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The photocatalytic activity and stability of a nanosized TiO_2 film prepared by carbon black modified method

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Abstract

Regard to the poor adsorbability of the fixing film photocatalyst, we prepared a new nanosized TiO_2 thin film modified by carbon black acting as the pore-forming agent and baked by a kind of new method. The film was characterized by XRD, TEM, SEM, DRS and FT-IR techniques. The results showed that the prepared TiO_2 films were mainly anatase structure, containing a little rutile. Their mean sizes of crystal grains are about 20–30 nm. Comparing to the ordinary TiO_2 film, we found that both carbon black modification and new baking method could make the characteristics of films change, such as more pores, looser structure, smaller crystal grains and longer excitation wavelength. It should be owed to these advantaged characteristics that the photocatalytic activity of the new film was largely improved during the degradation of benzamide. Furthermore, it also had wonderful stability, keeping its activity for 4 months applied to degrade reactive brilliant red X-3B in the continuous flow reactor.

Keywords: Nanosized TiO_2 thin film; Photocatalytic oxidation; Carbon black modification; Stability

1. Introduction

Semiconductor photocatalytic technology can effectively destroy and mineralize most of the organic pollutants attributed to the generation of the powerful oxidant •OH radical [1]. In the past years, it has attracted considerable interests for removal of volatile organic compounds (VOCs) in gas-phases [2,3], detoxification and disinfection of drinking water [4,5], advanced treatment of wastewater for reuse [6,7] and so on.

Some workers have developed pilot scale treatment systems employing suspended TiO_2 [8,9], which is efficient due to the large specific surface area of catalyst. But in slurry system the following separation of catalyst is requested, which enhances the overall capital and running cost of the plant. And aggregation of catalyst will also decrease its catalytic activity in slurry system. So immobilized catalyst is more fit for application, which has been given high regard in recent years. However, being another problem that limitation of transfer mass often occurs [10], activity of immobilized catalyst is very low. At present, this kind of immobilized system cannot be applied on a large scale, either.

In order to increase adsorbability of immobilized photocatalyst, many researchers chose adsorbent as carrier (e.g. granular activated carbon [11], molecular sieves [12], porous nickel [13], etc.). Some persons even added polymer such as polyethylene glycol [14,15] into sol of catalyst to increase the porosity of film. But more organic groups will be remained in film because polymer is difficult to oxidize and remove by baking.

In this work, carbon black (CB) with nanometer size was adopted as pore-forming agent and doped into the sol for coating film. After baked at high temperature, CB was oxidized and removed from film, while pores were formed. Thus, modified TiO_2 film (CB–TiO_2) with high photocatalytic activity was prepared through doping carbon black. And stability of modified film was also tested through the long-term use.

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2. Experimental

2.1. Preparation of films

TiO_2 films were prepared using sol–gel technology. Tetrabutylorthotitanate (10.0 ml, C.P.) and acetylacetone (3.0 ml, A.R.) were dissolved in *n*-propanol (70.0 ml, A.R.). After mixed to uniformity, ionized water (4.0 ml) was added drop wise to the above solution. Then, CB (23.5 mg, produced by Degussa Ltd.) was added to the sol acting as pore-forming agent. And dispersed by ultrasonic for 10 min, the suspending solution became the sol for coating films. Aluminum plate (150 mm × 75 mm × 1.0 mm) was used as the substrates and coated by dipping-withdrawing in an ambient atmosphere. After dried, gel films were baked at high temperature.

During the preparation of photocatalytic films, coating cycles are usually repeated for enough times to provide the loading mass of catalyst required by photocatalysis. The traditional baking method (marked by TM) follows that films are baked at higher temperature for a long time during every coating cycle. Thus, aggregation and growth of TiO_2 grains in the interior region of films, which undergo a repeated long-term baking, cause a decrease in the number of surface active sites [15]. On the other hand, the pore formed from the former coating cycles can be filled with sol during the consequent coating cycles. These are all disadvantages to improving photocatalytic activity.

We used a new baking method (marked by NM) according to the property of CB, which cannot be oxidized when baked below some temperature. During our preparation, the films from the initial coating cycles were baked at lower temperature (e.g. 300 °C) for shorter time (e.g. 30 min) in order to remove most of the organic group and hold CB as framework of films. While the films from the last coating cycle were baked at higher temperature (e.g. 450 °C) for longer time (e.g. 2 h) in order to remove residual organic group and CB and complete crystallization of TiO_2. The different color of films during preparation well showed the above courses (Table 1).

2.2. Characterization of films

The loading mass of TiO_2 on aluminum plate was determined by weight method using electronic balance. Composition of crystal phase and size of crystal grains were analyzed by X-ray diffraction (XRD) with a diffractometer (D/max-RB model) employing Cu Kα radiation. The accelerating voltage and the applied current were 40 kV and 120 mA, respectively. The morphology was observed using transmission electron microscopy (TEM, H-800 model) with an accelerating voltage of 20 kV and scanning electron microscopy (SEM, LEO-1530 model) with an accelerating voltage of 5 kV. Diffuse reflectance spectra (DRS) were obtained on a Shimadzu UV-2100s spectrophotometer, using $BaSO_4$ as the reference. Fourier transform infrared spectra (FT-IR) were taken on a spectrophotometer (Nicolet-560 model), using KBr pellets and working in the transmittance mode.

Table 1
Color of films baked at different conditions

Baking temperature	Color of films	Color-forming substance
No baking	Dull black	CB/organic group
300 °C	Bright black	CB
450 °C	White	TiO_2

2.3. Measurement of photocatalytic activity

Photocatalytic activities of TiO_2 films were measured using the plate reactor shown in Fig. 1. An aqueous solution of benzamide (2×10^{-5} mol l^{-1}, 200 ml) was used as model pollutant. Film was placed on the plate of reactor and the solution with pollutant was continually circulated from its surface driven by peristaltic pump. A 20 W low-pressure mercury lamp was used as the irradiation source. Through solution layer, UV light vertically irradiated the surface of photocatalytic film, where photocatalytic degradation took place. Reactor of glass body and silicone pipe was used to avoid adsorption of pollutant in system.

In order to get rid of the extrinsic influence on reaction rate (e.g. the change of light intensity of lamp after long-term used), a certain catalyst, which had already been measured, was introduced as "reference" during the preparation and photocatalytic measurement of every batch catalyst. So if photocatalytic activity of "reference" was defined as "1", the activity of measured catalytic just was the ratio of its photocatalytic reaction rate and that of "reference". That was,

$$a = \frac{K - k}{K_0 - k}$$

where a was the photocatalytic activity of film; k the photo degradation reaction rate, min^{-1}; K and K_0 the overall reac-

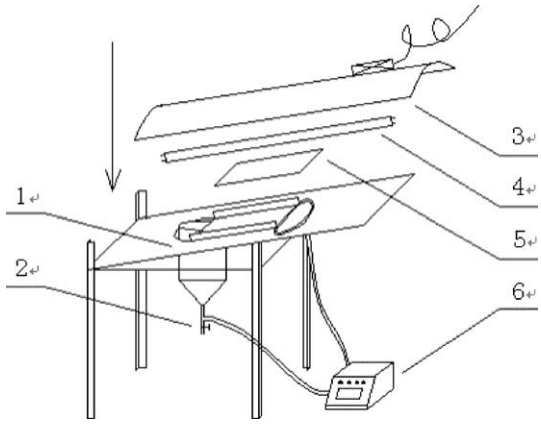


Fig. 1. Plate reactor for measurement of photocatalytic activity: (1) storage vessel; (2) drain valve; (3) shield; (4) UV lamp; (5) photocatalytic film; (6) pump.

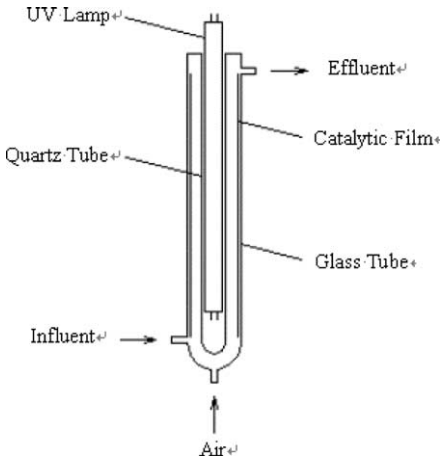


Fig. 2. Tube reactors for test of photocatalytic stability.

tion rates of measured catalyst and "reference", respectively, min^{-1}.

2.4. Stability test

Long-term stability of TiO_2 film was tested using the annular tube reactor operated with continuous flow, shown in Fig. 2. An aqueous solution of reactive brilliant red X-3B (5.0 mg l^{-1}) was used as model pollutant. An 8 W low-pressure mercury lamp was placed in the quartz tube located in the center of reactor. Film was closed to the inner wall of glass tube. Aeration from the bottom of reactor provided perfect mixing of solution and dissolved oxygen needed for reaction.

2.5. Analysis method

Benzamide concentrations were determined by Shimadzu LC10A HPLC with C18 column (length of 25 cm and inside diameter of 4.6 mm). The mobile phase was methanol and water with a flow rate of 1.0 ml min^{-1}. The column temperature was 40 °C.

Reactive brilliant red X-3B was analyzed on Shimadzu UV250 spectrophotometer. The determination wavelength was 538 nm.

3. Results and discussion

3.1. Characterization of films

3.1.1. Loading mass

Fig. 3 showed a linear relationship between loading mass of CB–TiO_2 and coating times. The slope of line is 0.3706; that is, the loading mass of film from every coating cycle is about 0.3706 g m^{-2}. Supposedly take no account of pores and estimated according to density of anatase in theory, the thickness of film from single coating cycle was approximately 94 nm.

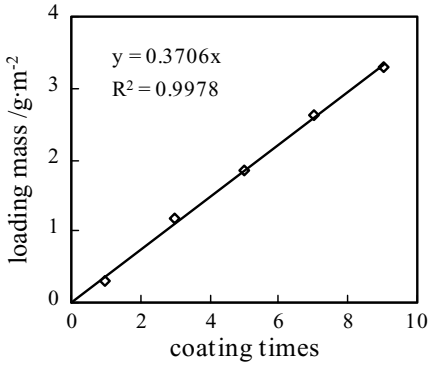


Fig. 3. Relationship between loading mass of CB–TiO_2 and coating times.

Table 2
Loading masses of the different films from single coating cycle

Films	Loading mass (g mm^{-2})
TiO_2 (TM)	0.3826
TiO_2 (NM)	0.3635
CB–TiO_2 (TM)	0.3899
CB–TiO_2 (NM)	0.3706

Table 2 showed loading mass of the different films from single coating cycle. We could see that their values of loading mass were very closed, ranged from 0.36 ∼ 0.39 g m^{-2}. But it was also obvious that new baking method made loading mass slightly decrease, while CB modification was opposite.

3.1.2. Composition of crystal phase and size of crystal grain

As shown in Fig. 4, all of TiO_2 films were mainly anatase structures (2θ = 25.3°) having little rutile content (2θ = 27.4°). Some results indicate that the photocatalyst with such composition will have higher activity [16]. It was observed that the peaks for anatase of TiO_2 films baked at 300 °C were a little lower than others, which showed that they did not completely crystallize. When the films were baked at 450 °C, their peaks for anatase rose and there were hardly the difference between the NM 450 °C and TM 450 °C. And their content of rutile was about 15 ∼ 120%.

The mean crystallite size of anatase from films prepared using different methods was summarized in Table 3. They were all the nanosized films with the mean crystallite size ranged from 20 ∼ 30 nm. CB doped into films enhanced steric hindrance for grain growth, so modification made the crystallite of films smaller. And the mean crystallite size of

Table 3
Crystallite size of anatase estimated by the broadening of the diffraction line (nm)

Baking condition	TiO_2	CB–TiO_2
TM 300 °C	25.0	21.4
NM 450 °C	27.3	24.2
TM 450 °C	31.5	28.9

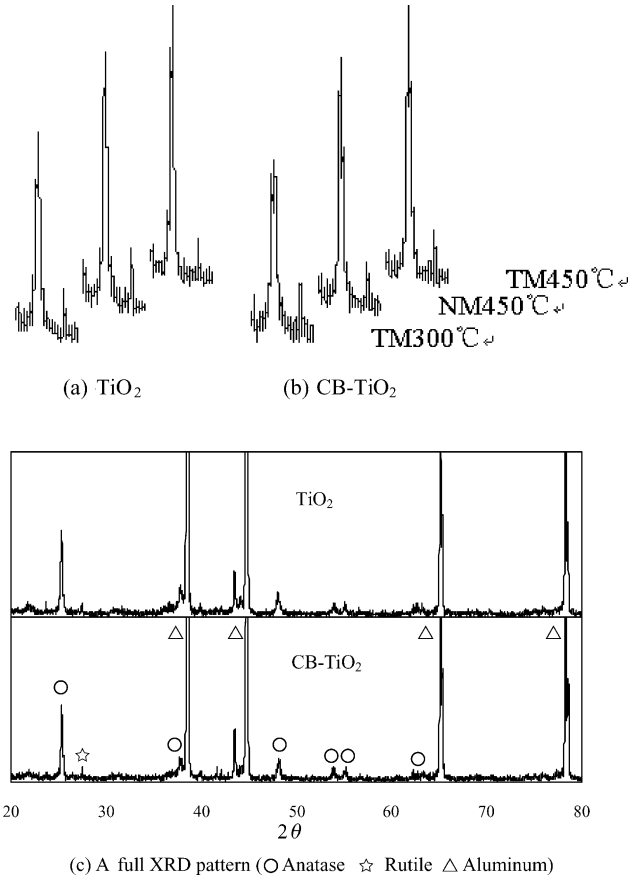


Fig. 4. XRD patterns of TiO_2 and CB–TiO_2 films under the different baking conditions.

films increased with increases of baking temperature and time. Generally, the smaller the crystallite is, the larger the specific surface area of films is. Among these films, the TM 300 °C had smallest crystal grains, but their content of anatase also was lowest, so their activities were not enough high. While the phase composition of the NM 450 °C and TM 450 °C were almost the same, and the crystal grains of the former were smaller, so their activities should be higher.

3.1.3. The morphology observation

Fig. 5 showed the transmission electron micrographs of the photocatalytic films prepared by TM 450 °C. Fig. 5(a)–(c) were the respective photographs of CB–TiO_2 films with the different amplification, while (d) was the one for TiO_2 films. It was observed that the crystallites of two kinds of films were all spherical grains about 30 nm, which was basically consistent with the results of XRD. Compared with the ordinary TiO_2 film, CB–TiO_2 film held more pores and the looser structure because of doping CB. In our experiment, TEM observation requires the coating cycles as few as 1 ∼ 2 times, so it is very difficult to distinguish the difference of TM 450 °C and NM 450 °C on morphology. So the scanning electron micrographs of the surface of the films were also shown in Fig. 6.

Table 4
Absorption edge for DRS of films (nm)

Baking condition	TiO_2	CB–TiO_2
NM 450 °C	375.5	378.5
TM 450 °C	371.5	374.5

We can find that the surface of TiO_2 film prepared by TM 450 °C was uniform and compact, there being the obvious crystal orientation. While the surface of CB–TiO_2 film prepared by TM 450 °C was not so regular as that of TiO_2 film, but their contrast was not very remarkable. The reason may be that the sol filled in the formed pores during the course of sequent coating. In contrast, the surface of CB–TiO_2 film prepared by NM 450 °C was very scraggly, which will equip the films with the larger specific surface area and the better adsorbability. So its photocatalytic activity will also be higher.

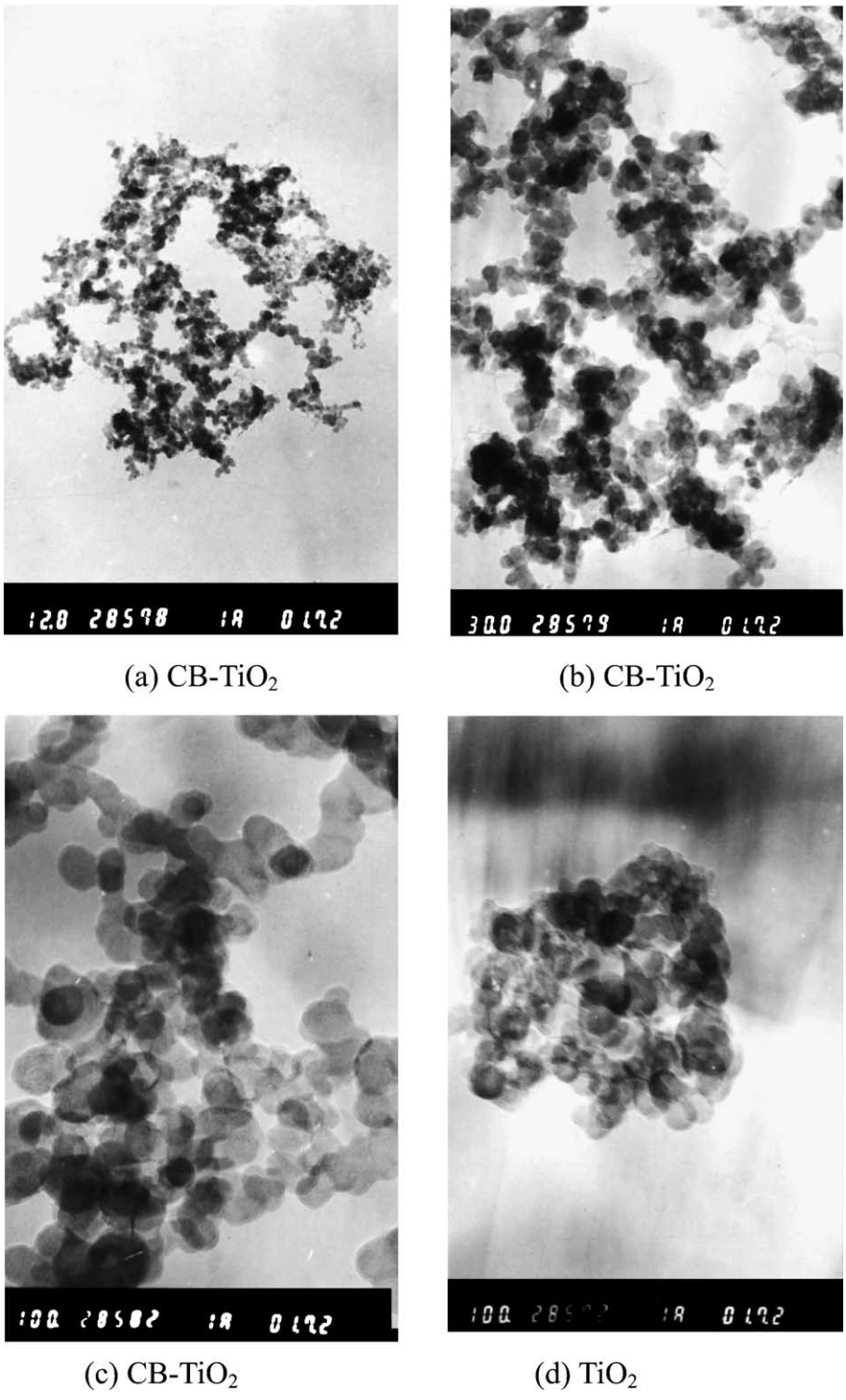
3.1.4. DRS analysis

According to diffuse reflectance spectra (Fig. 7), the films only showed strong absorption in the region of UV light, which is typical optical characteristic held by semiconductor. And the changes of the crystallite size and porosity brought that the films modified by CB or baked using new method showed stronger reflectance to visible light and stronger absorption to UV light, which will also favor the improvement of their photocatalytic activities.

The absorption edge of films can be compared with the inflections of reflectance curves [17]. They had already been achieved by the first derivative of DRS and the results were shown in Table 4. It was observed that CB modification and new baking method made the edge of film red shift about 3 and 4 nm, respectively.

3.1.5. FT-IR spectra

Figs. 8 and 9 were FT-IR spectra of TiO_2 and CB–TiO_2 films baked using different methods, respectively. Among these spectra, the band at 3460 cm^{-1} showed the stretching vibration of OH, attributing to surficial hydroxyl group and adsorbed water molecules, while the band at 1660 cm^{-1} could be ascribed to the blending vibration of H–O–H brought by adsorbed water molecules [18]. The strong absorption peaks at 1590, 1540 and 1370 cm^{-1} related to the symmetric and asymmetric vibrations of groups containing carbon. Doping CB caused the vibration of 1550 cm^{-1}. The weak absorption peak at 1040 cm^{-1} corresponded to the bands of Ti–O–C. The peak at 560 cm^{-1} was representative absorption of [TiO_6] octahedron [19]. The results showed that after the films dried, there were abundant organic groups on the their surface, but the precursor containing Ti was almost hydrolyzed completely, forming oxide or hydroxide. And the surficial species of the film doped by CB were simpler. This can be because the absorption of some tetrabutylorthotitanate, acetylacetone or the their hy-

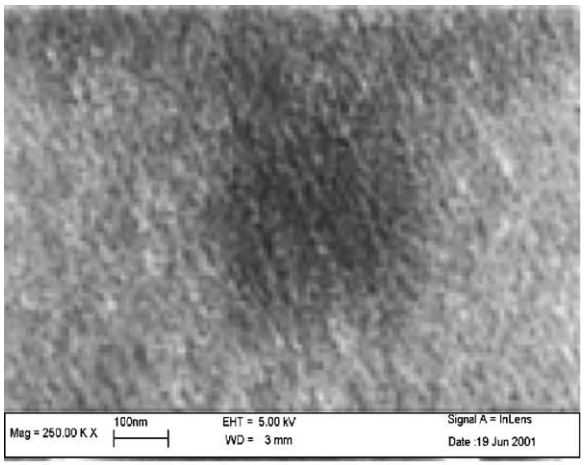


(a) CB-TiO_2 (b) CB-TiO_2

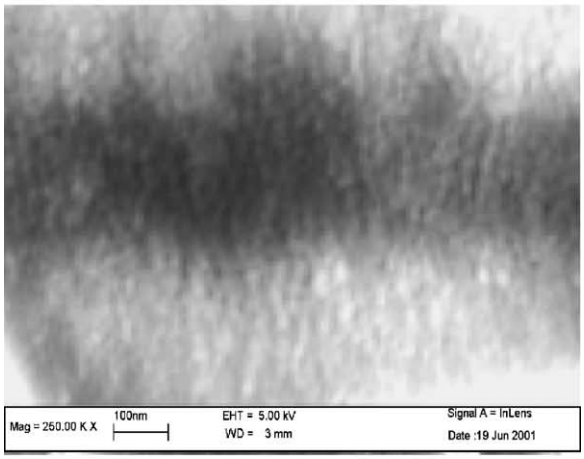
(c) CB-TiO_2 (d) TiO_2

Fig. 5. Transmission electron micrographs of the TM 450 °C films.

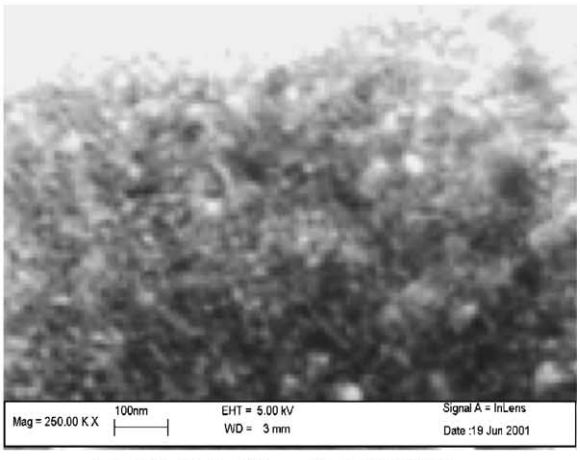
drolyzing/complexing products in the sol on CB induced the shift of reaction equilibrium between hydrolyzing and complexing, resulting in hydrolyzing rate in sol doped by CB decreased. Another fact was observed that after the films baked at 300 °C, organic groups almost completely disappeared, while CB was still kept. When the baking temperature went up to 450 °C, CB was also oxidized and removed from the films, in which there were only a little surficial hydroxyl group and absorbed water molecules and no group containing carbon. And the surficial groups from NM 450 °C films and TM 450 °C films were the same. Generally, it is considered that a proper amount of surfi-



(a) TiO_2 film of TM450 °C



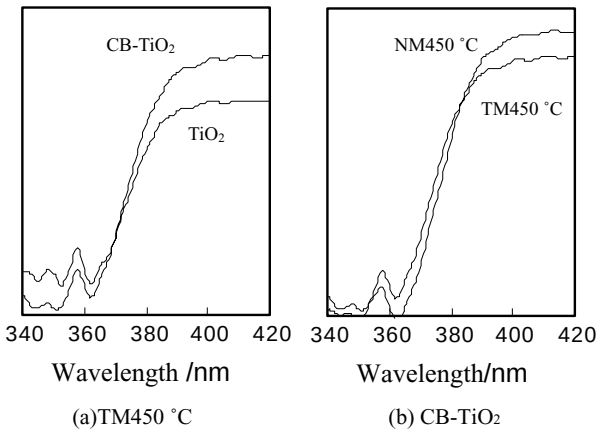
(b) CB-TiO_2 film of TM450 °C



(c) CB-TiO_2 film of NM450 °C

Fig. 6. Scanning electron micrographs of the surface of the films.

cial hydroxyl group favors trap of holes, but the excessive one and other groups can become the recombination center of the carriers, resulting in lower photocatalytic activities [20].



(a)TM450 °C (b) CB-TiO_2

Fig. 7. DRS analysis of photocatalytic films.

3.2. Photocatalytic activity of films

3.2.1. CB modification

Adsorbability is a main characteristic of photocatalyst as well as other catalytic processes. Generally, the adsorbing capacity of porous film for pollutant is larger. Thus, it will bring higher equilibrium concentration in aqueous pollutant and larger driving force of transfer mass. On the other hand, larger pollutant coverage on the surface of film will also increase the rate of photocatalysis, since one-order reaction occurs on catalytic surface. So improvement of adsorbability will remarkably increase the activity of photocatalyst in the immobilized film system, in which the conditions of transfer mass is ordinary worse.

In this work, CB was doped into sol for coating film as pore-forming agent in order to increase porosity of film and improve its activity. Fig. 10 showed that the photolysis, TiO_2 and CB–TiO_2 photocatalysis of benzamide all followed the pseudo-one-order kinetic relationship under our experimental condition. And as expected, TiO_2 film modified by CB had very high photocatalytic activity, which is about two times of that of ordinary TiO_2 film.

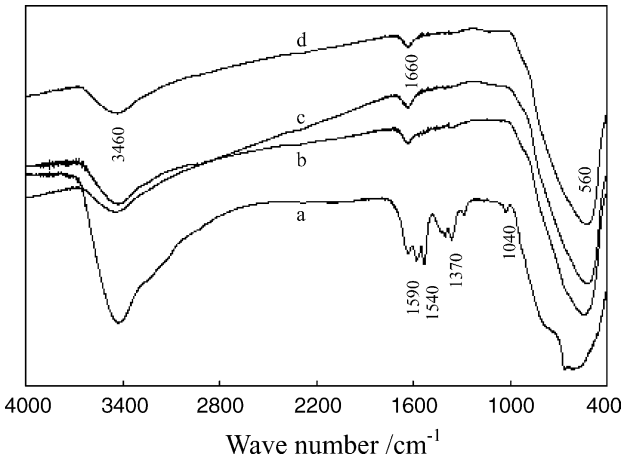


Fig. 8. FT-IR spectra of TiO_2 films prepared using different baking methods: (a) TM 110 °C; (b) TM 300 °C; (c) NM 450 °C; (d)TM 450 °C.

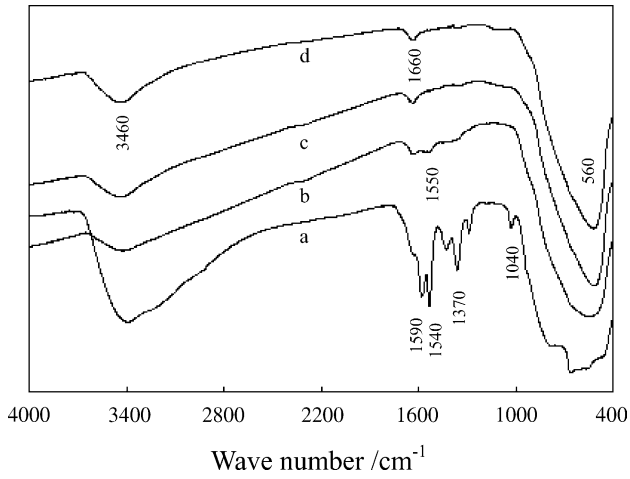


Fig. 9. FT-IR spectra of CB–TiO_2 films prepared using different baking methods: (a) TM 110 °C; (b) TM 300 °C; (c) NM 450 °C; (d) TM 450 °C.

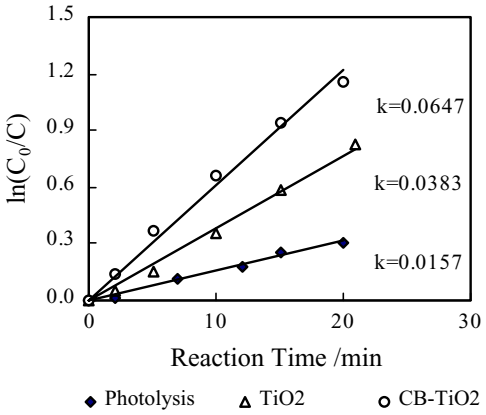


Fig. 10. Degradation rate of benzamide under the different reaction processes.

3.2.2. Baking method

As shown in Fig. 11, photocatalytic activities of CB–TiO_2 using new baking method were obviously higher than that of CB–TiO_2 using traditional method as expected. Moreover, both of them sharply increased with coating times and

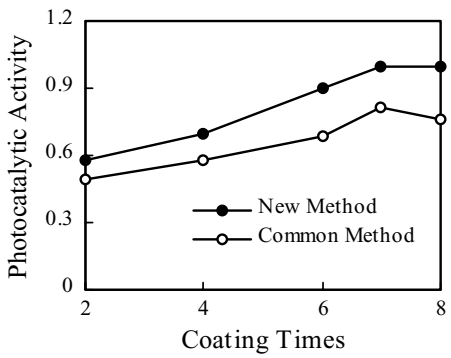


Fig. 11. Photocatalytic actives of CB–TiO_2 films using the different baking method.

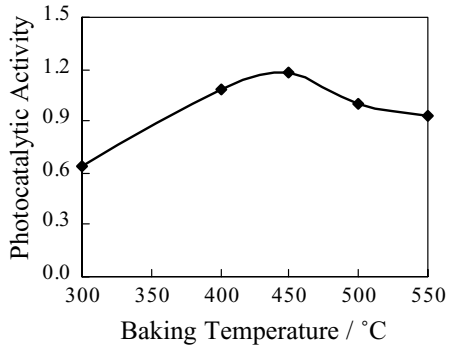


Fig. 12. Influence of the last baking temperature on photocatalytic activity of film.

achieved the maximum at the seventh coating. Then the former was almost kept, while the latter lightly decreased, which mainly resulted from excessive baking.

3.2.3. Baking conditions

According to experimental results, preferable conditions for new baking method is that films from coating of initial six times were baked at 300 °C for 30 min, and films from the seventh coating at 450 °C for 2 h. Here, only relationship between the last baking temperature and photocatalytic activity was given (Fig. 12), since it was more predominant than others were.

3.3. Stability of the nanosized photocatalytic film modified by CB

The key to the application of photocatalytic technique is the preparation of catalyst with higher activity and better stability. The former had already been shown by the above results, while the long-term stability experiment for 4 months in continuous flow reactor proved the latter. As shown in Fig. 13, the removal efficiency of reactive brilliant red X-3B, as model pollution, was kept above 95% all the time. This

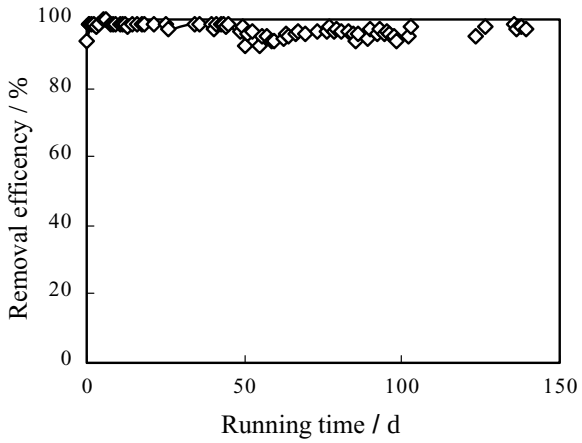


Fig. 13. Change of photocatalytic activity of the modified film applied in continuous flow reactor.

result showed that the photocatalytic film held very good stability. The stability of the film was also proved by its same TEM figure before and after test.

4. Conclusions

The nanosized TiO_2 thin films modified by CB have been prepared on aluminum plate substrate using a kind of new baking method. The structural properties, photocatalytic activity and stability of the TiO_2 films have been investigated as potential photocatalytic materials.

The TiO_2 films are mainly anatase structure, containing little rutile, and the mean size of whose crystal grains were about 30 nm. Compared to the ordinary TiO_2 films, the CB–TiO_2 films have more pores, looser structure, smaller crystal grains and longer excitation wavelength.

New baking method can avoid the repeat and excessive baking of films and strengthen the pore-forming action of CB.

Both the photocatalytic activity and stability of the CB–TiO_2 films are all higher. During the degradation of benzamide the activity is about two times of that of the ordinary films. And the film kept the degradation rate higher than 95% as long as 4 months in the continuous flow reactor.

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