Chem. Mater. **2006,** *18,* 5649−5651

Chemoresistive Gas-Phase Nitric Oxide Sensing with Cobalt-Containing Conducting Metallopolymers

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*Received August 25, 2006
Revised Manuscript Received October 9, 2006*

Nitric oxide (NO) has been implicated in a wide range of biological processes including but not limited to cellular signaling, coronary artery dilation, immune system response, and neurotransmission.[1] With this in mind, the development of direct, sensitive, and selective sensing schemes for NO has attracted a great deal of attention in recent years. Approaches to detect NO in solution have focused on EPR,[2] dye systems,[2] and binding events in metalloprotein structures.[3] Interfacial detection schemes have been reported on the basis of photoluminescence and electrochemical changes at modified semiconductor surfaces[4] and electrodes,[5] respectively. Additionally, the direct gas-phase detection of NO has been studied utilizing bulk resistance changes in several different electrode materials.[6]

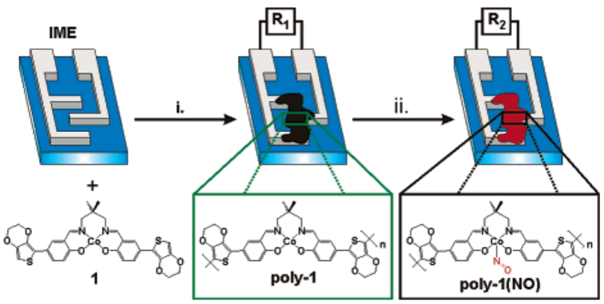

Figure 1. Schematic illustration of the fabrication of conducting metallopolymer/electrode devices: (i) electropolymerization of **1** across interdigitated microelectrodes (IME), (ii) chemoresistive response to NO gas exposure.

Whereas others have reported gas sensors based on either conducting polymers[7] or polymer hybrid materials,[8] our group has previously reported the development of a redox matched conducting metallopolymer[9] system and its use as a solution NO sensor.[10] This earlier work focused on the reversible detection of mM concentrations of NO in organic solution via attenuation of the electrochemical properties of an electrode-confined polymer film. Conducting metallopolymers are particularly well-suited for detection of small ligating molecules, such as NO, based on the electrochemical communication between the metal centers and the polymer backbone and the high propensity of the metal centers to bind target ligands.[9] Herein, we report the development of a selective, parts per million level, gas-phase NO detection system based on chemoresistive changes in a cobalt-containing metallopolymer film device.

Monomer **1** (Figure 1) was synthesized using modifications of literature procedures (see the Supporting Information), and all characterization data are fully consistent with the proposed structure. This monomer has been specifically designed for use in a conducting metallopolymer NO sensing scheme by virtue of several structural features. (1) The choice of EDOT (3,4-(ethylenedioxy)thiophene) polymerizable groups, which lowers the oxidation potential necessary for electropolymerization relative to thiophene or unfunctionalized salpen (*N,N*′-propylenebis(salicylidenimine) ligands and matches the ultimate redox potential of the polymer backbone to that of the metal center. (2) The use of the neopentyl linker in the salpen ligand both enhances solubility of the monomer and

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Table 1. XPS and FTIR Characterization of 1 and poly-1

	XPS elemental analysis[a,b]							
entry	% C	% O	% N	% S	% Co	% P	% F	FTIR[c]
1	59.24 (57.49)	18.54 (14.82)	3.04 (4.36)	10.10 (9.90)	9.07 (9.10)			1620
poly-**1**[d]	54.96 (54.64)	14.60 (9.29)	3.45 (4.07)	7.29 (6.21)	5.63 (5.70)	2.24 (3.00)	11.83 (11.03)	1621[e]

[a] Measured from thin films on stainless steel; drop cast from CH_2Cl_2 for **1** and electropolymerized for poly-**1**. [b] Calculated values given in parentheses. [c] C=N stretching frequency (cm^{-1}). [d] Calculated values for poly-**1** include one electrolyte molecule ($TBAPF_6$) per polymer repeat unit. [e] Measured from thin film on gold-coated PET using an ATR accessory.

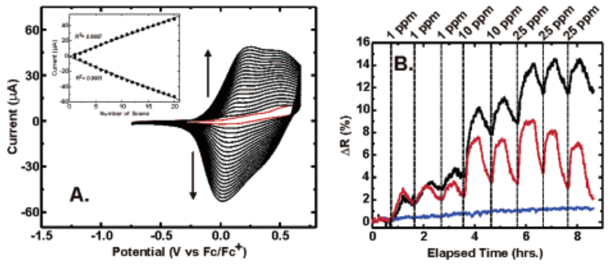

Figure 2. (A) Electropolymerization of **1** across an interdigiated microelectrode array (RT, CH_2Cl_2, 0.1 M $TBAPF_6$, 100 mV/s scan rate, 20 scans, Fc/Fc^+ is the redox couple of ferrocene). The first scan is shown in red. Inset: Plot of linear current growth vs number of scans of the CV. (B) Relative variations of resistance of polymer films to increasing concentrations of NO gas in dry N_2 at 40 °C. Unconditioned poly-**1** film shown in black, poly-**1** film conditioned at 0.262 V (vs Fc/Fc^+) for 2 min shown in red, and poly-EDOT film shown in blue. Each dashed line represents the beginning of a 30 min exposure to the indicated concentration of test gas, which is then followed by a 30 min recovery time prior to the next test gas exposure.

introduces a degree of flexibility to the ligand to accommodate conformational changes at the metal center that often accompany oxidation and expansion of the coordination sphere. (3) The choice of cobalt metal, which is known to readily bind NO but is less sensitive to ambient conditions (i.e., water and oxygen) than other metal centers such as Fe^{2+}.

Monomer **1** readily electropolymerizes onto a variety of working electrode surfaces (Figure 2A), granting access to conducting metallopolymer films for characterization and gas sensing purposes. The resulting conducting metallopolymer films were studied by electrochemical and surface techniques, including cyclic voltammetry (CV), in situ conductivity, profilometry, X-ray photoelectron (XPS), UV−vis, and FTIR spectroscopies (see the Supporting Information). For example, the elemental composition, ligand structure, and metal coordination environment were confirmed by XPS and FTIR analysis (Table 1). These data are completely consistent with the polymer structure shown in Figure 1.

For use in gas-phase testing, films of poly-**1** were prepared across arrays of commercially available interdigitated microelectrodes. These electrodes comprise a series of 50 pairs of interdigitated electrode fingers (15 μm) that are separated by 15 μm over a total distance of 1.5 mm. By spanning the gaps in these electrodes with poly-**1** through electropolymerization, we can prepare high-surface-area films (total exposed surface area ca. 7.5 mm^2, with surface area:volume ratio of ca. 700:1) that are then easily electrically interfaced for direct gas-phase testing (Figure 1).

Figure 2B shows the response of three polymer films when subjected to parts per million levels of NO in a stream of dry N_2. For the purposes of these tests, two different poly-**1** films were prepared, in addition to a poly-EDOT film for comparison/control purposes. The two variations of the poly-**1** film are identical, with the exception that one of these films was conditioned at a voltage corresponding to its peak conductivity/oxidation potential for 2 min after growth (see the Supporting Information). Both of the poly-**1** films display easily detected resistance changes (positive relative to initial resistance levels), even upon exposure to concentrations of NO as low as 1 ppm, whereas the poly-EDOT control film shows no appreciable change in resistance with any concentration of NO tested. The exposure of poly-**1** to NO undoubtedly results in the formation of poly-**1**(NO) (Figure 1), where the cobalt metal center has adopted a square pyramidal coordination arrangement to accommodate the addition of a bent NO ligand. This assignment is completely consistent with model studies of **1**, **1**(NO), poly-**1**(NO), and similar Co(NO) complexes previously reported.[11] The most diagnostic data for the assignment of **1**(NO) is the strong band observed in the FTIR ($\nu_{NO} = 1660\ cm^{-1}$).

The primary differences that were observed between the poly-**1** film that was conditioned and the film that was not are 2-fold. The conditioned film displayed a much faster and more complete recovery when the NO flow was stopped, and the conditioned film displayed saturation behavior within the 30 min exposure at the highest concentrations tested (25 ppm). Both of these effects can be rationalized by the fact that there are likely changes in film morphology with conditioning of the film. By conditioning the conducting metallopolymer film in electrolyte solution at its peak oxidation potential, it is assured that the film is fully swollen and at its highest density of incorporated electrolyte. This has the effect of increasing the overall porosity of the conducting polymer film, thus exposing the maximum amount of the internal volume to analyte gas molecules. As a result, one would expect more facile exchange of ligands, leading to a less diffusion-limited response and recovery, which is consistent with the observed NO response curves (Figure 2B).

Additionally, the response of poly-**1** and the poly-EDOT control films toward several possible interfering gases (i.e., O_2, NO_2, CO, and CO_2) were measured (Figure 3). The films showed no obvious response to the test gases with one exception: poly-**1** with NO_2. When exposed to NO_2, the poly-**1** film showed a large, irreversible resistance change negative to the initial resistance. The magnitude, direction, and irreversibility of this response can be easily explained as a one-electron electron transfer between the NO_2 analyte ($E^0_{red} = 0.11-0.35$ V vs Fc/Fc^+)[12] and the cobalt conducting

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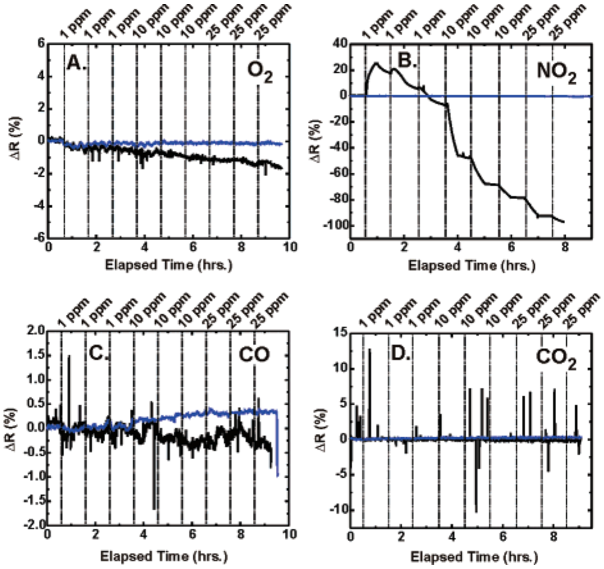

Figure 3. Relative variations in resistance of polymer films to increasing concentrations of possible interfering gases ((A) O_2, (B) NO_2, (C) CO, (D) CO_2) in dry N_2 at 40 °C for A and D and 30 °C for B and C. Unconditioned poly-**1** film shown in black and poly-EDOT films shown in blue. Each dashed line represents the beginning of a 30 min exposure to the indicated concentration of test gas, which is then followed by a 30 min recovery time prior to the next test gas exposure.

metallopolymer resulting in the formation of a Co^{3+}/nitrite complex. This agrees well with previous observations of the reversible reaction of NO with Co(salen) complexes and the irreversible reaction with NO_2.[13] Also, this reaction would leave the polymer in a more highly doped state, which accounts for the large and irreversible decrease in resistance that is observed.

In conclusion, we have herein demonstrated the rational design and synthesis of a conducting metallopolymer that is an effective and selective solid-state sensor material for nitric oxides (i.e., NO_x where $x = 1$ or 2). These films are easily prepared and electrically interfaced and have shown detection limits of NO_x below 1 ppm. Future studies will be aimed at diversifying this class of sensor materials and exploring the differentiation of NO vs NO_2 using sensor arrays.

Acknowledgment. This work was supported by the U.S. Army through the Institute for Soldier Nanotechnologies, under Contract DAAD-19-02-D-0002 with the U.S. Army Research Office. Dr. Michael Rakijas and Dr. Lawrence Schatzmann of the Raytheon Company are gratefully acknowledged for helpful discussions.

Supporting Information Available: Experimental details for the synthesis and characterization of the title ligand, **1**, poly-**1**, **1**(NO), and poly-**1**(NO); electrodeposition of polymer films and corresponding electrochemical characterization; description of gas-phase testing. This material is available free of charge via the Internet at http://pubs.acs.org.

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