Bull. Mater. Sci., Vol. 31, No. 5, October 2008, pp. 741–745. © Indian Academy of Sciences.

Characterization and photocatalytic activity of boron-doped TiO_2 thin films prepared by liquid phase deposition technique

NOOR SHAHINA BEGUM*, H M FARVEEZ AHMED and O M HUSSAIN†

Department of Studies in Chemistry, Central College Campus, Bangalore University, Bangalore 560 001, India
†Department of Physics, Sri Venkateswara University, Tirupati 517 502, India

MS received 28 December 2007; revised 16 March 2008

Abstract. **Boron doped TiO_2 thin films have been successfully deposited on glass substrate and silicon wafer at 30°C from an aqueous solution of ammonium hexa-fluoro titanate and boron trifluoride by liquid phase deposition technique. The boric acid was used as an F^- scavenger. The resultant films were characterized by XRD, EDAX, UV and microstructures by SEM. The result shows the deposited film to be amorphous which becomes crystalline between 400 and 500°C. The EDAX and XRD data confirm the existence of boron atom in TiO_2 matrix and a small peak corresponding to rutile phase was also found. Boron doped TiO_2 thin films can be used as photocatalyst for the photodegradation of chlorobenzene which is a great environmental hazard. It was found that chlorobenzene undergoes degradation efficiently in presence of boron doped TiO_2 thin films by exposing its aqueous solution to visible light. The photocatalytic activity increases with increase in the concentration of boron.**

Keywords. **B-TiO_2 thin film; LPD technique; photodegradation.**

1. Introduction

Since TiO_2 was found to be a well known photocatalyst, intense research was concentrated on anatase TiO_2 photocatalysis. However, this material is only active upon UV excitation because of its large energy bandgap of 3·2 eV. Recently, many researchers' work on the doping of TiO_2 with non-metal atoms has received a lot of attention (Asahi *et al* 2001; Khan *et al* 2002; Burda *et al* 2003; Irie *et al* 2003a, b; Lindgren *et al* 2003; Sakthival and Kisch 2003a, b; Umebayashi *et al* 2003; Gole *et al* 2004; Noor Shahina Begum and Farveez Ahmed 2008).

For example, Asahi *et al* (2001) and Khan *et al* (2002) reported that doping TiO_2 with nitrogen or carbon can lower its bandgap and shift its optical response to the visible region. Zhao *et al* (2004) observed remarkable improvement in the rate of degradation by doping TiO_2 with metal and non-metal atoms.

Here we report the photocatalytical activity of B-doped TiO_2 thin films grown by a simple technique known as liquid phase deposition (LPD). The LPD method is a unique soft solution process, and is performed by very simple procedures. In this method, metal oxide or hydroxide thin films are formed on the substrate through the ligand-exchange (hydrolysis) equilibrium reaction of metal-fluoro complex species. Addition of boric acid or aluminium metal acts as a free F^- scavenger and shifts the equilibrium to one side (Nagayama *et al* 1988; Richardson and Rubin 2000; Deki *et al* 2001; Noor Shahina Begum and Farveez Ahmed 2008).

Our findings suggest that incorporation of B into TiO_2 can extend the spectral response to the visible region and that the photocatalytic activity is greatly enhanced.

2. Experimental

2.1 *Preparation of boron doped TiO_2 thin films*

Ammonium hexa-flurotitanate and boric acid were dissolved in distilled water so that the concentration of Ti ion was about 0·15 mol/dm^3 and boric acid concentration, about 0·05 mol/dm^3. A boron trifluoride solution was mixed with the above precursor in different proportions (TiO_2-X, X = 1, 2 and 3% of B). The substrates [glass and Si wafer (111)] were degreased and washed ultrasonically and subsequently kept immersed vertically in treatment solution at 30°C for 40 h. After 40 h, the substrate was taken out, washed and dried at lab temperature. Calcination of the films was also carried out at various temperatures.

2.2 *Photocatalytic degradation*

B-doped TiO_2 thin film was settled in a solution of chlorobenzene of concentration, 10 ppm. The solution

*Author for correspondence (noorsb@rediffmail.com)

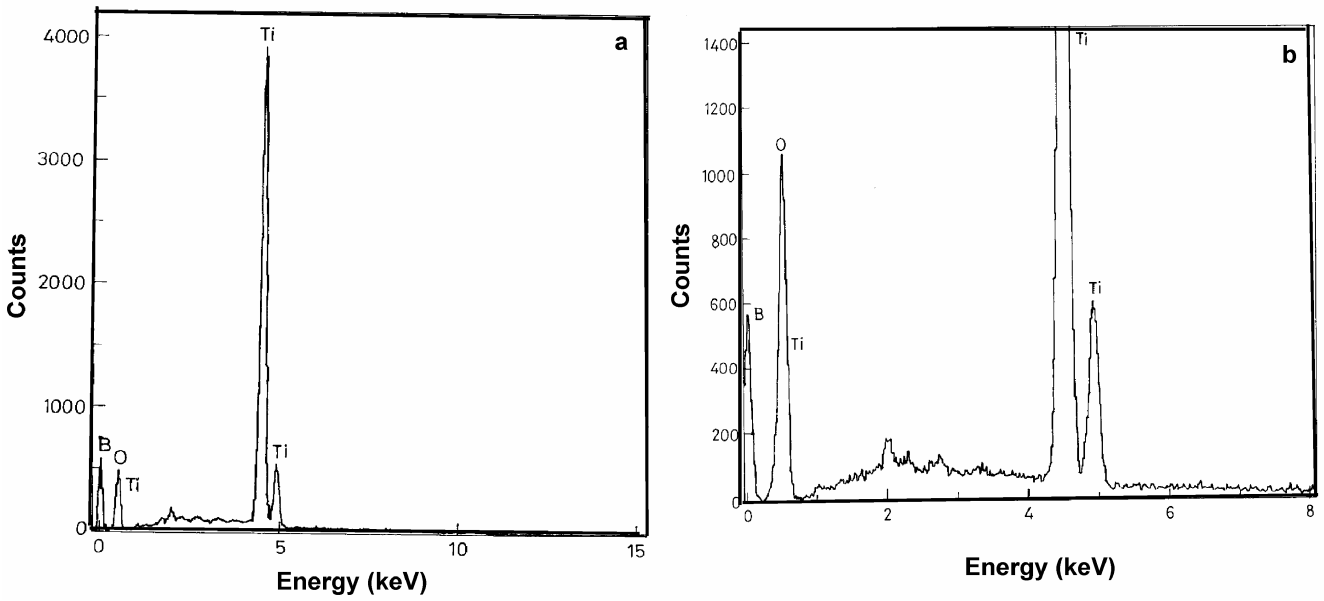

Figure 1. EDAX spectra of TiO_2 thin film doped with **a**. 2% B, grown on glass substrate and annealed at 500°C and **b**. 3% B, grown on glass substrate annealed at 500°C.

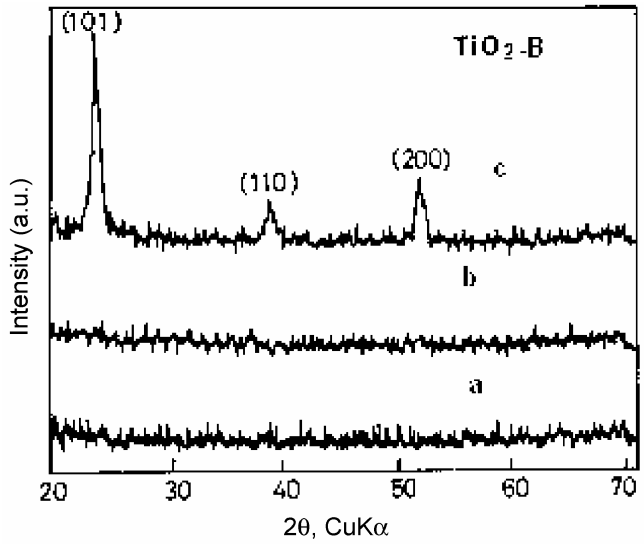

Figure 2. XRD pattern of B-doped TiO_2 thin films annealed at different temperatures: (a) as-deposited film, and films annealed at (b) 200 and (c) 500°C.

was exposed to sunlight at different irradiation times. The solution was bubbled frequently with air during irradiation. The concentration of chlorobenzene was determined with a UV-visible spectrophotometer by measuring the absorbance between 300 and 1200 nm.

3. Characterization of deposited films

X-ray diffraction spectra were obtained from an X-ray diffractometer (type PW 3710 based tube anode: CuKα_1: 1·54056 and Kα_2: 1·54439). Optical properties were studied by using UV-vis-NIR, scanning spectrophotometer (type, Shimadzu-2003, Japan) in the wavelength range 300–1400 nm. The structural properties and elemental analysis of coating were studied using scanning electron microscope and EDAX (type: Leica Cambridge Ltd./Leica S440i for SEM and Oxford link software for EDAX).

4. Results and discussion

4.1 *EDAX analysis*

The elemental analysis of boron doped TiO_2 thin film was analyzed by taking EDAX. Figures 1a and b show the EDAX spectra of experimental films calcined at 500°C with 2% and 3% boron dopants, respectively. The elementary analysis reveals the peaks for Ti, O and B but boron concentration was found to be very less.

4.2 *Structure and surface morphology*

Figure 2 shows XRD pattern of B-doped TiO_2 thin films annealed at different temperatures. The as deposited film and the film annealed at 200°C are amorphous in nature (curves a and b). Crystallinity begins only after 200°C (curve c). X-ray diffraction analysis also reveals that a structure composed only of anatase phase formed after calcinations at 500°C and that there was no observable structural difference between pure TiO_2 thin films and boron-doped TiO_2.

X-ray data reveals that there is slight change in lattice parameter of B-doped TiO_2 thin films (TiO_2-X, X = 3%B)

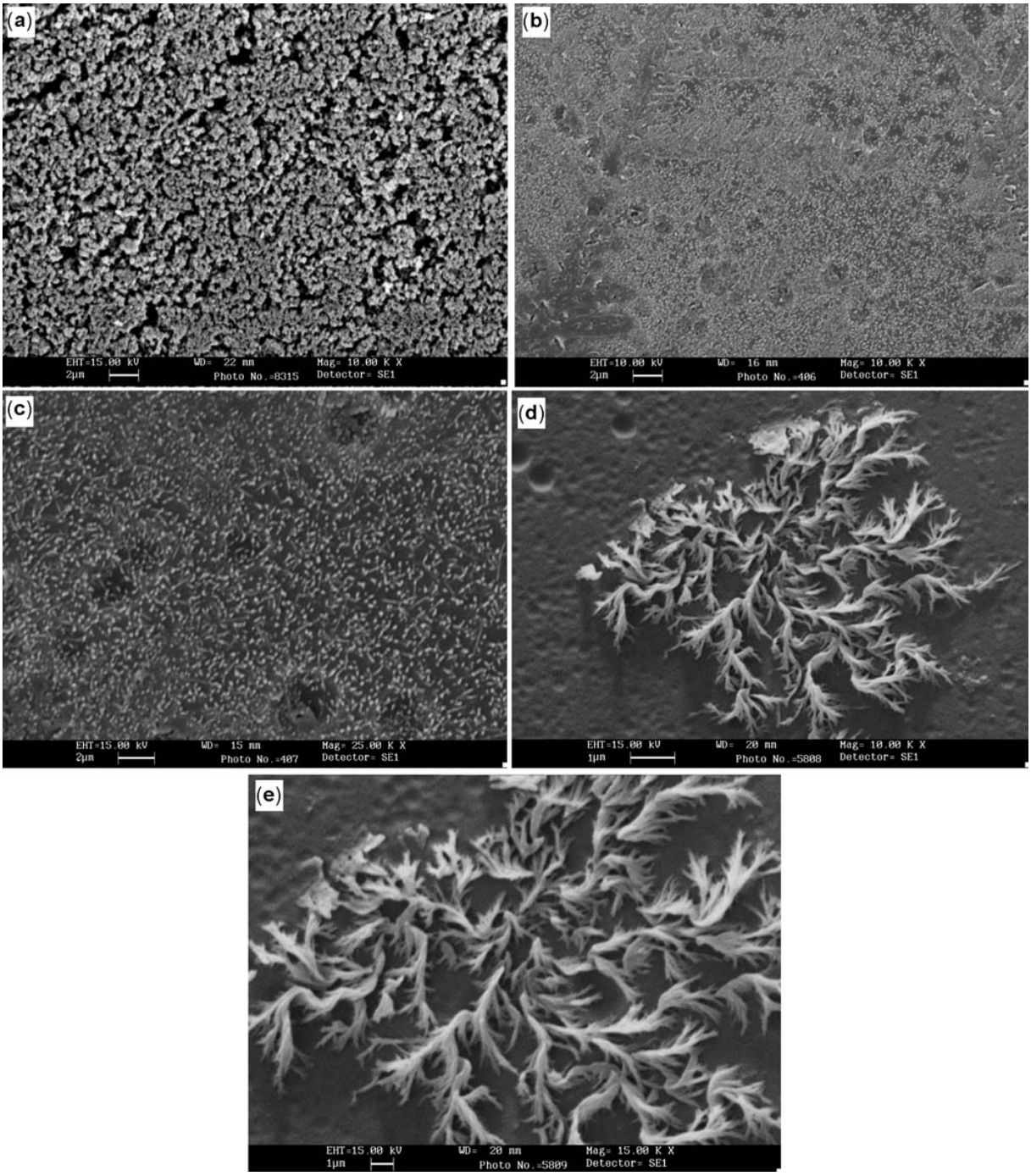

Figure 3. Scanning electron micrographs of (**a**) as deposited TiO_2 thin film doped with 3% B, grown on glass substrate showing amorphous background, (**b**) B-doped TiO_2 thin films (3% B), grown on glass substrate and annealed at 400°C showing the segregation of B atoms, (**c**) B-doped TiO_2 thin films (3% B), grown on glass substrate and annealed at 500°C showing the segregation of B atoms, (**d**) B-doped TiO_2 thin films (2% B), grown on Si wafer and annealed at 600°C showing the B atoms segregated like roots and (**e**) B-doped TiO_2 thin films (3% B), grown on Si wafer and annealed at 600°C showing the B atom segregated like roots.

at *c*-axis when compared to pure TiO_2, this confirms the existence of B atoms in TiO_2 thin films (9·5958) for pure TiO_2 and (9·6263) for B-doped TiO_2 (Zhao *et al* 2004; Chen *et al* 2006). However, a small peak (figure 2) corresponding to rutile phase was observed with the orientation [200].

Surface morphology of B-doped TiO_2 thin films was studied by using Leica S440i scanning electron microscope with Oxford link software used to evaluate surface topology of experimental films.

Figures 3(a)–(d) show scanning electron micrographs of 3% B-doped TiO_2 thin films grown on glass substrate and

annealed at different temperatures. The as deposited film is homogeneous with the amorphous background (figure 3(a)). The films annealed at 400°C and 500°C show the compact structure with the segregation of B atoms (figures 3(b)–(c)) and the average grain size of about 50 nm. However, B-doped TiO_2 thin films grown on Si wafer and annealed at 600°C show roots like morphology (figures 3(d) and (e)). These structures show the B on Si wafer to be segregated and not uniformly distributed.

4.3 *Optical property*

Figure 4 shows the UV-vis transmittance spectra of bare TiO_2 (curve a) and B-doped TiO_2 thin film samples (curve b), grown on glass substrate and annealed at 500°C. It was observed that the optical absorption edge of B-doped TiO_2 thin films (3% B) is significantly shifted towards visible region when compared to undoped TiO_2. The energy bandgap calculation of pure and doped TiO_2 shows remarkable changes in the bandgap. The graph of $(\alpha h\nu)^{1/2} \times h\nu$ shows bandgap energies of pure TiO_2, 3·2 eV and B-doped TiO_2, 2·95 eV (figure 5). From this observation, it is clear that the photocatalysis is possible under visible light. However, no significant differences were found in UV-vis transmittance spectra of 2% B-doped TiO_2 thin films when compared to bare TiO_2 thin films.

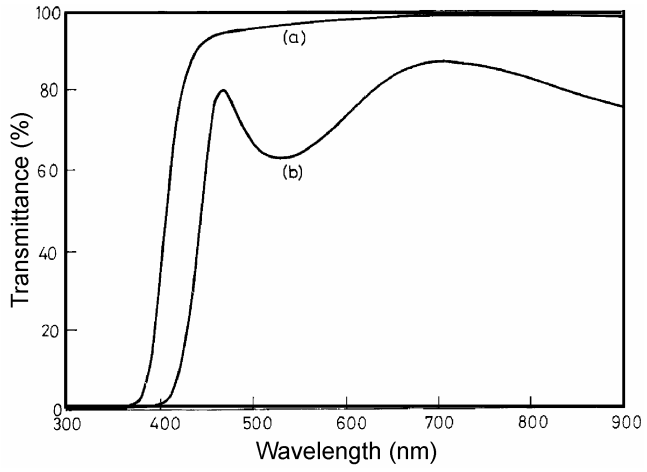

Figure 4. UV-vis transmittance spectra of (a) bare TiO_2 and (b) 3% B-doped TiO_2 thin films, grown on glass substrate and annealed at 500°C.

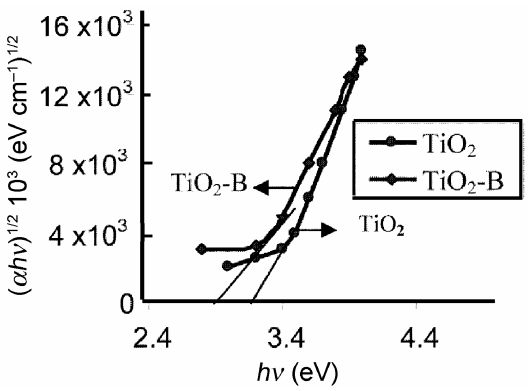

Figure 5. Bandgap energy of pure TiO_2 and B-doped TiO_2 thin films grown on glass substrate and annealed at 500°C.

4.4 *Photodegradation studies*

Photocatalytic activity of bare TiO_2 and B-doped TiO_2 films, grown on glass substrate and annealed at 500°C, were studied by taking chlorobenzene (Hussain 1991; Hoffmann *et al* 1995; Cheng *et al* 2004) which is environmentally hazardous. Figure 6 shows that B-doped TiO_2 exhibits much greater activity than pure TiO_2 thin films in the visible region. From the graph it can be concluded that the TiO_2 thin film with 3% boron dopant exhibits photocatalytic activity much efficiently when compared to 2% B-doped TiO_2 and bare TiO_2 thin films, respectively.

The mechanism of photocatalytic activity of B-TiO_2 was suggested by Grey *et al* (1996) that boron incorporation to TiO_2 leads to the partial reduction of Ti^{4+} to Ti^{3+}, which could improve the photocatalytic activity of TiO_2. Since Ti^{3+} sites could act as the photogenerated electron traps and thus facilitate the charge separation. This increases the stability of electron–hole pair and minimizes the recombination phenomena. In addition to that doping of B remarkably decreases the bandgap. It is also believed that segregation of boron in TiO_2 thin films may partially increase the surface area and hence photocatalytic activity is enhanced.

5. Conclusions

Boron-doped TiO_2 thin films have been prepared by a simple novel technique known as liquid phase deposition

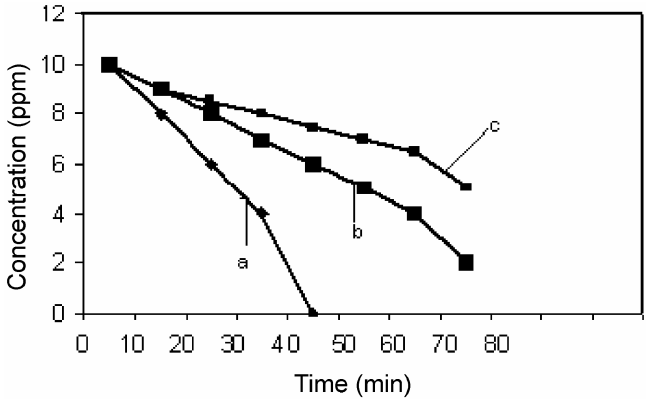

Figure 6. Photodegradation of chlorobenzene by bare TiO_2 and B-doped TiO_2 thin films, grown on glass substrate and annealed at 500°C. a. 3% B-doped TiO_2 thin film, b. 2% B-TiO_2 thin film and c. bare TiO_2 thin film.

technique. The prepared films were homogeneous and well adhered to the substrate and showed amorphous background. At higher temperature the films turn into crystalline form. The SEM images show the distribution of B atoms in the TiO_2 matrix. The root like morphology was observed for the films grown on silicon wafer. EDAX and XRD data confirm the existence of B in TiO_2 thin films. A small peak corresponding to rutile phase with the orientation [200] was observed. The photodegradation studies reveal that TiO_2 doped with 3% B degraded the chlorobenzene effectively when compared to 2% B-doped TiO_2 and bare TiO_2 thin films under visible light irradiation.

Acknowledgements

The authors are grateful to Dr K R Gunasekar, Indian Institute of Science, Bangalore and Mr D Basavaraj and Mr Kalyan Raj, BMS College of Engineering, Bangalore, for providing technical support.

References

Asahi R, Morikawa T, Ohwaki T, Aoki K and Taga Y 2001 *Science* **293** 269

Burda C, Lou Y, Chen X, Samia A C S, Stout J and Gole J L 2003 *Nano Lett.* **3** 1049

Chen Daimai, Wang Dong Yang and Jiang Zhongyi 2006 *Ind. Eng. Chem.* **45** 4110

Cheng Jen-hao 2003 *A study on photocatalytic oxidation of aqueous chlorobenzene solution by nanostructured film of TiO_2*, Master Thesis, National Sun Yat-Sen University, Taiwan

Deki S, Henin Yu Yu Ko, Fujita T, Akamatsu K, Mizuhata X and Kajinami A 2001 *Eur. Phys. J.D* **16** 325

Gole J L, Stout J D, Burda C, Lou Y and Chen X 2004 *J. Phys. Chem.* **B108** 1230

Grey I E, Li C and Macrae C 1996 *J. Solid State Chem.* **127** 240

Hoffmann M R, Martin S T, Choi W and Bahnemann D W 1995 *Chem. Rev.* **95** 69

Hussain Al-Ekabi 1991 *Proc. of workshop on 'Potential applications of concentrated solar energy'*, USA, p. 28

Irie H, Washizuka S, Yoshino N and Hashimoto K 2003a *Chem. Commun.* **11** 1298

Irie H, Watanabe Y and Hashimoto K 2003b *J. Phys. Chem.* **B107** 5483

Khan S U M, Al-Shahry M and Ingler W B Jr 2002 *Science* **297** 2243

Lindgren T, Mwabora J M, Avendano E, Jonsson J, Hoel A, Granqvist C and Lindquist S 2003 *J. Phys. Chem.* **B107** 5709

Nagayama H, Honda H and Kawahara H 1988 *J. Electrochem. Soc.* **135** 2013

Noor Shahina Begum and Farveez Ahmed H M 2008 *Bull. Mater. Sci.* **31** 43

Richardson T J and Rubin M D 2000 *4th Int. mtg. on electrochromism*, *Uppsala, Sweden*

Sakthivel S and Kisch H 2003a *Angew. Chem., Int. Ed.* **42** 4908

Sakthivel S and Kisch H 2003b *Chem. Phys. Chem.* **4** 487

Umebayashi T, Yamaki T, Tanaka S and Asai K 2003 *Chem. Lett.* **32** 330

Zhao Wei, Ma Wanhong, Chen Chuncheng, Zhao Jincai and Shuai Zhigang 2004 *J. Am. Chem. Soc.* **126** 4782