Doped and Dedoped Polyaniline Nanofiber Based Conductometric Hydrogen Gas Sensors

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Abstract: Template-free, rapid polymerisation was employed to synthesize polyaniline nanofibers using chemical oxidative polymerisation of aniline, with HCl as a dopant. The doped and dedoped nanofibers were deposited onto conductometric sapphire transducers for gas sensing applications. The sensors were exposed to various concentrations of hydrogen (H_2) gas at room temperature. The sensitivity was measured to be 1.11 for doped and 1.07 for dedoped polyaniline nanofiber sensors upon exposure to 1% H_2. Fast response times of 28 seconds and 32 seconds were observed for dedoped and doped sensors respectively. The dedoped nanofiber sensor outperforms the doped sensor in terms of baseline stability and repeatability. Due to its room temperature operation, the gas sensor is promising for environmental applications.

Keyword: Polyaniline; Nanofiber; Conductometric; Gas Sensor; Hydrogen

1. Introduction

Conducting polymers are of increasing importance in the development of smart sensors due to their room temperature operation, low fabrication cost, ease of deposition onto a wide variety of substrates [1][2] and their rich structural modification chemistry [3]. Polyaniline is unique among the family of conducting polymers since its doping level can be controlled through a non-redox acid doping/ base dedoping process [4]. By changing the doping level, conductivity of polyaniline can be modified to suit specific applications. Polyaniline in the emeraldine oxidation state can be reversibly switched between electrically insulating emeraldine base and conducting emeraldine salt forms. Polyemeraldine (Fig. 1: top) consists of amine (-NH-) and imine (=N-) sites in equal proportions. The imine sites can be protonated to achieve the intermediate bipolaron form (Fig. 1: middle) and finally by dissociation the polaron lattice form (Fig. 1: bottom), resulting in high conductivity [5]. It is widely agreed that polarons are the charge carriers responsible for the high conductivity of polyaniline. By controlling the pH of the dopant acid solution any desired quantity of dopant can be added until all imine nitrogen atoms are doped. The dopant can be removed by a reversible reaction with any strong base such as ammonium hydroxide (NH_4OH).

The conductivity of polyaniline depends on both the oxidation state of the main polymer chain and the degree of protonation on imine sites [6]. Any interaction with polyaniline that alters either of these processes will affect its conductivity. Unlike acids and bases, redox active chemicals and gases can change the conductivity of polyaniline by changing its inherent oxidation state.

Depending on the extent of the redox reaction, polyaniline can exist in a range of oxidation states: fully reduced leucoemeraldine, half oxidized emeraldine and fully oxidized pernigraniline. The emeraldine form of polyaniline shows the highest electrical conductivity after it had been doped with protonic acid [8]. Neutral, non-redox organic compounds, such as chloroform or toluene, are able to change the conductance of doped polyaniline films through swelling effects [9]. Functional additives incorporated into the polyaniline structural matrix, such as metals, metal oxides and enzymes can change the electrical characteristics of polyaniline. This versatility has made polyaniline attractive for a broad scope of design and development of smart sensors [10].

Recently, nanostructured materials, in the form of nanowires, nanotubes, nanofibers or nanobelts have received much attention. These one-dimentional materials process extremely high surface area without increasing the device dimension. Therefore, they should have improved performance in applications where a high surface contact area is needed between the device and its environment, such as in sensors [11-12]. Polyaniline nanofibers which have a cylindrical morphology form porous structures when deposited as thin films. Polyaniline nanofibers, with diameters in the nanometer range, possess larger surface areas per unit mass and permit easier addition of surface functionalities compared with traditional polyaniline which is highly agglomerated [13]. The three-dimensional porous structure of a polyaniline nanofiber film allows easy diffusion of gas molecules into and out of the film and the nano-scale fiber diameters lead to rapid diffusion of gas molecules into the polyaniline [14]. As a result, polyaniline nanofiber based sensors outperform conventional polyaniline thin film sensors in terms of sensitivity and dynamic performances upon exposure to a number of gases [11-12].

The sensitivity of conventional polyaniline thin film gas sensors depends on the film thickness [15]. Generally, sensor sensitivity increases with a reduction of film thickness as entire thickness of the film is affected by the reactions with gas species in a short period of time. On the other hand, sensitivity of a polyaniline nanofiber sensor is independent of film thickness, due to the porous structure of the film which leads to the predominance of surface phenomena over the bulk material phenomena. This advantage allows the fabrication of sensors with reproducible response that have a large tolerance in thickness variation [11].

Although nanostructured conducting polymers are very promising for sensors, there are few reports of them in the literature. Recently, we have reported [7] a surface acoustic wave based polyaniline nanofiber hydrogen sensor. To the best of our knowledge, polyaniline nanofibers have not yet been used as a conductometric sensor for hydrogen gas sensing. In this paper, we will present and compare the responses of doped and dedoped polyaniline nanofiber based conductometric H_2 gas sensors.

2. Experimental

The classical methods of synthesizing polyaniline nanostructures usually require structure-directing templates, such as zeolite channels [16], nanoporous membranes **Error! Reference source not found.**, or surfactants [17]. Complex synthesis conditions require removal of these templates at the end of the reaction, resulting in very low production rate. Recently, template-free, interfacial polymerisation was employed to synthesize polyaniline nanofibers using chemical oxidative polymerisation of aniline [19][20]. The polymerisation is performed in an aqueous solution where aniline is rapidly

polymerised in 1M acid by the quick addition of the oxidant. Due to the immediate interaction between the monomer and the oxidant, the primary reaction product, nanofibers, is the main morphology present. After completion of the reaction, the product is collected for purification. Washing or dialyzing with water gives pure HCl doped polyaniline nanofibers. The dedoped solution was prepared by washing or dializing doped solution with ammonia.

Hydrogen gas sensors were designed and fabricated to operate as a resistive element. They are made up of two important physical components: the sensitive polyaniline nanofiber layer, which interacts with the gas media and the transducer, which converts the chemical signal to an electrical signal. Platinum (Pt) sputtered inter digital electrodes and heater were fabricated on 3x3 mm^2 sapphire substrate to form a transducer. Doped and dedoped polyaniline nanofiber dispersions were drop cast onto the electrodes of two separate transducers. They were then left to dry in a clean, dry environment for one day. The electrodes are used directly to measure the resistance of the sensitive polyaniline nanofiber layer upon exposure to the H_2 gas. Two types of sensors were created: one with doped and the other with dedoped polyaniline nanofiber sensitive layer.

The sensors were mounted inside an enclosed environmental cell (Fig. 2). Four mass flow controllers (MFC) were connected to form a single output that supplied gas to the cell. The gas mixture was delivered at a constant flow rate of 0.2 liters per minute. A computerized gas calibration system was used to vary the concentration of H_2 gas in synthetic air. The sensors were exposed to a H_2 gas pulse sequence of 0.06%, 0.12%, 0.25%, 0.50%, 1%, and 0.12% in synthetic air at room temperature. Gas exposure time

was three minutes for each pulse of H_2 gas and the cell was purged with synthetic air for seven minutes between each pulse to allow the surface of the sensor to regain atmospheric conditions. A Keithley 2001 multimeter was used to measure the variation of sensor resistance.

3.   Results & Discussion

A Scanning Electron Microscope (SEM) image of the polyaniline nanostructures on the sapphire substrate is shown in Fig. 3. The SEM result indicates that the polyaniline layer deposited on the sapphire substrate consists of nanofibers. The average diameter of the both doped and dedoped polyaniline nanofibers is about 50 nm with a length of several microns. The average thickness measured for both of the thin films on sapphire substrate using a profilometer is 0.3 µm, and the deviation in thickness across the active area of the sensors is 0.05 µm.

Dynamic responses of the dedoped and doped polyaniline nanofiber sensors to H_2 gas at room temperature are shown in Fig. 4 and 5, respectively. It was observed that the conductivity of both doped and dedoped sensitive layers increase after exposure to H_2 gas. It is also observed that at high concentrations of H_2 (0.25%, 0.5% and 1%), fast conductivity increase followed by a slow decrease of the conductivity for both of the sensors. The observations indicate that either more than one type of reaction site is available or that a number of different reactions are possible. The results prove that the sensors are useful for detecting a low concentration range of H_2.

Although, the hydrogen storage properties of conducting polymers are being actively studied, the mechanism for polymer and hydrogen interactions is still not fully

understood. Cho et al. [21] believed 6-8% (wt) hydrogen storage in HCl doped polyaniline and polypyrrole at room temperature. The authors attributed this unusual phenomenon to the combined effects of the molecular sieving and metallic properties of the conducting polymer. This result could not be reproduce by Panella et al. [22] experiments and Huang et al. [23] observed a much lower hydrogen storage capacity of 1.44% (wt). The hydrogen may form a bridge between nitrogen atoms on two adjacent chains or there may be partial protonation of some imine nitrogen atoms [24]. These reactions lead to the protonation of polyaniline nitrogen atoms, resulting in more delocalized charge carriers (polarons and bipolarons) on the backbone for conduction and an increase of the film conductivity. It has also been suggested that the resistance change is caused by the formation of water [25]. The effects of water on the conductivity of polyaniline are well known [26,27] and have been established from nuclear magnetic resonance (NMR) spectroscopy studies that presence of water molecules in the polyaniline facilitates the charge transfer in the polyaniline backbone leading to an increase in polymer's conductivity. In the process of H_2 and polyaniline interaction, a proportion of the analyte is probably catalytically oxidized forming water, which decreases the resistance of the both doped and dedoped polyaniline. The sensitivity of the sensors is defined as: $S = R_{air}/R_{gas}$, where R_{air} is the resistance of the sensor in air, R_{gas} is the resistance of the sensor in presence of gas. The sensitivity of the sensors was calculated to be 1.11 for doped and 1.07 for dedoped polyaniline nanofiber sensors upon exposure to 1% of H_2 at room temperature. Fast response times of 32 seconds and 28 seconds were observed towards 1% H_2 for doped and dedoped sensors, respectively. Two significant observations were obtained from the tests. Firstly, the response curves show that the

doped polyaniline nanofiber sensor is more sensitive than the dedoped sensor (Fig. 6). Secondly, the baseline of the dedoped nanofiber sensor was more stable than the doped sensor. Additionally, the dedoped nanofiber sensor has better repeatability than the doped sensor. Repeatability and stability of the sensors were confirmed by testing the sensors continuously over a 7 day period. It is believed volatility of dopant acid HCl is responsible for instability of doped sensor.

4. Conclusion

Conductometric H_2 gas sensors based on doped and dedoped polyaniline nanofibers were developed. The sensors were investigated for concentrations of H_2 gas in synthetic air. Both of the sensors showed high sensitivity and good repeatability. For dedoped polyaniline nanofiber sensor, a 17 kΩ resistance shift from 260 kΩ baseline, which is equivalent to a sensitivity of 1.07, was observed when exposed to 1% H_2 at room temperature. For similar conditions, the doped polyaniline nanofiber sensor exhibited a 120 Ω resistance shift from 1.26 kΩ baseline, which is equivalent to a sensitivity of 1.11.

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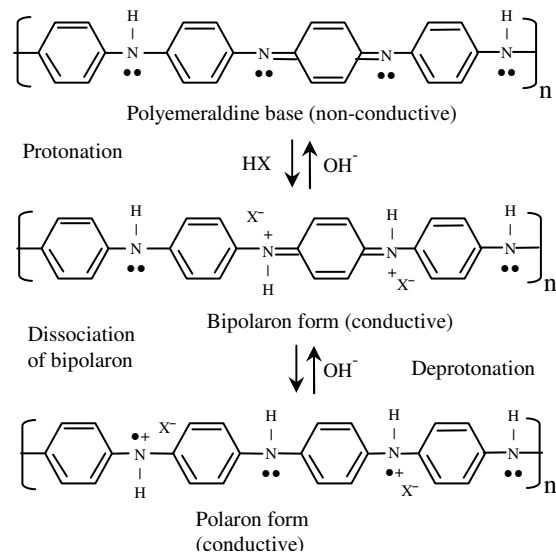
Figure 1. Polyemeraldine base form (top), intermediate bipolaron form (middle) and the fully doped acid form (bottom) [7].
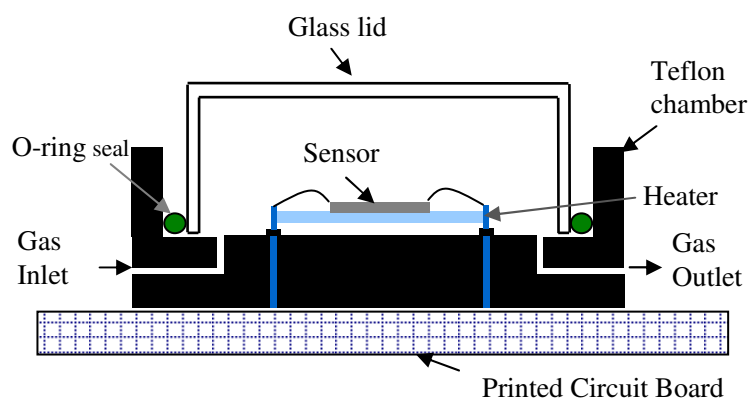

Figure 2. The experimental set-up for testing doped and dedoped polyaniline nanofiber sensor [7].
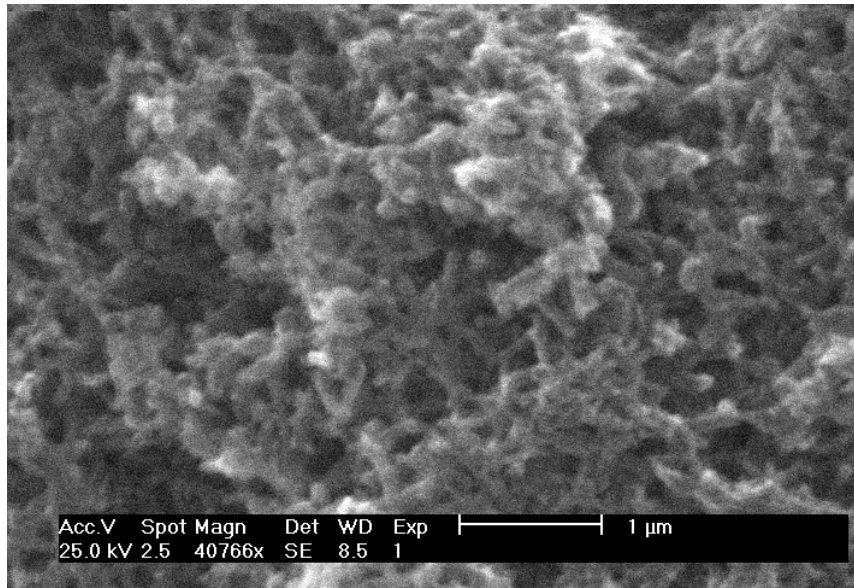
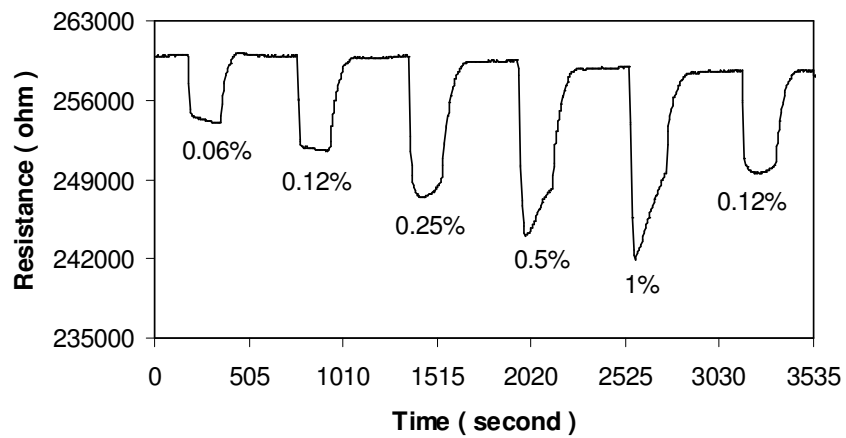Figure 3. SEM image of polyaniline nanofibers on the sapphire substrate.

Figure 4. Dynamic response of the dedoped polyaniline nanofiber based conductometric sensor to different H_2 gas concentrations in synthetic air.
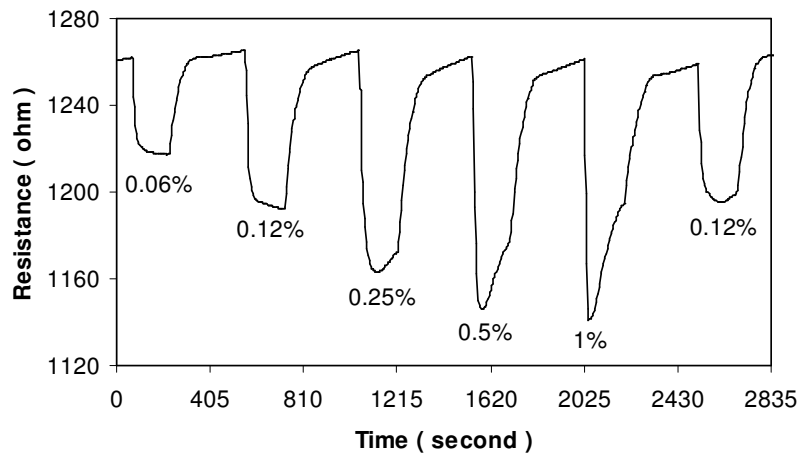
Figure 5. Dynamic response of the doped polyaniline nanofiber based conductometric sensor to different H_2 gas concentrations in synthetic air.
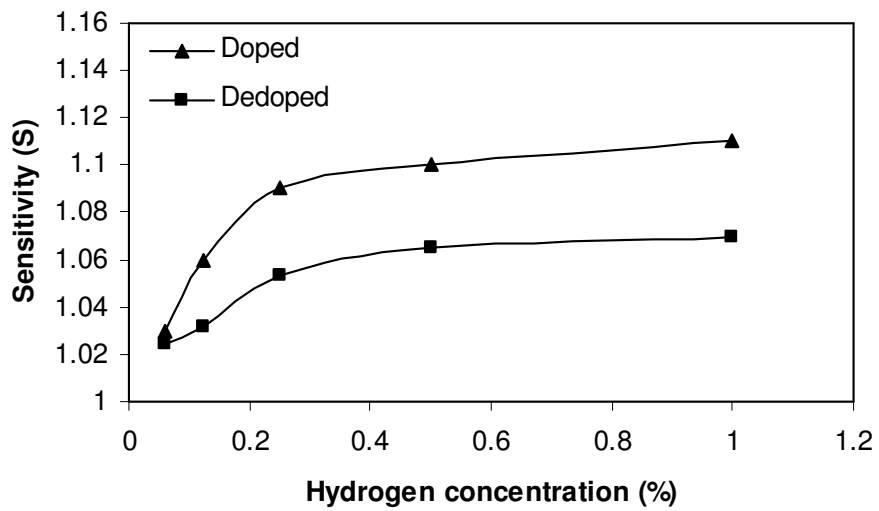

Figure 6. Sensitivity of doped and dedoped polyaniline nanofiber sensors towards different concentrations of H_2 in synthetic air.

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