Photodecomposition of amino acids and photocurrent generation on TiO_2/OTE electrodes prepared by pulse laser deposition

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The photoelectrical degradation of the amino acids L-aspartic acid (L-Asp), L-glutamic acid (L-Glu), L-leucine (L-Leu), L-α-alanine (L-α-Ala) and β-alanine (β-Ala) was examined on TiO_2/OTE electrodes prepared by a pulse laser deposition method. The disappearance of amino acids and their mineralization into CO_2 were determined with and without an applied anionic bias of 0.3 V. The generation of photocurrent was also measured during the photoelectrical degradation of substrates on the TiO_2/OTE electrode assembly considering it as a possible type of solar cell. The relationship between the photoelectrodegradation rate, the photocurrent and the structure of the amino acids was established.

Keywords: titanium dioxide, semiconductor electrode, amino acid, photocurrent, photooxidation, photodegradation

1. Introduction

The photocatalytic oxidation of organic compounds has been extensively investigated in TiO_2 aqueous dispersions [1–5]. However, TiO_2 particles have to be removed from the degraded solution by centrifugation and filtration after the photodecomposition of substrates. No such an operation is needed if the TiO_2 is fixed, and continuous wastewater treatment is possible. Recently, the photoelectrochemical degradation of organic compounds has been carried out with TiO_2 film electrodes prepared by a pasting procedure [6–12], a sol–gel method [13–17], and a Ti-firing technique [18].

In this study, the TiO_2/OTE electrodes were prepared by a pulse laser deposition procedure. The surface characteristics of these TiO_2 films were identified by SEM and XRD. The photodegradation of amino acids on these TiO_2/OTE electrodes was monitored by the disappearance of the amino acids and concomitant CO_2 evolution, with or without an anionic bias. A gas-phase synthesis by pulse laser photolysis deposition gives excellent fine and pure particles having uniform size. Laser pulse irradiation of H_2, O_2 and $TiCl_4$ mixed gases leads to the formation of superfine TiO_2 particles by dielectric gas breakdown. This gas-phase procedure using pulsed laser deposition yields a TiO_2 preparation with the following advantages: (1) excellent light absorption efficiency; (2) no impurities in the TiO_2 particles; and (3) easy control of the formation ratio of anatase/rutile mixed crystallites by the relative amounts of H_2, O_2 and $TiCl_4$. In general, the photodegradation of organic compounds on the TiO_2-coated glass electrode can be accelerated by applying an anionic bias owing to the virtual prevention of the recombination of electron/hole pairs. This work revealed that the effect of an applied anionic bias on the photooxidation rate of amino acids is related closely to the structure of the substrates, and particularly to the isoelectric point (pI) of the amino acids used. Furthermore, the possibility of photocurrent generation as a kind of wet solar cells was also examined in the photodecomposition of amino acids.

2. Experimental

2.1. Materials

The amino acids, L-aspartic acid (L-Asp, $HOOCCH_2C^*H(NH_2)COOH$), L-glutamic acid (L-Glu, $HOOCCH_2CH_2C^*H(NH_2)COOH$), L-leucine (L-Leu, $(CH_3)_2CHCH_2C^*H(NH_2)COOH$), L-$\alpha$-alanine (L-$\alpha$-Ala, $CH_3C^*H(NH_2)COOH$), and β-alanine (β-Ala, $NH_2CH_2CH_2COOH$) were all supplied by Tokyo Kasei Co., Ltd., and Ajinomoto Co., Ltd. They were used as received without further treatment.

2.2. Preparation of TiO_2/OTE

The optically transparent electrode (OTE) of SnO_2/sodalime glass (sheet resistance 5.6 Ω/□; film thickness of SnO_2; 960 nm, Haze 14%) was a gift from Asahi glass Co., Ltd. An OTE plate (20 mm × 40 mm) was employed for the electrode, on which an area of 20 mm × 30 mm was used to coat with TiO_2 and an area of 20 mm × 10 mm was covered with masking tape in order to conduct an outer circuit for the electrode.

The synthesis of TiO_2 (anatase and/or rutile) by the pulse laser technique using CO_2 laser pulses was previ-

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ously described by Oyama et al. [19]. In the present work, a TiO_2/OTE electrode was prepared by the pulse laser deposition method as follows: an OTE plate was put in a 3000 ml spherical glass photoreactor having a quartz window. A reactant mixture of $TiCl_4$, H_2 and O_2 gases was introduced into the photoreactor and then was irradiated with an intense laser pulse (a Nd-YAG laser; wavelength 1,064 nm; pulse energy 1 J; pulse width 10 ns) focused with a lens (fl = 200 mm) through the quartz window. The reaction occurs via many steps; the first step is the reaction of H_2 with O_2 to form $^{\bullet}OH$ and H_2O, and the second step is hydrolysis of $TiCl_4$ by $^{\bullet}OH$ and/or H_2O. As a result, TiO_2 particles (anatase and/or rutile) were formed and deposited on the OTE glass plate. The TiO_2 crystal type (the anatase/rutile ratio) depends on the mixing ratio of $TiCl_4$, H_2 and O_2.

TiO_2/OTE plates prepared by the laser pulse method were employed in the photodegradation of amino acids. Crystal types (anatase and/or rutile) of TiO_2 particles were analyzed by XRD measurements. The anatase/rutile fraction ($I_a/(I_a + I_r)$) was determined from the intensities of the highest peaks (I_a = anatase, $2\theta = 25.28°$; I_r = rutile, $2\theta = 27.42°$) in the XRD patterns [18]. The surface and cross-section of the TiO_2/OTE plates were determined by SEM.

2.3. Photoelectrochemical degradation procedure

The photoelectrochemical degradation device has been described previously [12]. The amino acid solution (0.1 mM, 50 ml) with NaCl (0.1 M) as an electrolyte was contained in a 124 ml Pyrex glass photoreactor. The electrode assembly consisted of the anode of a TiO_2/TCO plate, the counter electrode (the cathode) of a Pt plate (20×20 mm^2) and the reference electrode of a Ag/AgCl electrode was connected to the assembly via a salt bridge. The voltage of 0.3 V was applied through a dc potentiostat; the UV illumination (12.5 mW/cm^2 at $\lambda_{max} = 360$ nm) was provided by a 75 W Toshiba Hg lamp ($\lambda > 250$ nm). The potentials at the TiO_2 electrode were measured with an electrometer. The temporal evolution of CO_2 was followed by gas chromatography using a Porapack Q column with helium as the carrier gas. The quantity of primary amine was assessed in borate buffer solution (pH 9.18) using the fluorescence emission intensity at 480 nm upon excitation of the fluorescamine/acetone mixture at 390 nm. Only primary amines can be detected with the fluorescamine reagent (supplied by Fluka); secondary and tertiary amines are not detectable by this method [15].

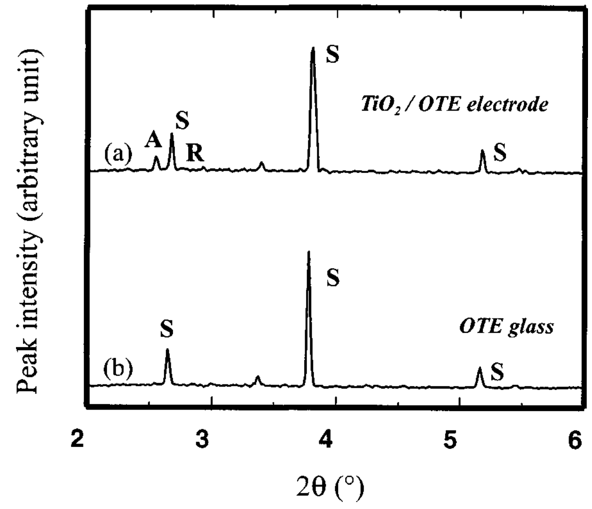

Figure 1. XRD patterns of (a) TiO_2/OTE electrode by pulse laser deposition method and (b) uncrated OTE plate (S: SnO_2, A: anatase, and R: rutile).

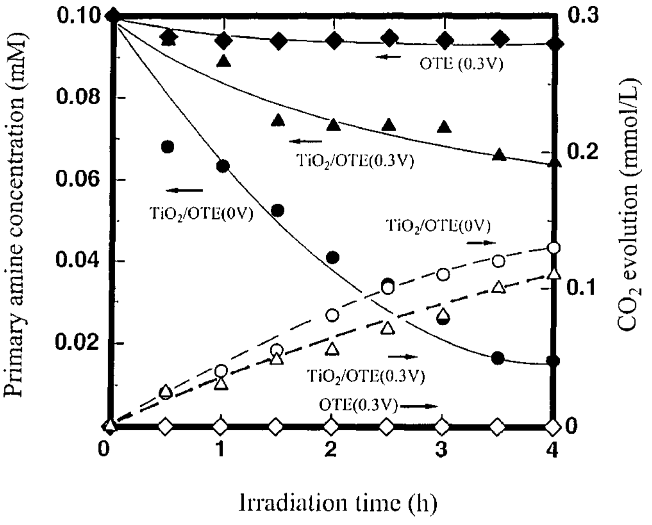

Figure 2. Disappearance of primary amine (black symbols) and CO_2 evolution (white symbols) in the photodegradation of L-α-Ala (0.1 mM) in the presence of NaCl electrolyte (0.1 M) on a TiO_2/OTE electrode with and without an anodic bias of 0.3 V. (▲, △) On a TiO_2/OTE electrode under a bias of 0.3 V; (◆, ◇) on a TiO_2-free OTE electrode under a bias of 0.3 V; and (●, ○) on a TiO_2/OTE electrode under no bias.

3. Results and discussion

It was found that only rutile TiO_2 was formed when a large excess of H_2 gas was used, while the formation of anatase TiO_2 occurred exclusively when equal amounts of H_2 and O_2 gases were present, and a TiO_2 mixture of anatase and rutile was obtained in the presence of an excess of O_2 gas. The rutile TiO_2/OTE electrode exhibited poor photocatalytic activity for the photooxidation of amino acids. Therefore, the anatase TiO_2/OTE electrode was used in this work. The TiO_2/OTE electrode prepared by the pulse laser deposition method had a homogeneous TiO_2 particulate film (film thickness: 0.5 μm, particle size: about 100 nm). The XRD pattern of the electrode is shown in figure 1.

The anatase content of TiO_2 on the electrode was determined to be 86%.

The disappearance of L-α-Ala and the evolution of CO_2 during photooxidation under UV irradiation are shown in figure 2.

Table 1
Initial disappearance rates of amino acids within 1 h.[a]

Amino acid	pI	Initial rates ($\times 10^{-7}$ mol/(l min))	
		No bias (0 V)	Applied bias (0.3 V)
L-Asp	2.77	7.9	10.5
L-Glu	3.22	7.8	8.7
L-Leu	5.98	8.8	5.3
L-α-Ala	6.00	6.0	2.0
β-Ala	6.90	6.2	2.3

[a] The experimental conditions are the same as in figure 2.

L-λ-Ala was scarcely photodecomposed and no CO_2 evolution was detected on the TiO_2-free OTE electrode even under an applied anionic bias of 0.3 V. On a TiO_2/OTE electrode without an applied bias, rapid degradation of L-α-Ala occurred under UV irradiation, and about 80% of the L-α-Ala disappeared after irradiation for 4 h. Concomitantly, the amount of CO_2 evolved increased with increasing irradiation time, and the mineralization yield of L-α-Ala into CO_2 was about 43% after 4 h of irradiation. In the previous paper [6,7], it was found that the photodegradation of organic compounds such as sodium dodecylbenzene sulfonate, sodium benzene sulfonate, 2-phenoxyethanol, ethyleneglycol, diethyleneglycol, acetic acid and formic acid on a TiO_2/OTE electrode prepared by pasting was accelerated under an applied anionic bias (0.3 V) owing to efficient prevention of the recombination of photogenerated electron/hole pairs. It should be noted that the photooxidation of L-α-Ala on the TiO_2/OTE electrode was depressed under an applied anionic bias of 0.3 V. Therefore, the effect of an applied anionic bias on the adsorption and migration of substrates onto the TiO_2 particles seems to be another important factor for the photoelectrochemical oxidation of organic compounds on the TiO_2/OTE electrodes, which depends on the nature of the substrates.

The initial photodegradation rates of several amino acids (within 1 h) on the TiO_2/OTE electrodes with and without an applied anionic bias (0.3 V) are summarized in table 1. The isoelectric points (pI) of these amino acids are also listed in table 1 in order to give insight into the migration and adsorption of amino acids onto the TiO_2/OTE electrode. Upon UV irradiation, the solution in the presence of TiO_2 particles (or TiO_2 electrodes) became acidic, the pH value of the irradiated solution shifting to 4–5 from an initially neutral or alkaline solution [21]. The effect of an applied anionic bias on the photodegradation rate is dependent upon the chemical structures of the amino acids, which are amphoteric. The acidic ones such as L-Asp (pI = 2.77) and L-Glu (pI = 3.22) exist in solution in an anionic state, and an applied bias of +0.3 V significantly accelerates the disappearance of L-Glu due to the enhancement of the migration and adsorption of amino acids to the TiO_2/OTE electrode. On the other hand, the photodegradation of amino acids with higher isoelectric points such as L-Leu (pI = 5.98), L-α-Ala (pI = 6.00) and β-Ala (pI = 6.90) was slowed down, as shown in table 1, by an applied bias of +0.3 V, since the migration and adsorption of these amino acids in their cationic state is hindered.

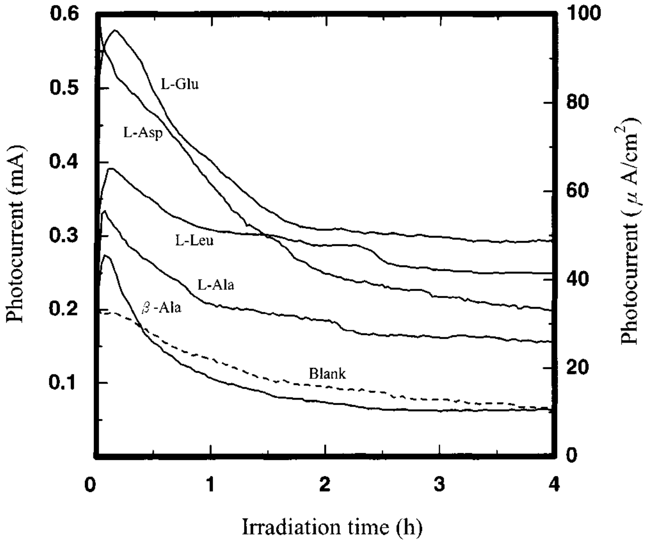

Figure 3. Evolution of photocurrent in the photoelectrodegradation of amino acids (0.1 mM) in the presence of NaCl electrolyte (0.1 M) on the TiO_2/OTE electrode under a constant bias of 0.3 V.

The temporal evolution of the photocurrent generated during the photoelectrochemical decomposition of amino acids on the TiO_2/OTE electrode under an applied anionic bias of 0.3 V (vs. Ag/AgCl reference electrode) is illustrated in figure 3. The photocurrent decreased gradually with increasing irradiation time, after an initial induction period. The actual value of photocurrent was closely related to the photodegradation rate of the substrate. The acidic amino acids L-Asp and L-Glu, with higher photodegradation rates under an applied anionic bias of 0.3 V, gave higher photocurrents, whereas the amino acids, L-Leu, L-α-Ala and β-Ala produced less photocurrent owing to their slower photodecomposition rates. The blank system in the absence of amino acids exhibited a much smaller photocurrent due to the slow photodecomposition of H_2O on the TiO_2/OTE electrode.

In summary, the amino acids can be easily degraded photoelectrochemically on a TiO_2/OTE electrode prepared by a pulse laser deposition method. As a possible kind of solar cells, the photocurrent can arise in the photodegradation of amino acids in the TiO_2/OTE electrode assembly. Under an applied positive bias, the photodegradation rate and the photocurrent are closely related to the structure of amino acids: acidic amino acids with a lower isoelectric point gave a larger photodegradation rate and more photocurrent owing to the easier migration and adsorption of the substrates onto the TiO_2/OTE electrode.

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