

Full Paper

Single Polypyrrole Nanowire Ammonia Gas Sensor

Sandra C. Hernandez, Debangshu Chaudhuri, Wilfred Chen, Nosang V. Myung,* Ashok Mulchandani*

Department of Chemical and Environmental Engineering and Center for Nanoscience and Engineering, University of California-Riverside, Riverside, CA-92521, USA

*e-mail: adani@engr.ucr.edu, myung@engr.ucr.edu

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Abstract

We report the synthesis, electrical characterization and ammonia gas sensing with single nanowire of conducting polypyrrole. Three hundred nanometer in diameter and 50 to 60 μm long polypyrrole nanowires were synthesized by chemical polymerization inside SiO_2 coated alumina membranes. Temperature dependent electrical resistance studies established that the chemically synthesized nanowires were more ordered compared to electrochemically synthesized nanowires. We further demonstrated that gas sensors based on single polypyrrole nanowire exhibited good sensitivity towards ammonia, and provided a reliable detection at concentration as low as approximately 40 ppm.

Keywords: Polypyrrole, Nanowires, Electrical resistivity, Disorder, NH_3 gas sensing

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1. Introduction

Over the last few decades, conducting polymers have come a long way from being a new class of materials with interesting electron-transport behavior to a material with immense potential in technological applications. Their ease of processing together with their chemically tunable properties makes them especially useful in electronic, optoelectronic and electromechanical devices. One such area where the conducting polymers have shown great promise is in sensory applications [1–4]. Delocalized electronic states combined with the restriction on the extent of delocalization leads to the formation of a large energy gap making most conductive polymers behave like p-type semiconductors. The fact that these polymers are redox-active, allows one to alter its conductivity by altering the electron count on the backbone by means of doping/dedoping, interactions of ions, functional groups, lone pairs, or charge transfer between polar molecules. A great deal of sensing applications is designed by exploiting the very nature of conducting polymers. The interaction of volatile components, gases, and liquids with conductive polymer films have shown to produce changes in color, mass, work function or electrical conductivity of the polymer, analyzable by photoluminescence, photocurrent, surface acoustic wave, quartz microbalance, conductometric, voltammetric or potentiometric measurements [5–11]. Past research work has focused on using conducting polymer, polypyrrole in particular, thin film based conductometric sensors for detection of volatile organic components (VOC), where it was shown that the polypyrrole thin film sensors were sensitive with good response to VOC showing larger responses to polar than nonpolar compounds [12].

Reliable sensing of ammonia (NH_3) is required in several situations like detecting leaks in air for environmental analysis [13], explosives and fertilizer industries [14], compressor of air-conditioners [15], breath analysis for medical diagnoses [16], and animal housing [17]. Further, its high toxicity also warrants a rapid detection at very low concentrations. However, one of the serious bottlenecks in using conducting polymers for sensing lies with the poor diffusion of the analyte molecules to the bulk of the polymer, thereby reducing the entire response to a surface effect. To alleviate this problem and increase the sensitivity of the device, several approaches have been taken to increase the effective surface area of the polymer. These involve using monolayer thin films, [18] coating polymers on porous substrates, [19] and synthesis of nanostructured conducting polymers [20]. However, to further improve the sensitivity, there is an obvious need to develop sensors based on single polymer nanowires. While several groups have demonstrated the enhanced sensitivity of conducting polymer nanowires, [21] there have been very few reports on developing single nanowire sensors [22]. In this work we report an ammonia sensor based on single nanowire of highly conducting polypyrrole. Being one of the most stable conducting polymers under ambient conditions, we selected polypyrrole for our studies.

2. Experimental**2.1. Materials**

Alumina membranes of 200 nm nominal pore size and 60 μm thickness were purchased from Whatman International Ltd (Maidstone, England). Pyrrole was obtained from

Sigma-Aldrich (St. Louis, MO, USA) and tetraethylorthosilicate was purchased from Gelest Inc. (Mossisville, PA, USA). Hydrofluoric acid, ferric chloride, hydrochloric acid, ethanol and sodium acetate were purchased from Fisher Scientific (Fair Lawn, New Jersey, USA). All reagents were analytical grade and solutions were prepared in double distilled deionized water.

2.2. Apparatus and Procedure

2.2.1. Polypyrrole Nanowire Fabrication

Alumina membranes, used as template for nanowires growth, were heated overnight at 150 °C (the polymer ring on the circumference of the membranes were removed prior to heating) in an oven (Model 281A, Fisher Scientific, Tustin, CA) to avoid swelling of templates and thus maintaining pore diameter through out the process. 5 mL of tetraethylorthosilicate (TEOS), 50 mL of ethyl alcohol (EtOH), and 1 mL of 1 M hydrochloric acid (HCl) were mixed for 5 min and left to sit for 1 h to stabilize. Alumina membranes were individually placed in the TEOS solution for 1 min and then sonicated for an additional min. Following sonication, the templates were pat dried with tissue paper (Kimwipes, Kimberly-Clark, Roswell, GA), washed with EtOH, air dried for 2 h and incubated in an oven overnight at 150 °C. The templates were then immersed in a freshly prepared and cooled (on ice for 30 min prior to use) 0.2 M pyrrole solution in 0.2 M sodium acetate followed by addition of an equal volume of cold 0.2 M ferric chloride solution in deionized water. The resulting mixture was placed on ice for 1 h followed by 24 h of incubation at 4 °C. Subsequently, the content was sonicated to release membranes from the container walls followed by rinsing with deionized water aided with sonication for five times. Polypyrrole embedded alumina membranes were then placed in a 10% (v/v) hydrofluoric acid (HF) over night to dissolve the template to release the nanowires. HF was removed by washing the nanowires with nanopure water until neutral pH was observed. This was followed by rinsing the nanowires with EtOH. The EtOH was then evaporated under vacuum to obtain dried nanowires.

2.2.2. Characterization of Nanowires

2.2.2.1. Morphology and Crystal Structure

X-ray diffraction patterns were obtained by using the dried post-ethanol rinsed polypyrrole nanowires on an evaporated gold substrate with Cu K α radiation and a scanning range of 10 to 80° with 0.1° increments (Bruker AXS Baltic Scientific Instruments D8 Advance). Nanowires were then imaged by scanning electron microscopy (SEM, Leo SUPRA 55, Model 1550).

2.2.2.2. Electrical Properties

A dilute solution of dispersed polypyrrole nanowires was made by suspending ca. 0.1 mg of dry nanowires in 1 mL of

ethanol and sonicating the mixture until contents were fully dispersed. A 5 μ L drop of well suspended nanowires was dispersed across microfabricated gold electrodes on SiO $_2$ /Si substrate and a flow of nitrogen gas was passed over the electrode (parallel to the chip) until the ethanol evaporated. The nitrogen gas provided a preferred orientation for nanowire alignment. Optical microscopy (Hirox HI-Scope Advanced KH-3000, River Edge, NJ, USA) was used for visual verification of single nanowire bridging two gold electrodes. A two point probes method was used to measure *I*–*V* characteristics for the nanowires bridging the two electrodes via sweeping the potential between –1 V to +1 V DC. Temperature dependent electrical resistance of nanowires was measured between 8 and 300 K with a physical property measurement system (PPMS) from Quantum Design (San Diego, CA, USA) in combination with the semiconductor parameter analyzer (Hewlett Packard Model 4155A, Austin, TX, USA) to obtain the *I*–*V* characteristics at each set temperature.

2.2.3. Gas Sensing

For gas sensing studies, electrodes with an aligned PPy nanowire were connected to a chip holder by wire bonding (West Bond Inc. Model 7443A, Anaheim, CA, USA). Subsequently, single nanowire PPy sensor was connected in series with a load resistance of comparable value to the resistance of the nanowire sensor in order to optimize resolution [22]. The sensor arrangement was subjected to 0.5 V DC potential and the current was continuously monitored with sample rate of one sample per second. Electrical resistance of the sensor was determined by continuous monitoring the voltage over the load resistor and applying Ohm's Law. A 1.3 cm 3 glass chamber with inlet and outlet ports was positioned over the microfabricated chip with a sandwiched O-ring and sealed by using a clamp. Gas at 150 std. cm 3 min $^{-1}$ flowed through the glass chamber. Argon (purity: 99.998%) and ammonia (purity: 99.99%) were used as the carrier and analyte gases, respectively (Airgas Inc., Riverside, CA, USA). The carrier gas was diluted with the analyte gas to obtain different ammonia concentrations. Analyte and carrier gas flow rates were regulated by mass flow controllers (Alicat Scientific Incorporated, Tucson, AZ). A custom LabView computer program was developed to control and monitor the voltage of the nanowire circuit using a Field Point analog module from National Instruments (Austin, TX, USA) [23].

3. Results And Discussion

3.1. Synthesis and Characterization

Figure 1 shows the schematic of the strategy employed for synthesizing polypyrrole nanowires. The technique employed in this work is slightly modified from that reported previously using porous alumina templates [24]. In the present work, instead of growing the nanowires inside as-is

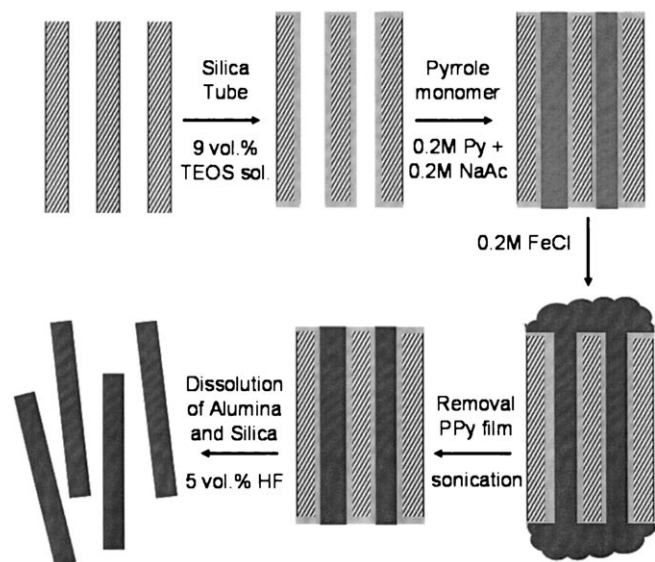


Fig. 1. Schematic of polypyrrole nanowires synthesis.

alumina membrane pores a thin layer of SiO_2 was first deposited on the inner walls of the alumina pores. This was followed by the chemical polymerization of pyrrole using FeCl_3 as the oxidizing agent. The average diameter of the polypyrrole nanowires was ca. 300 nm (Fig. 2B), which was larger than the manufacturer reported average pore diameter (200 nm) for the membrane. As evident in SEM images (Fig. 2), the surface of nanowires made using SiO_2 modified pores were smoother compared to unmodified pores. The smoother surface morphology in the SiO_2 coated pores can be attributed to the anionic sites on silica that act as molecular anchor to nascent cationic monomer providing preferential nucleation for polypyrrole along the pore walls and producing a continuous coating. The rough and irregular blob morphology obtained from unmodified pore was in accordance with the literature report and is hypothesized to the absence of molecular anchors on the alumina pores causing nucleation to happen at random positions within the

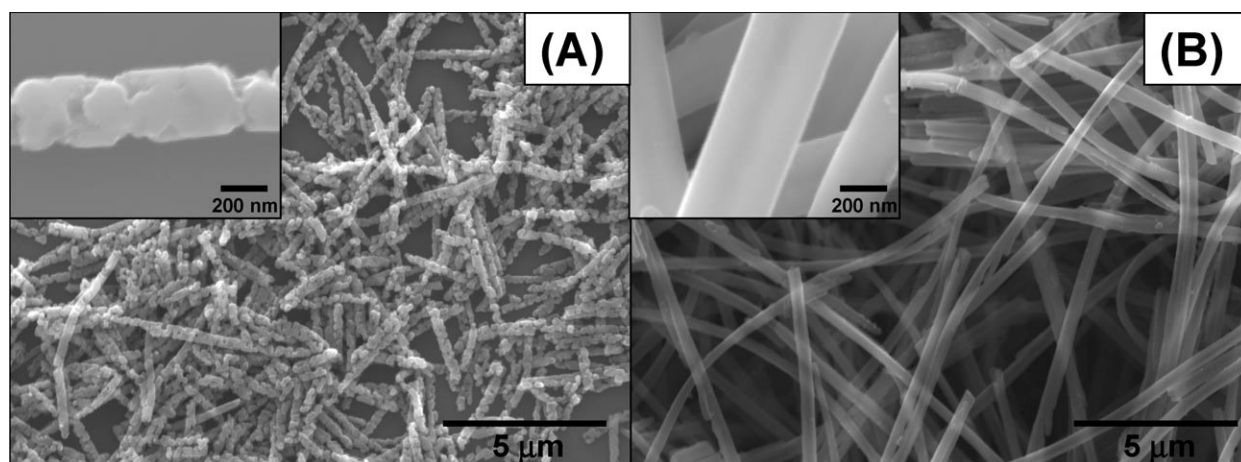


Fig. 2. Scanning electron micrographs of polypyrrole nanowires synthesized A) inside as obtained, unmodified alumina templates and B) inside alumina templates modified with an inner layer of silica.

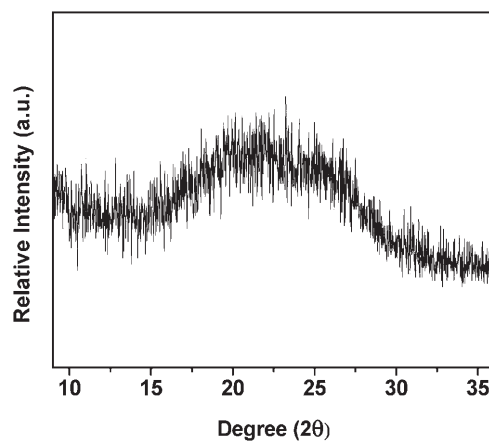


Fig. 3. X-ray diffraction pattern of polypyrrole nanowires.

pores as opposed to along the walls in case of silica coated pores [24].

The XRD pattern reveals that the resulting polypyrrole nanowires were amorphous (Fig. 3) showing a broad band in the region of $15^\circ < 2\theta < 30^\circ$ indicating that short-range chain arrangement dominates as has been similarly observed for electrochemically synthesized polypyrrole nanowires [25].

3.2. Electrical Characteristics

To be used as a conductometric gas sensor, the nanowire should be semiconducting and have good quality, i.e. low degree of disorder. Figure 4a shows the $I-V$ characteristic of a single polypyrrole nanowire as a function of temperature. The inset shows the corresponding SEM micrograph of the nanowire bridging the gold electrodes. The current-voltage plot is fairly linear about the 0 V bias, revealing an ohmic contact between nanowire and electrodes. A decreasing current response upon lowering the temperature is indicative of the inherent semiconducting nature of these

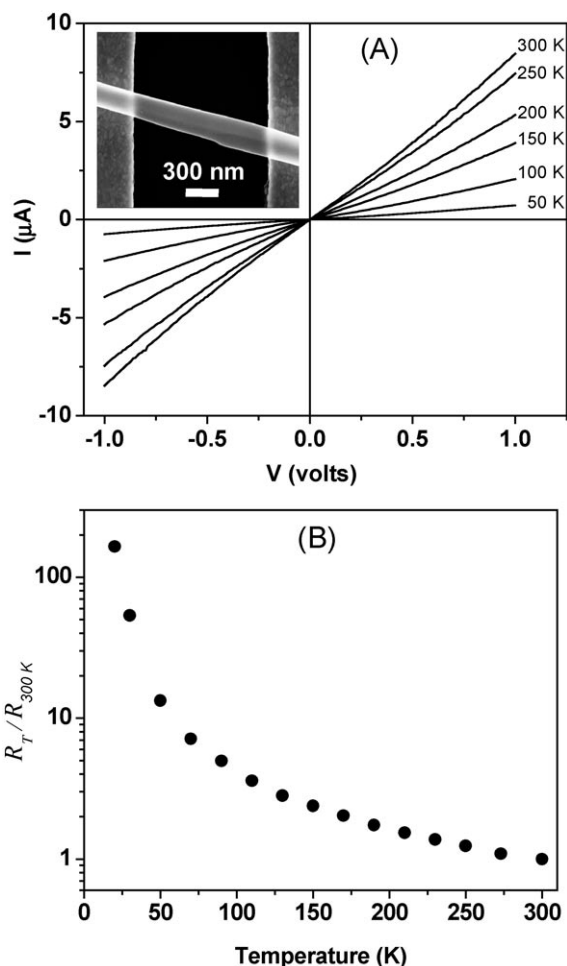


Fig. 4. A) Temperature dependent I - V characteristics of a single polypyrrole nanowire. The inset shows the SEM image of a single nanowire bridging across the gold microelectrodes. B) Low temperature to room temperature resistance ratio $R(T)/R(300\text{K})$, as a function of temperature.

nanowires. The room temperature conductivity estimated from the ohmic part of the I - V curve (between -0.1 to 0.1 V) was determined to be 5.1 S cm^{-1} . This is in good agreement with previously reported value for chemically synthesized polypyrrole [26].

To further corroborate the fact that the polypyrrole nanowires are of superior quality, effect of temperature on the single nanowire resistance was analyzed between 8 and 300 K. As shown in Figure 4B, over this temperature range the resistance of the nanowires increased with decreasing temperature. This is a typical behavior for doped semiconducting materials and is in accordance with the observations for electrochemically and chemically synthesized polypyrrole nanowires within pores of alumina and polycarbonate membranes [24, 27]. The degree of disorder in a sample is another parameter for the evaluation of the nanowires quality. It is well known that the rate of increase in resistivity at lower temperatures is higher in the case of disordered samples [28]. Therefore, by monitoring the ratio of low temperature to room temperature resistivity, it is

possible to obtain an indication of the degree of disorder in the sample. The ratio of the conductivity between 75 and 300 K for single nanowire synthesized in this work was found to be ca. 7. In comparison, the electrochemically synthesized chloride doped single polypyrrole nanowire exhibited a conductivity ratio of ca. 15, suggesting that the nanowires synthesized in the present work are much ordered. The difference in the degree of disorder is also reflected in the corresponding activation energies calculated by fitting the high temperature (100–300 K) resistivity data of the two samples to Arrhenius behavior, as per the following equation,

$$\rho = \rho_0 \exp(E_a/kT)$$

The activation energies (E_a) for single polypyrrole nanowire synthesized by chemical (present study), and electrochemical [28] polymerization were 19.4 and 25.9 eV, respectively.

3.3. Gas Sensing

Conductometric sensing of ammonia was carried out with a single polypyrrole nanowire and the results are presented in Figure 5. Argon was chosen as the carrier gas in order to achieve a faster stabilization of the background signal. Ammonia concentration was varied from 40–300 ppm by diluting ammonia gas with argon. After each exposure, the sensor resistance was recovered by purging with argon. The time required for a stable base line to be obtained upon the first imposition of the bias potential was 30 minutes (data not shown). The recovery time, defined as time required for the resistance to return to the original value upon switching to 100% carrier gas, was ca. 15 min. It is important to note that although the recovery was near-complete for lower concentrations, it was not the case at higher concentrations, thereby suggesting some irreversible binding between polypyrrole and NH_3 . This observation is consistent with previous studies on polypyrrole-based ammonia sensors [21], and the mechanism has been explained in terms of an irreversible electron transfer from ammonia to the doped polymer [29]. The response time, defined as the time to reach 90% of the total resistance change, of the sensor was found to be 15 min and 10 min, for the lower and higher ammonia concentrations, respectively. The slower response and recovery times in our samples could be due to the fact that the nanowire has very smooth surface morphology. Smoother surface morphology translates to less surface area for ammonia to diffuse into.

The sensitivity, determined from the slope of the linear range, was determined to be 0.06% per ppm of ammonia in the concentration range of 40–300 ppm (correlation coefficient, $r^2 = 0.9827$). The lower detection limit of the single polypyrrole nanowires sensor was 40 ppm, which is close to the recommended threshold limit value for human exposure (25 ppm) [30]. The sensitivity and lower detection limit of the sensor can be improved by operating the sensor in a field effect transistor mode with a back gate and changing the

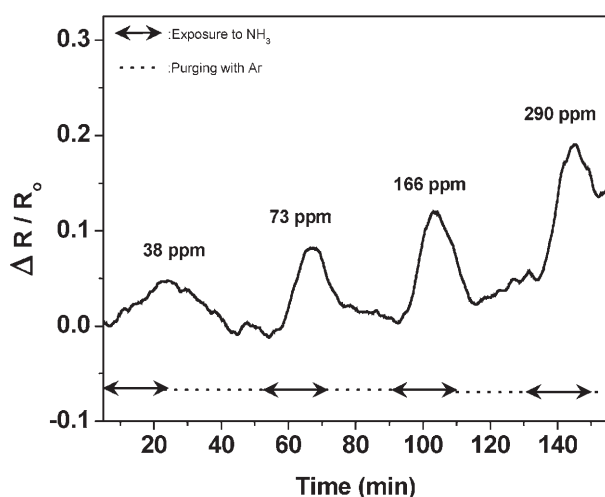


Fig. 5. Conductometric response of a single polypyrrole nanowire to ammonia at an applied DC bias of 0.5 V. Arrows indicate a 15 minute exposure time.

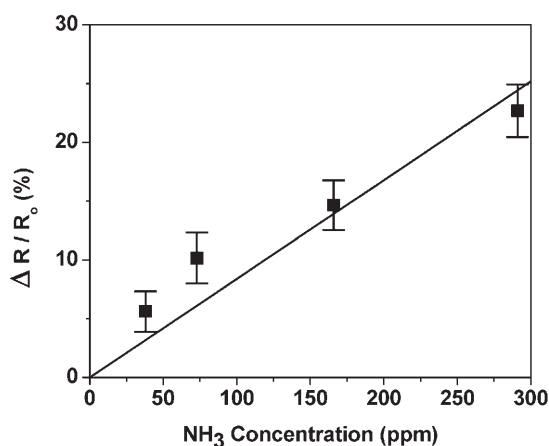


Fig. 6. Calibration for ammonia of a single polypyrrole nanowire using a two electrode configuration at an applied DC bias of 0.5 V. The error bars show the standard deviation from the average values ($n = 5$).

dopant to one that can promote enhanced changes in current due to the dual interaction of the dopant with the hydrocarbon chain and charged analyte.

The sensor exhibited an excellent selectivity towards ammonia with no detectable response to nitric dioxide (NO_2) even at concentration as high as 100 ppm. The absence of response to NO_2 is attributed to the highly doped state of the polypyrrole and therefore the inability for an electron acceptor like NO_2 to extract further electrons from the backbone. Polypyrrole-based gas sensors are reported to be sensitive to humidity with as much as 75% decrease in response resulting from a 5% increase in relative humidity [31]. The problem of humidity can be resolved by passing the sample through a desiccant before analyzing or replacing the chloride with a more hydrophobic dopant such as *p*-toluene sulfonate.

4. Conclusions

To conclude, high quality polypyrrole nanowires were prepared by template directed chemical synthesis. Temperature dependent electrical transport measurements showed the sample to be semiconducting with low degree of disorder. Single nanowires-based sensors showed good limit of detection and sensitivity and excellent selectivity for gaseous ammonia.

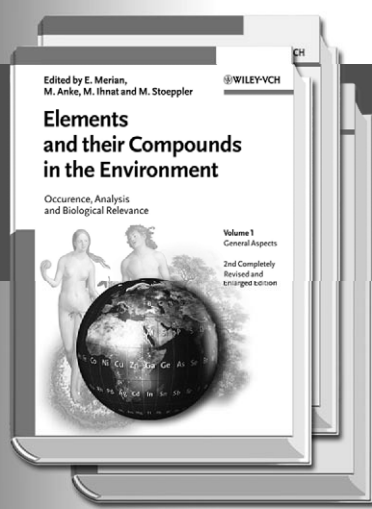
5. Acknowledgements

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