

A low temperature preparation and photocatalytical activities of PDVB@TiO₂ hybrid microspheres

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Abstract The core/shell anatase TiO₂ encapsulated poly(divinylbenzene) (PDVB@TiO₂) hybrid microspheres were prepared by the two steps: (1) the copolymer particles (PDVB) were prepared by the radical precipitation copolymerization of divinylbenzene (DVB) and γ -[(methacryloxy)propyl]trimethoxysilane (KH-570); (2) tetrabutyl titanate (TBOT) was co-hydrolyzed with the trimethoxysilyl groups on the surfaces of the PDVB cores and then the amorphous TiO₂ shell obtained was phase transformed to anatase TiO₂ by acid peptization. The products were characterized by FT-IR, UV-vis, scanning electron microscopy (SEM), X-ray diffraction (XRD) and thermal gravimetric analysis (TGA). Their photocatalytical activities were measured by the photo-degradation of methylene blue (MB). The polymer supported TiO₂ photocatalysts prepared at low temperature, had better repetition because of the coupled action of KH-570 between the PDVB core and TiO₂ shell. Furthermore, it could be easily separated from the solution by simple sedimentation.

Introduction

TiO₂ nano-semiconductor catalyst has been attracted a great deal of attention for its potential application in

decomposition of various environmental pollutants in both gaseous and liquid phase [1–3]. It is generally accepted that anatase is the most active photocatalyst among the three common polymorphs—anatase, rutile and brookite [4]. Under UV irradiation of photon energy greater than or equal to TiO₂ band gap energy ($h\nu > 3.2$ eV, i.e., $\lambda < 380$ nm), electron-hole pairs are formed, which once dissociated, generate free photoelectrons and holes able to interact with organic matter present at a TiO₂ particle surface. Thus, through a complex multi-step heterogeneous photocatalytic process, an oxidative decomposition of organic molecules can be induced. The photocatalytic degradation of various toxic compounds in aqueous solutions using TiO₂ nanoparticles under UV irradiation have been widely investigated [5]. Although high photoreaction interfacial area was obtained between reactants and TiO₂ particles, it was big problem how to effectively separate TiO₂ nanoparticles from aqueous solution in order to reuse the photocatalysts.

For the simple separation of the photocatalysts, the polymeric materials had been selected as the supports because of their better processing property. The photocatalysts supported by polymeric materials could be prepared by the two main processes. The amorphous titania is adsorbed onto the polymeric supports and then the phase transformation from the amorphous titania to anatase titania is carried out at a low temperature because the polymeric supports are poor heat-resistant [6–10]. And in the other process, the anatase readymade in titania sol is adsorbed on the polymeric supports directly [11–16]. In the reported photocatalysts supported by polymeric materials, prepared by the two processes above-mentioned, there is no chemical bond between the polymeric supports and

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the anatase titania. So the repetition properties might poor. It is doubted that the photo-degradation of the polymeric supports might happened in the process of the photo-degradation of the pollutants.

In this paper, the PDVB@TiO₂ photocatalyst, the anatase titania shell chemically bonded with the polymer core, had successfully prepared by the controlled co-hydrolysis of tetrabutyl titanate (TBOT) and the trimethoxysilyl groups on the surface of the polymer core in ethanol solution and then acid peptization. The photocatalytical activity of the PDVB@TiO₂ microspheres prepared was investigated for the photo-degradation of methylene blue (MB) in a suspension system.

Experimental

Materials

Divinylbenzene (DVB) (chemical purity, China Medicine (Group) Shanghai Chemical Reagent Corporation, China) was washed with 1 N 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, γ -[(methacryloxy)propyl]trimethoxysilane (KH-570), is industrial products purchased from Gaizhou Chemical Industrial Co. Ltd., Liaoning, China. Reagent grade 2, 2'-azobisisobutyronitrile (AIBN), was purified by recrystallization from methanol before use. TBOT (chemical purity, Shanghai Shanaishi Reagent Company) and methylene blue (MB, C₁₆H₁₈N₃S, reagent grade, Shanghai Chemical Reagent Factory) were used without any treatment. All other reagents were analytical grade and were used as received, and the distilled water is used throughout.

Preparation of copolymer cores

The radical precipitation copolymerization was carried out in a three-necked, round-bottom flask fitted with a stirrer, condenser, and nitrogen inlet tube. 7 ml DVB, 3 ml KH-570, 0.15 g AIBN and 150 ml 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 was initiated. Then the solution was heated to 70 °C with water bath and the polymerization was continued for 8 h under a nitrogen atmosphere. After cooling to room temperature, the copolymer cores were filtered with filter paper and the microspheres were washed several times with absolute ethanol and dried in vacuum oven.

Encapsulation of the cores with titania

3 ml TBOT was added into 50 ml ethanol with the help of ultrasonic agitation, and then dropped into the 50 ml ethanol suspension of the 3.0 g copolymer cores under ultrasonic treatment. Distilled water was added dropwise for controlled co-hydrolysis of TBOT and the trimethoxysilyl groups with vibration. After that, the solution was adjusted to pH 1.5 with 10% HCl, and heated to 80 °C for 8 h with stirring. The amorphous titania could be rearranged to form crystalline particles during the peptizing procedure. The microspheres were filtered and washed several times with ethanol and distilled water. Purified microspheres were dried in a vacuum oven at room temperature. The preparation process to the core/shell anatase TiO₂ encapsulated poly(divinylbenzene) (PDVB@TiO₂) could be schematically shown as Scheme 1.

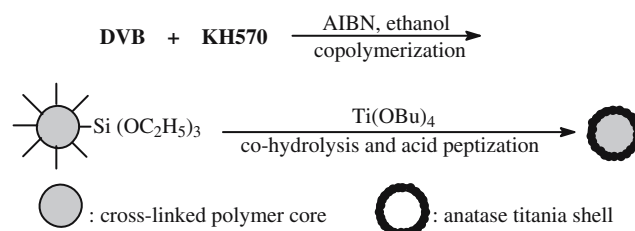
Instruments and analytical methods

X-ray diffraction (XRD) was used for identification of the crystalline phases of TiO₂. 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 α 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, κ is a constant of 0.89, λ is X-ray wavelength (0.15418 nm), β is half maximum line breadth, and θ is Bragg angle.

The surface morphologies of the copolymer cores and the PDVB@TiO₂ microspheres were observed using scanning electron microscopy (SEM) (XL-20, Philips Corporation, the Netherlands), operating at a 25 kV. The UV-vis absorption spectra of the copolymer cores and PDVB@TiO₂ microspheres were



Scheme 1 The preparation process to the PDVB@TiO₂ hybrid microspheres

measured by the diffuse reflection method using a spectrophotometer equipped with an integrating sphere (Lambda 35, Perkin-Elmer Corporation, USA), and BaSO₄ were used as a reference material. The UV–vis absorption spectra of MB solution were also measured with the same instrument. The chemical composition and structure of the copolymer cores, the PDVB@TiO₂ microspheres were analyzed with a Nicolet Avatar 360 FT-IR spectrometer (Nicolet Corporation, USA). Thermal Gravimetric Analysis (TGA) was carried out starting from room temperature up to 800 °C (heating rate 10 °C/min), under nitrogen atmosphere using ZRY-2P instrument (Shanghai Analytical Instrument Factory, China).

Photocatalytic experiment

The photocatalytic activities of prepared PDVB@TiO₂ microspheres were studied by the degradation experiments using MB dye as a model compound, because it has strong adsorption characteristics on many surfaces, good resistance to light degradation and a well defined optical absorption maximum in the visible region [17]. 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. The prepared PDVB@TiO₂ was acted as photocatalyst and UV light was supplied by a 300 W high-pressure mercury lamp (qe6, λ_{max} = 365 nm, Osram Corporation, Germany) as illuminating light source. 100 ml of the MB solution with an initial concentration (C₀) of 20 mg/l in the presence of 200 mg prepared PDVB@TiO₂ microspheres were illuminated with the high-pressure mercury lamp 25 cm high over the solution. The air was bubbled during the reaction. The changes of MB concentration with the illumination time were monitored by measuring the absorbance at 665 nm.

Results and discussion

Preparation of core/shell PDVB@TiO₂ microspheres

DVB was selected as the main monomer to obtain the cross-linked polymer core with better stability. 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 TiO₂ shell via copolymerization and co-hydrolysis. And the introduction of the KH-570 could

lead to another advantage. A SiO₂ layer might be formed between the polymer core and the TiO₂ shell. It could protect the polymer core from photo-degradation [8–10].

The preparation process to the core/shell anatase TiO₂ encapsulated poly (divinylbenzene) (PDVB@TiO₂) microspheres was conducted by the followed two steps as shown in Scheme 1. In the first step, the DVB and the C=C bonds of the silane couple agent were radical precipitation copolymerization in the 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 TiO₂ shell. And then the amorphous TiO₂ shell was phase transformed to anatase TiO₂ shell by acid peptization.

The adsorption bands at about 1724 cm⁻¹ of carbonyl group and 1087 cm⁻¹ of Si–O–C were found in the FT-IR spectrum of the copolymer cores (Fig. 1(a)). And the bands of Ti–O–Ti and Ti–O–Si at 1085 cm⁻¹, and Ti–O at 441 cm⁻¹ were also found in the FT-IR spectrum of the PDVB@TiO₂ microspheres (Fig. 1(b)). And the surface morphologies of the PDVB@TiO₂ microspheres became unshaped and their diameters were increased after the co-hydrolysis reaction with TBOT (Fig. 2).

Figure 3 depicts the thermogravimetric characteristics measured for copolymer cores and the PDVB@TiO₂ microspheres. There is a weight loss of about 2% in the TGA curve of the PDVB@TiO₂ microspheres below 100 °C due to the removal of adsorbed moisture.

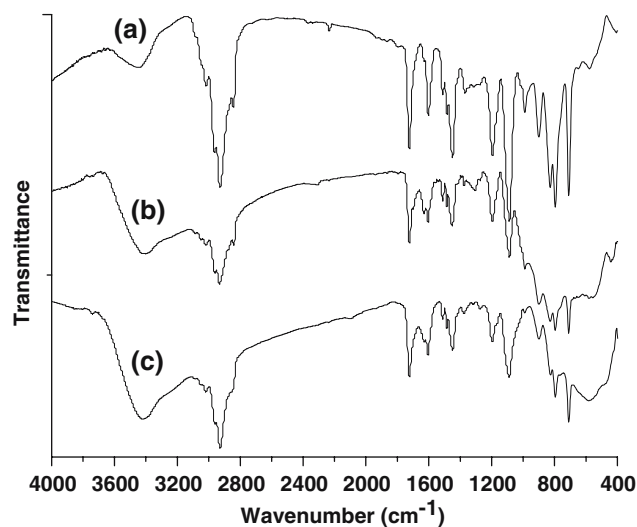


Fig. 1 FT-IR spectra of (a) the copolymer cores, (b) the PDVB@TiO₂ hybrid microspheres, and (c) the PDVB@TiO₂ hybrid microspheres after the tenth photo-degradation under UV irradiation

However, it is not found in the one of the copolymer cores because that its surfaces are hydrophobic before the encapsulation with TiO₂. Obviously, the significant loss of copolymer cores microspheres occurs between 270 °C and 660 °C, and the total weight loss up to 800 °C

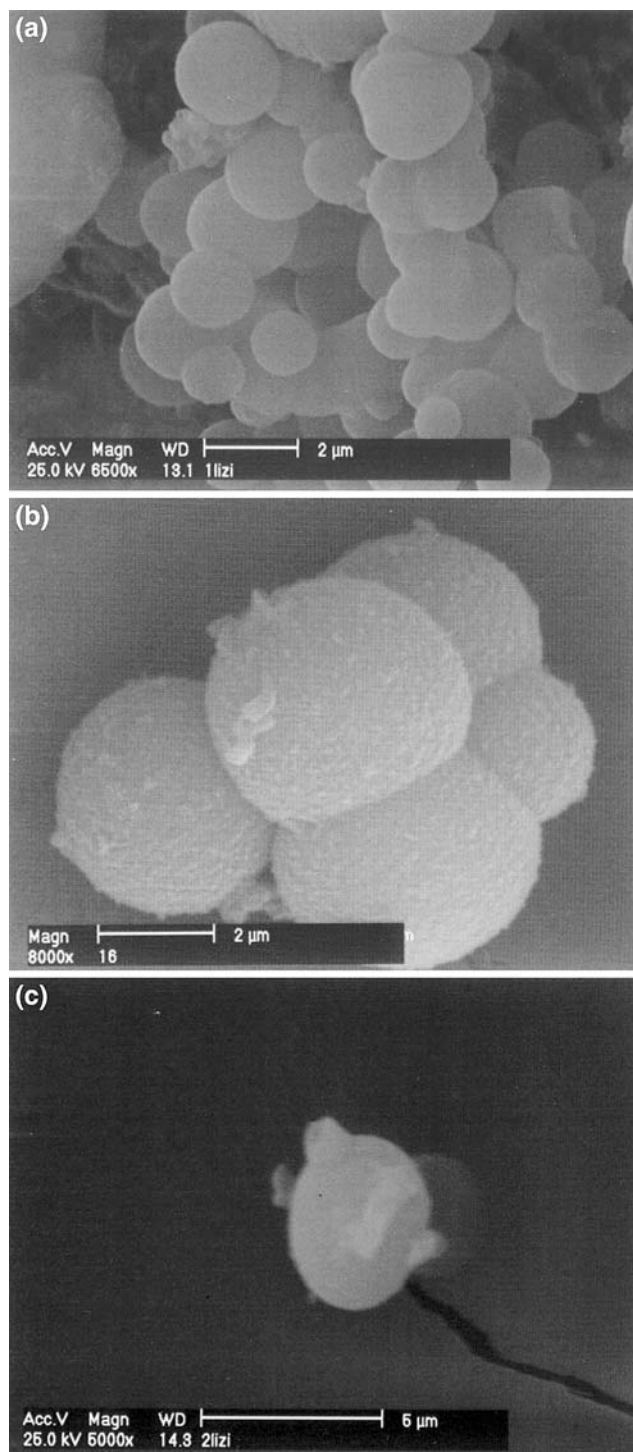


Fig. 2 SEM images of (a) copolymer cores, (b) and (c) PDVB@TiO₂ core-shell microspheres

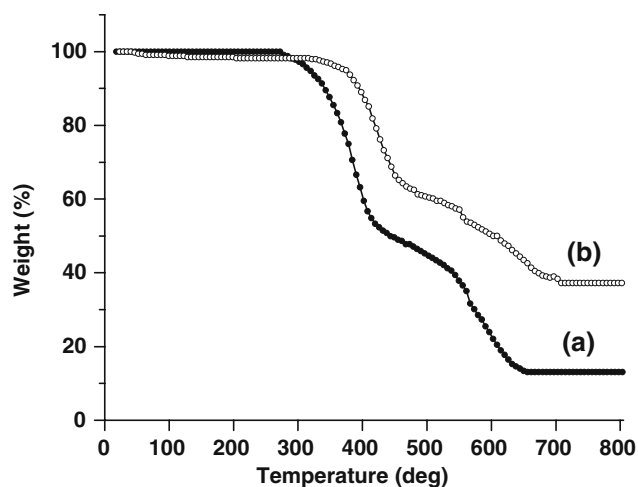


Fig. 3 TGA curves of (a) the copolymer cores, and (b) the PDVB@TiO₂ microspheres

is 86.9%. The residue is carbonized products and SiO₂. As for the PDVB@TiO₂ microspheres, the most significant loss occurs between 400 and 700, and the total weight loss monitored up to 800 °C is 62.8%. The weight loss comprised of the degradation of the polymer and the removal of the structure water of the TiO₂ shell. From the TGA data, we presume that TiO₂ shell had formed and the component of TiO₂ in the microspheres was about 27.7%.

Regarding the titania phase character, amorphous TiO₂ seldom displayed photocatalytic activity. And so, crystal structure of TiO₂ sample greatly affects the photoactivity. The crystalline phase of the titania encapsulated PDVB hybrid microspheres with and without acid peptization was studied by XRD. As shown in Fig. 4, the titania in the titania encapsulated PDVB hybrid microspheres as-prepared before acid peptization was amorphous. However, the XRD pattern indicated that titania in the titania encapsulated PDVB hybrid microspheres after acid peptization were anatase crystal phase due to the presence of attributive peaks ($2\theta = 25.4, 37.7, 47.8, \text{ and } 54.4^\circ$). It was same as that of calcinations at 450 °C for 2 h. It means that fresh prepared amorphous titania could be dissolved as transparent titania gel in stirred acidic solutions, phase transformation from amorphous to anatase structure, which requires commonly high temperature calcinations at least 350 °C, can be achieved by digesting and peptizing treatment of TiO₂ sol at moderate preparation condition [18]. Then after being aged for varying period at a desired temperature, crystalline re-precipitation could occur in solid-liquid interface (the copolymer core surfaces). Very broad diffraction peak at 101 plane ($2\theta = 25.4^\circ$) was due to its small crystalline size of TiO₂ particles.

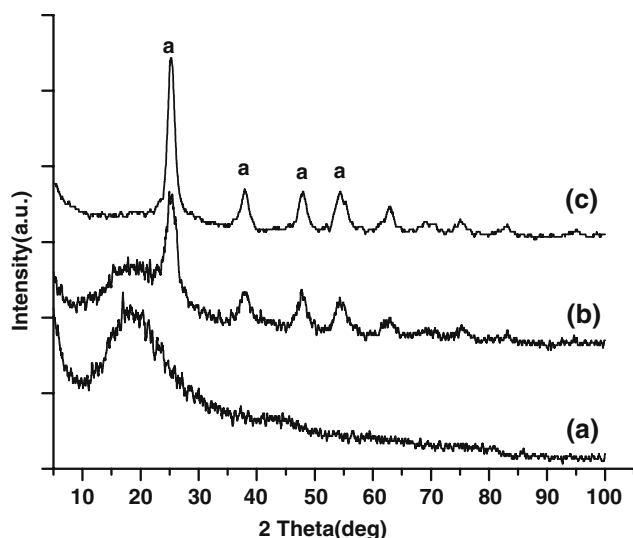


Fig. 4 XRD patterns of (a) amorphous titania encapsulated PDVB as prepared without acid peptized, (b) PDVB@TiO₂ microspheres after acid peptized, and (c) PDVB@TiO₂ microspheres after being sintered at 450 °C for 2 h. All peaks (a) can be assigned to the anatase characteristics of TiO₂

The size of the nanocrystals of anatase titania calculated from Scherrer's equation was about 4 nm. PDVB@TiO₂ samples did not appear any other diffraction peak of new crystal phase apart from anatase.

The UV-vis absorptions of the copolymer cores and PDVB@TiO₂ microspheres were measured in the wavelength range 190–800 nm and the results were shown as Fig. 5. In the visible light region (Wavelength > 400 nm), the adsorption of the PDVB@TiO₂ microspheres was a little lower than that of the bare copolymer cores. However, in the UV light region, the

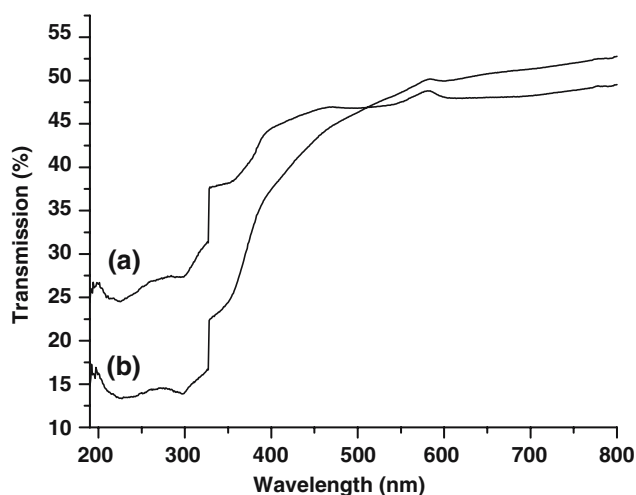


Fig. 5 UV-vis spectra of (a) the copolymer cores, and (b) the PDVB@TiO₂ microspheres

PDVB@TiO₂ microspheres showed much higher adsorptions, and it revealed that the anatase titania shell produced a high UV adsorption. This means the PDVB@TiO₂ microspheres prepared with the proposed method would be a candidate photocatalyst because there is a corresponding relation between the absorption intensity of UV radiation and the activity of the catalysts [19]. The stronger the UV absorption intensity, the higher the activity, where the stronger absorption intensity implied that more electrons could be promoted from the valence band into the conduction band and more separate electrons or holes could be produced, which will help to hence the photocatalytic activity.

Photocatalytic activity of the PDVB@TiO₂ microspheres

Photocatalytic activities of the samples were determined by MB decomposition in water under UV irradiation. Blue color of the solution was faded off with time due to the adsorption and decomposition of MB. Fading speed of color was followed by sampling about 2 ml of the solution at appropriate interval and by measuring the absorbance at a wavelength of 665 nm which was attributed to MB by using a calibration curve. In order to distinguish the adsorption and degradation of MB, the experiments were carried out with and without UV irradiation respectively. The photolysis effect of MB under UV irradiation was also checked without catalyst. The results were shown in Fig. 6. It was found that the concentration of MB in the

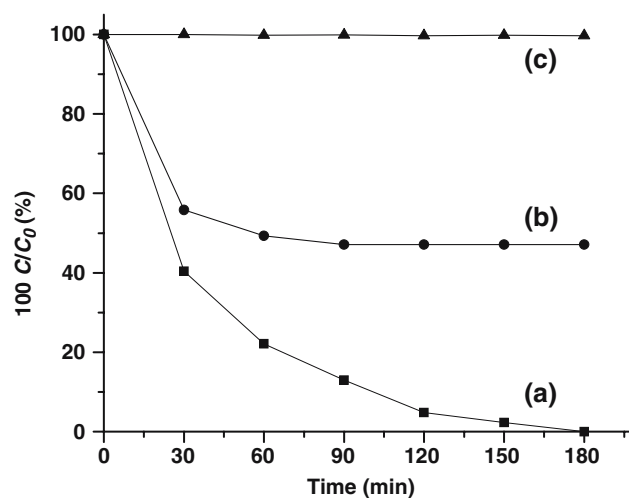


Fig. 6 Effect of the UV irradiation on the adsorption and/or photo-degradations of MB: (a) PDVB@TiO₂ with UV irradiation, (b) PDVB@TiO₂ without UV irradiation, and (c) UV irradiation without photocatalyst

glass vessel without the photocatalysts hardly decreased during the UV irradiation as the blank test and the direct decomposition of MB due to UV light can be negligible. The MB fading of aqueous solution with the PDVB@TiO₂ photocatalysts without UV irradiation was lead from the adsorption of MB on the catalysts and the adsorption reached saturate in 90 min. However, MB had been absolutely degraded under UV irradiation with the photocatalysts in 3 h (Fig. 6(a)).

The variation of UV-vis absorption spectra of MB aqueous solution containing PDVB@TiO₂ photocatalysts under UV irradiation was shown in Fig. 7. The absorption bands at ca. 290 and 665 nm are observed in the spectrum before UV irradiation and both of them decreased with UV irradiation. It typically indicated that MB is decomposed by the photocatalytic reaction with the PDVB@TiO₂ photocatalyst.

To confirm the cyclic usage of the PDVB@TiO₂ photocatalyst, the photo-degradation experiment of MB was repeated for ten times, and the result was shown as Fig. 8. It was found that the photocatalytic activity of the PDVB@TiO₂ photocatalysts kept above 90% of those as prepared and there was no significant loss of the photocatalytic activity after ten times used. It indicated that anatase TiO₂ supported on copolymer core was not easily detached and the adhesion between titania and the copolymer core was good. This is considered to be due to the coupled action of KH-570 between the copolymer core and TiO₂ shell. Moreover, the silica under-layer produced by the hydrolysis of KH-570 acted as a protective coating against the photocatalytic degradation of the copolymer core.

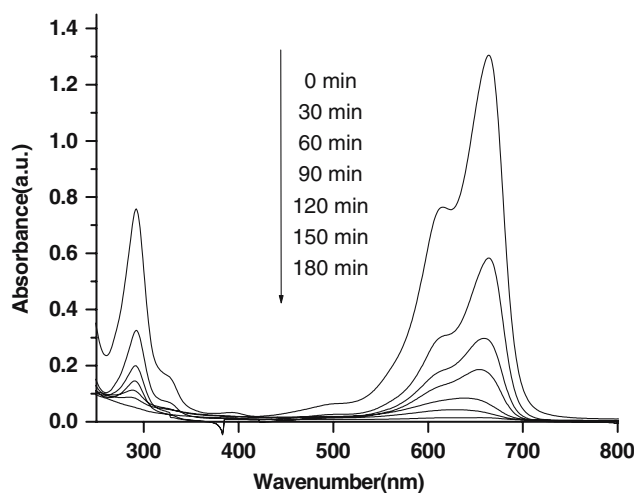


Fig. 7 Variation of the UV-vis absorption spectra of MB aqueous solution with the PDVB@TiO₂ microspheres after the saturated absorption under UV irradiation

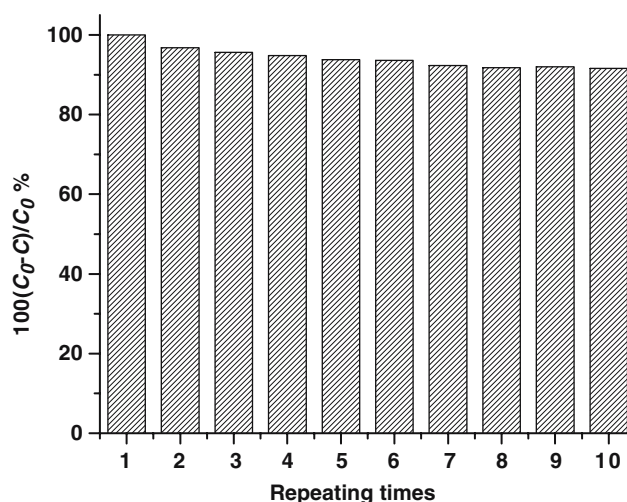


Fig. 8 The repetition of the PDVB@TiO₂ microspheres for the photo-degradation of MB under UV irradiation

The FT-IR spectra of the PDVB@TiO₂ hybrid microspheres did not change after the tenth photo-degradation under UV irradiation (Fig. 1c). [8–10].

The photocatalytic activity of the present photocatalyst is just slightly reduced in photo-degradation experiment of MB indicating that cyclic usage of the photocatalyst is possible and its stability in treating polluted water is satisfactory. Furthermore, it also proved that the final removal of MB from solutions was caused by the photocatalytic degradation other than the adsorption process that will lead to saturated adsorption of MB on the photocatalyst. And the PDVB@TiO₂ photocatalysts kept good photocatalytic activity after an exposure to the open air over 12 months.

Conclusion

The core/shell anatase TiO₂ encapsulated poly(divinylbenzene) hybrid microspheres (PDVB@TiO₂) were prepared successfully at low temperature by the co-hydrolysis of TBOT and the trimethoxysilyl groups on the surfaces of the copolymer cores of DVB and KH-570 and acid peptization. XRD patterns revealed that the titania was well crystalline and the size of titania crystal was about 4 nm. The PDVB@TiO₂ prepared showed high photocatalytic activities and better repetition on photo-degradation of MB because of the coupled action of KH-570 between the copolymer core and TiO₂ shell. Moreover, the photocatalysts can be easily separated from the solution by simple sedimentation and the silica under-layer produced by the hydrolysis of KH-570 acted as a protective coating

against the photocatalytic degradation of the copolymer core. The PDVB@TiO₂ prepared is expected to be applied as photocatalysts for purity of wastewater.

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