



## Analytical Methods

## A novel sensor for the detection of acetamiprid in vegetables based on its photocatalytic degradation compound

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## ABSTRACT

An electrochemical method for the indirect determination of acetamiprid was studied, using titanium dioxide photocatalysts coupled with a carbon paste electrode. The cyclic voltammetric results indicated that the photocatalytic degradation compound of acetamiprid had electroactivity in neutral solutions. The amount of acetamiprid was further indirectly determined by differential pulse anodic stripping voltammetric analysis as a sensitive detection technique. The experimental parameters were optimized with regard to the photocatalytic degradation time, pH of buffer solution, accumulation potential and accumulation time. Under optimal conditions, the proposed electrochemical method could detect acetamiprid concentrations ranging from 0.01 to 2.0  $\mu\text{M}$ , with a detection limit (3 S/N) of 0.2 nM. Moreover, the proposed method displays excellent selectivity, good reproducibility, and acceptable operational stability and can be successfully applied to acetamiprid determination in vegetable samples with satisfying results.

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## 1. Introduction

Acetamiprid, (E)-N-[(6-chloro-3-pyridyl)methyl]-N-cyano-N-methylacetamidine, belongs to the new neonicotinoid class of systemic broad-spectrum pesticide. Due to the relatively low chronic mammalian toxicity, and no long-term cumulative toxicity, it has been used to replace organophosphorus and other conventional pesticide for controlling the insects such as Hemiptera, Thysanoptera, and Lepidoptera on vegetables, fruits, and teas (Seccia, Fidente, Barbini, & Morrica, 2005; Tomlin, 2000). However, acetamiprid is one of the pesticides frequently detected in agricultural products owing to its widespread and extensive usage (Akiyama, Yoshioka, & Tsuji, 2002). When people are exposed to the primary route of food and water polluted by acetamiprid, potential human health risks will be caused by acetamiprid. The maximum residue limit (MRL) for acetamiprid in vegetables and fruits is set at  $\leq 5 \mu\text{g g}^{-1}$  by the Japanese Ministry of Health, Labour and Welfare (Henshushitsu, 1998) and at  $\leq 3 \mu\text{g g}^{-1}$  by the U.S. Environmental Protection Agency (EPA, 2005). Therefore, it is necessary to develop analytical methods for the detection of acetamiprid in food and environment to keep people from potential health risks.

Different analytical methods have been used to analyze acetamiprid residues in agricultural products such as gas chromatography (GC) (Zhang, Pan, et al., 2008), liquid chromatography (LC) (Di Muccio et al., 2006; Fidente, Seccia, Vanni, & Morrica, 2005), liquid chromatography coupled with thermal lens spectrometric method (Guzsvany, Madzgalj, Trebse, Gaal, & Franko, 2007), high-performance liquid chromatography (HPLC) (Obana, Okihashi, Akutsu, Kitagawa, & Hori, 2002), enzyme-linked immunosorbent assays (ELISAs) (Wanatabe, Ito, & Kamata, 2001) and electrochemical impedance spectroscopy (EIS)-based aptasensor (Fan, Zhao, Shi, Liu, & Li, 2013; Fei et al., 2015). However, these techniques suffer from such drawbacks as high cost, long processing time, requirement of technical skills, and sophisticated equipment (Xu, Du, Jin, Li, & Hu, 2011; Yang et al., 2015).

As a comparison, photoirradiation assisted electrochemical method, with its portability and low cost, fast or real-time detection, and environmental friendliness, has been recognized as one of the most promising technologies because of the advantage of both optical methods and electrochemical sensors (Dong et al., 2004; Zhao et al., 2013). Ultraviolet (UV) and sunlight induced photolysis was efficiently used for various pesticides degradation during the last decade (Barakat, Nassar, Farrag, & Mahmoud, 2014; Burrows, Canle, Santaballa, & Steenken, 2002; Chatterjee & Mahata, 2004; Devi & Murthy, 2009; Sharma, Sadanandam, Ratnamala, Kumari, & Subrahmanyam, 2009; Vicente et al.,

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2014). Numerous reports have been published concerning the photocatalytic degradation of some neonicotinoid insecticides, the majority of them being devoted to imidacloprid (Feng, Xu, & Liu, 2013; Philippidis, Sotiropoulos, Efstathiou, & Poullos, 2009; Rancan, Sabatini, Achilli, & Galletti, 2006; Zabar, Komel, Fabjan, Kralj, & Trebse, 2012). To the best of our knowledge, few works has reported the combination of photocatalytic degradation process with electrochemical method for the determination of neonicotinoid insecticide residues until now. Gaal, Guzsvany, and Bjelica (2007) and Guzsvany et al. (2008) have successfully detected imidacloprid, acetamiprid and some other neonicotinoids at bismuth film electrode or differently modified glassy carbon electrodes by cathodic voltammetry, respectively. They also reported the successful monitoring of the photocatalytic degradation process of imidacloprid and acetamiprid via their disappearance (Guzsvany et al., 2008). However, they didn't construct an analytical method for the indirect detection of these neonicotinoids based on their photocatalytic degradation products. Rancan et al. (2006) have reported that 6-chloronicotinic acid (6CNA) yielded by a post-column photochemical reaction was more electroactive. It can be easily oxidized and the current generated by a constant level of concentration was much higher than the parent compounds. But they didn't use the voltammetric method for the detection of the parent compound based on the electrochemical oxidation behavior of 6CNA.

Titanium dioxide ( $\text{TiO}_2$ ), an inexpensive, non-toxic, and chemically inert material, which is especially stable under solar irradiation (Li & Shang, 2009), is most widely used as a very effective photocatalyst due to its large production of hydroxyl radicals, and high efficiency of photoactivity (Fujishima & Honda, 1972; Gratzel, 2001; Lim, Huang, Lim, & Mazhar, 2014; Zheng et al., 2000). Photocatalytic decomposition of various organic molecules on  $\text{TiO}_2$  surfaces has been reported elsewhere (Burrows et al., 2002; Joo et al., 2010; Konstantinou & Albanis, 2004; Li, Li, Yang, Xu, & Hu, 2011; Rajeshwar et al., 2008).

Here we report a simple, sensitive, inexpensive, and selective sensor for acetamiprid based on titanium dioxide photocatalysis coupled with a carbon paste electrode (CPE). Scheme 1 was used to illustrate the detection process. Under UV light irradiation,  $\text{TiO}_2$  absorbs UV light to induce electron transition readily from the valence band (VB) to the conduction band (CB). The photo-

generated electrons ( $e^-$ ) are so active that they can react with  $\text{O}_2$  to yield superoxide radicals  $\cdot\text{O}_2^-$ , a positively charged hole ( $h^+$ ) could be formed by the electron on  $\text{TiO}_2$  valence band, which can react with  $\text{OH}^-$  or  $\text{H}_2\text{O}$  to generate  $\cdot\text{OH}$ . Acetamiprid could be degraded by the super-oxide radical ion  $\cdot\text{O}_2^-$  and the hydroxyl radical  $\cdot\text{OH}$  (Kumar & Devi, 2011; Zhang, Zong, Zhao, & Zhu, 2008).

Based on a few publications, 6-chloronicotinic acid (6CNA) was reported as the final main photocatalytic degradation compounds of the pyridyl ring of acetamiprid (Guzsvany, Csanadi, Lazić, & Gaal, 2009; Guzsvany et al., 2012; Zabar, Dolenc, Jerman, Franko, & Trebse, 2011). The proposed method was constructed based on the oxidative signal of this photocatalytic degradation product 6CNA. 6CNA has been reported to be the last stable product in the degradation chain before total mineralization (Guzsvany et al., 2008). Though the photocatalytic degradation of 6CNA has been reported (Zabar et al., 2011), 6CNA is the very stable produced compound (Dell'Arciprete et al., 2009). Some of it still existed in the degradation solution even after photocatalytic degradation for 120 min. This method has been applied to determine acetamiprid in vegetable samples with satisfying results.

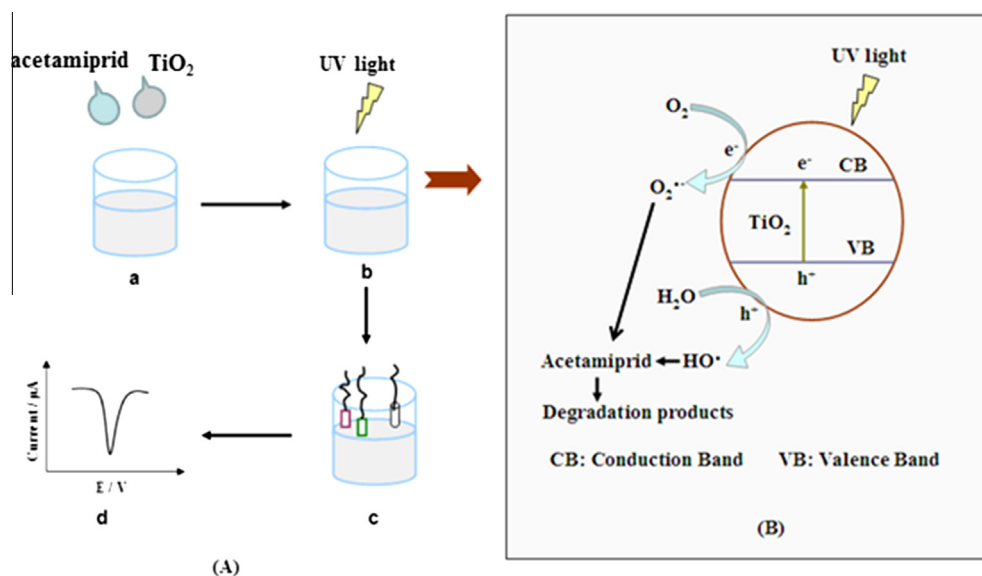
## 2. Experimental

### 2.1. Chemicals and solutions

Titanium dioxide ( $\text{TiO}_2$ ) (anatase, <25 nm, 99.7%), and acetamiprid ( $\geq 96\%$ ) were purchased from Sigma–Aldrich (St. Louis, MO). 6-Chloronicotinic acid (6CNA) (98%), acetonitrile, graphite powder, and paraffin oil used in this work were of analytical grade and were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) unless indicated otherwise. 0.1 M phosphate buffer was always employed as the supporting electrolyte. Deionized double-distilled water (18.6 M $\Omega$ ) (Millipore Co. Ltd.) was used throughout the experiment.

### 2.2. Apparatus

The UV light was obtained from an LED lamp (365 nm, Wisbay M&E Co., Ltd., Shenzhen, China). All the electrochemical experiments were performed on a CHI760D electrochemical workstation



**Scheme 1.** (A) Scheme of the electrochemical sensor for acetamiprid detection; and (B) photocatalytic degradation mechanism of acetamiprid by  $\text{TiO}_2$  under UV light irradiation; (a) the suspension of acetamiprid and  $\text{TiO}_2$  was dripped into the cylindrical cell, (b) the suspension was irradiated by UV light, (c) a conventional three electrode system, and (d) DPASV of the irradiated acetamiprid.

(Shanghai CH Instruments, China), using a conventional three-electrode system with a carbon paste electrode (CPE) as the working electrode, a platinum wire as the auxiliary electrode, and a saturated calomel electrode as the reference electrode. CPE was prepared by thoroughly mixing 0.5 g of spectroscopic grade graphite powder with 0.3 mL of paraffin oil, and then the paste was packed into an electrode body to obtain CPE. All experiments were performed at room temperature (25 °C) in this study. The cyclic voltammetry (CV) experiments were carried out with a scan rate of 100 mV s<sup>-1</sup>. The differential pulsed anodic stripping voltammetry (DPASV) were recorded with amplitude of 50 mV, pulse width of 0.2 s, and pulse period of 0.5 s. High-performance liquid chromatography (HPLC) was used to verify the application of the photocatalytic electrochemical method. HPLC system from Dionex Technologies consisted of an UltiMate 3000 Series liquid chromatograph, and a Dionex-C<sub>18</sub> Rapid Resolution Cartridge column (4.6 mm × 250 mm 5 µm particle size). The mobile phase, which was composed of acetonitrile and H<sub>2</sub>O (85:15), was pumped at a flow rate of 1.0 mL min<sup>-1</sup>. The injection volume was 5 µL. The column was in room temperature. Acetamiprid signal was detected at 245 nm and 6-CNA was measured at 224 nm.

### 2.3. Photocatalysis of acetamiprid under UV light and electrochemical determination

The photocatalysis experiments were conducted as follows. Acetamiprid stock solution (10 mL, 0.1 mM) in acetonitrile/water (20/80, V/V) containing 10 mg of TiO<sub>2</sub> photocatalyst were magnetically stirred in the dark for 30 min. Subsequently, the stock solution was irradiated for 40 min under the UV light, which is 10 cm above liquid level. The UV lamp was placed into the inner part of the photo system with a water circulation arrangement to maintain the temperature in the range of 25–30 °C and electrochemical response was measured in maintaining a room temperature. The samples were exposed to air throughout the experiment. For electrochemical detection, aliquots of the reaction mixture were diluted with 0.1 M phosphate buffer (pH 7.0). Afterward, the three-electrode system was inserted in the electrochemical cell. DPASV and CV were used to study the electrochemical behavior of the photocatalytic degradation compound of acetamiprid. After a 300 s accumulation at the potential of -0.4 V, DPASV were recorded in the potential range from 0.0 to 1.0 V. Before each measurement a preconditioning step (for cleaning of the electrode) at a potential of 1.1 V was applied for 60 s.

### 2.4. Samples preparation

To demonstrate the feasibility of the proposed method, we applied it to the determination of acetamiprid in vegetable samples. 50 g of commercially available vegetables (greens, tomatoes and cucumbers) were chopped in a conventional food processor for 10 min to obtain thoroughly mixed homogenates. A known quality of acetamiprid stock solution was evenly sprayed on vegetable samples. The samples were placed in a glass dish for 12 h. The contaminated samples were taken out and washed with water three times, placed in a centrifuge tube with the addition of 10.0 mL of acetonitrile, and then vigorously shaken for 2 min. Finally, the mixtures were centrifuged at 4000 rpm min<sup>-1</sup> for 10 min. Then the supernatant was filtered through a 0.45 µm membrane, and transferred into a 10 mL volumetric flask that was brought to volume with acetonitrile. Samples used for recovery studies were previously tested by the HPLC method and proved to be free from acetamiprid. The procedure described above was used for the preparation of blank vegetable samples and spiked with a known quantity of acetamiprid for recovery studies.

## 3. Results and discussion

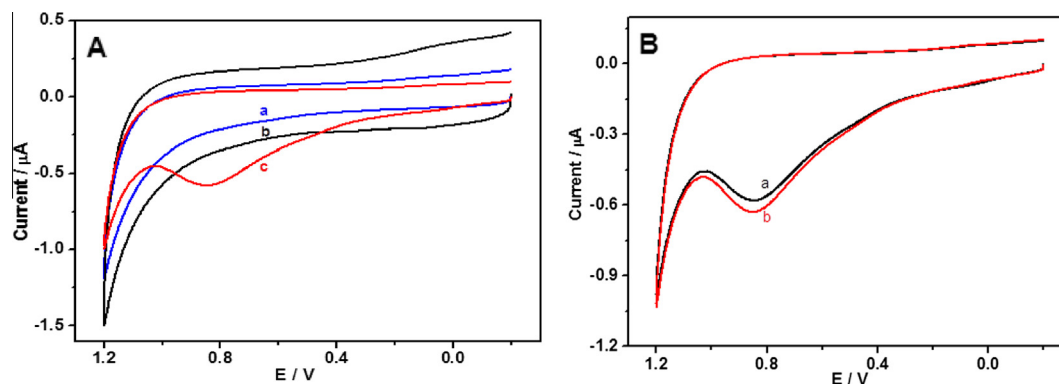
### 3.1. Characterization of acetamiprid before and after the photocatalytic degradation

Cyclic voltammetry was used to examine the electrochemical behaviors of acetamiprid before and after the photocatalytic degradation at CPE. Fig. 1A shows electrochemical responses of blank buffer (curve a), acetamiprid (curve b), and 12.0 µM of photocatalytically degraded acetamiprid (curve c) at CPE in the pH 7.0 phosphate buffer, respectively. No oxidation peak was observed in the studied potential range from -0.2 to 1.2 V for the blank buffer (curve a, Fig. 1A) and acetamiprid (curve b, Fig. 1A), indicating that acetamiprid was not electroactive in the studied potential range. However, an oxidation peak was observed clearly for the photocatalytically degraded acetamiprid (curve c, Fig. 1A), indicating that some electroactive compounds were formed after the photocatalytic degradation of acetamiprid. The photocatalytic degradation compounds of acetamiprid have been reported (Guzsvany et al., 2009, 2012; Zabar et al., 2011), and 6CNA was one of the species. Cyclic voltammetry was also used to check the electrochemical characters of 6CNA. Fig. 1B showed the CVs of the photocatalytically degraded acetamiprid (curve a) and 6CNA (curve b). Both of them showed an oxidation peak at almost the same potential (ca. 0.81 V), indicating 6CNA was the photocatalytic degradation of acetamiprid. It can be used for the indirect determination of acetamiprid by simple electrochemical methods.

HPLC-MS was carried out to test the photocatalytic degradation compounds of acetamiprid. Fig. S1A shows the chromatography of acetamiprid before photocatalytic degradation. Before photocatalytic degradation, only one peak was observed on the chromatography. After irradiating 40 min, three distinct peaks with different retention time were observed on the chromatograms (Fig. S1B). The intensity of the peak with the retention time of 6.19 (compound a) was decreased while other two peaks with the retention time of 4.99 (compound b) and 1.98–2.42 (compound c) were appeared. The peak at the retention time of 6.19 probably belonged to acetamiprid, and other peaks could be ascribed to the photocatalytic degradation products of acetamiprid. HPLC-MS has been used to identify these compounds (Fig. S1C–E) that were shown in Fig. S1B. The compound eluted at time 6.19 min with the major ESI<sup>+</sup> fragment *m/z* 223 [M+H]<sup>+</sup> can be attributed to the pseudo molecular ion of acetamiprid (222 g/mol) (Fig. S1C). The other two compounds with ESI<sup>+</sup> fragment *m/z* 158 [M+2H]<sup>+</sup>, and 186 [M+H]<sup>+</sup> are correlated to the 6CNA (Fig. S1D) and Cl-C<sub>5</sub>H<sub>3</sub>N-CH<sub>2</sub>-N-CH-CH<sub>2</sub>-OH (Fig. S1E), respectively. These HPLC-MS results correlate with previously published data. Moreover, these acetamiprid degradation products have already been reported (Carra et al., 2015; Yang et al., 2013). Therefore, 6CNA was one of the important photocatalytic degradation products of acetamiprid. Because we couldn't obtain the standard of Cl-C<sub>5</sub>H<sub>3</sub>N-CH<sub>2</sub>-N-CH-CH<sub>2</sub>-OH, the electrochemical characters of this compound could not be given. However, considering the structure differences between 6CNA and Cl-C<sub>5</sub>H<sub>3</sub>N-CH<sub>2</sub>-N-CH-CH<sub>2</sub>-OH, they should not have the same electrochemical characters. According to the electrochemical characters of 6CNA and the photocatalytic degradation product studied above, no obvious peak potential shift was observed, indicating that the electrochemical signal we used was coming from 6CNA.

### 3.2. Optimization of acetamiprid analysis conditions

In order to improve the sensitivity of the proposed method and obtain the best conditions for acetamiprid detection, we have explored the effects such as photocatalytic degradation time, pH of buffer solution, accumulation potential, and accumulation time.



**Fig. 1.** (A) CVs of blank buffer (a), 12.0 μM acetamiprid (b), and 12.0 μM photocatalyzed acetamiprid (c) at CPE in 0.1 M pH 7.0 phosphate buffer. (B) CVs of 12.0 μM photocatalyzed acetamiprid (a) and 2.0 μM 6CNA (b) in 0.1 M pH 7.0 phosphate buffer.

### 3.2.1. Optimum of photocatalytic degradation time conditions

The relationship between the photodegradation efficiency of acetamiprid and the photocatalytic degradation time was investigated by fixing the amount of  $\text{TiO}_2$  as 10 mg/10 mL. The results were shown in Fig. 2. The differential pulse voltammetric (DPV) peak currents increased sharply with the increase of the illumination time from 0 to 40 min, indicating photocatalytic degradation efficiency of acetamiprid sharply increased. When the illumination time was longer than 40 min, DPV peak current enhanced slowly, and then trended toward a maximum value. The probable reason is that, more photodegraded species 6CNA were produced with the increase in illumination time from 0 to 40 min. Meanwhile, some other small organic molecules are produced by photodegradation process and these small organic molecules adsorb on the surface of  $\text{TiO}_2$ , resulting in the decreased formation of hydroxyl radical  $\cdot\text{OH}$  and superoxide radical ion  $\cdot\text{O}_2^-$  that attack the pesticides, and therefore increase in illumination time does not lead to greater photodegradation efficiency of acetamiprid. For the optimal sensitivity and analysis efficiency, we chose 40 min as the optimum photocatalytic degradation time for the acetamiprid assay.

### 3.2.2. Optimum of pH conditions

The pH value of the base solution has a significant influence on the oxidation of 6CNA, the photocatalytic degradation compound of acetamiprid. The effect of pH of the supporting electrolytes on

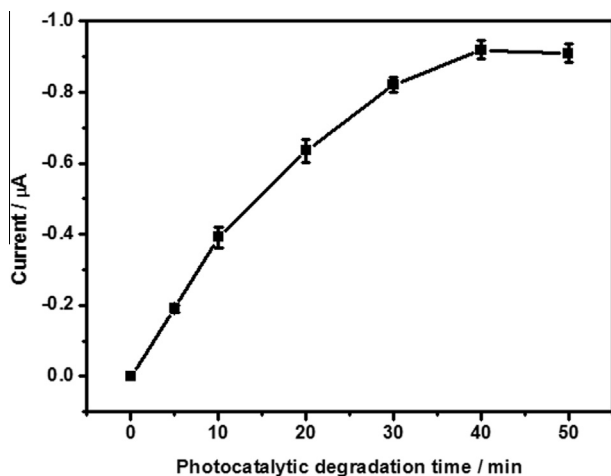
the DPV peak currents of 6CNA was studied in the pH range of 3.0–8.0, as described in the Supplementary material (Fig. S2). It was found that the peak current increased with the increase of pH from 3.0 to 7.0, and then decreased at higher pH. Therefore, the optimum pH value of 7.0 could be selected in the following experiments.

### 3.2.3. Optimum of accumulation potential and accumulation time

The effect of accumulation potential and accumulation time on the DPV response for acetamiprid was studied. The accumulation step proceeded in constantly stirred solution and the voltage scanning step was performed after 30 s of quiet time. Fig. 3A shows the effect of accumulation potential range from  $-0.8$  to  $0.2$  V on peak current of photocatalyzed acetamiprid with accumulation time 300 s. The peak current of 1.20 μM photocatalyzed acetamiprid was the highest at  $-0.4$  V. It may be explained that the concentration of 6CNA reached a maximum in pH 7.0 buffer solutions when the accumulation potential was set at  $-0.4$  V. So the potential of  $-0.4$  V was chosen as the accumulation potential of photocatalyzed acetamiprid. The effect of the accumulation time on the peak current of photocatalyzed acetamiprid was also shown in Fig. 3B. It showed that the peak current increased very rapidly with the increasing accumulation time, which indicated that photocatalyzed acetamiprid at the CPE surface was rapidly adsorbed on CPE. After 300 s, further increase in the accumulation time did not increase the amount of photocatalyzed acetamiprid on the electrode owing to surface saturation, and the peak current remained almost constant. Thus,  $-0.4$  V and 300 s were chosen as the accumulation potential and accumulation time in this work, respectively.

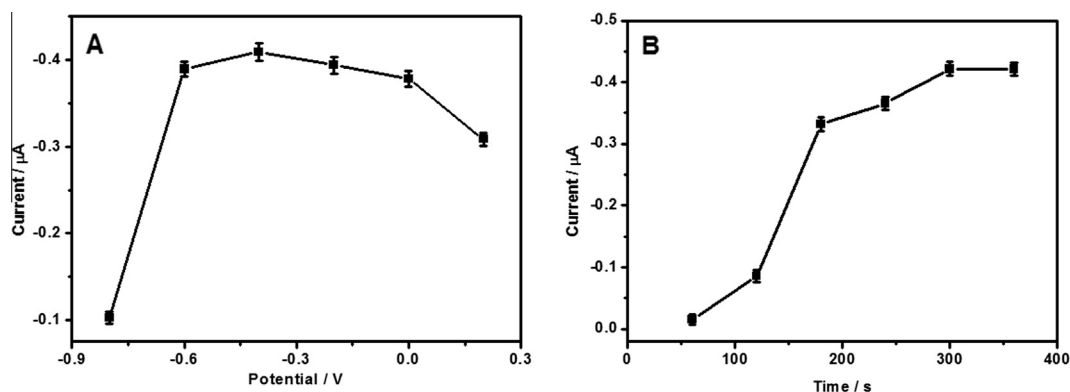
### 3.3. Analytical performance

In order to develop a voltammetric method for determining the pesticide, we selected DPASV mode, because DPASV analysis of acetamiprid showed a strong signal under optimum experimental conditions. Fig. 4 shows DPASV of different concentrations of acetamiprid after UV light irradiation under the optimized conditions. With the increase of acetamiprid concentration the stripping peak currents increased linearly. A good linear relationship ( $R = 0.999$ ) existed between the peak currents and the concentration of acetamiprid over the range from 0.01 to 2.0 μM ( $2.23\text{--}445.4 \mu\text{g kg}^{-1}$ ), with a detection limit ( $(3 S/N)$ ) of 0.2 nM ( $44.6 \text{ ng kg}^{-1}$ ). The analytical performance of different methods for acetamiprid detection was described in the Supplementary material (Table S1). The method is more sensitive than the SPE/LC–MS (Di Muccio et al., 2006), LC–MS (Fidente et al., 2005), HPLC–DAD (Obana et al., 2002), colorimetry (Xu et al., 2011; Yang et al., 2015) and

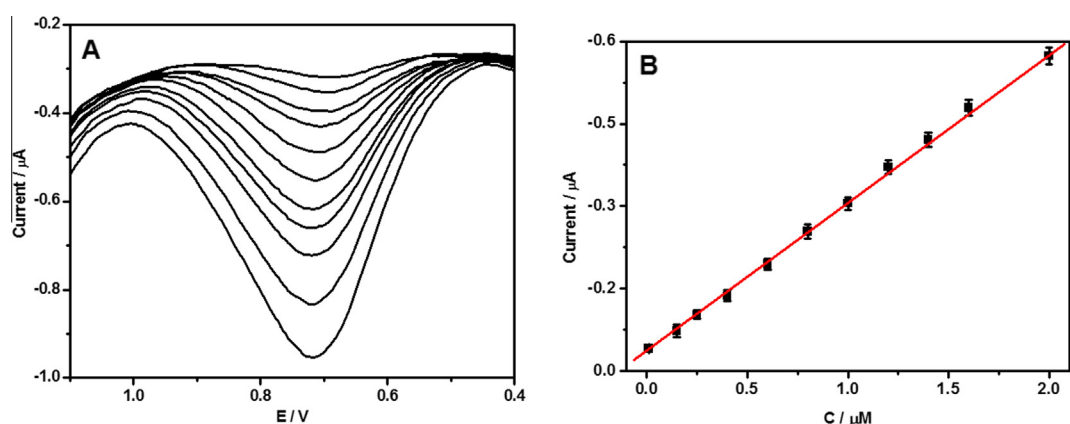


**Fig. 2.** Effects of photocatalytic degradation time of 0.1 mM acetamiprid stock solutions on DPV responses in 0.1 M pH 7.0 phosphate buffer containing 10.0 μM acetamiprid.





**Fig. 3.** Effects of accumulation potential (A) and accumulation time (B) on DPV peak current of photocatalyzed acetamiprid, in 0.1 M pH 7.0 phosphate buffer containing 1.20  $\mu\text{M}$  acetamiprid.



**Fig. 4.** (A) DPASV of acetamiprid with increasing concentration obtained after 40 min UV light irradiation in pH 7.0 phosphate buffer; curves from top to bottom, 0.01, 0.15, 0.25, 0.40, 0.60, 0.80, 1.00, 1.20, 1.40, 1.60 and 2.00  $\mu\text{M}$ , respectively. (B) Calibration plot of peak current vs acetamiprid concentration.

**Table 1**

Measurement results of acetamiprid in vegetable samples ( $n = 3$ ).

Sample	Spiked ( $\mu\text{M}$ )	Found by the proposed method ( $\mu\text{M}$ )	Recovery (%)	RSD (%)	Found by HPLC ( $\mu\text{M}$ )
Green vegetable	0.05	0.047	93.8	4.7	0.045
	0.10	0.105	105.0	2.3	0.098
	0.15	0.146	97.5	2.9	0.153
Tomato	0.06	0.058	96.7	2.7	0.056
	0.12	0.113	94.2	4.5	0.124
	0.18	0.177	98.3	1.7	0.176
Cucumber	0.05	0.051	102.0	2.8	0.047
	0.10	0.096	96.0	3.5	0.095
	0.15	0.142	94.7	2.3	0.153

electrochemical sensor (Guzsvany et al., 2008), but is less sensitive than ELISAs (Wanatabe et al., 2001) and EIS-based aptasensor (Fei et al., 2015). However, the detection limit of 0.2 nM is suitable enough for the electrochemical detection of acetamiprid in pesticide samples, because it is below the maximum residue limits set by the Japanese Ministry of Health, Labor and Welfare ( $\leq 5 \mu\text{g g}^{-1}$ ) (Henshushitsu, 1998) and those by the U.S. Environmental Protection Agency ( $\leq 3 \mu\text{g g}^{-1}$ ) (EPA, 2005). Moreover, the response could reach the steady signal within only 10 s. Thus, the detection time of acetamiprid was much shorter than that of the previous methods (Di Muccio et al., 2006; Fan et al., 2013; Fei et al., 2015; Fidente et al., 2005; Obana et al., 2002; Wanatabe et al., 2001). Obviously, the proposed titanium dioxide coupled with a carbon paste electrode shows promises for the application of monitoring acetamiprid with low detection limit and short detection time.

### 3.4. Repeatability, reproducibility and interferences

The repeatability measurement of the method was examined at a concentration of 0.80  $\mu\text{M}$  acetamiprid with the same electrode and the relative standard deviation (R.S.D.) was 3.1% for nine successive assays. To investigate the fabrication reproducibility, a 0.80  $\mu\text{M}$  acetamiprid solution was measured by six independent runs of titanium dioxide coupled with carbon paste electrodes prepared. The RSD of the peak current was 4.5%, revealing excellent reproducibility.

In order to demonstrate the selectivity of the developed method, possible interferences from coexisting pesticide were tested. The study was carried out by adding various concentrations of foreign substances into the solution containing 0.80  $\mu\text{M}$  acetamiprid and mixed with  $\text{TiO}_2$ , and then irradiated. The tolerance

limits for the interfering species were considered as the maximum concentration that gave a relative error less than 5%. The results showed that 1000-fold excess of  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$ ; 100-fold excess of glucose, and sucrose; 50-fold excess of  $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Ni}^{2+}$ ; and 10-fold excess of clothianidin, thiamethoxam have negligible effect the determination of acetamiprid. However, 20 nM 6CNA and imidacloprid have obvious current response and some interference for 0.80  $\mu\text{M}$  acetamiprid detection.

### 3.5. Analysis of vegetable sample

In order to evaluate the feasibility of the developed method for routine analysis, the method was applied to determine acetamiprid in vegetable samples. Since no acetamiprid residue was detected in those samples, they were spiked with acetamiprid at different concentrations, ranging from 0.05 to 0.20  $\mu\text{M}$ . The recovery of the added acetamiprid was determined in triplicate using the standard addition method. It was found that the proposed method demonstrated satisfactory recovery in the range of 93.8–105.0%, which was in good agreement with the amounts spiked. HPLC method was used to test the applicability of the proposed method. The results obtained by the sensor based on titanium dioxide photocatalysts and by the HPLC method were summarized in Table 1. There were agreed well with each other, implying that the developed method was capable of practical applications.

## 4. Conclusions

This work described the application of photoirradiation assisted electrochemical method for the analysis of the acetamiprid, based on the use of titanium dioxide photocatalysts coupled with CPE. Sample matrixes have no interferences on determination of acetamiprid. The recovery ratio was 93.8–105.0%; repeatability and reproducibility relative standard deviation (R.S.D.) were 3.1% and 4.5%, respectively, thereby demonstrating the high accuracy and precision of the assay. The proposed method was validated by its good correlation with HPLC results. Under optimal conditions, the proposed method could detect acetamiprid concentrations ranging from 0.01 to 2.0  $\mu\text{M}$  in vegetable samples, the limit of detection (LOD) of the optimized sensor was 0.2 nM. The proposed photoirradiation assisted electrochemical sensor has high sensitivity, high selectivity, rapid reaction time, low cost, and portability. Thus, the combination of a CPE with photocatalytic degradation process could be used as a feasible quantitative method for the acetamiprid analysis in vegetables.

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## 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.foodchem.2015.08.118>.

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