Preparation, Characterization and Photocatalytic Activity of N doped TiO$_2$

Dhanya T.P.[1], Sugunan S.[2]

[1]*(Department of Chemistry, NSS College, Ottapalam, India)*
[2]*(Departmenof Applied Chemistry,Cochin University of Science and Technology, India)*

Abstract : *In order to utilize visible light in a photocatalytic reaction, yellow nitrogen-doped titania was prepared by sol-gel method in mild condition, with the elemental nitrogen source from urea.The titania catalysts were characterized by XRD, BET Surface area, UV-Vis DRS,TEM and XPS . The results showed that all titania catalysts were anatase and doping of nitrogen extended the absorption into visible light region. Photocatalytic activity of the catalysts was evaluated based on the photodegradation of 2,4-D in aqueous solution under visible light. The experiments demonstrated that the nitrogen-doped titania exhibited higher visible-light activity compared to undoped one.*
Keywords – anatase, 2,4-D, nitrogen doped, photocatalytic activity, titania

I. Introduction

AOPs were based on the generation of very reactive species such as hydroxyl radicals (•OH) that oxidize a broad range of pollutants quickly and non selectively. Among AOPs, heterogeneous photocatalysis using TiO$_2$ as photo-catalyst appears as the most emerging destructive technology [1]. The key advantage of it is its inherent destructive nature: it does not involve mass transfer; it can be carried out under ambient conditions (atmospheric oxygen is used as oxidant) and may lead to complete mineralization of organic carbon into CO$_2$ [2,3]. Moreover, TiO$_2$ photocatalyst is largely available, inexpensive, non-toxic and show relatively high chemical stability [4].

However, because of the relatively high intrinsic band gap of anatase TiO$_2$ (3.2 eV), only 4% of the incoming solar energy on the Earth's surface can be utilized [5,6]. On the other hand, the hole and electron excited by the UV light can recombine easily, which will reduce the efficiency of photons. How to reduce the band gap to produce the visible-light photocatalysis and suppress the recombination of hole-electron pairs has been one of the most challenging topics [7].

Therefore, considerable efforts have been made to extend the photoactivity of titania-based systems into the visible-light region, using dopants. Asahi *et al.* [8] reported that nitrogen- doped titania could induce the visible-light activity and the doped nitrogen was responsible for the visible light sensitivity because of the narrowing of the band gap. It has initiated a new research area to extend the photo absorbance into the visible-light region using nitrogen-doped titania [7].

In this study, yellowish nitrogen doped titania was produced through sol-gel method in mild condition, using titanium tetra isopropoxide(TTIP) as the titanium source and urea as the nitrogen source. The titania catalysts were characterized by XRD, BET, TEM, XPS and UV-Vis diffuse reflectance spectroscopy. The photocatalytic activity was studied by the mineralization of a pesticide 2,4-D in aqueous solution. The nitrogen-doped titania photocatalysts was found to be more active for 2,4-D degradation under visible-light irradiation compared to undoped one. The effect of time, light source and dopant on the photocatalytic activity was also discussed.

II. Experimental

2. 1 Preparation of nitrogen doped titania.

Nitrogen doped TiO$_2$ catalyst was prepared through sol gel method using Titanium isopropoxide (TTIP) and urea. In this method titanium isopropoxide and urea was taken in the mole ratio 1:5. The urea solution was added drop wise to a mixture of titanium isopropoxide and ethanol. After stirring for 24 hours at room temperature it was dried at 60°C .The dried solids were ground in an agate mortar until fine and homogeneous powder was obtained. Before characterization, all the samples were calcined in air at 400°C for 4 hours. Different N doped catalysts with TTIP: urea in the mole ratio 1:2, 1:5 and 1:10mole ratios were prepared by the same method and were signed as U1, U2 and U3. Pure titania catalyst (signed as T) was also prepared to compare the results with the doped one.

2.2 Characterization Methods

The crystal phases of the catalysts were determined by X-ray diffraction (XRD) analysis. XRD patterns of the samples were obtained using Bruker AXS D8 advance X ray diffractometer using CuKα radiation. Data were collected over the angle of 2θ between 10° to 70°. Crystallite size was determined by using Scherrer's equation : $D=0.9\lambda/\beta(\Pi/180)\cos\theta$ (1) where D is the crystallite size λ is the wavelength of X ray radiation, β is the full width of half maximum and θ is the diffraction angle. BET Surface area was measured using Micrometritics Tristar 3000 surface area analyzer. The samples were activated at 90°C for 30 minutes and degassed at 350°C for 4 hours. The UV- DRS were obtained in the range 300-800nm on Labomed UV VIS DOUBLE BEAM UVD 500 Spectrophotometer equipped with an integrating sphere assembly using BaSO$_4$ as reflectance standard. The wavelength at the onset of reflection was taken and band gap was calculated using the equation: $E_{bg}=1240/\lambda$ (2) where λ is the wavelength in nanometer . The SEM micrographs of the samples were taken using JOEL Model JSM -6390LV scanning electron microscope with a resolution of 1.38eV. The TEM analysis was carried out in an ultra high resolution analytical electron microscope JOEL3010. XPS data were recorded in an indigenously developed electron spectrometer equipped with Thermo VG Clamp-2 Analyser and a Mg Kα X-ray source (1253.6 eV, 30mA × 8 kV). A thin sample wafer of 12 mm in diameter was used in these studies. As an internal reference for the absolute binding energy of C 1s peak at 284.6 eV was used.

2.3 Photocatalytic Activity Studies

Photocatalytic activity of the prepared samples was measured by studying the degradation 2,4-D in aqueous solution. The experiment was carried out using an Oriel Uniform Illuminator 150 W Xe ozone free lamp with filters. 280-420nm dichoric mirror for UV light, and 420-630nm dichoric mirror (cold mirror) for visible irradiation were used. The studies were carried out by taking 20 ml of 10^{-4} M solution of pesticide and 1g/L of catalyst. The solution was stirred for 30 minutes before irradiation to attain the adsorption desorption equilibrium. After irradiation the solution was centrifuged the percentage mineralisation was studied using TOC analysis. TOC was analysed using an Elemental Vario TOC analyser.

The percentage mineralisation= $(TOC_o –TOC_t/ TOC_o)$ x 100 (3) where TOC_o is the value of TOC for initial solution, TOC_t is the value after time t. The effects of operational parameters, such as time, light source, dopants were examined.

The structure of 2,4-D as follows
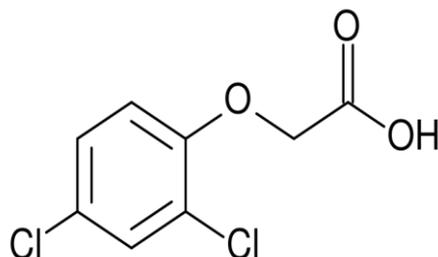
Fig. 1 Structure of 2,4-D

III.   Results and Discussion

a.   Structure and Properties of Photocatalysts

The XRD patterns of the synthesised N doped TiO$_2$ are shown in Fig. 2.
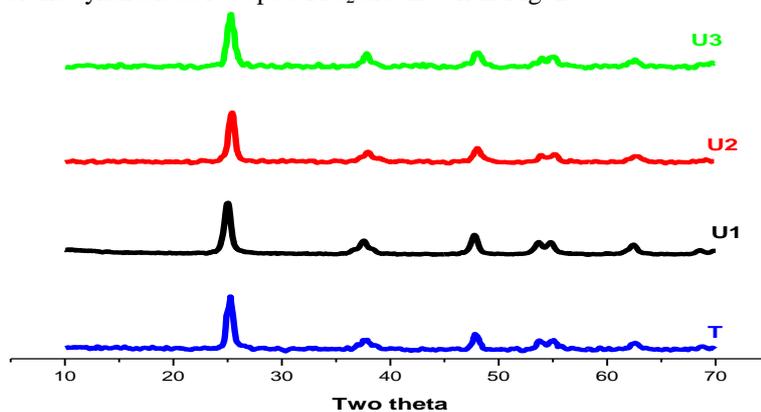
Fig.2 XRD pattern of N doped titania

The diffraction peak at 25.4 corresponds to anatase phase of titania. Usually amorphous–anatase transformation may complete in the temperature range 250-400°C. The peak positions are same and no extra peaks except for anatase TiO$_2$ was observed, suggesting that the structure of TiO$_2$ is not changed [9]. No peak was observed for dopants, may be due to the low amount of doped nitrogen so that it cannot be detected by XRD. The materials show a very high degree of crystallinity of fully anatase phase. The crystallite size of the sample are in arrange of 11-13, which is promising since nanocrystalline anatase is considered as the more photoactive form of titania [9,10].

Specific surface area is one of the important properties of photocatalyst, a greater surface area is generally favourable to yield a higher photoactivity [10]. In case of N doped catalysts the surface area first increases with dopant concentration and then decreases. It can be concluded that the present sol gel method adopted is a good route for the preparation of photocatalyst with high surface area, which is favourable in enhancing the photoactivity of TiO$_2$ based photocatalyst. The crystallite size and surface area of the catalysts are given in Table 1.

Table 1 Crystallite size and surface area of prepared catalysts

Catalyst	Crystallite size(nm)	BET surface area (m^2/g)
T	13.4	77
U1	12	91
U2	11.7	121
U3	11.6	46

Extending the absorption edge of TiO$_2$ to the visible region is considered as one of the main objective in this study. The UV-Vis diffuse reflectance spectroscopy method was used to record absorbance capacity of the powders and to estimate band-gap energies of the prepared TiO$_2$ samples .The minimum wavelength required to promote an electron depends upon the band-gap energy, E_{bg}, of the photocatalyst . The band gap of pure titania is 3.2eV (Fig.3) corresponding to a wavelength of 389nm which falls in the UV region [10,11].
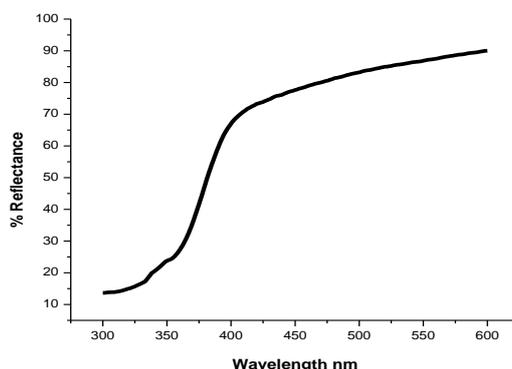
Fig. 3. UV-Vis.DRS of T

The UV DRS spectra were recorded for N doped catalysts (Fig.4). The doped samples are yellow in colour. The change in colour of the nanoparticles upon N incorporation demonstrates a profound effect on their optical response in the visible wave length [12].
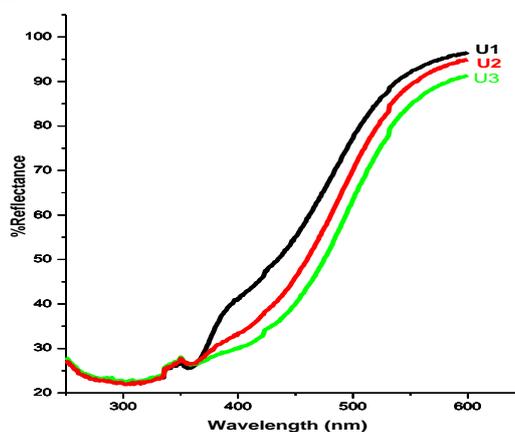
Fig.4 UV-Vis.DRS of N doped titania catalysts

As shown in Fig.4, N doping obviously affects light absorption characteristics of TiO_2. Unmodified TiO_2 nanoparticles hardly absorb visible light, while N-doped TiO_2 nanomaterials show a clear red shift towards visible light region, suggesting the formation of an energy level within the band gap. Moreover, the absorption in this range increases with the increase of doped N content. This clearly indicates a decrease of the band gap energy of TiO_2. N doping can extend the wavelength response range to the visible region and increase the number of photogenerated electrons and holes to participate in the photocatalytic reaction, which would enhance the photocatalytic activity of TiO_2. However there is no direct relation between light absorption and photocatalytic activity of samples, that stronger absorption of visible light does not mean the higher degradation of pollutants [9,13]. The band gap of N doped titania(U2) is 2.25eV corresponding to 550 nm. Various mechanisms have been proposed to explain the light absorption and photoactivity of N-doped TiO_2. Di Valentin et al. provided theoretical evidence that [14] in the case of substitutional N-doped anatase TiO_2, the visible light response arises from occupied N 2p localized states slightly above the valence band edge [15].Hashimoto and co-workers [16,17] provided the explanation that a localized N 2p state formed above the valence band was the origin for the visible light response of the nitrogen-doped TiO_2.

The surface morphology was studied by SEM analysis. Fig. 5 shows the SEM image of undoped TiO_2. Fig. 6 shows the SEM image of N doped catalyst. The images show that particles are somewhat spherical in nature. But most of them are in agglomerated form.
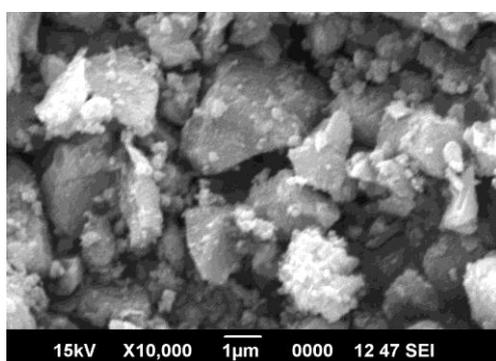
Fig.5 SEM image of undoped titania(T)   Fig.6 SEM image of U2
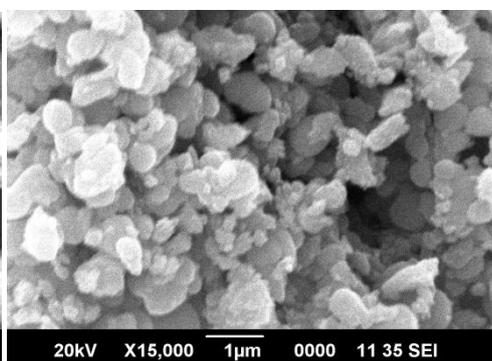
The TEM image of U2 is shown in Fig.7.The particles are agglomerated and exhibit spherical or rectangular shape. The HRTEM image of U2 is shown in Fig.8. The image indicates that particles are well ordered and highly crystalline in nature. The catalysts give the same d value (0.352nm) which is in correlation with the d value obtained from XRD and corresponds to101 anatase planes. This again confirms the presence of anatase phase. Fig.9 shows the selected area electron diffraction pattern of U2 catalyst. The electron diffraction image shows well distinct spots due to the high crystallinity of titania indicated as anatase phase with major 101 planes
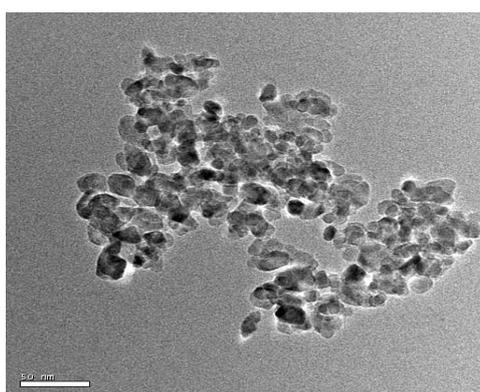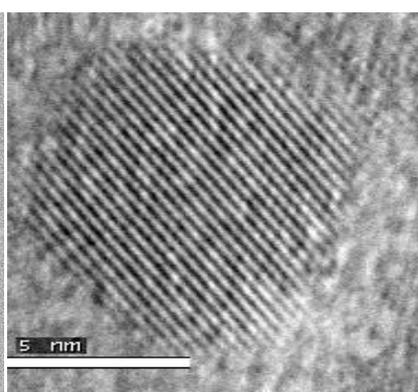
Fig.7 TEM image of U2   Fig.8 HRTEM image of U2
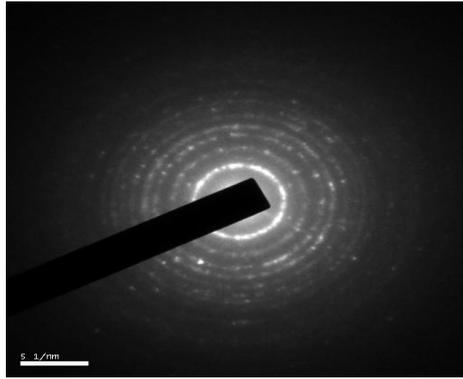
Fig.9 SAED image of U2

The XPS spectrum of nitrogen in U2 is shown in Fig.12. There are obvious nitrogen signals in the N-doped sample, although peak intensities are not so strong.
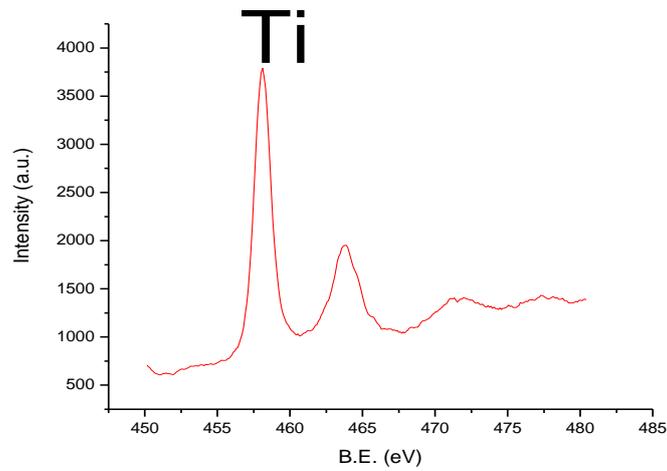
Fig.10 Ti 2p spectrum of sample U2
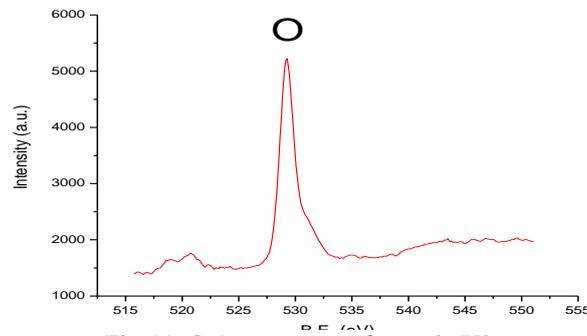
Fig.11 O 1s spectrum of sample U2
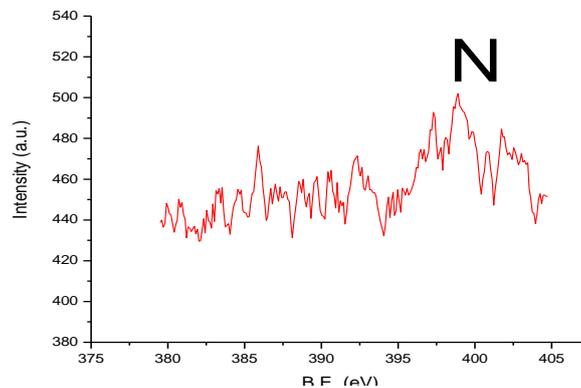
Fig. 12 N 1s spectrum of sample U2

There were two peaks for Ti 2p (Fig.10) at 458.2 and 464.2 eV. According to the literatures [18-20], the peak at 458.2 eV was attributed to Ti2p$_{3/2}$ and the peak at 464.2 eV was assigned to Ti2p$_{1/2}$, indicating that Ti remained in an octahedral environment [21]. Binding Energy values of Ti are attributed to its 4+ oxidation state. A shoulder seen in O 1s spectrum at higher B.E at ~ 531 eV (Fig.11) is associated with surface hydroxyl groups while the main peak at ~529. 3 is due to oxygen associated with titania[22]. Nitrogen 1s peak at ~ 399.2 eV appears to be very broad has relatively lower intensity. The XPS peak around 399.2 eV which is due to the formation of an O-Ti-N bond, suggesting that the nitrogen is doped in the lattice as an anion by the bond formation (O-Ti-N). This peak therefore can be attributed to the 1s electron binding energy of the N atom in the O-Ti-N environment [12,18] .This O-Ti-N bond formation occurs by the replacement of the lattice oxygen by nitrogen in [TiO$_6$]$^{2-}$ octahedra [23,24].

3.2 Photocatalytic Activity of the Catalyst

The effect of time on the degradation of 2,4-D was examined under visible light irradiation in the reaction time ranging from 30 to 180 minutes. Samples were withdrawn at different time intervals after photodegradation and centrifuged immediately and percentage mineralisation was studied using TOC analysis. The results of percentage mineralisation at different times are shown in Fig. 13.
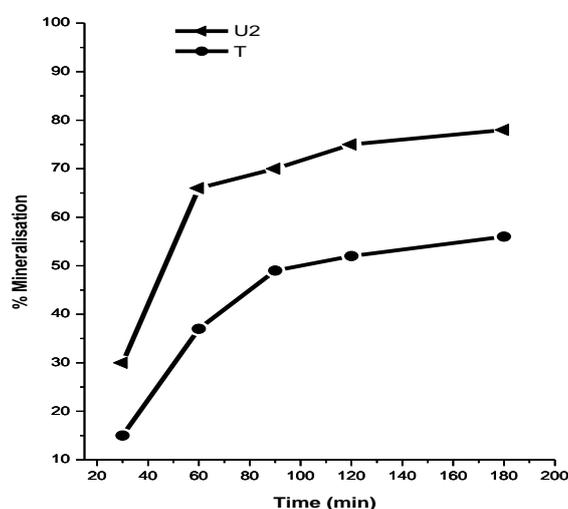
Fig.13 % Mineralisation of 2,4-D against time
Amount of catalyst 1g/L; Pesticide concentration 20ml of 10^{-4}M

Results show that as time increases the percentage mineralisation increases. It has been observed that the mineralisation of the compound proceeds much more rapidly in the presence of N doped catalyst in visible light. It was found that 78% TOC was removed after 3 hours when U2 was used as catalyst in visible light .The reason for better photoactivity could be attributed to the fact that the catalyst is composed of nanocrystalline anatase form. The bandgap energy is lower than that of pure titania, it shows a stronger absorption in visible light region and the presence of dopant prevents the recombination of photogenerated electrons and holes leading to better photocatalytic activity. In the case of N doped catalysts highest activity was observed with catalyst prepared in 1:5 mole ratio of TTIP and urea (U2). However, when the concentrations of dopant ions are above the optimum ratio, the dopant atoms become the recombination centres [25]. This can be seen from the reduced photocatalytic efficiency of the catalyst with doping ratio above the optimum value. The existence of the optimum value can also be associated with the amount of active sites on TiO$_2$. These active sites however will be easily blocked if the amount of dopants is too high or above the optimum value. So even though the U4 catalyst shows more absorption in visible region the photocatalytic activity is very low.

The effect of light source of different wavelength on the photodegradation of 2,4-D using undoped and doped TiO$_2$ also studied. When only UV light is used, degradation takes place slowly using the doped catalyst. Control experiment was performed by employing visible light irradiated blank solution. The degradation of 2,4-D was negligible when the aqueous solution was irradiated without TiO$_2$. Negligible mineralisation was observed when studies were carried out in absence of light. All these results suggest that mineralization of this compound takes place through photocatalytic mechanism [26].

Table 2 %Mineralisation of 2,4-D against light source

Irradiation time 1hour; Amount of catalyst 1g/L; Pesticide concentration 20ml of 10^{-4}M

Light	% mineralisation	
	U2	T
Visible light (420-630 nm)	66	37
UV light (280- 400nm)	52	48

Table 3 % Mineralisation of 2,4-D in absence of light/catalyst

Irradiation time 3hours; Amount of catalyst 1g/L; Pesticide concentration 20ml of 10^{-4}M

studies	% mineralisation 2,4-D
Without catalyst	3
Without light	5

IV.   Conclusions

Yellowish nitrogen-doped titania catalysts, with the elemental nitrogen source from urea, were prepared using the sol-gel method in mild condition. The nitrogen-doped titania had larger surface area than pure titania. The UV-Vis DRS results showed that the presence of small amount of nitrogen in the catalyst gives rise to a red shift of its absorbance wavelength and decreases the band gap of titania. The nitrogen incorporation in the lattice of TiO₂ formed a narrow N 2p band above the valence band, which exhibited a higher visible light absorption and was responsible for the higher visible-light activity by considering 2,4-D mineralisation.

References

[1]   Ioannis K. Konstantinou, Triantafyllos A. Albanis, Applied Catalysis B: Environmental 49 (2004) 1.
[2]   T.Aarthi ,Giridhar madras, Ind.Eng.Chem.Res.,46 (2007)7.
[3]   Hao-Li Qin, Guo-Bang Gu, Song Liu C. R. Chimie, 11 (2008) 95.
[4]   Fotini Kiriakidou, Dimitris I. Kondarides, Xenophon E. Verykios, Catalysis Today, 54 (1999) 119.
[5]   BeataWawrzyniak, AntoniWaldemarMorawski, and Beata Tryba,International Journal of Photoenergy 2006 (2006) 1.
[6]   Y.Liu,X.Chen, J.Li, C.Burda, Chemosphere 61(2005)11.
[7]   Qin Haoli, G.U Guobang, Liu Song, Rare Metals , 26 (2007) 254.
[8]   Asahi R., Morikawa T., Ohwaki T., Aoki K.Taga Y., Science, 2001,293: 269
[9]   Yi Xie, Qingam Zhao, Xiu Jian Zhao, Yuanzhi Li, Catal Lett., 118 (2007) 231.
[10]   Jian Yuan, Mingxia Chen, Jianwei Shi, Wenfeng Shangguan, International Journal of Hydrogen Energy, 31 (2006) 1326.
[11]   Clemens Burda, Yongbing Lou, Xiaobo Chen, Anna C. S. Samia, John Stout, James L. Gole, Nanoletters, 3(2003)1049.
[12]   L. Lin, R.Y. Zheng, J.L. Xie, Y.X. Zhu, Y.C. Xie, Applied Catalysis B: Environmental, 76 (2007) 196.
[13]   Rocıo Silveyra, Luis De La Torre Saenz, Wilber Antunez Flores, V. Collins Martınez, A. Aguilar Elguezabal ,Catalysis Today ,107–108 (2005) 602.
[14]   C. Di Valentin, G. Pacchioni, A. Selloni, S. Livraghi, E. Giamello, J. Phys. Chem. B, 109 (2005) 11414.
[15]   Feng Peng, Lingfeng Cai, Hao Yu, Hongjuan Wang, Jian Yang, Journal of Solid State Chemistry, 181 (2008) 130 .
[16]   H. Irie, S. Washizuka, N. Yoshino, K. Hashimoto, Chem.Commun.,11 (2003) 1298.
[17]   H. Irie, Y .Watanabe, K .Hashimoto, J. Phys. Chem. B, 107 (2003) 5483.
[18]   Y. Aita, M. Komatsu, S. Yin, T. Sato, J. Solid State Chem., 177 (2004) 3235.
[19]   T. Morikawa, R. Asahi, T. Ohwaki, K. Aoki, Y. Taga, Jpn.J. Appl. Phys. 40 (2001) L561.
[20]   R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, Science, 293 (2001) 269.
[21]   Xiang-Zhong Shen, Jun Guo, Zhi-Cheng Liu, Shan-Mei Xie, Applied Surface Science,   254 (2008) 4726.
[22]   Haimei Liu, Wensheng Yang, Ying Ma, Yaan Cao, Jiannian Yao,New J. Chem., 26   (2002) 975.
[23]   X. Chen, C.Burda, J. Phys. Chem. B, 107(2004) 5483.
[24]   Mingyang Xing, Jinlong Zhang, Feng Chen, Applied Catalysis B: Environmental, 89(2009)563.
[25]   Hao-Li Qin, Guo-Bang Gu, Song Liu, C.R. Chimie, 11 (2008) 95.
[26]   Razika Zouaghi, Abdennour Zertal, Journal of Water Science, 20 (2007)163.