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Development of supported boron-doping TiO_2 catalysts by chemical vapor deposition*

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Abstract: In this study, supported nonmetal (boron) doping TiO_2 coating photocatalysts were prepared by chemical vapor deposition (CVD) to enhance the activity under visible light irradiation and avoid the recovering of TiO_2. Boron atoms were successfully doped into the lattice of TiO_2 through CVD, as evidenced from XPS analysis. B-doped TiO_2 coating catalysts showed drastic and strong absorption in the visible light range with a red shift in the band gap transition. This novel B-TiO_2 coating photocatalyst showed higher photocatalytic activity in methyl orange degradation under visible light irradiation than that of the pure TiO_2 photocatalyst.

Key words: Chemical vapor deposition (CVD), TiO_2, Boron, Visible light, Photocatalysis
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INTRODUCTION

TiO_2 is a promising photocatalyst due to its low cost, outstanding stability, and highly efficient oxidative power. However, the wide use of TiO_2 in photocatalysis is limited by its wide band gap (3.2 eV for anatase), which facilitates response to UV light. Recently, nonmetal-doping of TiO_2, especially N-doping, through heat treatment ammonia (Vitiello *et al*., 2006) or by implantation (Ghicov *et al*., 2006) was found to be efficient to excite the photocatalytic activity under visible light due to band gap narrowing or the creation of surface oxygen vacancies. However, ammonia gas is hazardous, and ion implantation process tends to cause a disintegration of the morphological integrity, whereas anatase TiO_2 is amorphized. This amorphization leads to a certain decrease of photoresponse in the UV range. This detrimental effect needs twice thermal treatment to recover the anatase state of TiO_2 (Ghicov *et al*., 2006). Therefore, exploring a simple, safe and efficient approach to carry out nonmetal-doping of TiO_2 to improve its photocatalytic activity under visible light is needed. Recently, boron-doping has attracted attention in electrochemical and functional materials application studies because it is prompting the creation of electronic level acceptor. Some studies on boron-doping of TiO_2 were reported regarding its photocatalytic application (Moon *et al*., 2000), especially the visible-light-activated photocatalytic activity (Zhao *et al*., 2004). Actually, boron atoms can substitute oxygen atoms in the TiO_2 lattice and the p orbital of B is mixed with O 2p orbitals, which causes the band gap narrowing and, as a result, shifts the optical response to the visible range. Therefore, it is also a promising path towards photocatalysis under visible light.

Another obstacle preventing TiO_2 photocatalysis from industrial application is that separation of the insoluble catalyst from the suspensions is difficult. Moreover, the suspended particles tend to aggregate, especially at high concentrations. Therefore, great efforts have been made to prepare supported TiO_2 catalyst to improve the photocatalyst recovery and to get a high catalytic performance (Peill and Hoffmann,

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1996; Ding *et al.*, 2000).

In this study, the supported boron doping TiO_2 coating photocatalyst was prepared in one step by chemical vapor deposition (CVD). As we know, CVD is an industrial process applicable to large area deposition, and high quality TiO_2 films can be easily anchored on various substrates even bearing the complicated shapes. Activated carbon fiber (ACF), a widely used absorbent in wastewater treatment, was selected to be the photocatalyst support. The advantages expected from this work are: (1) Steps in traditional methods for supported catalysts preparation, such as saturation, aging, drying and reduction, can be eliminated; (2) The uniform distribution of boron within TiO_2 is expected due to its simultaneous formation; (3) The process of preparation and modification of TiO_2 is achieved in one CVD system, which leads to a significant reduction of the catalyst preparation steps such as transferring the TiO_2 catalyst from one reactor to another to modify TiO_2, so the process of catalyst preparation is simplified.

EXPERIMENTAL DETAILS

Materials

Titan-tetraisopropoxy (TTIP), used as TiO_2 precursor, was purchased from Shanghai Xingta Co., Ltd., China. HBO_4, used as boron precursor, was purchased from Shanghai Wusi Chemical Co., Ltd., China. The purity of nitrogen applied as carrier gas was greater than 99.99%. ACF selected as the photocatalyst support was purchased from Nantong Chemical Co., Ltd., China.

Preparation of B-TiO_2/ACF photocatalyst

The apparatus is shown in Fig.1. ACF was put into the silica reactor, and dehydrated in a stream of dry nitrogen at 573 K for 1 h. Then, the temperature of the reactor was adjusted to 973 K. After the reactor temperature stabilized, the deposition of TiO_2 was initiated by switching TTIP to the source temperature of 343 K and a carrier gas flow rate of 10 L/min for 3 h. The doping of boron was achieved still using the CVD method with the source temperature of 298 K (75 mg/L) and a carrier gas flow rate of 8 L/min for 2~6 h. The gas line was heated to avoid the precursor condensation. After the deposition was stopped, the reactor was purged by N_2 for about 1 h. Details of the apparatus can be found elsewhere (Ding *et al.*, 2000). The crystalline structures of TiO_2 and B-TiO_2 were mainly anatase (2θ=25.3°) determined by XRD.

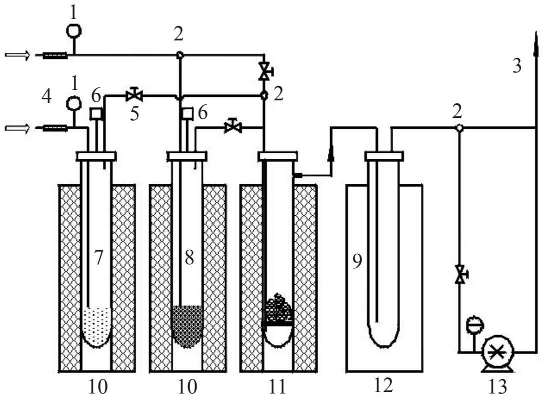


Fig.1 Schematic diagram of the CVD system
1: Moisture meter; 2: 3-way valve; 3: Vent; 4: Moisture trap; 5: Electrothermal trap, 6: T; 7: Dopant; 8: Precursor; 9: Water bath; 10: Evaporator; 11: CDV reactor; 12: Trap; 13: Vacuum pump

RESULTS AND DISCUSSION

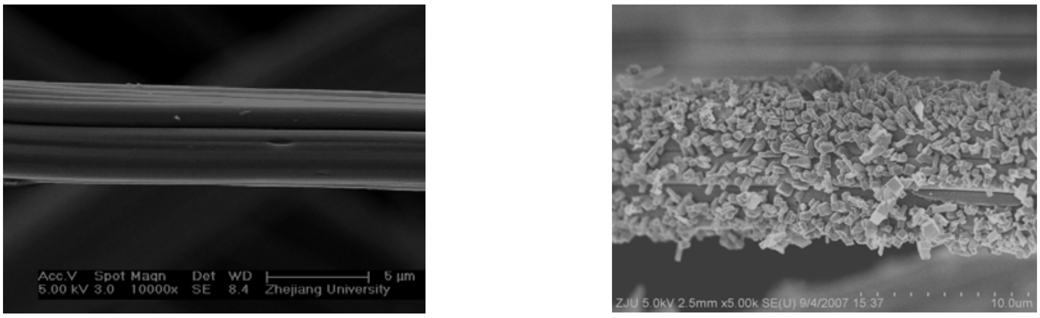
Fig.2 shows SEM analysis of surfaces of ACF and B-TiO_2/ACF samples. From the SEM photographs, it could be seen that the surfaces of ACF were covered by the B-TiO_2 catalysts, ascertained with the EDX microanalysis. It should be pointed out that the surface of ACF support could be completely covered with the B-TiO_2 coating if a long deposition time was used (not shown). Determination of the chemical state of the B-TiO_2 sample (700 °C) was carried out with XPS, as shown in Fig.3. Fig.3a shows that an unsymmetrical B 1s peak consists of a few obvious tailing peaks. This means that different chemical forms of B atoms might exist in TiO_2. Both peaks at 194.0 eV and 192.8 eV could pertain to B-O bonds in B_2O_3 (Lu *et al.*, 2004). The peak at 189.2 eV was attributed to Ti-B bonds in TiB_2 (Harris *et al.*, 2002). In addition, it is interesting to note that the peak at 191.2 eV was between those of B_2O_3 and TiB_2. This indicates some mixed state such as B-Ti-O appeared because the chemical environment surrounding boron is neither B-Ti-B nor B-O. The boron-doped TiO_2 was denoted as $TiO_{2-x}B_x$. Zhao *et al.*(2004) calculated the theoretical densities of states (DOSs) for the O substitution case and revealed that the p orbital of B was mixed with O 2p orbitals, which was responsible for the band gap narrowing, and then caused the optical response in the visible range. Besides, Ti and O spectra were also taken. Fig.3b shows that the spectrum of Ti $2p_{3/2}$ in TiO_2 could be fitted as one peak at 459.4 eV, indicating that Ti ions were mainly in an octahedral environment and their valence state was not influenced by a small amount of doping. Meanwhile, the binding energy of Ti $2p_{3/2}$ of 464.6 eV was larger than that of the standard value ((458±0.1) eV), which means that the surface acidity of TiO_2 was enhanced, and thus it was easy for the polar organic pollutants to be adsorbed on the TiO_2 surface (Lu *et al.*, 2000). Fig.3c depicts that the O 1s spectrum could be fitted by 3 peaks of 530.4, 531.6 and 533.3 eV, corresponding to the Ti-O bond in TiO_2, the surface hydroxyl groups and the B-O band.

Fig.4 shows the UV-vis diffuse reflectance absorption spectra of TiO_2 and B-doped TiO_2 samples. It can be seen that the B-doped TiO_2 samples clearly display drastic and strong absorption in the visible light range. This shows that doping with boron can shift the absorption edge of TiO_2 to the visible light range and narrow the band gap.

The activity of B-TiO_2/ACF samples prepared with different doping time was evaluated by degradation of methyl orange in a cylinder reactor, as shown in Fig.5. It is apparent that the pure TiO_2 photocatalyst showed rather low photocatalytic activity, while B-doped TiO_2 samples exhibited higher photocatalytic efficiency, indicating the positive effect of B-doping on the photoelectrocatalytic efficiencies. It should be noted that the activity of B-TiO_2/ACF with a B-doping time of 6 h was similar to that of B-TiO_2/ACF with a B doping time of 4 h, suggesting a B-doping time of 4 h was appropriate to obtain an active photocatalyst. It was noticed that the atomic B/Ti ratio of B-TiO_2/ACF with a B-doping time of 4 h was 0.016 as determined by XPS.

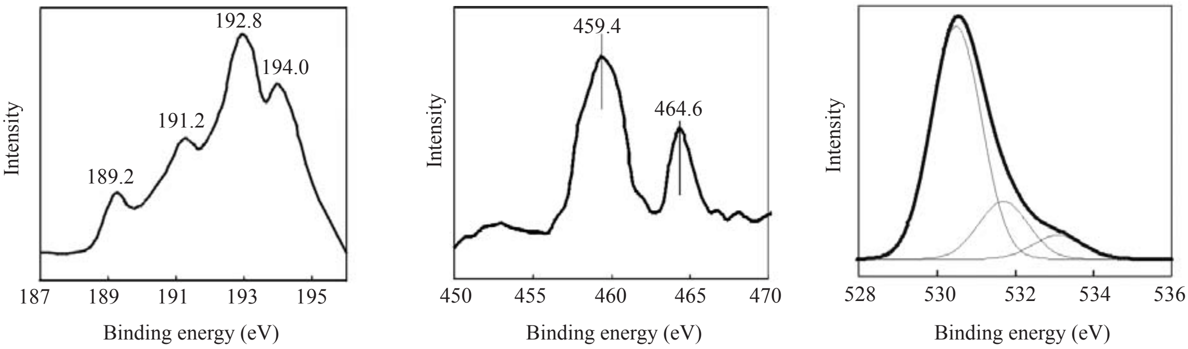
CONCLUSION

Supported B-TiO_2 coating photocatalyst was



(a) (b)

Fig.2 Typical SEM images of surface of samples. (a) ACF; (b) B-TiO_2/ACF



(a) (b) (c)

Fig.3 XPS spectra of B 1s (a), Ti 2p (b) and O 1s (c)

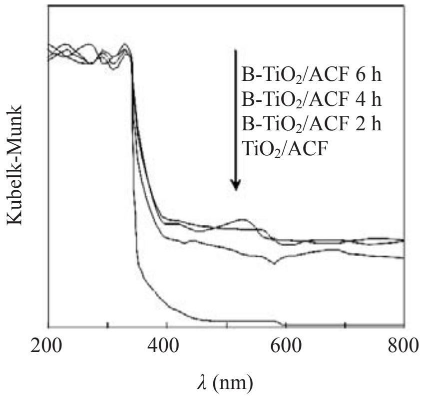


Fig.4 Diffuse reflectance electronic absorption spectra of pure TiO_2 and B-TiO_2 samples

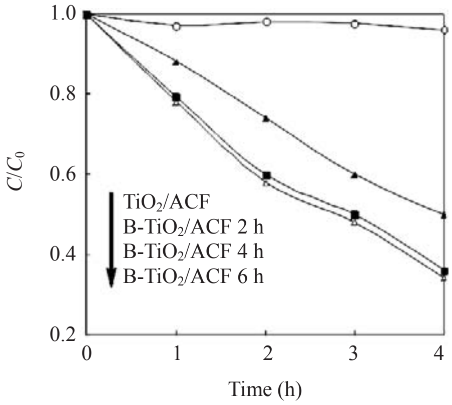


Fig.5 Comparison of photocatalytic efficiency of pure TiO_2 and B-TiO_2 samples

developed in one step through a novel method—CVD. Boron atoms were successfully doped into the lattice of TiO_2, and B-doped TiO_2 exhibited strong absorption in the visible light range with a red shift in the band gap transition. The catalytic performance of TiO_2 under visible light irradiation was enhanced after boron doping due to the band gap narrowing. This novel B-TiO_2 coating photocatalyst showed higher photocatalytic activity in methyl orange degradation under visible light irradiation than that of the pure TiO_2 photocatalyst.

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