

Enhancement of photocatalytic degradation of polyethylene plastic with CuPc modified TiO₂ photocatalyst under solar light irradiation

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Abstract

Solid-phase photocatalytic degradation of polyethylene (PE) plastic, one of the most common commercial plastic, over copper phthalocyanine (CuPc) modified TiO₂ (TiO₂/CuPc) photocatalyst was investigated in the ambient air under solar light irradiation. Higher PE weight loss rate, greater texture change; more amount of generated CO₂, which is the main product of the photocatalytic degradation of the composite PEC plastic can be achieved in the system of PE–(TiO₂/CuPc) in comparison with PE–TiO₂ system. The CuPc promoted charge separation of TiO₂ and enhanced the photocatalytic degradation of PE based on the analysis of surface photovoltage spectroscopy (SPS). During the photodegradation of PE plastic, the reactive oxygen species generated on TiO₂ or TiO₂/CuPc particle surfaces play important roles. The present study demonstrates that the combination of polymer plastic with TiO₂/CuPc composite photocatalyst in the form of thin film is a practical and useful way to photodegrade plastic contaminants under solar light irradiation.

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1. Introduction

Plastic waste such as polyethylene (PE) disposal has been recognized as a worldwide environmental problem. Though various kinds of techniques have been proposed for the conversion of waste PE plastic, it is generally accepted that material recovery is not a long-term solution to the present problem [1]. Due to their chemical stability and unbiodegradability, waste PE products are being mainly disposed by the incineration, which will release a lot of toxic by-products. Thermal or catalytic degradation of waste PE plastic into fuel oils was investigated in recent years [2–4]. However, this technique requires not only high temperature and cost, but also appropriate catalysts to guarantee narrow distribution of hydrocarbons [4]. Consequently, new technologies are being investigated for the treatment of plastic wastes.

Recently, photocatalytic techniques have been successfully applied in the disposal of air and wastewater pollutants [5–7]. Therefore, it is worthwhile to study the solid-phase photodegradation of waste plastic under the conditions of the atmosphere and solar light (since the polymer wastes are usually exposed to the solar light in the open air and sun is an unending resource). The composition of plastic and TiO₂ particles has been proven to be a new and useful way to decompose solid polymer in an open air [8–10]. They investigated the photocatalytic degradation of PVC and polystyrene (PS) plastic over photocatalysts. However, the degradation efficiency of their composite films is still low. In addition, the investigations are not systemic and the mechanism is inexplicit.

Composition of dye and TiO₂ can be thought to be an efficient method to modify the photo-response properties of photocatalyst and enhance the photocatalytic capacity [11–13]. Metal Pc may be an appropriate candidate because of its good chemical stability and high absorption coefficient within the solar spectrum [14]. Up to now, a number of studies regarding dye sensitization have been carried out in the aqueous solutions

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in order to seek an efficient method for water purification with solar light as energy source [15,16]. To our best knowledge, there has been no other research (except for one paper we published) on the degradation of solid-phase contaminants such as polymer plastic over dye and TiO_2 composite photocatalyst. It is very important to find an eco-friendly disposal of polymer wastes where they degrade under the ambient sunlight irradiation without the formation of toxic by-products.

Although degradation of polystyrene plastic has been performed in our previous work [10], it is still essential to investigate the degradation efficiency of polyethylene plastic by this method due to their different molecular structure. Thus, in this paper, solid-phase photocatalytic oxidation of PE with TiO_2 or TiO_2/CuPc as photocatalyst under solar irradiation was investigated. Enhancement of photocatalytic degradation of PE over CuPc modified TiO_2 composite film was observed, and the charge transfer mechanism in TiO_2/CuPc composite sample was suggested.

2. Experimental

2.1. Materials

PE was supplied by Yanshan Petrochemical Company Ltd. The average molecular weight (M_w) was about 100,000. The TiO_2 photocatalyst was Degussa P25, whose primary particles ranged in 20–40 nm diameters with mixed crystalline phases [17]. CuPc was supplied by Aldrich (dye content 97%).

2.2. Preparation and characterization of TiO_2 and TiO_2/CuPc photocatalysts

In a typical preparation of TiO_2/CuPc composite, 50 mg TiO_2 powder (P25: 80% anatase, 20% rutile) was added to a 50 ml of ethanol CuPc solution ($C_{\text{dye}}: 2 \times 10^{-5}$ mol/L), followed by stirring for 30 min to obtain absorption/desorption equilibrium. The mixed solution was centrifuged, and the precipitate was washed for several times with distilled water and dried at 80 °C. Finally, the blue TiO_2/CuPc photocatalyst was obtained with 1.1 wt% CuPc. UV–vis spectra of PE– TiO_2 and PE–(TiO_2/CuPc) composite films were measured using a UV-365 spectrophotometer. SPS was employed to study the charge separation characteristics. I – V measurements were performed by using a CHI 660B electrochemical workstation.

A three-electrode cell with platinum flake (50 mm × 4 mm × 0.2 mm) as a counter electrode and a saturated calomel electrode (SCE) as reference electrode was served. All experiments were conducted at 25 ± 2 °C.

2.3. Preparation of PE– TiO_2 and PE–(TiO_2/CuPc) composite films

The PE– TiO_2 or PE–(TiO_2/CuPc) composite film was cast as follows: The polymer stock solution was prepared by dissolving 0.5 g of PE in 40 ml cyclohexane at 70 °C under vigorous stirring for 60 min. 0.0075 g of the TiO_2 or TiO_2/CuPc powder was suspended uniformly in the above 40 ml solution, with the ratio of TiO_2 or TiO_2/CuPc to PE 1.5 wt%. Then 10 ml PE– TiO_2 or PE–(TiO_2/CuPc) solution was spread on a glass plate ($R = 4$ cm) and dried for 20 min at 70 °C, then dried for 48 h at room temperature. The thickness of the resulting films was measured to be 15–20 μm by SEM (KYKY 2000).

2.4. Photodegradation and characterization of the PE– TiO_2 and PE–(TiO_2/CuPc) films

The PE– TiO_2 and PE–(TiO_2/CuPc) samples were exposed in sunlight under the ambient conditions from 9:00 a.m. to 5:00 p.m. every sunny day. The PE– TiO_2 and PE–(TiO_2/CuPc) samples before and after irradiated at different time were all characterized by SEM. The concentration of generated CO_2 during the degradation was measured by GC equipped with a thermal conductivity detector (TCD) using GDX-403 steel column as described in ref. [10].

3. Results and discussion

3.1. Photocatalytic degradation of PE– TiO_2 and PE–(TiO_2/CuPc) samples

Fig. 1 shows the photoinduced weight loss of different samples with solar irradiation time. No noticeable weight loss is observed for the pure PE plastic with 160 h. Addition of TiO_2 leads to the weight loss of PE plastic. Furthermore, the weight loss rate for PE–(TiO_2/CuPc) samples, which varied with different CuPc content of composite photocatalysts, is much higher than PE– TiO_2 sample. The apparent degradation rate shows a maximum at $\text{CuPc}/\text{TiO}_2 \approx 0.7$ wt%, which corresponds

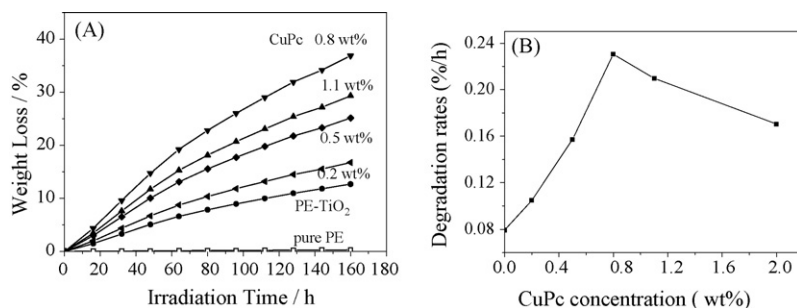


Fig. 1. (A) Weight loss of PE, PE– TiO_2 and PE–(TiO_2/CuPc) samples with solar irradiation time. (B) Apparent degradation rates vs. CuPc concentration in composite catalyst.

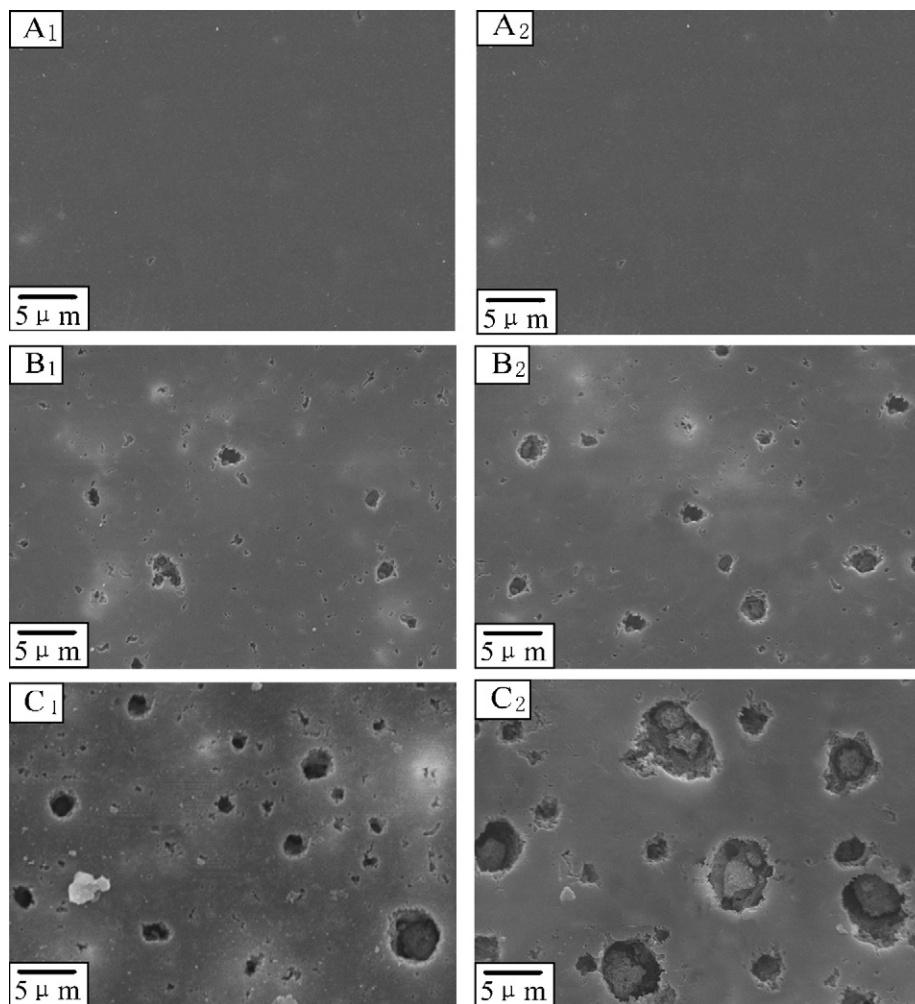


Fig. 2. SEM images of PE, PE-TiO₂ and PE-(TiO₂/CuPc) films. (A₁) PE film after solar-irradiation for 40 h; (A₂) PE film after solar-irradiation for 80 h; (B₁) PE-TiO₂ film after solar-irradiation for 40 h; (B₂) PE-TiO₂ film after solar-irradiation for 80 h; (C₁) PE-(TiO₂/CuPc) film after solar-irradiation for 40 h and (C₂) PE-(TiO₂/CuPc) film after solar-irradiation for 80 h.

to 0.3 monolayer of CuPc on TiO₂. This fact implies that the access of both TiO₂ and CuPc surface to PE polymer can introduce all the active species to the polymer and there exists an optimal surface concentration at submonolayer coverage. The above weight loss data indicate that the photocatalytic and photolytic reaction of PE-(TiO₂/CuPc) and PE-TiO₂ films led to the bond scission and produced a mass of volatile products.

Fig. 2 shows the texture of different film samples after solar irradiation. For PE-TiO₂ film, it can be seen that there are some 2 μm sized and 0.5–1 μm deep cavities on the film surface, and only a little increase in cavity density is observed with the extension of irradiation time. Therefore, it can be supposed that the photodegradation of PE mainly happens on the film surface. Apparently, photocatalytic reaction first starts at the interface between PE and exposed TiO₂ photocatalyst, which leads to the formation of cavities around TiO₂ particles. For PE-(TiO₂/CuPc) sample, the texture changed more significantly. After 40 h irradiation, the average size and depth of the cavities are 3–4 μm and 2 μm, respectively. After 80 h irradiation, the size and depth of the cavities increase to 5 μm and 4–5 μm. The SEM images revealed that the reaction rate of PE-(TiO₂/CuPc) sample is much higher than that of PE-TiO₂ sample.

As shown in Fig. 3, the amount of CO₂ released from PE-(TiO₂/CuPc) samples is always more than that from PE-TiO₂ samples. The formation of CO₂ and volatile organic compounds results in weight loss of films as shown in Fig. 2. The total amount of CO₂ during photodegradation process account for 90% and 96% of the weight loss of PE-TiO₂ and PE-(TiO₂/CuPc) after 50 h irradiation, respectively. It is obvious that CO₂ is the main product of the photocatalytic degradation of the composite PE plastic. In our previous work, degradation of PS-TiO₂ and PS-(TiO₂/CuPc) was performed under fluorescent light [10]. Degradation of PS-TiO₂ and PS-(TiO₂/CuPc) performed under same condition exhibited that degradation of PS-TiO₂ and PS-(TiO₂/CuPc) was slower than PE-TiO₂ and PE-(TiO₂/CuPc), which was mainly due to the complex molecule structure of PS than PE.

3.2. Photoelectrochemical properties of TiO₂ and TiO₂/CuPc photocatalysts in PE films

Fig. 4 shows the UV-vis spectra of different film samples. Pure PE film only absorbs little UV light ($\lambda < 240$ nm), while PE-TiO₂ film has strong absorption below 400 nm.

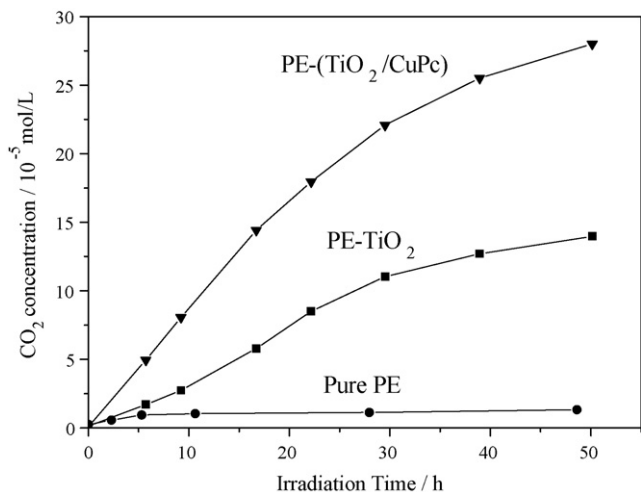


Fig. 3. The concentration of CO₂ for PE, PE-TiO₂ and PE-(TiO₂/CuPc) samples with solar-irradiation time.

PE-(TiO₂/CuPc) film exhibits a broader absorption range (480–800 nm) for the solar spectrum than PE-TiO₂ film. It is seen from Fig. 1(D) that after solar irradiation the spectra of CuPc did not change, which indicated the stability of the TiO₂/CuPc.

As can be seen from Fig. 5, from 300 to 400 nm the stronger photovoltage intensity of TiO₂/CuPc indicates the higher charge separation efficiency and the longer excitations lifetime as compared with that of TiO₂. Also, TiO₂/CuPc sample showed broader photovoltaic response range compared with pure TiO₂. However, there is no absorption in the visible region, which indicates no electron transfer between TiO₂ and CuPc under visible light. In Fig. 6, *I*-*V* curves of TiO₂/CuPc under visible irradiation and without irradiation are very similar, which indicates that there is almost no photocurrent under visible light irradiation. However, under UV-irradiation, the photocurrent produced from TiO₂/CuPc is higher than that from TiO₂, which imply that there is photoelectron transfer between TiO₂ and CuPc under UV light.

TiO₂ particles can absorb UV light ($\lambda < 387$ nm) to create mobile electrons (e^-) and holes (h^+) in the conduction band

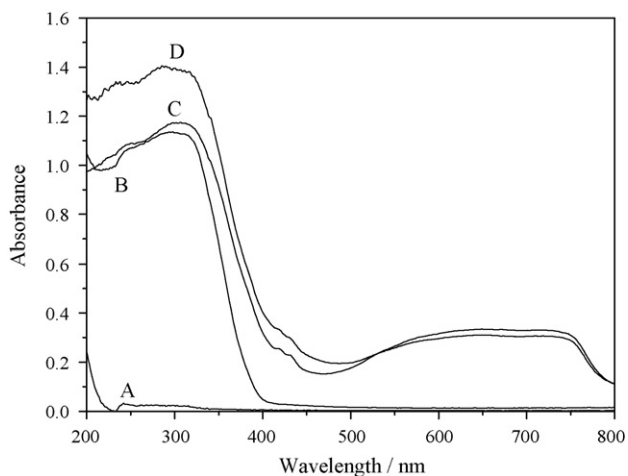


Fig. 4. The UV-vis absorption spectra of different films: (A) pure PE film; (B) PE-TiO₂ film; (C) PE-(TiO₂/CuPc) film and (D) PE-(TiO₂/CuPc) film after solar-irradiated for 50 h.

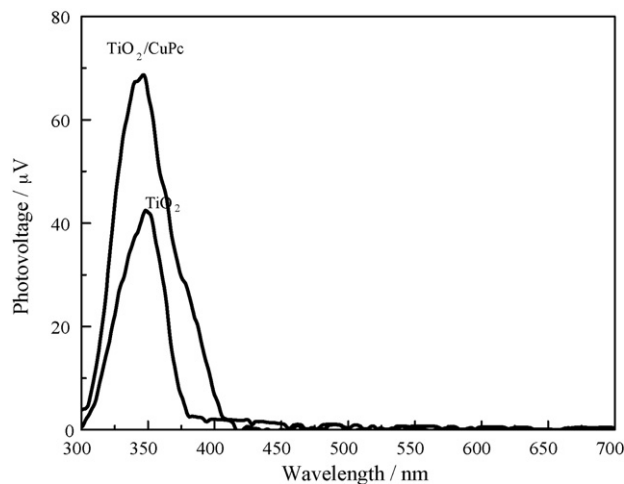


Fig. 5. The SPS of TiO₂ and TiO₂/CuPc photocatalysts.

(CB) and valence band (VB), respectively. Adsorbed oxygen molecules can capture electrons, producing O₂⁻, O and O⁻ species. At the same time, photogenerated holes can be trapped by hydroxyl ions or water adsorbed on the surface, producing hydroxyl radicals, •OH, which play important roles in photocatalytic reactions [18,19].

If the electrons and holes cannot be captured in time, they will recombine with each other within a few nanoseconds, which will reduce the photocatalytic efficiency of TiO₂.

The results in Section 3.1 exhibited that TiO₂/CuPc has much stronger photocatalytic activity than TiO₂ in PE films under solar irradiation. TiO₂ is optically excited by UV light, and a charge injection of photogenerated hole from the valence band of TiO₂ to the ground state of CuPc is thermodynamically permitted:



Resulting from the above process, the electrons and holes are separated effectively on the interface of TiO₂ and CuPc. The

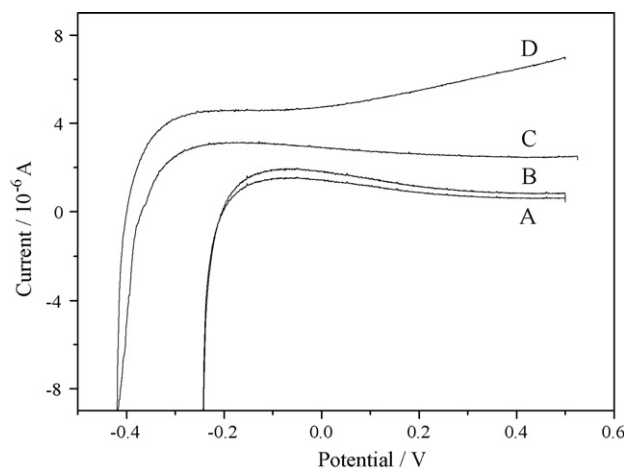
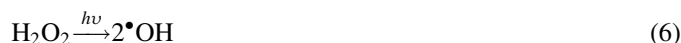
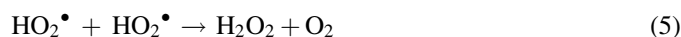
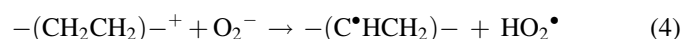
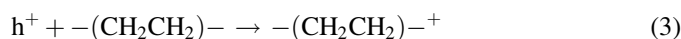


Fig. 6. The *I*-*V* curves of different photocatalysts: (A) TiO₂/CuPc without irradiation; (B) TiO₂/CuPc under visible irradiation; (C) TiO₂ under UV irradiation and (D) TiO₂/CuPc under UV.

recombination rate of photogenerated excitons in TiO₂/CuPc sample was reduced, which ensured more electrons or holes to initiate photocatalytic reaction.

3.3. Photocatalytic degradation mechanism of PE–(TiO₂/CuPc) samples

The photodegradation of pure PE has been extensively studied [20–22]. The reaction of PE under ultraviolet irradiation occurred via direct absorption of photons by the PE macromolecule to create excited states, and then undergo chain scission, branching cross-linking and oxidation reactions. For composite samples, the photocatalytic degradation is the main reaction, which is quite different from the photolytic degradation of pure PE sample. For PE–TiO₂, the photodegradation of PE mainly happens on the film surface where electrons or holes combine with adsorbed oxygen molecules or hydroxyl ion to produce O₂^{•−} or •OH, two very important reactive oxygen species for the degradation of PE. In the photocatalytic degradation of PE–(TiO₂/CuPc), not only O₂^{•−} and •OH play the important roles, but also the holes generated in the ground state of CuPc. As mentioned in Section 3.2, efficient holes production occurs in the ground state of CuPc under solar irradiation. Although holes in the ground state of CuPc have lower oxidative ability than those in valence band of TiO₂, it is energetically favorable for them to participate in the oxidation of PE polymer:



Therefore, embedded TiO₂/CuPc particles can generate enough •OH to photodegrade inner PE. The active oxygen species described above initiate the degradation reaction by attacking neighboring polymer chains. The degradation process spatially extends into the polymer matrix through the diffusion of the reactive oxygen species. Once the carbon-centered radicals are introduced in the polymer chain, their successive reactions lead to the chain cleavage with the oxygen incorporation and species containing carbonyl and carboxyl groups produced (Eqs. (3)–(6)). These intermediates can be further photocatalytically oxidized to CO₂ and H₂O by the aid of reactive oxygen species.

4. Conclusions

1. PE–(TiO₂/CuPc) shows better photocatalytic degradation than PE–TiO₂. The more reactive oxygen species generated, the faster plastic photodegradation goes on. Furthermore, the optimal surface concentration is 0.3 monolayer of CuPc on TiO₂.

2. TiO₂/CuPc in the PE film can be excited only by UV part in the sunlight. The higher charge separation efficiency of TiO₂/CuPc photocatalyst results in the more reactive oxygen species generation both on film surface and inside thin film, which is responsible for the faster and more complete mineralization over TiO₂/CuPc than over TiO₂ photocatalyst.
3. The development of this new kind of composite polymer can lead to an eco-friendly disposal of polymer wastes.

Acknowledgments

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