

# Synthesis and Fluorescence Spectroscopy of Sulphonic Acid-Doped Polyaniline When Exposed to Oxygen Gas

S.F.S. Draman, R. Daik, and A. Musa

**Abstract**—Three sulphonic acid-doped polyanilines were synthesized through chemical oxidation at low temperature (0-5 °C) and potential of these polymers as sensing agent for O<sub>2</sub> gas detection in terms of fluorescence quenching was studied. Sulphuric acid, dodecylbenzene sulphonic acid (DBSA) and camphor sulphonic acid (CSA) were used as doping agents. All polymers obtained were dark green powder. Polymers obtained were characterized by Fourier transform infrared spectroscopy, ultraviolet-visible absorption spectroscopy, thermogravimetry analysis, elemental analysis, differential scanning calorimeter and gel permeation chromatography. Characterizations carried out showed that polymers were successfully synthesized with mass recovery for sulphuric acid-doped polyaniline (SPAN), DBSA-doped polyaniline (DBSA-doped PANI) and CSA-doped polyaniline (CSA-doped PANI) of 71.40%, 75.00% and 39.96%, respectively. Doping level of SPAN, DBSA-doped PANI and CSA-doped PANI were 32.86%, 33.13% and 53.96%, respectively as determined based on elemental analysis. Sensing test was carried out on polymer sample in the form of solution and film by using fluorescence spectrophotometer. Samples of polymer solution and polymer film showed positive response towards O<sub>2</sub> exposure. All polymer solutions and films were fully regenerated by using N<sub>2</sub> gas within 1 hour period. Photostability study showed that all samples of polymer solutions and films were stable towards light when continuously exposed to xenon lamp for 9 hours. The relative standard deviation (RSD) values for SPAN solution, DBSA-doped PANI solution and CSA-doped PANI solution for repeatability were 0.23%, 0.64% and 0.76%, respectively. Meanwhile RSD values for reproducibility were 2.36%, 6.98% and 1.27%, respectively. Results for SPAN film, DBSA-doped PANI film and CSA-doped PANI film showed the same pattern with RSD values for repeatability of 0.52%, 4.05% and 0.90%, respectively. Meanwhile RSD values for reproducibility were 2.91%, 10.05% and 7.42%, respectively. The study on effect of the flow rate on response time was carried out using 3 different rates which were 0.25 mL/s, 1.00 mL/s and 2.00 mL/s. Results obtained showed that the higher the flow rate, the shorter the response time.

**Keywords**—conjugated polymer, doping, fluorescence quenching, oxygen gas.

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## I. INTRODUCTION

Polyaniline (PANI) is one of the most intensively studied conductive polymers which have been explored for use in electronic and optical applications. It has demonstrated significant potential for technological applications due to its simple and economical production routes, and relatively high environmental stability. There is particular interest in employing the protonated polyaniline or the emeraldine salt, their derivatives, or polyaniline-metal composites as sensing materials. The preference for a conductive polymer over a conventional metal as a sensing material stems from several factors: conductive polymer is light and less expensive in processing, it can be operated at lower applied voltages and temperatures, and it interacts more favorably with organic compounds [1].

The great potential of PANI is, however, masked by its serious disadvantages such as insolubility, infusibility and hence poor process ability. Attempts have been made to improve its solubility, of which the most widely adopted strategy is to dope PANI with organic acids such as sulphonic acid [2].

Recent applications of PANI as a gas and vapor sensing materials include detection of H<sub>2</sub>S and NO<sub>x</sub>, ammonia vapor, NH<sub>3</sub>, and more recently hydrogen, methane, ethylene, acetylene and carbon monoxide [1, 3]. In the present work, we investigated the effects of dopant type and doping level on the sensitivity of sulphuric acid-doped PANI (SPAN), DBSA-doped PANI and CSA-doped PANI solutions and films for O<sub>2</sub> gas detection in terms of fluorescence quenching.

## II. EXPERIMENTAL

### A. Materials

Aniline monomer (Riedel-de Haen) was used as the monomer and analytical grade ammonium persulfate, (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (Merck) was used as the oxidant. Ammonia solution, NH<sub>4</sub>OH (BDH Laboratory) was used as the base agent. Analytical grade calcium hydride, CaH<sub>2</sub> (Fluka) was used in drying the aniline monomer. Hydrochloric acid, HCl (R & M Chemicals), sulfuric acid, H<sub>2</sub>SO<sub>4</sub> (Ashland Chemicals), dodecylbenzene sulphonic acid, DBSA (Fluka) and camphor sulphonic acid, CSA (Merck) were used as the

protonic acids in the doping process. Dimethylformamide, DMF (BDH Laboratory) and 1-methyl-2-pyrrolidone, NMP (Merck) were used as the solvent for polymer solution and film preparation, respectively. Poly (vinyl alcohol), PVA was used to fabricate SPAN, DBSA-doped and CSA-doped PANI films. Oxygen and nitrogen gas of 99.0% purity were obtained from MOX.

#### B. Instrumentation

All UV-visible absorption spectra were recorded on a Varian Carry 100 UV-visible spectrophotometer instrument. The infrared spectra were recorded by using GX FTIR spectrometer. Elemental analysis (EA) was carried out using Fision (CARLO ERBA) EA 1108. Thermogravimetry analyzer (TGA) used was a Mettler Toledo TGA 851e. Differential Scanning calorimetry (DSC) was conducted using a Mettler Toledo DSC 822. All fluorescence measurements were conducted on a Perkin-Elmer LS-55 Luminescence Spectrometer. A gel permeation chromatography system (waters Breeze 1515) was used to determine the molecular weight of synthesized DBSA-doped and CSA-doped PANI. Toluene was used as the mobile phase and known molecular weight polystyrenes were used as the standards for the calibration curve.

#### C. Synthesis of Polyaniline emeraldine base(EB)

Aniline monomer (100 mL) was dried with calcium hydride (0.25 g) for 30 min. The dried aniline was then distilled (three times) under reduced pressure at 80 - 85 °C and the colorless aniline monomer obtained was stored in nitrogen atmosphere at 0 - 5 °C prior to use. Polyaniline emeraldine base was synthesized by the method reported previously [1] with a slight modification. HCl (1 M, 300 mL) containing aniline monomer (0.1 mol, 9.11 mL) was cooled down to 0 - 5°C.  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (22.8 g, 0.1 mol) in HCl (1 M, 100 mL) was added dropwise into the aniline solution within 30 min. The mixture was stirred vigorously at 275 rpm for 4 h. A color change from blue to dark green was observed. At the final stage of polymerization, the dark green precipitate of polyaniline emeraldine salt was recovered from the polymerization flask. The polymer was filtered and washed with HCl (1 M, 750 mL), deionized water (750 mL) and subsequently  $\text{NH}_4\text{OH}$  (1 M, 750 mL). The polyaniline emeraldine salt powder was mixed with  $\text{NH}_4\text{OH}$  (0.1 M, 500 mL) and the solution was stirred for 5 h. The dark blue powder of polyaniline base was filtered and washed with  $\text{NH}_4\text{OH}$  (0.1 M, 750 mL) and deionized water (750 mL). The powder was then dried in vacuum oven at 50 – 60 °C for 12 h to obtain EB (6.649 g, 71.4 %).

#### D. Synthesis of SPAN

Emeraldine base (2 g) was sulfonated by dissolving it in fuming sulfuric acid (30 %, 160 mL) with constant stirring at 5 °C. The colour of the solution changed from dark purple to dark blue in 2 h. The solution was then slowly added into methanol (200 mL) to precipitate most of the product. The temperature was held between 10 and 20°C by an ice bath.

Precipitation was completed by the addition of acetone (100 mL) [4]. The dark green powder was filtered by using Whatman no. 2 filter paper. SPAN powder was washed with methanol until the filtrate was colourless. The powder was then dried in vacuum oven at 50 – 60 °C for 12 h.

#### E. Synthesis of DBSA-doped PANI

A 500 mL deionized water containing 5.48 mL (0.06 mol) of aniline monomer and 21.6 g (0.06mol) of DBSA was cooled down to 4°C. The mixture was stirred vigorously for 3h. A solution of 13.69 g (0.06mol) of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  in 50 mL of deionized water was slowly added into the aniline solution and the polymerization was extent for 5h. The dark green precipitate of DBSA-doped PANI was recovered from the polymerization flask, filtered and then washed with 750 mL of methanol and dried in a vacuum oven at 60°C for 12h.

#### F. Synthesis of CSA-doped PANI

The mixture containing 5.0 mL (0.05 mol) of aniline monomer and 75 mL of CSA was cooled down to 0-5°C. A solution of 2.28 g (0.01mol) of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  in 25 mL of CSA was slowly added into the aniline solution within 30 min. The mixture was stirred vigorously for 1.5 h. The dark green precipitate of CSA-doped PANI was recovered from the polymerization flask, filtered and then washed with 400 mL of CSA (0.1 M) and 750 mL methanol. The powder was then dried in a vacuum oven at 60°C for 12h.

#### G. Preparation of polymer solution

Polymer solution of SPAN was prepared by dissolving SPAN (0.5 mg) in DMF (25 mL) in a sonification bath. Undissolved polymer powder was then filtered using Whatman no. 2 filter paper. The filtrate of polymer solution was used in fluorescence measurement. A similar procedure was used to prepare the polymer solution of DBSA-doped and CSA-doped PANI for fluorescence measurement.

#### H. Fluorescence measurement

SPAN, DBSA-doped and CSA-doped PANI solution (3 mL) was placed in quartz cuvette for all the fluorescence measurements.  $\text{O}_2$  gas was allowed to flow at a constant rate into the polymer solution. The fluorescent polymer was regenerated by using  $\text{N}_2$  gas after quenching with  $\text{O}_2$ .

#### I. Preparation of polymer films

The films of doped polyanilines were prepared by the following procedure. A 0.08 g sample of doped PANI was mixed with 0.02 g PVA in 10 mL of NMP and the solution was vigorously stirred for 12 h. Then 0.15 mL each of the various doped polyaniline solutions was cast on a glass slide and dried in vacuum oven at 50-60 °C for 96-120 h.

### III. RESULT AND DISCUSSION

SPAN, DBSA-doped PANI and CSA-doped PANI were successfully synthesized through chemical oxidation at low

temperature (0-5°C) with high yield which are 71%, 75% and 40%, respectively due to its exothermic reaction. Therefore, the low temperature of reaction lead to high conversion compared to high reaction temperature [2].

#### A. Polymer characterization

The UV-visible absorption spectrum of EB shows two peaks at 325 nm and 635 nm, respectively. These peaks represent the  $\pi$ - $\pi^*$  electron transition of the benzenoid segment and the  $\pi$ - $\pi^*$  electron transition of the quinoid segment, respectively [5]. It is anticipated that the UV-visible absorption spectrum of doped polyaniline (PANI) would have two peaks at 325 nm and 825 nm respectively, since the peak at 635 nm, that corresponds to the quinoid segments would disappear due to the conversion of quinoid segments into the polaron state. However, in this study UV-visible absorption spectra for EB and SPAN were almost identical. This is probably due to the green protonated emeraldine had been converted to protonated pernigraniline, which is blue and expected to be conducting when exposed to moisture [6]. The UV-visible absorption spectrum of CSA-doped PANI shows three peaks at 335 nm, 430 nm and 840 nm, respectively. This first peak represent the  $\pi$ - $\pi^*$  electron transition of the benzenoid segment and for the second peak is probably due to the protonated of PANI chain. The third peak represents the polaron state due to the doping process. For the synthesized DBSA-doped PANI, their spectra show nearly the same results as those of SPAN.

The FTIR spectrum of PANI emeraldine base exhibited five absorption peaks at 829, 1158, 1302, 1496 and 1590  $\text{cm}^{-1}$ . They represent the C-H bending vibration of para-coupled benzene ring, the vibration mode of quinoid ring, the stretching vibration of C-N, the stretching vibration of N-benzenoid ring and the stretching vibration of N-quinoid ring, respectively [7]. For the SPAN, DBSA-doped PANI and CSA-doped PANI, the spectra do not have the absorption peak at 1590  $\text{cm}^{-1}$  since all quinoid segments have presumably been converted to the bipolaron state.

The  $M_n$  and  $M_w$  of DBSA-doped PANI were 65700 g/mol and 88000 g/mol, respectively and the corresponding polydispersity was 1.34. For CSA-doped PANI, the  $M_n$  and  $M_w$  were 7400 g/mol and 24000 g/mol, respectively and the corresponding polydispersity was 3.22. The chromatograms of EB and SPAN have not been characterized because EB and SPAN were insoluble. However, based on published data [8], the  $M_n$  and  $M_w$  of EB with NMP as a mobile phase were 25000 g/mol and 64000 g/mol, respectively. In this study, EB was easily dissolved in NMP, thus it is expected that the  $M_n$  and  $M_w$  of this sample was quite high. High molecular weight of polymer is important to fabricate film as sensing agent.

Differential scanning calorimetry was carried out to determine glass transition,  $T_g$  of the synthesized polymers. Emeraldine base indicate  $T_g$  at 250°C, and that is consistent with previously published data [9,10]. Meanwhile,  $T_g$  of SPAN, DBSA-doped PANI and CSA-doped PANI is higher compared to EB which is around 314-320°C. This could be

due to the presence of doping agent that reduced the chain mobility and thus lead to higher  $T_g$ .

SPAN, DBSA-doped PANI and CSA-doped PANI obtained were 32.9%, 33.1% and 53.96%, respectively as calculated from S/N ratio. For PANI emeraldine base, TGA chromatogram shows a typical two step weight loss behavior. A 1-3% weight loss at 50-100°C can be attributed to the loss of water molecules [1,9,10]. Beyond that temperature, there is a gradual weight loss due to the loss of low molecular weight oligomer up to 400 where the skeleton of PANI emeraldine base back bone begins to decompose. For SPAN, DBSA-doped PANI and CSA-doped PANI, TGA chromatograms indicates a three step weight loss. The first weight loss between 50 and 100°C s due to the escape of water molecules and the second step weight loss at 150°C can be attributed to the elimination of dopant molecules. The third weight loss at 400°C is due to decomposition of PANI backbone [11].

#### B. Fluorimetric response of the SPAN, DBSA-doped PANI and CSA-doped PANI solutions

SPAN, DBSA-doped PANI and CSA-doped PANI are moderately soluble in strong polar organic solvent such as dimethyl sulfoxide (DMSO), DMF and N-methylpyrrolidone (NMP). In this study, fluorescence characteristics of SPAN, DBSA-doped PANI and CSA-doped PANI in DMF upon exposure to oxygen gas in terms of fluorescence quenching are discussed. Synthesis and characterization of SPAN, DBSA-doped PANI and CSA-doped PANI have been reported by other researchers [4,12,13]. However, to our present knowledge, an application of a simple concept that is fluorescence quenching of polyaniline and its derivatives has not been used in optical sensor studies for gas detection. The fluorescence spectrum of SPAN, DBSA-doped PANI and CSA-doped PANI in DMF are shown in Figures 1, 2 and 3, respectively. The maximum emission of SPAN, DBSA-doped PANI and CSA-doped PANI was observed at 363 nm, 373 nm and 395 nm, respectively, when the polymer solution was excited at 308 nm, 313 nm and 313 nm, respectively. The fluorescence spectra of DBSA-doped PANI and CSA-doped PANI have shifted to higher wavelength compared to SPAN because of two factors: the different of doping agent and doping level. The used of dodecyl group with long chain [14], and the highest doping level achieved in the case of CSA-doped PANI (53.96%) leading to maximum emission at higher wavelength. The emission spectrum of all the polymers solutions was noticed to be a mirror image of the excitation spectrum. This is probably due to the vibrational spacing in the ground state ( $S_0$ ) that is often similar to the first excited single state ( $S_1$ ) for large molecule [15].

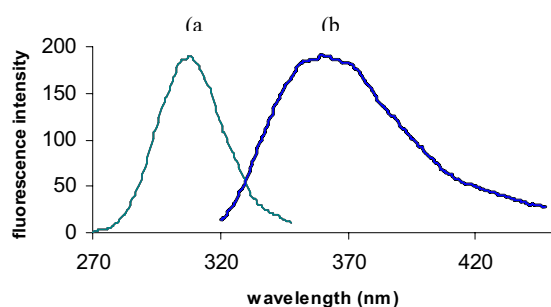


Fig. 1 The excitation (a) and emission (b) spectra of SPAN solution in DMF

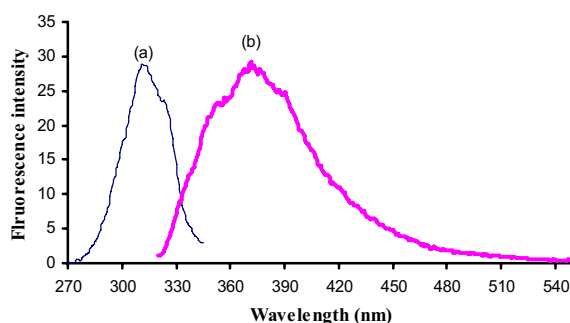


Fig. 2 The excitation (a) and emission (b) spectra of DBSA-doped PANI solution in DMF

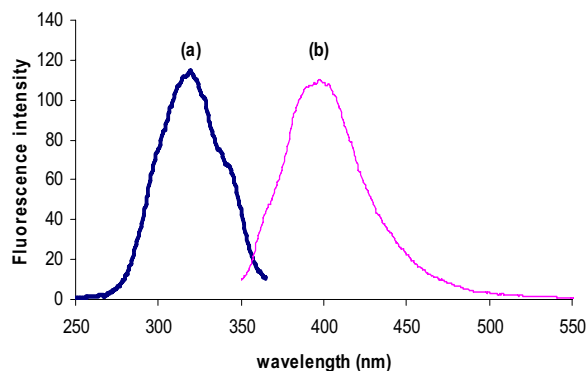


Fig. 3 The excitation (a) and emission (b) spectra of doped CSA-doped PANI solution in DMF

The fluorescence intensity of the SPAN, DBSA-doped PANI and CSA-doped PANI solution decreased when exposed to  $O_2$  gas, indicating  $O_2$  gas was able to quench the intensity of fluorescence emission (Figures 4, 5 and 6, respectively) until a steady state response is established. Chen et al. [16] suggested that the fluorescence of conjugated polymer can be described in terms of semiconductor band theory. Upon photo excitation of a conjugated polymer, the electrons from the valence band are excited to the conduction

band and then migrated along the polymer backbone. The excited electron and the oppositely charged "hole" attract one another. When the excited electron recombines with the hole, a photon is emitted (fluorescence). In solution, the quencher and the polymer form a weak complex. This static association prevents the transfer of electron on the conjugated chain, or induces ultra fast photo induced electron transfer to electron acceptor, resulting decrease of fluorescent intensity of conjugated polymer. This suggestion agreed to fluorescence quenching phenomena that being mentioned by Hobart et al. [18]. The energy loss in heat and photo forms because of collision phenomena occurs between different molecules called dynamic quenching. In other words, dynamic quenching is a process where quenching molecules deactivate the excited fluorophore (conjugated polymer).

In photostability study, all polymer solutions were irradiated with xenon light under  $N_2$  atmosphere. For a continuous irradiation period of 9 h, the result shows that the sensing material is considered stable. The relative standard deviation (RSD) for SPAN, DBSA-doped PANI and CSA-doped PANI are 0.34%, 1.21% and 0.95%, respectively.

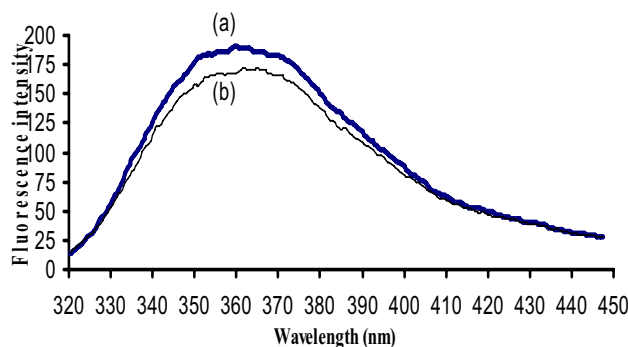


Fig. 4 The fluorescence spectra of SPAN solution before (a) and after (b) being exposed to  $O_2$  gas

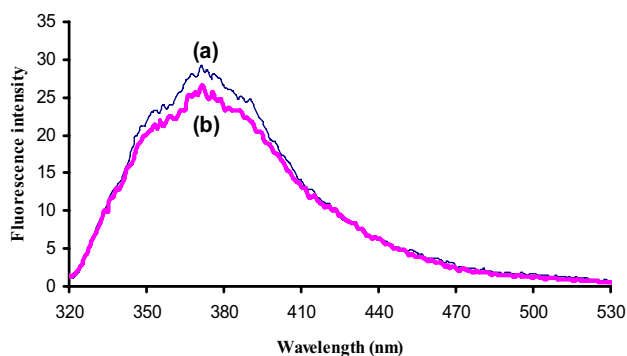


Fig. 5 The fluorescence spectra of DBSA-doped PANI solution before (a) and after (b) being exposed

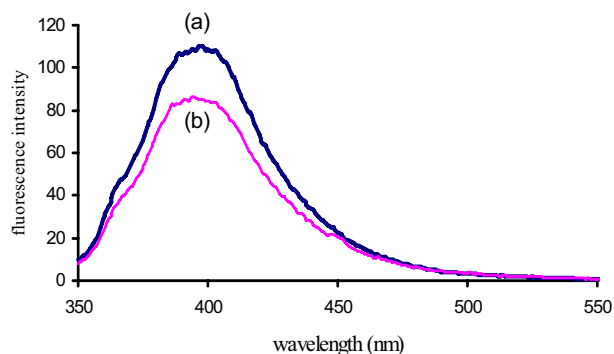


Fig. 6 The fluorescence spectra of doped CSA-doped PANI solution before (a) and after (b) being exposed to O<sub>2</sub> gas

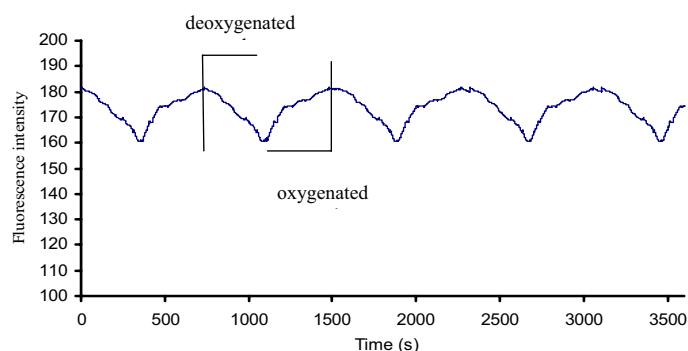


Fig. 7 Typical response of SPAN solution towards the same amount of O<sub>2</sub> gas.

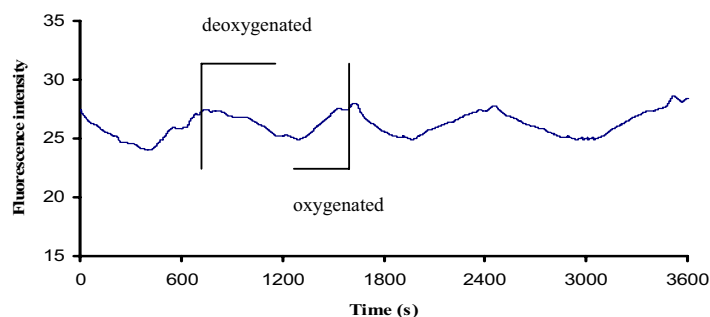


Fig. 8 Typical response of DBSA-doped PANI solution towards the same amount of O<sub>2</sub> gas.

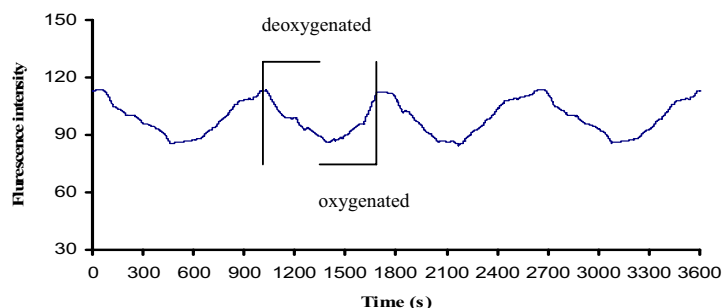


Fig. 9 Typical response of doped CSA-doped PANI solution

towards the same amount of O<sub>2</sub> gas

Fig. 7, 8 and 9 shows the typical dynamic response of the SPAN, DBSA-doped PANI and CSA-doped PANI solution upon exposure to fully oxygenated and deoxygenated atmospheres. In this study, SPAN, DBSA-doped PANI and CSA-doped PANI that have been exposed to oxygen were regenerated by flushing the polymer solution with N<sub>2</sub> gas. The steady state response time for O<sub>2</sub> detection was found to be at average 6 minutes and 23 seconds, 6 minutes and 32 seconds and 6 minutes and 36 seconds, respectively. Regeneration of the polymer solution with N<sub>2</sub> gas took an average 6 minutes and 37 seconds, 6 minutes and 36 seconds and 6 minutes and 42 seconds, respectively. This means that a complete regeneration cycle took about 13 minutes, 13 minutes and 8 seconds and 13 minutes and 18 seconds, respectively, and therefore 4 complete cycles were obtained in 60 minutes of testing. The changes of the signal were fully reversible and hysteresis was not observed.

Fig. 10, 11 and 12 show the reproducibility and repeatability of the SPAN, DBSA-doped PANI and CSA-doped PANI, respectively, as sensing materials towards O<sub>2</sub> gas. In this study, repeatability refers to the response generated by a single sensing reagent when used to determine the same amount of O<sub>2</sub> for several times. Reproducibility on the other hand, refers to the response generated by different sensing reagents when exposed to the same amount of O<sub>2</sub> gas. The RSD for the repeatability for SPAN, DBSA-doped PANI and CSA-doped PANI were 0.23%, 0.64% and 0.76%, respectively, and the RSD for reproducibility were 2.36%, 6.98% and 1.27%, respectively. The relatively high RSD value obtained for reproducibility is expected to be due to common errors during solution preparation that cause variation in fluorescence intensity when measurements were made.

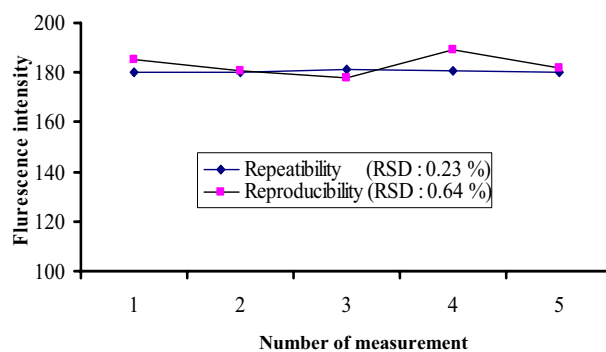


Fig. 10 The reproducibility (■) and repeatability (◆) of the sensing reagent upon exposure to O<sub>2</sub> gas (SPAN solution)

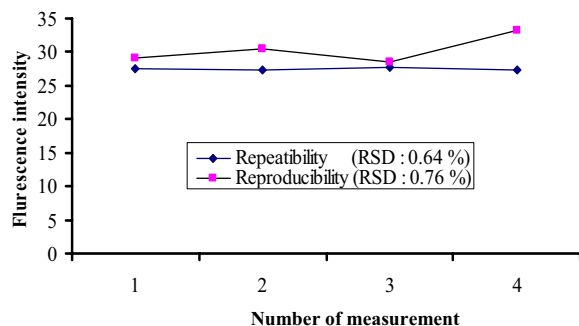


Fig. 11 The reproducibility (■) and repeatability (◆) of the sensing reagent upon exposure to O<sub>2</sub> gas (DBSA-doped PANI solution)

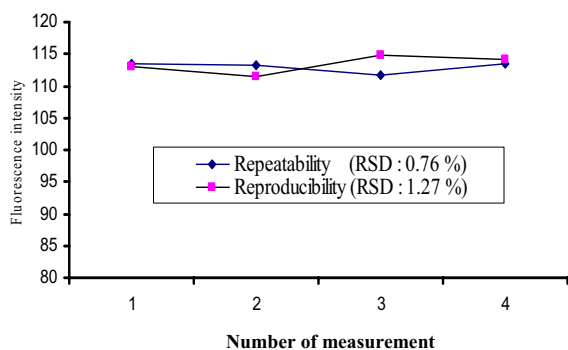


Fig. 12 The reproducibility (■) and repeatability (◆) of the sensing reagent upon exposure to O<sub>2</sub> gas (doped CSA-doped PANI solution)

As shown in Fig.13 (SPAN), the attainment of the steady state response is governed by the flow-rate of the gas. In this study, the flow rates used were 0.25 mL/s, 1.00 mL/s and 2.00 mL/s. The similar observation on the effect of the flow-rate on response time has been reported in the literature. Mehamod et al. [15] reported that the higher flow-rate offered higher reaction rate and shorter response time, whereas lower flow-rate gave the opposite effects. For DBSA-doped PANI and CSA-doped PANI, the effect of flow-rate on response time show was nearly the same as those of SPAN.

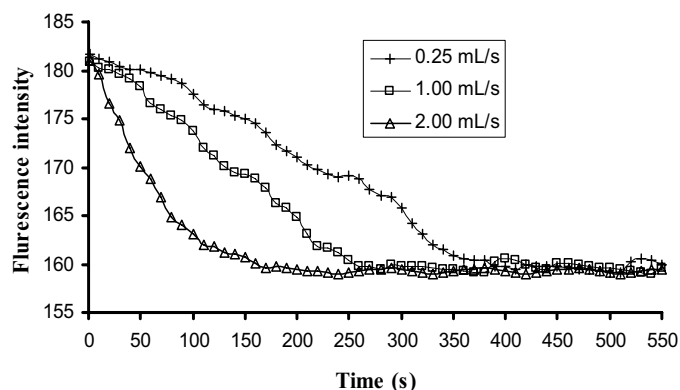


Fig. 13 The effect of flow rate of O<sub>2</sub> gas on the response time of SPAN solution

### C. Fluorimetric response of the SPAN film

Recently, a lot of research works deal with the use of a composite film with doped PANI as sensitive layer. In this study, PVA were used to blend with doped PANI. According to Eduardo and Azevedo [17], the formation of composite films allows to PANI to preserve its conductivity even with humidity or heat and this kind of blends allows also improving the solubility of conducting polymers and thus their processability

The fluorescence spectra of polymer films of SPAN, DBSA-doped PANI and CSA-doped PANI, are shown in Figures 14, 15 and 16, respectively. The maximum emission was observed at 389 nm, 395 nm and 408 nm, respectively, when the polymer film was excited at 334 nm, 325 nm and 335 nm, respectively. The emission spectrum of the polymer films did not form a mirror image of the excitation spectrum. This is probably due to the vibrational spacing in the ground state ( $S_0$ ) is different to the first excited single state ( $S_1$ ) for large molecule [15]. The fluorescence spectra of all polymer films are shifted to higher wavelength compared to all polymer solution. This is probably due to the molecules of SPAN, DBSA-doped PANI and CSA-doped PANI in film could not move as freely as in the solution causing part of the energy to be released to other form. This situation occur due to the release of molecule before fluorescence take over from the first excited single state to the ground state ( $S_1 \rightarrow S_0$ ) [18].

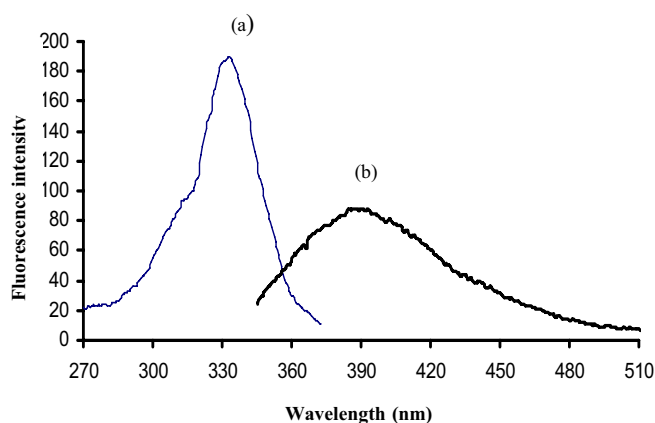


Fig.14 The excitation (a) and emission (b) spectra of SPAN film

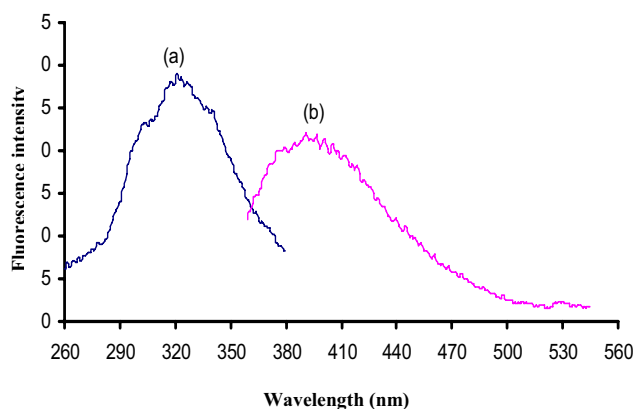


Fig. 15 The excitation (a) and emission (b) spectra of DBSA-doped PANI film

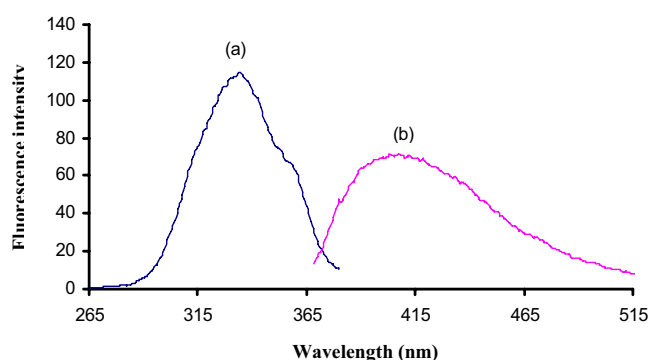


Fig. 16 The excitation (a) and emission (b) spectra of doped CSA-doped PANI film

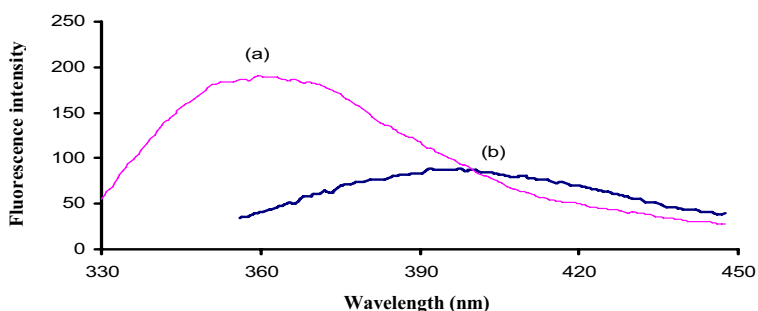


Fig.17 The comparison of fluorescence spectra of SPAN solution (a) and film (b)

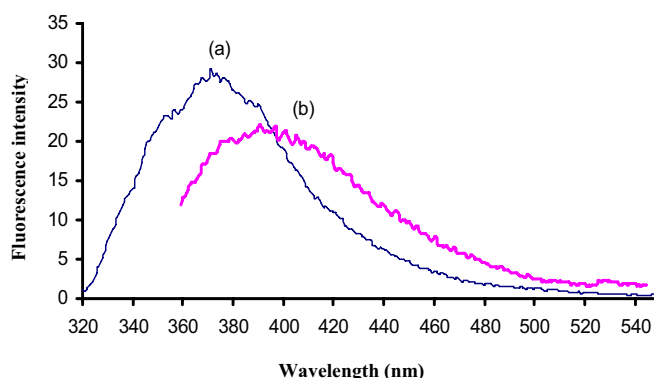


Fig.18 The comparison of fluorescence spectra of DBSA-doped PANI solution (a) and film (b)

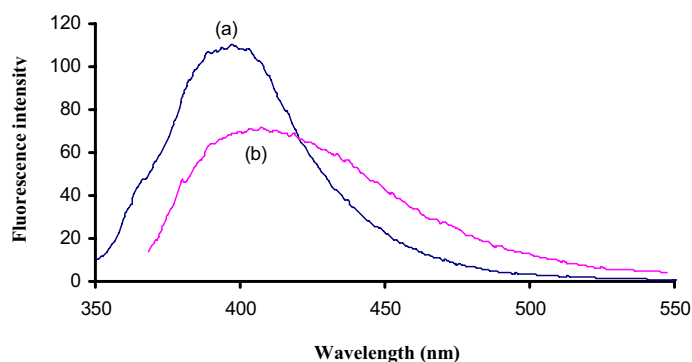


Fig. 19 The comparison of fluorescence spectra of CSA-doped PANI solution (a) and film (b)

The fluorescence intensity of the SPAN, DBSA-doped PANI and CSA-doped PANI films decreased when exposed to  $O_2$  gas, indicating  $O_2$  gas was able to quench the intensity of fluorescence emission until a steady state response is established. Figures 17, 18 and 19 show the comparison of the fluorescence spectra of SPAN, DBSA-doped PANI and CSA-

doped PANI, respectively, in solution and film. These results show that the fluorescence intensity of film is lower compared to solution. In photostability study, all polymer film was irradiated with UV light under N<sub>2</sub> atmosphere. For a continuous irradiation period of 9 h, the result shows that the sensing material in film form is considered stable.

Based on the typical dynamic response of the SPAN, DBSA-doped PANI and CSA-doped PANI films upon exposure to fully oxygenated and deoxygenated atmospheres, the steady state response time for O<sub>2</sub> detection and regeneration of the polymer film with N<sub>2</sub> gas took an average 6 minutes. These results were very similar to those of polymer solution.

The RSD for the repeatability of the sensing materials towards O<sub>2</sub> gas for SPAN, DBSA-doped PANI and CSA-doped PANI film were 0.52%, 4.05% and 0.90%, respectively. The RSD for the reproducibility were 2.91%, 10.05% and 7.42%, respectively. The relatively high RSD values obtained for reproducibility is expected to be due to variation in the thicknesses of films and the dispersion of polymer is not uniform. These common errors could be due to the difference of pores size and concentration of polymer during film preparations that cause variation in fluorescence intensity when measurements were made.

#### IV. CONCLUSION

SPAN, DBSA-doped PANI and CSA-doped PANI were successfully synthesized by oxidative chemical polymerization method with high yield 71.40%, 75.00% and 39.96%, respectively. Doped CSA-doped PANI had highest doping level (53.96%) compared to DBSA-doped PANI (33.13%) and SPAN (32.86%). The used of DBSA and CSA as a doping agent increases the solubility in organic solvent especially in toluene compared to SPAN and thus possible for molecular weight determination. Spectroscopic and thermal properties of the polymers are found to be affected by the type of the dopant used. Fluorescence characteristics of polymer solution/film upon exposure to O<sub>2</sub> gas showed a good potential to be exploited as sensing material for O<sub>2</sub> gas detection. A good repeatability and reproducibility of measurement were obtained. A complete regeneration cycle took about 13 minutes and 4 complete cycles were observed in 60 minutes of testing.

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