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Highly sensitive and selective chemiresistive sensors based on multidimensional polypyrrole nanotubes†

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Multidimensional polypyrrole nanotubes (MPPy NTs) were successfully fabricated as chemiresistors on a sacrificial nanofiber template by vapor deposition polymerization (VDP) and used to discriminate volatile organic compounds (VOCs) and toxic gases.

Extremely low concentrations (ppb to ppt) of metabolites and/or volatile compounds in exhaled breath can be used as diagnostic markers for diseases.[1] Liver diseases can be diagnosed by elevated levels of ethane (*ca.* 800 pmol L^{-1}) and pentane in breath.[2] Hepatic disease, hepatic encephalopathy which is a neuropsychiatric consequence of advanced liver disease, is marked by the presence (*ca.* 238 μg%) of ammonia.[3] Various detection methods have been applied to exhaled breath, including gas/liquid chromatography,[4] infrared spectroscopy,[5] mass spectrometry,[6] biological and chemical methods[7] with metallic materials, to meet the expanding need for more sensitive, specific, and non-invasive tests. Although these analyses have individual advantages, their limitations generally include lack of normalization and standardization. Depending on the method, they can also be time consuming and expensive, or may operate at high temperatures.

Chemiresistor-based sensors boast several potential advantages, including low power consumption, label-free detection, and highly precise resistance measurements.[8] Several materials, such as metal oxides, semiconductors, and hybrid nanomaterials, have been utilized as chemiresistors and have exhibited strong changes in resistance in response to various chemical gases, including volatile organic compounds (VOCs) and toxic gases. Although significant achievements have been made in the development of these sensors, they have been largely limited by poor selectivity and reproducibility, high temperatures, and low sensitivity. The development of novel chemiresistors with unique nanostructures remains a challenge.

We report herein a highly selective and sensitive chemiresistive sensor based on multidimensional conducting polymer

(CP) nanotubes. Unique substructures consisting of nanowires (NWs) and nanonodules (NDs) were grown on a polypyrrole surface that had been coated onto a sacrificial nanofiber template by vapor deposition polymerization (VDP). The resulting multidimensional polypyrrole nanotubes (MPPy NTs) exhibited an enhanced surface-to-volume ratio with an anisotropic tubular structure that provided efficient charge carrier transport along the rotational axis of the nanotube. Most importantly for the current application, the electrical resistance of the MPPy NTs was both sensitive and selective to specific VOCs. The minimum detection limit (MDL) for gaseous ammonia was 10 ppb, which is 2–3 orders of magnitude lower than that of previously reported ammonia sensors. It is still a challenge to precisely control the morphology of functional polymers on a nanometer scale for various future technologies. Thus it is believed that our approach provides a good example of how the morphology of functional polymers should be tailored for sensing applications.

Previously, we synthesized various conducting polymer nanomaterials for chemical gas sensing.[9,10] Continuously, MPPy NTs with nanonodules (ND) and nanowires (NWs) were fabricated for the current study (Fig. 1). Polypyrrole nanotubes with a smooth layer (SM) surface was also prepared as a control.

One-dimensional (1D) sensing architectures provide unparalleled advantages in terms of facilitating efficient charge carrier transport induced by molecular recognition events along the
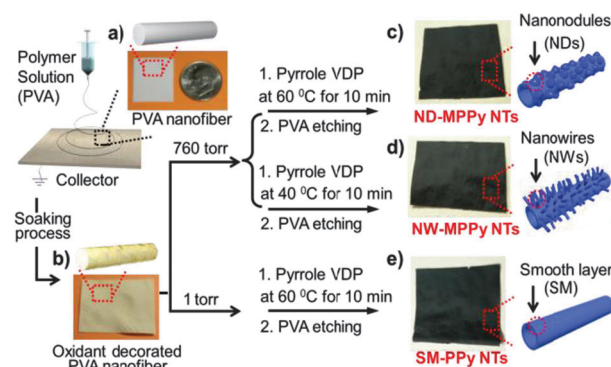
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† Electronic supplementary information (ESI) available: Detailed synthetic method, schematic diagram of the sensor substrates, real-time responses of MPNs toward HR. See DOI: 10.1039/c2cc35307e
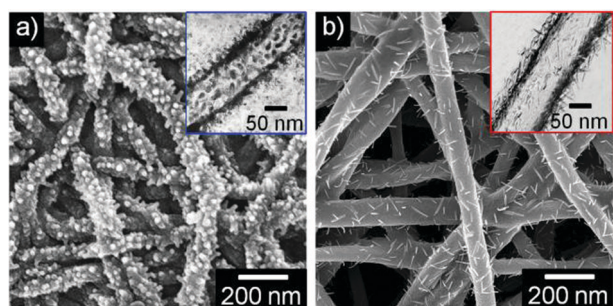‡ These authors contributed equally to this work.

Fig. 1 Synthetic protocol of MPPy NTs. (a)–(e) are photo images of the real samples. Each product shows the characterized color changes (a: polyvinyl acetate (PVA) nanofibers with white color, b: oxidant decorated PVA nanofibers with yellow, c and d: ND- and NW-MPPy NTs with black, and e: PPy NTs with black).

Fig. 2 FE-SEM images of MPPy NTs: (a) NDs and (b) NWs. The insets indicate HR-TEM images.

long-axis direction.[9–11] 1D tubular, nanostructure-based sensor devices are more sensitive and selective than nanowires or nanofibers due to their relatively larger surface area.[9] From a materials perspective, the MPPy NTs were constructed following a core-etching process and were observed by field-emission scanning electron microscopy (FE-SEM) and high-resolution transmission electron microscopy (HR-TEM) (Fig. 2). The surface morphologies of the MPPy NTs were tailored with specific structures: SM (Fig. S1, ESI†), NDs (Fig. 2a), and NWs (Fig. 2b). Most of these structures had outer diameters of about 100 nm with thin walls approximately 15 nm thick. Stable tubular nanostructures were also identified in HR-TEM micrographs, shown in the insets of Fig. 2. The Brunauer–Emmett–Teller (BET) surface area of the nanotubes increased in the following order: SM (28 m² g⁻¹) < ND (46 m² g⁻¹) < NW (57 m² g⁻¹). The NW-MPPy NTs had the most extensive surface area, twice that of conventional SM.

To use MPPy NTs as chemiresistive transistors in a chemical sensor system, the MPPy NTs were integrated into a circuit device fabricated in-house. MPPy NTs were transferred onto a polydimethylsiloxane (PDMS) substrate using a dry-transfer method. Micro-patterned gold electrodes were then deposited onto the MPPy NTs by thermal evaporation (Fig. S2 and S3, ESI†). The electrical properties of the MPPy NT-integrated chemiresistive sensors (MPNS) were determined by observing their current–voltage characteristics. Fig. 3a shows the *I–V* curves of MPPy NTs on the sensor substrate. All of the MPPy NTs displayed ohmic behaviors in their *I–V* characteristics, which indicates that the MPPy NTs were in reliable electrical contact with the sensor substrate. Interestingly, the d*I*/d*V* values increased slightly in the order SM < ND < NW, due primarily to inter-nanotube contact resistance, which allows for efficient charge transport along the long axis of the MPPy NTs. Accordingly, when the MPPy NTs were assembled between the source and drain electrodes, interactions with the target analyte were indicated by changes in electrical resistance through the MPNS.

To confirm their sensing performances, the MPNSs were implemented into chemical gas sensing systems. First, since exhaled air contains high levels of water vapor, the environmental stability of the MPNSs was investigated with regard to relative humidity (RH). The electrical resistance of the MPNSs was measured on a probe station in an RH-controlled and temperature-monitored chamber (Fig. S4, ESI†). Under optimized conditions (30–35% RH at RT), changes in resistance were recorded in real time during alternate exposures to ammonia
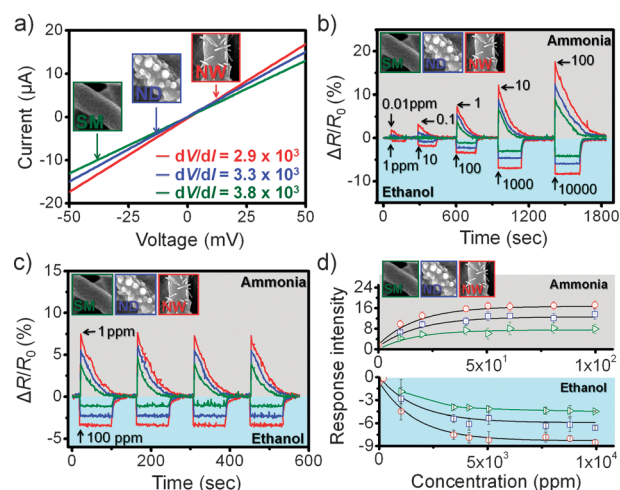

Fig. 3 (a) *I–V* characteristics of MPPy NTs integrated in the sensor substrate (scan rate, 1 mV s⁻¹). The d*V*/d*I* values indicate the slope of the resistance change. (b) Real-time responses of MPPy NTs upon cyclic exposure to ammonia (0.01 ppm to 100 ppm) and ethanol (1 ppm to 10 000 ppm). (c) Real-time responses of MPPy NTs on periodic exposure to 1 ppm ammonia and 100 ppm ethanol. (d) Changes in response intensity of MPPy NTs as a function of ammonia and ethanol vapor concentration: the response intensity was determined as the $\Delta R/R_o$(%) measured when the saturated value was reached after exposure to gases.

or ethanol vapor and pure N_2 (Fig. 3b). Exposure to ammonia and ethanol vapors elicited a precipitous rise in the resistance of the MPPy NTs and the signals were saturated continuously. In particular, we presented just a shorter saturation period (*ca.* 10 s) to show the overall response profile at the same cycle because the sensor showed much longer recovery time to ammonia than did ethanol (Fig. S5, ESI†). When the analyte flow was replaced with N_2, the resistance recovered to the original level. The signal intensities increased in the order SM < ND < NW. NW- and ND-MPNSs were more sensitive than SM-MPNS. The lowest detection limit of *ca.* 10 ppb gaseous ammonia (signal-to-noise: 3.2) was observed with NW-MPNS. This is approximately two orders of magnitude more sensitive than previously reported NH_3 sensors.[9] For ethanol vapor, the NW-MPNS also showed the highest sensitivity with an MDL of *ca.* 1 ppm (signal-to-noise: 3.0). In the previous study, we demonstrated that the charge carrier density was crucial to the sensing performance of devices based on CP nanostructures. In particular, MPPy NTs exhibit a p-type semiconductor characteristic which has holes as charge carriers. The responses from MPNSs can also change the charge carrier density in the MPPy NT backbone. Specifically, the introduction of electron-donating molecules (NH_3) into MPPy NTs reduces the charge carrier density (holes density), resulting in the increment of the electrical resistance. In contrast, analytes which possess electron-withdrawing groups, such as ethanol, methanol, and acetic acid, create new holes in the MPPy NT structure, leading to the opposite result.[9] These charge transfer behaviors allow the MPPy NTs to act as chemiresistors. Compared to conventional gas sensors, the MPNSs had rapid response (less than 1 s) and recovery times (0.01 ppm ammonia: 55–60 s, 1 ppm ethanol: 4–5 s) under various concentrations. In addition, the MPNSs demonstrated excellent reproducibility
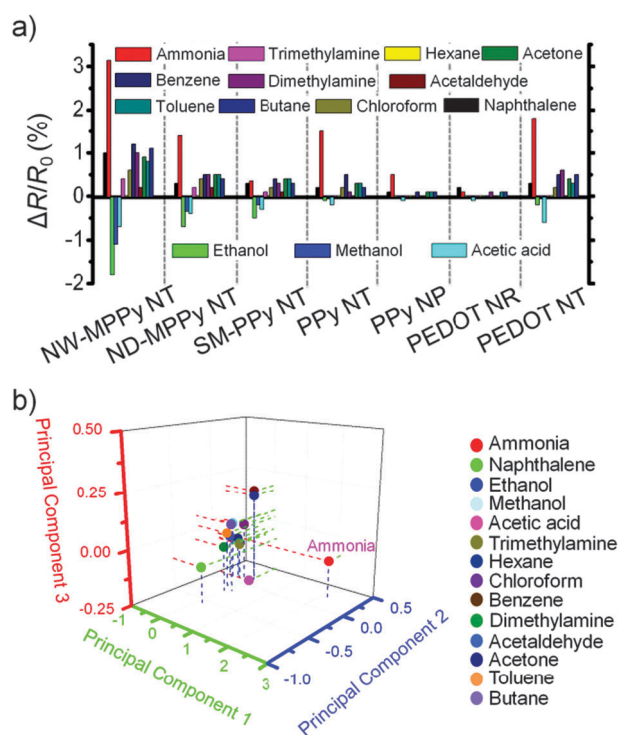
Fig. 4 (a) Histogram of sensing performances and (b) principal components analysis (PCA) plot of the dataset of response intensities inputted from six conducting polymer nanomaterials (NW-MPPy NT, ND-MPPy NT, SM, PPy NT, PPy NP, PEDOT NR, and PEDOT NT) to 14 analytes: each analyte concentration was fixed at around 10 ppm.

and reversibility (Fig. 3c). Fig. 3d shows the changes in resistance over concentration ranges of 0.01 ppm to 100 ppm of ammonia and 1 ppm to 10 000 ppm of ethanol vapor.

The MPNS resistance was then monitored in response to several representative VOCs and toxic gases frequently present in human breath.[1,12] For comparison, the responses of several other sensing materials were simultaneously evaluated. Fig. 4a shows the real-time responses of selected sensing materials to 14 gases. For the selectivity test, ammonia gas was calculated at 0.1 ppm for MPNS and the other gases were introduced at 10 ppm. Relative to the other chemiresistors, the responses from NW- and ND-MPNSs were highly selective for two gases: one (ammonia) is on the positive region and the other (ethanol) is on the opposite direction. Interestingly, there were no significant responses from the sensing nanomaterials (polypyrrole nano-particles (PPy NPs),[9a] PPy NTs,[9d] poly(3,4-ethylenedioxythio-phene) nanorods (PEDOT NRs),[9e] and PEDOT NTs[9e]) toward several of the analytes (dimethylamine, ethanol, methanol, triethylamine, and toluene).

Principal components analysis (PCA) was performed on the detection data shown in Fig. 4a. Fig. 4b shows the characteristic sensitivities of each sensing material for each of the analytes. The accuracy of the simulation results was satisfactory (>99%). Analytes were segregated into separate regions of the PCA plot, with sufficient resolution for the identification of individual analytes. The response of ammonia was particularly differentiable, demonstrating the selective recognition ability of MPPy NTs.

In summary, we demonstrated that chemiresistors composed of multidimensional conducting polymer nanotubes built on pat-terned PDMS substrates can be used to discriminate VOCs and toxic gases from human breath. This provides a convenient, safe, and non-invasive method of diagnosing and monitoring diseases. The MPNSs exhibited rapid response and recovery times with highly sensitive and selective responses. The NW-MPNS was especially sensitive with an MDL of *ca.* 0.01 ppm for ammonia. The sensing materials developed in this study are expected to be relatively portable and inexpensive, allowing their use in high-volume applications such as pre-screening events.

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