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An interdigitated ISFET-type sensor based on LPCVD grown graphene for ultrasensitive detection of carbaryl

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ABSTRACT

Consider advances are being made to develop new technologies capable of fast in-situ tracing of agricultural toxins. In this work, we reported a simple carbaryl sensor with very high sensitivity using graphene interdigitated ion selective field effect transistor (ISFET). The graphene films were first prepared on polycrystalline copper foil by a low-pressure chemical vapor deposition method, and then transferred onto the interdigitated electrodes of ISFETs by a chemical etching technique. The biorecognition is based on the enzymatic inhibition of carbaryl towards urease. As expected, the weaker enzymatic activity of urease in addition of carbaryl would result in the weaker current response. It was demonstrated that the interdigitated ISFET sensor could achieve high sensitivity to detect carbaryl as low as 10^{-8} μg mL^{-1} and the current response of the device showed a good linearity against the logarithm of carbaryl concentration $C_{carbaryl}$ with a regression equation $\Delta I_{ds} = -0.4 - 0.6 \log C_{carbaryl}$ (mA) ($R^2 = 0.99$) in the concentration range from 2.58×10^{-7} to 2.58×10^{-2} μg mL^{-1}. In conlusion, such convenient graphene-based ISFET configuration could be advantageously extended for on-line screening of other pesticide and herbicide agents.

1. Introduction

It was well-known that the excess use of carbaryl (1-naphthyl-*N*-methyl carbamate) for pest control in crops can cause its bioaccumulation in food or water, and then lead to bioconcentration through the food chain [1]. Up to now, many analytical methods have been developed for the determination of carbaryl in food and water, such as high performance liquid chromatography (HPLC) [2–4], high performance liquid chromatography-mass spectrometry [5], and gas chromatography-mass spectrometry (GC-MC) [6]. Although these above mentioned methods are accurate and selective, they require an extraction step using highly toxic organic solvents and expensive equipment. Moreover, they can only be performed by highly trained technicians and are not convenient for on-site detection [7]. Recently, biosensors have emerged as low-cost, easy operation, fast response, and ultra-sensitive tools for tracing pesticide residue [8–10].

Basically, one biosensor is consisted of one biological recognition element to sense targeted molecule and one transducing element to convert that biological recognition into measurable signals. To recognize carbaryl (one popular carbamate compound), enzymatic inhibition effect is often used. Several enzymes have been used to develop biosensors for carbaryl detection such as acetylcholinesterases (AChE) [8–13], butyrylcholinesterase (BChE) [14], organophosphorus hydrolase (OPH) [15], alkaline phos-

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phatase (ALP) [16], tyrosinase [17], and urease [18]. To translate the inhibition of carbaryl towards the above enzymes into measureable signals, various transducing techniques such as optical, electrochemical, FET, and so on have been employed. Several research groups have reported the optical biosensors based on quantum dots [19,20] and nanoparticles (gold, silver) [21,22] for carbaryl detection. For instance, Yinhui Yi and co-workers [19] have reported a novel carbaryl optical biosensor based on silicon quantum dots. The proposed sensor is able to detect carbaryl at concentrations ranging from 7.49×10^{-6} to 7.49×10^{-1} μg mL^{-1} with detection limit of 7.25×10^{-6} μg mL^{-1}. Many other works have demonstrated the possibility to use electrochemical biosensors based on hybrid films constructed from various conductive materials such as conducing polymers, novel metal nanoparticles, and carbonaceous nanomaterials. Abdolhamid and co-workers [23] have developed an electrochemical carbaryl biosensors based on the covalent immobilization of two enzymes (acetylcholinesterase (AChE) and cholineoxidase (ChO)) on self-assembled monolayer attached to a polycrystalline gold electrode. The linear range for the determination of carbaryl was found to be $\sim 2 \times 10^{-3}$–2×10^{-1} μg mL^{-1} and detection limit was estimated to be $\sim 1.2 \times 10^{-3}$ μg mL^{-1} [23]. Although the detection limit of the above mentioned carbaryl sensors (optical and electrochemical) is below the maximum residue level (5×10^{-2} μg mL^{-1}) established by European Union [24], their stability and reproducibility are still limited. To overcome this problem, field effect transistor (FET) has become a rising star to achieve much improved biosensing performances of carbaryl sensors.

Graphene (Gr), a single layer of carbon atoms assembled in a honey comb lattice, has attracted increasing attention of physicists, chemists, biologists and electronic engineers due to its extraordinary mechanical, thermal and electrical behaviors. With a large specific surface ~2630 m^2/g, an extremely high mobility ~10^5 cm^2 V^{-1} s^{-1} and a facile surface functionalization to immobilize various bio-molecules (antibodies, antigens, enzymes, cells, peptides, etc), this material is widely studied in the field of biological sensors [25–32]. For graphene-based FET biosensors, Gr is often utilized as conduction channel that allows the mobile charges to flow between drain and source electrodes in solution-gating configuration, whereas the biological processes on that graphene layer are monitored by characteristics of the FET (i.e., Dirac point) [33]. It was anticipated that the adsorption of ions (either OH^- or H^+) onto graphene channel can modulate channel conductance by doping holes or electrons, thus shifting position of charge neutrality point (Dirac point) in the right or left direction, respectively [34]. For this reason, various research groups have utilized graphene and its derivatives as conduction channel of FETs for pH sensing as well as biosensing applications [34–36]. In fact, Gr and reduced graphene oxide (rGO) were the most often used carbonaceous nanomaterials for constructing these devices. Until now, it is still questionable if Gr-based FETs or rGO-based FETs can provide better biosensing performances. It was sometimes reported that the presence of structural defects and oxygen moieties in imperfect Gr and rGO lattices might even create active sites to attract these ions. Otherwise, several works demonstrated lower performances in terms of filed-effect channel mobility in rGO-based FETs compared to Gr-based FETs [35].

In this study, a simple configuration of a graphene based on ISFET sensor is presented for the on-site monitoring of carbaryl. The few-layered graphene films prepared by LPCVD have been transferred onto a prepatterned interdigitated microelectrode array (IDA) of source (S) and drain (D) electrodes. The surface of these graphene-based electrodes was subsequently functionalized with urease. The sensing of carbaryl was recorded by the variation in position and intensity of Dirac point. The development of this simple sensing technology could probably lower the time and cost to control food safety in future.

2. Experimentals

2.1. Chemical agents

Urease enzyme (EC 3.5.1.5) was purchased from Merck. Phosphate buffer solution (PBS, pH 7.4) and glutaraldehyde (GA) were purchased from Sigma-Aldrich. All aqueous solutions were prepared in deionized water.

2.2. Fabrication of graphene films

The LPCVD process for the synthesis of graphene films on polycrystalline Cu foils (25 μm-thick) of 99.8% purity (Alfa-Aesar). First, Cu foils were cleaned in acetone and isopropanol (IPA) to remove all organic contaminants and electrochemically polished in 85% H_3PO_4 at 1.9 V using another Cu sheet as a cathode. The furnace was pumped down to a base pressure at 60 Torr and then heated from room temperature to 1000 °C in mixture of argon (Ar) (20 standard cubic centimeter/minute (sccm)/H_2 (50 sccm)) for 25 min. Then, the Cu foils were annealed at 1000 °C for 30 min in H_2 (20 sccm) to reduce the native Cu oxide and to facilitate Cu grain growth. Then, a flow of methane (CH_4, 0.3 sccm) was introduced to grow the graphene films. After 30 min, the CH_4 flow was turned off and the Cu foil was rapidly cooled to room temperature under a mixture gas flow of Ar (20 sccm)/H_2 (20 sccm). The pressure in the furnace was maintained at 60 Torr during CVD process.

2.3. FET fabrication

The schematic illustration of FET based on graphene films is detailed in ref [28]. In brief, an IDA was patterned on a silicon substrate with a top layer of 100 nm of silicon dioxide (SiO_2/Si) by lithography. The IDA consisted of a pair of chromium (20 nm)/platinum (100 nm) electrode bands with 19 fingers each, in which the bands served as source (S) and drain (D) electrodes, respectively. The configuration of IDA was 60 μm × 60 μm × 2.4 mm (width, interfinger gaps, long). Poly(methyl methacrylate) (PMMA) was spin coated on the graphene surface and baked at 120 °C for 1–2 min on top of a hot plate. Then, the PMMA/graphene/Cu film was placed in a baker containing 0.3 M $(NH_4)_2S_2O_8$ solvent until all the Cu foil layer was etched away. Following the etching, samples were rinsed with deionized (DI) water five times and then transferred onto top of the prefabricated IDA. After drying in air, a small amount of fresh PMMA was dropped onto the PMMA/graphene/FET electrodes to dissolve soak the previously coated dried PMMA. To remove the PMMA layers, the samples were immersed into an acetone bath for 2 h and then immersed into isopropanol (IPA) for 1 h. Finally, the graphene based FET was annealed in Ar gas at 110 °C for 30 min to enable the flattening of the graphene film on the substrate and remove the water completely.

2.4. Enzyme immobilization

10U urease was immobilized on the interdigitated electrodes using glutaraldehyde (GA) vapor as cross-linking agent. The electric pads were protected from GA vapor by using a parafilm. The incubation process was conducted at room temperature for 60 min. After that, the electrodes were washed several times to remove the unbound GA molecules.