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

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A R T I C L E   I N F O

Article history:
Received 4 June 2017
Received in revised form 30 November 2017
Accepted 29 December 2017
Available online 30 December 2017

Keywords:
Graphene
ISFET
Sensor
Interdigitated electrode array
Carbaryl

A B S T R A C T

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 \(10^{-4} \text{mg} \cdot \text{L}^{-1}\) and the current response of the device showed a good linearity against the logarithm of carbaryl concentration \(C_{\text{carbaryl}}\) with a regression equation \(\Delta I_D = -0.4 - 0.6 \log C_{\text{carbaryl}} \text{(mA)}\) (\(R^2 = 0.99\)) in the concentration range from 2.58 \(\times 10^{-2}\) to 2.58 \(\times 10^{-4}\) \(\mu\text{g} \cdot \text{L}^{-1}\). In conclusion, such convenient graphene-based ISFET configuration could be advantageously extended for on-line screening of other pesticide and herbicide agents.

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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-
phase (ALP) [16], tyrosinase [17], and urease [18]. To translate the inhibition of carbaryl towards the above enzymes into measurable 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, Yin-Hui Yi and co-workers [23] have reported a novel carbaryl optical biosensor based on silicon quantum dots. The proposed sensor is able to detect carbaryl at concentrations ranging from $7.49 \times 10^{-6}$ to $7.49 \times 10^{-1} \mu g mL^{-1}$ with detection limit of $7.25 \times 10^{-6} \mu g mL^{-1}$. Many other works have demonstrated the possibility to use electrochemical biosensors based on hybrid films constructed from various conductive materials such as conducting 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 choline oxidase (ChO)) on self-assembled monolayer attached to a polycrystalline gold electrode. The linear range for the determination of carbaryl was found to be $2 \times 10^{-3} \sim 10^{-1} \mu g mL^{-1}$ and detection limit was estimated to be $12 \times 10^{-3} \mu g mL^{-1}$ [23]. Although the detection limit of the above mentioned carbaryl sensors (optical and electrochemical) is below the maximum residue level ($5 \times 10^{-2} \mu g mL^{-1}$) 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. Experiments

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% H3PO4 at 19 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)/H2 (50 sccm)) for 25 min. Then, the Cu foils were annealed at 1000 °C for 30 min in H2 (20 sccm) to reduce the native Cu oxide and to facilitate Cu grain growth. Then, a flow of methane (CH4, 0.3 sccm) was introduced to grow the graphene films. After 30 min, the CH4 flow was turned off and the Cu foil was rapidly cooled to room temperature under a mixture gas flow of Ar (20 sccm)/H2 (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 (SiO2/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 (NH4)2S2O8 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.
2.5. Detection of carbaryl

In order to test the carbaryl detection, a saturated urea solution (30 mM) and various carbaryl solutions with concentrations ranging from $2.58 \times 10^{-2} \, \mu g \, mL^{-1}$ to $2.58 \times 10^{-2} \, \mu g \, mL^{-1}$ were prepared in deionized water. For each measurement, the FET sensors were incubated for 30 min at room temperature in the pesticide solution and then their electrical characterization was immediately processed in urea solution. The variations of the drain-source current as a function of the gate voltage have been recorded to evaluate the inhibition of carbaryl toward the enzymatic activity of urease.

The working principle of our carbaryl sensors is based on the inhibition of this carbamate compound toward urease in the hydrolysis reaction:

$$\text{CO(NH}_2\text{)}_2 + 3\text{H}_2\text{O} + \text{urease} \rightarrow \text{CO}_2 + 2\text{NH}_4^+ + 2\text{OH}^- \quad (1)$$

With a perfect and contamination-free graphene device, the Dirac point will be close to zero. The Dirac point of graphene will shift to positive or negative gate voltage if the surface of the graphene has adsorbed any chemicals and biological reagents. We can determine the change of graphene surface by observing the shift of the Dirac point. When no pesticide is added to the reaction solution and saturated concentration (30 mM) of urea sub-
substrate exists in solution, the ions (i.e., NH$_4^+$) born from enzymatic hydrolysis of urea would be adsorbed onto graphene surface, then cause n-doping of the material, and finally shifting Dirac point towards negative gate voltage. In contrast, the Dirac point will be shifted to the right direction in addition of carbaryl since less ions are born at the surface of the graphene channel compared with the shift of urea saturated concentration. Additionally, the slopes at both right and left sides of “V-shape” transfer characteristic curve should be somehow varied because of restricted field-effect mobilities of charges. Actually, the most widely used enzyme for biosensing systems to detect carbamate and/or organophosphorus pesticides is acetylcholinesterase [37] whereas urease-based biosensors are more promising for tracing heavy metals in water and foods [38–40]. However, it has been also reported in literature that carbamate and/or organophosphorus pesticides might significantly inhibit enzymatic reaction of urease. Noticably, the enzymatic inhibition of carbamates was found to be irreversible for acetylcholinesterase and reversible for urease. In the former case, carbamate molecules attach to active sites of acetylcholinesterase and binds covalently to them, therefore diminishing the enzymatic activity. In the latter case, these molecules create a flexible bridge between two nickel bi-nuclear active sites. Since the major character of the bonds between this bridge and nickel ions is not covalent but ionic, the carbamate molecules can be released from this complex after washing the electrodes and/or incubating the electrodes in a buffer solution. This enables us to develop a new-generation of pesticide sensors which can be easily regenerated after use.

It is also worth to notice that both carbaryl and natural substrates of urease (i.e. urea) possess amide groups (O=–C–NH–) which are able to attach to hydroxy group and other electronegative functional groups nearby nickel ions. This structural similarity allows carbaryl to act as a substrate-like inhibitor that reduces enzymatic activity of urease. Other inhibitors such as thiourea, hydroxyurea, hydroxamic acid, phosphazenes also work in this way [41]. Moreover, the intermediate product formed during the first step enzymatic hydrolysis of urea is actually one carbamate molecule (H$_2$N–CO–OH) [41]. Clearly, the presence of carbamate molecules like carbaryl probably reduces the rate of enzymatic reaction.

The inhibition level of carbaryl toward urease was determined from I–V$_g$ curves as follows:

\[ RI = 100% \times \left( \frac{\Delta I_{ds0} - \Delta I_{ds}}{\Delta I_{ds0}} \right) \]  

(2)

![Image](image1.png)

**Fig. 3.** (a) SEM of the graphene film grown on the Cu substrate after CVD process and (b) UV–vis transmittance spectrum of the graphene film after transferring from Cu substrate to glass substrate. Inset in (b) is its corresponding optical image.

![Image](image2.png)

**Fig. 4.** (a) AFM topography image and (b) Representative Raman spectrum of the graphene film after transferring from Cu substrate to a SiO$_2$/Si substrate. In (a) the inset shows a height profile between the bare SiO$_2$/Si substrate and the graphene film along the back line in the AFM image. In (b) the names and frequencies (in parentheses, unit cm$^{-1}$) of the main Raman peaks are labeled on the graph.
where RI is relative inhibition, (ΔIds0) and (ΔIds) are the output signals before and after inhibition (as shown in Fig. 2).

2.6. Sample characterizations

The surface morphologies of graphene films were investigated by field-emission scanning electron microscopy (FESEM) (Hitachi S-4800) and atomic force microscopy (AFM) (XE-100 Park Systems). The transmittance of the graphene film in the 350–800 nm range was measured using an UV–vis spectrophotometer (Model Jasco V-600 series). Raman spectra were recorded using an Acton spectrometer fitted with a Pylon CCD detector and a 600 grooves/mm grating (∼2.5 cm⁻¹ between each CCD pixel). The sample was characterized on Si/SiO₂ substrate and using a 532 nm (2.33 eV) laser. The full width at half-maximum of the focused laser spot was about 400 nm. Electrical measurements of the graphene based FET were carried out using a semiconductor parameter analyzer (Keithley, Model 4200-SCS). The source and drain measurement pads were protected from solution by covering the sample with a silicon rubber well (0.9 mm in radius). The Ag/AgCl reference electrode was immersed in urea solution to provide gate control. To evaluate the FET characteristics, the gate potential (Vg) was applied between the source electrode and the reference electrode immersed in the saturated urea solution.

3. Results and discussion

3.1. Graphene film-based field effect transistor elaboration

We have fabricated a layer-by-layer carbaryl FET sensor based on IDA configuration with graphene films. The whole procedure of sensor fabrication is schematically presented in Fig. 1. The graphene based FET sensor was fabricated with (i) the graphene film as the bottom layer which acts as the transducer material to amplify the detected signal; and (ii) an urease enzyme layer on top which acts as the receptor/identification element. Fig. 2(a) and (b, c) are photography and (b, c) SEM images of graphene film on interdigitated electrodes, respectively. From SEM images (Fig. 2(b,c)), we can see that the graphene film with the size of 1.8 mm x 1.8 mm was successfully transferred onto the surface of interdigitated electrodes.

3.2. Characterization of graphene films

Fig. 3(a) shows a FESEM image of a graphene film grown at 1000 °C under flow of CH₄ and H₂ (CH₄/H₂ = 20/0.3 sccm) and pressure 60 Torr with a CVD duration of 30 min. This image shows the presence of Cu surface steps, and graphene wrinkles (bright lines) which result from the difference between the thermal expansion coefficients of graphene and of the Cu substrate. The bright spots also visible in Fig. 3(a) correspond to rounded particles with diameters in the range of 10–40 nm which are attributed to amorphous carbon residues.

Fig. 3(b) shows the optical transmittance spectrum of a similar graphene film transferred on a glass substrate (see insert in Fig. 3(b)). The optical transmittance of the graphene film is 96.8% at 550 nm which is compatible with an average number of layer slightly higher than 1 [42].

The graphene films transferred on 100 nm SiO₂/Si substrate were characterized by AFM and Raman spectroscopy. A typical AFM image is shown on Fig. 4(a). According to the AFM image, the averaged thickness of the graphene film is about 0.91 nm which is compatible with a 1 layer thickness although AFM has been shown to be a poor reliability technique for number of graphene layer estimation [43]. This image also shows the presence of graphene wrinkles (bright lines) and of PMMA residues (white spots).

Fig. 5. Electrical properties of the fabricated sensor (a) current-voltage transfer characteristics of the bare graphene FET at different Vds, (b) Ids versus Vg curves measured after urea immobilization and for different carbaryl concentration at Vds = 1.5 V. As the carbaryl concentration increases, from 2.58 × 10⁻⁷ µg mL⁻¹ to 2.58 × 10⁻⁵ µg mL⁻¹, the minimum of Ids is shifted towards higher Vg. (c) The dependence of the differential drain-source current (ΔIds) on the concentration of carbaryl.
A typical Raman spectrum of the transferred graphene film is shown in Fig. 4(b). As expected, the two characteristic peaks assigned to G band (at 1587 cm$^{-1}$) and 2D band (at 2684 cm$^{-1}$) of graphene/few layer graphene (FLG) material are present on the Raman spectrum. The defect related peaks, D and D’ band located around 1346 cm$^{-1}$ and 1625 cm$^{-1}$, respectively, are also visible. In order to estimate the number of layers, we chose to analyze the G-band integrated intensity normalized versus the one of an highly oriented pyrolytic graphite (HOPG) reference sample ($A_G$) since the criteria based on the analysis of the 2D band have been shown to be misleading in many cases [44]. On about 70% of the probed areas, $A_G$ is found between 0.8 and 0.9 which is consistent with the presence of single layer graphene [45]. On the other part of the sample, thicker regions (few layer graphene) are observed by Raman and optical microscopy (not shown). Regarding defects, the intensity ratio between D and D’ bands, found around 7 on all measured positions, suggest that the defects are mainly vacancies [46]. To go further, the analysis of the integrated intensity ratio of D and G bands and of G band full width at half maximum indicates that the average distance between defects ($l_D$) is between 8 and 20 nm and the average grain size ($l_G$) is larger than 40 nm [47].

### 3.3. Charge mobility of graphene based FET

The hole and the electron mobility were also extracted from the transfer characteristic using [48]:

$$\mu = \frac{m_{in} (L/W) V_{ds} C_d}{\Delta \mu}$$  \hspace{1cm} (3)

where $m_{in}$ is the obtained slope from the linear fits in the $I_{ds} - V_g$ diagram. W and L are the channel width and length, respectively. $V_{ds}$ is the applied source-drain voltage and $C_d$ is the specific capacitance of top gate $= 1.2 (\mu F/cm^2)$ [28].

Fig. 5(a) shows the room temperature transfer characteristics of the bare graphene liquid gated FET device. From Fig. 5(a), we derive the mobility (using expression (3)) of holes and electrons for $V_g$ in the 1.3–1.55 V range (see Table 1). The $I_{on}/I_{off}$ ratios are also defined and calculated in Table 1 by measuring saturated drain-source current ($I_{ds}$) divided by drain-source current at the minimum conductance point (charge neutrality point) ($I_{cmp}$).

The calculated results show that, the mobility values of our bare graphene-FET are found around of 80 cm$^2$/Vs for both electrons and holes. The $I_{on}/I_{off}$ ratio is around of 1.3. This value is lower than that of the graphene-based FETs (2–3.5 [25] and ~2 [49]). This seems to be due to our ISFETs use single-layer graphene with large area and the existence of PMMA residues on the surface of graphene after transferring from Cu substrate to electrode substrate.

### 3.4. Carbaryl detection

The current responses of carbaryl interdigitated ISFET sensor at different sample concentrations are shown in Fig. 5(b). Interestingly, the carbaryl level can be monitored by either position or intensity of charge neutrality point ($V_g$ at the minimum conductance point or Dirac point). When the concentration of carbaryl increased from 0 to $2.58 \times 10^{-2}$ μg mL$^{-1}$, the position of Dirac point was shifted towards positive values. On the other hand, an increase in charge concentration was obtained. It must be noticed that graphene material should be intrinsically n-doping due to the existence of negatively charged oxygen moieties on its surface. Herein, the increase in charge concentration actually reflects decreasing number of positive ions (i.e., $NH_4^+$) absorbed on the surface due to restricted hydrolysis of urea in presence of pesticide.

As shown in Fig. 5(c), the differential drain-source current ($\Delta I_{ds}$) decreases from 3.58 mA to 0.56 mA when the carbaryl concentration increases (from $2.58 \times 10^{-7}$ to $2.58 \times 10^{-2}$ μg mL$^{-1}$). This response curve shows 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) ($R^2 = 0.99$). From the decrease of $\Delta I_{ds}$, the enzyme urease inhibition level of carbaryl for the different concentrations was calculated (using expression (2)). The highest inhibition level is up to 86% with a carbaryl concentration of $2.58 \times 10^{-2}$ μg mL$^{-1}$.

The analysis of the sensor response as a function of the carbaryl concentration (Fig. 5(c)) also shows a good inhibition rate with a LOD of $10^{-8}$ μg mL$^{-1}$ carbaryl. This LOD is far below the maximum residue level ($5 \times 10^{-2}$ μg mL$^{-1}$) established by the European Union [24]. This value is also lower than detection limit of carbaryl biosensors reported in previous works (see Table 2) which ranges from $10^{-7}$ μg mL$^{-1}$ to $10^{-2}$ μg mL$^{-1}$ [2,3,9–11,13,50–53]. Only few studies have demonstrated the ability for carbaryl detection with a detection limit as low as our system [8,54].

Additionally, the charge mobilities (both electron and hole) were decreased as pointed out by decreasing slopes of both sides of ‘V-shape’ curve. As the carbaryl concentration increases, i.e., from 0 to

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**Table 1**

<table>
<thead>
<tr>
<th>$V_{ds}$ (V)</th>
<th>1.3</th>
<th>1.35</th>
<th>1.40</th>
<th>1.45</th>
<th>1.50</th>
<th>1.55</th>
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<td>80</td>
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<td>77</td>
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<tr>
<td>Electron mobility (cm$^2$/Vs)</td>
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<td>77</td>
<td>76</td>
<td>76</td>
<td>77</td>
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<tr>
<td>$I_{on}/I_{off}$ ratio</td>
<td>1.32</td>
<td>1.32</td>
<td>1.31</td>
<td>1.32</td>
<td>1.32</td>
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**Table 2**

<table>
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<tr>
<th>Configuration</th>
<th>Measurement method</th>
<th>Linear range (μg/mL)</th>
<th>Limit of detection (μg/mL)</th>
<th>Reference</th>
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<td>ACHEn-CAMC/SPCE</td>
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<td>10$^{-2}$ to 0.5</td>
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<td>ACHEn-Sch/ASCH/CTO</td>
<td>Electrochemical</td>
<td>5 × 10$^{-3}$ to 10</td>
<td>2 × 10$^{-3}$</td>
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<td>ACHEn-e-pGON/GCE</td>
<td>Electrochemical impedance</td>
<td>3 × 10$^{-4}$ to 6.1 × 10$^{-3}$</td>
<td>1.5 × 10$^{-4}$</td>
<td>[9]</td>
</tr>
<tr>
<td>ACHEn/CHIT/JAM</td>
<td>Electrochemical impedance spectroscopy</td>
<td>10$^{-1}$ to 0.1</td>
<td>7.8 × 10$^{-4}$</td>
<td>[10]</td>
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<td>3.4 × 10$^{-4}$</td>
<td>[11]</td>
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<td>ACHEn/AgNPs-CGR-NF/GCE</td>
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<td>−1.1 × 10$^{-7}$</td>
<td>[13]</td>
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<td>NH$_2$-graphene-Numic</td>
<td>Electrochemical luminescence (ECL)</td>
<td>5 × 10$^{-4}$ to 10</td>
<td>2 × 10$^{-4}$</td>
<td>[50]</td>
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<td>Graphene-IL-Au/CS-AuNPs/GCE</td>
<td>HCA and PCA</td>
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<td>2.5 × 10$^{-3}$</td>
<td>[51]</td>
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<tr>
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<td>6 × 10$^{-3}$ to 1.2</td>
<td>1.6 × 10$^{-1}$</td>
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<td>[53]</td>
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<td>ISFET</td>
<td>10$^{-4}$ to 10$^{-3}$</td>
<td>1.6 × 10$^{-1}$</td>
<td>[54]</td>
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</table>

Notes: ACHEn, acetylcholinesterase; CAMC, cellulose acetate composite; SPCE, screen-printed carbon electrode; JAM, interdigitated array microelectrodes; CHIT, chitosan; e-pGON, electrochemically inducing porous graphene oxide network; HCA, hierarchical clustering analysis; PCA, principal component analysis; GA, glutaldehyde; NPs, nanoparticles; II, liquid-nanol; CS, chitosan; MWCNTs, multi-walled carbon nanotubes; GNRs, graphene oxide nanoribbons; SCH, thiocilone; ASC, acetylthiocholine; SEMmmix, mixed self-assembled monolayer; PDDA, poly(diallyldimethylammonium chloride); SWCNTs, single walled carbon nanotubes; GCR, carboxylic graphene.
to $2.58 \times 10^{-2}$ mg L$^{-1}$, the mobility (using expression (3)) of holes and electrons decreases, from 72 cm$^2$/Vs to 9 cm$^2$/Vs for holes and from 62 cm$^2$/Vs to 4 cm$^2$/Vs for electrons (see Fig. 6). The decrease of the carrier mobility of the graphene-based ISFET when increasing of the carbaryl concentration can be explained as following. The mobility of carrier in graphene-ISFET depends on the differential gate voltage. When the carbaryl molecules absorb onto the surface of the graphene electrode, the ions concentration ($\text{NH}_4^+$, $\text{OH}^-$) in the solution will be decreased, so the differential gate voltage and the carrier mobility will decrease.

4. Conclusion

In this study, we have demonstrated the realization of a carbaryl sensor using a LPCVD-grown graphene based ISFET. This sensor is able to detect carbaryl in the range of $2.58 \times 10^{-7}$--$2.58 \times 10^{-2}$ mg L$^{-1}$ with low limit of detection of $10^{-8}$ mg L$^{-1}$, which is among the lowest reported so far. Apart from the pesticide detection, the used sensor design can be extended for other biosensing applications to achieve high sensitivity and specificity.

Acknowledgments

This research was financially supported mainly by the Vietnam National Foundation for Science and Technology Development (No.103.99-2016.19). Raman measurement was done with the supporting by PICS-CNRS n° 6457.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.snb.2017.12.191.

References


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