JOURNAL OF Materials CHEMISTRY

Preparation, characterization and photoluminescence properties of mesolamellar titanium dioxide films

Ni Bai,[a] Shougui Li,[a] Haiyong Chen[b] and Wenqin Pang*[a]

[a]State Key Laboratory of Inorganic Synthesis & Preparative Chemistry, Department of Chemistry, Jilin University, Changchun 130023, P. R. China. Fax: +86-431-5671974; E-mail: wqpang@mail.jlu.edu.cn
[b]Key Laboratory of Superhard Materials, Jilin University, Changchun 130023, P. R. China

Received 2nd May 2001, Accepted 24th September 2001
First published as an Advance Article on the web 19th October 2001

Mesolamellar TiO_2 films, through self-assembly of titanium alkoxide and surfactants, have been prepared on glass substrates at 50 °C in air and under hydrothermal conditions, respectively. The multilayer composite materials thus obtained are different from the well-known nanocrystalline TiO_2 films. XRD and TEM results clearly show the formation of a lamellar structure and SEM results reveal that the lamellar TiO_2 films grow on the glass substrates in a layer by layer fashion. The thickness of the TiO_2 layer intercalated between the organic species is maintained around 1 nm, independent of the alkyl length of the surfactant used. Other techniques including IR, XPS and DR UV-vis spectroscopy were used to further characterize the nanostructured TiO_2 films. Room temperature photoluminescence of multilayered TiO_2 films is detectable with an excitation of 300 nm, which might arise from the interfacial effect between the titania layers and the surfactants.

Introduction

In recent years, the fabrication of nanostructured composites has been attracting considerable attention in the field of materials science.[1–4] In particular, the two dimensional layer semiconductor composites have received increasing interest because this type of material often exhibits novel properties making them potential candidates in electronic and optoelectronic devices, solar cells, photoelectrodes, photocatalysts, and sensors.[1–4] Layer semiconductor nanocomposites might be obtained based on the self-assembly process between inorganic and organic species,[1,4,5] a process which has been extensively used to guide the formation of mesoporous materials with nanometer scale periodicity since 1992.[6–8] To date, a series of layer semiconductor mesophases in which a semiconductor oxide is sandwiched between organic components have been successfully produced.[4,9–13] Among them are TiO_2 mesoporous materials which can be synthesized by employing different surfactants, titanium precursors and reaction conditions.[10,11,14–18] As a large-bandgap semiconductor and versatile photocatalyst, anatase, rutile and nanocrystalline TiO_2 have been widely studied.[19–22] In contrast, mesolamellar TiO_2–surfactant composites show well-defined multilayer structures to form layered TiO_2–surfactant superlattices. This peculiar structure might have a profound effect on the chemical and physical properties of titanium dioxide.[4]

One important step for diverse applications of mesoporous materials is control of the morphology, which is a currently widespreading subject. Over the past few years, considerable research has been focused on the formation of thin films of mesoporous silica with hexagonal,[23] cubic[24] and lamellar arrays;[25,26] however, much less is known about thin films of non-silica mesophases and their properties related to their unique structure. Here, we have explored the possibility of preparing non-silica films, with the aim of preparing nanostructured TiO_2 films. Although numerous nanocrystalline TiO_2 films composed of TiO_2 nanoparticles have been obtained by sol–gel technique associated with hydrolysis of titanium alkoxides followed by calcination,[27,28] it is clearly different from the case of nanostructured TiO_2–surfactant films featuring a two-dimensional layer structure. Techniques such as XRD, SEM, TEM, IR, DR UV-vis spectra and XPS have been used to characterize the layered TiO_2–surfactant films. Room temperature photoluminescence of TiO_2–surfactant films, undetectable for bulk TiO_2 materials, is also examined. The unusual room temperature photoluminescence might be influenced by interfacial effects between TiO_2 and the surfactant.

Experimental

Synthesis

Reagents used for the preparation of mesolamellar TiO_2 films included tetra-n-butyltitanate (C. P., TBOT), cationic surfactants $CH_3(CH_2)_nN(CH_3)_3Br$ ($n = 12, 14, 16$, $C_{12}TABr$, $C_{14}TABr$, $C_{16}TABr$, respectively, A.R.) and tetramethylammonium hydroxide (10% solution in water, C. P., TMAOH). All the reagents were purchased from Beijing Chemical Reagents Company and used as received.

Firstly, TiO_2–surfactant films were prepared at 50 °C in air.[23,29] The films were grown on glass substrates by allowing the glass substrates to be leveled at the bottom of the reaction vessel. The reactant mole ratios used for preparing a film with a thickness of *ca.* 2 μm were 2.7 TBOT : 1.3 C_nTABr : 1.0 TMAOH : 640 H_2O. The typical synthesis procedure is described as follows: 6.4 g of a $C_{16}TABr$ surfactant was mixed with 150 g of deionized water, then 12 ml of TMAOH solution (10%) was added to the mixture under stirring followed by the addition of 12 g TBOT. After the mixture was stirred at 50 °C in air for 4 h, the film grown on the substrate was removed from the solution, washed with water and air-dried. Calcined films were obtained by heating in air at 200 °C, 300 °C, 400 °C or 550 °C for 4 h.

In addition, the TiO_2–surfactant films were also obtained by crystallization from the mother liquor in a Teflon-lined autoclave at 100 °C, 140 °C or 180 °C for 24 h. Then, the films were removed, washed with water and air-dried.

DOI: 10.1039/b103930j

Characterization

The X-ray powder diffraction patterns were collected on a Siemens D5005 diffractometer with nickel-filtered Cu-Kα radiation ($\lambda = 0.15418$ nm). SEM images of glass-supported titania–surfactant films were obtained on a Hitachi X-156 scanning electron microscope. Transmission electron microscope (TEM) image was recorded on a Hitachi H-8100 microscope operating at an accelerating voltage of 200 kV. IR spectra were recorded on a Nicolet Impact 410 FTIR spectrometer using KBr pellets. The UV-vis diffuse reflectance spectra (DR UV-vis spectra) were obtained on a Perkin-Elmer Lambda 20 spectrometer. The X-ray photoelectron spectrum (XPS) was recorded on a VG ESCALABMIK II spectrometer with an Al-Kα X-ray source and constant pass energy of 50 eV. The C 1s peak (284.6 ev) was used as the reference for the correction of the XPS positions of the film obtained. Photoluminescence spectra were measured on a Shimadzu RF-5301 PC spectrometer.

Results and discussion

The XRD patterns of the as-prepared TiO_2–C_nTABr films obtained at 50 °C in air are shown in Fig. 1. In the presence of C_{16}TABr, three diffraction peaks in good order at *d*-spacings of 3.4 nm, 1.7 nm and 1.1 nm can be observed (Fig. 1a), indicating that the film possesses a periodic mesostructure. Similar to lamellar silicate[6–8,25,26] and aluminophosphate[30] mesophases, the peaks are attributed to the (001), (002) and (003) reflections, characteristic of a lamellar structure. When C_{14}TABr (Fig. 1b) and C_{12}TABr (Fig. 1c) were employed, respectively, the interlamellar spacing changed from 3.4 nm (C_{16}TABr) to 3.1 nm (C_{12}TABr), indicating that the interlamellar spacing is dependent on the surfactant chain length. Also, it can be seen that the first diffraction peak is weak and broad, suggesting that, under similar reaction conditions and reactant mole ratios, the order of the film structure decreases with the shortness of the surfactant chain length. With regard to the performance of the surfactant in the TiO_2–surfactant films, it is reasonable to note that the surfactant was incorporated into the TiO_2–surfactant films in the bilayer form, consistent with the lamellar silica films reported by Ogawa.[25,26] Moreover, C_nTABr bilayers may not be attached perpendicularly to the titania because the spacing between two TiO_2 sheets is smaller than twice the length of the C_nTABr molecule, as is the case for sodium dodecyl phosphate that has also been used as a surfactant in the TiO_2 mesophase.[17] The absence of diffraction peaks at $2\theta > 10°$ suggests that crystalline phases of the surfactant and TiO_2 are not present in the films, implying the amorphous nature of the wall (TiO_2 layer) in nanostructured TiO_2 films, which is different from nanocrystalline TiO_2 films composed of crystalline TiO_2 nanoparticles.[27,28] Calcining the as-prepared films in air at 200 °C results in a decrease of the intensity of the diffraction peaks until it completely disappears upon calcination above 300 °C. However, no sharp peaks could be detectable in wide angle XRD patterns for the films calcined at 550 °C for 4 h, which seems to contradict the phenomenon whereby the anatase phase should be generated at 450 °C. The absence of diffraction peaks might be a result of small TiO_2 clusters forming rather than crystalline anatase upon calcining the TiO_2–surfactant films above 550 °C.

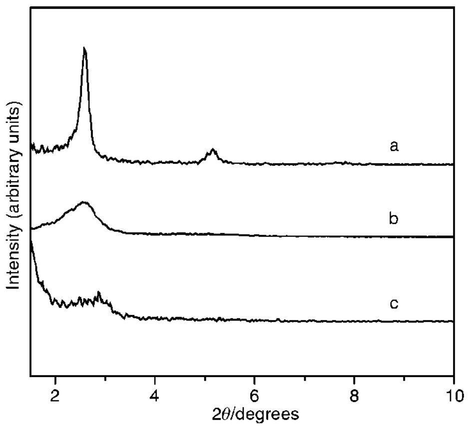

Fig. 1 XRD patterns of films prepared at 50 °C in air: (a) TiO_2–C_{16}TABr, (b) TiO_2–C_{14}TABr and (c) TiO_2–C_{12}TABr.

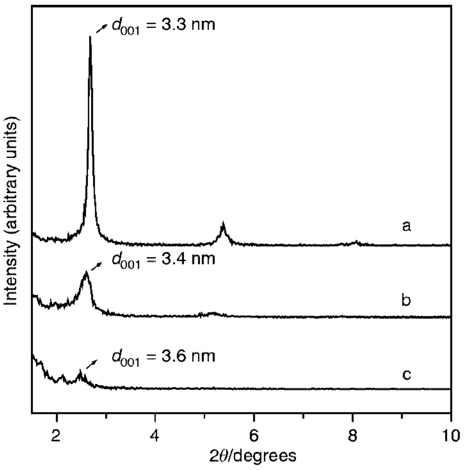

Fig. 2 XRD patterns of TiO_2–C_{16}TABr films crystallized hydrothermally at (a) 100 °C, (b) 140 °C and (c) 180 °C.

The TiO_2–C_{16}TABr films were further crystallized under hydrothermal conditions at 100 °C, 140 °C or 180 °C for 24 h. Intense and sharp diffraction peaks with a d_{001}-spacing of 3.3 nm are shown in Fig. 2a after crystallization at 100 °C, while the diffraction peaks decrease and broaden upon crystallization at 140 °C (Fig. 2b) or 180 °C (Fig. 2c) for 24 h. The increase of the d_{001}-spacing (3.4 nm at 140 °C and 3.6 nm at 180 °C) with the increase of the temperature might result from the incorporation of H_2O or TMAOH from the mother liquor into the TiO_2–surfactant multilayer structure, but it is as yet uncertain.

The growth and structure of the TiO_2–surfactant films were studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). In Fig. 3a, a continuous surface and little surface roughness are characteristic features of the films produced at 50 °C in air, although some cracks could be found which might arise from orientation forces and/or stress in the film. The overlapping part on the surface of the film as shown in Fig. 3a indicates that the film is composed of a

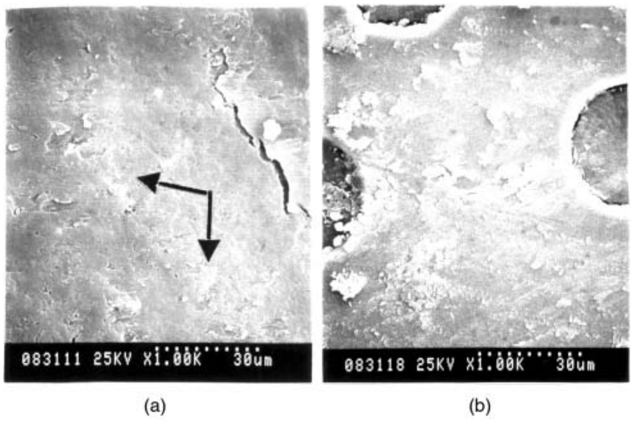

Fig. 3 SEM images of TiO_2–C_{16}TABr films obtained at (a) 50 °C in air and (b) 100 °C under hydrothermal conditions. The arrows in (a) point to the overlapping parts indicating that the growth of the films proceeds through layer-by-layer deposition.

Fig. 4 TEM image of a TiO_2–$C_{16}TABr$ film prepared at 50 °C in air.

layer structure parallel to the surface of the substrate. Moreover, the growth of the films proceeds through layer-by-layer deposition rather than deposition of preformed particles. For the films which were further crystallized hydrothermally at 100 °C for 24 h in precursor solutions, some circular pits can be clearly observed (Fig. 3b) but the origin of this defect is not completely clear. Fig. 4 displays a TEM image of a TiO_2–$C_{16}TABr$ film, in which well-defined parallel lines can be seen, confirming that the film is of lamellar structure,[6–8] consistent with the results of XRD and SEM. The interlamellar distance is found to be about 3.4 nm, in accordance with the *d*-spacing calculated from the first diffraction peak in the XRD pattern. In addition, from the TEM image, it can also be estimated that the thickness of the film is *ca.* 2 μm and the thickness of the titania sheets is *ca.* 0.9 nm, almost the same as that of silicate sheets of lamellar nanocomposites.[25,26] Although broad diffraction peaks were observed in the XRD patterns when $C_{14}TABr$ and $C_{12}TABr$ were employed, parallel lines of lamellar structure were still observed in TEM images. The change of the interlamellar spacing does not lead to any change of the thickness of the TiO_2 layer.

FT-IR spectroscopy was also used to characterize the nanostructured TiO_2–$C_{16}TABr$ films. In Fig. 5, the two sharp bands at 2830–2930 cm^{-1}, due to C–H stretches of the hydrocarbon chain of $C_{16}TABr$, are evidence that $C_{16}TABr$ is incorporated into titanium dioxide films. The presence of Ti–O groups, arising from the –Ti–O–Ti–O polymeric network, is demonstrated by the broader absorbance band between 400 and 800 cm^{-1}, which has been thought to be related to the amorphous nature of this structure.[14,18]

DR UV-vis spectra of nanostructured TiO_2–surfactant films are similar when $C_{16}TABr$, $C_{14}TABr$ and $C_{12}TABr$ are employed. As shown in Fig. 6a, the absorption band between 210 nm and 300 nm, centered at 250 nm, is an indication of the presence of the octahedral titania clusters rather than tetrahedrally isolated titanium sites.[31,32] In comparison with bulk TiO_2 (anatase, 387 nm; rutile, 413 nm),[27,28] the blue shift of the absorption band can be clearly seen, which is also observed in semiconductors as the particle size decreases due to the quantum size effect.[33] In our case, it seems to be reasonable to ascribe the blue shift to quantum size effects of TiO_2 layers with a thickness about 1 nm. However, it should be noted that the interfacial interaction between the titania layers and surfactants, differing from bulk and nanocrystalline TiO_2 films, might play an important role in the blue shift of the absorption band. To investigate the change of UV-vis absorption upon calcining TiO_2–surfactant films, DR UV-vis spectra of TiO_2 films calcined at 200 °C, 300 °C, 400 °C and 550 °C in air were also measured. As shown in Fig. 6(b–e), the absorption band is red shifted with increasing temperature, which might arise from the aggregation and growth of TiO_2 particles in the process of calcination. For the films calcined above 400 °C, three absorption bands at 200–220 nm, 250–317 nm and 320–410 nm, ascribed to different sized TiO_2 particles, are still blue-shifted compared with that of bulk TiO_2 as well as the quantum-sized TiO_2 (370 nm for 2.4 nm anatase;[34] 375.1 nm for 3.8 nm anatase and 398 nm for 5.5 nm rutile[35]), implying that small TiO_2 clusters formed,[31] which is consistent with the XRD results.

The XPS technique was used to determine the surface structure of the TiO_2–surfactant film. As shown in Fig. 7, the bonding energy located at 457.5 eV is related to the $Ti_{2p3/2}$ core electron, which is shifted in comparison with the corresponding value at 459.2 eV for TiO_2 rutile/anatase.[14,18] This result has also been observed in mesoporous titania synthesized by using glycotitanate and octadecylamine by the Ozin[14] and Zaban groups.[18] They attributed the shift to the interaction between titania and the surfactants that has an effect on the microenvironment of titanium.

Fig. 8 gives the room temperature photoluminescence spectra of the mesostructured TiO_2–$C_{16}TABr$, TiO_2–$C_{14}TABr$ and TiO_2–$C_{12}TABr$ films. A broad emission band between 400 and 550 nm, centered at 469 nm, can be observed with an excitation of 300 nm. To the best of our knowledge, it is difficult to observe any photoluminescence phenomenon at

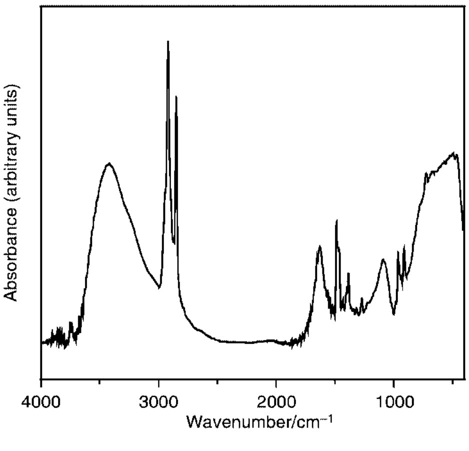

Fig. 5 FT-IR spectrum of a TiO_2–$C_{16}TABr$ film prepared at 50 °C in air.

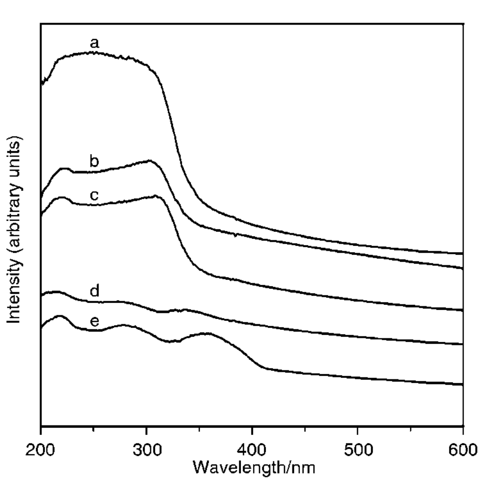

Fig. 6 DR UV-vis spectra of (a) an as-prepared TiO_2–$C_{16}TABr$ film at 50 °C in air, and TiO_2–$C_{16}TABr$ films calcined at (b) 200 °C, (c) 300 °C, (d) 400 °C and (e) 550 °C.

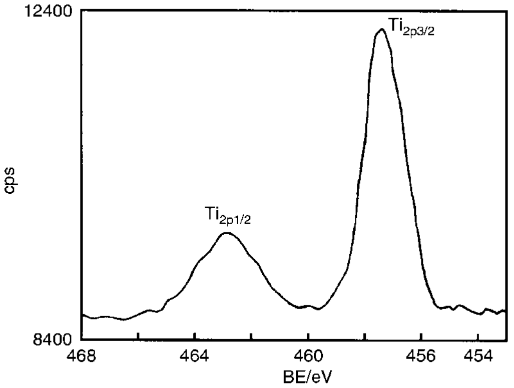

Fig. 7 XPS of a TiO_2–C_{16}TABr film obtained at 50 °C in air.

room temperature for bulk TiO_2, even in the monocrystal state, due to its indirect transition nature.[36,37] By contrast, some nanosized particles have been reported to exhibit room temperature photoluminescence.[36,37] For example, Zou *et al.*[36] reported room temperature photoluminescence of TiO_2 ultrafine particles coated with stearic acid and attributed this phenomenon to the modification of stearic acid on the TiO_2 surface. Despite the dimension difference between the present TiO_2 mesolamellar films and the coated TiO_2 particles reported by Zou *et al.*, the interfacial effect between TiO_2 and the organic surfactant might be similar. Therefore, in conjunction with DR UV-vis spectra and XPS of nanostructured TiO_2–C_nTABr films, it could be inferred that the light emission of TiO_2–surfactant films may be induced by the interface effect between titania and the surfactants, similar to the case reported by Zou.[36]

Conclusion

Mesolamellar TiO_2 films, based on the self-assembly process between inorganic and organic species, have been prepared at 50 °C in air and under hydrothermal conditions. XRD, SEM and TEM results clearly show that the TiO_2–surfactant films display a multilayer structure, in which TiO_2 layers and surfactants are arranged alternately to form a semiconductor–organic superlattice. Unusual room temperature photoluminescence of nanostructured TiO_2–surfactant films might be induced by the interfacial effect between TiO_2 and the surfactant. It can be anticipated that the manipulation of the layer dimensions and compositions of semiconductor oxides of this type would be attractive in the development of nanostructured materials.

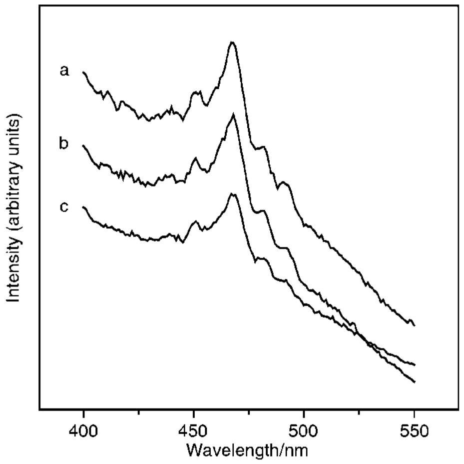

Fig. 8 Photoluminescence spectra of films prepared at 50 °C in air: (a) TiO_2–C_{16}TABr, (b) TiO_2–C_{14}TABr and (c) TiO_2–C_{12}TABr.

Acknowledgements

The authors gratefully acknowledge the financial support of the Ministry of Science and Technology of China through the State Basic Research Project (G200077507) and the National Natural Science Foundation of China (29871012, 29733070).

References

1 G. A. Ozin, *Adv. Mater.*, 1992, **4**, 612.
2 M. Trau, D. A. Saville and I. A. Aksay, *Science*, 1996, **272**, 706.
3 C. R. Marti, *Science*, 1994, **266**, 1961.
4 P. V. Braun, P. Osenar and S. I. Stupp, *Nature*, 1996, **380**, 325.
5 N. Kimizuke and T. Kunitake, *Adv. Mater.*, 1996, **8**, 89.
6 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
7 J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T.-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins and J. L. Schlenker, *J. Am. Chem. Soc.*, 1992, **114**, 10834.
8 Q. S. Huo, D. I. Margolese, U. Clesla, P. Y. Feng, T. E. Gier, P. Sieger, R. Leon, P. M. Petroff, F. Schüth and G. D. Stucky, *Nature*, 1994, **368**, 317.
9 Z. R. Tian, W. Tong, J. Y. Wang, N. G. Duan, V. V. Krishnan and S. L. Suib, *Science*, 1997, **276**, 926.
10 N. Ulagappan and C. N. R. Rao, *Chem. Commun.*, 1996, 1685.
11 D. M. Antonelli and Y. J. Ying, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2014.
12 K. G. Severin, T. M. Abdel-Fattah and T. J. Pinnavaia, *Chem. Commun.*, 1998, 1471.
13 J. Q. Li, L. Delmotte and H. Kessler, *Chem. Commun.*, 1996, 1023.
14 D. Khushalani, G. A. Ozin and A. Kuperman, *J. Mater. Chem.*, 1999, **9**, 1491.
15 D. T. On, *Langmuir*, 1999, **15**, 8561.
16 W. Y. Lin, W. Q. Pang, J. Z. Sun and J. C. Shen, *J. Mater. Chem.*, 1999, **9**, 641.
17 H. Fujii, M. Ohtaki and K. Eguchi, *J. Am. Chem. Soc.*, 1998, **120**, 6832.
18 Y. Q. Wang, S. G. Chen, X. H. Tang, O. Palchik, A. Zaban, Y. Koltypin and A. Gedanken, *J. Mater. Chem.*, 2001, **11**, 521.
19 P. Kluson, D. Kacer, T. Cajthaml and M. Kalaji, *J. Mater. Chem.*, 2001, **11**, 644.
20 D. Papoutsi, P. Lianos, P. Yianoulis and P. Koutsoukos, *Langmuir*, 1994, **10**, 1684.
21 L. Kavan, M. Grätzel, S. E. Gilbert, C. Klemenz and H. J. Scheel, *J. Am. Chem. Soc.*, 1996, **118**, 6716.
22 U. Bach, D. Lupo, P. Comte, J. E. Moser, F. Weissortel, J. Salbeck, H. Spreitzer and M. Grätzel, *Nature*, 1998, **395**, 583.
23 H. Yang, N. Coombs, I. Sokolov and G. A. Ozin, *Nature*, 1996, **381**, 589.
24 Y. Lu, R. Ganguli, C. A. Drewien, M. T. Anderson, G. J. Brinker, W. Gong, Y. Guo, H. Soyez, B. Dunn, M. H. Huang and J. I. Zink, *Nature*, 1997, **389**, 364.
25 M. Ogawa, *J. Am. Chem. Soc.*, 1994, **116**, 7941.
26 M. Ogawa, *Langmuir*, 1995, **11**, 4639.
27 I. Moriguchi, H. Maeda, Y. Teraoka and S. Kagawa, *J. Am. Chem. Soc.*, 1995, **117**, 1139.
28 I. Moriguchi, H. Maeda, Y. Teraoka and S. Kagawa, *Chem. Mater.*, 1997, **9**, 1050.
29 H. Yang, A. Kupermann, N. Coombs, S. Mamiche-Afara and G. A. Ozin, *Nature*, 1996, **379**, 703.
30 M. Froba and M. Tiemann, *Chem. Mater.*, 1998, **10**, 3475.
31 M. E. Raimondi, E. Gianotti, L. Marchese, G. Martra, T. Maschmeyer, J. M. Seddon and S. Coluccia, *J. Phys. Chem.*, 2000, **104**, 7102.
32 A. M. Prakash, H. M. Sung-Suh and L. Kevan, *J. Phys. Chem. B*, 1998, **102**, 857.
33 A. J. Aronson, C. F. Blanford and A. Stein, *Chem. Mater.*, 1997, **9**, 2842.
34 A. Kormann, D. W. Bahnemann and M. R. Hoffmann, *J. Phys. Chem.*, 1988, **92**, 5196.
35 M. Anpo, T. Shima, S. Kodama and Y. Kubokawa, *J. Phys. Chem.*, 1987, **91**, 4305.
36 B. Zou, L. Xiao, T. Li, J. Zhao, Z. Lai and S. Gu, *Appl. Phys. Lett.*, 1991, **59**, 1826.
37 N. Serpone, D. Lawless and R. Khairutdinov, *J. Phys. Chem.*, 1995, **99**, 16646.