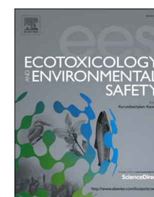
Ecotoxicology and Environmental Safety 148 (2018) 862–868

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

journal homepage: www.elsevier.com/locate/ecoenv



Inner filter effect-based homogeneous immunoassay for rapid detection of imidacloprid residue in environmental and food samples

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ARTICLE INFO

Keywords:
Imidacloprid
Upconversion nanoparticles
Gold nanoparticles
Inner filter effect
Immunoassay

ABSTRACT

This paper reports a novel and sensitive homogeneous immunoassay for rapid detection of imidacloprid residue in environmental and food samples. The assay signal was originated from inner filter effect (IFE) between upconversion nanoparticles (UCNPs) and gold nanoparticles (AuNPs). UCNPs (energy donor) were coupled to the antibody against imidacloprid, and AuNPs (energy acceptor) were used to label the antigen of imidacloprid. The competitive immunoreaction occurred between imidacloprid and antigen-AuNPs binding to antibody-UCNPs. The assay system, sensitivity, selectivity, accuracy, and reliability were investigated. Under the optimal assay condition, the limit of detection for imidacloprid was 0.79 ng/mL and the concentration recovering 50% saturation of the signal (SC_{50}) was 18.7 ng/mL. The linear detection range (SC_{10} to SC_{90}) was 1.39–335.81 ng/mL. Furthermore, the proposed method was successfully applied to determine imidacloprid in spiked water, Chinese cabbage, and honey samples, giving recoveries in the range of 78.1–97.9%. Through the blind sample tests, the IFE-based immunoassay demonstrated good correlation with ultra-performance liquid chromatography-tandem mass spectrometry (R^2 = 0.9866). Therefore, the new one-step immunoassay can be used as a promising tool for rapid detection of imidacloprid in field of environment and food safety.

1. Introduction

Imidacloprid is a systemic and contact neonicotinoid insecticide with low mammalian toxicity (Mullins, 2009). It affects the nervous system of insects (Mullins, 1993) and exhibits distinguished insecticidal activity against aphids, planthoppers, leafhoppers, whiteflies and thrips in crops such as corn, rice, cotton, potatoes, sorghum, and many vegetables such as cabbage (Delbeke et al., 1997). However, extensive and unreasonable use of neonicotinoid insecticides have resulted in the destruction of the ecological environment and harmed to non-target organisms such as honey bees (Cresswell, 2011; Goulson, 2013). Owing to their persistence and high solubility in water systems, they are found in the environment, which may present a threat to human health and environmental safety (Zhou et al., 2006). Maximum residue limit (MRL) for imidacloprid has been announced in different official legislations. For instance, the MRLs in cabbages and honey are 0.5 and 0.05 mg/kg respectively set by European Commission (http://ec.europa.eu/sanco_pesticides/public/index.cfm). Thus, it is urgent to regularly monitor imidacloprid residue in agricultural products and environment.

At present, there are various efficient methods to determine imidacloprid in food and water. Typically, instrumental analytical approaches, such as high-performance liquid chromatography (HPLC) (Fan et al., 2007), gas chromatography mass spectrometry (GC-MS) (Macdonald and Meyer, 1998), show favorable sensitivity and accuracy, but there are some problems such as being time-consuming, complex pretreatment technologies and high cost of instruments and technicians. In recent two decades, immunoassays are increasingly developed for rapid detection of imidacloprid. Most of them are heterogeneous assays, such as enzyme-linked immunosorbent assay (ELISA) (Kim et al., 2004), chemiluminescence enzyme-linked immunosorbent assay (CL-ELISA) (Girotti et al., 2008) and time-resolved fluoroimmunoassay (TRFIA) (Shi et al., 2015), which exhibit high sensitivity and reliability for measurement. However, they require several separation processes with strict washing and laborious reagent-adding steps, which are not ideal for the simple, efficient and high-throughput demands for screening purposes. Hence, it is imperative to develop a homogeneous, rapid, simple and sensitive method for detection of residual imidacloprid.

UCNPs has attracted an enormous attention due to the unique luminescence properties of rare-earth nanocrystals, such as sharp absorption and emission lines, long lifetimes, high quantum yields, and superior photostability (Wang et al., 2010). Contrary to traditional

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https://doi.org/10.1016/j.ecoenv.2017.11.062
Received 24 August 2017; Received in revised form 16 November 2017; Accepted 22 November 2017
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downconversion fluorescent materials (such as organic dyes and quantum dots), UCNPs can convert low-energy light (near-infrared or infrared) to higher-energy light (UV or visible) through multiple photon absorptions or energy transfers (Auzel, 2004). Thus, due to the absence of auto-fluorescence, the sensitivity and signal-to-noise ratio of the detection can be improved (Wang and Liu, 2009). In addition, the near-infrared radiation has stronger penetration ability and less harm to biological samples (Li et al., 2008). Therefore, UCNPs are promising alternatives to traditional fluorescent bio-labels for bioimaging (Liu et al., 2013; Song et al., 2017), fluorescence bioanalysis (Jiang and Zhang, 2010; Jin et al., 2017) and possess prominent potentials in clinical application (Idris et al., 2012; Wang et al., 2011a, 2011b).

Inner filter effect (IFE) refers to the absorption of the exciting radiation and/or emitted fluorescence radiation of fluorophores by absorbers in the detection system (Yuan and Walt, 1987). IFE only occurs effectively if the absorption band of absorbers possesses the complementary overlap with the excitation and/or emission bands of fluorophores (Chang and Ho, 2015). Different from fluorescence resonance energy transfer, the IFE-based approach does not require the link of absorbers with fluorophores, which offers considerable flexibility and more simplicity (Shang and Dong, 2009). Compared to other fluorescence analytical methods, IFE system possesses several advantages, such as the simplified synthesis (Li and Hu, 2007) and modification process of the fluorescent materials (Zhang et al., 2012), and higher sensitivity (Wang and Huang, 2007). In addition, the IFE-based immunoassay is homogeneous, which is superior to heterogeneous immunoassays in experiment operation (no coating and washing steps), reagent consumption and disposability (Cui et al., 2012). Up to now, the detection for pesticides in IFE process has been explored in some previous studies (Guo et al., 2013; Long et al., 2015; Yan et al., 2014). However, there are very few reports on employing UCNPs in IFE-based immunochemical methods for pesticide detection (You et al., 2017).

In this work, carboxylic acid-functionalized UCNPs (COOH-UCNPs) and gold nanoparticles (AuNPs) were served as energy donor and acceptor, respectively. COOH-UCNPs and AuNPs were further conjugated with imidacloprid antibody and competitive antigen, respectively. The IFE system was constructed as shown in Fig. 1. When there is no imidacloprid in the IFE system, the imidacloprid antibody of UCNPs can specifically bind with the competitive antigen of AuNPs, so that AuNPs can absorb the visible light emitted from the UCNPs upon the NIR irradiation. When imidacloprid is added into the IFE system, it will competitively bind with the imidacloprid antibody of UCNPs to prevent the process of IFE.

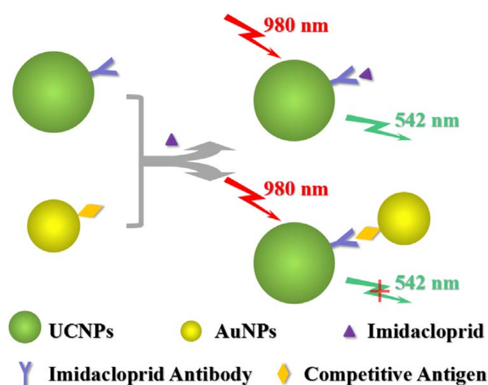

Fig. 1. Schematic of the IFE process between UCNPs (donor) and AuNPs (acceptor).

2. Experimental sections

2.1. Materials

Carboxylic acid-functionalized $NaYF_4$: Yb, Er was obtained from Fluo NanoTech Co., Ltd. (Hangzhou, China). N-Hydroxysuccinimide (NHS, 99%), 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC, 99%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Sodium dihydrogen phosphate (NaH_2PO_4, 99%) and sodium hydrogen phosphate (Na_2HPO_4, 99%) were provided by Huzhou Chemical Reagent (China). Bovine serum albumin (BSA) and ovalbumin (OVA) were obtained from Sino-American Biotechnology (Luoyang, China). Chloroauric acid ($HAuCl_4 \cdot 4H_2O$, 99%), sodium citrate (trisodium salt, dehydrate, 99%), sodium chloride (NaCl, 99.5%), hydrochloric acid (HCl, 36–38%) were purchased from Sinopharm Chemical Reagent (Shanghai, China). Tris (hydroxymethyl) aminemethane (99.9%), polyethylene glycol (PEG), trahalose (99%), Tween 20 were supplied by Aladdin Industrial Corporation (Shanghai, China). N-propyl-ethylenediamine (primary secondary amine, PSA) was obtained from Agela Technologies (Tianjin, China). The imidacloprid antigen and imidaclothiz antigen were prepared as described in literatures (Kai and Li, 2000; Fang et al., 2011). The antibody for imidacloprid was previously produced in our lab. All the other chemicals were commercially available as analytical grade and Milli-Q ultrapure water was used throughout the experiments.

2.2. Apparatus

Transmission electron microscopy (TEM) images were taken with the H-7650 TEM (Hitachi, Japan). The spectrum of UCNPs was determined by F-4500 fluorescence photometer (Hitachi, Japan) with an external 980 nm laser source (Changchun Laser Optoelectronics Technology, China) instead of the internal excitation source. The maximum power of the laser was 2 W. The absorption spectrum of AuNPs was detected by SpectraMax i3 multiscan spectrum (Molecular Devices, USA).

2.3. Preparation of imidacloprid antibody-UCNPs conjugates

The stock solution of COOH-UCNPs particles was first prepared to the concentration of 0.5 mg/mL in ultrapure water, and then 20 μL NHS (25 mg/mL) and 20 μL EDC (38 mg/mL) were added into 1 mL of the nanoprobe solution with simple vortex. The solution was shaken fiercely for 20 min in order to active particles. After that, the solution was centrifuged 10 min at 9000 rpm for precipitating active particles, 95% of the supernatant solution was discarded. The precipitate was rinsed with 1 mL of 0.01 M phosphate buffer (PB, pH 7.4) for 5 min under ultrasound. Afterwards, 19 μL of imidacloprid antibody (2.1 mg/mL) was added into the UCNPs activate suspension. The mixture was reacted for 2 h at 250 rpm, and then 1% BSA solution was added into the mixture to block for 30 min. After centrifugation, the supernatant was discarded and the sediment was resuspended in stock solution of 0.03 M PB (pH 7.4) containing 1% BSA (w/v), 0.1% Tween-20 (v/v), and 1% trehalose (w/v). The imidacloprid antibody-UCNPs were stored at 4 °C, and if particles turned to be aggregation or flocculation, ultrasonic dispersion was conducted prior to use.

2.4. Synthesis of AuNPs

AuNPs were synthesized by using sodium citrate as the reducing agent (Frens, 1973). First, 1 mL 1% gold chloride was added into the 100 mL water to form 0.01% gold chloride. Under reflux condensation conditions, the solution was heated to boiling point, and then 1.2 mL of 1% trisodium citrate solution was added rapidly with constant stirring. The solution was boiled for another 5 min when the mixture's color changed from deep blue to significant wine red. After cooling to room

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