

Polyelectrolyte nanocapsule probe for the determination of imidacloprid in agricultural food samples

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ABSTRACT

Layer-by-layer (LBL) technique is a well-established method for the formation of nanocapsules, which could encapsulate nanoparticles by polyelectrolyte and has received great interest in some areas of research. In this study, colloidal gold nanoparticles (AuNPs) were used as a vehicle for loading horseradish peroxidase (HRP), and AuNPs-HRP was encapsulated by using LBL technique to form a signal amplification nanocapsule probe. Based on the probe, an immunoassay was developed for the detection of imidacloprid in agricultural food samples (rice, pear and cabbage). The IC_{50} value of the assay was 0.11 ng mL^{-1} which was 8-9954 times lower than those of traditional ELISAs and well below the maximum residue limits (MRLs) permitted by the European Union (EU). The recoveries of imidacloprid from three different samples were 80.34–120.84% that had a good correlation ($R^2 = 0.9739$) with those obtained by the commercial kit. The developed assay could provide a sensitive method for detection of imidacloprid.

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1. Introduction

Imidacloprid (1-(6-chloro-3-pyridylmethyl)-N-nitroimidazolidin-2-ylideneamine) is a systemic and chloronicotinylic neonicotinoid insecticide (Gang, 2006; Wanatabe et al., 2001), which has been widely used in agricultural production for control of sucking and chewing insects including aphids, thrips, plant hoppers, diamondback moths and whiteflies (Li et al., 2007). Some studies showed that imidacloprid could induce histological alterations in bone (Mzid, Badraoui, Khedir, Sahnoun, & Rebai, 2017), liver (Toor, Sangha, & Khera, 2013) and adversely affect brain development (Kimura-Kuroda,

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Komuta, Kuroda, Hayashi, & Kawano, 2012) through their residues in agricultural products.

In the past decade, many efforts have been made to develop efficient methods to determine imidacloprid in agricultural food samples, including gas chromatography-mass spectrometry (GC-MS) (Liang et al., 2017), high-performance liquid chromatography (HPLC) (Seccia, Fidente, Montesano, & Morrica, 2008; Vichapong, Burakham, & Srijaranai, 2015), liquid chromatography combined mass spectrometry (HPLC-MS) (Di Muccio et al., 2006; Jovanov et al., 2013), gold immunochromatographic assay (GICA) (Fang et al., 2015), surface plasmon resonance (SPR) sensing (Lee et al., 2016) and selection of phage-displayed peptides based assay (Liu et al., 2015). Although these methods have high selectivity, specificity and accuracy, they either involve complicated sample pretreatment, sophisticated equipment and skilled analysts or just suit for laboratory detection and have relatively low sensitivity.

At present, enzyme-linked immunosorbent assays (ELISAs) have been reported for imidacloprid (Table 1). Compared with the above techniques, ELISAs have simple sample pretreatment and operation steps. However, the sensitivities of some ELISAs were not high enough to meet the demand of MRLs permitted by the EU. It is important to develop reliable signal amplification probe for the detection of imidacloprid in agricultural products.

Colloidal gold nanoparticles (AuNPs) have been proved to be an ideal candidate in the biotechnological platform because of their unique chemical and physical properties, such as easy preparation, high surface-to-volume ratio and good biocompatibility (Gao, Xu, Hou, Chen, & Tang, 2013; Lin et al., 2015; Tang, Tang, Niessner, Chen, & Knopp, 2011; Wu et al., 2014; Zhou, Lai, Zhuang, Tang, & Tang, 2013). AuNPs can facilitate variety surface reactions and load more biomolecules such as enzyme (Shu et al., 2016), antibody (Zhang et al., 2012), DNA (Howes, Chandrawati, & Stevens, 2014; Orza, Olenic, Pruneanu, Pogacean, & Biris, 2010) and other proteins for synthesis of probe to enhance the signal amplification.

Table 1. Comparison of the proposed assay with reported methods for imidacloprid detection.

Method	linear range (ng mL ⁻¹)	IC ₅₀ of target (ng mL ⁻¹)	LOD of target (ng mL ⁻¹)	Reference
ELISA	– ^a	35.00	–	Li and Li (2000)
ELISA	5.00–125.00	17.30	–	Lee, Ahn, Park, Kang, and Hammock (2001)
ELISA	1.30–50.00	3.30	–	Watanabe et al. (2001)
ELISA	1.00–39.00	8.00	0.50	Watanabe et al. (2004)
ELISA	–	995.40	30.00	Li et al. (2007)
ELISA	–	6.50	0.20	Ma et al. (2009)
ELISA	–	14.80	0.11	Girotti, Maiolini, Ghini, Eremin, and Ma Es (2010)
ELISA	–	1.20–3.00	0.03–0.16	Wang, Wang, Yang, Wang, and Deng (2012)
GICA	–	–	10.00	Fang et al. (2015)
Selection of phage-displayed peptides based assay	8.00–906.00	96.00	2.30	Liu et al. (2015)
Nanoplasmonic biochips	–	–	0.20	Lee et al. (2016)
ELISA	0.10–8.10	0.93	0.05	Commercial kit
Proposed assay	0.02–0.84	0.11	0.01	This study

^aNot mentioned.

Layer-by-layer (LBL) technique is a well-established method for the formation of microcapsules or nanocapsules, which could encapsulate almost all types of nanoparticles, such as lipid nanoparticles (Cui & Mumper, 2002), inorganic (Aqil et al., 2008; Neumann, Kovtun, Dietzel, Epple, & Heumann, 2009) and polymeric nanoparticles (Sheng et al., 2009). The capsule was produced by LBL deposition of polyelectrolyte around the surface of nanoparticulate templates where the composition, charge and thickness of the shell were dependent on the material of layer deposited (Pereira, Barros-Timmons, & Trindade, 2014). A primary property of this technique was the preparation of nanoparticles with core-independent (Del et al., 2014; Labouta & Schneider, 2010). This technique has attracted intensive attention in various technological fields such as drug (Ariga, Lvov, Kawakami, Ji, & Hill, 2011; Chen et al., 2017; Del et al., 2014; Luo, Venkatraman, & Neu, 2013) and vaccine delivery (Chong et al., 2009), biosensor (Kreft, Javier, Sukhorukov, & Parak, 2007; Xuan, Jia, Jiang, Abdel-Halim, & Zhu, 2012) and bioreactor (Matsusaki, Amemori, Kadowaki, & Akashi, 2011) mostly because they can protect the encapsulated bioactive agents from the surrounding environmental hazards (Balabushevich, Sukhorukov, & Larionova, 2005; Lvov & Caruso, 2001) and encapsulate nanoparticles to load more molecules to enhance the signal amplification of immunoassays (Harshala, Parab, & Ru-Shi Liu, 2009; Oaew, Charlermroj, Pattarakankul, & Karoonuthaisiri, 2012; Trau & Renneberg, 2003).

Take into account the advantages of the encapsulation ability of LBL technique and the surface functionalization ability of AuNPs, a signal amplified nanocapsule probe was synthesized for sensitive determination of imidacloprid (Figure 1A). Firstly, 20 nm AuNPs were employed to synthesize high surface-to-volume ratio protein vehicle to label with a large amount of horseradish peroxidase (HRP) on their surface. Then AuNPs-HRP were encapsulated into nanocapsule by poly (styrenesulfonic acid) sodium salt (PSS). Finally, goat anti-mouse IgG (Ab2) was absorbed on the nanocapsule surface by electrostatic interaction. Small molecule like 3, 3', 5, 5'-tetramethylbenzidine (TMB) could cross the polymer and interact with HRP to produce an amplified signal. Based on the synthetic nanocapsule probe, an immunoassay was developed for sensitive detection of imidacloprid in agricultural food samples (Figure 1B).

2. Materials and methods

2.1. Chemicals and reagents

Imidacloprid, thiacloprid, acetamiprid, clothianidin, imidaclothiz, thiamethoxam, nitenpyram and dinotefuran were purchased from Jiangsu Pesticide Research Institute (Jiangsu, China). Anti-imidacloprid monoclonal antibody (mAb) and coating antigen imidacloprid-BSA were purchased from Thpower Biotechnologies Co., Ltd. (Shenzhen, China). Horseradish peroxidase (HRP), 3, 3', 5, 5'-tetramethylbenzidine (TMB), Poly (styrene sulfonic acid) sodium salt (MW = 70,000) were purchased from Sigma Chemicals Co. (St. Louis, MO, USA). Chloroauric acid (HAuCl₄) and trisodium citrate were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Bovine serum albumin (BSA) was purchased from Sangon Biotech Co., Ltd. (Shanghai, China). Polyethylene glycol (MW = 20,000) was purchased from Alfa Aesar Chemical Co., Ltd. (Shanghai, China). Goat anti-mouse IgG was purchased from Bioss Biotech Co., Ltd. (Beijing,

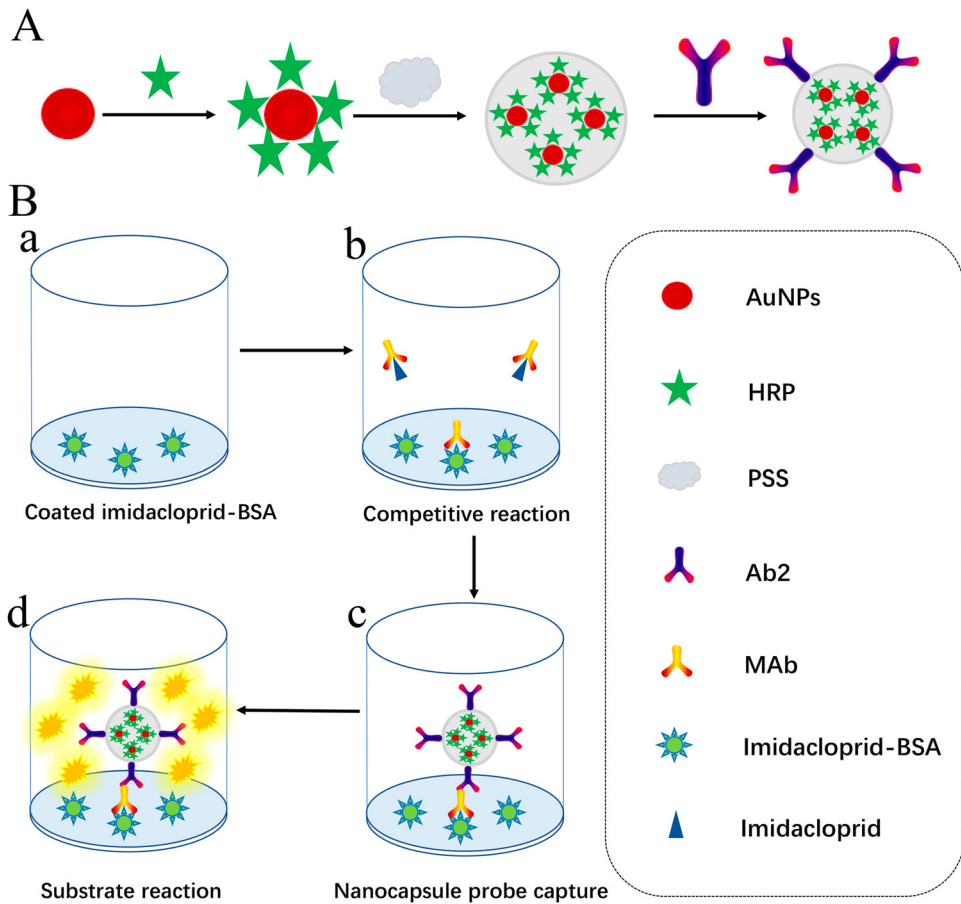


Figure 1. Schematic of preparation of nanocapsule probe and the probe-based assay procedure. (A) Synthesis illustration of nanocapsule probe and (B) protocol of the enhanced assay. (a) Coating antigen ($0.25 \mu\text{g mL}^{-1}$, $100 \mu\text{L}$) was added to 96-well plate and incubated 2 h at 37°C . (b) Imidacloprid ($100 \mu\text{L}$) and mAb ($0.125 \mu\text{g mL}^{-1}$, $100 \mu\text{L}$) were added and incubated 1 h at 37°C . (c) The probe ($100 \mu\text{L}$) was added and incubated 1 h at 37°C . (d) Substrate solution ($100 \mu\text{L}$) was added and incubated 15 min at 37°C .

China). Tween-20 was obtained from Amresco (USA). Commercial ELISA kit was purchased from Glory science Co., Ltd. (Hangzhou, China). The 96-well polystyrene plate was purchased from Costar Group, Inc. (USA). All other chemicals were of analytical grade and obtained from Beijing Chemical Reagent Co. (Beijing, China). Distilled water was used throughout all the experiments.

2.2. Buffers and solutions

PB solution: 10 mM sodium phosphate buffer (pH 6.0 and 6.3). PBS solution: 10 mM sodium phosphate buffer (pH 7.4) containing 140 mM NaCl. Coating buffer, carbonate-bicarbonate buffer (50 mM, pH 9.6). Washing buffer: PBST (0.05% (v/v) Tween in 0.01 M PBS) and PBT (0.05% (v/v) Tween in 0.01 M PB [pH 6.3]). Blocking buffer: 0.01 M PBS buffer containing 2% (w/v) BSA. Probe dilution buffer: 0.01 M PB (pH 6.3)

buffer containing 2% (w/v) BSA. Sample solution: 0.01 M PBS buffer containing 5% (v/v) methanol. TMB solution: citrate buffer (pH 5.0) containing 0.01% (w/v) TMB and 0.005% (v/v) urea hydrogen peroxide. Stop solution: 2 M H₂SO₄.

2.3. Preparation of the nanocapsule probe.

AuNPs 20 nm in diameter were prepared according to the reported method with minor modifications (Zhou et al., 2009). Briefly, a stirred aqueous solution of HAuCl₄ (10%, 0.1 mL) in 100 mL of Milli-Q purified water was heated to reflux, and trisodium citrate solution (1%, 2.6 mL) was added. The solution was heated under reflux with constant stirring for another 3 min, during which its colour changed from yellow to wine red. Finally, the colloidal gold solution was cooled to room temperature with a continuous and slow stirring. The solution was stored at 4°C. The dispersity of AuNPs was checked by a transmission electron microscope (TEM, H-7650).

The nanocapsule probe was synthesized using a modified method (Oaew et al., 2012). Briefly, 10 mL AuNPs was centrifuged at 11,360 × *g* for 30 min and resuspended into 1 mL of Milli-Q purified water. Then 20 μL HRP (5 mg mL⁻¹) was added to 1 mL AuNPs solution, and the mixture was further incubated for 1 h at room temperature under gentle stirring. Afterward, the mixture was centrifuged at 11,360 × *g* for 30 min at 4°C to remove the excess HRP. The obtained AuNPs-HRP was resuspended in 10 mL of PB (PH 6.0). In order to encapsulate AuNPs-HRP into capsules, 10 mL of AuNPs-HRP was added into PSS (30 mg mL⁻¹, 10 mL) in 1 mM NaCl, and the mixture was further incubated for 40 min at room temperature, the mixture was centrifuged at 9680 × *g* for 30 min to remove the excess PSS. Finally, Ab2 was added into AuNPs-HRP-PSS solution at a final concentration of 200 μg mL⁻¹ and incubated at room temperature for 2 h under gentle stirring. Following that, polyethylene glycol (20 mg mL⁻¹, 50 μL) was added into the mixture and incubated for 30 min, which was centrifuged at 9680 × *g* for 30 min and washed three times to remove unconjugated Ab2 and excess polyethylene glycol. The obtained AuNPs-HRP-PSS-Ab2 was resuspended in 1 mL of PB (PH 6.0) and stored at 4°C. The synthesis of AuNPs-HRP-PSS-Ab2 was confirmed by TEM and UV-spectra.

2.4. Procedure of the nanocapsule probe-based assay for imidacloprid detection

The 96-well polystyrene plates were coated with imidacloprid-BSA (0.25 μg mL⁻¹, 100 μL) for 2 h at 37°C. After washing the plates with PBST (200 μL), the plates were blocked with blocking buffer (100 μL) for 1 h at 37°C. After a washing step, imidacloprid (100 μg mL⁻¹, 100 μL) with the serial sample solution and mAb (0.125 μg mL⁻¹, 100 μL) diluted by PBS were added and incubated at 37°C for 1 h. After another washing step, the probe (100 μL) diluted 5-fold with probe dilution buffer was added and incubated at 37°C for 1 h. After a final washing step with PBT (200 μL), TMB substrate solution (100 μL) was added to each well and incubated for 15 min at 37°C. The reaction was terminated by stop solution (50 μL) and the OD values were measured with Epoch Microplate Spectrophotometer at 450 nm. The IC₅₀ value (50% inhibition) for each compound was measured by the inhibition formula (Meng et al., 2015): Inhibition (%) = [1 - B/B₀] × 100. B was the corresponding OD₄₅₀ values at different concentrations of imidacloprid, B₀ was the OD₄₅₀ value without imidacloprid.

2.5. Selectivity of the nanocapsule probe

The selectivity was evaluated by using the standard solution of imidacloprid and some analogues including thiacloprid, acetamiprid, clothianidin, imidaclothiz, thiamethoxam, nitenpyram and dinotefuran.

2.6. Samples analysis

Three different agricultural samples (rice, pear and cabbage) were chosen to evaluate the performance of the assay. All samples were collected from the local supermarket of Changchun (China). The samples were spiked with different concentrations of imidacloprid (2, 10 and 20 $\mu\text{g Kg}^{-1}$) and stirred for 10 min. Subsequently, all samples were extracted by ultrasonic extraction in 5% (v/v) methanol in PBS for 10 min and centrifuged for 10 min at $4000 \times g$. The supernatant was collected and the solutions were comparatively analyzed by the developed assay and commercial kit. The recoveries were calculated according to the following equation (Meng et al., 2015):

$$\text{Recovery (\%)} = [(C_D - C_N)/C_S] \times 100\%$$

where C_D was the detected concentration of the spiked sample, C_N was the concentration of the unspiked sample, C_S was the spiked concentration of imidacloprid. Analyses were always made in triplicate.

3. Results and discussion

3.1. Synthesis and confirmation of nanocapsule probe

In this study, AuNPs were chosen as a carrier for loading HRP, LBL technique was used to encapsulate AuNPs-HRP to enhance the signal amplification. The IgG had a net positive charge at pH 6.0 and the PSS-encapsulated AuNPs showed a negative charge on the surface due to the presence of anionic SO_3 groups of PSS (Harshala et al., 2009; Wang, Chen, Wang, Ma, & Su, 2007). Therefore, in the presence of PB solution (pH 6.0), IgG could be spontaneously immobilized onto the surface of AuNPs-HRP-PSS without using any cross-linking reagents mainly due to the electrostatic interaction between positively charged IgG and the negatively charged PSS.

The modification of nanocapsule was analyzed by TEM and UV-Vis absorption spectra. TEM image in Figure 2A (b) showed the AuNPs were encapsulated in PSS shell forming a polymer capsule. Fifty nanocapsules were counted, the average number of AuNPs in one nanocapsule were twenty-three. The UV-Vis absorption spectra of AuNPs, AuNPs-HRP, AuNPs-HRP-PSS and AuNPs-HRP-PSS-Ab2 were shown in Figure 2B. The AuNPs had surface plasmon resonance (λ_{SPR}) at 519 nm, the effect of immobilization caused λ_{SPR} of AuNPs-HRP redshift from 519 to 527 nm. After the LBL deposition process, AuNPs-HRP-PSS had a broader absorption peak than AuNPs-HRP, displaying a successful aggregation of AuNPs-HRP. The λ_{SPR} redshift of AuNPs-HRP-PSS-Ab2 was from 527 to 530 nm, indicating successful link interaction between IgG and AuNPs-HRP-PSS. There was no significant colour change in the synthesis process of the probe.

In the probe, the amount of Ab2 adsorbed on the surface of nanocapsule is one of the most important components, which can affect the sensitivity of the probe. As shown in

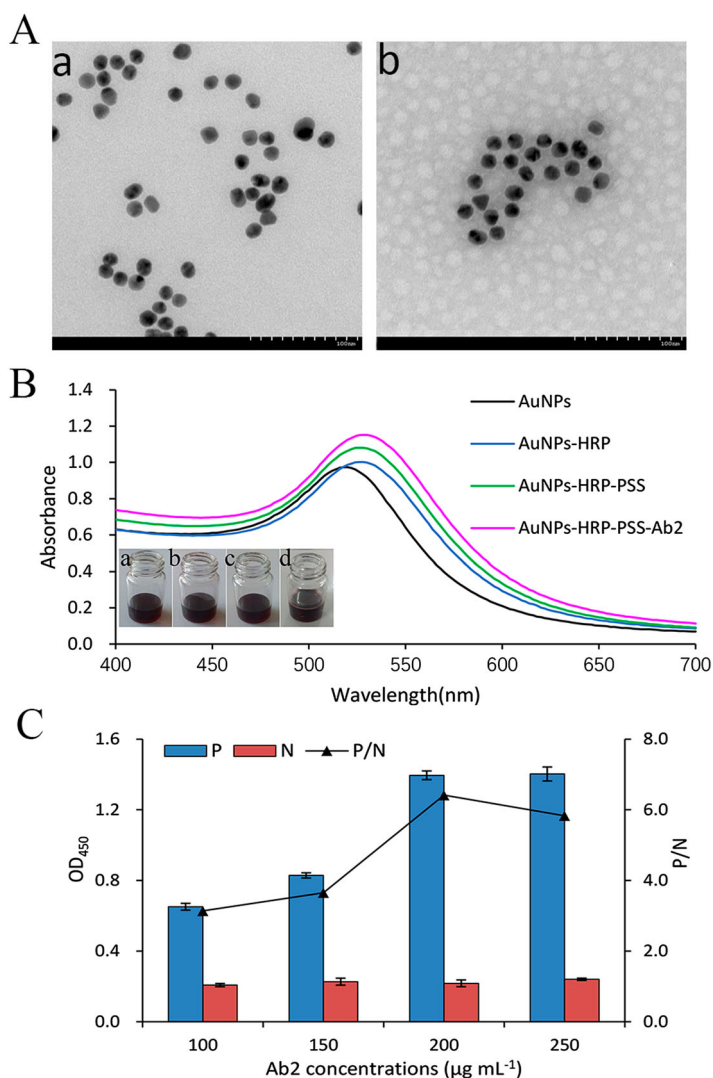


Figure 2. Synthesis confirmation of nanocapsule probe. (A) TEM images of the AuNPs (a) and the synthesized nanocapsule probe (b). (B) UV-spectra analysis of synthesis process of nanocapsule: AuNPs (a); AuNPs-HRP (b); AuNPs-HRP-PSS (c); AuNPs-HRP-PSS-Ab2 (d). (C) The relationship between the amount of Ab2 and the absorbance value. P/N value is the positive OD value/blank OD value.

Figure 2C, the absorbance and P/N values increased gradually along with the amount of IgG adsorbed on nanocapsule, and became almost constant at $200 \mu\text{g mL}^{-1}$. Thus, $200 \mu\text{g mL}^{-1}$ was chosen as the optimum amount.

3.2. Calibration curve and specificity

A calibration curve was obtained by plotting the values of inhibition and the logarithm of the concentrations of imidacloprid (Figure 3). The linear regression equation was $y = 39.719 \times -31.238$, with a correlation coefficient (R^2) of 0.9487. The linear range (IC_{15} -

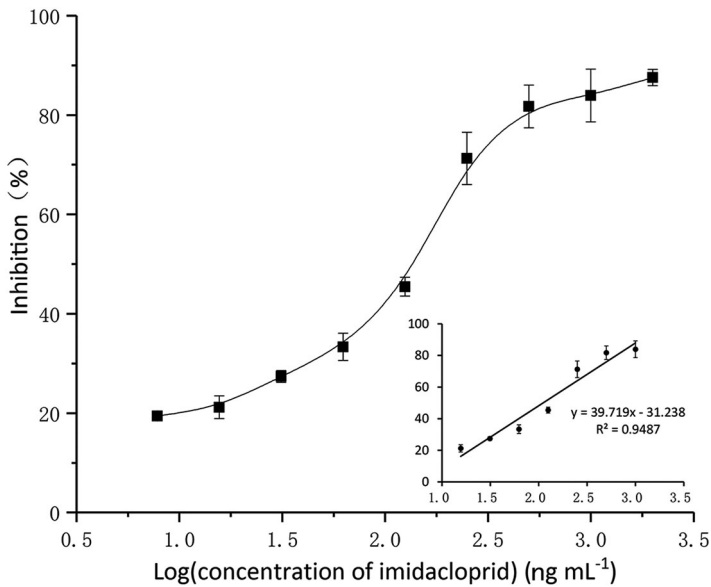


Figure 3. Standard curve of nanocapsule probe-based assay for imidacloprid. The curve was obtained by using the relationship between the values of inhibition and the logarithm of the concentrations of imidacloprid. Results are mean \pm SD ($n = 3$).

IC₈₅) was 0.02 to 0.84 ng mL⁻¹, the limit of detection (LOD, IC₁₀) and the IC₅₀ value was 0.01 and 0.11 ng mL⁻¹. The sensitivity of the developed method was higher than traditional ELISA, commercial kit and other reported methods (Table 1).

The specificity of the probe was evaluated by cross-reaction (CR) values with imidacloprid and seven other structurally similar neonicotinoid insecticides. As shown in Table 2, there was almost no CR with other analogues except thiacloprid, acetamiprid and clothianidin (CR < 10%). The results confirmed the good specificity of the probe for the detection of imidacloprid.

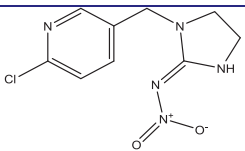
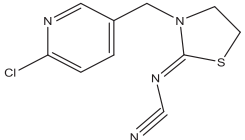
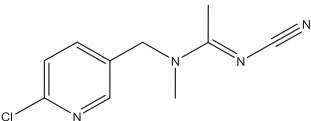
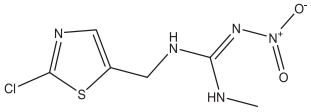
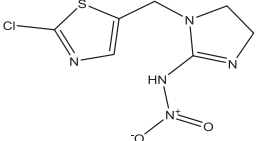
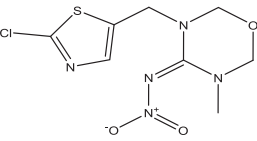
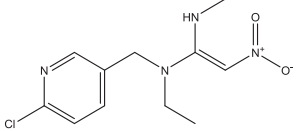
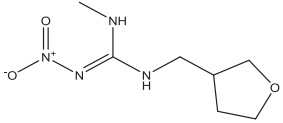
3.3. Spiked sample detection

In order to reduce matrix interference and correspond with the detection linear range of commercial kit, 50-fold matrix dilution was used for this analysis. As shown in Table 3, the recoveries of imidacloprid from rice, pear and cabbage were 88.05–117.02%, 89.53–109.50% and 80.34–120.84%, respectively, with the coefficient of variations (CVs) within 13%. The recoveries of imidacloprid had a good correlation ($R^2 = 0.9739$) between the developed method and commercial kit and were in accordance with the AOAC international standard which the recoveries should be in the range between 50% and 150% (Koerner et al., 2013). These data suggested that the developed method can be used as a quantitative tool for the determination of imidacloprid in agricultural food samples.

3.4. Stability of the probe

The stability of the probe was tested by using the same procedures described in section 2.4 except for no adding of the standard solution of imidacloprid. As

Table 2. Cross-reactivity (CR) of the probe with imidacloprid and its analogues.

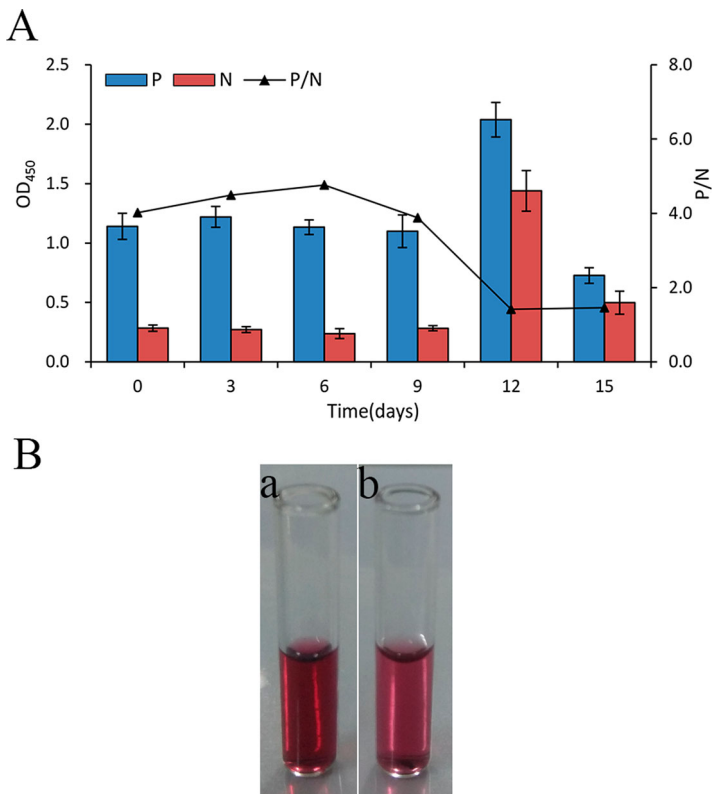
Analogues	Chemical structure	CR ^a (%)
Imidacloprid		100.00
Thiacloprid		<10.00
Acetamiprid		<10.00
Clothianidin		<10.00
Imidaclothiz		<1.00
Thiamethoxam		<0.10
Nitenpyram		<0.10
Dinotefuran		<0.10

^aData represent the means of three experiments.

shown in Figure 4A, The OD₄₅₀ values only change from 1.09 to 1.22 and the *P/N* values were almost constant in the first nine days, suggesting that the AuNPs-HRP-PSS-Ab2 conjugate has almost no major difference in stability after storage nine

Table 3. Recovery of spiked samples.

Samples	Spiked concentration ($\mu\text{g Kg}^{-1}$)	Mean recovery ^a (%) Developed method	CVs (%)	Commercial ELISA kit
Rice	2	88.05 \pm 7.23	8.21	109.19 \pm 7.01
	10	117.02 \pm 8.80	7.52	117.64 \pm 1.56
	20	109.02 \pm 10.56	9.69	92.62 \pm 1.35
	0	– ^b	–	–
Pear	2	89.53 \pm 7.11	7.94	90.05 \pm 4.96
	10	96.80 \pm 9.78	10.11	95.63 \pm 4.13
	20	109.50 \pm 13.73	12.54	83.81 \pm 1.45
	0	–	–	–
Cabbage	2	80.34 \pm 8.35	10.39	93.50 \pm 1.62
	10	92.55 \pm 6.11	6.61	90.08 \pm 3.44
	20	120.84 \pm 12.10	10.01	89.22 \pm 5.15
	0	–	–	–

^aData represent the means of three experiments.^bNot detected.**Figure 4.** (A) OD₄₅₀ value of assay for the nanocapsule probe stored for different time-periods. (B) The picture of the probe stored at 0 (a), 12 (b) days.

days. The AuNPs-HRP-PSS-Ab2 was clumped and became light in colour from day twelve (Figure 4B). These data indicated that the probe can be used for repeated measurements after 9 days storage at 4°C.

4. Conclusion

A signal amplified nanocapsule probe was synthesized using the LBL technique and an immunoassay was developed based on the probe for sensitive detection of imidacloprid in agricultural samples. The sensitivity of the developed assay was higher than traditional ELISA, commercial kit and well below the MRLs permitted by the EU. The values of recoveries and CVs had a good correlation with those from a commercial kit, indicated the accuracy and precision of the developed method. The synthesized nanocapsule probe could be used for sensitive and selective detection of imidacloprid in agricultural samples.

Disclosure statement

No potential conflict of interest was reported by the authors.

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