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Effect of HEC/PVDF coating on glass substrate for formaldehyde concentration sensing

***Abstract**. This paper has reported demonstration of simple and low cost formaldehyde sensor utilizing Hydroxyethyl cellulose/Polyvinylidene fluoride (HEC/PVDF) coated glass substrate. It was integrated with Arduino microcontroller for data acquisition of the variation of the transmitted light during the sensing. The formaldehyde detection is based on the change in refractive index (RI) of the HEC/PVDF as a sensitive material which modulate the output light intensity when the concentration level of the formaldehyde increases. A significant response towards formaldehyde concentrations level was observed with the output voltage reduced linearly from 1.5V to 0.8V. The sensitivity of the proposed sensor improves by a factor of 1.09 as compared to uncoated glass substrate. It also performed better in term of stability, response time and hysteresis. The proposed sensor evades the used of costly optical sensor fabrication and manufacturing process which are more practical for large production while maintaining a good sensing performances. Based on the experiment results, the proposed approach has exhibited convincing potential as a formaldehyde sensor.*

***Streszczenie.** W tym artykule przedstawiono demonstrację prostego i taniego czujnika formaldehydu wykorzystującego podłoże szklane powlekane hydroksyetylocelulozą/polifluorkiem winylidenu (HEC/PVDF). Został zintegrowany z mikrokontrolerem Arduino w celu akwizycji danych o zmienności przepuszczanego światła podczas wykrywania. Wykrywanie formaldehydu opiera się na zmianie współczynnika załamania światła (RI) HEC/PVDF jako wrażliwego materiału, który moduluje natężenie światła wyjściowego, gdy poziom stężenia formaldehydu wzrasta. Istotną reakcję na poziom stężeń formaldehydu zaobserwowano przy liniowym obniżeniu napięcia wyjściowego z 1,5V do 0,8V. Czułość proponowanego czujnika poprawia się o współczynnik 1,09 w porównaniu z niepowlekanym podłożem szklanym. Działał również lepiej pod względem stabilności, czasu odpowiedzi i histerezy. Zaproponowany czujnik pozwala uniknąć kosztownego wytwarzania i procesu produkcyjnego czujnika optycznego, które są bardziej praktyczne w przypadku dużej produkcji przy zachowaniu dobrych parametrów wykrywania. Na podstawie wyników eksperymentu zaproponowane podejście wykazało przekonujący potencjał jako czujnik formaldehydu. (**Wpływ powłoki HEC/PVDF na podłoże szklane do wykrywania stężenia formaldehydu**)*

Keywords: glass substrate, HEC/PVDF, formaldehyde sensor
Słowa kluczowe: podłoże szklane, HEC/PVDF, czujnik formaldehydu

Introduction

Formaldehyde is a chemical element that is well known as one of the Volatile Organic Compounds (VOCs) which could cause hazardous environmental effects and prolong danger to the human health [1]. It could be generated by several sources such as forest fires, burned fossil fuels, automobile fumes, rain water and surface waters [2-4]. It has been employ in various applications such as dry cleaning solutions, oil soluble resins, fabrics, cosmetics, cleaning products, fertilizer, house decoration, disposable sanitary products, plywood and textiles industries [5-9]. Due to Its pivotal impact to environment and human health, it has attracted numbers of researchers to develop a highly accurate formaldehyde detection and monitoring system.

Numerous studies on optical sensor has been conducted on various platforms such as plastic optic fiber [10] , silica microfiber [11], PEN substrates [12], paper substrates [13], ITO/PET substrates [14] and polyimide substrates [15]. However, most of the platforms are costly and required complicated design. Glass substrate is an alternative for cheap sensing platform. It could be realize by combining the glass substrate with sensing circuit contains of LED, photodiode, amplifier and Arduino microcontroller. The sensor does not need any power source from battery while in operation because it is using LED as the light source. The light source from LED is transmitted through the glass substrate and receive by photodiode to convert to voltage signal. The Arduino is used for signal processing of transmitted light to compute data of output voltage analysis.

However, the sensing response for uncoated glass substrate produces a low sensing performance because it has small refractive index contrast between the surround analyte. In order to increase the sensing response, a higher refractive index coating material is required. One of the sensitive material is Hydroxyethyl cellulose/Polyvinylidene fluoride (HEC/PVDF) which is a water-soluble cellulose derivative that is non-ionic. It is an odourless, tasteless, and non-toxic white to light-yellow powder that dissolves quickly in hot and cold water but not in most organic solvents. It also exhibits a stable, low-cost, and widely used material due to its porous character and strong water absorption capabilities and it has been previously employed as a coating material to improve relative humidity sensitivity of fibre sensor. The optical characteristics of the composite coating alter in response to variations of its surroundings analyte. [16]. The measurement is based on the intensity modulation approach, which examines the output intensity or voltage of transmitted light for variations in formaldehyde concentrations level.

Current optical formaldehyde detection mostly employed expensive laser source, optical spectrum analyser and photodetector which are not viable for mass production. A more practical sensor with low manufacturing cost is required for large scale production [17]. This paper reported the development of formaldehyde sensing device based on HEC/PVDF coated glass substrate which has been demonstrated for the first time to our knowledge. The sensing circuit contain several basic components such as light-emitting diode (LED) as a light source and the photodiode to convert the output light that travel through the glass substrate to the voltage signal. Green LED was chosen for the light source based on previous study conducted by [10]. Arduino microcontroller was used for signal processing and data acquisition to reduce costly equipment.

Experimental details

Prior of the coating procedure, the glass substrates need to be prepared. Microscope glass substrates (Heathrow Scientific LLC, USA) were first immersed in a container of soapy water, clear water and acetone [CH_3COCH_3] (Bendosen Laboratory Chemical, Germany) for 15 minutes in a sequence for the ultrasonic cleaning process. It was then located in an oven at 90^{o}C for 1 hour to remove organic material [18]. As for the preparation of Hydroxyethyl Cellulose/Polyvinylidene fluoride (HEC/PVDF), 1 g of PVDF powder (Mw=275,000) was dissolved in 120 ml dimethyl form amide (DMF) in a water bath at 90˚C for the HEC/PVDF . The PVDF solution was then mixed with 4 g of hydroxyethyl cellulose (HEC). The mixed solution was continually stirred at room temperature for around 10 hours to develop the mesh gel three-dimensional structure (hydrogel). The HEC/PVDF mixture was then gradually placed onto the glass substrate and allowed to dry for 48 hours [19].

Experimental setup of the proposed sensor is depicted in Figure 1. Green LED with wavelength between 495 nm to 570 nm was used as a light source based on report in [20]. Glass substrate was positioned between the LED and photodiode. They were set as closed as possible at both edges of the glass substrates. The function of the photodiode is to convert the light intensity into voltage. The LED was placed at the angle of 50^o to the edge of the glass substrate to ensure 60^o of incident angle which lead to total internal reflection. The amplifier circuit was used to amplify the voltage signal for signal processing using Arduino microcontroller [21]. The experiment was conducted in room temperature to emulate the real environment scenario. The experiment was repeated for formaldehyde concentration level from 0% to 100% in which the results were investigated with refer to 0% (pure water)

When the light transmits through the glass substrate, the scattering effect from the coated materials upon exposure to varying amounts of formaldehyde was mostly due to a decrease of light intensity during the sensing experiment. The sensing mechanism is shown in Figure 1. The output light intensity of the proposed sensor reduced when expose to the increasing concentrations level of the formaldehyde. This is due to the refractive index contrast between the coating layer and the glass substrates increase as the formaldehyde concentrations increase. Thus, greater light leakage would cause less light intensity reach to photodetector when concentrations increase. This decrease the output voltage from the photodetector. Furthermore, more light scattering occur which lead to higher leakage and lower output voltage value [21]. Other factors contributed to this phenomenon is the variation of the surrounding refractive index and change in electrical conductivity due to adsorption process when analyte applied to the coating layer.

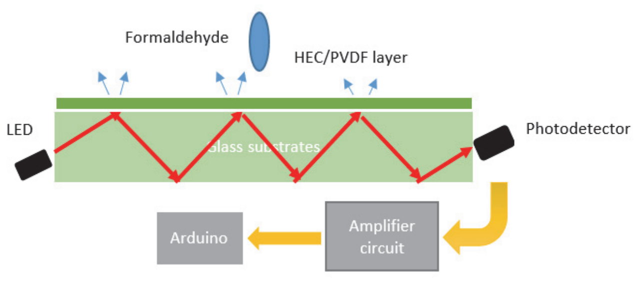


Fig.1. Setup of the HEC/PVDF gel coated glass substrate for formaldehyde sensing

Result and discussion

Figure 2 shows the sensing response of the proposed sensor when exposed to increasing formaldehyde concentrations level. It shows that the glass substrate coated with HEC/PVDF has the higher sensitivity and linearity for 0.0076 V/% with 97.69% respectively as compared to the uncoated glass with sensitivity of 0.007 V/% and linearity of 97.21%. Water has a refractive index of 1.333 whereas formaldehyde has a refractive index of 1.3746 [21], hence refractive index of the HEC/PVDF increase with the change of the surround molecule which has been measured by Abbe's refractometer [22]. The composite coating layer produce higher RI value as compared to the glass substrate which lead to lossy and decrease the output voltage. The reproducibility of the uncoated glass substrate when exposed to difference formaldehyde concentrations level is shown in Figure 3 (a) while for the HEC/PVDF coated glass substrate shows in Figure 3(b). The graphs reveal acceptable repeatability results for both samples. The output voltage when the measurements were conducted in forward and reverse measurement is shown in Figure 4. Based on Figure 4 (a), the uncoated glass substrate produces quite large difference output voltage which is around 0.12V at 80% concentration level while he HEC/PVDF coated glass substrate produces better hysteresis trend with smaller output voltage difference as shown in Figure 4 (b). The difference is due to the variation rates of adsorption and desorption of analyte molecules on the coating layer which leads to a slight deviation for the sensor response [23]

The response time and the recovery time for both samples were shown in Figure 5. Response time was performed by applying formaldehyde from minimum concentration value directly to maximum concentration value while recovery time was performed by applying formaldehyde from maximum concentration value directly to minimum concentration. Figure 5 (a) shows the overall time response graph for both samples. Response time and recovery time of both samples are shown in Figure 5 (b) and Figure 5 (c) respectively. The response time and recovery time of the uncoated glass are 0.5 seconds which is slower than the HEC/PVDF coated glass substrate with 0.25 seconds. This results proved that a glass substrate coated with HEC/PVDF improved the time response of the uncoated glass substrate. Eventually, stability test was performed by logging the output data for 10 minutes (600 seconds) in every second for five formaldehyde concentrations level to ensure the practicality of the sensor, Figure 6 (a) shows the stability data for the uncoated glass substrate. The graph shows significant attenuation as compared to the HEC/PVDF coated glass in Figure 6 (b) which has better stability.

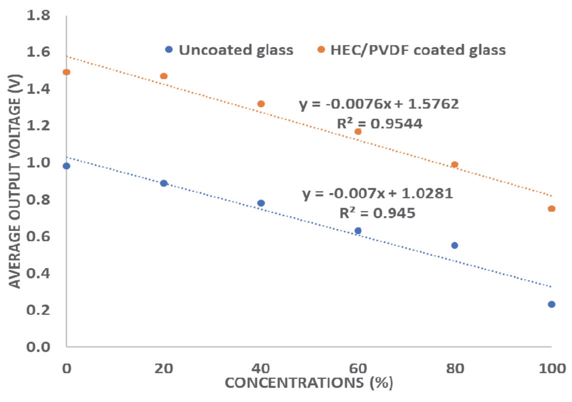
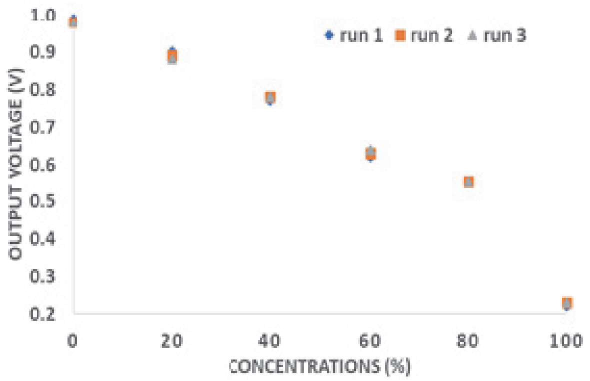
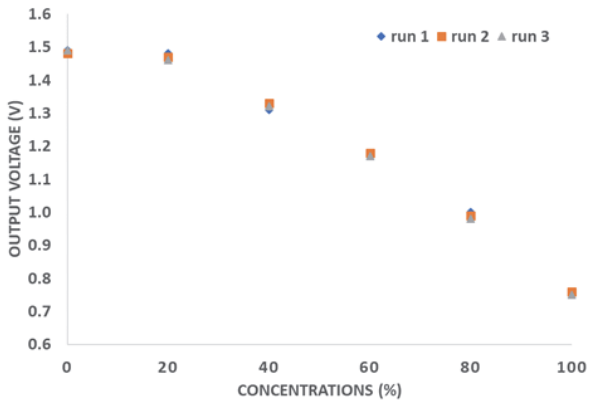


Fig.2. Trendline graph when exposed to increase formaldehyde concentrations level

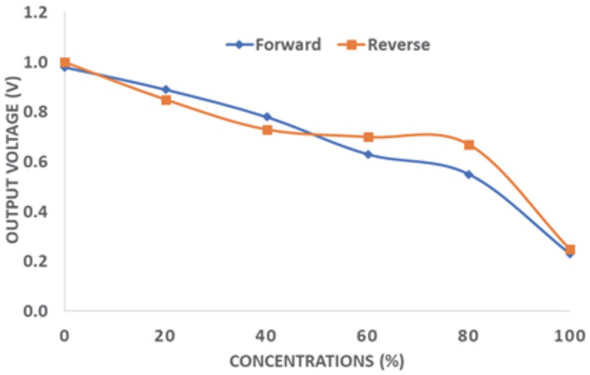


(a)

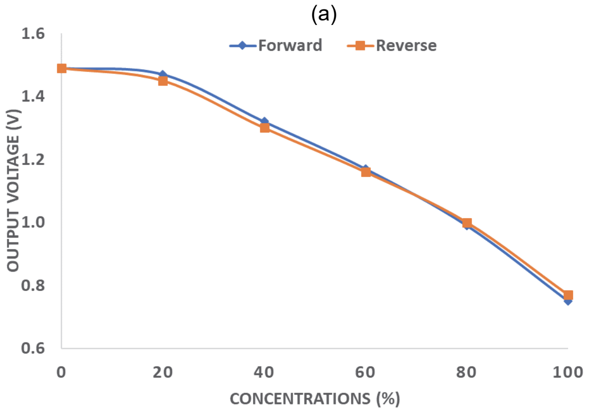


(b)

Fig.3. Reproducibility of; a) Uncoated glass and b) HEC/PVDF coated glass

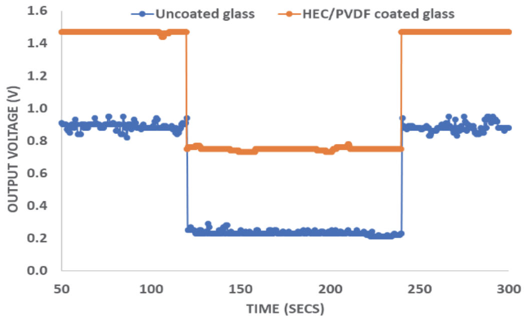


(a)

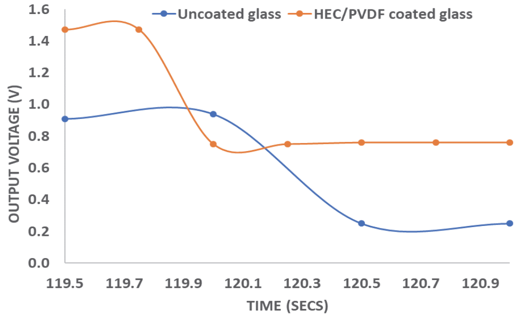


(b)

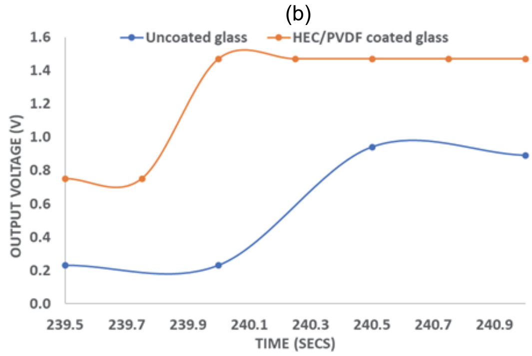
Fig.4. Hysteresis graph for; a) Uncoated glass and b) HEC/PVDF coated glass



(a)

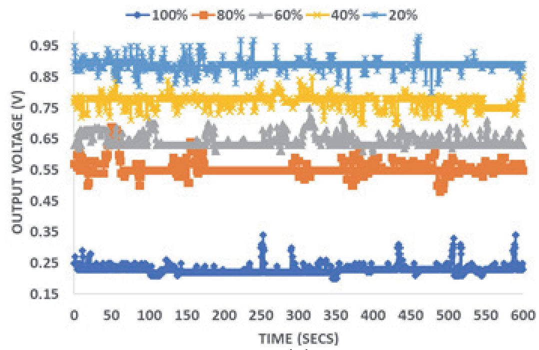


(b)

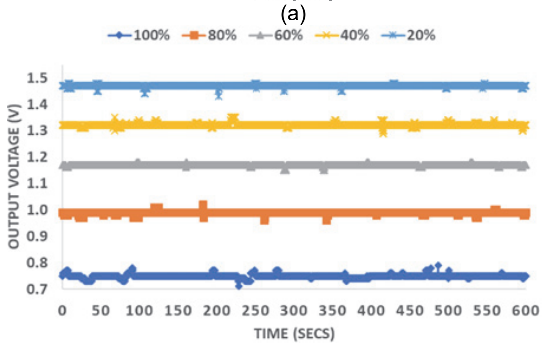


(c)

Fig.5. Time reponse for; a) Overall, b) Response time and c) Recovery time



(a)



(b)

Fig.6. Stability graph for; a) Uncoated glass and b) HEC/PVDF coated glass

Conclusion

A formaldehyde sensor based on HEC/PVDF coated glass substrates has been successfully demonstrated in this paper. The structure has superiority in term of evading the used of expensive laser source based equipment which is less viable for large scale production. The components used for the sensing circuit are widely available in the market which lead to more practical sensing devices. Overall the proposed sensor has shown better sensing performances results in term of sensitivity, linearity, response time, repeatability, stability and hysteresis as compared to its counterpart. This is because HEC/PVDF coated material improved the light interaction towards the variation of refractive index of the coating layer when the formaldehyde concentrations level increase. As for recommendation, other coating material could also be utilized as a sensitive material to analysed the sensing performance towards formaldehyde.

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