

Energy Band Structure and Photocatalytic Property of Fe-doped Zn₂TiO₄ Material

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Received September 1, 2009, Accepted November 4, 2009

Zn₂Ti_{1-x}Fe_xO₄ (0 ≤ x ≤ 0.7) photocatalysts were synthesized by polymerized complex (PC) method and investigated for its physico-chemical as well as optical properties. Zn₂Ti_{1-x}Fe_xO₄ can absorb not only UV light but also visible light region due to doping of Fe in the Ti site of Zn₂TiO₄ lattice because of the band transition from Fe 3d to the Fe 3d + Ti3d hybrid orbital. The photocatalytic activity of Fe doped Zn₂TiO₄ samples for hydrogen production under UV light irradiation decreased with an increase in Fe concentration in Zn₂TiO₄. Consequently, there exists an optimized concentration of iron for improved photocatalytic activity under visible light (λ ≥ 420 nm)

Key Words: Fe doped Zn₂TiO₄, Polymerized complex method, Photocatalysis, Visible light, Hydrogen production

Introduction

Photocatalysts could convert solar energy into chemical energy by producing hydrogen gas from water or hydrogen containing compounds.¹⁻⁵ Thus hydrogen production by use of photocatalysts has recently received much attention because of the depletion of fossil fuel source and related environmental problems. Zn₂TiO₄ has been a promising material for the photocatalytic water splitting as well as photocatalytic oxidation reaction under UV light because of its higher reduction potential and lower oxidation potential.⁶

But, Zn₂TiO₄ has a wide band gap (3.1 eV) and thus don't show the photocatalytic activity under visible light.⁶ Since visible light accounts for the largest portion (ca. 46%) of the solar spectrum, visible light-driven photocatalysts are needed for hydrogen production from water as well as the decomposition of toxic compounds. One promising approach to develop new photocatalysts is the tuning or modification of the optical properties of UV light active catalysts by doping, as demonstrated in La₂Ti_{2-x}MxO₇ (M = Fe, Cr),⁷ Zr-S co-doped TiO₂,⁸ SrTi_xM_{1-x}O₃ (M = Ru, Rh, Ir, Pt, Pd),⁹ TiO_{2-x}Cr_xO₂,¹⁰ AgGa_{1-x}In_xS₂,¹¹ TiO_{2-x}C_x,^{12,13} or TiO_{2-x}N_x¹⁴ for cation and anion doping.

Here we have tailored the band gap of Zn₂TiO₄ by doping of Fe metal ion with Ti site in Zn₂TiO₄ crystal lattice using the polymerized complex reaction and characterized it using UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS) and X-ray diffraction (XRD). This work further reports the photocatalytic activity for hydrogen production under UV and visible light irradiation (λ > 420 nm).

Experimental

Preparation of nanocrystalline Zn₂Ti_{1-x}Fe_xO₄ (0 ≤ x ≤ 0.7). Nanocrystalline Zn₂Ti_{1-x}Fe_xO₄ was synthesized by the PC method

according to the same procedure in our previous work.^{15,16} Zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, 98.0%, Aldrich), iron nitrate hydrate (Fe(NO₃)₃·9H₂O, 98%, Aldrich), titanium (IV) isopropoxide (Ti[OCH(CH₃)₂]₄, 97%, Aldrich), ethylene glycol (C₂H₆O₂, Kanto Chemicals), citric acid (C₆H₈O₇, Wako) were used as starting materials. The citric acid (CA) was added into ethylene glycol under constant agitation, at temperature of 60 - 70 °C. Ethylene glycol (EG) was added to the mixture to yield a mass proportion of 60% CA to 40% EG. Next, titanium (IV) isopropoxide was dissolved in citric acid-EG solution and then the salts of zinc nitrate hexahydrate and iron nitrate hydrate were dissolved in the above mixture to obtain metal citrate complex. Finally, the mixture was kept on the hot plate (80 °C) until it became a transparent solution. The well mixed solution was then heated at 130 °C for several hours to obtain a polymeric gel. The viscous polymeric product was pyrolyzed at about 300 - 500 °C to form the precursor powders. Thus obtained powder was pressed in the form of pellets, which were calcined at 1200 °C for 5 h in an electric furnace to obtain nanocrystalline Zn₂Ti_{1-x}Fe_xO₄. On the other hand, for the purpose of comparison, TiO_{2-x}N_x nanoparticle was also prepared by the hydrolytic synthesis method (HSM).¹⁷

Characterization. Zn₂Ti_{1-x}Fe_xO₄ (0 ≤ x ≤ 0.7) samples thus obtained were characterized by X-ray Diffractometer (Mac Science Co., M18XHF). X-ray diffraction (XRD) results were compared with the Joint Committee Powder Diffraction Standards (JCPDS) data for phase identification. The band gap energy and optical property of the as-prepared materials was measured by UV-Visible diffuse reflectance spectrometer (Shimadzu, UV 2401). The morphology was determined by scanning electron microscopy (SEM, Hitachi, S-2460N) and high-resolution transmission electron microscopy (HR-TEM, Philips, CM 200).

Photocatalytic activity. The rate of H₂ evolution was determined for water-methanol solution (distilled water 70 mL and

methanol 30 mL) containing 0.1 g catalyst. The concentration of H₂ was analyzed by gas chromatography equipped with a thermal conductivity detector (molecular sieve 5-Å column and Ar carrier). Before both reactions, 1 wt% of Pt was deposited on photocatalysts by photodeposition method under uv ($\lambda \geq 210$ nm) and visible light ($\lambda \geq 400$ nm).

Results and Discussion

Structural characterization of the samples was investigated to compare their crystallization behaviors with respect to the calcination temperatures. Figure 1 shows the XRD patterns of Zn₂Ti_{1-x}Fe_xO₄ ($0 \leq x \leq 0.7$) samples prepared by the conventional solid state reaction method. All the samples showed an inverse spinel with a lattice constant of 8.48 Å and space group Fd3m.¹⁸ But, undoped Zn₂TiO₄ and Zn₂Ti_{0.95}Fe_{0.05}O₄ samples represent pure crystal structure without Fe₂O₃ crystal phase among the as-synthesized samples. With the increase in the concentration of iron ($x = 0.05$), X-ray diffraction pattern of Fe₂O₃ in Zn₂Ti_{1-x}Fe_xO₄ ($0.1 \leq x \leq 0.7$) samples clearly appear the Figure 1. This indicates that only small amount of iron ion into Zn₂TiO₄ crystal structure can be substituted into the lattice of Ti site in Zn₂TiO₄ crystal structure.

The optical properties were studied by UV-Vis diffuse reflectance (UV-DR) spectroscopy for iron doped Zn₂TiO₄ samples with different contents. Figure 2 shows the UV-Visible diffuse reflectance spectra of Zn₂Ti_{1-x}Fe_xO₄ ($0 \leq x \leq 0.7$) samples ($0 \leq x \leq 0.7$). In case of undoped Zn₂TiO₄ sample, absorption edge appeared near 400 nm corresponding to 3.1 eV, consistent with the literature.⁶ However, the absorption spectra of Fe doped Zn₂TiO₄ samples exhibit new absorption shoulder in visible light region. In general, the absorption edge of Zn₂TiO₄ around 400 nm was ascribed to the band transition from O 2p to Zn 4s. Additionally, the absorption of Fe doped Zn₂TiO₄ samples was based on the transition from Fe e_g to Fe 4s. In this case, the interband may exist between the conduction and valence band of Zn₂TiO₄.

Figure 3 shows scanning electron microscopy (SEM) images of Zn₂Ti_{1-x}Fe_xO₄ ($x = 0.0, 0.05, 0.1, 0.2$) samples with different content of iron calcined at 1200 °C for 5 h, respectively. All samples represent the morphology of a well-developed crystal and the grain size of as-synthesized samples shows a similar value of 5 ~ 10 μm. But, with increasing the Fe doping level into the lattice site of Ti in Zn₂TiO₄ crystal structure, there exists the impurity crystal phase with small grain size. The existence of small grains possibly affects the photocatalytic activity of as-prepared samples.

We investigated the photocatalytic hydrogen production from methanol-water solution using undoped Zn₂TiO₄ and Zn₂Ti_{1-x}Fe_xO₄ ($x = 0.05, 0.1$), and TiO_{2-x}N_x samples under uv and visible light irradiation. Table 1 shows the results of H₂ evolution as well as respective band gaps of the samples calculated from respective DRS spectra. All the samples showed the photocatalytic activity for hydrogen production from methanol-water solution under uv light irradiation ($\lambda \geq 210$). Among the as-synthesized samples, undoped Zn₂TiO₄ photocatalyst showed the highest photocatalytic activity as compared to other samples. The Fe doped sample, Zn₂Ti_{0.95}Fe_{0.05}O₄, with low doping level only showed H₂ production as high as 6.2 mmol/gcat-hr under visible

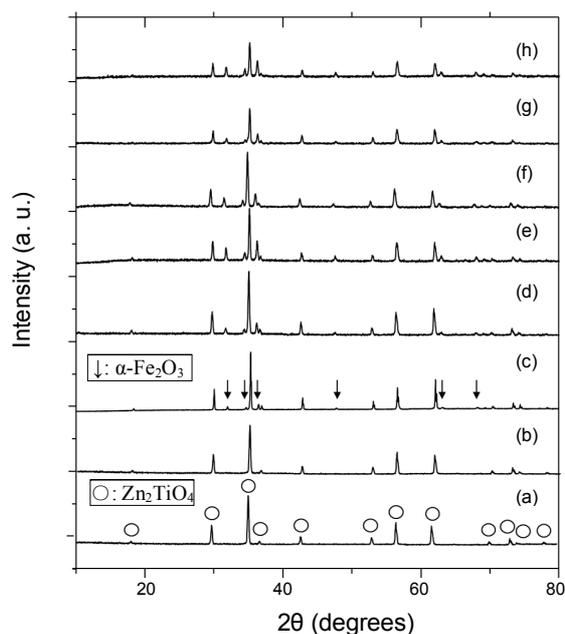


Figure 1. X-ray diffraction patterns of Zn₂Ti_{1-x}Fe_xO₄ photocatalysts for $x =$ (a) 0, (b) 0.05, (c) 0.1, (d) 0.2, (e) 0.3, (f) 0.4, (g) 0.6, and (h) 0.7.

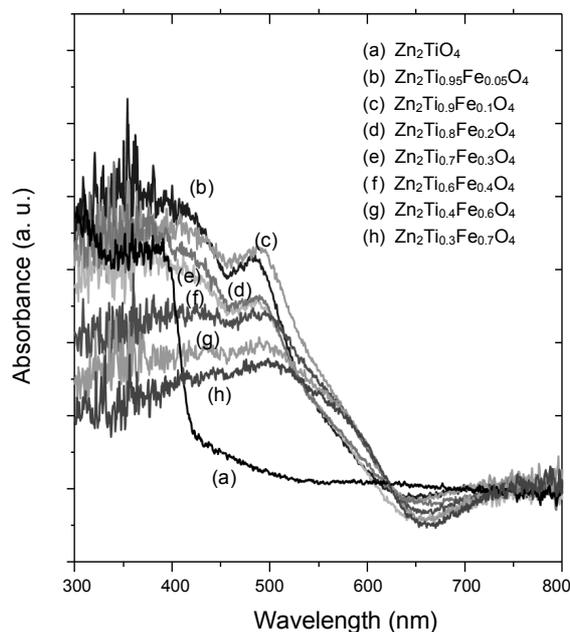


Figure 2. UV-vis diffuse reflectance spectra of Zn₂Ti_{1-x}Fe_xO₄ photocatalysts for $x =$ (a) 0, (b) 0.05, (c) 0.1, (d) 0.2, (e) 0.3, (f) 0.4, (g) 0.6, and (h) 0.7.

light irradiation ($\lambda \geq 420$ nm). But, Zn₂Ti_{0.9}Fe_{0.1}O₄ and TiO_{2-x}N_x samples showed a trace amount of H₂ production. This indicates that the Zn₂Ti_{0.95}Fe_{0.05}O₄ seems to be an optimum concentration which could lead to the proper bandgap as well as band position for producing hydrogen gas as compared to other samples. Possibly, the Fe doping concentration higher than Zn₂Ti_{0.95}Fe_{0.05}O₄ ($x = 0.05$) leads to Fe₂O₃ as an impurity phase, which could play a role of electron transfer medium towards a positive

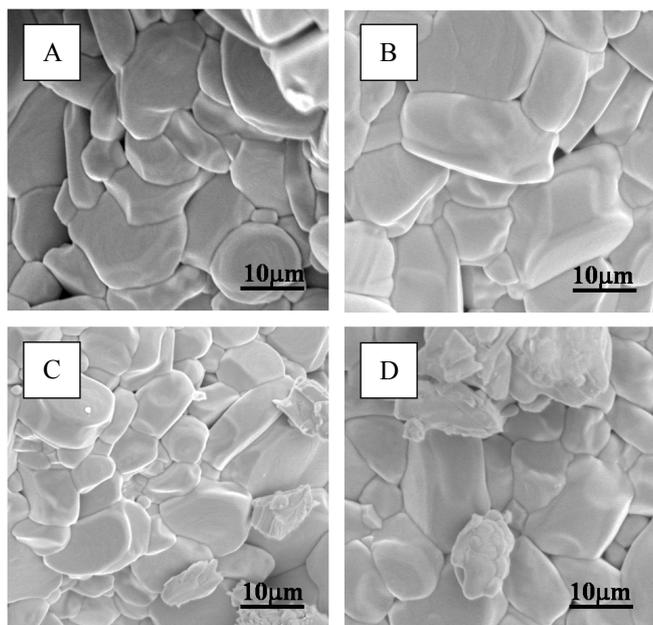


Figure 3. SEM images of $Zn_2Ti_{1-x}Fe_xO_4$ samples for $x =$ (a) 0, (b) 0.05, (c) 0.1, and (d) 0.2.

Table 1. Photocatalytic H_2 production from methanol-water solution over 1 wt% Pt/ $ZnTi_{1-x}Fe_xO_4$ ($x = 0.0, 0.05, 0.1$) and 1 wt% Pt/ $TiO_{2-x}N_x$ samples.

Catalyst	Energy band gap		H_2 evolution (mmol/gcat.hr)	
	E_g (eV)-1	E_g (eV)-2	UV light irradiation ($\lambda > 210$ nm)	Visible light irradiation ($\lambda > 420$ nm)
Pt/ Zn_2TiO_4	3.10	-	140	0
Pt/ $Zn_2Ti_{0.95}Fe_{0.05}O_4$	3.10	2.48	116	6.2
Pt/ $Zn_2Ti_{0.9}Fe_{0.1}O_4$	3.10	2.48	11	Trace
Pt/ $TiO_{2-x}N_x$	3.20	2.73	8	Trace

potential more than the reduction potential of H_2 .

Figure 4 shows time curve of the photocatalytic hydrogen production over $Zn_2Ti_{0.95}Fe_{0.05}O_4$ for 15 h with intermittent N_2 gas purging every 3 h (dotted line). There was no noticeable reduction in activity during the first two runs for 6 h. This implies that the $Zn_2Ti_{0.95}Fe_{0.05}O_4$ sample may be stable in water-methanol solution during photocatalytic reaction.

XPS measurements were carried out to analyze the oxidation state of Fe atoms in $Zn_2Ti_{0.95}Fe_{0.05}O_4$ photocatalyst. Figure 5 shows the XPS survey spectrum of $Zn_2Ti_{0.95}Fe_{0.05}O_4$ sample, which contains Zn, Ti, O, C and Fe elements, with photoelectron peaks appearing at binding energies of 1022 (Zn $2p_{3/2}$), 459 (Ti $2p_{3/2}$), 531 (O 1s) and 285 eV (C 1s) and a weak photoelectron peak at 711 eV (Fe $2p_{3/2}$). The inset in Figure 5 presents the core level spectra of the Fe $2p_{3/2}$ region of corresponding sample revealing that the peak at 711 eV is symmetrical and can be ascribed to the trivalent oxidation state of Fe (Fe^{3+}).

Figure 6A shows the bandgap position of $Zn_2Ti_{0.95}Fe_{0.05}O_4$ and $TiO_{2-x}N_x$ photocatalysts as suggested from the results of

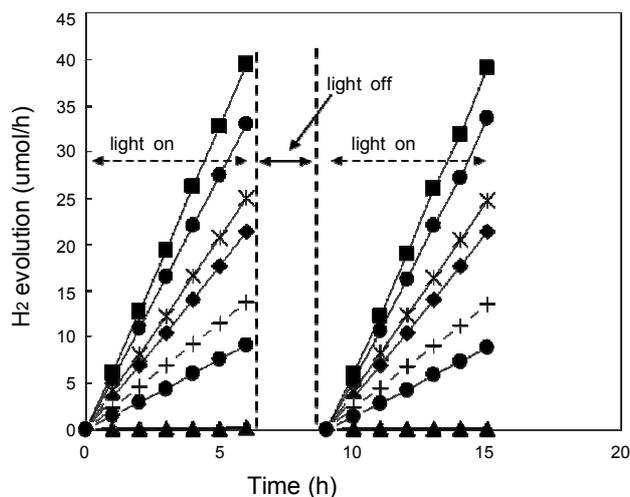


Figure 4. Time courses of hydrogen production over various $Zn_2Ti_{1-x}Fe_xO_4$ for $x =$ (■) 0.05, (●) 0.04, (×) 0.06, (◆) 0.07, (+) 0.03, (○) 0.02 and (▲), $TiO_{2-x}N_x$ photocatalysts.

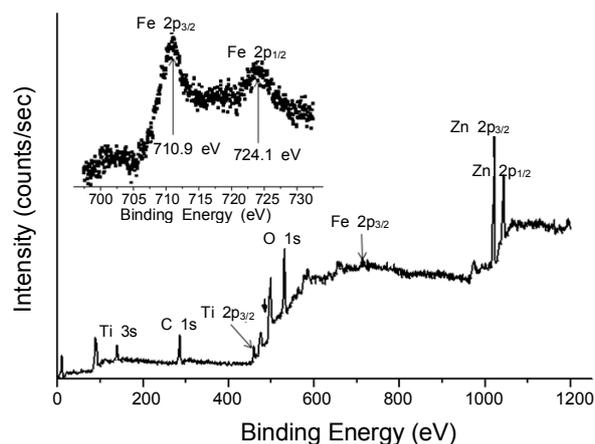


Figure 5. XPS survey spectrum of $Zn_2Ti_{0.95}Fe_{0.05}O_4$ sample. The insert shows the XPS core-level spectra of Fe 3d in $Zn_2Ti_{0.95}Fe_{0.05}O_4$ sample.

undoped Zn_2TiO_4 and TiO_2 reported by Matsumoto *et al.*⁶ and UV-DRS data of doped two materials.¹⁷ The bandgap energy of $Zn_2Ti_{0.95}Fe_{0.05}O_4$ and $TiO_{2-x}N_x$ are *ca.* 2.48, 2.73 eV, respectively. In general, in case of Fe-doped material an interband is formed between the conduction and valence band of undoped material.⁷ Thus, the doped material could absorb visible light due to the transition from interband to the conduction band of the original material. With knowledge of the band position of the undoped material, here we propose the schematic of band positions of doped material as shown in Figure 6A. Figure 6B represents the schematic describing the mechanism for photocatalytic hydrogen production over $Zn_2Ti_{0.95}Fe_{0.05}O_4$ from methanol-water solution under visible light irradiation ($\lambda \geq 420$ nm). $Zn_2Ti_{0.95}Fe_{0.05}O_4$ photocatalyst produced H_2 gas in the presence of aqueous methanol-water solution under visible light. Thus, in the case of Pt/Fe-doped Zn_2TiO_4 , an electron excited is to the conduction band due to sufficiently high reduction potential to reduce H^+ ion and a hole in the valence band also has lower oxidation potential for CH_3OH degradation to CO_2 . H_2 gas was

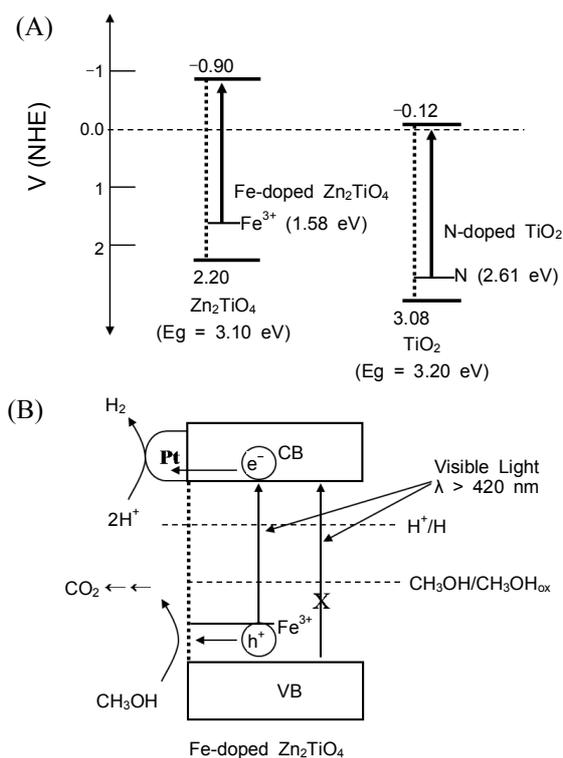


Figure 6. (A) The bandgap position of $\text{Zn}_2\text{Ti}_{1-x}\text{Fe}_x\text{O}_4$ and $\text{TiO}_{2-x}\text{N}_x$ photocatalysts. (B) The schematic describing the mechanism for photocatalytic hydrogen production from methanol-water solution.

generated only when the formation of an ohmic junction between Pt and Fe doped Zn_2TiO_7 might enhance the charge separation. Therefore, Fe doped Zn_2TiO_4 could be applied for photocatalytic reaction that requires a higher reduction potential as well as lower oxidation potential.

Conclusions

$\text{Zn}_2\text{Ti}_{1-x}\text{Fe}_x\text{O}_4$ photocatalysts were successfully prepared by the polymerized complex method. New band gap in the visible light range was obtained by Fe doping in Zn_2TiO_4 . $\text{Zn}_2\text{Ti}_{0.95}\text{Fe}_{0.05}\text{O}_4$ sample with low doping level was synthesized without impurity phase such as Fe_2O_3 and only showed the photoca-

talytic activity under visible light irradiation ($\lambda \geq 420$ nm). Further increase of the amount of Fe in Zn_2TiO_4 led to the formation of Fe_2O_3 crystal phase. Therefore, it is considered that Fe doping could play an important role in reducing the bandgap and showing the photocatalytic activity in the system of Zn_2TiO_4 under visible light irradiation.

Acknowledgments. This work has been supported by KBSI grant T29320, MKE-RTI04-0201, KOSEF grant (NCRCP, R15-2006-022-01002-0), Hydrogen Energy R&D Center, Korea.

Reference

- Lee, J. S. *Catal. Surv. Asia* **2005**, *9*, 217.
- Kudo, A.; Misaki, Y. *Chem. Soc. Rev.* **2009**, *38*, 253.
- Maeda, K.; Takata, T.; Hara, M.; Saito, N.; Inoue, Y.; Kobayashi, H.; Domen, K. *J. Am. Chem. Soc.* **2005**, *127*, 8286.
- Kim, H. G.; Hwang, D. W.; Lee, J. S.; *J. Am. Chem. Soc.* **2004**, *126*, 8913.
- Jang, J. S.; Ji, S. M.; Bae, S. W.; Son, H. C.; Lee, J. S. *J. Photochem. Photobiol. A: Chem.* **2007**, *188*, 112.
- Matsumoto, Y. *J. Solid State Chem.* **1996**, *126*, 227.
- Hwang, D. W.; Kim, H. G.; Lee, J. S.; Kim, J.; Li, W.; Oh, S. H.; *J. Phys. Chem.* **2005**, *B109*, 2093.
- Kim, S. W.; Khan, R.; Kim, T. J.; Kim, W. *Bull. Korean Chem. Soc.* **2008**, *29*, 1217.
- Bae, S. W.; Borse, P. H.; Lee, J. S. *Appl. Phys. Lett.* **2008**, *92*, 104107.
- Bae, S. W.; Borse, P. H.; Hong, S. J.; Jang, J. S.; Lee, J. S.; Jeong, E. D.; Hong, T. E.; Yoon, J. H.; Jin, J. S.; Kim, H. G. *J. Korean Phys. Soc.* **2007**, *51*, S22.
- Subramanian, E.; Baeg, J.; Kale, B. B.; Lee, S. M.; Moon, S.; Kong, K. *Bull. Korean Chem. Soc.* **2007**, *28*, 2089.
- Khan, S. U.; Al-Shahry, M. M.; Ingler, Jr., W. B. *Science* **2002**, *297*, 2243.
- Sakthivel, S.; Kisch, H.; *Angew. Chem. Int. Ed.* **2003**, *42*, 4908.
- Ashai, R.; Ohwaki, T.; Aoki, K.; Taga, Y. *Science* **2001**, *293*, 269.
- Kim, H. G.; Hwang, D. W.; Bae, S. W.; Jung, J. H.; Lee, J. S. *Catal. Lett.* **2003**, *91*, 193.
- Jung, E. D.; Borse, P. H.; Jang, J. S.; Lee, J. S.; Cho, C. R.; Bae, J. S.; Park, S.; Jung, O. S.; Ryu, S. M.; Kim, H. G. *J. Nanosci. Nanotech.* **2008**, *9*, 3568.
- Jang, J. S.; Kim, H. G.; Ji, S. M.; Bae, S. W.; Jung, J. H.; Shon, B. H.; Lee, J. S. *J. Solid State Chem.* **2006**, *179*, 1067.
- Rankin, R. B.; Campos, A.; Tian, H.; Siriwardane, R.; Roy, A.; Spiwey, J. J.; Sholl, D. S.; Johnson, J. K. *J. Am. Ceram. Soc.* **2008**, *91*, 584.