

# A new route for preparation of TiO<sub>2</sub>/C hybrids and their photocatalytic properties

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## Abstract

The TiO<sub>2</sub>/C hybrid photocatalysts were prepared by the followed three steps: (i) firstly the copolymer cores with surface rich trimethoxysilyl groups were obtained by the radical precipitation copolymerization of divinylbenzene and a silane coupling agent,  $\gamma$ -methacryloxypropyltrimethoxy silane (KH-570); (ii) secondly, the precursor tetrabutyl titanate were co-hydrolyzed with trimethoxysilyl groups at the surfaces of the copolymer cores; (iii) then the core/shell poly(PDVB)/TiO<sub>2</sub> (PDVB@TiO<sub>2</sub>) hybrids were heat-treated to the final temperatures of 400, 450, or 500 °C in a furnace under air for certain time and obtained TiO<sub>2</sub>/C hybrids with different carbon contents. The photocatalysts developed were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), elemental analysis, Brunauer–Emmett–Teller (BET), and UV–vis adsorption spectroscopy. It was found that the substrate carbon was in insignificant amount in the hybrids, but this amount was enough to support TiO<sub>2</sub> photocatalysts. Their adsorptivity and photoactivity properties were evaluated separately by the measurement of relative concentration of Methylene Blue (MB) remained in the solution either in darkness or under UV irradiation, respectively. The present catalysts show high adsorptivity and high photoactivity for the degradation of MB and can be very easily separated from the solution by sedimentation or simple filtration and it can be used repeatedly for MB removal with preservation of its photoactivity.

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**Keywords:** Carbon; TiO<sub>2</sub>; Photocatalyst; TEM; Catalytic properties

## 1. Introduction

As one of the most promising candidate photocatalyst of the application for photocatalysis in environmental protection and water treatment, nano-titania in its anatase crystallographic form has attracted great attention of scientists and engineers from the view point of practical applications because of its high stability against photocorrosion, high photocatalytic activity, low cost, and its environmental non-toxicity [1]. However, the low abilities of TiO<sub>2</sub> for adsorption of organic compounds caused low photocatalytic efficiency when it is used for very low concentration of organic pollutant in water for the lower collision probability of the pollutant with TiO<sub>2</sub>. Moreover, high cost and time consuming for the particle-fluid separation after radiation treatment for the reuse of the catalyst restrained its industrial applications [2]. So, development of

TiO<sub>2</sub> photocatalysts immobilized on a certain suitable adsorbent such as activated carbon, by which dilute polluted substances could be condensed, would be of great significance, not only to avoid the disadvantages of filtration of fine photocatalyst particles, but to lead to high photodecomposition efficiency [3–7].

The composites of titania and carbon can be prepared by the following three main ways: mounted titania on activated carbon, carbon coating the surface of TiO<sub>2</sub> particles, or carbon-doped TiO<sub>2</sub>. TiO<sub>2</sub>-mounted activated carbon has been studied and some success was obtained for the coupling of the photoactivity of anatase-type TiO<sub>2</sub> with the adsorptivity of activated carbon [8–17]. It has some benefits such as improving the crystalline structure of TiO<sub>2</sub> catalyst by using higher temperature of heat treatment and selection of the proper carbon precursor for carbonization. The adsorbent carbon should have high adsorbabilities for the substances of target but the diffusion of adsorbed substrates should not be seriously hindered.

Carbon-coated TiO<sub>2</sub> can be prepared by the heat treatment of powder mixtures of photocatalyst TiO<sub>2</sub> with different carbon

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precursors, such as poly(vinyl chloride), poly(vinyl alcohol), hydroxypropyl cellulose, and poly(ethylene terephthalate), at a high temperature from 500 to 1100 °C in inert atmosphere [10,18–23], pyrolysis of sucrose highly dispersed on the surface of titania in flowing N<sub>2</sub> [24] or heating at the high temperatures of titanium dioxide in an atmosphere of gaseous *n*-hexane [25]. Carbon coating of the photocatalysts had some advantages, such as the suppression of the phase transition to rutile and high adsorptivity, but also some disadvantages, such as a reduction in the amount of UV rays reaching the anatase surface. The most important is to get the balance among these factors in order to give a high performance of the catalysts, high photoactivity, and high adsorptivity.

Carbon-doped TiO<sub>2</sub> was fabricated by oxidative annealing of TiC [26], hydrolysis of titanium tetrachloride with tetrabutylammonium hydroxide followed by calcination at 400–550 °C for certain time [27] or carbonization of K-contained anatase under a flow of cyclohexane [28]. The most important property of these samples was they have visible-light sensitivity.

Compared with the reported works, in which the carbonizations were undertaken at 700–1100 °C for a long time in inert gas atmospheres, a novel process was developed for the preparation of the TiO<sub>2</sub>/C hybrid photocatalysts in the present work. The ready-made core/shell PDVB@TiO<sub>2</sub> microspheres were used as the precursors and carbonized at lower temperatures for shorter time in air. The TiO<sub>2</sub>/C hybrids were applied for the decomposition of MB in water. Adsorptions of MB by TiO<sub>2</sub>/C hybrid photocatalysts were quantitatively evaluated. Rate constants for the photodecomposition reaction of MB in water on anatase particles were determined in order to compare the photoactivity of the samples. The separation and reuse of the photocatalyst were also investigated.

## 2. Experimental

### 2.1. Materials

Divinylbenzene (DVB) (chemical purity, China Medicine (Group), Shanghai Chemical Reagent Corporation, China) was washed with 1 mol L<sup>-1</sup> NaOH and water to remove polymerization inhibitors and then purified by reduced pressure distillation and dried with anhydrous sodium sulfate before use. Silane coupling agent used,  $\gamma$ -methacryloxypropyltrimethoxy silane (KH-570), is an industrial product purchased from Gaizhou Chemical Industrial Co. Ltd., Liaoning, China, and used without any pre-treatment. Reagent grade 2,2'-azobisisobutyronitrile (AIBN) was purified by re-crystallization from methanol before use. Tetrabutyl titanate (TBOT, chemical purity, Shanghai Shanaishi Reagent Company) was used without any pre-treatment. Methylene blue (MB, C<sub>16</sub>H<sub>18</sub>N<sub>3</sub>S) is the reagent grade (Shanghai Chemical Reagent Factory) and used as received. A commercial TiO<sub>2</sub>, HR-3 (Mingri Nano-material Industrial Co. Ltd., Zhejiang, China), in anatase crystalline, with a diameter of 5–10 nm and surface area of 210 m<sup>2</sup> g<sup>-1</sup>, was used for the comparison of the photodegradation properties. All other reagents were of analytical grade, and the distilled water is used throughout.

### 2.2. Preparation of TiO<sub>2</sub>/C photocatalysts

The PDVB@TiO<sub>2</sub> hybrids were prepared as follows: The radical precipitation copolymerization was carried out in a three-necked, round-bottom flask fitted with a stirrer, condenser, and nitrogen inlet tube. Seven millilitre DVB, 3 mL KH-570, 0.15 g AIBN, and 150 mL absolute ethanol were mixed into the flask and the solution was purged with nitrogen in order to eliminate the inhibition effect of oxygen before the polymerization. Then the solution was heated to 70 °C and the polymerization was continued for 8 h under a nitrogen atmosphere. After cooling to room temperature, the copolymer microspheres were filtered with filter paper and the microspheres were washed several times with absolute ethanol and dried in vacuum oven.

Fifty millilitre ethanol solution of tetrabutyl titanate (containing 3 mL TBOT) was dropped into 50 mL ethanol suspension of the 3.0 g copolymer microspheres under ultrasonic agitation. The trimethoxysilyl groups on the surface of the microspheres were co-hydrolyzed with TBOT by the addition of distilled water. The microspheres were filtered and washed several times with ethanol and distilled water under ultrasonic agitation. Purified microspheres were dried in a vacuum oven at room temperature.

PDVB@TiO<sub>2</sub> microspheres were heated in Programmable Muffle Furnce (750-58, Fisher Scientific Co., USA) in air. The heating temperature was rising gradually to the final temperature of 400, 450, or 500 °C, respectively. The samples were kept at the final temperature for 2 h. The photocatalysts were assigned as TiO<sub>2</sub>/C 400, TiO<sub>2</sub>/C 450, and TiO<sub>2</sub>/C 500, respectively. For comparison, TiO<sub>2</sub> was also prepared following the same precipitation procedure but in the absence of PDVB and was heated to a final temperature of 450 °C for 2 h. The neat titania catalyst was assigned as TiO<sub>2</sub> 450.

### 2.3. Instruments and analytical methods

X-ray diffraction (XRD) was used for identification of the crystalline phases of TiO<sub>2</sub>. The XRD patterns were recorded in the range of  $2\theta = 10\text{--}100^\circ$  by step scanning with an X-ray diffractometer (XRD-6000, Shimadzu Corporation, Japan). Nickel-filter Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm) was used with a generator voltage of 40 kV and a current of 30 mA. Scherrer's equation was used to calculate the particles size of titanium dioxide crystal:

$$D = \frac{\kappa\lambda}{\beta \cos \theta}$$

where  $D$  is crystallite particle size,  $\kappa$  the constant of 0.89,  $\lambda$  the X-ray wavelength (0.15418 nm),  $\beta$  the half maximum line breadth, and  $\theta$  is Bragg angle.

The Brunauer–Emmett–Teller (BET) surface areas ( $S_{\text{BET}}$ ) of the powders samples were determined by nitrogen adsorption–desorption isotherm measurements at 77 K on a Micromeritics ASAP 2010 (USA) Area and Porosimetry Accelerated Surface System. All the samples measured were degassed at 180 °C before the actual measurements. Pore volumes were

determined using the cumulative adsorption of nitrogen by the BjH method.

The surface morphologies of TiO<sub>2</sub>/C photocatalysts were observed using scanning electron microscopy (SEM) (XL-20, Philips Corporation, The Netherlands), operating at 25 kV. For transmission electron microscopy (TEM) studies, the samples were suspended in distilled water, dispersed ultrasonically, and a drop of suspension was directly deposited on carbon-coated copper grids. Observations were made with a Hitachi 6000 microscope (Hitachi Corporation, Japan) working at 100 kV. The UV–vis absorption spectra of photocatalysts were measured by the diffuse reflection method using a spectrophotometer (Lambda 35, Perkin-Elmer Corporation, USA) equipped with an integrating sphere (BaSO<sub>4</sub> was used as a reference). The UV–vis absorption spectra of MB solution were also measured with the same instrument. Carbon content on calcined samples was analyzed by means of an elemental analyser Vario EL (Vario Corporation, Germany).

#### 2.4. Adsorption and photocatalytic degradation experiments

The photocatalytic activities of the TiO<sub>2</sub>/C photocatalysts were studied by the degradation experiments using MB dye as a model compound, because it has good resistance to light degradation and a well defined optical absorption maximum in the visible region. The experiment of photocatalytic reaction was conducted in a cubage 150 mL, cylindrical glass vessel surrounded with water-jacket to maintain the reaction temperature at ambient temperature of near 20 °C. Illuminating UV light source was supplied by a 300 W high-pressure mercury lamp 25 cm high over the solution (qe6, λ<sub>max</sub> = 365 nm, Osram Corporation, Germany). In each experiment, the catalyst of 0.100 g was placed into 100 mL of MB solution with concentration of 0.050 g L<sup>-1</sup>. MB was adsorbed on the catalyst surface without UV irradiation (in the darkness). Adsorption equilibrium for MB was established within 1.5 h and the adsorbed amount of MB on the catalyst (adsorption capacity, in mass%) was determined from the measurement of MB concentration before and after adsorption. After saturation of adsorption into catalysts UV lamp was switched on, and the decomposition of MB was followed by measuring the absorbance of the solution as a function of UV irradiation time. The changes of MB concentration with the illumination time were monitored by measuring the absorbance at 650 nm using a previously established calibration graph.

#### 2.5. Determination of decantability of the prepared photocatalysts

Certain amount (about 0.1 g) photocatalyst was dispersed in 100 mL of H<sub>2</sub>O and the suspension was irradiated with ultrasonic for 2 h, after then allowed to stand at room temperature. After a definite time, 5.0 mL of dispersion liquid was taken out with a pipet, and the photocatalyst dispersed was determined. The decantability of photocatalyst was estimated from the stability of the dispersion:

$$\text{Stability (\%)} = \frac{A}{B} \times 100$$

where *A* is the photocatalyst remained in the dispersed phase after standing (g), and *B* is photocatalyst added (g).

### 3. Results and discussion

#### 3.1. Structure and morphology of TiO<sub>2</sub>/C photocatalysts

DVB was selected as the main monomer to obtain the cross-linked polymer core and the silane couple agent (KH-570) was selected as the second monomer for the aim of the chemically link between the hydrophobic polymer core with the hydrophilic TiO<sub>2</sub> shell via copolymerization and co-hydrolysis. The preparation process to the core/shell anatase TiO<sub>2</sub> encapsulated poly(divinylbenzene) (PDVB@TiO<sub>2</sub>) microspheres was conducted by the following two steps. In the first step, the DVB and the C=C bonds of the silane couple agent were radical precipitation copolymerized in ethanol system. So the copolymer particles with most of the polar groups (trimethoxysilyl groups) on their surfaces were achieved. In the second step, the surface trimethoxysilyl groups were co-hydrolyzed with TBOT to form the amorphous TiO<sub>2</sub> shell.

Generally, amorphous titania usually changes to anatase crystallographic form after calcinations at temperatures >400 °C. However, the carbon element might be eliminated completely at the temperatures >500 °C. So 400, 450, and 500 °C were chosen as the carbonizing temperatures. The characteristics of the TiO<sub>2</sub>/C photocatalysts were summarized in Table 1. Upon calcination at 500 °C, all samples present one crystalline anatase phase observed by XRD (Fig. 1). With the increase of calcinations temperatures from 400 to 500 °C, diffraction peaks get sharper which indicate that the improvement in crystallinity of anatase type structure. The mean crystallite size of the anatase for TiO<sub>2</sub>/C photocatalysts calculated by using the Scherrer equation was also shown in Table 1. It was worth

Table 1  
Characteristics of photocatalysts prepared in the present work

Sample code	Calcinations temperature (°C)	Carbon content (%)	Color of catalysts	Mean size (nm) <sup>a</sup>	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	V <sub>p</sub> (cm <sup>3</sup> g <sup>-1</sup> )
TiO <sub>2</sub> /C 400	400	5.33	Black	–	89.79	0.27
TiO <sub>2</sub> /C 450	450	1.56	Gray	6.6	105.88	0.36
TiO <sub>2</sub> /C 500	500	0.66	Light gray	8.3	112.90	0.35
TiO <sub>2</sub> 450	450	0	White	9.1	33.56	0.12

<sup>a</sup> Calculated from the XRD results.

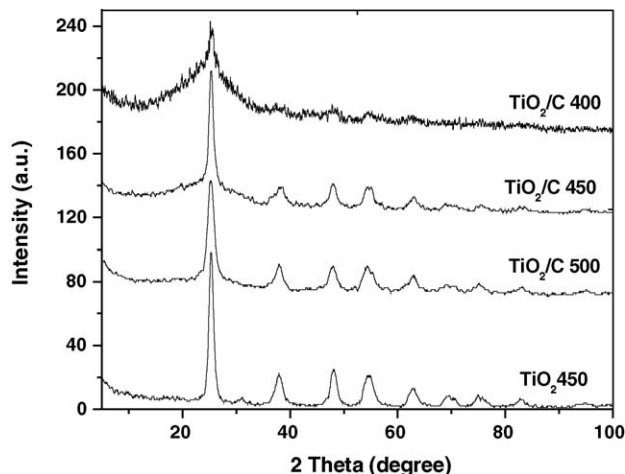


Fig. 1. XRD patterns of photocatalysts prepared at different calcinations temperatures.

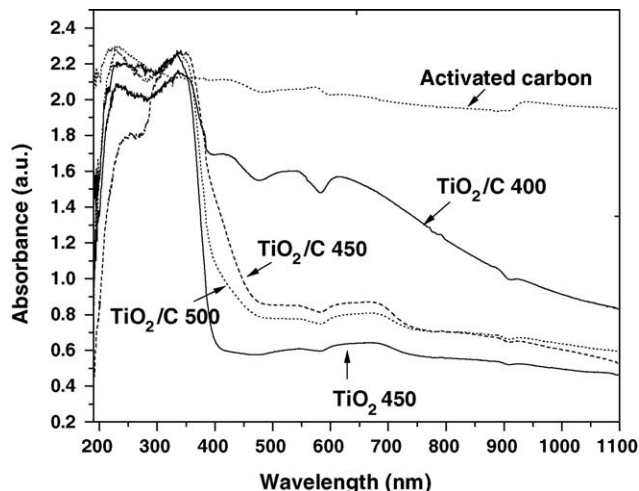


Fig. 2. UV-vis spectra of photocatalysts calcined at different temperatures.

noting that the mean crystallite size calculated seems to be related with the preparation procedure. The results indicated with the increase of calcination temperature, the size of anatase increased.  $\text{TiO}_2$  450 obtained in the absence of carbon present a mean crystallite size of 9.1 nm. On the other hand,  $\text{TiO}_2/\text{C}$  450 and  $\text{TiO}_2/\text{C}$  500 photocatalysts present a little smaller mean crystallite sizes of 6.6 and 8.3 nm separately, even in the higher calcination temperature. It seems that the presence of polymers can restrain the coarsening of grain during calcinations. This is similar to result reported by Colon et al. [30].

Diffuse reflectance spectroscopy gives information about the electronic absorption of the photocatalysts. In Fig. 2, the optical absorption spectra of  $\text{TiO}_2/\text{C}$  400,  $\text{TiO}_2/\text{C}$  450, and  $\text{TiO}_2/\text{C}$

500 are compared with the  $\text{TiO}_2$  450 and carbon powders.  $\text{TiO}_2$  of a single phase of anatase without carbon shows a clear absorption edge at around 360 nm, as reported in many papers on anatase photocatalysts. For carbon-contained photocatalysts, some absorption of visible light is observed. Absorption spectra of carbon-contained photocatalysts may be understood to comprise of overlapping absorption spectrum of carbon and anatase. For  $\text{TiO}_2/\text{C}$  500 photocatalyst, absorption of the visible light is rather small (because of a small amount of carbon), and the absorption edge due to anatase is obviously detected. With higher carbon content in photocatalyst  $\text{TiO}_2/\text{C}$  400, absorption of a visible light due to carbon becomes more pronounced and also the absorption edge due to anatase becomes more ambiguous, but the absorption edge is still observed.

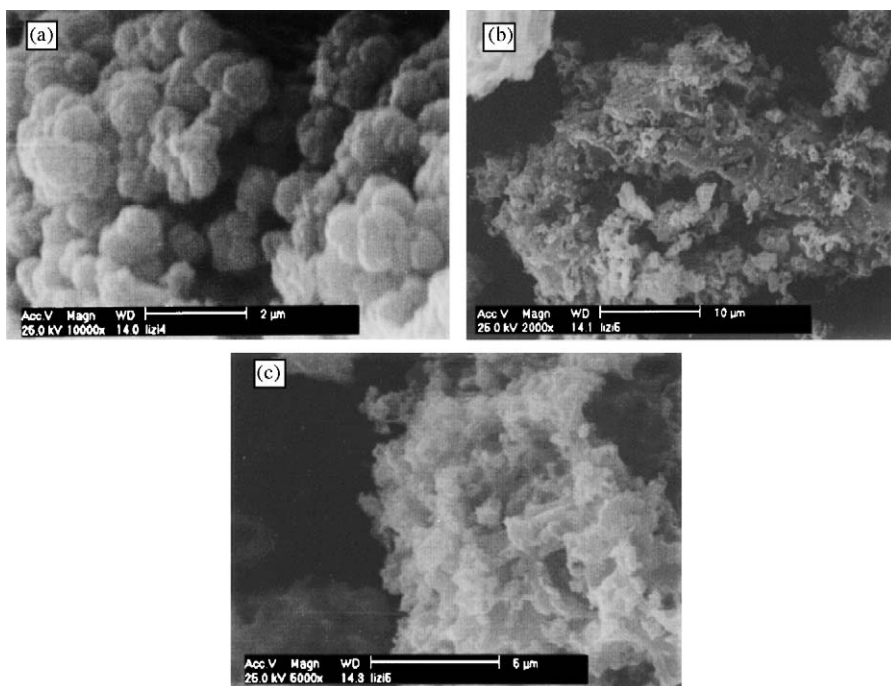


Fig. 3. Selected SEM images of  $\text{TiO}_2/\text{C}$  photocatalysts: (a)  $\text{TiO}_2/\text{C}$  400, (b and c)  $\text{TiO}_2/\text{C}$  500.



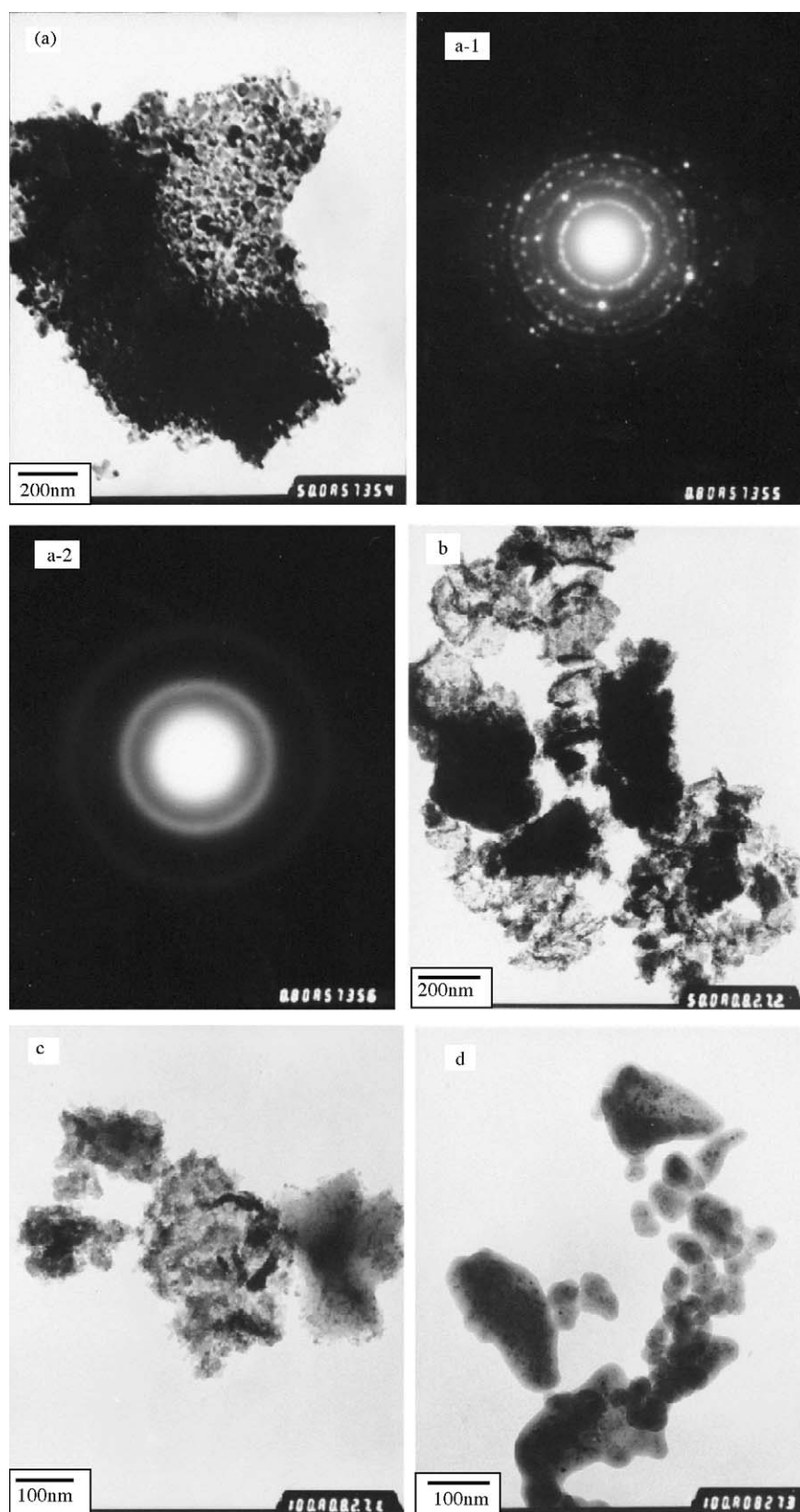


Fig. 4. TEM of  $\text{TiO}_2/\text{C}$  photocatalysts and neat  $\text{TiO}_2$ : (a)  $\text{TiO}_2/\text{C}$  400 and the corresponding SAED diffraction pattern of  $\text{TiO}_2$  (a-1) and carbon (a-2), (b and c)  $\text{TiO}_2/\text{C}$  450, (d)  $\text{TiO}_2/\text{C}$  500, (e)  $\text{TiO}_2$  400, (f)  $\text{TiO}_2$  450, and (g)  $\text{TiO}_2$  500.

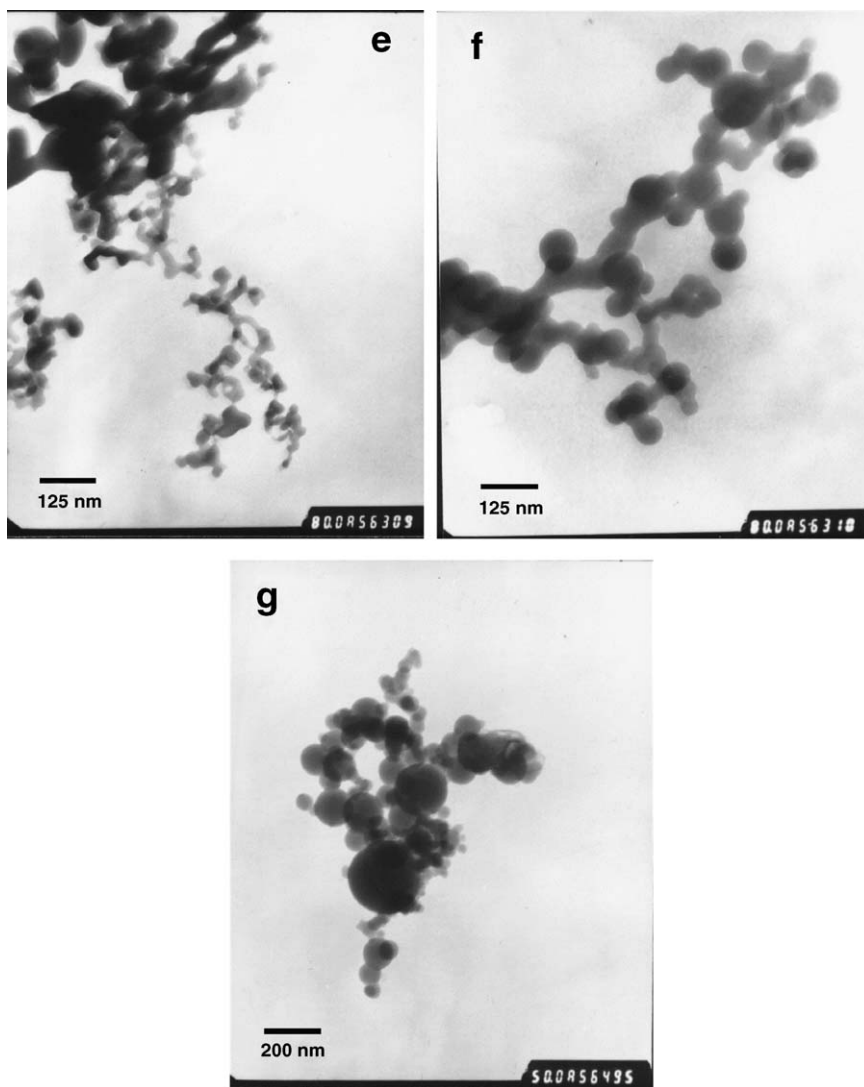


Fig. 4. (Continued).

SEM micrographs of  $\text{TiO}_2/\text{C}$  photocatalysts prepared from different calcination temperatures are shown in Fig. 3. After heat treatment at  $400^\circ\text{C}$ , the size of  $\text{TiO}_2/\text{C}$  400 photocatalyst was about a few hundreds of nanometers and kept mainly in round shell shapes (Fig. 3a). These images indicated that in the preparation procedure, the  $\text{TiO}_2$  was homogeneous deposited on the copolymer particles surface. When the calcinations temperature rose to  $500^\circ\text{C}$ , the surface of the sample  $\text{TiO}_2/\text{C}$  500 became very rough and porous and seemed to be consisted of aggregated  $\text{TiO}_2$  particles because of more elimination of polymer core at higher calcinations temperature (Fig. 3b and c).

For the sample  $\text{TiO}_2/\text{C}$  400, the smaller titania particles were connected by the relative higher content of carbon, so the photocatalyst particles were few hundreds nanometers to several microns (Fig. 4a). The SAED patterns indicated that presence of titania was anatase crystalline phase (Fig. 4a-1), and this is in accordance with the result from the XRD analysis. Moreover, the amorphous carbon was detected as shown by the corresponding SAED patterns (Fig. 4a-2) [29]. With the increase of the calcinations temperatures to 450 (Fig. 4b and c) and  $500^\circ\text{C}$

(Fig. 4d), the photocatalyst particles became smaller for several hundreds nanometers because of the less carbon contents. The TEM images clearly show that the aggregates of nanosized  $\text{TiO}_2$  are stabilized by the presence of carbon. In the  $\text{TiO}_2/\text{C}$  500 photocatalyst, the substrate carbon was in insignificant amount, but this amount was enough to support  $\text{TiO}_2$  photocatalyst. The morphologies of the  $\text{TiO}_2$  400,  $\text{TiO}_2$  450, and  $\text{TiO}_2$  500 prepared without PDVB was about 30–150 nm aggregate spherical particles, which quite different from the morphologies mentioned above (Fig. 4e–g).

### 3.2. Adsorption of Methylene Blue with $\text{TiO}_2/\text{C}$ photocatalysts

The study of MB ( $\text{C}_{16}\text{H}_{18}\text{N}_3\text{S}\cdot 3\text{H}_2\text{O}$ ) adsorption has been performed in darkness at room temperature on  $\text{TiO}_2/\text{C}$  400,  $\text{TiO}_2/\text{C}$  450,  $\text{TiO}_2/\text{C}$  500,  $\text{TiO}_2$  450, and HR-3 commercial  $\text{TiO}_2$ . The HR-3  $\text{TiO}_2$  was selected as the comparison because it has very small sizes about 5–10 nm and a very big surface area. Fig. 5 shows the residual concentration of MB versus its original

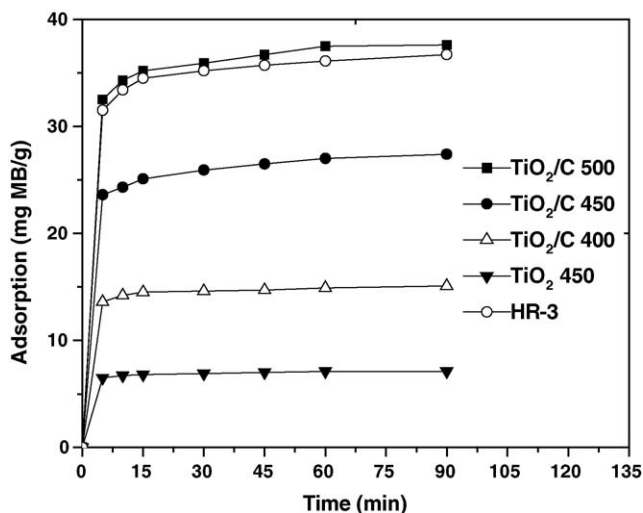


Fig. 5. Adsorption of MB in darkness with time ( $V=100\text{ mL}$ ;  $C_0=50\text{ mg/L}$ ;  $W_c=0.1000\text{ g}$ ).

concentration of  $50\text{ mg L}^{-1}$  as a function of adsorption time over various samples. The pH value of solution was about 7. It can be observed that most of adsorption occurred within 15 min. The equilibrium concentrations were determined using UV–vis spectrophotometer by monitoring MB concentration at wavelength 650 nm. The amounts of MB adsorbed are calculated as follows:

$$n_{(\text{ads})} = \frac{V\Delta C}{W_c} \quad (1)$$

where  $n_{(\text{ads})}$  is the amount of adsorbed MB (mg MB/g),  $\Delta C$  the difference between the initial concentration ( $C_0$ ) and equilibrium concentration ( $C_e$ ),  $V$  the volume (L) of the solution, and  $W_c$  is the weight of catalyst used.

As described in the preparation procedure, the  $\text{TiO}_2$  particles were deposited on the surface of copolymer cores homogeneously and there is an interaction between polymer and titania, the surface area of the PDVB@ $\text{TiO}_2$  particles was low. Upon calcinations, the polymer is eliminated leaving high surface area [29]. BET measurements show the surface areas of the powders increase from  $89.79$  to  $112.90\text{ m}^2\text{ g}^{-1}$  when the calcinations temperatures increase from  $400$  to  $500\text{ }^\circ\text{C}$  (Table 1). According to Fig. 5, the  $n_{(\text{ads})}$  order found for five solids were as follows:  $\text{TiO}_2/\text{C } 500 \approx \text{HR-3} > \text{TiO}_2/\text{C } 450 > \text{TiO}_2/\text{C } 400 > \text{TiO}_2$  450. This result indicated that there is an interaction between carbon and titania. With the increase of the calcinations temperature, the size of the powders get smaller and the surface area increased (see TEM Fig. 4). The  $\text{TiO}_2/\text{C } 500$  sample with higher surface area show higher adsorption capability of MB and this is similar to the result reported by Colon et al. [30].

### 3.3. Kinetics of photocatalytic degradability of MB

Photodegradation of MB was tested over selected samples under UV illumination. The concentration of dye was monitored after 1.5 h magnetically stirring in darkness to secure the establishment of adsorption–desorption equilibrium before

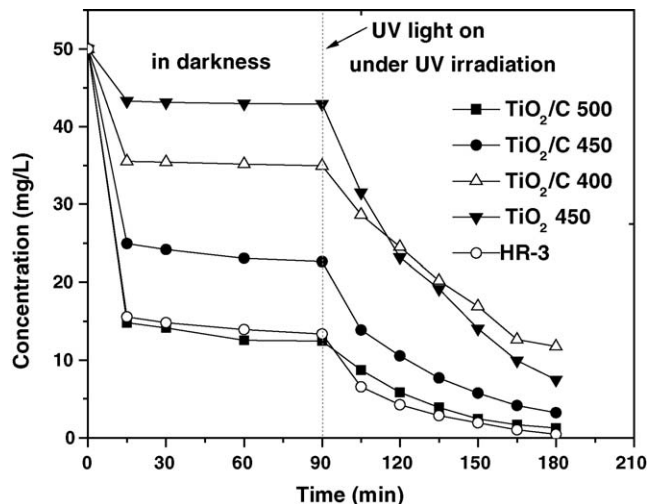


Fig. 6. Kinetics of MB depigmentation in the darkness and photodegradation (under UV) in the presence of different photocatalysts.

photocatalytic experiments. Fig. 6 shows the kinetics of depigmentation, as a function of reaction time, of illuminated MB with an initial concentration of  $0.050\text{ g L}^{-1}$  in presence of different photocatalysts. Direct photolysis without photocatalyst could be neglected with less than 3.2% of the conversion after 8 h of UV irradiation.

The curves in Fig. 6 are of the apparent first order process as confirmed by the linear transforms  $\ln(C_0/C)=f(t)$  as shown in Fig. 7 from which the apparent rate constants can be obtained. The apparent first order rate constants ( $k_{\text{app}}$ ) for the five photocatalysts are presented in Table 2.  $k_{\text{app}}$  has been chosen as the basic kinetic parameter for different systems, since it is independent of used concentration [20,31,32]. As shown in Table 2, the photocatalytic activities for MB photodegradation of  $\text{TiO}_2/\text{C } 500$  determined from the ( $k_{\text{app}}$ ) is higher, compared with the corresponding neat titania, but little lower than that of HR-3. HR-3 that was known to consist of fine powder of  $\text{TiO}_2$  exhibited higher dispersion in the aqueous solution (see decantability

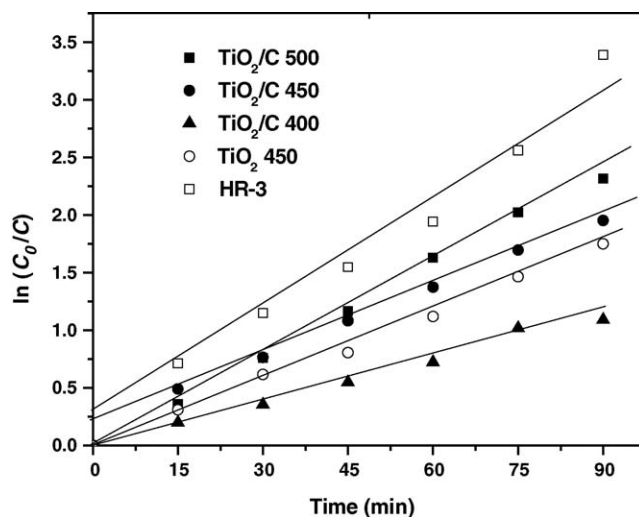


Fig. 7. Logarithmic dependence of the MB depigmentation with the irradiation time on the studied photocatalysts.

Table 2  
The apparent first-order rate constants of MB during UV-light degradation

Catalyst	$k_{app}$ ( $\text{min}^{-1}$ )
TiO <sub>2</sub> /C 400	$1.21 \times 10^{-2}$
TiO <sub>2</sub> /C 450	$1.94 \times 10^{-2}$
TiO <sub>2</sub> /C 500	$2.59 \times 10^{-2}$
TiO <sub>2</sub> 450	$2.03 \times 10^{-2}$
HR-3	$2.88 \times 10^{-2}$

result, Fig. 8) in comparison with the present TiO<sub>2</sub>/C photocatalysts, which was supposed to be one of the reasons for faster decomposition for MB. For the catalysts calcined at 400, 450, and 500 °C, the lower content of carbon in TiO<sub>2</sub>/C catalysts, the higher photocatalytic activity in MB degradation. In all the five samples, TiO<sub>2</sub>/C 400 show lowest activity, this may be caused by the lower crystallization of the titania and perturb of the UV-light transmission to the surface of titania because of the higher carbon content.

### 3.4. Catalyst separation and reuse

As it is well known, one of the main drawbacks of the use of TiO<sub>2</sub> photocatalysis is the catalysts separation from the treated suspension. In this study, it has been observed that the catalysts calcined at 450 and 500 °C with 0.6–1.5% carbon decanted very quickly with regard to the TiO<sub>2</sub> 450 particles and HR-3. Fig. 8 shows the results of a decantability comparative experiment which was estimated from the stability of the dispersion. As Fig. 8 shows, while the TiO<sub>2</sub>/C 500 and TiO<sub>2</sub>/C 450 catalysts are completely decanted after 5 h, the TiO<sub>2</sub> 450 and HR-3 catalysts still remain suspended. The TEM analyses show that these catalysts are formed by denser aggregated that justify their higher decantability (see Fig. 4). The result of certain suspend of TiO<sub>2</sub>/C 400 photocatalyst may be caused by the certain unaggregated particles calcined at lower temperature.

To confirm cyclic usage is possible for the TiO<sub>2</sub>/C photocatalysts, the photocatalyst TiO<sub>2</sub>/C 500 was selected. After

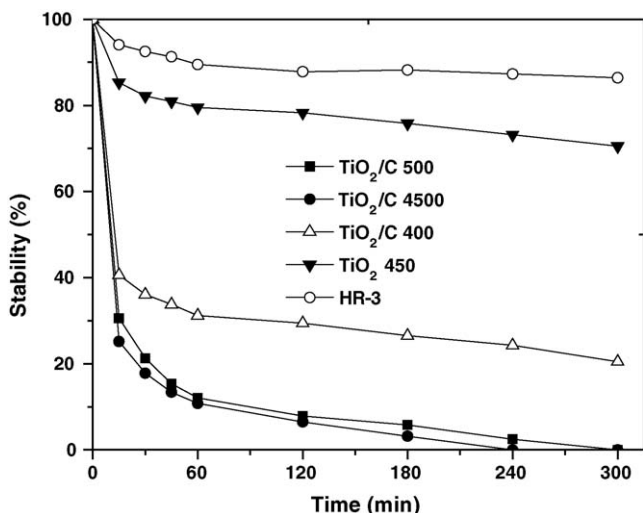


Fig. 8. Decantability of the studied photocatalysts.

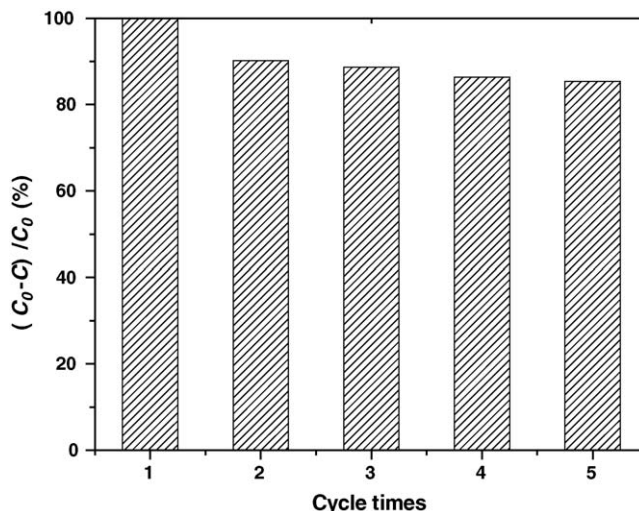


Fig. 9. Changes in relative concentration of MB with cycling operations of photodegradation using TiO<sub>2</sub>/C 500 as photocatalyst.

photodegradation of MB use TiO<sub>2</sub>/C 500 as photocatalyst, the solution was placed for 5 h and the catalyst decant at the bottom of the reactor, decanted the above clear solution very carefully and the catalyst was used for the degradation of fresh samples of MB under the same conditions. The change in relative concentration of MB with cycling operation with the same UV irradiation times are shown in Fig. 9.

The photocatalytic reactivity of the present photocatalyst is just slightly reduced in stirred aqueous solution, indicating that cyclic usage of the photocatalyst is possible and its stability in treating polluted water is satisfactory. At the same time, it also proves that the final removal of MB from the solution is caused by the photocatalytic degradation other than the adsorption process that will lead to saturated adsorption of MB on the photocatalyst.

## 4. Conclusions

A novel process has been developed for the preparation of TiO<sub>2</sub>/C hybrid photocatalysts via the calcination of the ready-made core/shell PDVB@TiO<sub>2</sub> microspheres to the final temperature of 400, 450, or 500 °C in a furnace under air for certain time. For model pollutants, Methylene Blue, the comparative experiments indicated that the developed photocatalysts TiO<sub>2</sub>/C 500 exhibited much higher adsorption capacity and photocatalytic activity than the neat TiO<sub>2</sub> prepared with the same condition.

One of the most important features of the resulting catalysts calcined at 450 and 500 °C is their fast decantability for comparison with that of neat TiO<sub>2</sub>. Interesting aggregates of nanosized TiO<sub>2</sub> are observed from TEM images stabilized by the presence of carbon. So the separation of the catalysts from solutions, one of the most important drawbacks of photocatalysis, was overcome by simple sedimentation and decantation. In particular, the typical features of the photocatalyst would make it very suitable for configurations and efficient photoreactor for purification of polluted water.



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