Available online at www.sciencedirect.com

SCIENCE DIRECT

Journal of Solid State Chemistry 179 (2006) 331–335

JOURNAL OF SOLID STATE CHEMISTRY

www.elsevier.com/locate/jssc

Rapid Communication

The role of NH_3 atmosphere in preparing nitrogen-doped TiO_2 by mechanochemical reaction

Gang Liu[a], Feng Li[a], Zhigang Chen[a], Gao Qing Lu[b,*], Hui-Ming Cheng[a,**]

[a]*Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, China*
[b]*Australian Research Council Centre for Functional Nanomaterials, School of Engineering, The University of Queensland, Qld. 4072, Australia*

Received 5 September 2005; received in revised form 21 October 2005; accepted 23 October 2005
Available online 23 November 2005

Abstract

NH_3 atmosphere in ball milling plays an important role in preparing $TiO_{2-X}N_X$ by a simple mechanochemical reaction. The results show that the structure transformation of titania milled in NH_3 is greatly delayed compared with that in air. The specific surface area of titania milled in NH_3 for 2 h is two times larger than that in air. It was also found that titania prepared in NH_3 has obvious absorbance for visible light. Mechanochemical milling in NH_3 atmosphere offers a new route to prepare $TiO_{2-X}N_X$ with high surface area.

Keywords: Titania; Nitrogen doping; Mechanochemical reaction; Phase transformation; Visible light absorption

1. Introduction

Titania (TiO_2) has been extensively studied as a photocatalytic material because of its unique properties (high redox ability, good stability and ready availability, etc.) [1–3]. However, its application has been mainly limited to UV light due to its large band gap. Many efforts have been made to extend its light absorption into the visible range by doping trace elements and formation of oxygen vacancies [4–6]. In recent years anion doping (C, N, S, F, Cl) has attracted much attention, especially since $TiO_{2-X}N_X$ by sputtering a TiO_2 target in an N_2 (40%)–Ar gas mixture followed by annealing in N_2 gas and carbon doping of *n*-TiO_2 to $TiO_{2-X}C_X$ were reported [7,8]. The optical absorption of both samples shifted to the visible region of $\lambda < 535$ nm. Meanwhile, varieties of methods to dope anions have been attempted in recent years [9–12].

Mechanical alloying as an effective technique of synthesizing a variety of nanocrystalline materials is also used to prepare nitrogen-doped titania or strontium titanate [13,14]. Conventionally, the organic substance (containing nitrogen element) and titania powder is milled together to prepare $TiO_{2-X}N_X$ by mechanochemical reaction in air atmosphere. During the process of ball milling in air, the anatase to srilankite and the srilankite to rutile transformations occur [17]. Fresh oxygen-rich surfaces are formed due to the mechanical breakage. Electrons are transferred from the fresh surfaces to the organic substance, as a result leading to the destruction of weak bonds in the organic substance and the formation of new bonds between the oxide and nonmetallic elements [17,18]. During this process NH_3 is released from the organic substance. It is generally believed that NH_3 is adsorbed on the surfaces of titania and reacts with activated surfaces, thus causing the growth of nitrogen-doped titania [13,15]. NH_3 released from organic substance seems to be an effective nitrogen source to dope nitrogen in mechnochemical reaction. During ball milling phase transformation from anatase to srilankite and then to rutile occurs [16]. However, it is still unclear how NH_3 affects the structure transformation of nitrogen-doped titania by mechanochemical reaction. The agglomeration caused by high surface energy of fresh surfaces can reduce surface area of titania. To increase the specific surface area, it is necessary to segregate the fresh surfaces from each

---

*Corresponding author. Fax: +61 7 3365 6074.
**Also for correspondence: Fax: +86 24 2390 3126.
E-mail addresses: maxlu@uq.edu.au (G.Q. Lu), cheng@imr.ac.cn (H.-M. Cheng).

0022-4596/$ - see front matter © 2005 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2005.10.030

other. It is thought that by introducing more active NH_3 to the ball-milling vial, strong interaction with fresh surfaces can occur. Meanwhile, gaseous NH_3 as a nitrogen source can avoid the residual organics remaining in titania which is the case where organic nitrogen sources are used.

In this paper, anatase titania powder is milled in gaseous NH_3 and air. The effects of gaseous NH_3 on the phase transformation, surface area, doping of nitrogen and UV–VIS absorbance of titania are investigated.

2. Experimental

Commercial anatase titania powder (99%, 8 wt% rutile) was used as the precursor material. A high-energy mill (Spex 8000 M) was used for grinding of the samples. Two Φ15 mm and four Φ5 mm hard steel balls with 1 g of titania powder were introduced to a hard steel vessel of 50 cm^3 inner volume. Prior to filling NH_3 gas in the vessel, the vial was evacuated to less than 20 Pa by a mechanical pump.

The phases of the samples were determined by X-ray diffraction (XRD). The relative content of srilankite was determined by the XRD peak intensity ratio as follows:

$$S\% = I_{S1\,1\,1}/(I_{S1\,1\,1} + I_{A1\,0\,1} + I_{R1\,1\,0}), \tag{1}$$

where $S\%$ is the fraction of the peak intensity of srilankite $d_{1\,1\,1}$, $I_{S1\,1\,1}$, $I_{A1\,0\,1}$ and $I_{R1\,1\,0}$ are the intensities of srilankite $d_{1\,1\,1}$, anatase $d_{1\,0\,1}$ and rutile $d_{1\,1\,0}$, respectively.

The absorption edge and band gap energy of the samples was determined from the onset of diffuse reflectance spectrum of the sample measured using a UV–VIS spectrophotometer (Shimadzu, UV-2550). The binding energy was identified by X-ray photoelectron spectroscopy (XPS) with Mg-$K\alpha$ radiation (PHI5300). The specific surface area (BET) was determined by nitrogen adsorption–desorption isotherm measurements at 77 K (ASAP 2010).

3. Results and discussion

3.1. Effect of NH_3 on the phase transformation

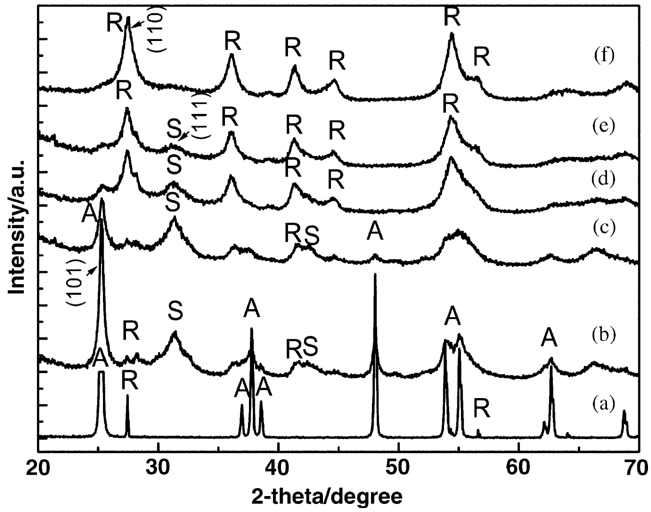

Fig. 1. XRD patterns of the samples milled in air: (a) raw, (b) 0.5 h, (c) 1 h, (d) 2 h, (e)3 h and (f) 5 h. A represents anatase, S srilankite and R rutile structure.

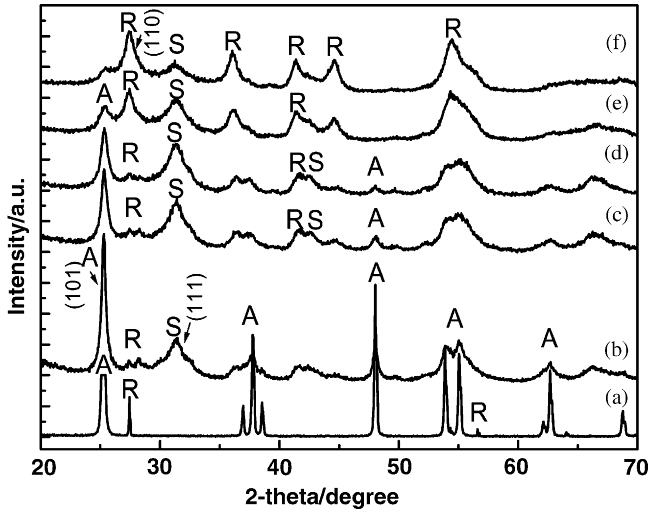

Fig. 2. XRD patterns of the samples milled in NH_3: (a) raw, (b) 0.5 h, (c) 1 h, (d) 2 h, (e) 3 h and (f) 5 h. A represents anatase, S srilankite and R rutile structure.

XRD patterns for the milled titania in air and NH_3 are shown in Figs. 1 and 2, respectively. It is obvious that the phase transformations of both anatase to srilankite and srilankite to rutile in NH_3 are delayed compared with that in air. The milled titania in air for 3 h mainly consists of rutile titania; however, much anatase and srilankite titania still exist when milled in NH_3 for 3 h. The relative content of srilankite rapidly reaches its maximum then decreases when titania is milled in air compared with that in NH_3. However, the content of srilankite in NH_3 is higher than that in air at 0.5 h from Fig. 3.

To understand the whole process of phase transformation, two factors are considered: oxygen partial pressure [19] and interaction of NH_3 with fresh surfaces. It has been proposed that the removal of oxygen ions, which generates oxygen vacancies, accelerates the anatase to rutile transformation because it involves an overall contraction of the oxygen structure, accompanied by shrinkage in volume, and breaking of two of the six Ti–O bonds [20]. Therefore the high oxygen partial pressure is not beneficial to the production of oxygen vacancies and the transformation rate of anatase in the high oxygen partial pressure is significantly slowed. On the other hand, the following process occurs when the mixture of titania and organic substance is milled. The mechanical stressing induces the formation of fresh oxygen-rich surfaces, which results in electron transfer from O^{2-} on the oxide surfaces to the organic substance. As a result, it leads to the destruction of weak bonds in the organic substance and the formation of new bonds between the oxide and non-metallic element [17,18]. The bond energies of N–N and N–H are 946 and

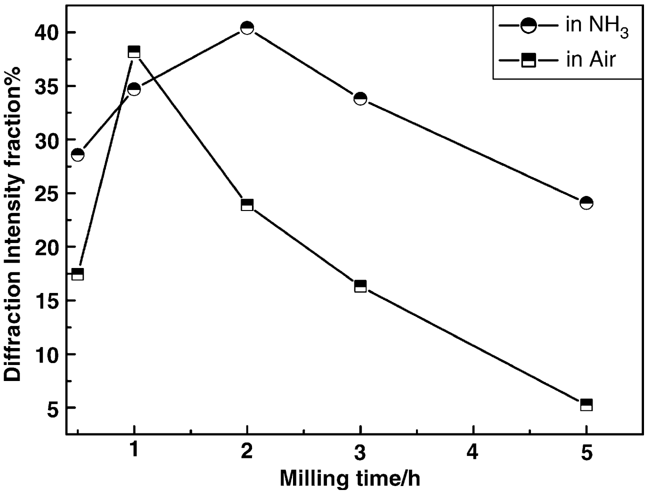

Fig. 3. Diffraction peak intensity of (111) fraction of srilankite phase determined by fomula (1).

380.5 kJ mol^{-1}, respectively and the bond energy of N–H is much weaker than the N–N bond. In other words, the N–H bond can be broken more easily. Therefore, a strong interaction between NH_3 adsorbed on the fresh surfaces and the activated surfaces exists and leads to the destruction of N–H bonds (in fact much hydrogen has been detected by the hydrogen detector). Such strong interaction can delay the phase transformation of anatase titania. However, this interaction is much weaker between gaseous N_2 and fresh surfaces because of the high energy of N–N bond and has less effect on the phase transformation. This can be confirmed by comparing N1s XPS spectra in Fig. 4. An obvious peak at near 396 eV attributed to the formation of Ti–N bond [7] is observed for the samples milled in NH_3 but no similar peak appears for the sample milled in air. It is thought that there must be a strong interaction between NH_3 adsorbed on the fresh surfaces and the activated surfaces before the formation of Ti–N, which delays the phase transformation.

The absence of oxygen is a favorable factor in phase transformation when titania is milled in NH_3 atmosphere. This is the reason why the content of srilankite phase is higher than that in air at 0.5 h. However, the strong interaction between fresh surfaces and NH_3 adsorbed on them can play a more important role in delaying phase transformation when the milling time increases. In other words, the role of this strong interaction in delaying phase transformation is more pronounced than oxygen absence in promoting phase transformation. The phase transformations both from anatase to srilankite and from srilankite to rutile are greatly restrained due to the strong interaction especially between 1 and 2 h in our experiments because of much created fresh surfaces and sufficient NH_3 existed in the vial.

3.2. The UV–visible spectroscopy

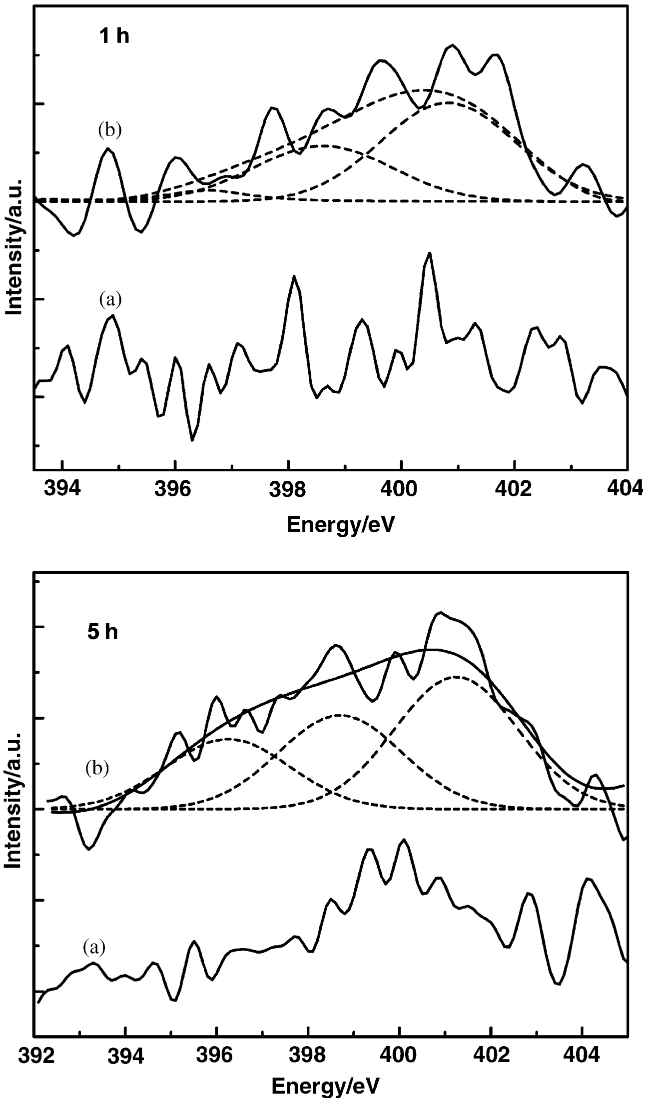

Fig. 4. N_{1s} XPS spectra of the samples milled in air and NH_3 for 1 and 5 h, respectively, (a) in air and (b) in NH_3.

Fig. 5 shows the diffusion reflectance spectra of the samples prepared by ball milling in air and NH_3 at various times. The absorption edge of the sample is determined by the following equation:

$$E_g = 1239.8/\lambda \qquad (2)$$

where E_g is the band gap (eV) of the sample and λ (nm) is the wavelength of the onset of the spectra. The samples milled in air have an absorption edge at 410–425 nm corresponding to a band gap of 3.02–2.92 eV. However, the samples milled in NH_3 show two absorption edges at 405–409 nm (3.03–3.06 eV) and 515–530 nm (2.34–2.41 eV), which is similar to the reported results on milling of titania and hexamethylenetetramine [13]. It seems that the first and second edges are attributed to the band structure of original TiO_2 and the newly formed N_{2p} band which is located above the O_{2p} valence band, respectively [7]. Fig. 4 shows the XPS spectra of the N_{1s} for the titania milled in air and NH_3, respectively. Besides two peaks corresponding to the molecularly chemisorbed γ-N_2, there is an obvious peak at near 396 eV for the titania milled in NH_3

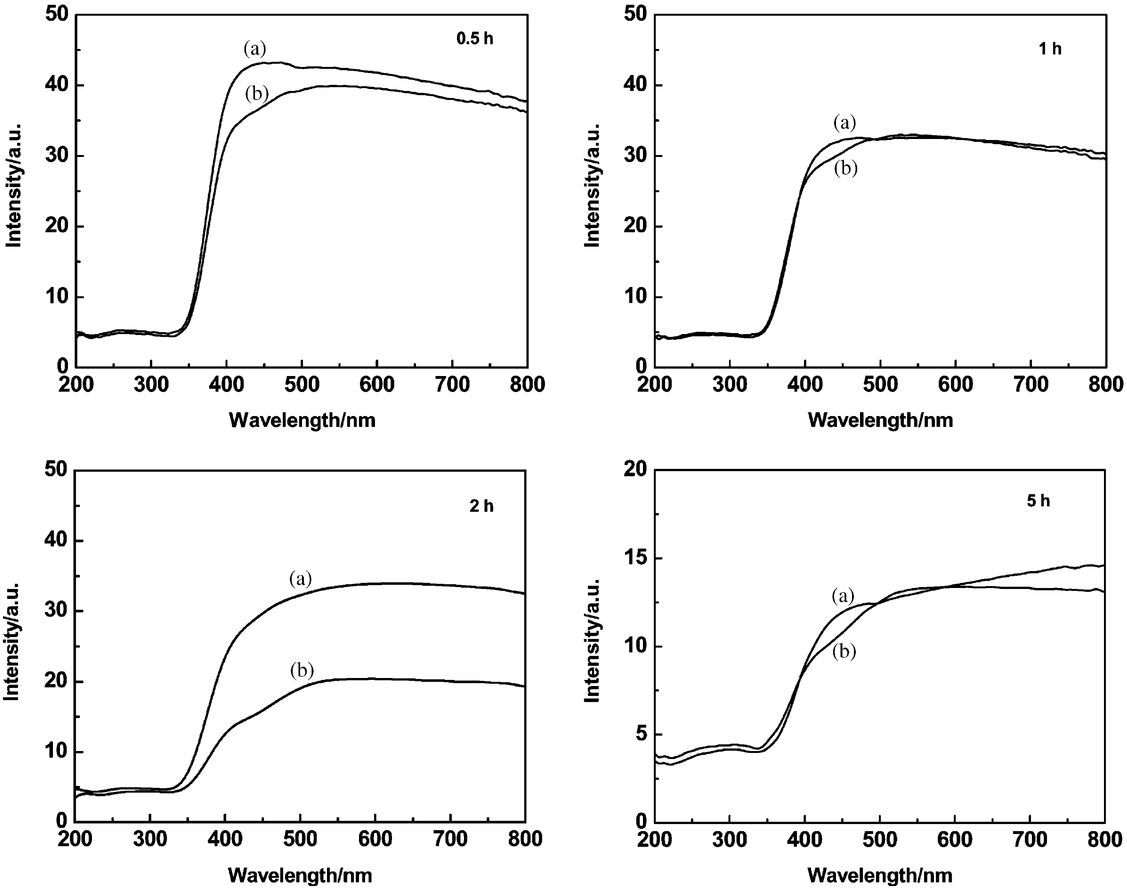

Fig. 5. UV–VIS spectra of the samples milled in air and NH_3 for different times, respectively, (a) in air and (b) in NH_3.

atmosphere. The peak at near 396 eV can be assigned to the formation of the Ti–N, which confirms the effective nitrogen doping. No peak at near 396 eV is detected in the N_{1s} spectra for the titania milled in air. Obviously, the band gap can be narrowed by mechanochemical reaction of gaseous NH_3 and titania. The absorption in visible light range increases up to 2 h milling time. However, the absorption at 5 h is lower than that at 2 h due to the mechanical stress inducing loss of substitution N atoms in titania lattices. At the same time, the substitution of O^{2-} with N^{3-} will result in the formation of anion defects for the charge compensation and the anion defects also seem to have affected high visible light absorption [21]. Much hydrogen was emitted when titania was milled in NH_3. Many oxygen vacancies are expected to form in the reduction atmosphere of H_2 and thus affect visible light absorption. Therefore, NH_3 can be an effective nitrogen source to easily dope nitrogen during simple ball milling.

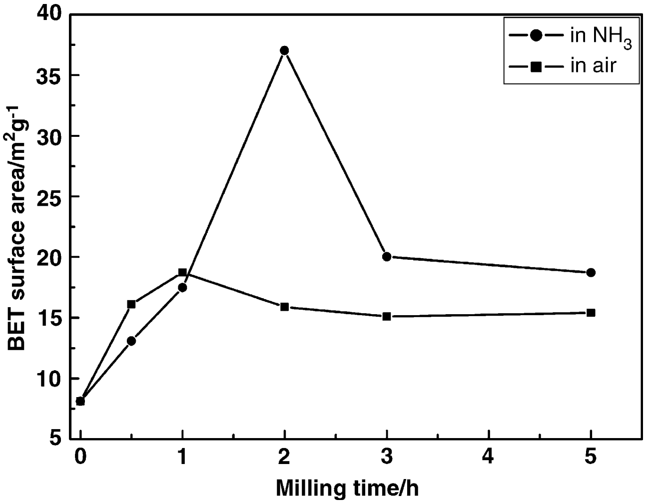

Fig. 6. BET surfaces area of the samples milled in air and NH_3 for different times.

3.3. The specific surface area (BET)

Fig. 6. shows the BET surface areas of the samples milled in air and gaseous NH_3. It is well known that mechanical alloying is an effective way to obtain nanocrystalline materials but the agglomeration often occurs due to the fact that the fresh surfaces formed by high-energy ball milling possesses high surface energy. It is very difficult to have nanocrystallinity with a high surface area by ball milling. However, gaseous NH_3 seems to play a key role in increasing the titania surface area in the process of milling. Surface area of the samples milled in air slowly reaches its maximum below 20 m^2/g at 1 h and then decreases. For the

samples milled in NH_3 there is a sudden increase between 1 and 2 h in its surface area with the highest above 35 m^2/g at 2 h, which is two times higher than that in air. In fact, there is only a little change in their XRD patterns and almost no change in crystal size determined by Scherer equation. So the surface area increase due to the decrease in crystal size can be neglected compared to the effects of NH_3 adsorbed on the fresh surfaces on the increase in surface area. The adsorbed NH_3 on the fresh surfaces can prevent active surfaces from contacting and agglomerating. To some extent, steric hindrance is formed due to strong adsorption of NH_3 on active surfaces. However, NH_3 molecules will decompose when electron transfers from surface O^{2-} to NH_3 molecules. Steric hindrance becomes weaker due to decomposition of NH_3 especially for longer milling time. Surface area of the sample in NH_3 is marginally larger than that in air when milling time is beyond 3 h. It seems there is an optimal time about 2 h to obtain a large surface area.

Considering the overall characteristics including phase structure, absorption in visible light range and BET surface area, an optimal milling time is about 2 h in our current experiments. With this milling time, both the amount of NH_3 in the vial and the activated surfaces are enough for the interaction of the adsorbed NH_3 with the activated surfaces to delay the phase transformation. The steric hindrance, caused by the large amount of adsorbed NH_3 on the fresh surfaces, can play a key role in decreasing agglomeration and increasing surface area. Meanwhile, a longer milling time can cause a decrease in the amount of nitrogen doping and bring about serious distortion of the lattice.

4. Conclusions

The transformation from anatase to srilankite and rutile in NH_3 is greatly delayed when titania is milled in NH_3 atmosphere compared with that in air. The interaction between fresh surfaces and NH_3 adsorbed on them plays an important role in delaying the phase transformation. There is absorption in the visible range when samples are prepared in NH_3 as NH_3 atmosphere facilitated the nitrogen doping due to the low bond energy of N–H. Meanwhile, NH_3 has obvious effect on increasing surface area due to steric hindrance and 2 h seems to be the optimal time to obtain high surface area titania. Therefore, milling in gaseous NH_3 instead of air could open an effective way to prepare nitrogen-doped titania with large surface area, which is beneficial for photocatalysis. We believe that there are several advantages of milling in gaseous NH_3 which include increased surface area, simple nitrogen doping particularly for continuous operation in large-scale production, and avoidance of organic residuals.

Acknowledgments

This work was supported by National Science Foundation of China (No. 50328204) and the support from the Shenyang Centre for Interfacial Materials, Chinese Academy of Sciences and the ARC Centre for Functional Nanomaterials, The University of Queensland, Australia is also acknowledged.

References

[1] A. Fujishima, K. Honda, Nature 238 (1972) 37–38.
[2] I.K. Konstantinau, T.A. Albanis, Appl. Catal. B 42 (2003) 319–335.
[3] Z. Ding, G.Q. Lu, P.F. Greenfield, J. Phys. Chem. B 104 (2000) 4815–4820.
[4] M. Anpo, M. Takeuchi, J. Catal. 216 (2003) 505–516.
[5] J.L. Gole, J.D. Stout, C. Burda, Y.B. Lou, X. B Chen, J. Phys. Chem. B 108 (2004) 1230–1240.
[6] I. Justicia, P. Ordejon, G. Canto, Adv. Mater. 14 (2002) 1399–1402.
[7] R. Aski, T. Morikawa, T. Ohwaki, K. Aoki., Science 293 (2001) 269–271.
[8] S.U.M. Khan, M. AL-shahry, W.B. Ingler Jr., Science 297 (2002) 2243–2245.
[9] J.M. Mwabora, T. Lindgren, E. Avendano, J. Phys. Chem. B 108 (2004) 20193–20198.
[10] Y.Z. Li, D.-S. Huang, N.H. Lee, S.-J. Kim, Chem. Phys. Lett. 404 (2005) 25–29.
[11] D. Li, H. Haneda, S. Hishita, N. Ohashi, N.K. Lahsetwar, J. Fluorine Chem. 126 (2005) 69–77.
[12] T. Sano, Nobuaki, Negishi, K. Koike, K. Takeuchi, S. Matsuzawa, J. Mater. Chem. 14 (2004) 380–384.
[13] S. Yin, H. Yamaki, M. Komatsu, Q.W. Zhang, J.S. Wang, Q. Tang, F. Saito, T. Sato, J. Mater. Chem. 13 (2003) 2996–3001.
[14] J.S. Wang, S. Yin, M. Komatsu, Q.W. Zhang, F. Satio, T. Sato., Appl. Catal. B: Environ. 52 (2004) 11–21.
[15] S. Yin, H. Yamaki, Q.W. Zhang, M. Komatsu, J.S. Wang, Q. Tang, F. Saito, T. Sato, Solid State Ion. 172 (2004) 205–209.
[16] J. Hu, H. Qin, Z. Sui, H. Lu., Mater. Lett. 53 (2002) 421–424.
[17] T. Ikoma, Q. Zhang, F. Saito, K. Akiyama, S. Tero, T. Kato, Bull. Chem. Soc. Jpn. 74 (2001) 2303–2309.
[18] J. Lee, Q. Zhang, F. Saito, Ind. Eng. Chem. Res. 40 (2001) 4785–4788.
[19] X.Y. Pan, X.M. Ma, J. Solid State Chem. 177 (2004) 4098–4103.
[20] R.D. Shannon, J.A. Pask, J. Am. Ceram. Soc. 48 (1965) 391–398.
[21] S.M. Prokes, J.L. Gole, X.B. Chen, C. Burda, W.E. Carlos., Adv. Funct. Mater. 15 (2005) 161–167.