

Photocatalytic decomposition of L-serine and L-aspartic acid over bare and silver-deposited TiO₂

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ABSTRACT

The photocatalytic degradation of L-serine and L-aspartic acid was investigated over bare and silver-deposited TiO₂ photocatalysts suspended into aqueous solutions of various pH. The conversion of the model compounds was followed by measuring the loss of the amine function and the formation of nitrogen containing ions, such as NH₄⁺, NO₂⁻ and NO₃⁻. In addition, the total organic carbon content (TOC), the total nitrogen content (TN) and the pH were also monitored. It is demonstrated that the initial rate of the photodegradation and the concentration of the surface complexes of amino acids increase with pH in that pH range where the zwitterionic form of amino acids is the principal species. The replacement of bare TiO₂ particles with silver-deposited TiO₂ particles results in an enhancement in the efficiency of the photocatalytic reaction. The increase in the initial rate has been found to be significant for serine and moderate for aspartic acid. The results of competitive kinetic measurements used oxalic acid as scavenger for photogenerated holes and that of the diffuse reflection Fourier transformed infrared (DRIFT) spectroscopy demonstrated the disappearance of model compounds on the surface of semiconductor particles of the UV irradiated samples have also been exploited for discussing the mechanism of photocatalytic decomposition of the amino acids.

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1. Introduction

TiO₂-mediated photochemical processes have been extensively investigated due to their applicability for various purposes, such as solar energy conversion, decontamination of pollutants in air and water [1–6]. Biochemical applications of TiO₂-based photocatalytic procedure have also been proven to be promising. Elimination of microorganisms such as fungi, bacteria and virus can be performed over light excited titania particles. Moreover, the suppression of cancer cells over illuminated TiO₂ has been observed [7–9]. To achieve further progress on application of TiO₂-based photocatalysis in living organisms a better understanding of the mechanism of the light induced reactions of elemental constituents of biological systems such as amino acids is needed.

A series of systematic researches on photodegradation of amino acids over UV-excited TiO₂ particles were carried out, and some remarkable results have been reported recently [10–19]. These articles clearly demonstrate that both functional groups of the amino acids play crucial role in the photocatalytic degradation. The carboxylate group provides the formation of relatively stable surface complexes [14]. In addition, the amino group can also contribute

to the surface complex formation by hydrogen bonding or ligand exchange mechanism [20]. Another important feature of the amino acids is the opposite character of their functional groups in electron transfer reactions undergoing at the surface of TiO₂ particles excited by photons of higher energy than the band gap. The carboxylate group can transfer electron to the valence band hole, while an electron may be accepted by the amino group from the conduction band.

The fate of seventeen amino acids and that of three related compounds upon exposure to aqueous titania suspension irradiated with UV-A and UV-B has carefully been investigated, and a reasonable mechanism for photodegradation has been proposed [10]. This study has been completed by theoretical calculations provided data sets for frontier electron density and point charges of the atoms of three selected amino acids; L-alanine, L-serine and L-phenylalanine [11]. Using these data the authors have strongly suggested that the chemisorption of the amino acids occurs through the carboxylate group, and they have confirmed the mechanism suggested earlier [10]. Recently, to follow the photodecomposition of L-alanine over UV-exposed TiO₂ ¹H NMR spectroscopy has been applied, and acetic acid, formaldehyde, formic acid, pyruvic acid and acetamide as intermediates have been identified [17]. The photocatalytic decomposition and adsorption of seven kinds of amino acids on a TiO₂ surface have been investigated by ¹H NMR spectroscopy and zeta potential measurements [19]. The kinetic and

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adsorption data have indicated that the amino acids interacting with the basic terminal OH groups of TiO₂ surface preferably by their side chain decompose faster and are more readily attacked by highly oxidizing species of photocatalytic system than the other amino acids.

The adsorption and photocatalytic decomposition of the alanyl-tryptophane dipeptide and its constituent amino acids, alanine and tryptophane on TiO₂ surface have been studied very recently [21]. It has been found that the decomposition rate of the tryptophane is relatively high compared to that of alanine. Moreover, the photocatalytic degradation of the dipeptide occurs with a rate lower than that of the thryptophane and higher than that of the alanine. It has also been shown that UV irradiation of the mixture of alanine and tryptophane leads to a significant suppressing of the photodecomposition of the alanine over anatase. Mutual suppressing of the photocatalytic degradation of the oxalic acid and aspartic acid in their reaction mixture has also been observed [18]. It has been explained by a mechanism in which the primary radical product of oxalic acid ([•]COOH) abstracts hydrogen atom from the species formed by electron transfer from the conduction band (CB) of excited TiO₂ to the protonated primary amine functional group of the aspartic acid (HAsp[•]).

In this article we compare the photodegradation of the amino acids involving oxygen atom in their side group R of electron withdrawing character. To get a better understanding on the features of the adsorption and the photocatalytic degradation of these amino acids, a series of carefully designed measurements have been performed. The initial pH values of the aqueous phase have been varied in a relatively wide range. The mechanism of the light induced processes occurring at the surface of the semiconductor particles are discussed by considering the results obtained by using bare and silver-deposited photocatalysts and oxalic acid as a reactant which efficiently competes with amino acids for the photogenerated holes. These competitive kinetic measurements have clearly indicated the inhibitory effect of oxalic acid over bare TiO₂ and a significant decrease in the inhibition over Ag-TiO₂. To study the surface complexes formed on TiO₂ and on Ag-TiO₂ and to follow the changes in the concentration of the surface complexes upon illumination diffuse reflection Fourier transformed infrared (DRIFT) spectroscopic measurements have been carried out, and the results of these investigations have also been exploited for supporting the mechanism involving primary electron transfer processes followed by reaction sequences and competitive steps.

2. Experimental

2.1. Materials

The amino acids and other chemicals used in this study were analytical reagent grade and were purchased from commercial sources. Doubly distilled and then doubly deionized and ultra-filtered water from Millipore Q system was used to prepare the stock solutions and the samples. Degussa titania (P25: 70% anatase, 30% rutile; with a surface area of 50 m² g⁻¹) was used as bare photocatalyst in the experiments. The silver-deposited TiO₂ was prepared by photocatalytic reduction of AgNO₃ or Ag₂SO₄ (concentration of Ag⁺ was 10⁻⁴ and 2 × 10⁻⁴ M) prior to use it as photocatalyst for the degradation of amino acids. The suspension containing 1 g dm⁻³ TiO₂ was irradiated in the photoreactor used for photocatalytic experiments. The color of the suspension was observed to be changed from white to pale-brown indicating the reduction of Ag⁺ and the deposition of silver on TiO₂. The photodeposition was completed within 40 min, which was checked by the procedure described in details elsewhere [22]. The irradiated mixture was centrifuged and then washed by high purity water given above. These procedures were repeated at least three times

to obtain nitrate or sulfate free washing water. Then Ag-TiO₂ photocatalyst was dried at 120 °C and investigated by scanning electron microscope (SEM) and Energy Dispersive X-Ray Analysis (EDAX) instrument: XL 30 ESEM (Philips). The images of Ag-TiO₂ samples demonstrated non-homogeneously distributed bright spots at the surface of the TiO₂ particles which were assigned as silver clusters by EDAX investigations (See supplementary: Figs. S1–S3). The silver content of the catalysts was ~1 m/m%.

2.2. Adsorption measurements

The adsorption studies of amino acids and oxalic acid were performed in dark. The initial concentration of the investigated amino acids was adjusted to different values between 0.075 mM and 1 mM, which was checked by the fluorescence method and TOC measurements detailed in Section 2.4. 200 cm³ of the solutions were transferred into a 500 cm³ flask and then 200 mg TiO₂ was added to solutions and dispersed by sonication. The suspensions were continuously stirred, and under this procedure aliquot samples were taken from suspensions after various time intervals. The samples were filtered as given in Section 2.4. The concentration of amino acids in the aqueous phase was measured by the fluorescence method and measuring the TOC content. It decreased continuously until the equilibrium concentration has been achieved. After 30 min stirring the concentration of amino acid was found to be constant in the homogeneous solutions filtered from the suspensions (Fig. S4). The residuals of the suspensions were also filtered and then the solid phases were dried in vacuum. These solid samples were used for DRIFT spectroscopy to characterize the surface complex of the amino acids. Same procedures were used to prepare Ag-TiO₂-based samples from suspension equilibrated in dark and from reaction mixtures irradiated over TiO₂ or Ag-TiO₂ particles with various time intervals. It is important to note that the adsorption isotherms clearly indicate that adsorption cannot proceed beyond monolayer coverage up to 1 mM solution concentration (see Fig. S5).

2.3. Photocatalytic experiments

A medium scale (2.8 dm³) photoreactor developed for irradiation of heterogeneous reaction mixture circulated by continuously fed air or other gases with a flow rate up to 50 dm³ h⁻¹ described elsewhere [22] was used for photocatalytic decomposition of amino acids. The experiments of the present study were performed by 40 dm³ h⁻¹ flow rate of air. The photon flux of the internal light source (40 W, λ_{max} ~ 350 nm) was checked by chemical actinometry using tris(oxalato)iron(III) complex as light sensitive material. The spectrum of the light source is given in our recently published article [23]. The initial volume of the suspension containing TiO₂ or silver-deposited TiO₂ in 1 g dm⁻³ concentration was set to be 2.8 dm³ prior to irradiation in all experiments. The initial pH of the reaction mixture was adjusted using HClO₄, H₂SO₄ and NaOH of pure reagent grade.

2.4. Sampling and analytical procedures

Before and during the continuous illumination aliquot samples were taken from the reaction mixture through a septum with a syringe. Samples containing TiO₂ were filtered through a Millipore Millex-LCR PTFE 0.45 μm membrane filter.

The pH of the aqueous phase of the reaction mixture was measured by SEN Tix 41 electrode. The concentration of the amine function of serine and aspartic acid was determined by fluorecamine [11]. The luminescence spectra originated from the product of the reaction of amino acid and fluorecamine (peaking at 480 nm, λ_{exc} = 393 nm) were measured by a PerkinElmer LS 50 B

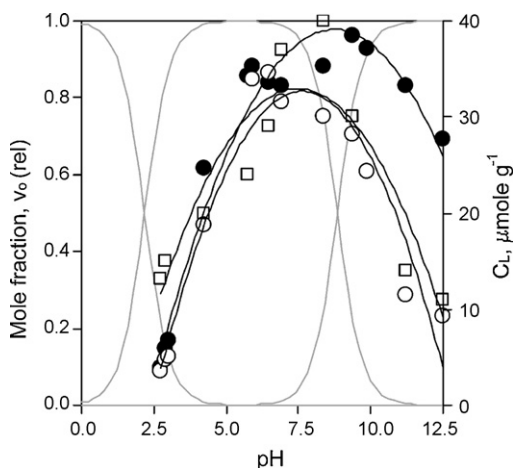


Fig. 1. The pH dependence of partial mole fraction of serine species (given by grey lines, from left to right; SerH⁺, Ser, and Ser⁻) and that of the relative initial rate of loss of the amine function (●) and NH₄⁺ formation (○) upon irradiation of the TiO₂ containing suspension and that of the equilibrium concentration of the surface complex measured in dark at 1 mM analytical concentration of serine (□): *c*₀ (serine) was 1 mM and the TiO₂ concentration was 1 g dm⁻³ in these experiments. The initial rates have been determined by polynomial fitting to the concentration vs. time data up to 300 min irradiation as it is demonstrated in Fig. 2 and have been normalized to *v*₀ (serine) = 7.5 × 10⁻⁶ M min⁻¹. The trend lines for data depicted by (●) (○) (□) have been obtained by second order polynomial fitting (black lines).

fluorimeter. The concentration of nitrite and nitrate ions was determined by spectrophotometric method using α-naphthylamine and sulfanilic acid in acidic conditions (CH₃COOH) and using 2,6-dimethylphenyl reagent in acidic conditions (H₂SO₄), respectively. The concentration of NH₄⁺ formed was measured by spectrophotometric method using sodium salicylate, nitropussid sodium, potassium citrate tribasic hydrate, sodium dichloroisocyanurate reagents in alkaline conditions. The mineralization of amino acids was followed by measuring the total organic carbon (TOC) and total nitrogen (TN) concentration, utilizing a Thermo Electron Corporation TOC-TN 1200 apparatus. The concentration of the oxalic acid was determined by classical permanganometry using the aliquot of the clear liquid sample as given in our paper published earlier [18].

IR spectroscopic measurements of surface-bounded reactants have been carried out by Bruker Equinox 55 FTS spectrometer using Harrick DRIFT adapter (it is of the so-called “praying monk” design) and DTGS detector. Reflected radiation was collected at ~50% efficiency. 50 ± 1 wt% sample was dispersed in KBr and 1024 scans were co-added at a resolution of 2 cm⁻¹, using KBr powder as a background.

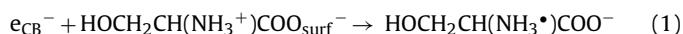
3. Results and discussion

3.1. Photodecomposition of L-serine

The photodegradation of L-serine has been investigated in the pH range of 2.5–12.5. Within this interval the zwitterionic form (HOCH₂CH(NH₃⁺)COO⁻; 2 < pH < 9.1) and the completely deprotonated form (HOCH₂CH(NH₂)COO⁻; 9.1 < pH) of the amino acid appear as dominant species. The initial rate of the loss of amine function and that of NH₄⁺ formation significantly increases with pH in the first pH range. Both reaction rates significantly decrease over pH 9. A similar trend has been observed for the concentration of surface complex vs. pH data (Fig. 1). The correlation between kinetic and equilibrium data indicates the crucial role of the surface complexes in the photocatalytic decomposition of serine. The surface charge of TiO₂ particles decreases with increasing pH. It changes from positive to negative at the isoelectric point (pH 6.25 [3]). It should be mentioned that this point can be shifted by surface

complex as it has been found for the TiO₂-aspartic acid suspension [19]. The electrostatic interaction of -NH₃⁺ and -COO⁻, respectively with TiO₂ surface should oppositely be changed with pH: the attraction becomes dominant for -NH₃⁺ and repulsion is expected for -COO⁻ over isoelectric point. Hence a significant increase in the concentration of surface complex with pH can partially be attributed to strengthening the interaction between the surface and the protonated amino group. This interaction is negligible over pH = p*K*_{a2}(serine) = 9.1, and thus, the electrostatic repulsion between the surface and the negatively charged form of serine increases. It should be noted that the rate of NH₄⁺ formation starts to deviate from that of loss of amine function at pH ~ 7, and the difference between them increases monotonously with pH. These findings may be explained by: (i) increasing probability of hydroxyl radical attack on serine with pH in alkaline reaction mixtures, (ii) an increase in the photooxidation efficiency of NH₄⁺/NH₃ with pH [24], and (iii) carrying out some ammonia from the alkaline reaction mixture by the continuously fed air.

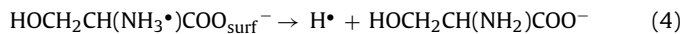
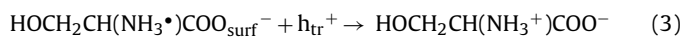
The first step of the reaction sequence leading to the loss of amine function is the primary electron transfer from the conduction band of the excited TiO₂ particle:



It is well documented that the molecular oxygen is an efficient acceptor for conduction band electron, and therefore the reaction (1) competes with reaction (2) in aerobic condition:



The products of reactions (1) and (2) are negatively charged. Hence, in acidic condition, at pH lower than the isoelectric point of TiO₂, their charge is opposite to that of the surface of semiconductor particles. It means that there is an attraction between the product of reactions (1) and (2) and the surface. This effect promotes the formation of surface complex and restrains the migration of the primary products to the bulk of aqueous phase. Hence it increases the probability of the further reactions of radicals occurring at the surface. The possible reactions of the radical HOCH₂CH(NH₃[•])COO⁻ are the direct backward electron transfer to the hole trapped at the surface of the semiconductor and the indirect electron transfer to hole through the formation of hydrogen radical:



Thus, the release of ammonia:



competes with reactions (3) and (4), respectively. The rate coefficients of bimolecular reaction of hydrogen atoms with serine and with the other amino acid investigated in this work are small in aqueous solution (*k*_{serineH⁺} = 3.6 × 10⁶ M⁻¹ s⁻¹, *k*_{asparticH⁺} = 7 × 10⁵ M⁻¹ s⁻¹, *k*_{aspartic⁻} = 2.7 × 10⁶ M⁻¹ s⁻¹ [25]), hence an efficient attack by H[•] on these amino acids can be excluded. However other reactions of hydrogen atoms can also take place in the presence suitable reactants.

Several characteristic changes, such as the disappearance of amine function of serine, the formation of ammonium ion along with the increase of pH of the aqueous phase upon irradiation of acidic reaction mixture are depicted in Fig. 2. The differences between the initial TOC (TOC₀) and that of measured after irradiation (TOC_t), which are expected to be equivalent to the formation of CO₂, are also given in this figure. The initial rate of the formation of this species has been estimated by fitting a second order polynomial to the experimental data. The reaction rate obtained by this

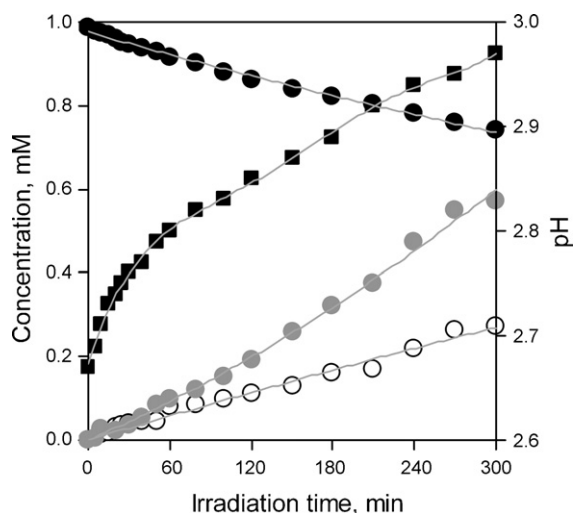


Fig. 2. Characteristic changes observed under photocatalytic decomposition of serine (c_0 (serine) = 1 mM) in acidic aqueous suspension of TiO_2 (1 g dm^{-3}): concentration of serine (●), ammonium ion (○), $\text{TOC}_0\text{-TOC}_t$ (●) and the pH (■). The trend lines (grey) have been obtained by polynomial fitting.

Table 1

Initial rate (v_0) for various species determined by polynomial fitting to data obtained by photocatalytic decomposition of serine over bare and silver-deposited P25 TiO_2 (1 g dm^{-3}); initial concentration of serine was 1 mM in these experiments.

Species	v_0 (M min^{-1})		v_0 (Ag- TiO_2)/ v_0 (TiO_2)
	TiO_2 (pH ₀ 2.68)	Ag- TiO_2 (pH ₀ 2.76)	
- NH_2	$(9.9 \pm 0.3) \times 10^{-7}$	$(7.4 \pm 0.3) \times 10^{-6}$	7.5
NH_4^+	$(9.8 \pm 0.3) \times 10^{-7}$	$(6.6 \pm 0.2) \times 10^{-6}$	6.7
$\text{TOC}_0\text{-TOC}_t$	$(1.4 \pm 0.1) \times 10^{-6}$	$(10.9 \pm 0.7) \times 10^{-6}$	7.9

procedure is higher than the rate of the loss of amine function. It should be noted that the latter value is identical with the initial rate of NH_4^+ formation, considering the experimental errors (Table 1).

The photocatalytic decomposition of serine has been found to be more rapid over silver-deposited TiO_2 than over bare TiO_2 although the difference between the initial pH values of the aqueous phases was only 0.08 (Fig. 3 and Table 1). Such a significant increase in

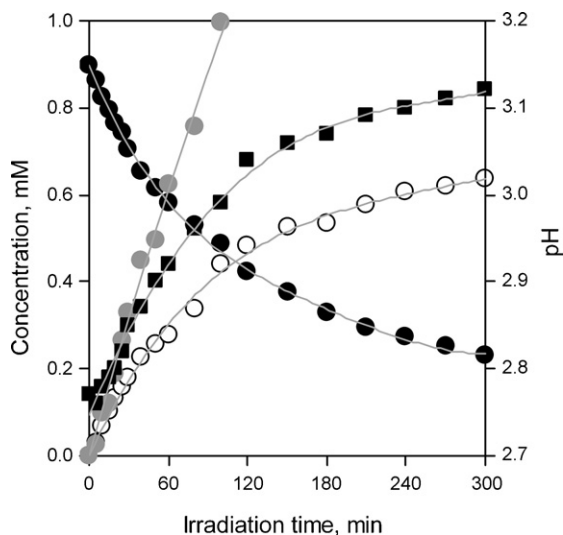


Fig. 3. Characteristic changes during photodecomposition of serine (c_0 (serine) = 1 mM) in acidic aqueous suspension of Ag- TiO_2 (1 g dm^{-3}): concentration of serine (●) and ammonium ion (○), $\text{TOC}_0\text{-TOC}_t$ (●) and the increase of pH (■). The trend lines (grey) have been obtained by polynomial fitting.

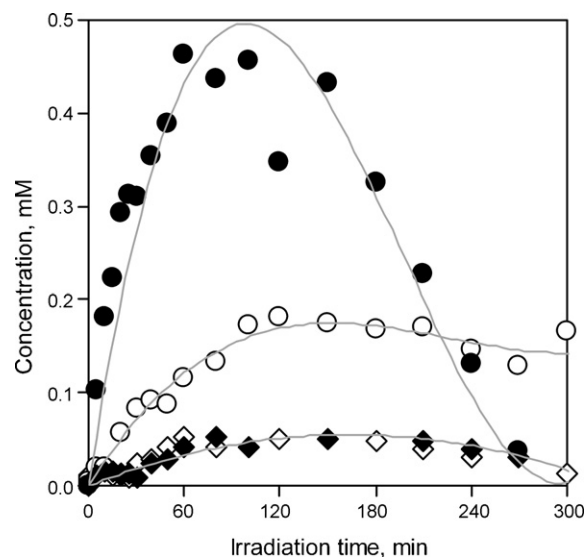


Fig. 4. Changes in carbon content (CCOI) and nitrogen content (DNB) of intermediates formed under photocatalytic decomposition of serine over TiO_2 and Ag- TiO_2 , respectively: (○) CCOI using TiO_2 , (●) CCOI using Ag- TiO_2 , (◇) DNB using TiO_2 and (◆) DNB using Ag- TiO_2 . The trend lines (grey) have been obtained by polynomial fitting.

reaction rate (~ 7 times) has not been observed under photocatalytic decomposition of aspartic acid. The increase in the rate of all reactions connected with the primary electron transfer processes occurring at the surface of the excited semiconductor particles is identical (within the experimental error). This experimental fact proves that the light initiated charge separation, which is crucial for these primary electron transfer processes, is more efficient at the surface of Ag- TiO_2 than at the surface of bare TiO_2 .

Moreover the figures in Table 1 also demonstrate that the decrease of TOC is significantly faster than that of NH_4^+ formation over both photocatalyst. The difference between them can partly be explained by the efficient scavenging of conduction band electrons with O_2 (reaction (2)). This process competes with the electron transfer to the amino acid (reaction (1)), and thus it can reduce the formation of $\text{NH}_3/\text{NH}_4^+$. On the other hand, the further reactions of $\text{O}_2^{\bullet-}$ may contribute to the decrease in the concentration of TOC.

The difference between TOC and the carbon content of serine, which can be assigned as carbon content of organic intermediates (CCOI), are compared in Fig. 4. The defect of nitrogen balances (DNB) obtained by subtracting the sum of measured nitrogen containing species (amine function of serine, NH_4^+ , NO_2^- , NO_3^-) from the initial nitrogen content (initial concentration of the serine) are also displayed on this figure. The features of the dashed trend lines obtained by polynomial fitting are typical for intermediates. The temporal changes of DNB estimated for bare and silver-deposited TiO_2 are identical and the apparent concentration of these species are relatively small compared to that of CCOI. Moreover, a significant difference is obtained for the two series of CCOI data. Namely, these species are formed more rapidly over Ag- TiO_2 particles than over TiO_2 . The relatively high CCOI, especially over Ag- TiO_2 , is a consequence of the very efficient NH_3 formation that leads to carbon containing intermediates of low photodecomposition rate.

3.2. Photodecomposition of L-aspartic acid

We have recently reported on some initial studies on the photocatalytic decomposition of aspartic acid in aqueous TiO_2 and Ag- TiO_2 dispersions, respectively [18]. It has been pointed out that

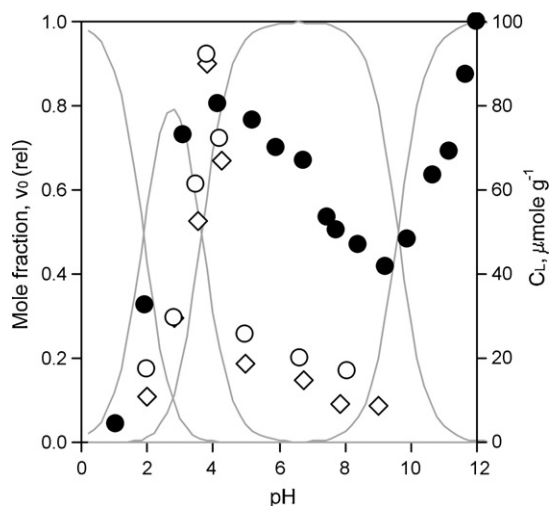


Fig. 5. Comparison of the pH dependence of photocatalytic decomposition (●) and that of the adsorption characteristics (○, ◇) of aspartic acid with the partial mole fraction of various species of aspartic acid appearing in aqueous solution (given by grey lines, from left to right; AspH^+ , Asp , Asp^- and Asp^{2-}). The equilibrium concentration of the surface complex of aspartic acid was measured at 1×10^{-3} M (○) and 5×10^{-4} M (◇) analytical concentration respectively. The initial concentration of aspartic acid and the concentration of TiO_2 were c_0 (aspartic acid) = 2.5×10^{-4} M and 1 g dm^{-3} , respectively in the photocatalytic experiments. The initial rate of loss of amine function related to the highest value measured at pH 12 ($v_0 = 4.5 \times 10^{-6} \text{ M min}^{-1}$).

the rate of loss of the amine function and the fate of the primary product of this light initiated electron transfer are rather different in acidic and alkaline reaction mixtures. As a continuation of these studies we have investigated the rate of loss of amine function and the change of adsorption characteristics of aspartic acid with the pH up to 12.

The change in the initial rate of photocatalytic reaction, the amount of substrate adsorbed on the surface of P25 TiO_2 particles in equilibrium and the distribution of the various forms of aspartic acid as functions of pH are compared in Fig. 5. A significant increase in the rate of photodegradation is observed in the narrow pH range, where the zwitterionic form is the dominant species. On the other hand, at pH values higher than 4, where the monoanionic form (Asp^-) has the highest mole fraction, the rate of light induced reaction, similarly to that observed for photocatalytic degradation of serine, decreases with increasing pH. Finally, the rate of loss of the amine function increases rapidly with pH in strongly alkaline solutions, where the mole fraction of Asp^{2-} is higher than that of the other species.

The quantity of adsorbed amino acid in equilibrium are peaking at pH 4, as it was found by other researchers [19]. The local maximum of the concentration of the surface complex and that of the initial rate of the photocatalytic degradation of aspartic acid appear at the same pH value. This clearly indicates the significant role of the surface complex in the photodegradation, as it has been pointed out for serine. It is important to note, that similar trends of pH dependence of reaction rate and that of the equilibrium concentration of surface complex, respectively have been found for both compounds in the pH range where their zwitterionic and monoanionic forms are the dominant species ($2.5 < \text{pH} < 14$ for serine and $1.6 < \text{pH} < 9.8$ for aspartic acid). However, at $\text{pH} > 9.8$, where $^- \text{OOC}-\text{CH}_2-\text{CH}(\text{NH}_2)\text{COO}^-$ is the principal species the initial rate of photocatalytic degradation of aspartic acid monotonously increases, that can be explained by a change in the mechanism. It is reasonable to assume the crucial role of hydroxyl radicals within pH range of 9.8–12, where the dominance of unprotonated hydroxyl radical $\cdot\text{O}^-$ cannot be excluded because $\text{p}K_a(\cdot\text{OH}) = 11.8$ [26].

Table 2

Initial rate of the light induced decomposition (v_0) of serine and aspartic acid measured using bare and silver-deposited TiO_2 , respectively; total initial concentration of the amino acids was adjusted to 1 mM in these experiments.

Amino acid	v_0 (M min^{-1})		$v_0(\text{Ag-TiO}_2)/v_0(\text{TiO}_2)$	Initial pH
	TiO_2	Ag- TiO_2		
Serine	9.9×10^{-7}	6.6×10^{-6}	6.7	2.68 (TiO_2)
				2.76 (Ag- TiO_2)
Aspartic acid	6.6×10^{-6}	9.7×10^{-6}	1.5	3.40 (TiO_2)
				3.40 (Ag- TiO_2)

The estimated error of the rate constants is ~8%.

The initial rate of photodecomposition of aspartic acid determined using silver-deposited TiO_2 is higher than that of measured over bare photocatalyst (Table 2). The relative change in v_0 is significantly smaller than that observed for serine. Comparing the pH dependence of the photodegradation rate of the investigated amino acids and the enhancement of their decomposition rate due to the replacement of TiO_2 with Ag- TiO_2 we can state that: (i) Photodegradation rate of these amino acids and the equilibrium concentration of their surface complexes increases with pH within the pH range of zwitterionic forms. (ii) These characteristics decrease for both compounds at higher pH values. (iii) The influence of silver-deposited photocatalyst is small for photodegradation of aspartic acid, while the enhancement in the reaction rate induced by silver clusters is very significant for serine.

To elucidate the origin of these differences and similarities and to get a better understanding on the mechanism of photoinduced reactions occurring at the semiconductor surface competitive kinetic measurements using oxalic acid as typical hole scavengers and DRIFT spectroscopic investigations of surface complexes using TiO_2 and Ag- TiO_2 samples originated from the reaction mixtures prior to irradiation and after irradiation of various time intervals have been carried out.

3.3. Inhibition of amino acid photodecomposition by oxalic acid: kinetic and DRIFT spectroscopic studies

In a recent paper we demonstrated that oxalic acid as efficient hole scavenger significantly suppresses the photocatalytic decomposition of aspartic acid occurring over light excited TiO_2 particles [18]. Moreover, photooxidation of oxalic acid has also slowed down in the presence of aspartic acid. Similar phenomenon has been observed during photocatalytic degradation of serine, as demonstrated by Fig. 6.

As it has been shown in Section 3.1, the rate of photocatalytic decomposition of serine strongly depends on pH in that range where the zwitterionic form is the dominant species. Namely, the rate of the light induced reaction of serine increases more than ten times with pH between 2 and 8. Thus, addition of oxalic acid to the reaction mixture containing amino acid and TiO_2 results in a decrease in pH. This change in pH leads to a considerable decrease in the photodecomposition rate of serine. To eliminate this pH effect the initial pH of the reaction mixture containing only serine has been adjusted by addition of suitable amount of sulfuric acid to achieve the pH value measured for reaction mixture containing serine and oxalic acid. Comparison of the disappearance of amine function in time upon UV excitation of both reaction mixtures clearly demonstrates the inhibitory effect of oxalic acid at early stage of the photolysis (Fig. 7). The initial decomposition rate of serine is significantly higher in reaction mixture *a* than in reaction mixture *b*. However, as the conversion of oxalic acid to CO_2 has nearly been completed the pH starts to increase due to the formation of ammonia from serine.

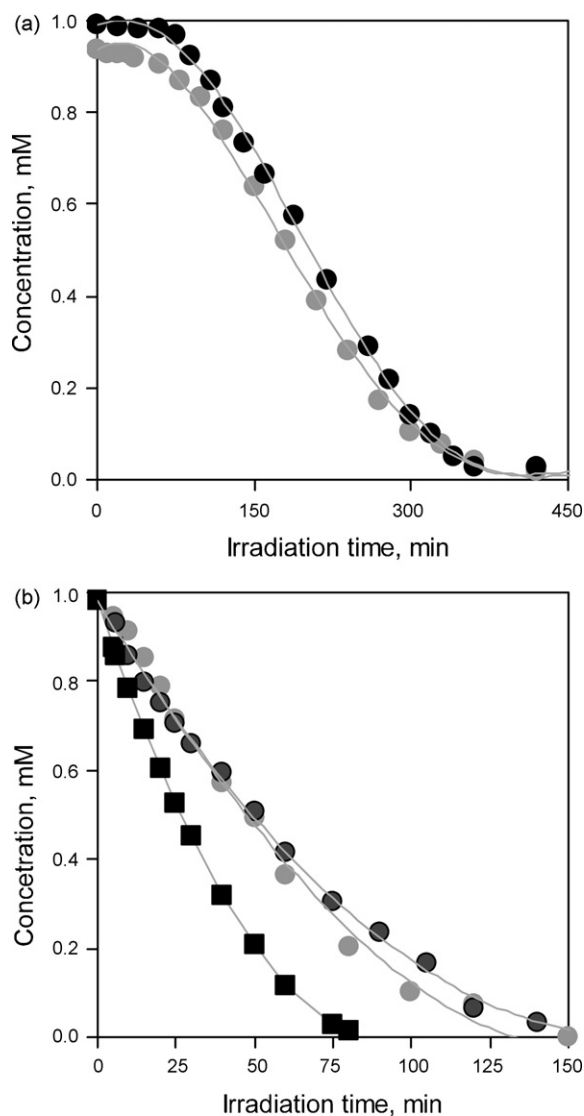
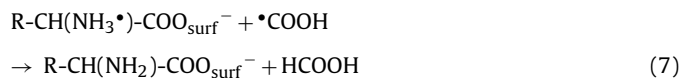


Fig. 6. Change in the concentration of amino acid (a) and oxalic acid (b) under irradiation of various reaction mixtures containing TiO_2 (1 g dm^{-3}): (○) 1 mM serine and 1 mM oxalic acid; (●) 1 mM aspartic acid and 1 mM oxalic acid; (■) 1 mM oxalic acid. The trend lines (grey) have been obtained by polynomial fitting.

Under prolonged irradiation the two reaction rates become to be reversed. Namely, the rate of loss of the amine function and the pH for reaction mixture *b* become significantly higher than those of reaction mixture *a*. It is important to note that decomposition of serine starts after ~ 200 min irradiation in the reaction mixture *c* indicating the higher concentration of oxalic acid the longer period inhibition of serine.

The results of competitive kinetic studies using either bare TiO_2 (Fig. 6) or silver-deposited TiO_2 (Fig. 8) demonstrate that a very similar inhibition in the photocatalytic decomposition of serine and aspartic acid occurs in the presence of oxalic acid. Hence, we can conclude that the release of ammonia from α -carbon atom of L-serine or L-aspartic acid (reaction (6)) competes with the following reaction, which is responsible for the mutual retardation of the photocatalytic decomposition of both reactants [18].



A strong influence of aspartic acid on photodegradation of oxalic acid is manifested by silver-deposited TiO_2 . It may be interpreted

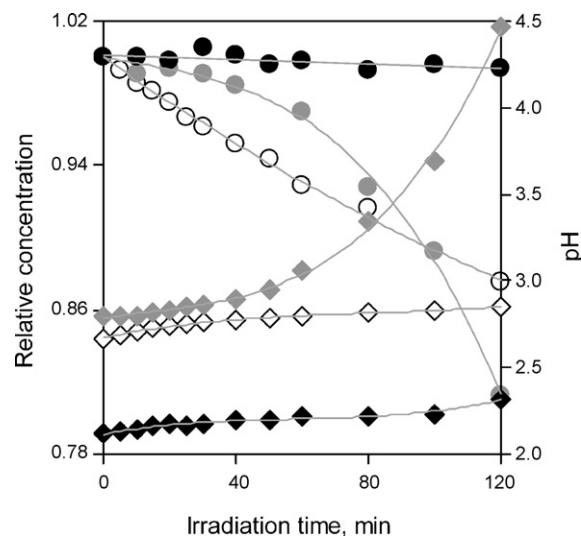


Fig. 7. The early stage of photocatalytic degradation of serine and the change of pH upon irradiation of the reaction mixtures containing P25 TiO_2 (1 g dm^{-3}): (a) c_0 (serine) = 1 mM and pH adjusted by H_2SO_4 given by empty symbols, (b) c_0 (serine) = 1 mM and c_0 (oxalic acid) = 1 mM given by grey symbols and (c) c_0 (serine) = 1 mM and c_0 (oxalic acid) = 5 mM given by black symbols. Circles represent the concentration of serine, while diamonds show the pH values. The trend lines (grey) have been obtained by polynomial fitting.

by its two carboxylate groups that efficiently compete with oxalic acid for holes or surface bonded hydroxyl radicals. Another plausible explanation is that, the L-aspartic acid requires more highly oxidizing species, such as $h\nu_{\text{VB}}^+$, *OH , $\text{O}_2^{\bullet-}$, for its complete mineralization than serine due to the higher amount of carbon atoms of L-aspartic acid molecule.

We have also investigated the surface complex formation of amino acids and the competitive surface complex formation between amino acids and oxalic acid. First, we have compared the IR spectra of model substances bounded to bare and silver-deposited TiO_2 (Fig. S6). These spectra indicate the same surface complex formation on the two photocatalysts possessing rather different photocatalytic efficiencies. The features of oxalic acid spectra are very similar to that of reported earlier [27,28] suggesting the appearance of three surface complexes of various Langmuir stability constants, K_L ($\log(K_L/M)$) = 6.38, 4.48 and 3.48 respectively). The most stable surface species has been assigned as a five-ring chelate complex. The next is bonded to the surface by one Ti–O bond and by hydrogen bond to one of the surface hydroxyl groups and the third forms the surface complex by one Ti–O bond only. The analysis of the spectra of surface complexes of the two amino acids in detail was not in the scope of this research. However, it was assumed that the competitive surface complex formation and the mutual effect of amino acid and oxalic acid on their photocatalytic decomposition could be demonstrated by these spectra. It is important to note, that the spectrum of aspartic acid adsorbed on TiO_2 surface shows more complex feature than that of reported by other authors earlier [29].

A significant difference is observed between the spectrum of the mixture of oxalic acid and aspartic acid prepared by TiO_2 and that of prepared by Ag- TiO_2 , respectively. The former spectrum (spectrum *a* in Fig. 9I) can be reproduced by a weighted superposition of the spectrum of pure oxalic acid and that of pure aspartic acid (spectra A and C). On the other hand, the relative intensity of the strongest band peaking at 1723 cm^{-1} in the spectrum of the surface complexes formed on Ag- TiO_2 in the reaction mixture of oxalic acid and aspartic acid is irradiated, which is characteristic for the surface complexes of weakly bonded oxalic acid, is smaller than that of expected by superposition of spectra B and D. In addition all bands of aspartic acid (1608 , 1513 , 1406 cm^{-1}) show higher rela-

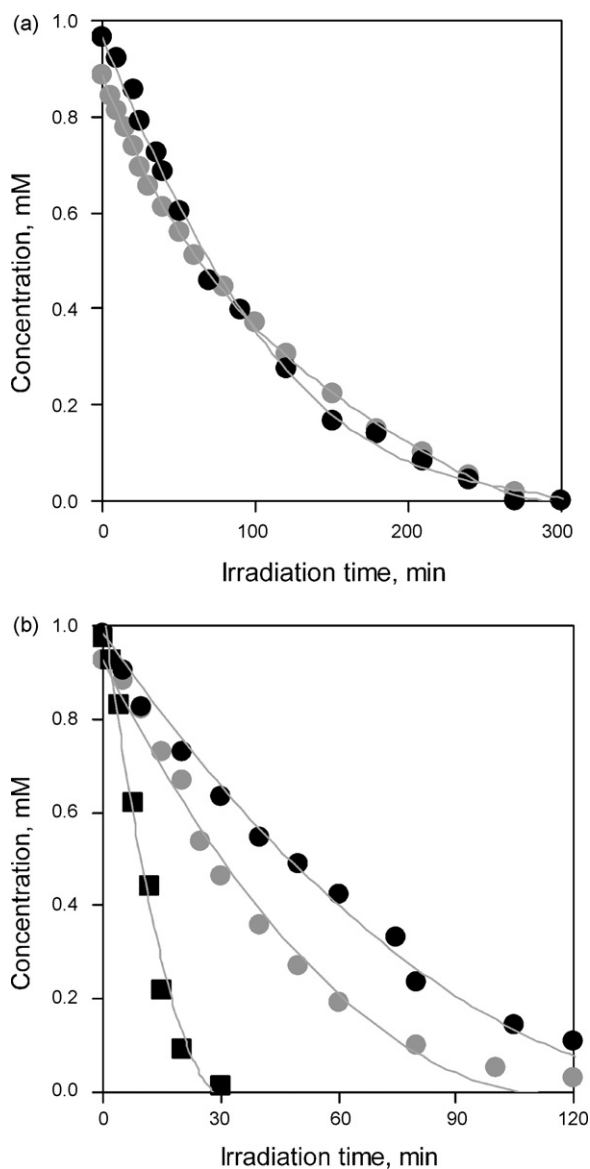


Fig. 8. Change in the concentration of amino acid (a) and oxalic acid (b) under irradiation of various reaction mixtures containing Ag-TiO₂ (1 g dm⁻³): (●) 1 mM serine and 1 mM oxalic acid; (●) 1 mM aspartic acid and 1 mM oxalic acid; (■) 1 mM oxalic acid. The trend lines (grey) have been obtained by polynomial fitting.

tive intensity in spectrum a-II, than in the spectrum of a-I in Fig. 9. Very similar differences can be seen in the spectra of the mixtures of oxalic acid and serine (compare a spectra in Fig. S7 I and II).

These observations suggest that the formation of weakly bonded surface complex of oxalic acid on Ag-TiO₂ is suppressed by aspartic acid and serine, respectively. This competitive surface complex formation may explain the experimental fact, whereas the photocatalytic decomposition of oxalic acid over UV irradiated Ag-TiO₂ is significantly restrained by aspartic acid. On the other hand, no apparent induction period is observed in the photocatalytic decomposition of aspartic acid or serine upon UV excited Ag-TiO₂ in the presence of oxalic acid (see Fig. 8a).

4. On the mechanism of the photocatalytic degradation

As it has been suggested in Section 3.2, the primary electron transfer reaction of the surface complexes can initiate the photo-

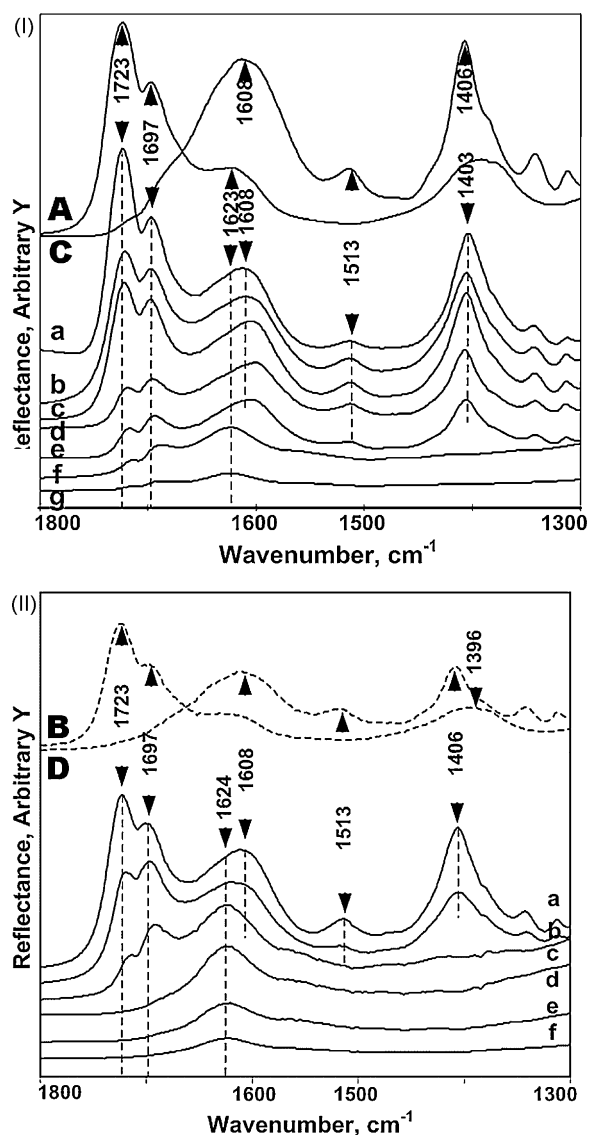
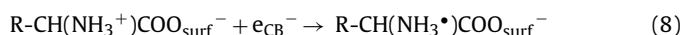
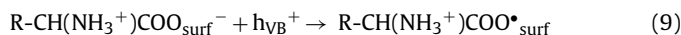


Fig. 9. Comparison of the DRIFT spectra of oxalic acid and aspartic acid and those of obtained from their reaction mixture irradiated over bare (I) and silver-deposited (II) P25 TiO₂ by various time intervals. Notation: oxalic acid (A) and aspartic acid (C) and samples irradiated, $t=0, 40, 80, 120, 170, 270, 300$ min (a–g spectra) in I, oxalic acid (B) and aspartic acid (D), and samples irradiated $t=0, 60, 120, 180, 240, 300$ min (a–f spectra) in II. Concentration of acids was 1 mM and the concentration of photocatalysts was 1 g dm⁻³ in the suspensions.

catalytic degradation of amino acids.

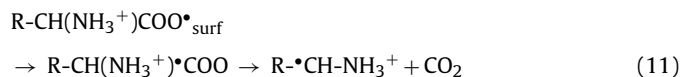


In principle, the carboxylic group of the surface-bound amino acid can readily transfer electron to the photogenerated hole.



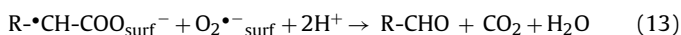
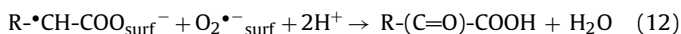
It is reasonable to suppose that this reaction efficiently competes with the backward electron transfers from R-CH(NH₃[•])COO_{surf}⁻ radical (reaction (4) and reactions (5) and (6) respectively), because the concentration of the surface complex of amino acid must be higher than that of the radical formed by reaction (8). Thus, the primary electron transfer steps mutually contribute to the consumption of the suitable constituent of {e⁻;h⁺} pairs and to the decrease of the efficiency of the backward electron transfers and to the release of the small molecule from the product of reactions (8)

and (9):



It has been pointed out (Section 3.2) that the loss of amine function from serine occurs with slightly lower reaction rate than the CO₂ formation. It should be noted that a very similar relation was reported by Hidaka et al. for the first order rate constants of these reactions [10]. Moreover, the rate of CO₂ formation was found to be slightly higher ($1.1 \times 10^{-5} \text{ M min}^{-1}$) than that of the loss of amine function from aspartic acid ($6.6 \times 10^{-6} \text{ M min}^{-1}$) [18]. Oxygen molecules, the concentration of which was kept to be constant in our experiments by the continuously fed air, are readily reduced by CB electrons. Thus, the reaction (8) must compete with the reaction (2), which explains the slightly lower reaction rate of the loss of amine function than that of CO₂ formation.

The reactivity of primary radicals R·CH-COO⁻ and R·CH-NH₃⁺ strongly depends on the nature of R group and the pH of the bulk of aqueous phase of the reaction mixture. The pH determines the surface charge of semiconductor particles and the distribution of protonated and deprotonated form of radicals in homogeneous aqueous phase. Therefore it influences the surface complex formation of radicals. The radical produced by reaction (2) appears as deprotonated or protonated species (O₂^{•-}, HO₂[•]) in slightly acidic conditions (pK=4.8 [30]) in the aqueous phase. The anionic form is preferably adsorbed on the semiconductor surface of positively charged [31]. This radical can react with R·CH-COO⁻ at the surface and the appearance of the suitable keto acid and aldehyde can be explained by the following reactions:



The rate of these reactions and that of reactions (10) and (11) may be influenced by the characteristics of TiO₂ particles, such as crystalline structure, size and size distribution of particles, the impurities (doped elements) of the crystals and the elements deposited on the surface in relatively low concentrations. Thus, these competitions can be regarded as the sources of the different time profiles of intermediates formed upon photocatalytic degradation of L-alanine over various TiO₂ particles [17]. The products of reactions (12) and (13) have higher photocatalytic reactivity for serine than for aspartic acid. This shows that higher molecular weight and more complicated structure of R significantly higher the yield of TOC content of intermediates.

We have demonstrated that the photocatalytic decomposition of serine decreases with pH over pH 9.8, where HO-CH₂-CH(NH₂)COO⁻ is the principal species (Fig. 1). In contrast, the rate of photocatalytic degradation of aspartic acid monotonously increases over pH 9.8, where ⁻OOC-CH₂-CH(NH₂)COO⁻ is the dominant species (Fig. 5). We strongly suggest that it is the consequence of a change in the mechanism due to the followings: (i) surface complex formation hindered by the strong electrostatic repulsion between the surface of the semiconductor particles and the double-charged negative ion (Asp²⁻), and therefore the primary electron transfer reactions (8) and (9) must be very slow, (ii) electron transfer is not preferred to the unprotonated amino group (-NH₂), (iii) the efficiency of hydroxyl radical formation at the surface increases with pH, (iv) the hydroxyl radical attack becomes the main primary step resulting in the decomposition of the amino acid.

Using silver-deposited TiO₂ instead of bare photocatalyst the efficiency of reactions (8) and (9) is significantly enhanced because the electron promoted to conduction band (e_{CB}⁻) and the hole left in the valence band (h_{VB}⁺) are significantly separated due to the electron trapping by silver clusters [21]. Thus the probability of recombination of {e⁻;h⁺} is significantly lower in Ag-TiO₂ than in bare TiO₂. We have observed small increase in the rate of loss of the amine function for aspartic acid, while considerable increase in the rate of this reaction has been found for serine. Due to the enhancement in the efficiency of the primary electron transfer steps (reactions (8) and (9)) a significant accumulation of the carbon containing intermediates is expected in the early stage of the photocatalytic decomposition of serine as it is demonstrated by Fig. 4.

The results of competitive kinetic experiments using oxalic acid as typical hole scavenger with bare and silver-deposited TiO₂, respectively, confirm suggestions outlined above and our recent proposal [18], whereas the suppression of the photocatalytic degradation of amino acid over bare TiO₂ by oxalic acid can be attributed to two effects: (i) oxalic acid readily transfers electron to the photo-generated hole preventing the CO₂ formation from amino acid via reactions (9) and (11). (ii) The [•]COOH radical abstracts hydrogen atom from R-CH(NH₃[•])COO_{surf}⁻ radical which is formed by reaction (8) (see reaction (7)).

Although the decomposition of amino acid has not been completely inhibited by oxalic acid, some mutual suppresses in the decomposition rate of the two reactants have been observed over silver-deposited TiO₂ (Fig. 8). Moreover, the photocatalytic decomposition of the oxalic acid as well as that of amino acid is significantly faster than that of observed using bare TiO₂ photocatalyst (compare Figs. 6 and 8). These experimental facts can be explained: (i) by strong surface complex formation of amino acid on silver-deposited photocatalyst, which suppresses the formation of weakly bonded surface complexes of oxalic acid, and (ii) by a significant enhancement of the efficiency of reaction (8) due to the very effective charge separation by trapping of CB electron by silver clusters.

5. Conclusions

The influence of solution pH on the equilibrium concentration of surface complexes and on the rate of the photocatalytic decomposition of L-serine and L-aspartic acid has been investigated using P25 TiO₂ nano-particles. A correlation between kinetic and equilibrium data has been found to be significant confirming the crucial role of the surface complexes in the photocatalytic decomposition of these amino acids. A considerable enhancement in the photocatalytic performance and in the yield of carbon containing intermediates has been observed in experiments performed by Ag-TiO₂ photocatalyst. Considering the results of competitive kinetic experiments applied oxalic acid as sacrificial electron donor and TiO₂ and Ag-TiO₂ as photocatalysts and analyzing qualitatively the DRIFT spectra of surface complexes a reasonable mechanism involving primary electron transfer steps and some competitive reactions following the primary events has been proposed.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2010.04.017.

References

- [1] A. Fujishima, K. Honda, Electrochemical photolysis of water at a semiconductor electrode, *Nature* 238 (1972) 37–39.
- [2] B. O'Regan, M. Gratzel, A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films, *Nature* 353 (1991) 737–740.
- [3] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Environmental applications of semiconductor photocatalysis, *Chem. Rev.* 95 (1995) 69–96.
- [4] A. Mills, S.L. Hunte, An overview of semiconductor photocatalysis, *J. Photochem. Photobiol. A: Chem.* 108 (1997) 1–35.
- [5] M. Kaneko, I. Ohkura (Eds.), *Photocatalysis—Science and Technology*, Kodansha-Springer, Tokyo, 2002.
- [6] A. Fujishima, T.N. Rao, D.A. Tyrk, Titanium dioxide photocatalysis, *J. Photochem. Photobiol. C: Photochem. Rev.* 1 (2000) 1–21.
- [7] R. Cai, K. Hashimoto, K. Itoh, Y. Kubota, A. Fujishima, Photokilling of malignant cells with ultra-fine TiO₂ powder, *Bull. Chem. Soc. Jpn.* 64 (1991) 1268–1273.
- [8] R. Cai, K. Hashimoto, Y. Kubota, A. Fujishima, Increment of photocatalytic killing of cancer cells using TiO₂ with the aid of superoxide dismutase, *Chem. Lett.* (1992) 427–430.
- [9] H. Shakai, R. Baba, K. Hashimoto, A. Fujishima, Selective killing of a single cancerous T24 cell with TiO₂ semiconducting microelectrode under irradiation, *Chem. Lett.* (1995) 185–186.
- [10] H. Hidaka, S. Horikoshi, K. Ajisaka, J. Zhao, N. Serpone, Fate of amino acids upon exposure to aqueous titania irradiation with UV-A and UV-B radiation. Photocatalyzed formation of NH₃, NO₃[−], and CO₂, *J. Photochem. Photobiol. A: Chem.* 108 (1997) 197–205.
- [11] S. Horikoshi, N. Serpone, J. Zhao, H. Hidaka, Towards a better understanding of the initial steps in the photocatalyzed mineralization of amino acids at the titania/water interface. An experimental and theoretical examination of L-alanine, L-serine and L-phenylalanine, *J. Photochem. Photobiol. A: Chem.* 118 (1998) 123–129.
- [12] H. Hidaka, K. Ajisaka, S. Horikoshi, T. Oyama, J.C. Zhao, N. Serpone, Photodecomposition of amino acids and photocurrent generation on TiO₂/OTE electrodes prepared by pulse laser deposition, *Catal. Lett.* 60 (1999) 95–98.
- [13] S. Ikeda, N. Sugiyama, B. Pal, G. Marci, L. Palmisano, H. Noguchi, K. Uosaki, B. Ohtani, Photocatalytic activity of transition-metal-loaded titanium(IV) oxide powders suspended in aqueous solutions: correlation with electron-hole recombination kinetics, *Phys. Chem. Chem. Phys.* 3 (2001) 267–273.
- [14] G. Martra, S. Horikoshi, M. Anpo, S. Coluccia, H. Hidaka, FTIR study of adsorption and photodegradation of L-α-alanine on TiO₂ powder, *Res. Chem. Intermed.* 28 (2002) 359–371.
- [15] M.A. Strehle, P. Rosch, R. Petry, A. Hauck, R. Thull, W. Kiefer, A Raman spectroscopic study of the adsorption of fibronectin and fibrinogen on titanium dioxide nanoparticles, *J. Popp. Phys. Chem. Chem. Phys.* 6 (2004) 5232–5236.
- [16] Y.K. Takahara, Y. Hanada, T. Ohno, S. Ushiroda, S. Ikeda, M. Matsumura, Photooxidation of organic compounds in solution containing hydrogen peroxide and TiO₂ particles under visible light, *J. Appl. Electrochem.* 35 (2005) 793–797.
- [17] M. Matsushita, T.H. Tran, A.Y. Nosaka, Y. Nosaka, Photooxidation mechanism of L-alanine in TiO₂ photocatalytic systems as studied by proton NMR spectroscopy, *Catal. Today* 120 (2007) 240–244.
- [18] E. Szabó-Bárdos, E. Pétervári, V. El-Zein, A. Horváth, Photocatalytic decomposition of aspartic acid over bare and silver deposited TiO₂, *J. Photochem. Photobiol. A: Chem.* 184 (2006) 221–227.
- [19] T.H. Tran, A.Y. Nosaka, Y. Nosaka, Adsorption, Photocatalytic decomposition of amino acids in TiO₂ photocatalytic systems, *J. Phys. Chem. B* 110 (2006) 25525–25531.
- [20] C.E. Giacomelli, M.J. Avena, C.P. De Pauli, Aspartic acid adsorption onto TiO₂ particles surface – experimental data and model calculations, *Langmuir* 11 (1995) 3483–3490.
- [21] T.H. Tran, A.Y. Nosaka, Y. Nosaka, Adsorption and decomposition of a dipeptide (Ala-Trp) in TiO₂ photocatalytic systems, *J. Photochem. Photobiol. A: Chem.* 192 (2007) 105–113.
- [22] E. Szabó-Bárdos, H. Czili, A. Horváth, Photocatalytic oxidation of oxalic acid enhanced by silver deposition on a TiO₂ surface, *J. Photochem. Photobiol. A: Chem.* 154 (2003) 195–201.
- [23] H. Czili, A. Horváth, Photodegradation of chloroacetic acids over bare and silver-deposited TiO₂: identification of species attacking chloroacetic acids, a mechanistic approach, *Appl. Catal. B: Environ.* 89 (2009) 342–348.
- [24] C.H. Pollema, E.B. Milosavljevic, J.L. Hendrix, L. Solujic, J.H. Nelson, Photocatalytic oxidation of aqueous ammonia (ammonium ion) to nitrite or nitrate at TiO₂ particles, *Monatshefte Chem.* 123 (1972) 333–339.
- [25] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (*OH/*O[−]) in aqueous solution, *J. Phys. Chem. Ref. Data* 17 (1988) 513–886.
- [26] K.E. O'shea, C. Cardona, The reactivity of phenol in irradiated aqueous suspensions of TiO₂. Mechanistic changes as a function of solution pH, *J. Photochem. Photobiol. A: Chem.* 91 (1995) 67–72.
- [27] S.J. Hug, B. Sulzberger, In situ Fourier transform infrared spectroscopic evidence for the formation of several different surface complexes of oxalate on TiO₂ in the aqueous phase, *Langmuir* 10 (1994) 3587–3597.
- [28] C.B. Mendive, D.W. Bahnemann, M.A. Blesa, Microscopic characterization of the photocatalytic oxidation of oxalic acid adsorbed onto TiO₂ by FTIR-ATR, *Catal. Today* 101 (2005) 237–244.
- [29] A.D. Roddick-Lanzilotta, A.J. McQuillan, An *in situ* infrared spectroscopic study of glutamic acid and of aspartic acid adsorbed on TiO₂: implications for the biocompatibility of titanium, *J. Colloid Interface Sci.* 227 (2000) 48–54.
- [30] J. Rabani, S.O. Nielsen, Absorption spectrum and decay kinetics of O₂^{•−} and HO₂[•] in aqueous solutions by pulse radiolysis, *J. Phys. Chem.* 73 (1969) 3736–3744.
- [31] T. Hirakawa, T. Daimon, M. Kitazawa, N. Ohguri, C. Koga, N. Negishi, S. Matsuzawa, Y. Nosaka, An approach to estimating photocatalytic activity of TiO₂ suspension by monitoring dissolved oxygen and superoxide ion on decomposing organic compounds, *J. Photochem. Photobiol. A: Chem.* 190 (2007) 58–68.