

Photodynamics of NaTaO₃ Catalysts for Efficient Water Splitting

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Electrons photoexcited in catalysts based on NaTaO₃ were observed by time-resolved infrared (IR) absorption spectroscopy. The electrons excited by 266-nm pump pulse exhibited a monotonic absorption of mid-IR light. The recombination kinetics of the excited electrons with holes was monitored in a vacuum as a function of time delay ranging from 100 ns to 1 s. When the Na content and La dopant were optimized to achieve high activity in the steady-state reaction of water splitting, the recombinative decay was hindered to increase the amount of electrons. The electrons were transferred to NiO ultrafine particles, loaded as a cocatalyst, within 1 μ s following the pulse excitation. Exposing the catalysts to water vapor affected the electron decay and efficient electron transfer to water via the cocatalyst was evidenced.

1. Introduction

Gaseous hydrogen is a promising fuel that is free from CO₂ release. The photocatalytic water-splitting reaction may provide a large amount of hydrogen when driven by solar light. Many inorganic catalysts, such as TiO₂,^{1–3} SrTiO₃,^{4,5} K₄Nb₆O₁₇,⁶ Na₂Ti₆O₁₃,⁷ BaTi₄O₉,⁸ ZrO₂,⁹ Ta₂O₅,¹⁰ K₂La₂Ti₃O₁₀,¹¹ Sr₂Nb₂O₇,^{12,13} and ZnNb₂O₆¹⁴ have been synthesized since photochemical water splitting was found on TiO₂.¹⁵ Some of the catalysts developed exhibited reasonably high activity when excited by ultraviolet (UV) light. Intense efforts^{16–18} are now being made to find catalysts that efficiently produce hydrogen with visible light.

Among the catalysts examined to date, NaTaO₃ doped with La has demonstrated the highest quantum yield of water splitting, exceeding 50% when irradiated by UV light.^{19–21} However, only little is known about what happens with the catalyst composed of mixed metal oxide doped with a heterogeneous element and assisted by NiO cocatalyst. The photoinduced dynamics of TiO₂-based catalysts has been extensively studied.^{22–24} Although some of the knowledge accumulated on TiO₂ can be transferred to other catalysts, the dynamics of photoexcited carriers should be observed on the highly efficient catalyst itself to promote further development toward the goal.

In the present study, electrons photoexcited in the NaTaO₃-based catalysts were observed by time-resolved infrared (IR) absorption spectroscopy. The kinetics of electrons recombining with holes and reacting with water vapor was traced as a function of catalyst modifications—Na content, doping of La, and loading of NiO. Time-resolved IR absorption spectroscopy

has proven its feasibility in tracing the kinetics of electrons photoexcited in TiO₂ raw,²⁵ platinumized,^{26,27} and dye-sensitized.^{28–30} This method is expected to work with other photocatalysts, because electrons excited in the conduction band of semiconductors absorb mid-IR light.³¹ Another advantage of this IR-based method is the freedom from scattering of probe light, which causes a problem in visible spectroscopy of micrometer-sized particles.

2. Experimental Section

The solid-state reaction to synthesize NaTaO₃ has been reported in detail.¹⁹ Mixtures of Na₂CO₃ and Ta₂O₅ with different atom ratios of Na/Ta were calcined at 1420 K in air. Lanthanum was doped by mixing La₂O₃ in the starting materials. NiO was impregnated with an aqueous solution of Ni(NO₃)₂ and calcined at 540 K. The catalyst powder was fixed on a CaF₂ plate with a density of 2 mg cm^{–2} and placed in a gas cell evacuated at 10^{–5} Torr (1 Torr = 133 Pa). The catalyst on the plate was heated to 573 K in 20-Torr O₂ prior to each measurement.

Transient IR absorption of photoexcited catalysts was observed with a home-built spectrometer.²⁶ The catalyst was irradiated by the fourth harmonic light of a Q-switched Nd:YAG laser. The wavelength, time width, and energy of the pump pulse were 266 nm, 10 ns, and 1 mJ/pulse, respectively. The diameter of the irradiated spot was 6 mm. Continuous-wave IR probe light passing through the catalyst was dispersed in a grating monochromator. A photovoltaic MCT detector received the monochromatized IR output. The MCT signal was amplified in ac-coupled amplifiers and accumulated as a function of time delay. Transient absorbance change as small as 10^{–6} was detected by signal averaging of 100 flashes at intervals of 30 s. The response of the detector determined the time-resolution to be 50 ns. The absorbance response observed at different wavenumbers was transformed to transient absorption spectrum at different time delays.

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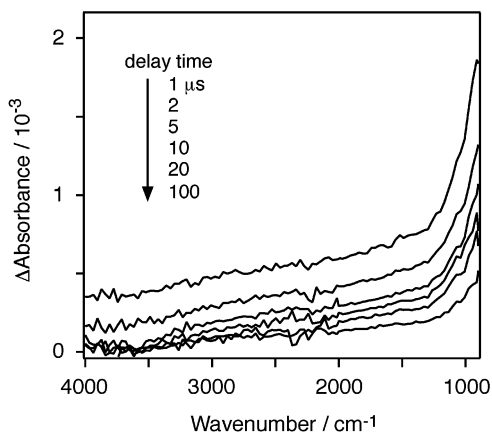


Figure 1. Transient IR absorption spectra of NaTaO₃ (Na/Ta = 1.05) irradiated by a 266 nm UV pulse at 1 mJ.

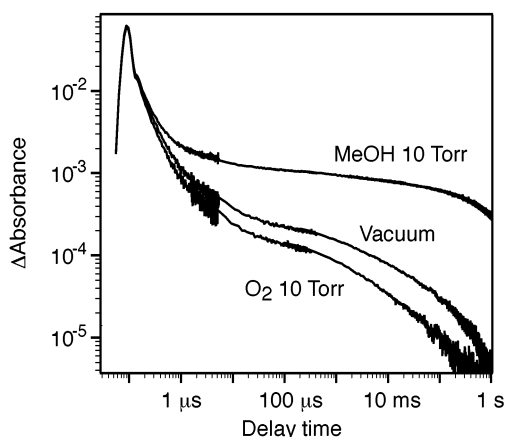


Figure 2. Temporal profiles of the transient IR absorption at 2000 cm⁻¹ by the irradiation of a 266 nm UV pulse at 1 mJ. These decay curves were obtained in a vacuum and in the presence of 10 Torr O₂ or 10 Torr CH₃OH gas.

3. Results and Discussion

3.1. Transient Absorption Spectrum of UV-Irradiated NaTaO₃. Figure 1 shows the transient absorption spectrum of NaTaO₃ with Na/Ta ratio = 1.05 in the starting material. The catalyst was placed in a vacuum and pumped by the 266-nm pulse. A broad absorption appeared upon the irradiation and diminished with time delay. The spectrum was monotonically increased in intensity with decreasing wavenumber from 4000 to 1200 cm⁻¹. We assigned this absorption to optical transitions of electrons excited in the conduction band (CB) and then trapped in shallow mid-gap states. One possible transition is the intra-CB transition of free electrons. Free electrons give absorption characterized by a monotonic spectrum when the momentum required for the intra-band transition is provided by phonons.³¹ Although the free electrons are quickly trapped in mid-gap states, a finite fraction of the trapped electrons can be thermally excited to the CB. Another possible mechanism is the direct optical transition of the trapped electrons to the CB. A monotonic absorption of IR light was found on TiO₂ and similarly assigned in our previous study.²⁶

To evidence the assignment to the electrons on NaTaO₃, the decay of the IR absorption was observed in the presence of an electron scavenger or a hole scavenger. Figure 2 presents the decay of absorbance at a fixed wavenumber, 2000 cm⁻¹. The decay observed in the vacuum simply reflected the recombination of the electrons and complementary holes. The decay was accelerated at 1 μs and later by exposure to an O₂ ambient of

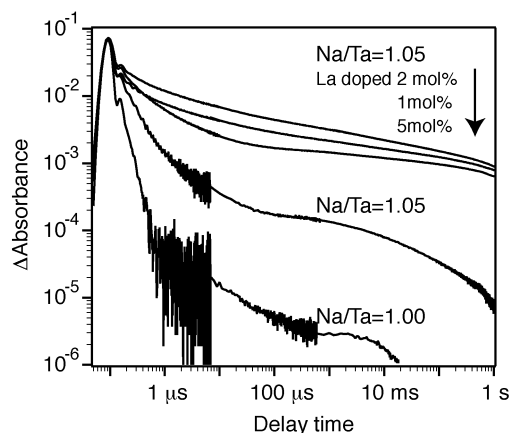
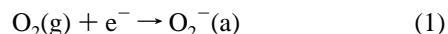


Figure 3. The decay of photogenerated electrons on NaTaO₃ (Na/Ta = 1.00), NaTaO₃ (Na/Ta = 1.05), and La-doped NaTaO₃ (Na/Ta = 1.05) in a vacuum. A 266 nm UV pulse at 1 mJ was irradiated on the catalysts and the transient absorption was observed at 2000 cm⁻¹.

10 Torr. The accelerated decay was ascribed to the electron capture by O₂:



where (g) and (a) represent gas phase and adsorbed phase, respectively. When the catalyst was exposed to methanol vapor of 10 Torr, the decay was retarded. Holes to recombine with the electrons were captured by a methanol-derived adsorbate (probably adsorbed methoxy):



The fact that the absorbance was nearly constant at 10 μs and later indicated that the holes were exhausted within the first 10 μs. The IR absorption responded to the composition of the reactant vapor as expected on our assignment to the transition of excited electrons. This assignment claimed, on the other hand, that holes photogenerated in the valence band (VB) did not absorb mid-IR light. The absence of hole-induced absorption is rationalized when the mid-gap states trapping the holes are energetically deep as in the case of TiO₂ catalysts.^{32,33} Holes trapped at such deep mid-gap states can neither be thermally excited to the VB nor absorb mid-IR light via the direct optical transitions. In the following sections, therefore, the absorbance at 2000 cm⁻¹ is interpreted to be the relative amount of excited electrons in NaTaO₃-based catalysts.

In Figure 1, absorbance at wavenumbers lower than 1200 cm⁻¹ was rapidly diminished with time delay when compared with the absorbance at higher wavenumbers. Two different transitions are behind the spectrum, probably reflecting energetic heterogeneity of electron traps.

3.2. Na Content in the Starting Material. The content of Na in the starting material is the first parameter controlling the activity of the calcined catalyst. The H₂-production activity of the catalyst prepared with the stoichiometric (Na/Ta ratio = 1.00) mixture was improved 15-times by adding 5% excess Na in the starting material.²⁰ The IR absorption of the two catalysts (Na/Ta ratio = 1.00 and 1.05) was observed in a vacuum and is compared in Figure 3. The catalyst with the excess Na presented more intense absorption, i.e., an enhanced population of excited electrons. The excess Na in the starting material suppressed recombination. The hump at 0.2 μs was an artifact caused by the limited response of our electronics.

The suppressed recombination of the electrons observed in Figure 3 was consistent with the picture that the excess Na

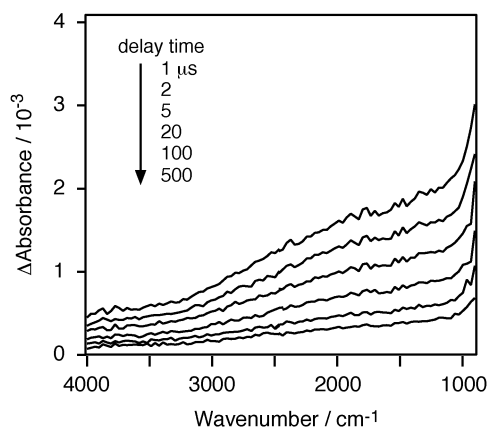


Figure 4. Transient IR absorption spectra of La-doped NaTaO₃ (Na/Ta = 1.05, La 2 mol %) irradiated by a 266 nm UV pulse at 0.2 mJ.

compensated for the sublimated loss in the calcination and improved the crystallinity of the calcined particles. Catalyst particles were transformed into the orthorhombic shape expected for single-crystalline NaTaO₃, and the size of each crystal enlarged up to 2 μm . The number of recombination centers such as Na vacancies and grain boundaries was reduced as a result.

3.3. Doping La. Another dimension of optimizing the catalyst is doping lanthanides. Lanthanum exhibited the most significant promotion of the nine lanthanides examined.¹⁹ When the catalyst of Na/Ta ratio = 1.05 was doped with La of 1 and 2 mol %, its H₂-production activity was improved by 3.3 and 2.6 times. Further doping at 5 mol % reduced the activity to almost the original value of the nondoped catalyst.²¹ The decay of the IR absorption was observed with the three La-doped catalysts (Figure 3). The La dopants at 1 mol % and 2 mol % enhanced the IR absorption at 1 μs or later by more than 1 order of magnitude, while doping at 5 mol % partially reduced the absorbance. The optimized doping of La hindered the recombination and increased the population of excited electrons. The electron population observed by the IR absorption correlated with the catalytic activity, suggesting that those electrons worked in the water-splitting reaction.

An interesting and important issue is how the lanthanum dopants suppressed the recombination. The La³⁺ ion was assumed to replace a part of Na⁺ in NaTaO₃ of perovskite structure on the basis of X-ray diffraction analysis.²¹ When one La³⁺ replaces one Na⁺ ion, two more Na⁺ ions should be removed to balance the ionic charge. Electrostatic potential can be modulated on the replaced lattice to promote the separation of electrons and holes photoexcited in pairs. In addition, the lanthanum was preferably populated close to the surface rather than in the bulk of particles.²¹ The localized distribution of La³⁺ makes the gradient of electrostatic potential from the surface to the bulk. The gradient may promote carrier separation.

The transient absorption spectrum of the catalyst with 2 mol % La is shown in Figure 4. Comparison with Figure 1 indicated the spectrum is sensitive to La dope. A broad rise appeared at 3000–1500 cm⁻¹ in addition to the monotonic spectrum. The La dopants perturbed the energetic profiles of the bands and mid-gap states leading to the additional feature of the spectrum.

3.4. Loading NiO. NiO is an effective cocatalyst to enhance the hydrogen evolution in the water splitting. This is first found on SrTiO₃ by Domen et al.^{34,35} Loading a small amount of NiO drastically activated the water splitting on our NaTaO₃ (Na/Ta ratio = 1.05) with 2 mol % La. When NiO was loaded at 0.2 wt %, the H₂-production activity was improved by 44 times to achieve the maximum apparent quantum yield of 56% with

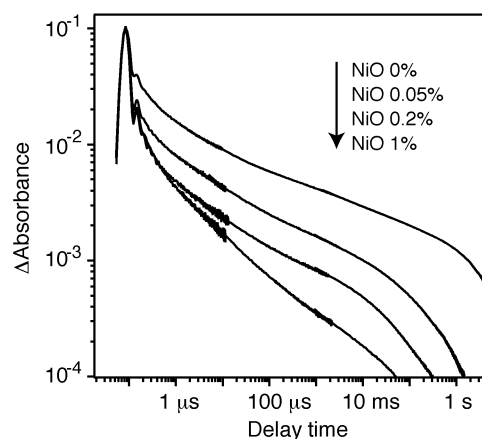


Figure 5. The decay of photogenerated electrons on NiO-loaded NaTaO₃ (Na/Ta = 1.05, La 2 mol %) catalyst at 0, 0.05, 0.2, and 1 wt %. These decay curves were obtained at 2000 cm⁻¹ in a vacuum.

irradiation by 270-nm light.²¹ Figure 5 shows the IR absorption of the catalyst with NiO loaded at 0.05, 0.2, or 1 wt % as a function of time delay. The absorbance at 2000 cm⁻¹ diminished with increased amount of NiO at any delay. We attributed the NiO-induced attenuation of the IR absorption to the transfer of photoexcited electrons from the La-doped NaTaO₃ to the NiO cocatalyst. The conduction band of NiO estimated to be more positive by 0.1 eV than that of NaTaO₃²⁰ was ready to receive the electrons. If the electrons quickly recombined with holes in NiO-loaded catalysts, as the alternative interpretation of the attenuated IR absorption, the quantum efficiency of the water-splitting reaction should have decreased. This was not the case. The curve of the loaded catalysts deviated downward at 1 μs or earlier from the curve of the unloaded catalyst, whereas the rest of the decay remained nearly parallel. This feature suggested that the electrons were transferred within 1 μs following the photoexcitation and afterward equilibrated between NiO and La-doped NaTaO₃.

The proposed interpretation of electron transfer is based on a supposition that the transferred electrons do not absorb IR light. Our previous study²¹ revealed NiO particles of smaller sizes than the resolution of transmission electron microscopy. Such ultrafine particles provide density of state energetically separated like molecular orbitals rather than continuous bands. The optical absorption of the electrons transferred to the ultrafine NiO particles may be observed at shorter wavelengths than those probed in the present study.

The transient absorption spectrum of the catalyst loaded at 0.2 wt % is shown in Figure 6. The broad rise at 3000–1500 cm⁻¹ lost intensity in comparison with the spectrum of the unloaded catalyst in Figure 4.

3.5. Electrons Consumed in the Water-Splitting Reaction on the NiO-Loaded Catalysts. In the preceding sections, the IR absorption of the catalysts was observed in a vacuum and interpreted with the electron recombination with the hole and electron transfer to the cocatalyst. The current section reports electrons consumed in the water-splitting reaction. Figure 7 presents the absorption decay observed on three catalysts exposed to 10-Torr water vapor. Compare the two curves observed in the vacuum and in the water atmosphere on each catalyst. The decay in water was initially retarded and then accelerated. The two curves consequently crossed at 2 s without NiO, at 20 ms with 0.05 wt % NiO, and at 1 μs with 0.2 wt % NiO. The retarded decay on the last catalyst, which presented the highest quantum yield of 56%,²¹ was not very evident.

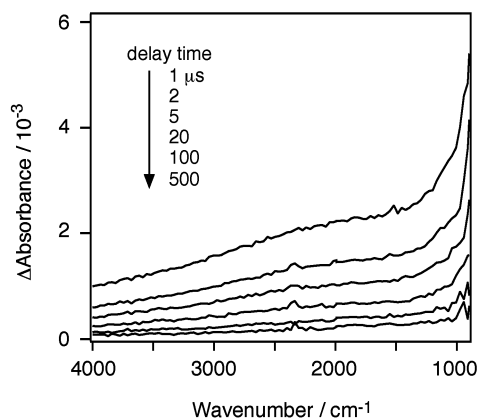


Figure 6. Transient IR absorption spectra of NiO-loaded NaTaO₃ (Na/Ta = 1.05, La 2 mol %, NiO 0.2 wt %) irradiated by a 266 nm UV pulse at 1 mJ.

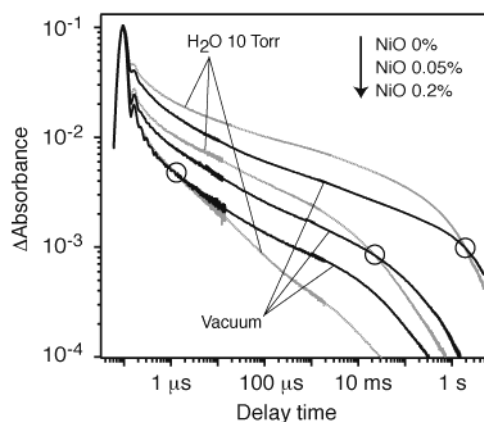


Figure 7. The decay of photogenerated electrons on the bare and NiO-loaded NaTaO₃ (Na/Ta = 1.05, La 2 mol %) catalysts. The amount of NiO is indicated in the figure. The transient absorption was observed at 2000 cm⁻¹ in the presence of 10 Torr H₂O gas.

We propose that holes oxidized water and then the electrons left behind reduced water. The preceding hole-consuming reaction caused retardation of the electron decay, and the following electron-consuming reaction accelerated the decay. The reductive reaction launched at the time delay when the electron decay in water vapor accelerated comparing with the decay in the vacuum. Similar kinetics of the water-splitting reaction—hole transfer followed by electron transfer—was proposed on platinized TiO₂ (P-25).²⁵ NaTaO₃ was designed by utilizing 5d orbitals of tantalum to raise its CB, i.e., the photoexcited potential of electrons, and to favor the electron transfer in the reductive reaction to produce H₂. The results in Figure 7 show that the reductive reaction still made a bottleneck in the water splitting on La-doped NaTaO₃ without the aid of the cocatalyst.

The catalytic activity showed a correlation with the characteristic time of launching the reduction. More active catalyst presented launching at an earlier time delay in Figure 7. This relationship confirmed that the ultrafine NiO particles provided an efficient site for the reductive reaction. This is consistent with the reported photochemical activity of the oxidative and reductive half reactions determined in the presence of sacrificial reagents.²¹ H₂ production in a methanol solution was enhanced by loading NiO, whereas O₂ production with a silver nitrate solution was not affected at all.

3.6. Excitation Strength. Our pump–probe study of IR absorption was aimed at simulating the steady-state kinetics of the water-splitting reaction. The excitation strength employed

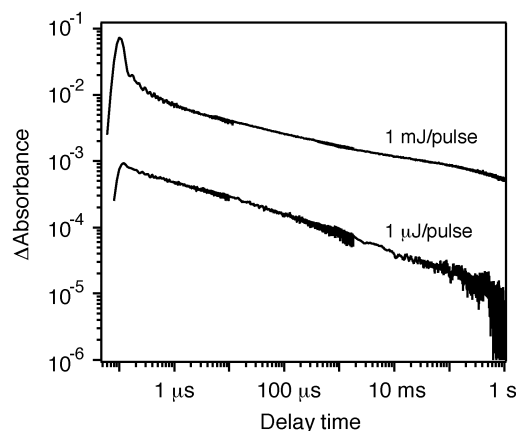


Figure 8. Dependence of electron decay kinetics on the pump pulse energy. NaTaO₃ (Na/Ta = 1.05, La 2 mol %) was irradiated by a 266 nm UV pulse at the indicated energies.

in the pump–probe and steady-state conditions are estimated. The photochemical reactions observed with the nanosecond-pulse may have been affected by the excitation strength. In the steady state²¹ the maximum quantum efficiency (56%) was achieved on the optimized catalyst of 50 mg irradiated by a photon flux of 300 μmol h⁻¹. By assuming the catalyst particle to be a cube of 1 μm and 3 g cm⁻³, one particle received 3 × 10⁶ photons s⁻¹. In the pulsed excitation, a catalyst disk with a diameter of 6 mm and density of 2 mg cm⁻² was irradiated by a 1-mJ pulse. One particle received 7 × 10⁶ photons pulse⁻¹. A peak flux 7 × 10¹⁴ photons s⁻¹ was estimated for the 10-ns pulse, which was 2 × 10⁸ times as intense as the steady-state flux.

The naked NaTaO₃ doped with 2 mol % La was excited with the 266-nm pulse of different pulse energy to examine the effect of the excitation strength. Figure 8 shows the decay curves observed in the vacuum. A sharp peak within the first 200 ns was evident at 1-mJ excitation and diminished at 1-μJ excitation. The two curves decayed in a parallel manner at 1 μs and later. The parallel decay suggested the electron dynamics at 1 μs and later was insensitive to the excitation strengths examined. Hence we consider that the electron dynamics reported in the present paper represented the reaction kinetics working in the steady-state splitting of water.

4. Conclusions

The dynamics of electrons photoexcited in NaTaO₃-based catalysts was traced by time-resolved IR absorption spectroscopy. Excited electrons presented a monotonic absorption of mid-IR light. The amount of the electrons in La-doped catalysts showed a correlation with their activity in the steady-state reaction of water splitting, which suggested that those electrons worked in the reaction. When NiO was deposited as a cocatalyst, the electrons excited in the La-doped NaTaO₃ were transferred to the cocatalyst within 1 μs following the pulse excitation. Electron dynamics obtained in water vapor evidenced that the cocatalyst mediated efficient electron transfer to water.

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References and Notes

- (1) Yamaguchi, K.; Sato, S. *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 1237.

- (2) Kudo, A.; Domen, K.; Maruya, K.; Onishi, T. *Chem. Phys. Lett.* **1987**, *133*, 517.
- (3) Sayama, K.; Arakawa, H. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 1647.
- (4) Lehn, J.-M.; Sauvage, J.-P.; Ziessel, R. *Nouv. J. Chim.* **1980**, *4*, 623.
- (5) Domen, K.; Kudo, A.; Onishi, T.; Kosugi, N.; Kuroda, H. *J. Phys. Chem.* **1986**, *90*, 292.
- (6) Kudo, A.; Sayama, K.; Tanaka, A.; Asakura, K.; Domen, K.; Maruya, K.; Onishi, T. *J. Catal.* **1989**, *120*, 337.
- (7) Inoue, Y.; Ogura, S.; Kohnno, M.; Sato, K. *Appl. Surf. Sci.* **1997**, *121/122*, 521.
- (8) Inoue, Y.; Kohnno, M.; Kaneko, T.; Ogura, S.; Sato, K. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 89.
- (9) Sayama, K.; Arakawa, H. *J. Phys. Chem.* **1993**, *97*, 531.
- (10) Sayama, K.; Arakawa, H. *J. Photochem. Photobiol. A: Chem.* **1994**, *77*, 243.
- (11) Takata, T.; Shinohara, K.; Tanaka, A.; Hara, M.; Kondo, J. N.; Domen, K. *J. Photochem. Photobiol. A: Chem.* **1997**, *106*, 45.
- (12) Kim, H. G.; Hwang, D. W.; Kim, J.; Kim, Y. G.; Lee, J. S. *Chem. Commun.* **1999**, 1077.
- (13) Kudo, A.; Kato, H.; Nakagawa, S. *J. Phys. Chem. B* **2000**, *104*, 571.
- (14) Kudo, A.; Nakagawa, S.; Kato, H. *Chem. Lett.* **1999**, 1197.
- (15) Fujishima, A.; Honda, K. *Nature* **1972**, *238*, 37.
- (16) Domen, K.; Hara, M.; Kondo, J. N.; Takata, T.; Kudo, A.; Kobayashi, H.; Inoue, Y. *Korean J. Chem. Eng.* **2001**, *18*, 862.
- (17) Asahi, R.; Morikawa, T.; Ohwaki, T.; Aoki, K.; Taga, Y. *Science* **2001**, *293*, 269.
- (18) Zou, Z.; Ye, J.; Sayama, K.; Arakawa, H. *Nature* **2001**, *414*, 625.
- (19) Kudo, A.; Kato, H. *Chem. Phys. Lett.* **2000**, *331*, 373.
- (20) Kato, H.; Kudo, A. *J. Phys. Chem. B* **2001**, *105*, 4285.
- (21) Kato, H.; Asakura, K.; Kudo, A. *J. Am. Chem. Soc.* **2003**, *125*, 3082.
- (22) Fox, M. A.; Dulay, M. T. *Chem. Rev.* **1993**, *93*, 341.
- (23) Linsebigler, A. L.; Lu, G.; Yates, J. T., Jr. *Chem. Rev.* **1995**, *95*, 735.
- (24) Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. *Chem. Rev.* **1995**, *95*, 69.
- (25) Yamakata, A.; Ishibashi, T.; Onishi, H. *J. Phys. Chem. B* **2001**, *105*, 7258.
- (26) Yamakata, A.; Ishibashi, T.; Onishi, H. *Chem. Phys. Lett.* **2001**, *333*, 271.
- (27) Yamakata, A.; Ishibashi, T.; Onishi, H. *J. Phys. Chem. B* **2002**, *106*, 9122.
- (28) Ghosh, H. N.; Asbury, J. B.; Lian, T. *J. Phys. Chem. B* **1998**, *102*, 6482.
- (29) Heimer, T. A.; Heilweil, E. J. *J. Phys. Chem. B* **1997**, *101*, 10990.
- (30) Takeshita, K.; Sasaki, Y.; Kobashi, M.; Tanaka, Y.; Maeda, S.; Yamakata, A.; Ishibashi, T.; Onishi, H. *J. Phys. Chem. B* **2003**, *107*, 4156.
- (31) Pankove, J. I. *Optical Processes in Semiconductors*; Dover: New York, 1975.
- (32) Martin, S. T.; Herrmann, H.; Choi, W.; Hoffmann, M. R. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 3323.
- (33) Yamakata, A.; Ishibashi, T.; Onishi, H. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 1019.
- (34) Domen, K.; Naito, S.; Soma, M.; Onishi, T.; Tamaru, K. *J. Chem. Soc., Chem. Commun.* **1980**, 543.
- (35) Domen, K.; Kudo, A.; Onishi, T. *J. Catal.* **1986**, *102*, 92.