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Photo-induced super-hydrophilic property and photocatalysis on transparent Ti-containing mesoporous silica thin films

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Abstract

The transparent Ti-containing mesoporous silica thin films can be prepared on quartz plate using a spin-coating sol–gel method. The spectroscopic characterization has revealed that the Ti-containing mesoporous silica thin films contain isolated and tetrahedrally-coordinated titanium oxide moieties in the frameworks. Compared with the common mesoporous silica thin films, these Ti-containing mesoporous silica thin films have demonstrated a strong hydrophilic surface property even before UV-irradiation. After UV-light irradiation, the contact angle of water droplet on the Ti-containing mesoporous silica thin films became lower, indicating the appearance of the super-hydrophilic property. Under UV-light irradiation Ti-containing mesoporous silica thin films also exhibited highly selective activity for the photocatalytic oxidation of propylene. The isolated and tetrahedrally-coordinated titanium oxide moieties are responsible for these photo-induced surface reactions.

Keywords: Mesoporous thin film; Titanium oxide; Super-hydrophilic property

1. Introduction

It is special interest to design the ion and/or cluster size catalysts within the microporous zeolite and mesoporous molecular sieve materials, because these fascinating supports offer unique nano-scaled pore systems, unusual internal surface topology, and ion-exchange capacities. Especially, the unique and fascinating properties of mesoporous silica involving transition metals within the cavities and framework have opened new possibilities for many application areas not only in catalysis but also for various photochemical processes [1–5]. The transition metal ions in mesoporous silica are considered to be highly dispersed at the atomic level and also to be well-defined catalysts, which exist in the specific structure of the framework. Unique photocatalytic properties, which cannot be realized in normal catalytic systems can be realized in modified reaction spaces. The photocatalytic activity of a highly dispersed titanium oxide catalyst anchored onto porous silica glass or zeolites was also investigated and it was found that the highly dispersed titanium oxide catalyst exhibits a high and unique photocatalytic activity as compared to bulk TiO_2 powder. Among them, Ti-containing mesoporous silica catalysts have been found to demonstrate efficient and selective photocatalytic activity for several significant reactions such as the reduction of CO_2 with H_2O [6–9], NO decomposition into N_2 and O_2 [10,11], and the selective photoepoxidation of alkene with O_2 [12].

Although the mesoporous silica is generally in the form of fine powder, a simpler method to synthesize mesoporous silica films has been developed recently using the spin-coating [13–15] and dip-coating [16] methods. These thin films of silica-surfactant mesostructured materials have an ideal morphology for possible applications in various fields. By the addition of titanium ions within the mesoporous silica thin films it becomes possible to design of unique surface active sites in the modified spaces. The design of Ti-containing mesoporous silica thin film

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anchored on transparent supports or embedded onto transparent materials would provide one of the most promising efficient photocatalyst systems [17]. TiO_2 thin films prepared by the sol–gel method and the dry process have been utilized in many fields not only for their photocatalytic properties but also their super-hydrophilic properties [18]. The developments of TiO_2 thin films having efficient photocatalytic activity and high mechanical stability are strongly desired while being supported on various substrates. Although the super-hydrophilicity of TiO_2 thin films has already been observed under UV-irradiation, the photo-induced surface properties of Ti-containing mesoporous silica films are also of special interest. The Ti-containing mesoporous silica embedded onto the transparent quartz plate is desired strongly as the efficient photocatalyst and unique photo-functional materials.

In this study, using the spin-coating sol–gel method Ti-containing mesoporous silica thin films have been prepared on quartz plate. Their photo-induced hydrophilic property and photocatalytic activity have been investigated.

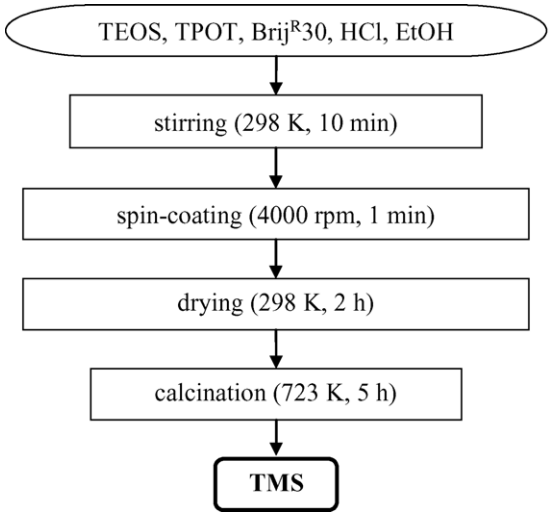

Fig. 1. Procedure of preparation for Ti-containing mesoporous silica (TMS) thin films by the spin-coating and sol–gel method.

2. Experimental

2.1. Preparation of Ti-containing mesoporous silica thin films

The Ti-containing mesoporous silica (TMS) thin films deposited on the plate of quartz (1 cm× 1 cm) were prepared by the spin-coating sol–gel method using tetraethyl orthosilicate (TEOS) and tetraethyl orthotitanate (TEOT) as silica and titania precursors, $C_{12}H_{25}(OCH_2CH_2)_4OH$ (Brij^{R}30) as surfactant, hydrochloric acid and ethanol (TEOS + TEOT:Brij30:HCl:EtOH = 8:0.9:0.8:50) (TEOS:TEOT = 100:x; x = 0, 1, 2, 5, 10). The mixtures were stirred for 10 min at 298 K, dripped onto a quartz substrate (10 mm × 10 mm × 1 mm), spread evenly and spun coated at a spinning rate of 4000 rpm for 1 min. Thus obtained thin films were calcined in air at 723 K for 5 h to remove the surfactant from the film materials. The mesoporous silica (MS) thin films without Ti was also prepared by the same method [14,15].

2.2. Characterization

The diffuse reflectance absorption spectra were recorded with a Shimadzu UV-2550 spectrometer at 295 K. The XRD patterns were recorded with a Rigaku Mini-flex using Cu Kα radiation of λ = 1.5418 Å. The XAFS spectra (XANES and EXAFS) were measured at the BL-9A facility [19] of the Photon Factory at the National Laboratory for High-Energy Physics, Tsukuba. A Si(1 1 1) double crystal was used to monochromatize the X-rays from the 2.5 GeV electron storage ring. The Ti K-edge absorption spectra were recorded in the fluorescence mode at 295 K. In a typical experiment, the sample was loaded into the in situ cell having the plastic windows. The normalized spectra were obtained by a procedure described in previous literature [20] and Fourier transformation was performed on k^3-weighted EXAFS oscillations in the range of 3–10 $Å^{-1}$. The preedge peaks in the XANES regions were normalized for atomic absorption, based on the average absorption coefficient of the spectral region from 5050 to 5200 eV (Fig. 1).

2.3. Measurement of contact angle of water droplet

The water-repellency of the film surface was checked by the contact angle of pure water (0.01 ml). A 10 mW He–Ne laser, a bandpass filter, a high-resolution (2000 × 1312 pixels) digital camera with a remote controller, a video and an image automatic transmission and processing system were used for the measurement. Because the band-pass filter can cut all other wavelengths except for the laser beam (632 nm), the reflection light can be removed and high definition drop profiles can be obtained.

2.4. Photocatalytic reaction

The photocatalytic activity of Ti-containing mesoporous silica thin film for the oxidation of propylene was investigated in a quartz cell with a flat bottom (85.55 cm^3) connected to a conventional vacuum system. Before the reaction, the catalysts were heated in O_2 at 723 K for 2 h, and evacuated at 523 K for 2 h. The photocatalytic oxidation of propylene with O_2 was carried out in the presence of propylene (8 μmol) and O_2 (16 μmol) under UV-light irradiation using a 100 W high-pressure Hg lamp at 273 K and products in the gas phase and the products desorbed by heating to 573 K were analyzed by GC [21,22].

3. Results and discussion

3.1. Characterization

The synthesized conventional mesoporous silica (MS) and Ti-containing mesoporous silica (TMS) thin films were transparent and well-fixed on the substrate of quartz plate.

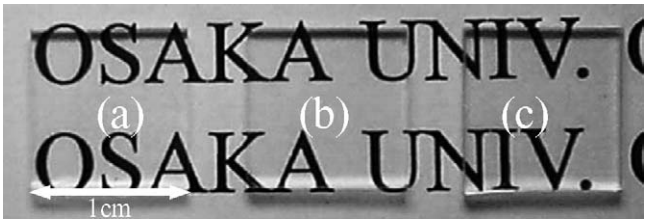

Fig. 2. Sample photography of (a) quartz plate, and plates coated with (b) mesoporous silica thin film, and (c) Ti-containing mesoporous silica thin film (Ti/Si = 0.05).

Fig. 2 shows the photo images of mesoporous silica and Ti-containing mesoporous silica thin films fixed on quartz plate. As shown in Fig. 2, the mesoporous silica and Ti-containing mesoporous silica thin films are colorless and totally transparent like original quartz plate.

The X-ray diffraction patterns of the mesoporous silica thin film and Ti-containing mesoporous silica thin films prepared at various Ti/Si ratios are shown in Fig. 3. The conventional mesoporous silica and Ti-containing mesoporous silica thin films with Ti/Si ratio of 0.01–0.05, exhibit a diffraction peak at around 2–3°, indicating the presence of mesoporous structure. The d-spacing of Ti-containing mesoporous silica changes depending on the Ti/Si ratios. The d-spacing of Ti-containing mesoporous silica film was larger than the mesoporous silica film. The X-ray diffraction patterns of Ti-containing silica thin film exhibited no peak corresponding to crystalline phase at the higher angle, indicating that Ti-oxide moieties are highly dispersed in the mesoporous structure, while no other phases are formed. On the other hand, the sample prepared with the Ti/Si ratio of 0.10 exhibited no peak due to the ordered mesoporous structure indicating that mesoporous structure can not be maintained after the calcination. These results obtained from SEM observation and XRD analysis indicate that the transparent Ti-containing mesoporous silica thin films with the Ti/Si ratio 0.01–0.05 can be prepared on quartz plate by the present spin-coating sol–gel method.

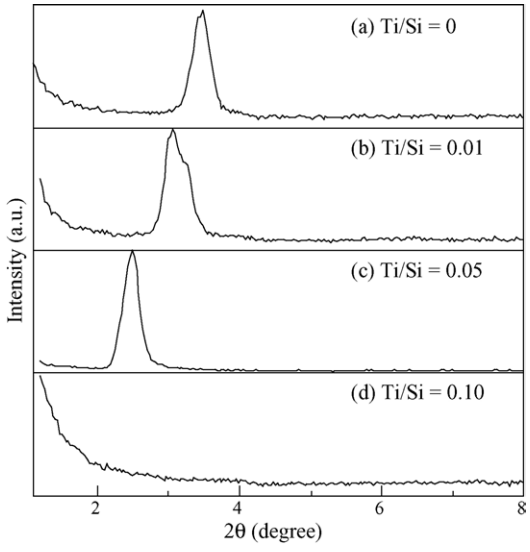

Fig. 3. XRD patterns of (a) mesoporous silica (MS) and (b–d) Ti-containing mesoporous silica (TMS) thin films.

Fig. 4 shows the XANES spectra at the Ti K-edge of TiO_2 powder (P25: anatase 80%, rutile 20%) and Ti-containing mesoporous silica thin films. The XANES spectra of the Ti containing compounds at the Ti K-edge show several well-defined preedge peaks. These relative intensities of the preedge peaks are related to the local structures surrounding the Ti atom and provide useful information on the coordination number surrounding the Ti atom [23,24]. As shown in Fig. 4, Ti-containing mesoporous silica thin films exhibit an intense single preedge peak. Because a lack of an inversion center in the regular tetrahedron structure causes an intense single preedge peak, the observation of this intense single preedge peak indicates that the titanium oxide moieties in Ti-containing mesoporous silica thin films has a tetrahedral coordination. Fig. 4 also shows the FT-EXAFS spectra of the samples and all data are given without corrections for phase shifts. The Ti-containing mesoporous silica thin films exhibit only a strong peak at around 1.6 Å (uncorrected for the phase shift), which can be assigned to the neighboring oxygen atoms (a Ti–O bond), indicating the presence of the isolated titanium oxide species on these samples.

Fig. 5 shows the UV–vis absorption spectra of the mesoporous silica and Ti-containing mesoporous silica thin films as well as TiO_2 powder (P-25). Absorption bands of Ti-containing mesoporous silica thin films are observed in the UV wavelength region. When the Ti/Si ratio of Ti-containing mesoporous silica thin films becomes the lower, the absorption edge shifts towards the wavelength region shorter than 250 nm. These bands can be attributed to the ligand-to-metal charge transfer (LMCT) band of the tetrahedrally-coordinated titanium oxide moieties [3]. These results indicate the formation of the isolated and tetrahedrally-coordinated titanium oxide moieties in the Ti-containing mesoporous silica thin films. The presence of the tetrahedrally-coordinated titanium oxide moieties was also confirmed by XAFS analysis.

3.2. Measurement of contact angle of water droplet

Fig. 6 shows the images of water droplets on the mesoporous silica and Ti-containing mesoporous silica thin film deposited on quartz plate. The results observed on TiO_2 thin film deposited on quartz plate using mirrortron sputtering technique were also shown as a reference. The water contact angles on Ti-containing mesoporous silica thin films were much smaller than on mesoporous silica thin film and TiO_2 thin film even before UV-light irradiation as shown in Figs. 6 and 7. After UV-light irradiation, the water contact angle on Ti-containing mesoporous silica thin film and TiO_2 thin film become very small, while the water contact angle on mesoporous silica thin films do not make any changes. These observations indicate that Ti-containing mesoporous silica thin films can perform the super-hydrophilic property under UV-light irradiation as well as TiO_2 thin film. The charge transfer excited state of the tetrahedrally coordinated titanium oxide moieties formed under UV-light irradiation play a significant role in the photo-induced super-hydrophilic property.

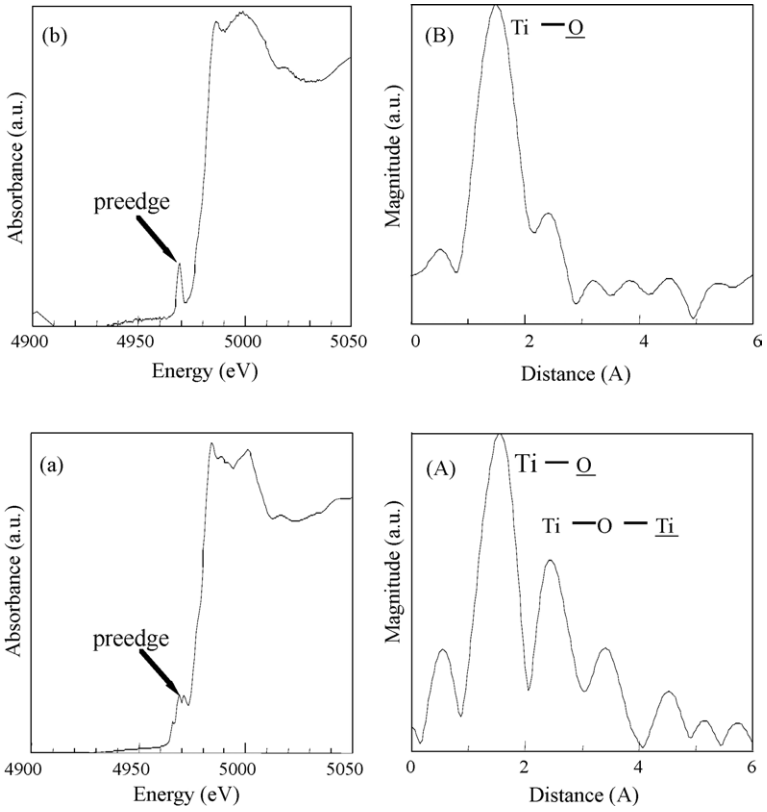

Fig. 4. XANES (a, b) and FT-EXAFS (A, B) spectra of (a, A) TiO_2 powder (P25) and (b, B) Ti-containing mesoporous silica (TMS) thin films (Ti/Si = 0.02).

3.3. Photocatalytic reaction

The photocatalytic property of Ti-containing mesoporous silica thin films for the oxidation of propylene with molecular oxygen was investigated. Under UV-light irradiation in the presence of propylene and oxygen, the Ti-containing mesoporous silica thin films catalyzed the photocatalytic oxidation of propylene to produce ethanol, acetone, CO/CO_2, etc. Activity of Ti-containing mesoporous silica thin films (Ti/Si = 0.01) for propylene oxidation per weight of TiO_2 was 0.454 μmol/s g-TiO_2

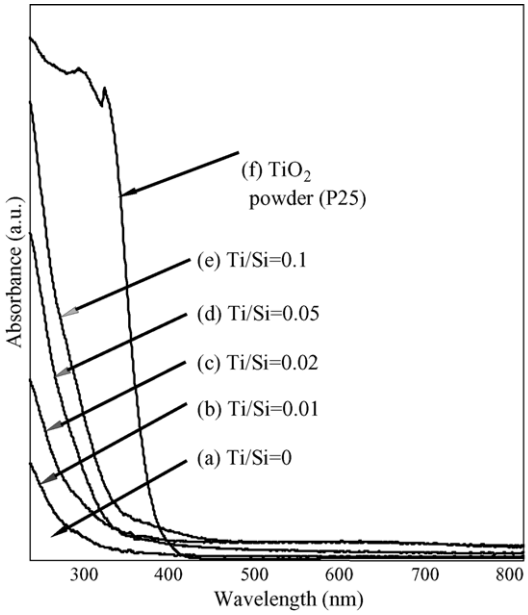

Fig. 5. UV–vis spectra of (a) mesoporous silica (MS) and (b–e) Ti-containing mesoporous silica (TMS) thin films.

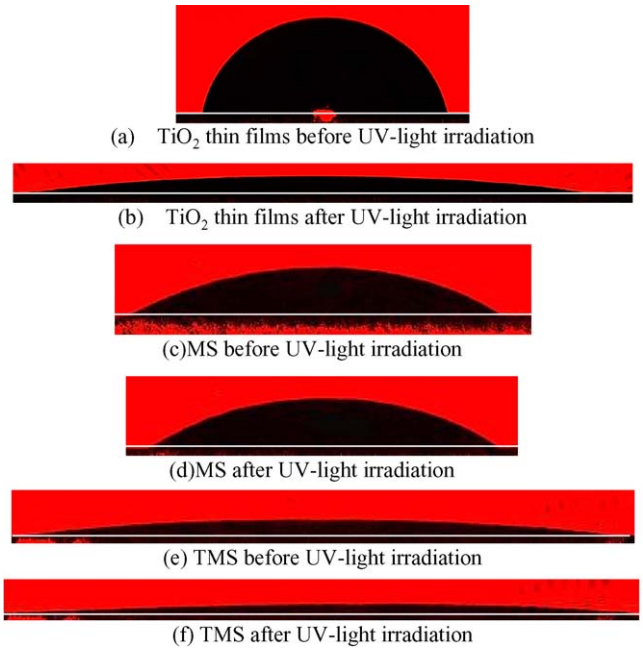

Fig. 6. The images of water droplets observed before (a, c, e) and after (b, d, f) UV-light irradiation on (a, b) TiO_2 thin film prepared by the mirrartron sputtering method, (c, d) the mesoporous silica (MS) and (e, f) Ti-containing mesoporous silica (TMS) thin films (Ti/Si = 0.02).

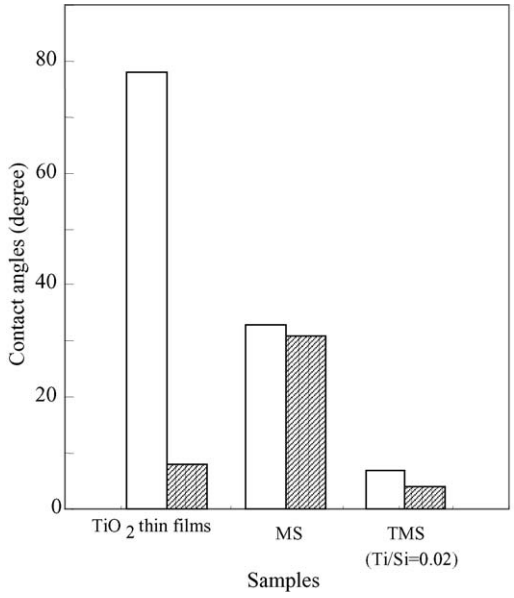

Fig. 7. The changes in the contact angles of water droplets observed before and after UV-light irradiation on TiO_2 thin film prepared by the mirrartron sputtering method, the mesoporous silica (MS) and Ti-containing mesoporous silica (TMS) thin films (Ti/Si = 0.02).

Table 1
Product yields and distribution in the photocatalytic oxidation of propylene on Ti-containing mesoporous silica (TMS) thin films (Ti/Si = 0.01) after UV-irradiation for 2 h

	C_2H_5OH	$(CH_3)_2O$	CO_x
Yields (mmol)	0.013	0.65	0.053
Selectivity (%)	1.3	96.1	2.6

which was higher than that of commercial TiO_2 (P-25) powder. Partial oxidation of propylene with a high selectivity for the production of oxygen containing hydrocarbons such as ethanol and acetone (96% at 2 h irradiation) proceeded under UV-light irradiation, as shown in Table 1. These results indicate that the tetrahedrally-coordinated isolated titanium oxide moieties in Ti-containing mesoporous silica thin films can exhibit the efficient photocatalytic activity for the oxidation of propylene under UV-light irradiation with a high selectivity for the partial oxidation of propylene.

4. Conclusion

The Ti-containing mesoporous silica thin films can be prepared on the quartz plate using the spin-coating sol–gel method with polyoxyethylene(4)lauryl ether (Brij 30) as surfactant. These Ti-containing mesoporous silica thin films are colorless transparent and well-fixed on the substrate of quartz plate. With Ti/Si ratio of 0.01–0.05, the Ti-oxide species were present as tetrahedrally-coordinated titanium oxide moieties in the Ti-containing mesoporous silica thin films. These Ti-containing mesoporous silica thin films have demonstrated a strong hydrophilic surface property even before UV-irradiation. After UV-light irradiation on the Ti-containing mesoporous silica thin films, the appearance of the super-hydrophilic property was observed. Furthermore, the Ti-containing mesoporous silica thin films exhibited the highly selective photocatalytic activity for the oxidation of propylene to produce the partially oxidized products under UV-light irradiation.

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References

[1] P. Wu, T. Tatsumi, Catl. Suv. Asia 8 (2004) 137.
[2] J.M. Thomas, R. Raja, J. Organometal. Chem. 689 (2004) 4110.
[3] H. Yamashita, M. Anpo, Curr. Opin. Solid State Maters Sci. 7 (2004) 471.
[4] M. Anpo, M. Che, Adv. Catal. 44 (1999) 119.
[5] B. Notari, Adv. Catal. 41 (1996) 253.
[6] H. Yamashita, M. OkazakiI, M. Anpo, Stud. Surf. Sci. Catal. 153 (2004) 289.
[7] H. Yamashita, K. Ikeue, T. Takewaki, M. Anpo, Topics Catal. 18 (2002) 95.
[8] H. Yamashita, Y. Fujii, Y. Ikeue, S.G. Zhang, K. Ikeuchi, D.R. Park, K. Koyano, T. Tatsumi, M. Anpo, Catal. Today 45 (1998) 221.
[9] M. Anpo, H. Yamashita, Y. Ichihashi, Y. Fujii, M. Honda, J. Phys. Chem. B 101 (1997) 2632.
[10] H. Yamashita, S.G. Zhang, Y. Ichihashi, Y. Matsumura, Y. Souma, T. Tatsumi, M. Anpo, Appl. Surf. Sci. 121 (1997) 305.
[11] H. Yamashita, Y. Ichihashi, M. Anpo, C. Louis, M. Che, J. Phys. Chem. 100 (1996) 16041.
[12] H. Yamashita, K. Kida, K. Ikeue, Y. Kanazawa, K. Yoshizawa, M. Anpo, Stud. Surf. Sci. Catal. 146 (2003) 597.
[13] S. Tanaka, N. Nishiyama, Y. Oku, Y. Egashira, K. Ueyama, Micropor. Mesopor. Mater. 63 (2003) 105.
[14] N. Nishiyama, S. Tanaka, Y. Egashira, Y. Oku, K. Ueyama, Chem. Mater. 14 (2002) 4229.
[15] M. Ogawa, N. Masukawa, Micropor. Mesopor. Mater. 38 (2000) 35.
[16] Y. Lu, R. Ganguli, C.A. Drewien, M.T. Anderson, C.J. Brinker, W. Gong, Y. Guo, H. Soyez, B. Dunn, M.H. Huang, J.I. Zink, Nature 389 (1997) 364.
[17] M. Ogawa, H. Ishikawa, T. Kikuchi, J. Mater. Chem. 8 (1998) 1783.
[18] H. Irie, K. Sunada, K. Hashimoto, Electrochemistry 72 (2004) 807.
[19] M. Nomura, A. Koyama, J. Synchrotron Rad. 6 (1999) 182.
[20] H. Yamashita, M. Matsuoka, K. Tsuji, Y. Shioya, M. Anpo, J. Phys. Chem. 100 (1996) 397.
[21] H. Yamashita, K. Yoshizawa, M. Ariyuki, S. Higashimoto, M. Che, M. Anpo, Chem. Commun. 435 (2001).
[22] H. Yamashita, S. Ohshiro, K. Kida, K. Yoshizawa, M. Anpo, Res. Chem. Intermed. 29 (2003) 881.
[23] G. Sankar, J.M. Thomas, C.R.A. Catlow, C.M. Barker, D. Gleeson, N. Kaltsoyannis, J. Phys. Chem. B 105 (2001) 9028.
[24] J.M. Thomas, G. Sankar, Acc. Chem. Res. 34 (2001) 571.