Enhancement of photoelectrocatalytic degradation of diclofenac with persulfate activated by Cu cathode

Shanshan Liu^{a,b}, Xu Zhao^{a,*}, Huabin Zeng^{a,b}, Yanbin Wang^a, Meng Qiao^a, Wei Guan^{a,c}

^a Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

^b University of Chinese Academy of Sciences, Beijing 100049, China

^c Chongqing Key Laboratory of Environmental Materials & Remediation Technologies, Chongqing University of Arts and Sciences, Chongqing 402160, China

HIGHLIGHTS

- Photoelectro-oxidation of diclofenac was largely enhanced with persulfate addition.
- Cu₂O was identified at copper cathode by in situ Raman technique.
- Activation mechanism of persulfate to SO₄^{•−} at copper cathode was proposed.

GRAPHICAL ABSTRACT

ARTICLE INFO

Article history:

Received 21 December 2016

Received in revised form 1 March 2017

Accepted 14 March 2017

Available online 18 March 2017

Keywords:

Photoelectrocatalysis

Persulfate

Cu cathode

Cu₂O

Diclofenac

ABSTRACT

In this work, persulfate ($S_2O_8^{2-}$, PS) was introduced to the photoelectrocatalytic (PEC) system, which consisted of a γ -Bi₂MoO₆ photoanode and a copper foil cathode (Bi₂MoO₆/Cu/PEC/PS system). Significant enhancement of diclofenac sodium (DCF) degradation efficiency was observed in this system under visible light irradiation. At an applied bias of 1.5 V and initial solution pH of 5.62, the removal efficiency of DCF with an initial concentration of 10 mg/L was increased from 19.4% in the PEC process to 86.3% in the PEC process with 10 mM PS addition. The pseudo-first-order kinetic rate constant of DCF degradation was increased from 0.1112 h^{−1} to 1.0498 h^{−1}. Active free radicals involving $SO_4^{\bullet-}$ and $HO^{\bullet}$ were produced in this process, which were confirmed by electron spin resonance analysis. Furthermore, the surface variation of copper foil cathode was characterized by FE-SEM, GI-XRD, XPS and in situ Raman spectroscopy. It was demonstrated that Cu₂O formed on the surface in the reaction process with the $S_2O_8^{2-}$ addition, which was further confirmed by the photoelectrochemical analysis of the cathode. The surface Cu(0)–Cu(I)–Cu(II)–Cu(0) redox cycle of cathode was proposed, which was responsible for the persulfate activation, leading to the generation of free radicals. This work may provide a new perspective on the combined utilization of different technologies for catalytic contaminant removal.

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1. Introduction

Pharmaceuticals and personal care products (PPCPs) have received an increasing attention of their occurrence and transfer

* Corresponding author at: P.O. Box 2871, 18 Shuangqing Road, Haidian District, Beijing 100085, PR China.

E-mail address: zhaoxu@rcees.ac.cn (X. Zhao).

in aquatic systems and soils over the past few years [1,2]. Diclofenac sodium (DCF), which is considered as a common non-steroidal anti-inflammatory drug and meanwhile, a persistent toxic pollutant, may produce adverse effect on animal kidney, liver and cause renal lesions [3,4]. Due to its low biodegradability, DCF cannot be effectively removed by conventional biochemical processes [5]. In recent years, the application of UV, UV/H₂O₂ and ozonation treatments in its degradation was largely investigated. For instance, it

has been proved that DCF could be removed effectively by UV irradiation with H_2O_2 addition [2,6], and ozonation technology also achieved a complete conversion of chlorine to ions and 32% mineralization of DCF for 1.5 h treatment [7].

Photoelectrocatalytic (PEC) oxidation process in which a small positive potential is applied on the semiconductor photoanode has proven to be more efficient than single photocatalytic process [8]. In PEC system, the application of a small external bias decreases the recombination rate of photogenerated electron-hole pairs and thus increases the photocatalytic activity of the semiconductor photocatalyst [9]. It has been largely investigated on the application of PEC processes in degrading refractory organics in aquatic system and water splitting recently [10]. In a PEC system, the semiconductor film electrode is usually used as the photoanode for organics oxidation, while the role of the cathode beyond a counter electrode is not fully exploited. Studies about cathode utilization such as reticulated vitreous carbon as a counter electrode for H_2O_2 generation to enhance PEC oxidation were reported [11]. But the amount of generated H_2O_2 via the cathodic reduction is limited due to the low applied bias used in PEC system. Therefore, it is desired to simultaneously improve the oxidation efficiency of organic contaminants and cathode utilization in the PEC system.

Recently, sulfate radical ($\text{SO}_4^{\cdot-}$) based processes have been paid more attention on the removal of organic contaminants. It has been proved that persulfate ($\text{S}_2\text{O}_8^{2-}$, PS) can be activated to generate sulfate radicals with a redox potential of 2.5 ~ 3.1 V which can efficiently decompose organics in water [12]. Generally, persulfate can be activated by physical means such as heating [13], UV irradiation [14] and microwave [15] as shown in Eq. (1).

Driven by the need of overcoming the drawback of above physical means, transition metal activation (Eq. (2)) has an advantage on high efficiency without high energy consumption and could be achieved under room temperature. For example, Fe(0) [16], Fe(II) [17] and Ag(I) [18] could be used as PS activators.

Owing to its rich abundance and high catalytic efficiency, copper-based catalyst has attracted a particular attention nowadays. PS activation by copper ion was proven to be efficient for propachlor degradation [19]. Zhang et al. discovered that magnetic CuFe_2O_4 spinel showed high activity on inducing peroxymonosulfate (PMS) activation; iopromide as target contaminant can be removed completely within 10 min at the PMS dosage of 20 μM [20]. It was also reported that almost 100% phenol was removed in 120 min with addition of 5 mM PS and 0.3 g/L $\text{CuO-Fe}_3\text{O}_4$ composite catalyst [21]. Above studies propose that the $\text{Cu(II)-Cu(III)-Cu(II)}$ redox cycle activates PS to form free radicals. However, Zhang suggested that peroxydisulfate (PDS) activation can be achieved not relying on sulfate radical generation but electrons rearrangement of PDS [22]. These results indicate the high efficiency of copper-based catalysts for the PS activation through different mechanisms.

To further improve the contaminant degradation efficiency, above two techniques are considered to be combined. Fu et al. investigated the response surface methodology (RSM) on optimizing the photoelectrocatalytic degradation of fulvic acid (FA) [23]. A. A. El-Zomrawy reported photoelectrocatalytic degradation of dye with ammonium persulfate (APS) addition [24]. However, the mechanism remained unclear about the interaction between PS and PEC reaction. Zeng et al. reported that PS was added to a photoelectrocatalytic system driven by UV light in order to enhance

the Cu-EDTA decomplexation and Cu recovery [25]. This paper indicated the PS activation through cathodic electron and served as a bridge between two techniques. To the best of our knowledge, there have been no published work about the PS activation through cathode itself in PEC system under visible light irradiation.

Herein, Cu cathode was used in a PEC system to activate PS and to improve the PEC degradation efficiency of target contaminant, DCF. In situ Raman spectroscopy combined with photoelectrochemical analysis was employed to analyze the copper cathode variation and generation of Cu_2O on the surface was confirmed. The variation of copper species was investigated in detail. In this variation process, PS was activated and free radicals such as $\text{HO}^{\cdot}$ and $\text{SO}_4^{\cdot-}$ were produced, which were responsible for the enhanced degradation efficiency of DCF. The activation mechanism was investigated in details.

2. Material and methods

2.1. Chemicals

Sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$, 98 + % purity) and sodium sulfite (Na_2SO_3 , 98.5% purity) were bought from Acros Organics. Diclofenac sodium ($\text{C}_{14}\text{H}_{10}\text{Cl}_2\text{NNaO}_2$, 98% purity) was procured from TOKYO Chemical Industry Co., Ltd. Sodium sulfate (Na_2SO_4 , 99% purity), Bismuth(III) nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 99% purity), Molybdenum oxide (MoO_3 , 99.5% purity), Diethylenetriamine-pentaacetic acid ($\text{C}_{14}\text{H}_{23}\text{N}_3\text{O}_{10}$, 99.0 + % purity), Diethanolamine ($\text{C}_4\text{H}_{11}\text{NO}_2$, 98–102% purity), sodium acetate (CH_3COONa , 99% purity) and acetic acid (CH_3COOH , 99.8% purity) were all purchased from Sinopharm Chemical Reagent Co., Ltd. The 5,5-dimethyl-1-pyrrolidine N-oxide (DMPO) was obtained from Aladdin, China. The copper foil was bought from Beijing Heng Li Ti Co., Ltd. All reagents used were at least analytical grade and without further purification. All solutions were prepared to required concentration in Milli-Q water ($\rho = 18.2 \text{ M}\Omega \cdot \text{cm}$).

2.2. Experimental section

Degradation experiments were carried out in a rectangular quartz reactor with DCF solution (120 mL, 10 mg/L). The PEC reaction was driven by an electrochemical workstation (CHI 660E; Shanghai Chenhua Instruments Co., Ltd, Shanghai, China) connected with a working photoelectrode (the $\gamma\text{-Bi}_2\text{MoO}_6$ film deposited onto the Indium-tin oxide glass, active area of 13 cm^2), a counter electrode (copper foil, active area of 13 cm^2) and a reference electrode (saturated calomel electrode). The visible light source was from a Xe lamp (PLS-SXE300; Beijing PerfectLight Co., Ltd, Beijing, China) with a UV cutoff filter ($\lambda > 420 \text{ nm}$). Linear sweep voltammetry (LSV) was also conducted in a single-compartment with Na_2SO_4 electrolyte, three electrode cell on the same workstation. Electrochemical impedance spectra (EIS, presented in [Supplementary material](#)) were measured at 0 V (vs. open circuit potential) on an electrochemical workstation (Interface 1000, Gamry, America). The initial pH (pH_0) adjustments were achieved by moderate addition of H_2SO_4 (0.1 M) or NaOH (0.1 M). Samples were taken from the reactor every 30 min and filtered through 0.22 μm membrane prior to analysis.

As reported in our previous work [26], $\gamma\text{-Bi}_2\text{MoO}_6$ film was deposited onto indium tin oxide (ITO) substrate from an amorphous heteronuclear complex solution by dip-coating method. Before each experiment, the anode film was rinsed by Milli-Q water and the copper foil used as a cathode was rinsed by hydrochloric acid, cleaned with 800-grit sandpapers to remove any rusts or solid deposits and double rinsed with Milli-Q water.

2.3. Analytical procedures

The concentration of DCF was determined by high performance liquid chromatography (HPLC; Shimadzu LC-20AT, Tokyo, Japan) with a C18 (250 mm × 4.6 mm × 5 μm) reversed-phase column (GL Sciences Inc., Tokyo, Japan) and a UV detector. The mobile phase was a mixture of acetate buffer (pH = 5.0) and methanol (V/V = 40/60) with a flow rate of 1 mL/min. The injection volume was set as 20 μL.

For the intermediates identification, samples were filtered and analyzed by UPLC-Q-TOF-MS (ACQUITY UPLC, Quattro Premier XE, Waters, America) with C18 (50 mm × 2.1 mm × 1.7 μm) reversed-phase column. The mobile phase contained A (0.2% formic acid in water) and B (0.1% formic acid in acetonitrile) at the flow rate of 0.3 mL/min. The gradient was 90% A for 1 min, linearly increasing to 95% B for 8 min, 95% B and 5% A for 5 min, decreasing back to 90% A and maintaining for 1 min. The mass spectrometer was operated with negative electrospray ionization recorded from 50 to 1000 *m/z*.

The mineralization of DCF was measured with an Elementar vario TOC analyzer (Germany). The pH adjustment was completed on PHS-3E. The metal ions were quantified by inductively coupled plasma-optical emission spectrometer (ICP-OES, Optima 8300, PerkinElmer, America).

The surface morphology of electrodes was characterized by field emission-scanning electron microscope (FE-SEM; HITACHI SU8020, Tokyo, Japan). The X-ray diffraction (XRD) patterns of electrodes were recorded on an X-ray diffractometer (XPert Pro MPD) with a Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) was measured on ESCALAB 250Xi (Thermo Fisher Scientific) to determine the chemical state of copper. In situ Raman spectroscopic studies were performed with a confocal Raman microscope (LabRAM HR 800, Horiba, Tokyo, Japan), equipped with an Ar laser (514 nm) and a 40× objective.

For the involved radical studies, experiments were detected on Bruker A300-10/12 (Germany) using DMPO as trapping agent. The measurements were conducted using a radiation of 9.85 GHz (X band) with center field of 3512.170 G, modulation frequency of 100 kHz, sweep width of 200 G, sweep time of 81.92 s, time constant of 40.96 ms, and microwave power of 21 MW at room temperature.

3. Results and discussion

3.1. Characterization of γ-Bi₂MoO₆ film anode

XRD pattern and SEM image of γ-Bi₂MoO₆ were shown in Fig. 1 (a). The peaks of prepared electrode are in conformity with the standard Bi₂MoO₆ (JCPDS: 21-0102). Both the sharpness of XRD reflections and small half peak width clearly demonstrate that the synthesized γ-Bi₂MoO₆ film is highly crystalline. The cell parameters are *a* = 5.50 Å, *b* = 16.24 Å, *c* = 5.49 Å and the principal crystalline phase is orthorhombic structure. As Fig. 1(a) inset graph shows, the film consists of small particles with a porous structure. In recent years, Bi-based photocatalysts are getting more and more attention [27,28]. The electrochemical behavior of photoanode was also investigated by LSV in solution with 0.05 M Na₂SO₄ at a potential range from 0.0 V to 1.5 V (vs. SCE). As shown in Fig. 1(b), the Bi₂MoO₆ electrode shows a strong photocurrent under visible light irradiation. The transient photocurrent response of prepared Bi₂MoO₆ electrode was examined. As shown in Fig. 1(c), the photocurrent with good reproducibility for prepared photoanode is observed when irradiated by visible light. After several cycles, the current remains stable and this indicates that the electrode photoresponse is repeatable and reversible. Under 1 V applied bias,

Fig. 1. XRD pattern and SEM image (inset) (a), LSV curves at a potential range of 0.0 to 1.5 V (vs. SCE) (b) and the transient photocurrent response (c) of the prepared Bi₂MoO₆ electrode. Conditions: [Na₂SO₄] = 0.05 M, λ > 420 nm.

the photocurrent density of electrode is 5 μA·cm⁻². The optical property of prepared anode was conducted by UV-Vis diffuse reflectance spectroscopy and presented in Supplementary material (Fig. S1). The bandgap of the prepared γ-Bi₂MoO₆ is determined to be 2.58 eV and it exhibits a strong ability to utilize the visible portion of solar spectrum. The above result demonstrated that the prepared photoanode represented a good response to visible light.

3.2. Enhancement performance for DCF degradation

As shown in Fig. 2(a), only 19.4% of DCF is removed in 2 h in the PEC system using Bi₂MoO₆ as photoanode and Cu as cathode, and

Fig. 2. Effect of PS concentration on the DCF removal (a), kinetic rate constants (b) and removal ratio of TOC (c). Conditions: [DCF] = 10 mg/L; applied bias, 1.5 V; pH_0 , 5.62.

the removal efficiency of DCF by PS or copper alone is negligible. When copper itself is put into the solution with 1 mM PS, 30.6% of DCF is removed. Interestingly, a remarkable enhancement of DCF removal is observed with the addition of 1 mM PS into the PEC process, and nearly 70% DCF is removed in 2 h. Meanwhile, the effect of PS concentration on the DCF degradation was examined. It is observed that the removal efficiency of DCF increases with the PS concentration. With 10 mM PS, 86.3% DCF is removed. All these results indicate that the combination of PS and PEC process is an efficient way to degrade the target contaminant from water.

The kinetic investigations exhibit that the degradation reaction of DCF follows a pseudo-first-order kinetics equation and the rate constant versus the concentration of PS is shown in Fig. 2(b). It is estimated to be 0.1112 h^{-1} ($R^2 = 0.993$) in the PEC system without the addition of PS. By contrast, corresponding to PS concentration of 1, 5 and 10 mM, the rate constants are 0.5561 h^{-1} ($R^2 = 0.992$),

0.7290 h^{-1} ($R^2 = 0.995$) and 1.0498 h^{-1} ($R^2 = 0.987$), respectively. These results strongly confirm the enhancement of DCF degradation efficiency in PEC process with the PS addition.

With respect to TOC variation, in PEC system, the TOC removal ratio is less than 10%. As shown in Fig. 2(c), when 1, 5 and 10 mM PS is added to the solution, it increases to 20.5%, 35.9% and 45.1%, respectively. It is demonstrated that DCF can be degraded more thoroughly in the PEC process with an increasing addition of PS.

3.3. Influence of applied bias and initial pH

The effect of applied bias on the DCF removal in PEC process was investigated with 1 mM PS addition. As illustrated in Fig. 3(a), the degradation efficiency of DCF increases with the increasing applied potential. For example, when the applied bias increases from 0 V to 0.5 V, the removal ratio of DCF increases from 17.3% to 25.3%. As the potential is increased to 2 V, a 72.4% removal of DCF is achieved within 2 h. It can be seen from Fig. 3(b) that the kinetic rate constant increases as the applied bias increases. When the applied bias increases from 0 V to 2 V, the rate constant increases from 0.0912 h^{-1} ($R^2 = 0.980$) to 0.6431 h^{-1} ($R^2 = 0.990$).

The increased degradation efficiency is due to firstly, the increased bias promotes the separation of the photogenerated electron-hole pairs and reduces their recombination possibility [29]. As a result, the photocatalytic oxidation of DCF at the photoanode is increased [30,31]. Secondly, as shown in Fig. 3(c), the copper concentration in the solution decreases obviously when the applied bias increases to be 2 V. It is clear that the increased applied bias is beneficial to the cathodic reduction of the liberated copper ions in PEC system within a certain range. The Cu cathodic leakage and reduction in the long-term run was also evaluated (Text S1, Fig. S2).

The effect of pH_0 on the DCF removal and solution pH variation in the PEC process were illustrated in Fig. 4. As shown in Fig. 4(a), when the pH_0 increases from 5.62, 7.00 to 10.00, the removal ratio of DCF decreases from 67.4%, 64.5% to 46.3% at 2 h. As shown in the inset graph of Fig. 4(a), the degradation rate of DCF is well fitted with a pseudo-first-order reaction model at each initial solution pH and the kinetic rate constants are determined to be 0.5561 h^{-1} ($R^2 = 0.992$), 0.4882 h^{-1} ($R^2 = 0.982$) and 0.3217 h^{-1} ($R^2 = 0.987$), respectively.

Thus, it is clear that the rate of DCF degradation efficiency decreases with an increase of pH_0 . DCF has a pK_a of 4.0, it deprotonates in the pH_0 range of 5.62 to 10.0 thus is always negative charged. Therefore, the effect from the charge interaction between electrode and DCF can be excluded. There may be some other factors which influence the DCF degradation in this system. From the view of free radicals, the redox potential of $\text{SO}_4^{\cdot-}$ is confirmed as 2.5 ~ 3.1 V, even higher than $\text{HO}^{\cdot}$ (potential of $\text{HO}^{\cdot}$ is about 2.7 V in acid solution and 1.8 V in neutral solution) [32–35]. As shown in Eq. (3), the conversion of $\text{SO}_4^{\cdot-}$ to $\text{HO}^{\cdot}$ occurs easily in alkaline conditions [36]. Therefore, more $\text{SO}_4^{\cdot-}$ are generated at acid conditions, which may be partly responsible for the efficient DCF degradation under acid conditions.

Moreover, PS was reported to be further catalyzed under acid conditions according to the literature [37] indicated by Eqs. (4) and (5):

On the other hand, solution pH may affect the generation of Cu species and the liberation of copper ions in solution. As shown in Fig. 4(b), the leached copper concentration is decreased from acid

Fig. 3. Effect of applied bias on the DCF removal (a), kinetic rate constants (b) and leached copper concentration (c) in PEC system. Conditions: [DCF] = 10 mg/L; [PS] = 1 mM; pH_0 , 5.62.

to alkaline conditions. Copper ions in alkaline conditions are inclined to precipitate. By contrast, acid condition is beneficial to copper electrodeposition [38], which will be discussed subsequently.

The pH variations with the reaction evolution under different conditions were shown in Fig. 4(c). It can be observed that the solution pH decreases as the reaction proceeds under both acid and alkaline conditions. This phenomenon is caused by the acidification stems from the transformation of SO_4^- to $\text{HO}^\bullet$, which consumes OH^- in the solution according to Eq. (3). The result was consistent with the research reported by Gu et al. [37].

3.4. Involved active radicals

According to previous literatures [14,22], there are two major proposed mechanisms to explain the PS activation process: radical

Fig. 4. Effect of pH_0 on the DCF removal (a), leached copper ions concentration (b) and pH variation (c) during the reaction in the PEC system. Conditions: [DCF] = 10 mg/L; applied bias, 1.5 V; [PS] = 1 mM.

processes and nonradical processes. In most cases, it was illustrated that SO_4^- and $\text{HO}^\bullet$ were produced in the process of activation which was responsible for the pollutant degradation [16,39]. As shown in Fig. 5(a), SO_4^- and $\text{HO}^\bullet$ are both detected at the Cu cathode and Bi_2MoO_6 anode in our PEC system. In PEC system, the photoanode produces electron-hole pairs and the holes can move to the surface of semiconductor to react with water and form $\text{HO}^\bullet$ [30]. The detected $\text{HO}^\bullet$ at the anode stem from this process. It can be concluded that the relative intensity of free radicals generated at the cathode is much higher than those generated at the anode and in the bulk solution. The above results indicate that free radicals are produced in this PS activation process and it mainly occurs at the surface of the copper cathode in this PEC system.

In order to investigate the role of Cu foil cathode in the generation process of free radicals, the control experiments were conducted by using Ti, Fe and Co foil as cathodes (the ESR analyses

Fig. 5. Comparison of ESR spectrum in bulk solution, at the anode and at the cathode in $\text{Bi}_2\text{MoO}_6/\text{Cu}/\text{PEC}/\text{PS}$ system (a); Comparison of ESR spectrum in aqueous solution, at Ti cathode and at Cu cathode in PEC system (b). Conditions: Applied bias, 1.5 V; $[\text{PS}] = 5 \text{ mM}$; pH_0 , 5.62.

of Fe, Co cathodes were shown in Fig. S3). As shown in Fig. 5(b), the peak intensities of $\text{HO}^\bullet$ and $\text{SO}_4^{\bullet-}$ generated at the Cu cathode are obviously higher than other metal cathodes. Some literatures

demonstrate that photogenerated electrons could activate PS in the photocatalytic process [40,41]. In our case, the photogenerated electrons transferred to the cathode is limited for activating PS. Meanwhile, the Cu cathode plays the key role in activating PS. The effects of PS concentration, applied bias and pH_0 on ESR signals of $\text{SO}_4^{\bullet-}$ and $\text{HO}^\bullet$ are further investigated in detail. As illustrated in Fig. S4(a)–(b), as the PS concentration and applied bias increases, the peak intensities of $\text{HO}^\bullet$ and $\text{SO}_4^{\bullet-}$ at the Cu cathode increase which leads to an increased degradation efficiency of DCF. As shown in Fig. S4(c), more free radicals may exist in the form of $\text{HO}^\bullet$ in alkaline conditions according to Eq. (3) as stated.

3.5. Characterizations of the Cu cathode variation

It was noticed that the fresh copper foil cathode became dark red with the addition of PS during the PEC reaction. The surface change of copper cathode was firstly checked using the FE-SEM technique. As shown in Fig. 6, the surface of copper foil is relatively smooth and uniform before the PEC reaction. The scratches observed are caused by copper pretreatment by sandpaper polish. However, the smooth surface is destroyed with the generation of porous structure at the PEC reaction time of 0.5 and 1 h. With the reaction evolution, this structure can be always observed and nearly covers the copper surface fully at 2 h.

Furthermore, copper cathode samples at various times in the PEC reaction with PS addition were analyzed by GI-XRD. This technique has a smaller incident angle of 0.2° and it could obtain a more intense signal than conventional XRD from surface in order to reduce the effect of Cu substrate. As shown in Fig. 7, before the PEC reaction, no other peaks except copper are observed. After one hour, peaks at $2\theta = 36.4^\circ$, 42.3° and 61.4° are obviously observed, which are corresponded well with Cu_2O (JCPDS: 78-2076). Moreover, the peak intensity of Cu_2O increases with the reaction evolution. It is demonstrated that some reactions may occur on the copper foil, leading to the formation of Cu_2O .

In addition, XPS technique was used to determine the variation of the copper valence. It can be clearly seen from Fig. 8(a) that nearly no change of the major elements on the copper surface is observed after the PEC reaction. As shown in Fig. 8(b), before the

Fig. 6. FE-SEM images of copper foil at various time in $\text{Bi}_2\text{MoO}_6/\text{Cu}/\text{PEC}/\text{PS}$ system. Conditions: $[\text{DCF}] = 10 \text{ mg/L}$; applied bias, 1.5 V; $[\text{PS}] = 5 \text{ mM}$; pH_0 , 5.62.

Fig. 7. GI-XRD patterns of copper foil at various times in $\text{Bi}_2\text{MoO}_6/\text{Cu}/\text{PEC}/\text{PS}$ system. Conditions: $[\text{DCF}] = 10 \text{ mg/L}$; applied bias, 1.5 V; $[\text{PS}] = 5 \text{ mM}$; pH_0 , 5.62.

Fig. 9. In situ Raman spectroscopic analysis of the copper cathode in the PEC reaction process. Conditions: Applied bias, 1.5 V; $[\text{PS}] = 5 \text{ mM}$; pH_0 , 5.62.

Fig. 8. XPS full scan spectra of copper cathode before and after reaction (a); XPS Cu 2p spectra of the copper cathode before and after reaction (b). Conditions: $[\text{DCF}] = 10 \text{ mg/L}$; applied bias, 1.5 V; $[\text{PS}] = 5 \text{ mM}$; pH_0 , 5.62.

reaction, the major $\text{Cu } 2p_{3/2}$ peaks centered at 932.6 eV and major $\text{Cu } 2p_{1/2}$ peaks centered at 952.45 eV are assigned to zero-valent copper [42,43]. After the reaction, there are three peaks related to copper valence appearing in the graph. The binding energies are 933.05, 952.5 and 935.08 eV, respectively. The major $\text{Cu } 2p_{3/2}$ peak centered at 933.05 eV is assigned to Cu [44]. In addition, the major $\text{Cu } 2p_{1/2}$ peak centered at 952.5 eV is assigned to Cu_2O [45]. Combined with XRD analysis, this evidence once again indicates that Cu(I) generates on the copper foil cathode in the PEC

process. In addition, a major $\text{Cu } 2p_{3/2}$ peak centered at 935.08 eV is also detected and it is assigned to Cu^{2+} [46].

The variation of the copper foil cathode during the PEC reaction was further examined by in situ Raman spectroscopy. As shown in Fig. 9, no obvious peak is observed at 0 min, demonstrating that the copper remains metallic. Five peaks at 145, 214, 414, 527 and 624 cm^{-1} appear at 5 min, which are assigned to Cu_2O [47]. The intensity of these peaks remains low before the first 30 min and enhances gradually from 30 min to 120 min. Besides, in situ Raman spectra of copper foil under different pH_0 are compared which are shown in Fig. S5. It can be concluded that pH_0 do not have an

Fig. 10. LSV curves of Bi_2MoO_6 (a) and Cu_2O (b) electrode in the presence and absence of visible light irradiation and persulfate in Na_2SO_4 electrolyte solution. Conditions: $[\text{PS}] = 5 \text{ mM}$; $[\text{Na}_2\text{SO}_4] = 5 \text{ mM}$; $\lambda > 420 \text{ nm}$; scan rate = 10 mV/s.

obvious influence on the generation of Cu_2O . From above, the generation of Cu_2O in the reaction process is confirmed.

3.6. Photoelectrochemical analysis

Photoelectrochemical characteristics of the Bi_2MoO_6 electrode and Cu_2O electrode were further discussed in the presence and absence of the persulfate by LSV measurements. As shown in Fig. 10(a), under visible light irradiation, the Bi_2MoO_6 photoanode shows a significant enhancement in photocurrent response. A slight difference was observed in the presence or absence of persulfate. In Fig. 10(b), the photoelectrochemical performance of the generated Cu_2O on the Cu cathode was presented. Under visible light irradiation, an enhancement of current is observed and the generated Cu_2O shows a good response to visible light with a p-type semiconductor characterization. Furthermore, it is clear that the current is largely increased with the persulfate addition both in the dark and under visible light irradiation, which indicated the interaction between generated Cu_2O and persulfate.

The IPCE plots and EIS Nyquist plots were shown in Fig. S6. IPCE increases slightly with the increase of persulfate concentration using the copper foil as cathode (Fig. S6(a)). As shown in Fig. S6(b), the arc radius of the Bi_2MoO_6 photoanode without

visible light irradiation is larger than that with visible light irradiation. Smaller arc radius implies a higher efficiency of charge transfer. But the arc radius of system with persulfate is nearly similar with the system without persulfate under visible light irradiation. Above results demonstrate that the introduction of persulfate to this PEC system do not obviously change the transfer efficiency of photogenerated electron-hole pairs.

3.7. Identification of intermediates and proposed reaction pathways

The main intermediates of DCF in the reaction were identified by UPLC-Q-TOF-MS. A possible reaction pathway was proposed in Fig. 11. Besides DCF itself, there were four intermediates identified in the reaction (the structures were in Table S1 and the mass spectra were shown in Fig. S7). We formulated these detected products from P1 to P4, respectively. The MS spectrum of DCF shows a molecular ion peak at 294 m/z and 250 m/z . The loss of 44 could be attributed to CO_2 loss, which is consistent with previous studies about DCF. The MS spectrum of P1 shows a strong peak at 177 m/z . Previous studies reported that peak at 161 m/z might be the major product in the degradation process of DCF [48]. P1 might be the product derived from addition reaction with $\text{OH}^\cdot$. In the mass spectrum of P2, the fragments are 228, 264 and 310 m/z . The most

Fig. 11. Proposed degradation pathways of DCF in the $\text{Bi}_2\text{MoO}_6/\text{Cu}/\text{PEC}/\text{PS}$ system (intermediates with * were deduced).

important fragment 228 m/z corresponds to the loss of HCl from fragment 264 m/z . The fragment 264 m/z corresponds to the loss of OH and CH₂ groups from 310 m/z . In the mass spectrum of P3, the most important fragment is 266 m/z and it corresponds to the loss of CO₂ from 310 m/z . P1 can be formed by cleavage of C–N bond from P8*. There is an interchange between P4 and P8*. P5* results from decarboxylation of DCF. P3 and P6* possess the same elemental compositions and they are derived from hydroxylation as a result of HO• attack. P2 is probably obtained by dehalogenation and oxidation of P6*. It can be concluded that most of the identified intermediates are generated by the attack of HO• in the reaction. This result is consistent with the ESR analyses and it is demonstrated that the main oxidizing species are HO• in this system.

3.8. A proposed enhanced mechanism

The above results indicated that HO• and SO₄•[−] were produced from the copper foil cathode with the addition of PS; and Cu₂O was generated during the PEC reaction process. Considering the above analyses, a proposed reaction process was expressed by Eqs. (6)–(9) and Scheme S1.

As illustrated in Scheme S1, PS could be activated by receiving an electron from the copper when PS was added into the PEC system. As a result, SO₄•[−] and HO• were generated, which were responsible for DCF oxidation. Meanwhile, Cu₂O was generated on the surface of copper cathode. In order to test its activation capacity for PS, the Cu₂O thin film was prepared with an electrodeposition method on ITO glass [49]. As shown in Fig. S8, there is nearly no removal of DCF observed by the prepared Cu₂O film with addition of 1 mM PS. It is known that Cu₂O is more inclined to undergo disproportionation reaction, leading to the generation of Cu and Cu²⁺ in acid conditions. Cu²⁺ absorbed on the surface according to XPS results may diffuse into the solution. In the meantime, Cu²⁺ could be deposited onto the copper surface again by cathodic reduction, which benefited the copper recycle between electrode and solution. This copper recovery process can be confirmed by the compared experiments between PEC system and chemical oxidation system in which copper just puts into solution with PS and DCF. The leached copper ion concentration in PEC system is 37% fewer than in chemical oxidation process when the PS and copper dosage is definite. This result demonstrates that the leached copper ions can be recovered by the cathodic reduction in the PEC system. In a word, the copper surface redox cycle of Cu(0)–Cu(I)–Cu(II)–Cu(0) would be probably responsible for the PS activation in this system.

3.9. Stability analysis

In order to evaluate the reproducibility of the system, the experiments were conducted for three times. As shown in Fig. 12, the removal efficiency of DCF does not change significantly in each cycle (67%, 72% and 71%, respectively). The final removal efficiency remains steady and consistent in the three cycles. From the above results, the system shows high reproducibility for DCF removal.

Fig. 12. The residual rate of DCF for cycles. Conditions: [DCF] = 10 mg/L; applied bias, 1.5 V; [PS] = 1 mM; pH₀, 5.62.

4. Conclusions

In summary, DCF can be efficiently removed in the PEC system with γ-Bi₂MoO₆ as photoanode and copper as cathode with the PS addition. The generation of hydroxyl radicals and sulfate radicals was detected, which was responsible for the enhanced DCF degradation. It was deduced that the copper provided electrons to PS with the generation of Cu₂O on the surface and PS was activated in this process. Then Cu(I) disproportionated in the acid solution, leading to the production of Cu(0) and Cu(II). Cu(II) was deposited onto the copper again by the cathodic reduction. Above results of this study showed the PS oxidation catalyzed with copper cathode may be an available method for contaminant removal. This work also provides a new perspective towards PS activation and efficient utilization of the cathode in the PEC system.

Acknowledgements

The authors gratefully acknowledge financial support from National Natural Science Foundation of China (No. 21377148, 51438011), Natural Science Foundation of Yongchuan, Chongqing (Ycstc, 2014ac4001).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2017.03.047>.

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