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High-sensitivity gas sensors based on arranged polyaniline/PMMA composite fibers

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ABSTRACT

Aligned poly(methyl methacrylate) (PMMA) fibers were fabricated by electrospinning and then nanostructured polyaniline (PANI) was grown on the surface of the parallel PMMA fibers *via in situ* solution polymerization. The structure and morphology of the aligned PANI/PMMA composite fibers were characterized by scanning electron microscopy (SEM) and Raman spectrometry. The gas sensing properties of the composite fibers were investigated under ultra-low ammonia concentrations at room temperature. It is found that the arranged fibers exhibited high sensitivity and fast response upon exposure to ammonia vapor of 1–30 ppm. The normalized resistance R/R_0 increased linearly with the ammonia concentration increasing. The sensing mechanism was also discussed. The results indicate that aligned PANI/PMMA composite fibers are promising candidate for fast detection of toxic ammonia gas.

1. Introduction

Electrospinning is an efficient, highly versatile and promising technique for fabricating one-dimensional (1D) continuous micro-/nanoscale fibers [1]. The principle of electrospinning is very simple. Under the action of electric field force, a charged jet of polymer solution ejects from Taylor cone at the tip of spinneret, and undergoes an instability and elongation/splitting process to become very long and thin. Meanwhile, the solvent evaporates, and ultrathin fibers are randomly deposited on the collector [1–4]. Numerous organic or inorganic materials have been fabricated into not only nonwoven fiber mats, but also well aligned or crossed fiber arrays [5] with fiber diameter ranging from tens of nanometer to several micrometers, and their potential applications in optoelectronics, sensors, catalysis, fiber reinforcement, tissue engineering, drug delivery, *etc.* have also been extensively explored [6–8].

Polyaniline (PANI) is one of the most important intrinsically conducting polymers due to its advantages of simple preparation, good chemical stability, high conductivity, *etc.* [9]. Generally, the blend of PANI and other polymers such as polyethylene oxide (PEO), PMMA and polystyrene (PS) were co-electrospun into nonwoven fibers [10–12]. Only few publications reported that pure PANI could be electrospun directly [13–16] due to the limitations on molecular weight and solubility unsuitable for electrospinning. Gong et al. synthesized PANI nanotubes by using electrospun PVA fiber mats as a template [17]. Electrospun fibers based on PANI and their composites have been investigated as gas sensing materials for the detection of a number of chemicals, including NO_2, CO, N_2H_4 and NH_3 [18–21]. Dobroczyńska et al. presented a simple construction of an ammonia sensor based on PANI nanostructures *in situ*-synthesized on the surface of conductive glue [22]. Liu et al. [23] reported that individual PANI/PEO composite nanofiber responded rapidly to 0.5 ppm ammonia vapor by scanned-tip electrospinning deposition method. Pinto et al. [24] detected that the normalized resistance of single PANI nanofiber exhibited about 1.5

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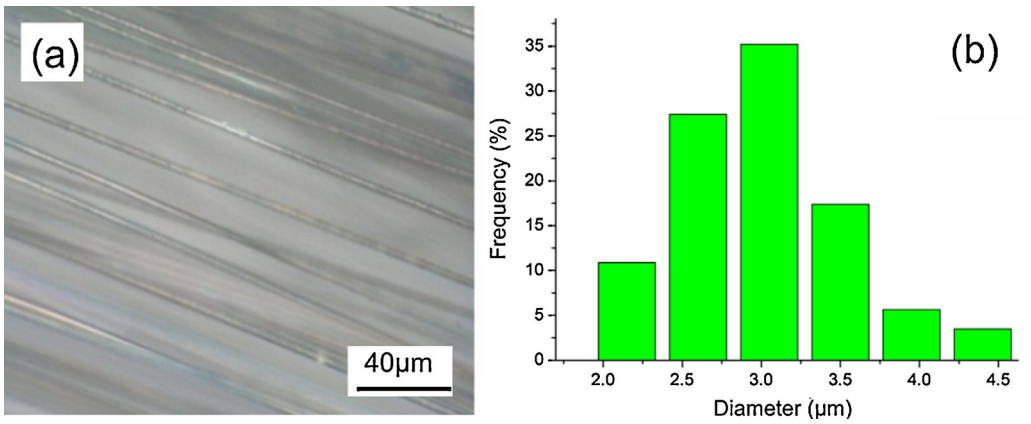

Fig. 1. (a) Photograph and (b) histogram showing the size distribution of aligned PMMA fibers.

times larger than that of PANI nanofiber mat to alcohol vapor. Ji et al. [25] prepared PANI/PMMA nonwoven mat gas sensor to triethylamine vapor. Although many conducting polymers were prepared into fibers *via* electrospinning and measured as gas sensors, the fibers were almost in the form of nonwoven mat with different porosities and without regular arrangement, and single fiber sensor was also reported occasionally. So the results of gas sensors based on conducting polymer composite fibers are not consistent. Up to now, aligned PANI/PMMA fibers prepared by electrospinning and *in situ* solution polymerization and their gas sensing properties have not been reported yet.

Ultrathin fibers in the form of nonwoven mat are commonly fabricated by conventional electrospinning setup. Parallel arrangement of electrospun fibers is in favor of electron transfer, which may enhance sensing performance of nano-devices. So it is necessary to modify the conventional electrospinning technique to obtain aligned fibers. In this paper, aligned PMMA fibers were prepared by a modified electrospinning setup with a rotating Cu wire-framed drum as collector, and then PANI nanostructures were grown on the PMMA fiber surface by *in situ* solution polymerization. These PANI/PMMA fibers have advantages of high order and controllability. The aligned composite fibers exhibit good ammonia sensing properties for concentrations of 1–30 ppm.

2. Experimental

Poly(methyl methacrylate) (PMMA) (Alfa Aesar, Tianjin) 20% weight percentage was stirred thoroughly in tetrahydrofuran (THF) for 3 h as the electrospinning precursor. The electrospinning setup is different from the conventional electrospinning setup, a Cu wire-framed drum acts as a collector [26], and the drum has two circular nonconducting plexiglas disks with 10 cm in diameter. The speed of the rotating collector was 650 rpm with an applied voltage of 7 kV and the distance is 6 cm from needle to the drum. The synthesis of PANI on PMMA fibers by *in situ* polymerization has been reported in detail [27]. And the reaction solution was prepared as follows: Firstly, 0.01 mol sulfosalicyclic acid dehydrate (SSA) was dissolved thoroughly in 50 ml deionized water. Then 0.02 mol aniline was added and stirred to form a stable solution named *A*. Secondly, 0.02 mol ammonium peroxodisulfate (APS) was dissolved and stirred in 50 ml deionized water to form solution *B*. Both solution *A* and solution *B* were kept in a refrigerator with temperature of 5 °C for 1 h. Then solution *A* and solution *B* were mixed together and the arranged PMMA fibers pasted on the polyethylene (PE) substrate was fully immersed in the mixed solution and kept steady at 5 °C for 6.5 h. At last, the aligned PMMA fibers were taken out and one can see PANI clusters self-assembled on the fibers. Because the micro gaps exist between the fibers and the nanofiber membrane is not thick, all the PMMA fibers were equally coated by PANI. The PANI clusters were still remained on the PMMA fibers after washed by deionized water for three times and dried in air.

The PANI/PMMA composite fibers were characterized by scanning electron microscopy (SEM, Hitachi TM-1000) and Raman spectrum analysis (Jobin Yvon S.A., the excitation wavelength was 532.16 nm). The electrical and gas sensing properties of the fibers were measured by a Keithley 6517 high resistance meter and a home-made gas sensing system. The sample was placed in a sealed glass chamber of 5 L. The chamber contains one inlet port and one outlet port. Moreover, the inlet port links up with a pipeline which connects the air and NH_3 diluted by N_2. Fresh air and NH_3 in N_2 were supplied. Flowmeter was used to obtain different NH_3 concentrations. The change in resistance was recorded automatically by a computer.

3. Results and discussion

Fig. 1a shows the photograph of the arranged PMMA fibers prepared by the modified electrospinning setup. The surface of the as-spun fibers is quite smooth because of the amorphous nature of the PMMA composite. Each fiber is quite uniform. And the fiber diameter ranges from 2.5 to 3.5 μm (Fig. 1b). The aligned PMMA fibers were used as template to grow PANI structures.

The microstructure of the electrospun fiber and surface features of the parallel fiber arrays were characterized by SEM. Fig. 2 shows the SEM image of aligned PANI/PMMA fiber arrays after the *in situ* chemical polymerization, which indicates that the highly ordering of the PMMA fiber template was maintained. One can see that the PANI nanostructures grew on the PMMA fibers. Namely, the PMMA fiber template was coated by nanostructured PANI with the increase of polymerization time. Bai et al. [12] reported that, generally, a thin PANI coating firstly grew evenly on the surface of PMMA fiber because of interfacial compatibility of PANI to PMMA. Then PANI nano-clusters were self-assembled on the surface of the PANI nanostructures. The inset in Fig. 2 clearly shows the surface structure of a single PANI/PMMA fiber. The surface nano-clusters are scale of dozens of nanometers to several micrometers. The aggregation of some PANI nanostructures could be attributed to the high-surface tension of PANI molecules.

The PANI/PMMA fibers were also characterized by Raman spectrum analysis (Fig. 3) with an incident light wavelength of 532.16 nm. Compared to electrospun PMMA fibers, the Raman spectrum of PANI/PMMA composite fibers match typical PANI Raman shift peaks. Five representative peaks arising from PANI can be indexed to C–H bending of the quinoid ring at 1176 cm^{-1}, C–H bending of the benzenoid ring at 1251 cm^{-1}, C–N stretching at 1342 cm^{-1}, and C–C stretching of the benzene ring at 1597 cm^{-1},

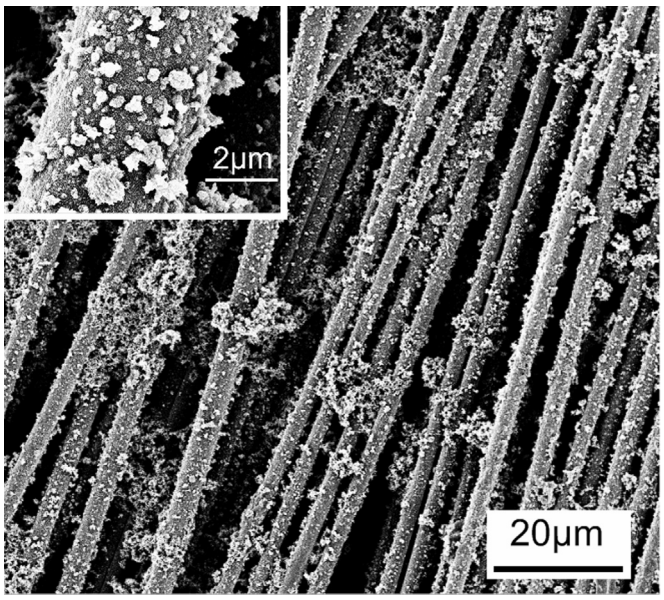

Fig. 2. SEM image of the aligned PANI/PMMA composite fibers. The inset shows the coated PANI nanostructures on the surface of a single PMMA fiber.

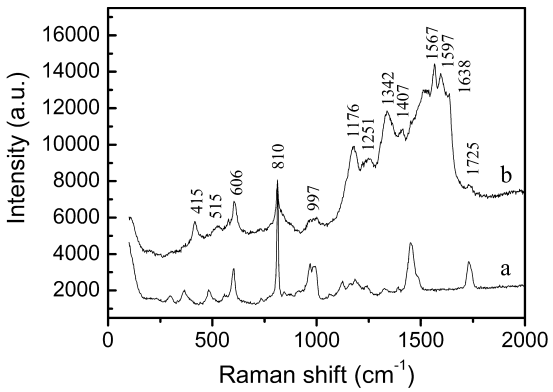

Fig. 3. Raman shifts of (a) pure PMMA fibers and (b) PANI/PMMA composite fibers.

respectively [28]. In addition, it can be seen that the peaks of 606 cm^{-1}, 810 cm^{-1}, 997 cm^{-1} and 1725 cm^{-1} of the PANI/PMMA spectrum come from PMMA. Since the laser jet was focused on the surface of the fiber, this result suggests that PMMA fiber is coated by PANI and thus a structure of PMMA fiber covered with PANI forms.

The detection of NH_3 in air is of interest for environmental monitoring and process control applications because of its high toxicity. The gas sensor based on PANI/PMMA aligned fibers was attributed to the diffusion of ammonia into the aligned fibers and the reaction of NH_3 molecules with doped PANI. The electrical properties of the fibers were measured at different ammonia concentrations. Fig. 4a shows the real-time PANI/PMMA response to 1, 2, 4, 5 and 7 ppm ammonia gas, respectively, which indicates the gas-concentrations effect on the transport behavior. The sensitivity S ($S = R/R_0$, R_0 is the initial resistance in the absence of NH_3, and R is the resistance measured exposure to gas for 800 s) is 1.38 at NH_3 concentration as low as 1 ppm. When the fibers was exposed to gas for 10 s, the sensitivity R/R_0 is about 1.07, which is similar to the result before [23,29,30]. And with the concentration increasing to 2, 4, 5 or 7 ppm, the sensitivity is 1.58, 2.19, 2.67, 3.46, respectively, attributed to more NH_3 molecules diffusing into the fibers at higher concentrations.

Fig. 4a shows the time response of resistance upon exposure to different gas concentrations. When exposed to fresh air the recovery time of the fiber resistance is much longer for 1 ppm gas (shown in Fig. 4b) than those of higher concentrations (shown in Fig. 4c). The sensitivity R/R_0 of the PANI/PMMA aligned fibers at 30 ppm

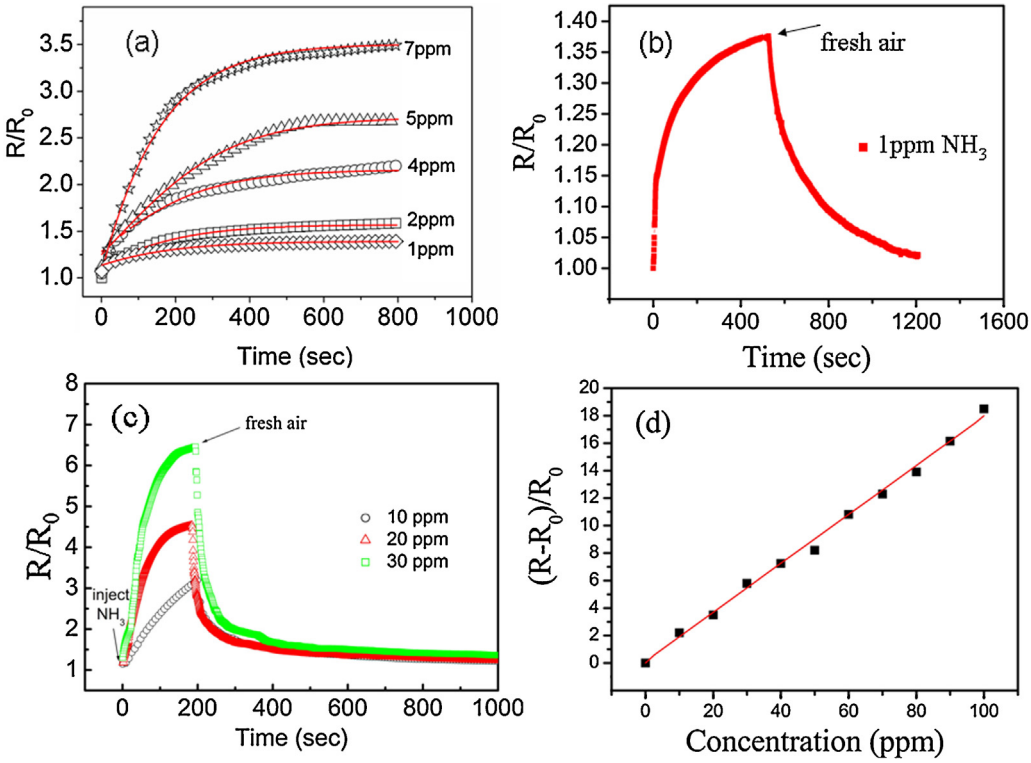

Fig. 4. Ammonia sensing properties of the arranged PANI/PMMA composite fibers: (a) Time response of the resistance upon exposure to different NH_3 concentrations. Scatters represent experimental curves and solid lines represent fitting curves. (b and c) Recovery curves. (d) Sensitivity of the PANI/PMMA fibers upon exposure to different concentrations of NH_3 gas. (For interpretation of the references to color in this figure citation, the reader is referred to the web version of this article.)

ammonia was approximately four times higher than that of the non-woven fiber mat [27]. Moreover, the value of $(R/R_0 - 1 = 0.56)$ was more than two times higher than that of PANI or its composition sensor [23,31] when exposure to gas at about 20 ppm for 10 s. Compared to random mats of fibers, aligned fibers may be its mechanical stability and well-defined current path so that variations in the interconnect resistance through the many contacts in a fiber network are eliminated.

And the recovery coefficient of resistance η $(\eta = (R_m - R')/(R_m - R_0)$ was measured, where R_m is the maximum resistance marked by dotted line in Fig. 4b and c, R' is the recovery resistance exposed to fresh air for 1000 s, and R_0 is the initial resistance in air) is 97%. To further characterize the recovery feature, the aligned fibers were measured at 10, 20 and 30 ppm NH_3 gas, respectively (as shown in Fig. 4c). When the sensitivity is 1.3, the response time is only 10 s, 4 s and 0.5 s for concentrations of 10, 20 and 30 ppm, respectively. So with the NH_3 concentration increasing, the response is faster for higher concentrations of NH_3. And the recovery coefficient η are 95%, 93% and 92.8%, respectively, which indicates the recovery coefficient decrease with the concentration increasing, that is to say, η tends to increase at lower concentration. As shown in Fig. 4d, the sensitivity of the arranged PANI/PMMA fibers reveals a nearly linear relationship to the concentration of ammonia. The solid line is a linear fitting to the data.

The mechanism of the gas sensor is originated from the diffusion of ammonia into the PANI/PMMA fibers and the reaction of NH_3 with PANI [32]. As we know, through doping the PANI conjugated molecule chain becomes more conductive by increasing the amount of polarons (charge carriers). A model of diffusion into solid cylinders can be considered to illustrate the diffusion process. The least-squares fits was applied to the experimental data by using the diffusion equation for solid cylinders as follows [33]:

$$\frac{R}{R_0} = \left[1 - A\left(1 - \sum_{n=1}^{\infty} \frac{4}{{a_n}^2} e^{-{a_n}^2 t}\right)\right]^{-1} \quad (1)$$

where a_n are the roots of the Bessel function of the first kind of order zero. A is the concentration ratio of NH_3 and carriers. As shown in Fig. 4a, the red solid curves are fitted well with the experimental data by using Eq. (1). The parallel microfibers may accelerate the electron transfer, and thus improve the response and recovery properties of the fiber-based sensor. Upon interaction with NH_3 gas, the protons in the –NH– sites in the conjugated PANI are withdrawn by adsorbed NH_3 molecules, and PANI in the form of emeraldine salt is reduced to emeraldine base. As a result, de-doping processes on the PANI chains occur, leading to a decrease of polaron amount and an increase of electrical resistance. Replacing NH_3 with air, this process is reversed. With the decrease of ammonia concentration around nanostructured PANI, more ammonia molecules are released and as a consequence more current carriers are freed, which makes the electrical conductance increase.

4. Conclusion

In summary, aligned PANI/PMMA composite fibers are successfully fabricated by electrospinning technique and followed *in situ* solution polymerization. The PANI/PMMA fibers coated with PANI nano-clusters have a larger surface area and thus higher gas sensitivity and faster sensing response, which can be used to detect trace level of ammonia (1 ppm). This sensitivity is approximately four times higher than that of the PANI/PMMA non-woven fibers sensor. The recovery coefficient tends to be higher at lower concentration. These results demonstrate that the aligned PANI/PMMA fibers may have practical usage in the alarm system and concentration determination of toxic gases like ammonia due to their good environmental stability, high sensitivity and low cost.

Acknowledgments

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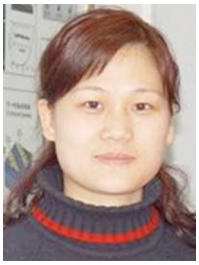
Biographies



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