

# High Sensitivity Ammonia Sensor Using a Hierarchical Polyaniline/Poly(ethylene-co-glycidyl methacrylate) Nanofibrous Composite Membrane

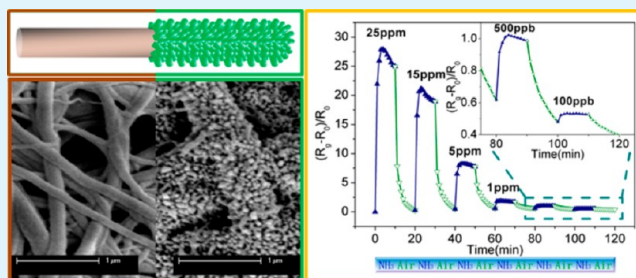
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**ABSTRACT:** A hierarchically structured three-dimensional network nanofibrous composite membrane was prepared through in situ growing uniform polyaniline nanofibers on the surfaces of poly(ethylene-co-glycidyl methacrylate) (PE-co-GMA) nanofibers. And the nanocomposite membrane was fabricated into a super sensitive sensor of ammonia gas in ambient temperature. Morphological analysis of the nanocomposite membranes revealed uniform small nanofibers of PANI rooted on the surface of PE-co-GMA large nanofibers and a three-dimensional porous nanocomposite structure formed. Because of the ultrahigh surface areas and three-dimensional porous architecture, the prepared sensor demonstrated high sensitivity in the parts per billion range and quick response with good reproducibility to ammonia gas.

**KEYWORDS:** ammonia, nanofiber, nanofibrous composite membrane, polyaniline, sensor



## INTRODUCTION

Sensors for toxic and hazardous chemicals have attracted considerable attentions in recent years because of the increased human safety concerns and environmental monitoring requirements. Taking advantage of the large surface areas of nanoscale structures, researchers have found significant applications for one-dimensional (1D) nanostructured materials, such as carbon nanotubes and semiconductor nanowires, in detecting trace amount of harmful gases.<sup>1,2</sup> Craighead and co-workers<sup>3</sup> used a nonlithographic deposition process to form an oriented polymeric nanowire, and the microfabricated nanowire sensor showed good response to NH<sub>3</sub> at parts per millions levels. Although the use of nanotubes and nanowires offers the prospect of high sensitivity and rapid detection, the application of nanowire sensor device is limited by the difficulty in manipulating and locating the nanostructures with respect to the microsized electrodes.

On the other hand, conductive polymers such as polyaniline (PANI) have been widely studied as a sensing material for a variety of toxic gases such as CO, NO<sub>2</sub>, and NH<sub>3</sub> because of its simple and reversible doping/dedoping chemistry.<sup>4–7</sup> PANI possesses a range of excellent properties such as environmental stability in both its doped, conducting and dedoped, insulating forms, highly tunable conductivity and easy fabrication processes.<sup>8,9</sup> PANI can be produced as bulk powders, cast films, or fibers, which in conjunction with the feasibility of low-cost and large-scale production makes it an ideal candidate for various applications.<sup>10</sup> Potential applications of PANI include anticorrosion coatings, rechargeable batteries, separation

membranes, photovoltaic cells, sensors, and conducting biocomposites.<sup>8,11,12</sup> More recently, there have been rapid developments in the subject area of PANI nanofibers and their composite, which provides an effective strategy for producing versatile sensor materials with enhanced sensing properties.<sup>13,14</sup> However, the surface areas and sensitivities could be limited if the chemical sensors are fabricated by directly using PANI nanofibers or blending the nanofibers with others substrates.<sup>15,16</sup>

High active surface areas and easy substrate penetration structures of the sensor materials are key factors for improved sensing performance. As an example, two-dimensional poly(acrylic acid) nanonets comprising of interlinked ultrathin nanowires with diameters of 10–30 nm exhibited a quick response (180 s), low detection limit (1 ppm) and ideal selectivity at room temperature for trimethylamine detection.<sup>17</sup> Chen et al.<sup>18</sup> prepared a three-dimensional porous CuO/TiO<sub>2</sub> nanocomposite electrode to detect glucose, which exhibited a high sensitivity (1321  $\mu\text{A mM}^{-1} \text{cm}^{-2}$ ) and low detection limit (390 nM) and good stability due to its hierarchical components and porous structure. Recently, a high throughput procedure was developed to fabricate nanofibrous membranes as ideal ultralight and breathable materials with ultrafine fibers and pore size, highly open porous structure and extraordinary high surface area to volume ratio.<sup>19,20</sup> In this work, we employed the

Received: June 7, 2013

Accepted: July 9, 2013

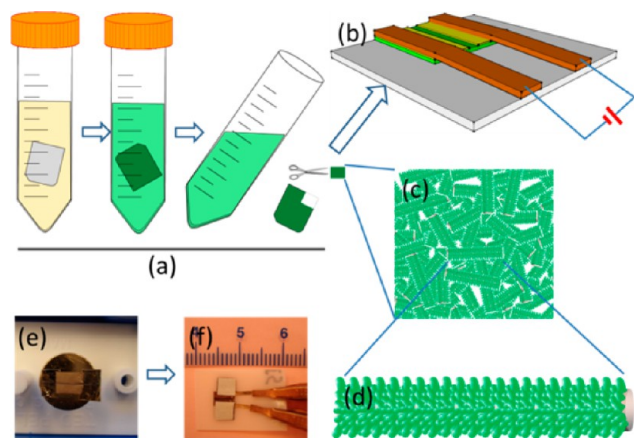
Published: July 9, 2013

nanofibrous membranes as a base to in situ grow chemical sensing conductive polymer nanofibers to form a novel three-dimensional (3D) nanofiber composite. Such 3D porous networks not only form ultrahigh active surface area materials but facilitate easy access of target gas chemicals. The assembled sensor represents a promising application in ammonia detection because of its special hierarchical structure of the nanocomposite membrane.

## EXPERIMENTAL SECTION

**Preparation of PE-co-GMA Nanofiber and Nanofibrous Membranes.** The PE-co-GMA nanofibers were prepared according to a previously published procedure.<sup>20,21</sup> Typically, mixtures of cellulose acetate butyrate (CAB)/PE-co-GMA powders with a blend ratio of 80/20 by weight were gravimetrically fed into a Leistritz corotating twin-screw (18 mm) extruder (model MIC 18/GL 30D, Nurnberg, Germany) at a feed rate of 12 g/min. Barrel temperature profiles were 150, 170, 180, 195, 205, and 210 °C. The blends were extruded and hot drawn by a take-up device with a draw ratio of 25 (the area of cross-section of the die to that of the extrudates) and cooled to room temperature. The PE-co-GMA nanofibers were prepared by the extraction of CAB/PE-co-GMA composite fibers cut into 5 mm for 24 h with acetone to remove the CAB matrix. To fabricate a PE-co-GMA nanofibrous membrane, the prepared nanofibers were dispersed in a solution with a high speed shear mixer to form a stable suspension. The suspension was then air-spray-coated on smooth surfaces of Teflon films to form nanofibrous membranes, which were then peeled off after being dried in air.

**Preparation of PANI/PE-co-GMA Nanofibrous Composite Membranes.** To form a hierarchical PANI/PE-co-GMA nanofibrous composite membrane, PANI nanorods and small nanofibers should grow on surfaces of PE-co-GMA nanofibers in the nanofibrous membrane via a modified chemical oxidative polymerization of aniline (Figure 1a).<sup>22,23</sup> The polymerization was carried out in an ice–water



**Figure 1.** Schematic illustrations of preparation of nanofibrous composite membrane and the assembling of the sensor. (a) The process of in situ polymerization for forming nanofibrous composite membranes. (b) The structure of the chemical sensor. (c) & (d) Schematic presentations of a nanofibrous composite membrane and a single PE-co-GMA nanofiber coated with PANI nanofibers and nanorods. (e) The nanofiber composite membrane sputtered with gold. (f) The gas sensor for measurement.

bath as follows: First, a piece of  $2 \times 2 \text{ cm}^2$  as formed PE-co-GMA nanofibrous membrane was soaked into 16 mL solution of aniline ( $1.25 \text{ g L}^{-1}$ ) dissolved in 1 M HCl solution in a vial in an ice–water bath. After 10 min, 6 mL of a cold solution of ammonium persulfate (APS) ( $5.5 \text{ g L}^{-1}$ ) dissolved in 1 M HCl solution was added with vigorous shaking. After the addition, the mixture was left in the ice–water bath with a frequent shaking by a vibrator. After 24 h, a dark-

green PANI/PE-co-GMA nanofibrous composite membrane was formed. Finally, the membrane was taken out and washed with deionized water several times and dried under ambient temperature.

**Characterizations.** The morphologies of the nanocomposite membranes were examined by using a scanning electron microscopy (SEM) (XL 30-SFEG, FEI/Philips, USA) at 5 kV accelerating voltage on gold sputter coated samples. Raman spectra were also obtained by using a Renishaw Laser Raman spectroscopy system (Spectra-Physics Ar-ion 514.5 nm).

**Sensor Assembling and Sensing Measurements.** A sensor for ammonia sensing test was fabricated by the following steps (Figure 1b, e, f). A piece of  $3 \times 5 \text{ mm}^2$  PANI/PE-co-GMA nanofibrous composite membrane was doped 2 h in 5 mL of 0.2 M  $\text{H}_2\text{SO}_4$  solution at room temperature. The doped nanocomposite membrane was covered with a mask and coated with gold by using a Sputter Coater to form a 0.2 mm sensing gap and two Au stripes on its surface, and then the membrane was pasted with two copper electrodes onto a piece of  $14 \times 20 \text{ mm}^2$  polystyrene sheet to form a sensor as shown in Figure 1b, e, and f.

Gas-sensing properties were investigated on a steady-state testing system by placing the sensor in a sealed 125 mL chamber with an electrical feed-through, a gas inlet, and a gas outlet, respectively.<sup>15</sup> Data recording started when the target gas was completely injected into the chamber. Dry air was used as both a carrier and a dilution gas. All measurements were performed at room temperature ( $26 \text{ }^\circ\text{C} \pm 1 \text{ }^\circ\text{C}$ ) with a relative humidity of  $25\% \pm 3\%$ . The sensitivity ( $S$ ) and resistance change ( $\Delta R$ ) are expressed in the following:

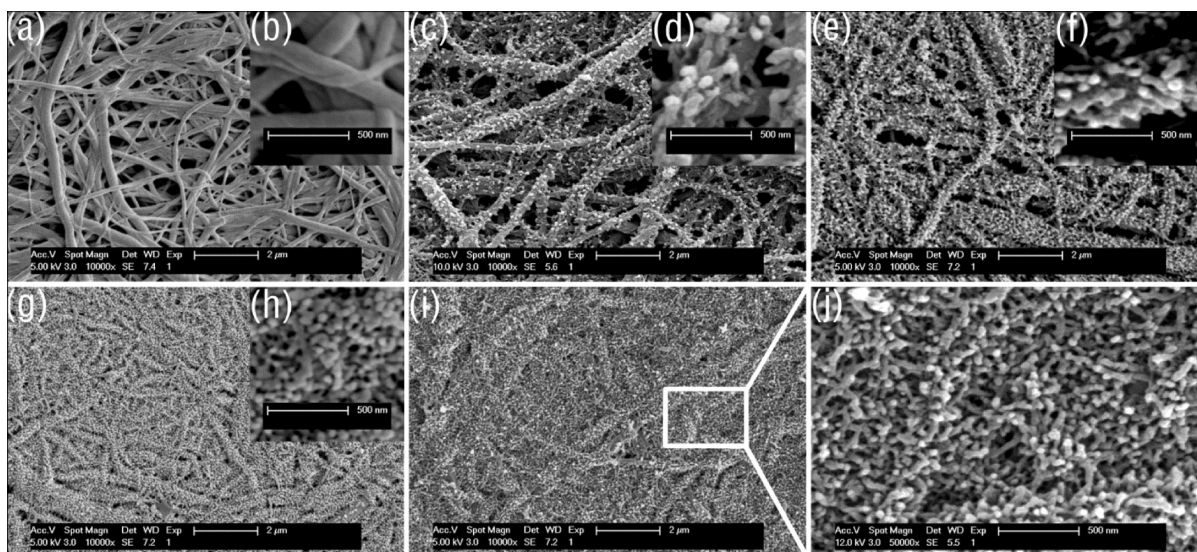
$$S = \frac{\Delta R}{R_0} (\%) = 100 \frac{R_g - R_0}{R_0} \quad (1)$$

Where  $R_0$  is the resistance in dry air, and  $R_g$  is the resistance upon exposure to target gas molecules.

## RESULTS AND DISCUSSION

**Morphologies of Nanofibrous Composite Membranes.** To fabricate sensors with improved sensitivity to toxic gases, substrate materials should possess ultrahigh surface areas and easy accessibility to the gases. Thus, a hierarchical nanofibrous composite membrane with a 3D nanoporous structure shown in Figure 1c was designed. As an effort of fabricating such a novel structure with capacity of self-standing and mass production, recently developed poly(ethylene-co-glycidyl methacrylate) (PE-co-GMA) nanofibrous membranes, which were fabricated by air-spraying melt spun PE-co-GMA nanofibers onto a Teflon film,<sup>20,24</sup> were employed. As shown in images a and b in Figure 2, PE-co-GMA nanofibers have an average diameter of 235 nm and a diameter distribution in the range of 100–400 nm. Micrometer-sized pores are clearly visible in the membrane and the surface of the nanofibers was smooth.

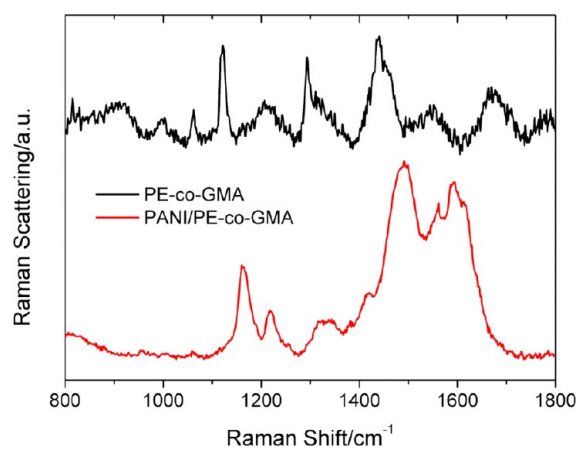
Then, polyaniline nanofibers were grown on the PE-co-GMA nanofibrous membranes by an in situ polymerization of aniline on the surface of the nanofibers, which formed the hierarchical PANI/PE-co-GMA nanofibrous composite membranes. The SEM images of the composite membranes in the PANI nanofiber growing process are shown in Figure 2c–j. As shown in Figure 2c, it can be found that PANI nanodots or nanorods are uniformly grown on the surface of PE-co-GMA nanofibers. Many of the up-pointing ends of the nanorods can be observed in the inset image (Figure 2d). The diameters of the nanodots and nanorods are in the range of 20–40 nm, and the lengths of the nanorods are about 100 nm. Moreover, all of the PANI nanodots and nanorods are rooted on the surface of the larger PE-co-GMA nanofibers and nearly all grown perpendicularly to the large fibers, whereas a few nanorods overlie on the surface. According to a well-proved mechanism, during the formation of



**Figure 2.** SEM micrographs of (a, b) PE-co-GMA nanofibrous membrane, and (c–j) PANI/PE-co-GMA nanofibrous composite membranes prepared by different in situ polymerization durations: (c, d) 4, (e, f) 6, (g, h) 12, and (i, j) 24 h.

PANI nanofibers and nanorods, there are two possible nucleation sites, both in bulk solution and on solid substrates, in the in situ polymerization system.<sup>22</sup> If concentrated aniline and/or oxidant are used in the polymerization system, PANI will be induced to form in bulk solution at a faster rate than it can deposit on solid substrates. In contrast, dilute aniline and/or oxidant induce heterogeneous nucleation occurs first on solid substrate and PANI will form nanorods that grow from the active nucleation centers in the competition of two phase reaction. The mechanism is similar to the model proposed by Liu et al.<sup>25</sup> to account for the stepwise electrochemical polymerization of PANI. With prolonged polymerization durations, more PANI nanorods appeared and grown, shown in Figure 2e–h. The pore size of the membranes gradually decreased and the outlines of PE-co-GMA nanofibers became more inconspicuous. After reacting for 24 h, a hierarchical PANI/PE-co-GMA nanofibrous composite membrane in a 3D network structure formed, with dense small PANI nanofibers completely covering the surfaces of large size PE-co-GMA nanofibers (Figure 2i–j). Figure 1c and d show the schematic of PANI nanofibers growing around PE-co-GMA nanofibers in the 3D porous membrane. The formed PANI nanofibers interconnected with each other, and the average diameters of the small PANI nanofibers are about 35 nm. It is well-known that the active surface areas of sensitive materials would have great effect on the sensitivity and other sensing properties.<sup>17,18</sup> Therefore, the hierarchical nanofiberous composite membrane are expected to have good gas sensing properties because of the dramatically increased surface areas which are derived from the 3D architecture of two kinds of nanofibers with different diameters.

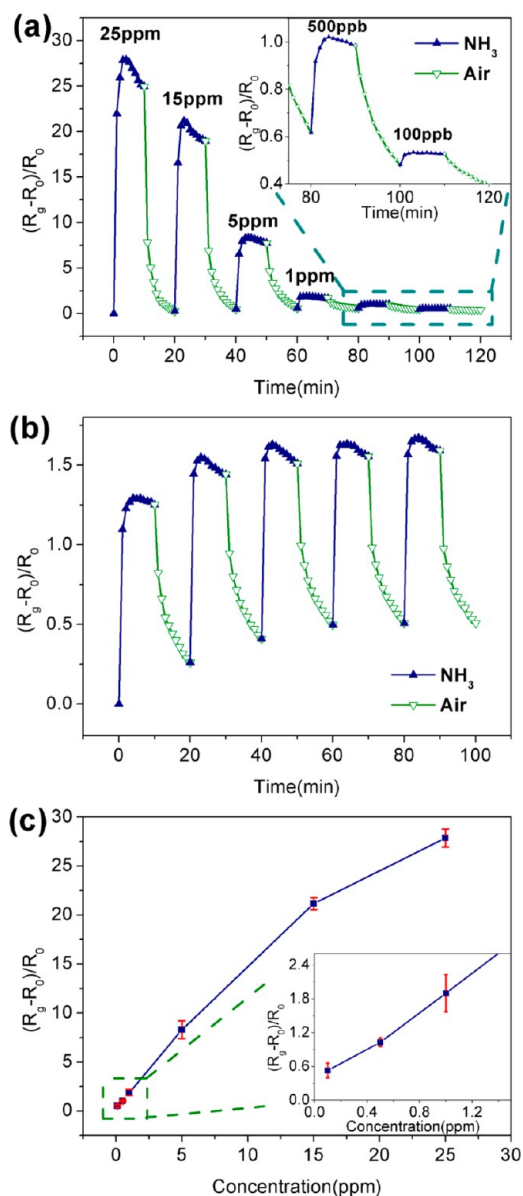
**Raman Spectra of the Membranes.** Figure 3 shows Raman spectra of the neat PE-co-GMA nanofibrous membrane and the as-formed PANI/PE-co-GMA nanofibrous composite membrane. In the spectrum of the neat PE-co-GMA nanofibrous membrane, the peak at  $1121\text{ cm}^{-1}$  is attributed to the symmetric stretching of C–C, while the  $\text{CH}_2$  twist near  $1293\text{ cm}^{-1}$  and the multiple peaks around  $1450\text{ cm}^{-1}$  are due to the correlation splitting of the  $\text{CH}_2$  bending vibrations of the polymer crystalline regions.<sup>26,27</sup> In the spectrum of the



**Figure 3.** Raman spectra of the neat PE-co-GMA nanofibrous membrane and the PANI/PE-co-GMA nanofibrous composite membrane.

composite membrane, the peaks of characteristic PE-co-GMA almost could not be seen. The peaks between the bands of  $1300$  and  $1350\text{ cm}^{-1}$  (C–N<sup>+</sup> stretching),  $1491\text{ cm}^{-1}$ , and  $1609\text{ cm}^{-1}$  (C–C stretching of the benzene ring) are attributed to the doped PANI in the form of emeraldine salt (PANI-ES).<sup>27</sup> At the same time, the peaks at  $1160$  and  $1217\text{ cm}^{-1}$  (C–H bending of the quinoid ring) revealed the presence of PANI in the emeraldine base form (PANI-EB).<sup>28,29</sup> Thus, the Raman spectrum indicated that the as-formed PANI in the membrane is a mixture of PANI-ES and PANI-EB, which almost totally covers the surface of PE-co-GMA nanofibers.

**Gas Sensing Properties of the Sensors Fabricated from Nanofibrous Composite Membranes.** To demonstrate the desired sensing properties of the 3D hierarchical PANI/PE-co-GMA nanofibrous composite membrane, it was assembled into a sensor according to the structure shown in Figure 1, and ammonia ( $\text{NH}_3$ ) was chosen as a testing gas. The variations of electronic resistance of the sensor are shown in Figure 4a when it was exposed to decreasing  $\text{NH}_3$  concentrations ranging from 25 to 100 ppb. Once  $\text{NH}_3$  gas was introduced, the resistance of the sensor increased sharply



**Figure 4.** (a) Response of the sensor exposed to  $NH_3$  gas with different concentrations. (b) Response and recovery curves of the sensor exposed to 1 ppm  $NH_3$  repeatedly in dry air. (c) Sensitivity ( $S$ ) values of the sensor exposed to  $NH_3$  gas. The error bars denote the standard errors of the mean values of three independent measurements.

and dramatically within several seconds and reached saturation or slightly decreased after several minutes because of the gas diffusion. The results demonstrate that the sensor has a surprisingly high and quick response to  $NH_3$ . For example, it was observed that the sensitivity  $S$  of the sensor was 2496% for 25 ppm  $NH_3$  in air, with the  $S$  value approximately 350 times and 570 times larger than the values reported for sensors prepared by the in situ polymerized PANI nanostructures and drop-casting PANI nanofibers (7.10 and 4.37%, respectively, for 92 ppm  $NH_3$ ).<sup>6</sup> Figure 4a also shows that the sensor possesses a much lower detection limit at 100 ppb of ammonia gas, which is even lower than that of the single PANI nanowire sensor (500 ppb)<sup>3</sup> and the vast majority of sensors fabricated by using other materials and methods for  $NH_3$  detection.<sup>30</sup> The excellent sensing properties are indeed due to the ultrahigh

surface areas and porosity of the 3D framework of the hierarchical nanofibrous composite membrane. As a result, during the exposure to low concentrations of  $NH_3$  gas, the gas can diffuse into the membrane and be absorbed by the PANI nanofiber surfaces more rapidly. This further verified the results of previous work<sup>6,17,18</sup> that the morphologies of sensing materials have important effect on its sensitivity.

To investigate the reproducibility of the sensor, it was exposed to  $NH_3$  at a fixed concentration of 1 ppm, as shown in Figure 4b, repeatedly. The sensor was cycled 5 times while the resistance showed a relatively limited drift during the initial 2 rounds. After the  $NH_3$  gas was replaced by pure dry air flow, the resistance of the sensor decreased quickly, but could not return to the original level at the initial round. It was roughly estimated that the response time was about 75 s to reach 90% of the maximum value for each  $NH_3$  gas exposure at a concentration of 1 ppm. The sensitivity ( $S$ ) values of the sensor for  $NH_3$  gas are shown in Figure 4c. The plot shows an initial linear sensitivity when the  $NH_3$  concentrations were in a range of 100 ppb to 5 ppm, and gradually moving toward to lower increasing rates because of absorption saturation in higher concentrations of  $NH_3$  gas.

## CONCLUSION

A 3D hierarchical nanofibrous composite membrane with high detection sensitivity to  $NH_3$  gas at room temperature was successfully prepared by in situ growing PANI nanofibers on a thermoplastic nanofibrous membrane. PANI nanofibers possessed good rooting on the surface of PE-co-GMA nanofibers and formed high porosity networks with super large active surface areas which facilitate easy access of target gas chemicals. This macroscale self-standing membrane material can be easily fabricated into resistive sensors through a simple method. Moreover, the assembled sensor demonstrated ultrahigh sensitivity to  $NH_3$  gas in the ppb range with good reproducibility and in higher concentration as well. The high-performance, low-cost sensor developed here could be used in a wide variety of practical applications.

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### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

S.C. is grateful for a scholarship from China Scholarship Council (Grant. 2011624553) for conducting this research at the University of California, Davis.

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