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A simple poly(3,4-ethylene dioxythiophene)/poly(styrene sulfonic acid) transistor for glucose sensing at neutral pH

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We demonstrate a simple transistor based on the conducting polymer poly(3,4-ethylene dioxythiophene)/poly(styrene sulfonic acid), capable of sensing glucose in a neutral pH buffer solution by a mechanism involving sensing of hydrogen peroxide.

Organic thin film transistors (OTFTs), in which small molecules (such as pentacene) or polymers (such as polythiophene) are used as the semiconductor layer, have attracted enormous attention due to their potential applications in flexible, low-cost electronics and optoelectronics.[1] In these devices, the conductivity of the semiconductor layer is modulated by applying a potential on a gate electrode, which is electrically isolated from the semiconductor by means of a dielectric layer (gate dielectric). The possible application of OTFTs in chemical and biological sensing is beginning to be explored.[2] Advantages of OTFT-based sensors include high sensitivity and selectivity that can be achieved by covalent integration of recognition groups directly on the organic semiconductor, and low manufacturing cost associated with the ease of processing of organics on a variety of substrates, including plastics.

In a parallel effort, conducting polymers, which are the heavily doped form of polymeric semiconductors, have also been investigated in electrochemical transistors for sensing applications.[3] These devices operate in an electrochemical mode, where the conductivity of the polymer is modulated by oxidation or reduction using a standard counter and reference electrode configuration. Their breadth of application is limited by the properties of the polymers used—typically electrochemically grown polyaniline or polypyrrole. Polyaniline, for example, loses its electrochemical activity (hence its ability to sense analytes) in neutral pH environment.[3,4] Although this problem has been mitigated to a certain extent by using polymeric counterions or modified polyanilines,[4,5] there is a need for conducting polymers that operate over a wide pH range and can be prepared at large quantities.

Recently, a commercially available conducting polymer, poly(3,4-ethylene dioxythiophene) (PEDOT) doped with poly(styrene sulfonic acid) (PSS), has been used for the fabrication of OTFTs.[6,7] In one configuration, a fully solid-state device was fabricated by using an insulating polymer layer as the gate dielectric. The conductivity of PEDOT : PSS decreased when a positive voltage was applied to the gate, which was attributed to migration of ions from the gate dielectric into the PEDOT : PSS layer (ion-leveraged mechanism).[6] In a slightly different configuration, the gate voltage was applied through an electrolyte, leading to switching of the conducting polymer between different redox states (electrochemical mechanism).[7] A humidity sensor was developed based on this transistor.[7]

In this communication, we demonstrate a PEDOT : PSS device configuration that can be used for glucose sensing. The main feature of this device is its simple fabrication: sensors can be readily built on a variety of substrates, using solution processing techniques. PEDOT : PSS (Baytron P) is commercially available, and yields sensors capable of operating in a wide range of pH environments. The device can be easily extended to be used in the detection of other biological analytes. The operation mechanism of this device is fundamentally different from traditional potentiometric and amperometric sensors, where the conducting polymer is used as an electrode. We discuss possible mechanisms based on electrochemical[7] and ion-leveraged[6] scenarios.

The device configuration is shown in the inset of Fig. 1. The PEDOT : PSS is spin-coated on a glass substrate, patterned by wiping off the excess material to form a 5 mm wide, 25 mm long stripe, and baked in a vacuum oven at 150 °C for 30 minutes. The gate voltage is applied through a Pt wire electrode, which is immersed in a phosphate buffer saline (PBS) with a pH of 7.14. The solution is confined by an elastomeric well made from poly(dimethyl siloxane) (PDMS) and is in contact with the PEDOT : PSS layer.

Fig. 1 shows that the current that flows in the PEDOT : PSS film (drain current, I_d) can be modulated by the application of a gate voltage (V_g) through the buffer solution. The drain voltage (V_d) in this experiment was set to 0.2 V, and V_g was pulsed according to the sequence shown in Fig. 1. The modulation of I_d is reversible, but also slow, which is indicative of ionic motion in and out of the polymer (see below). In this configuration, V_g and V_d are small, so there is no hydrolysis of the electrolyte. Moreover, at a given V_g, I_d varies linearly with V_d (not shown here) in the range of the measurement. The gate current (I_g) was found to be negligible compared to I_d. In addition, we observed a stable baseline current with V_d = 0.2 V and V_g = 0 V, indicating that there is no degradation of the PEDOT : PSS film under these experimental conditions.

The gating effect observed in Fig. 1 is caused by a decrease in the conductivity of PEDOT : PSS upon the application of a gate voltage that is consistent with, and can be interpreted by either the electrochemical,[7] or the ion-leveraged mechanism.[6] In PEDOT : PSS, PEDOT is doped by PSS and is positively charged, *i.e.* as $PEDOT^+$. According to the electrochemical mechanism, the

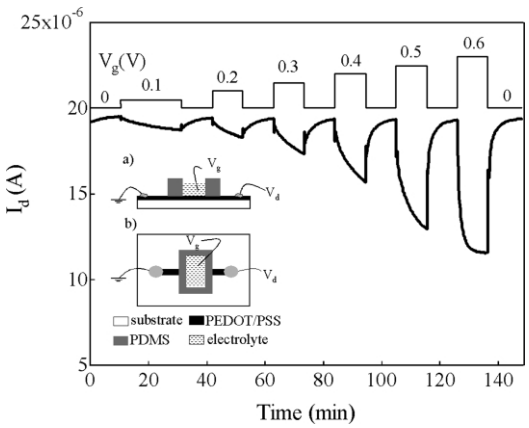

Fig. 1 Drain current I_d of PEDOT : PSS device as a function of time. The gate voltage V_g is modulated from 0 to 0.6 V as shown above. The drain voltage V_d is set to 0.2 V. Inset shows the device configuration. (a) is the side view, and (b) is the top view.

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reaction PEDOT$^+$: PSS$^-$ + Y$^+$ + e^- ⇔ PEDOT + Y$^+$: PSS$^-$ takes place, where Y$^+$ are positively charged ions in the solution.[7] It is this reduction of the polymer that leads to the observed decrease in conductivity upon gating. Charge balance in the device is maintained by an oxidation reaction at the Pt electrode. On the other hand, according to the ion-leveraged mechanism, positively charged ions from the solution drift into the PEDOT : PSS film and disrupt hole tunnelling.[6] This causes a metal to insulator transition which results in a decrease in the conductivity. These two mechanisms should be viewed as representing limiting cases, and can possibly occur at the same time. According to both mechanisms, removal of the gate voltage causes the positively charged ions to diffuse back to the solution and the conductivity of PEDOT : PSS is restored, as observed in Fig. 1.

The device characteristics change dramatically when *both* glucose and the enzyme glucose oxidase (GOx) are present in the buffer solution. In Fig. 2, I_d is monitored as a function of time, where V_d = 0.2 V and V_g is pulsed three times between 0 and 0.6 V. In this experiment, the gate voltage is kept on for only 1 min, resulting in a modulation in the current that is now only 10% for PBS. When GOx is added to PBS, the magnitude of this modulation does not change. In sharp contrast, a large gating effect is observed when glucose is introduced into the solution. Namely, the current decreases by 70% upon gating. A control experiment was performed (not shown here), where first glucose and then GOx were introduced into the solution. The experiment confirmed that a large modulation is observed only in the presence of both enzyme and glucose. Therefore, the mechanism appears to involve a reaction of glucose and GOx.

It should be noted that the I_d baseline in Fig. 2 increases slightly when GOx and glucose are added to PBS, but the change is minor compared to the magnitude of the modulation induced by the gate. The inset of Fig. 2 shows the relative change in I_d as a function of V_g. The plot indicates that the magnitude of the effect can be modulated by the gate voltage.

Fig. 3 shows the relative change in I_d as a function of glucose concentration. For this experiment, various amounts of glucose were added to a PBS solution that contained GOx. A response is seen even at concentrations as low as 0.1 mM of glucose, and reaches saturation above 1 mM. It should be noted however, that these two values depend on parameters such as the amount of GOx present in the PBS solution and the thickness of the PEDOT : PSS film, and have not been optimised in this work.

It is well known that GOx catalyses the reaction of glucose in the presence of oxygen to produce hydrogen peroxide (H_2O_2) and gluconic acid.[8] The latter changes the pH of the solution, and this is what some glucose sensors detect. The modulation in I_d was measured in standard buffer solutions with pH in the range from 5 to 9, and found to be independent of the pH. Therefore, a change in the pH is not the reason for the current modulation in the PEDOT : PSS transistor. This observation indicates that the PEDOT : PSS transistor can be used as a sensor over a wide range of pH environments. The modulation in I_d was found to be extremely sensitive to the presence of H_2O_2. This is shown in Fig. 3, where the relative change in I_d is plotted as a function of H_2O_2 concentration in PBS, indicating that the transistors can be used to detect H_2O_2 in the ppm range. However, the response of the transistor to glucose and to H_2O_2 is not identical, indicating that there are other factors that play a role too.

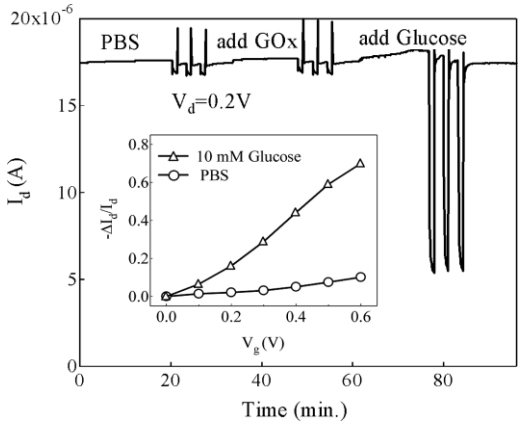

Fig. 2 I_d *vs.* time for the device in PBS solution, in which first GOx, and then glucose are added. V_d = 0.2 V, and V_g is pulsed to 0.6 V for 1 min. Inset shows the relative change of I_d (*i.e.* $-[I_d(V_g = 0\ V) - I_d(V_g)]/[I_d(V_g = 0\ V)]$) as a function of V_g for different solutions.

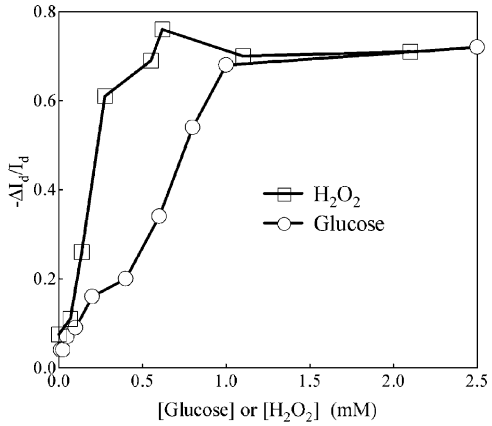

Fig. 3 Relative change of I_d for various amounts of glucose and H_2O_2. Change of $\Delta I_d/I_d$ is defined as $[I_d(V_g = 0\ V) - I_d(V_g = 0.6\ V)]/[I_d(V_g = 0\ V)]$.

The detection of glucose is consistent with an electrochemical mechanism of operation.[7] H_2O_2 is oxidized at the Pt electrode, and, in order to maintain charge balance, PEDOT$^+$ in the film is reduced. An alternative interpretation is that the oxidation of H_2O_2 leads to a redistribution of the potential at the PBS/PEDOT : PSS interface. A standard counter and reference electrode configuration can help discriminate between the two possibilities. Such experiments are now in progress.

In summary, we demonstrate a simple transistor based on the commercially available conducting polymer PEDOT : PSS, capable of sensing glucose in a neutral pH buffer solution. The mechanism involves sensing of hydrogen peroxide. This work is supported by Alliance for Nanomedical Technology, Center for Advanced Technology (CAT), the New York State Office of Science, Technology, and Academic Research (NYSTAR). Terri Wilson is acknowledged for helpful discussions.

Notes and references

1 A. R. Brown, A. Pomp, C. M. Hart and D. M. de Leeuw, *Science*, 1995, **270**, 972; G. Horowitz, *Adv. Mater.*, 1998, **10**, 365; H. Klauk, D. J. Gundlach, M. Bonse, C. C. Kuo and T. N. Jackson, *Appl. Phys. Lett.*, 2000, **76**, 1692; C. D. Dimitrakopoulos and P. R. L. Malenfant, *Adv. Mater.*, 2002, **14**, 99.

2 G. Guillaud, J. Simon and J. P. Germain, *Coord. Chem. Rev.*, 1998, **178**, 1433; B. Crone, A. Dodabalapur, A. Gelperin, L. Torsi, H. E. Katz, A. J. Lovinger and Z. Bao, *Appl. Phys. Lett.*, 2001, **78**, 2229; Z.-T. Zhu, J. T. Mason, R. Dieckmann and G. G. Malliaras, *Appl. Phys. Lett.*, 2002, **81**, 4643.

3 P. N. Bartlett and Y. Astier, *Chem. Commun.*, 2000, 105.

4 D. Raffa, K. T. Leung and F. Battaglini, *Anal. Chem.*, 2003, **75**, 4983.

5 P. N. Bartlett and J. H. Wang, *J. Chem. Soc. Farady Trans.*, 1996, **92**, 4137.

6 J. Lu, N. J. Pinto and A. G. MacDiarmid, *J. Appl. Phys.*, 2002, **92**, 6033; A. J. Epstein, F.-C. Hsu, N.-R. Chiou and V. N. Prigodin, *Curr. Appl. Phys.*, 2002, **2**, 339.

7 D. Nilsson, M. Chen, T. Kugler, T. Renonen, M. Armgarth and M. Berggren, *Adv. Mater.*, 2002, **14**, 51; D. Nilsson, T. Kugler, P.-O. Svensson and M. Berggren, *Sens. Actuators B*, 2002, **86**, 193.

8 A. J. Cunningham, *Introduction to Bioanalytical Sensors*, Wiley, New York, 1998.

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