

Fluorescence Characteristics of Sulfonated Polyaniline Solution in DMF when Exposed to Oxygen Gas

Sarifah Fauziah Syed Draman, Rusli Daik* and Musa Ahmad

School of Chemical Sciences and Food Technology, Faculty of Science and Technology
Universiti Kebangsaan Malaysia, 43600 Bangi Selangor, Malaysia

*corresponding author

Fax : 603-89215410, Email address : rusli@pkriscc.ukm.my

Abstract : Aniline monomer was polymerized by oxidation with ammonium persulfate in hydrochloric acid at 0 °C. Sulfonated polyaniline (SPAN), a fluorescent conjugated polymer was obtained when emeraldine base (EB) was doped with sulfuric acid. Both EB and SPAN were characterized by UV-visible absorption and FTIR spectroscopy. The doping level of SPAN obtained was about 32% as measured by using thermogravimetry analysis and elemental analysis, indicating that on average, one aniline unit in every three repeat units was sulfonated. The optical response of the SPAN solution upon exposure to O₂ gas was described in terms of fluorescence quenching. The maximum emission was observed at 363 nm when the polymer solution was excited at 308 nm. The fluorescence intensity of the SPAN solution decreased when exposed to O₂ gas. The calculated relative standard deviation (RSD) of repeatability and reproducibility were 0.23% and 2.36, respectively. The fluorescent polymer was regenerated by flushing the polymer solution with N₂ gas. A complete regeneration cycle took about 13 minutes and 4 complete cycles were obtained in 60 minutes of testing.

Keywords : conjugated polymer, doping, fluorescence quenching, oxygen gas

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Introduction

Conjugated polymers have been extensively studied for the last few decades due to the substantial π -electron delocalization along the polymer backbones which gives interesting optical properties and allow them to become good semiconductors when oxidized or reduced [1]. Among the most interesting conjugated polymers for various applications is polyaniline (PANI). PANI is a phenylene-based polymer with -NH- group in the polymer main chain flanked either side by phenylene (Figure 1).

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.

PANI, also known as 'aniline black' that was first prepared in 1834, has attracted particular interest amongst researchers due to the fact that its electrical properties can be reversibly controlled by changing the oxidation state of the main chain and by protonating the nitrogen atoms [2]. Another advantage is the fact that PANI can be easily synthesized, the latter being relatively simple and inexpensive. The excellent environmental and thermal stability of the conducting form, the variety of optical properties, and low cost make PANI an attractive material for application in several areas such as energy storage devices [3], light-emitting diodes [4], EMI shielding [5], lightweight batteries [6] and now in sensors either biosensors [7] or chemical sensors [8].

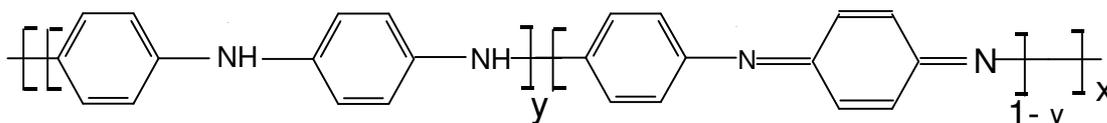


Figure 1 : General chemical structure of polyaniline

However, PANI like other conjugated polymers is infusible and insoluble or only partly soluble in common organic solvents and is therefore, intractable. Good solubility is essential for a polymer in order to facilitate post synthetic processing. The solubility of PANI is greatly improved by the presence of the $-\text{SO}_3^-$ groups [9]. Therefore, in this study self-doping of PANI using sulfuric acid as doping agent was used to obtain sulfonated polyaniline (SPAN). Being able to dope itself, the polymer is anticipated to exhibit better optical and electrical response as compared with the parent polyaniline [10]. Furthermore, $-\text{SO}_3^-$ groups might induce greater electron delocalization in SPAN compared to that in polyaniline. In this case, SPAN would probably exhibit semiconducting properties such as fluorescence with small band gap between HOMO and LUMO

Previously, conductivity measurement has been widely used in polyaniline-based gas sensors to detect ammonia gas [11-14], SO_2 [15] and volatile organic compounds (VOC) [16]. There have been only limited reports on polyaniline optical gas sensors. Jin et al. [17] have successfully developed an optical ammonia gas sensor by employing absorption spectroscopy as a detection method. 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.

In the past, a variety of sensing material based on fluorescence quenching has been reported. These include the use of pyrene derivatives chemisorption layers [18], metalloporphyrin complexes [19,20] and ruthenium complex entrapped in sol-gel film [21] for O_2 sensing. In this study, fluorescence characteristics of sulfonated polyaniline (SPAN) upon exposure to oxygen gas is discussed.

Experimental

Materials

Aniline monomer (Riedel-de Haen) was used as the monomer and analytical grade ammonium persulfate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (Merck) was used as the oxidant. Ammonia solution, NH_4OH (BDH Laboratory) was used as the base agent. Analytical grade calcium hydride, CaH_2 (Fluka) was used in drying the aniline monomer. Hydrochloric acid, HCl (R & M Chemicals) and sulfuric acid, H_2SO_4 (Ashland Chemicals) were used as the protonic acids in the doping process. Dimethylformamide, DMF (BDH Laboratory) was used as the solvent for polymer solution preparation. Both oxygen, O_2 and nitrogen, N_2 gas of 99.0% purity were obtained from MOX.

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. All fluorescence measurements were conducted on a Perkin-Elmer LS-55 Luminescence Spectrometer.

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 [15] 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 NH_4OH (1 M, 750 mL). The polyaniline emeraldine salt powder was mixed with NH_4OH (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 NH_4OH (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 %).

Synthesis of sulfonated polyaniline (SPAN)

Emeraldine base (2 g) was sulfonated by dissolving it in fuming sulfuric acid (30 %, 160 mL) with constant stirring at 5 °C. The color 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) [9]. The dark green powder was filtered by using Whatman no. 2 filter paper. SPAN powder was washed with methanol until the filtrate was colorless. The powder was then dried in vacuum oven at 50 - 60 °C for 12 h.

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.

Fluorescence measurement

SPAN solution (3 mL) was placed in quartz cuvette for all the fluorescence measurements. O₂ gas was allowed to flow at a constant rate into the polymer solution. The fluorescent polymer was regenerated by using N₂ gas after quenching with O₂.

Results and Discussion

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 [22]. 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 [23].

The peaks at 700 and 616 cm⁻¹ in the FTIR spectrum of SPAN (Figure 2) are consistent with the presence of -SO₃⁻ groups attached to the aromatic groups [10]. The peaks at 798 and 877 cm⁻¹ are due to out-of-plane bending of aromatic hydrogen for 1,2,4-trisubstitution of the phenyl ring. These peaks are not present in the FTIR spectrum of EB.

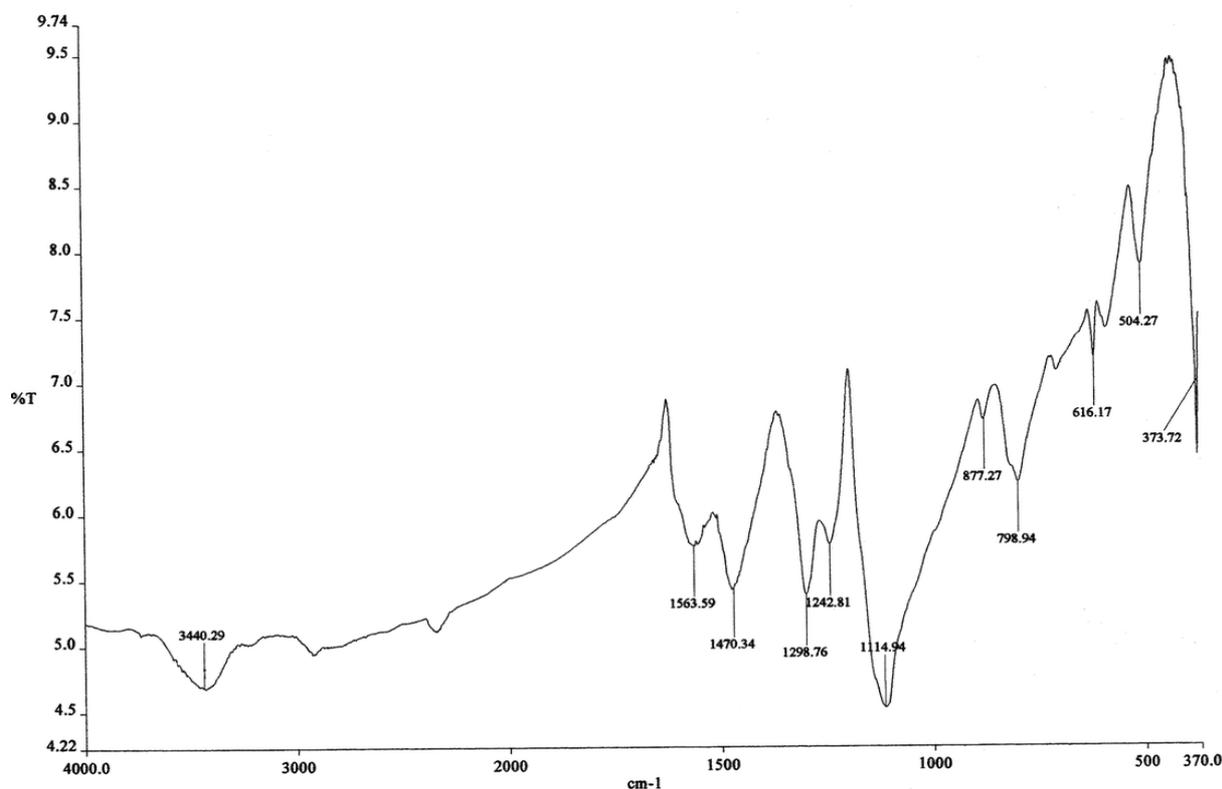


Figure 2 : FTIR spectrum of SPAN

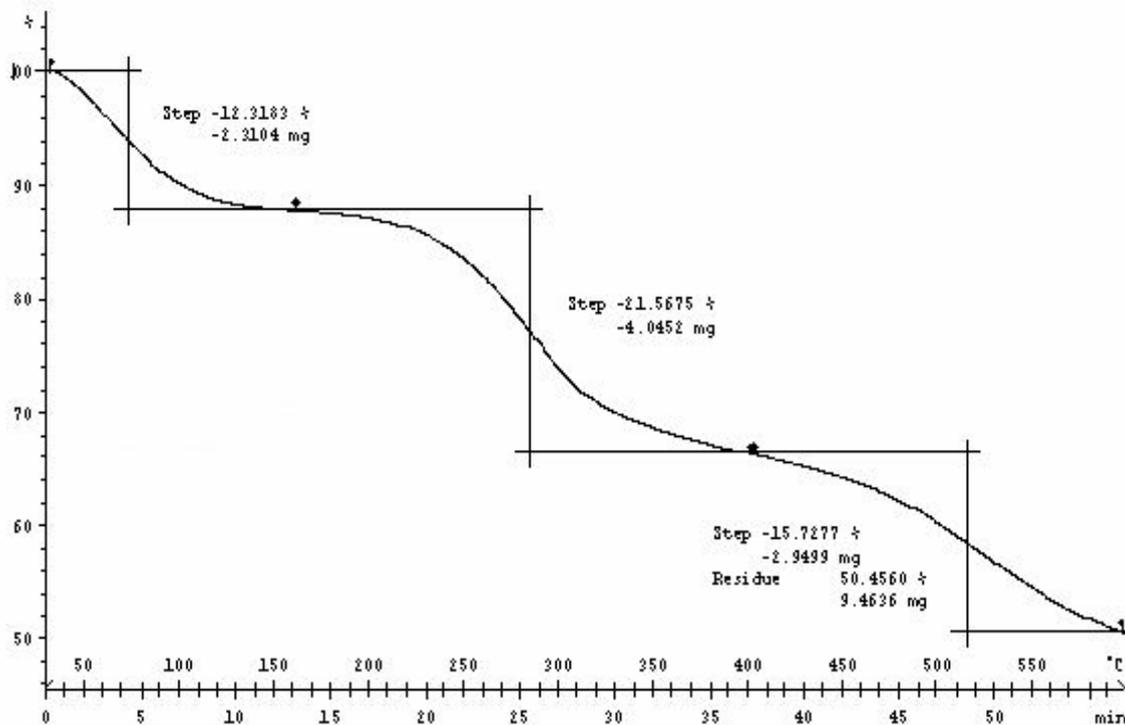


Figure 3 : TGA thermogram of SPAN

Based on elemental analysis, doping level of SPAN obtained was 32.18%, as calculated from S/N ratio. Figure 3 shows TGA thermogram of SPAN with three steps of weight loss. The first weight loss of 12%, between 50 and 100 °C indicates the escape of water molecules and the second 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 SPAN backbone [24]. From the second weight loss, doping level of SPAN was found to be 31.51%.

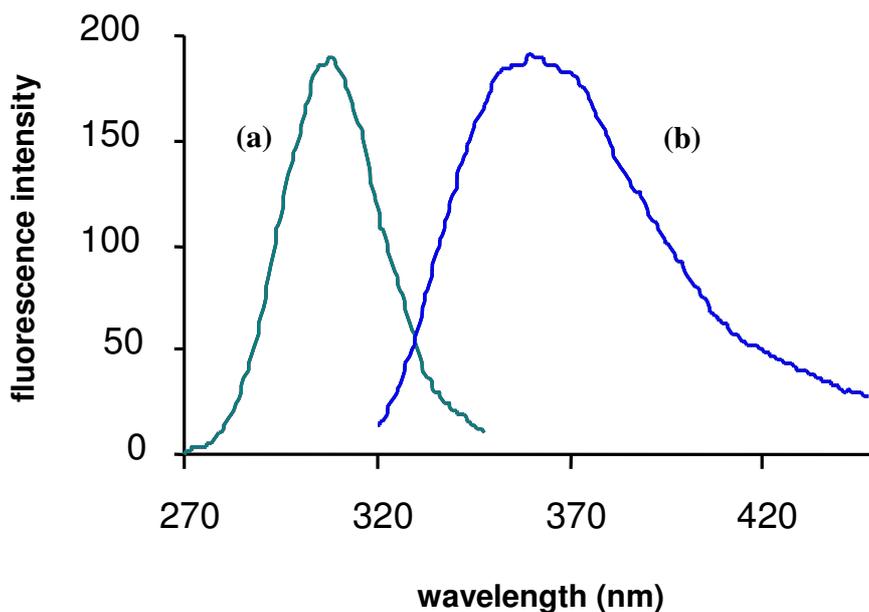


Figure 4 : The excitation (a) and emission (b) spectra of SPAN solution in DMF

Fluorimetric response of the SPAN solution

Fluorescent polymer, SPAN is moderately soluble in strong polar organic solvent such as dimethyl sulfoxide (DMSO), DMF and N-methylpyrrolidone (NMP). The fluorescence spectrum of polymer in DMF is shown in Figure 4. The maximum emission was observed at 363 nm when the polymer solution was excited at 308 nm. The emission spectrum of the polymer solution 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 [25].

study, SPAN that has been used as sensing material was regenerated by flushing the polymer solution with N_2 gas. The steady state response time for O_2 detection was found to be at average 6 minutes and 23 seconds. Regeneration of the polymer solution with N_2 gas took an average 6 minutes and 37 seconds. This means that a complete regeneration cycle took about 13 minutes 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.

Figure 7 shows the reproducibility and repeatability of the sensing materials towards O_2 gas.

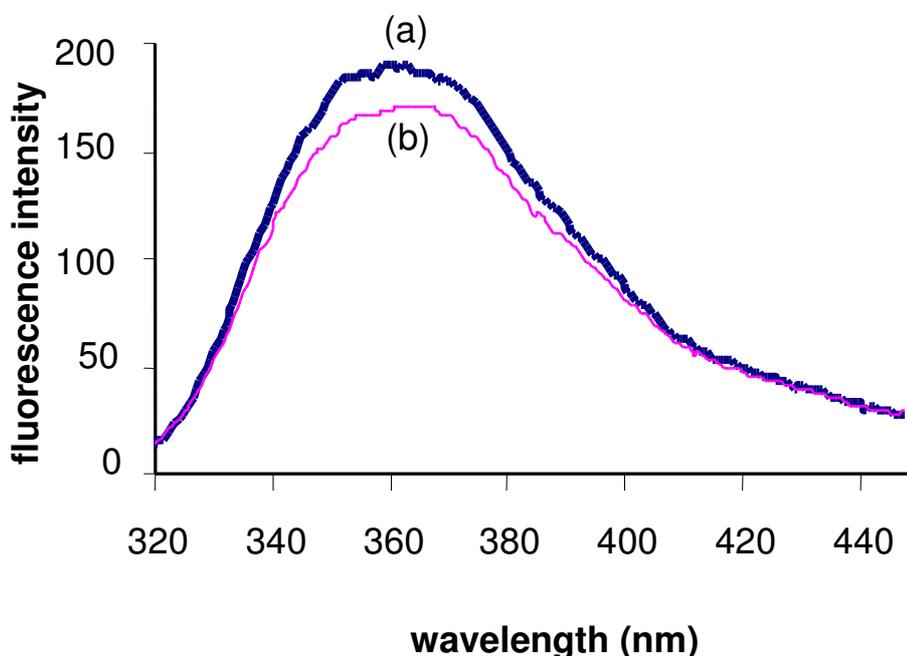


Figure 5 : The fluorescence spectra of SPAN solution before (a) and after (b) being exposed to O_2 gas

The fluorescence intensity of the SPAN solution decreased when exposed to O_2 gas, indicating O_2 gas was able to quench the intensity of fluorescence emission (Figure 5) until a steady state response is established. In photostability study, polymer solution was irradiated with UV 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 the study is 2.21% or 0.25% per hour.

Figure 6 shows the typical dynamic response of the SPAN solution upon exposure to fully oxygenated and deoxygenated atmospheres. In this

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. Reproducibility on the other hand, refers to the response generated by different sensing reagents when exposed to the same amount of O_2 gas. The RSD for the repeatability and reproducibility were 0.23% and 2.36%, respectively for 5 measurements. The similar observations have been reported in the literature [21] for repeatability and reproducibility. 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.

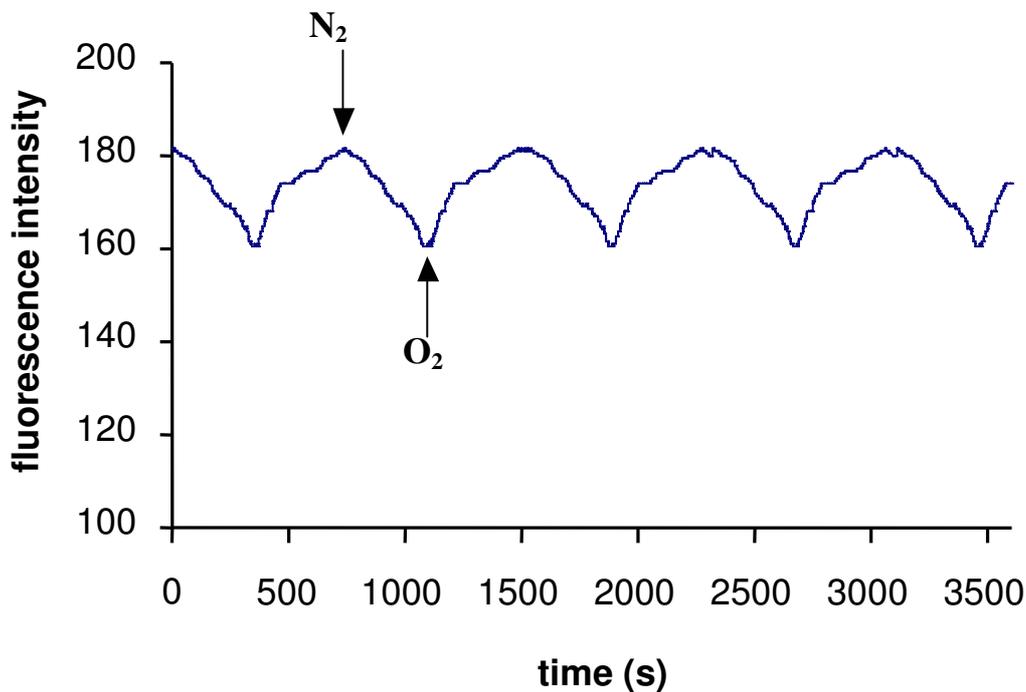


Figure 6 : Typical response of SPAN solution towards the same amount of O₂ gas. The N₂ gas was used to regenerate the polymer every after O₂ gas exposure.

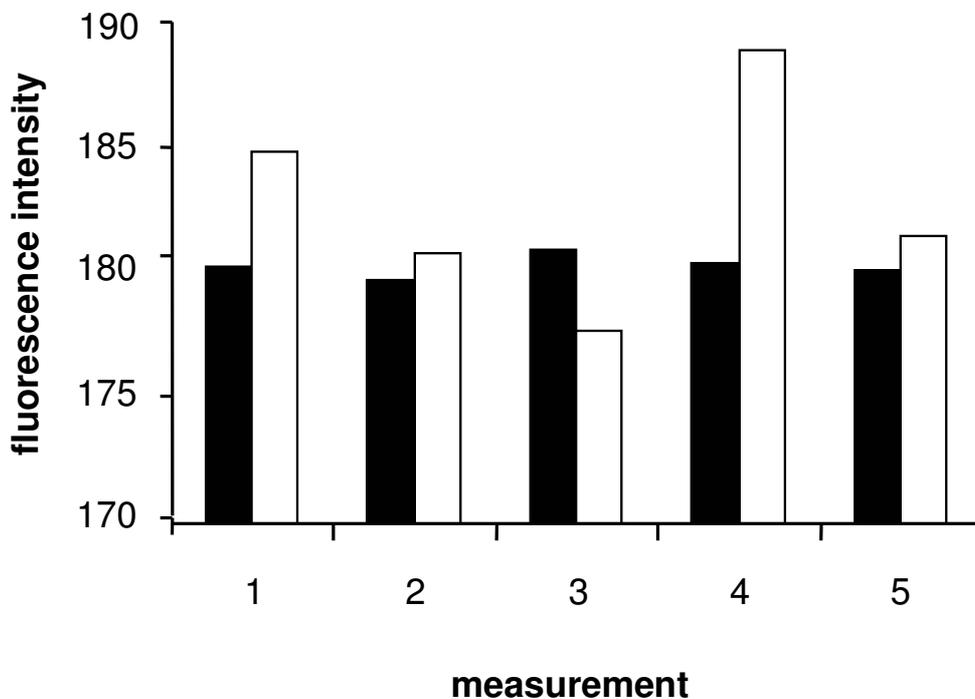


Figure 7 : The reproducibility (□) and repeatability (■) of the sensing reagent upon exposure to O₂ gas

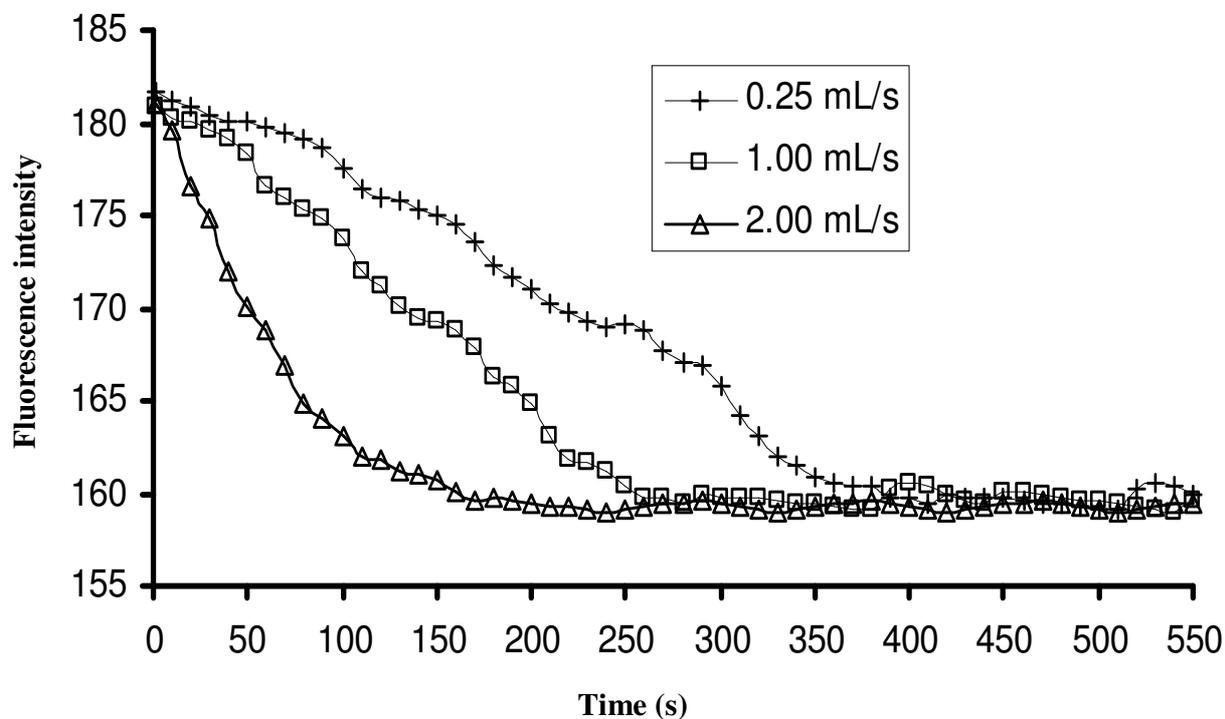


Figure 8 : The effect of flow rate of O₂ gas on the response time of SPAN solution

As shown in Figure 8, 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 2.50 mL/s. The similar observation on the effect of the flow-rate on response time has been reported in the literature. Mehamod et al. [25] reported that the higher flow-rate offered higher reaction rate and shorter response time, whereas lower flow-rate gave the opposite effects.

Conclusion

SPAN was successfully obtained when EB was doped by using sulfuric acid with doping level of about 32% as determined by TGA and elemental analysis. Fluorescence characteristics of SPAN solution upon exposure to O₂ gas showed that SPAN has the potential to be exploited as sensing material for O₂ 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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