RSC Advances

RSC Advances

PAPER

Hierarchical polyaniline microspheres loading on flexible PET films for NH₃ sensing at room temperature

Shouli Bai, Jingyao Ye, Ruixian Luo*, Aifan Chen, Dianqing Li*

Hierarchical polyaniline microspheres was prepared on polyethylene terephthalate (PET) film by facile and rapid in situ chemical oxidative polymerization of aniline，in presence of ZnO microspheres, to construct a smart sensor for detection of NH₃. The sensor not only exhibits high sensitivity, good selectivity and low detection limit at room temperature but also possesses the features of flexibility, portability and optical transparency compared with traditional sensors based on substrates of glass, quartz slide or ceramic tube. Particularly, the low operating temperature of 21°C is favorable to saving energy, safety and long life of the sensor. The mechanism of the ZnO microspheres enhanced sensing properties of polyaniline is attributed to the morphology design, enhancement of crystallinity and protonation degree, which has been confirmed by XRD, SEM and XPS analysis. The study will also open a new window to develop a type of portable electronic devices.

1 Introduction

In recent years, with rapid development of portable electronics and the deterioration of our living environment, there is an urgent demand to develop portable gas sensors with small size, low cost and room temperature operating for online monitoring of hazardous gases. As ammonia is utilized extensively in many chemical industries, fertilizer factories, refrigeration systems, etc., a leak in the system would be a catastrophe for humans and animals alike [1]. The lowest limit of NH₃ is 25 ppm perceiving by human smell [2]. However, NH₃ is irritating to the respiratory system, skin and eyes below this limit. Therefore, it is necessary to develop ammonia gas sensors. During the past years, a lot of reliable sensing materials for detecting NH₃ have been developed, such as metal oxides, conducting polymers and their composites. Polyaniline (PANI) as a conducting polymers attracts a considerable attention due to the ease of synthesis, environmental stability, low cost, sensing to some of VOCs gases at room temperature and their good interfacial adhesion with organic film [3, 4], which makes the PANI a promising candidate in the field of gas sensing. However, it has disadvantages of low sensitivity, long response time and incomplete desorption of gas molecules in previous studies [5, 6]. PANI can be synthesized through various methods. While template synthesis is one of the most popular methods, because it is simple and low cost compared with other methods. In particular, the soft template is easy operating and need not post-treatment compared with hard template. We had used silver nanowire as a soft template for the synthesis of polyaniline networks and the sensitivity is greatly improved, but the high cost of the silver nanowire makes it cannot be widely used [7]. To improve the feasibility of application, the metal oxide can be soft template to synthesize PANI with different morphology can be achieved due to cheapness, structure stability and controllable morphology. As a "classical" metal oxide, ZnO has attracted great interest for using in electronic devices, energy generators, optoelectronic device, sensors etc [8-10]. On the other hand, ZnO also allows versatile processes to form low-dimensional and three-dimensional micro-/nano-structures, such as nanobelt [11], nanorod [12], nanosheet [13], micro-pyramid [14] and hierarchical microsphere [15]. Among them, the 3D microsphere structures of ZnO are even more appealing because of their robust structure, large surface-to-volume ratio and easily accessible inner surface to guest molecules [16, 17]. These properties make them highly promising for using in functional devices with excellent performance. Consequently, the microsphere structures of ZnO are chosen to be the template for the synthesis of hierarchical PANI microspheres. The hierarchically nanostructured conductive films could be fabricated by a combination of conducting polymers from the ZnO microspheres as template, then they were loaded on flexible polyethylene terephthalate (PET) substrates for high-performance room temperature portable gas sensing device.

Herein, we report the fabrication of conducting films of hierarchical PANI microspheres on PET substrates by coating ZnO microspheres and subsequently in situ chemical oxidative polymerizing aniline. The as-prepared conductive film could be assembled into chemical gas sensor devices for high sensitive detection of toxic gases at room temperature.

2 Experimental

2.1 Synthesis ZnO microspheres

All the chemical reagents were of analytical grade and were used without further purification. In a typical procedure, 0.015 mol ZnSO$_4$•7H$_2$O and 0.0375 mol urea were dissolved in 150 mL of deionized water under magnetic stirring to form a clear solution. After stirred for 0.5 h, the resultant mixture was transferred into a Teflon-lined stainless steel autoclave and kept at 120°C for 6 h. After cooling to room temperature, the precipitation was filtered and washed with deionized water several times, and dried at 80°C for 4 h. The precursors were calcined at 600°C for 4 h in air to obtain ZnO powders, with a heating rate of 5°C/min.

2.2 Synthesis of HCl doped PANI nanofibers and hierarchical PANI microspheres

The PET films (1cm×1cm) was pretreated in a 20 g/L NaOH solution at 95°C for 90 min and washed with ethanol and dried at 50°C. Polyaniline nanofibers were synthesized by chemical oxidative polymerization method. In a typical procedure: 1.5mmol aniline monomer in 15mL 1M HCl was treated with ultrasonic wave for 15 min followed by magnetic stirred at 5°C. Then 15mL 1M HCl solution containing 1.5mmol ammonium persulfate (APS) which was precooled at 5°C was added to above solution, after that, a piece of blank PET was immersed in the solution. This polymerization action was kept for 30 min at 5°C. The polymerized salt was filtered, washed repeatedly with distilled water and ethanol to remove impurities, and dried in an air oven at 50°C for 1 h. The precipitates in the above beaker were collected for characterization.

To prepare hierarchical polyaniline microspheres, same procedure was followed with a piece of blank PET by simple coating with paint brush with a series of different amount of zinc oxide (0.1, 0.2, 0.3, and 0.4mg) to aniline hydrochloride solution during polymerization. The precipitates in the above beaker were collected for characterization. The resultant products with 0.1 mg, 0.2 mg, 0.3 mg, and 0.4 mg ZnO are named as S0.1, S0.2, S0.3 and S0.4, respectively.

2.3 Characterization

Field emission scanning electron microscopy (FESEM) images were obtained with a Hitachi S-4700 instrument operated at 20.0 kV. Powder X-ray diffraction (XRD) patterns of the products were recorded on a Rigaku D/MAX-2500 X-ray diffractometer at 30 kV and 100 mA with copper Kα radiation (λ= 1.54Å). Scanning rate of 5° min^{-1} was applied to record the patterns in range of 10–70° (2θ). Fourier transform infrared (FT-IR) spectra were recorded on a FT-IR absorption spectrometer (Nicolet 6700) in the range of 400–4000 cm^{-1} at room temperature. The samples were mixed with KBr at a mass ratio of 1:100. X-ray photoelectron spectra (XPS) were recorded on a VG ESCALAB-MK electron spectrometer with Al Kα as the excitation source. The UV–Vis absorption spectra of the samples in methanol solvent were recorded in the range

of 200–800 nm with a Shimadzu UV-2550, UV–Vis spectrophotometer (Japan)

2.4 Sensor fabrication and gas-sensing test

The PET film with PANI nanofibers and hierarchical PANI microspheres was welded on a special pedestal with six poles by silver pulp to make of sensor element. The gas sensing properties of PANI nanofibers and hierarchical PANI microspheres were measured using a JF02E gas sensor test system (Guiyang Jinfeng Technology Co., Kunming, China). The sensor elements were infixed into an 18L air chamber. Different concentrations of NH$_3$ (10-100ppm) were used as the target gas to test the gas performance of PANI and hierarchical PANI microspheres at room temperature. The definition of gas sensitivity S was the ratio of R$_g$/R$_a$, where the R$_a$ is the initial resistance of the sensor and the R$_g$ is the resistance of the sensor when it was exposed to the testing gases. The response time is the time for the resistance of the sensor change to reach 90% of the total change from R$_a$ to R$_g$, while the recovery time is the time necessary for the sensor return to 10% above the initial resistance in air.

3 Results and discussion

3.1 Morphology and structure

Fig. 1 represents FESEM images of ZnO powder, PANI nanofibers and S0.3. Fig. 1a and b show the typical SEM images of the ZnO precursor and the samples calcined at 600°C in air for 4h. The low-magnification SEM image of the ZnO precursor sample (shown in Fig. 1a) shows that it is mainly made up of microspheres with ca.15 mm in diameters, and the high-magnification SEM image of the ZnO precursor sample suggest that microspheres are assembled by nanosheets with a thickness of about 75 nm as shown in Fig. 1a inset. Fig. 1b shows the SEM images of the samples calcined at 600 °C in air for 4h. It can be seen that the structure of the microspheres and the nanosheets has been changed to particles after calcinations and the average thickness of the nanoparticles is approximately 50 nm, which could be attributed to the increase of the crystallinity and the loss of volatile gas such as H$_2$O and CO$_2$
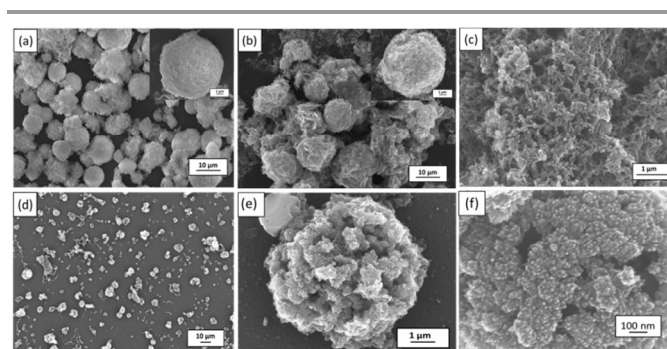

Fig. 1 FESEM micrograph of (a) ZnO microsphere precursor; (b) ZnO microspheres calcined at 600°C for 4h; (c)PANI nanofibers; (d)-(f) S0.3 at different magnifications.
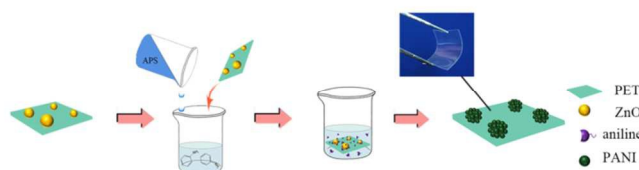
Fig. 2 Schematic illustration formed of hierarchical PANI microspheres conductive film.

in Fig. 1(c), the PANI shows fussy agglomerated nanofibers. The sample of S0.3 shows hierarchical microspheres morphology owing to the addition of ZnO microspheres as shown in Fig. 1(d). The hierarchical PANI microspheres in Fig. 1(d) show a rough surface because the surface is composed of many PANI nanoparticles. The hierarchical PANI microspheres were formed by in-situ chemical oxidation polymerization of aniline monomers adsorbed on the surface of ZnO microspheres and loaded on the PET thin film. Polymerization of aniline and dissolution of zinc oxide are happen at the same time. During the polymerization of aniline, the ZnO gradually dissolved in the acidic solution and converted to zinc chloride in solution, which got removed during washing and filtration. Finally, hierarchical PANI microspheres are formed with the assistance of zinc oxide. The formation process of hierarchical PANI can be schematized in Fig. 2.

XRD patterns of the prepared ZnO microspheres samples calcined at $600^{o}C$ are shown in Fig. 3(a). All the reflection peaks of the samples can be indexed to hexagonal ZnO with a wurtzite structure (JCPDS file No. 36-1451) [18]. Fig. 3(b) and (c) represents the X-ray diffraction pattern of PANI nanofibers and S0.3. The characteristic peaks of polyaniline were found at 25.18 corresponding to (200) crystal planes of polyaniline in all the two samples [19]. In addition, the XRD pattern of polyaniline samples S0.3 show two peaks at 20 and 15.2 which corresponds to (020) and (011) crystal plane of PANI. We can see from the XRD plot that the crystalline nature of PANI enhanced significantly with the addition of ZnO microspheres during polymerization. In addition, the characteristic peaks of zinc oxide are not detected, confirming that the ZnO microspheres play a role as soft template.

Fig. 4 represents IR spectrum of PANI nanofibers and S0.3. From Fig. 4(a), the sample prepared by in situ polymerization contains all the characteristic peaks of PANI. The band at 1558 cm^{-1} is due to quinoid ring deformations of aromatic ring. The peaks at 1473 cm^{-1} and 1301cm^{-1} are the results of the stretching vibrations of C–N$^+$ and C–N, respectively [20]. The peaks at 1124 cm^{-1} and 800 cm^{-1} are attributed to the aromatic C–H bending in the plane and out of the plane for the 1,4-disubstituted aromatic ring [21, 22]. All the above observed absorption characteristics confirm the formation of PANI. In Fig. 4(b), the characteristic peaks of PANI were found to shift to higher wave number side. The corresponding peaks of PANI fibers at 1558 cm^{-1} shifted to 1560 cm^{-1}, 1473 cm^{-1} shifted to 1476 cm^{-1}, 1301 cm^{-1} shifted to 1302 cm^{-1}, 1238 cm^{-1} shifted to 1242 cm^{-1}, 1124 cm^{-1} shifted to 1136 cm^{-1} and 800 cm^{-1} shifted
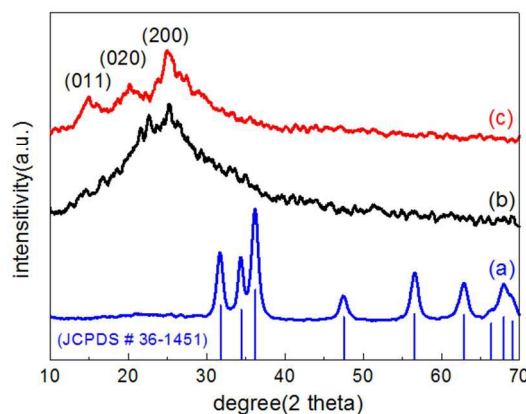

Fig. 3 The XRD patterns of (a) ZnO microspheres, (b)PANI nanofibers and (c) S0.3.

to 801 cm^{-1} wave numbers in hierarchical PANI microspheres, which indicates the action of ZnO microspheres in polymerization process of aniline although both the samples are not significant different in IR spectra.

The UV/visible spectrum corresponding to pure ZnO powder, PANI nanofibers and S0.3 are shown in Fig. 5. The absorption spectrum of the ZnO microspheres (Fig. 5a) presents a sharp absorption peak around 374 nm which is the characteristic single peak of hexagonal ZnO microspheres [23, 24]. PANI nanofibers strongly absorbs visible light, with a characteristic peak at 445 nm [25], which related to doping level. The of PANI samples S0.3 is exhibited in Fig. 5(c). The UV–visible spectrum of PANI sample S0.3 has an absorption peak at 454 nm, which is red shifted compared with the absorption peaks of PANI nanofibers (445 nm). This may be because of the addition of ZnO microspheres. No characteristic peak of ZnO was observed in S0.3.

Fig. 6 shows XPS spectra of the N1s region of PANI nanofibers and S0.3. The asymmetric N1s core level of PANI nanofibers is composed of three subpeaks centered at about 399.5 eV (-NH-), 400.25 eV (=NH$^+$=) and 402.1 eV (-NH$_2$$^+$-), respectively (Fig. 6a) [26]. The area fractions of these three peaks are 0.45, 0.4 and 0.15, respectively, where the total area from protonated nitrogen atoms is 54.6%, indicating that the doping level of PANI nanofibers is 54.6%. Likewise, the three subpeaks appear at about 399.14, 400.1 and 402.2 in sample
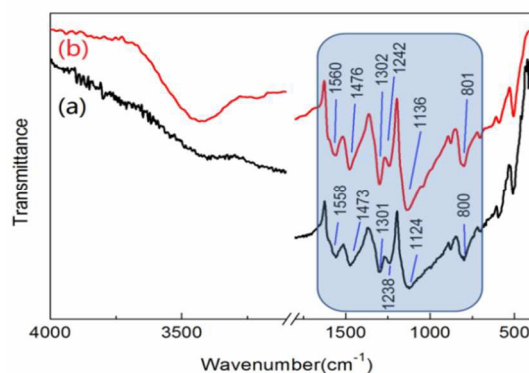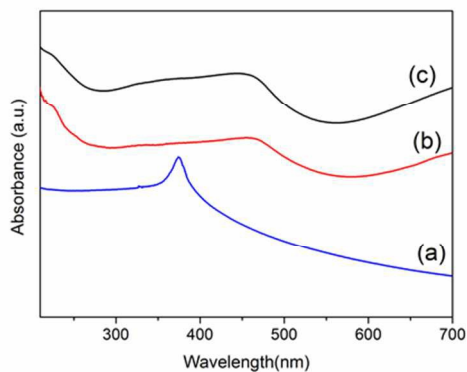

Fig. 4 FTIR spectra of (a)PANI nanofibers and (b) S0.3.

Fig. 5 UV–vis spectra of (a) ZnO microspheres; (b)PANI nanofibers and (c) S0.3.

S0.3 (Fig. 6b). The area fraction of these three peaks is 0.20, 0.64 and 0.15, respectively, where the total area from protonated nitrogen atoms is 79.55%, indicating that the doping level of S0.3 was 79.55%. We can see from the experimental results of XPS spectra, the level of protonation increased significantly by adding ZnO microspheres as template during polymerization.

3.2 Gas-sensing properties of PANI nanofibers and hierarchical PANI microspheres based sensors

Fig. 7 represents the sensor response of PANI nanofibers and S0.1, S0.2, S0.3 and S0.4 for 100 ppm of ammonia gas at room temperature. It indicates that the NH_3 sensing properties are strongly influenced by ZnO content. It was found that the sensor response increases in the addition of ZnO and the maximum response is obtained with the addition of 0.3mg ZnO. For PANI sample prepared with addition of 0.3mg ZnO, a significant enhancement in its sensor response has been observed. With further increase of ZnO powder during synthesis the sensor response decreased.

Fig. 8(a) represents variation in actual sensor response of PANI nanofibers, S0.3 and ZnO for different ammonia gas concentration. It was observed that the sensitivity increases with the increase in the gas concentration in the range of 10–100 ppm. It is found that the response of S0.3 is much higher than the PANI nanofiber and ZnO. When the gas concentration is 10ppm, the sensor response has reached 24. The optimum sensor response is much better than other PANI
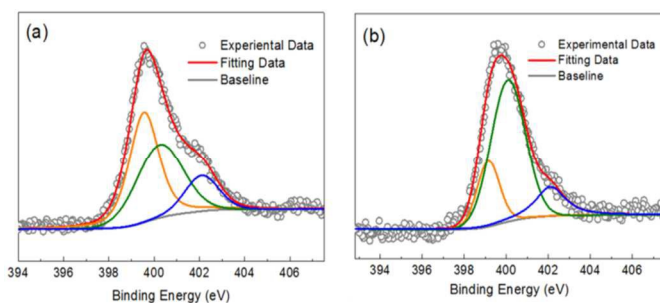

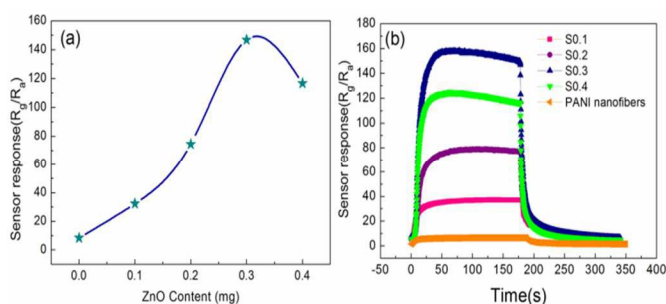Fig. 6 XPS spectra of the N1s region of (a) PANI nanofibers and (b)S0.3.

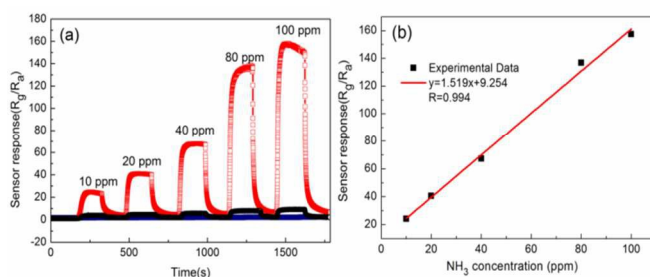Fig. 7 (a) Effect of ZnO content on NH_3 gas-sensing properties and (b) shows the raw data of responses.

Fig. 8 (a)Transient response curves of sensors based on pure ZnO annealed at 600°C (blue curves); PANI nanofibers (black curves) and S0.3 samples (red curves) to 10–100 ppm ammonia gas, (b) linear relationship of the sensitivity and NH_3 concentration for S0.3 at room temperature.

sensors reported as shown in table 1. The response obtained from PANI sample S0.3 is 157 to 100 ppm NH_3, which is 18 times and 157 times higher than that of PANI nanofibers and ZnO, respectively. It can be seen from Fig. 8(b) that the sensitivity of the sample S0.3 showing a linear relationship with the increasing of the concentration of NO_2. Such a good linear dependence of responses on the gas concentration indicates that the hierarchical PANI microspheres can be used as a promising material for detecting low concentration of NH_3.

Fig. 9 depicts the sensor response as a function of NH_3 concentration for PANI nanofibers and S0.3. When the responses are plotted in log–log scale, linear trends are observed for both pure PANI nanofibers and S0.3. This suggests that both the sensors have advantages of detecting low concentration of NH_3, with the S0.3 displays much larger response rate to NH_3. Generally, the response at a given gas concentration and the detection limit (D_L) is defined as the lower concentration at which the response is differentiated from the background level [32]. When the criterion for gas detection was set to 3 times the standard deviation of noise, The detection limit of this sensing device was calculated equal to 300 ppb and 900 ppb for the sensors based on PANI nanofibers and S0.3, respectively. This result demonstrates that the hierarchical PANI microspheres extremely lowers the detection limit and capable of detecting low concentration of NH_3.

Fig. 10 shows the selectivity of NH_3 gas to ethanol, methylbenzene, acetone, methanol and methanal (100 ppm) for

Table 1 Response of PANI sensors to NH₃ reported in literatures

Gas sensor	Gas concentration	Operating temperature	Sensitivity (R_g/R_a)
ZnO assisted PANI[5]	100 ppm	Room temperature(RT)	2.5
PANI[27]	100 ppm	RT	1.96
PANI-ZnO[28]	300000 ppm	110°C	14
PANI-ZnO[29]	150000 ppm	RT	1.2
PANI[30]	100 ppm	70°C	12
PANI-SnO₂[21]	100 ppm	RT	1.72
PANI-SnO₂[31]	94 ppm	RT	5
PANI-TiO₂[31]	94 ppm	RT	6
PANI-In₂O₃[31]	94 ppm	RT	0.9
This work	100 ppm	RT	157

the sensor based on hierarchical S0.3. It indicates that the sensor not only has high response to NH₃ gas but also exhibits high selectivity to ethanol, methylbenzene, methanol and methanol due to the different of their sensing mechanism. For the electron-donating gas of NH₃ has the performance of withdrawing protons from polyaniline, While the sensing responses to some of VOCs (reducing gases) result from the oxidizing reaction between gas and adsorbed oxygen species (O_2^-) on surface of material. But the reducing activity of adsorption oxygen is lower at room temperature, so, their response is lower too. So, hierarchical PANI microspheres synthesized by in situ polymerization is a promising sensing material for NH₃ gas detection.

3.3 Transient response and nonlinear fit of NH₃ sensor based on PANI nanofibers and hierarchical PANI microspheres

In order to obtain the accurate transient parameters, we have analyzed the transient response (S (t)) according to the Langmuir–Hinshelwood model:

$$S(t) = S_{max}(1 - exp^{-k \cdot Ca \cdot t}) \quad (1)$$

Where S_{max} is the maximum response when the sensor is saturated; k is the surface rate constant; C_a is the initial gas concentration. Fig. 11 (a) shows the exponential fitting of these
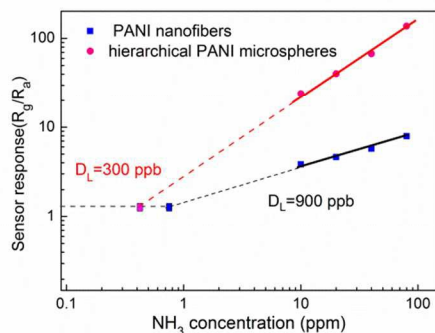

Fig. 9 Dilogarithm curve of the relationship between the sensor response and NH₃ concentration in range of 10-80 ppm.
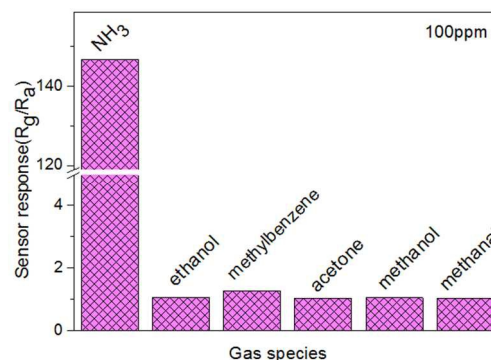

Fig.10 Response of sensor based on S0.3 to different tested gases at room temperatures.

transient data, in which the distinguishable values of S_{max} and $k \cdot C_a$ are estimated. For the response time (τ90%) is the time taken for the response reaches 90% of its maximum value. Solving the equation of "1- $e^{-k \cdot Ca \cdot t}$ = 90%", the value of τ90% is obtained as 2.303/ (k·Ca). Fig. 11 (b) shows the characteristic response time (τ90%) change with NH₃ concentration, it is obviously observed that the response time decreases with increasing NH₃ concentration, and the characteristic response time reduces disproportionately with the increase of the NH₃ concentration for the irreversible-type gas sensor.

3.4 Sensing mechanism of PANI nanofibers and hierarchical PANI microspheres on NH₃

PANI is much useful in the detection of many gases as doping of PANI can be controlled by acid/base reactions. In most cases the fast and reversible reactions of PANI with bases (when it is in doped state-emeraldine salt, ES) and acids (when it is in undoped state-emeraldine base, EB) are the chemical basis of these registration principles [33]. The two forms can be reversibly interconverted by the application of acid or base as shown below. Corresponding chemical changes in PANI during such reactions are shown in Scheme 1:

When polyaniline gas sensors exposed to ammonia, deprotonation occurs and the conductivity changes from the conducting emeraldine salt form to the insulating emeraldine base form [34,34]. Full doping consists of the addition of a proton and counterion for every imine nitrogen in the backbone (half the total nitrogens in the polymer). This conductivity change can be easily measured and makes polyaniline attractive as a sensor material. Ammonia gas molecules withdraw protons from N^+–H to form NH_4^+ leading to the increase in resistance and further improve the sensitivity. Conversely, when the sensor was exposed in air, the process is reversed.

4 Conclusion

In conclusion, PANI nanofibers and hierarchical PANI microspheres films were successfully prepared by facile and rapid in situ chemical oxidation polymerization under a very low monomer concentration, and loading on flexible PET films substrate in the presence of ZnO microspheres. The better
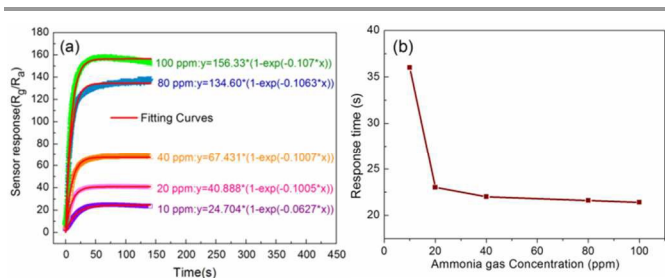
Fig. 11 (a) Experimental and fitting (red line) transient responses of the S0.3 sample and (b) Variation of response time with ammonia concentrations.

quality of hierarchical PANI microspheres can be obtained by adding 0.3mg ZnO. The polyaniline microspheres with 0.3 mg ZnO as the novel sensing material exhibits high sensitivity which is 18 times higher than PANI nanofibers at room temperature, and the detecting limit is 300 ppb. The fabricated sensor also shows good selectivity toward ammonia compared with ethanol, methylbenzene, methanol and methanal. The mechanism of the ZnO microspheres enhanced sensing properties of polyaniline is attributed to the morphology change and enhancement of deprotonation level and crystallinity of the synthesized PANI. This work provides a novel and cost-effective route for the synthesis of hierarchical PANI microspheres as well as creates opportunities for application in electronic circuitry and optoelectronic devices.

Acknowledgements
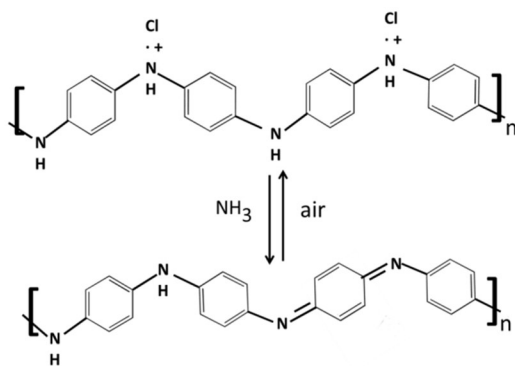
Scheme 1. PANI changes during acid–base reactions.

Notes and references

State Key Laboratory of Chemical Resource Engineering, Beijing Key Laboratory of Environmentally Harmful Chemicals Analysis, Beijing University of Chemical Technology, Beijing 100029, China.

E-mail: luorx@mail.buct.edu.cn, lidq@mail.buct.edu.cn.

1. A. R. Bari, L. A. Patil, I. G. Pathan, D. N. Surawanshi and D. S. Rane, *Procedia Materials Science*, 2014, **6**, 1798-1804.
2. B. Timmer, W. Olthuis and A. v. d. Berg, *Sens. Actuators, B*, 2005, **107**, 666-677.
3. H. Ullah, A.-u.-H. A. Shah, S. Bilal and K. Ayub, *J. Phys. Chem. C*, 2013, **117**, 23701-23711.
4. M. C. Arenas, G. Sanchez, M. E. Nicho, J. Elizalde-Torres and V. M. Castano, *Appl. Phys. A: Mater. Sci. Process.*, 2012, **106**, 901-908.
5. V. Talwar, O. Singh and R. C. Singh, *Sens. Actuators, B*, 2014, **191**, 276-282.
6. A. J. Heeger, *Synthetic. Met.* , 2001, **125**, 23-42.
7. S. Bai, C. Sun, P. Wan, C. Wang, R. Luo, Y. Li, J. Liu and X. Sun, *Small*, 2014, n/a-n/a.
8. X. Li, Y. Chang and Y. Long, *Mat. Sci. Eng.* , 2012, **32**, 817-821.
9. T. T. Trinh, N. H. Tu, H. H. Le, K. Y. Ryu, K. B. Le, K. Pillai and J. Yi, *Sensors and Actuators B: Chemical*, 2011, **152**, 73-81.
10. H. S. Al-Salman and M. J. Abdullah, *Measurement*, 2013, **46**, 1698-1703.
11. S. Park, H. Ko, S. Lee, H. Kim and C. Lee, *Thin Solid Films*, 2014, **570**, 298-302.
12. C. J. Lin, S. J. Liao, L. C. Kao and S. Y. Liou, *J. Hazard. Mater.*, 2015, **291**, 9-17.
13. W. X. Zhang, T. Li, C. He, X. L. Wu, L. Duan, H. Li, L. Xu and S. B. Gong, *Solid State Commun.*, 2015, **204**, 47-50.
14. E. Bacaksiz, S. Yılmaz, M. Parlak, A. Varilci and M. Altunbaş, *J. Alloy. Compd.*, 2009, **478**, 367-370.
15. Q. Li, K. Cheng, W. Weng, P. Du and G. Han, Thin Solid Films, 2013, 544, 466-471.
16. X. Zhou, Z. Hu, Y. Fang, W. Ding and N. Xu, *Mater. Chem. and Phy.*, 2008, **112**, 592-595.
17. Q. Zhu, J. Chen, Q. Zhu, Y. Cui, L. Liu, B. Li and X. Zhou, *Mater. Res. Bull.*, 2010, **45**, 2024-2030.
18. Q. Xiao and T. Wang, *Mater. Res. Bull.*, 2013, **48**, 2786-2791.
19. L. Ding, Q. Li, D. Zhou, H. Cui, H. An and J. Zhai, *J. Electroanal. Chem.*, 2012, **668**, 44-50.
20. M. Sajimol Augustine, P. P. Jeeju, S. J. Varma, P. A. Francis Xavier and S. Jayalekshmi, *Thin Solid Films*, 2014, **562**, 84-89.
21. G. D. Khuspe, M. A. Chougule, S. T. Navale, S. A. Pawar and V. B. Patil, *Ceram. Int.*, 2014, **40**, 4267-4276.
22. B. K. Sharma, A. K. Gupta, N. Khare, S. K. Dhawan and H. C. Gupta, *Synthetic Met.*, 2009, **159**, 391-395.
23. K. Khun, S. Elhag, Z. H. Ibupoto, V. Khranovskyy, O. Nur and M. Willander, *Solid State Sci.*, 2015, **41**, 14-18.
24. J. He, W. Shao, L. Zhang, C. Deng and C. Li, *J. Appl. Polym. Sci.*, 2009, **114**, 1303-1311.
25. N. R. Panda, D. Sahu, B. S. Acharya and P. Nayak, *Curr. Appl. Phys.*, 2015, **15**, 389-396.
26. Z. Tong, Y. Yang, J. Wang, J. Zhao, B.-L. Su and Y. Li, *J. Mater. Chem. A*, 2014, **2**, 4642-4651.
27. G. D. Khuspe, D. K. Bandgar, S. Sen and V. B. Patil, *Synth. Met.*, 2012, **162**, 1822-1827.
28. S. B. Kondawar, P. T. Patil and S. P. Agrawal, *Adv. Mat. Lett.*, 2014, **5**, 389-395.
29. A. A. Khan and M. Khalid, *J. Appl. Polym. Sci.*, 2010, NA-NA.
30. S. Virji, J. Huang, R. B. Kaner and B. H. Weiller, *Nano Lett.*, 2004, **4**, 491-496.
31. Y. J. Huiling Tai, Guangzhong Xie and Junsheng Yu, *J. Mater. Sci. Technol.*, 2010, **26**, 605.
32. T. Krishnakumar, R. Jayaprakash, N. Pinna, N. Donato, A. Bonavita, G. Micali and G. Neri, *Sens. Actuators, B*, 2009, **143**, 198-204.
33. I. Duboriz and A. Pud, *Sens. Actuators, B*, 2014, **190**, 398-407.
34. H. Yin and J. Yang, *Mater. Lett.* , 2011, **65**, 850-853.

Hierarchical polyaniline microspheres loading on flexible PET films for NH$_3$ sensing at room temperature

Shouli Bai, Jingyao Ye, Ruixian Luo*, Aifan Chen, Dianqing Li*

State Key Laboratory of Chemical Resource Engineering, Beijing Key Laboratory of Environmentally Harmful Chemicals Analysis, Beijing University of Chemical Technology, Beijing 100029, China
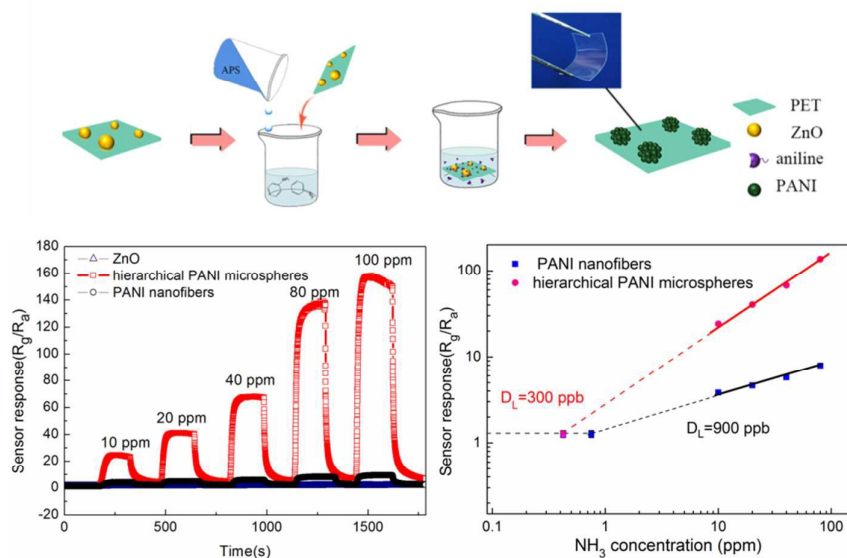
Hierarchical polyaniline microspheres was prepared on polyethylene terephthalate (PET) film by in situ chemical oxidative polymerization of aniline using ZnO as sacrificial template to construct a smart sensor for NH$_3$ detection, which not only exhibits high sensitivity, good selectivity and low detection limit at room temperature, but also possesses features of flexibility, portability and optical transparency compared with traditional sensors based on substrates of glass, quartz slide or ceramic tube.