



## Enhanced photoelectrocatalytic degradation of phenols with bifunctionalized dye-sensitized TiO<sub>2</sub> film

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### ARTICLE INFO

#### Article history:

Received 26 August 2011

Received in revised form 24 October 2011

Accepted 31 October 2011

Available online 7 November 2011

#### Keywords:

Photoelectrocatalytic degradation

Dye-sensitized TiO<sub>2</sub> film

Phenols

Degradation efficiency

### ABSTRACT

A degradation device containing a bifunctionalized TiO<sub>2</sub> film electrode and an anode electrode was described. The bifunctionalized TiO<sub>2</sub> film electrode is composite of an area of dye-sensitized TiO<sub>2</sub> film, electrolyte and counter electrode, which is similar to the structure of dye-sensitized solar cells (DSSCs). Electrons and positive charges induced by visible light absorption of dyes could arrive at the degradation region of the bifunctionalized TiO<sub>2</sub> film electrode and the anode electrode, respectively. Both could produce hydroxyl radicals (<sup>•</sup>OH) to participate in the degradation reaction. The degradation efficiency was enhanced remarkably by an external potential. Meanwhile, the effects of dye-sensitized TiO<sub>2</sub> film area and pH value on the degradation of 4-chlorophenol (4-CP) were tested. An insight into degradation pathway, plausible mechanism for 4-CP and degradation of other phenols were also discussed here.

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### 1. Introduction

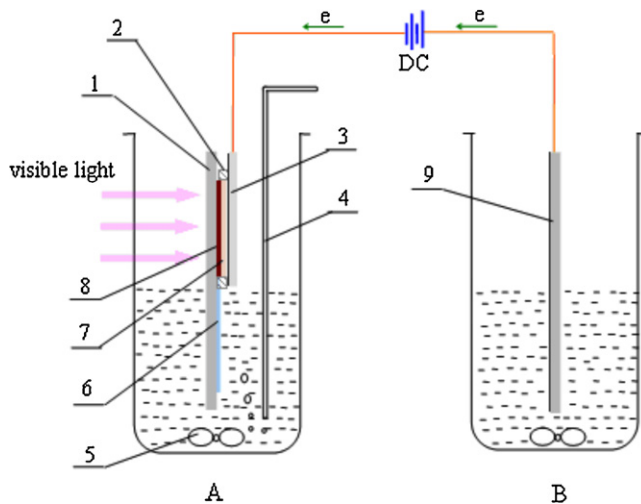
Titanium dioxide (TiO<sub>2</sub>) has been extensively studied being a photocatalytic material for environmental applications, including the purification of water and wastewater because of its high photocatalytic activity, long-term chemical stability, non-toxicity and low price [1–3]. The photocatalysis process uses ultraviolet (UV) light to excite an electron from the valence band of TiO<sub>2</sub> to its conduction band, leaving a hole to oxidize organics. It is preferable of utilizing TiO<sub>2</sub> in the form of film rather than slurry because the former avoids the nuisance recovery procedure for the nanoparticles from an aqueous phase. The rapid recombination of photogenerated electrons and holes often results in low quantum yield, limiting the photocatalytic efficiency and obstructing the practical application of the photocatalytic process. Photoelectrocatalytic (PEC) process has proven to be an efficient way of affording good quantum yield, which is through immobilization of TiO<sub>2</sub> on a conducting substrate and application of a potential bias [4,5]. The photogenerated electron is withdrawn to counter electrode by external bias in the PEC process, which could counteract charge recombination [6–8]. However, the wide-band gap of TiO<sub>2</sub> can only capture less than 5% of solar irradiance. To obtain a more efficient utilization of solar irradiation, many attempts were made to shift its photocatalytic activity to the visible region [9–11].

Polymers [12–14] and metal-organic complexes [15,16] have been applied into modify TiO<sub>2</sub>, giving high photocatalytic degradation of organics under visible irradiation. Likewise, dye sensitization is one of the efficient methods for extending the light absorption of TiO<sub>2</sub> to a visible region. As these dyes sensitized TiO<sub>2</sub> produce hydroxyl radicals (<sup>•</sup>OH) through trapping conduction band electrons to reduce oxygen to superoxide, many dyes cannot withstand this severe oxidative stress for long time and were degraded gradually. In order to avoid dye decomposition, it is desired to develop new sensitization systems with high activity, visible-response, and high stability.

Herein, a new double-region-structured TiO<sub>2</sub> film was fabricated with one region of dye-sensitized site providing photogenerated electrons and the other region of the photocatalytic site supplying an effective degradation of organic pollutants [17]. This bifunctionalized TiO<sub>2</sub> film is composite of an area of dye-sensitized TiO<sub>2</sub> film, electrolyte and counter electrode, which is similar to the structure of dye-sensitized solar cells (DSSCs) [18] except for the deposition substrate for TiO<sub>2</sub> film. The reason for use of ordinary glass sheet in place of FTO conductive glass for deposition of TiO<sub>2</sub> film was discussed in our previous report [17]. The fabricated device could accomplish separation of electron from the positive charge. Thus electrons and positive charges had opportunities to participate in degradation reaction, which caused to increase the quantity of active species. Consequently, the degradation efficiency increased obviously. Positive charges and electrons transferred into photocatalytic sites of the bifunctionalized TiO<sub>2</sub> film and anode, which afforded 97% and 96% removal of 4-chlorophenol (4-CP) after 5 h, respectively.

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**Fig. 1.** Degradation of 4-chlorophenol in reactors A and B (salt bridge is not shown in the figure). 1, ordinary glass sheet; 2, sealing film; 3, counter electrode (Pt/FTO); 4, bubbling pipe; 5, magnetic stirrer; 6, degradation region of TiO<sub>2</sub> film; 7, electrolyte; 8, dye-sensitized TiO<sub>2</sub> film; and 9, anode (Pt/FTO).

The degradation reaction catalyzed by the bifunctionalized TiO<sub>2</sub> film together with the anode governed the degradation process and high degradation efficiency in the former could lead to high efficiency in the latter. On the other hand, the latter degradation promoted the former degradation because of the anode withdrawing electron from water oxidation and supplying electron for regeneration of the oxidized dye through the iodide/triiodide redox couple. If the oxidized dyes could be regenerated faster through the iodide/triiodide redox couple, much more electrons will be injected into the conduction band of TiO<sub>2</sub> from the dyes under light irradiation, which will provide higher degradation efficiency. To test this idea, an electrical potential was applied into the reaction through a potentiostat. Here, we hope to report the result of external potential on the photocatalytic degradation of 4-chlorophenol (4-CP). Further, effects of dye-sensitized TiO<sub>2</sub> film area and pH value, an insight into the degradation mechanism and other possible phenols are also presented here.

## 2. Experimental

### 2.1. Preparation of the degradation device

TiO<sub>2</sub> colloid was prepared according to the literature method [19], which was used for the preparation of the nanocrystalline

films. An area of TiO<sub>2</sub> film (14 mm × 28 mm) was deposited on an ordinary glass sheet by screen printing. Half area of the film (14 mm × 14 mm) was stained by immersing it into a dye solution containing 300 μM *cis*-Ru(dcbpy)<sub>2</sub>(NCS)<sub>2</sub> (N719) as dye sensitizer. The cell of a dye-sensitized region was fabricated according to the reported procedure [17], which was composed of the dye-sensitized TiO<sub>2</sub> film, electrolyte, and a counter electrode. Pt catalyst was deposited on a FTO glass (16 mm × 16 mm) to give a counter electrode. The electrolyte employed was a solution of 0.6 M 1,2-dimethyl-3-n-propylimidazolium iodide (DMPII), 0.1 M LiI, 0.05 M I<sub>2</sub>, and 0.5 M *tert*-butylpyridine in acetonitrile. Another Pt/FTO electrode with an area of 14 mm × 28 mm was employed as an anode. The degradation region of TiO<sub>2</sub> film and the anode were inserted into solutions of 4-CP in reactors A and B, respectively, as shown in Fig. 1. An electrical DC potential was applied by a potentiostat. A U-tube salt bridge is contacted between reactors A and B, which is not shown in Fig. 1.

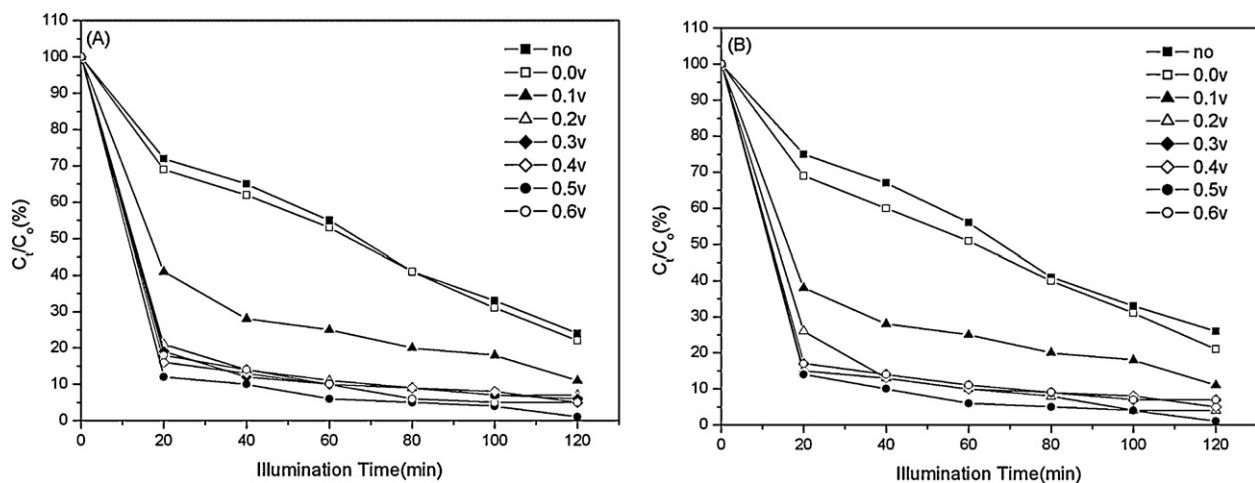
### 2.2. The degradation experiment

A 300 W Xe lamp (L25, λ<sub>max</sub> = 500 nm) was used as the visible light source, which irradiated at a distance of 20 cm to the device surface through 420 nm cutoff filters. The degradation experiment was conducted in two wide-mouth glass flask reactors with 14 mL of 4-CP and magnetically stirred by a Teflon stirrer. Air was bubbled through the pipe during the reaction. Light intensity, as measured by a visible-irradiance meter, was about 4.0 mW/cm<sup>2</sup> at the position of the dye-sensitized region located. The concentration of 4-CP was determined by a HPLC using an Agilent 1100 chromatograph equipped with a ZORBAX Eclipse XDB-C18 reversed phase column. HPLC was detected by a UV detector adjusted to 280 nm. The mobile phase was a mixture of water and methanol (20:80, v/v) with a flow rate of 1.0 mL/min. The total organic carbon (TOC) was measured using SHIMADZU TOC-VCPH instrument to evaluate the mineralization degree of 4-CP. Hydrogen peroxide concentration was determined by a spectrophotometric method using the potassium titanium (IV) oxalate method [20], and then the absorbance was measured at 400 nm in a 1 cm quartz cell. The fluorescence emission of 7-hydroxycoumarin was measured at 332 nm excitation using a spectrofluorometer. The 2 M H<sub>2</sub>SO<sub>4</sub> and 2 M NaOH solutions were used to adjust pH to the desired values.

## 3. Results and discussion

### 3.1. Effect of external voltage on the degradation of 4-CP

The experiments were conducted in two reactors A and B using a DC power source. The negative pole of the power was connected



**Fig. 2.** Effect of external voltage on the degradation of 4-chlorophenol in reactors A and B.

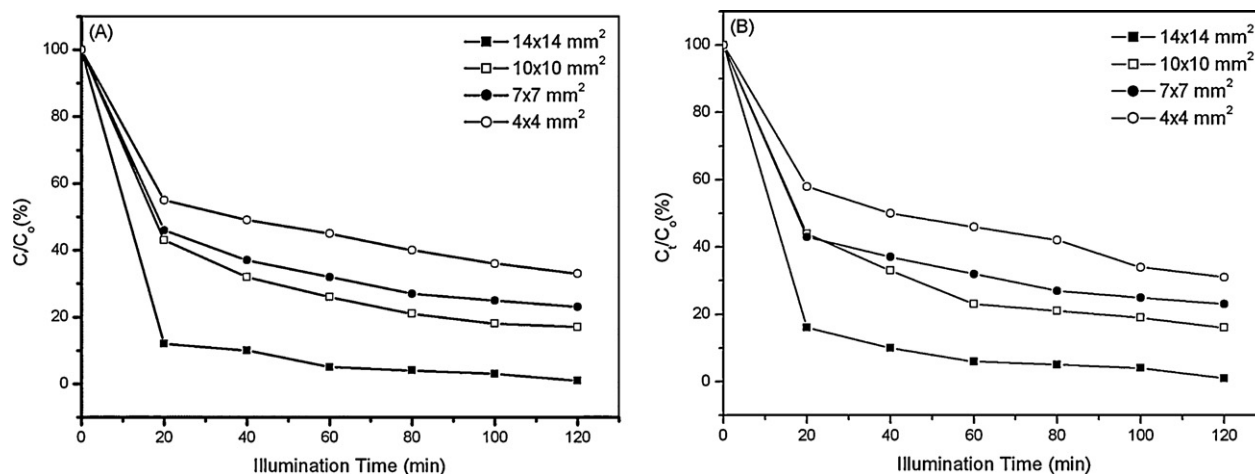


Fig. 3. Effect of dye-sensitized TiO<sub>2</sub> film area on the degradation of 4-chlorophenol in reactors A and B.

to the counter electrode in reactor A, and its positive electrode was with the anode in reactor B. The effect of applied external voltage was designed at 0.6, 0.5, 0.4, 0.3, 0.2, 0.1, and 0.0 V. No applied external voltage was also tested when the counter electrode is connected with the anode by a copper wire. The degradation reaction was under the conditions of 10 mg/L 4-CP, pH 4, bubbling air 5 L/h, and light intensity 4.0 mW/cm<sup>2</sup>. The results are shown in Fig. 2. The degradation efficiency of 4-CP was increased in both reactors A and B from the external potential of 0.0 to 0.5 V. 99% and 98% of 4-CP were removed at a potential of 0.5 V after 2 h in reactors A and B, respectively, whereas they were only 76% and 74% removal without external potential supply. It was also observed that any further increase in the applied potential beyond 0.2 V did very little to enhance the degradation rate. However, with the higher potential of 0.5 V, a little lower efficiency of the degradation was observed. The concentration of total organic carbon (TOC) in reactors A and B decreased 61% and 60%, respectively, after 2 h at a potential of 0.5 V. For comparison, a set of experiments in darkness were set up to perform electrolysis degradation. Almost no removal of 4-CP in both reactors was found in the absence of light irradiation, although at a potential of 0.5 V. The degradation reaction did not occur under electrolysis conditions because there is no current in electrolysis system.

In our previous report [17], the glass substrate for depositing the bifunctionalized TiO<sub>2</sub> film and oxygen atmosphere both played crucial role in degradation of 4-CP. As seen in Fig. 2, the external voltage had enhanced the degradation efficiency remarkably. The other parameters, such as dye-sensitized TiO<sub>2</sub> film area and pH value, were also tested at an external potential of 0.5 V.

### 3.2. Effect of dye-sensitized TiO<sub>2</sub> film area on the degradation of 4-CP

The amount of dye sensitizer is one of the important parameters in photocatalytic degradation. In order to study the effect of dye-sensitized TiO<sub>2</sub> film area, other three bifunctionalized TiO<sub>2</sub> film electrodes with an area of 10 × 20, 7 × 14, and 4 × 8 (mm<sup>2</sup>) were prepared according to the same procedure. Half areas of these films with 10 × 10, 7 × 7, and 4 × 4 (mm<sup>2</sup>) were sensitized by dye N719 and fabricated to cells. The other corresponding half areas without dye sensitization were used for degradation region. These devices for degradation of 4-CP were carried out under the typical conditions (4-CP 10 mg/L, pH 4, bubbling air 5 L/h, light intensity 4.0 mW/cm<sup>2</sup>, and DC 0.5 V), and these results are shown in Fig. 3. The removal of 4-CP was increased with the increase of dye-sensitized TiO<sub>2</sub> film area. Larger area of dye-sensitized TiO<sub>2</sub> film

will absorb much more amounts of dyes in the procedure for fabricating a degradation device, which generate more electrons under the same light irradiation. The more electrons cause to enhance the degradation efficiency through increasing the quantity of active species.

### 3.3. Effect of pH on the degradation of 4-CP

The degradation of 4-CP at different initial pHs is shown in Fig. 4. The variation of pH had an obvious influence on the degradation of 4-CP. Higher degradation rates were obtained when experiments were conducted in acidic solutions than that in alkaline solutions. For example, 99% of 4-CP disappeared at pH 4 after 2 h under visible light irradiation, whereas 75% of 4-CP was removed at pH 10. At the alkaline conditions, 4-CP is ionized with negative charges, and becomes more water-soluble, which slackens the reaction. However, at the acidic conditions, 4-CP is presented in the molecular form with more hydrophobic property. Thus, the acidic solution facilitates 4-CP in the molecular form adsorption on the surface of TiO<sub>2</sub> and promotes better degradation [21]. On the other hand, TiO<sub>2</sub> surface becomes negatively charged at the alkaline condition, and becomes positively charged at acidic condition. The interaction between positively charged catalyst surface and 4-CP shows high adsorption capacity at low pH and favors good degradation [22]. In addition, the super oxide ions generated by the reaction of dissolved oxygen are more readily producing the active species of hydroxyl radicals in the acidic solutions than the alkaline solutions from the reaction of O<sub>2</sub><sup>•−</sup> and H<sup>+</sup>, which is beneficial to the degradation reaction. With further lowering pH value (pH = 2), the removal efficiency decreases to 86%, which may be partly ascribed to the increasing concentration of SO<sub>4</sub><sup>2−</sup> by addition of H<sub>2</sub>SO<sub>4</sub> to adjust pH.

### 3.4. Degradation of other phenols

To extend the degradation substrate, 2-chlorophenol (2-CP), phenol and 4-nitrophenol (4-NP) were submitted to this device, and the results are shown in Fig. 5. Degradation of 2-CP and phenol by this process had a similar tendency to that of 4-CP, although the observed degradation rate had some difference. The concentration of 2-CP in reactors A and B decreased 96% and 94% after 2 h, respectively. However, in the degradation of 4-NP, only 78% and 76% removals of the substrate were obtained in reactors A and B under the same conditions, respectively. Buxton et al. [23] reported that the degradation rate constants for •OH with phenolic compounds

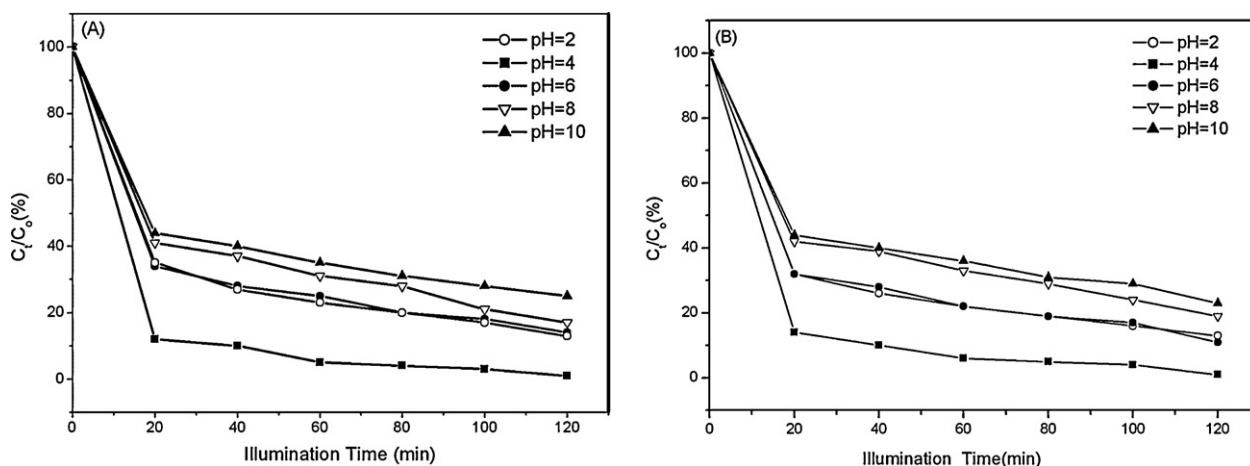


Fig. 4. Effect of pH on degradation of 4-CP in reactors A and B.

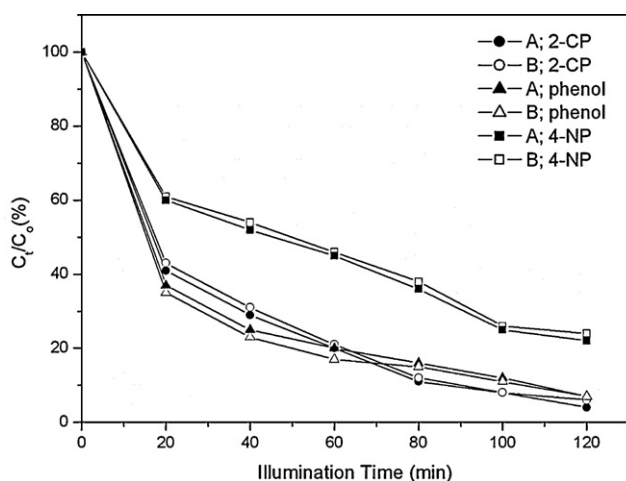


Fig. 5. Removal of 2-CP, phenol, and 4-NP in the reactors A and B.

were 4-CP > phenol > 4-NP. The degradation efficiency by our process was coincident with the order of reported rate constants.

### 3.5. Formation of hydrogen peroxide

The formation of hydrogen peroxide ( $H_2O_2$ ) was detected by a spectrophotometric method [20], which can be converted into  $\cdot OH$  by attack of electron. Fig. 6 shows the formation of  $H_2O_2$  in reactors A and B at an external potential of 0.5 V and no external potential. In the reactor A,  $H_2O_2$  was formed quickly once the reaction was initiated under no external potential conditions. The concentration of  $H_2O_2$  increased steadily with the reaction time, reaching 43.8 mg/L after 25 min. The formation of hydrogen peroxide is promoted by external potential. For example, the concentration of  $H_2O_2$  reached 25.2 mg/L after 5 min and 52.2 mg/L after 25 min, increasing remarkably with the reaction time. This enhancement in the formation of  $H_2O_2$  was in consistent with the degradation of 4-CP. However, small amount of  $H_2O_2$  was produced in the reactor B with 2.9 mg/L  $H_2O_2$  after 25 min at a potential of 0.5 V and 0.11 mg/L  $H_2O_2$  after 25 min under no external potential conditions. These results indicated that hydrogen peroxide was formed efficiently in the reactor A, followed by generation of active species  $\cdot OH$  to degrade pollutants. While the degradation of 4-CP occurred in the reactor B was not mainly derived from hydrogen peroxide.

The degradation of 4-CP was compared in the absence or presence of *tert*-butanol (*t*-BuOH), which is a widely used hydroxyl

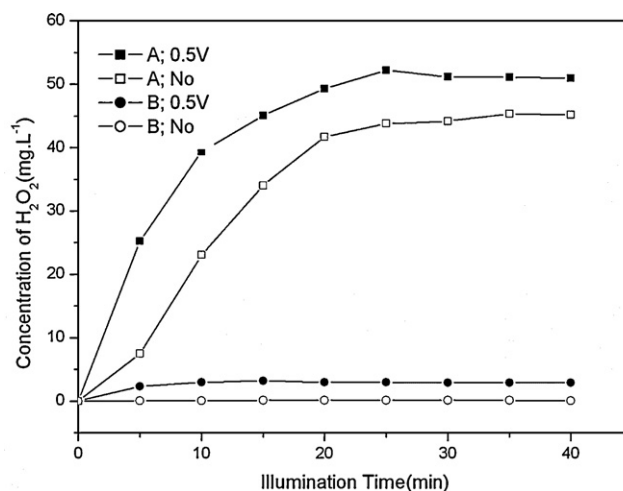


Fig. 6. Formation of  $H_2O_2$  in reactors A and B at an external potential of 0.5 V and no external potential.

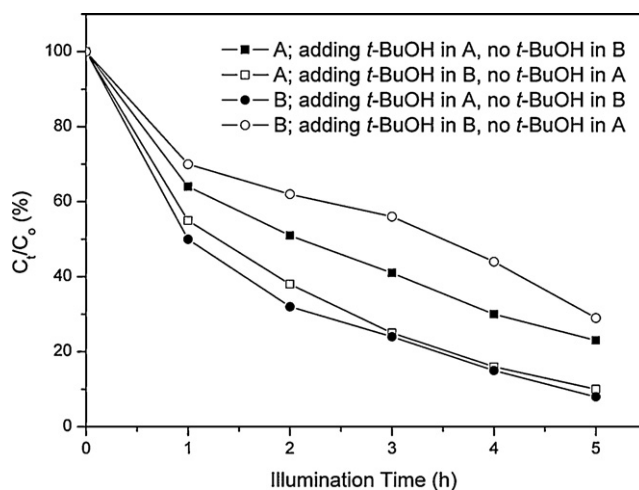


Fig. 7. Effect of *tert*-butanol on the degradation of 4-CP in reactors A and B.

radicals ( $\cdot OH$ ) scavenger [24]. The degradation was carried out under no external voltage conditions. As shown in Fig. 7, when adding 1 mM *t*-BuOH in reactor A and no *t*-BuOH in reactor B, the degradation of 4-CP in the reactor A slowed down with 77% removal after 5 h. However, the addition of *t*-BuOH in the reactor B had a



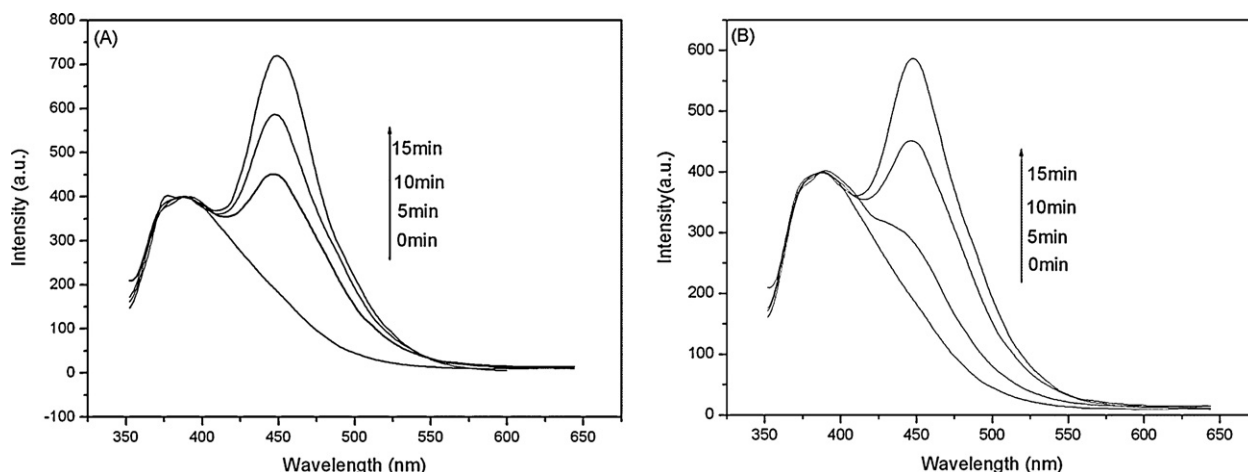


Fig. 8. The fluorescence emission intensity of 7-hydroxycoumarin was measured under the excitation of 332 nm.

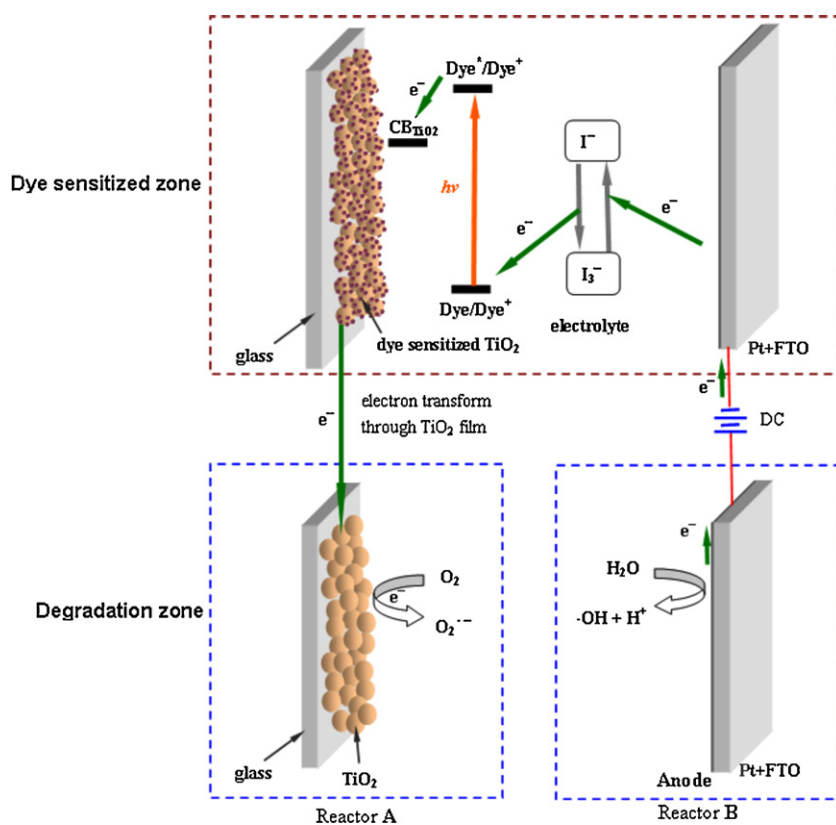
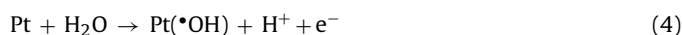


Fig. 9. Possible mechanism for the degradation reaction.

more significant effect on the degradation of reactor B when adding 1 mM *t*-BuOH in reactor B and no *t*-BuOH in the reactor A. The presence of *t*-butanol impeding the degradation of 4-CP showed that both degradation processes in reactors A and B should be mediated by hydroxyl radicals. The *t*-BuOH caused more serious retardation in reactor B than that in reactor A partly due to the presence of other active species, such as hydroperoxide and/or superoxide radicals ( $\cdot\text{OOH}/\text{O}_2^{\cdot-}$ ) in the reactor A.

To further provide the direct evidence of  $\cdot\text{OH}$  generation, coumarin was added as a reagent trap of  $\cdot\text{OH}$  to form the production of the coumarin-OH adduct (7-hydroxycoumarin), which can be quantified by measuring its fluorescence emission intensity [25]. As shown in Fig. 8, the coumarin-OH adducts were produced in proportion to the irradiation time, which demonstrated that

hydroxyl radicals were indeed generated in the reactors A and B. The production of  $\cdot\text{OH}$  in the reactor A should proceed through the reductive reactions of Eqs. (1)–(3). Hydroxyl radicals ( $\cdot\text{OH}$ ) in the reactor B should be produced from water discharge by Eq. (4), since the degradation reaction in reactor B is induced by the positive charge. The formation of 7-hydroxycoumarin in the reactor B indicated the active species was mainly the physically absorbed hydroxyl radicals.





attack of benzoquinone **2** causes a cleavage of C–C bond to give acid **3**, which undergoes C–C bond cleavage to produce maleic acid **4** and intermediate **5**. Maleic acid is degraded to be compound **6** by elimination of carbonic acid ( $\text{H}_2\text{CO}_3$ ). The compound **6** by attack of  $\bullet\text{OH}$  also generates intermediate **5**, which gives oxalic acid **9** via compounds **7** and **8**. Oxalic acid **9** is easily decomposed to  $\text{H}_2\text{CO}_3$  in the presence of  $\bullet\text{OH}$ . The  $\bullet\text{OH}$  attack of *ortho* position of 4-CP gives 4-chloro-1,2-benzenediol **10**, followed by elimination of  $\bullet\text{Cl}$  and  $\bullet\text{H}$  to generate compound **12**. The compound **12** undergoes C–C bond cleavage to give acid **13**, which produces maleic acid **4** and intermediate **14**. The intermediate **14** by attack of  $\bullet\text{OH}$  forms compound **8**, which produces  $\text{H}_2\text{CO}_3$  through the formation of oxalic acid **9**.

#### 4. Conclusions

A new device containing bifunctionalized  $\text{TiO}_2$  film and Pt/FTO electrode was designed to degrade phenols in reactors A and B. The bifunctionalized  $\text{TiO}_2$  film was composed of a dye-sensitized region providing photogenerated electron and a degradation region supplying effective degradation of organic pollutants. In the dye-sensitized region, a similar structure of dye-sensitized solar cells was fabricated to segregate the dye from pollutants avoiding dye decomposition. Both electrons and positive charges induced by light absorption of dyes could participate in degradation reaction. The degradation efficiency was enhanced remarkably by an external electrical potential. The concentration and TOC of 4-CP in the reactor A decreased 99% and 61%, respectively, after 2 h visible light irradiation at an external potential of 0.5 V. The similar result was obtained in reactor B as well. Degradation efficiency was increased with the increase of dye-sensitized  $\text{TiO}_2$  film area. Larger area of dye-sensitized  $\text{TiO}_2$  film generated much more electrons, which caused formation of more amounts of active species. Other phenolic compounds were also degraded in this device. The fabricated device, which is promoted efficiently by external DC potential, is promising for degradation of organic pollutants.

#### Acknowledgments

We are grateful to the National Natural Science Foundation of China (21072152, 21101115), the Tianjin Natural Science Foundation (09JCZDJC24400) for financial supports.

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