Chemical sensors using peptide-functionalized conducting polymer nanojunction arrays

Alvaro Díaz Aguilar, Erica S. Forzani, Xiulan Li, and Nongjian Tao

Department of Electrical Engineering and The Center for Solid State Electronics Research, Arizona State University, Tempe, Arizona 85287

Larry A. Nagahara, Islamshah Amlani, and Raymond Tsui

Embedded Systems and Physical Sciences Lab, Motorola Labs, Tempe, Arizona 85284

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We demonstrate a heavy metal-ion sensor for drinking water analysis using a conducting polymer nanojunction array. Each nanojunction is formed by bridging a pair of nanoelectrodes separated with a small gap (<60 nm) with electrodeposited peptide-modified polyanilines. The signal transduction mechanism of the sensor is based on the change in the nanojunction conductance as a result of polymer conformational changes induced by the metal-ion chelating peptide. The nanojunction sensor allows real-time detection of Cu$^{2+}$ and Ni$^{2+}$ at ppt range. © 2005 American Institute of Physics. [DOI: 10.1063/1.2128038]

A basic requirement for a chemical or biological sensor is to convert a molecular binding event into a measurable signal. Conducting polymers have been attractive for sensor applications because they can directly convert the binding event into an electrical signal. They can also be modified chemically with appropriate functional groups for specific recognition and detection of different analytes. An additional advantage is that conducting polymers can be scaled all the way down to the nanoscale or even a single molecule dimension, which provides one with a unique opportunity to study molecular binding events on the nanoscale. Because of these unique properties, conducting polymers have been applied to chemical and biosensors by many groups.

In the present work, we demonstrate chemical sensor applications using a nanoscale peptide-functionalized conducting polymer junction array. Each nanojunction is formed by bridging a pair of gold electrodes separated with a small gap (20–60 nm) with polyaniline and oligopeptides. In contrast to the previous efforts, our sensor offers several distinctive features: (1) By reducing the junctions down to nanoscale, the conductance of even a poorly conductive polymer is measurable. This is important because a polymer is often much less conductive once a molecular probe is attached to it, which makes the conductance measurement difficult if one uses films or micron-scale junctions. This is also significant for polymers (e.g., polyaniline) that are poorly conductive under physiological conditions (near neutral pH). (2) The nanojunctions have a large surface to volume ratio which rise to extremely high sensitivity and fast response time. (3) The reduced dimension requires only small amounts of probes and samples, and promises a highly integrated device. (4) The number of different oligopeptides is virtually unlimited by choosing different amino acid sequences, which allows one to tune the specificity of the sensor via the combinatorial chemistry approach.

We note that sensors using nanoscale materials have been actively pursued recently. Feldheim et al. have explored sensor applications based on the single electron charging effect in metallic nanoparticles using a scanning tunneling microscope. We have shown that metallic quantum wires are sensitive to molecular adsorption. Penner et al. have used Pd nanowires for a novel H$_2$ sensor. Several groups have reported that the resistance of a single-walled carbon nanotube changes upon exposure to chemical and biological species. Lieber’s group has used silicon nanowires to detect biological and chemical species. Huang et al. have shown that polyaniline nanofibers can provide sensitive detection of HCl and NH$_3$ vapors.

Although the nanojunction sensor described here can be applied to detect various species by selecting appropriate peptides, we focus here on the detection of heavy metal ions in drinking water. To minimize the effect of detecting non-specific adsorption of impurities in the sample solution, we used a reference junction consisting of regular polyaniline without the peptide group. Using this approach, we demonstrated detection of metal ions in the ppt concentration range.

Each nanojunction was formed by electropolimerization of a mixture of aniline and peptide-modified aniline in presence of poly(styrenesulfonic acid) (PSS) to bridge two electrodes separated with a nanometer-scale gap (<60 nm) on an oxidized Si substrate [Fig. 1(a)]. The electrode arrays (Au) were fabricated using electron beam lithography or gold electroplating on 1 μm gap electrodes to decrease gap size. The electrodes were coated with Si$_3$N$_4$ except for a small portion near the end of each nanoelectrode to minimize leakage current due to ionic conduction through electrolyte. We chose Gly-Gly-His and (His)$_6$-modified meta-aniline (GGH-ANI and H$_6$-ANI) because of specific binding to Cu$^{2+}$ and Ni$^{2+}$, respectively [Fig. 1(b)]. We bridged the gap between each pair of electrodes with polyaniline or peptide-modified polyaniline by cycling the electrode potential in 0.1 M aniline+supporting electrolyte solution (0.5 M NaHSO$_4$+10 mg/mL PSS+1.9 M H$_2$SO$_4$). The aniline solution contained either 100% regular ANI for the reference nanojunction, 75% GGH-ANI+15% ANI for GGH-modified nanojunction (for Cu$^{2+}$) or 90% H$_6$-ANI+10% ANI for (His)$_6$-modified nanojunction (for Ni$^{2+}$). The use of PSS as counter ions allows us to maintain large polya-
Aniline conductivity near neutral pH for long periods of time.\textsuperscript{17} After the formation of the polymer nanojunctions, we thoroughly rinsed the chip and then characterized the electrical properties of the nanojunctions as a function of electrochemical gate [Fig. 1(c)]. The electrochemical gate potential ($V_g$) and the source-drain bias $V_{sd}$ were controlled with a homemade bipotentiostat. Figure 1(c) shows a typical source-drain current ($I_{sd}$) vs $V_g$ (Ref. 18) of poly(GGH-ANI) nanojunction with $V_{sd}$=−50 mV in 50 mM H$_2$SO$_4$ solution. The result is similar to that of unmodified conductive PANI nanowires.\textsuperscript{19} The peak width at half height (∼0.35 V) is smaller than that reported for micron ($\mu$m)-polymer junctions (∼0.5 V) (Ref. 20) which is probably due to a smaller amount of heterogeneous broadening in the nanoscale junctions.\textsuperscript{19,21} Control experiments performed in the absence of aniline under same experimental conditions for PANI electropolymerization detected a current smaller than 2 pA, of aniline under same experimental conditions for PANI/H$_2$O and PANI/H$_2$O/H$_2$SO$_4$ junctions.\textsuperscript{19,21} Control experiments performed in the absence of heterogeneous broadening in the nanoscale conductance in Fig. 1 shows a typical $I_{sd}$−$V_g$ curve of poly(GGH-ANI) nanojunction in free aniline solution (50 mM H$_2$SO$_4$) at 60 mV s$^{-1}$ ($V_{sd}$=-50 mV). The PANI redox states are indicated. (d) Reflection-absorption FTIR spectrum for poly(GGH-ANI) and regular PANI films on gold surfaces. For comparison, the spectra absorbance is normalized by the corresponding absorbance at 1585 cm$^{-1}$ which is assigned to non symmetric C$_3$ ring stretching of quinoid ring (imine groups of PANI units).

We simultaneously monitored the current through both peptide modified-PANI nanojunctions and reference (regular PANI) nanojunctions upon exposure to water containing various amounts of heavy metal ions [Fig. 2(a)]. Figure 2(a) plots the current through a poly(GGH-ANI) nanojunction upon injections of different Cu$^{2+}$ concentrations at a constant voltage bias of 0.4 V. Each injection of Cu$^{2+}$ causes a transient spike due to mechanical disturbance and then a decrease in the current. In contrast, the current through the unmodified polyaniline changes little during the same process. This experiment demonstrates that the current decrease in the poly(GGH-ANI) nanojunction is due to the binding of Cu$^{2+}$ to GGH. Previous electrochemical studies have shown that Cu$^{2+}$ can bind to GGH specifically.\textsuperscript{22} Figure 2(b) shows that current change is linearly proportional to the logarithm of Cu$^{2+}$ concentration. Similar effect was observed on poly(H6-ANI) nanojunctions when they were exposed to Ni$^{2+}$ solutions [Fig. 2(c)]. The detection limits on poly(GGH-ANI) and poly(H6-ANI) nanojunctions are 63 pM (4 ppt) and 0.4 nM (23 ppt) for Cu$^{2+}$ and Ni$^{2+}$, respectively. We believe that the current decrease is due to a change in the polymer conformation from the peptide-metal ion complexation and also the change in the charge distribution in the polymer nanojunctions. Further studies will be needed to pin down the exact mechanisms of the current decreases.

From analysis of the $I_{sd}$−metal ion concentration plots through Langmuir-like isotherm equation,\textsuperscript{16} dissociation constants of few nanomolar are assessed for the Cu$^{2+}$−poly(GGH-ANI) and Ni$^{2+}$−poly(H6-ANI) nanojunctions. These values agree with those found for the same peptides from SPR studies\textsuperscript{16} and accounts for the relatively strong metal ion-peptide binding on the polymer nanojunction.

We tested the nanojunction sensor performance by detecting Cu$^{2+}$ in drinking water (tap water) on a poly(GGH-ANI) and PANI nanojunction array using an internal stan-
poly/H20849 concentration. The injection of Cu
in drinking water and Cu2+-peptide dissociation constant.
in drinking water. Numbers indicate Cu2+ final concentrations.
fitting to Langmuir-like equation used to calculate Cu2+ concentration in
water solutions by atomic absorption spectroscopy /H20849
dard addition method (Fig. 3). Namely, we first exposed the
nanojunctions to the drinking water sample, and then to solutions with known concentrations for calibration. The Cu2+
concentration determined using the method was (0.14 ± 0.03) ppm, which is consistent with the one obtained by atomic absorption spectroscopy (0.1 ppm). We estimated the dissociation constant for Cu2+-poly(GGH-ANI) for drinking water to be ~1 nM (Fig. 3), which shows high affinity binding of the peptide-modified conducting polymer nanojunctions even for real drinking water sample.

The polymer nanojunction arrays allow selective real-time detection of metal ions without the need of accumulation, and their sensitivity is several orders of magnitude higher than the µm-scale devices.24 The nanojunctions are stable at room temperature for at least 6 weeks (tested so far) and can be regenerated multiple (>5) times through a 10 min acidic treatment (50 mM H2SO4).

In summary, we have fabricated polymer nanojunction arrays on Si substrate. By attaching peptides with different sequences of amino acids, we have demonstrated sensitive and selective detection of heavy metal ions in drinking water. The high sensitivity, fast response, and small size of each sensing elements promises a highly integrated device consisting a large array of individual sensing elements, each is functionalized with different peptides for simultaneous detection of different analytes.

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18All gate potential values are referred to SCE for the sake of clarity and comparison with previous references.