Photocatalytic ozonation of dibutyl phthalate over TiO$_2$ film

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Abstract

A novel carbon black modified nano-TiO$_2$ film photocatalyst (CB-TiO$_2$) was prepared by a sol–gel method and used for degrading and mineralizing dibutyl phthalate. The film was characterized by XRD, SEM, and DRS techniques. Carbon black modification could make TiO$_2$ film more pores, looser structure, smaller crystal sizes and longer excitation wavelength. The photocatalytic activity of the CB-TiO$_2$ films was 1.4 times higher than that of TiO$_2$ films in degrading dibutyl phthalate. The results showed that ozone concentrations had an important effect on degradation and mineralization of dibutyl phthalate. The combined photocatalysis with UV irradiation and ozonation (TiO$_2$/UV/O$_3$) process considerably improved mineralization and degradation of dibutyl phthalate compared to combined photocatalysis with UV irradiation (TiO$_2$/UV) process, combined ozonation with UV irradiation (UV/O$_3$) process and ozonation alone (O$_3$) process. Dibutyl phthalate can be quickly mineralized in TiO$_2$/UV/O$_3$ and UV/O$_3$, its mineralization followed pseudo-zero-order kinetics dependent upon ozone concentration and indicated its concentration did not affect the kinetics during TiO$_2$/UV, UV/O$_3$ and TiO$_2$/UV/O$_3$ processes. The kinetic study showed the mineralization rate constants of dibutyl phthalate with TiO$_2$/UV/O$_3$ are 1.2–1.8 times higher than that of UV/O$_3$ with the same ozone concentration and 3.5 times higher than that of TiO$_2$/UV.
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1. Introduction

Dibutyl phthalate is an important additive in special paints and adhesives [1]. As a consequence, it is released into the natural environment during manufacture, use, disposal and leaching from plastic materials. It is found to accumulate in the environment and to be toxic to a variety of aquatic organisms, which are at the base natural food chain in both marine and fresh environments [2]. Its toxic properties are even more important considering its high bioaccumulation rate (range from 100 to 3000) in different organisms [3]. And it is also one of endocrine disruptors [4,5]. In the past, some studies focused on the biodegradation of several phthalate esters from soil, synthetic or real waste waters by activated sludge treatment [6–8]. However, dibutyl phthalate is a rather stable compound in the natural environment. Its hydrolysis half-life was estimated to be about 20 years [1].

Heterogeneous photocatalysis, on the other hand, has received wide interest as a promising technology for removing refractory organic pollutants in water. Photcatalysis has proven effective in degrading dibutyl phthalate, but its mineralization requires a long time [1]. In TiO$_2$-photocatalytic oxidation processes, oxygen is widely used as an additional oxidant. The disadvantage is the slow electron transfer from TiO$_2$ to O$_2$ [9]. Ozone is a powerful oxidant ($E^0 = 2.07$ V) and reacts with many compounds via direct or indirect reactions (mainly, OH). Electrophilic attack by ozone molecules may occur at atoms with a negative charge density or double/triple bonds such as carbon–carbon etc. Indirectly, ozone can react by OH ($E^0 = 2.80$ V), which is a powerful and nonselective oxidant and can react with almost all organic compounds. Therefore, it is necessary to develop more powerful oxidation methods allowing mineralization of the total organic content. There are a few publications on the photocatalytic ozonation for removing refractory organic pollutants [10–15]. Most authors applied a suspension of fine TiO$_2$ particles. According to some reports, TiO$_2$ in

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suspension are more effective than immobilized film catalysts because of mass transfer limitations in immobilized photocatalytic treatment systems [16,17]. Industrial-scale use of TiO_2 suspensions would be problematic because of difficulty of recycling the catalyst from the treated water. This problem can be solved by immobilizing the catalyst on a support and improving immobilized film catalysts' absorbability. And there are many TiO_2 fixed film applications [18,19].

In this study, we demonstrate the advantages of the carbon black modified TiO_2 thin films supported on Al sheet. They include a higher photocatalytic activities and avoidance of separating solid–liquid phase. We chose dibutyl phthalate as a model compound because some phthalate esters, including dibutyl phthalate, were found in the secondary effluent of some waste water plants in Beijing.

2. Materials and methods

2.1. Catalysts preparation

TiO_2 films were prepared by a sol–gel method. The procedure was as follows: tetrabutyl titanate, acetyl acetone (inhibitor), and water were added to *n*-propyl alcohol (solvent) orderly to obtain a sol. Carbon black (CB) (Printex L6, made in Degussa; particle diameter, 18 nm) was then added to the sol to increase porosity and the fraction of rutile, which can improve the activities of the catalysts [15,20]. The components of the TiO_2 sol are shown in Table 1. The mixed sol was sonicated for a few minutes. The Al sheet (L2m) was then submerged in the mixed sol for several minutes before being withdrawn at a constant rate of 2 mm/s. It was dried at room temperature and sintered at 300 °C for 30 min. The coating procedure was repeated several times and the last film coat was sintered at 450 °C for 2 h to obtain CB-TiO_2 (carbon black modified TiO_2) thin films.

2.2. Photo-oxidation procedure

A 0.5 L tubular photoreactor ($h = 500$ mm, $\phi_{in} = 45$ mm) was employed for the photocatalytic oxidation and ozonation experiments. The reactor is a borosilicate glass column, which consists of the CB-TiO_2 thin films supported on cylindrical Al sheet which is against the interior glass surface, a coaxial UV source (a 15 W low-pressure UV lamp with a characteristic wavelength of 254 nm (intensity of UV light source: 40 mw/cm^2)) surrounded by quartz thimble

Table 1
Proportions of the mixed sol

Component	Proportion
Carbon black (mg)	23.5
n-propyl alcohol (mL)	70
Tetrabutyl titanate (mL)	10
Acetyl acetone (mL)	3.0
Water (mL)	4.0

($\phi_{out} = 30$ mm). Ozonized oxygen (ozone input rate: 12.5, 25.0, and 50.0 mg/L) was continuously bubbled into the solutions through a porous glass plate and flowed upward in the annular section between the UV lamp and the cylindrical vertical catalyst. Ozonation time is 60 min. Ozone was produced from pure oxygen using a DHX-SS-001 ozone generator (made in China).

2.3. Films characterization

The BET surface area was determined by nitrogen adsorption using Quantasorb surface area analyzer (USA). Grain size as well as crystalline phase of TiO_2 and CB-TiO_2 films was determined using an X-ray diffractometer (D/max-RB) 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 surface morphology of the calcined samples was visualized using a scanning electron microscope (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.

2.4. Analytical methods

Test solutions were prepared with 15.0 mg/L dibutyl phthalate, pH = 6.4. Its concentration was analyzed by means of a high-performance liquid chromatography (Shimadzu, LC10A HPLC) with a Kromasil C18 column (eluting solvent rate = 1.0 mL/min, column temperature = 40 °C). An aqueous solution of methanol and water was used as an eluting solvent. The total organic carbon (TOC) was determined by a Shimadzu TOC 5000 analyzer.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. XRD spectra of the films
XRD patterns, which were obtained from film, are shown in Fig. 1. Two films were mainly polycrystalline anatase structures ($2\theta = 25.3$), which have little rutile content ($2\theta = 27.4$). Some researches indicate that the photocatalyst with such composition will have higher activity [21]. And their content of rutile was 14.4 and 18.7%, respectively. The mean crystallite size of anatase and BET surface area from films was summarized in Table 2. Their mean crystallite grains are 27.3 and 24.2 nm, respectively. Doping CB into

Table 2
BET surface area, average pore size of the samples

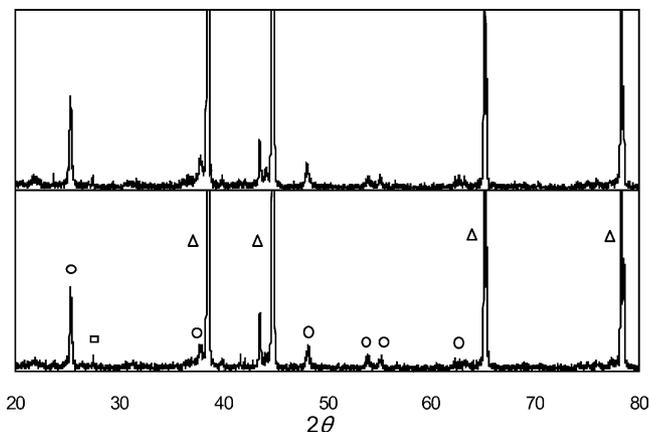| Sample	BET (m^2/m^2)	Average pore size (nm)
TiO_2	54.3	27.3
CB-TiO_2	91.8	24.2

Fig. 1. X-ray diffraction pattern of CB-TiO$_2$ and TiO$_2$ films: (○) anatase; (□) aluminium; (△) rutile.

films enhanced steric hindrance for grain growth and made the crystallite smaller. The smaller the crystallite is, the larger its surface area is. While the phase composition of the CB-TiO$_2$ and TiO$_2$ were almost same, and the crystal grains of the former were smaller, so their activities should be higher.

3.1.2. DRS analysis

Fig. 2 shows the diffuse reflectance spectra of CB-TiO$_2$ and TiO$_2$ films. They only showed strong absorption in the region of UV light, which is typically optical characteristic held by semiconductor. And the changes of the crystallite size and porosity, which is brought by CB modification, showed stronger reflectance to visible light and stronger absorption to UV light, which will also favour the improvement of their photocatalytic activities. The absorption edge of films can be compared with the inflections of reflectance curves [22]. It was observed that CB modification made the edge of film red shift from 375.5 to 378.5 nm.

3.1.3. SEM images

Fig. 3 shows the SEM images of CB-TiO$_2$ and TiO$_2$ films. It was observed that the crystalline grains of two kinds of films
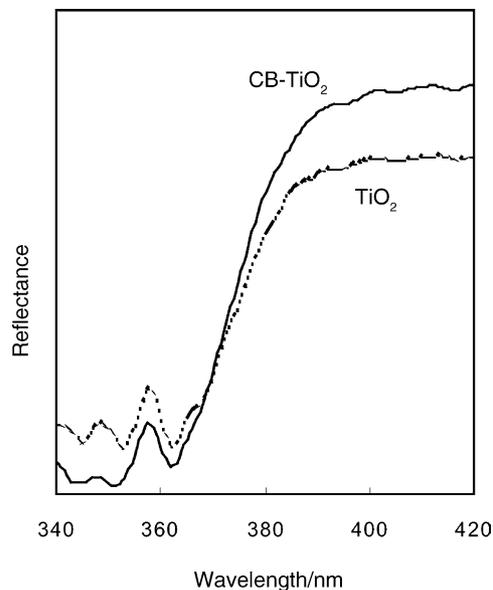

Fig. 2. DRS analysis of photocatalytic films.

were about 30 nm, which was basically consistent with the results of XRD. But doping CB made the film more pores and looser structure, which could improve the absorbability of TiO$_2$ film.

3.2. The photocatalytic activity evaluation of the CB-TiO$_2$ thin films

Absorbability is a main characteristic of photocatalytic processes. So improving photocatalyst absorbability will remarkably increase its activity in the immobilized film system. In this study, in order to increase porosity of film and improve its activity, CB was doped into sol. Table 3 showed the first-order rate constants in degrading dibutyl phthalate (initial concentration = 15 mg/L) with TiO$_2$ and CB-TiO$_2$ film photocatalysis. As expected, the modified TiO$_2$ film by CB had
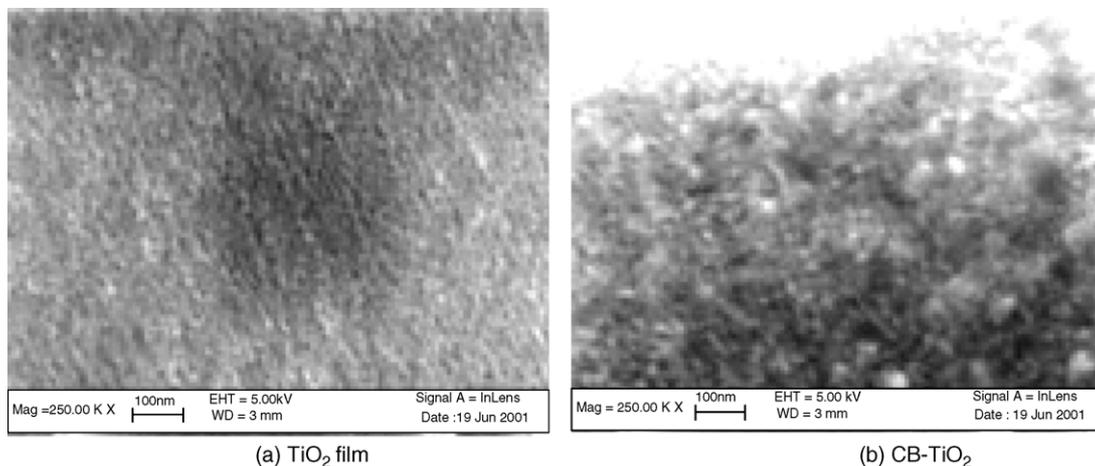

(a) TiO$_2$ film

(b) CB-TiO$_2$

Fig. 3. SEM images of catalysts.

Table 3
The first-order rate constants of dibutyl phthalate degradation by photocatalysis

Catalyst	k (min^{-1})
TiO$_2$ films	0.0146
CB-TiO$_2$ films	0.0207

very high photocatalytic activity, which was 1.4 times higher than that of TiO$_2$ films.

3.3. Degradation and mineralization of dibutyl phthalate

3.3.1. Effect of ozone dosage on degradation and mineralization of dibutyl phthalate in different oxidation process

Fig. 4 shows the degradation of dibutyl phthalate was very quick at the first 15 min in O$_3$ process and gradually slowed down with the increase of oxidation time. TOC removal rate was not quick and much slower compared to its degradation rate (C/C_0). At 50 mg/h ozone dosage, TOC removal rate is only 46% in 60 min. It indicated the intermediate compounds produced during the ozonation process of dibutyl phthalate, which are not easy to be mineralized, and accorded with former reports [15]. Some organic acids are produced in the oxidation process of aromatics, such as formic acid and oxalic acid etc. Ozonation alone can only achieve a very limited mineralization of formic and oxalic acids because their ozonation rate constants are 5 and $<4 \times 10^{-2}$ M^{-1} s^{-1} in the acidic pH, respectively [15]. TOC removal rate increased

with ozone dosage, but the rate of their reduction is immediately declined. These results indicated dibutyl phthalate was immediately oxidized into the intermediate compounds.

Fig. 5 shows that the degradation of dibutyl phthalate with UV/O$_3$ process. The presence of UV greatly improved its degradation compared to ozonation alone. At 25–50 mg/h ozone dosage, it degraded 60–69% in first 5 min, because dibutyl phthalate was easily photolyzed at the irradiation of 254 nm UV. The presence of UV also considerably improved TOC removal compared to ozonation alone. Dibutyl phthalate was mineralized over 85% in 60 min when ozone dosage was 25 mg/h. TOC removal rate was over 73% after 30 min when ozone dosage was 50 mg/h. The presence of UV could transform ozone into secondary radicals such as OH to initiate a radical-type chain reaction in the aqueous phase, so that the reaction of organic matters with ozone was accelerated [15]. The reaction rate constants of formic acids and oxalic acids with OH were 1.3×10^8 and 1.4×10^6 M^{-1} s^{-1}, respectively [15]. That meant the indirect reaction, which was advantageous to the mineralization of the intermediate compounds, played a major role.

Figs. 5 and 6 shows the degradation of dibutyl phthalate by using TiO$_2$/UV/O$_3$ is similar to UV/O$_3$. The addition of ozone considerably improved TOC removal compared to TiO$_2$/UV, which conformed with former reports [9]. The presence of TiO$_2$ also considerably improved TOC removal compared to UV/O$_3$. After 30 min, TOC removal rate was over 75% when ozone dosage was over 25 mg/h, while only 73% using UV/O$_3$ when ozone dosage was 50 mg/h. These
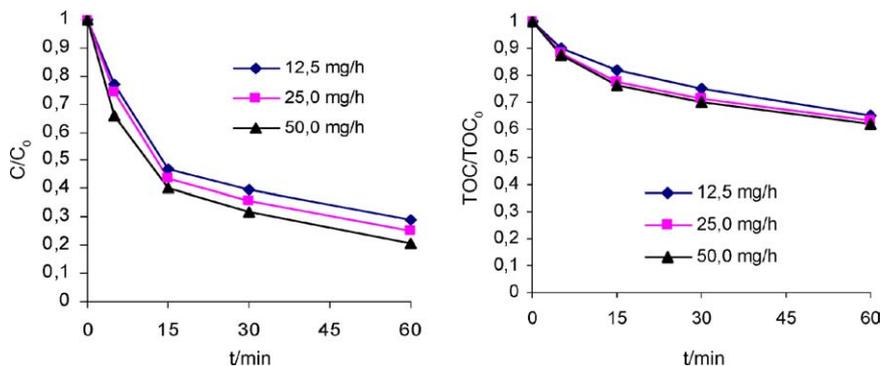

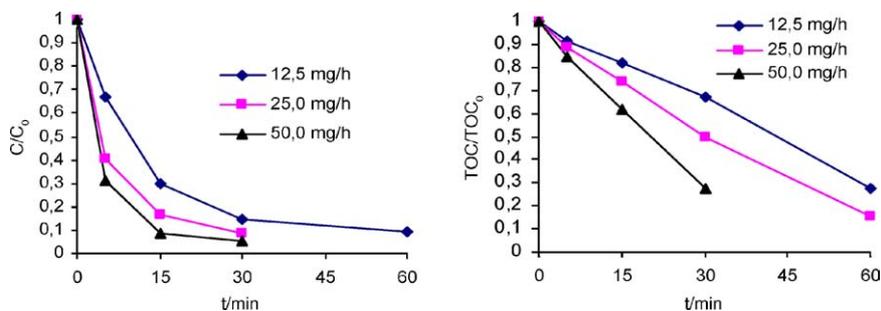Fig. 4. Degradation of dibutyl phthalate and TOC removal in the O$_3$ alone processes.

Fig. 5. Degradation of dibutyl phthalate and TOC removal in the UV/O$_3$ process.
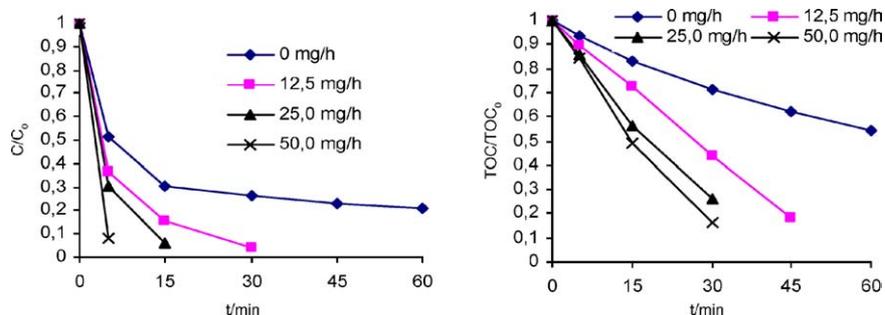
Fig. 6. Degradation of dibutyl phthalate and TOC removal in the $TiO_2/UV/O_3$ process.

Table 4
TOC removal kinetics of UV/O_3 and $TiO_2/UV/O_3$ processes with various ozone dosages

O_3 (mg/h)	UV/O_3		$TiO_2/UV/O_3$	
	Equations of kinetics	R^2	Equations of kinetics	R^2
0			$-dTOC/dt = 0.0083$	0.9621
12.5	$-dTOC/dt = 0.0119$	0.9951	$-dTOC/dt = 0.0186$	0.9987
25.0	$-dTOC/dt = 0.0148$	0.9808	$-dTOC/dt = 0.0260$	0.9878
50.0	$-dTOC/dt = 0.0246$	0.9960	$-dTOC/dt = 0.0294$	0.9860

results showed the synergetic effect of the UV/O_3, TiO_2/UV and TiO_2/O_3 [23–25]. When semiconductor is in contact with water, the surface of TiO_2 is readily hydroxylated. Under near-UV illumination, electron–hole pairs are formed in the semiconductor, the oxidation potential of hydroxylated TiO_2 must lie above the position of the semiconductor valence band, the oxidation of surface-bound OH^- and H_2O by TiO_2 valence band holes to form OH is thermodynamically possible and expected [26]. So the mineralization of dibutyl phthalate was accelerated.

3.3.2. Kinetics of photocatalytic oxidation of dibutyl phthalate

The kinetic data of semi-batch experiments with various ozone dosage are listed in Table 4. The linear trends appeared to follow pseudo-zero-order kinetics dependent upon ozone concentration and indicated that dibutyl phthalate concentrations did not affect the kinetics of TiO_2/UV, UV/O_3 and $TiO_2/UV/O_3$ processes. These results also indicated the indirect reaction of ozone may play a dominant role for the mineralization of dibutyl phthalate. The mineralization rate constants of dibutyl phthalate with $TiO_2/UV/O_3$ are 1.2–1.8 times higher than that of UV/O_3 with the same concentration of ozone, 3.5 times higher than that of TiO_2/UV.

4. Conclusions

A novel carbon black modified nano-TiO_2 film photocatalyst was prepared by a sol–gel method. The film was characterized by XRD, SEM, and DRS techniques. Carbon black modification could make TiO_2 films more pores, looser structure, smaller crystal sizes and longer excitation wavelength. The photocatalytic activity of the CB-TiO_2 films was 1.4 times higher than that of TiO_2 films in degrading dibutyl phthalate.

For degradation and mineralization of dibutyl phthalate, the presence of TiO_2 (O_3) considerably improved their removal compared to UV/O_3 (TiO_2/UV). And the presence of UV also considerably improved their removal compared to ozonation alone. Dibutyl phthalate can be quickly mineralized in $TiO_2/UV/O_3$ and UV/O_3, TOC removal rate is over 85 and 73% after 30 min, respectively, only 46% using O_3 in 60 min, when ozone dosage is over 50.0 mg/h.

In the TiO_2/UV, UV/O_3 and $TiO_2/UV/O_3$ processes, the mineralization of dibutyl phthalate follows pseudo-zero-order kinetics dependent upon ozone concentration and indicated that its concentration did not affect the kinetics of $TiO_2/UV/O_3$ and UV/O_3 processes.

The kinetic study showed the mineralization rate constants of dibutyl phthalate with $TiO_2/UV/O_3$ are 1.2–1.8 times higher than that of UV/O_3 with the same ozone concentration, 3.5 times higher than that of TiO_2/UV.

Acknowledgements

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