Sulfonated Poly(ether ether ketone)/Polypyrrole Core−Shell Nanofibers: A Novel Polymeric Adsorbent/Conducting Polymer Nanostructures for Ultrasensitive Gas Sensors

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S *Supporting Information*

ABSTRACT: Conducting polymers-based gas sensors have attracted increasing research attention these years. The introduction of inorganic sensitizers (noble metals or inorganic semiconductors) within the conducting polymers-based gas sensors has been regarded as the generally effective route for further enhanced sensors. Here we demonstrate a novel route for highly-efficient conducting polymers-based gas sensors by introduction of polymeric sensitizers (polymeric adsorbent) within the conducting polymeric nanostructures to form one-dimensional polymeric adsorbent/conducting polymer core−shell nanocomposites, via electrospinning and solution-phase

polymerization. The adsorption effect of the SPEEK toward NH_3 can facilitate the mass diffusion of NH_3 through the PPy layers, resulting in the enhanced sensing signals. On the basis of the SPEEK/PPy nanofibers, the sensors exhibit large gas responses, even when exposed to very low concentration of NH_3 (20 ppb) at room temperature.

KEYWORDS: electrospinning, gas sensor, polypyrrole, polymeric sensitizer, sulfonated poly(ether ether ketone), one-dimensional core−shell structure
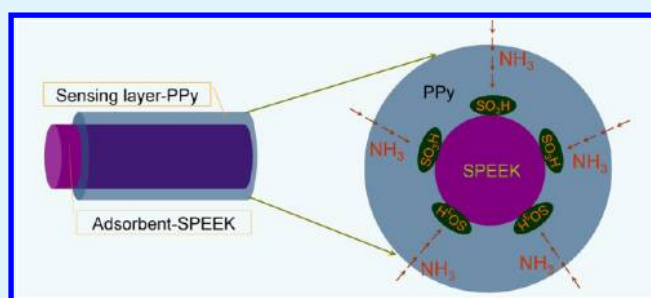
■ INTRODUCTION

The past several decades have witnessed the big progress on fabricating gas sensors based on conducting polymer sensing materials, driven by their advantages such as tunable electrical behavior from insulator to near metallic, good flexibility, room temperature operation, environmental stability, low density, relatively low cost and ease of functionalization.[1−5] In recent years, conducting polymer sensing materials are usually synthesized at the nanoscale owing to their large surface areas and the increased physical adsorption of the tested gases.[6−8] However, their intrinsic shortcomings such as low mechanical strength and low sensitivity of conducting polymers hinder their potential for future applications.[9] By far, many efforts have been devoted to improving the sensitivities of conducting polymers-based gas sensors, which are frequently focused on the introduction of inorganic sensitizers: (I) combination of n-type inorganic semiconductors within p-type conducting polymers for the synergic effect of these two components,[10−13] or (II) introduction of noble metal additives to activate the sensing system.[14−16] Despite some successes, those reported approaches still suffer from the intrinsic brittleness and high-cost of the inorganic sensitizers, which is not helpful to develop low-cost and flexible sensing devices in practice. Introduction of

polymer sensitizers may be an effective method but has attracted little research attention. It is well-known that NH_3 is harmful for the human health and environment, and its monitoring has aroused great concerns worldwide.[17] Furthermore, elevated concentrations of ammonia in exhaled breath, 50−100 ppb, can be used as a noninvasive diagnosis of renal disorders or ulcers.[18] Thus in this study, taking NH_3 as the target gas, we established a novel all-organic sensing structure consisting of one-dimensional polymeric adsorbents/conducting polymers core−shell nanostructures, in which the polymeric adsorbent was chosen as the sensitizer. The designed sensing materials were demonstrated based on sulfonated poly(ether ether ketone) (SPEEK)/polypyrrole (PPy) core−shell nanofibers via electrospinning[19,20] and solution-phase polymerization.[21] Such sensing structure possesses the following two advantages. (i) The polymeric adsorbents (SPEEK) can provide excellent mechanical flexibility. (ii) During the test, the adsorption effects of the SPEEK toward NH_3 are expected to facilitate the tested gases diffusion within and react with the

conducting polymer shells, hence increasing the sensing response, even when exposed to a very low concentration of NH_3 (20 ppb) at room temperature.

■ EXPERIMENTAL SECTION

Materials. The sulfonated poly(ether ether ketone) (SPEEK) used in the present work was synthesized in our lab. The detailed synthesis experiment and characterization data have been provided in our former work.[22] (The molecular formula of the SPEEK is presented in Scheme S1 in the Supporting Information). Polyacrylonitrile (PAN, M_w = 80 000) was obtained from Jilin Carbon Group, China. Pyrrole (AR, Shantou Xilong Chemicals Co., China) was distilled twice under reduced pressure before use. N,N-Dimethylformamide (DMF) and $FeCl_3 \cdot 6H_2O$ were purchased as analytically pure reagents from Tianjin Tiantai Fine Chemicals Co. (China) and used without further purification. Distilled water was used for all experiments.

Fabrication of the Nanofibers and Sensors. *Preparation of SPEEK Nanofibers.* The SPEEK is a kind of ionic polymer, with inherently poor electrospinnability. Thus PAN was used as the fiber-forming facilitating additive to facilitate the formation of SPEEK electrospun nanofibers. First, 0.4 g of SPEEK and 0.04 g of PAN were dissolved in 2 mL of DMF, under vigorous stirring at 60 °C for 2 h. After cooling to room temperature, the mixture was loaded into a glass syringe. A 15 kV potential was applied between the cathode (a flat aluminum foil) and the anode (the syringe tip), which were separated by 20 cm.

Preparation of SPEEK/PPy Core−Shell Nanofibers. The collected SPEEK nanofiber films were immersed in an aqueous solution of pyrrole (0.025 g of pyrrole in 50 mL of distilled water). After adding $FeCl_3$ solution as the oxidant (0.1 g of $FeCl_3 \cdot 6H_2O$ in 5 mL of water), the PPy layer gradually formed on the SPEEK nanofibers. After the solution-phase polymerization, the as-prepared products were rinsed 6 times and dried in air for 24 h.

Fabrication of the Sensors. The as-prepared SPEEK/PPy nanofiber films were then coated onto a ceramic substrate (7 mm × 5 mm × 0.5 mm) with three pairs of carbon interdigital electrodes to form sensing films. To improve the adhesion between nanofiber films and the device substrates, the substrates with attached nanofibers were immersed in water for 1 min and dried at 60 °C in air.

Characterization and Measurement. The products were characterized by transmission electron microscopy (TEM; JEM-2000EX), UV−vis absorption spectrometry (Shimadzu UV-3101 PC Spectrometer), scanning electron microscopy (SEM, Shimadzu SSX-550, Japan) attached with energy dispersive X-ray spectrometry (EDX). Gas sensing properties were measured using a static test system. The electrical properties of sensors were measured by the CGS-8 intelligent gas-sensing analysis system (Beijing Elite Tech Co. Ltd., China). The source of voltage used by the system is 220 V, and the sensor test voltage supplied by the system is 5 V. When the resistances of all the sensors were stable, saturated target gas was injected into the test chamber (20 L in volume) by a microsyringe through a rubber plug. The saturated target gas was mixed with air (the relative humidity was controlled in the range of 30−40%, and room temperature was about 25 °C) by two fans in the analysis system. After the sensor resistances reached a new constant value, the test chamber was opened to recover the sensors in air. All the measurements were performed in a laboratory fume hood. The sensor resistance and response values were acquired by the analysis system automatically. The gas response was defined as response (%) = (Rg − Ra)/Ra × 100, where Rg and Ra denote the sensors resistances in the tested gas and in the air, respectively.

■ RESULTS AND DISCUSSION

The fabrication of the NH_3 sensors using SPEEK/PPy core−shell nanofibers can be divided into three steps. First, template nanofibers comprised of SPEEK and polyacrylonitrile (PAN) were electrospun from a dimethylformamide (DMF) solution and collected, the mass ratio of PAN to SPEEK is 1/10.
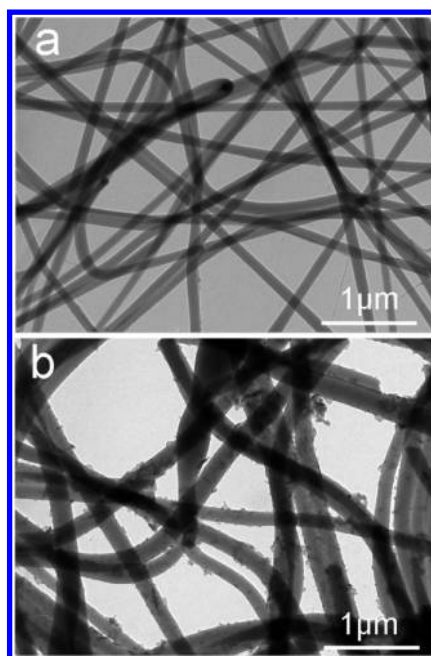

Figure 1. TEM images of (a) SPEEK nanofibers (containing PAN) and (b) SPEEK/PPy core−shell nanofibers.
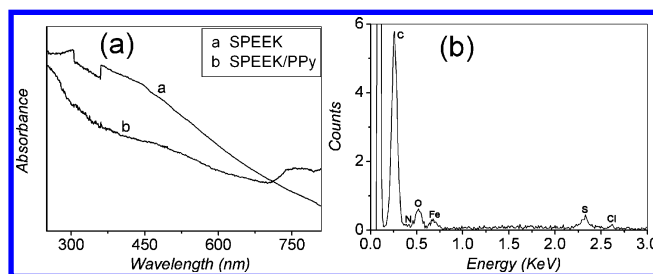

Figure 2. (a) UV−vis spectra of the SPEEK (containing PAN) nanofibers and SPEEK/PPy core−shell nanofibers. (b) EDX spectra based on SPEEK/PPy naofibers (polymerization time of 3 h).

Second, the collected nanofiber films were then immersed in a solution of polymerizing PPy and used to direct the synthesis of the core−shell nanofibers in aqueous medium.[21] Finally, the as-prepared SPEEK/PPy core−shell nanofiber films were transferred onto device substrates (with three pairs of carbon interdigital electrodes) to detect NH_3. Figure 1a shows the TEM images of the template nanofibers (SPEEK/PAN), indicating the average diameter is ∼90 nm and the surface is smooth. Figure 1b presents the TEM image of the SPEEK/PPy core−shell fibers, after the solution-phase polymerization of PPy for 3h. The average diameter of the composite nanofibers increases to about 190 nm, indicating the formation of the PPy shell on the SPEEK nanofibers. To further confirm the formation of PPy after the solution polymerization, the UV−vis spectra of the samples were performed and shown in Figure 2a. An absorption band after 730 nm can be observed, confirming the formation of polypyrrole.[23] The SPEEK/PPy core−shell nanofibers were also characterized by EDX, as shown in Figure 2b. One can clearly see the corresponding peaks of the elements of C, N, O, S from the pattern, confirming the components of the SPEEK/PPy nanofibers. It is noteworthy that Fe and Cl elements were also detected in the EDX pattern, which is in good agreement with a previous report.[24] It is because Fe and Cl elements often remain in

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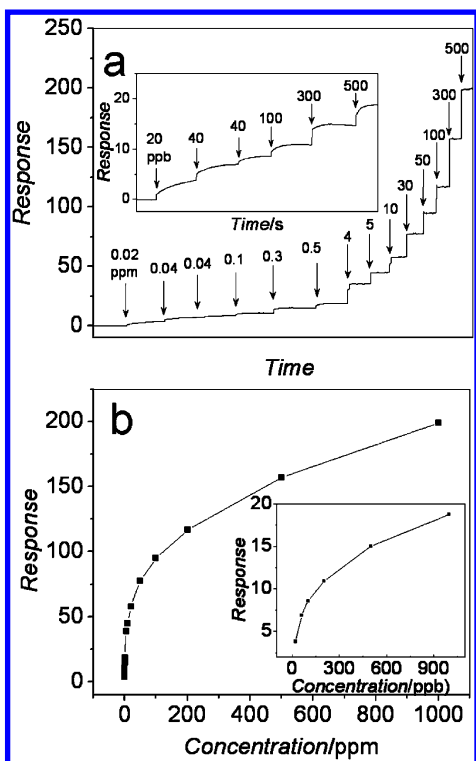
Figure 3. Part a and the inset show the stepwise increase in gas response of SPEEK/PPy nanofibers (polymerization time of 3 h) obtained with successive injection of NH_3 into the test chamber. (b) The sensor response as a function of the NH_3 concentration. The inset of part b shows the response curve in the range of 20−1000 ppb.

Scheme 1. Schematic Diagram the SPEEK/PPy Core−Shell Nanofibers, During NH_3 Sensing
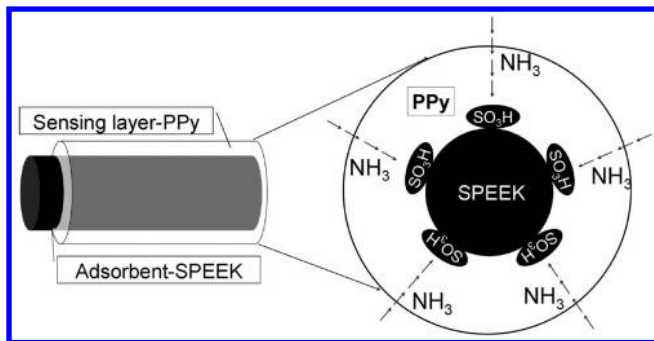
chemically prepared PPy in the form of $[FeCl_x]^{n-}$ species, which serve as the counterions to dope PPy, when $FeCl_3$ serves as the oxidant.

In this study, the gas sensing properties of the SPEEK/PPy core−shell nanofibers toward NH_3 have been studied by recording its electrical response upon exposure to NH_3 gas of different concentrations at room temperature. Figure 3a displays the stepwise increase in gas response of the sensor based on SPEEK/PPy core−shell nanofibers (polymerization time of 3 h) at room temperature, upon the successive addition of NH_3 into the testing chamber.[25] (The data were collected tens of seconds after each injection of NH_3.) Stable and distinct responses can be observed for that sample. Figure 3b and the inset plot the response of the gas sensor as a function of concentration of NH_3. When exposed to a very low concentration of NH_3 (20 ppb), it exhibits a response of as
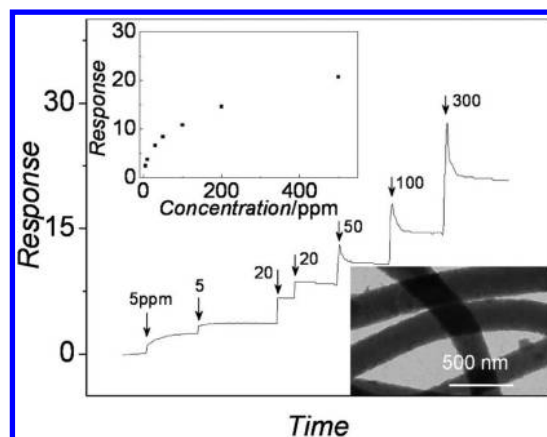

Figure 4. Step-wise increase in gas response of PAN/PPy nanofibers. Top inset: response versus NH_3 concentration for PAN/PPy nanofibers. Bottom inset: TEM image of PAN/PPy nanofibers.
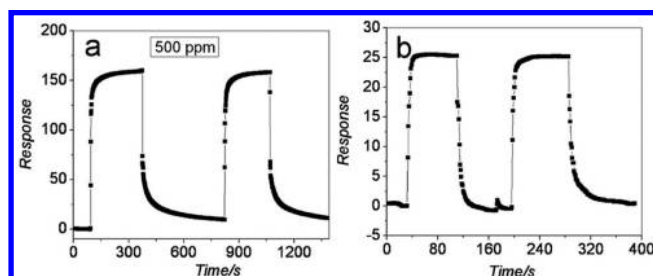

Figure 5. Response/recovery curves at ammonia concentrations of 500 ppm at room temperature (a) for SPEEK/PPy nanofibers and (b) for PAN/PPy nanofibers.
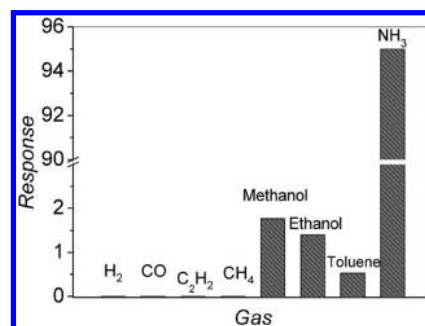

Figure 6. Anti-interference performance of SPEEK/PPy nanofibers to 100 ppm of H_2, CH_4, C_2H_2, CO, methanol, ethanol, toluene, and NH_3.
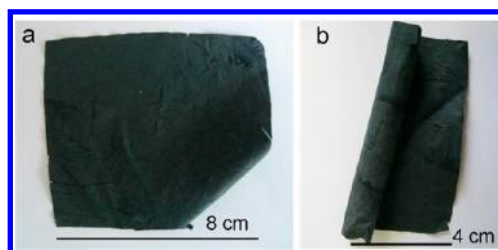

Figure 7. Photographs of a SPEEK/PPy core−shell nanofiber film with larger area (polymerization time of 3 h): (a) before and (b) after curling up.

high as 3.8 (inset of Figure 3b). With increasing the concentration of NH_3, the response is greatly increased. The response values are about 8.6, 15.0, 18.8, 45.0, and 95.1 to 100 ppb, 500 ppb, 1 ppm, 10 ppm, and 100 ppm NH_3, respectively.
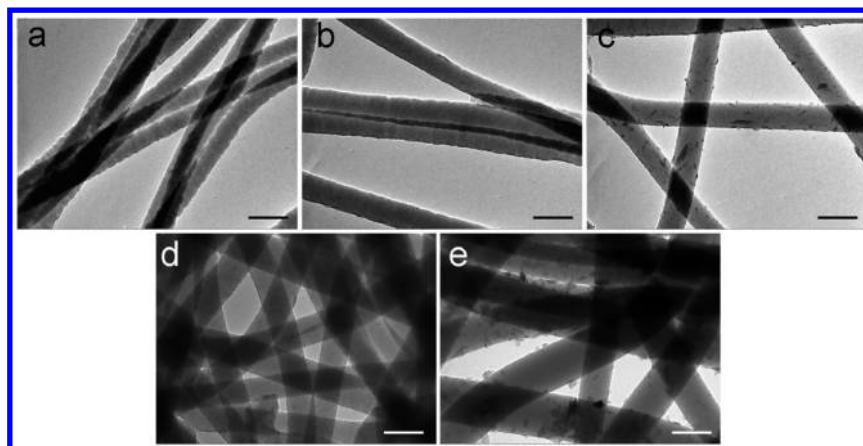
Figure 8. TEM images of SPEEK/PPy nanofibers having different polymerization times: (a) 5 min, (b) 10 min, (c) 20 min, (d) 40 min, and (e) 3 h. The scale bar: 200 nm.
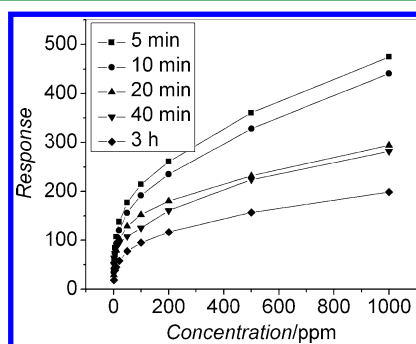

Figure 9. Response versus NH_3 concentration for SPEEK/PPy nanofibers having different polymerization times.

These results obtained for the SPEEK/PPy nanofiber are much better than most previously reported PPy gas sensors.[6,11,15,18,26,27] Specifically, the detection limit has surpassed all those reports on PPy based (pure and hybrid) NH_3 sensors.[6,9,11,15,18,25−28]

The excellent sensing performance (large responses and low detection limit) of the SPEEK/PPy nanofibers is supposed to originate from the sensitization of the polymeric adsorbent (SPEEK) cores. There are lots of sulfonic groups in the SPEEK molecule (Scheme S1 in the Supporting Information). So we propose that the ionic interaction between SPEEK cores and NH_3 will enhance the diffusion of NH_3 within the PPy layers, accordingly, more NH_3 will pass through the PPy layers and react with them. So the response values and detection limit will be improved. The proposed sensitization process is shown in Scheme 1. To prove our hypothesis, auxiliary experiments have been carried on. We substituted SPEEK core nanofibers by polyacrylonitrile (PAN, average diameter, ∼100 nm, Figure S1 in the Supporting Information) and fabricated PAN/PPy core−shell nanofibers through the similar process. The average diameter of the PAN/PPy nanofibers is controlled to be about 200 nm, which is similar with the SPEEK/PPy fibers (bottom inset of Figure 4). Figure 4 and the top inset show the NH_3 response of the PAN/PPy nanofibers. The PAN/PPy nanofibers respond to NH_3, only when the concentration is higher than 5 ppm. Additionally, the response is only about $^1/_{12}$th of the SPEEK/PPy nanofibers (toward 10 ppm NH_3).

The response-recovery behavior of the sensors can also provide the evidence to prove the effect of the SPEEK cores. Figure 5a presents the response-recovery behavior of the

SPEEK/PPy nanofibers (3 h) toward NH_3 gas of 500 ppm during the test. Air was chosen as the carrier gas in experiments in order to simulate the most common sensing environment. One can see that the response of SPEEK/PPy nanofibers increases rapidly upon exposure to NH_3 and then gradually levels off. By purging with air, the sensor response can be recovered quickly near the initial stage and then slowly afterward. The response and recovery time are about 10 and 180 s, respectively. (It is important to note that the time taken by a sensor to achieve 90% of the total impedance change is defined as the response time in the case of adsorption or the recovery time in the case of desorption). However, from the response-recovery behavior of the PAN/PPy nanofibers (the thickness of the PPy is close to that of SPEEK/PPy) toward 500 ppm NH_3 gas (Figure 5b), it is clear to see that the recovery time is less than 25 s, which is much shorter than that of SPEEK/PPy nanofibers based sensor (180 s). The phenomenon suggests that the adsorption effect of the SPEEK cores toward NH_3 slow down the desorption of NH_3 during the recovery process.

Generally, a single chemical sensor has cross-sensitivity, which hinders it from practical application. Herein, the anti-interference performance is carried out by injecting 100 ppm of H_2, CO, C_2H_2, CH_4, methanol, ethanol, toluene and NH_3 separately into the test chamber in turn at room temperature, and the results are shown in Figure 6. The sensor exhibits a large response to NH_3 but neglectable response to C_2H_2, CO, CH_4, and H_2 at the same concentration of 100 ppm. Additionally, the responses of the sensor to methanol, ethanol, and toluene are all less than 2% of that to NH_3. These results clearly confirm the good selectivity of the as-prepared sensor, which makes the SPEEK/PPy core−shell nanofibers a good candidate for fabricating NH_3 sensor in practice. The good selectivity may originate from that the SPEEK cores can selectively increase the adsorption of NH_3. Flexibility is another important advantage of our SPEEK/PPy nanofiber sensing films, as opposed to pure and hybrid conducting polymer sensing materials. Figure 7 shows the photograph of a SPEEK/PPy nanofiber film which can be curled up, indicating the potential application in flexible sensing devices.

The sensing performance of the SPEEK/PPy core−shell nanofiber sensing films can be further turned by adjusting the thickness of the PPy shells. Figure 8 shows the TEM images of the SPEEK/PPy nanofibers having different polymerization

times (for PPy). It can be clearly seen that the shorter the polymerization time, the smaller the fibers' diameters, which indicates that the thickness of the PPy shells can be controlled by polymerization time (The photographs are shown in Figure S2 in the Supporting Information). Figure 9 plots the responses of those core−shell nanofibers as a function of concentration of NH_3, and it can be seen that the shorter the polymerization time, the higher the response. When the polymerization time is reduced to 5 min, the response of the sensors is increased to more than 2 times as compared with the sample of 3 h. (Further reduced polymerization time would make the formation of PPy difficult.) The above experiment can be explained by the following reasons. (i) The reduced thickness of PPy shells can increase the exposure of the SPEEK cores to NH_3, accordingly increase the adsorption effect of SPEEK toward NH_3. (ii) Sensing layers are penetrated by analyte molecules, thus a lower sensing layer thickness can accelerate the gas diffusion within it.[29]

CONCLUSIONS

In summary, a successful example of polymer sensitized gas sensors was reported based on polymeric adsorbents/conducting polymers one-dimensional core−shell nanostructure: sulfonated poly(ether ether ketone) (SPEEK)/polypyrrole (PPy) core−shell nanofibers, via electrospinning and solution-phase polymerization. The sensing materials exhibit large gas responses, even when exposed to a very low concentration of NH_3 (20 ppb) at room temperature. Additionally, rapid response behavior, good selectivity can also be obtained for the SPEEK/PPy nanofiber gas sensors. Most importantly the introduction of polymer sensitizers can provide excellent flexibility for gas sensors in practical application. The present work can be extended to other polymeric sensitizers and can develop a new platform to understand and design high-performance conducting polymer gas sensors.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, the molecular formula of the SPEEK, SEM of electrospun PAN nanofibers, and photographs of SPEEK/PPy nanofibers having different polymerization times. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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