



In-situ nitrogen doping and boron modification of nanocrystalline titania powders by chemical vapour synthesis

Imteyaz Ahmad Md.^{1,2}, Subramshu S Bhattacharya^{1*}, Horst Hahn^{2,3}

¹Department of Metallurgical & Materials Engineering, Indian Institute of Technology Madras, Chennai-600036, India

²Joint Research Laboratory Nanomaterials, Technische Universität Darmstadt and Forschungszentrum Karlsruhe, 64287 Darmstadt, Germany

³Institute for Nanotechnology, Forschungszentrum Karlsruhe, Postfach 3640, 76021 Karlsruhe, Germany

Received 12 January 2009; received in revised form 1 May 2009; accepted 16 June 2009

Abstract

During the chemical vapour synthesis (CVS) of nanocrystalline titania doping and/or modification can be directly carried out in-situ by using an additional precursor. In this study, nitrogen doped nanocrystalline titania powders and boron modified nanocrystalline titania powders were synthesised by CVS. The resultant powders were characterised by X-ray diffraction (XRD) and UV-vis spectroscopy. In both cases, a red shift in the band gap of titania was seen. Electron paramagnetic resonance spectroscopy (EPR) showed the presence of nitrogen in the titania lattice. Solid state nuclear magnetic resonance (NMR) spectroscopy showed that boron in titania was present in BO_4 coordination with the oxygen atoms.

Keywords: chemical vapour synthesis, doping, titania

1. Introduction

Nanocrystalline titania is an important oxide ceramic, having potential applications in various fields like catalysis, solar cells, water purification, self cleaning coatings etc., to name a few [1–3]. Titania exists in three crystallographic modifications: rutile, anatase and brookite. Out of the three polymorphs, anatase has the highest functional value, especially for applications in solar cells, catalysis and nonlinear optics. However, as a wide band gap semiconductor (3.2 eV) anatase titania exhibits photoactivity only in the UV light regime. Since, about 45% of the sunlight comprises of visible light, it is of interest to bring down the band gap of anatase to the visible range. To this end, many studies have been dedicated to the doping of titania with metals as well as non-metals. Doping with metals such as Ni, Fe, Cr, Co etc. have the primary drawback of thermal instability and formation of intermediate phases [4]. By far, doping with non-metal N, B, S, C etc. have shown encouraging results [5–9].

During the last decade, various methods were employed to obtain N-modified TiO_2 by calcining tita-

nium hydroxide with aqueous ammonia or with an ammonium salt [10], calcining TiO_2 at 550 to 600°C under an atmosphere of ammonia and argon [11–13], treating TiO_2 nanoparticles with triethylamine at room temperature [14], mechanochemical methods, DC magnetron or radio-frequency sputtering [15,16], ion implantation [17] and by calcining solid mixtures of titania or titanium hydroxide with urea. However, all these methods are either two-step processes or involve complicated and expensive equipment. In all the cases, nitrogen doping resulted in a red shift in the band gap of titania.

Few reports are available in the literature on boron modified titania synthesised through wet chemical routes. There are contrary reports on the effect of boron modification on the band gap. Zhao et al. [8] showed lowering, while Daimei et al. [18] reported an increase in the band gap of titania on boron modification.

In the present study, nitrogen doped nanocrystalline titania and boron modified nanocrystalline titania powders were synthesised in-situ by a chemical vapour synthesis process. The resultant powders were characterised by different techniques and the results presented.

* Corresponding author: tel: ++91 44 22574765
fax: +91 44 22570545, e-mail: ssb@iitm.ac.in

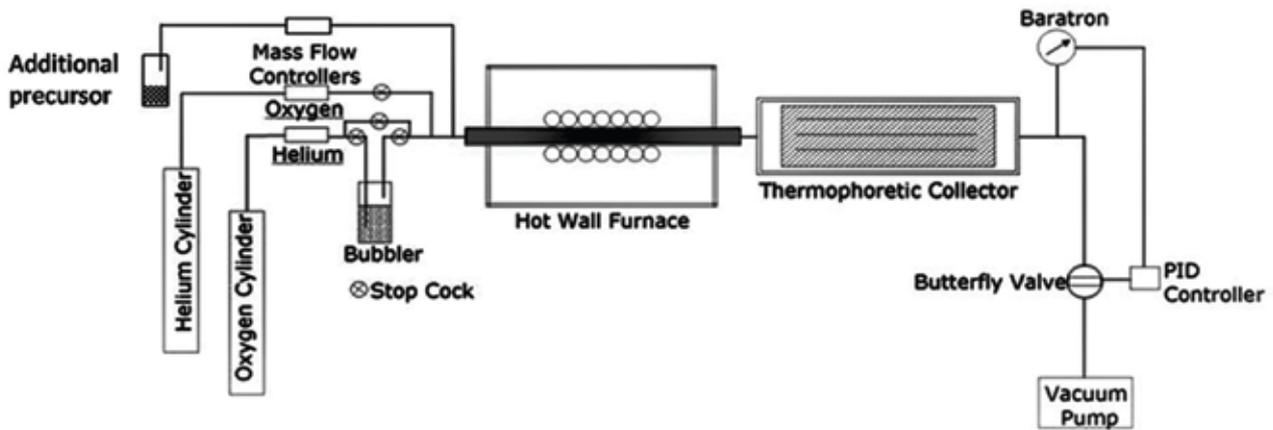


Figure 1. CVS setup for synthesising doped titania

II. Experimental

Chemical vapour synthesis of pure nanocrystalline titania is typically carried out by the high temperature pyrolysis of a metallorganic precursor, titanium tetra iso-propoxide (TTIP) within the well defined reaction zone of a hot wall reactor and the resultant powders are deposited in a thermophoretic collector [19–22]. In-situ preparation of doped/modified nanocrystalline powders by CVS were carried out by using an additional precursor along with TTIP which resulted in doped/modified titania powders (see Fig. 1). NH_4OH was used as the additional precursor for nitrogen doping while triethyl boron was used for boron modification. The temperature of the hotwall was maintained at 800°C with the system pressure at 10 mbar. Helium was used as a carrier gas through a bubbler for the TTIP precursor supply into the furnace. The helium and oxygen flow rates were maintained at 500 sccm and 1000 sccm respectively.

The resultant powders were characterised by X-ray diffraction in a Bruker D8 machine to detect the phases and crystallite size. The UV-vis absorption spectra were recorded in a Cary 5E UV-vis-NIR spectrometer. Nitrogen in the samples was detected using electron paramagnetic resonance spectroscopy (EPR) (Bruker ESP 300E), while boron modified titania was characterised by X-ray photoelectron spectroscopy (XPS) and nuclear magnetic resonance spectroscopy (NMR) using a Bruker Advanced® 400 NMR spectrometer.

III. Results and discussion

Fig. 2 depicts the XRD patterns of nitrogen doped and boron modified titania. No intermediate phases could be observed in XRD and the major phase in both the cases was anatase. However, about 16% by weight of rutile, as estimated from XRD [22,23], was observed in case of nitrogen doped titania.

Nitrogen was detected by EPR spectra measured at X-band frequency of 9.5 GHz at room temperature

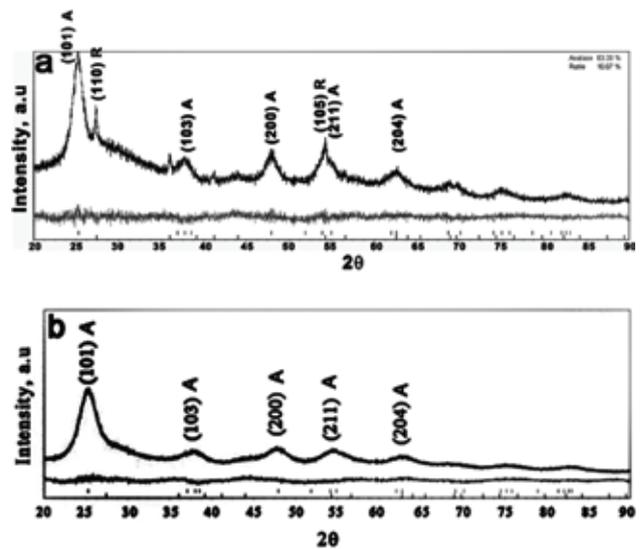


Figure 2. XRD pattern of the as-synthesised (a) nitrogen doped and (b) boron modified nanocrystalline titania powders

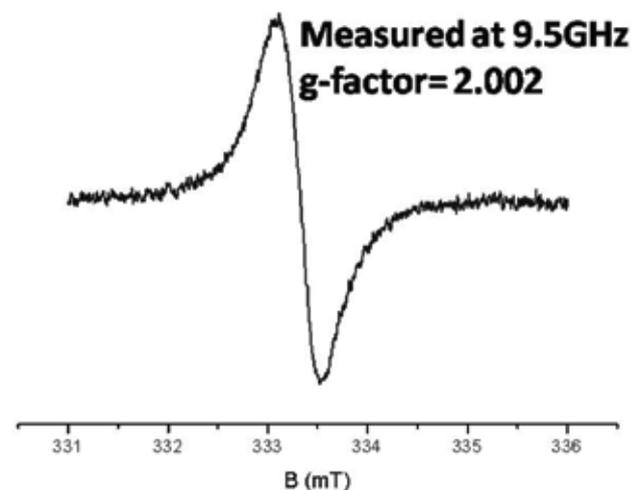


Figure 3. EPR spectrum of nitrogen doped titania

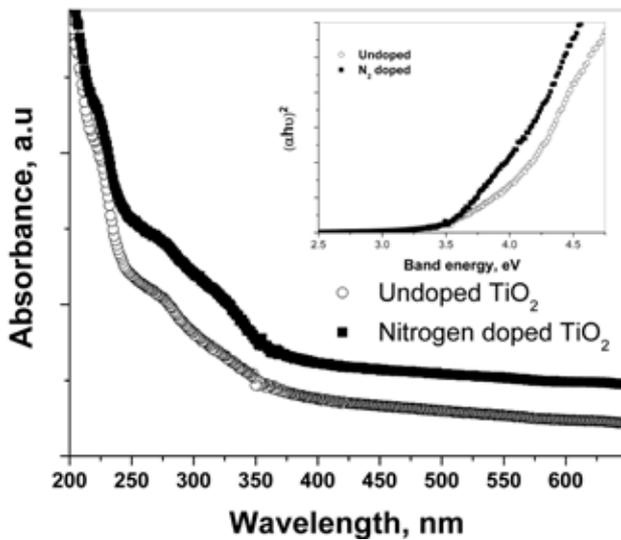


Figure 4. UV-vis spectra of undoped and nitrogen doped titania

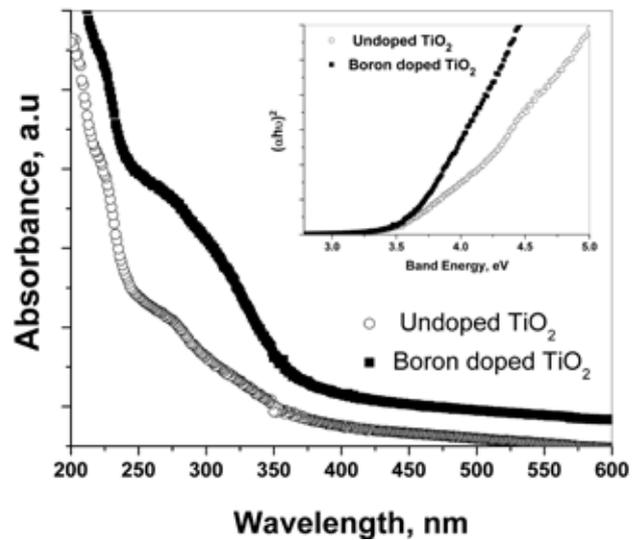


Figure 7. UV-vis spectra of unmodified and boron modified titania

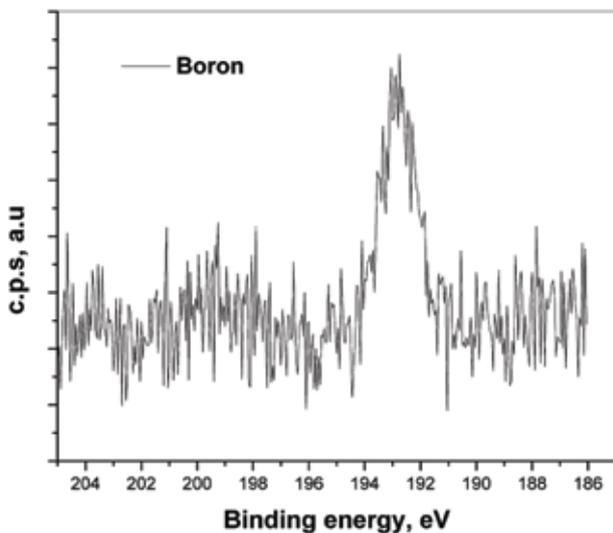


Figure 5. XPS of boron in the boron modified titania powders

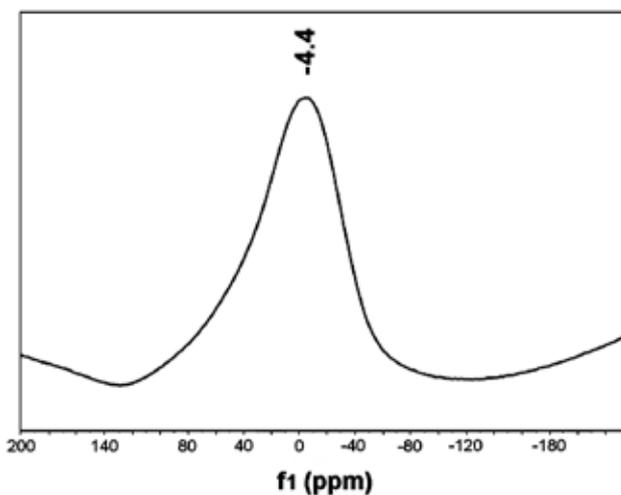


Figure 6. ¹¹B-NMR-MAS spectrum of boron modified titania

(Fig. 3). The estimated *g*-factor was about 2.002, which indicated the presence of a lone electron spin suggesting the presence of nitrogen in the crystal structure of titania [24]. The UV-vis spectra showed greater absorption in the visible range in case of the nitrogen doped sample, as can be seen from Fig. 4. The inset in Fig. 4 gives the variation of $(\alpha \cdot h \cdot \nu)^2$ with the band energy, where α is the absorbance, h the Planck's constant and ν the frequency. The shift in the direct band gap was estimated from these plots and a red shift in the band gap was observed which was in agreement with the earlier reports on nitrogen doping [11–13].

Fig. 5 depicts the X-ray photoelectron spectrum for boron taken from the boron modified nanocrystalline titania powders. B1s emission was observed at a binding energy of 192.6 eV. The signal to noise ratio of boron peak was low due the fact that the boron atom has a lower photo electron emission cross section when compared to the relatively heavier Ti atoms. It has been reported earlier [18,25] that boron in titania assumes a chemical environment very similar to that of boron in boron oxide because of which it becomes difficult to make any unequivocal attribution regarding the presence of boron in titania from XPS results. The ¹¹B-MAS-NMR spectra is depicted in Fig. 6. It has been shown earlier that boron could be present in either BO₃ or BO₄ coordination [26–28]. Presence of 4 oxygen atoms in coordination with boron causes higher deshielding and a lower quadrupole interaction resulting in a relatively symmetrical peak at a lower chemical shift in NMR [29]. Therefore, the chemical shift of -4.4 ppm observed here was attributed to the presence of boron in the form of BO₄ structural units as reported by Dong et al. [30] for sodium borophosphate glasses. The UV-vis spectra for boron modified titania is depicted in Fig. 7. Evidently, a red shift can be observed in the direct band gap of boron modified titania when compared to the unmodified

tania and is confirmed from the $(\alpha \cdot h\nu)^2$ vs energy (eV) plot shown as inset in Fig. 7. This result is in accordance with the earlier report of Zhao et al. [8].

VI. Conclusions

Nitrogen doped nanocrystalline titania and boron modified nanocrystalline titania powders were synthesised by a one step method using chemical vapour synthesis (CVS). Nitrogen doping lowered the band gap of titania. Boron modification of titania also resulted in a red shift in the band gap. NMR spectra showed that boron in the titania structure was present in BO_4 coordination.

Acknowledgments Imteyaz Ahmad Md. would like to thank DAAD, Bonn, Germany for providing financial support to work at Materialwissenschaft, Technische Universität, Darmstadt, Germany for six months. S.S. Bhattacharya would like to thank the Alexander von Humboldt Foundation, Bonn, Germany for providing financial support for a month stay at Materialwissenschaft, Technische Universität, Darmstadt, Germany.

References

1. P.V. Kamat, N.M. Dimitrijevic, "Colloidal semiconductors as photocatalysts for solar energy conversion", *Sol. Energy*, **44** [2] (1990) 83–98.
2. S.A. Larson, J.L. Falconer, "Characterization of TiO_2 photocatalysts used in trichloroethene oxidation", *Appl. Catal. B*, **4** [4] (1994) 325–342.
3. T. Ohno, K. Sarukawa, M. Matsumura, "Crystal faces of rutile and anatase TiO_2 particles and their roles in photocatalytic reactions", *New J. Chem.*, **26** (2002) 1167–1170.
4. A.D. Paola, G. Marc, L. Palmisano, M. Schiavello, K. Uosaki, S. Ikeda, B. Ohtani, "Preparation of polycrystalline TiO_2 photocatalysts impregnated with various transition metal ions: Characterization and photocatalytic activity for the degradation of 4-nitrophenol", *J. Phys. Chem. B*, **106** (2002) 637–645.
5. R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, "Visible-light photocatalysis in nitrogen doped titanium oxides", *Science*, **293** [5528] (2001) 269–271.
6. E. Broborini, A.M. Conti, I. Kholmanov, P. Piseri, A. Podesta, P. Milani, C. Cepek, O. Sakho, R. Macovez, M. Sancrotti, "Nanostructured TiO_2 films with 2 eV optical gaps", *Adv. Mater.*, **17** (2005) 1842–1846.
7. T. Umebayashi, T. Yamaki, H. Itoh, K. Asai, "Band gap narrowing of titanium dioxide by sulfur doping", *Appl. Phys. Lett.*, **81** (2002) 454–456.
8. Z. Wei, W. Ma, C. Chen, J. Zhao, Z. Shuai, "Efficient degradation of toxic pollutants with $\text{Ni}_2\text{O}_3/\text{TiO}_{2-x}\text{B}_x$ under visible irradiation", *J. Am. Chem. Soc.*, **126** (2004) 4782–4783.
9. J.C. Yu, J. Yu, W. Ho, Z. Jiang, L. Zhang, "Effects of F-doping on the photocatalytic activity and microstructures of nanocrystalline TiO_2 powders", *Chem. Mater.*, **14** (2002) 3808–3816.
10. E.A. Reyes-Garcia, Y. Sun, K. Reyes-Gil, D. Raftery, " ^{15}N solid state NMR and EPR characterization of N-doped TiO_2 photocatalysts", *J. Phys. Chem. C*, **111** (2007) 2738–2748.
11. J. Zhang, Y. Wang, Z. Jin, Z. Wu, Z. Zhang, "Visible-light photocatalytic behaviour of two different N-doped TiO_2 ", *Appl. Surf. Sci.*, **254** (2008) 4462–4466.
12. Y. Wang, C. Feng, Z. Jin, J. Zhang, J. Yang, S. Zhang, "A novel N-doped TiO_2 with high visible light photocatalytic activity", *J. Mol. Catal. A: Chem.*, **260** (2006) 1–3.
13. H. Irie, Y. Watanabe, K. Hashimoto, "Nitrogen-concentration dependence on photocatalytic activity of $\text{TiO}_{2-x}\text{N}_x$ powders", *J. Phys. Chem. B*, **107** [23] (2003) 5483–5486.
14. Y. Cong, J. Zhang, F. Chen, M. Anpo, "Synthesis and characterization of nitrogen-doped TiO_2 nanophotocatalyst with high visible light activity", *J. Phys. Chem. C*, **111** (2007) 6976–6982.
15. Y. Nakano, T. Morikawa, T. Ohwaki, Y. Taga, "Origin of visible-light sensitivity in N-doped TiO_2 films", *Chem. Phys.*, **339** (2007) 20–26.
16. K. Prabakara, T. Takahashia, T. Nezukaa, K. Takahashia, T. Nakashimab, Y. Kubotac, A. Fujishima, "Visible light-active nitrogen-doped TiO_2 thin films prepared by DC magnetron sputtering used as a photocatalyst", *Renew. Energy*, **33** (2008) 277–281.
17. H. Shen, L. Mi, P. Xu, W. Shen, P.-N. Wang, "Visible-light photocatalysis of nitrogen-doped TiO_2 nanoparticulate films prepared by low-energy ion implantation", *Appl. Surf. Sci.*, **253** (2007) 7024–7028.
18. D. Chen, D. Yang, Q. Wang, Z. Jiang, "Effects of boron doping on photocatalytic activity and micro structure of titanium dioxide nanoparticles", *Ind. Eng. Chem. Res.*, **45** (2006) 4110–4116.
19. K.K. Akurati, S.S. Bhattacharya, M. Winterer, H. Hahn, "Synthesis, characterization and sintering of nanocrystalline titania powders produced by chemical vapour synthesis", *J. Phys. D: Appl. Phys.*, **39** (2006) 2248–2254.
20. S. Klein, M. Winterer, H. Hahn, "Reduced-pressure chemical vapour synthesis of nanocrystalline silicon carbide powders", *Chem. Vapor Depos.*, **4** (1998) 143–149.
21. M. Winterer, *Nanocrystalline ceramics: Synthesis and structure*, Springer, 2002.
22. I. Ahmad Md., S.S. Bhattacharya, "Effect of process parameters on the chemical vapour synthesis of nanocrystalline titania", *J. Phys. D: Appl. Phys.*, **41** (2008) 155313–155320.
23. A. Kobata, K. Kusakabe, S. Morooka, "Growth and transformation of TiO_2 crystallites in aerosol reactor", *AIChE J.*, **37** (1991) 357–359.
24. S. Livraghi, M.C. Paganini, E. Giamello, A. Selloni, C. D. Valentin, G. Pacchioni, "Origin of photoactivity of nitrogen-doped titanium dioxide under visible light", *J. Am. Chem. Soc.*, **128** [49] (2006) 15666–15671.

25. V. Gombac, L.D. Rogatis, A. Gasparotto, G. Vicario, T. Montini, G.B.D. Barreca, P. Fornasiero, E. Tonello, M. Graziani, “TiO₂ nanopowders doped with boron and nitrogen for photocatalytic applications”, *Chem. Phys.*, **339** (2007) 111–123.
26. A. Delmastro, G. Gozzelino, D. Mazza, M. Vallino, G. Busca, V. Lorenzelli, “Characterization of microporous amorphous alumina-boria”, *J. Chem. Soc., Faraday Trans.*, **88** (1992) 2065–2070.
27. B.-Q. Xu, S.-B. Cheng, S. Jiang, Q.-M. Zhu, “Gas phase beckmann rearrangement of cyclohexanone oxime over zirconia-supported boria catalyst”, *Appl. Catal., A*, **188** (1999) 361–368.
28. H. Geng, S. Yin, X. Yang, Z. Shuai, B. Liu, “Geometric and electronic structure of the boron doped photocatalyst TiO₂”, *J. Phys.: Condens. Matter*, **18** (2006) 87–96.
29. W. Kemp, *Organic Spectroscopy*, Macmillan, 1991.
30. D. Qiu, P. Guerry, I. Ahmed, D.M. Pickup, D. Carta, J.C. Knowles, M.E. Smith, R.J. Newport, “A high-energy X-ray diffraction, ³¹P and ¹¹B solid-state NMR study of the structure of aged sodium borophosphate glasses”, *Mater. Chem. Phys.*, **111** [2-3] (2008) 455–462.