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Studies on Potential of Sulphonic Acid-Doped Polyaniline as Oxygen Sensor

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ABSTRACT

Potential of three conjugated polymers namely sulphonic acid-doped polyanilines (sulphuric acid-doped polyaniline (SPAN), dodecylbenzene sulphonic acid-doped polyaniline (DBSA-doped PANI) and champor sulphonic acid -doped polyaniline (CSA-doped PANI)) as sensing agents for O_2 *gas detection in terms of fluorescence quenching was studied. Sensing tests were carried out on polymer samples in the form of solution by using fluorescence spectrometer. SPAN solution was excited at 308 nm and the maximum emission was observed at 363 nm. DBSA-doped PANI solution and CSA-doped PANI solution were excited at 313 nm. Meanwhile, the maximum emission for DBSA-doped PANI solution and CSA-doped PANI solution were observed at 373 nm and 395 nm, respectively. Samples of polymer solution showed positive response towards* O_2*. Results showed that the intensity of the fluorescence decreased when exposed to* O_2 *gas. All polymer solutions were fully regenerated by using* N_2 *gas within 1 hour period. Photostability study showed that all samples of polymer solution 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. The study on effect of the flow rate on the response time was carried 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*

Introduction

The discovery of conjugated polymer has opened up many new possibilities for making devices with combined optical, electrochemical, and electrical properties (Nalwa, 1997). Among them, polyaniline (PANI) has received widespread attention because of its simple synthesis, good environmental and thermal stability. Gas sensors based on PANI materials have been attracting considerable attention in recent years (Dhawan et al., 1997; Kiattubur et al., 2002; Sadek et al., 2007) due to their unique properties. The conductivity of PANI depends on both the ability to transport charge carriers along the polymer backbone and the ability to hop the carriers between polymer chains. Thus PANI molecules can readily react with protonating and deprotonating, or reductive and oxidative agents, to change their conductivity at room temperature. PANI is a phenylene-based polymer having chemically flexible –NH- group in the polymer main chain flanked either side by phenylene as shown in Figure 1.

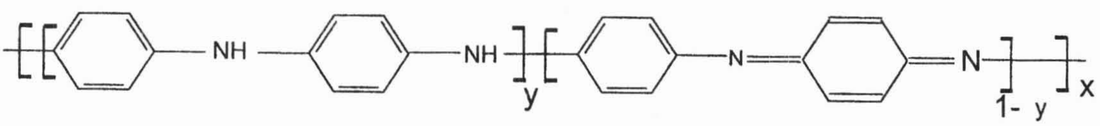


Figure 1: General Chemical Structure of PANI

The value of y represents the oxidation state, and can be varied from y =1, which represents the completely reduced polymer (leucoemeraldine), to y = 0, which represents the completely oxidized polymer (pernigraniline). When y = 0.5, the PANI is in emeraldine oxidation state. These advantages make PANI an attractive material for application in several areas such as energy storage devices, light-emitting diodes, microelectronics, lightweight batteries and now in sensors, i.e biochemical or chemical sensors. However, major problems related to successful utilization of PANI such as its poor mechanical property and solubility remained unsolved. Therefore, sulfonic acid was used as doping agent in order to improve the solubility of PANI. Good solubility is essential for a polymer in order to facilitate post synthetic processing.

Yue et al. (1991) discussed the effect of sulfonic acid group on polyaniline backbone. The solubility of PANI is greatly improved by the presence of the $-SO_3^-$ groups. In this study, three sulfonic acids were used which are sulphuric acid, dodecylbenzene sulphonic acid (DBSA) and camphor sulphonic acid (CSA). Sulfonic acid-doped PANI have been synthesized via oxidative polymerization of aniline with ammonium persulfate as the oxidant at 5 °C. Synthesis and characterizations for sulphuric acid-doped polyaniline (SPAN), DBSA-doped polyaniline (DBSA-doped PANI) and CSA-doped polyaniline (CSA-doped PANI) have been reported in our previous paper (Draman et al., 2004; 2006; 2008).

In the past, a variety of sensing material based on fluorescence quenching has been reported. These include the use of pyrene derivatives chemisorption layers (Fujiwara & Amoa, 2003), metalloporphyrin complexes (Marco & Lanzo, 2000) and ruthenium complex entrapped in sol-gel film (Musa et al., 2001) for O_2 sensing. Chen et al. (2007) also reported that metal cation can be used as sensing material based on fluorescence quenching concept. To our present knowledge, the application of a simple concept that is fluorescence quenching of polyaniline and its derivatives has not been used in optical sensor studies. In this study optical response of SPAN, DBSA-doped PANI and CSA-doped PANI solutions upon exposure to oxygen gas are discussed.

Methodology

Polymer Solution Preparation

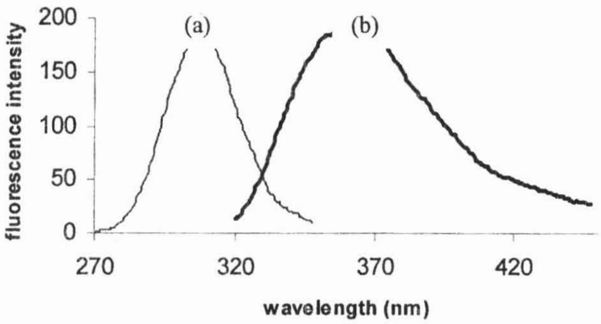
Polymer solution was prepared by dissolving 0.5 mg SPAN in 25mL dimethylformamide, DMF (BDH Laboratory). The same procedure was followed for DBSA-doped PANI and CSA-doped PANI.

Fluorescence Measurement

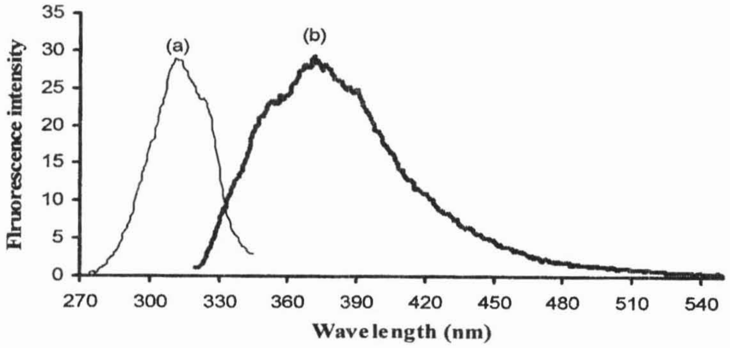
3 mL of SPAN solution was placed in quartz cuvette for all the fluorescence measurements (Perkin-Elmer LS-55 Luminescene Spectrometer). O_2 gas was allowed to flow at a constant rate into the polymer solution. The fluorescent polymer was regenerated by using N_2 gas after quenching with O_2. The similar measurements were done for DBSA-doped PANI and CSA-doped PANI.

Results and Discussion

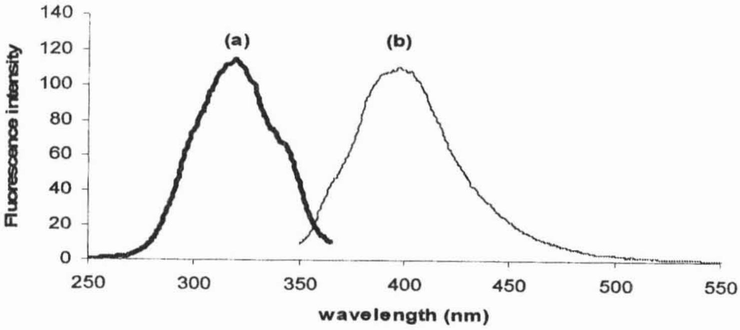
For SPAN solution, the maximum emission was observed at 363nm when the polymer solution was excited at 308nm. As shown in Figure 2, the maximum excitation and emission spectra of DBSA-doped PANI solution in DMF were observed at 313nm and 373nm, respectively. Meanwhile, CSA-doped PANI solution was excited at 313nm and the maximum emission was observed at 395nm. The emission spectra of the polymer solutions were noticed to be a mirror image of the excitation spectrum. This is probably due to the vibrational spacing in the ground state (S_o) that is often similar to the first excited single state (S_1) for large molecule as discussed by Mehamod et al. (2003).



SPAN Solution in DMF



DBSA-doped PANI Solution in DMF



CSA-doped PANI Solution in DMF

Figure 2: Excitation (a) and Emission (b) Spectra of Sulfonic Acid-doped PANI Solution in DMF

Figure 3 shows the fluorescence intensity of the of SPAN, DBSA-doped PANI and CSA-doped PANI solutions decreased when exposed to O_2 gas, indicating O_2 gas was able to quench the fluorescence. Chen et al. (2007) 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 conducting band and then migrate 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 aqueous 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 in fluorescent intensity of conjugated polymer.

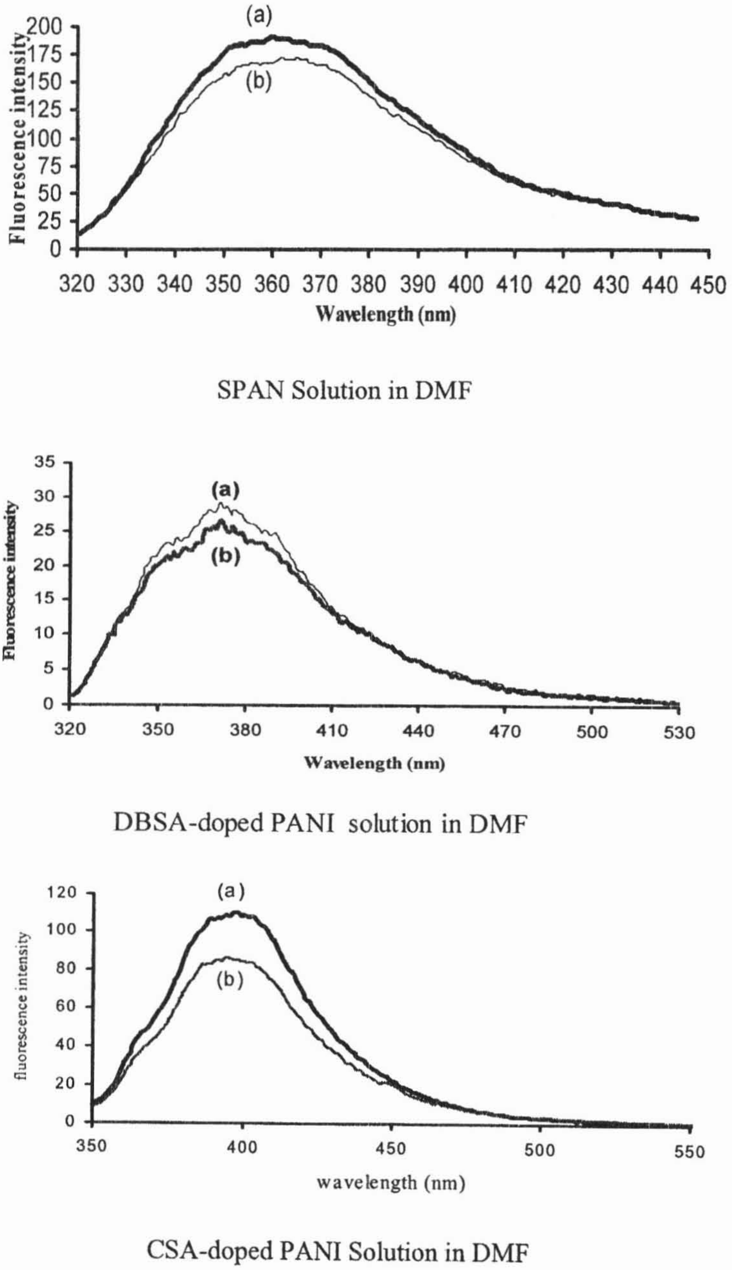


Figure 3: The Fluorescence Spectra of Sulfonic Acid-doped PANI Solution before (a) and after (b) being Exposed to O_2 Gas

In photostability study, polymer solutions were irradiated with UV light under N_2 atmosphere. For a continuous monitoring period of 9 h, the result shows that the polymer solutions are stable. The relative standard deviation (RSD) for SPAN, DBSA-doped PANI and CSA-doped solutions in this study are 0.34%, 1.21% and 0.95%, respectively as shown in Figure 4.

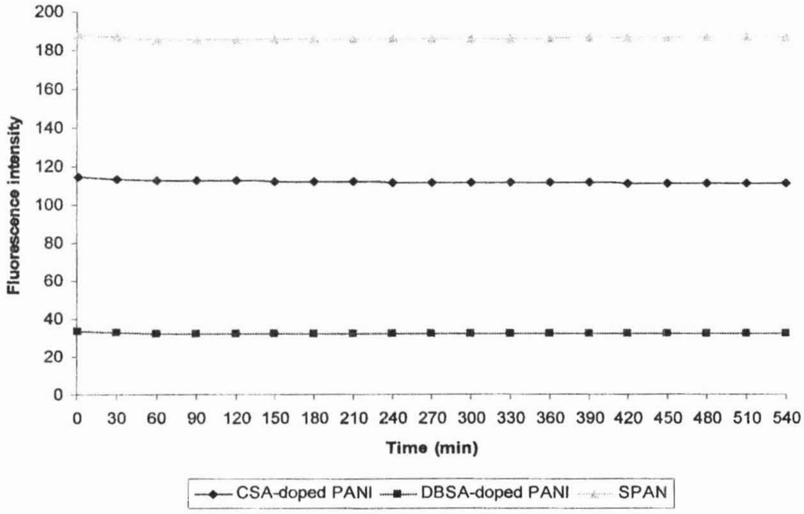
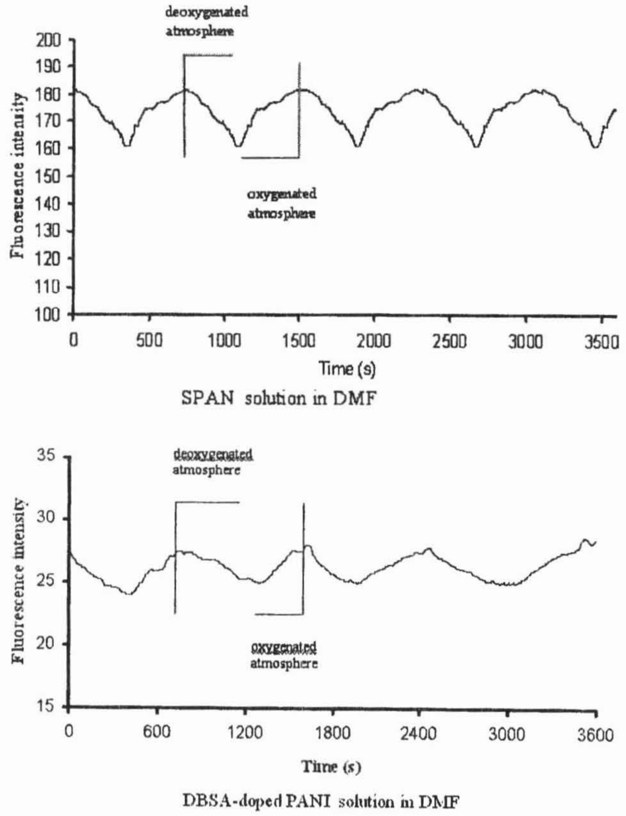
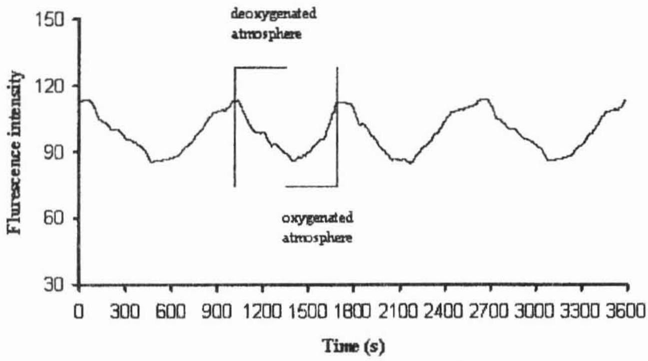


Figure 4: The Results of Photostability Study for SPAN, DBSA-doped PANI and CSA-doped PANI Solutions.

Figure 5 shows the typical dynamic response of the sensing material upon exposure to fully oxygenated and deoxygenated atmospheres. In this study, the polymer solutions were regenerated by flushing the polymer solution with N_2 gas. The response time for all polymer solutions were found to be about 6 min.

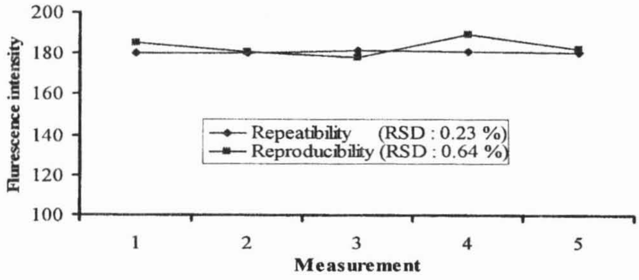




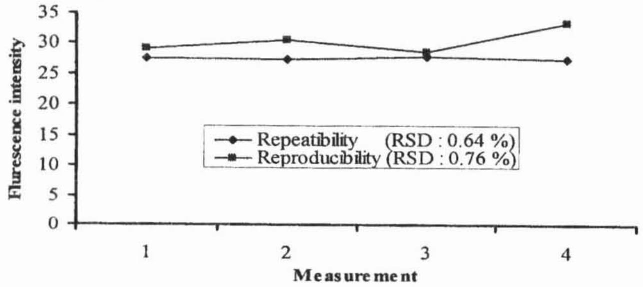
CSA-doped PANI solution in DMF

Figure 5: Typical Response of Sulfonic Acid- doped PANI Solutions Towards the Same Amount of O_2 Gas. The N_2 Gas was used to Regenerate the Polymer every After O_2 Gas Exposure.

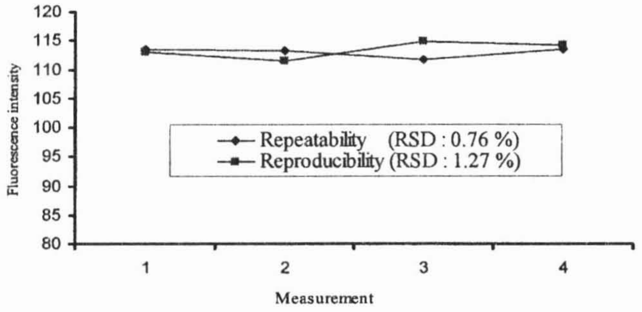
The reproducibility and repeatability of the polymer solutions towards O_2 gas were also studied (Figure 6). In this study, repeatability refers to the response generated by a single sensing reagent when used to determine the same amount of O_2 for several times. Meanwhile, reproducibility refers to the response generated by different samples of polymer solution when exposed to the same amount of O_2 gas. The RSD for the repeatability and reproducibility were 0.76% and 1.27%, respectively for 4 measurements. The relatively high RSD value obtained for reproducibility is expected to be due to common errors during solution preparation which causes variation in fluorescence intensity when measurements were made. Similar observations were reported by Musa et al. (2001) for repeatability and reproducibility.



SPAN Solution in DMF



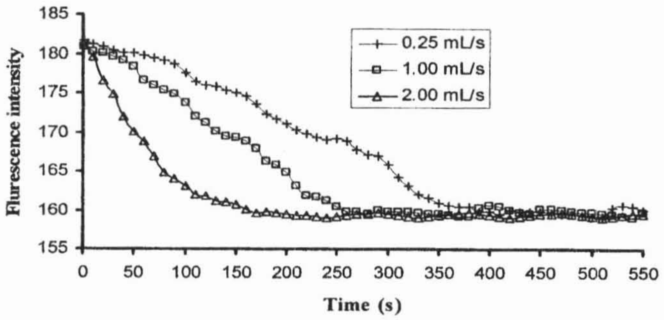
DBSA-doped PANI Solution in DMF



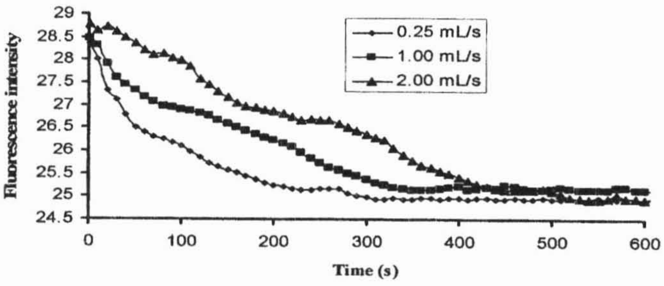
CSA-doped PANI Solution in DMF

Figure 6: The Reproducibility and Repeatability of the Polymer Solutions upon Exposure to O_2 Gas

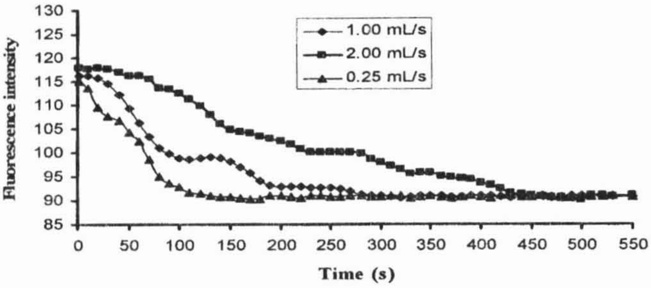
Figure 7 shows the effect of flow rate of O_2 gas on the response time of SPAN, DBSA-doped PANI and CSA-doped PANI solutions. Three flow rates were used in this study which is 0.23mL/s, 1.00mL/s and 2.50mL/s. The result shows that the higher flow-rate offered higher reaction rate and shorter response time, whereas lower flow-rate gave the opposite effects. Similar observations have been reported by Mehamod et al. (2003).



SPAN Solution in DMF



DBSA-doped PANI solution in DMF



CSA-doped PANI Solution in DMF

Figure 7: The Effect of Flow Rate of O_2 Gas on the Response Time of Sulfonic Acid-doped PANI

Conclusion

Based on the studies in optical fluorimetric response of SPAN, DBSA-doped PANI and CSA-doped PANI solutions in DMF upon exposure to O_2 gas shows that these polymers have the potential to be exploited as sensing material.

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