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Photocatalytic properties of TiO_2 bonded active carbon composites prepared by SOL-GEL ①

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Abstract: Photocatalyst of TiO_2 bonded active carbon (TiO_2/AC), was prepared via sol-gel method from a mixture of TiO_2 sol with active carbon. Post heat treatment was performed at 250 ℃ for 2 h in air and then kept at 400 ℃ to 600 ℃ under a flow of nitrogen for 2 h. The TiO_2/AC composites obtained were characterized by SEM, XRD, UV-vis and BET. The photocatalytic activities of the TiO_2/AC composites were studied in comparison with TiO_2, AC, P-25 and a mixture of TiO_2 and AC, respectively. The Ramnant rate of Rhodamine B absorbed by the active carbon is found to be almost 70% and the remnant rates of the Rhodamine B decolorized by TiO_2 and the mixture of TiO_2 and the active carbon are 30% and 25%, respectively. However, nearly complete removal of Rhodamine B is observed for a TiO_2/AC composite after 200 min under UV irradiation, which will take the P-25 commercial product 5 h. Therefore, the TiO_2/AC composite is much more effective in decolorization of aqueous Rhodamine B. In addition, the composite can be easily separated from solutions.

Key words: TiO_2-bonded composite; sol-gel; photoactivity; active carbon
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1 INTRODUCTION

Environmental purification using photocatalysts has attracted a great deal of attention due to the increasing environmental problems in the world[1]. Recently, their application has been focused on the purification and treatment of water and air[2]. TiO_2 is the a promising and wildly used photocatalyst because of its high activity, chemical stability, robustness against photocorrosion, low toxicity, no-twain pollution and availability at low cost[3-5]. However, shortcomings of conventional powder catalysts are owing to the low efficiency in making use of light, difficulty in stirring during reaction and separation after reaction and low-concentration contamination near TiO_2[6, 7]. These disadvantages of TiO_2 result in low efficiency in photocatalytic activity in practical application. Correspondingly, catalysts such as TiO_2 bonded active carbon(TiO_2/AC) were prepared to overcome these disadvantages and to extend its industrial applications. It is efficient to shelter low-concentration contamination that the higher BET surface area of active carbon act as the carrier of TiO_2 powder[8]. Some papers reported on preparation of the composites between TiO_2 and carbon[9-12] and TiO_2-mounted exfoliated graphite[13, 14]. It was reported that the addition of active carbon to titania slurry could increase decomposition of some organic compounds during the photocatalytic process[15]. In other group's work, mounting of TiO_2 onto various active carbons was reported to result in certain reduction of specific surface area of carbons and TiO_2 broke away from active carbon[12]. This was reasonably supposed to be owing to the preferential deposition of TiO_2 particles at the entrance of the miniature pores of active carbon and TiO_2 particles felted on the surface of active carbon by fixed glue . In the present work, the sol-gel technique is applied in order to introduce TiO_2 into the inside and outside of active carbon and increase their binding energy, aiming to avoid precipitation of TiO_2 into miniature pores of active carbon by adjusting the ratio of active carbon to TiO_2 sol and restrict TiO_2 desquamating from active carbon by heat treatment. In this work, composites of TiO_2/AC with high photocatalytic activity are successfully prepared and their photocatalytic properties are studied.

2 EXPERIMENTAL

2.1 TiO_2/AC composites preparation

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Precursor solutions for TiO_2/AC were prepared by the method[3] as follows. Tetrabutylorthotitanate(Aldrich, 99.9%, 17.02 mL) and diethanoiamine(4.8 mL) were dissolved in ethanol(64.82 mL). The solution was stirred vigorously for 2 h at 20 ℃ followed by addition of a mixture of distilled water(0.9 mL) and ethanol(10 mL) on stirring. The resulted alkoxide solution was left standing at 20 ℃ for 2 h for hydrolysis reaction, resulting in the TiO_2 sol. The chemical composition of the starting alkoxide solution was $x[Ti(OC_4H_9)_4]:x(C_2H_5OH):x(H_2O):x[NH(C_2H_4OH)_2] = 1:25.5:1:1$. Then a desired amount of active carbon particles(AC) (pure chemicals) was used as the carriers and was added into TiO_2 sol. After this sol changed to gel, TiO_2 gel bonded active carbon was heat treated at 250 ℃ for 2 h in air and then heating temperature was increased gradually to the end temperature form 400 ℃ to 600 ℃ for 2 h in nitrogen using an electric oven. The concentration of TiO_2 sol in active carbon was adjusted by the quantity of active carbon added to TiO_2 sol.

2.2 Photocatalytic activity evaluation

Photocatalytic activity of the TiO_2/AC was determined by aqueous Rhodamine B decolorization in water under UV irradiation. The same mass (0.5 g) of TiO_2/AC, AC, TiO_2 and mixture of TiO_2 with AC(the amount of TiO_2 in mixture is equal to that of TiO_2 in TiO_2/AC) were added respectively into aqueous Rhodamine B with a concentration of 5 mmol/L in a quartz cell(280 mL), as presented in Fig. 1. An ultraviolet lamp of 40 W, fixed in the middle of the quartz cell, was used as a light source, with wavelength range and peak wavelength of 320 – 400 nm and 365 nm, respectively. The solution was sparged with air during irradiation. The concentration of Rhodamine B after decolorization was determined by an UV-visible spectrophotometer. The photocatalytic decolorization of Rhodamine B is a pseudo-first-order reaction and its kinetics may be expressed as $\ln\left[\frac{C_0}{C}\right] = k_{app}C$.

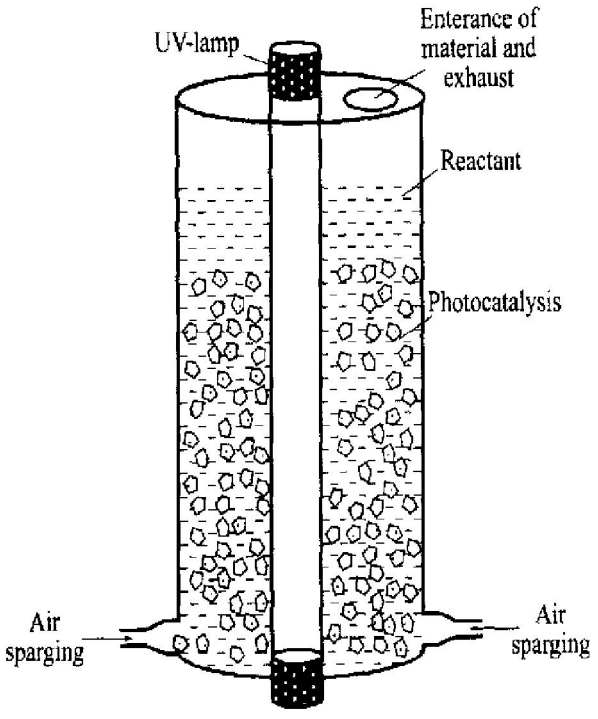

Fig. 1 Setup of photocatalytic reaction

2.3 Characterization

The crystallinity of the TiO_2/AC was determined by X-ray diffraction(XRD) using an HZG4-PC diffractometer with Cu K_α radiation, the accelerating voltage and the applied current were 35 kV and 20 mA, respectively. The crystalline size of TiO_2/AC and TiO_2 was calculated from XRD measurement by supplied computer program. The concentration of anatase was estimated from integrated intensities of the reflection of(101) and(110) phases. The amount of TiO_2 bonded on the carbon surface was determined from ignition loss at 700 ℃ in air by using TG apparatus(STA 449 C Jupiter 8 thermobalance of Netzsch Company, Germany). The structure of prepared catalysts was observed on using scanning electron microscope (SEM, SX-100) with an accelerating voltage of 20 kV. The size of TiO_2 grains in TiO_2/AC composites and TiO_2 was observed using an UV-visible spectrophotometer (Helios α of Unicam company, England) with a wavelength range of 200 – 1 000 nm. BET surface area was determined with a monosorb BET analyzer(Quantachrome Company, USA).

3 RESULTS AND DISCUSSION

3.1 Photocatalytic activity of TiO_2/AC

The results of Rhodamine B removal under UV irradiation are presented in Fig. 2. The remnant rate of Rhodamine B, decolorized by active carbon under UV irradiation without photocatalysis, was found to be 70% after 200 min. The remnant rate of the Rhodamine B decolorized by the TiO_2 and UV irradiation are 30% and 96% after 200 min, respectively. However, heated to an end temperature of 500 ℃ for 2 h, the TiO_2/AC containing both anatase and rutile phase reaches almost 100% of the Rhodamine B removal. This seems to suggest that the effect of the active carbon carriers must appear remarkably. To demonstrate further the utility of the active carbon carriers for TiO_2 loading, photodecomposition of Rhodamine B was studied using the naked TiO_2 in the presence of dispersed active carbon. As shown in Fig. 2, the reaction rate of the naked TiO_2 was increased by introducing the active carbon into the TiO_2 suspension, The remnant rate of the Rhodamine B decolorized by the mixture of TiO_2 with active carbon was 25%, but the enhancement was not so great as that obtained at the 26.3%-loaded TiO_2/AC. It may attribute

this to the active carbon with high surface area, which worked well as an effective adsorbate to concentrate Rhodamine B around the loaded TiO_2. The adsorbed Rhodamine B seems to be supplied to the loaded TiO_2 mostly by surface diffusion. In addition, active carbon can possibly prevent recombination of electron-hole pairs. The presence of Ti^{3+} ion, which could capture generated electrons, is confirmed by XPS survey spectra under effect of active carbon. UV irradiation was essential to photodegradation of Rhodamine B by TiO_2/AC, because the remnant rate of the Rhodamine B decolorized by the TiO_2/AC without UV is 68%.

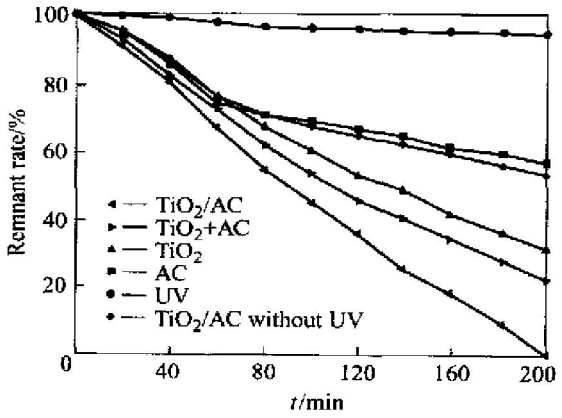

Fig. 2 Photocatalytic degradation properties of TiO_2/AC, TiO_2, AC and mixture of TiO_2 powder with AC, pyrolyzed under same condition at 500 ℃

The photoactivity was compared to commercially available TiO_2 P-25 (Degussa, Germany) that consists of both anatase (80%) and rutile (20%) phases of TiO_2. The same experimental conditions were selected for P-25. From the comparison between catalysts P-25 and the TiO_2/AC composite (in Fig. 3.), it can be seen that Rhodamine B undergoes decomposition much faster in the case of the latter catalyst. After 200 min of irradiation almost 100% Rhodamine B removal was observed, but the former needed at least 5 h.

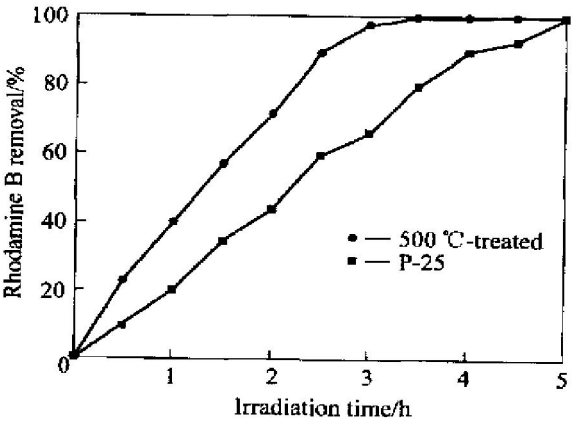

Fig. 3 Rhadamine B removal under UV irradiation with P-25 and 500 ℃-treated catalysts

IR spectra of Rhodamine B show that some organic compounds emerged after it was photodegraded, as illustrated in Fig. 4. The new bands in the range of 1 150 – 1 270 cm^{-1} are attributed to C=O vibration of carbonate or ether species. The apparent reaction rate constants of the photocatalytic decolorization of Rhodamine B was 0.007 7 min^{-1} for TiO_2/AC and 0.005 0 min^{-1} for TiO_2, respectively.

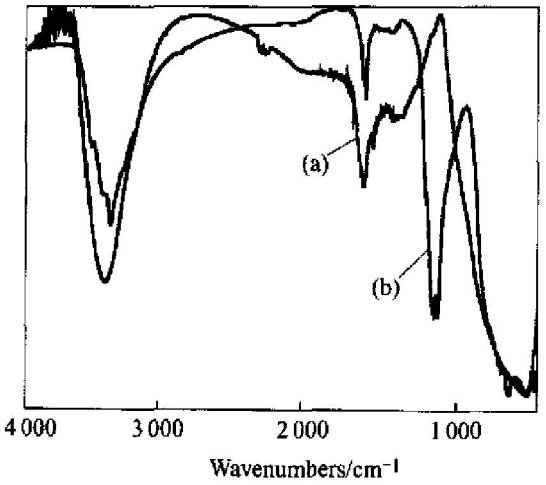

Fig. 4 IR spectra of Rhodamine B before (a) and after (b) decolorization

3.2 XRD results

XRD patterns of TiO_2/AC and TiO_2 under different heat-treated temperatures are presented in Fig. 5 and Table 1. The TiO_2/AC heated to 450 ℃ for 2 h consists only of anatase phase of TiO_2, while that heated at 500 ℃ consists of both anatase (65%) and rutile (35%). Crystalline phase of anatase was developed in TiO_2/AC with the increase of heat-treatment temperature. The higher the heat-treatment temperature, the larger the amount of rutile formed. When the heat-treatment temperature was 550 ℃ for 2 h, TiO_2/AC consists of only rutile. However, the TiO_2 consists of both anatase (95%) and rutile (5%) phases at heat-treatment temperatre of 450 ℃ for 2 h. When the TiO_2 was heated from 500 ℃ to 550 ℃, the content of anatase of TiO_2 varied from 45% to 0. The crystallite size of TiO_2/AC and TiO_2 were rising with the increasing heat-treatment temperature. At the same heat-treatment temperature, the crystallite size of TiO_2 was greater than that of TiO_2/AC and the increasing degree of the grain size of TiO_2 is faster than that of TiO_2/AC. This may be attributed to the fact that the active carbon has such a great surface area that it retards the growth of TiO_2 crystallite bonded active carbon.

3.3 UV-vis spectra

Fig. 6 shows the UV-vis spectra in the wave-

Table 1 Anatase content and crystalline grain size of TiO_2/AC and TiO_2 under different heat-treatment conditions for 2 h

Temperature/ ℃	Mass fraction of anatase/ %		Crystalline grain size/ nm	
	TiO_2/AC	TiO_2	TiO_2/AC	TiO_2
450	100	95	26.8	34.7
475	88	71	30.2	40.3
500	65	45	37.5	47.2
525	32	25	39.1	49.8
550	0	0	42.7	53.3

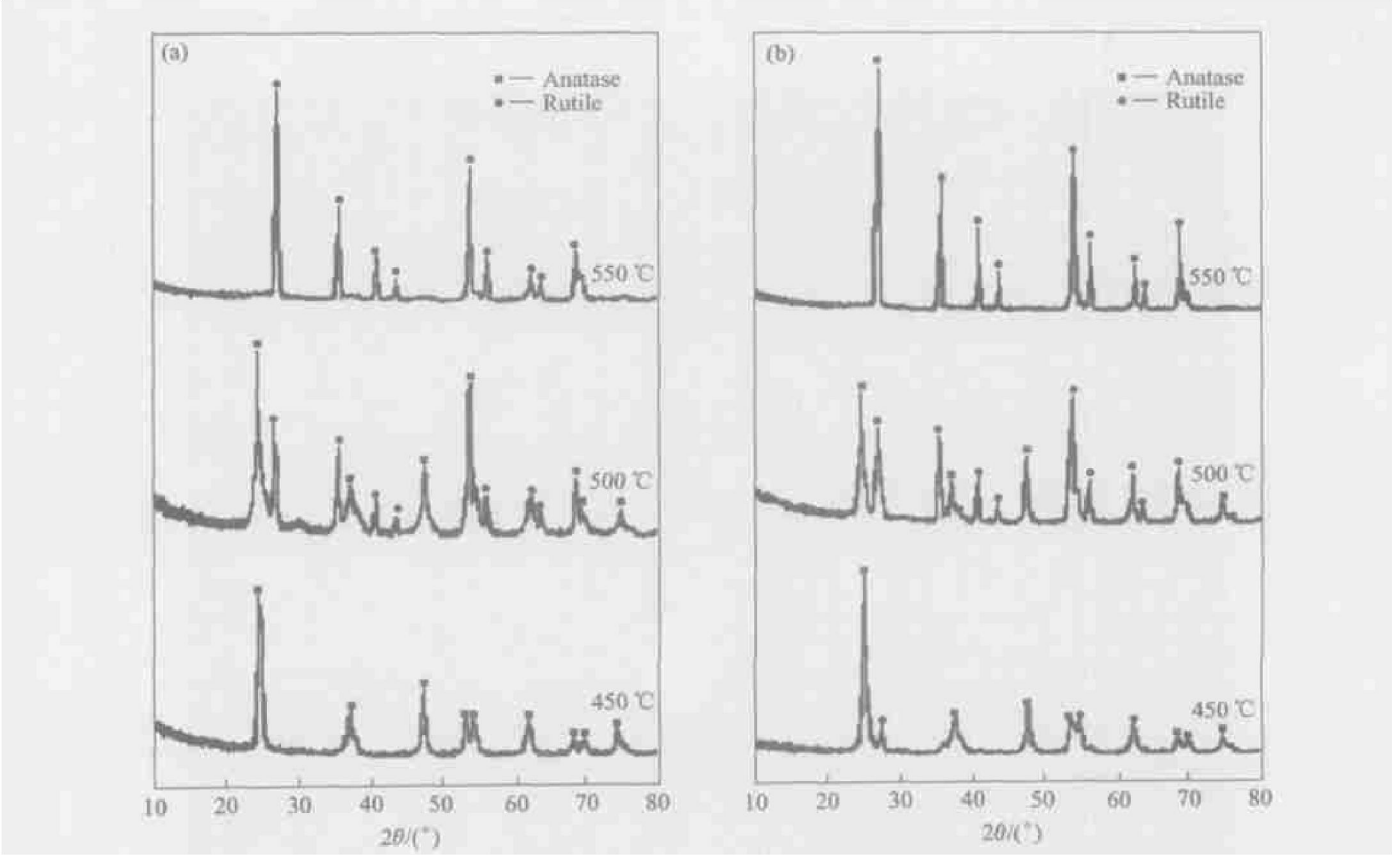

Fig. 5 XRD patterns of TiO_2/AC composites(a) and TiO_2 nano-powders(b) pyrolyzed at different temperatures

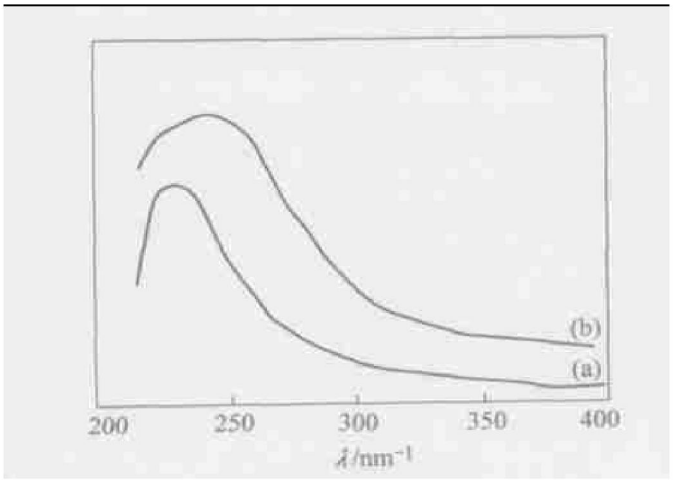

Fig. 6 UV-vis absorption spectra of TiO_2/AC(a) and TiO_2(b)

length range 200 – 400 nm for TiO_2 grains in composites and TiO_2 grains, respectively. The absorption edge of the TiO_2/AC(Fig. 6(a)) is observed at a lower wavelength range than that of the TiO_2(Fig. 6(b)). The shift is ascribed to the difference in particle size. The TiO_2/AC composites contain relatively small particle and show a bseudo"blue shift". This is adapt to the obtained results by XRD. The BET surface areas of TiO_2/AC, TiO_2 and active carbon are presented in Table 2. The BET surface area of the active carbon in TiO_2/AC rises slightly with the increasing heat-treatment temperature. At the same time, the BET surface area of TiO_2 reduces as the grain size of TiO_2 raised. It causes development of surface area of TiO_2/AC that the big carves in active carbon changes into small carves with the decreasing mass of TiO_2/AC.

3.4 SEM results

Fig. 7 shows the scanning electron micrograph of the surface of TiO_2/AC and TiO_2. It is observed

Table 2 BET surface area of TiO_2/AC and TiO_2 under different heat-treatment conditions

Heat-treatment temperature/ ℃	$w(TiO_2)$/%	BET surface area/ ($m^2 \cdot g^{-1}$)		
		TiO_2/AC	TiO_2	AC
450	17.8	510.97	76.13	434.8
475	21.6	519.86	74.31	436.3
500	26.3	526.03	70.71	440.1
525	30.2	538.78	68.65	444.8
550	34.1	556.94	66.44	447.1

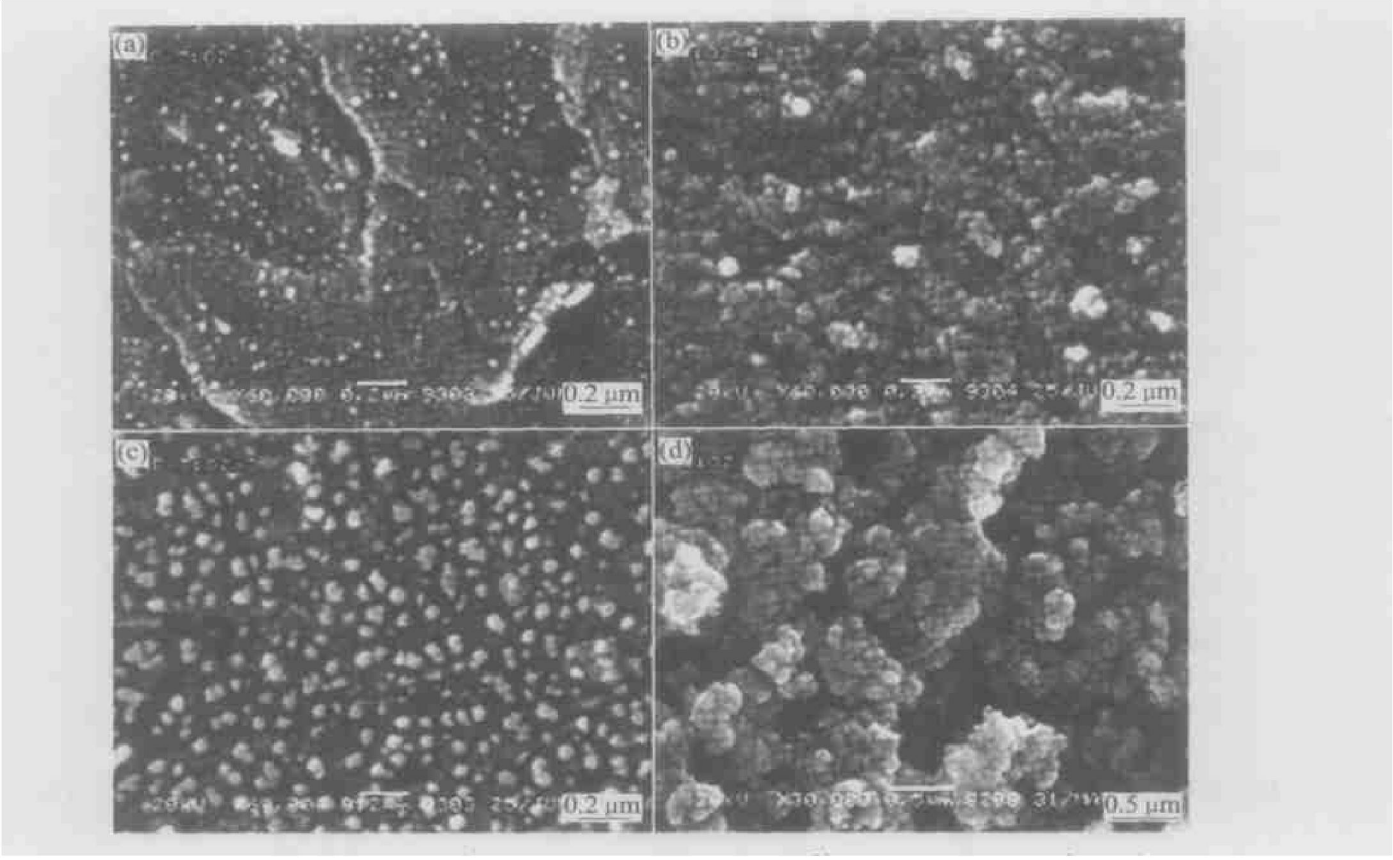

Fig. 7 SEM images after heat-treated under different conditions for 4 h
(a) —TiO_2/AC at 400 ℃; (b) —TiO_2 at 400 ℃; (c) —TiO_2/AC at 500 ℃; (d) —TiO_2 at 500 ℃

that the TiO_2/AC has spherical microstructure and dispersing texture, composed of 30 – 50 nm sphere particles. However, the grain size of TiO_2 with reuniting microstructure is bigger than that of TiO_2/AC. In accordance with the increasing heat-treatment temperature, the grain sizes of TiO_2/AC and TiO_2 increase, but the increasing degree of the grain size of TiO_2 is faster than that of the grain size of TiO_2/AC. This is due to the great surface area of the active carbon that has a great "absorbing energy" to retard growth of TiO_2 grains.

4 CONCLUSIONS

In order to prepare TiO_2 bonded active carbon composite with higher photoacativity, the active carbon was added into TiO_2 sol by properly controlling the ratio of active carbon to TiO_2 sol. Introducing active carbon into the TiO_2 composite would not decrease its surface area, instead, some advantages can be obtained, such as suppression of anatase onto rutile phase and retarding growth of TiO_2 grains . The prepared catalysts can effectively remove rhodamine B under UV irradiation and can be easily separated from solutions, which is due to the active carbon carrier

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