Hybrid Amperometric and Conductometric Chemical Sensor Based on Conducting Polymer Nanojunctions

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We report on a hybrid chemical sensor that can perform either amperometric or conductometric detection alone or simultaneously. It consists of an array of electrode pairs in which the two electrodes in each pair are separated with micrometer to nanometer-scale gaps. The gaps are bridged with conducting polymer (polyaniline) so that one can measure the conductance of the polymer bridge like a conventional Chem-FET. The electrode geometries are designed to allow simultaneously detection of electrochemical current like a conventional microelectrode amperometric sensor. The hybrid device provides increased selectivity for detection of analytes in complex matrices and may provide new insights into the electrochemical reaction mechanisms of analytes. As an example, we have demonstrated the detection of dilute neurotransmitter (dopamine) in the presence of its concentrated major physiological interferent, ascorbic acid, which is not possible using either the amperometric or the conductometric techniques alone.

Electrochemical detection principles have been widely used in chemical sensors and biosensors.1–3 One of the most successful electrochemical techniques is the amperometric method, which detects electrochemical reaction currents related to target analytes.4,5 Another successful signal transduction mechanism is to detect target species-induced change in the electrical conductance of a sensing element made of materials such as silicon,6,7 conducting polymers,8–10 carbon nanotubes,11,12 metal oxides,13,14 and metals.15 These conductometric approaches have shown particular advantages when the size of the sensing element is shrunk down to nanometer scale. Examples include significant improvements in the sensitivity and time response of the sensors, due to the increased surface to volume ratio of the sensing element.6–9,11,13–15 In addition, the conductivities of many sensing materials may be controlled with a gate voltage in the fashion of field effect transistors (FET), which provide further flexibility for chemical and biosensor applications.10,16 However, both amperometric and conductometric detections have their intrinsic limitations. Electrochemical detection can be rather selective and sensitive, but they are susceptible to electroactive interferents that also contribute to the measured total electrochemical reaction current. For example, the amperometric method can detect dopamine (Dpm), a neurotransmitter, via measuring the oxidation current of Dpm.4,17,18 But ascorbic acid (AA) in physiological fluid is more easily oxidized and more concentrated than Dpm and, thus, a serious interferent for electrochemical detection of Dpm.5,19 The selectivity of conductometric methods relies primarily on specific binding or interaction of a target species onto the sensing materials functionalized with receptor molecules,8 which is often inadequate due to nonspecific binding.

In this paper, we demonstrate a hybrid amperometric and conductometric device that retains the advantages of both amperometric and conductometric methods while removing some of the serious drawbacks associated with each of them when used alone (Figure 1A). The hybrid device can detect an analyte via either an electrochemical current signal or conductance signal separately or both signals simultaneously. This hybrid approach enhances selectivity for detection of analyte in complex matrices, even in the presence of interferents with much higher concentrations than the analyte itself. Using the device, we have detected Dpm in the presence of AA at 3 orders of magnitude higher concentration.19 This capability cannot be achieved using either the amperometric or the conductometric methods alone.

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EXPERIMENTAL SECTION

Device Fabrication. We used a 360-µm-thick Si (100) wafer (7–13 Ω-cm resistivity) covered with a 50-nm thermal SiO₂ insulation layer. We then patterned the Si substrate with an array of Au electrode pairs using standard photolithography tools (Figures 1B and 2A). The separation between the two electrodes in each pair was ~1–2 µm. The Au electrodes were thermally evaporated with a thickness of 60–100 nm on top of ~8-nm Cr adhesion layer. A 400-nm-thick Si₃N₄ layer was deposited by chemical vapor deposition on the entire wafer except for a 10-µm-wide strip that exposes the gap regions of all the electrode pairs. The Si₃N₄ layer served as an insulation layer to minimize leakage current due to ionic conduction, which is important for carrying out electrical measurement in electrolytes. The leakage

Amperometric: \[ I_{2,ec} = I_2 - I_d \sim I_1 \]

Conductimetric: \[ I_d = I_1 \cdot I_{1,ec} \sim I_1 \]

Figure 1. (A) Schematic illustration of a hybrid amperometric and conductometric sensor. WE₁ and WE₂ represent two working electrodes (source and drain electrodes) connected with a conducting polymer bridge. RE and CE are reference and counter electrodes, respectively. The electrochemical gate potential \( (V_g = E_1) \) is applied between the drain electrode (WE₁) and RE, and a bias voltage \( (V_{bias}) \) is applied between WE₁ and WE₂. (B) Optical and scanning electron microscope images of the device made of an array of polymer bridges on a silicon chip. (C) Simultaneous conductometric \( (I_d) \) and amperometric \( (I_{2,ec}) \) detection of HQ. The first 2 injections (labeled “1 and 2”) are supporting electrolyte. The injections of HQ (labeled “3 and 4”) induce increases in \( I_{2,ec} \) due to the oxidation of HQ to quinone (Q) (or HQ \( \rightarrow Q + 2e + 2H^+ \)) and decreases in \( I_d \) due to the oxidation of the polymer bridge by the reaction product, Q. \( V_g (E_1) = 0.2 \) V, \( V_{bias} = 0.25 \) V. See text for details.

Figure 2. Dark-field optical images of (A) a bare electrode pair, (B) electrode pair after Au electrodeposition onto WE₂, (C) Au electrodeposited electrode pair after the formation of polyaniline nanojunction, (D) \( I_d \) vs \( V_g \) curve of polyaniline nanojunction in supporting electrolyte (forward swept at 60 mV/s), and (E) sensitivity of the amperometric–conductometric device \( (\Delta I_d/\Delta I_{2,ec}) \) as a function of \( G_{max} \), which measured the amount of polymer deposition. Labels, P2–P6, represent 4 different devices. Inset: sensitivity of two devices as a function of HQ concentration.
current was typically a few picoamperes. In order to decrease the gap between the two Au electrodes in each pair, we electrochemically deposit Au onto one of the two electrodes using a method reported elsewhere.\(^{20}\) A Pt coil and a Ag wire were used as counter electrode and as quasi-reference electrode, respectively. The quasi-reference electrode was calibrated against the more commonly used Ag/AgCl (in 3.0 M KCl). The electrode potentials were controlled using a homemade bipotentiostat. The electrodeposition of Au was carried out by holding the electrode potential at \(-0.35\) V versus Ag/AgCl 0.4 M citric acid (pH 4) containing 10 mM NaAu\((\text{S}_2\text{O}_3)^-\). During the electrodeposition process, the current between the two electrodes was monitored continuously. Initially, the current was small and entirely due to ionic leakage current. The process was performed at different time deposition to obtain a different gap size.

**Polymer Deposition.** After completing the fabrication of the electrodes, we thoroughly rinsed the chip with 18 M\(\Omega\) cm water to remove Au deposition solution and dried it out with \(\text{N}_2\) gas. The device was transferred to a probe station with a hydrophobic cell made by PDMS on top of the device. Polyaniline was deposited onto the electrodes by sweeping the electrode potentials between 0 and 0.9 V (vs Ag/AgCl) at 50–70 mV/s in 0.12 M aniline + 0.5 M H\(_2\)SO\(_4\) + 0.13 M NaH\(_2\)SO\(_4\)+ 2.7 mg/mL poly(4-styrene-sulfonate) (7000 g mol\(^{-1}\)). The bias voltage applied between two working electrodes was 10–50 mV using the homemade bipotentiostat. When the growing polyaniline strands started to bridge the gap, the current increased sharply. By controlling the number of potential cycles before stopping the deposition process, different amounts of polyaniline bridged between the gaps were obtained. After fabrication of the polymer bridge, the entire chip was then gently rinsed with DI water.

**Amperometric—Conductometric Sensor Measurements.** We performed the amperometric and conductometric measurements using the homemade bipotentiostat. The bipotentiostat was used to control the potential of the two electrodes in each pair with respect to the quasi-reference electrode. It also has a current amplifier for amperometric detection. To perform the conductometric measurement, we used an electrometer (Keithley, model 617). All measurements described here were carried out in 50 mM H\(_2\)SO\(_4\) to demonstrate the concept of the hybrid amperometric—conductometric device. However, other conducting polymer materials work at or near neutral pH (pH 7.2–7.4).\(^{21}\)

**RESULTS AND DISCUSSION**

**Principle of the Hybrid Device.** We describe here briefly the working principle of the device. The key component of the device is a pair of asymmetric working microfabricated electrodes (WE\(_1\) and WE\(_2\)) on the silicon chip, one (WE\(_2\)) has a much larger (>20 times) area than the other one (WE\(_1\)) (Figure 1A). The two electrodes are separated by a gap varying from a few hundreds to a few tens of nanometers, which is bridged with conducting polymer. This electrode design, based on the following consideration, allows one to simultaneously measure the conductivity of the polymer bridge and the current due to electrochemical reactions of analytes taking place on WE\(_2\). The potentials of WE\(_1\) and WE\(_2\) are independently controlled with respect to the quasi-reference electrode using the bipotentiostat, and the associated currents, \(I_1\) and \(I_2\), of the two electrodes are monitored. The potential difference, \(E_2 - E_1 = V_{\text{bias}}\), is the bias voltage between the two electrodes, which drives a current, \(I_b\), through the polymer bridge. This current \((I_b)\) measures the conductivity of the polymer bridge, which is related to \(I_1\) and \(I_2\) by \(I_1 = I_0 + I_{\text{ec}}\) and \(I_2 = I_0 + I_{\text{tec}}\), where \(I_{\text{ec}}\) and \(I_{\text{tec}}\) are currents due to electrochemical reactions. We minimize the electrode area of WE\(_1\) so that \(I_{\text{ec}}\) \(\sim\) 0. So \(I_2 \sim I_1\) gives the conductivity of the polymer bridge (conductometric) and \(I_{\text{tec}} \sim I_3 - I_0\) measures the electrochemical reaction current (amperometric). Since the device operation is analogous to an electrochemically gated field effect transistor, \(I_3\) in this paper is also referred to as the drain current.

Many electrochemical reaction schemes can induce changes in \(I_3\) and \(I_{\text{tec}}\). In the present paper, we analyze two cases: (1) Independent amperometric—conductometric detection. The analyte, such as AA, is electrochemically active and irreversible. When AA arrives at the device surface, it is electrochemically oxidized and the associated oxidation current through WE\(_2\) is detected. In the meantime, AA interacts with the polymer, which changes the conductivity of the polymer bridge due to the reducing property of AA (see scheme in Figure 3C and details below). (2) Dependent amperometric—conductometric detection. The analyte is electrochemically active and quasi-reversible. Dpm and hydroquinone (HQ) are two examples studied here. As with the first case, Dpm and HQ can be oxidized electrochemically and are detected in amperometric mode. However, unlike the previous case, Dpm and HQ do not affect the conductivity of the polymer bridge. Instead, the reaction products, dopaminequinone (DQ) and quinone (Q), of the two analytes are detected on the polymer bridge due to the changes in the redox activity of the polymer by the reaction products. Figure 1C shows an example of simultaneous measurement of \(I_3\) and \(I_{\text{tec}}\) upon successive injections of supporting electrolyte (1–2) and HQ (3–4). The injections of supporting electrolyte cause only transient spikes in the currents due to mechanical disturbance, but the injections of HQ induce increases in \(I_{\text{tec}}\) due to the oxidation of HQ to Q at WE\(_2\) and decreases in \(I_3\) values as the reaction product, Q, tends to oxidize the polymer (see below).

**Optimization of Amperometric—Conductometric Device.** In order to achieve the best performance of the hybrid device, several device parameters were optimized. First, as we have discussed already, small WE\(_1\) and large WE\(_2\) are preferred. This is because small WE\(_1\) (area) reduces electrochemical current on WE\(_1\), so that \(I_1\) is essentially the same as the drain current that measures the conductivity. A relative large WE\(_2\) is important since it collects the electrochemical current, which is proportional to the area of the electrode (Figure 1A).

Second, the size of the gap between the two electrodes is a key to reach low detection levels and fast response in the conductometric mode. We have demonstrated picomolar-range detection limit (ppt)\(^{22}\) and few-millisecond time response\(^{23}\) for detection of heavy metal ions\(^{22}\) and glucose\(^{23}\) by using polymer bridges of few tens of nanometers. The starting gap size of the microfabricated electrodes in the present work was 2 \(\mu\)m, which was further reduced by selectively depositing metal on WE\(_2\).\(^{20}\) This

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\(^{21}\) Kim, B.-H.; Díaz, A.; Forzani, E. S.; et al. unpublished results.


method has allowed us to control the gap size from micrometers down to a few nanometers. Figure 2A,B shows dark-field optical images of a device before and after electrodeposition of Au, which shows a decreased electrode gap and roughened WE2 (larger electrode). Figure 2C shows images of the same device after the formation of the polymer nanojunction (bridge). The best gap sizes have been defined between hundreds of nanometers and tens of nanometers for HQ or dopamine detection (Figure 1B). Smaller gaps allow us to fabricate small polymer bridges, which give higher sensitivity in the conductometric mode because of the large surface to volume ratio of polymer material. It also allows electrochemical reaction products generated at the relative large WE2 to quickly diffuse and reach the entire polymer bridges for conductometric measurements.

We have studied the dependence of the device sensitivity on the polyaniline bridge size. The conductance of polyaniline obtained at small bias voltage ($V_{bias}$) is strongly dependent on the potentials of the electrodes ($E_1$ and $E_2$). Note, at a small bias voltage, $E_1$ and $E_2$ are about the same. Figure 2D shows the drain current of a polymer nanojunction as a function of $E_1$ ($V_g$) at a constant bias voltage. At low gate potentials, the polymer is in the reduced state (leucoemeraldine), which is insulating, and the conductance ($I_d$) is small. The conductance increases with the increase of gate potential ($V_g$ or $E_1$) as the polymer is transformed.
into the conducting oxidized state (emeraldine). Further increasing the gate potential oxidizes the polymer to a second insulating state (perigraniline), which results in a decrease in the conductance.24 $G_{max}$, the maximum conductance of the polymer bridge, provides a good measure of the size of the polymer bridge. We fabricate the polymer bridge by cycling the potentials of the electrodes in the presence of aniline. The potential cycling polymerizes aniline into polyaniline and deposits the polymer across the electrodes. By controlling the number of potential cycles (c.), we can control the size of the polymer bridge.

One way to characterize the sensitivity of the conductometric mode is to determine $\Delta I_d/\Delta I_{2,ec}$ at a constant HQ concentration, where $\Delta I_d$ is the change due to Q (HQ electrochemical product) reaction on the polymer, and $\Delta I_{2,ec}$ is the electroxidation current of HQ (Figure 1C). For a given set of electrodes of constant geometry, $\Delta I_{2,ec}$ is constant if the HQ concentration and electrode potentials are fixed, but $\Delta I_d$ depends on the size of the polymer bridge. We found that $\Delta I_d/\Delta I_{2,ec}$ increases rapidly when the amount of polymer bridging the gap decreases (Figure 2E). This observation can be attributed to the large surface to volume ratio for small polymer bridges. This trend was observed at different HQ concentrations (inset of Figure 2E).

In addition to optimizing the device geometry for sensitive and selective detection of analytes, we can also tune the performance of the device by adjusting the potentials of the electrodes. The potentials control the conductance of the polymer nanojunctions via control of the redox state of the conducting polymer (Figure 2D). They also control electrochemical reactions of analytes on the two electrodes. The potential difference is the bias voltage, which allows one to control the drain current. By adjusting the potentials, one can optimize the selectivity of the device for detecting an analyte in a complex matrix. We describe below how one may achieve selective detection of Dpm in the presence of high-concentration AA by properly controlling the potentials and by combing the amperometric and conductometric methods. Such a hybrid approach may also provide new insight into the reaction mechanisms of analytes.

**Case A: Independent Amperometric—Conductometric Detection. Detection of Ascorbic Acid.** Figure 3A shows a cyclic voltammogram ($I_{2,ec}$ vs $V_g$) of 2.2 mM AA on a polyaniline-modified microelectrode (WE$_2$), where the rapid increase near 0.2 V (vs Ag/AgCl) in current is due to the oxidation of AA. First, we show the detection of AA by operating the device at the conductometric mode alone (Figure 3B). This was achieved by holding the potentials ($E_1 = V_g = 0.20$ V and $E_2 = 0.45$ V). In this case, $I_{2,ec}$ increased upon AA injection due to electrochemical oxidation of AA on WE$_2$ (Figure 3C, red curve). In parallel, an increase in $I_d$ was also observed (Figure 3C, blue curve). The observed increase in the conductivity is because the device was operated on the right side of the bell curve maximum at $E_1$ (or $V_g$) = 0.2 V and AA reduces the polymer (Figure 2D, right side arrow, upward direction). These experiments indicate that AA can be detected by operating the hybrid device either in the conductometric or the amperometric mode alone.

**Case B: Dependent Amperometric—Conductometric Detection.** We now turn to the case where the analytes by themselves do not affect the conductivity of the polymer bridges, but their reaction products can interact with and change the conductivity of the polymer bridges. In other words, we must turn on the amperometric mode in order to use the conductometric mode in this case. This dependent operation can provide better discrimination against possible interferents.

**Detection of HQ or Dpm.** Figure 4A is a cyclic voltammogram of 3.9 mM HQ on a polyaniline-modified microelectrode, which shows a large increase in current, due to the electrooxidation of HQ, when increasing potential above 0.2 V. The reaction pathway

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Figure 5. Amperometric–conductometric detections of HQ (A), AA (B), and a mixture of HQ and AA (C). $V_{bias}$ = 0.25 V, and $E_2$ = 0.45 V. Labels 1 and 2 are injections of supporting electrolyte, and labels 3 and 4 are injections of the analytes. (D) $\Delta I_d/\Delta I_{2,ec}$ and $\Delta I_d$ vs AA/ HQ concentration ratio. Insets in (A–C) illustrate the reaction mechanisms.

**Detection of Dpm in the Presence of High Concentrations of AA.** The amperometric method has been used to monitor neurotransmitters such as Dpm through oxidation currents. One of the major difficulties is the presence of a large amount of AA, which is also oxidizable. To demonstrate the usefulness of the hybrid sensor, we performed detection of dilute Dpm (hundreds nM—few µM range) in the presence of highly concentrated AA (1–2 mM range). Figure 6A shows the time course of simultaneous amperometric and conductometric operations with the hybrid device. Dpm was successively injected in the presence of 3 orders of magnitude more concentrated AA. As before, initial injections of supporting electrolyte are performed to monitor the stability of the conducting bridge toward injections (1–3) to ensure no significant changes in the currents due to mechanical disturbance of solution injections. After that, AA was injected to bring AA concentration to the level of millimolar range (4), which causes large increases in both $I_d$ and $I_{2,ec}$. After $I_d$ and $I_{2,ec}$ reached steady states, Dpm was injected (5–7). Since AA is much more concentrated ($\sim 10^3$) than Dpm, the injection of Dpm did not result...
in a measurable amount of change in the electrochemical current ($I_{2,ec}$) (Figure 6A,B). However, the electrochemical product of Dpm (dopaminoquinone) even at relatively low concentration causes significant change in the conductivity of the polymer bridge (see inset scheme in Figure 6A). The experiment demonstrated that dilute or small changes in Dpm ($\geq 100 \text{ nM}$) can be detected continuously in the presence of a major physiological interferent (AA) ($\sim 1 \text{ mM}$) with the hybrid amperometric–conductometric device.

CONCLUSIONS

We have demonstrated a hybrid device that can detect analytes using either conductometric or amperometric mode, or both modes simultaneously. The device consists of an array of conducting polymer nanojunctions; each nanojunction is polyaniline bridged between two electrodes. By carefully designing and optimizing the electrode geometries and separations, the device allows conductivity and electrochemical reaction current to be detected independently. It overcomes many drawbacks associated with the conventional electrochemical and conductometric (or Chem-FET) sensors. The major advantages of the hybrid device include the following: (a) improved selectivity and sensitivity over devices based on either amperometric or conductometric detection alone; (b) detection of an analyte in the presence of interferents at orders of magnitude of higher concentrations; (c) integration of both detection methods (amperometric and conductometric)
using an array of many parallel devices on a single chip, which promises a miniaturized sensor for detecting multiple analytes. We have illustrated the applications of the hybrid device using Dpm and HQ in the mixed medium with AA. We anticipate that the hybrid approach will lead to other chemical or biochemical applications for detection of analytes in gas phase, cultures, and tissues.

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