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Camphor Sulfonic Acid Doped Polyaniline Nanofiber Based 64° YX LiNbO₃ SAW Hydrogen Gas Sensor

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ABSTRACT

A template-free, rapidly-mixed reaction was employed to synthesize polyaniline nanofibers using chemical oxidative polymerization of aniline. Camphor sulfonic acid (CSA) was used in the synthesis to obtain 50 nm average diameter polyaniline nanofibers. The nanofibers were deposited onto a 64° YX LiNbO₃ SAW transducer. The sensor was tested towards hydrogen (H₂) gas while operating at room temperature. A fast response and recovery with high sensitivity and good repeatability were observed.

Keywords: Polyaniline, Nanofiber, Hydrogen, Gas sensor

1. INTRODUCTION

Conducting polymers have received increasing interest for smart sensors due to their operation in room temperature, low production cost, ease of deposition onto a wide variety of substrates [1] and their rich chemistry for structural modifications [2]. Among the family of conducting polymers, polyaniline is the most highly studied material because of its simple synthesis, good stability and simple non-redox acid doping/base dedoping process to control conductivity [3]. By changing the doping level, the conductivity of polyaniline can be tuned for specific applications such as sensors, actuators, rechargeable battery electrodes, anticorrosion coatings, gas-separation membranes, display devices and field effect transistors [4].

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. Polyaniline in the emeraldine oxidation state can be reversibly switched between electrically insulating and conducting forms. The polyemeraldine form consists of amine (-NH-) and imine (=N-) sites in equal proportions. The imine sites are protonated in preference to achieve an intermediate bipolaron form (Fig. 1: middle) which further undergoes a dissociation to form delocalized polaron lattice (Fig. 1: bottom). A polaron can be considered a type of electronic defect that occurs within the π orbitals of the polymer backbone and is the charge carrier responsible for the high conductivity of doped polyaniline [5]. By controlling the pH of the dopant acid solution any desired quantity of dopants can be added until all imine nitrogens are doped. Dopants can be removed by a reversible reaction with any common base such as ammonium hydroxide.

The conductivity of polyaniline depends on both the degree of protonic acid doping of the imine sites and the redox states of the main polymer chain [3]. Any interaction with polyaniline that alters either of these processes will affect its conductivity. As a result, redox active gases can affect the conductivity of polyaniline by changing its inherent oxidation state.

Nanostructured polyaniline, in the form of nanofibers have received increasing attention for sensing applications due to their predominant surface phenomena over the bulk counterpart. Polyaniline nanofibers when used as a sensitive layer in gas sensors, can greatly improve carrier diffusion due to their high surface to volume ratio and large penetration depth for gas molecules [6].
Conventional polyaniline thin film sensors have a dependency on the deposited film thickness in their sensitivity [8]. Generally, sensor sensitivity increases with a reduction of film thickness. Probably due to porous nature of films, polyaniline nanofiber based sensor sensitivity is independent of layer thickness. This allows the fabrication of sensors with reproducible responses that have a large tolerance in thickness variation [6].

2. EXPERIMENTAL

The previous approaches for making polyaniline nanostructures usually require structure-directing templates which must be removed at the end of the reactions, resulting in low production rates. Recently, we have introduced template-free, rapidly mixed reaction approach to synthesize polyaniline nanofibers using chemical oxidative polymerization of aniline [9]. The polymerization is performed in an aqueous solution where aniline is rapidly polymerized in 1M CSA acid by the quick addition of the oxidant (ammonium peroxydisulfate ((NH₄)₂S₂O₈)). Due to the immediate interaction between the monomer and the oxidant, the primary reaction product, nanofibers, is the main morphological component present. After completion of the reaction, the product is collected for purification. Washing or dialyzing with water gives pure doped polyaniline. The average diameter of the polyaniline nanofibers is about 50 nm with length up to several microns. A transmission electron microscope (TEM) image in Fig. 2 reveals that the polyaniline nanofiber layer consists of a large...
quantity of fiber-like nanostructures. Nanofiber dispersions were drop cast onto the active area of the 64° YX LiNbO₃ SAW transducer using a micro pipette. They were then left to dry in a clean, dry environment for one day.

The sensor was mounted inside an enclosed environmental cell. The four mass flow controllers (MFCs) were connected to form a single output that supplied gas to the cell. A constant flow rate of 0.2 liters per minute was delivered via the MFCs. A computerized gas calibration system was used to vary the concentration of H₂ gas in synthetic air and to measure the operating frequency of the sensors. The sensor responses were displayed in real-time and saved for off-line processing and analysis. Gas exposure time was fixed for each pulse of H₂ gas and the cell was purged with synthetic air between each pulse to allow the surface of the sensor to recover to atmospheric conditions. The sensor was exposed to a hydrogen gas pulse sequence of 0.06%, 0.12%, 0.25%, 0.50%, 1%, and 0.12% concentrations in synthetic air at room temperature. A Fluke high-resolution counter (PM66860B) was used to measure the operational frequency.

![TEM image of CSA doped polyaniline nanofibers.](image)

**3. RESULTS**

The sensor was placed in a multi-channel gas calibration system and exposed to H₂ gas. Dynamic response to a sequence of different H₂ gas concentrations in synthetic air is shown in Fig. 3. It was observed that the resonant frequency of the sensor decreases with the H₂ exposure. It proves that the conductivity of polyaniline nanofiber layer increase resulted in a decrease in acoustic wave velocity, thereby decreasing the resonant frequency. The hydrogen sensing mechanism is still not fully understood. The hydrogen may form a bridge between nitrogen atoms on two adjacent chains or there may be partial protonation of some imine nitrogen atoms [10]. The sensor response, defined as the variation in operating frequency of oscillation due to the introduction of the gas, was 79 kHz towards 1% of H₂ in synthetic air. A fast response of 1 min and a recovery of 5 min with good repeatability were observed at room temperature. Fig. 4 shows the frequency shift vs H₂ concentration.

Reproducibility was observed as indicated when a second pulse of 0.12% of H₂ was introduced into the sensor chamber. It was found that the polyaniline nanofiber composite based sensor produce repeatable responses of the same magnitude with good baseline stability. Repeatability was confirmed by testing the sensor continuously over a 5 day period.
Fig. 3. Dynamic response of a polyaniline nanofiber based 64° YX LiNbO₃ SAW sensor towards H₂ at room temperature.

Fig. 4. Frequency shift (kHz) versus H₂ gas concentration (%) at room temperature.

**4. CONCLUSION**

We have fabricated SAW gas sensor based on CSA doped polyaniline nanofiber composite synthesized by chemical oxidative polymerization. The sensor has been investigated towards H₂ gas. The sensor showed a repeatable and large response towards H₂ gas. A fast response and recovery time with stable base-line frequency was observed at room temperature. Due to room temperature operation, the gas sensor is promising for environmental and industrial applications.
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