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RESEARCH ARTICLE

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Effect of carbon content on photocatalytic activity of C/TiO_2 composite

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Abstract A series of carbon-covered titania (CCT) were prepared via pyrolysis of sucrose highly dispersed on titania surface in flowing N_2. The samples were characterized by XRD, BET, DTA-TG, UV—Vis, and their photocatalytic properties were evaluated with two model pollutants, methylene blue (MB) and rhodamine B (RB), at room temperature. The effect of carbon content on photocatalytic activity of the C/TiO_2 composite was investigated. It was found that the effect of carbon content is different for different pollutants or different light sources. For three tested samples, under UV illumination CCT01 has the highest activity for MB photocatalytic degradation, while in the case of RB, CCT02 is the most active photocatalyst. Under visible light illumination, CCT005 has the highest activity for both MB and RB photocatalytic degradation.

Keywords titania, carbon, photocatalysis, methylene blue, rhodamine B

1 Introduction

Among the various semiconductive materials, maximum attention has been given to anatase TiO_2 because of its high photocatalytic activity, resistance to photocorrosion, photostability, low cost, and nontoxicity. However, titania has a large band gap (3.20 eV for anatase TiO_2) and therefore only the small UV fraction of solar light, about 2%−3%, can be utilized. Many attempts have been made to sensitize titania for the much larger visible fraction, such as transition metal deposition or anionic species doping [1]. Among various modified titanias, carbon—titania composites have been reported as a kind of promising photocatalyst. There are different methods reported to prepare C/TiO_2 responsive to visible light. Kisch and co-workers [2] prepared carbon-containing titania (CCT) by a modified sol—gel process using different alkoxide precursors, but the content of carbon is obviously difficult to be controlled. Carbon-doped titania can also be prepared by oxidation of a titanium metal sheet in a natural gas flame [3], but this method shows poor reproducibility and expedience. Oxidative annealing of TiC is another method reported to prepare carbon-modified titania, but the expensive material makes this method unpractical [4]. Recently, a simple process has been developed by our group for the preparation of uniform carbon-covered alumina (CCA) [5,6] and titania (CCT) [7] via pyrolysis of sucrose highly dispersed on the surface of alumina and titania. The carbon content can be easily controlled by tuning the sucrose content in the precursors. Additionally, this simple method has good reproducibility. It is proved that the as-prepared C/TiO_2 shows unique surface properties and ability to adsorb pollutant in the aqueous solution. For the model pollutant, methylene blue (MB), it is found that the adsorption capacity of C/TiO_2 catalysts is much higher than that of the mixture of corresponding titania and carbon with the same composition, or the summation of their respective adsorption capacity. Carbon covering the surface of titania can inhibit the phase transformation of TiO_2 during calcination, that is, titania in the as-prepared C/TiO_2 catalyst can maintain its anatase phase at high temperature and not be transformed to rutile phase. Photocatalytic tests show that under UV illumination, the kinetics of the elimination of MB in the suspension of CCT powders follows an apparent first-order rate as in pure titania suspension, but the rate constant is much higher than that of pure titania, even commercial Degussa P-25 TiO_2. Under visible light illumination, CCT shows similar kinetic features for the photodegradation of the dyes to that under UV illumination, different from the apparent zero-order rate of pure titania. The detection of the products of MB degradation, and the absorption spectra of MB solution after the photocatalytic reaction proved that MB is decomposed over CCT samples under visible light illumination, whereas it is simply bleached over pure titania at the same condition. In the previous work, the effect of calcination temperature on the

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photocatalytic properties of catalysts has been investigated, and it was proved that the catalyst treated at 500°C showed the highest activity of the photocatalytic degradation of MB [7]. In the present paper, two common dyes, methlene blue (MB) and rhodamine B (RB), have been chosen as model pollutants to study the effect of carbon content in the C/TiO_2 composites calcined at 500°C on their photocatalytic activity.

2 Experimental

2.1 Catalyst preparation

TiO_2 was prepared by dropping aqueous solution of $Ti(SO_4)_2$ and 3 mol/L $NH_3{\cdot}H_2O$ simultaneously into a beaker containing a small amount of 0.5 mol/L NH_4HCO_3 solution with subsequent filtering and washing until no SO_4^{2-} could be detected by 0.5 mol L^{-1} barium nitrate solution in the filtrate. The product was dried at 110°C for 12 h and then calcined in a muffle furnace at 450°C for 4 h.

Sucrose/TiO_2 precursors were prepared by impregnating titania with aqueous solutions of sucrose. After drying at 80°C, the precursors were calcined at 500°C in flowing N_2 with a rate of 50 mL min^{-1} for 2 h. In the present paper, the C/TiO_2 catalyst was denoted with the sucrose content. For example, the C/TiO_2 composite prepared by 0.1 g sucrose/g TiO_2 was labeled as CCT01.

2.2 Catalyst characterization

Phase composition of the samples was determined with a Rigaku D/MAX-200 X-ray powder diffractometer with Ni-filtered Cu-Kα radiation at 40 kV and 100 mA. The UV—Vis spectra of the powder samples were recorded on a Shimadzu UV 3100 PC, UV-VIS-NIR scanning spectrophotometer equipped with a diffuse reflectance accessory. Specific surface area was determined by using BET method based on N_2 adsorption at 77 K with a Micromeritics ASAP 2010 Analyzer. Carbon content in the sample was determined by DTA-TG test performed on a Dupont model 1090 apparatus.

2.3 Photocatalytic activity estimation

Photocatalytic experiments in aqueous phase were carried out with catalyst powder suspended in a water-cooled cylindrical 250-mL Pyrex glass vessel; the suspension was stirred magnetically in darkness or under visible light or UV illumination. The visible light source was a 150 W halogen—tungsten lamp (Phillips) equipped with a UV cut-off filter to remove the UV portion of the illumination (< 420 nm). UV illumination was provided by an 8 W medium-pressure mercury lamp with a main emission peak at 365 nm (Institute of Electrical Light Source, Beijing, China). MB and RB were dissolved in distilled water to the concentrations of 1.2×10^{-5} and 1.0×10^{-5} mol L^{-1}, respectively. Powder sample of 50.0 mg was dispersed into 200 mL MB solution. After 2 h of magnetic stirring in darkness to secure the adsorption—desorption equilibrium, variations in the concentration of dyes were monitored by UV—Vis spectroscopy at the wavelengths of 665 and 554 nm for MB and RB, respectively. A certain amount of suspension was taken out at given time intervals and immediately centrifuged at 80 r/min for 15 min, and then filtered through a 0.2 μm membrane filter to remove the particles before subjecting to UV—Vis spectroscopy.

3 Results and discussion

3.1 The physicochemical properties of C/TiO_2 composites

In our previous paper, it has been proved that sucrose can disperse onto the surface of alumina [5,6,8] and titania [7] to form a monolayer, and the threshold is about 0.38 g sucrose/100 m^2 TiO_2. The surface area of titania in our present work is about 97 m^2 g^{-1} (Table 1), sucrose is monolayer-dispersed on the surface of titania when its content is lower than 0.37 g sucrose/g TiO_2. Then in C/TiO_2 samples prepared from sucrose/TiO_2 with low sucrose loading, carbon is uniformly distributed on the surface of titania, and the special structure might lead to some changes of the physicochemical properties of the catalysts. Because of the high adsorption capacity of C/TiO_2 composites for organic pollutant MB, only three samples with low carbon content, as shown in Table 1, have been chosen for the photocatalytic activity test.

As can be seen in Table 1, the carbon content of the as-prepared C/TiO_2 composites increases linearly with the increase of sucrose loading in precursors. The surface areas of these three C/TiO_2 composites are all close to that of pure titania, indicating that the as-prepared carbon via pyrolysis of sucrose is uniformly distributed on the surface of titania [9].

Table 1 Precursor composition, carbon content, and BET surface area of different samples

Sample code	Weight ratio of sucrose to titania in precursor	Carbon content / wt%	BET surface area / (m^2 g^{-1})
TiO_2		0	97
CCT005	0.05 : 1	1.1	92
CCT01	0.1 : 1	2.1	89
CCT02	0.2 : 1	3.9	99

CCT: carbon-covered titania

3.2 The photocatalytic properties of C/TiO_2 composites

3.2.1 The photocatalytic properties of C/TiO_2 composites under UV illumination

Under UV illumination, the kinetic curves of the photocatalytic disappearance of MB and RB versus reaction time over C/TiO_2 composites and pure titania are shown in Fig. 1(a) and Fig. 2(a), respectively. It has been proved that the kinetic

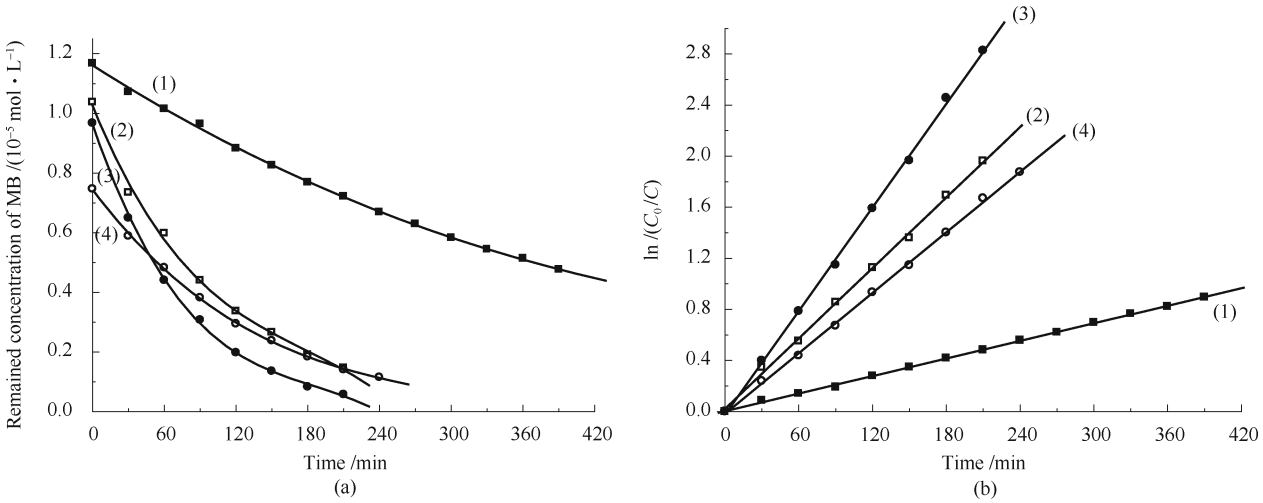

Fig. 1 Kinetic curves of MB disappearance versus reaction time in the presence of various catalysts under UV-illumination (a), and linear graph of $\ln(c_0/c)$ versus time, transformed from (a) : (1) TiO_2, (2) CCT005, (3) CCT01 and (4) CCT02

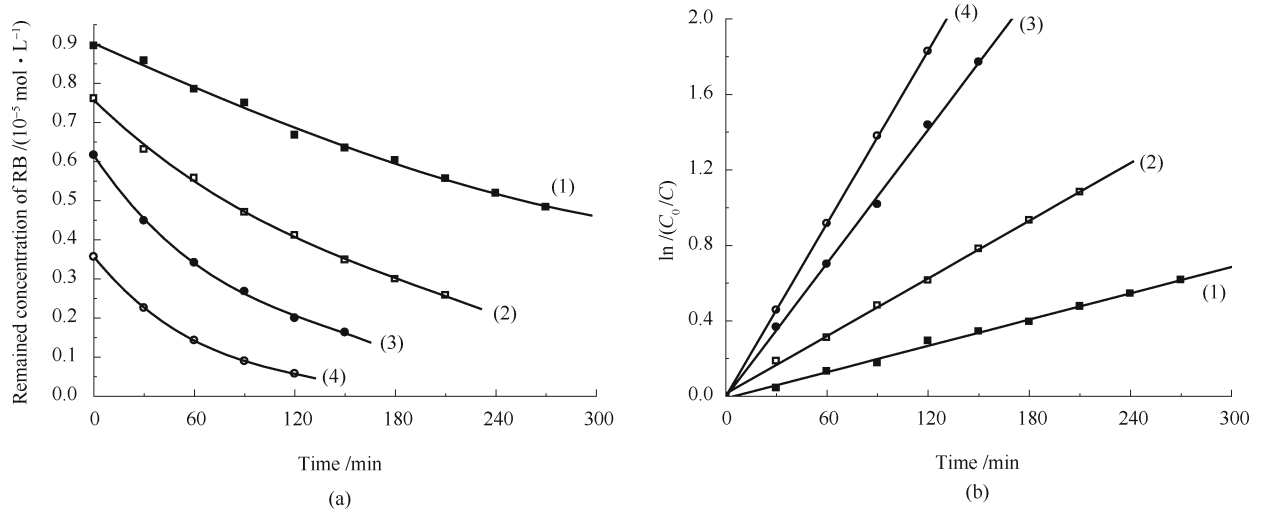

Fig. 2 Kinetic curves of RB disappearance versus reaction time in the presence of various catalysts under UV-illumination (a), and linear graph of $\ln(c_0/c)$ versus time, transformed from (a) : (1) TiO_2, (2) CCT005, (3) CCT01 and (4) CCT02

curve of photocatalytic degradation of MB [10] and RB [11] is of apparent first order. If c stands for the instant concentration of organic pollutant, c_0 stands for the concentration after adsorption equilibrium, k stands for the apparent rate constant, and t stands for the reaction time, then

$$-\mathrm{d}c/\mathrm{d}t = kc$$

and it can be transformed to

$$\ln(c_0/c) = kt$$

The kinetic curves in Fig. 1(a) and Fig. 2(a) are of the apparent first order as confirmed by the linear transforms of $\ln(c_0/c)$-t as shown in Fig. 1(b) and Fig. 2(b).

In addition, it can be found that the C/TiO_2 composites exhibit much higher activity for RB and MB photodegradation when compared with the corresponding titania. It has been well accepted that there are some key factors influencing the activity of titania photocatalysts [12]: crystalline structure, crystalline particle sizes, and surface area, etc. C/TiO_2 composites and pure titania exhibit similar surface area (Table 1) and crystalline particle sizes (XRD figures not shown), then the higher activity of C/TiO_2 composites might be explained by the following two reasons. One is the high adsorption capacity for pollutants, and the high concentration difference obviously benefits the transfer of pollutants and accordingly the reaction activity on the catalysts surface. The other is the carbon covering the titania surface, which will perturb the transmission of UV-light to the surface of titania and is adverse to the activity of photocatalysts. For different pollutants, the effect of carbon content on the photocatalyst's activity differs. For example, CCT01 shows the highest activity for MB, while for RB the activity of CCT02 is higher than the other two catalysts, which is obviously attributed to the catalysts' different adsorption capacity for MB and RB. According to Fig. 2(a), the modification of carbon increases

the adsorption capacity of RB markedly, and the capacity of CCT02 is as high as 65%. Differently, although the carbon covering also increases the adsorption capacity of the catalysts for MB, the increase extent is lower than that of RB. Therefore, the influence of the adsorption capacity on the photocatalytic decomposition of RB is crucial. When carbon content increases, the adsorption capacity of the catalysts for RB increases, and accordingly the photocatalytic activity increases. Therefore, the activity order of these three tested catalysts is: CCT02 > CCT01 > CCT005 > TiO_2. For MB system, the two factors might influence the activity reciprocally, and accordingly lead to the following activity order: CCT01 > CCT005 > CCT02 > TiO_2.

3.2.2 The photocatalytic properties of C/TiO_2 composites under visible light illumination

The kinetic curves of the photocatalytic disappearance of MB and RB versus reaction time are presented in Fig. 3(a) and Fig. 4(a), respectively. MB and RB degrade by an apparent zero-order kinetics in the presence of pure titania powder, while by an apparent first-order kinetics on CCT. It is well known that the dyes undergo two different pathways under different light illuminations [7,11]: the photocatalytic one by an apparent first-order kinetics under ultraviolet light and the photosensitization pathway by an apparent zero-order kinetics under visible light.

The photocatalytic pathway can be summarized as follows

$$TiO_2 + h\nu \rightarrow TiO_2(e^- + h^+) \quad (1)$$

$$h^+ + OH^- \rightarrow {}^{\cdot}OH \quad (2)$$

$$e^- + O_2 \rightarrow {}^{\cdot}O_2^- \quad (3)$$

$$\text{dye}_{\text{ads}} \xrightarrow{h^+, {}^{\cdot}OH, {}^{\cdot}O_2^-} CO_2 + H_2O + \text{mineral acids} \quad (4)$$

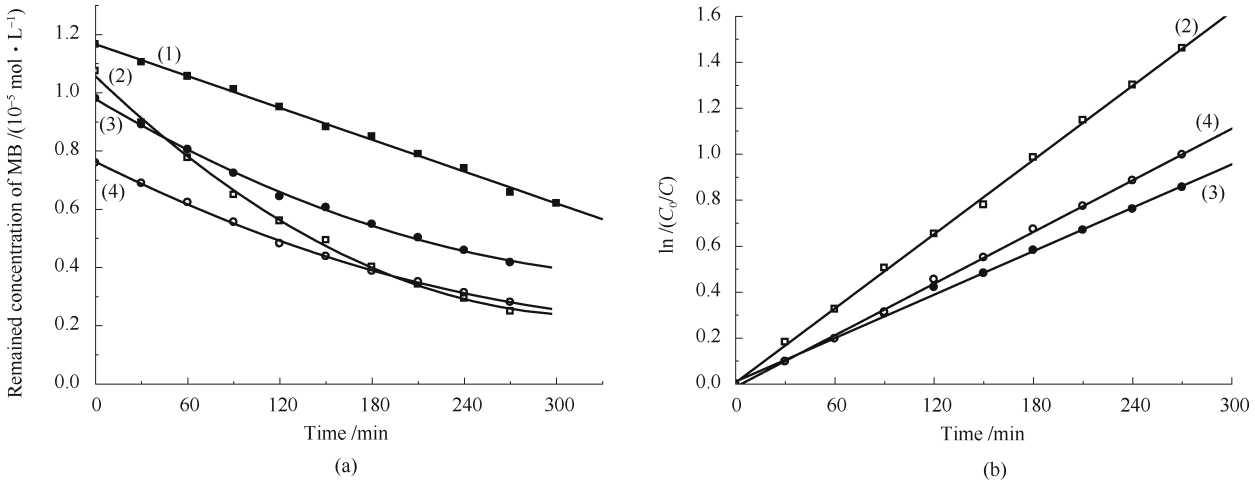

Fig. 3 Kinetic curves of MB disappearance versus reaction time in the presence of various catalysts under visible-light illumination (a), and linear graph of ln(c_0/c) versus time, transformed from (a) : (1) TiO_2, (2) CCT005, (3) CCT01 and (4) CCT02

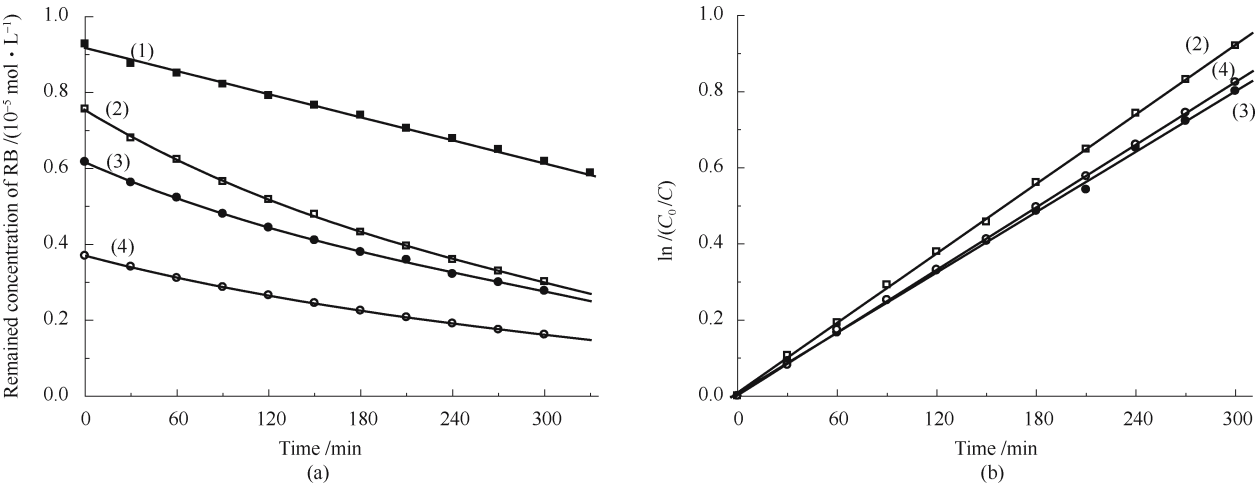

Fig. 4 Kinetic curves of RB disappearance versus reaction time in the presence of various catalysts under visible-light illumination (a), and linear graph of ln(c_0/c) versus time, transformed from (a) : (1) TiO_2, (2) CCT005, (3) CCT01 and (4) CCT02

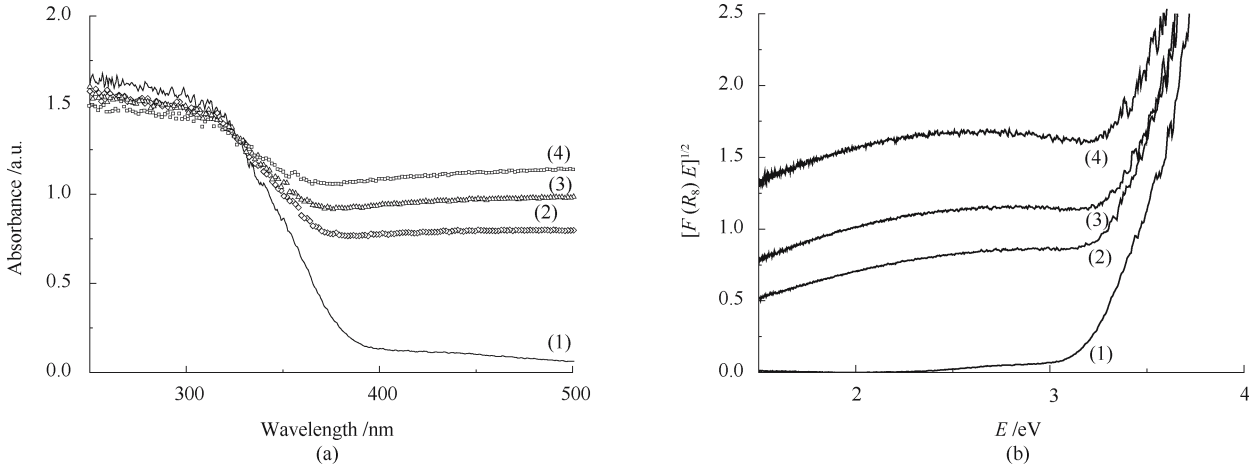

Fig. 5 UV-Vis diffuse reflectance spectra of different samples (a) and plot of transformed Kubelka–Munk function versus the energy of the light absorbed (b) : (1) pure titania, (2) CCT005, (3) CCT01 and (4) CCT02

The photosensitization pathway of dyes under visible light has been characterized as

$$\text{dye} + h\nu \rightarrow \text{dye}^* \quad (5)$$

$$\text{dye}^*_{\text{ads}} + \text{TiO}_2 \rightarrow \text{dye}^+_{\text{ads}} + \text{TiO}_2(e^{-1}) \quad (6)$$

$$\text{dye}^+_{\text{ads}} \xrightarrow{h^+, \cdot OH, \cdot O_2^-} CO_2 + H_2O + \text{mineral acids} \quad (7)$$

In our previous work [7], it has been proved that under visible light illumination, MB was photocatalytically degraded rather than simply photobleached over C/TiO_2 composites. In the present paper, MB and RB were both photocatalytically degraded over the three tested CCT samples, but their activity order was different from that under UV light. For MB, the order is CCT005 > CCT02 > CCT01, while it is CCT005 > CCT02 ≈ CCT01 for RB. It is worth noting that these three samples show similar photocatalytic activity order for different pollutants (MB or RB), which is different from that under UV light. This might result from the difference in absorption of catalysts for visible light and UV light, which needs further study.

Figure 5(a) shows the UV—Vis diffuse reflectance spectra of C/TiO_2 composites and pure titania. It can be found that the new absorption of CCT005, CCT01, and CCT02 above 400 nm is related to the carbon. Fig. 5(a) can be transformed to plots of the modified Kubelka—Munk function versus the energy of exciting light, as shown in Fig. 5(b), and their absorption edges can be estimated from the tangent lines in the plots. Obviously, with the increase of carbon content, the absorption edge of catalyst red-shifts, making the catalysts responsive to the visible light. Lettmann *et al.* [13] assumed that it was the modified carbon working as a sensitizer. The observed generation of a photocurrent supports an electron transfer from the sensitizer (coke) to the conduction band of the titania, resulting in the catalysts responsive to visible light. Similarly, the carbon materials uniformly covering the titania surface in the as-prepared C/TiO_2 composites might be also considered as a sensitizer.

4 Conclusions

Uniformly carbon-covered titania was prepared via pyrolysis of sucrose monolayer dispersed on the titania surface. For the photocatalytic degradation of MB and RB, the as-prepared composites show higher activity than that of pure titania under UV light illumination. Furthermore, the C/TiO_2 composites show favorable activity under visible light illumination. For different pollutants or illuminating lights, the effect of carbon content is different.

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