The utilization of the dye sensitization effect on powdered semiconductors appears to be a promising method for extending the effective wavelength into the visible region [23, 24]. In addition to the exploitation of new semiconductors, the development of new catalysts to replace expensive noble metal catalysts such as platinum and RuO_2 is also important. The effect of these catalysts, particularly that of RuO_2, on the semiconductors under irradiation is still a subject of controversy [25, 26].

3. Effect of the nature of the semiconductor on the photocatalytic decomposition of lactic acid [27]

Platinized TiO_2 and CdS have been found to decompose lactic acid and to produce hydrogen very efficiently. The quantum yields of hydrogen production are 71% (at 360 nm) for Pt–TiO_2 and 38% (at 440 nm) for Pt–CdS. Interestingly the reaction products differ depending on the type of semiconductor used. For Pt–TiO_2 the main products are hydrogen, CO_2 and acetaldehyde, whereas for Pt–CdS they are hydrogen and pyruvic acid.

This result suggests that the following reactions take place:

$$CH_3CH(OH)COOH \longrightarrow H_2 + CO_2 + CH_3CHO \qquad \text{(III)}$$

for Pt–TiO_2 and

$$CH_3CH(OH)COOH \longrightarrow H_2 + CH_3COCOOH \qquad \text{(IV)}$$

for Pt–CdS. The difference between the reactions can be explained by the difference between the oxidation powers of the photogenerated holes in the valence band of each semiconductor.

The photocorrosion of CdS was suppressed during the reaction and the photocatalytic activity was maintained during irradiation for more than 300 h.

4. Highly efficient photocatalytic production of amino acids from organic acids [28] and its application to asymmetric synthesis [29]

The production of amino acids by irradiating mixtures of various organic compounds and ammonia with UV light has been investigated mainly from the viewpoint of chemical evolution [30, 31]. Bard and coworkers [32, 33] have demonstrated that various amino acids were produced from methane–ammonia–water mixtures with a Pt–TiO_2 photocatalyst under near-UV irradiation. Kawai *et al.* [34] have recently reported the formation of polypeptides as well as various amino acids from glucose–ammonia–water

mixtures with a Pt–TiO_2 catalyst. The efficiency of the above reactions is rather low and the reaction mechanism seems to be very complicated because of the simultaneous production of various amino acids. Here we report a highly efficient photocatalytic synthesis of amino acids from organic acids in ammonia–water mixtures by using various dyes and semiconductors as photocatalysts. The quantum yields of these reactions using visible light are 20% - 40% in the absence of metal catalysts such as platinum. Moreover the reactions are highly selective and depend strongly on the type of semiconductor used. We also applied this method to the asymmetric synthesis of amino acids using asymmetric catalysts. A rather high optical yield of 50% was achieved for L-phenylalanine (L-Phe) synthesis.

Among various organic acids, ketocarboxylic, hydroxycarboxylic and unsaturated carboxylic acids were found to produce the corresponding amino acids efficiently. The reactions are classified into three types, examples of which are shown in Fig. 2.

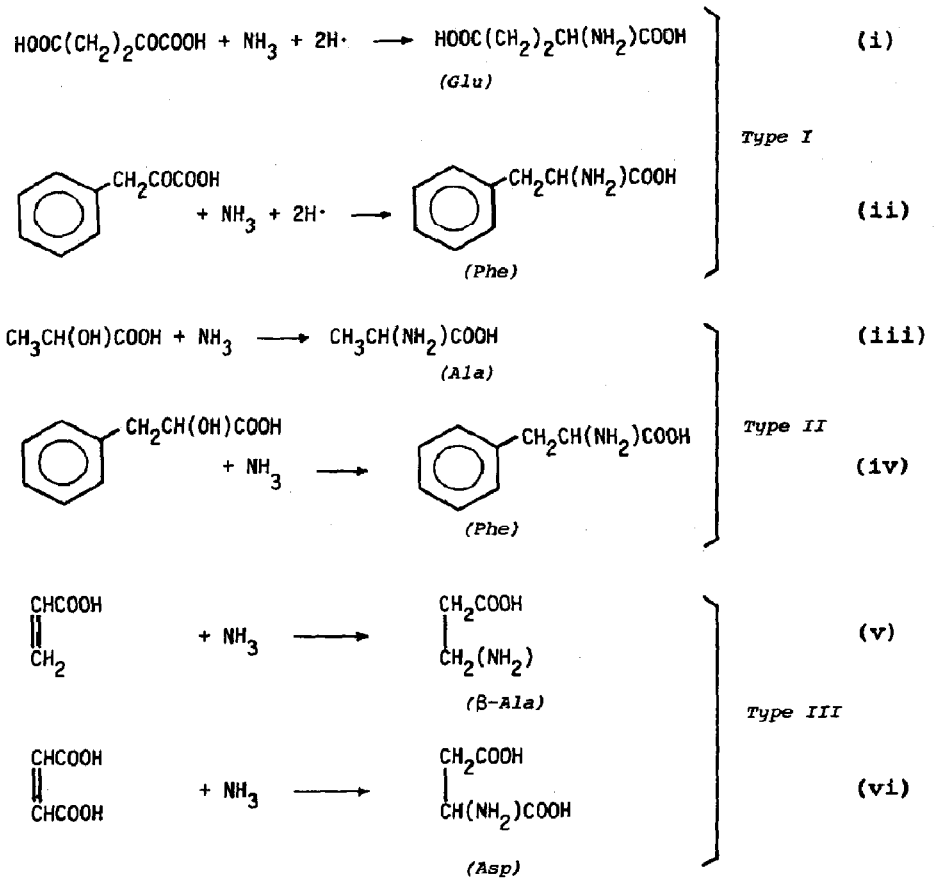


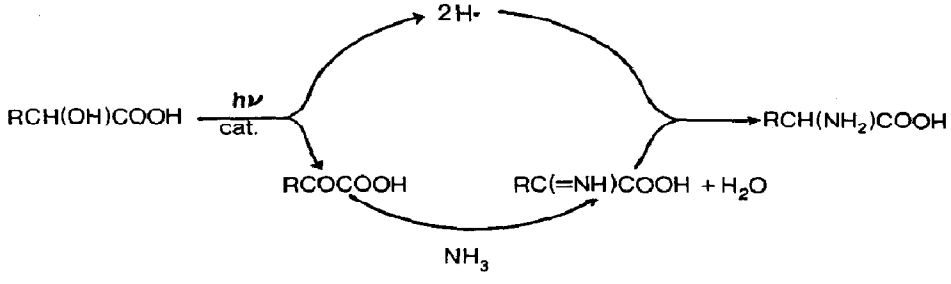
Fig. 2. Typical examples of the photocatalytic synthesis of amino acids from organic acid–ammonia–water mixtures using dyes or powdered semiconductors as photocatalysts.

In the first type of reaction, ketocarboxylic acid, ammonia and a sacrificial agent such as triethanolamine (TEOA) are used:

$$\mathrm{RCOCOOH} + \mathrm{NH_3} \longrightarrow \mathrm{RC(=NH)COOH} + \mathrm{H_2O}$$
$$\xrightarrow{2\mathrm{H}^{\cdot}} \mathrm{RCH(NH_2)COOH} + \mathrm{H_2O} \qquad \text{(V)}$$

This reaction resembles the Knoop reaction [35] in which imino acid is reduced thermally by hydrogen and a platinum catalyst or by ethanol and an alkali metal. However, in the present photocatalytic reaction an excited dye or an excited semiconductor oxidizes a sacrificial agent such as TEOA. In the case of a dye, the dye itself is reduced in this reaction. Fluorescein derivatives and $Ru(bpy)_3^{2+}$ (bpy ≡ 2,2′-bipyridine) are known to undergo one-electron reduction under alkaline conditions [36, 37]. These reduced dyes are believed to reduce the imino acid since they have a strong reducing power. For a semiconductor photocatalyst, hydrogen atoms on the semiconductor surface, which are produced by the photocatalytic reaction of water (or H^+) with electrons in the conduction band of the semiconductor, are believed to be responsible for the reduction of the imino acid. Unlike the Knoop reaction, in the present reaction platinum is not necessary. Both the semiconductor and the dye were found to function as good photocatalysts. For instance, 2-ketoglutaric acid in a 7% ammonia–water mixture produced 1.2 mmol of glutamic acid after irradiation ($\lambda > 450$ nm) for 7 h with zinc tetra-*p*-sulphonatophenylporphyrin (ZnTPPS) as a photocatalyst. In similar reactions, pyruvic acid, glyoxylic acid and phenylpyruvic acid were found to produce efficiently the corresponding amino acids, *i.e.* alanine (Ala), glycine (Gly) and phenylalanine (Phe) respectively. Various dyes such as ZnTPPS, riboflavine, dibromofluorescein, $Ru(bpy)_3^{2+}$ and copper chlorophyrine were found to function as good photocatalysts. By analogy with the Knoop reaction, the first type of reaction can be called the photo-Knoop reaction. Tabushi *et al.* [38] have recently reported the efficient reduction of ketocarboxylic acid derivatives to dihydro derivatives on a functionalized micelle by using a ZnTPPS photocatalyst. Their reactions seem to be very similar to the present reactions.

In the second type of reaction hydroxycarboxylic acids are used instead of ketocarboxylic acids. Ala, Gly and Phe are produced efficiently from lactic acid, glycol acid and phenyllactic acid respectively. In this type of reaction no sacrificial agent is necessary because the hydroxycarboxylic acids act as reducing agents. The reaction scheme is believed to be as follows:



(VI)

This type of reaction can be regarded as a modification of the first type and can also be called a photo-Knoop reaction. Most dyes do not work as photocatalysts in the second type of reaction, probably because of the weak oxidation power of their excited states. For semiconductor photocatalysts the efficiency depends strongly on the type of semiconductor used. For instance, 2.4 mmol of Ala was produced from lactic acid after 10 h irradiation in the presence of CdS, whereas only 12 μmol of Ala was produced in the presence of TiO_2 under the same conditions. This corresponds well to the fact that the main product of the photocatalytic decomposition of lactic acid in an aqueous medium is pyruvic acid for Pt–CdS and acetaldehyde for Pt–TiO_2 because of the difference between the oxidation powers of CdS and TiO_2 [27]. A similar result was obtained for the formation of Gly from glycol acid. The formation of amino acids was strongly suppressed in the presence of oxygen. A similar effect was observed for reactions of the first type. This is expected from reaction schemes (V) and (VI), since in the presence of oxygen the excited electrons reduce oxygen rather than the imino acid. NH_2OH instead of ammonia was found to be effective as a nitrogen source for the photocatalytic production of amino acids. It is believed that in this case oxyimino acids are reduced to produce amino acids.

In addition to the photo-Knoop reactions, we investigated the addition of NH_3 to unsaturated carboxylic acids such as maleic acid, cinnamic acid and acrylic acid. Several of these reactions were successful. For instance, β-Ala was produced efficiently and selectively by the addition of NH_3 to acrylic acid using ZnTPPS as a photocatalyst. This reaction is expressed as

$$\begin{array}{l} CHCOOH \\ \| \\ CH_2 \end{array} + NH_3 \longrightarrow \begin{array}{l} CH_2COOH \\ | \\ CH_2NH_2 \end{array} \qquad \text{(VII)}$$

Interestingly, no α-Ala was produced in this case which suggests a Michael-type reaction mechanism for reaction (VII). Letokhov *et al.* [39] reported efficient production of aspartic acid (quantum yield, about 0.35) by means of the two-photon excitation of maleic acid with a picosecond UV laser at a very high laser power of 3×10^8 W cm^{-2}. In our method, however, the reactions proceed efficiently with visible light under mild conditions. Table 2 shows some examples of these reactions and their quantum yields. As shown in this table, the quantum yields of these reactions with visible light are very high.

Amino acids of L chirality are frequently produced in natural organisms. The asymmetric synthesis of various organic compounds is also one of the interesting subjects in organic chemistry. Several methods have been used for electrochemical asymmetric synthesis [40]. We have applied these methods to the photocatalytic asymmetric synthesis of amino acids by using semiconductor surfaces modified with asymmetric compounds. The use of chiral compounds such as L-Glu, dibenzoil-L-tartaric acid and (2,2′-bis-(diphenylphosphino)-1,1′-binaphthylrhodium(I) complex [41] resulted in the efficient asymmetric synthesis of L-Phe from phenylpyruvic acid (type I reaction in Fig. 2) or L-phenyllactic acid (type II reaction) by

TABLE 2

Quantum yields of the photocatalytic production of amino acids using visible light

Reaction	*Photocatalyst*	*Quantum yield (%)*	*Wavelength (nm)*
2-Ketoglutaric acid + NH_3 + 2H· $\xrightarrow{2h\nu}$ Glu[a]	ZnTPPS	30	436
Lactic acid + NH_3 $\xrightarrow{2h\nu}$ Ala[b]	CdS	18	430
Acrylic acid + NH_3 $\xrightarrow{h\nu}$ β-Ala[c]	Acridine yellow	42	450
	ZnTPPS	38	436

[a]3.5 g of 2-ketoglutaric acid, 10 ml of ammonia water (28% NH_3), 30 ml of distilled water, 10 ml of triethanolamine and 0.88×10^{-4} M ZnTPPS. Two-electron reduction of imino acid was assumed for the quantum yield calculation.
[b]10 ml of lactic acid, 10 ml of ammonia water (28% NH_3), 40 ml of distilled water and 300 mg of powdered CdS. Two-electron reduction of imino acid was assumed for the quantum yield calculation.
[c]5 ml of acrylic acid, 10 ml of ammonia water (28% NH_3), 30 ml of distilled water and 4.6×10^{-4} M acridine yellow or 0.97×10^{-4} M ZnTPPS.

using powdered CdS as a photocatalyst [29]. Interestingly, in the synthesis of phenylalanine from L-phenyllactic acid an equal amount of D-Phe and L-Phe was produced in the absence of the asymmetric catalyst: the asymmetric memory of L-phenyllactic acid was lost in the photocatalytic reaction. However, rather high optical yields of 50% were attained using asymmetric catalysts. A similar result was obtained when phenylpyruvic acid was used as the starting material.

Because of its simplicity and high efficiency, this method may be a promising means of amino acid synthesis. The high quantum yields of the reactions and the high optical yields of the asymmetric reaction suggest that photocatalytic processes play an important role in chemical evolution [32, 33] since various organic acids including lactic acid and glycol acid can easily be produced in experiments of the type described by Miller [42] and Miller and Urey [43] and the largest energy source on the Earth is sunlight.

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