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Visible-Light Photocatalytic Degradation of Aromatic Contaminants with Simultaneous H_2 Generation: Comparison of 2,4-Dichlorophenoxyacetic Acid and 4-Chlorophenol

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Abstract Aromatic contaminants, 2,4-dichlorophenoxyacetic acid (2,4-D) and 4-chlorophenol (4-CP), were photocatalytically degraded in aqueous solutions under visible light illumination. 2,4-D was degraded more rapidly with more amount of simultaneous hydrogen generation than 4-CP. This is due to their difference in oxidative potentials, hydrophobic effects, electrostatic interactions and chemisorptions on the photocatalyst 3%WO_x/TiO_2.

Keywords Photocatalysis · Visible light · Degradation · 2,4-Dichlorophenoxyacetic acid · 4-Chlorophenol · Hydrogen generation

1 Introduction

Organic compounds, such as hydrocarbons and fossil fuels, have been used as sacrificial electron donors (SEDs) for photocatalytic hydrogen generation [1]. Accordingly, organic pollutants have been suggested to act as SEDs [2]. This process can degrade pollutants and meantime transfer the energy of light and the chemical energy of pollutants into the chemical energy of hydrogen, a promising future energy carrier. A photogalvanic mode has been reported to confirm the suggestion. 4-CP, 2,4,5-trichlorophenol and 4,4′-dichlorophenol are photocatalytically decomposed on TiO_2 anode, and H_2 is generated on the platinum black cathode [3]. More recently, in the suspension mode containing UV illuminated Pt/TiO_2, model pollutants such as oxalic acid, formic acid, formaldehyde and chloroacetic acids have been photocatalytically degraded with simultaneous H_2 generation [4–6].

Compared to UV light [3–6], visible-light photocatalysis has much more promise in applications. Since visible light cannot excite TiO_2, azo-dyes have been employed to sensitize the TiO_2-based photocatalysts, while they are photocatalytically degraded [7, 8]. In fact, most pollutants are not sensible to visible light. Thus, it is significant to utilize pollutants except dyes in the H_2 generation. Since aromatic pollutants are ubiquitous in the environment and refractory to bio-degradation, they should be paid more attention to.

In this study, 2,4-D and 4-CP were selected as model aromatic pollutants. The performances of the aromatic pollutants on the photocatalytic H_2 generation were compared on visible light illuminated 3%WO_x/TiO_2. Then, the difference in the performances was investigated from the views of oxidative potentials, hydrophobic effects, electrostatic interactions and chemisorptions on the photocatalyst. The results benefit the evaluation of the abilities of aromatic contaminants as SEDs for visible-light photocatalytic H_2 generation.

2 Experimental Section

The experimental setup consists of a glass photoreactor, a vacuum system to collect the gaseous products, and a gas chromatogram (Varian CP-3800, US) (Fig. 1). Argon gas was introduced into the system as base gas. A 250 W high

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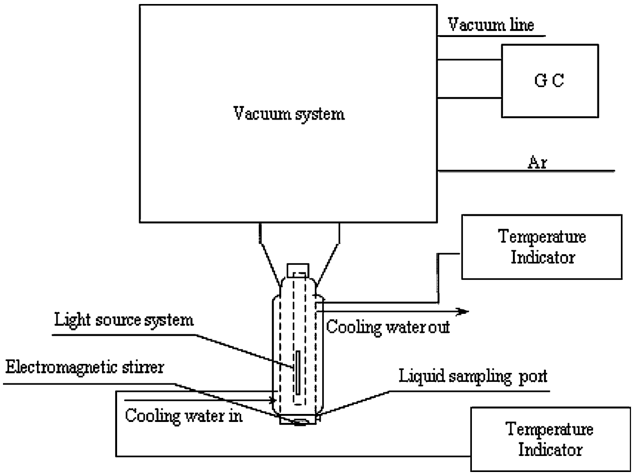

Fig. 1 Sketch of the setup for the photocatalytic experiments

pressure sodium lamp was used as the light source whose UV light was removed by sodium nitrite solution filter. The photocatalyst was 3%WO_x/TiO_2 obtained as a gift from Prof. Li et al. [9], and was dispersed with 1.0 g/L concentration into the reactant solutions by magnetic stirring. The volume of the suspension was 160 mL. Water and the solution of 1.0 mmol/L 4-CP were adjusted to pH 3.1 by nitric acid, which matched the natural pH of 2,4-D solution with the concentration of 1.0 mmol/L. The reaction temperature was kept at 20 C by a thermostat with circular water. The concentrations of 2,4-D and 4-CP were detected by a high pressure liquid chromatography (P200II, Elite, China) at 280 nm. The column used was a Hypersil ODS2 column (200 × 4.6 mm, 5 μm), and the mobile phase was a mixture of 60% acetonitrile, 40% water and 1.0‰ acetic acid with a flow rate of 1.0 mL/min.

Differential pulse voltammetry (DPV) measurements were carried out in a conventional 3-electrode cell on an electrochemical workstation (ZAHNER IM6e, Germany). A rotating disc electrode of glass carbon coated with a film of 3%WO_x/TiO_2 was used as the work electrode, a platinum flake as the counter electrode, and Ag/AgCl electrode as the reference electrode. The concentration of 2,4-D and 4-CP was 1.0 mmol/L. Sodium sulfate solution with 0.1 mol/L concentration was used as the supporting electrolyte, and nitrogen was purged into the solution during the measurements.

Theoretical calculations were carried out by the Gaussian 03 program [10], employing the hybrid Becke exchange and Lee, Yang, and Parr correlation density functional method, B3LYP [11–13]. In the geometry optimization, molecular orbital characteristics and electrostatic potential (ESP) analysis, 6-311++G(d,p) basis set was used. Aqueous solvation effect was considered by a polarized continuum model (PCM) [14].

3 Results and Discussion

3.1 H_2 Generation and Organic Degradation

Figure 2 demonstrates the amount of H_2 and the concentration decays of the pollutants in the visible-light photocatalytic reaction system with the illumination time. When the dark adsorption reached equilibrium after 1 h, the adsorption amount of 2,4-D was bigger than that of 4-CP. When the illumination was initiated, it could be seen that no H_2 was detected in water without the presence of any pollutant, while a small amount of 0.007 μmol of H_2 was detected with the presence of 4-CP after about 10 h illumination. Interestingly, the amount of H_2 generated from 2,4-D solution was about 7.6 times of that from 4-CP solution after about 10 h illumination. At the same time, 18.1% of 4-CP and 32.0% of 2,4-D were removed. Thus, both 2,4-D and 4-CP accelerated visible-light photocatalytic H_2 generation from water, and the promotion by 2,4-D was more notable than that by 4-CP.

Figure 2 also showed that the amount of hydrogen produced is much less than the amount of aromatic pollutants degraded. This phenomenon is discussed below according to the energy level diagram of the photocatalyst WO_x/TiO_2 (Fig. 3).

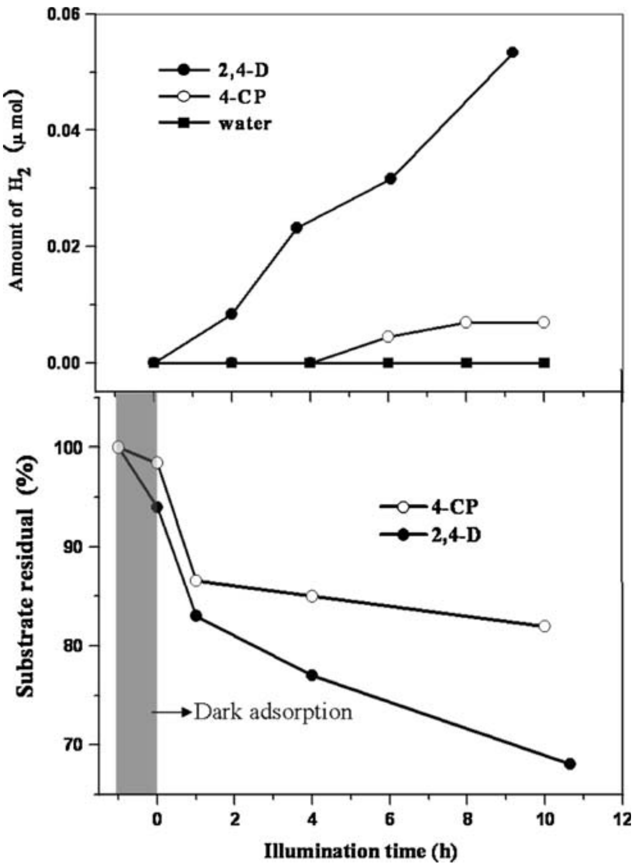

Fig. 2 Amount of hydrogen produced and decay of the concentrations of 2,4-D and 4-CP

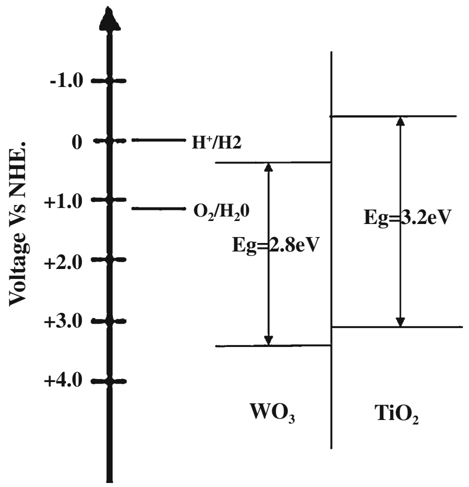

Fig. 3 Energy level diagram of WO_3/TiO_2

Tungsten in the photocatalyst WO_x/TiO_2 mainly presents in the valence of W^{6+} [9]. The bandgap of WO_3 is 2.8 eV and it can absorb visible light. While the bandgap of TiO_2 is 3.2 eV and it can only absorb UV light. Visible light can excite the electrons on the valent band of WO_3 to the conductive band and induce holes on the valent band. These holes are of so strong ability of oxidation that they obviously degraded the aromatic pollutants. Meanwhile, since the valent band potential of WO_3 and TiO_2 are rather close, photoinduced holes on the valent band of WO_3 may partly transfer onto the valent band of TiO_2. This can prolong the lifetime of the photoinduced carriers and accelerate the photocatalytic reactions.

On the other side, the potential of the conductive band of WO_3 is more positive than the potential of hydrogen generation (Fig. 3). This is not favorable for the photocatalytic hydrogen production. The most possible reason for the hydrogen production in this paper is that the photoinduced electrons can reduce tungsten to lower valence and generate states with more negative potential. Some of these states have more negative potential than that of hydrogen generation, so a little hydrogen is released and much less than the amount of aromatic pollutants degraded. We should say that the WO_x/TiO_2 is not an ideal visible-light photocatalyst for hydrogen generation. But anyway, with this photocatalyst, we showed that aromatic pollutants can be photocatalytically degraded with simultaneous hydrogen production with visible light illumination.

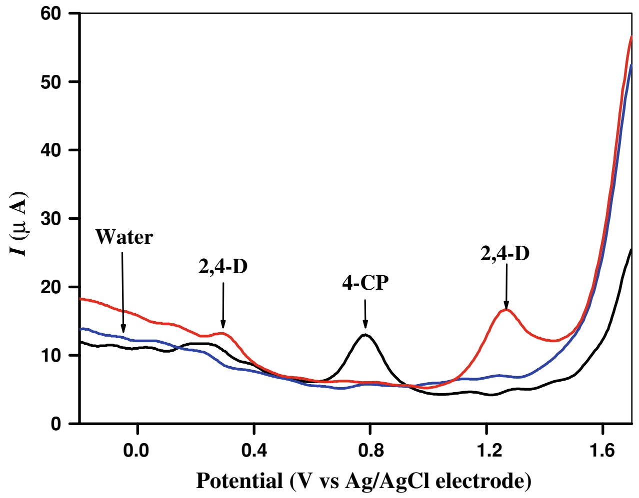

Fig. 4 DPV results of 2,4-D, 4-CP and water on the surface of $3\%WO_x/TiO_2$ at pH 3.1

3.2 Difference in Oxidative Potentials of 2,4-D and 4-CP on $3\%WO_x/TiO_2$

DPV has been employed to determine the oxidative potentials [15–17] as an electrochemical technique for its high resolution and sensitivity. In this study, DPV measurements were performed to compare the oxidative potentials of 2,4-D and 4-CP on the surface of $3\%WO_x/TiO_2$ at pH 3.1, and the results were shown in Fig. 4. It could be seen that for water, no oxidative peak was observed within the potential window. This was in accord with the fact that water has negligible visible-light photocatalytic H_2 generation. An oxidative peak was observed for 4-CP at 0.786 V, while two oxidative peaks were observed at 0.308 and 1.259 V for 2,4-D, respectively. The peak at lower oxidative potential value of 0.308 V indicated that 2,4-D was more readily to be oxidized than 4-CP, thus easier to donate its electrons to generate H_2 in the photocatalytic process.

3.3 Difference in Adsorption of 2,4-D, 4-CP and Water on Photocatalyst

Adsorption of the organic pollutants is considered as a prerequisite step for the photocatalytic degradation in a TiO_2 suspension system, and a stronger adsorption appears to speed up the degradation rates and electron donation of the organic pollutants [4, 18]. The adsorption of 2,4-D, 4-CP and water on $3\%WO_x/TiO_2$ consists of physical adsorption and chemisorption. The physical adsorption was mainly determined by hydrophobic effects of the pollutants and the electrostatic interactions between the substrates and the photocatalyst.

The hydrophobic effects of these pollutants can be evaluated by *n*-octanol/water partition coefficient (K_{ow}) [19]. K_{ow}s for 2,4-D and 4-CP are 646 [20] and 245 [21], respectively. 2,4-D is more hydrophobic than 4-CP due to more hydrophobic groups involved. Then, 2,4-D is more prone to aggregate and migrate onto the interfaces of the photocatalyst. Since the directionality of electrostatic interaction and chemisorption, the negative polar head of the pollutants came nearest to the positively charged surface of the photocatalyst, while the hydrophobic effect can drive the pollutants onto the interface and arrange the non-polar head of the pollutants. By this way, hydrophobic effect promoted electrostatic interactions and chemisorption. The hydrophobic effect in 2,4-D solution was stronger than that in 4-CP solution, this partly contributed to the difference of their performances as SEDs for visible-light photocatalytic hydrogen production.

Since electrostatic interactions are relevant to electric properties of the species involved, the component analysis is necessary. The pKa of 2,4-D, 4-CP and H_2O in water are 2.64 [22], 9.41 [23] and 7.0, respectively. As the pH value of the solutions was 3.1, the species distribution in the reaction solution can be calculated. The concentration of H_3O^+ was always 0.753 mmol/L. 2,4-D is 75.3% dissociated while 4-CP and water is hardly dissociated. Thus, the concentrations of the dissociated species of 4-CP (4-CP^{-1}) and hydroxyl ion could be neglected, while the concentration of nitrate ion in 4-CP and water was 0.753 mmol/L.

The electrostatic potentials (ESP) of the species were calculated by B3LYP method and the results are illustrated in Fig. 5. Since the isoelectric point of 3%WO_x/TiO_2 is 5.0 [9], and the pH value for the reaction solution is 3.1, thus the photocatalyst surface is positively charged. It is more prone to interact with species with negative ESP. The dissociated species of 2,4-D (2,4-D^{-1}) has largest value of ESP of −0.309. So, it has strongest electrostatic interactions with the photocatalyst. The molecular states of 2,4-D, 4-CP and H_2O have low values of local negative ESP, thus weak electrostatic interactions exist between the molecule states and the photocatalyst. Nitrate ion in 4-CP solution and water may screen the molecular states for it has bigger electrostatic interaction than the molecule states. So, strongest electrostatic interactions exist between 2,4-D and the photocatalyst. This strong interaction enhances the physical adsorption of 2,4-D on the photocatalyst.

Chemisorptions between the substrates and the photocatalyst can be discussed with the theory of hard and soft acid and base (HSAB) [24], which emphasizes that hard acids prefer to interact with hard bases, and soft acids prefer to interact with soft bases (HSAB) [25].

Absolute hardness (η), a quantitative index for HSAB theory, is defined as the half of the difference between the orbital energies of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) [26]. The η-values calculated by the B3LYP method are listed in Table 1, in light of which the chemical adsorption of the species on the 3%WO_x/TiO_2 can be evaluated. The surface acidity of TiO_2, a hard acid, is

Table 1 Absolute hardness (η) of the species in the reaction solution

Species	E_{HOMO} (eV)	E_{LUMO} (eV)	η (eV)
4-CP^{-1}	−4.907	−0.193	2.357
2,4-D^{-1}	−6.387	−0.986	2.700
OH^-	−5.626	0.118	2.872

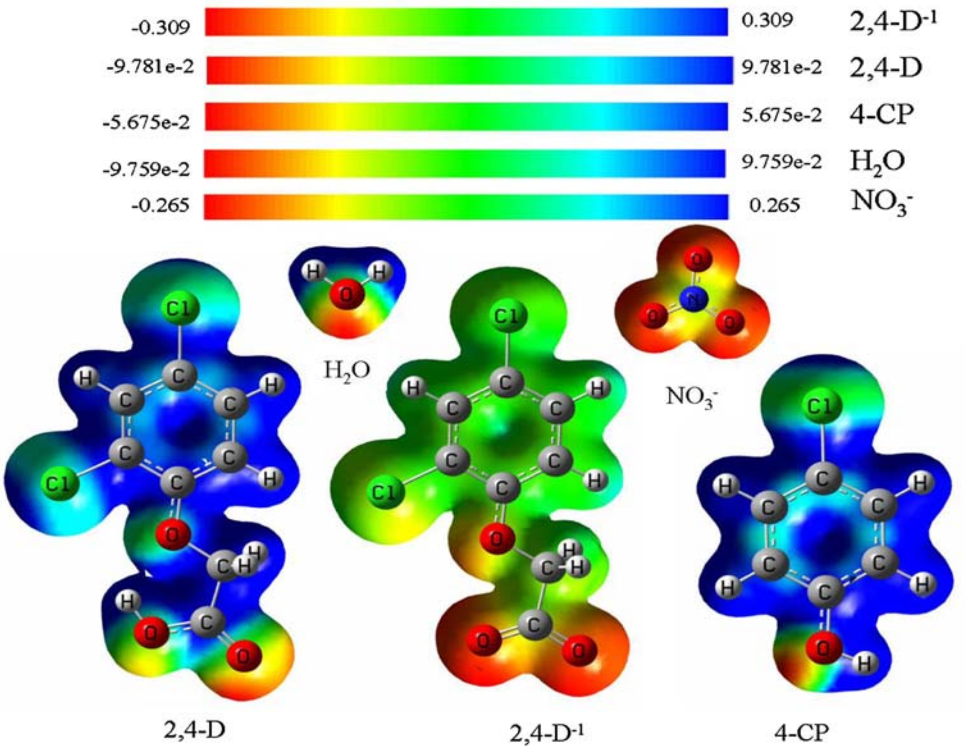

Fig. 5 Electrostatic potential pictures of the species at total electron density isosurface with value of −0.0200

significantly increased by a factor of 15 after the loading of 3% WO_3 [27], so the surface of the photocatalyst 3%WO_x/TiO_2 is mainly covered with hard acid. Besides, 2,4-D and 4-CP have been reported to be dissociatively chemisorbed on the surfaces of the photocatalysts [28–30]. Then, the adsorption of the dissociated species as base is considered. Clearly, the adsorption of 2,4-D^{-1} on the surface of 3%WO_x/TiO_2 is stronger than that of 4-CP^{-1} since the η value of 2,4-D^{-1} (2.700 eV) is larger than that of 4-CP^{-1} (2.357 eV). Hydroxyl ion (2.872), the dissociative part of water, has even bigger absolute hardness value than 2,4-D. This indicates that water is theoretically easier to be chemisorbed. Since the pH value of the photocatalytic systems was 3.1 and pKa of water is 7.0, the concentration of hydroxyl ion is very low, so the dissociation chemisorption of water on 3%WO_x/TiO_2 is quite kinetically limited.

The above results indicate that both physical adsorption and chemical adsorption of 2,4-D on the 3%WO_x/TiO_2 are stronger than those of 4-CP and water. The stronger adsorption benefited the photocatalytic degradation of 2,4-D and enhanced the simultaneous evolution of H_2.

4 Conclusions

Both 2,4-D and 4-CP promoted photocatalytic hydrogen generation and were simultaneously degraded in water on visible light illuminated 3%WO_x/TiO_2. 2,4-D was a better SED than 4-CP. This was originated from the difference in oxidative potentials, hydrophobic effects, electrostatic interactions and chemisorptions on the photocatalyst.

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