High photocatalytic degradation activity of the polyvinyl chloride (PVC)–vitamin C (VC)–TiO$_2$ nano-composite film

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ABSTRACT

A novel photodegradable polyvinyl chloride (PVC)–vitamin C (VC)–TiO$_2$ nano-composite film was prepared by embedding VC modified nano-TiO$_2$ photocatalyst into the commercial PVC plastic. The solid-phase photocatalytic degradation behavior of PVC–VC–TiO$_2$ nano-composite 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 UV–Vis spectroscopy, scanning electron microscopy (SEM), weight loss monitoring, and X-ray diffraction spectra (XRD). The results show that PVC–VC–TiO$_2$ nano-composite film has a high photocatalytic activity; the photocatalytic degradation rate of it is two times higher than that of PVC–TiO$_2$ film and fifteen times higher than that of pure PVC film. The optimal mass ratio of VC to TiO$_2$ is found to be 0.5. The mechanism of enhancing photocatalytic activity is attributed to the formation of a Ti^{IV}–VC charge-transfer complex with five-member chelate ring structure and a rapid photogenerated charge separation is thus achieved.

1. Introduction

Polyvinyl chloride (PVC) and related plastic products are non-biodegradable in natural environment because of their chemical inertness. The waste PVC plastics become one of the main sources of "white pollution". Traditional processing methods, such as garbage deposit or incineration, cause a serious secondary pollution [1–4]. Therefore, the development of degradable PVC plastics becomes an important issue. Several biodegradable PVC plastics have been reported elsewhere [5–7]. There are some disadvantages in these PVC plastics, mainly the long degradation cycle and the incompleteness of the degradation, which limit their practical applications. On the other hand, the photodegradable PVC by embedding photocatalysts into the plastics demonstrate a high potential in rapid decomposition of the plastics. Particularly, the photocatalytic degradation of PVC generates no dioxins and the decomposition process is easily to occur under natural environmental conditions [8–13]. The photocatalytic degradation of polymers by means of TiO$_2$ has been proved an attractive and efficient decomposition technique for treatment of waste polymers, in open-air under UV light irradiation or solar exposure [11–20].

However, slow reaction rate and poor solar efficiency have already hindered the practical application of this technology. To eliminate these drawbacks, many attempts have been carried out to modify TiO$_2$ characteristics by surface modifiers through three ways: (a) by inhibiting charge recombination; (b) by expanding the wavelength response range; and (c) by changing the selectivity or yield of a particular product [21]. Recent studies indicate that the surface modification of TiO$_2$ by metallophthalocyanine shows a high photocatalytic activity for degradation of polymers [22–24]. Vitamin C (VC), a naturally available compound, has been used as a modifier in a solid-state cell based on TiO$_2$ and CuI, where the photo-excited dye molecules inject electrons into the conduction band of TiO$_2$ and holes into the valence band of CuI. It is proved that VC can satisfy the charge separation requirements and increase the photo-effects of the cell [21,25]. Ou et al. [26] reported that the surface modification of TiO$_2$ with VC greatly enhanced the methyl orange photocatalytic decolorization rate due to the formation of a charge-transfer bidentate complex. To our best knowledge, there is no research on waste plastics treatment by VC modification of nano-TiO$_2$.

In this paper, a new kind of photodegradable PVC–VC–TiO$_2$ nano-composite film was synthesized using VC modified nano-TiO$_2$ as the photocatalyst. The photodegradation performance has been investigated. The PVC–VC–TiO$_2$ nano-composite film shows much higher photodegradation efficiency under UV light irradiation than the PVC–TiO$_2$ composite film and the pure PVC film.

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2. Experimental

2.1. Surface modification of nano-TiO$_2$ with VC

First, 0.1 g VC was dissolved in 10 mL tetrahydrofuran (THF), and then a thimbleful of water was added. 0.2 g nano-TiO$_2$ powder (Degussa P25, 70% in anatase and 30% in rutile phase, whose primary particle diameter is in the range of 30–50 nm) was dispersed into 30 mL THF solution by ultrasonic vibration for 3 min to obtain a uniform suspension. Then the 10 mL VC–THF solution was added to the nano-TiO$_2$ suspension dropwise with magnetic stirring, forming a light yellow suspension. The color change implies that a chemical reaction occurred in this process.

2.2. Preparation and characterization of the composite films

10 g PVC powder particles (from Wuhan Gehua Co. Ltd.) were dissolved in 70 mL THF under vigorous stirring for 2 h to obtain the transparent PVC solution. The colored suspension mentioned above was added to PVC solution. The solution was under continuous stirring for 5 h. The 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 for 72 h at room temperature. The PVC–VC–TiO$_2$ nano-composite films containing different amounts of VC (from 0.02 g to 0.2 g) were thus prepared. The PVC–TiO$_2$ film, PVC–VC film and pure PVC film were also prepared in a similar procedure, in order to compare their photocatalytic activities. Pure PVC and PVC–VC films both were transparent and colourless, while PVC–TiO$_2$ film was of slightly white and PVC–VC–TiO$_2$ film was light yellow.

The thickness of these films was measured to be 20 μm by a micrometer. A UV–Vis spectrophotometer (Shimadzu UV-3100) was used to obtain the absorption spectra of films before irradiation. The surface morphologies of the composite films were observed by Field Emission Scanning Electron Microscope (JEOL JSM-6700F).

2.3. Photocatalytic degradation of the composite films

The typical surface area of the film samples was 16 cm^2 (4 cm × 4 cm). Each film was washed several times with the deionized water and ultrasonic vibration to remove the traces of THF solvent before irradiation. 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 24 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 surface morphologies of all samples after irradiation were observed by SEM. The X-ray diffraction (XRD) patterns were obtained on a D8 Advance Bruker X-ray diffractometer using Cu Kα irradiation.

3. Results and discussion

3.1. Spectroscopic characterization

Fig. 1 shows the UV–Vis absorption spectra of the four types of PVC films. The absorption of the pure PVC film is interrupted above 250 nm, while all the composite films have obvious absorption over this threshold, due to the addition of dopants. The PVC–VC film has absorption above 250 nm because of the unsaturated bonds of VC, and the PVC–TiO$_2$ film demonstrates strong absorption until 400 nm owing to the characteristic absorption of TiO$_2$. The absorption range of the PVC–VC–TiO$_2$ film is remarkably broader than
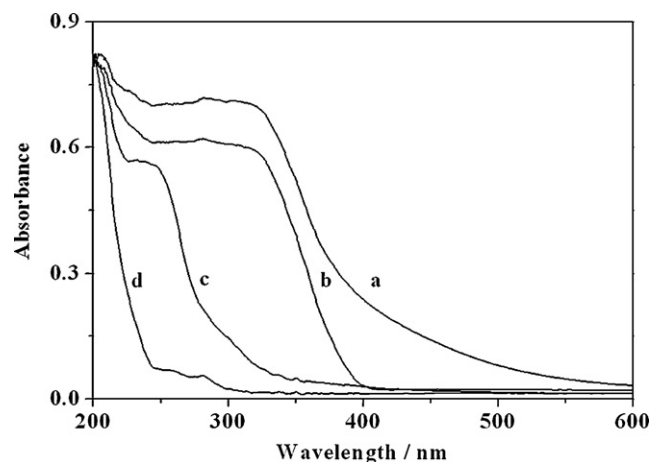

Fig. 1. UV–vis absorption spectra of different films before irradiation. (a) PVC–VC–TiO$_2$ film (TiO$_2$: 2 wt%;VC: 1 wt%); (b) PVC–TiO$_2$ film (TiO$_2$: 2 wt%); (c) PVC–VC film (VC: 2 wt%); (d) pure PVC film.

both the PVC–TiO$_2$ film and PVC–VC film. The red shift of absorption threshold of it is up to around 600 nm, this phenomenon can be explained that bidentate binding of α-substituted surface modifiers results in the formation of a five-membered ring at surface titanium atoms [21,27]. The specific binding of VC to the surface of TiO$_2$ is supported by the fact that the titanium ions can readily form complexes with oxygen atom from various containing oxygen ligands, so the bidentate binding between TiO$_2$ and VC not only enhances the ultraviolet photoresponse of TiO$_2$, but also shifts the onset of the photoresponse of TiO$_2$ up to visible region. The following drawing is the proposed structure of the surface charge-transfer complex (Fig. 2).

3.2. Surface morphologies of the samples after photodegradation

Fig. 3 shows the surface morphologies of PVC–TiO$_2$ film and PVC–VC–TiO$_2$ film before and after 70 h and 100 h of irradiation. It can be observed that both of PVC–TiO$_2$ film (Fig. 3a) and PVC–VC–TiO$_2$ film (Fig. 3d) before irradiation are smooth. After irradiation, the composite films are obviously decomposed as showed in Fig. 3b, c, e and f. There are lots of cavities, indicating the photocatalytic reaction starts at the interface between polymer and photocatalyst [18]. It is interesting that the cavity size and depth of PVC–VC–TiO$_2$ film is much larger than the PVC–TiO$_2$ film, the results imply that the VC evidently promotes the degradation of PVC film by modifying nano-TiO$_2$.

3.3. XRD analysis

The crystalline phase of the TiO$_2$ is important for its photocatalytic activity. Fig. 4a shows the characteristic peaks of the anatase and rutile crystalline phase of TiO$_2$. These peaks are still observable in the samples after 216 h of irradiation (Fig. 4d and e), indicating the stability of TiO$_2$ in long time of UV light irradiation. There is an obvious diffraction peak centered at 17.5° (2θ value)
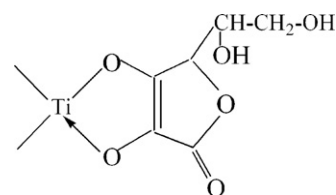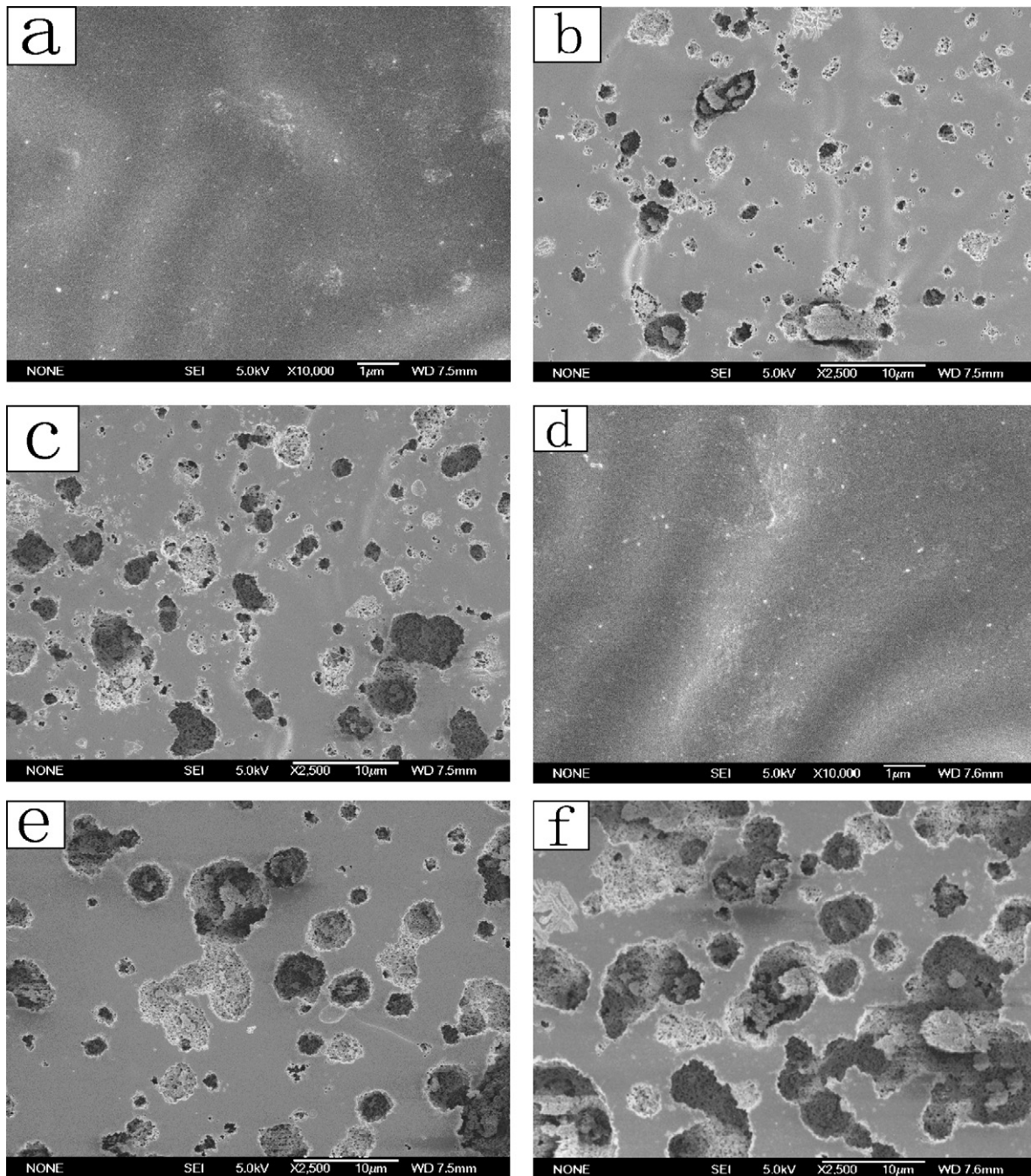

**Fig. 2.** Proposed structure of the surface charge-transfer complex.

Fig. 3. SEM images after irradiation with 1.0 mW/cm^2 UV light intensity. (a) The PVC–TiO$_2$ film 0 h irradiation; (b) the PVC–TiO$_2$ film after 70 h irradiation; (c) the PVC–TiO$_2$ film after 100 h irradiation; (d) the PVC–VC–TiO$_2$ film 0 h irradiation; (e) the PVC–VC–TiO$_2$ film after 70 h irradiation; (f) the PVC–VC–TiO$_2$ film after 100 h irradiation.

in the PVC films before irradiation. This peak is considered as the semi-crystalline phase of the PVC. After 216 h of irradiation of the PVC–VC–TiO$_2$ film (Fig. 4e), this peak disappears completely. Meantime, a new diffraction peak centered at 13.4° (2θ value) appears. This observation suggests that the inherent structural of PVC has been changed due to the chain scission in the backbone under irradiation. According to the literature, the average molecular weight (M_W) of the PVC composite film decrease under UV light irradiation [12], so it could be that the vanished semi-crystalline phase belongs to high M_W and the new semi-crystalline phase belongs to low M_W for the PVC polymer. The intensity of new peak for PVC–TiO$_2$ film is much weaker than the PVC–VC–TiO$_2$ film, implying that the PVC–VC–TiO$_2$ film has more strong chain scission in the backbone of the PVC polymer under UV light irradiation.

3.4. Weight loss analysis

The photodegradation extent of the films can be evaluated directly by their weight loss. Fig. 5 demonstrates the photo-induced weight loss curves of the pure PVC film and composite films. The weight loss rate of the pure film (Fig. 5c) and PVC–VC film (Fig. 5d) is about 5% after 216 h irradiation, which shows that VC itself has basically no photocatalytic activity. The weight loss rate of the PVC–VC–TiO$_2$ film (Fig. 5a), which reaches about 71% after 216 h irradiation, is the highest among these four kinds of films, while the PVC–TiO$_2$ film (Fig. 5b) reduction is only 35%. This result proves that the modifier of VC remarkably promotes the photocatalytic degradation of nano-TiO$_2$-containing PVC film.
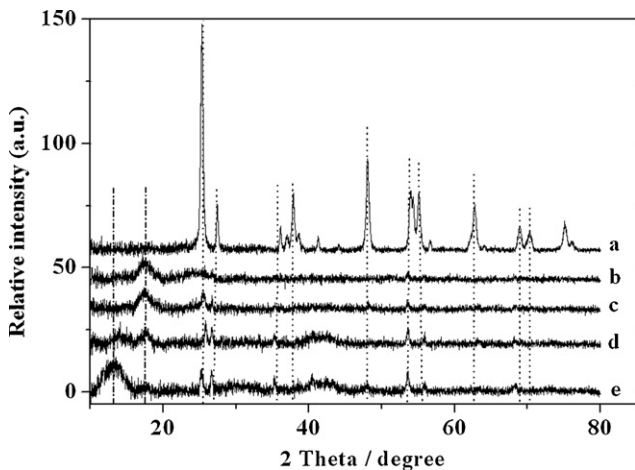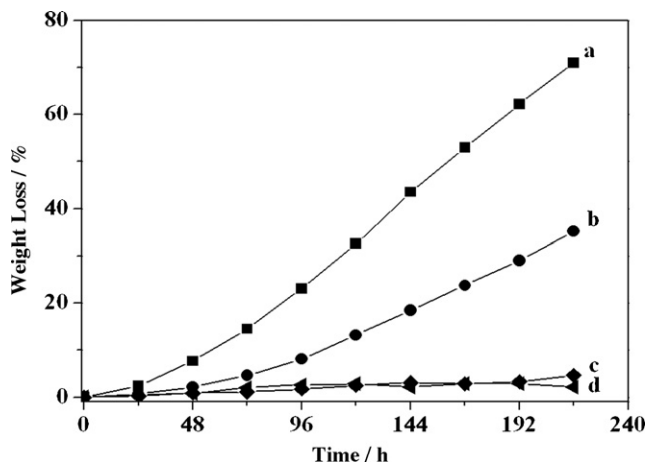
Fig. 4. X-ray diffraction patterns of TiO_2 powder and different films. (a) TiO_2 powder; (b) pure PVC film; (c) PVC–VC–TiO_2 film before irradiation; (d) PVC–TiO_2 film after 216 h irradiation; (e) PVC–VC–TiO_2 film after 216 h irradiation.

Fig. 6. The weight loss rate at different mass ratios of VC to TiO_2 in PVC–VC–TiO_2 film under $1.0\,mW/cm^2$ UV light intensity irradiation 216 h (TiO_2: 2 wt%). (a) $WVC/WTiO_2 = 0$; (b) $WVC/WTiO_2 = 0.1$; (c) $WVC/WTiO_2 = 0.4$; (d) $WVC/WTiO_2 = 0.5$; (e) $WVC/WTiO_2 = 1$.
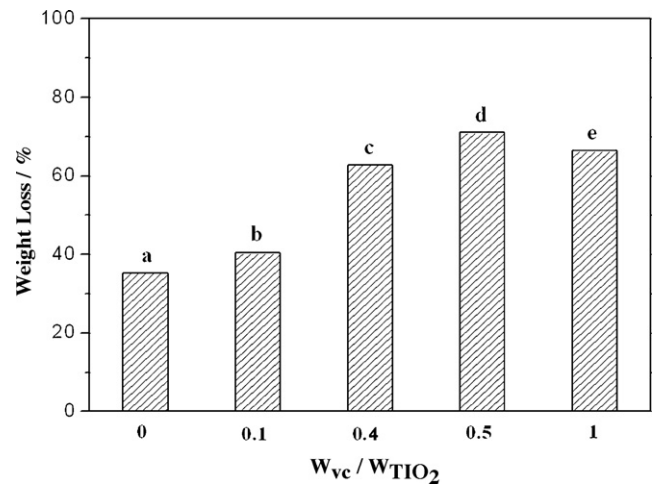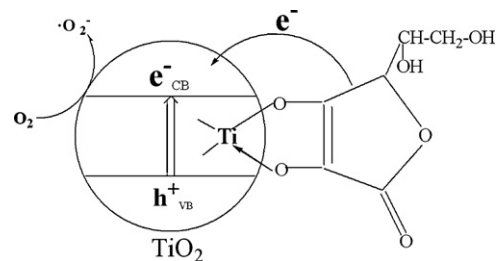
With the increasing of irradiation time the light yellow of the composite film slowly faded, it means the dissociation of the charge-transfer complex, for VC is oxidized in the charge separated process. However, it cannot be seen that the dissociation of the complex decreases the weight loss rate of PVC from Fig. 5a. The possible reason is that the key step of the solid-phase photocatalytic degradation is photoinitiation, subsequent reaction of photocatalytic degradation will be continuously generated due to the photoinitiation. So the weight loss rate of PVC–VC–TiO_2 film can steadily increase in the later photocatalytic process while the charge-transfer complex has been dissociated.

3.5. Effect of the addition amount of VC

Fig. 6 shows a comparison of weight loss rate of different mass ratios of VC to TiO_2 in PVC–VC–TiO_2 films. When the mass ratio is below 0.5, addition of VC always promotes the weight loss rate of composite films; it increases with the amount of VC increasing. However, when the mass ratio exceeds 0.5, such as 1, the weight loss rate of the PVC–VC–TiO_2 film does not increase any longer. The optimal mass ratio of VC to TiO_2 is 0.5 for the photocatalytic activity. It means the VC coverage on the surface of TiO_2 will greatly affect the photocatalytic activity. When the amount of VC

reaches saturation on the surface of TiO_2, the excess VC cannot be bound to TiO_2 and cannot form charge-transfer complex, so they have no effect on the photocatalytic degradation of PVC–VC–TiO_2 film. Therefore, there exists an optimal mass ratio of VC to TiO_2.

3.6. Photocatalytic degradation mechanism

TiO_2 is stimulated by UV light whose wavelength is lower than 387 nm to generate electrons (e^-) and holes (h^+). Adsorbed oxygen molecules and water on the surface can capture electrons and holes respectively, producing various active species [28,29]. Among them, 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 initiate the degradation reaction in solid-phase same as in other liquid-phase and gas-phase photocatalytic reactions [17,30,31]. These reactive species attack the neighboring PVC polymer chains to abstract a hydrogen atom and to form carbon-centered radicals such as $-(CH_2{}^\bullet CCl)-$ and $-(^\bullet CHCHCl)-$ [12]. 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 VC, a Ti^{IV}–VC charge-transfer complex is formed, the initial stage of photocatalytic reaction of the modified system has a significant feature different from pure TiO_2 due to charge-transfer complex [32]. The electrons transfer from VC to conduction band of TiO_2 (Fig. 7). The superoxide radicals which would attack neighboring polymer chains and induce the degradation of PVC are formed acceleratively through one-electron reduction of surface oxygen by conduction band electrons. The photocatalytic activity is thus enhanced by synergetic effect of VC and TiO_2.

Fig. 5. Weight loss of the pure film and composite films under UV light irradiation with $1.0\,mW/cm^2$ light intensity. (a) PVC–VC–TiO_2 film (TiO_2: 2 wt%;VC: 1 wt%); (b) PVC–TiO_2 film (TiO_2: 2 wt%); (c) pure PVC film; (d) PVC–VC film (VC: 2 wt%).

Fig. 7. The mechanism scheme of photocatalysis process for TiO_2 modified by VC.

4. Conclusions

This study demonstrates that the VC modified nano-TiO$_2$, forming the Ti^{IV}–VC charge-transfer complex having a five-member chelate ring structure, greatly promotes the solid-phase photocatalytic degradation of PVC. The weight loss rate of PVC–VC–TiO$_2$ film is two times greater than that of PVC–TiO$_2$ film and fifteen times than that of pure PVC film under the identical experimental condition. The PVC–VC–TiO$_2$ nano-composite is a potential environment-friendly photodegradable polymer material.

Acknowledgement

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