

The Interaction of CO to the Co(salen) Complex in to PEDOT:PSS Film and Sensor Application

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The interaction between carbon monoxide (CO) and a cobalt-salen complex (Co(salen)) was studied and applied to detect CO. The metal complex doped PEDOT:PSS film exhibited good sensitivity to CO and differentiate CO from other gases. The response of the composite to CO was reversible (RSD < 5%) change in resistance upon removal of CO gas from the test chamber. The effects of adding Co(salen) in the probe film on the response of the sensor were investigated using AFM, XPS, and FT-IR spectroscopy. The sensitivity of the sensor increased as the Co(salen) concentration enhanced as it increased from 0.0 to 1.5 wt. %, where the highest sensitivity ($\% \Delta R/R_0$) of $-25.0 \pm 0.05\%$ was achieved with 1.0 wt. % Co(salen). The sensor containing probe exhibited a linear response ($R^2 = 0.983$) in the range of 0.5 to 10.0% CO (v/v) N₂, and the detection limit was 1.74% CO (v/v) in N₂.

Key Words : Chemical sensor, PEDOT:PSS, Co(salen), Carbon monoxide

Introduction

A reliable carbon monoxide (CO) sensor must be able to qualitatively and quantitatively detect of the toxic CO gas.¹ There are two main classes of gas-sensing materials; organic and inorganic compounds. Inorganic gas-sensing materials are sensitive to gases at high operating temperatures.^{2,3} Organic materials such as conductive polymers have received considerable attention in recent years because they can operate at room temperature.⁴ The electrical conductivity of a conductive polymer changes when it is exposed to a particular gas; thus, conductive polymers can be used as gas-sensing probes. Among conductive polymers, poly(thiophene) is an important class of gas-sensing polymers due to its many applications in sensing.^{5,6} It has been used in many different kinds of chemical and electrochemical sensors such as gas sensors and biosensors.^{4,7-12} In recent, poly(3,4-ethylenedioxy) thiophene-poly(styrenesulfonate) (PEDOT:PSS) has been used in recent studies and is an important conductive polymer (its conductivity is approximately 10 S/cm).^{13,14} PEDOT:PSS has been used as a base substrate for gas sensors because it has several advantages in comparison with other conductive polymers, namely, high conductivity, high stability, abundance, and low cost.¹⁵⁻¹⁸ PEDOT:PSS has a polar structure where PEDOT is positively charged and PSS is negatively charged. Therefore, PEDOT:PSS is more sensitive to polar species such as water vapor, NO and CO.¹⁹ There are some reports on the incorporation of metals, metal oxides, and organometallic complexes into intrinsically conductive polymers to enhance the electron or ion mobility and improve conductivity and stability.²⁰ For example, an Fe-Al doped polyaniline film exhibited a fast response and

excellent sensitivity to CO in a previous study.²¹ The response of ultra thin films of polyaniline-SnO₂ and polyaniline-TiO₂ nanocomposites to CO have also been studied.²² Several metal organic complexes have also been added to conductive polymer sensors to enhance sensor selectivity and sensitivity.²³ PEDOT:PSS has been doped separately with materials such as Fe, Al, Kryptofix-21 (Kr 21), Kryptofix-22 (Kr 22), 1,4-dioxane, and piperazine and in some cases with mixtures of these materials.¹⁶ Among doped PEDOT:PSS polymers, a morpholine doped PEDOT:PSS film behaves as a sensor for CO sensor. Cobalt compounds have also been added to PEDOT:PSS as selective CO gas adsorbents to improve selectivity of the resulting sensor.²⁴⁻²⁶ Therefore, in this study, we enhanced the performance of a PEDOT:PSS CO sensor by adding a Co(salen) complex to a PEDOT:PSS film.

In the present study, the CO sensor probe was fabricated by doping PEDOT:PSS with a Co(salen) complex. A PEDOT:PSS film containing Co(salen) complex was characterized using atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and fourier transform infrared (FT-IR) spectroscopy. Experimental parameters such as the gas flow rate and Co(salen) concentration were controlled to optimize the sensitivity of the CO sensor. In addition, the performance of sensors with and without the Co(salen) complex were compared.

Experimental

Materials and Instruments. Chemical reagents were purchased from Fluka and Aldrich Co. (U.S.A.) and were used without further purification. The solid content, maximum

viscosity, and maximum surface resistance of the PEDOT:PSS was approximately 1.0 wt. % (solids contained both PEDOT and PSS polymers), 15 mPa·s, and 20 M Ω , respectively. Glass pieces with interdigitated Au electrodes (size: 10.0 mm \times 15.0 mm, gap width between electrodes: 10.0 μ m, electrode width: 10.0 μ m) were used as a substrate. A homemade spin coater was used to prepare a thin film of the composite conductive polymer on the substrate. The response of the sensor probe (PEDOT:PSS doped with different concentrations of Co(salen)) was evaluated separately with O₂, CO₂, N₂, and CO gases. Gas cylinders containing high purity gas were provided by PS Chem Co., Ltd (South Korea).

Bare interdigitated Au electrodes were washed with distilled water and cleaned using an ultrasonic cleaner. Each electrode was cleaned with acetone, dried, and then coated with polymer. Four different compositions of doped polymer were spun cast on top of the substrates, at a velocity of 1200 rpm for 5 seconds. The prepared sensor probe was then placed in a chamber with a controlled atmosphere wherein the gas inlet and outlet pressure was measured and controlled. An electrometer/high resistance meter (Keithley, CIMS model 6517A, U.S.A.) was used to monitor variations in the resistance of the thin films. The ratio of the gas mixture was controlled using a precision gas flow meter (KOFLOC, model RK1200, Japan). Atomic force microscope (AFM) images were obtained with tapping mode using a Digital Instrument NanoscopeTM 3D ADC5, Multi mode (Veeco Instruments Inc., CA).

Synthesis of the Co(salen) Complex. The Co(salen) complex was synthesized as illustrated in Scheme 1. A mixture of benzene-1,2-diamine (0.11 g, 1.0 mmol), 2-hydroxybenzaldehyde (0.12 g, 1.0 mmol) and *p*-toluenesulfonic acid (*p*-TSA) (0.1 g) was stirred for 5 hr in ethanol (5.0 mL) under reflux. The reaction was monitored by thin layer chromatography (TLC), and the reaction mixture was cooled down to room temperature after completion. Precipitated product was then filtered and washed with ethanol (10.0 mL)

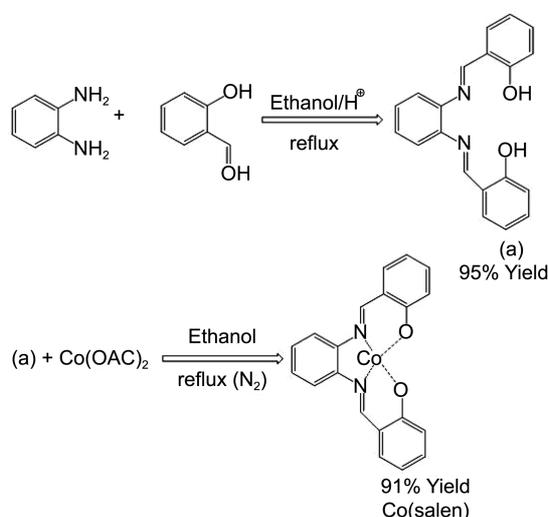
to give a yellow powder (0.30 g, yield 95%) as the pure product. A mixture of this compound (1.0 mmol, 0.32 g) and Co(OAc)₂ (1.0 mmol, 0.18 g) was stirred in ethanol (5.0 mL) at 80 °C under a nitrogen atmosphere in a 50.0 mL, tri-necked flask equipped with a reflux condenser. The reaction was monitored by TLC, and stirring continued for 8 hr until the reactants were consumed. After completion of the reaction, the mixture was cooled to room temperature and the precipitated product was filtered and washed with ethanol (2.0 \times 10.0 mL) to give brown powders (0.34 g, yield 91%) as the pure product. The structure of the product was analyzed by FT-IR spectroscopy (KBr) and mass spectrometry (MS). The FT-IR peaks (at 3030, 1637, 1610, 1540, 1461, 1200, and 750 cm⁻¹) and MS peaks (C₂₀H₁₄CoN₂O₂: *m/z*: 373.042 [M⁺]) confirmed that the product had the expected structure and molecular weight.

Preparation of Co(salen) Doped PEDOT:PSS. Different concentrations of Co(salen) were stirred into an aqueous solution of the polymer for several hours to prepare the Co(salen) doped PEDOT:PSS. During this process, PEDOT:PSS and the Co(salen) complex mixed together completely. The concentration of Co(salen) varied from 0.2 to 2.0 wt. %. Spin-coating was used to prepare a transparent thin film of doped PEDOT:PSS on interdigitated electrodes. A few drops of PEDOT:PSS containing Co(salen) was added to the base substrate, and the substrate was then spun at 3000 rpm to produce the doped polymer film. The resulting sensor probes were exposed to different gases in a chamber, and the variation in resistance was monitored. An electrometer/high resistance meter (CIMS model 6517A) was used in series with the doped PEDOT:PSS thin film to record variations in sensor resistance. The percent variation in resistance of the sensor relative to that of the base (in-vacuum/in-room air) substrate was plotted versus the time of gas exposure.

Results and Discussion

Response of Co(salen) Doped PEDOT:PSS to CO. Polymer films doped with different concentrations of Co(salen) were prepared on interdigitated Au electrodes and were then exposed to CO at a flow rate of 19.0 mL/min at atmospheric pressure. Figure 1(a) shows the dependence of the Co(salen) concentration doped in the polymer on the sensitivity of the sensor to CO at room temperature. Sensitivity (*S*) is defined as the ratio of resistance measured in air (*R*_a) to that measured in each gas (*R*_g). A concentration of 1.0 wt. % Co(salen) in the PEDOT:PSS thin film resulted in the maximum sensitivity to CO. Increasing the Co(salen) concentration above 1.0 wt. % resulted in decreased sensitivity to CO. As shown in Figure 1(b), there is a linear relationship between probe sensitivity and CO concentration a slight increase in the concentration of CO results in an increase in probe sensitivity.

Selectivity of Co(salen) Doped PEDOT:PSS to CO. The response of the PEDOT:PSS thin film doped with 1.0 wt. % Co(salen) to O₂, N₂, CO, and CO₂ was evaluated. Each gas was flowed in a vacuum chamber at a rate of 17.0 mL/



Scheme 1. Synthetic route for preparation of the Co(salen) complex.

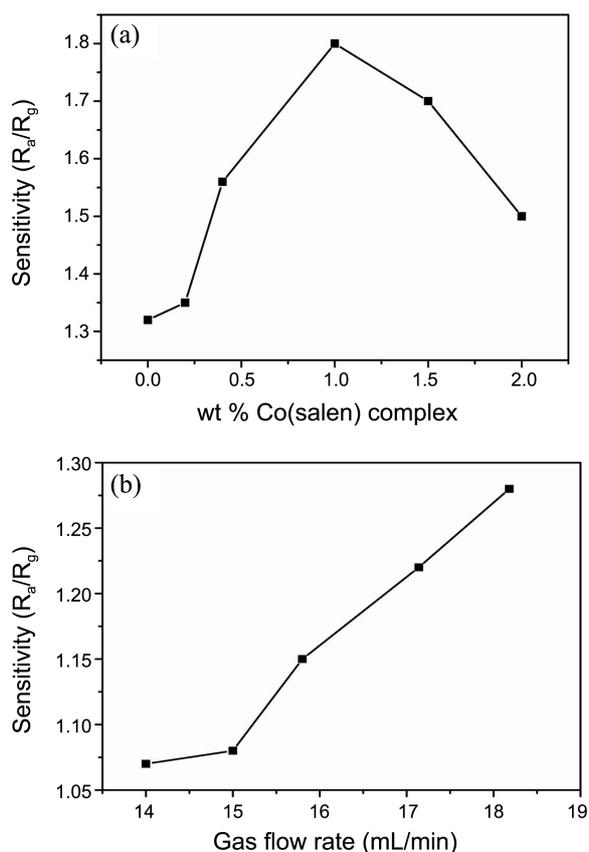


Figure 1. (a) Sensitivity of Co(salen) doped PEDOT:PSS vs. Co(salen) concentration at room temperature. (b) The change of sensitivity of the PEDOT:PSS/1.0 wt. % Co(salen) composite vs. the CO concentration at room temperature.

min. Figure 2(a) shows the percent variation in resistance of the sensing probe to the different gases tested. The sensor exhibited a better response to polar gases such as CO because PEDOT:PSS has a polar structure. However, there was a weak response to O_2 and CO_2 . In addition, there was an unexpected decrease in the resistance of the sensor upon exposure to N_2 gas. The desired vacuum pressure was not achieved completely in the testing chamber; therefore, it is possible that flowing nitrogen over the sensor removed trapped moisture on the surface of the sensor, explaining the drop in sensor resistance observed in a N_2 atmosphere. Because the PEDOT:PSS has a polar structure, it can retain water moisture; contamination of the sensor by moisture in the atmosphere thus causes changes in its resistance. To mitigate this, a drying silicate was used to dry the inside of the testing chamber. Figure 2(b) illustrates the response of the probe versus the gas exposure time. As seen in this figure, the resistance of the probe rapidly increased when the CO gas exited the chamber. However, this resistance change is not completely reversible after repeated exposure to CO gas.

As shown in Figure 3, the response of the Co(salen) doped sensor to CO gas occurred relatively quickly at room temperature, with a response time (t_p) of approximately 60 sec. Doping Co(salen) in the polymer film improved the

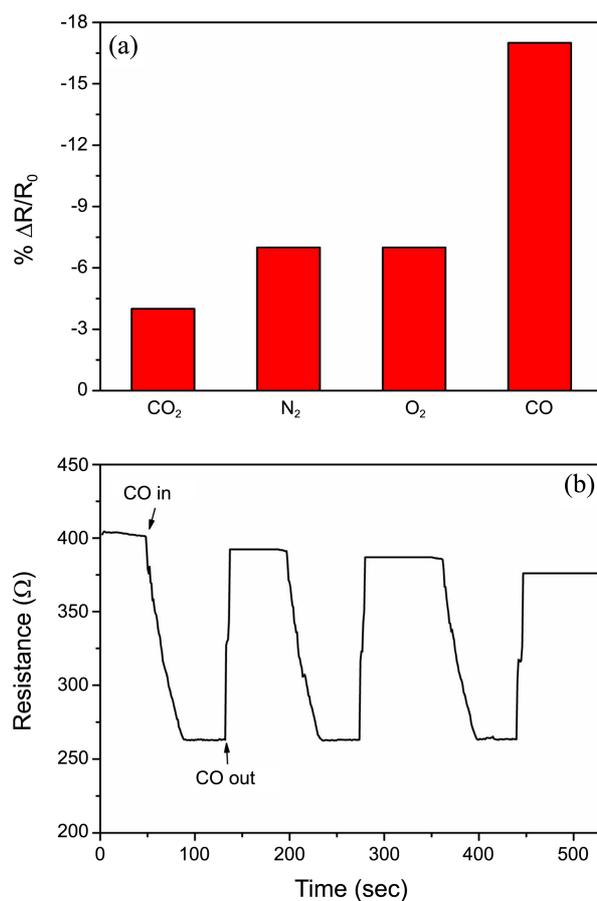


Figure 2. (a) Response of the PEDOT:PSS/1.0 wt. % Co(salen) composite to common gases in atmosphere. (b) Reversibility of PEDOT:PSS/1.0 wt. % Co(salen) composite in the presence of CO in the atmosphere background.

response time of the sensor to CO by increasing the reactivity of the CO oxidation reaction to CO_2 in the presence of O_2 -captured Co(salen).²⁴ Because the cobalt complex has a stronger affinity to oxygen than CO, the oxygen-Co(salen) complex is primarily formed in air.²⁷ Hence, CO gas, as an active species, reaches a stable state to form CO_2 gas *via* reaction with O_2 supplied by the oxygen-Co(salen) complex formed in air.²⁵ The response of the probe to CO gas was therefore enhanced by this process occurring in the presence of the oxygen-Co(salen) complex. The slope of the response curve depends on the rate of interaction between the sensor probe and the gas. Figure 3(b) shows that the response rate between the Co(salen) doped probe and CO is higher than that of the undoped probe.

Figure 4(a) shows a typical resistance response of the sensor to various concentrations of CO gas at room temperature. The performance of the sensor was tested in a gas mixture containing N_2 and various concentrations of CO. The resistance change of the sensor increased with increasing CO concentration. The data show that the sensor yielded a 7.8% change in resistance upon exposure to 10% CO gas (v/v) in N_2 . A variation in the resistance of approximately 1% was observed with CO gas concentrations as low as 0.5% CO gas (v/v) in N_2 . A calibration curve, shown in

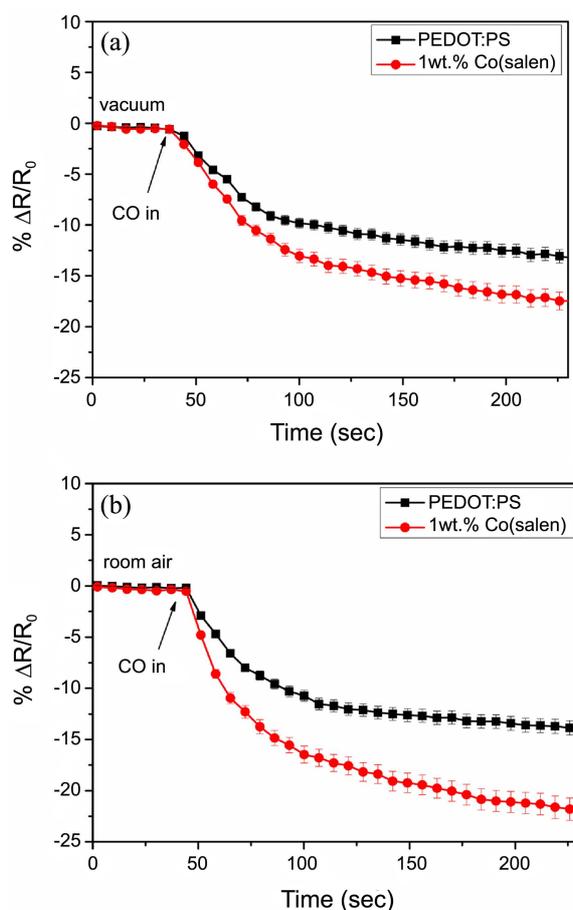


Figure 3. Resistance variation of pure PEDOT:PSS and its composite exposing to the CO gas in (a) vacuum and (b) room air background.

Figure 4(b), was obtained by plotting the change in resistance obtained for different concentrations of CO gas. The magnitude of the resistance response is expressed relative to that of the base substrate ($\Delta R/R_0$)/concentration (v. %). A response magnitude of 0.77125 ± 0.04467 ($\% \text{ v/v}$)⁻¹ was obtained from the slope of a linear fit to the calibration curve shown in Figure 4(b). A correlation coefficient (R^2 value) of 0.9835 was obtained for the calibration curve, demonstrating that the doped PEDOT:PSS exhibits a linear response to CO gas. The detection limit (D.L.) of the Co(salen) doped PEDOT:PSS was calculated from the linear calibration curve in Figure 4 to be 1.74% CO (v/v) in N₂ according to Eqs. (1) and (2).

$$B.L. = \text{mean}_{\text{blank}} + 1.645(SD_{\text{blank}}) \quad (1)$$

$$D.L. = B.L. + 1.645(SD_{\text{low concentration sample}}) \quad (2)$$

The *B.L.* (blank limit) was estimated by measuring replicates of a blank sample and by calculating the mean result and the standard deviation (SD).

AFM Analysis. AFM images of the surface topography of Co(salen) doped PEDOT:PSS film can be seen in Figure 5. These images showed that the sensor surface has a roughness of approximately 1.73 nm, indicating uniform

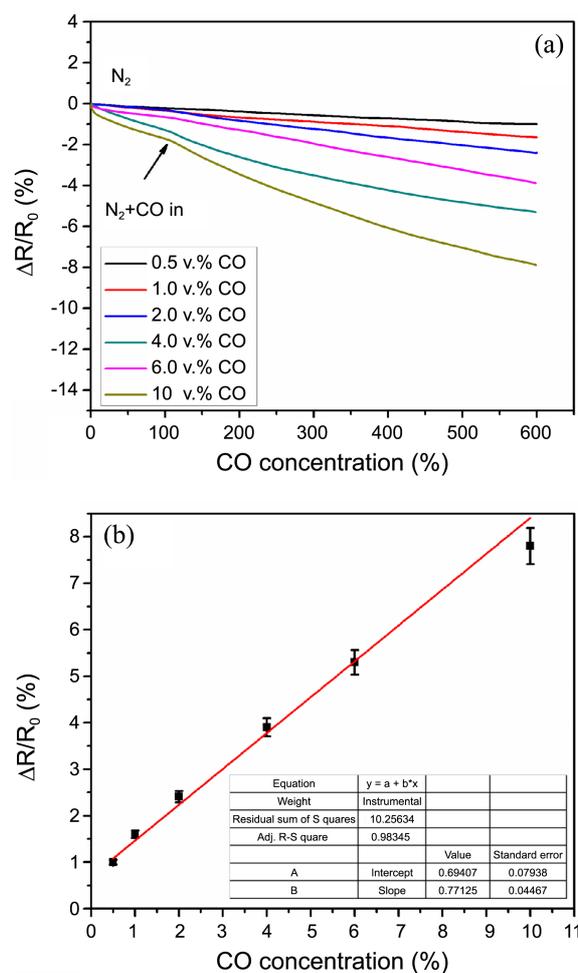


Figure 4. (a) Response of the Co(salen) doped PEDOT:PSS sensors to various concentrations of the CO gas. (b) Calibration plot of the resistance responses of the sensor versus the concentration of the CO gas.

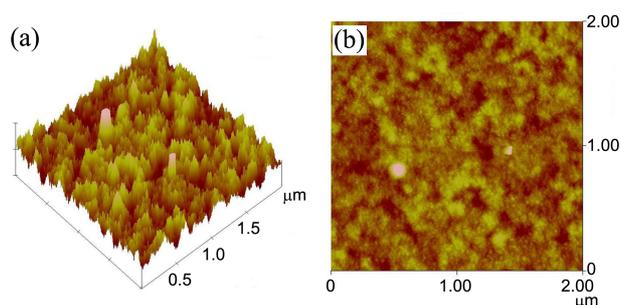


Figure 5. AFM images of (a) 3-D and (b) 2-D of the Co(salen) doped PEDOT:PSS (1.0 wt %) film.

coverage of the silicon substrate by the doped polymer. The doping of 1.0 wt. % Co(salen) complex in the PEDOT:PSS film slightly increased the roughness from 1.24 to 1.73 nm, indicating that the addition of Co(salen) did not noticeably change the morphology of the film. The thickness of the coated polymer film layer was determined to be approximately 3.5 nm. This result indicates that spin coating produced a homogenous surface layer without cracks, pores, or other kinds of defects.

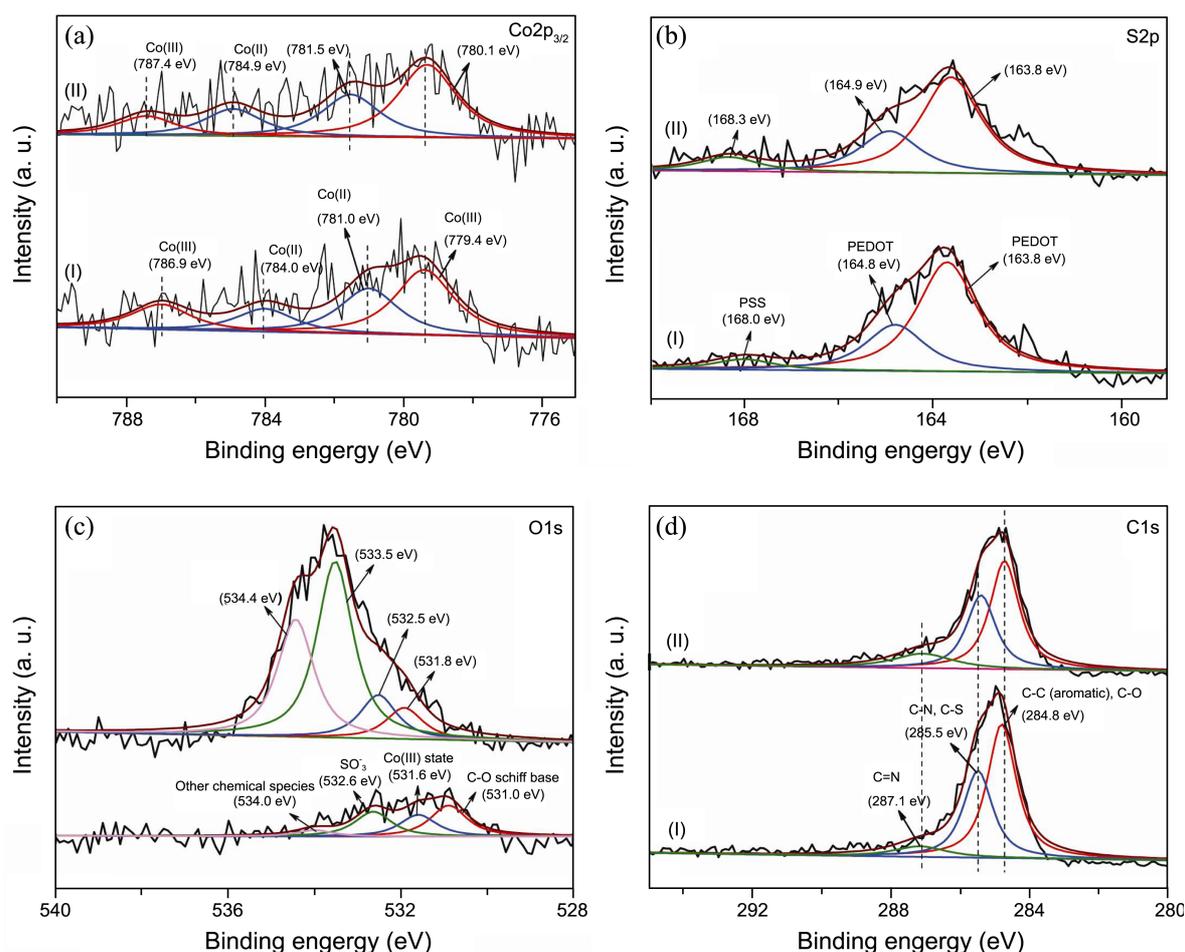
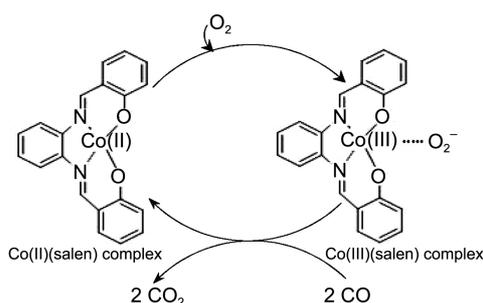


Figure 6. XPS spectra of (a) Co $2p_{3/2}$, (b) S $2p$, (c) O $1s$, and (d) C $1s$ for Co(salen)-doped PEDOT:PSS (I) before and (II) after the reaction with the CO gas.

XPS Analysis. To investigate the interaction between Co(salen) and CO gas, XPS spectra were obtained for the Co(salen) doped PEDOT:PSS film before and after exposure to CO gas. Figure 6 shows the XPS spectra for (a) Co $2p$, (b) S $2p$, (c) O $1s$, and (d) C $1s$ in the sensor before (I) and after (II) reaction with CO gas. The XPS spectrum of Co $2p_{3/2}$ before exposure to CO gas (Figure 6(a(I))) contain two peaks at 779.4 and 781.0 eV, corresponding to the Co(III) and Co(II) ions, respectively.²⁸ Furthermore, additional satellite peaks were observed at approximately 784.0 and 786.9 eV and are probably due to the Co (II) and Co (III) ions. Interestingly, a distinct peak shift from 781.0 to 781.5 eV towards a higher binding energy was observed for the Co(III) and Co(II) ions after reaction with CO as shown in Figure 6(a(II)), confirming the an interaction between the Co(salen) and CO gas. The S $2p$ spectrum exhibited peaks at 163.8 and 164.8 eV corresponding to the C-S bond present in PEDOT. The spectrum showed an additional peak after doping of PSS at a higher binding energy of 168.0 eV, confirming successful doping of PSS on PEDOT (Figure 6(b(I))).²⁹ In a control experiment, however, we obtained XPS spectra for only PEDOT wherein the peak at 168.0 eV was not found (data not shown). After reaction with CO, distinct peak shifts from 168.0 to 168.3 eV and from 164.8 to 164.9 eV were

observed due to the interaction between the polar groups of PEDOT:PSS and the CO gas (Figure 6(b(II))). This result again confirms an interaction between CO gas and the sensor. The O $1s$ spectrum exhibited four peaks at 531.0, 531.6, 532.6, and 534.0 eV, corresponding to Schiff base, Co(III) ion, sulfonate (PSS), and other chemical species, respectively (Figure 6(c(I))).²⁸ Surprisingly, a peak shift with high intensity was observed after interaction of the sensor with CO gas (Schiff base (531.8 eV), Co(III) state (532.5 eV), sulfonate (533.5 eV), and other chemical species (534.4 eV)), as shown in Figure 6(c(II)). This reconfirms the successful interaction between the sensing probe and CO gas.³⁰ Of the observed peaks, the SO $_3^-$ peak exhibited the highest intensity due to water vapor adsorbed on the surface of sensing probe. Peaks at 284.8, 285.5, and 287.1 eV corresponded to C-C (Co(salen)), C-O (PEDOT), C-N (Co(salen)), C-S (PEDOT), and C=N (Co(salen)), respectively. As seen in Figure 6(d), there was no apparent change in the binding energy of C for the doped polymer.

The Interaction Between Co(salen) and CO. Usually, reactions between O $_2$ and metal complexes proceed irreversibly by cleavage of the oxygen-oxygen bond producing oxides, hydroxides or water. With the appropriate ligand configuration the reversible binding of dioxygen with tran-



Scheme 2. A tentative reaction mechanism for the operation of Co(salen) in the presence of CO.

sition metal complexes is also possible.³² The Co(salen) complex binds O₂ reversibly.^{33,34} The cobalt complex has a very low tendency for interaction with CO whereas it has a high tendency for interaction with oxygen. CO gas, as an active species, reaches a stable state (CO₂ gas) via reaction with O₂ binding to Co(III). The resistance of the Co(salen) doped PEDOT:PSS sensor changes upon immersion in CO gas due to interaction between CO and the dioxygen Co complex. Oxygen lost during this interaction is replaced by oxygen present in the atmosphere and then again oxidizes cobalt. During this process, the refreshed Co(salen) complex undergoes the same reaction again.³⁵ In this way, detection of CO gas by the Co(salen) doped polymer becomes reversible. If the detection of CO occurs via the mechanism shown in Scheme 2, the resistance of the Co(salen) doped PEDOT:PSS composite changes accordingly and can be used to detect CO gas.

Conclusions

Co(salen) doped PEDOT:PSS acts as a sensing material for detection of CO gas under ambient conditions. The sensitivity of the PEDOT:PSS film to CO increased from 12 ± 0.05 to $22 \pm 0.05\%$ when a very low concentration of Co(salen) complex was added. The response of the Co(salen) doped PEDOT:PSS thin film to CO was quite fast and reversible. The optimum concentration of Co(salen) complex in the polymer matrix was 1.0 wt. % and resulted in the highest sensitivity to CO gas. Further effort and research on this novel material may lead to a cost effective and high performance sensor for detection of CO poisoning.

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