ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 4, pp. 611–616. © Pleiades Publishing, Ltd., 2014.
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Photocatalytic Activity of TiO_2–MO_x Composites in the Reaction of Hydrogen Generation from Aqueous Isopropanol Solution

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Received November 21, 2013

Abstract—The photocatalytic activity of the composites TiO_2–MO_x (M = Ni, Cu, Zn, Fe, Cr) was studied in the reaction of hydrogen generation from aqueous alcoholic suspensions under UV light. The samples modified by the oxides of the metals capable of being reduced from oxides under photocatalytic conditions showed a high catalytic activity. The studied modifiers were divided in three groups in terms of their effect of the photocatalytic activity of TiO_2: activating (NiO, CuO), inhibiting (Fe_2O_3), and indifferent (ZnO, Cr_2O_3).

Keywords: titanium dioxide, photocatalysis

DOI: 10.1134/S107036321404001X

In modern science considerable effort is devoted to search for an efficient way of introducing alternative environmentally friendly, and inexhaustible power sources. Much researcher's attention is focused on photoinduced processes which allow accumulation of the light energy in chemical reaction products. Among such reactions the greatest promise is held by the photocatalytic decomposition of water into hydrogen and oxygen, because water is an accessible reagent, and the reaction product is hydrogen which is considered by the fuel of the future. The discovery of photoinduced water decomposition dates back to 1972, when Fujishima and Honda observed this process on UV irradiation of titanium dioxide in a photoelectron-chemical cell [1]. Since then much emphasis was put on the development of high-efficiency photocatalytic systems both by modification of titanium dioxide [2–4] and by testing other catalysts, not infrequently having quite a complicated composition and structure [5–8].

The most challenging problem is to shift the working spectral range from UV to visible for efficient utilization of sunlight. The present applications of photocatalysis include purification and disinfection of air [9], development of self-cleaning surfaces [10], sterilization of surgical instruments, as well as oxidation of organic water pollutants [11]. Since in this case artificial UV sources are allowed, the most popular catalyst is titanium dioxide owing to its chemical stability, safety, and ability to oxidize almost all organic compounds under irradiation [9, 12].

The mechanism of heterogeneous photocatalysis on semiconductor catalysts involves light absorption and generation of electrons and holes which further take part in redox reactions of particles adsorbed on the surface [13]. Titanium dioxide is a widely used photocatalyst [14], but individual TiO_2 is not active enough to be used in practice, especially for hydrogen production. Therefore the TiO_2 surface is usually modified by platinum particles (cocatalyst) [15]. This results in, on the one hand, in spacial separation of the oxidation and reduction centers (via transfer of the photogenerated electrons onto the metal), and on the other, the overvoltage of hydrogen reduction. At the same time, platinum as a cocatalyst has certain drawbacks, specifically, it can catalyze the reverse dark reaction of hydrogen with oxygen and also has a high cost. There are other possible cocatalysts for TiO_2 in reactions accompanied by hydrogen release, specifically nickel and copper oxides [16, 17]. Zinc oxide, Fe_2O_3, and Cr_2O_3 oxides can enhance the photocatalytic activity of TiO_2 in some other processes [18–20].

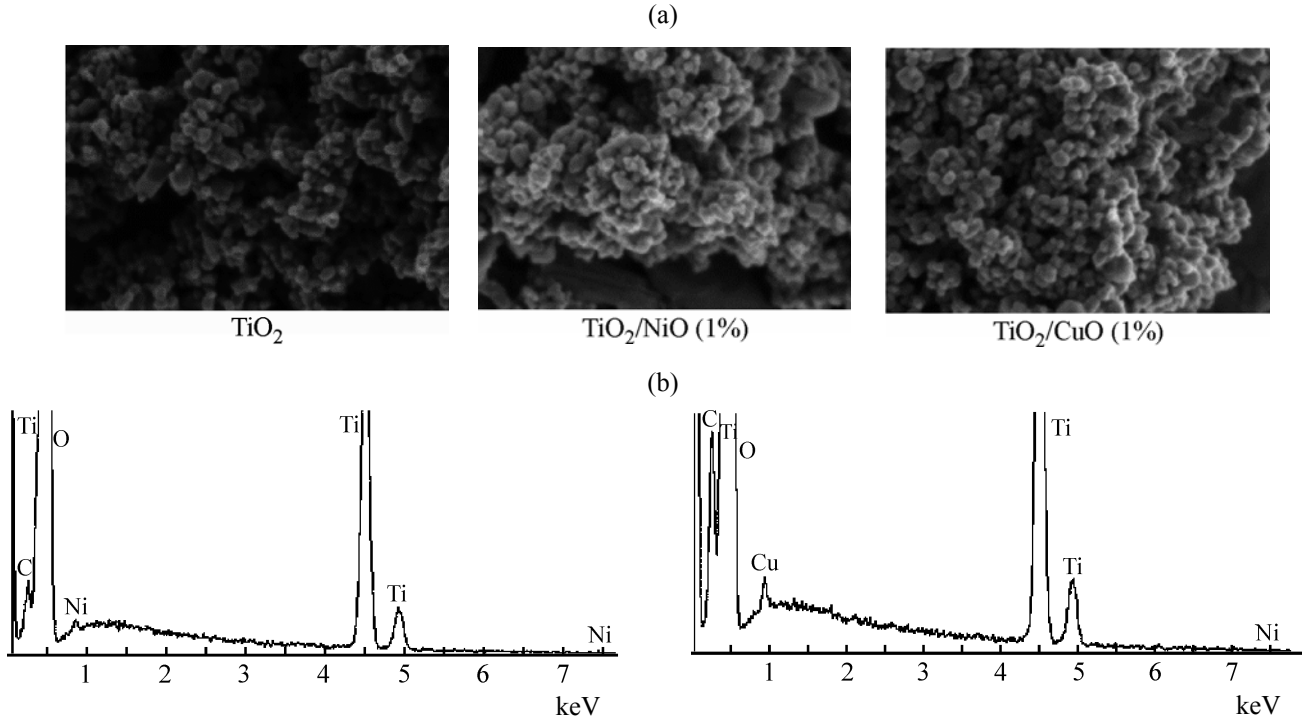

Fig. 1. (a) Electron micrographs of titanium dioxide before and after modification and (b) results of elemental analysis of TiO_2–NiO (1%) and TiO_2–CuO (1%).

The photocatalytic activity can sometimes be enhanced two orders of magnitude by a rightly chosen co-catalyst. However, at present the problem of optimization of cocatalyst nature and amount is solved exclusively at the experimental level, because no reliable methods for theoretical predictions have yet been developed. In this connection, useful information can be obtained only if photocatalytic activity studies on modified samples are performed in identical and reproducible conditions.

The aim of the present work was to compare the photocatalytic activity of NiO-, CuO-, ZnO-, Fe_2O_3-, Cr_2O_3-, and Pt-modified titanium dioxide in the model reaction of hydrogen generation from aqueous isopropanol solution.

The samples containing oxide modifiers were prepared by wet impregnation from TiO_2 powder. According to electron microscopy data, the modification of TiO_2 by transition metal oxides had no appreciable effect on the morphology of its particles (Fig. 1a), whereas elemental analysis detected Cu and Ni in the studied samples (Fig. 1b). X-ray phase analysis showed defined reflexes from the modifier phase only when the CuO fraction had become higher than 10%. The fact that we did not observe modifier oxide particles in the micrographs is most likely explained by their small size (<5 nm). Because of the large surface area of TiO_2 (50 m^2/g), the number of crystallization nuclei is large, and the crystal size is small.

The kinetic curves obtained for the TiO_2–NiO sample (NiO fraction 0.25–1.5%) are presented in Fig. 2. In the case of individual TiO_2, the hydrogen generation rate decreases with time and reaches 48 μL/h by the end of the experiment. This retardation is likely to be associated with poisoning of the photocatalyst surface and decrease in the number of active centers. With TiO_2 modified with NiO, the hydrogen generation rate gets much higher, and a self-acceleration effect is observed: the curves corresponding to modified samples have a concave shape, and the larger the fraction of NiO, the stronger acceleration is observed. This effect is apparently associated with the partial reduction of NiO to nickel metal under the photocatalytic reaction conditions. Evidence for this suggestion is provided by an appreciable darkening of the reaction suspension by the end of the experiment, which has not been observed for individual TiO_2. The darkening becomes especially evident at high NiO concentrations. In view

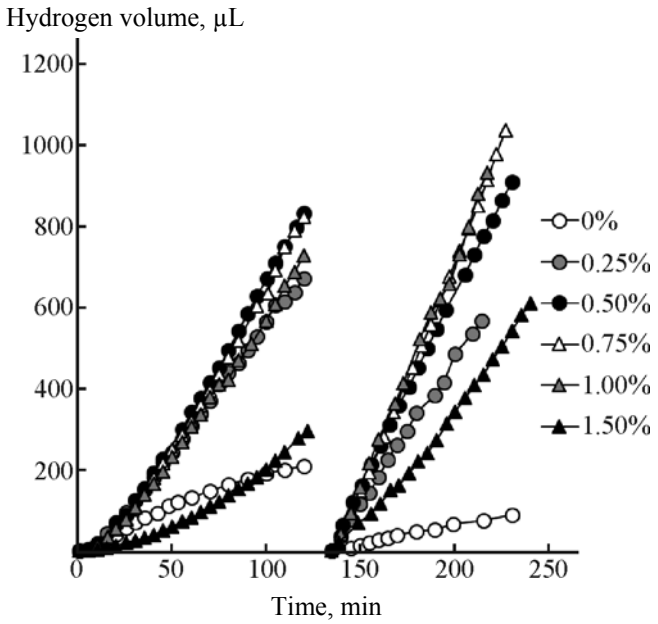

Fig. 2. Dependence of generated hydrogen volume on the time of irradiation of TiO_2 suspensions with different contents of the NiO surface modifier.

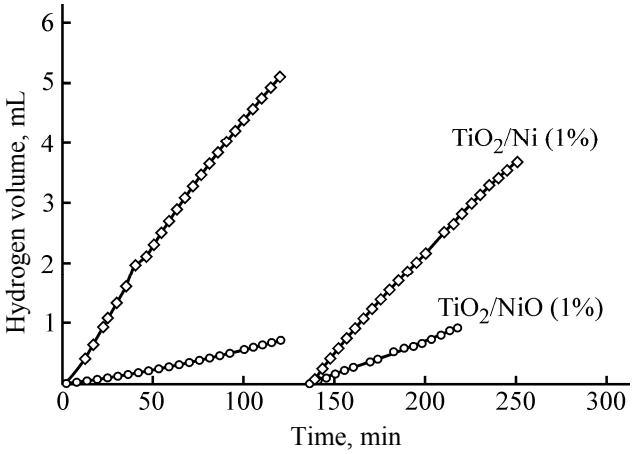

Fig. 3. Dependence of generated hydrogen volume on the time of irradiation of TiO_2-NiO and TiO_2–Ni suspensions.

of the fact that the hydrogen generation rate tends to increase in the course of the experiment, we can conclude that just nickel metal is an efficient cocatalyst of this process. On the one hand, nickel, indeed, exhibits electrocatalytic properties in hydrogen generation reactions. On the other hand, its function may consist in forming ohmic contact with titanium dioxide, which facilitates the outflow of photogenerated electrons and favor spatial charge separation.

After the reduction in hydrogen (NiO fraction 1%), the sample has acquired a dark gray color. The hydrogen generation rate compared to the unreduced sample has increased ~5 times (3150 μL/h). This finding gave further evidence to show that just nickel metal works as an efficient cocatalyst (Fig. 3).

The deceleration of hydrogen generation during the experiment with the TiO_2–Ni catalyst can be associated with the fact that the concentration of isopropanol decreases by the end of the experiment. This decrease can no longer be ignored in view of the high reaction rate (the taken amount of isopropanol is enough to form 68 mL of H_2 at the stoichiometric ratio of 1 : 1). Under the photoreaction conditions, complete reduction of NiO to Ni [reaction (1)], obviously does not occur, because the increasing amount of reduced nickel makes more and more competitive the generation of gaseous hydrogen by reaction (2). Therefore, the rate of hydrogen generation first increases to a certain value and then no longer changes.

$$NiO + 2H^+ + 2e^- \rightarrow Ni + H_2O, \quad (1)$$

$$2H^+ + 2e^- \xrightarrow{[Ni]} H_2. \quad (2)$$

The modification of TiO_2 with CuO resulted in a strong enhancement of the catalytic activity, too (Fig. 4).

Like with TiO_2–NiO, self-acceleration of the photocatalytic reaction at high CuO concentrations (> 1%) is observed. At the concentrations of 5 and 10%, a well-defined induction period takes place, and its duration correlates with the CuO concentration. This finding suggests that photogenerated electrons have a more favorable reaction route at the beginning of the reaction than to reduce H^+ to gaseous hydrogen. Obviously, this route involves CuO reduction. The kinetic curves become linear earlier than with NiO, implying earlier stabilization of the hydrogen generation rate. This fact can be explained by that copper has a higher reductive potential and a less expressed capacity to adsorb hydrogen than nickel. By the end of the experiment all TiO_2–CuO suspensions got dark (or black, when the CuO concentration was higher than 1%).

All kinetic curves for ZnO-, Cr_2O_3-, and Fe_2O_3-containing composites lie below the curve for individual TiO_2 (Fig. 5).

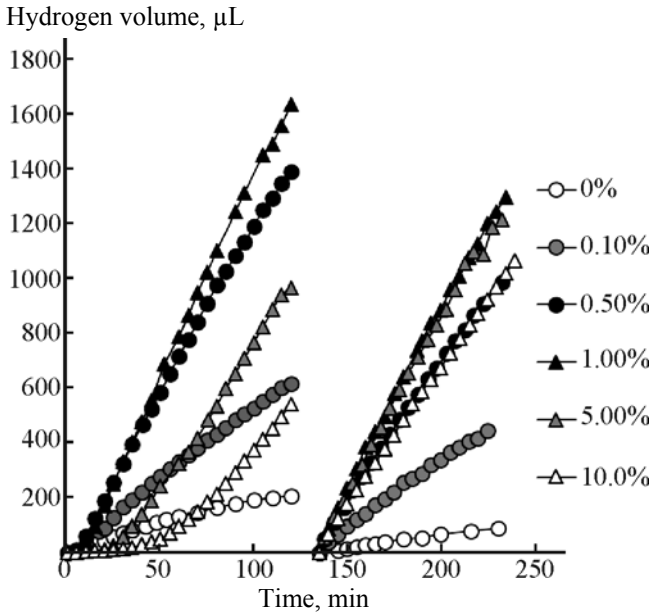

Fig. 4. Dependence of generated hydrogen volume on the time of irradiation of TiO_2 suspensions with different contents of the CuO surface modifier.

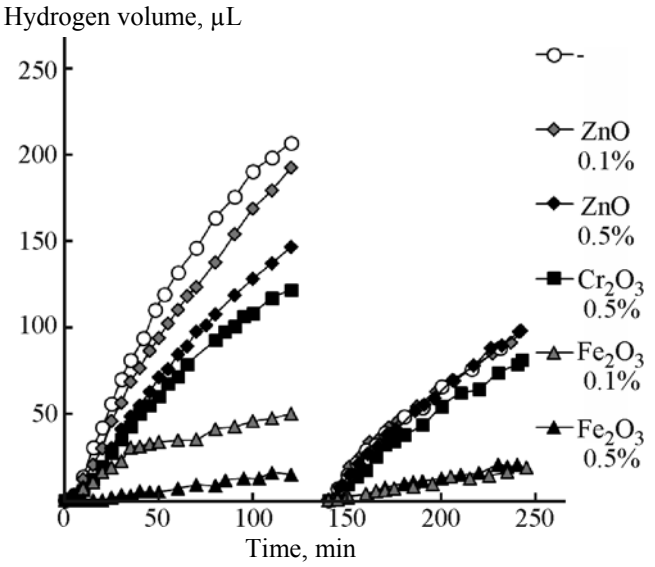

Fig. 5. Dependence of generated hydrogen volume on the time of irradiation of TiO_2 suspensions with different contents of the ZnO, Cr_2O_3, and Fe_2O_3 surface modifiers.

Suspensions did not change color both before and after experiment. The absence of the catalytic effect is probably associated with the absence of an efficient mechanism of charge separation in the system and the low tendency of the metals to be reduced from the corresponding oxides under the photoreaction conditions because of their low reductive potentials. As to Fe_2O_3, during the reaction iron can reversibly change its oxidation state from +3 to +2, thereby inducing the chain reaction (3), decreasing the yield of the photocatalytic reaction.

$$Fe^{3+} + e^- \rightarrow Fe^{2+}; Fe^{2+} + h^+ \rightarrow Fe^{3+}. \quad (3)$$

Since the hydrogen generation rate changed over the course of the reaction, we took as the measure of the photocatalytic activity of a sample the rate at the end of the experiment, when it is almost constant. Thus estimated hydrogen generation rates are listed in the table, and their ratios for different samples is illustrated in Fig. 6.

Thus, the resulting data allowed us to divide the surface oxide modifiers of TiO_2 into 3 groups in terms of their activity in photoinduced hydrogen generation in catalyst suspensions in aqueous isopropanol: activating (NiO, CuO), inhibiting (Fe_2O_3), and indifferent (ZnO, Cr_2O_3). The activating effects of NiO and CuO were very close to each other, up to the mofidier concentration of 1%. As would be expected, platinum proved to be the most efficient cocatalyst for titanium dioxide: It was 4 times superior in activity that the reduced nickel composite.

EXPERIMENTAL

X-Ray phase analysis was performed on an ARL X'TRA powder diffractometer (CuK_α radiation, 2θ range 5°–60°).

The particle morphology was studied using ZeissSupra 40VP and Zeiss Merlin scanning electron microscopes equipped by an Oxford Instruments INCAx-act detector for X-ray microanalysis.

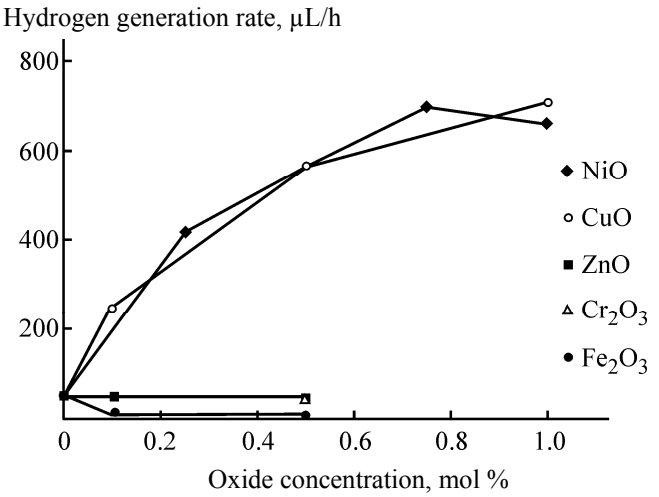

Fig. 6. Dependence of the hydrogen generation rate on the concentration of nanoparticles loaded on the TiO_2 surface.

Photoinduced hydrogen generation rates at different modifier concentrations in composites

Sample	Modifier concentration, %	Hydrogen generation rate, μmol/h
TiO_2	–	2.1
TiO_2–NiO	0.25	18
	0.5	25
	0.75	31
	1	29
	1.5	12
TiO_2–Ni	1	141
TiO_2–CuO	0.1	11
	0.5	25
	1	32
	5	31
	10	27
TiO_2–ZnO	0.1	2.1
	0.5	2.1
TiO_2–Cr_2O_3	0.5	2.0
TiO_2–Fe_2O_3	0.1	0.5
	0.5	0.5
TiO_2–Pt	0.5	581

Composite oxide photocatalysts were prepared by the wet impregnation technique. The starting materials were Degussa (Evonik) P25 TiO_2 (particle size 20–30 nm, specific surface area 50 m^2/g) and transition metal nitrates of no less than analytical grade. A solution of metal nitrate of required concentration, 2 mL, was poured onto 1 g of TiO_2, and the mixture was thoroughly triturated in an agate mortar at 35°C until water evaporated completely. The resulting powder was dried for 10 h at 80°C and then calcined at 350°C in a silit furnace for 1 h. Nitrates decomposed according to Eqs. (4) and (5).

$$Me(NO_3)_2 \rightarrow MeO + 2NO_2\uparrow + 1/2O_2\uparrow, \quad (4)$$

$$2Me(NO_3)_3 \rightarrow Me_2O_3 + 6NO_2\uparrow + 3/2O_2\uparrow. \quad (5)$$

Nickel reduction in the composite samples was performed in hydrogen flow at 400°C for 1 h.

Composite TiO_2–Pt. Hexachloroplatinic acid $H_2PtCl_6 \cdot 6H_2O$, 0.0045 g, was dissolved in a suspension of 0.07 g of TiO_2 in 70 mL of 0.1% isopropanol, and was placed into a reactor to precipitate platinum onto the TiO_2 surface by the photocatalytic reduction of the hexachloroplatinate anion under UV irradiation [Eq (6)].

$$PtCl_6^{2-} + 4e^- \rightarrow Pt + 6Cl^-. \quad (6)$$

Photocatalytic activity measurements were performed at the device described in [8], radiation source being a DRT-125 mercury lamp. A light filter (temperature-controlled $CuSO_4$ solution, 15°C, cell thickness 22 mm) was used to cut off the IR and short-wave UV ($\lambda < 280$) radiation. A suspension of 0.055 g of catalyst (grounded in a mortar) in 55 mL of 0.1% aqueous isopropanol was loaded into the reactor and left to stand for a day for equilibration. Immediately before experiment the suspension was ultrasonicated for 10 min (SAPFIR UV bath, 55 W) to disintegrate coarse catalyst particles. The duration of one photocatalytic experiment was 4 h. The quantity of released hydrogen was determined by gas chromatography (Tsvet-800, thermal conductivity detector), samples for analysis were taken every 5–10 min.

ACKNOWLEDGMENTS

The work was financially supported by the Russian Foundation for Basic Research (project no. 12-03-00761) and St. Petersburg State University (contract no. 12.0.105.2010).

The work was performed using the equiment of the Interdisciplinary Resourse Center for Nanotechnology, St. Petersburg State University.

REFERENCES

1. Fujishima, A and Honda, K., *Nature,* 1972, vol. 238, p. 37
2. Pal, U., Ghosh, S., and Chatterjee, D., *Transition Metal Chem*., 2012, vol. 37, p. 93.
3. Stengl, V., Bakardjieva, S., and Murafa, N., *Mater. Chem. Phys*., 2009, vol. 114, p. 217.
4. Gavrilov, A.I., Rodionov, I.A., Gavrilova, D.Yu., Zvereva, I.A., Churagulov, B.R., and Tret'yakov, Yu.D., *Dokl. Chem.,* 2012, vol. 444, no. 2, p. 133.
5. Maeda, K., *J. Photochem. Photobiol. C*, 2011, vol. 12, p. 237.
6. Chen, X., Shen, S., Guo, L., and Mao, S.S., *Chem. Rev.,* 2010, vol. 110, p. 6503.
7. Osterloh, F.E., *Chem. Mater.,* 2008, vol. 20, p. 35.
8. Rodionov, I.A., Silyukov, O.I., Utkina, T.D., Chislov, M.V., Sokolova, Yu.P., and Zvereva, I.A., *Russ. J. Gen. Chem.*, 2012, vol. 82, no. 7, p. 1191.

9. Carp, O., Huisman, C.L., and Reller, A., *Prog. Solid State Chem*., 2004, vol. 32, p. 33.
10. Nakata, K. and Fujishima, A., *J. Photochem. Photobiol. C*, 2012, vol. 13, p. 169.
11. Kostedt, I., William, L., Drwiega, J., Mazyck, D.W., Lee, S.W., Sigmund, W., Wu, C.Y., and Chadik, P., *Environ. Sci. Technol*., 2005, vol. 39, p. 8052.
12. Fujishima, A., Rao, T.N., and Tryk, D.A., *J. Photochem. Photobiol. C,* 2000, vol. 1, p. 1.
13. Pleskov, Yu.V., *Fotoelektrokhimicheskoe preobrazovanie solnechnoi energii* (Photoelectrochemical Transformation of Solar Energy), Moscow: Khimiya, 1990, p. 59.
14. Cassaignon, S., Colbeau-Justin, C., and Durupthy, O., *Nanomaterials: A Danger or a Promise?: A Chemical and Biological Perspective*, Brayner, R., Fiévet, F., and Coradin, T., Eds., London: Springer, 2013, p. 153.
15. Li, M., Li, Y.,Peng, S., Lu, G., and Li, S., *Front. Chem. China*, 2009, vol. 4, p. 32.
16. Kudo, A., Domen, K., Maruya, K., and Onishi, T., *Chem. Phys. Lett*., 1987, vol. 133, p. 517.
17. Xu, S. and Sun, D.D., *Int. J. Hydrogen Energy*, 2009, vol. 34, p. 6096.
18. Chen, S., Zhao, W., Liu, W., and Zhang, S., *Appl. Surf. Sci*., 2008, vol. 255, p. 2478.
19. Liu, H., Shonb, Sun, X., Vigneswaran, S., and Nan, H., *Appl. Surf. Sci*., 2011, vol. 257, p. 5813.
20. Jung, Y.-S., Kim, K.-H., Jang, T.-Y., Tak, Y., and Baeck, S.-H., *Curr. Appl. Phys*., 2011, vol. 11, p. 358.