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A derivative photoelectrochemical sensing platform for herbicide acetochlor based on TiO_2–poly (3-hexylthiophene)–ionic liquid nanocomposite film modified electrodes

Dangqin Jin [a,b], Qin Xu [a], Yanjuan Wang [a], Xiaoya Hu [a,*]

[a] College of Chemistry and Engineering, Yangzhou University, Yangzhou 225002, PR China
[b] Department of Chemical Engineering, Yangzhou Polytechnic Institute, Yangzhou 225127, PR China

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ABSTRACT

Nonelectroactive acetochlor can be indirectly determined through the photocatalytical degradation of acetochlor. A derivative visible light photoelectrochemical sensor for indirect detection of the herbicide acetochlor using TiO_2–poly(3-hexylthiophene)–ionic liquid nanocomposite is constructed. Poly (3-hexylthiophene) (P3HT) was synthesized via chemical oxidative polymerization with anhydrous $FeCl_3$ as oxidant, 3-hexylthiophene as monomer, chloroform as solvent, and the functional TiO_2 nanoparticles were facilely prepared by blending TiO_2 nanoparticles and P3HT at room temperature ionic liquid, 1-Butyl-3-methylimidazolium hexafluorophosphate solution. Operational parameters, including the photolysis time, ratios of TiO_2 to P3HT, bias voltage and pH of buffer solution have been optimized. Under optimal conditions, the proposed photoelectrochemical method could detect acetochlor ranging from 0.5 to 20 μmol L^{-1} with a detection limit of 0.2 nmol L^{-1} at a signal-to-noise ratio of 3. The assay results of acetochlor in water samples with the proposed method were in acceptable agreement with those of the gas chromatograph–mass spectrometer (GC–MS) method. The promising sensor opens a new opportunity for fast, portable, and sensitive analysis of acetochlor in environmental samples.

1. Introduction

Acetochlor (2-chloro-N-(ethoxymethyl)–N-(2-ethyl-6-methyl-phenyl)-acetamide) (Fig. 1), as one of the most important herbicides in the world, is a pre-emergent herbicide used to control competing grasses and some broadleaf weeds in corn. It was used extensively for the first time in the United States after its conditional registration by the U.S. Environmental Protection Agency (USEPA) in March 1994 [1]. However, acetochlor has had a multi-year history of international use prior to its registration in the United States [2–4].

Acetochlor has clear limits in many countries [5] because it has been classified by the USEPA as a B-2 carcinogen [1]. Acetochlor undergoes transformation in the environment to form the corresponding ethanesulfonic (ESA) acids [6,7]. There are some evidences that the ESA acids might migrate into ground and surface waters due to their solubility and mobility [8–10], and they have a weak genotoxic [11] and carcinogenic effects [12]. The registration for acetochlor states that concentrations of acetochlor should not exceed 0.10 μg L^{-1} in groundwater or 2.0 μg L^{-1} as an annual average in surface water [1]. In view of the major concerns regarding the toxicity of acetochlor, the determination of acetochlor residues in environment samples is urgently needed. Although instrumental methods such as gas chromatography (GC) [13–17], liquid chromatography (LC) [18–20], immunosorbent assay [21], gas chromatogram mass spectrometer(GC–MS) and liquid chromatogram mass spectrometer (LC–MS) [22] offer high sensitivity and specificity and have the potential for simultaneous determination of multiple analogs, which require associated high costs and time-consuming labor . Searching for a new, simple, low-cost, portable, and sensitive analytical method is of considerable interest.

Photoelectrochemical measurement is a newly developed technique for the sensing platform, which is based on the electron transfer among analyte, semiconductor, and electrode with photoirradiation [23,24]. Coupling photoirradiation with electrochemical detection, photoelectrochemical sensors has the advantages of both optical methods and electrochemical sensors [25,26]. Thus, this technique has attracted considerable interests as a newly developed and promising analytical technique. Moreover, the utilization of electronic detection makes the photoelectrochemical instruments simpler and low-cost compared with those of the conventional optical methods. During the recent decades,titanium dioxide has been demonstrated to be a very efficient catalyst for

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[*] Corresponding author. Tel.:+86 51487971818; fax:+86 51487975244.
E-mail address: xyhu@yzu.edu.cn (X. Hu).

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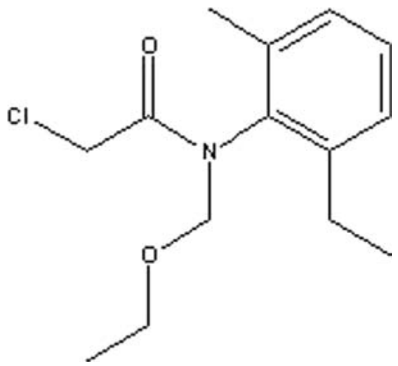


Fig. 1. Structure of acetochlor.

decomposition of organic compounds, sterilization, cancer treatment, etc. due to its high photocatalytic activity, abundant resource, biological and chemical inertness, and nontoxicity [27–30]. Titanium dioxide is especially suitable to work by solar UV light [31]. However, the wide band gap (3.2 eV) of TiO_2 only allows it to absorb the ultraviolet light ($<$ 387 nm) that limits the utilization of solar light since UV light in solar light is less than 5% [32]. Hence, much effort has been devoted to develop a TiO_2 based photocatalyst which is capable of efficient utilization of the visible light.

Poly(3-hexylthiophene) (P3HT), as one of the excellent photoelectric materials, has a higher charge carrier mobility, dissolubility, and processability, long-term stability, and a broad and strong absorption in visible region (with band gap of 1.9–2.0 eV) [33,34]. P3HT–functionalized TiO_2 nanoparticles can efficiently promote the separation of holes and electrons. Therefore, it should be a good candidate for a sensitizer of TiO_2. In a recent study, P3HT–TiO_2 composites were described for their application in rapid degrading organic dye methyl orange with visible light irradiation [34]. We have reported the application of P3HT–TiO_2 nanoparticle-functionalized electrodes for visible light and low potential photoelectrochemical sensing of organophosphorus pesticide chlopyrifos [35].

Room temperature ionic liquid (IL) 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF_6) has attracted much attention as extraordinarily high chemical and thermal stability, good conductivity, wide electrochemical windows, no requirement for additional supporting electrolytes and good dissolving capability. It has been widely used in organic synthesis, liquid–liquid extraction, photoelectrochemistry and inorganic synthesis [36–38]. So far, the application of IL in electrochemistry has been stretched in many areas, such as the electrodeposition of metals or semiconductors [39], the electropolymerization of organic compounds [40], the fabrication of gas sensors and supercapacitors [41] and as medium for photochemical reactions [38].

To the best of our knowledge, little work has been done on the photocatalytic activity of TiO_2–-poly(3-hexylthiophene)–-ionic liquid nanocomposite film modified electrodes under visible light irradiation as a photoelectrochemical sensing platform of the acetochlor. In this paper, we have prepared TiO_2 nanoparticles modified by a small amount of P3HT (TiO_2–P3HT) at room temperature ionic liquid ([bmim]PF_6)(IL) solution and investigated the visible light photocatalytic activities of TiO_2–P3HT–IL towards acetochlor and developed a derivative method for the sensitive detection of acetochlor.

2. Material and methods

2.1. Reagents and solutions

3-Hexylthiophene (99%), TiO_2 nanopowder (anatase, $<$ 25 nm, 99.7%), and acetochlor (96% EC) were purchased from Sigma-Aldrich (St. Louis, MO). The room temperature IL, 1-butyl-3-methylimidazolium hexafluorophosphate([bmim]PF_6), was purchased from Aladdin-Reagent Company(Shanghai, China). All other chemicals were of analytical grade. In this work, Phosphate–NaOH buffer solutions were prepared with a pHS-25 pH-meter (Shanghai Leici Instrument Plant, China) at room temperature by mixing 0.1 M Na_2HPO_4 and 0.1 M NaH_2PO_4, and then adjusting to the desired pH by 0.1 M HCl or 0.1 M NaOH. It was always employed as the supporting electrolyte after being deaerated with high-purity nitrogen. Aqueous solutions were prepared with twice-distilled water, and the pH value of buffer solution was 9.0 unless indicated otherwise.

2.2. Apparatus

Photoelectrochemical measurements were performed with a home-built photoelectrochemical system. A 250 W halogen lamp light was used as the irradiation source. Photocurrent was measured by the current–time curve experimental technique on a CHI760D electrochemical workstation (CH Instruments, Shanghai, China) connected to a personal computer with visible light irradiation. All experiments were carried out at room temperature(25 °C) using a conventional three electrode system with a modified glassy carbon electrode (GCE) as the working electrode, a platinum wire as the auxiliary electrode, and a saturated calomel electrode as the reference electrode. The model surveyor apparatus used in this study was a GC/MS [Trace 2000 Shimadzu equipped with capillary column (HP-5, 30 m × 0.32 mm × 0.25 μm)]. For GC–MS, the column temperature was maintained at 50 °C for 1 min and then programmed to 140 °C at 30 °C min^{-1}, to 220 °C at 5 °C min^{-1}, and then to 280 °C at 10 °C min^{-1}, and held for 7 min. The carrier gas at a rate of 1.0 mL min^{-1} was helium, with purity of 99.999%. The injection port temperature was 260 °C, and the splitless mode was used for injection of 1 μL volume with the valve opened for 30 s. The ionization energy was 70 eV. The ion source and the GC–MS interface were kept at 200 and 280 °C, respectively.

2.3. Preparation of TiO_2, TiO_2-P3HT P3HT-IL and TiO_2–P3HT–IL modified GCE

The TiO_2–P3HT–IL nanocomposites were prepared according to the following steps: first, poly(3-hexylthiophene) (P3HT) was synthesized via chemical oxidative polymerization with anhydrous $FeCl_3$ as oxidant, 3-hexylthiophene as monomer, chloroform as solvent by the reported procedure [42]. Then, 2.0 g TiO_2 nanoparticles were added to chloroform solutions (50 mL) of P3HT with the different mass ratios of titania to P3HT (40:1, 60:1, 80:1, 100:1 and 120:1). After continuously ultrasonicated for 3 h, the above suspension mixtures were filtered. Finally, the product was dried at 60 °C under vacuum till the constant mass was reached. TiO_2–P3HT suspension dispersed in the DMF solution (1 mg mL^{-1}), and then 1 μL IL was added into 1 mL of TiO_2–P3HT suspension. After a GCE had been polished with Al_2O_3 (0.3 μm), washed with acetone and twice-distilled water, and dried at room temperature, 10 μL of the TiO_2-P3HT-IL suspension was coated onto the GCE and dried at room temperature to obtain a TiO_2-P3HT–IL modified GCE. A TiO_2–P3HT modified GCE and a TiO_2 modified GCE were prepared similarly.

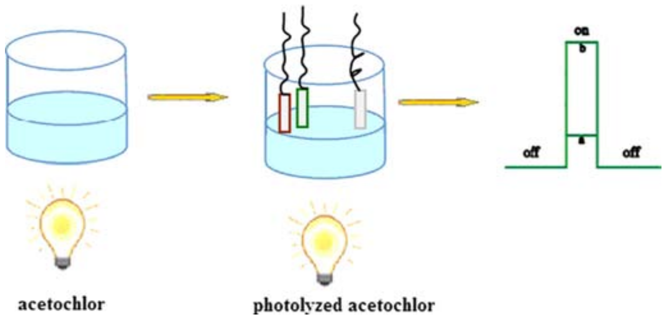
2.4. Photolysis and photoelectrochemical detection

Acetochlor solution was irradiated under the visible light radiation for 30 min with the distance of 10 cm between the 250 W Whalogen lamp light and liquid level. The lamp was placed in the inner part of a home-built photoelectrochemical system and a fan was used to avoid uncontrolled heating of the irradiated solution and photocurrent was measured in maintaining room temperature. There are 12 kinds of photolysis compounds of acetochlor [43,44]. Some of them are readily oxidizable materials (alcohols, aromatics,…). Afterward acetochlor solution was irradiated under the visible light radiation for 30 min, the electrodes were inserted into the solution to detect the concentrations of photolysis compounds of acetochlor by photocurrent responses. The procedure is shown in Scheme 1. The acetochlor solution was heated at 90 °C for 30 min without light irradiation to check whether a thermal hydrolysis played an important fact or not. There is no obvious difference on the photocurrent responses of acetochlor before and after heating in 0.1 mol L^{-1} pH 9.0 buffer solution. Therefore, this is not the thermal hydrolysis.

3. Results and discussion

3.1. Electrochemical behavior of acetochlor and its photolysis compound

The electrochemical behaviors of acetochlor (Fig. 2 b) and its photolysis compound (Fig. 2 c) were studied, respectively. As can be seen in Fig. 2, there is no obvious difference in photocurrent at the TiO_2–P3HT–IL modified GCE in the absence (Fig. 2 a) and presence (Fig. 2 b) of 5.0 µmol L^{-1} acetochlor in buffer solution (pH 9.0), which indicates that the photocurrent responses of acetochlor do not take place in 0.1 mol L^{-1} pH 9.0 buffer solution. However, one of photocurrent responses markedly appears (Fig. 2 c) for the 5.0 µmol L^{-1} photolyzed acetochlor, which demonstrates that the photolysis compound of acetochlor has good photoelectrochemical activity. Different photocurrent responses, before and after photolysis, showed good selectivity against other pesticides and possible interferences. Therefore, acetochlor can be indirectly detected by its photolysis compounds.



Scheme 1. Scheme of photoelectrochemical sensor to detect the sample.

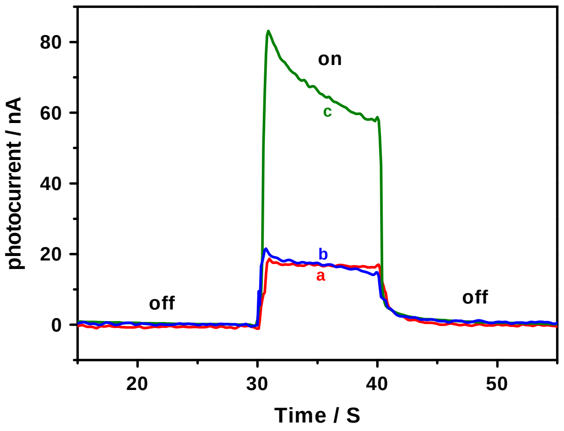


Fig. 2. Photocurrent responses of 5.0 µmol L^{-1} acetochlor before and after photolysis in 0.1 mol L^{-1} pH 9.0 buffer solution at TiO_2 –P3HT–IL modified GCE: (a) blank buffer, (b) in the presence of acetochlor, and (c) in the presence of photolyzed acetochlor.

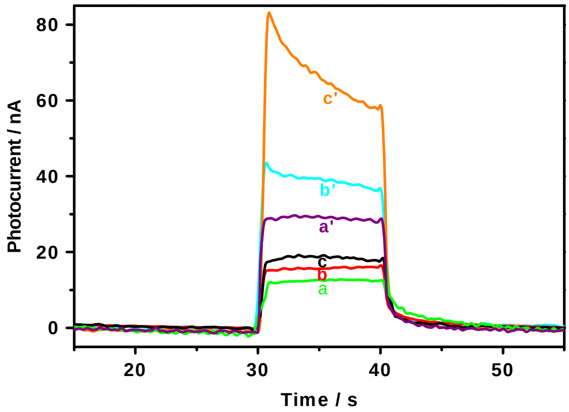
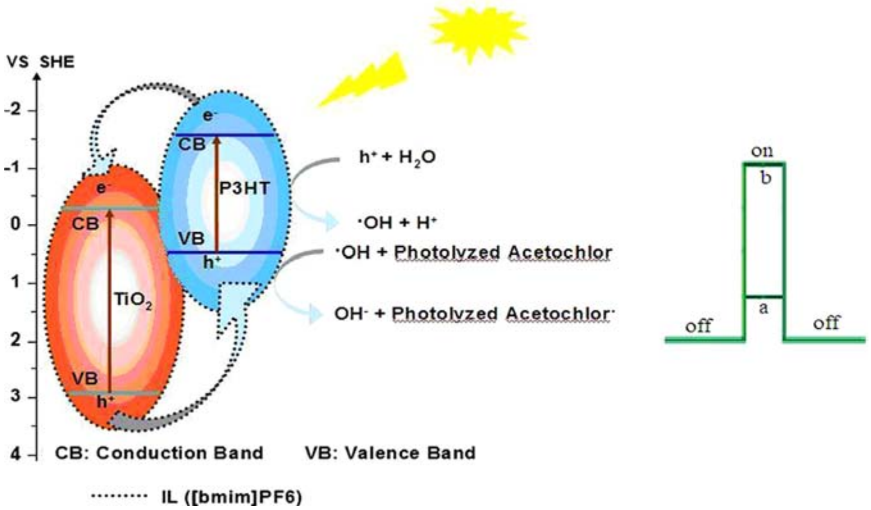


Fig. 3. Photocurrent responses of (a,a') TiO_2,(b,b') TiO_2–P3HT and (c, c') TiO_2–P3HT–IL (80:1) modified GCEs in 0.1 M pH 9.0 buffer solution in the (a, b and c) absence and (a',b' and c') presence of 5.0 µmol L^{-1} acetochlor at 0.2 V with visible light excitation.

3.2. Photoelectrochemical oxidation of photolyzed acetochlor

Upon photoexcitation with visible light, the TiO_2 modified GCE showed a photocurrent of 12.7 nA (Fig. 3 a), the TiO_2–P3HT modified GCE showed a photocurrent of 15.6 nA (Fig. 3 b), whereas the TiO_2–P3HT–IL modified GCE showed a photocurrent of 18.7 nA (Fig. 3 c) at a bias voltage of 0.2 V, indicating the improvement of the photocurrent conversion efficiency of TiO_2 by the addition of P3HT because of the strong electronic coupling between the excited-state P3HT and the conduction band of TiO_2 [35]. Furthermore, the improved photocurrent conversion efficiency could be further amplified by an electron-transfer process from photolyzed acetochlor to P3HT by addition of IL because of ionic conductivity enhancement due to large number of free charge carriers provided by IL. Upon addition of 5.0 µmol L^{-1} acetochlor, the photocurrent of TiO_2–P3HT–IL modified GCE increased by 66.3 nA (Fig. 3 c and c'), which was 1.7 times the photocurrent increment of 39.5 nA observed at the TiO_2–P3HT modified GCE (Fig. 3 b and b'), which was 2.3 times the photocurrent increment of 29.5 nA observed at the TiO_2 modified GCE. The increase of 132.3% at the TiO_2 modified GCE is attributed to the oxidization of photolyzed acetochlor by the TiO_2 holes. The different sensitizing effects at TiO_2–P3HT–IL modified GCE with an increase of 254.5% resulted from the efficient charge separation of the TiO_2–P3HT–IL system to form holes for the photoelectrochemical oxidation of photolyzed acetochlor.

Photo-anodic processes on TiO_2 showed a stable photoelectrochemical response that could be caused by the pre-concentrated analyte as well as be further sensitized by a P3HT and IL. Photolysis compound of acetochlor contain aromatic rings with π-electrons [43,44], and thiophene and IL contain alkyl hydrogens. Therefore, thiophene and IL could interact with the photolysis compounds of acetochlor through H–π interaction, thus pre-concentrate photolysis compound of acetochlor on electrodes. The relative energy levels of P3HT and TiO_2 (conduction band, CB; and valence band, VB) are shown in Scheme 2. On the basis of the results of photoelectrochemical tests, the photoelectrochemical mechanism for photolyzed acetochlor oxidation under visible light irradiation can be inferred as follows. P3HT absorbs visible light to induce and transport electron from VB to CB transition. The CB and VB edge potentials of TiO_2 are at −0.29 eV and 2.91 eV, respectively. The CB and VB edge potentials of P3HT are at −1.5 eV and



Scheme 2. Schematic illustration of proposed photoelectrochemical mechanism for photolyzed acetochlor oxidation at TiO_2–P3HT–IL modified GCE.

0.6 eV, respectively. P3HT absorbs visible light to induce and transport electrons, the excited-state electrons could be injected from the CB of P3HT to CB of TiO_2 readily. Because CB edge potentials of TiO_2 is at −0.29 eV, the CB edge potentials of P3HT is at −1.5 eV. The CB of TiO_2 and P3HT match well in energy level, which can cause a synergic effect. On the basis of the synergic effect, the excited-state electrons could be injected into the d-orbital (CB) of TiO_2 readily and subsequently transferred to the GCE surface, leading to a sharp increase of the photocurrent [45]. The improved photocurrent conversion efficiency could be further amplified by the electron-transfer process from photolyzed acetochlor to P3HT by addition of IL because of ionic conductivity enhancement due to large number of free charge carriers provided by IL. At the same time, a positive charged hole (h^+) of TiO_2 may form and migrate to the VB of P3HT [46], which can react with H_2O to generate $^\bullet$OH and then it is the responsibility of hydroxyl radical ●OH for the oxidation of photolyzed acetochlor to photolyzed acetochlor●. Subsequently, more generated photolyzed acetochlor● can promote the amplifying photocurrent response.

3.3. *Optimization of the experimental conditions for acetochlor measurement*

Since the proposed method for the indirect determination of acetochlor is based on the photoelectrochemical signal being proportional to the concentration of acetochlor with visible light irradiation, it is more important to improve the sensitivity of the proposed method. The effect factors for measurements concerning photolysis time, ratios of TiO_2 to P3HT, bias voltage, and pH of buffer solution were studied in detail.

3.3.1. *Optimal conditions for photolysis time*

The analytical performance of the photoanalysis was related to the concentration of electroactive hydroxyl-substituted aromatic ring compounds in the measuring system. As can be seen in Fig. 4, the photocurrent response increased with the increasing photolysis time from 5 to 40 min and became stable after 30 min (inset of Fig. 4). Longer photolysis time did not obviously improve the response. It can be explained that more photodegraded species of acetochlor were produced as the photodegradation progresses with the increase of the time. Considering the optimal sensitivity and analysis efficiency, the photolysis time of 30 min was chosen as the optimal photolysis condition for the detection of acetochlor.

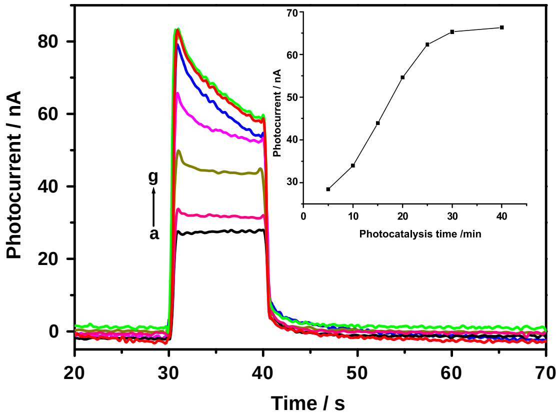


Fig. 4. Photocurrent responses of the photoelectrochemical sensor with increasing photolysis time in 0.1 mol L^{-1} pH 9.0 buffer solution containing 5.0 μmol L^{-1} acetochlor (a–g). The inset shows the effects of photolysis time of acetochlor on the amperometric response of the photoelectrochemical sensor.

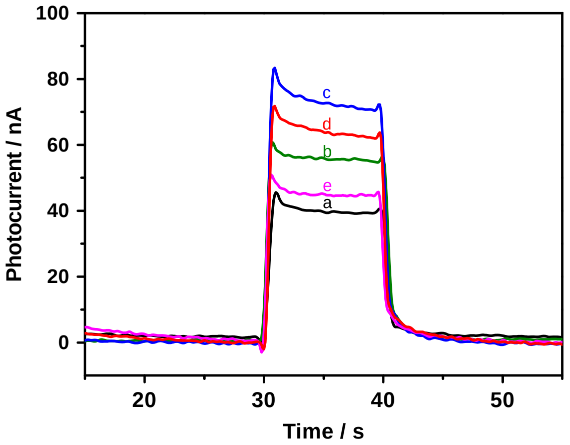


Fig. 5. Effects of mass ratio of TiO_2 to P3HT (a) 40:1, (b)60:1, (c) 80:1, (d) 100:1, and (e) 120:1 at room temperature ionic liquid and 0.1 M pH 9.0 buffer solution containing 5.0 μmol L^{-1} acetochlor.

3.3.2. *Optimum of ratios of TiO_2 to P3HT*

The mass ratios of functionalized TiO_2 to P3HT (40:1, 60:1, 80:1, 100:1 and 120:1) at room temperature ionic liquid were investigated for their photocurrent response. As shown in Fig. 5, upon addition of 5.0 μmol L^{-1} acetochlor, the photocurrent increased until the mass ratio of TiO_2/P3HT is 80:1 at the bias voltage of 0.2 V with visible light excitation and then decreased. It can be explained that the more positive charged holes (h^+) of P3HT–TiO_2 system can be generated and promote the deep oxidation of photolyzed acetochlor; however, the thicker P3HT film may prevent the electron transporting from the CB of P3HT to TiO_2 and further decreased the photocurrent response. Therefore, the ratio of 80:1 is favorable for the further study.

3.3.3. *Optimum of the bias voltage*

The bias voltage is an important parameter for producing the photocurrent. Upon addition of 5.0 μmol L^{-1} acetochlor, the photocurrent sharply increased as the bias voltage increased from 0 to 0.1 V and then trended toward a maximum value (Fig. 6). The bias voltage effectively gets inhibited by simply compositing the photo-generated electrons and holes, which increases the photocurrent response. However, when the bias voltage increases to 0.2 V, the photocurrent almost does not increase. So it is not that when bias voltage is greater, photocurrent response efficiency will increase. 0.2 V was chosen for the photoelectrochemical sensor of photolyzed acetochlor.

3.3.4. *Optimal pH*

The effect of solution pH on the photoelectrochemical response of 5.0 μmol L^{-1} acetochlor at TiO_2–P3HT–IL/GCE was investigated with buffer solution in the pH range from 4.0 to 12.0. As can be seen in Fig. 7, the photocurrent response increased rapidly with the increase of pH when pH was below 9.0, and then remained practically constant down to 12.0. Therefore, pH 9.0 was chosen as the optimum pH in the subsequent measurements.

3.4. *Photoelectrochemical detection of acetochlor*

The photocurrent – time curve of TiO_2–P3HT–IL modified GCE clearly illustrates the rapid response of the modified electrode to photolyzed acetochlor at a bias voltage of 0.2 V with visible light irradiation (Fig. 8). Under the optimal conditions, the response displayed a linear increase as the acetochlor concentration increased from 0.5 to 20 μmol L^{-1} (0.13–5.4 mg L^{-1}) with a detection limit of 0.2 nmol L^{-1} (54 ng L^{-1}). Although the detection limit of 54 ng L^{-1} was higher than that of GC–MS (10 ng L^{-1}) [22], the lower detection limit of 54 ng L^{-1} is suitable enough for the photoelectrochemical detection of acetochlor in pesticide samples, because it is below the maximum residue limits set by the USEPA (0.10 μg L^{-1}) [1], let alone it was lower than that of the HPLC method (200 ng L^{-1}) [22]. Moreover, the response could reach the steady signal within only 10 s. Thus, the detection time of acetochlor was much shorter than that of the previous methods [22]. Obviously, the proposed TiO_2–P3HT–IL based photoelectrochemical sensor shows promise for application in the monitoring of acetochlor with low detection limit and short detection time.

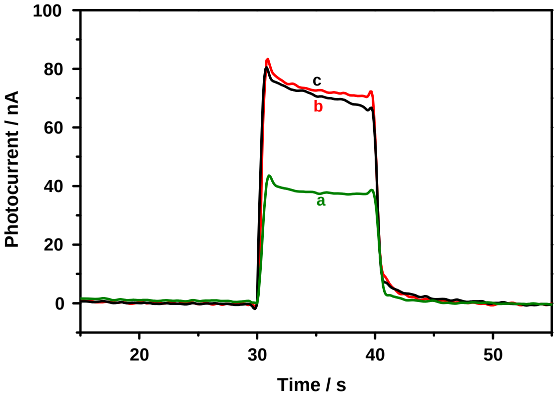


Fig. 6. Bias voltage of 0, 0.1 and 0.2 V (from a to c) on photocurrent response of TiO_2-P3HT–IL modified GCE in 0.1 M pH 9.0 buffer solution containing 5.0 μmol L^{-1} acetochlor.

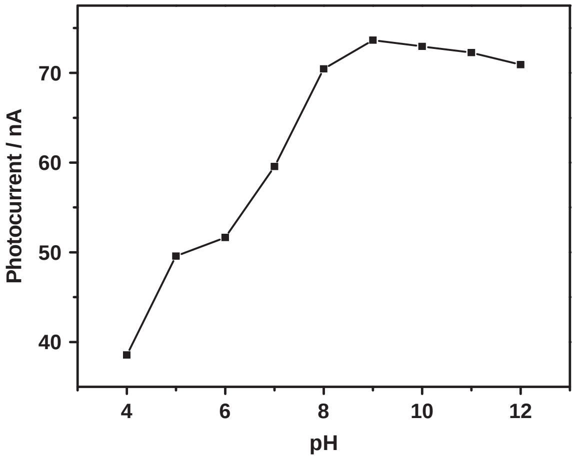


Fig. 7. Effect of buffer solution pH on photocurrent response of 5.0 μmol L^{-1} photolyzed acetochlor at TiO_2–P3HT–IL modified electrode at 0.2 V with visible light excitation.

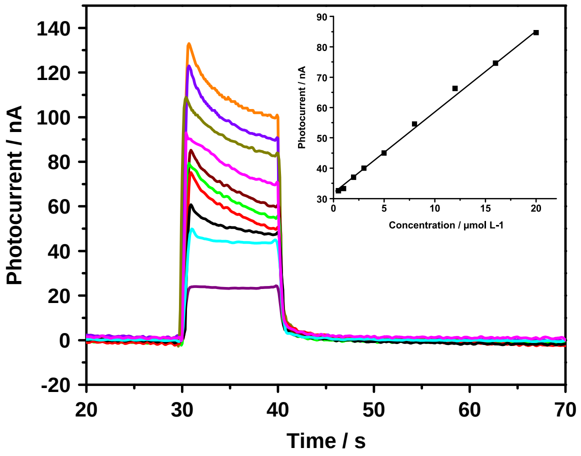


Fig. 8. Photocurrent responses at TiO_2–P3HT–IL modified GCE in 0.1 M pH 9.0 buffer solution in the presence of 0, 0.5, 1.0, 2.0, 3.0, 5.0, 8.0, 12, 16 and 20 μmol L^{-1} acetochlor (from bottom to top) at 0.2 V with visible light excitation. Inset: linear calibration curve.

3.5. *Reproducibility, stability and interferences*

For investigating the fabrication reproducibility, a 5.0 μmol L^{-1} acetochlor solution was measured by six TiO_2–P3HT–IL modified electrodes prepared independently and the RSD of the photocurrent was 3.2%, revealing excellent reproducibility. After the electrode was stored for 7 days at 4 °C in humid environment, it could retain 94.7% of its original response, suggesting acceptable storage stability.

Because acetochlor is one of the most important herbicides in the world, the effects of other herbicides and water sample matrix as interfering species on the photoelectrochemical sensing response were examined. Each one was considered as an interfering agent, when the photoelectrochemical signal exhibited a deviation more than ±5%. For example, 1000-fold mass ratio of NH_4^+, K^+, Na^+, Zn^{2+}, Ca^{2+}, Mg^{2+}, Al^{3+}, Cu^{2+}, Ba^{2+}, SO_4^{2-}, Cl^-,

Table 1
Measurement results of acetochlor in water sample ($n=3$)[a].

Analyte	GC–MS (μmol L^{-1})	This method (μmol L^{-1})	Added (μmol L^{-1})	Found (μmol L^{-1})	Recovery (%)
acetochlor	0.62	0.61	1.0	1.57	95.1
	0.68	0.65	3.0	3.71	103.1
	0.77	0.75	6.0	6.72	98.8

[a] n is the repetitive measurements number.

NO_3^- and PO_4^{3-}. 100-fold mass ratio of glucose, and sucrose. 50-fold mass ratio of Fe^{3+}, Fe^{2+}, Co^{2+}, Pb^{2+}, and Ni^{2+}. and 10-fold mass ratio of prometryn, paraquat had no influence on the determination of acetochlor. Thus, the photoelectrochemical sensor had an excellent specificity against other herbicide and water sample matrices for the detection of herbicide acetochlor in water samples.

3.6. *Analysis of real sample*

To demonstrate the feasibility of the sensor applied to the practical samples, the determination of acetochlor in water sample was performed. The water samples were pretreated by toluene and diluted with methyl cyanide to the required volume. The sample solution was injected directly into 10 mL of buffer solution (pH 9.0), and the residual acetochlor content was detected by means of photocurrent–time curve using the acetochlor sensor. Subsequently, an amount of standard acetochlor solution was added into the above solution, and the recovery of the added acetochlor was observed to be good for three determinations. The results obtained by the proposed method also accorded very well with those obtained by GC–MS. The results were summarized in Table 1. These results implied that the sensor was capable of practical applications.

4. Conclusions

We have demonstrated a sensitive, simple, fast, and portable photoelectrochemical sensing protocol for the herbicide acetochlor based on the TiO_2–P3HT–IL modified GCE. The promising photocurrent–time curve provide the facile quantitative method for acetochlor. The results obtained from this work implied that the fast photoelectronic communication among photolyzed acetochlor, P3HT, TiO_2, IL and GCE led to a derivative method for the photoelectrochemical indirect detection of acetochlor with good analytical performance, such as visible light irradiation, using 0.2 V bias voltage, rapid response, low detection limit, and good reproducibility and stability. Under optimized conditions, the proposed method was applied to the detection of acetochlor in water samples and the value was consistent with that obtained by GC/MS, indicating acceptable accuracy of the photoelectrochemical sensor.

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