High-Performance, Flexible NO₂ Chemiresistors Achieved by Design of Imine-Incorporated n-Type Conjugated Polymers

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Flexible and mechanically robust gas sensors are the key technologies for wearable and implantable electronics. Herein, the authors demonstrate the high-performance, flexible nitrogen dioxide (NO₂) chemiresistors using a series of n-type conjugated polymers (CPs: PNDIT2/IM-x) and a polymer dopant (poly(ethyleneimine), PEI). Imine double bonds (C = N) are incorporated into the backbones of the CPs with different imine contents (x) to facilitate strong and selective interactions with NO₂. The PEI provides doping stability, enhanced electrical conductivity, and flexibility. As a result, the NO₂ sensors with PNDIT2/IM-0.1 and PEI (1:1 by weight ratio) exhibit outstanding sensing performances, such as excellent sensitivity (ΔR/R₀ = 240% @ 1 ppm), ultralow detection limit (0.1 ppm), high selectivity (ΔR/R₀ < 8% @ 1 ppm of interfering analytes), and high stability, thereby outperforming other state-of-the-art CP-based chemiresistors. Furthermore, the thin film of PNDIT2/IM-0.1 and PEI blend is stretchable and mechanically robust, providing excellent flexibility to the NO₂ sensors. Our study contributes to the rational design of high-performance flexible gas sensors.

1. Introduction

Considering the growing demand for wearable/portable electronics, flexible gas sensors are one of the most important devices that can be integrated into health/environmental monitoring and/or implantable biomedical devices.[1–4] Conjugated polymers (CPs) are promising materials for flexible gas sensors owing to their superior optoelectrical properties, mechanical resilience, and facile solution processability compared to the conventional materials.[5–7] The sensing performances (i.e., sensitivity, selectivity, reversibility, limit of detection (LOD), cycling stability, and reliability) of CPs are typically determined by the electrical modulations in the CP films during interaction with the target analytes.[8,9] CPs consist of alternating single and double bonds, which provide delocalized π electrons (π-conjugations) along the backbone and allow fast charge transport. When CPs interact with gas analytes, the extent of their π-conjugation can be reinforced or reduced by the partial charge transfer between the molecules and/or swelling of sensing layers, enabling transduction of chemical signals to electrical signals in the sensors. To utilize the high potential of CPs in flexible chemiresistive sensors (e.g., chemiresistors), many efforts have been made to tune the intrinsic electrochemical properties of CPs and their composites.[10,11]

Doping is a promising strategy to amplify the sensing performance of CP-based chemiresistors, as it can modulate the charge density and transform the base material from a semiconducting state to a highly conductive state.[12,13] The intensity of the electrical signal and the operation durability of the sensors are strongly influenced by the doping level and the doping stability, respectively.[14,15] For example, the sensing properties of p-type polyaniline (PANI) fibers are enhanced significantly by doping with (+)-camphor-10-sulfonic acid (CSA). The resistive sensor based on PANI/CSA can detect very low concentrations (1 ppm) of nitrogen dioxide (NO₂) gas.[16] Recently, an ionic liquid (IL) based on imidazolium cation and hexafluorophosphate anion has been reported for achieving the stable doping of CP sensing layers through the coupling of electronic/ionic charges.[17,18] The resulting CP/IL blends exhibit enhanced sensing signals, reversibility, and analyte selectivity for volatile organic compounds.
Therefore, it is important to choose an appropriate dopant for the CPs, in accordance with the molecular structures of the CPs and target analytes.\(^{[19]}\)

Development of new molecular structures of CPs, consisting of specific sites for selective interactions with analytes, is imperative to enhance the electrical response of the sensors. Through these interaction sites, CPs can easily donate/withdraw the electrons to/from the analyte gases and lead to large changes in electrical properties. For example, polypyrrole (PPy) was modified to include covalently linked n-butylamine substituents, of which the amine bonds could transfer the electrons from the polymer to the target analyte.\(^{[20]}\) The modified PPy sensing layers exhibited enhanced sensitivity (e.g., 15% @ 1 ppm) with good selectivity for trinitrotoluene, whereas pristine PPy did not show any electrical response. Polythiophene (PT) block copolymers were developed to exhibit large electrical signals, where the polar polymers of second blocks could interact effectively with volatile organic compounds.\(^{[10]}\) However, these CP-based sensors exhibit relatively poor sensitivity and LOD. This is mainly because the designated interaction sites were not highly selective to the target analytes.\(^{[8,21,22]}\) Therefore, it is important to develop CPs, in which the strong interaction sites for analytes are directly integrated into the conjugated backbone. In particular, monitoring NO\(_2\) at very low concentrations is crucial for human health or living things, because even trace levels of NO\(_2\) (≤1 ppm) can cause pulmonary edema and throat irritation, serving as an acute health hazard.\(^{[11]}\) Moreover, there have been only a few studies on CP-based flexible chemiresistors.\(^{[23]}\) Therefore, the development of CP-based NO\(_2\) sensors with a flexible device platform is crucial.

In this study, we develop high-performance flexible NO\(_2\)-sensing chemiresistors based on imine-incorporated n-type CPs, PNDIT2/IM\(_x\) (\(x = \) mole fraction of imine bond). Films consisting of PNDIT2/IM\(_x\) and a polymer dopant (poly(ethylenimine), PEI) are employed to construct the NO\(_2\) chemiresistors with excellent performance and mechanical flexibility. Optimal performance with a sensitivity (\(\Delta R/R_b\)) of 240% at 1 ppm of NO\(_2\) is obtained with the PNDIT2/IM-0.1 film blended with PEI (1:1 by weight ratio). In this condition, the polymer-blend film exhibits excellent selectivity against interfering gases (\(\Delta R/R_b < 8\% @ 1\) ppm for interfering analytes). In particular, the sensor shows one of the lowest LODs (0.1 ppm) and the highest cycling stability (240% of constant sensitivity under 15 cycles of NO\(_2\)/N\(_2\) exposure) among the reported CP-based NO\(_2\) chemiresistors. Based on analyses using X-ray photoelectron spectroscopy (XPS) and Raman scattering, these high sensing characteristics are mainly attributed to the strong interactions of imine bonds of the CPs with NO\(_2\). As the electron delocalization is disturbed by sharing the lone pair electron of N of imine bond to NO\(_2\) molecules, the electrical conductivity of the sensing layer decreases rapidly. Owing to the flexible nature of the PNDIT2/IM\(_x\) and PEI blends, we also demonstrate the feasibility of a flexible sensor platform using our CP blends as a sensing element.

### 2. Results and Discussion

#### 2.1. Design Strategy and Characterization of System

To develop high-performance flexible NO\(_2\)-sensing chemiresistors, we designed and synthesized a series of imine-incorporated PNDIT2/IM\(_x\) polymers by the following procedure in the previous literature\(^{[24]}\) (Figure 1; Figure S1, Supporting Information). Naphthalene diimide (NDI), which is a major repeating unit of high-performance n-type CPs,\(^{[25-29]}\) was selected as one of the building blocks for the polymer backbone to generate transport pathways for the charge carriers during the sensing measurements.\(^{[30-32]}\) Another building block, (E,E)-N',N'-1,4-phenylenebis[1-(2-thienyl)methanimine] (IM) containing C=N bonds, was prepared to achieve high-performance sensors according to the following two considerations: (1) imine bonds (C=N) strongly interact with NO\(_2\), by sharing their lone pair electrons (N); (2) these interactions affect the overall π-conjugation of PNDIT2/IM\(_x\), enabling rapid changes in the electrical signals. The two different key blocks of NDI and IM were integrated to produce the PNDIT2/IM\(_x\) polymers by Suzuki cross-coupling reactions (Figure S1, Supporting Information).\(^{[33,34]}\) The mole fractions of the imine bonds (\(x\)) in the PNDIT2/IM\(_x\) polymers were varied from 0 to 0.1, and then, to 0.3. The structures of the polymers were confirmed by \(^1\)H nuclear magnetic resonance spectroscopy (\(^1\)H NMR) (Figure S2, Supporting Information). The three different PNDIT2/IM\(_x\) had similar, high number-average molecular weights (\(M_n = 50–65\) kg mol\(^{-1}\)). These molecular weights of NDI polymers are higher than the critical molecular weight required to form an entanglement network in the thin film.\(^{[35-37]}\) Therefore, we expect the thin films fabricated from these polymers exhibit a high tensile strength and crack-on-strain (COS), which are important properties for their applications in flexible and wearable devices. To investigate the intrinsic electrical properties of the PNDIT2/IM\(_x\) films and explore their feasibility in the sensors, their electron mobilities (\(\mu_e\)) were examined with organic field-effect transistors (OFETs) (Figure S3, Supporting Information).\(^{[38]}\) PNDIT2/IM\(_x\) exhibited a sufficiently high \(\mu_e\) of 0.23, 0.27, and 0.04 cm\(^2\) V\(^{-1}\) s\(^{-1}\) at \(x = 0, 0.1,\) and 0.3, respectively. All the details of the methods used for the measurements and information on PNDIT2/IM\(_x\) are described in the Experimental Section and Table S1 (Supporting Information), respectively.

We incorporated PEI (\(M_i \approx 10\) kg mol\(^{-1}\)) as a polymeric dopant in the PNDIT2/IM\(_x\) films to develop CP-based chemiresistors, because of the advantages of PEI, including high n-doping stability and mechanical ductility. Chemiresistors have a simple and effective architecture and are suitable for the flexible sensors, whereas transistor-based sensors require additional dielectric and electrode layers, which limit the diffusion of analytes into the buried channel.\(^{[39,40]}\) The doping effects of PEI on the properties of the PNDIT2/IM\(_x\) thin films were examined with UV–vis absorption spectra (Figure 1b; Figure S4, Supporting Information) and electrical conductivity (Figure S5, Supporting Information). After doping, the absorption spectra of all PNDIT2/IM\(_x\) exhibited blue shifts of 6–15 nm and the bandgaps reduced by 0.02–0.04 eV. Their bandgaps decreased from 1.49 to 1.43 eV when the films were doped with PEI ratios from 0.0 to 3.0 (Figure 1b). In addition, PNDIT2/IM-0.1 showed higher electrical conductivities with larger PEI blend ratios (e.g., 1.0 × 10\(^{-4}\) and 3.1 × 10\(^{-4}\) S cm\(^{-1}\) at PEI weight ratios of 0.4 and 3.0, respectively), indicating that PNDIT2/IM\(_x\) doped with PEI could provide sufficient electrical signals for chemiresistors. Next, we investigated the feasibility of PNDIT2/IM\(_x\) films doped with PEI as chemiresistor sensors, utilizing the set-up...
Figure 1. a) Schematic illustration of CP-based sensing materials (IM-x/P-y) for high-performance flexible NO₂ chemiresistors. b) UV–vis absorption spectra of PNDIT2/IM-x films blended with different weight ratios of dopant (y). c) Stability and recovery of IM-x/P-y-based NO₂ sensors with different dopants (i.e., PEI and n-DMBI with the same y = 1.0). d) Stress–strain curves of PNDIT2/IM-0.1 films and those with different dopants (y = 1.0).

Their sensing properties and stability were measured and compared with those of PNDIT2/IM-x films doped with 4-(1,3-dimethyl-2,3-dihydro-1H-benzoimidazol-2-yl)phenyl)dimethylamine (n-DMBI), which is one of the representative small-molecule n-doping reagents (Figure 1c). The blend films (thickness ≈ 0.1–0.2 μm) consisting of dopant and PNDIT2/IM-0.1 (1:1 by weight ratio) were prepared by drop-casting the polymer solutions (5 mg mL⁻¹ in chloroform) onto alumina substrates on which Au parallel electrodes (25 and 70 μm of width and separation distance, respectively) were deposited. The resistance of the sensor was measured and converted into a sensitivity value, i.e., $\Delta R = (R_{\text{gas}} - R_b)/R_b$ (%), where $R_{\text{gas}}$ and $R_b$ denote the resistance in target gas and baseline gas (N₂), respectively. As
evident in Figure 1c, the resistance increased upon exposure to 0.1–0.8 ppm of NO\textsubscript{2} gas in N\textsubscript{2} balance at a slightly elevated temperature (∼60 °C). Importantly, the sensor functionalized with a PEI dopant showed a good reversibility of resistance during NO\textsubscript{2} sensing, which could be attributed to the high doping stability of PEI onto PNDIT2/IM-0.1 even with NO\textsubscript{2} injections. They also enabled scalable detection with a gradual increase of AR (from 2.7 to 32.6 M\textohm) when the concentration of NO\textsubscript{2} was increased from 0.2 to 0.8 ppm. However, the sensor with n-DMBI showed a continuous upward drift of the resistance even after the recovery process (N\textsubscript{2} injection), indicating a poor reversibility of the sensor. Similar to the most organic n-type dopants, n-DMBI is intrinsically unstable in the composite, owing to the high-lying level of the highest occupied molecular orbital (HOMO) and/or low compatibility with CP chains.\[43,44\]

Next, we investigated the mechanical properties of the sensing layers with different dopants through the pseudo-free-standing tensile test.\[45\] This method enables the measurement of intrinsic tensile properties of thin films without any influence from the substrate. For example, the tensile strength and COS, which are highly correlated with the flexibility and ductility of the films in the sensors, can be obtained by this method.\[6,46,47\]

In the stress–strain curves and optical images of the tensile films (Figure 1d; Figure S7, Supporting Information, respectively), the film of PNDIT2/IM-0.1 exhibited excellent mechanical resilience with a high COS value of 22%, which was consistent with the previous results from NDI-based CP films with molecular weights higher than the critical molecular weight.\[37\] Notably, the PNDIT2/IM-0.1 film doped with PEI (1:1 by weight ratio) exhibited very similar mechanical properties with a high COS value (above 20%). This indicates that the incorporation of PEI polymer chains does not compromise the mechanical properties of the film, which is important for their use in flexible sensors. In contrast, the film with n-DMBI showed cracks at a very low external strain (∼6%) because the n-DMBI molecules in thin films served as the initial crack point and led to high roughness of the films. Therefore, the blend films of PNDIT2/IM-x with PEI polymer dopant are employed for constructing NO\textsubscript{2} sensors in this study.

### 2.2. Gas Sensing Properties of CP-Based Chemiresistors

To obtain the optimal sensitivity of PNDIT2/IM-x with PEI dopants, a series of PNDIT2/IM-x films with different weight ratios of PEI (IM-x/Y/P-y) were compared, where Y is the weight ratio between PEI and PNDIT2/IM-x in the blend film. We systematically investigated the sensing characteristics of the IM-x/P-y-based sensors at different operating conditions (e.g., operating temperature, gas concentration, etc.). First, the effect of the operating temperature was examined using the IM-0.1/P-1.0 sensor by varying the temperature from room temperature (RT ∼ 20 °C) to 90 °C (Figure S8, Supporting Information). Not only the reversibility but also the sensitivity (∆R/R\textsubscript{0} ∼ 2400 @ 1 ppm NO\textsubscript{2}) increased significantly at an elevated temperature (60 °C), while a very high operation temperature (90 °C) led to a large decrease in the sensitivity (∆R/R\textsubscript{0} ∼ 20% @ 1 ppm NO\textsubscript{2}). According to the Schaefer–Siebert–Roth model, the use of high temperatures can promote the hopping of charge carriers through CPs, resulting in enhanced conductivity and sensor performance.\[48\]

However, the dedoping process can be accelerated at elevated temperatures, which decreases the sensitivity.\[12\] Thereafter, we varied the PEI doping content (y) from 0.2 to 3.0 in the blend with IM-0.1 to observe the effect on sensitivity (Figure 2a). The baseline resistance of the IM-x/P-y-based sensors decreased from 11.1 to 7.0, 6.1, and 4.2 M\textohm as the y value increased from 0.2 to 0.4, 1.0, and 3.0, respectively. Based on the sensitivity graph at each gas concentration (0.1–1 ppm), we observed that the IM-0.1/P-1.0 sensor exhibited the highest sensitivity (∆R/R\textsubscript{0} = 4.7% @ 0.1 ppm and 240.4% @ 1 ppm) toward NO\textsubscript{2} (Figure 2b). These sensitivities were 20.9- and 18.3-fold enhanced at 0.1 and 1 ppm, respectively, compared to that of the IM-0.1/P-0.2 sensor. Moreover, the IM-0.1/P-1.0 sensor exhibited high sensitivity with the detection of an extremely low concentration of 0.1 ppm NO\textsubscript{2}.

We further investigated the effect of imine content (x) on the electrical resistance of the blend films and gas sensing properties (Figure S9, Supporting Information). As x increased from 0.0 to 0.1 and to 0.3, the baseline resistance changed from 6.3 to 4.6 and to 12.5 M\textohm, respectively, following a similar trend of the electron mobility of the pristine PNDIT2/IM-x films depending on the x values. In terms of the sensing characteristics, the sensor with IM-0.3/P-1.0 showed a reduced sensitivity (e.g., 33.5% degradation at 0.1–1 ppm NO\textsubscript{2}) compared to the sensor with IM-0.1/P-1.0, indicating that 0.1 is the optimal mole fraction of the imine bonds for the NO\textsubscript{2} sensors.

Next, we investigated the selectivity and humidity/cycling stability of the sensors (Figure 2; Figures S10 and S11 and Table S2, Supporting Information). We selected the IM-0.1/P-1.0-based sensor as it showed optimal selectivity. The selective gas-sensing characteristics of the IM-0.1/P-1.0 sensor were examined upon exposure to 1 ppm of the representative environmentally hazardous gas analytes including NO\textsubscript{2}, nitric oxide (NO), formaldehyde (HCHO), carbon monoxide (CO), carbon dioxide (CO\textsubscript{2}), methane (CH\textsubscript{4}), acetylene (C\textsubscript{2}H\textsubscript{2}), ethylene (C\textsubscript{2}H\textsubscript{4}), ethanol (C\textsubscript{2}H\textsubscript{5}OH), propane (C\textsubscript{3}H\textsubscript{8}), hydrogen sulfide (H\textsubscript{2}S), hydrogen (H\textsubscript{2}), acetone (C\textsubscript{3}H\textsubscript{6}O\textsubscript{2}), and water vapor (H\textsubscript{2}O) with 30%, 55%, and 90% relative humidity (RH) conditions (Figure 2c; Figure S10, Supporting Information). A high cross-selectivity value (S\textsubscript{NO2}/S\textsubscript{inter} > 32.2, where S\textsubscript{NO2} and S\textsubscript{inter} denoted the sensitivity toward NO\textsubscript{2} and interfering gas analytes, respectively) was obtained, which is superior to those of the previously reported CP-based gas sensors.\[49–51\]

Long-term stability is a major challenge for CP-based gas sensors, as they often experience an incomplete recovery of conductivity after chemical reactions with target analytes. To investigate the cycling stability of the IM-0.1/P-1.0 sensor, cycling gas exposure tests, i.e., 1 ppm NO\textsubscript{2} for 15 cycles of NO\textsubscript{2}/N\textsubscript{2} injections were conducted (Figure 2d). During the cycling tests, consistent and reversible resistance variations were obtained without a noticeable degradation of sensitivity (∆R/R\textsubscript{0} = 240.4 (±1.6)% @ 1 ppm). For real-world applications of CP-based gas sensors, the sensing characteristics should be measured in air and under various humid conditions. Therefore, we investigated the sensing behaviors of the IM-0.1/P-1.0 sensor under different conditions of RH, including 1.5% (dry air), 55%, and 90% in air atmosphere (Figure S11, Supporting Information). Stable baseline resis-
2.3. NO₂ Sensing Mechanism

The sensing mechanism of the IM-x/P-y-based NO₂ sensor was investigated through XPS measurements of the sensing layers before and after NO₂ exposure (Figure 3). To clarify the effect of each component during NO₂ sensing, pristine PNDIT2/IM-0.0, pristine PNDIT2/IM-0.3, and IM-0.3/P-0.4 blend films were compared in terms of their chemiresistive sensing measurements (Figure 3a). All the films were prepared by the same
Table 1. State-of-the-art CP-based NO$_2$ sensors operating at mild temperature (<90 °C). Types of CPs and their abbreviations: polypyrrole (= PPy), polythiophene (= PT), poly(phenyl vinylene) (= PPV), polyaniline (= PANI), polyacetylene (= PA), polyethylene glycol (= PEG), poly(3-hexylthiophene) (= P3HT), poly(methylsiloxane) (= PMS).

| Sensing element | Sensing temperature [°C] | Sensitivity [%] | LOD [ppm] | Cyclability [# of cycles] | Recovery Time [S] | Ref |
|-----------------|--------------------------|----------------|-----------|---------------------------|-------------------|-----|
| PPy thin film   | RT                        | 36 @ 100 ppm   | 10        | 3                         | 2170 @ 100 ppm    | [49] |
| 15-layers PANI film | RT                        | 65 @ 20 ppm   | 10        | 2                         | 17% @ 100 ppm     | [64] |
| PT film         | 60                       | 400 @ 1000 ppm | 100       | 4                         | 17% @ 100 ppm     | [65] |
| PT thin film    | RT                        | 33 @ 100 ppm   | 10        | 2                         | 35% @ 100 ppm     | [66] |
| Interconnected nanofibrous PT thin film | RT                        | 48 @ 100 ppm   | 25        | 4                         | 17% @ 100 ppm     | [67] |
| PEDOT nanotubes | RT                        | 52 @ 63 ppm    | 0.2       | 2                         | 17% @ 100 ppm     | [51] |
| PANI thin film  | RT                        | 11 @ 10 ppm    | 10        | 2                         | 17% @ 100 ppm     | [68] |
| Ag-PPy          | RT                        | 68 @ 100 ppm   | 5         | 2                         | 17% @ 100 ppm     | [69] |
| PANI-fibers     | RT                        | 80 @ 1 ppm     | 1         | 6                         | 17% @ 100 ppm     | [16] |
| PEDOT film      | 80                       | 22 @ 100 ppm   | 10        | 2                         | 17% @ 100 ppm     | [50] |
| PEDOT-rGO       | 80                       | 7 @ 100 ppm    | 1         | 5                         | 17% @ 100 ppm     | [70] |
| DBSA-doped PPy-WO$_3$ | RT                        | 71 @ 100 ppm   | 5         | 3                         | 17% @ 100 ppm     | [71] |
| Ppy-NiO         | RT                        | 47 @ 100 ppm   | 10        | 4                         | 17% @ 100 ppm     | [72] |
| PPy-Fe$_2$O$_3$ nanorod | RT                        | 12 @ 50 ppm    | 1         | 5                         | 17% @ 100 ppm     | [73] |
| PT-WO$_3$       | 90                       | 500 @ 100 ppm  | 10        | 4                         | 17% @ 100 ppm     | [74] |
| PT-SnO$_2$      | 90                       | 400 @ 100 ppm  | 10        | 5                         | 17% @ 100 ppm     | [75] |
| rrP3HT-PMS Graft | 50                       | 2300 @ 5 ppm   | 5         | 3                         | 17% @ 100 ppm     | [76] |
| PEGSi-H         | 50                       | 900 @ 5 ppm    | 1         | 5                         | 17% @ 100 ppm     | [77] |
| IM-0.1/P-1.0    | 60                       | 240 @ 1 ppm    | 0.1       | 15                        | 17% @ 100 ppm     | This Study |

methods of sensor measurements. The XPS data of three different samples were mainly discussed through the N 1s spectra, as no distinct changes were observed in O 1s and C 1s spectra. First, PNDIT2/IM-0.0 exhibited a single imide (O=C–N–C=O) peak from the NDI moiety at 400.2 eV (NDI-peak), which is well-matched with the results of the previous studies.[53–55] Meanwhile, after the integration of IM into NDI, PNDIT2/IM-0.3 showed an additional peak at 398.5 eV, associated with the strong interaction between C–N–C and NO$_2$, as evidenced by no noticeable change in the 1H NMR and UV–vis absorption spectra of PNDIT2/IM-x films before and after continuous NO$_2$ exposure for 3 d (Figure S12, Supporting Information). Furthermore, the IM-0.3/P-0.4 blend exhibited the same additional peak of –N•••– and larger decreases in A$_{IM}$ + A$_{NO_2}$ (≈35%) than pristine PNDIT2/IM-0.3. The decreases could be attributed to not only the weakened imine bonds (A$_{IM}$), but also the dedoping of PEI (A$_{PEI}$) by NO$_2$ interactions (Figure 3b). Supported by the XPS analysis of PNDIT2/IM-0.0 with PEI (i.e., IM-0.0/P-0.4), the influence of PEI dedoping might be the same in IM-x/P-y-based sensors with different imine contents (x), because the decreasing ratios of A$_{PEI}$ were very similar in both imine contents (decreasing ratio of A$_{PEI}$ = 17% and 18% at x = 0.0 and 0.3, respectively, in Figure S13, Supporting Information). For both the PNDIT2/IM-0.3 and IM-0.3/P-0.4 blend samples, NDI-peak shifted toward a lower binding energy (≈0.2–0.3 eV) because of the electron localization by the weakened conjugations (Figure 3c). In short, the adsorption of NO$_2$ onto PNDIT2/IM-x was driven by two mechanisms. First of all, C=N bond of PNDIT2/IM-x donates its lone pair electrons (N) to NO$_2$ molecules. This causes a larger electron-deficiency of the C=N bond, which disturbs the push-pull structures of PNDIT2/IM-x and weakens the backbone conjugation.[58] Second, dedoping of PEI from the PNDIT2/IM-x composites reduces the charge-carrier density of CPs.[53,55] These changes resulted in a rapid increase in the electrical resistance, enabling the detection of very low concentrations of NO$_2$. is formed and the imine bonds might be weakened via NO$_2$ interactions. We note that the molecular structures of PNDIT2/IM-x can be preserved even after long-term exposure of NO$_2$, despite the strong interaction between C=N and NO$_2$, as evidenced by no noticeable change in the 1H NMR and UV–vis absorption spectra of PNDIT2/IM-x films before and after continuous NO$_2$ exposure for 3 d (Figure S12, Supporting Information). Furthermore, the IM-0.3/P-0.4 blend exhibited the same additional peak of –N•••– and larger decreases in A$_{IM}$ + A$_{NO_2}$ (≈35%) than pristine PNDIT2/IM-0.3. 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The decreases could be attributed to not only the weakened imine bonds (A$_{IM}$), but also the dedoping of PEI (A$_{PEI}$) by NO$_2$ interactions (Figure 3b). Supported by the XPS analysis of PNDIT2/IM-0.0 with PEI (i.e., IM-0.0/P-0.4), the influence of PEI dedoping might be the same in IM-x/P-y-based sensors with different imine contents (x), because the decreasing ratios of A$_{PEI}$ were very similar in both imine contents (decreasing ratio of A$_{PEI}$ = 17% and 18% at x = 0.0 and 0.3, respectively, in Figure S13, Supporting Information). For both the PNDIT2/IM-0.3 and IM-0.3/P-0.4 blend samples, NDI-peak shifted toward a lower binding energy (≈0.2–0.3 eV) because of the electron localization by the weakened conjugations (Figure 3c). In short, the adsorption of NO$_2$ onto PNDIT2/IM-x was driven by two mechanisms. First of all, C=N bond of PNDIT2/IM-x donates its lone pair electrons (N) to NO$_2$ molecules. This causes a larger electron-deficiency of the C=N bond, which disturbs the push-pull structures of PNDIT2/IM-x and weakens the backbone conjugation.[58] Second, dedoping of PEI from the PNDIT2/IM-x composites reduces the charge-carrier density of CPs.[53,55] These changes resulted in a rapid increase in the electrical resistance, enabling the detection of very low concentrations of NO$_2$.
The molecular interactions between NO₂ and the IM-x/P-y films were also supported by Raman spectra (Figure 3d). Before NO₂ exposure, IM-0.3/P-0.4 represented similar spectra with those of conventional NDI-based CPs, reported in the previous literature.[59] An additional peak at ≈1574 cm⁻¹ was observed from the intensity of C=N stretching vibrations.[60] After NO₂ exposure, the band from C=N stretching was decreased and the overall Raman spectra exhibited upward shifts (≈6.5 cm⁻¹). The upward shift of Raman spectra was highly correlated with the reduction of electron delocalization in the CP chains.[61,62] Considering all these observations, the NO₂ sensing mechanism of the IM-x/P-y-based sensor is proposed (Figure 3e). Before NO₂ exposure, a high charge-carrier density in the active channel by PEI doping and extended conjugations of CPs chains successfully lead to a high electrical conductivity and low baseline resistance of sensors. After NO₂ exposure, the CP chains are influenced by two effects: (1) the weakening of the conjugations by donating the lone pair electrons of C=N bond to NO₂ analytes; and (2) the reduction of the charge-carrier density in CPs by the dedoping of PEI. Accordingly, rapid increases in resistance enable the sensors to detect very low concentrations of NO₂ gas with high sensitivity, long-term stability, and high selectivity.
2.4. Applications in Flexible and High-Performance NO\textsubscript{2} Sensor

To demonstrate the feasibility of IM-\textit{x}/P-\textit{y} in flexible sensor applications, we fabricated a flexible and stretchable device as follows. We used a mechanically stable thermoplastic polyurethane (TPU) substrate\textsuperscript{[63]} (thickness \(\approx 300\) μm) with Cu/Au bilayer electrodes (5 nm/100 nm) (Figure 4a). The polymer solutions of IM-0.1/P-1.0 were drop-casted on the prepared poly(sodium 4-styrenesulfonate) (PSS)-coated glass; Thereafter, the polymer films were floated on water by dissolving the PSS sacrificial layer and transferred onto the TPU substrates. Next, we measured the performance of the flexible sensors under three different measurement conditions; (i) flat state (Flat), (ii) bent state (Bent), and (iii) flat state after 500 cycles of bending tests (Flat500) (Figure 4b). The bending tests were conducted using a homemade bending machine with a bending angle of \(\approx 80^\circ\) and a bending radius of 1.9 mm. The NO\textsubscript{2} sensing properties were analyzed upon exposure to 0.2–5 ppm of NO\textsubscript{2} in N\textsubscript{2} atmosphere at RT. All the sensors showed similar baseline resistances (130, 144, and 138 kΩ at Flat, Bent, and Flat500, respectively) and reliable reversibility (Figure 4c,d). As the IM-\textit{x}/P-\textit{y} based sensing material features excellent flexibility and mechanical stability, the sensor with IM-0.1/P-1.0 could monitor very low concentration (0.2 ppm) of NO\textsubscript{2} analytes in both Bent and Flat500 states at RT.
3. Conclusion

In this study, we demonstrated high-performance flexible chemiresistive NO\textsubscript{2} sensors with a newly designed CP-based system (IM-x/P-y). The incorporation of imine bonds into the conjugated backbone could facilitate good interaction with NO\textsubscript{2}, while all-polymer-based sensing materials provided excellent mechanical stability. The sensing properties were investigated systematically under different operating conditions, such as different sensing temperatures, mole fractions of imine bonds, weight ratios of PEI dopants, RH in atmosphere, and cyclic exposure of gas. IM-0.1/P-0.1 exhibited outstanding performances in terms of high sensitivity (ΔR/R\textsubscript{0} = 240% @ 1 ppm of NO\textsubscript{2}), selectivity (S\textsubscript{NO\textsubscript{2}}/S\textsubscript{max} > 32.2), ultralow LOD (≈0.1 ppm), and high long-cycling stability. Based on XPS and Raman spectroscopic analyses, the unique sensing mechanisms were identified: the effective modulations of the conjugations in IM-x/P-y were derived by donating the lone pair electrons of the imine bond to NO\textsubscript{2} analytes and dedoping of PEI dopant, leading to large modulations in the electrical signals. Furthermore, we successfully demonstrated the substantial potential of IM-x/P-y as a flexible sensor platform. The resulting sensor in the bent state or after subjecting to 500 bending cycles could monitor sub-ppm level of NO\textsubscript{2} gas with high sensitivity.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

conjugated polymer-based chemiresistors, flexible sensors, high-performance chemiresistors, imine bonds, NO\textsubscript{2} gas sensors

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