Fluorescence Sensing of Nitrite Ions on Polyvinylpyrrolidone/Zinc Oxide Composites Prepared by Impregnation Method

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Abstract. A series of polyvinylpyrrolidone/zinc oxide (PVP/ZnO) composites with different loading amounts of PVP was prepared by an impregnation method. Successful formation of the composites was analyzed by the Fourier transform infrared (FTIR), diffuse reflectance ultraviolet-visible (DR UV-Vis) and fluorescence spectroscopies. Prepared composites were then further tested as fluorescence sensors by conducting quenching studies in the presence of nitrite ions (NO$_2^-$). Among the prepared composites, the ZnO with 1% PVP exhibited the highest sensing performance for the NO$_2^-$ detection ($K_{sv} = 0.07 \mu M^{-1}$). The efficiency of the composite was ca. 1.7 and 1.4 times higher than the bare ZnO and the best composite prepared by the physical mixing method, respectively. These results suggested that impregnation method is a suitable method to prepare the PVP/ZnO composites as fluorescence sensor for the NO$_2^-$ detection.

Keywords: polyvinylpyrrolidone/zinc oxide, composite, impregnation, fluorescence sensor, nitrite ion

1. Introduction
Nitrite (NO$_2^-$) is commonly used as a preservative and fertilizing agent for food as well as an inorganic fertilizer. Since NO$_2^-$ has a high level of solubility in water, these ions also have high mobility, which has led to constant threats whenever agriculture processes are involved [1]. The emergence of NO$_2^-$ as one of the hazardous contaminants has become a grave concern since NO$_2^-$ can react with secondary or tertiary amines to form nitrosamines, which are carcinogenic compounds [2-4]. Ingestion of NO$_2^-$ might cause endogenous nitrosation that is probably carcinogenic to human [5] and associated with colorectal and stomach cancers [6]. Furthermore, NO$_2^-$ is also known to result in respiratory deficiencies as NO$_2^-$ would react with hemoglobin forming methemoglobin, which disturbs the transport of oxygen [7, 8]. Therefore, it is a must to develop tools or methods that are simple, non-toxic, selective and sensitive to detect the presence of NO$_2^-$.
For nitrite/nitrate determination, one of the most generally reported methods is spectroscopy method owing to its great limit of detection and easy protocols [1]. Particularly, fluorescence sensors have attracted many attentions since they are simple, their signal can be amplified, they can be fabricated easily into devices, and they can be combined with various outputs [9]. One of the best candidates for a simple, inexpensive, and non-toxic solid material in the detection of NO$_2^-$ is a semiconductor-based sensor. Particularly, zinc oxide (ZnO) has been widely used as a sensor for the detection of various gasses, pollutants, and biomolecules [10-13].

As semiconductor gas sensor, ZnO has been extensively investigated for the detection of gas leaks and environmental monitoring of gaseous pollutants. For instance, ZnO showed excellent sensitivity to detect some flammable gasses as well as corrosive vapors with fast response-recovery characteristic, great selectivity, and stability [10]. ZnO was also reported serving as a sensor for sensing liquefied petroleum gas (LPG) and ethanol [11]. It was observed that ZnO also has good sensitivity at low temperature and it also showed better response and shorter recovery time. The application of ZnO as a sensor for methanal and xylene has also been investigated [12]. In addition, ZnO was also pointed out to improve signal in DNA sensor arrays [13].

In order to enhance the performance of ZnO as a sensor, ZnO can be modified with polymers [14-17]. It is recognized that grafting polymers onto the surface of ZnO was an effective way to improve its dispersion in a polymer matrix and the composites showed improved properties [14]. One of the potential polymers is polyvinylpyrrolidone (PVP), which has been reported to be a potential fluorescence sensor for the detection of nitrate (NO$_3^-$) [18]. Recently, the addition of PVP to ZnO by a physical mixing method has been reported to be able to increase the sensing efficiency of ZnO towards the NO$_2^-$ detection [15]. In this study, we newly reported a higher enhancement of the fluorescence sensing capability for NO$_2^-$ detection when the PVP/ZnO composites were prepared by an impregnation method.

2. Experimental Method

2.1. Materials

The materials used were zinc acetate dehydrate 99.5% (Zn(CH$_3$COO)$_2$.2H$_2$O, QRëc), sodium hydroxide pellet 99 % (NaOH, QRëc), cetyltrimethylammonium bromide (C$_{16}$H$_{33}$BrN, CTAB, Fischer Scientific), polyvinylpyrrolidone 45% in H$_2$O ((C$_6$H$_9$NO)$_n$, PVP, Sigma-Aldrich), sodium nitrite 99.5% (NaNO$_2$, Merck), and distilled water.

2.2. Methods

2.2.1. Preparation of ZnO. Zinc acetate dihydrate, Zn(CH$_3$COO)$_2$.2H$_2$O was used as a precursor to synthesize the ZnO. The Zn(CH$_3$COO)$_2$.2H$_2$O (4.5 g) was dissolved in distilled water (100 ml) as solution A. For the preparation of solution B, NaOH (6.4 g) was dissolved in distilled water and followed by the addition of CTAB (7.28 g) into the mixture and stirred for 1 hour to obtain a homogeneous solution. After 1 hour, solution A was added into solution B and heated at 70 °C for 1 hour. The remaining solid was subsequently filtered and washed with distilled water. The solid powder was dried at room temperature and then calcined at 500 °C at a rate of 1.0 °C min$^{-1}$ and further tempered for another 1 h at the same temperature.

2.2.2. Preparation of PVP/ZnO composites. Various PVP/ZnO composites were prepared by an impregnation method, in which the concentration ratios were varied to 0.1, 1 and 3 % (v/w). The samples were labeled as PVP(x)/ZnO, with x that shows the ratio of PVP to the ZnO. For a typical synthesis of PVP (1)/ZnO composite, the ZnO (1 g) was dispersed in distilled water (30 mL). The PVP (0.2020 mL) from 5 % PVP solution was then added dropwise to the mixture containing ZnO and distilled water, followed by stirring and drying at 80 °C on a hot plate.
2.2.3. Characterizations. As for characterizations of the prepared ZnO and PVP/ZnO composites, FTIR spectroscopy (Thermo Scientific, Nicolet iS50) was applied to investigate the functional groups in the prepared ZnO and PVP/ZnO composites. For the measurement, potassium bromide (KBr) pellet technique was used. The FTIR spectra were measured in the range of 400 to 4000 cm\(^{-1}\) with 32 scan number. Nitrogen gas was purged into the system before analysis to exclude moisture for better background correction. DR UV-Vis spectroscopy (UV-2600 with an integrating sphere, Shimadzu) was used to measure the absorption spectra of the samples. The absorption spectra were recorded in the wavelengths range from 250 to 500 nm. Scan speed was at the rate of 300 nm min\(^{-1}\) and the slit width was set at 1 nm. As a reference, barium sulfate (BaSO\(_4\)) was used in the measurement. The fluorescence spectra were recorded on the fluorescence spectrophotometer (FP-8500, JASCO) at room temperature. The emission spectra were measured when the excitation wavelength was 365 nm.

2.3. Sensor tests
Sensor tests for the detection of NO\(_2^−\) were carried out based on the quenching study, by monitoring the decreases in the emission intensity of the sensor when various concentrations of the NO\(_2^−\) were added into the sensor. Typically, the sensor sample (0.3 g) was transferred into a fluorescence sample holder and placed at the fluorescence instrument. Initial readings for excitation and emission peaks were firstly recorded in the absence of the NO\(_2^−\). As for the quenching test, the selected concentration of NO\(_2^−\) (2−10 μM) with a volume of 10 μL was added slowly on top of the sample. The emission spectra were then recorded at an excitation wavelength of 365 nm for ZnO and all the PVP/ZnO composites. The efficiency for the detection of the NO\(_2^−\) was further determined by Stern-Volmer plot on each of the prepared sample.

3. Results and Discussion

3.1. Functional groups
The functional groups of PVP, ZnO, and PVP/ZnO composites were examined by using the FTIR spectroscopy. FTIR spectroscopy gives qualitative information on the type of functional groups that present in the samples. As shown in Figure 1(a), PVP gave OH stretching vibration from a water molecule at around 3447 cm\(^{-1}\) due to the hydrophilic nature of the PVP, while the peaks observed around 2800-3000 cm\(^{-1}\) were assigned to C−H stretching. The characteristic peaks of PVP could be seen at 1655 and 1461 cm\(^{-1}\), which were corresponding to C=O and C−N stretching, respectively. The presence of C−N stretching was also shown at around 1370 cm\(^{-1}\) and the peaks below 700 cm\(^{-1}\) gave the evidence of C−C chains and N−C=O bending [19].

![Figure 1. FTIR spectra of (a) PVP, (b) ZnO, (c) PVP(0.1)/ZnO, (d) PVP(1)/ZnO and (e) PVP(3)/ZnO samples](image-url)
Displayed in Figure 1(b) is the FTIR spectrum of ZnO. The ZnO showed a sharp peak at around 420 cm$^{-1}$ that could be assigned as the stretching mode of Zn–O [20, 21]. Figures 1(c)–(e) show the FTIR spectra for the PVP/ZnO composites. All the composite samples gave the presence of Zn–O stretching as well as two peaks appeared at 1647 and 1434 cm$^{-1}$ that could be related to C=O and C–N stretching, respectively. Both of the latter peaks came from the PVP. It has been suggested that the peak shift can be related to the hydrogen bond formation [19, 20]. Therefore, the shifting observed on the PVP/ZnO samples might be the outcome of the hydrogen bonding interaction between the surface hydroxyl of ZnO and the functional group in the PVP. Another responsibility that can be proposed was the existence of a strong coulombic interaction between the ZnO and the polymeric matrix [22]. When the amount of PVP in the PVP/ZnO composite increased, the intensity of C=O stretching and C–N stretching also increased owing to the increment amount of PVP contained in the PVP/ZnO composites. The FTIR spectra suggested the successful preparation of the PVP/ZnO composites.

3.2. Optical properties
The optical properties of the PVP, ZnO, and PVP/ZnO composites were investigated using the DR UV-Vis spectroscopy and are displayed in Figure 2. As shown in Figure 2(a), PVP exhibited intense narrow bands centered at 265 and 370 nm, which might be due to the presence of C=O and N–C groups, respectively [19]. On the other hand, Figure 2(b) shows a strong absorption peak of ZnO in the UV region, which was centered at 330 nm due to the electron charge transfer in the Zn–O linkage [23, 24]. The DR UV-Vis spectra of the PVP/ZnO composites are shown in Figures 2 (c)–(e). All the composite samples showed similar absorption peak to each other, where the main absorption peak of ZnO was clearly observed and the loading amount of PVP also slightly increased the absorption band of PVP. It can be observed that the addition of PVP did not give considerable influence to the band structure of the ZnO.

3.3. Fluorescence properties
Fluorescence spectroscopy is a powerful non-destructive technique to explore the fluorescence properties of the materials. Figure 3 shows the emission spectra of the prepared ZnO and PVP/ZnO composites. Shown in Figure 3(a) is the emission spectrum for ZnO when the excitation wavelength at 365 nm was used. ZnO gave one broad emission peak at 517 nm, which has been recognized as the green emission of ZnO, reflecting the presence of oxygen defect on the surface and deep level of the ZnO [22]. As can be seen from Figure 3(b)–(d), all PVP/ZnO composites have a lower emission intensity as compared to the ZnO. In addition to the reduced fluorescence intensity, the addition of PVP also shifted the emission peak to a longer wavelength. The decrease in fluorescence intensity and
the strong peak shifting indicated that there were interactions existed between the PVP and the ZnO. The most possible interactions between PVP and ZnO would occur via hydrogen bonding and/or coulombic interaction.

3.4. Sensing performance
The sensing performance of the ZnO and the PVP/ZnO composites towards the NO$_2^-$ was evaluated via quenching tests by monitoring the decreases in the emission intensity after the additions of various concentrations of the NO$_2^-$ (0–10 μM) to the ZnO and the PVP/ZnO composites. All samples showed similar results, where the emission intensity was reduced gradually with the increase in the concentration of the NO$_2^-$.

As a representative, the changes of the emission spectra in the absence and presence of NO$_2^-$ for the PVP(1)/ZnO composite are illustrated in Figure 4(a).

The relative emission intensity can be strongly related to the concentration of NO$_2^-$ that investigated by a Stern-Volmer plot. In the plot, the relative emission intensity is expressed as a function of the NO$_2^-$ concentrations, following the Stern-Volmer plot as shown in Equation (1).

$$\frac{I_o}{I} = K_{SV} [Q] + 1$$

Where $I_o$ and $I$ show the fluorescence intensity without and with NO$_2^-$, respectively, $Q$ shows the concentrations of NO$_2^-$, and $K_{SV}$ is the Stern-Volmer quenching constant. The calculated $K_{SV}$ indicated the efficiency of the sensor. Higher $K_{SV}$ value suggested a larger efficiency of the sensor. All the ZnO and PVP/ZnO composites gave almost linear curves, suggesting that the ZnO and the PVP/ZnO composites can be potential fluorescence sensors in the detection of NO$_2^-$.

As a representative of the samples, Figure 4(b) illustrates the linear Stern-Volmer plots of the ZnO and the PVP(1)/ZnO composite in the presence of NO$_2^-$.

$K_{SV}$ values of the ZnO and the PVP/ZnO composites are given in Figure 5. The $K_{SV}$ value of the ZnO was determined to be 0.04 μM$^{-1}$. It was evident that the addition of PVP from 0.1 to 1% improved the ZnO sensing performance, where the $K_{SV}$ value increased from 0.04 to 0.05 and 0.07 μM$^{-1}$, respectively. Unfortunately, the sensing performance decreased to 0.026 μM$^{-1}$ when the loading amount of PVP was too high (3%). It was shown that the addition of PVP reduced the ZnO intensity, thus, when the loading of PVP was too high, the reduced emission intensity would decrease the sensitivity of the sensor. This study showed that the PVP(1)/ZnO was the best sample showing the highest efficiency towards the detection of NO$_2^-$.

![Figure 4. (a) Emission spectra of PVP(1)/ZnO in the absence and presence of different concentrations of NO$_2^-$ and (b) Stern-Volmer plots of PVP(1)/ZnO and ZnO samples](image-url)
Figure 5. Comparison of $K_{SV}$ values of ZnO and PVP-ZnO composites

It was reported that the best PVP/ZnO composite prepared by physical mixing, the PVP(0.1)/ZnO, gave $K_{SV}$ value of 0.05 $\mu$M$^{-1}$ [15]. Comparison to the best PVP/ZnO composite prepared by physical mixing showed that the best PVP/ZnO composite developed by the impregnation method gave a higher $K_{SV}$ value of 0.07 $\mu$M$^{-1}$. It was proposed that better interaction between the PVP and the ZnO prepared by the impregnation method would be the crucial factor to get a higher efficiency. Since the impregnation method employed a sonication step, the PVP would be dispersed better on the ZnO than that prepared by physical mixing. This study demonstrated that the impregnation method was better than the physical mixing to prepare the PVP/ZnO composites as fluorescence sensor of the $NO_2^{-}$.

4. Conclusion

The PVP/ZnO composites were successfully prepared by an impregnation method as evidenced by FTIR, DR UV-Vis, and fluorescence spectroscopies. The prepared ZnO and composites gave good linear Stern-Volmer plots with various concentrations of $NO_2^{-}$, suggesting the potential capability of these samples as fluorescence sensors for the $NO_2$ detection. The best composite, which was PVP(1)-ZnO, gave $K_{SV}$ value of 0.07 $\mu$M$^{-1}$, which was 1.7 times higher than that of the ZnO.

5. References

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Acknowledgements
The work was financially supported by the Ministry of Higher Education (MOHE, Malaysia) and the Universiti Teknologi Malaysia (UTM, Malaysia) through a Tier-1 Research University Grant (cost center code: Q.J130000.2509.06H66).