

## Visible Light Activity and Photoelectrochemical Properties of Nitrogen-Doped TiO<sub>2</sub>

Shanmugasundaram Sakthivel,<sup>†</sup> Marcin Janczarek,<sup>‡</sup> and Horst Kisch<sup>\*,†</sup>

*Institut für Anorganische Chemie der Universität Erlangen-Nürnberg, Egerlandstr. 1, D-91058 Erlangen, Germany, and Department of Chemical Technology, Gdansk University of Technology, ul. Narutowicza 11/12, 80-952 Gdansk, Poland*

*Received: July 15, 2004; In Final Form: September 29, 2004*

Nitrogen-doped titania photocatalysts were prepared from titanium tetraisopropoxide or titanium tetrachloride and thiourea. The yellow powders obtained after calcination at 400–600 °C photocatalyze the mineralization of 4-chlorophenol by visible light ( $\lambda \geq 455$  nm). Different from previously published data these materials do not contain sulfur but instead nitrogen as the doping component inducing visible light photocatalysis. The measured band gap narrowing of 40–80 meV and the anodic shift of the quasi Fermi potential of 40–90 mV are in agreement with recent results on nitrogen-doped titania.

### Introduction

The application of titanium dioxide as mutual photocatalyst for daylight-induced chemical conversions is hampered by the fact that it absorbs only the very small UV part (2–3%) of solar light arriving at the earth's surface. To obtain a more efficient utilization of solar irradiation, many attempts were made to shift its photocatalytic activity to the visible. Earlier investigations dealt with transition metal doping, and in a very few cases the resulting materials were active under visible light irradiation.<sup>1,2</sup> Also, surface modification with a transition metal halide complex afforded a type of hybrid semiconductor active even in diffuse indoor daylight.<sup>3–7</sup> Later it was found that also doping or modification with nonmetals such as carbon,<sup>8–10</sup> nitrogen,<sup>11–18</sup> and sulfur<sup>19–21</sup> leads to visible light photocatalysis. Whereas the band edge and surface state positions of the carbon- and nitrogen-doped titania materials were estimated from photoelectrochemical experiments and wavelength dependence of OH radical formation,<sup>10,14</sup> no corresponding data were available for the sulfur-doped titania. In connection with our corresponding experiments with nitrogen- and carbon-doped titania we therefore intended to measure also the quasi Fermi level. According to literature, sulfur-doped titania may be prepared by two methods. The first method consists of annealing titanium disulfide at 500 °C for 90 min. The resulting powder exhibited in the X-ray photoelectron spectrum (XPS) a sulfur 2p(3/2) peak at 160.0 eV and photocatalyzed the decolorization of methylene blue by UV and visible light.<sup>19,20</sup> In the second method, titanium tetraisopropoxide was mixed with thiourea in ethanol solution and was followed by evaporation of ethanol under reduced pressure and calcination at 500 °C.<sup>21</sup> From the XPS S2p(3/2) peak at 170.0 eV it was concluded that the material contains sulfur in the oxidation state +6, probably as sulfate since washing with water and HCl considerably lowered the peak intensity. This novel material photocatalyzed the disappearance of methylene blue by visible light ( $\lambda \geq 440$  nm).<sup>21</sup> It is recalled that methylene blue also absorbs visible light and since the redox potential of its lowest excited state is located at about  $-0.71$

V, it cannot be excluded that a minor part of this reaction proceeds via *indirect semiconductor photocatalysis*.<sup>22</sup> When we repeated this preparation<sup>21</sup> we obtained also a yellow powder but surprisingly it did not contain sulfur but instead nitrogen as the dopant. In the following section we report on some basic photoelectrochemical properties and on the visible light activity of this nitrogen-doped titania in the mineralization of the pollutant 4-chlorophenol. Different from methylene blue this compound does not absorb in the visible, and therefore the presence of indirect semiconductor photocatalysis can be excluded.

### Results and Discussion

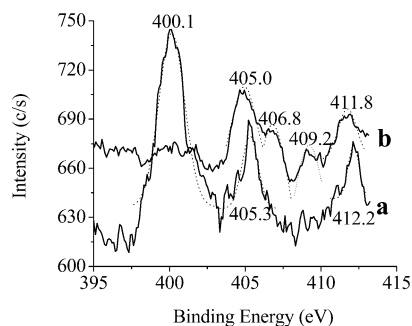
Following the experimental procedure as reported for the preparation of sulfur-doped titania,<sup>21</sup> we also obtained a yellow powder (TiO<sub>2</sub>-N/1) which according to elemental analysis contained nitrogen (0.09 wt %) and smaller amounts of carbon (0.03 wt %) but no sulfur. Even when the concentration of thiourea was increased five times, sulfur could not be found. In accord with this result is the observation that the XPS spectrum did not contain peaks in the range of 160–170 eV and FT-IR measurements gave no evidence for the presence of sulfate. In a further attempt to obtain a sulfur-doped titania we used water instead of ethanol as the solvent. Elemental analysis of the resulting TiO<sub>2</sub>-N/1a evidenced the presence of sulfur (0.8%), nitrogen (0.3%), and carbon (0.1%). According to literature sulfur should be present as sulfate<sup>21</sup> which on the other hand is known to decrease the photoactivity of titania.<sup>23</sup> In agreement with this we observed that washing with water and HCl removes all sulfur and improves the activity in the mineralization of 4-chlorophenol by 5%.

The results presented above indicate that nitrogen and not sulfur is responsible for the visible light activity of TiO<sub>2</sub>-N/1 prepared according to the published procedure.<sup>21</sup> Since this catalyst exhibited only poor photocatalytic activity in 4-chlorophenol mineralization with visible light ( $\lambda \geq 455$  nm), we searched for improvement. This was achieved by increasing the concentrations of titanium tetraisopropoxide and thiourea from 0.35 and 1.40 M to 0.56 and 2.24 M, respectively, and by elevating the calcination temperature from 500 °C to 600 °C (TiO<sub>2</sub>-N/2). Furthermore, replacing titanium tetraisopropoxide

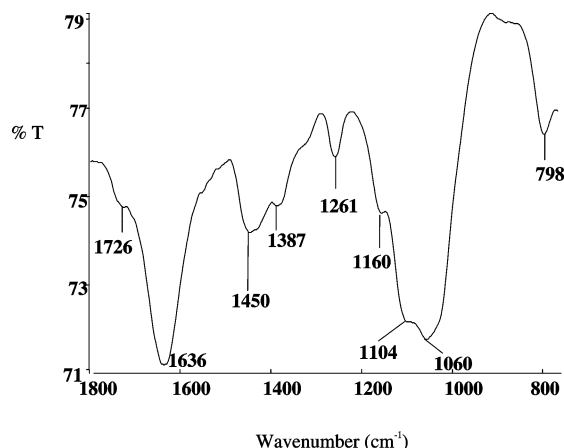
\* Author to whom correspondence should be addressed. Fax: (+49)-9131-8527363. E-mail: kisch@chemie.uni-erlangen.de.

<sup>†</sup> Institut für Anorganische Chemie der Universität Erlangen-Nürnberg.

<sup>‡</sup> Gdansk University of Technology.

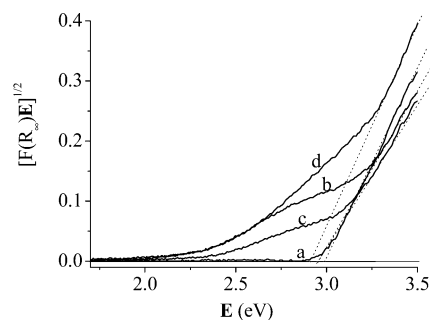


**Figure 1.** N-1s XPS spectrum of TiO<sub>2</sub>-N/1. Dotted curves were obtained from Gaussian fits of experimental data. (a) Before sputtering, (b) after sputtering.



**Figure 2.** FT-IR spectrum of TiO<sub>2</sub>-N/1.

by titanium tetrachloride afforded an even better photocatalyst (TiO<sub>2</sub>-N/3). According to elemental analysis, TiO<sub>2</sub>-N/2 and TiO<sub>2</sub>-N/3 contain 0.07 and 0.30 wt % of nitrogen, and 0.05 and 0.16 wt % of carbon, respectively, but no sulfur. This is corroborated by XPS data. Figure 1 displays the N 1s spectra of TiO<sub>2</sub>-N/1 analyzed before and after sputtering. By comparison with literature data the most intense peak observed before sputtering (Figure 1a) at the binding energy of 400.1 eV is assigned to hyponitrite,<sup>24</sup> whereas the two less intense peaks at 405.3 and 412.2 eV most likely originate from nitrite ions.<sup>24,25</sup> After sputtering for 2 min, which corresponds to removal of a 5 nm surface layer, the hyponitrite peak had disappeared, whereas the nitrite peaks were slightly shifted to 405.0 and 411.8 eV and two new weak peaks appeared at 406.8 and 409.2 eV. According to literature,<sup>24</sup> the former can be assigned to nitrate, whereas the latter still falls in the range of binding energies reported for nitrite. These data clearly reveal that hyponitrite is located in the surface region while nitrite and nitrate are present also in the bulk. Correspondingly, the atomic composition (%) of the specimen before and after sputtering changes from Ti 17.9, O 56.3, C 24.4, and N 1.4 to Ti 28.2, O 61.4, C 9.7, and N 0.7. Further evidence stems from the IR spectrum of TiO<sub>2</sub>-N/1 exhibiting hyponitrite peaks at 1387, 1104, and 1060 cm<sup>-1</sup>, and nitrite peaks at 1450, 1261, and 1160 cm<sup>-1</sup> (Figure 2).<sup>24</sup> Two further peaks at 1726 and 798 cm<sup>-1</sup> suggest that carbonate is present, in accordance with previous results for nitrogen-<sup>14,26</sup> and carbon-doped titania.<sup>10</sup> It is noted that carbonate is not responsible for visible light photocatalysis since it is also present in unmodified titania prepared from titanium tetrachloride and sodium carbonate; this material is not photoactive upon irradiation at  $\lambda \geq 455$  nm. According to XRD measurements all nitrogen-doped powders consist of anatase and contain only trace quantities of rutile, as also reported for the material described



**Figure 3.** Transformed diffuse reflectance spectra of (a) TiO<sub>2</sub>, (b) TiO<sub>2</sub>-N/1, (c) TiO<sub>2</sub>-N/2, (d) TiO<sub>2</sub>-N/3.

**TABLE 1: Photoelectrochemical Data,<sup>a</sup> Band Gap Energies, and Initial Disappearance Rates**

catalyst	pH <sub>0</sub>	*E <sub>f</sub> [V, NHE] <sup>b</sup>	E <sub>bg</sub> [eV] <sup>b</sup>	r <sub>i</sub> [10 <sup>-9</sup> mol L <sup>-1</sup> s <sup>-1</sup> ] <sup>c</sup>
TiO <sub>2</sub>	3.00	-0.68	2.99	0.26
TiO <sub>2</sub> -N/1	3.70	-0.64	2.95	1.83
TiO <sub>2</sub> -N/2	3.75	-0.64	2.95	6.40
TiO <sub>2</sub> -N/3	4.60	-0.59	2.91	7.52

<sup>a</sup> Measured according to ref 29 and calculated for pH = 7.

<sup>b</sup> Reproducibility was better than  $\pm 0.01$  V and  $\pm 0.01$  eV, respectively.

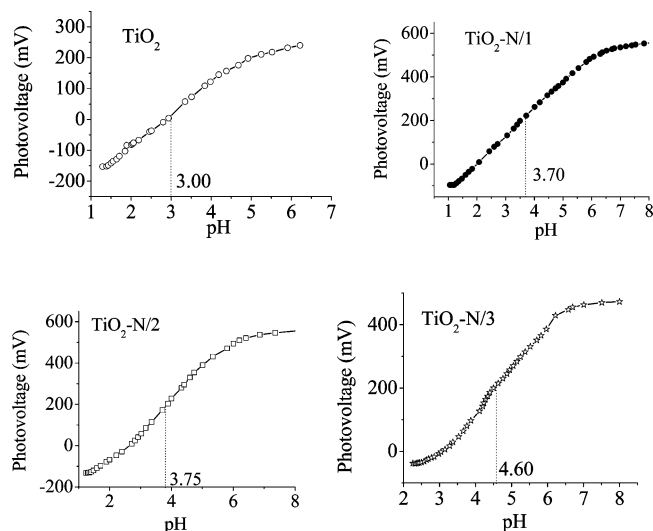
<sup>c</sup> r<sub>i</sub> represents initial reaction rate.

in the literature.<sup>21</sup> Employing Scherer's equation, crystal sizes of 18, 22, 7, and 35 nm can be estimated for TiO<sub>2</sub>-N/1, TiO<sub>2</sub>-N/2, TiO<sub>2</sub>-N/3, and undoped TiO<sub>2</sub>, respectively, from the anatase (101) peak broadening. The latter was prepared from an ethanolic solution of titanium tetraisopropoxide by hydrolysis with humid air; according to XRD analysis it contains approximately 5–10% of rutile.

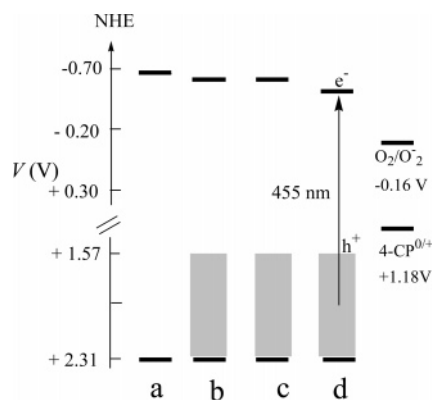
Diffuse reflectance spectra reveal that the new absorption shoulder at 400–520 nm is related to the presence of nitrogen since it increases with nitrogen content. This absorption pattern is the same as that observed for our previously reported nitrogen-doped titania.<sup>14</sup> Assuming the materials to be indirect semiconductors, as is TiO<sub>2</sub>, a plot of the modified Kubelka–Munk function  $[F(R_{\infty})E]^{1/2}$  vs the energy of absorbed light  $E$ ,<sup>27</sup> affords band gap energies of 2.99, 2.95, 2.95, and 2.91 eV for unmodified titania, TiO<sub>2</sub>-N/1, TiO<sub>2</sub>-N/2, and TiO<sub>2</sub>-N/3, respectively (Figure 3, Table 1).<sup>28</sup> This results in a maximum band gap narrowing of 0.08 eV for TiO<sub>2</sub>-N/3, whereas a value of 0.04 eV is found for TiO<sub>2</sub>-N/1 and TiO<sub>2</sub>-N/2. Similarly, nitrogen-induced band gap narrowing of 0.03 to 0.05 eV was observed for other nitrogen-doped titania materials.<sup>14</sup>

To verify whether a shift of the valence or conduction band edge is responsible for this decrease of band gap energy, the position of the quasi Fermi level (\*E<sub>f</sub>) was determined through measuring the photovoltage as a function of the suspension pH value (Figure 4).<sup>29</sup> The \*E<sub>f</sub> values as obtained from the corresponding inflection points (pH<sub>0</sub>) of the voltage–pH curves were converted to the values at pH 7.<sup>29,30</sup> A lower pH<sub>0</sub> value corresponds to a more negative Fermi potential. The value of -0.68 V found for the self-prepared unmodified titania is cathodically shifted as compared with -0.46 V reported for the quasi Fermi level of commercial anatase powder.<sup>30</sup> Values of -0.64, -0.64, and -0.59 V were measured for TiO<sub>2</sub>-N/1, TiO<sub>2</sub>-N/2, and TiO<sub>2</sub>-N/3, respectively (Table 1). The anodic shifts of 40 mV and 90 mV are a little larger than the values of 30–50 mV measured previously for nitrogen-doped titania samples prepared in aqueous medium through hydrolysis of titanium tetrachloride with a nitrogen base.<sup>14</sup>

Assuming that the distance between the quasi Fermi level and the conduction band edge is vanishing for these probably



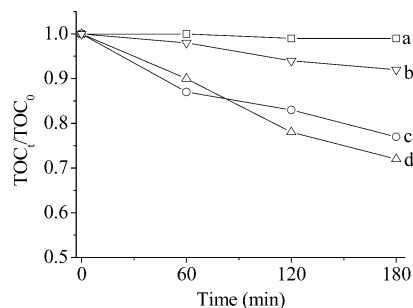
**Figure 4.** Dependence of photovoltage (V vs Ag/AgCl) on pH value of electrolyte.



**Figure 5.** Electrochemical potentials (vs NHE) of band edges and surface states (shaded areas) at pH 7. (a)  $\text{TiO}_2$ , (b)  $\text{TiO}_2\text{-N/1}$ , (c)  $\text{TiO}_2\text{-N/2}$ , (d)  $\text{TiO}_2\text{-N/3}$ .

highly doped n-type materials, the position of the valence band edge can be located from the corresponding band gap energies as +2.31 V for all samples (Figure 5). The same observation was made for the previously prepared nitrogen-doped titania,<sup>14</sup> although in this case the valence band edge is located at +2.64 V. Recalling that light absorbance starts already at 520 nm (2.38 eV), a manifold of surface states must exist. The position of these states is close to the valence band edge as evidenced by the wavelength dependence of salicylic acid formation from benzoic acid in the presence of electron scavengers<sup>14</sup> and by theoretical calculations.<sup>12</sup> In two recent articles the same surface states positions were assumed.<sup>15–16</sup>

To explore the photocatalytic activity of the catalysts, degradation of 4-chlorophenol ( $2.5 \times 10^{-4}$  M) was investigated with artificial visible light ( $\lambda \geq 455$  nm). In the presence of the various photocatalysts, 8, 23, and 30% mineralization was observed after irradiation in the presence of  $\text{TiO}_2\text{-N/1}$ ,  $\text{TiO}_2\text{-N/2}$ , and  $\text{TiO}_2\text{-N/3}$  for 3 h, respectively, whereas no mineralization occurred in the case of unmodified titania (Figure 6). The initial rates of 4-chlorophenol disappearance for  $\text{TiO}_2\text{-N/2}$  and  $\text{TiO}_2\text{-N/3}$  were about 3 to 4 times larger than that for  $\text{TiO}_2\text{-N/1}$  (Table 1). Among these catalysts,  $\text{TiO}_2\text{-N/3}$ , prepared from titanium tetrachloride, exhibited the highest activity. This may be due to the highest nitrogen content and the smallest particle size of this material. However, the photocatalytic activity is more than two times lower as compared to our previously reported nitrogen-doped titania photocatalysts.<sup>14</sup> The higher oxidation



**Figure 6.** Photomineralization of 4-chlorophenol ( $2.5 \times 10^{-4}$  M) at  $\lambda \geq 455$  nm in the presence of various titania powders (1 g/L): (a)  $\text{TiO}_2$ , (b)  $\text{TiO}_2\text{-N/1}$ , (c)  $\text{TiO}_2\text{-N/2}$ , (d)  $\text{TiO}_2\text{-N/3}$ .  $\text{TOC}_0$  and  $\text{TOC}_t$  = Total Organic Carbon content at times 0 and  $t$ .

potential of reactive holes in these materials as suggested by the fact that the valence band edge is shifted anodically by 0.33 V (vide supra) could be responsible for this difference.

## Experimental Section

Elemental analyses were measured with a Carlo Erba (CHNS-O, E.A.1108), X-ray powder diffraction (XRD) data were collected with a Philips X'Pert PW 3040/60, X-ray photoelectron spectra were measured on a Phi 5600 ESCA spectrometer (pass energy of 23.50 eV, Al standard, 300.0 W,  $45.0^\circ$ ), and diffuse reflectance spectra were obtained with a Shimadzu UV-2401 UV-Vis recording spectrophotometer equipped with a diffuse reflectance accessory. IR spectra were recorded on a Perkin-Elmer spectrometer (FT-IR, 16PC), using KBr pellets. Quasi Fermi energies ( $*E_f$ ) were measured according to the literature;<sup>29</sup> 30 mg of catalyst and 6 mg of methyl viologen dichloride were suspended in a 100 mL two-necked flask in 50 mL of 0.1 M  $\text{KNO}_3$ . A platinum flag and Ag/AgCl served as working and reference electrodes and a pH meter for following the proton concentration.  $\text{HNO}_3$  (0.1 M) and NaOH (0.1 M) were used to adjust the pH. The suspension was magnetically stirred and purged with nitrogen gas throughout the experiment. Initially the pH of the suspension was adjusted to pH 1 before measurement. The light source was the same as that used in the photodegradation. Stable photovoltages were recorded about 30 min after changing the pH. The obtained  $\text{pH}_0$  values were converted to the Fermi potential at pH 7 by the equation  $*E_f(\text{pH } 7) = -0.445 + 0.059(\text{pH}_0 - 7)$ .<sup>29</sup> Reproducibility of  $\text{pH}_0$  values was better than 0.1 pH units.

$\text{TiO}_2\text{-N/1}$  was prepared as described.<sup>21</sup>  $\text{TiO}_2\text{-N/1a}$  was synthesized analogously but with replacement of ethanol by water. In the washing experiment three drops of concentrated HCl were added to a suspension of 0.5 g of  $\text{TiO}_2\text{-N/1a}$  in 100 mL of  $\text{H}_2\text{O}$ . After sonication and stirring for 15 min and 2 h, respectively, the solid was separated by centrifugation followed by washing 4 times with 100 mL portions of water. The resulting powder was dried in air for 1 h at  $100^\circ\text{C}$ . Elemental analysis: N 0.30, C 0.11, and S 1.10 before washing, and N 0.31, C 0.15, and S 0.00 after washing.

$\text{TiO}_2\text{-N/2}$  and  $\text{TiO}_2\text{-N/3}$  were prepared from titanium tetraisopropoxide (0.56 M) and titanium tetrachloride (0.56 M) with thiourea (2.24 M) in ethanol (80 mL). In a dry vessel the titanium precursor was slowly added to 40 mL of absolute ethanol (HPLC grade) and mixed thoroughly for 30 min by magnetic stirring (mixture 1). Similarly, thiourea was dissolved in 40 mL of absolute ethanol and magnetically stirred for 30 min (mixture 2). Thereafter mixture 1 was added dropwise to mixture 2, and stirring was continued overnight. After removal of ethanol under reduced pressure,  $\text{TiO}_2\text{-N/2}$  and  $\text{TiO}_2\text{-N/3}$  were

calcined for 3 h at 600 and 400 °C, respectively. The calcination temperature was attained at a heating rate of about 5 °C min<sup>-1</sup>.

For comparison, undoped titania was prepared by two methods. In the first method, ethanol was evaporated from mixture 1 and the residue was left in contact with humid air for 4 h. The resulting solid was ground and calcined at 600 °C for 3 h; Elemental analysis: C 0.34. In the second method, a solution of 0.25 M of sodium carbonate was added dropwise to 200 mL of 0.25 M TiCl<sub>4</sub> at 0 °C until a pH of 5.5 was reached. After aging the suspension for 24 h at room temperature, the precipitate was filtered and dried under air at 70 °C. The residue was crushed to a fine powder and calcined in a muffle furnace at 400 °C for 4 h under air; the calcination temperature was attained at a heating rate of about 5 °C min<sup>-1</sup>; Elemental analysis: C 0.44.

Photodegradation of 4-chlorophenol was carried out in a jacketed cylindrical 15 mL quartz cuvette attached to an optical train. Irradiation was performed with an Osram XBO 150 W xenon arc lamp installed in a light-condensing lamp housing (PTI, A1010S). A water filter and a 455 nm cutoff filter were placed in front of the cuvette. Running water was circulated through the jacket to ensure constant temperature of the reaction mixture, which was stirred magnetically. TOC measurements were made on a Shimadzu Total Carbon Analyzer TOC-500/5050 with NDIR optical system detector. Initial reaction rates were calculated from the disappearance rate of 4-chlorophenol. Concentration of 4-chlorophenol was monitored through its absorbance at 224 nm. A Varian CARY 50 Conc UV–Vis spectrophotometer was used for recording absorption spectra.

**Acknowledgment.** This work was supported by Deutsche Forschungsgemeinschaft.

**Supporting Information Available:** Graphs showing the FT-IR spectrum of unmodified TiO<sub>2</sub> and the XRD patterns of modified and unmodified TiO<sub>2</sub>. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References and Notes

(1) Yamashita, H.; Ichihashi, Y.; Takeuchi, M.; Kishiguchi, S.; Anpo, M. *J. Synchrotron Radiat.* **1999**, *6*, 451.

- (2) Klosek, S.; Raftery, D. *J. Phys. Chem. B* **2001**, *105*, 2815.  
(3) Kisch, H.; Zang, L.; Lange, C.; Maier, W. F.; Antonius, C.; Meissner, D. *Angew. Chem.* **1998**, *110*, 3201; *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3034.  
(4) Zang, L.; Lange, C.; Maier, W. F.; Abraham, I.; Storck, S.; Kisch, H. *J. Phys. Chem. B* **1998**, *102*, 10765.  
(5) Zang, L.; Macyk, W.; Lange, C.; Maier, W. F.; Antonius, C.; Meissner, D.; Kisch, H. *Chem. Eur. J.* **2000**, *6*, 379.  
(6) Macyk, W.; Kisch, H. *Chem. Eur. J.* **2001**, *7*, 1862.  
(7) Burgeth, G.; Kisch, H. *Coord. Chem. Rev.* **2002**, *230*, 41.  
(8) Lettmann, C.; Hildenbrand, K.; Kisch, H.; Macyk, W.; Maier, W. *F. Appl. Catal. B* **2001**, *32*, 215.  
(9) Khan, S.; Al-Shahry, M.; Ingler, W. B. *Science* **2002**, *297*, 5590.  
(10) Sakthivel, S.; Kisch, H. *Angew. Chem.* **2003**, *115*, 5057; *Angew. Chem., Int. Ed. Engl.* **2003**, *42*, 4908.  
(11) Sato, S. *Chem. Phys. Lett.* **1986**, *123*, 126.  
(12) Asahi, R.; Morikawa, T.; Ohwaki, T.; Aoki, A.; Taga, Y. *Science* **2001**, *293*, 269.  
(13) Morikawa, T.; Asahi, R.; Ohwaki, T.; Aoki, A.; Taga, Y. *Jpn. J. Appl. Phys.* **2001**, *40*, 561.  
(14) Sakthivel, S.; Kisch, H. *ChemPhysChem* **2003**, *4*, 487.  
(15) Irie, H.; Watanabe, Y.; Hashimoto, K. *J. Phys. Chem. B* **2003**, *107*, 5483.  
(16) Lindgren, T.; Mwabora, J. M.; Avendano, E.; Jansson, J.; Hoel, A.; Granqvist, C.-G.; Lindqvist, S.-E. *J. Phys. Chem. B* **2003**, *107*, 5709.  
(17) Gole, J. L.; Stout, J. D.; Burda, C.; Lou, Y.; Chen, X. *J. Phys. Chem. B* **2004**, *108*, 1230.  
(18) Diwald, O.; Thomson, T. L.; Zubkov, T.; Goralski, Ed. G.; Walck, S. D.; Yates, J. T. *J. Phys. Chem. B* **2004**, *108*, 6004.  
(19) Umebayashi, T.; Yamaki, T.; Itoh, H.; Asai, K. *Appl. Phys. Lett.* **2002**, *81*, 454.  
(20) Umebayashi, T.; Yamaki, T.; Tanaka, S.; Asai, K. *Chem. Lett.* **2003**, *32*, 330.  
(21) Ohno, T.; Mitsui, T.; Matsumura, M. *Chem. Lett.* **2003**, *32*, 364.  
(22) Kisch, H.; Macyk, W. *ChemPhysChem* **2002**, *3*, 399.  
(23) Abdullah, M.; Low, G. K. C.; Matthews, R. W. *J. Phys. Chem.* **1990**, *94*, 6820.  
(24) Navio, J. A.; Cerrillos, C. C.; Real, C. *Surf. Interface Anal.* **1996**, *24*, 355.  
(25) Honda, F.; Hirokawa, K. *J. Electron Spectrosc. Relat. Phenom.* **1977**, *10*, 125.  
(26) Sakthivel, S.; Kisch, H. Unpublished results.  
(27) Karvaly, B.; Hevesy, I. Z. *Naturforsch. Teil A* **1971**, *26*, 245.  
(28) This corresponds to absorption onsets of 415, 420, 420, and 426 nm, respectively.  
(29) Roy, A. M.; De, G. C.; Sasmal, N.; Bhattacharyya, S. S. *Int. J. Hydrogen Energy* **1995**, *20*, 627.  
(30) Ward, M. D.; White, J. R.; Bard, A. J. *J. Am. Chem. Soc.* **1983**, *105*, 27.