



Dye-sensitized TiO₂ film with bifunctionalized zones for photocatalytic degradation of 4-chlorophenol

Guohui Qin^a, Zhe Sun^a, Quanping Wu^{b,*}, Lin Lin^a, Mao Liang^a, Song Xue^{a,**}

^a School of Chemistry & Chemical Engineering, Tianjin University of Technology, Tianjin 300384, China

^b School of Electric Engineering, Tianjin University of Technology, Tianjin 300384, China

ARTICLE INFO

Article history:

Received 2 April 2011

Received in revised form 16 May 2011

Accepted 19 May 2011

Available online 27 May 2011

Keywords:

Photocatalytic degradation

Dye-sensitized TiO₂ film

Anode

4-Chlorophenol

ABSTRACT

A new strategy to photocatalytic degradation of 4-chlorophenol (4-CP) under visible light irradiation was described. The TiO₂ film deposited on an ordinary glass sheet was distributed into two zones. One zone was sensitized by N719 dye and fabricated to be a sandwich type cell with a similar structure of dye-sensitized solar cells. The other zone was inserted into pollutants solution for degradation. A highly oxidized overvoltage anode was achieved from the dye-sensitized zone. The bifunctionalized TiO₂ film and the anode could degrade 4-chlorophenol in two separate reactors with 97% and 96% removal of 4-CP after 5 h, respectively. The degradation efficiency could be improved by addition of FeSO₄. The as-prepared bifunctionalized TiO₂ film was comparably stable in the process of degradation.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

With rapid industrialization in the world, chemical pollutants, such as dyes, sulphates and toxic compounds, are dumped into rivers and are polluting soil and water. These pollutants affecting on environment is particularly serious in developing countries. Moreover, there is a continually growing problem due to the rising population and increasing demands for water sources. Efforts should be made on the development of various treatment technologies to decrease environmental pollution. Heterogeneous photocatalysis using titanium dioxide has attracted extensive attention in the field of degradation of chemical pollutants in aqueous phases [1–3]. Though titanium dioxide possesses merits of low-cost, non-toxicity, inert nature and long-term stability, two major problems of the recombination of photogenerated charge carriers and the filtration step of suspended particles after water treatment obstruct the practical application in the environmental areas [4–7]. Photoelectrocatalytic (PEC) process has proven to be an efficient method to solve these two problems, which is through immobilization of TiO₂ on a conducting substrate and application of a potential bias [8,9]. However, the wide band gap of TiO₂ can only capture about 5% of solar irradiance on earth's surface. To obtain a more efficient utilization of solar irradiation, many attempts,

such as metal or nonmetal elements doping [10–15], were made to shift its photocatalytic activity from UV illumination to the visible region. Although exciting improvements on the photocatalytic activity of TiO₂ under visible light irradiation, have been achieved through those modifications, some problems for doped materials with thermal instability and carrier-recombination probability still exist and affect practical utilization.

Another way of extending absorption to visible region is through dye sensitization, such as polymers [16–19] and metal–organic complexes [20,21] modified TiO₂. As these dyes sensitized TiO₂ produce hydroxyl radicals (*OH) through trapping conduction band electrons to reduce oxygen to superoxide, many dyes cannot withstand this severe oxidative stress for long time. So from the point of remedying the environment, it is desired to develop new sensitization system with high activity, visible-response, and high stability.

In order to avoid dye decomposition in the degradation progress of pollutants, the dye should be not mixed with pollutants. At the same time, electron induced by light through dye could be separated from positive charge and transferred to pollutants solution. Based on this idea, a thin film of TiO₂ with bifunctionalized zones was designed. One zone was sensitized by a dye, namely dye-sensitized zone. The other was used for insertion into pollutants solution for degradation, namely degradation zone. In the dye-sensitized zone, a similar structure of dye-sensitized solar cells (DSSCs) [22,23] was fabricated to segregate the dye from pollutants. Here we hope to report the result of degradation of 4-chlorophenol (4-CP) with the bifunctionalized TiO₂ film under visible light irradiation.

* Corresponding author.

** Corresponding author. Tel.: +86 22 60214250; fax: +86 22 60214252.

E-mail address: xuesong@ustc.edu.cn (S. Xue).

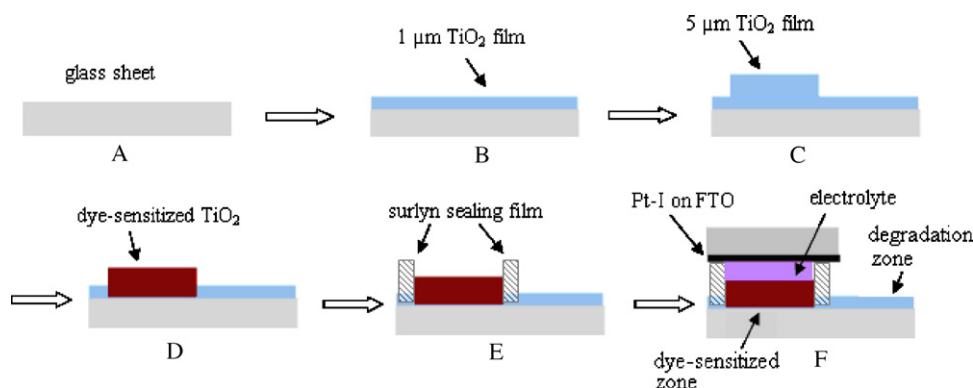


Fig. 1. The procedure for preparation of bifunctionalized TiO₂ film. (A) Glass sheet (16 mm × 36 mm, FTO or OR); (B) 1 μm thick TiO₂ film by screen printing; (C) a area of TiO₂ film (14 mm × 14 mm) with 5 μm thickness; (D) TiO₂ film sensitized by N719 dye; (E) the dye-sensitized TiO₂ surrounded by surlyn sealing film; (F) covering Pt-I and injecting electrolyte.

2. Experimental details

2.1. Preparation of bifunctionalized TiO₂ film

The bifunctionalized TiO₂ film was composite of a dye-sensitized zone and a degradation zone, which was prepared as shown in Fig. 1. TiO₂ colloid was prepared according to the literature method [24], which was used for the preparation of the nanocrystalline films. The TiO₂ paste consisting of 18 wt% TiO₂, 9 wt% ethyl cellulose and 73 wt% terpineol was firstly prepared, which was printed on a glass sheet using a screen printing technique. FTO conducting glass sheet (16 mm × 36 mm, fluorine doped SnO₂, sheet resistance 10 Ω/sq, transmission > 90% in the visible) or an ordinary glass sheet (OR) was cleaned by a standard procedure [24]. The thickness of the TiO₂ film was controlled by repetition of printing. The film was dried in air at 120 °C for 30 min and calcined at 500 °C for 30 min under flowing oxygen before cooling to room temperature. A area of TiO₂ film (14 mm × 14 mm) with ca. 5 μm thickness was stained by immersing it into a dye solution containing 300 μM *cis*-Ru(dcbpy)₂(NCS)₂ (N719) as dye sensitizer, which is among the best photosensitizers used in mesoporous TiO₂-based dye sensitized solar cells (DSSCs). After 48 h at room temperature, the dye-stained film was rinsed with dry ethanol and dried by a dry air flow. Pt was deposited on FTO glass by coating with a drop of H₂PtCl₆ solution (40 mM in ethanol) with heat treatment at 395 °C for 15 min to give a Pt electrode, coded as Pt-I. The dye-sensitized TiO₂ film and Pt-I electrode were separated by a surlyn spacer film (50 μm thick) and sealed by heating to form a sandwich type cell. Electrolyte was then injected into the cell gap to form bifunctionalized TiO₂ film. The electrolyte was a solution of 0.6 M 1,2-dimethyl-3-n-propylimidazolium iodide (DMPImI), 0.1 M LiI, 0.05 M I₂, and 0.5 M tertbutylpyridine in acetonitrile.

2.2. The degradation experiment of 4-chlorophenol

The degradation experiment was conducted in a wide-mouth glass flask reactor with 14 mL of 4-CP and magnetically stirred by a Teflon stirrer. The degradation zone of bifunctionalized TiO₂ film was immersed into the solution of 4-CP. Another Pt electrode, coded as Pt-II, was placed at a distance of 5 mm to the TiO₂ film and connected with the Pt-I electrode by a copper conductor wire, as shown in Fig. 2. A 300 W Xe lamp (L25, λ_{max} = 500 nm) was used as the visible light source, which was irradiated at a distance of 20 cm to the dye-sensitized zone of TiO₂ film through 420 nm cutoff filters. Air was bubbled through the pipe during the reaction. Light intensity, as measured by a visible-irradiance meter, was about 4.0 mW/cm² at the position of the TiO₂ film 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. The 2 M HCl and 2 M NaOH solutions were used to adjust pH to the desired values.

3. Results and discussion

3.1. Effect of substrates for the bifunctionalized TiO₂ film

In our initial degradation of 4-CP, two types of TiO₂ film were fabricated and investigated. One was TiO₂ deposited on an ordinary glass (OR). The other was TiO₂ on a FTO conducting glass. The typical degradation reaction was carried out under the conditions of 20 mg/L 4-CP, pH 4, bubbling air 5 L/h, and visible light intensity 4.0 mW/cm². The variation of relative concentration of 4-CP (*C_t/C₀*) as a function of reaction time was shown in Fig. 3. It was obviously

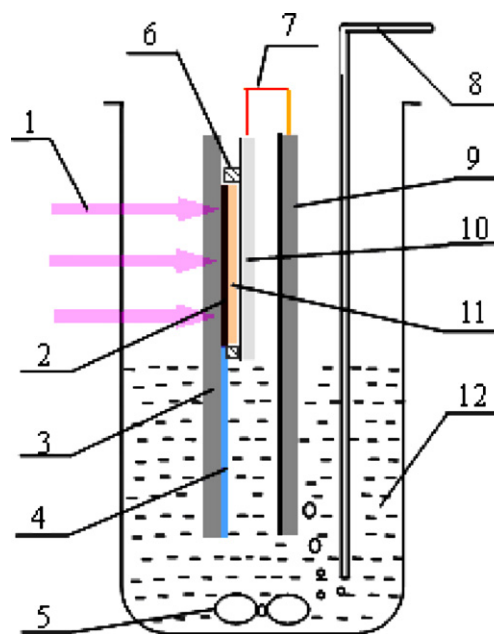


Fig. 2. Photocatalytic degradation of 4-chlorophenol under visible light irradiation. (1) Visible light (λ ≥ 420 nm); (2) dye-sensitized TiO₂ film; (3) ordinary glass sheet or FTO glass; (4) TiO₂ film without dye sensitization (degradation zone); (5) magnetic stirrer; (6) sealing film; (7) copper wire; (8) bubbling pipe; (9) Pt-II electrode; (10) Pt-I electrode; (11) electrolyte; (12) wide-mouth glass flask with 4-CP solution.

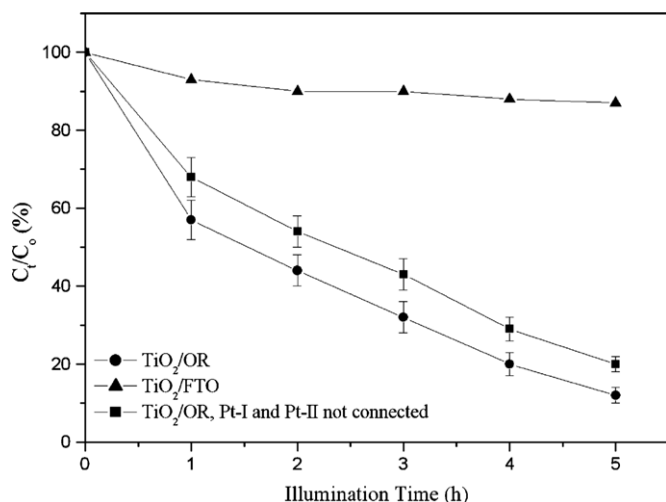


Fig. 3. Effect of two substrates for the bifunctionalized TiO₂ film on the degradation of 4-CP. ●: TiO₂ deposited on an ordinary glass (TiO₂/OR); ▲: TiO₂ on a FTO conducting glass (TiO₂/FTO); ■: TiO₂/OR, Pt-I electrode not connected with Pt-II electrode.

illustrated that the TiO₂ film on an ordinary glass exhibited significant activity for the removal of 4-CP. The concentration of 4-CP decreased 88% after 5 h under visible light irradiation. However, when 4-CP was degraded using the TiO₂ deposited on a FTO conductor glass, only 13% removal of the concentration of 4-CP was obtained under the same conditions. The reduction rate of total organic carbon (TOC) was slower than that of the degradation of 4-CP. The concentration of TOC decreased 38% after 5 h for the TiO₂ film on the ordinary glass sheet. The slow mineralization was due to the formation of aromatic intermediates in the process of degradation, which concentrations remain almost unchanged [25,26]. The results indicated that the TiO₂ deposited on the ordinary glass was efficient for the degradation of 4-CP under the reaction conditions. So the following experiments were performed by the TiO₂ film on an ordinary glass sheet.

3.2. Effect of Pt-II electrode

The effect of Pt-II electrode was studied on the basis of the bifunctionalized TiO₂ film. The degradation became a little slower under the typical degradation conditions when Pt-II electrode was not connected with Pt-I electrode in the absence of copper wire. The concentration of 4-CP decreased 80% after 5 h under visible light irradiation, and the variation concentration of 4-CP was shown in Fig. 3 as well. The relative low degradation efficiency implied that the Pt-II electrode had a positive effect on degradation performance when it was connected with Pt-I electrode by copper wire. To further show the degradation effect of Pt-II electrode, the bifunctionalized TiO₂ film and Pt-II electrode were inserted into two wide-mouth glass flask reactors A and B, respectively, as shown in Fig. 4. The two reactors with 14 mL of 4-CP and stirrer bar were carried out under the same conditions of 20 mg/L 4-CP, pH 4, bubbling air 5 L/h, and light intensity 4.0 mW/cm². The results were shown in Fig. 5. The reactor A degraded by the bifunctionalized TiO₂ film gave 81% removal of 4-CP after 5 h and almost no degradation of 4-CP (7% removal) was observed in the reactor B by the Pt-II electrode when degradation reaction was carried out in the absence of copper wire. The slight removal of 4-CP in the reactor B may be due to the absorption of Pt-II electrode surface. It was found that when Pt-II electrode was connected with Pt-I electrode by a copper wire, the concentration of 4-CP in the reactor B decreased 85% after 5 h and a little enhanced degradation efficiency was achieved in the reactor A (87% versus 81%). Degradation reaction occurring

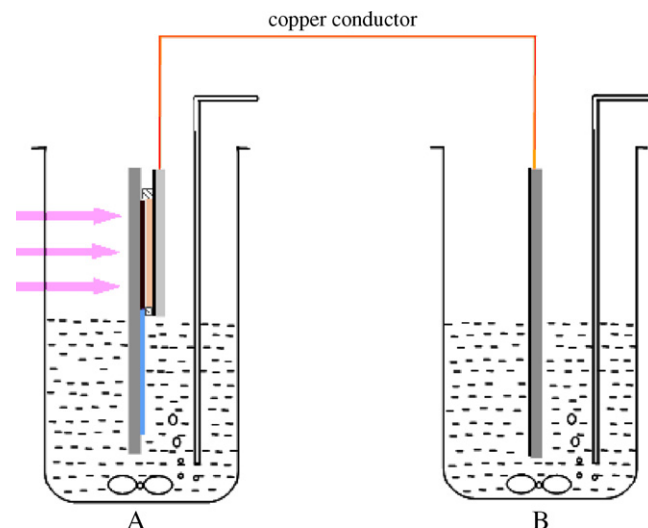


Fig. 4. Degradation of 4-CP performed in separate reactors A and B.

in reactor B showed that Pt-II electrode produced active species, causing the decomposition of 4-CP. At the same time, degradation in reactor B promoted the degradation in reactor A.

3.3. Effect of ferrous ions

Ferrous ions have a remarkable promoting effect on degradation reaction in the Fenton process, which involves the reaction of Fe²⁺ with hydrogen peroxide (H₂O₂), giving rise to hydroxyl radicals. If hydrogen peroxide was generated in our degradation conditions, addition of FeSO₄ would promote the degradation of 4-CP. The effect of ferrous ions by addition of 0.5 mM FeSO₄ in reactors A and B was shown in Fig. 6. After irradiation of 5 h, the removal of 4-CP in reactors A and B was obtained in 97% and 96%, respectively, when adding 0.5 mM FeSO₄ in reactor A but no FeSO₄ in reactor B. The removal of 4-CP in both reactors was greatly accelerated by the presence of FeSO₄ in reactor A. However, their degradation efficiencies were not enhanced by the addition of FeSO₄ in reactor B. For example, 87% and 88% of 4-CP were removed in reactors A and B, respectively, when adding 0.5 mM FeSO₄ in reactor B and no FeSO₄ in reactor A. These results demonstrated that formation of hydroxyl radicals was promoted by the addition of Fe²⁺ in reac-

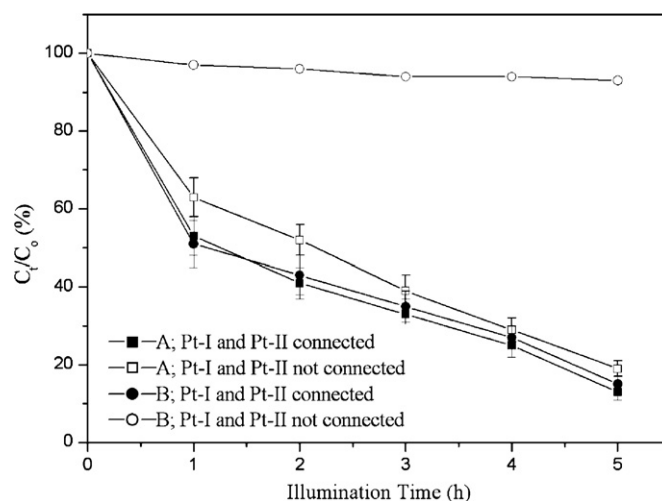


Fig. 5. Effect of Pt-II electrode on the removal efficiency of 4-CP in separate reactors A and B.

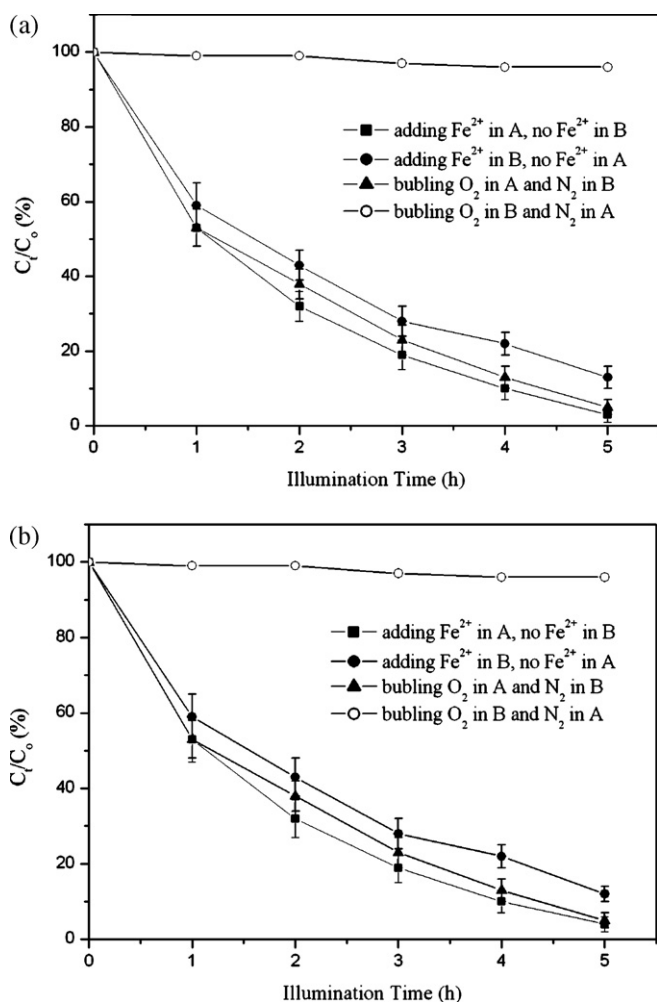


Fig. 6. Effects of Fe^{2+} and O_2 on the removal efficiency of 4-CP in separate reactors A and B. (a) Degraded by TiO_2 film in reactor A; (b) degraded by Pt-II electrode in reactor B.

tor A, resulting in enhanced degradation efficiency. The addition of $FeSO_4$ in reactor B had no obvious enhancement of the degradation efficiency, indicating that there was no H_2O_2 involved in this case.

3.4. Effects of O_2

To obtain insight into the role of O_2 in the present study, experiments under O_2 and N_2 atmospheres were undertaken. In the atmosphere of N_2 by bubbling nitrogen in reactors A and B, the degradation reaction in both reactors did not occur after 5 h under our reaction conditions. It was found that degradation reaction occurred and the removal of 4-CP in both reactors was obtained in 95% and 92%, respectively, when bubbling air in reactor A and bubbling nitrogen in reactor B (Fig. 6). However, when bubbling nitrogen in reactor A and bubbling air in reactor B, almost no degradation reaction was observed in the reactor A, nor did degradation in the reactor B. These results clearly demonstrated that the presence of O_2 was crucial for degradation in reactor A, but was not crucial for reactor B.

3.5. Degradation mechanism

A schematic mechanism for the degradation reaction was shown in Fig. 7. In dye-sensitized zone, light absorption takes place in the dye under irradiation, with subsequent electron transfer from the dye's excited states (dye^*) into the conduction band (CB) of

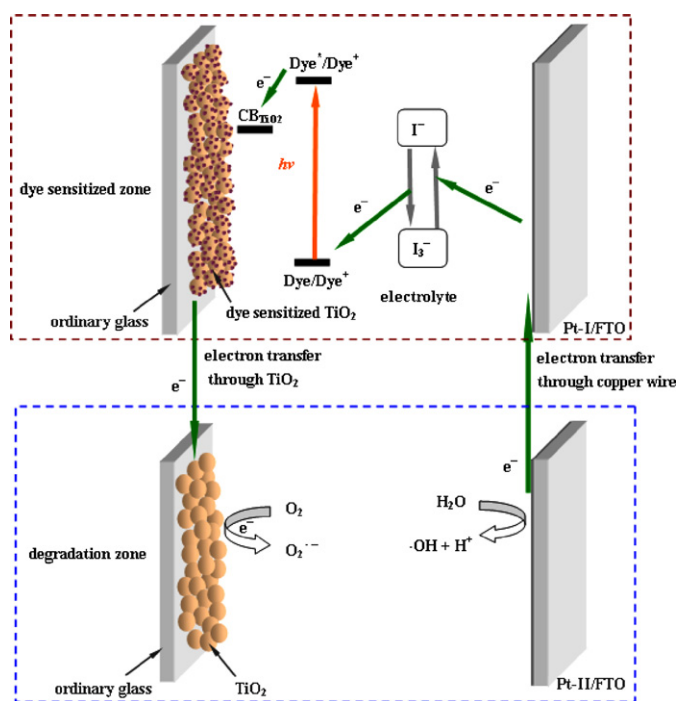
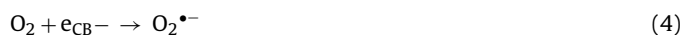
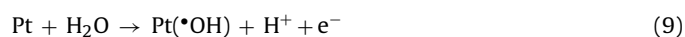


Fig. 7. Working principle of the degradation system.

the TiO_2 . As for the TiO_2 film deposited on an ordinary glass, the electrons transport to the degradation zone via diffusion of electrons through the network of TiO_2 nanoparticles. The oxidized dyes (dye^+) are regenerated by the iodide/triiodide redox couple through reactions of Eqs. (1) and (2), followed by electron exchange transporting the positive charge to the Pt-I electrode via Eq. (3). In degradation zone, the electron transporting at conduction band of TiO_2 is at high energy level and can react with oxygen in solution to produce $O_2^{\bullet-}$, followed by reaction with H^+ to form high active species of hydroxyl radicals ($\cdot OH$) through Eqs. (4)–(8) for degradation of 4-CP [27]. As for the TiO_2 film deposited on a FTO conducting glass, electrons generated in dye-sensitized zone prefer transporting through FTO conducting glass rather than through semiconductor TiO_2 film because the former has superior conductivity to the latter. Thus, electrons transfer through FTO conducting glass from the dye-sensitized zone to the degradation zone. It is known that the resistance of TiO_2 is much higher than that of FTO glass. Therefore, the electrons in degradation zone are hard to arrive at the surface of TiO_2 film because there is no sufficient driving force for electron injection from FTO glass to TiO_2 surface under the reaction conditions. Few electrons at the surface of TiO_2 film afford few active species, which results in low degradation efficiency. Therefore, the reason for high degradation efficiency of TiO_2 film based on the ordinary glass is that electrons induced by light directly transform from the dye-sensitized zone to the degradation zone through the TiO_2 film.



Pt-II electrode had an important affection on the degradation. In the reported electrochemical degradation method, hydroxyl radicals ($\cdot\text{OH}$) generally was produced at the surface of a highly oxidized overvoltage anode from water oxidation via Eqs. (9) and (10) [28,29]. The active species of either physically adsorbed hydroxyl radical ($\cdot\text{OH}$) or chemisorbed metal oxide (MO) in the lattice of metal may be formed from water discharge along with electron release [8]. The degradation by Pt-II electrode working smoothly in reactor B showed that there was highly oxidized overvoltage on the electrode. The high overvoltage on the Pt-II electrode should be originated from the oxidized dyes with the positive charge transfer through the iodide/triiodide redox couple to the Pt-I electrode. The oxidized dye was regenerated by reduction reaction with I^- , and I^- was converted to I_3^- (Eqs. (1) and (2)). When I_3^- was catalytically converted into I^- through Pt-I electrode with electron exchange, positive charge was transported from Pt-I to Pt-II through copper wire. As dyes repeated the process of light absorption and regeneration, the oxidized overvoltage of the Pt-II electrode with arrival of the positive charges from the Pt-I electrode became high enough for production of $\cdot\text{OH}$ through water oxidation. Then the degradation reaction by the Pt-II electrode occurred. Moreover, in the process of Pt-II electrode production of $\cdot\text{OH}$, electron was released from water oxidation and reacted with I_3^- to generate I^- via Pt-I. If there is no electron supplied for the recover of I^- from I_3^- , the concentration of I^- in electrolyte would decrease and gradually be consumed. When the oxidized dyes were not regenerated in the absence of I^- , the degradation reaction would stop. Therefore, the degradation by Pt-II electrode was driven by photo-generated positive charge in dye-sensitized TiO_2 film, and also afforded electron for regeneration of the oxidized dye, promoting the degradation of TiO_2 film.



FeSO_4 has an obvious influence on degradation reaction. Addition of Fe^{2+} in reactor A enhanced the degradation efficiency in reactors A and B. The bifunctionalized TiO_2 film in reactor A produced H_2O_2 , which was promoted by Fe^{2+} to form active species $\text{HO}\cdot$ as shown in Eq. (11). More active species were generated, much higher degradation efficiency was achieved. The catalyst of Fe^{2+} could be regenerated through electrolysis reduction of Fe^{3+} via Eq. (12). The higher degradation efficiency in reactor A would consume more electrons, which would produce more positive charges for Pt-II and caused higher degradation efficiency in reactor B. Addition of Fe^{2+} in reactor B gave no enhancement in both reactors due to no formation of H_2O_2 in reactor B.



Oxygen is crucial for the degradation. The photogenerated electrons can reduce the adsorbed molecular oxygen on the TiO_2 surface to produce $\text{O}_2^{\cdot-}$, followed by reaction with H^+ to form superoxide radical anion $\text{HO}_2\cdot$. The high active species of hydroxyl radicals ($\cdot\text{OH}$) are generated through Eqs. (5)–(8) [27,30]. It is known that $\cdot\text{OH}$ radicals are nonselective and strong electrophilic oxidizing species [31]. When bubbling N_2 in reactor A, no active species was formed in the absence of O_2 , leading to no degradation. On the other hand, electrons at conduction band of TiO_2 could not be consumed without O_2 and would come back to the dye cation with recombination or into electrolyte solution reacting with I_3^- [32]. The positive charge transported into Pt-I electrode would be limited and the oxidized overvoltage on the Pt-II electrode could not be accumulated enough high to oxidize H_2O to form hydroxyl radicals. Therefore, when bubbling nitrogen in reactor A,

the degradation reaction did not occur in reactor A, neither did in reactor B.

For the practical application of such bifunctionalized TiO_2 film, not only the degradation efficiency is important, but its durability or lifetime is also critical. The degradation of 4-CP for five cycles of the bifunctionalized TiO_2 film was tested. The degradation effectiveness decreased from 98% to 92% after five repeated uses, which demonstrated the as-prepared bifunctionalized TiO_2 film was comparably stable under the studied conditions.

4. Conclusions

A new bifunctionalized TiO_2 film was designed for degradation of 4-CP under visible light irradiation. The bifunctionalized TiO_2 film was composite of an area of dye-sensitized TiO_2 film and an area of un-sensitized TiO_2 film. The effects of substrates for TiO_2 film, Pt-II electrode, FeSO_4 , and O_2 on degradation of 4-CP were studied. When the bifunctionalized TiO_2 film was deposited on an ordinary glass sheet, the concentration and TOC of 4-CP decreased 88% and 38%, respectively, after 5 h irradiation at initial concentration of 20 mg/L, pH at 4, and light intensity of 4.0 mW/cm² with bubbling air. The concentration of 4-CP decreased only 13% when TiO_2 film was deposited on a FTO conducting glass under the same conditions. Pt-II electrode afforded comparable degradation efficiency when it was connected with Pt-I electrode by a copper. The degradation efficiency could be improved by addition of FeSO_4 , which promoted H_2O_2 to form $\cdot\text{OH}$. Oxygen is crucial for the degradation reaction. The as-prepared device was comparably stable in the process of degradation after five recycles. The device worked smoothly for degradation of 4-CP under visible light irradiation without external power supply. This process is promising for degradation of organic pollutants due to its saving-energy, low cost, and sustainability.

Acknowledgements

We are grateful to the National 863 Program (2009AA05Z421), the Tianjin Natural Science Foundation (09JCZDJC24400), and the Tianjin High Education Science & Technology Development Fund (20090507) for financial supports.

References

- [1] M.A. Fox, M.T. Dulay, Heterogeneous photocatalysis, *Chem. Rev.* 93 (1993) 341–357.
- [2] A.L. Linsebigler, G. Lu, J.T. Yates, Photocatalysis on TiO_2 surfaces: principles, mechanisms, and selected results, *Chem. Rev.* 95 (1995) 735–758.
- [3] D.S. Bhatkhande, V.G. Pangarkar, A.C.M. Beenackers, Photocatalytic degradation using TiO_2 for environmental applications: a review, *J. Chem. Technol. Biotechnol.* 77 (2002) 102–116.
- [4] D.F. Ollis, H. Al-Ekabi (Eds.), *Photocatalytic Purification and Treatment of Water and Air*, Elsevier, Amsterdam, 1993.
- [5] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Environmental applications of semiconductor photocatalysis, *Chem. Rev.* 95 (1995) 69–96.
- [6] D.W. Chen, F.M. Li, A.K. Ray, External and internal mass transfer effect on photocatalytic degradation, *Catal. Today* 66 (2001) 475–485.
- [7] K. Kabra, R. Chaudhary, R.L. Sawhney, Treatment of hazardous organic and inorganic compounds through aqueous-phase photocatalysis: a review, *Ind. Eng. Chem. Res.* 43 (2004) 7683–7696.
- [8] C.A. Martinez-Huitle, E. Brillas, Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: a general review, *Appl. Catal. B: Environ.* 87 (2009) 105–145.
- [9] K. Vinodgopal, U. Stafford, K.A. Gray, P.V. Kamat, Electrochemically assisted photocatalysis. 2. The role of oxygen and reaction intermediates in the degradation of 4-chlorophenol on immobilized TiO_2 particulate films, *J. Phys. Chem.* 98 (1994) 6797–6803.
- [10] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, Visible light photocatalysis in nitrogen-doped titanium oxides, *Science* 293 (2001) 269–271.
- [11] C.C. Chen, X.Z. Li, W.H. Ma, J.C. Zhao, H. Hidaka, N. Serpone, Effect of transition metal ions on the TiO_2 -assisted photodegradation of dyes under visible irradiation: a probe for the interfacial electron transfer process and reaction mechanism, *J. Phys. Chem. B* 106 (2002) 318–324.

- [12] G.S. Li, D.Q. Zhang, J.C. Yu, A new visible-light photocatalyst: CdS quantum dots embedded mesoporous TiO₂, *Environ. Sci. Technol.* 43 (2009) 7079–7085.
- [13] Q. Li, M.A. Page, B.J. Marin, J.K. Shang, Treatment of coliphage MS₂ with palladium-modified nitrogen-doped titanium oxide photocatalyst illuminated by visible light, *Environ. Sci. Technol.* 42 (2008) 6148–6153.
- [14] X.C. Wang, J.C. Yu, Y.L. Chen, L. Wu, X.Z. Fu, ZrO₂-Modified mesoporous nanocrystalline TiO₂-N as efficient visible light photocatalysts, *Environ. Sci. Technol.* 40 (2006) 2369–2374.
- [15] L.C. Chen, Y.C. Hoa, W.S. Guo, C.M. Huang, T.C. Pan, Enhanced visible light-induced photoelectrocatalytic degradation of phenol by carbon nanotube-doped TiO₂ electrodes, *Electrochim. Acta* 54 (2009) 3884–3891.
- [16] H. Zhang, R.L. Zong, J.C. Zhao, Y.F. Zhu, Dramatic visible photocatalytic degradation performances due to synergetic effect of TiO₂ with PANI, *Environ. Sci. Technol.* 42 (2008) 3803–3807.
- [17] H.C. Liang, X.Z. Li, Visible-induced photocatalytic reactivity of polymer-sensitized titania nanotube films, *Appl. Catal. B: Environ.* 86 (2009) 8–17.
- [18] X.Y. Li, D.S. Wang, G.X. Cheng, Q.Z. Luo, J. An, Y.H. Wang, Preparation of polyaniline-modified TiO₂ nanoparticles and their photocatalytic activity under visible light illumination, *Appl. Catal. B: Environ.* 81 (2008) 267–273.
- [19] D.S. Wang, J. Zhang, Q.Z. Luo, X.Y. Li, Y.D. Duan, J. An, Characterization and photocatalytic activity of poly(3-hexylthiophene)-modified TiO₂ for degradation of methyl orange under visible light, *J. Hazard. Mater.* 169 (2009) 546–550.
- [20] Q. Sun, Y. Xu, Sensitization of TiO₂ with aluminum phthalocyanine: factors influencing the efficiency for chlorophenol degradation in water under visible light, *J. Phys. Chem. C* 113 (2009) 12387–12394.
- [21] W. Zhao, Y. Sun, F.N. Castellano, Visible-light induced water detoxification catalyzed by Pt dye sensitized titania, *J. Am. Chem. Soc.* 130 (2008) 12566–12567.
- [22] B. O'Regan, M. Grätzel, A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films, *Nature* 353 (1991) 737–740.
- [23] A. Hagfeldt, M. Grätzel, Molecular photovoltaics, *Acc. Chem. Res.* 33 (2000) 269–277.
- [24] S. Ito, T.N. Murakami, P. Comte, P. Liska, C. Grätzel, M.K. Nazeeruddin, M. Grätzel, Fabrication of thin film dye sensitized solar cells with solar to electric power conversion efficiency over 10%, *Thin Solid Films* 516 (2008) 4613–4619.
- [25] S. Kim, H. Park, W. Choi, Comparative study of homogeneous and heterogeneous photocatalytic redox reactions, *J. Phys. Chem. B* 108 (2004) 6402–6411.
- [26] A. Mylonas, A. Hiskia, E. Papaconstantinou, Contribution to water purification using polyoxometalates. Aromatic derivatives, chloroacetic acids, *J. Mol. Catal. A: Chem.* 114 (1996) 191–200.
- [27] Y.B. Wang, C.S. Hong, TiO₂-mediated photomineralization of 2-chlorobiphenyl: the role of O₂, *Water Res.* 34 (2000) 2791–2797.
- [28] C. Cominellis, Electrocatalysis in the electrochemical conversion/combustion of organic pollutants for waste water treatment, *Electrochim. Acta* 39 (1994) 1857–1862.
- [29] C.A. Martínez-Huitle, S. Ferro, Electrochemical oxidation of organic pollutants for the wastewater treatment: direct and indirect processes, *Chem. Soc. Rev.* 35 (2006) 1324–1340.
- [30] Y.B. Xie, Photoelectrochemical application of nanotubular titania photoanode, *Electrochim. Acta* 51 (2006) 3399–3406.
- [31] L.A. Pérez-estrada, S. Malato, W. Gernjak, A. Agüera, E.M. Thurman, I. Ferrer, A.R. Fernández-alba, Photo-Fenton degradation of diclofenac: identification of main intermediates and degradation pathway, *Environ. Sci. Technol.* 39 (2005) 8300–8306.
- [32] A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, Dye-sensitized solar cells, *Chem. Rev.* 110 (2010) 6595–6663.