



A flexible and multifunctional electronic nose using polyaniline/cotton fibrous membrane with a hierarchical structure

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ABSTRACT

A novel flexible electronic nose (E-nose) with multiple sensing capabilities of gas/pressure/temperature is achieved by coating interfacial polymerized polyaniline (PANI) nanofibers on porous cotton textile. The E-nose has a competitive detecting ability of ammonia gas compared to the reported PANI-based material, achieving super low detection limit (1 ppm) as well as high sensitivity (10.3 for 50 ppm) due to the high surface area of hierarchical PANI nanofibers. Furthermore, the as-prepared E-nose possesses highly sensitive pressure response (0.073 kPa^{-1}) and effective monitoring of temperature ($0.44 \text{ }^\circ\text{C}^{-1}$). This work significantly enriches the E-nose's functions to three further, which makes the E-nose more humanoid with sensing capabilities of smell, tactility, and hot/cold perception.

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1. Introduction

Recently, with the developments of soft robots, E-nose, as a key component of robot, also needs to be flexible and multifunctional for reproducing human nose senses [1,2]. In this case, PANI has drawn many attentions in fabricating flexible E-nose with gas and force sensing abilities simultaneously due to its intrinsic flexibility, conductivity, and gas-detectivity [3–6]. However, increasing sensitivity in both gas and force capturing is still a challenge, which restricts their practical application [7,8].

To overcome the limitations and increase the performances of E-nose, the key is developing enough gas effusion channels and conducting contact points [9,10]. In our previous work, we have demonstrated that a hierarchical structure has impressive advantages in overcoming the low sensitivity in force detection [11]. However, the hierarchical structure is seldom explored or developed in fabrication of flexible and multifunctional E-nose. What's more, most of the reported E-noses only focus on the development of gas and force sensing capacities, whereas the sensing of temperature is also necessary to make the nose smarter.

Herein, we introduce the hierarchical structure into the development of our PANI-based E-nose by coating interfacial polymerized PANI nanofibers on cotton textile. Due to enough gas effusion channels and conducting contact points derived from the ultrahigh surface areas of the nanofibers, porous substrate

and hierarchical structure, the E-nose has a more competitive ammonia gas sensing performance (10.3 for 50 ppm) than many PANI-based materials. Meanwhile, combined with unique semi-conductive properties of PANI nanofibers, the E-nose possesses excellent pressure (0.073 kPa^{-1}) and temperature ($0.44 \text{ }^\circ\text{C}^{-1}$) sensing performances. The developed flexible E-nose with three detecting capabilities will have a huge potential application in soft robots.

2. Experimental

The PANI nanofibers were synthesized by an interfacial polymerization developed by Richard B. Kaner [12], which were further washed and dispersed in anhydrous ethanol with a concentration of 0.2 mg/mL . The commercial cotton textiles (Huiming Fiber, China; $1 \text{ cm} \times 2 \text{ cm} \times 200 \text{ }\mu\text{m}$) were immersed into different volumes of PANI nanofiber suspensions for 1 min following dried at $50 \text{ }^\circ\text{C}$ for 10 min respectively, which was repeated several times until the suspensions was absorbed fully. The E-nose was obtained by attaching electrodes to each end of the cotton textiles with conductive adhesive.

The structures of PANI and E-nose were characterized with a FT-IR spectrometer, X-ray diffraction and FE-SEM instrument. The gas sensing was measured with a gas sensor tester (WS-30A). The pressure was applied with a tensile testing machine (KJ-1065A). A hot plate was used as the heat source. The resistance changes were collected by micro-ohmmeter (TEGAM 1740) synchronizing with the stimuli exertion.

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3. Results and discussion

FT-IR and XRD spectrums of the PANI are illustrated in Fig. S1a and S1b (ESI). FT-IR characteristic peaks exhibit the PANI with well-supported information of PANI (Table S1, ESI), and XRD spectrum implies the crystalline regions dispersed in amorphous medium, which is similar to the previous report [13]. The SEM image of PANI is exhibited in Fig. 1a and the typical nanofiber-shape morphology with an average diameter of about 60 nm is revealed. The uniform distribution of PANI nanofibers on interlaced cotton microfibers with a diameter of 10–20 μm is observed clearly through SEM image (Fig. 1b). The resistance change as a function of PANI contents is illustrated in Fig. 1c, reflecting conductive percolation threshold between 0.25 wt% and 0.5 wt%. Besides, the resistance change tends to be relatively smooth when the PANI content increases to 0.75 wt% due to the nanofibers coating on the cotton microfiber entirely.

For gas sensing of the E-nose, sensitivity (S_g) is defined as R_g/R_a (where R_g and R_a refers to resistance of E-nose in test gas and air atmosphere respectively). Towards NH_3 gas, see Fig. 2a, the contents of PANI have an evident promoting influence on S_g (increase from 2.9 to 10.3 with contents from 0.36 to 1.45 wt%). Thus, the E-nose with a PANI content of 1.45 wt% was chosen to study the following gas performances.

The effects of NH_3 concentration on S_g were also evaluated. Fig. 2b illustrates the plot of S_g as a function of NH_3 gas concentration, exhibiting a linear relation from 1 ppm to 500 ppm, after which point the sensor becomes saturated. The E-nose also displays a high selectivity for amine bases. As displayed in Fig. 2c and d, S_g of VOCs is lower than 12% while surpasses 2 for ethylenediamine and triethylamine and 6 for NH_3 . Fig. 2e exhibits the resistance changes when E-nose exposed to 5 ppm NH_3 gas. Although the peak trend arises in first exposure and tends to be consistent in the following exposure, its S_g is relatively consistent, which also demonstrates the E-nose's good response reversibility even in low concentrations.

The E-nose has a more competitive NH_3 response than many PANI-based gas sensors, even hybrid-based sensors (Fig. 2f) thanks to the high surface area of the interfacial polymerized PANI [14] and enough gas effusion channel of the porous hierarchic structure. The gas sensing mechanism of the E-nose is doping mechanism (Fig. S2, ESI) to bases while swelling mechanism to other VOCs [15].

For pressure sensing, the resistance changes of E-nose with different PANI contents to the applied pressure from 0 to 20 kPa are shown in Fig. 3a. The contents of PANI have a prominent influence on sensitivity ($S_p = \frac{R/R_0}{\Delta P}$, where ΔP is the applied pressure on the E-nose). The S_p of the E-nose with a PANI content approaching the

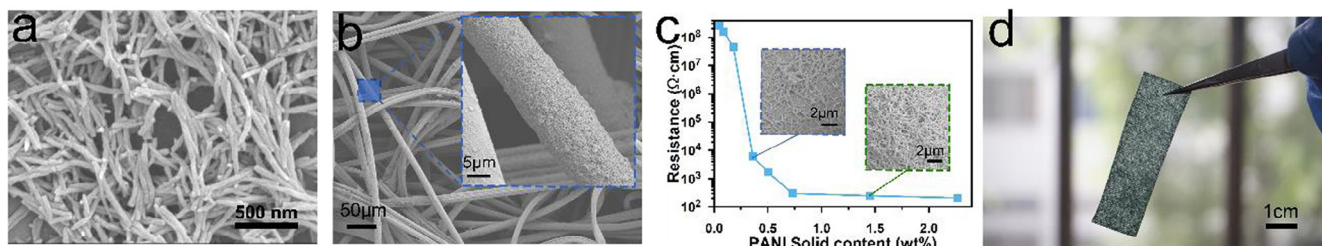


Fig. 1. SEM image of PANI nanofibers (a), PANI coated cotton textile and high magnification of the selected area in inset (b). Resistance changes of the E-nose to PANI solid content and corresponding SEM image of PANI in inset (c). (d) The digital photograph of E-nose (1.45 wt%).

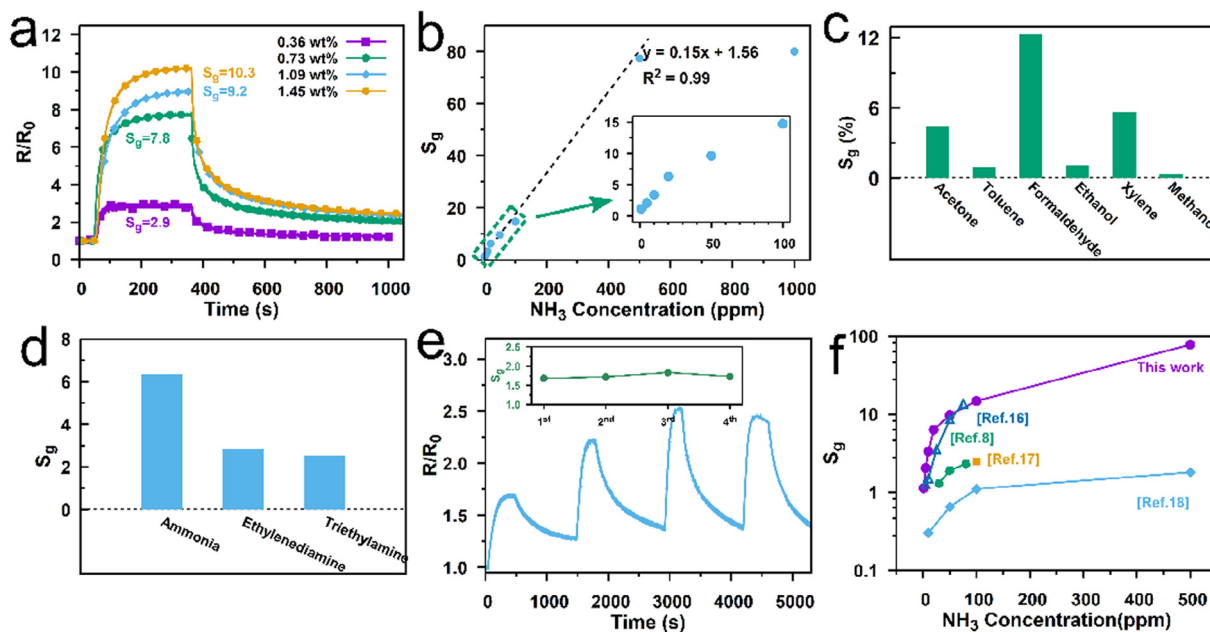


Fig. 2. (a) Response curves of different contents PANI based E-nose towards 50 ppm NH_3 . The S_g of E-nose (1.45 wt%) towards to different concentration (inset is high magnification of low concentration) (b), 20 ppm VOC gas species (c), and amine bases (d). (e) Reproducibility in low 5 ppm NH_3 (inset is S_g changes curve with times) of the E-nose (1.45%). (f) The contrasts of NH_3 gas response with other reports [9,16–18].

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