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Enhanced Detection of Nitrite Ions Over Copper Acetylacetonate/Polymeric Carbon Nitride Composites

Siti Maryam Jasman,[1] Hendrik O. Lintang,[2,3] Leny Yuliati*[2,3]

Summary: Nitrogen containing compounds such as nitrite ions (NO_2^-) may cause contaminations to the environment, food and drinking water, and they have a negative effect on human health. In this study, a novel fluorescence sensor was developed by modification of polymeric carbon nitride (CN) with copper(II) acetylacetonate ($Cu(acac)_2$). The polymeric CN was prepared by using urea as a precursor via thermal polymerization technique, while the $Cu(acac)_2$ was introduced onto the polymeric CN via an impregnation method. The formation of polymeric CN can be confirmed from the Fourier transform infrared (FTIR) and the diffuse reflectance ultraviolet visible (DR UV-Vis) spectroscopies. The polymeric CN exhibited three excitation peaks at 277, 315, and 370 nm owing to the presence of C=N, C=O, and C−N groups, respectively, while there was only one emission peak observed at 455 nm. The emission intensity was decreased with the increase of $Cu(acac)_2$ loading, suggesting certain interactions between the polymeric CN and the added $Cu(acac)_2$. The performances of the polymeric CN and $Cu(acac)_2$/CN composites as fluorescence sensors were evaluated for NO_2^- detection with concentration range of 0.5-4 μM. It was revealed that the C=N sites in the polymeric CN were the most favored quenching sites for the NO_2^-. With the addition of $Cu(acac)_2$ (0.1 mol%), the quenching rate for C=N sites was enhanced two times higher than that of the polymeric CN. This study demonstrated that the composite is a promising fluorescence sensor for the detection of NO_2^-.

Keywords: composites; copper(II) acetylacetonate; fluorescence sensors; nitrite; polymeric carbon nitride

Introduction

Polymeric carbon nitride (CN) is an N-substituted graphite framework consisting of π-conjugated graphitic planes formed by sp^2 hybridization of carbon and nitrogen atoms.[1] The polymeric CN is categorized as a semiconductor with band gap energy of ∼ 2.7 eV[2] and it contains graphitic stacking of CN layers, which are constructed from tri-s-triazine units connected by planar amino groups.[3] It can be produced on a large scale with low cost by bulk condensation of N-rich precursors, including urea, cyanamide and melamine.[1] The polymeric CN has been reported to show high photoluminescence (PL) intensity, good photostability, and excellent biocompatibility. All of these characteristics make the polymeric CN an ideal platform for catalysis,[4] bioimaging, drug delivery and sensing applications.[5–8] Previous studies reported

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the potential applications of the polymeric CN as chemosensors for DNA,[5] metal ions, such as Cu^{2+}, Ag^+, and Fe^{3+},[6,7] as well as nitrogen-containing compounds, such as N-nitrosopyrrolidine[8] and nitrate ions (NO_3^-).[9]

In this study, copper species/polymeric CN composites were prepared by a modification of the polymeric CN with certain amount of copper(II) acetylacetonate $(Cu(acac)_2)$ via a simple impregnation method. The $Cu(acac)_2$ has been commonly used in many applications not only as catalysts and inhibitors in chemical reactions but also as oxygen pressure sensors in thin films and p-type semiconductors.[10] In addition, the immobilization of transition complexes onto the solid support or polymer is a subject of current interest.[11–12]

On the other hand, nitrite (NO_2^-) is an important target analyte presented in soil, water, food and widely exists in an environment that has caused serious hazards to human health.[13] Reactions of the NO_2^- with secondary amines and amides from natural breakdown products of proteins can form compounds known as nitrosamines, which are regarded as carcinogenic compounds. Consequently, monitoring the concentration of NO_2^- is of great important.[14] In addition, when the NO_2^- is present at high concentration in blood, it can react with the iron(II) of the haemoglobin, forming methemoglobin that has no oxygen binding ability; this medical condition is called methemoglobinemia or "blue baby syndrome".[15,16] Owing to its potential toxicity, detection of the NO_2^- is important for public health, industrial and environmental fields. Therefore, it is necessary to develop a reliable and sensitive sensor to detect the NO_2^- in food, waste water and environmental samples.[17–19]

In this report, the polymeric CN was modified by $Cu(acac)_2$ and used for detection of the NO_2^-. To the best of our knowledge, this is the first report on the use of $Cu(acac)_2$/polymeric CN composite for detection of the NO_2^- by using fluorescence spectroscopy, whilst the polymeric CN and its composites have been characterized by using FTIR, DR UV-Vis, surface area analyzer and fluorescence spectroscopy.

Experimental Section

Materials

All chemicals used in this study were commercially available and used as received without any treatments. Urea $(CON_2H_4$, Sigma-Aldrich) was used as the precursor for the synthesis of polymeric CN while the copper acetylacetonate, $Cu(acac)_2$ $(Cu(C_5H_7O_2)_2$, Merck) was used for the preparation of $Cu(acac)_2$/polymeric CN. Sodium nitrite $(NaNO_2$, Merck) was used as the NO_2^- source. In addition, sodium nitrate $(NaNO_3$, Merck), sodium chloride $(NaCl$, Fisher Scientific), sodium sulfate $(Na_2SO_4$, Fisher Scientific) and orthophosphoric acid $(H_3PO_4$, Merck) were used as the source of interference ions.

Preparation of Polymeric CN and Cu(x)/Polymeric CN Composites

Polymeric CN was prepared by using urea as a precursor via a thermal polymerization technique at 823 K for 4 hours in the similar way to the reported literatures.[9,20] The $Cu(acac)_2$/polymeric CN composites were prepared by an impregnation method. Certain amount of $Cu(acac)_2$ was dissolved in ethanol (10 mL) and mixed with the polymeric CN (0.5 g). The loading amounts of the $Cu(acac)_2$ were fixed at 0.1 and 0.5 mol%. The mixture was heated at 90°C until all the ethanol was evaporated. The samples were denoted as $Cu(x)$/polymeric CN, which x shows the loading of $Cu(acac)_2$ (mol%).

Characterizations of Polymeric CN and Cu(x)/Polymeric CN Composites

Fourier transform infrared (FTIR) spectra of the polymeric CN and its composites were recorded using a Nicolet iS50 spectroscopy by mixing the samples with potassium bromide as a pellet. The diffuse reflectance UV-Visible (DR UV-Vis) spectra were recorded in the range of 250–800 nm at room temperature on

a Shimadzu UV-Vis spectrophotometry (UV-2600), in which barium sulfate was used as the reference. The emission spectra were recorded on a JASCO FP-8500 fluorescence spectrophotometer at room temperature. The nitrogen adsorption-desorption profiles and Brunauer-Emmett-Teller (BET) specific surface area of the polymeric CN and its composites were determined at 77 K by using a Quantachrome NOVA TOUCH LX^4. Prior to the measurements, the samples were heated under vacuum at 373 K for 3 h.

Quenching Tests

In order to study the performance of the materials to detect the NO_2^-, the quenching tests with various concentrations of NO_2^- (0.5-4 μM) were carried out on the polymeric CN and the Cu(*x*)/polymeric CN composites at room temperature using the fluorescence spectrophotometer. Typically, various concentrations of the NO_2^- aqueous solution (10 μL) was introduced onto the sample (0.05 g) and the changes in the emission intensity were measured at each excitation wavelength.

Reproducibility, Stability, and Selectivity Tests

Reproducibility of the Cu(*0.1*)/polymeric CN was evaluated by conducting the quenching test under similar conditions as mentioned above for five times. The reproducibility of the composite was determined from the low value of relative standard deviation (RSD) calculated at each concentration of NO_2^- when measured at different sensing sites. Stability test was carried out similarly to the quenching test by reusing the Cu(*0.1*)/polymeric CN composite as the fluorescence sensor for detection of NO_2^- at three consecutive measurements. Prior to the second and third measurements, the used composite was washed with distilled water and dried at 353 K for 24 hours. In order to evaluate the selectivity of the Cu(*0.1*)/polymeric CN composite towards the detection of NO_2^-, the performance of the composite was recorded in the presence of other interference ions, which were NO_3^-, Cl^-, SO_4^{2-} and

PO_4^{3-}. Typically, the NO_2^- aqueous solution (1 μM, 10 μL) was introduced onto the sample (0.05 g), followed by measurements of emission intensity as shown above. The interference ion in aqueous solution (300 μM, 10 μL) was then added onto the same sample and the emission intensity was compared to the one without the presence of the interference ion.

Results and Discussion

Functional Groups

FTIR spectroscopy was used to identify the functional groups of the materials. As shown in Figure 1, the polymeric CN showed vibration bands at around 3300-3400 cm^{-1} due to the overlapping bands from the secondary and primary amines and incomplete graphitic condensation and $v(O-H)$ group.[21] The stretching mode of the v (C−N) heterocycles originated from the extended CN network were observed at 1200-1700 cm^{-1},[3] while the vibration bands at 809 cm^{-1} was corresponded to the heterocyclic tri-*s*-triazine ring (C_6N_7) units with single and double bonds, which showed the characteristics of the graphitic polymeric CN.[22,23] The presence of these peaks confirmed the successful formation of the polymeric CN.

The FTIR spectra of the Cu(*x*)/polymeric CN composites are also shown in Figure 1. The composites showed similar vibration bands to those of the polymeric CN, suggesting that the addition of Cu(acac)$_2$ did not affect the functional groups of the

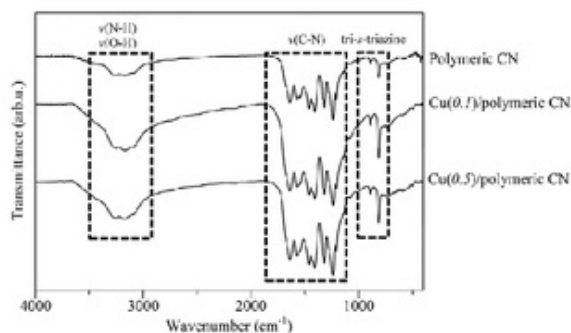**Figure 1.**
FTIR spectra of polymeric CN and its composites.

polymeric CN. The vibration modes of the $Cu(acac)_2$ have been reported to be observed at 1577 and 1529 cm^{-1} that were assigned to $\nu(C=C)$ coupled with $\nu(C=O)$ and $\nu(C=O)$ coupled with $\nu(C=C)$, respectively.[24] Unfortunately, these peaks were not observed clearly in the $Cu(x)$/polymeric CN composites, which might be due to the low amount of the added $Cu(acac)_2$ and/or the overlapping bands between the added $Cu(acac)_2$ and the polymeric CN.

## Optical and Physical Properties

The optical properties of the polymeric CN and its composites were obtained by using a DR UV-Vis spectroscopy. As shown in Figure 2, all the synthesized samples showed absorption bands in the UV and visible region below 450 nm. The polymeric CN exhibited intense absorption bands at ca. 277, 315 and 370 nm in good agreement to the reported paper.[9] As has been reported, the absorption peak at 277 nm would be originated from the C=N group (π-π^*) in the conjugated aromatic 1,3,5-triazine ring, the peak at 315 nm would be attributed from the C=O (mixture of n-π and π-π^*), while the peak at 370 nm would be due to the terminal C—N group (n-π^*).

The DR UV-Vis spectra of the composites are also displayed in Figure 2. With the addition of $Cu(acac)_2$, the absorption peaks below 350 nm were found to be increased with the increase of the $Cu(acac)_2$ amount. It was reported that the maximum band at 277 nm was attributed to the ligand to metal charge transfer (LMCT) transition between Cu^{2+} ion and oxygen in mononuclear species, while a small shoulder at around 300 nm indicated the presence of oligomeric cluster-like moieties through the charge transfer between Cu^{2+} and oxygen.[25] The increased absorption bands clearly suggested the presence of the $Cu(acac)_2$ in the composites.

The band gap energy (Eg) of the polymeric CN and its synthesized composites was calculated according to the Tauc plot derived from the DR UV-Vis spectra, taking into account the indirect semiconductor.[8] As shown in Figure 3, the band gap energy of the polymeric CN was estimated to be around 2.88 eV. On the other hand, the band gap energy of the composites were estimated to be 2.84-2.85 eV, suggesting that the addition of the $Cu(acac)_2$ did not give much influence on the band gap energy of the polymeric CN. This is reasonable since the $Cu(acac)_2$ was loaded onto the polymeric CN at room temperature. Therefore, the $Cu(acac)_2$ would not affect the structure of the polymeric CN and would be only deposited on the surface of the polymeric CN.

The nitrogen adsorption-desorption curve of the polymeric CN and it composites are shown in Figure 4. The gas sorption curves were mostly close to type III isotherm for nonporous solids. There are no changes occurred on the isotherm when the $Cu(acac)_2$ was added onto the samples,
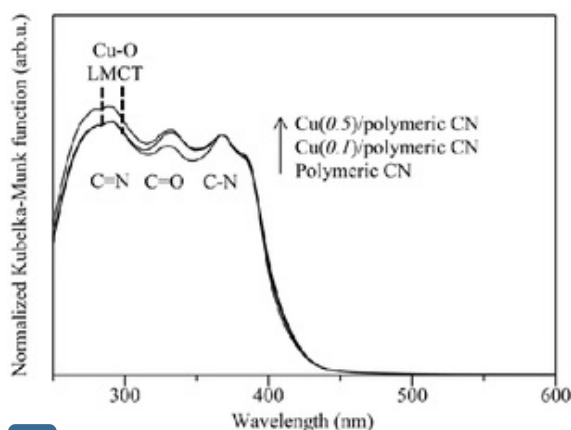
Figure 2.
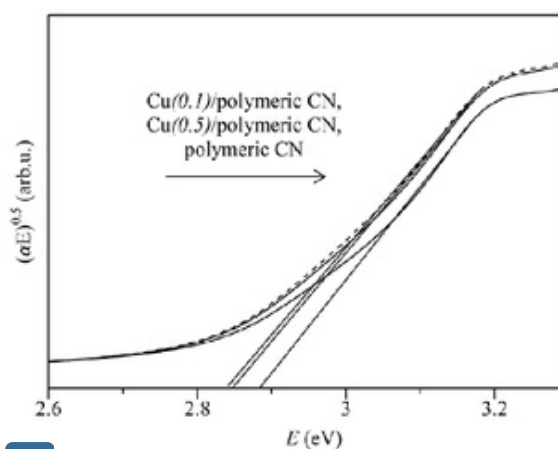Normalized DR UV-Vis spectra of polymeric CN and its composites.

Figure 3.
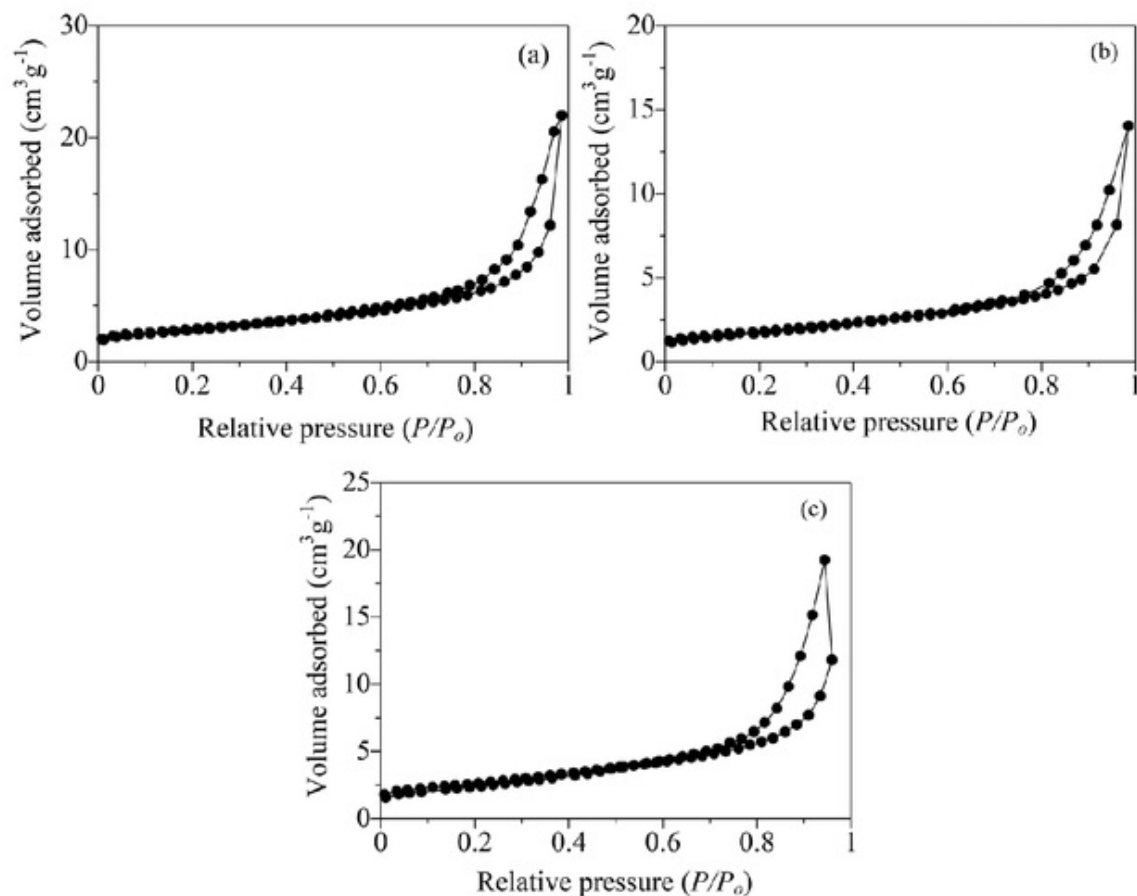Tauc plots of polymeric CN and its composites.

Figure 4.
N$_2$ adsorption-desorption isotherm of (a) polymeric CN, (b) Cu(0.1)/polymeric CN and (c) Cu(0.5)/polymeric CN.

suggesting that the added Cu(acac)$_2$ did not affect the physical properties of the polymeric CN. The BET specific surface areas of the polymeric CN, the Cu(0.1)/polymeric CN, and the Cu(0.5)/polymeric CN were determined to be 91, 62 and 75 m^{2}g^{-1}, respectively. In general, the surface area of the polymeric CN was found to be decreased with the addition of the Cu(acac)$_2$ as the Cu(acac)$_2$ might cover the surface of the polymeric CN.

Fluorescence Properties
Polymeric CN and its composites were applied as fluorescence sensors since the polymeric CN has been reported to exhibit an excellent fluorescent property.[9] As shown in Figure 5 (a), the polymeric CN and its composites gave three excitation peaks at 277, 315, and 370 nm in good agreement with their DR UV-Vis spectra. On the other hand, only one emission was observed at 455 nm when polymeric CN

and its composites were excited at 277, 315, and 370 nm (Figure 5(b)-(d)). Under all excitation wavelengths, the addition of Cu(acac)$_2$ was found to decrease the emission intensity of the polymeric CN. The lower emission intensity indicated the presence of certain interactions between the copper species and the polymeric CN.

Quenching Tests
In order to investigate the interactions between the polymeric CN and its composites towards the NO$_2^-$, the emission spectra of the polymeric CN and its composites were measured at excitation wavelengths of 277, 315, and 370 nm in the absence and presence of NO$_2^-$ with various concentrations in the range of 0.5–4 μM. Figure 6 illustrates the detailed fluorescence response of polymeric CN towards the NO$_2^-$ concentration ranging from 0.5 to 4 μM. In the absence of the NO$_2^-$, the emission intensity of the polymeric CN was
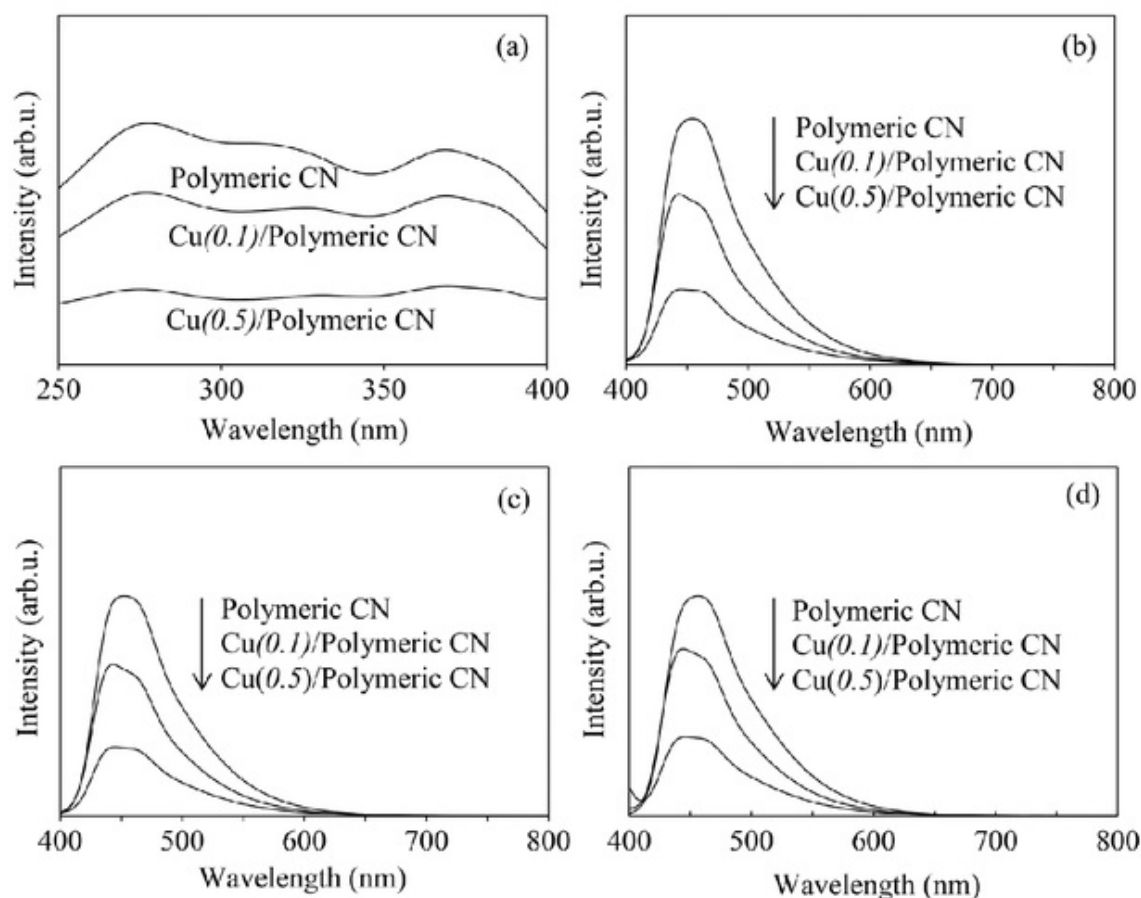
Figure 5.

(a) Excitation spectra of polymeric CN and its composites monitored at the emission wavelength of 455 nm, and the emission spectra monitored at excitation wavelengths of (b) 277, (c) 315, and (d) 370 nm.

high. Upon increasing the concentration of the NO_2^-, the emission intensities of the polymeric CN were reduced regardless the excitation wavelengths. These phenomena were also observed for all composite samples as shown in Figures 7 and 8.

The decrease in the emission intensity strongly suggested that the NO_2^- molecules acted as quencher molecules and interacted with the emission sites of the polymeric CN and the composites. The quenching efficiency of the polymeric CN and its composites
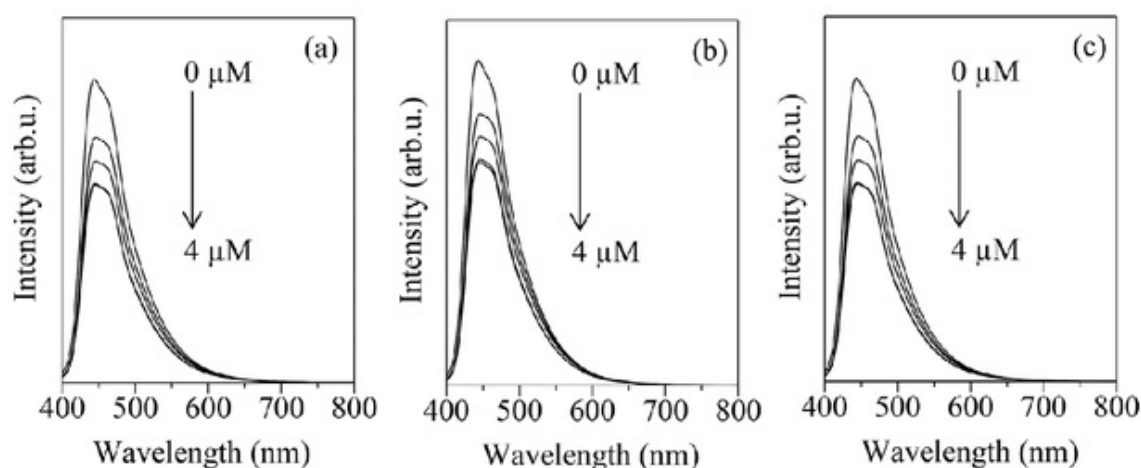

Figure 6.

Changes of the emission intensity of polymeric CN monitored at excitation wavelengths of (a) 277, (b) 315 and (c) 370 nm with various concentrations of NO_2^-.
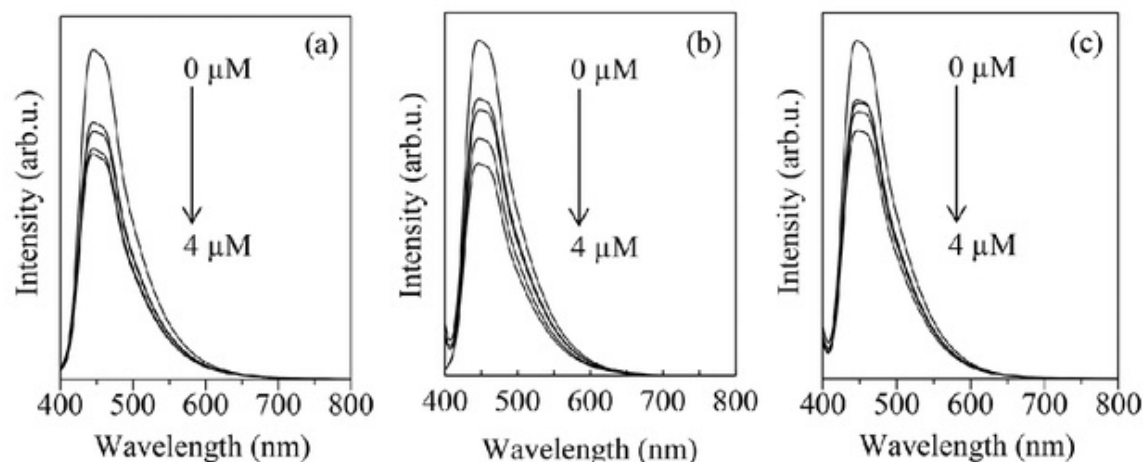
Figure 7.
Changes of the emission intensity of Cu(0.1)/polymeric CN monitored at excitation wavelengths of (a) 277, (b) 315 and (c) 370 nm with various concentrations of NO_2^-.

towards NO_2^- ion were then calculated by the following Stern-Volmer equation:

$$\frac{I_o}{I} = K_{sv}[Q] + 1 \qquad (1)$$

where I_o and I are fluorescence intensities observed in the absence and the presence of NO_2^-, respectively, Q is the NO_2^- concentration and K_{sv} is the Stern-Volmer plot quenching constant.

The linear plot would indicate that the material can be used as a potential fluorescent sensor for the detection of NO_2^-. The quenching efficiencies towards NO_2^- were revealed from the slopes of the linear plots, which were corresponding to the K_{SV} value. As representative, Figure 8

shows the Stern-Volmer plots derived from the relative emission intensity of the polymeric CN and the Cu(*x*)/polymeric CN to the concentration of added NO_2^- monitored at excitation wavelength of 277 nm. As shown in Figure 9, the polymeric CN and its composites gave almost linear plots in the presence of NO_2^- up to 4 μM, indicating that the decrease in the emission intensity of all the materials was a linear function to the concentration of NO_2^-. This result suggested that the polymeric CN and the composites can be considered as potential fluorescence sensors for the detection of NO_2^-.

The K_{sv} values of the polymeric CN and its composites for each excitation wavelength
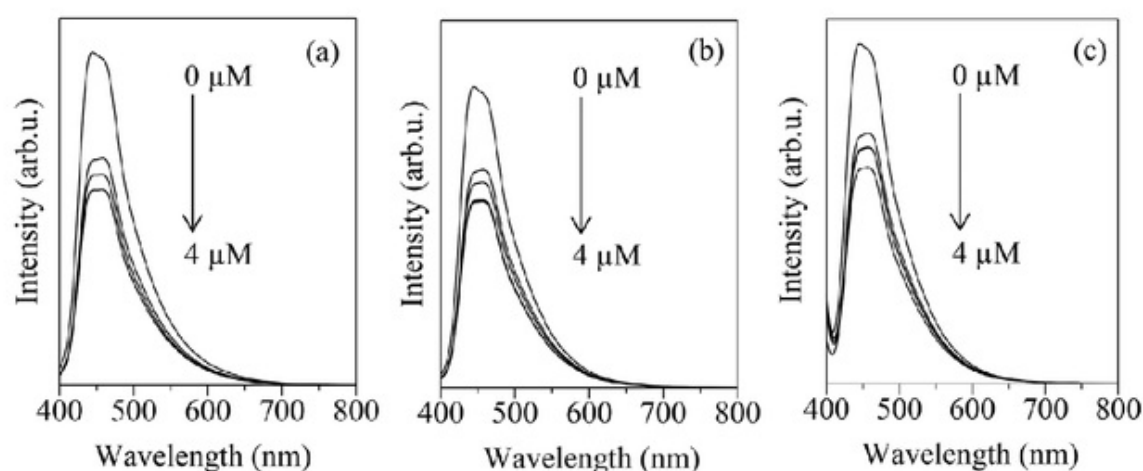

Figure 8.
Changes of the emission intensity of Cu(0.5)/polymeric CN monitored at excitation wavelengths of (a) 277, (b) 315 and (c) 370 nm with various concentrations of NO_2^-.
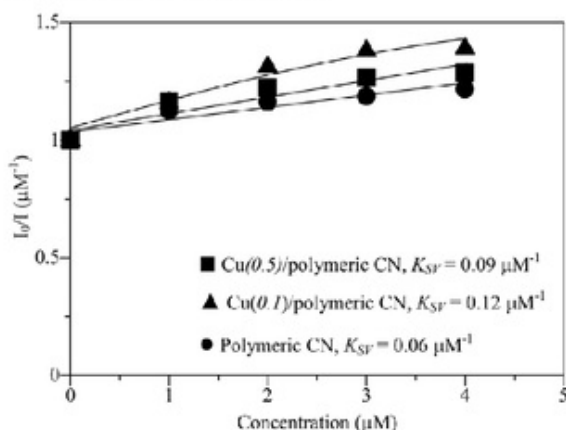
Figure 9.
Stern-Volmer plots between the relative emission intensity of polymeric CN and Cu(x)/polymeric CN and the concentration of NO_2^-, monitored at excitation wavelength of C=N sites (277 nm).

are shown in Figure 10. It was obvious that the highest K_{SV} values on all samples were obtained at excitation wavelength of 277 nm, which was the C=N sites. This result suggested that the C=N sites were the most favored sites to have interactions with the NO_2^- molecules. The presence of copper species clearly enhanced the K_{SV} values of the polymeric CN for all emission sites. With optimum amount of 0.1 mol%, the sensing capability of the polymeric CN towards the NO_2^- was increased two times higher from 0.06 to 0.12 μM^{-1} for the C=N sites. It was proposed that the added Cu(acac)$_2$ would act as additional new sites to interact more with the NO_2^- molecules.
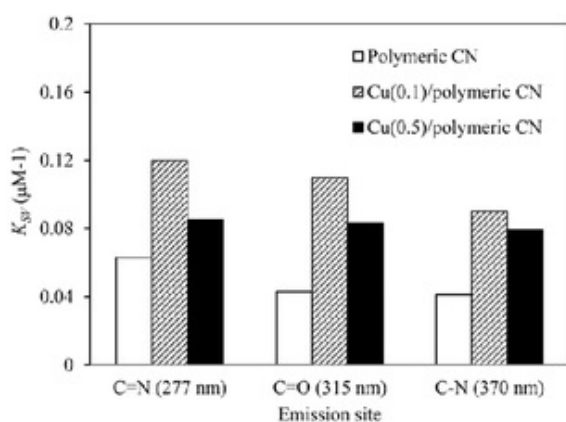

Figure 10.
The K_{SV} values for polymeric CN and Cu(x)/polymeric CN for all the emission sites.

Reproducibility, Stability, and Selectivity Tests

Further investigations were carried out on the best fluorescence sensor, which was Cu(0.1)/polymeric CN. As for reproducibility tests, the Cu(0.1)/polymeric CN were evaluated for the detection of NO_2^- at five repetitions. It was confirmed that the Cu(0.1)/polymeric CN showed good reproducibility at all emission sites. The RSD values for the C=N, the C=O, and the C-N sites were calculated to be in the range of 0.7–5, 2.4–4.8, and 3.8–5.1%, respectively.

The lowest concentration level at which the fluorescence sensor still provides a reliable result can be represented as limit of detection (LOD). The LOD on the Cu(0.1)/polymeric CN towards the detection of NO_2^- was determined according to equation (2).

$$LOD = \frac{3 \times SD}{slope} \qquad (2)$$

where the SD shows the standard deviation of the response at the intercept values and the slope shows the average K_{SV} values. It was obtained that the LOD was 0.5 μM when measured at the C=N sites. This value was much lower than that observed on the polymeric CN, which was 0.9 μM, supporting the better sensitivity of the Cu(0.1)/polymeric CN.

The stability test was carried out by reusing the Cu(0.1)/polymeric CN after it was washed and dried for three consecutive times. It was confirmed that the K_{SV} values of the Cu(0.1)/polymeric CN were not much affected, suggesting the stability and potential reusability of the composite. The K_{SV} values at the C=N sites were found to be in the similar range of 0.10-0.12 μM^{-1}.

As for selectivity test, the sensing performance of the Cu(0.1)/polymeric CN was evaluated in the presence of NO_3^-, Cl^-, SO_4^{2-} and PO_4^{3-} as the interference ions. The extent of interferences (E) were calculated according to equation (3) and shown in Table 1.

Table 1.
Extent of interferences of ions towards NO_2^- detection on Cu(0.1)/polymeric CN

Interference ions	Extent of interferences (*E*, %)		
	C=N (277 nm)	C=O (315 nm)	C—N (370 nm)
NO_3^-	4.1	3.7	2.9
Cl^-	5.2	5.0	3.7
SO_4^{2-}	4.2	3.9	2.4
PO_4^{3-}	3.9	3.1	1.3

$$E = \frac{I_o - I}{I_o} \times 100\% \qquad (3)$$

where I_o and I show the fluorescence emission intensity for the Cu(*0.1*)/polymeric CN with the presence of NO_2^- ions only and the presence of both NO_2^- and interference ions, respectively. As listed in Table 1, regardless the type of the interference ions, the extent of interference was in the range of 3.9–5.2, 3.1–5.0, 1.3–3.7% for C=N, C=O, and C—N sensing sites, respectively. Such low values of the extent of interference indicated the low interference effect of the ions towards the performance of the Cu(*0.1*)/polymeric CN for the detection of NO_2^-. These results clearly demonstrated that the Cu(*0.1*)/polymeric CN still can be used selectively to detect NO_2^- in the presence of other ions mentioned above.

Conclusions

In conclusion, polymeric CN and its composites were successfully synthesized and characterized by FTIR, DR UV-Vis, N_2 adsorption-desorption and fluorescence spectroscopies. Stern-Volmer plots showed the linear relationship between the relative emission intensity and the concentration of the NO_2^-. The addition of $Cu(acac)_2$ (0.1 mol%) increased two times the quenching efficiency of the polymeric CN for the C=N sites. Moreover, the composite gave good reproducibility and stability, low LOD, and high selectivity for the detection of NO_2^- in the presence of

other interference ions (NO_3^-, Cl^-, SO_4^{2-} and PO_4^{3-}). This work demonstrated that the polymeric CN and its composite can be applied as a fluorescence sensor for the detection of NO_2^-.

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