

# Surface Characterization of Nanoparticles of $\text{NiO}_x/\text{In}_{0.9}\text{Ni}_{0.1}\text{TaO}_4$ : Effects on Photocatalytic Activity

Zhigang Zou,<sup>\*,†</sup> Jinhua Ye,<sup>‡</sup> and Hironori Arakawa<sup>\*,†</sup>

Photoreaction Control Research Center (PCRC), National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan, and Ecomaterials Center (EMC), National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

Received: July 17, 2002; In Final Form: September 12, 2002

The highly crystalline nanoparticles of  $\text{In}_{0.9}\text{Ni}_{0.1}\text{TaO}_4$ , with a wolframite-type structure, were prepared by a solid-state reaction method. The band gap  $E_g$  of  $\text{In}_{0.9}\text{Ni}_{0.1}\text{TaO}_4$  is about 2.3 eV, and particles with sizes in the range of 300–500 nm were observed by TEM measurements. We loaded 1.0 wt % partially oxidized nickel as electron-trapping and hydrogen-evolution sites onto the  $\text{In}_{0.9}\text{Ni}_{0.1}\text{TaO}_4$  surface from an aqueous  $\text{Ni}(\text{NO}_3)_2$  solution. The TEM measurements show that nearly spherical nano  $\text{NiO}_x$  particles with a size of about 15 nm are distributed on the surface of  $\text{In}_{0.9}\text{Ni}_{0.1}\text{TaO}_4$ . Stoichiometric amounts of oxygen and hydrogen were evolved under visible-light irradiation using  $\text{NiO}_x/\text{In}_{0.9}\text{Ni}_{0.1}\text{TaO}_4$  with a quantum yield of about 0.66%. This system behaves as a short-circuited microphotoelectrochemical cell. The surface of  $\text{NiO}_x$  is the cathode, and the surface of  $\text{In}_{0.9}\text{Ni}_{0.1}\text{TaO}_4$  is the anode.

## Introduction

It is believed that upon excitation of a photon a separated electron and hole can move to the surface of a semiconductor particle. If the conduction-band potential level of a semiconductor is more negative than that of hydrogen evolution and the valence-band potential level is more positive than that of oxygen evolution, then it is possible to split water into  $\text{H}_2$  and  $\text{O}_2$ .<sup>1</sup> This process takes place in  $\text{H}_2\text{O} + \text{photocatalyst} + h\nu \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2$  (the standard potential  $E^0$  of water is  $-1.23$  eV (SHE, pH = 0.0)). However, from the viewpoint of the efficient use of solar energy, the water-splitting photocatalysts should be active in the visible light region, which is the rich portion of the solar spectrum.<sup>2–5</sup>

Very recently, we have observed a new series of photocatalysts,  $\text{NiO}_x$ - or  $\text{RuO}_2$ -loaded semiconductors  $\text{In}_{1-x}\text{Ni}_x\text{TaO}_4$  ( $x = 0.0\text{--}0.2$ ), which induces the direct splitting of water into stoichiometric amounts of oxygen and hydrogen under visible-light irradiation.<sup>6,7</sup> The photocatalytic activity changed with the variation of  $x$  in  $\text{In}_{1-x}\text{Ni}_x\text{TaO}_4$ , with the photocatalyst at  $x = 0.1$  showing the highest activity. Since the reaction of photocatalysis occurs on the surface of the photocatalyst, various parameters in models predicting the conversion efficiency of solar water splitting may be combined to characterize the surface on the photocatalyst in a solar photocatalysis system using semiconductors.<sup>6–9</sup>

To know the details of the preparation conditions of visible-light-driven photocatalysts that yield an overall solar photocatalysis efficiency, in the present study, we have chosen the  $\text{NiO}_x/\text{In}_{0.9}\text{Ni}_{0.1}\text{TaO}_4$  system. Here, we report the surface characteristics of the  $\text{NiO}_x/\text{In}_{0.9}\text{Ni}_{0.1}\text{TaO}_4$  photocatalyst and the effects of surface characteristics on photocatalytic activity.

## Experimental Section

The powdered semiconductor  $\text{In}_{0.9}\text{Ni}_{0.1}\text{TaO}_4$  was prepared by a solid-state reaction method at 1100 °C. Predried  $\text{In}_2\text{O}_3$ ,  $\text{Ta}_2\text{O}_5$ , and  $\text{NiO}$  with a purity of 99.99% were used as starting materials.<sup>6,7</sup> The powder X-ray diffraction (XRD) pattern of  $\text{In}_{0.9}\text{Ni}_{0.1}\text{TaO}_4$  was measured with Cu K $\alpha$  radiation ( $\lambda = 1.54178$  Å). XRD data were collected with a step-scan procedure in the range of  $2\theta = 5\text{--}100^\circ$ . The step interval was  $0.024^\circ$ , and the scan speed,  $1^\circ \text{ min}^{-1}$ . The chemical composition of the samples before and after the photocatalytic reactions was determined by TEM-EDAX analysis. UV–vis diffuse reflectance spectra of the photocatalysts were measured at room temperature with a UV–vis spectrometer.

We loaded 1.0 wt % partially oxidized nickel as electron-trapping and hydrogen-evolution sites onto the  $\text{In}_{0.9}\text{Ni}_{0.1}\text{TaO}_4$  surface from an aqueous  $\text{Ni}(\text{NO}_3)_2$  solution by an impregnation method. The Ni-loaded photocatalyst was first calcined at 350 °C for 1 h in air and reduced in a  $\text{H}_2$  atmosphere at 500 °C for 2 h and then treated in an  $\text{O}_2$  atmosphere at 200 °C for 1 h. The double-layered structure of metallic Ni and NiO (denoted  $\text{NiO}_x$ ) was formed on the surface of  $\text{In}_{0.9}\text{Ni}_{0.1}\text{TaO}_4$  by a reduction–oxidation procedure.<sup>6,10</sup>

The photocatalytic reaction was examined using a closed gas-circulation system. The powdered photocatalyst (0.5 g) was suspended in 250 mL of pure water in a Pyrex glass cell. A 300-W Xe arc lamp was focused through a shutter window, and a 420-nm-long pass filter was placed on the surface of the cell. The gases that evolved were identified with TCD gas chromatograph that was connected to the glass-made gas-circulation line attached to the Pyrex glass cell.

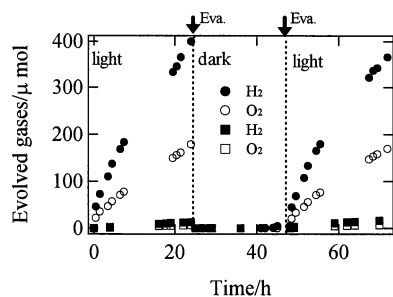
## Results and Discussion

Figure 1 shows the stoichiometric evolution of  $\text{H}_2$  and  $\text{O}_2$  from pure water with  $\text{In}_{0.9}\text{Ni}_{0.1}\text{TaO}_4$  and a loaded 1.0 wt % partially oxidized nickel  $\text{NiO}_x/\text{In}_{0.9}\text{Ni}_{0.1}\text{TaO}_4$  photocatalyst suspension under visible light irradiation ( $\lambda > 420$  nm). The

\* Corresponding authors. E-mail: z.zou@aist.go.jp and h.arakawa@aist.go.jp.

<sup>†</sup> National Institute of Advanced Industrial Science and Technology (AIST).

<sup>‡</sup> National Institute for Materials Science (NIMS).



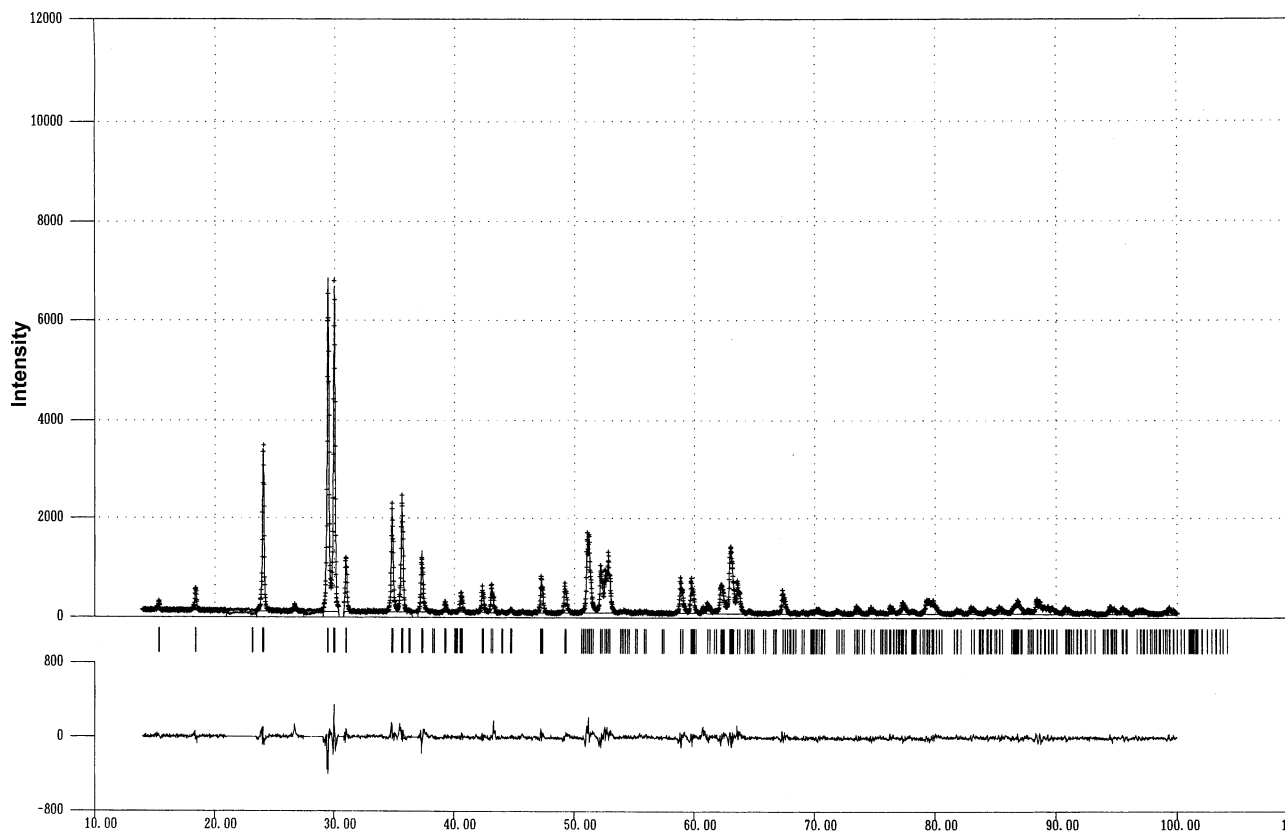
**Figure 1.** Reaction time course of the photocatalytic water splitting into  $\text{H}_2$  and  $\text{O}_2$  under visible light irradiation ( $\lambda > 420 \text{ nm}$ ) using a suspension of  $\text{In}_{0.9}\text{Ni}_{0.1}\text{TaO}_4$  (■,  $\text{H}_2$ ; □,  $\text{O}_2$ ) and  $\text{NiO}_x/\text{In}_{0.9}\text{Ni}_{0.1}\text{TaO}_4$  (●,  $\text{H}_2$ ; ○,  $\text{O}_2$ ) as a catalyst. Eva. means evacuating the system. The photocatalytic reaction was carried out in a closed gas-circulation system. The 0.5 g powder sample was suspended in 250 mL of pure water using a Pyrex glass cell. A 300-W Xe arc lamp was focused through a shutter window, and a 420-nm cut filter was placed onto the window face of the cell. The gases evolved were determined with TCD gas chromatography, which was connected to a gas-circulation line.

gas evolution stopped when the light was turned off, showing that the reaction is induced by the absorption of visible light. The rates of  $\text{H}_2$  and  $\text{O}_2$  evolution were about  $16.6$  and  $8.3 \mu\text{mol h}^{-1}$ , respectively, on  $\text{NiO}_x/\text{In}_{0.9}\text{Ni}_{0.1}\text{TaO}_4$ . The activity increases by about 4000% over that of nonloaded  $\text{NiO}_x$ . This means that the loaded  $\text{NiO}_x$  on the surface of  $\text{In}_{0.9}\text{Ni}_{0.1}\text{TaO}_4$  led to an increase in the activity of the photocatalyst. The quantum yield at 402 nm was estimated to be 0.66% by using an interference filter ( $\lambda = 402 \text{ nm}$ , half width = 15.3 nm). Figure 1 shows that after evacuating the system, almost the same rate was reproduced in the second; furthermore, the ratio of the total amount of gas evolved to the amount of catalyst (mol) was greater than 1.0 at 80 h, indicating that the reaction occurs catalytically.

The light-absorption properties of  $\text{In}_{0.9}\text{Ni}_{0.1}\text{TaO}_4$  were investigated. The visible absorption spectra of these compounds are extremely characteristic.<sup>6,7</sup> This means that the photocatalysts have the ability to respond to visible light. The band gap was estimated to be 2.3 eV from plots of the square root of Kubelka–Munk functions  $F(R)$  versus photon energy.<sup>11</sup>

To better understand the origin of the photocatalysts, we examined the atomic ratio and crystal structure of these photocatalysts before and after reaction. XRD analysis showed that the change in the samples before and after reaction was unobservable. Full-profile structure refinement of XRD data was performed using the Rietveld program RIETAN.<sup>12</sup> Figure 2 shows the final result of the refinement, which indicated good agreement between the observed and calculated intensities for the monoclinic wolframite-type structure with a space group of  $P2_1/a$ . The lattice parameters are  $a = 5.1532(1)$ ,  $b = 5.7729(2)$ , and  $c = 4.8218(1) \text{ \AA}$  and  $\beta = 91.3525(3)^\circ$ . TEM-EDAX analysis shows that these photocatalysts before and after reaction have a homogeneous atomic distribution. The chemical composition is close to the starting stoichiometric amounts of the precursors. From these experimental results, we confirmed that these photocatalysts have not changed in either the crystal structure or the chemical composition after reaction.

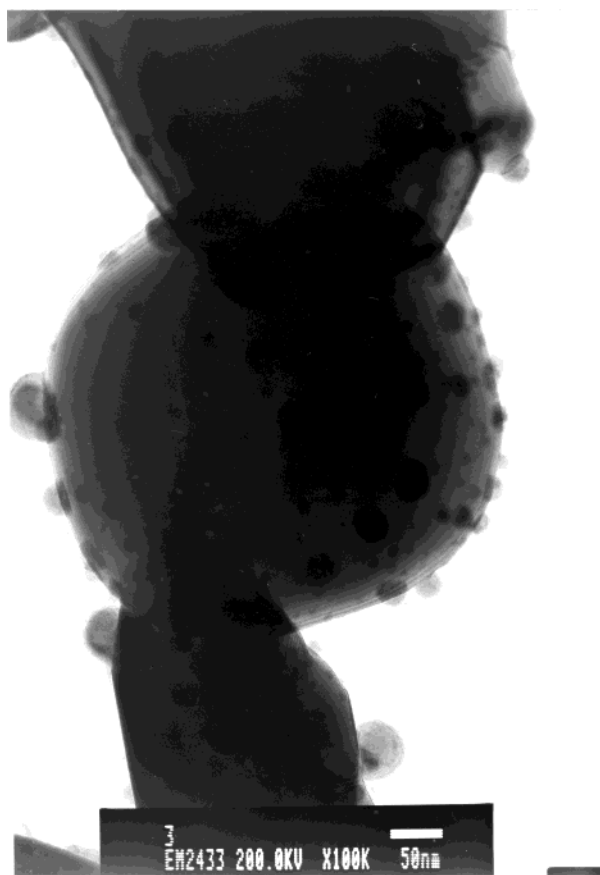
Figure 3 shows a TEM micrograph of  $\text{In}_{0.9}\text{Ni}_{0.1}\text{TaO}_4$ . Fine particles with high crystallinity were observed. Particles with sizes in the range of 300–500 nm are dominant. Since the surface area of the photocatalyst affects the number of active sites in a photocatalytic reaction and the particle size influences the distance that photogenerated electrons and holes have to migrate in the bulk of the semiconductor particle to reach the active sites,<sup>13</sup> it is possible to increase the activity by increasing the surface area. However, the suppression of recombination of the separated electron and hole excited by the absorption of



**Figure 2.** Rietveld refinement of XRD data for  $\text{In}_{0.9}\text{Ni}_{0.1}\text{TaO}_4$  by a solid-state reaction method at 1100 °C for space group  $P2_1/a$ . A difference (obsd – calcd) profile is shown beneath. The tic marks represent reflection positions.

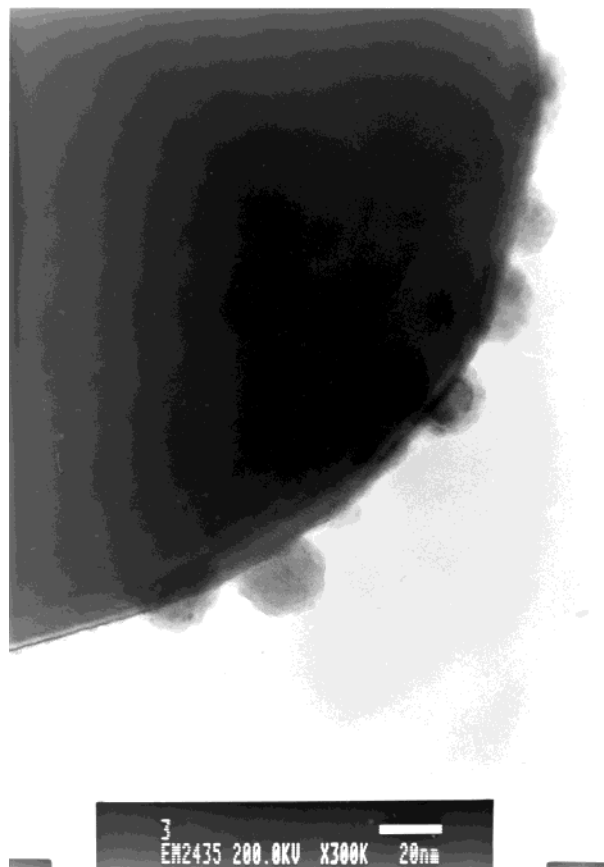


**Figure 3.** TEM micrograph of the  $\text{In}_{0.9}\text{Ni}_{0.1}\text{TaO}_4$  particles.



**Figure 4.** TEM micrograph of  $\text{NiO}_x/\text{In}_{0.9}\text{Ni}_{0.1}\text{TaO}_4$  photocatalyst.

a photon seems to be more important than increasing the surface area and decreasing the particle size<sup>14</sup> because the deficiency



**Figure 5.** TEM image of the extending surface structure of the  $\text{NiO}_x/\text{In}_{0.9}\text{Ni}_{0.1}\text{TaO}_4$  photocatalyst.

in the crystal is usually the center of recombination of the separated electron and hole. The high crystallinity and fineness of semiconductor particles might be efficient in suppressing the recombination, resulting in increasing conversion efficiency.

It is interesting that the growth steps formed in the process of crystallization were observed clearly on the particle surface (see Figure 3). The stage of the steps is about 3–5 nm. From a study of photocatalytic water splitting for the  $\text{NiO}_x/\text{NaTaO}_3$  photocatalyst, it was found that the characteristic step structure on the surface of the  $\text{NaTaO}_3$  semiconductor may contribute to the creation of highly active sites, resulting in an increase in the photocatalytic activity for water splitting.<sup>14</sup> A multielectron transfer reaction of water oxidation to form  $\text{O}_2$  seems to proceed more favorably on the step than on the flat surface because of a geometric effect.<sup>14</sup> Mallouk et al.<sup>15</sup> studied the photochemical hydrogen evolution from nonsacrificial electron donors. They found that layered metal oxide semiconductor particles evolve hydrogen more easily because the photogenerated electron–hole pairs can move effectively to the surface.<sup>15</sup> It is hard to conclude at the present level of experimental accuracy that the step structure on the surface of our photocatalysts led to high activity. However, judging from the result for  $\text{NaTaO}_3$ , the activity of the photocatalyst with the step structure is much higher than that with the flat surface. The step structure on the surface might contribute to higher photocatalysis efficiency, but further investigation is necessary.

We loaded 1.0 wt % partially oxidized nickel as electron-trapping and hydrogen-evolution sites onto the  $\text{In}_{0.9}\text{Ni}_{0.1}\text{TaO}_4$  surface. The treatment was conducted to suppress the backward reaction of water splitting on the nickel metal surface. Figure 4 shows a TEM micrograph of the  $\text{NiO}_x/\text{In}_{0.9}\text{Ni}_{0.1}\text{TaO}_4$  photocatalyst. Nearly spherical  $\text{NiO}_x$  particles are distributed on

the surface of  $\text{In}_{0.9}\text{Ni}_{0.1}\text{TaO}_4$ . EDAX analysis of the  $\text{NiO}_x/\text{In}_{0.9}\text{Ni}_{0.1}\text{TaO}_4$  photocatalysts indicated that  $\text{NiO}_x$  is localized on the surface of the semiconductor  $\text{In}_{0.9}\text{Ni}_{0.1}\text{TaO}_4$ . Figure 5 shows a TEM image of the magnified surface structure of  $\text{NiO}_x/\text{In}_{0.9}\text{Ni}_{0.1}\text{TaO}_4$ . The  $\text{NiO}_x$  particles with sizes of about 15 nm were localized on the surface of  $\text{In}_{0.9}\text{Ni}_{0.1}\text{TaO}_4$ . This system behaves as a short-circuited microphotoelectrochemical cell. The surface of  $\text{NiO}_x$  is the cathode, and the surface of  $\text{In}_{0.9}\text{Ni}_{0.1}\text{TaO}_4$  is the anode. Band-gap excitation in the bulk of the  $\text{In}_{0.9}\text{Ni}_{0.1}\text{TaO}_4$  semiconductor injects negatively charged electrons into the  $\text{NiO}_x$  particles and positively charged holes into the surface of the  $\text{In}_{0.9}\text{Ni}_{0.1}\text{TaO}_4$  particles. Trapped electrons on the surface of  $\text{NiO}_x$  reduce water to hydrogen, and the holes on the surface of  $\text{In}_{0.9}\text{Ni}_{0.1}\text{TaO}_4$  oxidize water to oxygen. The presence of  $\text{NiO}_x$  significantly enhances  $\text{H}_2$  and  $\text{O}_2$  production. Additional research is clearly necessary to enhance the efficiency of the photocatalyst by modifying the surface state. Studies to help us understand the photocatalytic mechanism are also currently underway in our laboratory. Nevertheless, the work described here suggests that surface characteristics of photocatalysts strongly affect their activity.

In conclusion, we have demonstrated the surface characteristics of  $\text{NiO}_x/\text{In}_{0.9}\text{Ni}_{0.1}\text{TaO}_4$ . One of the most important factors for increasing their activity might be to suppress the recombina-

tion of the separated electron and hole by excitation with a photon. Our results showed that the catalytic efficiency of the photocatalyst could be improved by increasing its crystallinity and by suitable modification of the surface sites.

## References and Notes

- (1) Honda, K.; Fujishima, A. *Nature (London)* **1972**, 238, 37.
- (2) Kawai, T.; Sakata, T. *Nature (London)* **1980**, 286, 474.
- (3) Linsebigler, A. L.; Lu, G.; Yates, J. T., Jr. *Chem. Rev.* **1995**, 95, 735.
- (4) Geoffrey, B. S.; Thomas, E. M. *J. Phys. Chem. B* **1997**, 101, 2508.
- (5) Kim, Y., II; Salim, S.; Huq, M. J.; Mallouk, T. E. *J. Am. Chem. Soc.* **1991**, 113, 9561.
- (6) Zou, Z.; Ye, J.; Sayama, K.; Arakawa, H. *Nature (London)* **2001**, 414, 625.
- (7) Zou, Z.; Ye, J.; Arakawa, H. *J. Mater. Res.* **2002**, 17, 1419.
- (8) Mills, A.; Hunte, S. L. *J. Photochem. Photobiol., A* **1997**, 108, 1.
- (9) Zou, Z.; Ye, J.; Arakawa, H. *Chem. Phys. Lett.* **2000**, 332, 271.
- (10) Kudo, K.; et al. *J. Catal.* **1989**, 120, 337.
- (11) Kim, Y., II; Atherton, S.; Brigham, E. S.; Mallouk, T. E. *J. Phys. Chem.* **1993**, 97, 11802.
- (12) Izumi, F. *J. Crystallogr. Assoc. Jpn.* **1985**, 27, 23.
- (13) Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. *Chem. Rev.* **1995**, 95, 69.
- (14) Kudo, A.; Kato, H. *Chem. Phys. Lett.* **2000**, 331, 373.
- (15) Kim, Y. II; Atherton, S.; Brigham, E. S.; Mallouk, T. E. *J. Phys. Chem.* **1993**, 97, 11802.