CONDUCTOMETRIC H$_2$ GAS SENSOR WITH DOPED AND DEDOPED ELECTROPOLYMERIZED POLYANILINE NANOSTRUCTURES

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Abstract. In this work, the structural and gas sensing properties of polyaniline nanostructures deposited on 36° lithium tantalite (LiTaO$_3$) conductometric transducers was investigated. The polyaniline nanostructures were synthesized via an electropolymerization method. The morphology of the nanostructured polyaniline was characterized using Scanning Electron Microscopy (SEM). It was observed that the electropolymerised film was a three-dimensional (3D) porous structure of polyaniline fibers and nanotips. The conductometric sensors were exposed to different concentrations of hydrogen (H$_2$) gas at room temperature.

Keywords: H$_2$ sensor; polyaniline; nanostructures; electropolymerization; doped and dedoped

Abstrak. Dalam kertas kerja ini, struktur dan prestasi pengesanan gas oleh polianilin yang berskala nano yang dimendap di atas transduser lithium tantalate. Polimer berkonduksi ini disintesiskan melalui teknik *electropolymerization*. Struktur permukaan polianilin dicirikan dengan menggunakan Mikroskop Pengesan Elektron (Scanning Electron Microscopy). Didapati bahawa polianiline yang terhasil dipermukaan transducer adalah 3-dimensi struktur dan poros. Pengesan ini kemudian disiasat prestasinya terhadap konsentrasi gas yang berbeza dan berada dalam keadaan suhu bilik.

Kata kunci: Pengesan H$_2$; polianilin, berskala nano; *electropolymerization*; dop dan nyah-dop

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1.0   INTRODUCTION

Hydrogen (H$_2$), a colourless and odourless gas has attracted a great deal of attention due to the fact that it can be used as a clean energy source when coupled with fuel cell technology. It is a highly flammable gas and will burn in air at concentrations as low as 4%. Furthermore, H$_2$ has a low ignition energy, posing significant risk to start a deflagration [1]. Recently, H$_2$ gas sensing based on conducting polymers have garnered great interest in the scientific community [2-4], despite the fact that they were discovered in 1977 [5]. H$_2$ sensors are important for application in aerospace, chemical refining and biomedical systems [6].

Polyaniline is one of the most attractive conducting polymers due to its facile synthesis, room temperature operation as a gas sensing material, availability of the inexpensive monomer, and its unique electrical properties. Polyaniline exists in three different oxidation states and can be reversibly switched between; fully oxidised pernigraniline, half-oxidised emeraldine and fully reduced leucoemeraldine. Emeraldine salt is the most conducting form of polyaniline [7]. It appears green in colour and has a characteristic absorbance at around 430 and 800 nm [8]. When the emeraldine salt is treated with a base (eg: NaOH), the colour changes from green to blue with characteristic absorbance peaks centered at 300 nm and 600 nm. This dedoped form of polyaniline has a lower electrical conductivity compared to the emeraldine salt, and it is known as emeraldine base. This emeraldine base can be converted back to salt form upon treatment with acid (eg.HCl) [7].

Nanostructured polyaniline possess large surface area per unit mass. These nano-scale structures permit easier addition of surface functionality and interaction compared to traditional polyaniline which is highly agglomerated. When deposited as a thin film, polyaniline nanostructures form porous structure, hence have higher surface to volume ratio [9] and larger penetration depth [10] than the traditional thin film polyaniline. There have been several reports on improving polyaniline based sensors sensitivity by depositing polyaniline nanostructured form as a sensing layer [4]. As a result, most literature reports on polyaniline nanostructures indicate that nanostructured outperforms conventional polyaniline for sensing applications [11-13]. Compared to the conventional polyaniline, the porous structure of polyaniline nanofibers film allows gas molecules diffused easily into and out of the film, therefore lead to rapid diffusion of gas molecules.

In depositing polyaniline nanofibers as a sensing layer, most researchers employed drop-casting method for polyaniline deposition on their devices. Except for electropolymerization method, others required separate polymerization (chemical polymerization) before being deposited onto the transducers. The synthesis of polyaniline via an electropolymerization technique [14, 15] is quite common, however the use of inter-digitated transducers (IDTs) as a working

electrodes is difficult to carry out.   In this research, the electropolymerization technique is the authors' interest in deposition of polyaniline nanofibers onto transducers. This method shows the ability to polymerize and deposit the polyaniline at the same time. Kalantar-zadeh *et al.* [16] have pioneered the deposition of polyaniline nanofibers on SAW device via this technique. They electropolymerized continuous films even in between electrodes and obtained a 6.2 kHz frequency shift when a polyaniline nanofibers based 64° YX LiNbO$_3$ SAW sensor was exposed to 0.125% H$_2$ gas. They observed that non-agglomerated, continuous and homogenous films could be obtained when the gaps on the working electrodes were smaller than several tens of microns. Then Arsat *et al.* [17] investigated the dedoped electropolymerized nanofibers and obtained a frequency shift of 9.2 kHz towards 1%Hz. In this work we employ the IDTs of conductometric transducer as the working electrode so that the polyaniline nanostructures deposited directly onto the transducer. The conductometric sensors were then exposed to various concentrations of H$_2$ gas at room temperature

2.0   EXPERIMENTAL

2.1   Conductometric Transducer

Transducers were fabricated on LiTaO$_3$ substrates and photolithograpic process were used to form 16 pairs of electrode structures. This conductometric transducer consists of electrodes with Ti and Au metallization layer film thicknesses of 20 nm and 80 nm, respectively. The aperture width of the transducer was 700 µm, whereas the finger width was 10 µm.

2.2   Electropolymerization

In this study, electropolymerization technique has been employed to fabricate polyaniline nanofibers on the surface of LiTaO$_3$ substrate. This deposition was conducted in agitated 1 M HCl electrolyte solution containing 0.3 M aniline monomer at room temperature. Platinum foil was employed as the counter electrode and the IDTs of the conductometric transducer were used as the working electrode. Two different voltages were applied during this deposition. A voltage of 0.75 V was supplied for the first 5 minutes before it was decreased to 0.65 V for the next 25 minutes. The sensor then was washed with de-ionized water and dried in a stream of N$_2$. Dedoping of the polymer was achieved by immersing

the conductometric sensor in diluted NaOH until the green colour of the as deposited polyaniline, turned Prussian-blue in color.

2.3   GAS TESTING

Gas testing of the conductometric device was carried out in gas testing chamber by exposing the sensor to H_2 at concentration ranging from 0.06% to 1% in a synthetic air balance. Testing was conducted before and after dedoping the conductometric device with diluted NaOH

3.0   RESULTS AND DISCUSSIONS

3.1   SEM

FE-SEM image in Figure 1 indicates that the electropolymerised polyaniline, comprises of dendritically interconnected fibers, with smaller nanotips growing away from the surface of the fiber (refer Figure 2). With the resultant structure forming a 3D porous network. The diameters of such fibers, are in a range between 150 nm to 350 nm, while the diameters of the nanotips are ~30-60 nm.
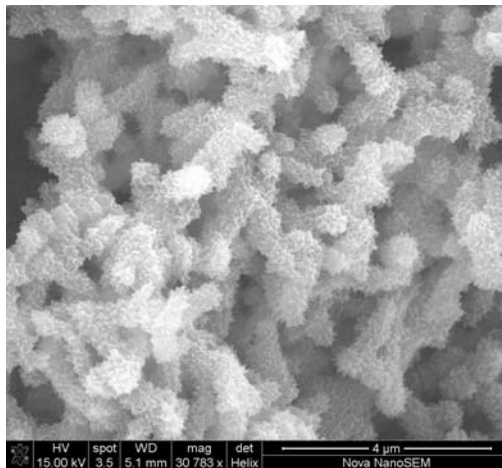

Figure 1   SEM image of electropolymerized polyaniline nanostructured on $LiTaO_3$
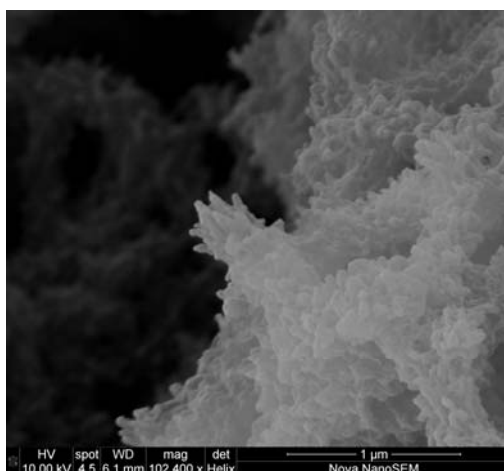
Figure 2   SEM image of nanotips grown away from the surface of the fiber

3.2 Gas Testing

The dynamic responses for doped and dedoped polyaniline nanofibers sensor towards different H$_2$ gas concentrations at room temperature are shown in Figure 3 and Figure 4, respectively. Both conductometric sensors were tested independently in a computerised multi-channel gas calibration system, ensuring repeatable and accurate results. This system was used to deliver five pulses of H$_2$ gas in synthetic air at a constant flow rate of 200 sccm. The synthetic air was used as a carrier gas and reference (baseline) gas. The H$_2$ gas concentration of each of the five pulses in the sequence was 0.06, 0.12, 0.25, 0.50 and 1.0%, with all experiments conducted at room temperature.
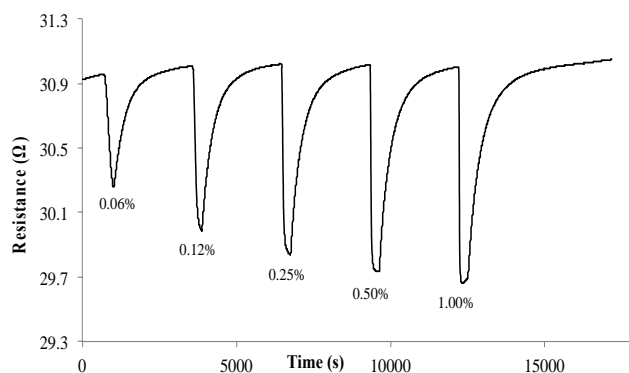

Figure 3 Dynamic response of doped polyaniline based conductometric sensors towards H$_2$ at room temperature
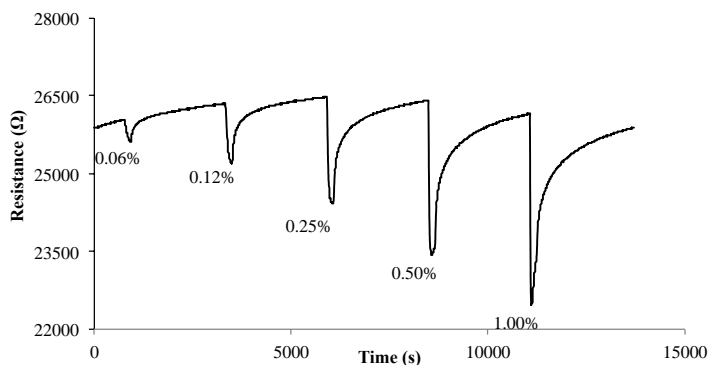
Figure 4 Dynamic response of dedoped polyaniline based conductometric sensors towards H_2 at
room temperature

Since H_2 is a reducing gas, the device sensitivity, denoted as S is the ratio of resistance for synthetic air (R_{air}) to the resistance of the test gas (R_{gas});

$$S_{reducing} = R_{air}/R_{gas}$$

The plotted graph in Figure 5 shows the devices' sensitivities of the electropolymerized doped and dedoped polyaniline nanofibers based conductometric sensors. From the plotted curves, the sensitivity of the doped and dedoped polyaniline nanofibers sensors was observed to be 1.04 and 1.16, respectively upon exposure to 1% of H_2 gas in synthetic air at room temperature.
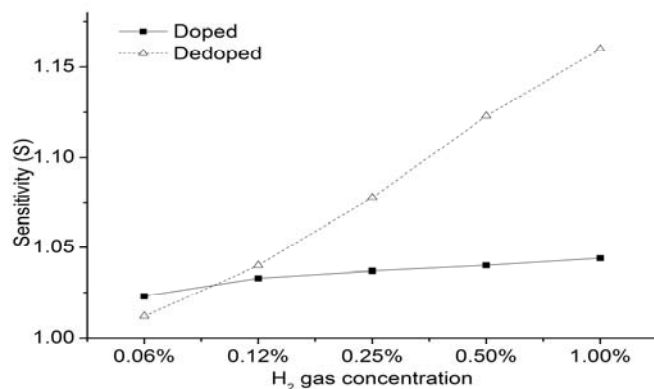

Figure 5 Sensitivity of doped and dedoped polyaniline nanofibers based sensors for different
concentrations of H_2 at room temperature

The graph in Figure 6 shows the comparison between response and recovery time for doped and dedoped conductometric sensors, demonstrating similar response times for both doped and dedoped conductometric sensors. Optimal responses of 36 s for 0.5% and 1% towards H$_2$ gas at room temperature was also observed for dedoped and doped devices, respectively. However, these conductometric sensors exhibit a slow recovery time. Doped conductometric sensors required approximately 4 minutes to fully recover to the original baseline after exposure to 1% H$_2$, while for the same concentration, dedoped conductometric required 38 minutes to recover. At elevated temperature, the probability of desorption increases [18]. Therefore, the slow recovery was expected as the experiments were conducted at room temperature.

During the interaction between H$_2$ and polyaniline, a proportion of the analyte gas (H$_2$) is probably catalytically oxidised forming water. The presence of water molecules in the polyaniline backbone leading to an increase in polymer's conductivity [19, 20]. Therefore, it was observed that the resistance of both doped and dedoped polyaniline based sensors decreased upon exposure to H$_2$ gas. This observation is similar to that of Sadek *et al.* [21] who obtained doped and dedoped polyaniline via chemical polymerization.

Furthermore, it was suggested that the H$_2$ may form a bridge between nitrogen atoms on two adjacent chains, or there may be partial protonation of some amine nitrogen atoms [22]. These reactions lead to the protonation of polyaniline nitrogen atoms which result in more delocalized charge carriers on the polymer's backbone and an increase of film conductivity.
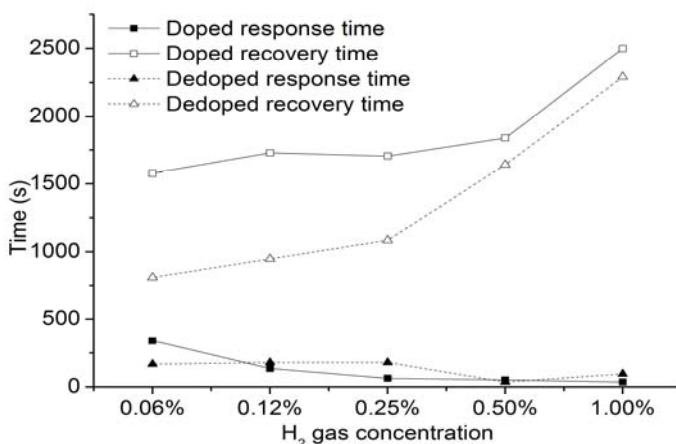

Figure 6 Response and recovery time versus H$_2$ gas concentrations

4.0   CONCLUSIONS

Doped and dedoped polyaniline nanostructures were successfully electropolymerized and deposited onto the conductometric transducers for H_2 gas sensing applications. The morphology of the nanostructures was characterized by SEM and showed that the diameters of the polyaniline fibers and nanotips were ~150-350 nm and ~30-60 nm, respectively. The gas sensing results of the doped and dedoped polyaniline nanofibers based conductometric sensors towards H_2 gas showed that dedoped polyaniline nanofibers based sensor was more sensitive than that of doped polyaniline nanofibers one. However doped polyaniline nanofibers based sensor possessed better baseline stability than the dedoped polyaniline nanofibers sensor.

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