Available online at www.sciencedirect.com
ScienceDirect
Journal of Photochemistry and Photobiology A: Chemistry 183 (2006) 171–175
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Influence of NH_3/Ar plasma irradiation on physical and photocatalytic properties of TiO_2 nanopowder

Hiroya Abe*, Tsukasa Kimitani, Makio Naito

Joining and Welding Research Institute, Osaka University, 11-1, Mihogaoka, Ibaraki, Osaka 567-0047, Japan

Received 24 August 2005; received in revised form 5 March 2006; accepted 11 March 2006
Available online 17 March 2006

Abstract

NH_3(10%)/Ar plasmas were generated at different gas pressures in a mechanical milling chamber, and were uniformly irradiated on an anatase TiO_2 powder with 300 m^2/g of which corresponding diameter was 7 nm. Crystal structures of the plasma irradiated powders were the same as that of the raw powder, regardless of the gas pressure. On the other hand, the optical property of the resultant powders was varied with regard to the gas pressure. When plasma generated and irradiated at 300 Pa, the powder had the specific surface area (SSA) of 283 m^2/g and noticeable absorption in vis light range was observed. In addition, the powder showed an improvement of the photocatalytic oxidation activity of CH_3CHO under vis light. These results indicated that the present plasma treatment is capable of modifying TiO_2 nanopowder for improving photoactivity without large SSA reduction, which is often seen in the modification with annealing.

Keywords: TiO_2; Photocatalysis; Nitrogen doping; NH_3/Ar plasma

1. Introduction

Titanium dioxide (TiO_2) of anatase phase is recognized as the most efficient photocatalytic material. It can only be excited by UV irradiation ($\lambda < 380$ nm) due to its large band gap energy of 3.2 eV. Since UV light accounts for only small fraction of the sun's energy compared to visible light, any shift in the optical response of TiO_2 from the UV to the visible spectral range will have a profound positive effect on the photocatalytic activity of the material. To realize the shifting, several modifications of TiO_2 have been attempted. These include oxygen deficient TiO_2 [1], cation-doped TiO_2 [2,3] or anion-doped TiO_2 [4–8].

It has been shown that the desired band gap narrowing of TiO_2 can be better achieved using the anionic dopant of nitrogen rather than cationic ions [4–6], and considerable efforts have been performed to dope TiO_2 powders with nitrogen by annealing TiO_2 at 500–600 °C under NH_3 flow [4,5]. It is known that NH_3 decomposes into nitrogen and hydrogen at the temperatures [9]. The annealing, however, often resulted in significant decrease of the specific surface area of powders due to grain growth, which would decrease the number of photoactive sites. Yin et al. have carried out nitrogen doping mechanochemically using P-25 titania and $C_6H_{12}N_4$ [10]. In this processing, however, an annealing (400 °C) was needed to remove residual $C_6H_{12}N_4$, and there is a concern that the thermal treatment of the milled powder would limit the keeping the initial large specific surface area.

Since NH_3 plasma consists of various nitriding species and excited hydrogen [11], effective NH_3 plasma irradiation on the surface of powder material may be a possible method for the TiO_2 modification without the high temperature annealing. Mechanical milling with electric discharge will present a uniform plasma irradiation of powder materials. The milling was firstly carried out by Calka and Wexler [12]. Their apparatus was a modified magneto-ball milling in which external magnets control the ball motion. The electrical discharge in the chamber was generated when the balls contacted a wire, which connected to a high voltage source. Although this technique promoted particle–particle and particle–gas reactions, the plasma condition cannot be fully controlled (for example, the distance between electrodes is uncontrollable).

Recently, the authors have developed a new apparatus for mechanical milling with electric discharge [13,14]. The illus-

---

* Corresponding author. Tel.: +81 6 6879 4366; fax: +81 6 6879 8680.
E-mail address: h-abe@jwri.osaka-u.ac.jp (H. Abe).

1010-6030/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2006.03.013

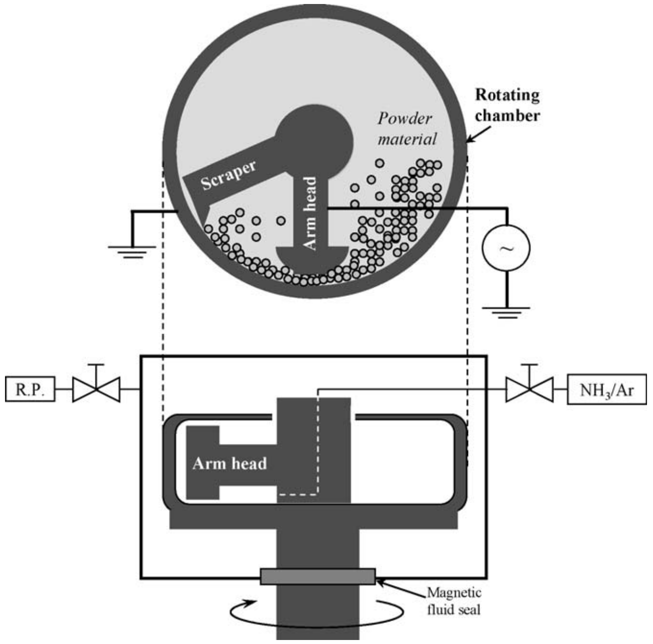

Fig. 1. An illustration of the apparatus used in this study.

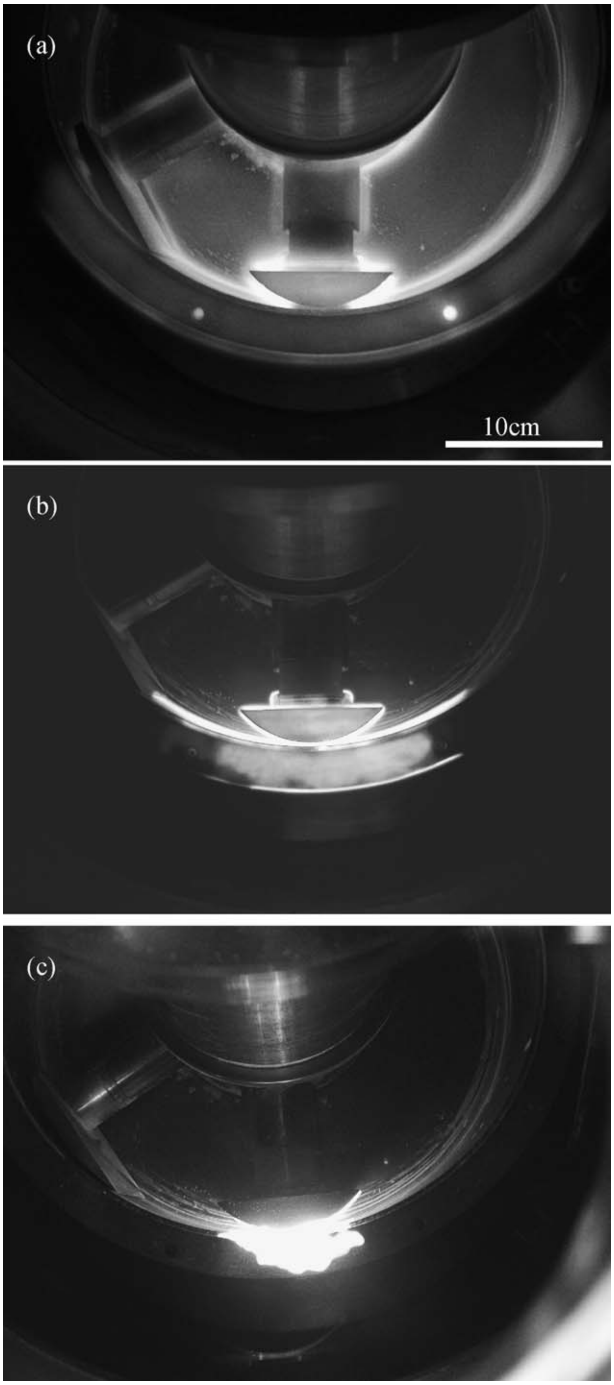

Fig. 2. Photographs of NH_3/Ar plasmas generated at (a) 50 Pa, (b) 300 Pa and (c) 1000 Pa.

tration of the apparatus is shown in Fig. 1. The main parts of the apparatus are a rotating chamber and an arm head fixed with a clearance against the inside wall of the chamber. An electric discharge can be formed by applying an electric power at the clearance with gaseous species. Plasma condition can be changed by controlling the power, distance of the clearance and gas pressure. When the chamber rotates, the powder material moves onto the inside wall of the chamber by centrifugal force and compressed in the clearance. The compressed powder on the inside wall can be successfully dispersed into the chamber by using the scraper, after the plasma is efficiently irradiated on the powder material. These actions are repeated during the chamber rotating, giving a well powder mixing under plasma, i.e., a homogeneous irradiation of plasma.

In this study, NH_3(10%)/Ar plasmas were generated at different gas pressures in the apparatus shown in Fig. 1, and were uniformly irradiated on an anatase TiO_2 nanopowder. The influences of the plasma irradiation on specific surface area, crystal structure, optical property and photocatalytic activity of the powder were investigated.

2. Experimental

2.1. Plasma treatment

The commercially available anatase TiO_2 powder (ST-01, Ishihara Sangyo, Japan) was used as a raw material. The specific surface area of the powder was 300 m^2/g and the corresponding diameter was 7 nm. The NH_3/Ar plasma treatment of the powder was carried out as follows. Five hundred grams of the powder was dried at 150 °C for 6 h to remove physically adsorbed water, and then placed in the chamber of the apparatus as shown in Fig. 1. The apparatus was evacuated for 10 min (reached 0.1 Pa), and NH_3(10%)/Ar gas was admitted into the chamber. To generate NH_3/Ar plasma, the alternative electric power (60 Hz, 30 W) was applied between the arm head and the chamber, with the chamber rotating of 1000 rpm. The clearance was set to 2 mm in gap. Time of the plasma irradiation was 1 h. Any heating was not employed during the treatment. The gas pressure in the chamber was controlled to be 50, 300 and 1000 Pa. Fig. 2 shows the photographs of the generated plasmas under the three different gas pressures. With increasing the gas pressure, the plasma became localized around the clearance.

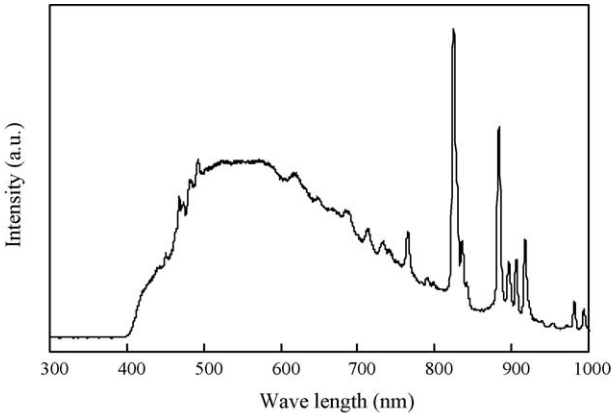

Fig. 3. Emission spectrum of the light used for photodegradation of acetaldehyde.

2.2. Powder properties

The phase structure of the plasma treated powders were characterized by X-ray diffraction (JDX-3530M, JEOL, Japan) using Ni filtered Cu Kα radiation. The specific surface area (SSA) of the samples was measured using a nitrogen gas absorption instrument (micromeritics ASAP 2010, Shimadzu, Japan), based on the BET method. The diffuse reflectance spectroscopy (DRS) of the powders was performed in a UV–vis spectrometer (UV-2450, Shimadzu, Japan), equipped with an integrating sphere attachment (ISR-2200, Shimadzu, Japan). The measurement of X-ray photoelectron spectroscopy (ESCA-34000, Shimadzu, Japan) was performed for the raw and the processed powders.

2.3. Photocatalytic activity

The photocatalytic oxidation activity was evaluated by the decomposition of gaseous CH_3CHO into CO_2 when irradiating light. A light was obtained by a Xe lamp (L2174, 75 W, Hamamatsu Photonics, Japan) with an optical filter (Achillesviniras, Achilles, Japan). Fig. 3 shows the emission spectrum of this light. As can be seen, UV light was well filtered out, and the light used in this study consisted of wavelength larger than 400 nm. The irradiation area was approximately 35 cm^2. A 2 g sample of the powders was uniformly spread over the irradiation area in a vessel. After pumping the vessel, CH_3CHO (500 ppm)/N_2 mixture gas was injected into it. The samples were kept in the dark for 3 h and then irradiated. CO_2 gas concentrations produced from decomposition of CH_3CHO were measured using a gas chromatograph (GC-8A, Shimadzu, Japan).

3. Results and discussion

3.1. XRD and BET results

Fig. 4 shows the XRD patterns of the raw TiO_2 and the NH_3/Ar plasma irradiated powders. Only peaks correspond to an anatase structure were observed in the raw powder. Almost the same patterns were observed in the NH_3/Ar plasma irradiated powders, regardless of the gas pressure. The results indicate that the crystal structure and the crystallinity of TiO_2 do not change with the present treatments. It has been reported that a high-energy ball milling of titania induced the phase transformation of anatase [10]. Since the phase transformation was not observed in Fig. 4, the mechanical energy in the present milling was not strong enough.

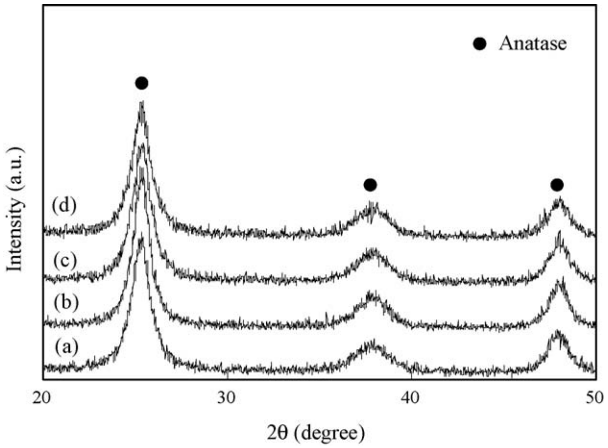

Fig. 4. XRD patterns of (a) the raw TiO_2 and NH_3/Ar plasma irradiated powders at (b) 50 Pa, (c) 300 Pa and (d) 1000 Pa.

Table 1 shows SSAs of the raw and the NH_3/Ar plasma treated powders. Although the SSAs of the NH_3/Ar plasma treated powders were lower than that of the raw powder, they were relatively high, exceeding 200 m^2/g. The maximum value (283 m^2/g) was obtained when plasma irradiated at 300 Pa. For comparison, the raw powder was calcinated at 500 °C under NH_3 flow for 3 h, and the resultant powder was of 65 m^2/g. The present method did not result in large reduction of the initial SSA of the powder.

3.2. DRS results

Fig. 5 shows the reflectance spectra of the raw and the NH_3/Ar plasma irradiated powders. Shifts of the absorption shoulders into the vis light region were obtained for the plasma irradiated powders. When plasma irradiated at 50 Pa, the absorption of the light at less than about 550 nm was observed. When plasma irradiated at 300 Pa, the increase in absorption at the same range was observed, and the absorption of the wavelengths greater than 550 nm was observed as well. When plasma irradiated at 1000 Pa, more strong absorption in the both regions was observed.

The change of the reflectance spectra of the powders with increasing the gas pressure showed a similar trend to that of the spectra obtained for $TiO_{2-x}N_x$ with increasing x [5]. The x values

Table 1
The specific surface area of the raw and the processed powders

	Specific surface area (m^2/g)
Raw	300
NH_3/Ar plasma at 50 Pa	211
NH_3/Ar plasma at 300 Pa	283
NH_3/Ar plasma at 1000 Pa	251
Calcination at 500 °C for 3 h	65

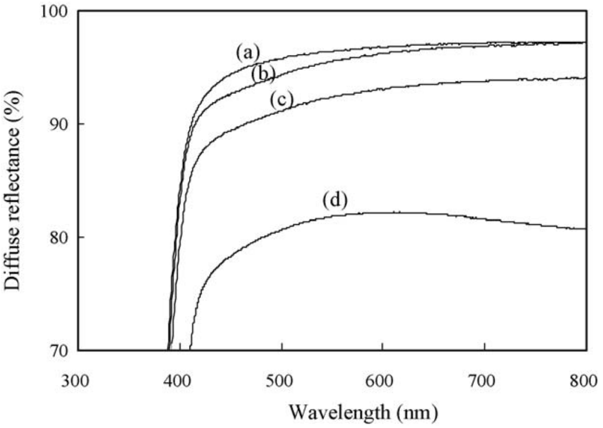

Fig. 5. UV–vis DRS spectra of (a) the raw TiO_2 and NH_3/Ar plasma irradiated powders at (b) 50 Pa, (c) 300 Pa and (d) 1000 Pa.

were controlled by annealing temperature under NH_3 flow. The shift of the absorbance shoulder into the vis light region was seen at low x (<0.01), and the increase in absorbance greater than 550 nm was also seen at relatively higher x (>0.01), which corresponds to Ti^{3+} [5]. The change of the reflectance spectra observed in this study may have resulted from the increase of the nitrogen amount.

NH_3 plasma consists of various nitriding species and excited hydrogen [10]. In the present case, these are the sources of nitridation and reduction of TiO_2, and can increase with increasing gas pressure. For the plasma irradiated powders, the increase of absorption in vis light range with increasing gas pressure can be attributed to the increase of nitriding and reducing species with it.

3.3. Photodegradation of acetaldehyde

Fig. 6 shows the change of CO_2 concentration as a function of time in the presence of the raw and the NH_3/Ar plasma treated powders while irradiating with the light as shown in Fig. 3. As can be seen, the produced CO_2 from the raw powder increased with increasing time. The reason for the photoactivity is presently unclear. It is noted that the raw powder had a slight absorption in entire vis light region as shown in Fig. 5, and the similar reflectance feature was seen in ref. [7].

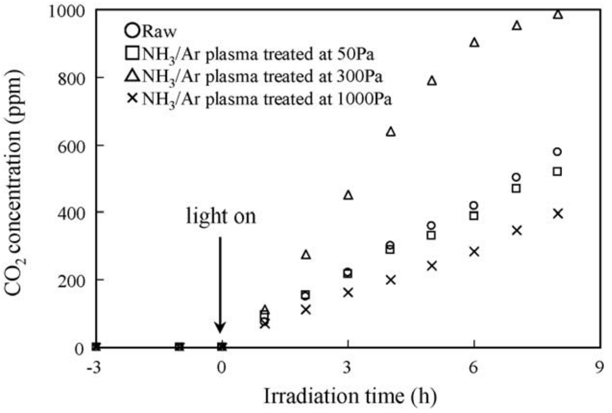

Fig. 6. CO_2 concentration changes for the raw TiO_2 and NH_3/Ar plasma irradiated powders under the light (Fig. 3).

The photocatalytic activity of the plasma irradiated powder at 50 Pa was almost the same as that of the raw powder, although the shift of the absorption shoulder was observed. One of the possible causes is the reduction of SSA. The SSA of the powder decreased down to by about 30% compared with the raw powder, which suggested the decrease of photoactive sites.

The plasma irradiated powder at 300 Pa showed the highest photocalatylic activity, almost twice of that of the raw powder. It decomposed almost completely the injected CH_3CHO for 8 h, since the evolved CO_2 concentration was 1000 ppm, which was twice of the initial CH_3CHO concentration. The SSA of the powder decreased down to by only 6% with the plasma-milling treatment. For the powder, the shift of the absorption shoulder and the absorption of the wavelength greater than 550 nm were observed, and the absorption was almost twice larger than that of the raw powder as shown in Fig. 5. The higher photocatalytic activity observed in this powder, compared to the raw powder and the plasma irradiated powder at 50 Pa, was probably due to the larger amount of adsorbed photons.

The plasma irradiated powder at 1000 Pa showed the lowest photocatalytic activity. As shown in Fig. 5(d), the powder had strong absorption in vis light region, including wavelength greater than 550 nm which corresponds to Ti^{3+}. The similar absorption characteristic was seen for $TiO_{2-x}N_x$ ($x = 0.019$), which was prepared by annealing under NH_3 flow, and the $TiO_{2-x}N_x$ ($x = 0.019$) showed the lower photocatalytic activity than those with lower x values [5]. The nitrogen doping caused an increase in oxygen vacancy and the amount of Ti^{3+}, and the oxygen vacancy state originated from Ti^{3+} could serve as a recombination center for holes and electrons under vis light irradiation [5]. For the present processed powders, the reflectance spectra in Fig. 5 indicate that the amount of Ti^{3+} increased with increasing the gas pressure. The decreased photocatalytic activity under vis light for the plasma irradiated powder at 1000 Pa can be considered to be due to the increased amount of Ti^{3+}.

The change of photocatalytic activity as well as reflectance feature of the plasma treated powders can be ascribed to difference of nitrogen amounts associated with gas pressure. Estimation of the amounts was tried by comparing the peak areas of N1s and O1s of XPS spectra. However, it was quite difficult because of a small difference in the ranges and the influence of background signal. As examples, the N1s XPS spectra of the raw and the plasma irradiated (300 Pa) powders are shown in Fig. 7. According to literatures [4–6], the XPS peak of N1 around 396 eV was assigned as atomic nitrogen bonded to titanium. The intensity in the range was small for the plasma irradiated powder, suggesting that the amount of doped nitrogen was low. The quantitative analysis of the nitrogen amount of the present samples is under investigation and will be reported in a future.

In this study, it was demonstrated that the present method is capable of modifying TiO_2 nanopowder for improving photoactivity without large SSA reduction, which is often seen in the modification with annealing. The decrease of SSA was quite low when the nanopowder was mechanically milled with plasma generated at relatively high gas pressure (300 Pa). The change

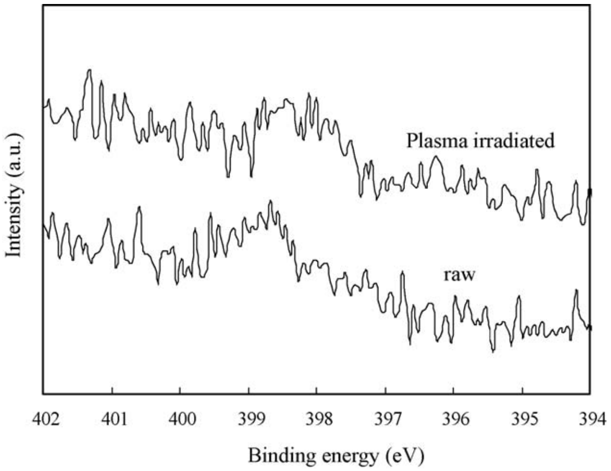

Fig. 7. N1s XPS spectra of raw TiO_2 and NH_3/Ar plasma irradiated powder at 300 Pa.

of the reflectance feature indicated the particle-gas reaction promoted with the treatment. We think this method is one of the promising approaches for modifying nanopowder materials.

4. Conclusion

The NH_3/Ar plasma irradiation was carried out on an anatase TiO_2 powder (300 m^2/g) using the newly developed apparatus (Fig. 1). The influence of the NH_3/Ar gas pressures (50, 300 and 1000 Pa) on the physical and photocatalytic properties of the powder was investigated. The crystal structure and crystallinity of TiO_2 did not change regardless of the gas pressures, and relatively high specific surface areas exceeding 200 m^2/g were observed for all resultant powders. The noticeable improvement in the photocatalytic activity under vis light was obtained when plasma irradiated at 300 Pa.

Acknowledgements

This work was partially supported by the Grant-in-Aid for Scientific Research (B) from Ministry of Education, Sports, Culture, Science and Technology of Japan. The authors also wish to acknowledge Prof. Tanaka of Osaka University for many fruitful discussions.

References

[1] I. Nakamura, N. Negishi, S. Kutsuna, T. Ihara, S. Sugihara, K. Takeuchi, J. Mol. Catal. A: Chem. 161 (2000) 161.
[2] Y. Bessekhouad, D. Robert, J.-V. Weber, N. Chaoui, J. Photochem. Photobiol. A: Chem. 167 (2004) 49.
[3] M. Anpo, M. Takeuchi, K. Ikeue, S. Dohshi, Curr. Opin. Solid State Mater. Sci. 6 (2002) 381.
[4] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, Science 293 (2001) 269.
[5] H. Irie, Y. Watanabe, K. Hashimoto, J. Phys. Chem. B 107 (2003) 5483.
[6] T. Morikawa, R. Asahi, T. Ohwaki, K. Aoki, Y. Taga, Jpn. J. Appl. Phys. 40 (2000) L561.
[7] T. Ihara, M. Miyoshi, Y. Iriyama, O. Matsumoto, S. Sugihara, Appl. Catal. B: Environ. 42 (2003) 403.
[8] H. Irie, S. Washizuka, N. Yoshino, K. Hashimoto, Chem. Commun. (2003) 1298.
[9] C.H. Shin, G. Bugli, G. Dweight-Mariadassou, J. Solid State Chem. 95 (1991) 11802.
[10] S. Yin, Q. Zhang, F. Saito, T. Sato, Chem. Lett. 32 (2003) 358.
[11] S. Luan, G.W. Neudeck, J. Appl. Phys. 68 (1990) 3445.
[12] A. Calka, D. Wexler, Nature 419 (2002) 147.
[13] M. Naito, H. Abe, Ceram. Trans. 157 (2005) 69.
[14] H. Abe, T. Kimitani, K. Sato, M. Naito, K. Nogi, J. Soc. Power Technol. Jpn. 42 (2005) 409.