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Polyaniline (PAni) optical sensor in chloroform detection

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ABSTRACT

A novel Fiber Bragg grating (FBG) coated with PAni film was used as a sensitive optical sensor for chloroform detection. In this study, the effect of synthesis parameters such as different dopant ratios (Ani: AOT = 5: 3, 5: 5 and 5: 7) and different polymerization temperatures (−5 °C, 0 °C and 25 °C) toward the efficiency of sensors were being investigated. Among the PAnis, PAni 5: 5 (0 °C) possessed the highest conductivity (1.627×10^{-2} S/cm) and the best efficiency (sensitivity = 0.0015) with response time of 7 s. The mechanism during chloroform detection was studied through Fourier Transform Infrared (FTIR) and Ultraviolet-visible (UV–vis) analysis, and the results showed clearly the physical interaction of the partial negative charge ($Cl^{\delta-}$) of chloroform with the partial positive charge ($NH^{\delta+}$) on PAni chain. Besides, the sensor performance such as recyclability, selectivity, limit of detection (LOD), limit of quantitation (LOQ) and real sample analysis was studied in details in this study.

1. Introduction

Chloroform is released into the environment through several anthropogenic sources where industrial sites using it in the production line. Exposure to 50 ppm of chloroform can damage human health. Traditional methods in chloroform detection include spectrophotometer and metal oxide [1,2]. These methods are not suitable for on-line monitoring because they are easily affected by the environmental factors such as surrounding temperature and air humidity.

To overcome these problems, sensing devices based on the optical fiber has been developed due to their advantages such as electrical immunity, small size, remote real-time sensing, tolerant of harsh environment (not easy to corrode) and long term stability. Optical fiber sensor is a device that has the ability to convert a physical and chemical into a detectable signal such as current, absorbance, acoustic variable and so on [3]. One of the most popular optical fibers used in sensor application is fiber Bragg grating (FBG).

Nowadays, many researchers have made progress on conducting polymers (CPs) because of their incredible electrical conductivity that range from semiconductor to near-metallic behavior [4]. Among CPs, polyaniline (PAni) is the most widely studied in numerous applications due to its promising properties such as ease of synthesis, low fabrication cost and low density. Besides, a key property that distinguishes PAni from other CPs is that it can exist in different oxidation states with different colour changes [5]. This unique property of PAni makes it potentially applicable as a sensor device in chemical detection.

Based on our knowledge, the novel PAni coated FBG sensor for chloroform detection has not been reported before. The sensitivity of PAni coated FBG in the chloroform detection was monitored by adjusting the synthesis parameter such as different dopant ratios and different polymerization temperatures. After obtaining the optimum synthesis parameter for PAni, the mechanism for the interaction between chloroform and PAni was investigated through Fourier Transform Infrared (FTIR) and Ultraviolet-visible analysis. The limit of detection (LOD), limit of quantitation (LOQ), interference study, real sample analysis, recovery and reusability of the sensor were also investigated in detail in this study.

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2. Experimental

2.1. Chemicals and materials

Aniline (Ani), dioctyl sodium sulfosuccinate (AOT), ammonium persulphate (APS), toluene (99.8%), and lithium chloride (LiCl, 96.5%) and acetone (99.5%) were purchased from Sigma- Aldrich, USA while hydrochloric acid (HCl, 37%) was purchased from RCl Labscan, Thailand. Chloroform (99%) and hydrofluoric acid (HF, 48%) were purchased from MERCK, Germany. Distilled water was purified by using Millipore water purification system. Another material used in this study is a single mode Fiber Bragg Grating (FBG) with reflectivity of >90%, bandwidth of <0.3 nm and centre wavelength of 1557 nm was purchased from Kumpulan Abex. Sdn. Bhd., Malaysia.

2.2. Synthesis and characterization of PAni

PAni was synthesized through chemical oxidation method using Ani as a monomer, AOT dopant and APS as oxidant. PAni was synthesized using different synthesis parameters such as different dopant ratios, different polymerization temperatures and etc.

For the synthesis of PAni with Ani: AOT ratio of 5: 5, AOT (6.6684 g) was dissolved in 1 M of HCl aqueous solution. Then, Ani (1.3970 g) was slowly added into AOT solution and stirred for two hours in order to obtain a uniform Ani/AOT mixture. It was followed by the slow addition of APS (3.423 g, dissolved in 33.33 mL of 1 M HCl solution) solution into the mixture to initiate the polymerization. Reaction was carried out at 0 °C in the ice bath for 24 h. The polymerization process was terminated by adding excess amount of toluene. PAni was extracted into toluene phase, unreacted Ani monomer, AOT and APS were in the aqueous phase and removed by the separating funnel. The organic phase was then washed with more distilled water to remove the left over water soluble impurities. The desired concentration of PAni solution (3%) was obtained by extraction using rotary vapour. Concentration of PAni solution was expressed as weight percentage (w/w%).

The synthesis route was repeated for different molar ratios of Ani: AOT (5: 3 and 5: 7) at 0 °C. Besides, the similar synthesis routes were also repeated for different polymerization temperatures such as 25 °C and −5 °C. At sub-zero polymerization temperature (−5 °C), the reaction was carried out in the circulating cooling bath for 24 h and the LiCl was added to avoid the freezing of the polymer solution. In this study, PAni samples with different molar ratios of Ani: AOT are labelled as PAni 5: 3, PAni 5: 5 and PAni 5:7.

The PAni solution in toluene was coated on glass slide using spin coater (model: SPS, Spin 150-NPP) with 3000 rpm for the film preparation for further characterizations such as FTIR analysis, UV–vis analysis and conductivity study. The chemical structure of PAni was investigated by using FTIR-ATR spectrometer (Perkin Elmer RX 1 model) from wavelength range of 400 cm^{-1} to 4000 cm^{-1} with resolution of 4 cm^{-1} and UV–vis spectrometer (UV-1650 PC model) in the wavelength range of 300 nm to 900 nm. The conductivity of PAni film was measured by using four-point probe, Loresta HP in conductivity range of 10^{-7} to10^{7} S/cm.

2.3. Application of PAni coated FBG sensor in chloroform detection

The optical FBG was modified by remove the cladding part using HF (46%) solution and rinsed with distilled water to remove excess HF left on the FBG. Then, PAni toluene solution was dropped coated onto the FBG surface and dried at room temperature.

In this study, PAni coated FBG sensor was connected to the three-directional coupler. The incident wave (E_{in}) from laser entered into port 1 and exited by passing through port 2 before it entered into the PAni coated FBG sensor. The output wave (E_{out}) was produced when light passed through the FBG device and exited from port 3 of the coupler, and recorded by using OSA detector. Data obtained from optical sensor analysis were interpreted by using “Lab View” software.

PAni coated FBG sensor was immersed into different concentration of chloroform solutions (10 ppm, 30 ppm, 50 ppm, 70 ppm and 100 ppm). Before chloroform detection, the initial Bragg wavelength of PAni coated FBG sensor was recorded as λ_o. After immersion in chloroform solutions for 10 s, the final Bragg wavelength of sensor in chloroform solution was recorded as λ. Then, sensor was immersed into distilled water and dried at room temperature in order to recover the sensor back to its initial state. Thus, the Bragg wavelength shift is represented by $\lambda_B = \lambda - \lambda_{o.}$

2.4. Proposed mechanism for the interaction between chloroform and PAni

For the sensor application part, the proposed mechanism for the interaction between chloroform and PAni was investigated in detail by using FTIR and UV–vis analysis.

2.5. Sensor performance of PAni coated FBG in chloroform detection

In this study, the sensor was evaluated for the following aspects; recyclability, selectivity, LOD, LOQ, real sample analysis and recovery.

3. Results and discussion

3.1. Chemical characterizations of PAni

3.1.1. FTIR analysis

The FTIR spectrum of PAni with Ani: AOT ratio of 5: 5 that synthesized at 0 °C is shown in Fig. 1. In general, PAni with Ani: AOT ratios of 5: 3, 5: 5 and 5: 7 and different polymerization temperatures (−5 °C, 0 °C and 25 °C) exhibit similar FTIR spectra form 400–4000 cm^{-1}. The vibration bands at 879–894 cm^{-1} and 1189–1206 cm^{-1} correspond to the C—H bending out of plane of the aromatic ring and the C=O symmetric and asymmetric stretching from AOT dopant, respectively. The band at 1286–1298 cm^{-1} represents the C—N stretching vibration in the benzenoid ring. The presence of two vibration bands at 1613–1619 cm^{-1} and 1466–1470 cm^{-1} are assigned to the C=C stretching vibration mode of quinoid and benzenoid ring, respectively. The bands at 2954–2960 cm^{-1} and 3242–3246 cm^{-1} are attributed to the C—H and N—H stretching, respectively [6].

3.1.2. UV–vis analysis

In principle, PAni with different dopant ratios and different polymerization temperatures exhibit similar UV–vis spectra form 300–900 nm as shown in Fig. 2(a) and (b), respectively. The absorption peak at ~350 nm refers to the π-π* transition of benzenoid rings, while the peak at ~420 nm indicates the polaron to π* transition and localized polaron bands of protonated imines C=N. In addition, the strong absorption peak at ~765 nm significantly proved all the resulted PAnis are in the form of ES state (conductive form) [7]. Both characterizations of FTIR and UV–vis analysis significantly confirmed the chemical structure of the resulted PAni.

3.1.3. Conductivity analysis

The conductivity of PAni (different dopant ratios) and (different polymerization temperatures) are shown in Fig. 3. Increasing of AOT dopant ratio from 3 to 5 will significantly increased the conductivity of PAni from 1.157×10^{-2} S/cm to 1.627×10^{-2} S/cm. It is