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Nitrogen-doped graphene quantum dots-based fluorescence molecularly imprinted sensor for thiacloprid detection

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ABSTRACT

In this paper, a test strip-based sensor was developed for thiacloprid quantitative detection based on PDA molecularly imprinted polymer (MIP) and nitrogen-doped graphene quantum dots (N-GQDs). Thiacloprid is a new type of nicotine insecticide, which can block the normal neurotransmitter delivery process in insects. In the sensing system, N-GQDs were immersed into filter paper at first. Then, dopamine (DA) with thiacloprid can be self-polymerized on test strip surface to form the uniform PDA film. After removed thiacloprid template, the established poly dopamine (PDA) MIP can selectively recognize thiacloprid. As a result, captured thiacloprid can enhance the fluorescence intensity of N-GQDs into the test strip. As a result, the fluorescence intensity of N-GQDs can be linearly related within a certain range of thiacloprid concentration. Under the optimum conditions, the proposed sensor for thiacloprid detection exhibited a linear ranging from 0.1 mg/L to 10 mg/L with a low detection limit of 0.03 mg/L. The N-GQDs based test strip-based sensor for thiaclopridis reported for the first time. The sensing system has high selectivity to thiacloprid and provides new opportunities in the pesticide detection.

1. Introduction

Thiacloprid is a novel member of the neonicotinoid family of systemic insecticides, which acts as agonists of the post-synaptic ligand operated ion channels of the nervous system [1,2]. Because thiacloprid can act on receptors of neurotransmitters, it can interfere with the normal nerve conduction of insects. As a result, it can cause the accumulation of a large amount of nerve conduction medium in the insect body and make the insects over-excited and ultimately die of the whole body spasm paralyzing. Therefore, in 2013, the European Food Safety Authority (EFSA) enforced a 2 year Europe wide ban on the use of the three neonicotinoids, imidacloprid, thiacloprid and clothianidin [3]. Currently, the analytical methods of thiacloprid detection mainly depend on chromatography and MS analysis [4]. Although these detection methods are effective and have low detection limit, the common technologies are limited by complicated synthesis, long reaction time and high detection cost. Thus, a simple and rapid sensor for thiacloprid determination with high sensitivity and selectivity is needed urgently.

With the development of fluorescence sensor [5], more and more nanomaterials have been employed in the novel sensing systems. Graphene quantum dots (GQDs), as a novel type of fluorescent material have attracted the notice of researchers due to their excellent properties of chemical inertness, ease of production, low cytotoxicity and superior biocompatibility [6,7]. These excellent properties of GQDs make them have a wide range of applications of biological imaging, optical sensing, and organic photovoltaic devices [8]. However, the surfaces of GQDs can be modified hardly, which make the GQDs have low quantum yield (QY) and limit the potential application [9]. So the surface of GQDs we can be modified by doping other hetero-atoms, which not only maintain their intrinsic properties, but also improve the quantum yield of GQDs. For example, nitrogen-doped graphene quantum dots (N-GQDs) have high quantum yield, superior fluorescent stability, stable photoluminescence characteristics and electrocatalytic activities. Therefore, they have more and more widely applications of sensors, fuel cells, and optoelectronics and so on. Xue et al. have used electrochemical method to prepare N-GQDs with fluorescence and electrochemical catalytic activity [10]. N-GQDs-based electrochemiluminescence sensors have also used to detect small molecules, organic compounds and proteins [11].

In this paper, we used test strip-based fluorescence sensor to detect thiacloprid with molecularly imprinted polymer (MIP) and N-GQDs. Molecular imprinting technique is a technology to identify target molecule specifically by making molecularly imprinted polymer. Recently, MIP is applied in more and more fields. Compared to traditional methods, MIP has higher mechanical and chemical stability, high specific recognition ability, and low cost. The interaction of polymers and the template molecule mainly includes covalent bonding and non-covalent bonding [12]. Scheme 1 described the thiacloprid sensing

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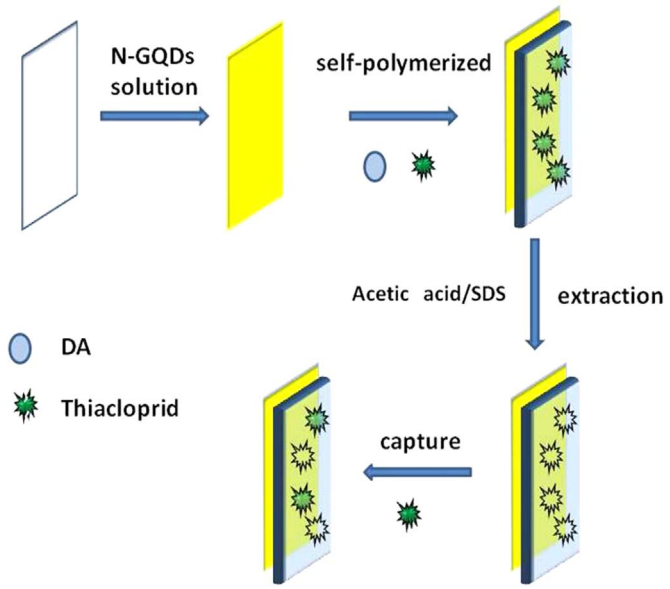

Scheme 1. The process of the molecularly imprinted N-GQDs based fluorescence strip preparation.

process of test strip-based fluorescence sensor. DA with thiacloprid was self-polymerized on test strip surface to form the uniform PDA MIP film in this work. DA is a neurotransmitter. The main role is to help the cells send pulses of chemical substances [13]. DA can be self-polymerization in aqueous solution conditions, and absorbed on the metal, glass, wood and a series of solid materials on the surface [14]. So, the PDA films formed on the test stripcan work as a biocompatible matrix for the molecules immobilization and reduce nonspecific absorption. Based on the enhanced photoluminescence characteristics of N-GQDs with thiacloprid and high selectivity of MIP, a novel sensor for thiacloprid was presented in this work. It is the first report that N-GQD based thiophanate sensor by utilizing MIP and using test strip as the solid matrix.

2. Experimental section

2.1. Materials and apparatus

All chemicals and reagents were analytical grade and used directly without further purification. Thiacloprid, citric acid (CA), ammonia, DA, Tris, sodium dodecyl sulfate (SDS) were obtained from Beijing Dinggguo Chemicals Co. (Beijing, China). All reagents were prepared using ultrapure water with a resistivity of greater than 18 MΩ cm^{-1}. The water samples were collected from the underground water in Jilin University. All experiments were carried out at room temperature.

Photoluminescence (PL) spectra measurements were performed on a Shimadzu RF-5301 PC spectrofluorophotometer (Shimadzu Co., Kyoto, Japan). The ultraviolet-visible (UV–vis) absorption spectra were acquired on a UV-1200 UV–vis Spectrophotometer with a 1 cm quart cell. Fourier transform infrared spectrometry (FT-IR) was conducted on a Thermo Nicolet 360 FT-IR spectrometer using KBr pellets. Transmission electron microscopy (TEM) images were obtained with a Hitachi electron microscope operating at 200 kV. TEM samples were prepared by dropping the silica microspheres onto carbon-coated copper grids and allowing the excess solvent to evaporate.

2.2. Preparation of N-GQDs and quantum yield (QY) measurements

N-GQDs were synthesized by carbonization of CA with ammonia according to the previous reports [15]. 2 g of citric acid and 0.3 mL of ammonia were transferred into a Teflon-lined autoclave and heated at 210 °C for 1 h. The resultant dark brown mixture (2 g) was dissolved to 10 mL with ultrapure water. Subsequently, pH of N-GQDs dispersion was tuned to 7.0 with adding NaOH solution. The supernatant was collected by removing the large dots through centrifugation at 12,000 rpm for 10 min. Then the obtained liquid was diluted to 20 mL with water acquiring N-GQDs stock solution with concentration of 0.1 g/mL. Finally, the as-prepared N-GQDs were stored at 4 °C for further characterization and use.

The QY of the resultant N-GQDs was calculated according to the follow equation [20]:

$$Y_u = Y_s I_u / I_s A_s / A_u n_u^2 / n_s^2$$

where Y represents the quantum yield, I represents the measured integrated emission intensity, A represents the absorbance intensity, n is the refractive index of the solvent, u represents the N-GQDs, and s represents the quinine sulfate standard sample (QY = 0.54).

2.3. Preparation of test strip based MIP sensor

Firstly, we diluted the solution of N-GQDs with a concentration of 0.1 g/L. The filter paper was immersed in the diluted N-GQDs solution for 10 min. And then the test strip was dried with absorbed by N-GQDs.

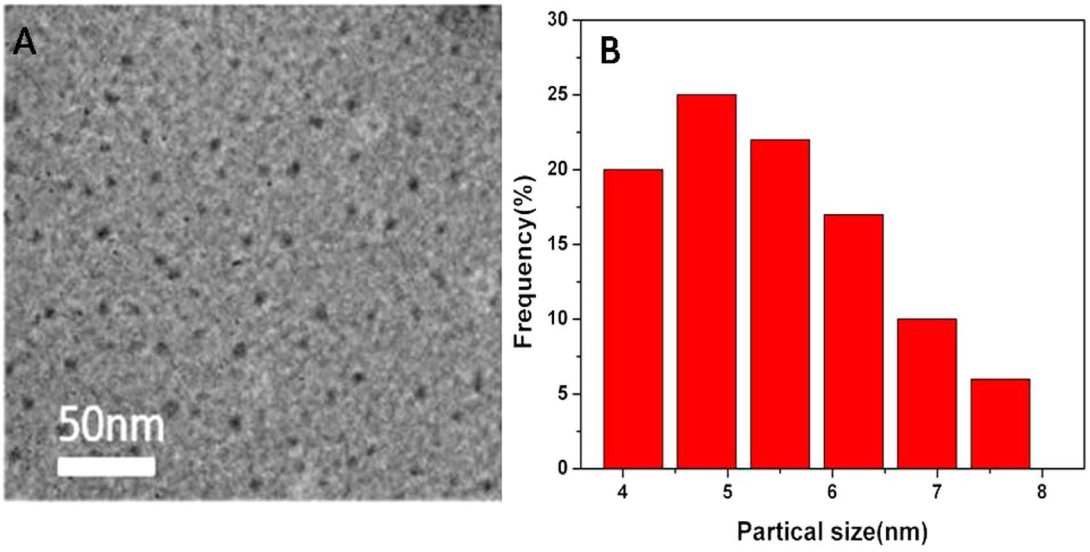

Fig. 1. (A) The TEM image of N-GQDs. (B) Size distribution histograms of QDs in the optimal procedure.