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ARTICLE

Heterostructures of polyaniline@SnO₂ loading on flexible PET thin films for triethylamine detection at room temperature

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A p-n heterostructure hybrid based on polyaniline-SnO₂ was synthesized by a rapid and facile in situ chemical oxidation polymerization under very low monomer concentration, and the hybrid was loaded on a flexible polyethylene terephthalate (PET) film substrate to structure a smart triethylamine (TEA) sensor. The structure, morphology and composition of hybrid have been characterized by various analysis methods. The sensor not only exhibits high sensitivity, good selectivity to some of other volatile organic compounds and wide linear response to 10-100 ppm triethylamine (TEA) at room temperature but also has flexible, structure simple and wearable performance. The mechanism of enhanced gas sensing properties is discussed in detail, which is attributed to the thickening of the depletion layer due to the formation of p-n heterojunction at interface in hybrid. The research is expected to open a new window for development of a kind of portable and wearable electronic device based on various p-n heterostructure hybrids.

1 Introduction

Environmental pollution problems get more and more serious with the rapid development of economy. Triethylamine (TEA), as a Volatile organic compound (VOC), releases from wastewater and the dead fish and marine products¹. Besides environmental problems, TEA also causes health hazards, especially hazard on respiratory system due to its strong pungency, causing pulmonary edema and even death. The threshold of exposure limit to triethylamine issued by National Institute for Occupational Safety and Health (NIOSH) for workplace and human being is 10 ppm and 25 ppm, respectively^{2, 3}. However, TEA is also widely used as organic solvent, catalyst in polymerization, preservative and synthetic dye⁴. Therefore, it is very necessary to develop highly sensitive sensors to detect TEA gas.

So far, there are various TEA gas sensors, such as cataluminescence sensors⁴, optical sensors^{5, 6}, semiconductor sensors⁷⁻¹⁰ and conducting polymer sensors¹¹, have been

researched. Among them, semiconductor metal oxide based sensors such as ZnO³, SnO₂², TiO₂¹², MoO₃¹³ and Fe₂O₃⁸ have been developed for TEA detection. These results indicate that the semiconductor metal oxide sensors are promising in TEA detection due to their high sensitivity, low cost, well thermal stability and mechanical stability. However, the high operating temperature leads to high power consumption, safety hazards and low stability of the sensing materials, limiting their practical applications in gas detection. While the conducting polymers such as polyaniline (PANI), polypyrrole (PPy) and polythiophene (PTH) are sensitive to VOCs at room temperature and have advantages of environmental stability, low cost and facile synthesis^{14, 15}. The PANI and PPy are the most extensively researched conducting polymers by far due to their potential applications in chemical and biological sensors, electronic devices, as well as solar cells. Weng et al. reported one-dimensional (1D) polyaniline-polypyrrole coaxial nanofibers as TEA sensor which exhibits a response of 1.5 to 100 ppm TEA at room temperature¹⁶. From these reports, it is obvious that conducting polymer based sensors exhibit a rather low sensitivity as well as poor thermal stability and mechanical stability. It is a feasible strategy to combine the characters of polyaniline and SnO₂, and then the sensing performance of the new gas sensing material will over the constituent counterparts due to the synergistic and

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Table 1. Sensing properties of PANI/SnO₂ and other reported TEA gas sensors.

Sensing material	[TEA] (ppm)	Tsens (°C)	Response
V ₂ O ₅ spheres ¹⁰	500	370	9.7
Hexagonal SnO ₂ ²	100	160	70
Prism-like ZnO ³	50	100	267
Urchin-like α-Fe ₂ O ₃ ⁸	18	350	5.9
Flower-like α-MoO ₃ ¹³	100	250	416
NiFe ₂ O ₄ nanorods ⁷	100	175	100
TiO ₂ nanorod arrays ¹²	100	290	14
NiO/SnO ₂ hollow spheres ¹⁷	100	220	267
Polyaniline/polypyrrolone coaxial nanofibers ¹⁶	100	Room temperature (RT)	1.5
Polyaniline/poly(methyl methacrylate) nanofibers ¹⁸	500	RT	1.77
This work	100	RT	30

complementary effects between the polyaniline and metal oxide. As far as we know, there are some reports about metal oxides or polymers sensitive to TEA. To comparison, these materials are listed in Table 1^{2, 3, 7, 8, 10, 12, 13, 16-18}. However, there is no report about using organic/inorganic hybrids to detect TEA yet. In here, a TEA sensor based on the heterojunction of p-type PANI/n-type semiconducting SnO₂ was designed by a rapid and facile in situ chemical oxidation polymerization under very low monomer concentration¹⁹.

After the formation of P–N junction, the sensing performance to TEA is enhanced obviously compared with the reported data, which indicates a great potential application of TEA detection. More, room-temperature operation of the hybrid film brings energy saving, safety and long-term stability of the sensing materials. Moreover, a concept of this work is using the flexible PET thin film to replace ceramic tube with Pt electrodes which is usually used in sensing property tests^{20, 21}, for structuring a flexible, economic, room-temperature operating and wearable smart sensor being ultrasensitive to TEA²². Especially, the wearable device has become the trend of research nowadays. This research is expected to open a new window for potential applications of p–n heterojunction in diodes and other electronic devices.

2 Experimental

2.1 Synthesis of SnO₂ nanoparticles

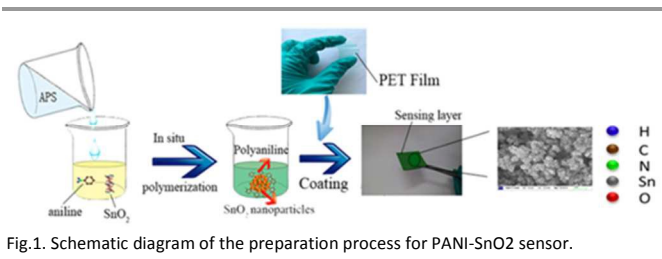


Fig.1. Schematic diagram of the preparation process for PANI-SnO₂ sensor.

To synthesize the SnO₂, 0.1M SnCl₂·2H₂O and 0.1M PEG were added into 50mL of distilled water followed by continuous stirring for 30 min at room temperature, after that, few drops of NH₃·H₂O were added to maintain the pH value of the solution is 10. The solution was vigorously stirred for 4 h at 80 °C, and then cooled down at room temperature gradually. The white precipitates were centrifuged, washed with distilled water and acetone several times, and finally dried at 50 °C overnight. The as-synthesized products were then annealed at 500 °C for 5 h, thus nanoparticles were attained at last.

2.2 Synthesis of HCl doped PANI nanomaterials and their hybrids with SnO₂

Polyaniline was synthesized by in situ chemical polymerization method. In a typical experimental procedure, 1.5 mmol of aniline monomer and stoichiometric amounts of SnO₂ nanoparticles (SnO₂/aniline monomer = 0, 0.5, 1.0, 1.5, 2.5, 3 and 3.5) were added into 15 mL of 1M HCl (A solution) followed by ultrasonic for 15 min, at the same time 1.5 mmol of ammonium persulfate (APS) was dissolved in 15 mL of 1M HCl (B solution), then both A and B solution were cooled at 5°C and B solution was poured into A solution, the polymerization process was kept for 30min at 5°C. The precipitates attained in the beaker were centrifuged, washed with distilled water and ethanol several times, and dried at 50 °C in an air oven. The resultant products obtained were marked as samples PANI, PS0.5, PS1.0, PS1.5, PS2.5, PS3 and PS3.5, respectively. The overall fabrication procedures for the hybrid sensor are schematically demonstrated in Figure 1.

2.3 Characterization

The product morphology was examined by field emission scanning electron microscopy (FESEM, Hitachi S-4700, and 20.0 kV). Crystallographic information for the samples was collected by using powder X-ray diffraction (XRD, Shimadzu XRD-600 diffractometer, copper Kα radiation with λ = 0.15406 nm), operated at 45kV and 40mA, with a scanning speed of 10° min⁻¹ for 2θ in a range from 10° to 80°. Fourier transform infrared spectra of materials were recorded with a FTIR absorption spectrometer (Nicolet 6700) in the range of 400–4000 cm⁻¹ at room temperature (mass ratio of sample and KBr is 1:100). The UV–Vis absorption spectra of the samples in methanol solvent were recorded in the range of 200–800 nm with a UV–Vis spectrophotometer (Japan, Shimadzu UV-2550). The thermogravimetric (TG) analysis was carried out in dynamic air atmosphere (75 mL min⁻¹) with a heating rate of 10 °C min⁻¹ using NETZSCH STA 449 F3 thermal analyzer. X-ray

photoelectron spectra (XPS) were recorded on a VG ESCALAB-MK electron spectrometer with Al K as the excitation source.

2.4 Sensor fabrication and gas-sensing test

The PET film was pretreated in a 20 g/L NaOH solution at 95 °C for 90 min. The PANI and its hybrids with SnO₂ were mixed with N - methyl pyrrolidone to form paste, and then coated onto the hydrophilic surface of PET film (Fig.1), which were welded on a special pedestal with six poles by silver glue to constitute sensor element. The sensing responses of samples to different concentrations of triethylamine (10-100ppm) were measured using a JF02E gas sensor test system (Guiyang Jinfeng Technology Co., Kunming, China). The change of the sensors' resistance was recorded. The response is defined as the ratio of R_{gas}/R_{air} , where the R_{air} is the resistance of the sensor in air and the R_{gas} is that in testing gases.

3 Results and discussion

3.1 Morphology, structure and thermal stability

FESEM is used to investigate the surface morphology of the synthesized PANI/SnO₂ hybrid material. As shown in Fig.2 (a), PANI shows coarse nanofibrous structure with diameter of 60 - 80 nm. The uniformly distributed spherical SnO₂ nanoparticles are shown in Fig.2 (b), with diameter of 20 nm. It can be seen in Fig.2 (c, d) that the SnO₂ nanoparticles are embedded within netlike structure built by PANI chains, the SnO₂ nanoparticles are closely packed and no bare nanoparticle is observed, which implies that hybrid is highly micro porous and is able to increase the liquid-solid interfacial area, provides a path for insertion and extraction of ions, and ensures a high reaction rate²³.

Fig.3 represents the X-ray diffraction patterns of pure PANI, SnO₂ nanoparticles and PS2.5 hybrid. As shown in Fig.3 (a), the characteristic peaks of polyaniline are found at $2\theta=15.3^\circ$, 20.6° and 25.24° corresponding to (011), (020) and (200) crystal planes of polyaniline²⁴. The well resolved and sharp peaks in

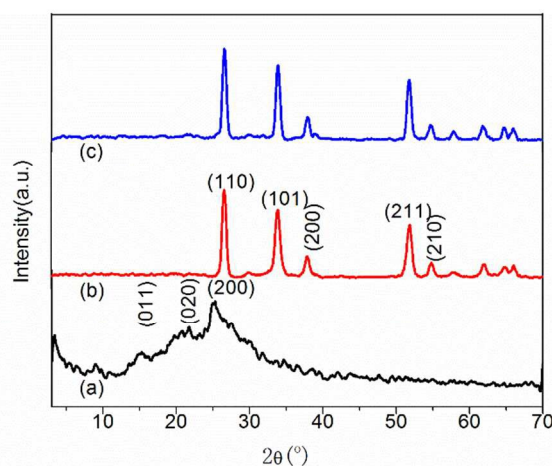


Fig.3 XRD patterns of (a) PANI, (b) SnO₂ nanoparticle and (c) PS2.5 hybrid.

Fig.3b are compared with the standard data (JCPDS # 77-0449) which confirms that powder is pure SnO₂. For PS2.5 hybrid (Fig.3(c)), all the main peaks presented in pure SnO₂ are also observed, which proves the existence of SnO₂ in hybrid. The formation of PANI-SnO₂ hybrids is evidenced by FTIR spectra, as shown in Fig. 4. The characteristic absorption peaks of PANI appearing at 1554 cm^{-1} , 1473 cm^{-1} , 1301 cm^{-1} and 1124 cm^{-1} are related to C=C stretching mode of quinoid rings, the stretching vibrations of C-N⁺, the stretching mode of C-N and the aromatic C-H bending in the plane, respectively²⁵. The PS2.5 hybrid shows the same absorption peaks with PANI and a new peak at 628 cm^{-1} can be observed, which is attributed to the characteristic peak of SnO-N⁺, confirming the interaction between SnO₂ and PANI. In comparison with the IR spectra of PANI and PANI-SnO₂ hybrids, a slight red shift of the four characteristic absorption peaks of PANI is found, which points to a change in the environment of the PANI, and may be the formation of hydrogen bonding between SnO₂ and the NH group of PANI on the surface of the SnO₂ nanoparticles²⁷. UV-vis spectroscopy is applied to characterize the optical

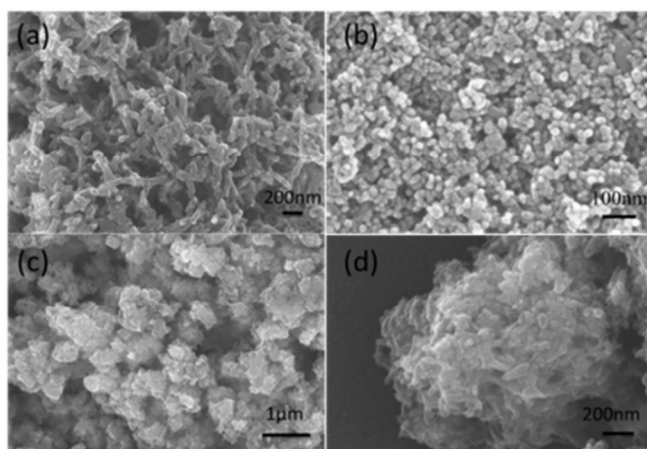


Fig.2. FESEM images of (a) PANI, (b) SnO₂ nanoparticles, (c) and (d) PANI-SnO₂ hybrid.

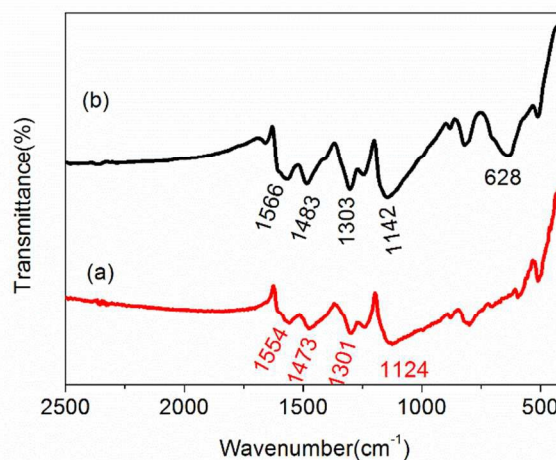


Fig.4 FTIR spectra of (a) PANI and (b) PS2.5 hybrid.

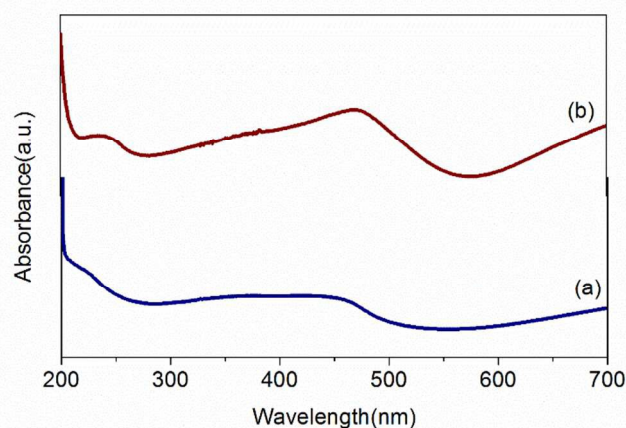


Fig.5 UV-vis spectra of (a) PANI and (b) PS2.5 hybrid.

properties of the synthesized hybrids. Fig.5 shows the UV-visible spectra of pure PANI and sample PS2.5 hybrid. It can be seen that polyaniline strongly absorbs visible light and shows two peaks. One distinctive peak at 228 nm and another broad peak at 300 nm-500 nm, which are due to the π - π^* conjugated ring systems and polaron- π^* ²⁸. While the UV-visible spectrum of sample PS2.5 hybrid has a broad absorption peak at 300 nm-550 nm, and this red shift compared with PANI may be attributed to interactions between PANI chains and SnO₂ nanoparticles²⁹.

Thermal stability of the hybrid was investigated by TG analysis as shown in Fig. 6. It is clearly observed that TG curve of PANI exhibits a four-step mass loss. The initial less mass loss at temperature ranging from 25°C to 100°C is mainly attributed to the thermal elimination of residual water and solvent in samples³⁰. The second and third mass losses are due to the elimination of doped species like HCl and low molecular weight polymer fragments. For PANI, the main mass loss after 400°C is caused by the decomposition of PANI backbone. Comparing the curves of the two samples, it can be obviously found that the pure PANI exhibits a total mass loss of 57% at 785°C, while the data of PS2.5 is only 36%. This result confirms

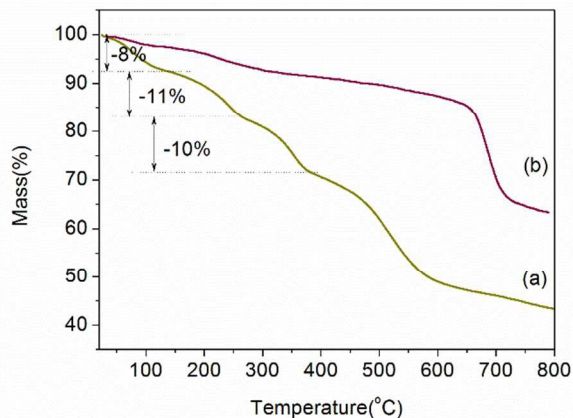


Fig.6 TG curves of (a) PANI and (b) sample PS2.5 hybrid.

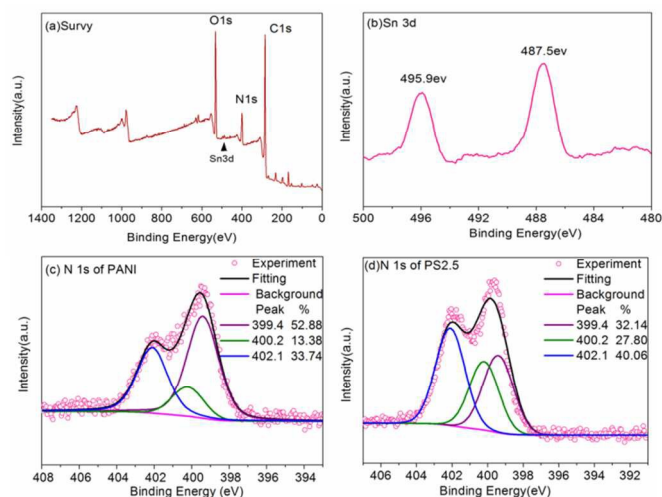


Fig.7. XPS spectra of PANI-SnO₂ hybrid: (a) Wide energy, (b) Sn 3d, (c) N 1s of PANI and (d) N1s spectra of PANI-SnO₂ hybrid.

that the hybridization of organic PANI with inorganic SnO₂ leads to a more thermally stable material, implying its prospects as sensing layer in chemical sensors.

XPS analysis is employed to further determine the surface composition of hybrid and chemical oxidation valence state of the as-obtained heterojunction hybrid. It can be observed in Fig.7b that the Sn 3d spectrum displays a spin-orbit doublet centered at 495.9 eV and 487.5 eV corresponding to Sn 3d_{3/2} and Sn 3d_{5/2}, and the splitting binding energy between the Sn 3d_{3/2} and Sn 3d_{5/2} core level is 8.3 eV, indicating a normal oxidation valence state of Sn⁴⁺ in the SnO₂ crystals³¹. The N 1s spectrum of PANI can be deconvoluted into three peaks (Fig.7c, d): the peak appearing at 399.4 eV is associated with uncharged amine sites (-NH-), the peak at 400.2 eV may be assigned to the radical cationic nitrogen atoms (=NH⁺=)³², and the peak at 402.1 eV is due to interaction between N⁺ and protons introduced by the acid doping (-NH²⁺-)³³. The area fraction of these three peaks is 0.5288, 0.1338 and 0.3374 in PANI, namely, the total area from protonated nitrogen atoms of PANI is 47.12%, while that for PS2.5 is 67.86%, and this may be due to the synergistic and complementary effects between the polyaniline and SnO₂.

3.2 Gas sensing properties

The response of sensor varies with concentration of target gas. Fig.8 presents the transient responses of sensors based on SnO₂, PANI and sample PS2.5 to triethylamine gas of different concentrations at room temperature. It can be observed clearly that the responses of sensor based on PS2.5 to 10-100 ppm TEA are much higher than those of SnO₂ or PANI. To be specific, the obtained response of sensor based on PS2.5 to 100ppm TEA is 30, which is 10 times and 30 times higher than that obtained from pure PANI and SnO₂ respectively.

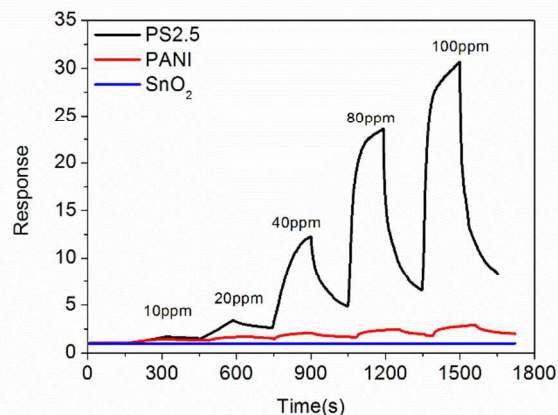


Fig.8. Transient response curves of sensors based on SnO₂, PANI and sample PS2.5 to TEA at room temperature.

From the viewpoint of practical application, a sensor should present rather high selectivity³⁴. Therefore, the selectivity of sensors was studied towards other reducing gases such as toluene, formaldehyde, methanol, ethanol and acetone. The observed response amplitudes at room temperature are shown in Fig. 9. It is apparent that triethylamine leads to significantly higher response compared to other targets. This result clearly demonstrates the high selectivity of PANI-SnO₂ hybrid and it is a promising sensing material for triethylamine detection. The content of components has a significant effect on the sensing properties of hybrid. Fig.10 shows the responses of PANI-SnO₂ hybrids with different SnO₂ content to 100ppm TEA at room temperature. It is obviously found that the sensor response increases first and then decreases with the increase in the content of SnO₂ during synthesis. Thus, the optimal mass ratio of SnO₂ to PANI is 2.5.

The linear tendencies are observed for both PANI and PS2.5 hybrid from Fig.11a, and the PS2.5 has a better linear response to 10-100ppm TEA. Generally, the detection limit (D_L) is defined as the lower concentration in which the response significantly differentiated from the noise signal, i.e. 3 times the standard deviation of noise, the detection limit is estimated to be ≥ 6.8 ppm for the sensor based on PS2.5.

3.3 Sensing mechanisms of PANI and PANI-SnO₂ hybrid to TEA

The sensing mechanism of pure PANI to TEA is proposed to be a deprotonation/protonation process. PANI is protonated by doping of HCl during the in situ polymerization process, producing an emeraldine salt of high conductivity. Once the PANI based sensor is exposed to TEA vapor (electron-donor), the protons from N⁺-H sites of PANI are withdrawn by adsorbed TEA molecules, and PANI in the form of emeraldine salt is reduced to emeraldine base, resulting in conductance decreases (resistance increases). When the TEA is replaced by air, the process is reversed and the initial protonation level and resistance are recovered, which causes the sensing

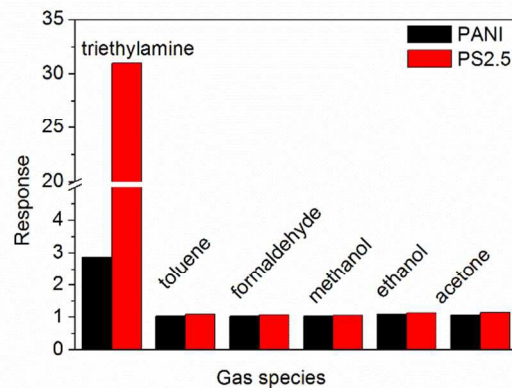


Fig.9 Response of sensor based on PANI and PS2.5 to 100ppm different tested gases at room temperatures.

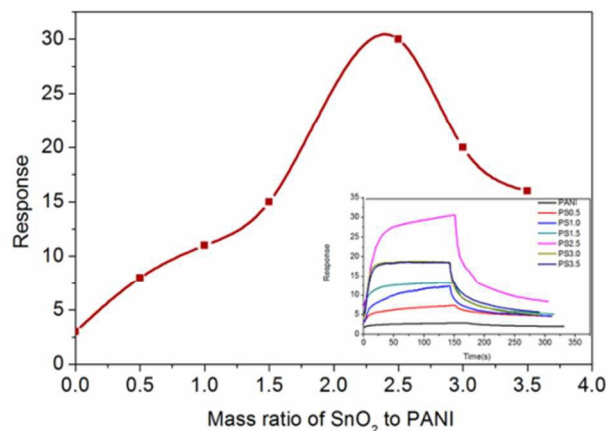


Fig.10. Effect of SnO₂ content on 100ppm TEA-sensing properties. Insert shows the raw data of responses.

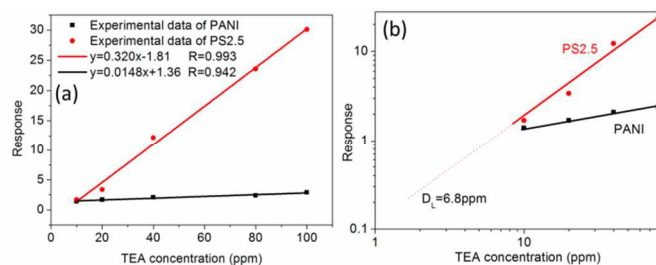


Fig.11. Relationship between the sensor response and TEA concentration: (a) fit curve and (b) dilogarithm curve.

response to TEA. In addition, several possible reasons are believed to be responsible for the high sensing properties of the hybrid film based sensor. As mentioned above XPS analysis the possibly enhanced protonation level in hybrid. Besides, the loose and porous structure on PET film makes the hybrid has a higher surface area to volume ratio, which enhances the gas diffusion process and provides a fine pathway for electron transfer in the gas sensing process, thereby improving the

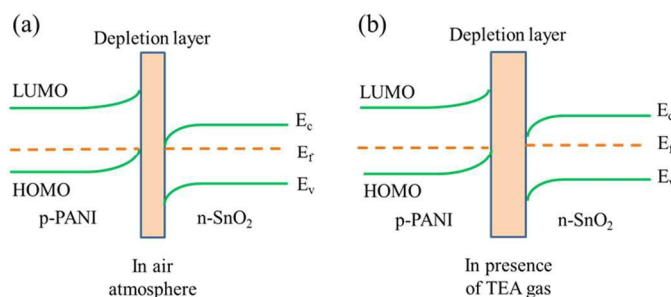


Fig.12 Proposed energy band diagram for PANI/SnO₂ hybrid film with the interaction of TEA gas.

sensing performance. On the other hand, it is inferable that upon compositing PANI and SnO₂, the electrons in SnO₂ and holes in PANI diffuse in opposite direction due to the great gradient of the same carrier concentration until establishment of equilibrium. As a result, the energy band bends in the interface and the system gets a uniform Fermi level (E_f). The formation of p-n heterojunction at interface in hybrid leads to the increase of depletion barrier height, thus leading to an improvement of response for the hybrid³⁵. However, once the hybrid is exposed to TEA gas, the TEA molecules adsorbed on surface of hybrid release electrons into the hybrid material, particularly into PANI in the junction region. That leads to the decrease in carriers density due to electron donating nature of TEA gas, resulting in the depletion layer widens (shown in Fig.12, where HOMO presents the highest occupied molecular orbital level, and LUMO is the lowest unoccupied molecular orbital level), and further increase of the hybrid resistance. Thus, the response of the PANI/SnO₂ hybrid to TEA is greatly improved³⁶. This description can also be used to interpret other systems with their response improved by p-n junction.

4 Conclusions

A heterojunction based on PANI-SnO₂ loading on PET film was fabricated by in situ chemical polymerization. The sensor based on PS2.5 hybrid not only exhibits the highest response of 30 to 100 ppm TEA at room temperature, which is 10 times and 30 times higher than that of pure PANI and SnO₂ respectively, but also has excellent selectivity to other VOCs such as toluene, formaldehyde, methanol, ethanol and acetone. The improvement of sensing performance except for the possibly enhanced protonation/deprotonation level, mainly attributes to the formation of p-n junction at interface in the hybrid. In particular, our fabricated sensor can operate at room temperature and has the flexible, economic and wearable characteristics. Thus, the combination of n-type SnO₂ nanoparticles and p-type PANI provides an effective strategy to design and fabricate a novel and promising TEA gas sensor operable at room temperature. Besides, there are papers studying the optical effects induced from interaction between

the sensors and analysts, which implies the possible implication value in optical sensors.

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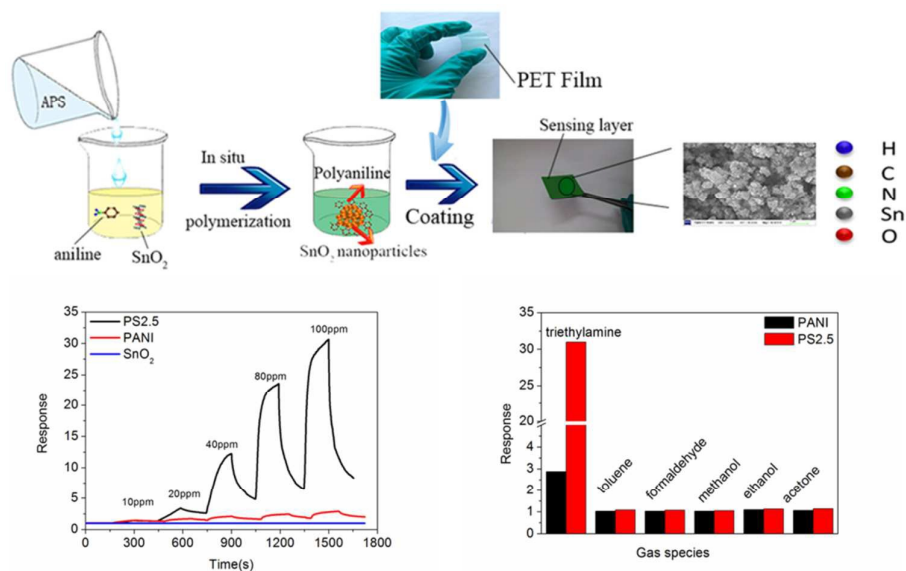
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Heterostructures of polyaniline@SnO₂ loading on flexible PET thin films for triethylamine detection at room temperature

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A p-n heterojunction based on PANI-SnO₂ hybrid loading on PET thin film was fabricated by in situ chemical oxidation polymerization, which not only exhibits high sensitivity and selectivity to triethylamine under room temperature, but also has flexibility, fabricating simplified, economical and wearable characters compared with the recently existing in literatures.