Int. J. Electrochem. Sci., 7 **(2012)** 11519 - 11527

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Enhanced Photocatalytic Activity of Ga-N Co-doped Anatase TiO_2 for Water Decomposition to Hydrogen

XiaoBo Li[*], *Qianfeng Liu, XiaoYing Jiang, Jianhua Huang*

Henan Institute of Science and Technology, Xinxiang, Henan 453003, China
*E-mail: lxb0620@163.com

Received: 5 September 2012 / *Accepted:* 27 September 2012 / *Published:* 1 November 2012

Pure TiO_2, single-doped and Ga+N co-doped TiO_2 nanoparticles were successfully prepared by sol-gel method. Detailed analysis shows that the TiO_2 samples possess anatase phase. Nitrogen and gallium atoms are incorporated into the titania oxide lattice and the Ga+N co-doped TiO_2 exhibits the highest absorption of visible light. The experimental results obtained from hydrogen evolution via water splitting showed that the photocatalytic activity of Ga+N co-doped TiO_2 was significantly higher than that of single-doped TiO_2, indicating the photocatalytic efficiency could be effectively enhanced by the co-modification of Ga and N. The increase of the quantity of oxygen vacancy and the band gap realignment leading by the synergistic effect of Ga and N codopant may be responsible for the enhancement of photocatalytic activity.

Keywords: Ga+N co-doped TiO_2, Photocatalytic activity, Hydrogen evolution, Water splitting

1. INTRODUCTION

In recent years, the development of hydrogen energy has attracted tremendous attention. Many researchers have been interested in the production of hydrogen in a clean and convenient way. In 1972, Fujishima and Honda [1] reported photocurrent evolution by using semiconductor electrodes. The scientific community has started to explore the potential applications of semiconductor materials for solar energy conversion lately. Hydrogen evolution via photocatalytic decomposition of water is one of the possible applications [2-5]. Among the photocatalysts available so far, TiO_2 is the most promising material with respect to its much more advantages such as low cost, high catalytic efficiency and chemical stability. With adequate energy band gaps (anatase: 3.23 eV, 384 nm; rutile: 3.02 eV, 411 nm) as well as band position, the electron hole pairs generated by the light irradiation can be used efficiently for various redox reactions on the particle surface. In general, rutile is preferred for optical applications because of its higher refractive index, whereas anatase is preferred for all the applications related to photocatalytic activity and solar cells, thanks to its higher mobility and catalytic properties [6, 7]. Amongst various TiO_2 nanostructures, titania nanoparticles have specific advantages in the enhancement of light absorption due to the large fraction of surface atoms. Despite its promising properties, however, the major disadvantage of TiO_2 is that the large band-gap necessitating wavelengths below 400 nm for excitation limits the photosensitivity to the ultraviolet region, which comprises less than 5% of the overall solar energy spectrum [8].

Up to now, one of the most effective ways to improve the photocatalytic efficiency of TiO_2 is the generation of defects in the lattice through selective metal or nonmetal ions doping, such as Sn [9], Gd [10], Cr [11], Ag [12], Ni [13], V [14], W [15], Bi [16], Pt [17], C [18], S [19], F [20], and Cl [21] which can suppress the recombination of photo-induced electron hole pairs and give rise to band gap narrowing so as to significantly extend the absorption of TiO_2 even into the visible region [22, 23]. However, the photocatalytic activity of metal-doped TiO_2 photocatalysts strongly depends on the dopant ion species and their concentration as well as the preparation technique and the process parameters. In parallel, since the discovery of N-doped TiO_2 with a visible light absorption by Asahi et al. [24], great attention has been given to modifying the electronic band gap of TiO_2 by nitrogen doping [25–27]. Compared to the other nonmetal elemental doping, N-doped TiO_2 materials exhibit a significant photocatalytic activity and strong absorption in the various reactions performed under visible light irradiation. [28-30] More recently, Yang et al reported the highly visible-light active N-doped TiO_2 photocatalyst over decomposition of Methylene blue and Methyl orange [31]. Moreover, many of the recent efforts revealed that the synergetic effect of doped different atoms contributes to a highly efficient photocatalytic activity [11, 32–35]. Because, the carrier recombination centers inside TiO_2 generated from monodoping could be passivated [36, 37] and the doping concentrations could be enhanced significantly by the Columbic attraction between opposite charge dopants [38–41].

It is well known that Sol-gel method is very simple and does not require any special equipment. TiO_2 prepared by this method has stable thermal stability, well-crystalline phase, small particle sizes and large surface area, which are beneficial to its photocatalytic. In this study, Ga-N co-doped anatase TiO_2 photocatalysts were synthesized by Sol-gel method and hydrogen evolution from water in the presence of methanol in order to overcome the rapid recombination in water splitting was set up to screen out the photocatalysts.

2. EXPERIMENTAL

2.1 Catalysts Preparation

Titanium tetraisopropoxide (TTIP, 99.95%, Junsei Chemical, Japan) and gallium chloride ($GaCl_3$, 99.50%, Junsei Chemical, Japan) were used as the titanium and gallium precursors, respectively, with ethanol as the solvent to prepare the sol mixture. Typically, at room temperature, 0.5 mol% $GaCl_3$ solution (0.6 mol/L) was mixed with 40 mL of anhydrous ethanol. After mixing, 12 mL of TTIP was added dropwise to the solution under vigorous stirring. A concentrated HCl solution was added until the final pH of this mixture was about 3.0. The gel was prepared by aging the sol for 48 h at room temperature, dried and then triturated to powder in an agate mortar. The as-prepared Ga-doped TiO_2 (GT) was calcined under pure nitrogen at 400 °C for 2 h, and the Ga content determined by ICP-AES (TJAIRIS 1000) was 0.48 mol% which was close to the nominal ratio. Pure TiO_2 (RT) was prepared by the same procedure but by replacing the $GaCl_3$ solution with deionized water. N doped TiO_2 (NT) and Ga-N co-doped TiO_2 (GNT) were prepared by annealing obtained TiO_2 powders under gaseous ammonia and nitrogen (1/2 (*V*/*V*)) at 400 °C for 2 h.

2.2 Characterization

XRD experiments were carried out in a Rigaku D/Max-γA X-ray diffractometer using Cu Kα radiation (λ=0.154 nm). The accelerating voltage and applied current were 40 kV and 30 mA, respectively. X-ray photoelectron spectroscopy (XPS) measurements were performed on an AXIS His spectrometer (Kratos Analytical) using Mg Kα X-ray (1253.6 eV) at 15 kV and 400 W, with an energy resolution of 0.8 eV. All the binding energies were referenced to the C 1s peak at 284.7 eV of the surface adventitious carbon. The morphology of the samples was measured through a scanning electron microscope (Hitachi S-4800). A Shimadzu UV-1601PC spectrophotometer was used to record the diffuse reflectance spectra of samples. Surface texture properties of the samples were measured at 77 K by nitrogen adsorption experiment using a Micromeritics ASAP 2000 system in the static measurement mode. Specific surface areas were calculated by the Multipoint BET method based on N_2 adsorption isotherm.

2.3 Determination of photocatalytic activity

Photocatalytic decomposition of water was carried out in an inner irradiation closed gas circulating flask-shaped Pyrex reaction cell system described in a previous work [42]. A photocatalyst was dispersed in 70 mL of an aqueous solution composed of 7 mL methanol (99.85%) and 63 mL distilled water, with the solution being stirred. A Philips HPR 125 W mercury lamp with a 400 nm cut-off filter was used as a visible light source. Argon gas, which flowed through the cell during reaction at an optimized flow rate 15 mL/min, was used to remove traces of oxygen and moistures. Irradiation started after the suspension had been mixed using ultrasonication (1 h). The hydrogen and the oxygen evolved were collected in a Tedlar bag and analyzed with a gas chromatograph (HP 6890C) equipped with a thermal conductivity detector (TCD).

3. RESULTS AND DISCUSSION

3.1 Characterization

XPS analysis was used to investigate whether the implementation of Ga-N co-doping is successful. As can be seen from figure, Ti 2p XPS spectrum shows that the Ti 2p3/2 and Ti 2p1/2 core levels of GNT appear at 457.7 and 463.5 eV, respectively, which agrees with previously reported XPS data for N-doped TiO_2 and arise from the presence of Ti^{4+} in pure anatase titanium [43, 44].

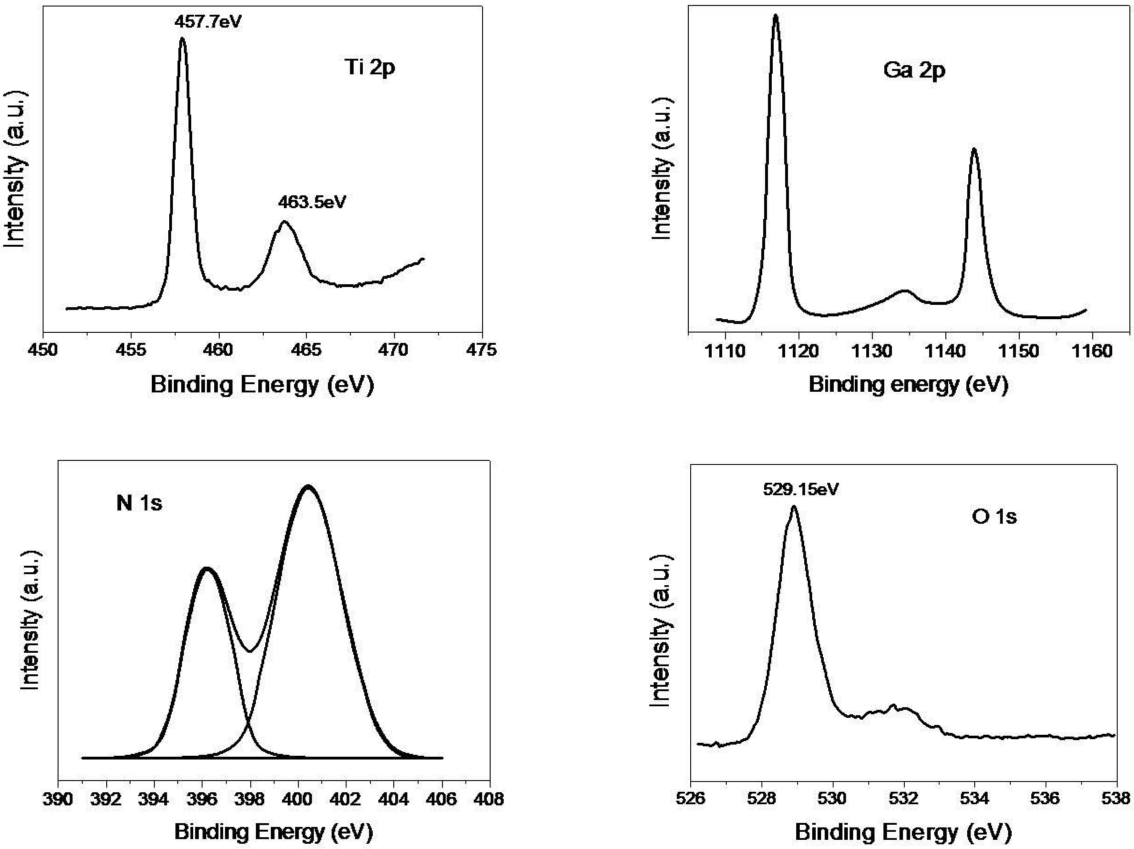

Figure 1. X-Ray photoelectron spectroscopy spectra of GNT.

Meanwhile, in O 1s XPS spectrum, the peak at 529.15 eV was due to metal-O in TiO_2 crystal lattice. Deconvolution results exhibited another peak centered at 532.2 eV, which was assigned to Metal-OH indicating that the particles are more hydrophilic, and thus produce more OH radicals during photocatalysis, resulting improved photocatalytic activity when the gallium ion is added [45, 46]. The N 1s peak at 401.6 eV can be attributed to the nitrogen in the form of a Ti–N–O linkage, and the low bonding energy component located at 396.5 eV is generally known as the N atom replacing the oxygen atoms in the TiO_2 crystal lattice to form an N–Ti–N bond [47]. However it is also could be attributed to N-Ga-N bond since Ga has a presence [48]. Two peaks situated at binding energies of 1117 and 1144 eV in Ga 2p XPS spectrum were assigned to Ga 2p3/2 and Ga 2p1/2, respectively, corresponding to Ga^{3+} [49], whereas some researchers have turned out that the Ga 2p 3/2 peak situated at 1118 eV is typically for Ga–N bond [48, 50]. This probably could explain how the doping concentrations are enhanced in metal-nonmetal codoping.

XRD patterns (Fig.2) shows that the four synthesized samples have the highest diffraction peak in (101) crystal plane (2θ = 25.6^{o}), and the other diffraction peaks are consistent with crystalline phases of (004), (200), (105), (211), and (204). It can be evidently seen that the crystal phase of each sample is manly in anatase form and the different dopants in TiO_2 did not affect the crystal form. In spite of the addition of the Ga into the TiO_2 framework, no clear peaks assigned to Ga_2O_3 (mainly peaks: 2theta = 45 and 52°) indicating that the gallium ions were safely incorporated into the titania anatase framework.

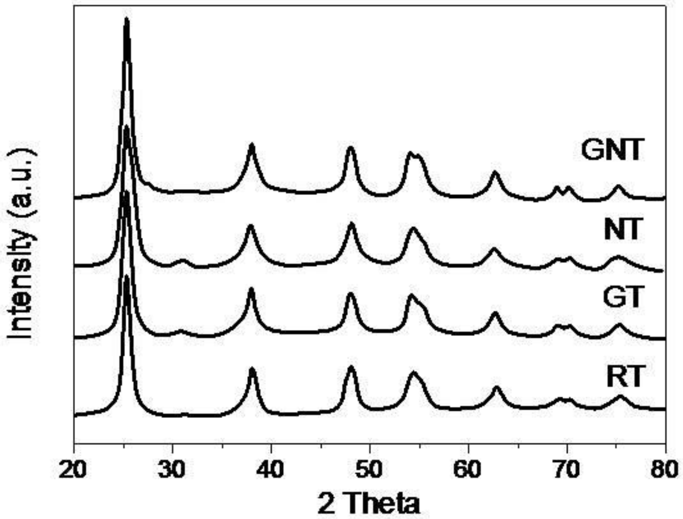

Figure 2. X-Ray diffraction data of samples

However, the [004] plane peak intensities were smaller with the amount of gallium components compared to other peaks, indicating that the smaller Ga ions (0.62 Å) insert to [004] site by substitution of the larger Ti ions (0.68 Å). Furthermore, the average Scherer crystallite sizes of the samples were roughly estimated approximately as 21.5, 18.7, 20.5, and 19.3 nm for RT, GT, NT, and GNT, respectively. As can be seen from the values, the crystallite sizes of GNT are smaller than those of RT, indicating that GNT are highly crystallized, whereas, bigger than those of GT since a considerable amount of nitrogen has been introduced during calcination. The BET surface areas were 87.89, 103.74, 91.39, and 101.31 m^2g^{-1} for RT, GT, NT, and GNT, respectively. Doped TiO_2 owns a larger specific surface area, and it is consistent with the fact that smaller crystals offer greater specific surface area [51, 52] and thus induce better surface absorbability of hydroxyl/water, which in-turn acts as an active oxidizer in the photocatalytic reaction [53].

The SEM images of RT and GNT are shown in figure 3. It can be seen that the average size of pure TiO_2 particles is significantly larger than that of GNT. It appears that GNT particles are spherical or square shaped with a primary particle size of from 18 to 20 nm.

As is shown in figure 4, the UV-vis adsorption spectrum of RT has a sharp absorption edge at about 393 nm due to its intrinsic band gap showing that absorption only in the ultraviolet light region. However, the red shift of absorption thresholds for doped TiO_2 implies the decrease in the band gap energy and demonstrates that the visible light absorption of TiO_2 has been effectively enhanced by the incorporation of Ga and N, in turn, may considerably enhance the photocatalytic activity of TiO_2 under visible light irradiation. Moreover, the more red shifts of NT and GNT clearly indicated that the more decrease of band gap energy by N-doping. The corresponding response to visible light is very important for utilizing sunlight in photocatalytic reaction processes.

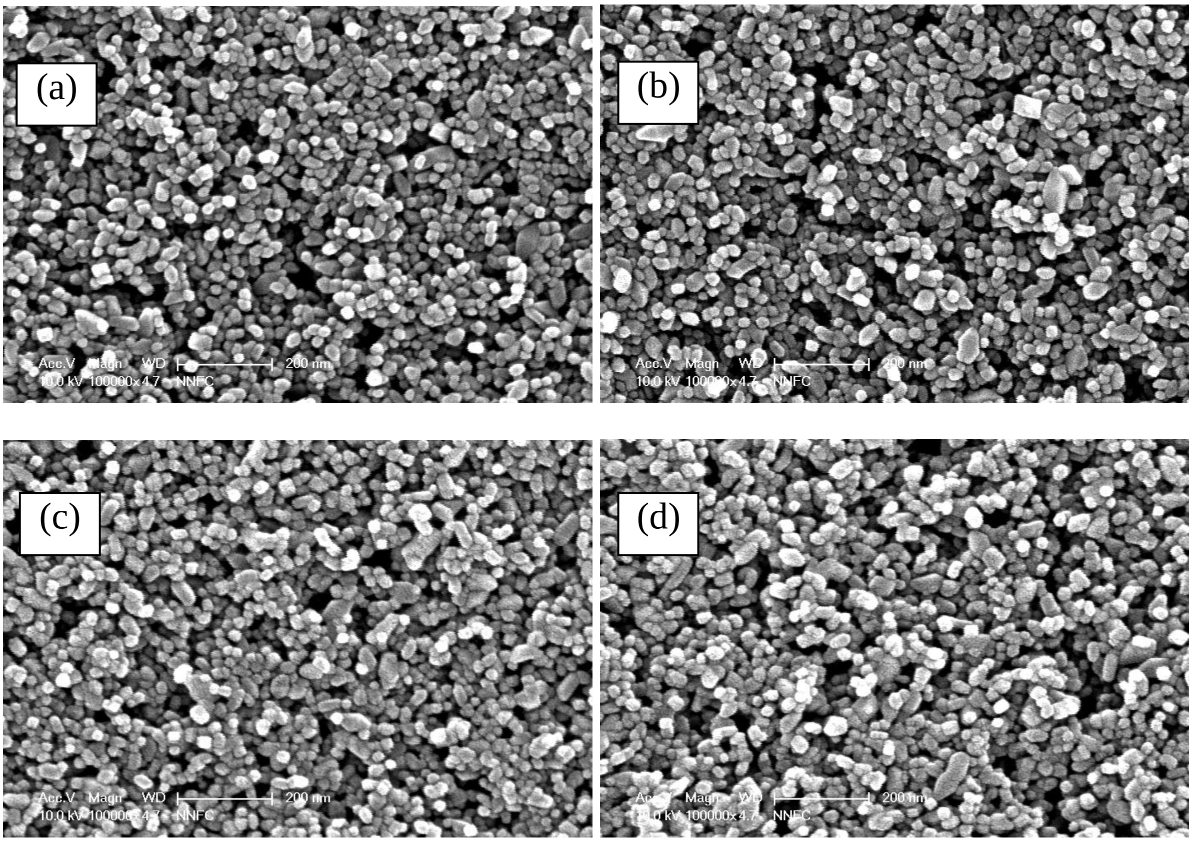

Figure 3. SEM images of samples: (a) RT; (b) GT; (c) NT; (d) GNT.

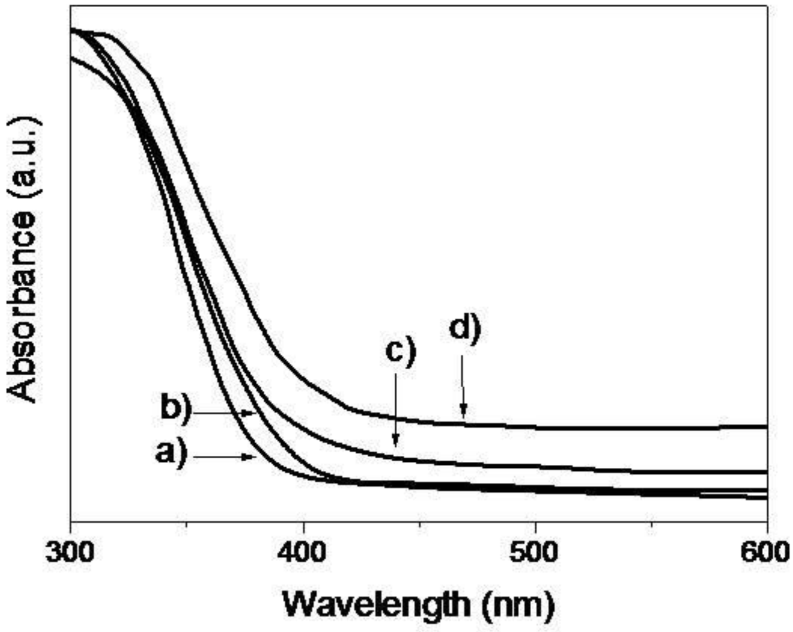

Figure 4. UV-vis diffuse reflectance spectra of samples.

3.2 Photocatalytic activities

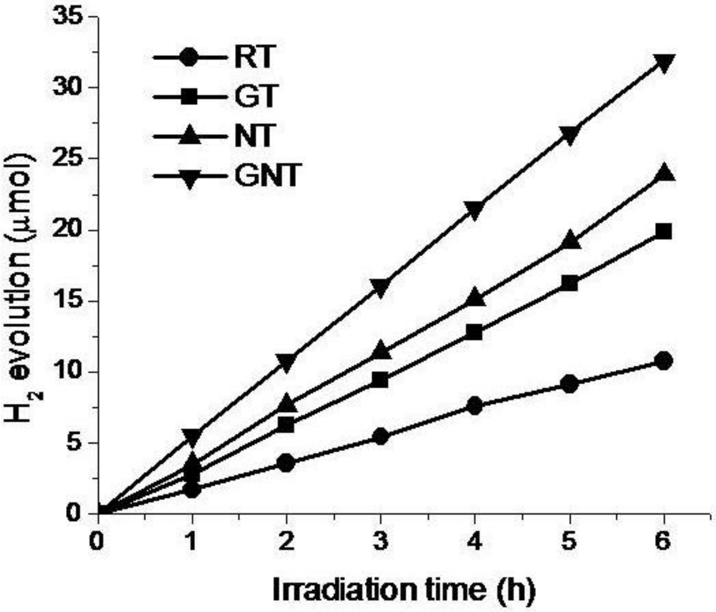

Figure 5. Reaction time profiles of H_2 evolution.

All the four synthesized photocatalysts were subjected to water splitting reaction under visible light irradiation. The photocatalytic activities to H_2 evolution are shown in figure 5 which are in the order of the GNT>NT>GT>RT. The GNT shows the best photocatalytic activity and leads to hydrogen evolution rate up to 5.32 μmol h^{-1} in 6 hours.

As to the origin of visible-light sensitivity in Ga, N and Ga-N co-doped TiO_2, the possible mechanism can be discussed here. It is generally known that the band gap of TiO_2 can be tailored by doping with nonmetal or metal elements. Herein, for the Ga-doped sample, the absorption edge red shift could be understood by the band gap narrowing, which is the result of the induced sub-band-gap transition [54, 55] or a defect level within the bandgap of TiO_2 [56] and electrons can be excited from this state to the TiO_2 conduction band by photons with energy less than the bandgap energy. Additionally, the metal doping creates trapping centers for electrons to decrease the electron-hole recombination during irradiation to enhance the photoactivity [57]. In nitrogen doped case, N doping can also lead to the formation of the oxygen vacancies [55] or a new substitution N 2p band formed above O 2p valance band [58]. Moreover, N impurity can cooperatively act with Ti^{3+} generated by untraped or uncombined electrons to narrow the band gap of N-doped TiO_2, resulting in the visible light activity of N-doped TiO_2 [31]. Therefore, For co-doped sample, the gallium is introduced into the lattice of TiO_2 as the oxide state of Ga^{3+} which is a p-type doping to increase the oxygen vacancies induced by the hole doping of N, similar as [36, 59]. Consequently, the co-doped TiO_2 results in the best response to visible-light and the largest red-shift because of the synergistic effect of Ga and N codopant.

4. CONCLUSION

In conclusion, anatase TiO_2 was synthesized by a sol-gel method. Doping with nitrogen or gallium could enhance the visible light absorption and the photocatalytic activity of TiO_2. The Ga+N co-doped TiO_2 possesses the highest visible light absorption and the best photocatalytic activity for catalyzing the hydrogen evolution via water splitting. The increase of the quantity of O vacancy and the band gap realignment leading by the synergistic effect of Ga and N codopant may be responsible for the increase of photocatalytic activity in the Ga + N codoped sample.

References

1. A. Fujishima and K. Honda, *Nature*, 37(1972) 238.
2. T. C. Yuan, R. D. Li and K. C. Zhou, *Trans. Nonferrous Met. Soc.*, 12(2007)762.
3. A. F. Heyduk and D. G. Nocera, *Science*, 293(2001)1639.
4. T. Kida, G. Q. Guan and A. Yoshida, *Chem. Phys. Lett.*, 371(2003)563.
5. R. Abe, K. Sayama and K. A. Domen, *Chem. Phys. Lett.*, 344(2001)339.
6. B. O’Regan and M. Gratzel, *Nature*, 353(1991)737.
7. H. Tang, K. Prasad, R. Sanjines, and F. Levy, *Sens. Actuators B*, 26(1995)71.
8. U. Diebold, *Surf. Sci. Rep.*, 48(2003)5.
9. R. Sasikala, V. Sudarsan, C. Sudakar, R. Naik, T. Sakuntala and S. R. Bharadwaj, *Int. J. Hydrogen Energy*, 33(2008)4966.
10. J. Xu, Y. Ao, D. Fu, and C. Yuan, *Colloids and Surfaces A*, 334(2009)107.
11. R. Dholam, N. Patel, M. Adami and A. Miotello, *Int. J. Hydrogen Energy*, 34(2009)5337.
12. M. S. Park and M. Kang, *Mater. Lett.*, 62(2008)183.
13. D. W. Jing, Y. J. Zhang and L. J. Guo, *Chem. Phys. Lett.*, 415(2005)74.
14. J. Zhou, M. Takeuchi, A. K. Ray, M. Anpo and X. S. Zhao, *J. Colloid Interface Sci.*, 311(2007)497.
15. T. Hathway, E. M. Rockafellow, Y. C. Oh, and W. S. Jenks, *J. Photochem. Photobiol. A: Chem.*, 207(2009)197.
16. H. Li, D. Wang, P. Wang, H. Fan and T. Xie, *Chem. Euro. J.*, 15(2009)12521.
17. Y. Ishibai, J. Sato, T. Nishikawa and S.Miyagishi, *Appl. Catal. B*, 79(2008)117.
18. J. H. Park, S. Kim and A. J. Bard, *Nano Letters*, 6(2006)24.
19. T. Ohno, M. Akiyoshi, T. Umebayashi, K. Asai, T. Mitsui and M. Matsumura, *Appl. Catal. A*, 265(2004)115.
20. D. Li, H. Haneda, N. K. Labhsetwar, S. Hishita and N. Ohashi, *Chem. Phys. Lett.*, 401(2005)579.
21. K. Lv, H. Zuo, J. Sun, K. Deng, S. Liu, X. Li and D. Wang, *J. Hazard. Mater.*, 161(2009)396.
22. W. Choi, A. Termin and M. R. Hoffmann, *J. Phys. Chem.*, 98(1994)13669.
23. S. U. M. Khan, M. Al-Shahry and W. B. Ingler Jr., *Science*, 297(2002)2243.
24. R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki and Y. Taga, *Science*, 293(2001)269.
25. R. Asahi and T. Morikawa, *Chem. Phys.*, 339(2007)57.
26. X. B. Chen and S. S. Mao, *Chem. Rev.*, 107(2007)2891.
27. Y. Guo, X. W. Zhang, W. H. Weng and G. R. Han, *Thin Solid Films*, 515(2007)7117.
28. X. C. Wang, J. C. Yu and Y. L. Chen, *Environ. Sci. Technol.* 40(2006)2369.
29. J. Premkumar, *Chem. Mater.*, 16(2004)3980.
30. S. Z. Chen, P. Y. Zhang, D. M. Zhuang and W. P. Zhu, *Catal. Commun.*, 5(2004)677.
31. G. D. Yang, Z. Jiang, H. H. Shi, T. C. Xiao and Z. F. Yan, *J. Mater. Chem.*, 20(2010)5301.
32. H. Liu, Z. Lu, L. Yue, J. Liu, Z. H. Gan, C. Shu, T. Zhang, J. Shi and R. Xiong, *Appl. Surf. Sci.*, 257(2011)9355.
33. J. Yang, J. Dai, and J. Li, *Appl. Surf. Sci.*, 257(2011)8965.

34. X. Zhang and Q. Q. Liu, *Appl. Surf. Sci.*, 254(2008)4780.
35. M. Bettinelli, V. Dallacasa, D. Falcomer, P. Fornasiero, V. Gombac, T. Montini, L. Romanò and A. Speghini, *J. Hazard. Mater.*, 146(2007)529.
36. Y. Gai, J. Li, S. S. Li, J. B. Xia and S. H. Wei, *Phys. Rev. Lett.*, 102(2009)036402.
37. T. Umebayashi, T. Yamaki, H. Itoh and K. Asai, *J. Phys. Chem. Solids*, 63(2002)1909.
38. W. Zhu, X. Qiu, V. Iancu, X. Qiu, V. Iancu, X. Chen, H. Pan, W. Wang, N. M. Dimitrijevic, T. Rajh, H. M. Meyer III, M. P. Paranthaman, G. M. Stocks, H. H. Weitering, B. H. Gu, G. Eres, and Z. Y. Zhang, *Phys. Rev. Lett.*, 103(2009)226401.
39. P. Romero-Gomez, A. Borras, A. Barranco, J. P. Espinos and A. R. Gonzalez-Elipe, *ChemPhysChem*, 12(2011)191.
40. Y. Sakatani, J. Nunoshige, H. Ando, K. Okusako, H. Koike, T. Takata, J. N. Kondo, M. Hara and K. Domen, *Chem. Lett.*, 32(2003)1156.
41. H. Y. Wang, J. H. Wei, R. Xiong and J. Shi, *J. Magn. Magn. Mater.*, 324(2012)2057.
42. X. B. Li,
43. K. Nagaveni, M. S. Hegde, N. Ravishankar, G. N. Subbanna and G. Madras, *Langmuir*, 20(2004)2900.
44. M. Sathishi, B. Viswanathan, R. P. Viswanath and C. S. Gopinath, *Chem. Mater.*, 17(2005)6349.
45. X. Chen and C. Burda, *J. Phys. Chem. B*, 108(2004)15446.
46. J. L. Gole, J. D. Stout, J. C. Burda, Y. Lou and X. Chen, *J. Phys. Chem. B*, 108(2004)1230.
47. M. M. Joshi, N. K. Labhasetwar, P. A. Mangrulkar, S. N. Tijare and S. S. Rayalu, *Appl. Catal. A: Gen.*, 357(2009)26.
48. M. Dinescu, P. Verardi, C. Boulmer-Leborgne, C. Gerardi, L. Mirenghi and V. Sandu, *Appl. Surf. Sci.*, 127-129(1998)559.
49. J. F. Mouider, W. F. Stickle, P. E. Soboi and K. D. Bomben, *Handbook of X-ray Photoelectron Spectroscopy*; Perkin-Elmer Coporation, USA (1992).
50. M. Joseph, H. Tabata and T. Kawai, *Jpn. J. Appl. Phys.*, 38(1999)L1205.
51. M. Seyler, K. Stoewe and W. F. Maier, *Appl. Catal. B: Environ.*, 76(2007)146.
52. M. Anpo and M. Takeuchi, *J. Catal.*, 216(2003)505.
53. X. Chen, X. Wang, Y. Hou, J. Huang, L. Wu and X. Fu, *J. Catal.*, 255(2008)59.
54. W. Choi, A. Termin, and M. R. Hoffmann, *J. Phys. Chem.*, 98(1994)13669.
55. K. Tan, H. Zhang, C. Xie, H. Zheng, Y. Gu, and W. F. Zhang, *Catal. Comm.*, 11(2010)331.
56. A. N. Banerjee, S. W. Joo and B. K. Min, *J. Nanomater.*, 2012(2012)201492.
57. A. Zaleska, *Recent Patents on Engineering*, 2(2008)157.
58. J. Yu, Q. Xiang, and M. Zhou, *Appl. Catal. B: Environ.*, 90(2009)595.
59. K. S. Ahn, Y. F. Yan, S. Shet, T. Deutsch, J. Turner, and M. Al-Jassim, *Appl. Phys. Lett.*, 91(2007)231909.