Enhancement of Photocatalytic Degradation Activity of Poly(Vinyl Chloride)-TiO$_2$ Nanocomposite Film with Polyoxometalate

Changjun Yang,[1] Lihong Tian,[1] Liqun Ye,[1] Tianyou Peng,[1] Kejian Deng,[2] Ling Zan[1]

[1]*College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China*
[2]*Key Laboratory of Catalysis and Materials Science of the State Ethnic Affairs Commission and Ministry of Education, South-Central University for Nationalities, Wuhan 430074, China*

ABSTRACT: A novel photodegradable poly(vinyl chloride)-polyoxometalate/TiO$_2$ (PVC-POM/TiO$_2$) nanocomposite film was prepared by embedding nano-TiO$_2$ photocatalyst modified by POM into the commercial PVC plastic. The solid-phase photocatalytic degradation behavior of as-prepared film under UV light irradiation was investigated and compared with those of the PVC-TiO$_2$ film and the pure PVC film, with the aid of FTIR spectroscopy, scanning electron microscopy (SEM), and weight loss monitoring. The results show that PVC-POM/TiO$_2$ nanocomposite film has a high photocatalytic activity. The optimal ratio of POM to TiO$_2$ is found to be 2 wt %, the degradation rate of PVC-POM/TiO$_2$ film is 1.5 times higher than that of PVC-TiO$_2$ film under the identical conditions. The enhancement of photocatalytic activity is due to the achievement of a rapid photogenerated charge separation with the assistance of POM which can mediate photogenerated electron transfering from TiO$_2$ conduction band to dioxygen. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 2048–2053, 2011

Key words: composites; degradation; photochemistry; plastics; poly(vinyl chloride) (PVC)

INTRODUCTION

As a conventional plastic material, a large amount of poly(vinyl chloride) (PVC) is produced and consumed globally every year. Due to its chemical inertness and nonbiodegradability, waste plastic products hardly decompose in landfills, causing a serious white pollution. Therefore, it is indispensable to dispose the waste polymers for remediation of natural environment. Traditional processing methods such as garbage deposit or incineration, not only require plenty of land and high cost, but also cause a serious secondary pollution.[1–4] Usually, the waste polymers are exposed to the sunlight in the open air, so the photodegradable PVC plastic as an ecofriendly technology is being investigated for treatment of waste polymers. In comparison with those traditional processing methods, the photocatalytic degradation process generates no dioxins and easily occurs under the ambient air condition, thus the practical application of this novel technology is much easier to be carried out.[5–10]

It is well-known that nano-TiO$_2$ has been widely used as a photocatalyst for treatment of environmental contaminants because of its outstanding characteristics such as inexpensiveness, nontoxicity, good photostability, and high reactivity. It has been proved that the blending of nano-TiO$_2$ particles into the polymer plastics is an attractive and efficient decomposition technique for treatment of waste polymers, under UV light irradiation or solar exposure in open-air.[11–17] For TiO$_2$ particles can absorb UV light wavelength less than 387 nm to generate active electron-hole pairs which can react with the surface-absorbed molecules and form active radicals, such as $^\bullet O_2^-$, $^\bullet OH$ and so on, these active radicals are able to attack the neighboring polymer chains and lead to the degradation of polymer. However, these photogenerated charge carriers are unstable, recombination of the electrons and holes can occur within a few nanoseconds, and brings about negative influence on the quantum yields and photocatalytic efficiency of TiO$_2$. To facilitate the electron-hole separation and increase the TiO$_2$ photocatalytic efficiency, the approach of surface modifying TiO$_2$ by mediating electron transfer from the TiO$_2$ conduction band to dioxygen has been extensively investigated.[18–22]

Among various electron scavengers for enhancing charge separation of TiO$_2$, the polyoxometalates (POMs) seem mostly to be interesting because of their particular characteristics, namely, POMs can undergo stepwise multielectron redox reactions while

their structure remains intact.[23] Therefore, POMs can act as electron relays to accept and donate electrons. Recent researches demonstrate that POMs are more effective than dioxygen alone at removing electrons of TiO$_2$ conduction band. In the POMs/TiO$_2$ associate systems, POMs have been employed as electron scavengers to retard the electron-hole recombination, consequently show positive influence on enhancing the TiO$_2$ photocatalytic efficiency for degradation of pollutants. For example, Ozer and Ferry found that addition of POMs, such as $PW_{12}O_{40}^{3-}$, $SiW_{12}O_{40}^{4-}$, and $W_{10}O_{32}^{4-}$, to TiO$_2$ suspension can significantly enhance the photocatalytic degradation rate of 1,2-dichlorobenzene.[24] Chen et al. have also reported a similar result for photocatalytic degradation of 1, 2-dichlorobenzene by using $PW_{12}O_{40}^{3-}$/TiO$_2$ system in aqueous media.[25] In addition, the photocatalytic degradation efficiency for 2, 2-*bis* (4-hydroxyphenyl) propane (BPA) and reactive brilliant red X-3B is much higher than pure TiO$_2$ by using $PW_{12}O_{40}^{3-}$/TiO$_2$ system,[26,27] $PW_{11}O_{39}^{7-}$/TiO$_2$ system also exhibited much higher photoactivity than that of pure TiO$_2$ and $PW_{11}O_{39}^{7-}$/SiO$_2$ system toward Congo Red (CR) dye degradation under UV irradiation.[28]

All reports about POM/TiO$_2$ system photoactivity are carried out in aqueous media. To the author's best knowledge, there is no research on the solid-phase photoactivity of POM surface modification of nano-TiO$_2$. Herein, the solid-phase photocatalytic degradation of PVC with POM surface modifying nano-TiO$_2$ has been investigated. A new kind of photodegradable PVC-POM/TiO$_2$ nanocomposite film was synthesized using a representative polyoxometalate, phosphotungstic acid ($PW_{12}O_{40}^{3-}$, POM), surface modifying nano-TiO$_2$ as the photocatalyst. The photodegradation performance has been researched. The PVC-POM/TiO$_2$ nanocomposite film shows much higher photodegradation efficiency under UV light irradiation than the PVC-TiO$_2$ composite film and the pure PVC film.

EXPERIMENTAL

Materials

Commercial poly(vinyl chloride) (PVC) powder particles were supplied by Wuhan Gehua Co. Ltd. Phosphotungstic acid was purchased from Sinopharm Chemical Reagent Co.Ltd. Nano-TiO$_2$ powder was Degussa P25, 70% in anatase phase and 30% in rutile, whose primary particle diameter is in a range of 30–50 nm.

Preparation of the composite films

The preparation of PVC-POM/TiO$_2$ nanocomposite film was cast as follows: First, 3 mg phosphotungstic acid was dissolved in 50 mL tetrahydrofuran (THF) which was added a thimbleful of water. Then 100 mg nano-TiO$_2$ powder was dispersed into the above solution by ultrasonic vibration for 25 min to obtain a uniform POM/TiO$_2$ suspension. Then 5 g PVC powder particles were added, the solution was under continuing vigorous stirring for 5 h. The nanocomposite film was then prepared on a spin-coater machine. About 20 mL viscous solutions were spread on a smooth tile surface (15 cm × 15 cm), and dried in airtight system at room temperature. PVC-POM/TiO$_2$ nanocomposite films containing different amounts of POM (from 1 mg to 3 mg) were prepared by the same way.

The PVC-TiO$_2$ film, PVC-POM film, and pure PVC film were also prepared in a similar procedure, to compare their photocatalytic activities. Pure PVC and PVC-POM films both were transparent and colorless, while PVC-POM/TiO$_2$ and PVC-TiO$_2$ films were of slightly white.

Photocatalytic degradation of the composite films

The typical surface area of the film samples was 16 cm^2 (4 cm × 4 cm). The photocatalytic degradation was performed under 30 W UV lamp (ZW30S19W, Jiangyin Feiyang Appliance Co. Ltd.) in the ambient air and the sample was weighted every 48 h. The light intensity was measured as 1.0 mW/cm^2 by a UV intensity meter (UV-I, Beijing Shida Instrument Factory) at primary wavelength 254 nm. The degradation extent of the film was evaluated directly by the weight loss.

The samples of FT-IR analysis were in the form of strips, the width and length of which were 0.8 cm and 4 cm, respectively. The samples were cut out from the composite films before and after different irradiating intervals. To analyze the change of concentrations of C-H group and the carbonyl (C=O) group, PVC-POM/TiO$_2$ and PVC-TiO$_2$ films both have the same surface area and weight before the irradiation.

Characterization of the composite films

The thickness of these films was measured to be 25–35 μm by a micrometer. An FT-IR spectrophotometer (NEXUS670, Nicolet) monitored the spectrum character of these films before and after irradiation. The surface morphologies of the composite films were observed by Field Emission Scanning Electron Microscope (Quanta 200).

RESULTS AND DISCUSSION

Surface modification of nano-TiO$_2$ with POM

The nano-TiO$_2$ surface is positively charged in acidic media,[29] while the $PW_{12}O_{40}^{3-}$ is negatively charged, thus facilitating adsorption of the $PW_{12}O_{40}^{3-}$ on the surface of nano-TiO$_2$ by simple Coulombic interactions.[25] By the embedding technique, POM
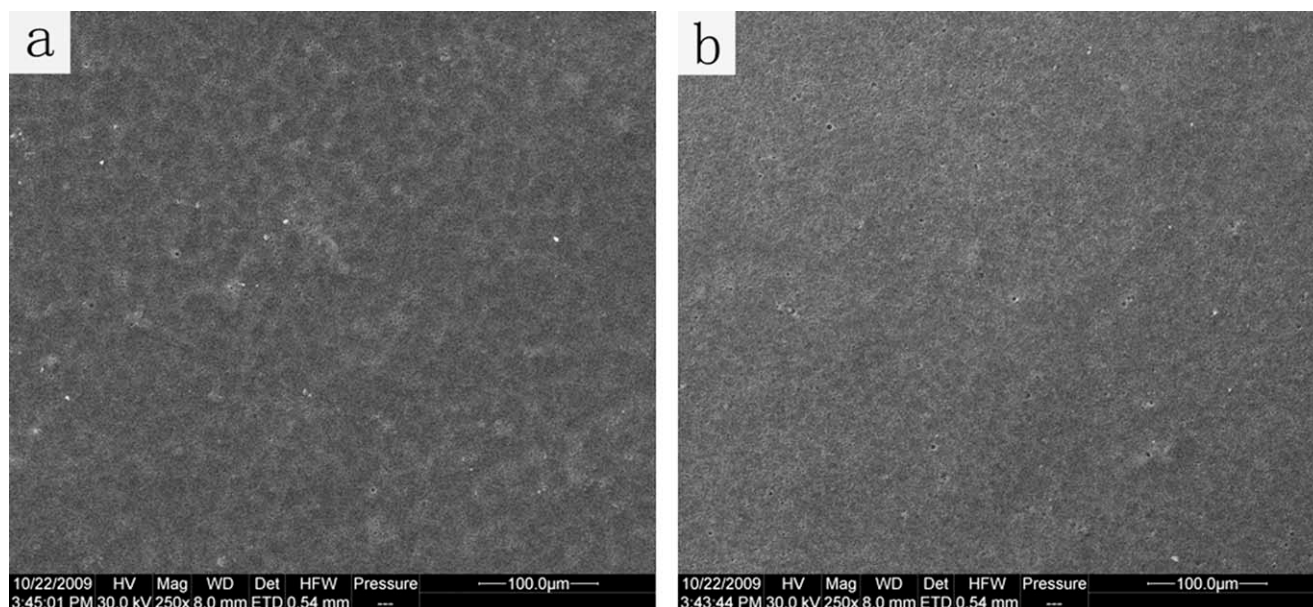
Figure 1 SEM images before irradiation. (a) The PVC-TiO$_2$ film. (b) The PVC-POM/TiO$_2$ film.

modifying nano-TiO$_2$ or naked nano-TiO$_2$ particles were blended into the commercial PVC. Figure 1 shows the surface morphologies of PVC-TiO$_2$ film and PVC-POM/TiO$_2$ film before irradiation. The both surfaces are smooth. It can be observed that the dispersions of nano-TiO$_2$ and POM/TiO$_2$ particles in PVC polymer are no different.

FTIR analysis

The photocatalytic degradation of PVC-POM/TiO$_2$ film can be examined by FT-IR analysis. Figure 2 shows the FTIR spectra of the composite film before and after irradiation for 10 h, 15 h, and 40 h. The bands in the region 2700–3100 cm^{-1} and 1680–1800 cm^{-1} are the characteristic absorptions of C-H group and C=O group in PVC film, respectively. It can be seen that the intensities of C-H group absorption peak decrease gradually [Fig. 2(a)], while that of the C=O group peak increase continually with increasing irradiation time [Fig. 2(b)]. In the composite film, owing to the catalytic action of POM/TiO$_2$ photocatalyst, active species were generated under irradiation and oxidized the C-H group to form the C=O group. This phenomenon suggests that the photooxidized reaction has taken place in the composite film.

The change of C=O group for PVC-POM/TiO$_2$ film and PVC-TiO$_2$ film have also been investigated. Figure 3 shows the plot of ratio of C=O group peak areas for PVC-POM/TiO$_2$ film to that for PVC-TiO$_2$ film. The ratio increases step by step with increasing irradiation time, which indicates the existence of higher concentration of oxygenated groups in PVC-
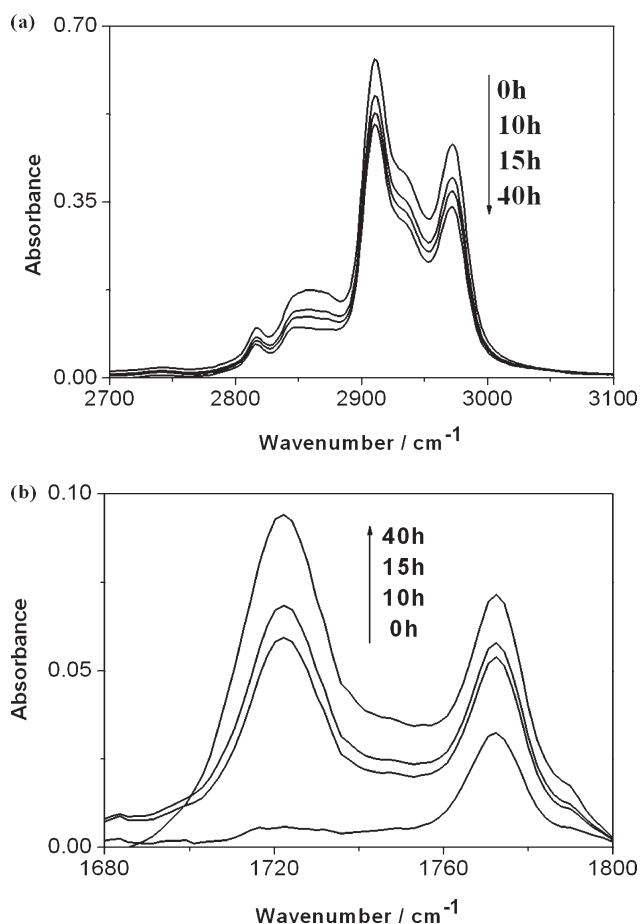
Figure 2 The FTIR spectra of the C-H group (a) and the carbonyl (C=O) group (b) of PVC-POM/TiO$_2$ film before and after photodegradation.
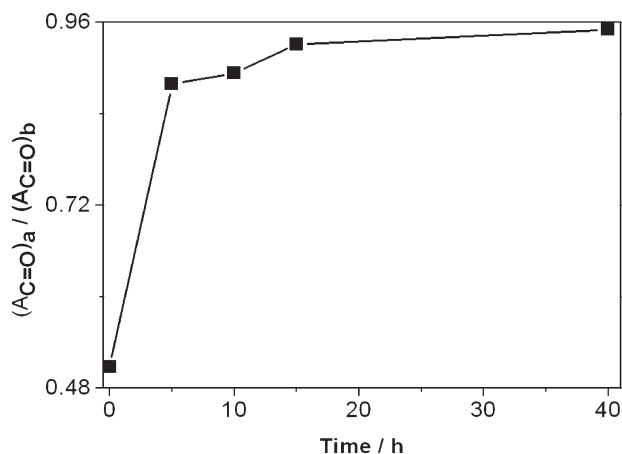
Figure 3 Plot of ratio of carbonyl (C=O) group peak areas for PVC-POM/TiO$_2$ film (a) to that for PVC-TiO$_2$ film (b).

POM/TiO$_2$ film than that in PVC-TiO$_2$ film. It means that the POM/TiO$_2$ composite catalyst has a higher catalytic activity than the untreated-TiO$_2$.

Surface morphologies of the samples after photodegradation

Figure 4 shows the surface morphologies of PVC-TiO$_2$ film and PVC-POM/TiO$_2$ film after 72 h and 120 h irradiation. After irradiation for 72 h, it can be observed that lots of cavities appeared on the surface of these

composite films, which reveals both of them are obviously decomposed. Apparently, for PVC-POM/TiO$_2$ film, the surface was destroyed more seriously comparing to the PVC-TiO$_2$ film with the increase of irradiation time. The increase of density, size, and depth of the cavities are observed. Even big holes are formed on the local surface, which shows that the structure of the polymer has been destroyed completely. The results imply that the POM evidently promotes the degradation of PVC film by modifying nano-TiO$_2$.

Weight loss analysis

The photodegradation extent of film can be evaluated directly by the weight loss. Figure 5 shows the photoinduced weight loss curves of the pure PVC film and various composite films under UV light irradiation. The weight loss rates of pure film [Fig. 5(c)] and PVC-POM composite film [Fig. 5(d)] have no noticeable difference. Both rates are about 14% after 384 h irradiation due to the direct photolysis reaction, which implies that a farthing POM has basically no photocatalytic activity. Obviously, the weight loss rate of PVC-POM/TiO$_2$ film is the highest among the four kinds of films, which reaches about 70% after 384 h irradiation [Fig. 5(a)], while the reduction of PVC-TiO$_2$ film is only 47% under the same condition [Fig. 5(b)]. It displays the POM modifier playing an important role in promoting the
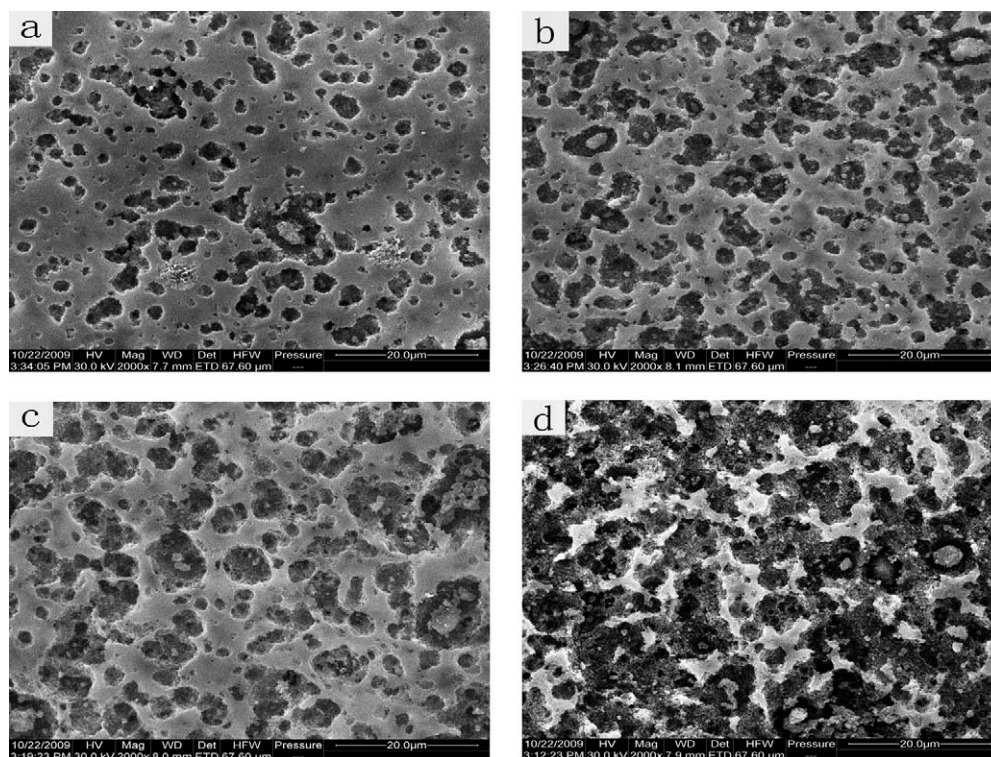

Figure 4 SEM images after irradiation with 1.0 mW/cm^2 UV light intensity. (a) The PVC-TiO$_2$ film after 72 h irradiation. (b) The PVC-POM/TiO$_2$ film after 72 h irradiation. (c) The PVC-TiO$_2$ film after 120 h irradiation. (d) The PVC-POM/TiO$_2$ film after 120 h irradiation.
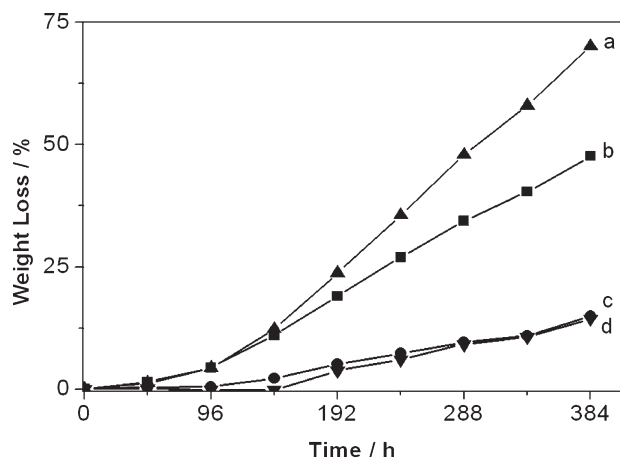
Figure 5 Weight loss of the pure film and composite films under UV light irradiation with 1.0 mW/cm^2 light intensity. (a) PVC-POM/TiO$_2$ film (TiO$_2$: 2 wt %; POM: 0.04 wt %; WPOM/WTiO$_2$ = 2%); (b) PVC-TiO$_2$ film (TiO$_2$: 2 wt %, without POM); (c) pure PVC Film; (d) PVC-POM film (POM: 0.04 wt %, without TiO$_2$).

photocatalytic degradation of nano-TiO$_2$-PVC composite film.

Figure 6 shows the photoinduced weight loss curves of the PVC-TiO$_2$ composite film with different film thickness under UV light irradiation. After irradiation for 288 h, the weight loss of composite film with the film thickness of 25 μm reached about 34.4% [Fig. 6(a)], which is much higher than that of the film thickness of 35 μm [Fig. 6(b)]. It means that the film thickness of composite film will greatly affect the photocatalytic degradation efficiency. Light penetration into the composite film is a function of the thickness of the film,[5] therefore, the thin thickness of composite film is beneficial to the UV light penetrating through the composite film that can excite TiO$_2$.
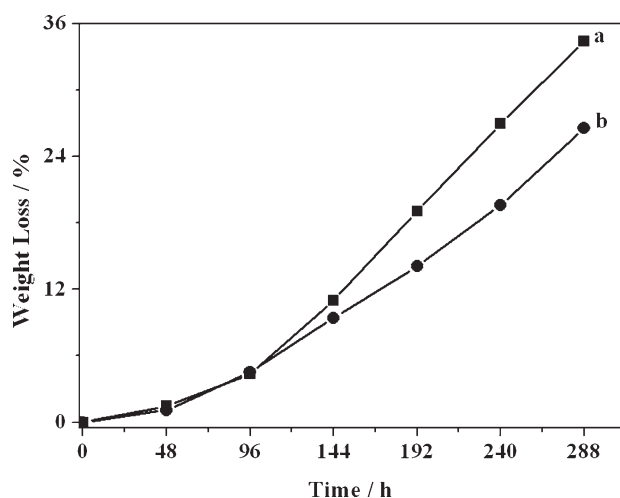

Figure 6 Effect of film thickness on the weight loss of PVC-TiO$_2$ composite film (TiO$_2$: 2 wt %) under UV light irradiation. (a) 25 μm; (b) 35 μm.
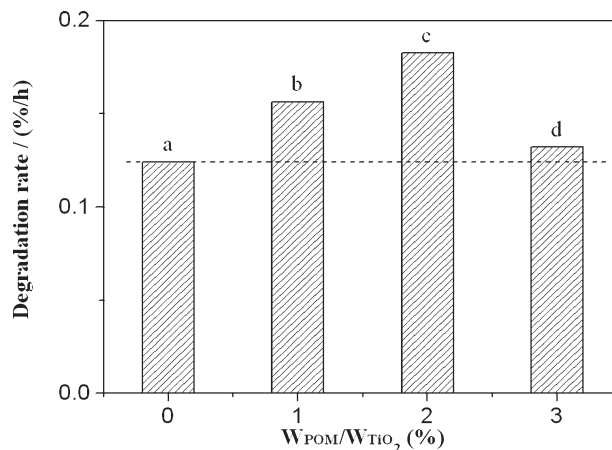
Figure 7 Comparison of apparent degradation rates of different POM concentration in PVC-POM/TiO$_2$ composite film. (a) WPOM/WTiO$_2$ = 0%; (b) WPOM/WTiO$_2$ = 1%; (c) WPOM/WTiO$_2$ = 2%; (d) WPOM/WTiO$_2$ = 3%.

Figure 7 shows that the apparent degradation rates of the PVC-POM/TiO$_2$ films containing different POM concentration are much higher than that of PVC-TiO$_2$ film. When the ratio of POM to TiO$_2$ is below 2 wt %, addition the amount of POM can observably promote the degradation of composite films, the weight loss rate of composite film increases with the amount of POM increasing; it reveals the POM will greatly affect TiO$_2$ photocatalytic activity. However, when the ratio exceeds 2 wt %, such as 3 wt %, the weight loss rate of PVC-POM/TiO$_2$ film does not increase any longer though it is also higher than that of PVC-TiO$_2$ film. It was possibly attributed to the saturation of active sites
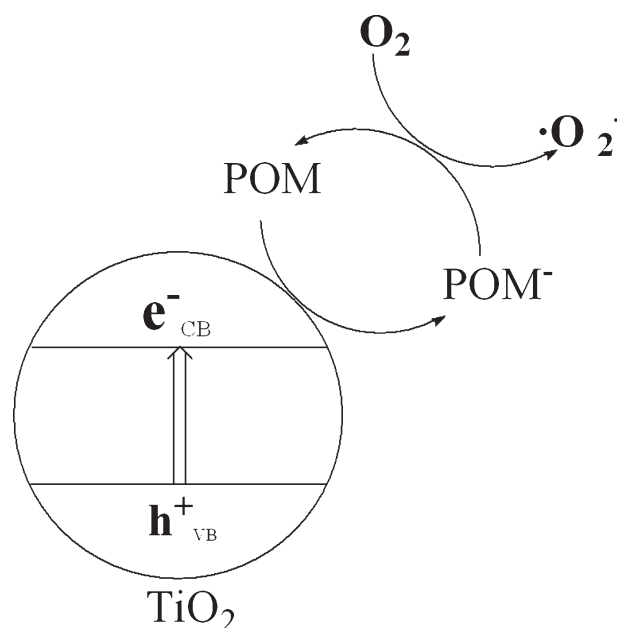
Figure 8 The possible process of POM mediated electron transferring from TiO$_2$ conduction band to dioxygen.

on the surface of TiO$_2$ when the amount of POM exceeds 2 wt %. Therefore, there exists an optimal ratio of POM to TiO$_2$ for the photocatalytic activity, W_{POM}/W_{TiO2} is 2 %.

Photocatalytic degradation mechanism

Thanks to the stimulation of TiO$_2$ particles by absorbing UV light, photogenerated electron (e$^-$) and hole (h$^+$) were formed. They can react with the adsorbed molecules, such as dioxygen and water, to produce various active species.[30,31] In particular, the superoxide anion ($^\bullet$O$_2^-$) and hydroxyl radical ($^\bullet$OH) are two very important reactive species for the solid-phase photocatalytic degradation process, which can attack the neighboring polymer chains to abstract a hydrogen atom and form carbon-centered radicals such as —($^\bullet$CHCHCl)—.[5] Once the carbon-centered radicals are introduced in the polymer chain, the successive reactions result in polymer chains cleavage. Finally, volatile species, such as carbon dioxide, are evolved until the complete degradation of polymer.

When nano-TiO$_2$ is modified by POM, the modification of POM has no effect on the dispersion of nano-TiO$_2$ in PVC polymer according to the previous surface morphologies of composite films. But the photocatalytic degradation rate of PVC-POM/TiO$_2$ film is much higher than that of PVC-TiO$_2$ film; one possible explanation for this photocatalytic activity enhancement is that POM promotes the separation of photogenerated electron-hole pair.[24,25] When POM and adsorbed dioxygen coexists in the surface of nano-TiO$_2$, there exists a competition of photogenerated TiO$_2$ conduction band electrons between these two electron scavengers. For one-electron reduction potential of PW$_{12}$O$_{40}$$^{3-}$ is + 0.218 V versus NHE, which is more positive than that of dioxygen, electron is favored to transferring to POM but not to dioxygen in the existence of POM.[32–34] Then POM donates the acceptant electrons to dioxygen forming superoxide anion ($^\bullet$O$_2^-$), resulting in the rapid separation of electron and hole during the reaction. The possible process of electron transfer can be displayed in Figure 8.

Thus, with the assistance of POM, the PVC film containing nano-TiO$_2$ has much higher photocatalytic degradation efficiency.

CONCLUSIONS

This study demonstrates that the modification of POM promotes the nano-TiO$_2$ photocatalytic activity in solid-phase photodegradation for POM is a better electron acceptor than dioxygen in the photocatalytic process and can retard the electron-hole recombination, that is, the PVC-POM/TiO$_2$ composite film shows higher photocatalytic degradation efficiency under UV light irradiation comparing with the PVC-TiO$_2$ composite film and

pure PVC film. It is a novel way to produce the environment-friendly photodegradable polymer material.

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