High-Performance Dopamine Sensors Based on Whole-Graphene Solution-Gated Transistors

*Meng Zhang, Caizhi Liao, Yanli Yao, Zhike Liu, Fengfei Gong, and Feng Yan**

Solution-gated graphene transistors with graphene as both channel and gate electrodes are fabricated for the first time and used as dopamine sensors with the detection limit down to 1 nM, which is three orders of magnitude better than that of conventional electrochemical measurements. The sensing mechanism is attributed to the change of effective gate voltage applied on the transistors induced by the electro-oxidation of dopamine at the graphene gate electrodes. The interference from glucose, uric acid, and ascorbic acid on the dopamine sensor is characterized. The selectivity of the dopamine sensor is dramatically improved by modifying the gate electrode with a thin Nafion film by solution process. This work paves the way for developing many other biosensors based on the solution-gated graphene transistors by specifically functionalizing the gate electrodes. Because the devices are mainly made of graphene, they are potentially low cost and ideal for high-density integration as multifunctional sensor arrays.

1. Introduction

Graphene has shown promising applications in optoelectronics devices, high frequency transistors and sensors etc. for its unique physical properties and the 2D structure.[1,2] A solution-gated graphene transistor (SGGT) is a device in which the graphene channel is in contact with electrolyte instead of gate insulator.[3] The SGGT operates in solution with the gate voltage applied on the graphene channel via the electrolyte/graphene interface, i.e., electric double layer.[3] So the SGGT is suitable for chemical and biological sensors after the device gets surface modification on either the gate electrode or the channel. Recently, SGGTs have been successfully used in sensing different analytes, including DNA,[4] glucose,[5] ion,[3,6] bacteria,[7] protein[8] and dopamine[9] etc. There are many advantages of using SGGTs as sensors. First, the devices can show much higher sensitivity than conventional electrical measurements for its inherent amplification function.[3,4] Here, the sensitivity is usually evaluated by the detection limits: the minimum concentration of the analyte that can be distinguished from a blank value. Second, the device can be miniaturized without the degradation of performance because the channel current is proportional to the channel width/length ratio instead of the device size. So the SGGTs can be used in high-density sensor arrays for high throughput detections.[3] Most of the reported SGGT-based sensors have the sensing mechanism due to the interactions between the analytes and the graphene channels.[4–9] However, very few people noticed that biosensors can be developed based on the SGGTs with functionalized gate electrodes,[3] which will be reported in this paper for the first time.

Dopamine being a neurotransmitter has been extensively studied since 1950s.[10] Because dopamine plays an important role in the functions of central nervous system, renal, hormonal, and cardiovascular system, etc.,[11,12] abnormal dopaminergic neuron process may lead to various neurological diseases.[13,14] Therefore, rapid detection of dopamine in biological system is very important for the routine analysis and diagnosis of neurological disorders.[15] Various analytical methods for measuring dopamine, including high performance liquid chromatography (HPLC),[16] mass spectroscopy,[17] electrochemical detection,[18] and transistor-based sensing,[19] have been developed. However, these methods have some limitations in practical applications. HPLC and mass spectroscopy are not suitable for portable and low-cost analytical measurement. Electrochemical analytical technique for dopamine determination is an attractive method due to low cost, easy operation and fast response while the detection limit is relatively high (normally ~1 μM). Si nanowire transistors showed ultrahigh sensitivity to dopamine being attributed to their small size and large surface-to-volume ratio while the selectivity of the devices was not characterized.[19] Actually, graphene shows higher surface-to-volume ratio than Si nanowires. He et al. firstly reported dopamine sensors based on SGGTs.[9] The sensing mechanism of the device is attributed to the π–π interaction between dopamine and graphene channel. Unfortunately, the devices showed the detection limit of only about 1mM, which is much worse than typical analytical techniques and the Si nanowire transistors.

In this paper, we present a whole-graphene SGGT-based dopamine sensor with a novel sensing mechanism.[9] The

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gate electrodes used in SGGTs reported before are Ag/AgCl electrodes or metal wires.[3–9] Considering graphene being a semimetal with zero bandgap,[20,21] we fabricated SGGTs with graphene as both channel and gate electrodes for the first time. So the device is mainly made of graphene, which is potentially low-cost and convenient for high-density integration. The device shows stable performance, high sensitivity and the low detection limit down to 1nM to dopamine, which is sensitive enough for characterizing dopamine levels in many biological systems.[22,23] We also find that conventional electrochemical measurements with the same graphene electrode only show the detection limit to dopamine of ~3 μM, which further indicates the advantage of using SGGTs in biosensors. The selectivity of the dopamine sensor is improved by modifying the gate electrode with the biocompatible polymer Nafion.[24] The sensing mechanism can be attributed to the electrochemical reaction of dopamine at the gate electrode, which leads to the change of effective gate voltage applied on the transistor.[3] This work also indicates that the SGGTs with suitable surface modification on the graphene gate electrode can be used as many other types of biosensors with high sensitivity.

2. Results and Discussion

Figure 1a shows the structure of a SGGT with graphene channel and gate. Au electrodes were deposited on glass substrates by thermal evaporation through a shadow mask. Single-layer graphene was prepared by chemical vapor deposition (CVD) method on copper foils and transferred on the substrates with Au electrodes.[20,21] Then the graphene layer was patterned on the substrates with the gate area of 3 mm × 3 mm. The channel width and length of the transistor are 3 mm and 0.2 mm, respectively. The device was then packaged by covering silicone on part of the Au electrodes with only graphene films in contact with electrolyte. So the device can be regarded as a whole-graphene transistor with metal contacts.[25] The device was then immersed in PBS solution and characterized with a semiconductor parameter analyzer (Agilent 4156C). It is notable that the osmolarity and ion concentrations of the PBS solution usually match those of the human body. Therefore, the success of the measurements in PBS solution implies the possible practical applications. The quality of the single-layer graphene film on a glass substrate was characterized by atomic force microscopy (AFM) and Raman Spectrometer (see Supporting Information, Figure S1 and Figure S2).

Figure 2a shows the transfer characteristic (I_{DS} versus V_G) of a SGGT with V_{DS} = 0.05 V. The device shows a typical ambipolar behavior with the Dirac point at about 0.4 V. It is reasonable to find the positive voltage of the Dirac point because graphene is p-type doped in air and water.[1] Then the device was characterized in 1 μM dopamine PBS solution at the same voltages. It is interesting to find that the transfer curve shows a horizontal shift of about 0.3 V to lower gate voltage. To better understand the effect, we fabricated another SGGT device with an Ag/AgCl (sat. KCl) gate electrode (control sample) and characterized it in PBS solution before and after the additions of 1 μM and 10 μM dopamine. However, the control device showed little change after the addition of dopamine (see supporting information, Figure S3). So the response of the device with graphene gate electrode was due to the electrochemical reaction of dopamine at the gate as shown in Figure 1b. Because the transfer curve of the device was characterized at positive gate voltages, the graphene gate can be regarded as an anode. So dopamine is electro-oxidized to *o*-dopaminequinone at the surface of the gate and generates faradic current.[26] To confirm the electrochemical reaction of dopamine, the graphene gate electrode was characterized in 1 mM dopamine PBS solution by cyclic voltammetry (CV) measurements. A redox peak current at about 0.65 V vs. Ag/AgCl was observed (see Supporting Information, Figure S4), which corresponds to the electro-oxidation of dopamine at the graphene electrode.

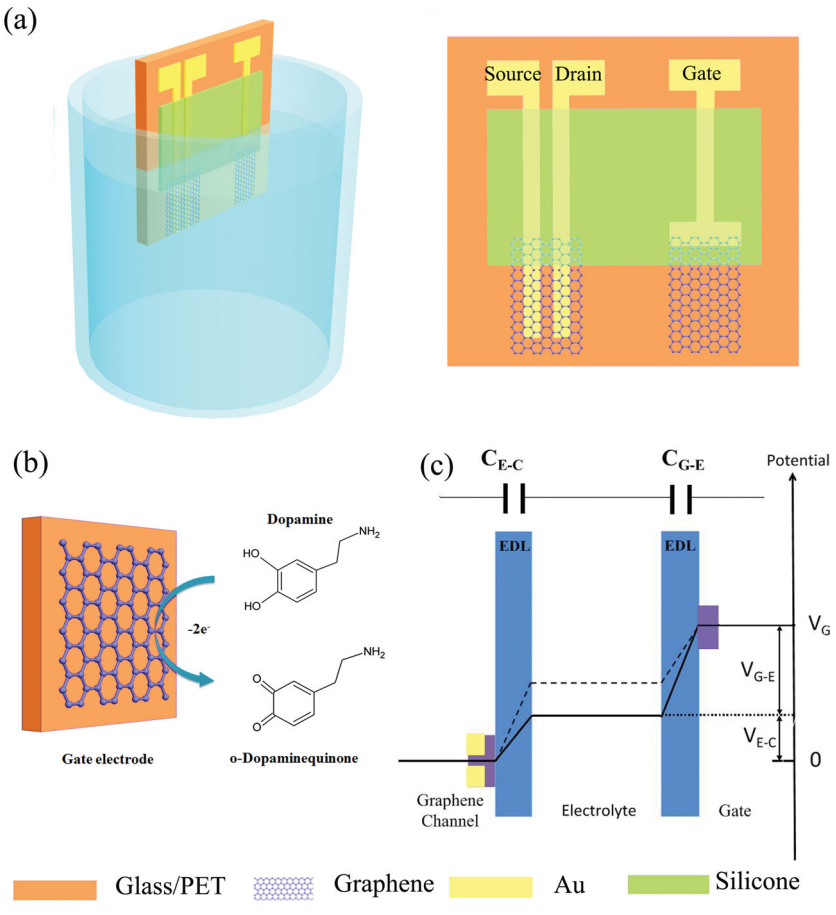

Figure 1. a) Schematic diagram of a SGGT with graphene channel and a graphene gate electrode characterized in electrolyte. b) Electrochemical reaction of dopamine on the graphene gate electrode. c) Potential distribution between the gate and the channel of a SGGT in electrolyte.

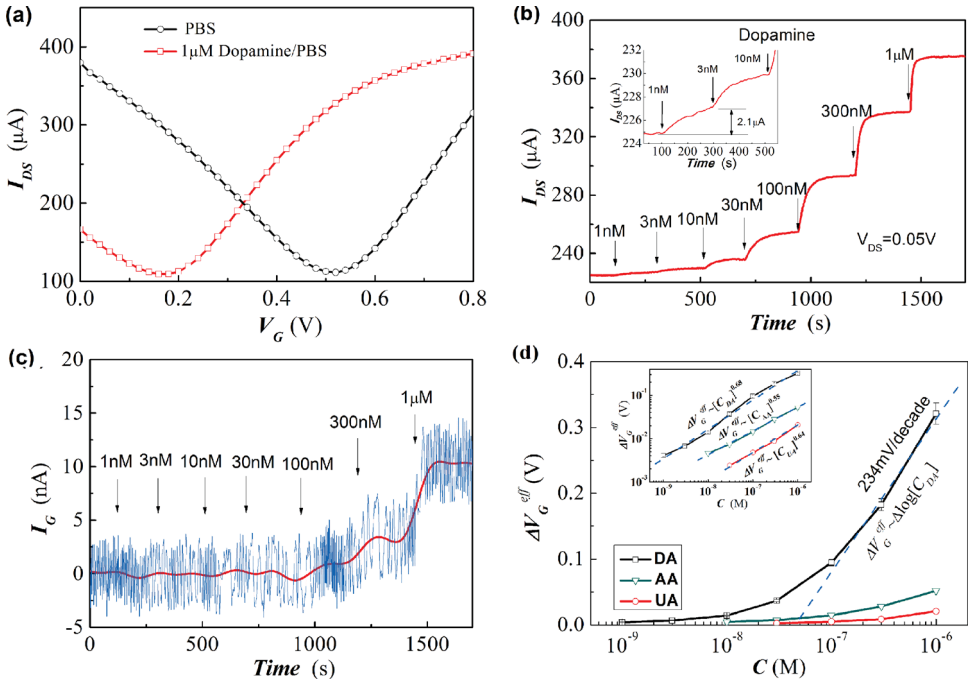

Figure 2. a) Transfer characteristics (I_{DS} vs. V_G, V_{DS} = 0.05 V) of a SGGT measured in PBS solution (pH = 7.4) before and after the addition of dopamine with the concentration of 1 μM. b) Channel current response of the SGGT to additions of dopamine with different concentrations. V_{DS} = 0.05 V, V_G = 0.7 V. c) Gate current of the SGGT during the additions of dopamine with different concentrations. Blue curve: measured gate current. Red curve: average current. d) The change of effective gate voltage (ΔV_G^{eff}) as functions of the concentrations of dopamine (DA), ascorbic acid (AA) and uric acid (UA). Inset: the results fitted with Equation (8).

In blank PBS solution, the potential drop between the gate and the channel under a gate voltage V_G is shown as the solid lines in Figure 1c. The gate voltage was actually applied on the gate/electrolyte and electrolyte/channel interfaces.[3] Assuming V_{G-E} and V_{E-C} are the voltages applied on the gate/electrolyte and electrolyte/channel interfaces, respectively, the gate voltage applied on the transistor is given by: $V_G = V_{G-E} + V_{E-C}$. Similar to the equivalent circuit in other solution-gated transistors,[26,27] the two interfaces can be regarded as two capacitors and thus the gate voltage is given by:

$$V_G = \left(\frac{C_{E-C}}{C_{G-E}} + 1\right) V_{E-C} = (\gamma + 1) V_{E-C}, \quad (1)$$

where $\gamma = \frac{C_{E-C}}{C_{G-E}}$, C_{G-E} and C_{E-C} are the capacitances of the electrolyte/gate and electrolyte/channel interfaces, respectively.[27] Each interface capacitance contains the two series connected capacitors, including electric double layer capacitance and graphene quantum capacitance.[28,29] The capacitance of an electric double layer (10 to 40 μF/cm^2) is dependent on the ion concentrations in the electrolyte and the applied bias voltage.[29] The quantum capacitance of graphene is between zero to tens of μF/cm^2, which is lower than or comparable to double-layer capacitance.[28]

After the addition of dopamine, the electrochemical reaction of dopamine at the gate electrode decreases the potential drop at the electrolyte/gate interface because of the faradic current. Consequently, the voltage applied on the electrolyte/channel interface is increased, as indicated by the dash line in Figure 1c, which leads to the increase of the effective gate voltage applied on the transistor and the shift of the transfer curve of the SGGT to a lower gate voltage.

In sensing applications, it is more convenient to measure the channel current response of the SGGT at fixed gate and drain voltages.[3] Figure 2b shows the response of the channel current (V_{DS} = 0.05 V and V_G = 0.7 V) to different concentrations of dopamine. It is notable that the device can measure dopamine concentrations down to 1 nM (signal/noise ratio > 3). Some devices even show the detection limit down to 0.1 nM (see Supporting Information, Figure S5). On the other hand, as shown in Figure 2c, the gate leakage current measured simultaneously is only about 10 nA, which is four orders of magnitude lower than the channel current of the device. So the channel current response is different from the faradic current due to dopamine reaction at the gate electrode, indicating that the SGGT-based dopamine sensor has a different working principle from the typical electrochemical methods.[18]

The voltage applied on the electrolyte/gate interface V_{G-E} is given by the Nernst equation and an overpotential due to the faradic current:[29]

$$V_{G-E} = E_0 + \eta - 2.30\frac{kT}{ne}\log C_{DA}, \quad (2)$$

where E_0 is a constant; k is the Boltzmann's constant; T is temperature, e is electron charge; n (= 2) is the number of electrons transferred during the electro-oxidation of dopamine; C_{DA} is the concentration of dopamine in the PBS solution, η is the overpotential on the gate related to the faradic current. So the voltage applied on the electrolyte/channel interface is:

$$V_{E-C} = V_G - V_{G-E} = V_G - E_0 - \eta + 2.30\frac{kT}{ne}\log C_{DA}. \quad (3)$$

In the above experiments, the gate voltage (V_G) applied on the transistor is constant. So the increase of channel current can be regarded as the increase of the effective gate voltage V_G^{eff} applied on the transistor. According to Equation (1), we assume $V_G^{eff} = (\gamma + 1)V_{E-C}$ and thus the effective gate voltage corresponding to a channel current can be decided from the transfer curve of the WGSGT characterized in blank PBS solution. The increase of $V_{E\text{-}C}$ will lead to the increase of effective gate voltage V_G^{eff} given by:[26,27]

$$V_G^{eff} = 2.30(\gamma + 1)\frac{kT}{ne}\log C_{DA} - (\gamma + 1)\eta + \text{constant}. \quad (4)$$

Considering the SGGT being a potentiometric transducer that has very low faradic current at the gate as show in Figure 2c, the overpotential η is very low,[29] which is similar to other types of transistor-based biosensors.[27] The relationship between the faradic current density j and the overpotential η at low current is given by Butler-Volmer equation:[29]

$$j = j_0(e^{-\alpha ne\eta/kT} - e^{(1-\alpha)ne\eta/kT}), \quad (5)$$

where j_0 is the exchange current density; α is called standard rate constant, which is normally between 0.3 and 0.7. Figure 2c shows that the faradic current on the gate (area: 0.9 $cm^{[2]}$ is about 10 nA when dopamine concentration is 1 μM, so the current density is about 1×10^{-7} A/cm^2. The exchange current is given by:[29]

$$j_0 = nFk^0C, \quad (6)$$

where C is the dopamine concentration, k^0 is the standard rate constant, F = 9.63×10^4 C/mole. k^0 was measured to be 1.34×10^{-3} cm s^{-1} (See supporting information and Figure S6). So the exchange current is $j_0 \approx 2.6 \times 10^{-7}$A/cm^2 when dopamine concentration is 1 μM.[29,30] Assuming $\alpha = 0.5$, the overpotential is estimated to be about $\eta \approx 5$ mV, which is negligible compared with the effective gate voltage change (~300 mV). So the effective gate voltage can be approximately given by:

$$V_G^{eff} \approx 2.30(\gamma + 1)\frac{kT}{ne}\log C_{DA} + \text{constant}, \quad (7)$$

Figure 2d shows the change of effective gate voltage ΔV_G^{eff} as a function of dopamine concentration C_{DA}. Equation (7) can be used to fit the curve when dopamine concentration is higher than 0.1 μM. However, the curve in the lower concentration region cannot be fitted with this equation for the very weak reaction of dopamine on the graphene gate.

As shown in the inset of Figure 2d, we find that the relationship can be fitted very well with the following equation:

$$\Delta V_G^{eff} = AC_{DA}^{\alpha} \quad (8)$$

where A and α are constants. Such power function has been successfully used in many other transistor-based sensors such as photo sensitive transistors, although it is difficult to be derived analytically.[21,31–33]

In practical dopamine analysis, the main interference comes from ascorbic acid (AA), uric acid (UA), ions and glucose.[34,35] The device did not show any response to glucose when the concentration of glucose was increased up to 10 mM (see Supporting Information Figure S7). Regarding the interference from ions, a SGGT with high quality graphene is not sensitive to ion concentrations as reported in our previous paper.[3] On the other hand, the ion concentrations in body fluids are relatively stable. For example, sodium ion (Na^+) is the major cation in plasma and its concentration is finely maintained within the narrow range of 135–145 mM (less than 8% variation) despite great variations in water and salt intake of human beings.[36] Our device characterized in NaCl aqueous solutions with the concentrations of 100 mM and 300 mM shows very little difference in the transfer curves although the ion concentration is increased for 200% (see Supporting Information Figure S8). It is easy to understand this result. First, even if some SGGTs are sensitive to ion concentrations because of the impurities on the surface of graphene,[3] the shift of transfer curve is normally less than the ideal value given by Nernst equation (59 mV/decade for Na^+).[3] It can be estimated that 8% change of ion concentration in body fluid will lead to less than 2 mV shift of the transfer curve, which is negligible in the measurements. The second factor is the change of double layer capacitance induced by the change of ion concentrations on the surface of graphene, which can induce slope changes of the transfer curves.[3b] It can be found that this effect is negligible in practical applications as shown in Figure S8 in the Supporting Information. Therefore, the influence of ion concentrations in practical applications of the SGGT is negligible.[36]

Then the selectivity of the device was characterized by adding AA and UA in PBS solution (see Supporting Information Figure S9 and S10). The detection limits to AA and UA are 10 nM and 30 nM, respectively. The changes of effective gate voltage as functions of the analyte concentrations are shown in Figure 2d. The responses of the SGGT to AA and UA can be attributed to the direct electro-oxidation of AA and UA on the graphene gate electrode. The curves for AA and UA can be fitted with the functions similar to Equation (8). So the sensitivities of the SGGT to AA and UA are about 1 and 2 orders of magnitude lower than that to dopamine, respectively. However, the concentration of AA is normally two orders of magnitude higher than that of dopamine in human body fluids (e.g., plasma, urine, etc), which severely restricts the effective dopamine determination by using the SGGT.[33,37]

To improve the selectivity of SGGTs to dopamine, the graphene gate electrode was modified with a biocompatible polymer Nafion, which has been used to modify electrodes in biosensors. Because Nafion is negatively charged in PBS (pH = 7.4) solution, it could effectively alleviate the interference from other substances at negatively charged states, e.g., UA and AA, by electrostatic interaction.[24] **Figure 3**a–c shows the channel current responses of the SGGT to additions of dopamine, AA and UA, respectively. The device exhibited detection limits of 1 nM to dopamine, 1 μM to AA and 10 μM to UA, indicating the improved selectivity of the device to dopamine. The induced changes of effective gate voltages were calculated and shown in Figure 3d. The voltage change of the device to dopamine can be fitted very well with Equation (8) down to 5 nM as shown in the inset of Figure 3d. The sensitivities of the device to AA and UA are about 3 and 4 orders of magnitude lower than that to dopamine, respectively. So the selectivity of the SGGTs to dopamine was dramatically improved by the Nafion modification on the gate electrodes.

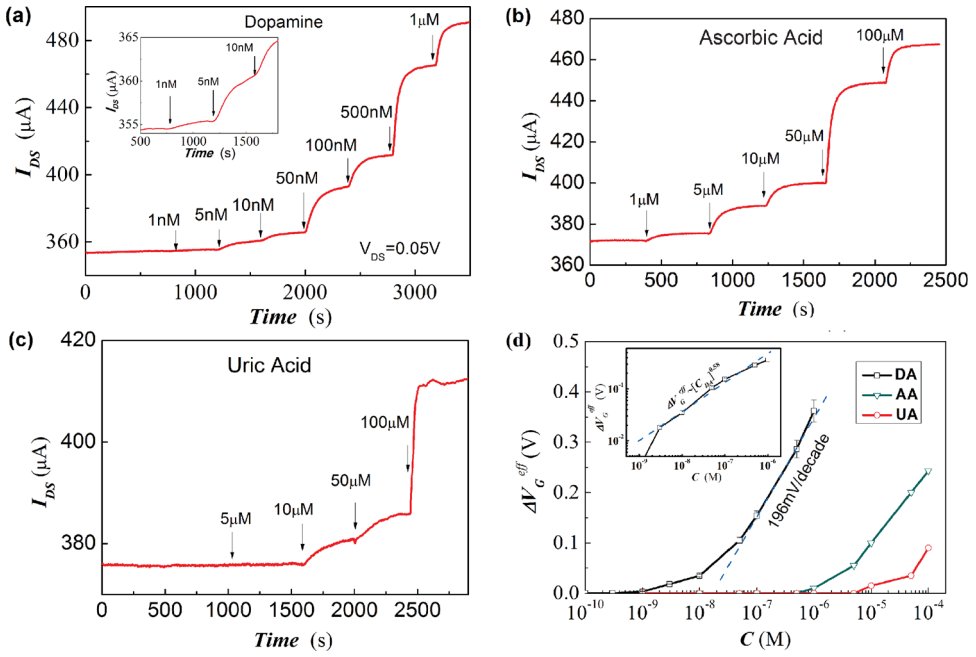

Figure 3. Channel current response of a SGGT modified with Nafion on the graphene gate to additions of a) dopamine, b) AA and c) UA with different concentrations, V_{DS} = 0.05 V, V_G = 0.7 V. d) The change of effective gate voltage (ΔV_G^{eff}) of the SGGT as functions of the concentrations of dopamine (DA), AA and UA. Inset: the response to dopamine fitted with Equation (8).

We found that the SGGT with a graphene gate electrode is even better than a device with a Pt gate electrode in sensing dopamine although Pt electrodes have been popularly used in the electrochemical detections of dopamine.[26] A SGGT with a Pt gate electrode (size: 3 mm × 3 mm) was characterized in PBS solution. **Figure 4**a shows the transfer curve of the device before and after the addition of 1 μM dopamine in PBS solution, which shifts for about 70 mV to lower gate voltage induced by dopamine. Figure 4b shows the current responses of the SGGT to additions of dopamine with different

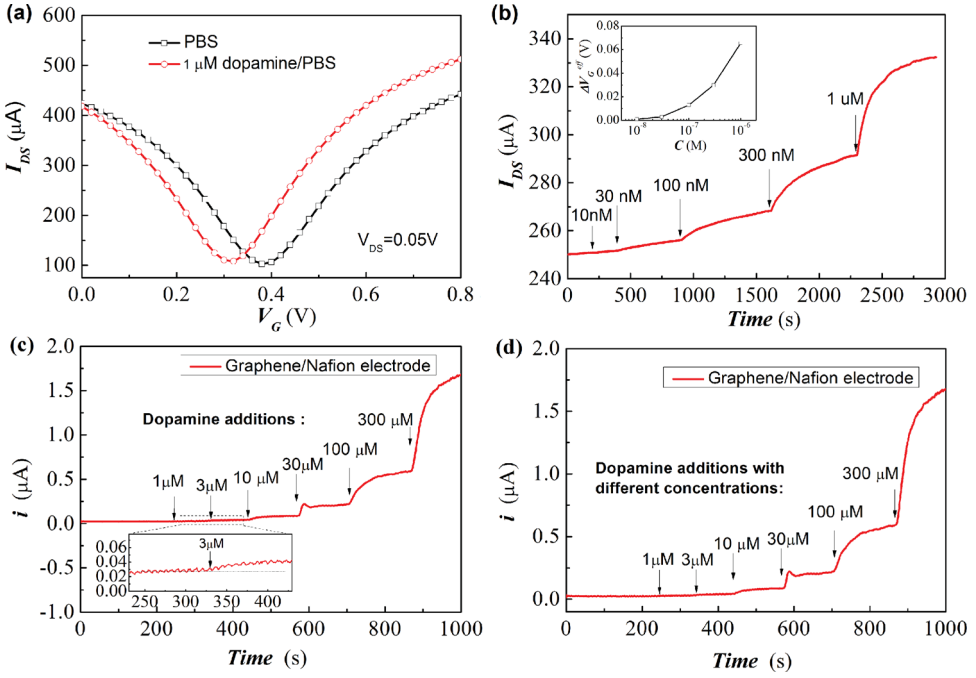

Figure 4. a) Transfer characteristics (V_{DS} = 0.05 V) of a SGGT with Pt gate electrode measured in PBS solution before and after the addition of dopamine with the concentration of 1 μM. b) Channel current response of the SGGT to additions of dopamine with different concentrations. V_{DS} = 0.05 V, V_G = 0.7 V. Inset: the change of effective gate voltage (ΔV_G^{eff}) for different dopamine concentrations.

concentrations. The device exhibits a detection limit of ~10 nM, which is not as good as the device with the graphene gate. The Pt gate electrode was also characterized in pure PBS solution and 1 mM dopamine PBS solution by CV measurements (see Supporting Information, Figure S11). The electro-oxidation of dopamine on the Pt electrode can be observed. It is notable that the current density across the Pt electrode in blank PBS solution is much higher than that of the graphene electrode (see Supporting Information, Figure S4). Therefore, the device with Pt gate electrode shows a high faradic current in PBS solution even without dopamine, which leads to worse selectivity, stability and detection limit of the dopamine sensor.

The changes of effective gate voltage at different dopamine concentrations were calculated and shown in the inset of Figure 4b. For the same dopamine concentration, the gate voltage change is lower than that of the devices with the graphene gates as shown in Figures 2d and 3d. According to Equation (7), the effective gate voltage change is proportional to the value of γ, which is inversely proportional to the capacitance of the gate/electrolyte interface C_{G-E}. A graphene gate electrode has lower interface capacitance than a Pt gate electrode with the same area due to the quantum capacitance of the graphene layer. Consequently, the device with the graphene gate electrode exhibits a higher value of γ and thus a bigger gate voltage change to dopamine than the device with a Pt gate electrode.

To further indicate the advantage of the SGGT-based dopamine sensor, the Nafion modified graphene gate electrode was characterize in PBS solution with a typical electrochemical method. Amperometric responses of the electrode to additions of dopamine are shown in **Figure 5** and exhibit a detection limit of about 3 μM (signal to noise ratio > 3), being similar to the reported results.[38] So the SGGT-based dopamine sensor shows much higher sensitivity than the conventional electrochemical measurements, which is consistent with various transistor-based biosensors reported before.[26]

The SGGTs with graphene gate electrodes are much more sensitive to dopamine than the graphene transistors reported before due to the different sensing mechanism based on the electrochemical reaction of dopamine at the gate electrode.[9] The detection limit of the SGGTs to dopamine is much better than that of many other electrochemical approaches. For example, Zhao et al. reported the electrochemical detection of dopamine with the minimum concentration of 0.55 μM by using poly(sulfosalicylic acid) modified glass carbon electrode.[18] Sheng et al. fabricated electrochemical sensors based on nitrogen-doped graphene and successfully detected dopamine down to 0.5 μM.[39] Guo et al. reported electrochemical dopamine sensors using electrodes modified with carboxylated carbonaceous spheres with the detection limit down to 20 nM.[38] Our group recently reported a dopamine sensor based on an organic electrochemical transistor with the detection limit of 5 nM,[26] which is inferior to the SGGT-based dopamine sensors. Considering the dopamine levels in urine and plasma being in the ranges of μM and nM levels, respectively, the SGGTs are potentially useful for clinical applications in the future.[22,23] The low detection limit of the SGGTs can be attributed to the fact that the devices are sensitive to potential changes given by Equation (7) even when faradic currents are too low to be detected.

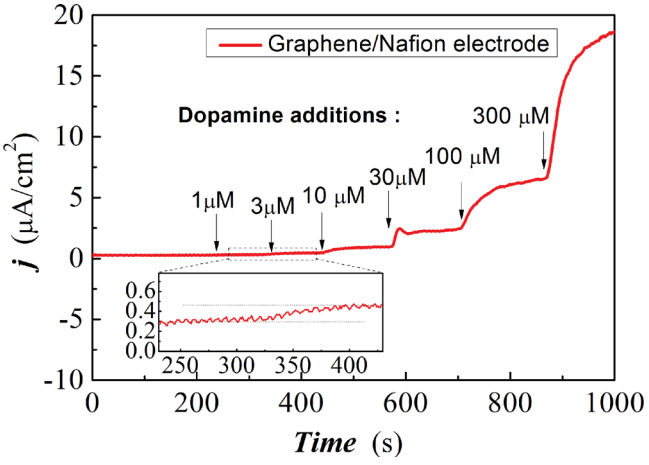

Figure 5. Amperometric response of a Nafion modified graphene electrode (area: 3 mm × 3 mm) to additions of dopamine with different concentrations. The applied potential is fixed at 0.7 V vs. Ag/AgCl. Inset: the detection limit is about 3 μM (signal/noise > 3).

Electrochemical biosensors presently hold a leading position in many sensing applications, including clinical, healthcare, environmental, food, and national defense detections. One main goal in designing new biosensor systems is to achieve greater sensitivity.[40] Besides dopamine sensors, graphene has shown promising applications in many other electrochemical biosensors for its large surface area, high electrical conductivity, good biocompatibility and electrochemical activity, and has been successfully used in modifying electrochemical electrodes with enhanced sensitivity in the detections of AA, UA, cytochrome c, nicotinamide adenine dinucleotide, hemoglobin, cholesterol, H_2O_2 and so on.[41] Due to the high electrochemical activity of graphene, the whole-graphene SGGT devices consequently can be operated as many other sensors with the sensing mechanism based on the electrochemical reaction of analytes on the graphene gates. Obviously, the gate electrodes of the SGGTs should be modified with suitable functional materials to improve the selectivity of each type of biosensors, which is similar to conventional electrochemical biosensors.[37]

3. Conclusion

A highly sensitive dopamine sensor was realized by using a SGGT with a graphene gate electrode. The sensing mechanism of the device is attributed to the electrochemical reaction of dopamine at the gate electrode, which changes the potential distribution at the interfaces on the graphene gate electrode and the graphene channel. The device shows excellent selectivity to dopamine after the modification of the graphene gate electrode with a thin layer of Nafion. The interference from AA and UA is 3 to 4 orders of magnitude lower than the response of the device to dopamine. The device shows the detection limit to dopamine down to 1 nM, which is good enough for analyzing dopamine levels in clinical applications. Because the channel and the gate of the device are all made of graphene, it can be fabricated on various substrates including flexible ones at low temperature by convenient techniques. Based on the same mechanisms, many other types of biosensors can be

developed in the future. Therefore, the whole-graphene SGGT is a promising candidate for disposable, flexible and highly sensitive biosensors.

4. Experimental Section

Preparation of SGGTs: The device design is shown in Figure 1a. Source, drain and gate Cr/Au electrodes were deposited on glass substrates by thermal evaporation through a shadow mask. Single-layer graphene was synthesized on copper foils by CVD method.[3,20] A thin poly(methyl methacrylate) (PMMA) film (~500 nm) was spin coated on graphene and then annealed at about 100 °C for 30 min. Then, it was immersed in an aqueous solution of iron chloride to etch the Cu substrate and washed by distilled water. The graphene/PMMA film was then transferred on the target substrate with Cr/Au electrodes. The PMMA layer was dissolved and removed from graphene by toluene. The graphene layer was then patterned on the susbtrates.[3] In the end, the Au electrodes were packaged with silicone layer.

Nafion solution (5% in a mixture of lower aliphatic alcohols and water) was purchased from Sigma-Aldrich Company. The solution was mixed with 2-propanol with volume ratio 1:1. For the SGGTs with Nafion modified on the gate electrode, 5 μL of the mixture was drop coated onto graphene gate electrode and kept at 4 °C for 4 h to get solvent completely evaporated. The formed Nafion film was rinsed by DI water and dried for future use.

Device Characterization: Before measurements, all of the as-prepared electrodes were immersed in PBS (pH 7.4) for 15 min to remove the residua. The SGGTs were tested at a fixed V_D = 0.05 V at different gate voltages (V_G: 0~0.8 V) and PBS was used as the electrolyte for all measurements. The device performance, including transfer curves (I_{DS} vs V_G) and time-dependent channel currents (I_{DS} vs time), was characterized by using two Keithley 2400 source meters controlled by a computer with a Labview program.

Electrochemical Measurements: Additionally, EG&G PAR2273 Potentiostats-Electrochemistry Workstation was used to characterize the electrochemical properties of the different gate electrodes. The electrochemical responses of the graphene or Pt electrodes to dopamine in PBS solutions were investigated by cyclic voltammetry (CV) with a scan rate of 50 mV/s. Amperometric measurement of a graphene electrode was carried out in a stirred PBS solution by adding dopamine with different concentrations. The applied potential is fixed (+0.7 V) relative to an Ag/AgCl reference electrode.

Graphene Characterization: The surface morphology of the graphene film was characterized by an atomic force microscopy (AFM, Digital Instruments). The graphene film was also characterized under Raman spectroscopy (HORIBA JOBIN YVON, HR800) to check the quality.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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F.Y. conceived the experiments. M. Z. and C. L. fabricated and characterized the devices. Y. Y and Z. L assisted the experiments. F.Y., M. Z., and F. G. discussed the results. F. Y. and M. Z. wrote the paper together. This work is financially supported by the Research Grants Council (RGC) of Hong Kong, China (project number: PolyU5322/10E) and the Hong Kong Polytechnic University (project number: A-PL49, G-YM45 and 1-ZV8N).

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