HTML ABSTRACT + LINKS

Magnetic-field-assisted assembly of metal/polymer/metal junction sensors

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We present a method to assemble Au/polyaniline/Au junctions and demonstrate a chemical sensor application. The building blocks consist of an array of microelectrodes on a silicon chip, microfabricated metallic bars, and a thin polyaniline layer deposited on the microelectrodes or on the bars. The individual bars suspended in solution are placed, with the help of a magnetic field, across the microelectrodes to form the junctions. The polyaniline layer is ~30 nm thick and modified with glycine-glycine-histidine oligopeptides. Strong binding of Cu^{2+} to the oligopeptide is converted into a conductance change of the junctions, allowing selective detection of trace amounts of Cu^{+2} ions. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1633678]

Nanostructured materials are attractive for sensor applications because of their unique properties that promise high sensitivity and fast response time. A number of sensor concepts based on nanostructures have been demonstrated.[1–9] Despite these advances,[10–14] the following challenges remain in many device applications based on nanostructures. The first one is to find a practical way to assemble and wire individual nanostructures into a circuit. The second challenge is to modify individual nanostructures with different molecular probes such that each one can detect a specific target species. In this letter, we present a magnetic-field-assisted method to assemble an array of electrically wired polymer junctions functionalized with oligopeptides for chemical sensor applications. This array of polymer junctions is an attractive approach to building sensors to detect simultaneously a variety of chemical species.

Our sensor consists of three basic building blocks: (1) (Au/Ni/Au) metallic bars formed by thermal evaporation and suspended in aqueous solution, (2) an array of parallel microelectrodes on a silicon chip, and (3) a thin layer of peptide-functionalized polyaniline deposited on the bars or on the microelectrodes (Fig. 1). We assemble the building blocks into a sensor by exposing the microelectrodes to the solution containing metal bars in the presence of a magnetic field. The magnetic field lead the bars to the surface of the chip and at the same time aligns them perpendicular to the microelectrodes, allowing each bar to bridge two microelectrodes. After removing the solution, the bars are immobilized onto the microelectrodes due to interfacial forces between the bars and the substrate. For each bar bridging two microelectrodes, two polymer junctions are formed. A single polymer junction can be simply formed by leaving one microelectrode free of conducting polymer to form an ohmic contact between the bar and the microelectrode. The dimensions of the metallic bars are $4\,\mu m \times 1\,\mu m \times 0.17\,\mu m$, which can be scaled down.

The thin conducting polymer layer sandwiched between the microelectrodes and the bars allows us to directly convert a chemical binding event into an electrical signal. To date, many conducting polymer-based sensors have been reported for various applications.[15–17] A key parameter is the thickness of the junction, which is controlled by that of the polymer layer. In the present experiment, the thickness of the junction is about 30 nm. This value is determined from images obtained with a tapping mode atomic force microscope (AFM). The ability to form a thin layer is essential for electrical measurements because polyaniline is a poor conductor near $pH=7$ (required for most biosensors). We note that a junction of this thickness cannot be easily fabricated using conventional lithography techniques.

In order to selectively detect different species, we have attached an oligopeptide to the carboxylic groups of the poly(acrylic acid)[18,19] incorporated into the polyaniline thin layer during polymerization. We choose peptides because the number of peptides with different sequences is virtually unlimited,[20–22] and yet different peptides can be attached to the polymer junctions with the same procedure. By attaching different peptides to the bars, it is possible to form, on the same chip, many polymer-based junctions that selectively detect different species. We demonstrate the principle using a simple 3-amino acid oligopetide, glycine-glycine-histidine (GGH)[23] to selectively detect Cu^{2+} up to 10 ppt.

The microelectrode array with bonding pads for external electrical connections was fabricated using conventional photolithography. The microelectrodes are 100 nm thick Au

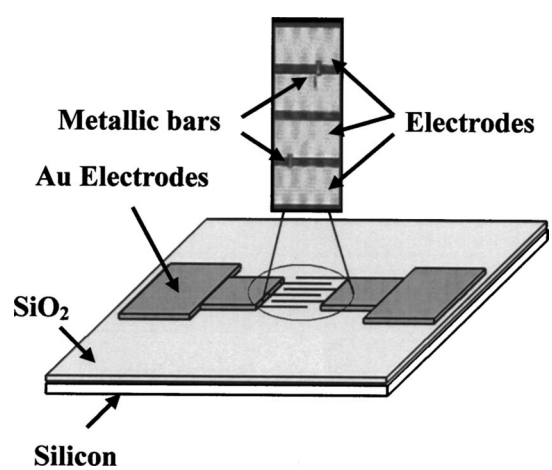

FIG. 1. Schematic diagram of the magnetic-field-assisted assembly of the Au/polymer/Au junctions. Top is an optical image of an actual device.

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lines on a 5 nm thick Cr layer deposited on oxidized silicon wafer (~200 nm SiO_2). The width of the microelectrodes is 10 μm and the separation between them is 3 μm. The Au/Ni/Au bars' suspension is prepared using the following procedure. First, a thin layer (100 nm) of aluminum "sacrificial layer" is evaporated on a silicon wafer. A large array of bars is then printed on the photoresist/Al/wafer using photolithography. After evaporating 50 nm Au, 70 nm Ni, and 50 nm Au in sequence, the Ni layer is magnetized along the long axis with an external magnetic field. The wafer is sonicated in acetone for 15 min to remove excess photoresist, leaving an array of metallic bars on the wafer. Finally, the metallic bars are freed from the wafer by sonicating the wafer in a solution containing 0.1 M sodium hydroxide for 20 min and then transferred into a vial containing pure water.

We deposited polyaniline on the microelectrodes or bars electrochemically using the procedure described subsequently. In the case of the bars, the deposition occurred before lifting the bars off the Si wafer, so that only one side of each bar is covered with a thin polymer layer. The electrolyte was 0.1 M H_2SO_4+0.5 M Na_2SO_4 (pH$<$0.2) containing 0.2 mM aniline and 15 mg/mL poly(acrylic acid). The potential was controlled with a bipotentiostat using a platinum wire as counter-electrode and a silver wire as quasi reference electrode. By cycling the potential between -0.2 and 0.6 V at a scan rate of 0.1 V/s, aniline was polymerized into polyaniline with poly(acrylic acid) as counter ions. The thickness of the polymer layer was controlled by the number of potential cycles. For metal ion detections, we attached GGH oligopeptide to the mixed polymer layer via peptide bonding between GGH and the carboxylic groups of poly(acrylic acid).

We assembled the functionalized polymer junctions by placing a microelectrode chip into the vial containing metal bars suspended in solution. A magnet was then positioned under the chip to direct the suspended bars toward the microelectrode chip. The microelectrode chip with the bars on its surface was then rinsed with pure water while resting on a magnet, keeping the bars to the desired orientation. Finally, the excess solution was removed and the bars were immobilized onto the microelectrodes to form Au/polymer/Au junctions. The bars adhere well to the microelectrodes, so that the junctions stay intact after repeated rinsing of the chip.

As a preliminary test, we studied the response of the Au/polyaniline/Au junction sensor to hydrochloric acid (HCl) and butylamine vapors (Fig. 2). We should mention that the polymer layer used for this test is free of polyacrylic acid and oligopeptides. The current is very small before exposing the junction to HCl [Fig. 2(a)]. After exposure to 5 ppm of HCl, the current increases immediately and reaches a plateau in a few seconds. The current increase as a result of exposure to HCl is due to the well-known proton doping effect. The fast response is due to the small volume (1 μm $\times$0.5 μm$\times$30 nm) of the metal/polyaniline/metal junction, which can be improved by further decreasing the bar dimensions. We then exposed the same junction to 20 ppm butylamine, which triggers an immediate current drop from [Fig. 2(b)]. The current drop can be attributed to the deprotonation of polyaniline by butylamine. Both the sensitivity and response time of our Au/polymer/Au junction sensor exceed the recently reported chemical sensor based on polyaniline nanofibers for HCl and butylamine.[9]

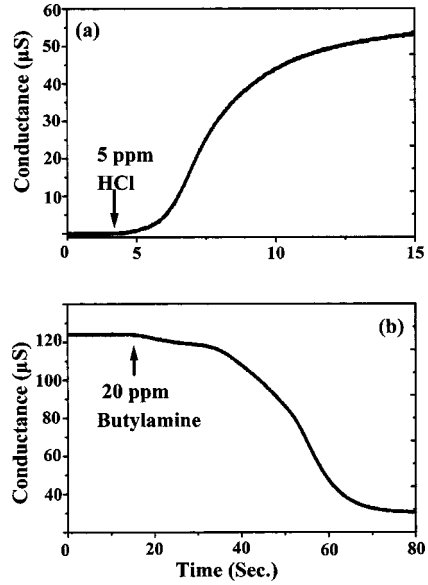

FIG. 2. Conductance response of Au/polyaniline/Au junction to vapors of (a) HCl and (b) butylamine.

Conducting polymers alone are limited both in the number of species that can be detected and in the selectivity of the detection. For these reasons, many biological molecules, such as DNA and enzymes have been attached or incorporated in polymers. In this work, we present a method to attach oligopeptides to polyaniline. We demonstrate the principle using GGH, a three-amino-acid oligopeptide that binds strongly and selectively to Cu^{2+}.

We have measured the $I-V$ characteristics of the GGH functionalized polyaniline junction by exposing the junction to solutions of various Cu^{2+} concentrations. Figure 3(a)

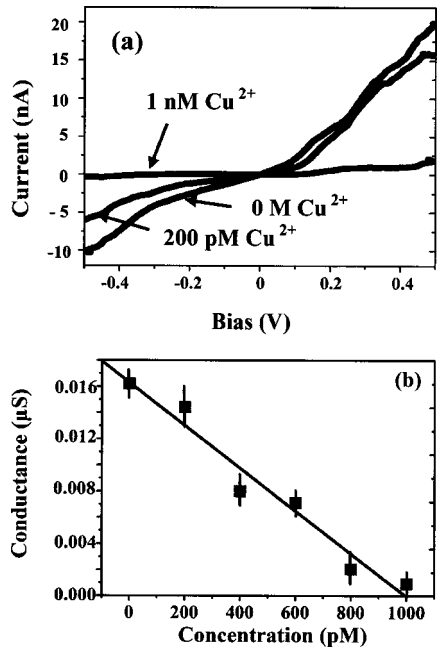

FIG. 3. (a) $I-V$ characteristic response of GGH peptide-incorporated in polyaniline/poly(acrylic acid) composite junction to Cu^{2+} ions. (b) Conductance of the Au/functionalized polymer/Au junction as function of concentration of Cu^{2+} at -0.4 V applied bias.

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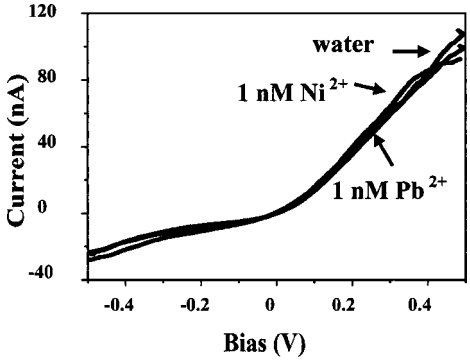

FIG. 4. Lack of response of GGH peptide-incorporated in polyaniline/poly(acrylic acid) composite junction to other ions, which demonstrates the selectivity of the sensor.

shows the $I-V$ plot at different Cu^{2+} concentrations. The pH of the solution is 7. In the absence of Cu^{2+} ions, the $I-V$ plot is approximately linear when the potential is below 0.1 V, but the slope increases significantly above 0.1 V. The asymmetry and nonlinearity in the $I-V$ plots have been discussed previously.[24] Immediately after exposing the functionalized polymer junction to 200 pM Cu^{2+}, the current decreases significantly at negative bias. With exposure to 1 nM Cu^{2+}, the current decreases almost to zero at negative bias. The conductance of the junction as a function of Cu^{2+} concentration at a fixed bias (-0.4 V) is plotted in Fig. 3(b). It shows that the current decreases linearly with the ionic concentration and ~100 pM (10 ppt) Cu^{2+} constitute the lower limit. This linearity depends on the bias voltage. For example, the conductance at $+0.4$ V is a nonlinear function of the Cu^{2+} concentration. We have also performed the same measurement in acidic solution ($p\mathrm{H}=1$). The conductivity of the polymer junction is much greater than that in neutral solution, but the current is much less sensitive to the Cu^{2+} ions.

As a control experiment, we have measured the $I-V$ characteristics of many junctions without GGH attached. We found that the presence of up to 1 μM Cu^{2+} did not change the $I-V$ plots. This experiment shows that the sensitivity of the junction to Cu^{2+} is due to the presence of GGH in the polymer. The binding of Cu^{2+} to GGH is expected to lead to two possible changes in the polyaniline junction. One is the release of protons from the peptides, which should cause an increase in the conductance. This clearly cannot explain the observed decrease in the conductance. Another one is the conformational change of the peptide as the nitrogen groups of the amino acids wrap around the Cu^{2+}. Further experiments are needed to pin down the mechanism.

In order to examine the selectivity of the metal/polymer/metal junction sensor for Cu^{2+}, we have measured $I-V$ characteristics after exposure to 10 nM Ca^{2+}, Ni^{2+}, Mg^{2+}, and Pb^{2+}. We found that the $I-V$ plots are unchanged by these ions at a rather high concentration (Fig. 4), which demonstrates excellent selectivity of the sensor. We note that a variety of methods have been demonstrated or proposed to detect trace level of metal ions to date. The distinctive features of our peptide-polymer-based sensor are: (1) direct conversion of an ionic binding event into an electrical signal, (2) small sensing element, and (3) different ions can be detected simultaneously using peptides with different sequences.

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