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Synthesis, characterization and photocatalytic activity of N-doped TiO_2 modified by platinum chloride

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Abstract

Structures and photocatalytic performance of N-doped TiO_2 modified by platinum chloride ($PtCl_x$/N-TiO_2) was investigated. It was found that the $PtCl_x$/N-TiO_2 forms anatase structure of TiO_2 involving nitrogen, chloride species and platinum ions (+IV) as major species, and it exhibits higher photocatalytic activity than either N-TiO_2 or $PtCl_x/TiO_2$ for the decomposition of acetic acid or acetaldehyde in aqueous solutions under visible light irradiation ($\lambda > 420$ nm). An enhancement of the photocatalytic activity on $PtCl_x$/N-TiO_2 has been proposed as a Z-scheme mechanism for charge separation between platinum chloride and N-TiO_2.

Keywords: Visible light; Photocatalyst; N-doped TiO_2; Platinum chloride; Z-scheme mechanism

1. Introduction

Since Honda-Fujishima effect was discovered [1], TiO_2 photocatalysts have been extensively studied for environmental applications to reduce toxic agents in the polluted atmosphere or water. However, TiO_2 (anatase) works as a photocatalyst only under UV-light (3.2–3.4 eV) irradiation, so that it is desired that sunlight can be more effectively utilized in photocatalysis. One of the most promising photocatalysts are nitrogen-doped TiO_2 (N-TiO_2), which works for various photocatalytic reactions under visible light irradiation [2–12]. Since Asahi et al. have reported photocatalytic activities and photofunctional properties of N-TiO_2 under visible light irradiation [2], many researchers have endeavored to synthesize and characterize N-TiO_2 in order to improve the photocatalytic activity. However, by doping nitrogen atoms, the oxygen vacancy is created in N-TiO_2 prepared by sol–gel method for a charge compensation. The excess oxygen vacancy works as the recombination center for the photo-induced holes and electrons. In order to suppress the recombination, Morikawa et al. reported that photocatalytic decomposition of acetaldehyde in the gas phase was enhanced on N-TiO_2 by loading with copper ions under visible light irradiation [13]. Ohno et al. also reported that the photocatalytic activities for oxidation of 2-propanol on S- or N-doped TiO_2 adsorbed Fe^{3+} ions are markedly improved compared to those of S- or N-doped TiO_2 under both UV-light and visible light irradiation [14].

Recently, we reported that the photocatalytic activity of N-TiO_2 modified by platinum chloride ($PtCl_x$/N-TiO_2) was remarkably improved compared with N-TiO_2 or $PtCl_x/TiO_2$ [15]. Here, we report on details of the characterization and the photocatalytic reactions under visible light irradiation, and have proposed a possible reaction mechanisms on the $PtCl_x$/N-TiO_2.

2. Experimental details

2.1. Materials

The N-doped TiO_2 (N-TiO_2) was prepared by the hydrolysis of 35 mL of tetra-isopropyl titanate (TiPOT) with 100 mL of an ammonium aqueous solution (28–30 wt.% as NH_3) at room temperature under vigorous stirring, washed

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several times with distilled water, recovered by filtration, dried at 343 K for 12 h and calcinated at various temperatures (473–873 K) for 3 h in air. As far as condition is not described, the N-TiO_2 calcinated at 673 K was utilized for the characterization and the photocatalytic reactions. Commercial TiO_2 samples, P-25 (a mixture of anatase and rutile phases; BET: ~50 m^2/g) supplied by Degussa and ST-01 (anatase, BET: ~320 m^2/g) by Ishihara were used for comparison. The N-TiO_2 and TiO_2 were modified by adsorption of platinum chloride from an aqueous solution of 0.01M H_2PtCl_6 at room temperature in the dark for 1.5 h. The solid products were washed several times with distilled water, recovered by filtration, dried at 343 K for 12 h, then the Pt-loaded N-TiO_2 and TiO_2 were labeled $PtCl_x$/N-TiO_2 and $PtCl_x/TiO_2$, respectively. Here, x is an unidentified number. The amount of Pt loadings for the sample was determined by atomic absorption spectroscopy.

2.2. Sample characterizations

The X-ray diffraction (XRD) patterns were obtained with a RIGAKU RINT2000 using Cu Kα radiation (λ = 1.5417 Å). The UV–vis spectroscopic measurements were carried out using a UV–vis recording spectrophotometer (UV-2200A, Shimadzu). The atomic composition of samples was analyzed with X-ray photoelectron spectroscopy (ESCA 3400, Shimadzu). The Au $4f_{7/2}$ (83.8 eV) as an internal standard was used for an energy calibration. The ESR spectra were recorded with a JEOL-2X spectrometer (X-band) at 77 K. The flatband potentials of the samples were measured by the Motto–Schottky plots in an aqueous solution of 0.5 M of acetic acid using a potentiostat (HZ3000, Hokuto Denko). In order to measure the flatband potentials, working electrodes were prepared by spreading a paste of catalysts with water onto the ITO-glass (10 Ω cm^{-2}) and drying at 343 K in air for 1 h. The film mass of electrodes is adjusted to be 1.20 ± 0.050 mg/cm^2 (film thickness: ca. 80–90 μm).

2.3. Photocatalytic reactions

Photocatalytic tests of samples were carried out in the Pyrex tube (20 mL) involving 10 mL of aqueous solutions of 0.5 M of acetic acid or acetaldehyde purged by O_2 in gas phase at room temperature. Photo-irradiation was performed with a 500 W xenon lamp (Ushio Inc.) through a low cut-off filter, Y-45 ($\lambda > 420$ nm) (Asahi Technoglass Co. Ltd.). The photoreaction cell was placed at photo-intensity by 10 mW cm^{-2} at 365 nm under full arc from xenon lamp. The products were analyzed by a gas chromatograph equipped with a thermal conductivity detector (TCD) for analysis of CO_2. In blank tests, photo-irradiation of catalysts suspended in distilled water evolved small amounts of CO_2. On the other hand, no decomposition of reactants took place under photo-irradiation without any catalysts. From these results, the photocatalytic activity was evaluated after subtracting the CO_2, yielded by blank tests from those by the photocatalytic decomposition of reactants.

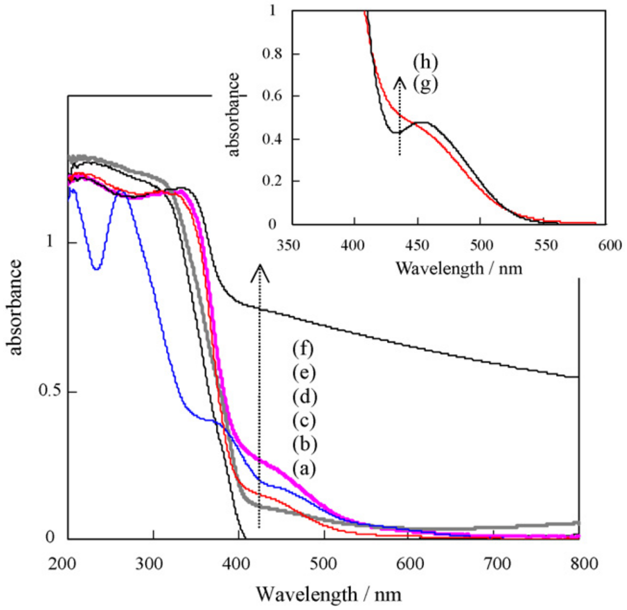

Fig. 1. UV–vis absorbance spectra of (a) TiO_2, (b) $PtCl_x/TiO_2$ (0.7 wt.% as Pt), (c) N-TiO_2, (d) $PtCl_x/SiO_2$, (e) $PtCl_x$/N-TiO_2 (0.8 wt.% as Pt) and (f) Pt^0/N-TiO_2 (0.8 wt.% as Pt). Inset shows the absorbance of 0.01 M of aqueous solutions of (g) H_2PtCl_6 and (h) $PtCl_4$.

3. Results and discussion

Crystal structures of N-TiO_2 are influenced by calcination temperatures of as-prepared N-TiO_2. Structures of N-TiO_2 are amorphous structures at ~473 K, anatase structures at 573–773 K, and a mixture of anatase and rutile phases at 873 K from XRD analysis.

The N-TiO_2 calcinated at 673 K for 3 h turns pale yellow, having a band gap at around 400 nm (3.1 eV) together with a sub-band gap at ~540 nm (~2.3 eV) as shown in Fig. 1. This sub-band in the visible light region cannot be observed in pure TiO_2. The absorption of visible light region in the spectrum of N-TiO_2 is caused by the excitation of electrons from localized N doping level in the band gap [8]. Furthermore, $PtCl_x$/N-TiO_2 exhibits an absorption band at around ~2.3 eV, which can be superimposed on the absorption bands of N-TiO_2 and aqueous solutions of H_2PtCl_6 or $PtCl_4$ (Inset of Fig. 1). The visible light absorption band at ~2.3 eV of H_2PtCl_6 or $PtCl_4$ is assignable to the charge transfer from the ligand (Cl^-) to platinum (+IV) ions [16]. On the other hand, the Pt^0/N-TiO_2 thermally reduced in the flow of H_2 at 473 K for 1 h become grey, having broad absorption band towards near infrared region, owing to the formation of platinum particles evidenced by XPS as shown in Fig. 2(e). The $PtCl_x/SiO_2$ also exhibits the absorption band at around ~2.3 eV in the visible region.

The states of platinum chloride on N-TiO_2 were investigated. The platinum chloride from aqueous solutions of H_2PtCl_6 or $PtCl_4$ is not adsorbed on the N-TiO_2 or TiO_2 treated by 5% (v/v) hydrofluoric acid, while the platinum chloride are easily adsorbed on the surface of N-TiO_2 or TiO_2. It was reported that the fluoride ions react with the hydroxyl groups of TiO_2 to form ≡Ti–F species [17]. These results suggest that

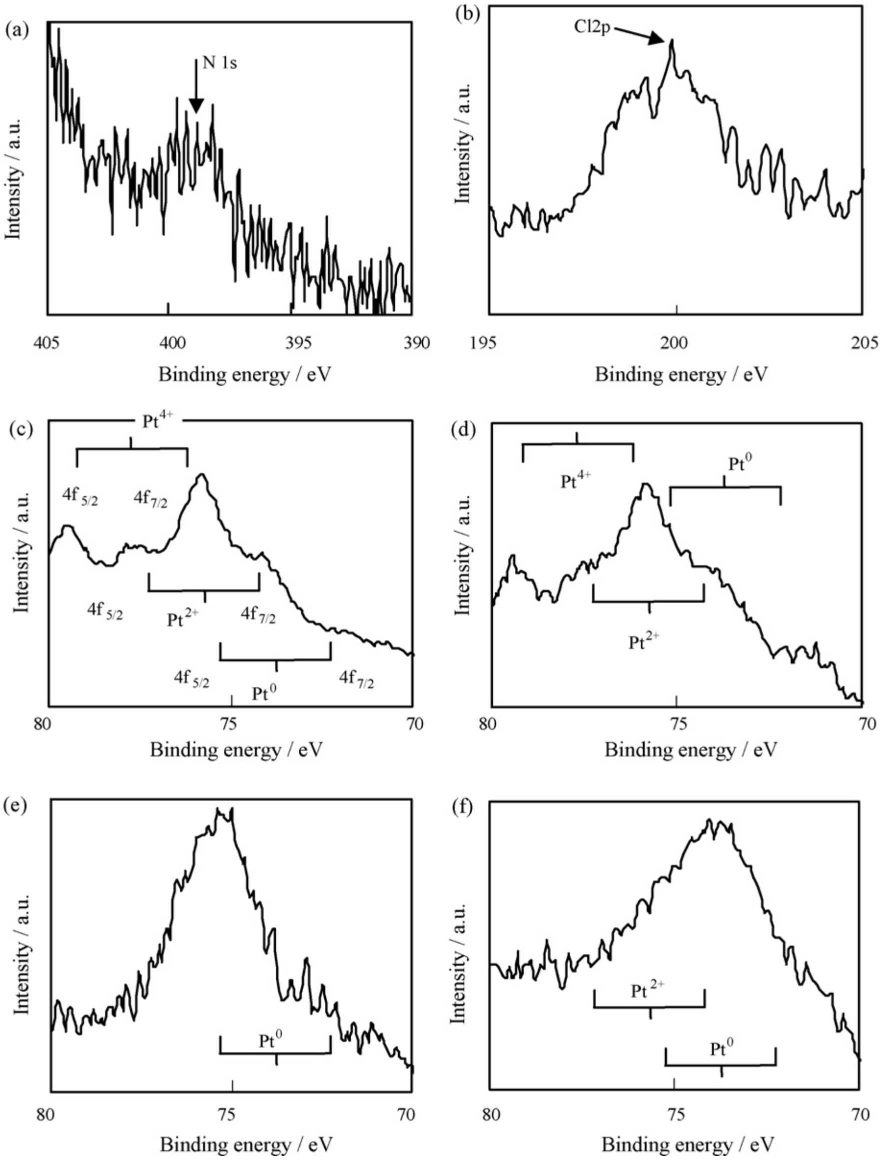

Fig. 2. N 1s, Cl 2p and Pt 4f XPS spectra: (a) N 1s, (b) Cl 2p and (c) Pt 4f for $PtCl_x/N\text{-}TiO_2$; Pt 4f for (d) $PtCl_x/TiO_2$, (e) $Pt^0/N\text{-}TiO_2$ and (f) $PtCl_x/SiO_2$.

platinum chloride strongly interacts with Ti–OH to form Ti–O–$PtCl_x$.

Fig. 2 shows the N 1s, Cl 2p and Pt 4f XPS spectra of $PtCl_x/N\text{-}TiO_2$, $PtCl_x/TiO_2$ and $PtCl_x/SiO_2$. The N 1s peak at 397–400 eV is observed on N-TiO_2 or $PtCl_x/N\text{-}TiO_2$, which is assignable to nitrogen species (Fig. 2(a)) [18,19]. The ratio of N/Ti on N-TiO_2 and $PtCl_x/N\text{-}TiO_2$ are roughly estimated to be 0.34 and 0.29 at.%, respectively. Thus, the N-TiO_2 prepared by hydrolysis involves low quantity of N calcinated at 673 K, as reported by Sato et al. [5]. On the other hand, the ESR signal owing to $^-$N radicals is observed on N-TiO_2 and $PtCl_x/N\text{-}TiO_2$. These species are considered to play a vital role in visible light response [8]. The Cl 2p peak at 197–201 eV is observed on the $PtCl_x/N\text{-}TiO_2$, $PtCl_x/TiO_2$ and $PtCl_x/SiO_2$ (Fig. 2(b)). On the other hand, the $PtCl_x/N\text{-}TiO_2$ exhibits three different types of doublet peaks ($4f_{5/2}$ and $4f_{7/2}$) at 79.3 and 76.2 eV for Pt^{4+} as major species, at 77.3 and 74.2 eV for Pt^{2+}, 75.4 and 72.3 eV for Pt^0 as minor species (Fig. 2(c)). Moreover, the $PtCl_x/TiO_2$ also exhibits similar Pt 4f spectrum with that of the $PtCl_x/N\text{-}TiO_2$ (Fig. 2(d)). On the other hand, $Pt^0/N\text{-}TiO_2$ thermally reduced at 473 K for 1 h exhibits doublet peaks at 75.4 and 72.3 eV for Pt^0, while the $PtCl_x/SiO_2$ shows those at 77.3 and 74.2 eV for Pt^{2+}, and at 75.4 and 72.3 eV for Pt^0 (Fig. 2(e and f)). Thus, platinum species with different oxidation states is deposited on the supports, and, in particular, the N-TiO_2 or TiO_2 are modified by platinum(+IV) chloride as a major species.

When the photocatalytic activity was compared with samples calcinated at each temperature (473–873 K), the N-TiO_2 calcinated at 673 K showed the highest photocatalytic activity. Fig. 3 shows the reaction time profile on the yields of CO_2 for the photocatalytic decomposition of acetic acid in an aqueous solution on the N-TiO_2 calcinated at 673 K. It is observed that the yields of CO_2 increases with a linearity against the reaction time on N-TiO_2 under $\lambda > 420$ nm, while no products are observed in the dark. Furthermore, the $PtCl_x/N\text{-}TiO_2$ (0.8 wt.% as Pt) showed seven times higher photocatalytic

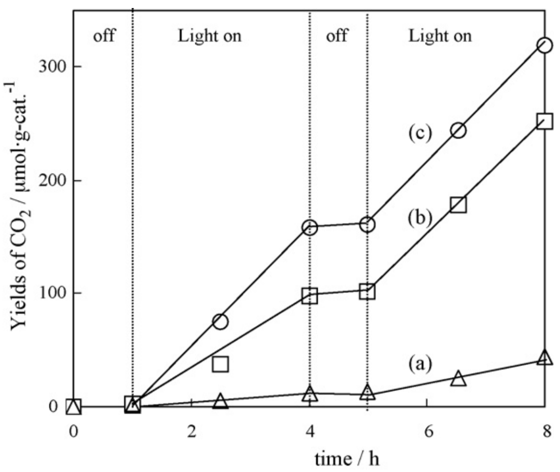

Fig. 3. Reaction time profiles for the photocatalytic decomposition of (a) acetic acid on N-TiO_2, (b) acetic acid and (c) acetaldehyde on $PtCl_x$/N-TiO_2 (0.8 wt.% as Pt) under $\lambda > 420$ nm.

Table 1

Yields of photo-formed CO_2 for the photocatalytic decomposition of acetic acid and acetaldehyde under $\lambda > 420$ nm on various samples

Samples	Yields of CO_2 (μmol h^{-1} g-cat^{-1})	
	Acetic acid	Acetaldehyde
TiO_2 (P-25)	≈0	≈0
$PtCl_x/TiO_2$ (P-25)	2.0	1.2
TiO_2 (ST-01)	≈0	≈0
$PtCl_x/TiO_2$ (ST-01)	4.5	2.8
Pt^0/TiO_2 (ST-01)	≈0	≈0
N-TiO_2	7.5	6.3
$PtCl_x$/N-TiO_2	54	32
Pt^0/N-TiO_2	14.5	10.8
$PtCl_x/SiO_2$	≈0	≈0

activity than N-TiO_2 under $\lambda > 420$ nm. The turnover numbers (TONs), defined as the number of acetic acid molecules consumed per number of total platinum ions, were estimated to be about 4 on $PtCl_x$/N-TiO_2 (0.8 wt.% as Pt) within 6 h. It is also observed that acetaldehyde in an aqueous solution is photocatalytically decomposed into CO_2 under $\lambda > 420$ nm.

Fig. 4 shows the dependence of platinum loadings on the photocatalytic activity of the $PtCl_x$/N-TiO_2 under both UV-light and visible light irradiation. This result suggests as follows: (1) the photocatalytic activity is optimized at the content of 0.8 wt.% as Pt and (2) the activity on the $PtCl_x$/N-TiO_2 is enhanced by seven times under visible light irradiation, and by 1.5 times under UV-light irradiation, compared with that of N-TiO_2.

Table 1 shows the yields of CO_2 for the decomposition of acetic acid or acetaldehyde in the presence of O_2 on various samples under $\lambda > 420$ nm. The photocatalytic activities of samples for the decomposition of acetic acid or acetaldehyde are in the following order: $PtCl_x$/N-TiO_2 $\gg$ Pt^0/N-TiO_2 > N-TiO_2 > $PtCl_x/TiO_2$ (ST-01 or P-25) > TiO_2 ≈ $PtCl_x/SiO_2$ ≈ 0. In fact, the $PtCl_x$/N-TiO_2 retains pale yellows under photocatalytic reactions in the presence of O_2. XPS analysis also supports that the Pt^{4+} ions are still predominant in the $PtCl_x$/N-TiO_2 used by photocatalytic reactions, while the platinum ions are photo-reduced in the absence of O_2. These results indicate as follows: (1) the photo-induced electrons and holes on platinum chloride by itself do not directly participate in the photocatalytic reaction, and the surface of N-TiO_2 or TiO_2 plays a major role in the charge separation; (2) the presence of O_2 as an electron acceptor is important for the formation of active oxygen species; (3) the presence of platinum(+IV) chloride adsorbed on N-TiO_2 causes a drastic enhancement of photocatalytic activity rather than platinum metal particles.

Kisch et al. proposed a reaction mechanism for the degradation of 4-chlorophenol, i.e., a photo-induced electron transfer takes place from Cl^- to Pt^{4+} on $PtCl_4/TiO_2$ under visible light irradiation, so that the photo-formed chlorine atoms oxidize the substrate, while the photo-formed electrons trapped in the TiO_2 matrix induces the reduction of oxygen to form super oxide anion radicals, O_2^- species, followed by the oxidation of the substrate [20–24].

In our system, a schematic diagram of the photo-induced charge separation on $PtCl_x$/N-TiO_2 has been proposed in Fig. 5.

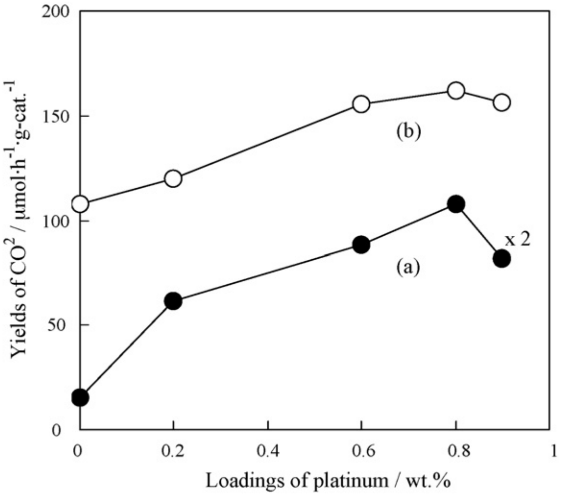

Fig. 4. Dependence of platinum loadings on $PtCl_x$/N-TiO_2 for the photocatalytic decomposition of acetic acid under (a) $\lambda > 420$ nm and (b) $\lambda > 320$ nm.

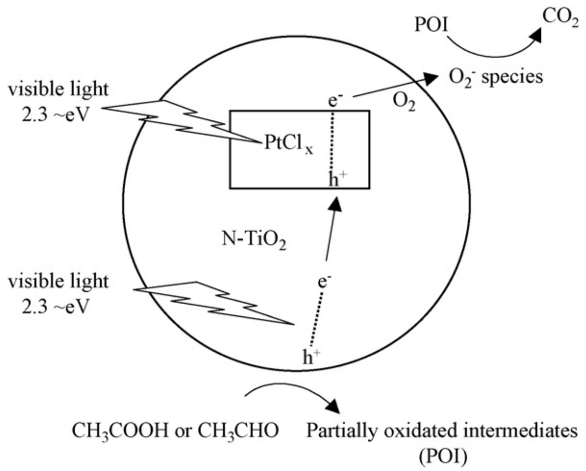

Fig. 5. Schematic diagram of the photo-induced charge separation on $PtCl_x$/N-TiO_2 for the photocatalytic reactions under visible light irradiation.

Charge separation of the photo-induced holes and electrons ($h^+\cdots e^-$) is seen to take place on $PtCl_x$/N-TiO_2 by double excitation of both N-TiO_2 and $PtCl_x$ under visible light irradiation. The photo-induced holes on N-TiO_2 can oxidize the reactants, and electrons are scavenged by the holes on $PtCl_x$ as electron acceptors. From an analysis of Motto–Schottky plots of N-TiO_2 or $PtCl_x$/N-TiO_2 in an aqueous solution of acetic acid, the flatband potentials of N-TiO_2 and $PtCl_x$/N-TiO_2 were estimated to be at -0.20 and -0.18 V versus NHE, respectively. Judging from the flatband potential of $PtCl_x$/N-TiO_2 at -0.18 V and the redox potential of O_2/O_2^- couple at -0.16 V versus NHE [25], the photo-induced electrons on the surface of $PtCl_x$/N-TiO_2 transfer to form O_2^- species, leading to the multi-step reactions. Thus, the mechanism for the photocatalytic decomposition of acetic acid or acetaldehyde on $PtCl_x$/N-TiO_2 under visible light irradiation could be proposed as a Z-scheme reaction.

4. Conclusions

Simply prepared N-TiO_2 works as visible light sensitive photocatalyst. Moreover, the photocatalytic activity was remarkably improved when the N-TiO_2 was modified by platinum chloride. It was concluded that this enhancement is caused by the double excitation between platinum(+IV) chloride and N-TiO_2 as a Z-scheme mechanism for charge separation. These materials show promise for applications in various photocatalytic systems.

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References

[1] A. Fujishima, K. Honda, Nature 238 (1972) 37.
[2] R. Asahi, T. Morikawa, K. Aoki, Y. Taga, Science 293 (2001) 269.
[3] S. Sato, Chem. Phys. Lett. 123 (1986) 126.
[4] M. Anpo, S. Dohshi, M. Kitano, Y. Hu, Chem. Ind. 108 (2006) 595.
[5] S. Sato, R. Nakamura, S. Abe, Appl. Catal. A 284 (2005) 131.
[6] H. Irie, Y. Watanabe, K. Hashimoto, J. Phys. Chem. B 108 (2003) 5483.
[7] M. Bazil, E.H. Morales, U. Diebold, Phys. Rev. Lett. 96 (2006) 26103.
[8] S. Livraghi, M.C. Paganini, E. Giamello, A. Selloni, C. Di Valentin, G. Pacchioni, J. Am. Chem. Soc. 128 (2006) 15666 (references therein).
[9] S. In, A. Orlov, F. Garcia, M. Tikhov, D.S. Wright, R.M. Labbert, Chem. Commun. (2006) 4236.
[10] S. Sakthivel, M. Janczarek, H. Kisch, J. Phys. Chem. B 108 (2004) 19384.
[11] T. Morikawa, R. Asahi, R. Ohwaki, K. Aoki, Y. Taga, Appl. Phys. Lett. 86 (2005) 132104.
[12] K. Hashimoto, H. Irie, A. Fujishima, Jpn. J. Appl. Phys. 44 (2005) 8269.
[13] T. Morikawa, Y. Irokawa, T. Ohwaki, Appl. Catal. A 314 (2006) 123.
[14] T. Ohno, Z. Miyamoto, K. Nishijima, H. Kanemitsu, F. Xueyuan, Appl. Catal. A 302 (2006) 62.
[15] S. Higashimoto, K. Takamatsu, M. Azuma, M. Kitano, M. Matsuoka, M., in press. Anpo, Catal. Lett.
[16] W. Macyk, H. Kisch, Chem. Eur. J. 7 (2001) 1862.
[17] V. Maurino, C. Minero, G. Mariella, E. Pelizzetti, Chem. Commun. (2005) 2627.
[18] J.A. Rodriguez, T. Jirsak, J. Dvorak, S. Sambasivan, D. Fischer, J. Phys. Chem. B 104 (2000) 319.
[19] O. Diwald, T.L. Thompson, T. Zubkov, E.G. Goralski, S.D. Walck, J.T. Yates Jr., J. Phys. Chem. B 108 (2004) 6004.
[20] L. Zang, C. Lange, I. Abraham, S. Storck, W.F. Maier, H. Kisch, J. Phys. Chem. B 102 (1998) 10765.
[21] L. Zang, W. Macyk, C. Lange, W.F. Maier, C. Antonius, D. Meissner, H. Kisch, Chem. Eur. J. 6 (2000) 379.
[22] H. Kisch, W. Macyk, Chemphyschem 3 (2002) 399.
[23] H. Kisch, L. Zang, C. Lange, W.F. Maier, C. Antonius, D. Meissner, Angew. Chem. Int. Ed. 37 (1998) 3034.
[24] W. Macyk, G. Burgeth, H. Kisch, Photochem. Photobiol. Sci. 2 (2003) 322.
[25] D.T. Sawyer, J.S. Valentine, Acc. Chem. Res. 14 (1981) 393.