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COPPER MODIFIED CARBON NITRIDE AS FLUORESCENCE SENSOR FOR NITRATE IONS

(Karbon Nitrida Terubah Suai Kuprum Sebagai Sensor Pendafluor Ion Nitrat)

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Abstract

In this study, newly developed copper modified CN composites were prepared and tested as a fluorescence sensor for detection of nitrate ions (NO_3^-). The structure and chemical properties of CN and copper modified CN composites were investigated via X-ray diffraction (XRD), Fourier transform infra-red (FTIR), diffuse reflectance ultraviolet-visible (DR UV-Vis) and fluorescence spectroscopies. Three emission sites represented as C=N, C=O and C-N moieties were suggested to contribute as sensing sites in CN and copper modified CN composites. The sensing capabilities of CN and copper modified CN composites toward NO_3^- in the range of 300 to 1800 µM were determined via a quenching technique. The quenching efficiencies (K_{SV}) of CN and copper modified CN composites were obtained from the Stern-Volmer plot. Among three emission peaks of CN, C=N sites were found to be the most sensitive site having the strongest interaction with NO_3^-. By addition of Cu(0.5 mol%), the K_{SV} of CN was improved from 2.11 x 10^{-4} to 5.27 x 10^{-4} μM^{-1}. This study showed that with the addition of copper as modifier, the performance of CN can be improved and the composite can be used as potential fluorescence sensor for the detection of NO_3^-.

Keywords: copper modified carbon nitride, fluorescence sensor, nitrate ion

Abstrak

Dalam kajian ini, karbon nitrida terubah suai kuprum yang baru telah disediakan dan diuji sebagai sensor pendafluor untuk mengesan ion nitrat (NO_3^-). Struktur dan sifat kimia bagi CN telah disiasat melalui pembelauan sinar-X (XRD), transformasian infra-merah Fourier (ETIR), spektroskopi pantulan serakan ultralembayung-cahaya nampak (DR UV-Vis) dan spektroskopi pendafluor. Tiga tapak pelepasan diwakili sebagai moiti C=N, C=O dan C-N telah dicadangkan untuk menyumbang sebagai tapak penderiaan CN dan komposit CN terubah suai kuprum. Keupayaan penderiaan CN dan komposit CN terubah suai kuprum terhadap NO_3^- dalam lingkungan 300 hingga 1800 µM telah ditentukan melalui teknik pelindapan. Kecekapan pelindapan (K_{SV}) bagi CN dan komposit CN terubah suai kuprum telah diperoleh daripada plot Stern-Volmer. Di antara tiga tapak pelepasan CN, tapak C=N telah ditemui menjadi tapak yang paling sensitif dan mempunyai interaksi paling kuat dengan NO_3^-. Dengan penambahan Cu(0.5 mol%), nilai K_{SV} bagi CN telah bertambah baik daripada 2.11 x 10^{-4} kepada 5.27 ×10^{-4} μM^{-1}. Kajian ini menunjukkan bahawa dengan penambahan kuprum sebagai pengubahsuai, prestasi CN boleh ditingkatkan dan komposit tersebut boleh digunakan sebagai potensi sensor pendafluor untuk mengesan NO_3^-.

Kata kunci: karbon nitrida terubah suai kuprum, sensor pendafluor, ion nitrat

Introduction

Nitrate (NO_3^-) is a widespread contaminant of groundwater which can be easily detected in the environment and cause hazard to human health. The NO_3^- is largely used for food preservative, drinking water and fertilizing agents [1, 2]. Excessive consuming of food and drinking water containing high level of NO_3^- can cause severe risk to human health especially infants. Human may metabolize NO_3^- in blood and finally transform it into carcinogenic nitrosamine causing the condition known as methemoglobinemia or also called as baby blue syndrome [3, 4]. In addition, it has been reported that the healthy human urine range of NO_3^- is in the range of 300 to 1800 μM [5]. Therefore, determination of NO_3^- is an important aspect to human health and environment. Griess reagent has been used widely for detection of NO_3^- ion. Basically, Griess reaction involved several steps starting from reduction of NO_3^- to NO_2^- ion by using vanadium (III) chloride [6]. The mixture was subsequently reacted with sulfanilamide and *N*-(1-naphtyl) ethylenediamine to produce pink coloured azo dye product which strongly absorbed light at 540 nm [5, 7-9]. However, it presents several disadvantages such as using high concentration of hazardous reagent in the reaction, complicated detection procedure and cannot be reused [10]. Thus, development of reusable and sensitive sensor for detection of NO_3^- ion is highly required.

Recently, carbon nitride (CN) has become a current interest because of its unique properties such as non-toxicity, low cost, high photoluminescence intensity [11] and good photostability [12]. CN is a graphite like layered material where *s*-triazine (C_3N_3) or tri-*s*-triazine (C_6N_7) units connected with amino groups (-NH/NH_2) are held together through hydrogen bonds between the amino groups [13, 14]. The principal application of the CN in the environment is mainly in photocatalysis for photodegradation of environmental pollutants [15, 16], while only few studies have been reported on its application in optical detection of environmental pollutant [17-22]. For instances, the CN has been reported to act as fluorescence sensor for detection of Cu^{2+} and Fe^{3+} ions [16-18] and *N*-Nitrosopyrrolidine [19]. Recently, metal-free CN was used as a fluorescence chemical sensor for detection of NO_3^- [23]. Unfortunately, CN alone still has low sensitivity towards the detection of the NO_3^-. Therefore, further investigation is still required to improve the performance of the CN.

The objective of this study is to design a sensitive sensing material based CN by improving the sensing sites of the CN for detection of the NO_3^-. In order to improve the sensing sites of the CN, copper species was used as the modifier. Copper based material has attracted a great interest due to its low cost as compared to noble metals such as Au, Pt, or Pd. It has been reported that the amino groups from the CN can interact with copper ion to form a stable complex due to the strong coordination force between the amino group and copper ion [24]. Herein, this study reported the modification of the CN by using copper species prepared by impregnation followed by a reduction method. The synthesized composites were demonstrated to show better sensing performances towards the NO_3^-.

Materials and Methods

Material preparation

CN was prepared by using urea (CON_2H_4, Sigma-Aldrich, 98%) as precursor via thermal polymerization technique at 823 k for 4 hours [21, 25]. As for the preparation of composites, certain amount of $Cu(acac)_2$ ($Cu(C_5H_7O_2)_2$, Merck, 99.99%) was dissolved in ethanol and mixed with CN via an impregnation process. The mixture was heated up to 363 K until all the ethanol was evaporated. The obtained solid was underwent thermal hydrogenation process at 473 K for 2 hours under hydrogen flow of 5 ml/min to produce copper species modified CN composites. Composites were denoted as Cu(*x*)/CN composites where *x* showed the mol ratio of Cu to CN, which were fixed at 0.1 and 0.5 mol%. As a reference, the $Cu(acac)_2$ was heated under thermal hydrogenation process at 473 K or 2 hours to obtain Cu metal.

Characterizations

Properties of CN and Cu(*x*)/CN composites were investigated by several instruments. The structure of the CN and its composite was identified by using powder X-ray difractometer recorded with a Bruker D8 Advanced using Cu Kα irradiation (λ = 1.5406 Å). The surface area of CN and its composites was confirmed by using Brunauer-Emmett-Teller (BET) equation obtained from a Quantachrome NOVA TOUCH LX^4. The functional groups present in the CN and its composites were recorded by 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 by using

Shimadzu UV-Vis spectrophotometry (UV-2600) in the range of 250 – 800 nm. The emission spectra were determined via JASCO FP-8500 fluorescence spectrophotometer at room temperature.

Quenching test

The interactions between the CN and its composites with NO_3^- were studied via fluorescence spectroscopy at room temperature. The quenching tests were carried out by exposing various concentrations of NO_3^- in the range of 300 to 1800 μM onto the CN and its composites. The various concentrations of NO_3^- (10 μL) were introduced into the sample (0.05 g) and the emission spectra were measured at excitation wavelengths of 277, 320 and 370 nm. The interaction between the samples and the NO_3^- can be observed from the changes in the emission intensity measured at each excitation wavelength and evaluated from the Stern-Volmer plot.

Results and Discussion

Characterization of CN and Cu(x)/CN composites

To investigate the chemical structure and optical properties of CN and its composites, XRD, FTIR, DR UV-Vis and fluorescence spectroscopies measurements were performed. The XRD patterns of CN and its composites are given in Figure 1. The XRD pattern of the prepared Cu metal is also shown as a reference. Cu metal gave three obvious peaks at 2θ of 44.3, 50.4 and 74.1° as the characteristics of copper (0) species (JCPDS no. 00-004-0836), which pattern was virtually the same as the reported one [26]. On the other hand, the CN exhibited two diffraction peaks at 2θ of 13.10 and 27.30°, corresponding to in-planar repeating units and the distance between the nitride pores, respectively [20, 23, 27-30]. The Cu(*x*)/CN composites showed similar diffraction patterns to those of the CN, suggesting that the added Cu might be too low to be detected by XRD or the Cu was highly dispersed on the CN.

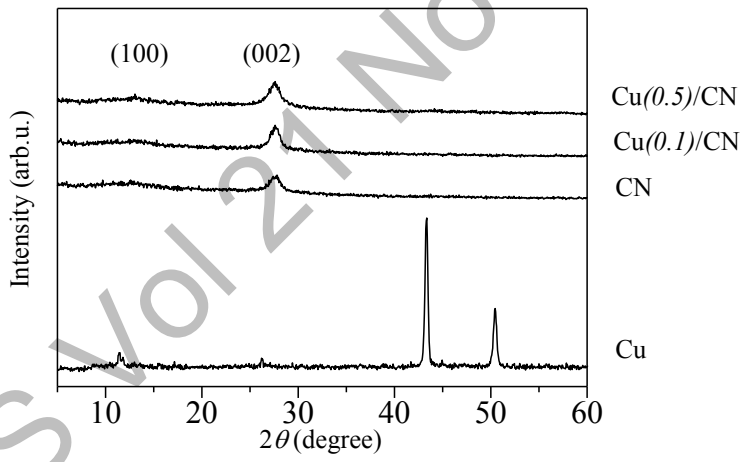


Figure 1. XRD patterns of Cu, CN and Cu*(x)*/CN composites

The FTIR spectra of CN and the Cu*(x)*/CN composites are shown in Figure 2. The CN showed vibration bands at around 3300 – 3400 cm^{-1} that can be attributed to the overlapping bands of primary and secondary amine, *v*(N-H) and *v*(O-H) groups [21-24, 31-35]. The stretching modes of *v*(C-N) heterocycles were observed at 1200 –1700 cm^{-1}, while the heterocyclic tri-*s*-triazine (C_6N_7) was found at around 809 cm^{-1}. Even though the presence of amino groups in the synthesized CN is difficult to be analysed by FTIR spectroscopy, it has been reported by XPS analysis [31]. It was obvious that the Cu(*x*)/CN composite exhibited almost similar peaks to those of the CN, which indicated that the structure of CN was kept to be almost the same even after addition of copper species on the samples, similar to other reported literatures [24, 32].

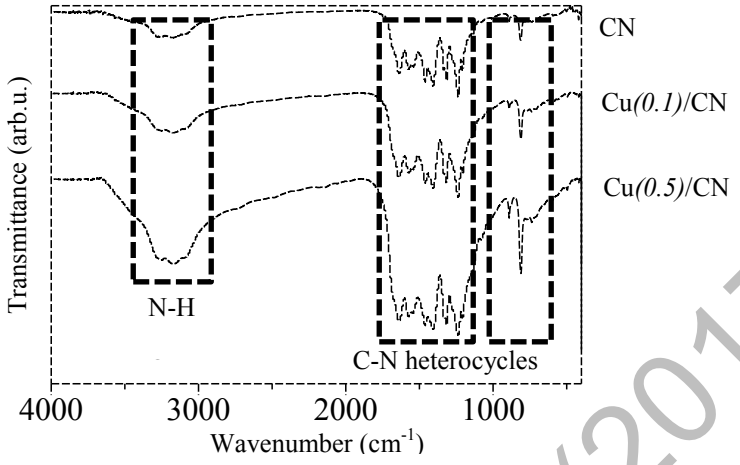
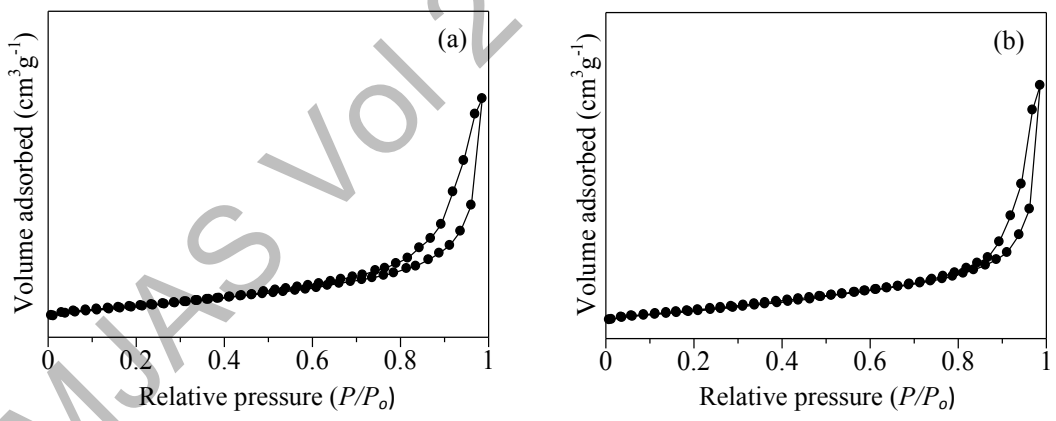


Figure 2. FTIR spectra of CN and Cu*(x)*/CN composites

Figure 3 shows N_2 adsorption-desorption isotherms of CN and its composites. It was obvious that they exhibited type III isotherm, which referred to nonporous solids. There were no change occurred on the isotherm when the Cu species were added onto the samples, suggesting that the added copper species did not affect the physical properties of the CN. The BET specific surface areas of CN, Cu *(0.1)*/CN, and Cu *(0.5)*/CN were measured to be 91, 93 and 56 m^2g^{-1}, respectively. Addition of 0.1 mol% of Cu did not affect much the specific surface area, but the addition of 0.5 mol% of Cu significantly decreased the specific surface area. The decrease in the surface area has been also reported when $Cu(acac)_2$ was dispersed on the CN [32].



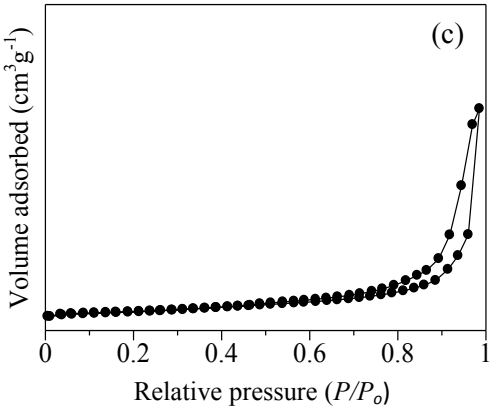


Figure 3. N_2 adsorption-desorption of (a) CN, (b) Cu*(0.1)*/CN and (c) Cu*(0.5)*/CN composites

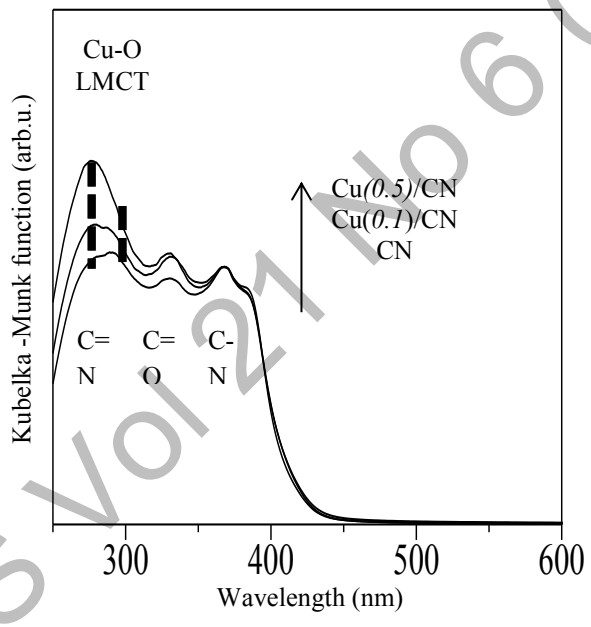


Figure 4. DR UV-Vis spectra of CN and Cu*(x)*/CN composites

The optical properties of CN and its composites were investigated by DR UV-Vis spectroscopy. As shown in Figure 4, CN and its composites exhibited three strong absorption bands at 277, 320 and 370 nm. The peak at 277 nm was corresponded to C=N groups (π-π*) in the conjugated aromatic triazine ring [20, 23, 31, 32], while the peak at 320 nm would be related to the presence of C=O moiety (π-π* and n-π*) due to the low condensation during the polymerization process of urea [30, 32, 36]. The peak at 370 nm was originated from the C-N terminal moiety (n-π*) [20, 23, 31, 32]. The Cu(x)/CN composites also gave similar absorption peaks to the CN, but with increased absorption peak intensities below 350 nm. The increase was more prominent for Cu*(x)*/CN composite with higher Cu loading amount. This would be the evidence of the presence of Cu on the samples since the peaks were contributed from the ligand to metal charge transfer (LMCT) transition between Cu and oxygen species in the composites [37].

The fluorescence properties of CN and Cu*(x)*/CN composites were studied by using fluorescence spectroscopy. Similar to the DR UV-Vis spectra, CN and its composites also shows three excitation peaks at 277, 320 and 370 nm, which referred to C=N, C=O and C-N terminal groups, respectively. On the other hand, only one emission peak was observed when CN and its composites were excited at 277, 320 or 370 nm [23]. As can be seen in Figure 5 (a), the intensity of the excitation spectra of the composites decreased with the increase in the loading amount of Cu species. This is believed due to certain interactions occurred between Cu species and CN. The same phenomenon also can be monitored from the emission spectra of CN and its composites at 455 nm for all excitation wavelengths, as can be seen in Figure 5 (b), (c) and (d), which illustrates the emission spectra of CN and its composites when excited at 277, 320 and 370 nm, respectively.

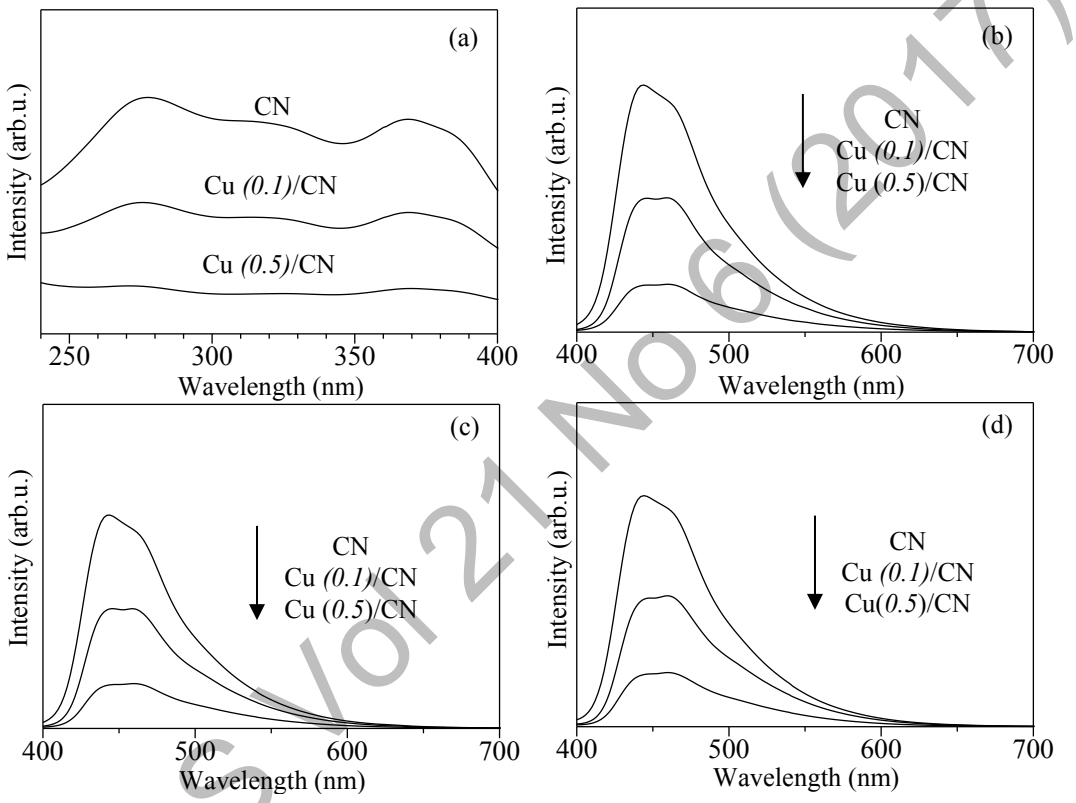


Figure 5. (a) Excitation spectra of CN and Cu*(x)*/CN composites monitored at emission wavelength of 455 nm, and emission spectra of CN and Cu*(x)*/CN composites monitored at excitation wavelengths of (b) 277, (c) 320 and (e) 370 nm

Sensing performance of CN and Cu(*x*)/CN composites toward NO_3^- ion

The fluorescence responses of CN and its composites to various concentrations of NO_3^- (300-1800 µM) were studied by using a quenching technique. Since the CN and its composites have three emission sites, which are C=N, C=O and C-N terminal groups, it is important to determine which emission site has the strongest interaction to NO_3^-. Figure 6 shows the emission spectra of CN at 277, 320 and 370 nm before and after addition of various concentrations of NO_3. Based on the spectra, it is clearly seen that the intensity of CN decreased with the increase of the NO_3^- concentration at all sensing sites, suggesting that the NO_3^- ion interacted with C=N, C=O and C-N terminal sites and acted as a quenching agent to deactivate the emission sites of the CN. It is believed that there is an electrostatic interaction between the CN and its composites with NO_3^- due to different charge between the sensing sites of the sensor samples and the NO_3^- [38]. The same phenomena also can be observed for Cu*(0.1)*/CN and Cu*(0.5)*/CN samples, which spectra are shown in Figures 7 and 8, respectively.

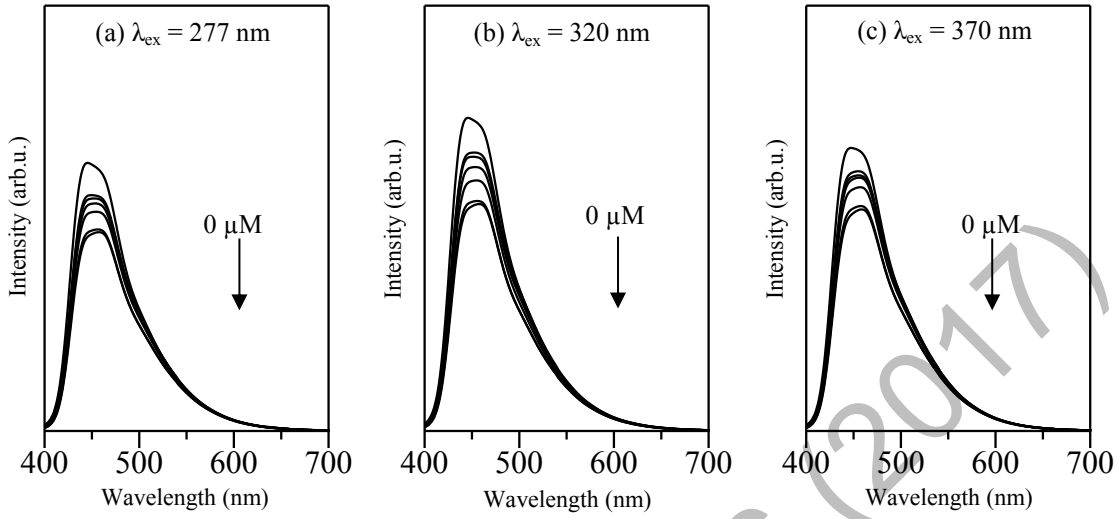


Figure 6. Emission spectra of CN in the absence and presence of NO_3^- with various concentrations, monitored at excitation wavelength of (a) 277, (b) 320 and (c) 370 nm

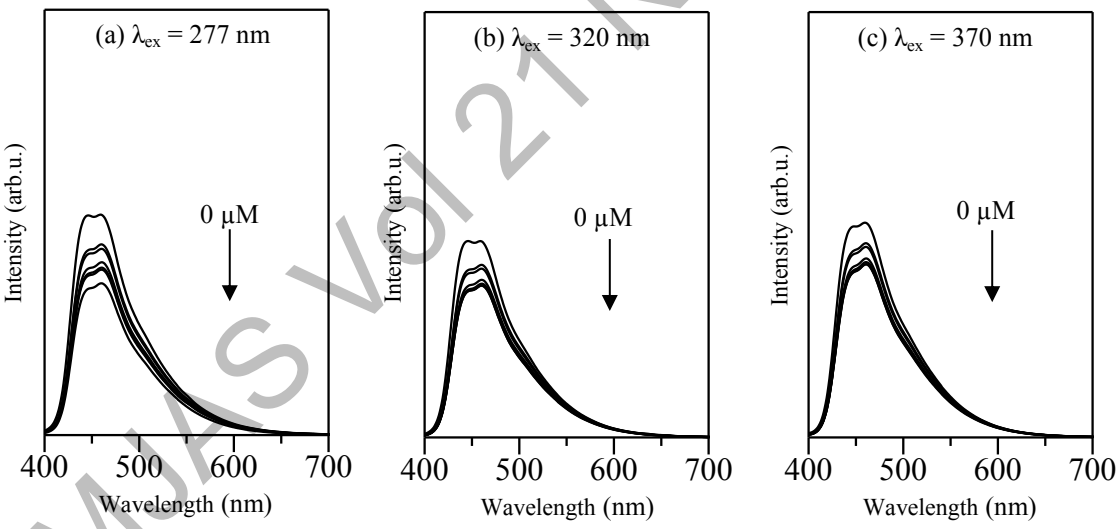


Figure 7. Emission spectra of Cu *(0.1)*/CN in the absence and presence of NO_3^- with various concentrations, monitored at excitation wavelength of (a) 277, (b) 320 and (c) 370 nm

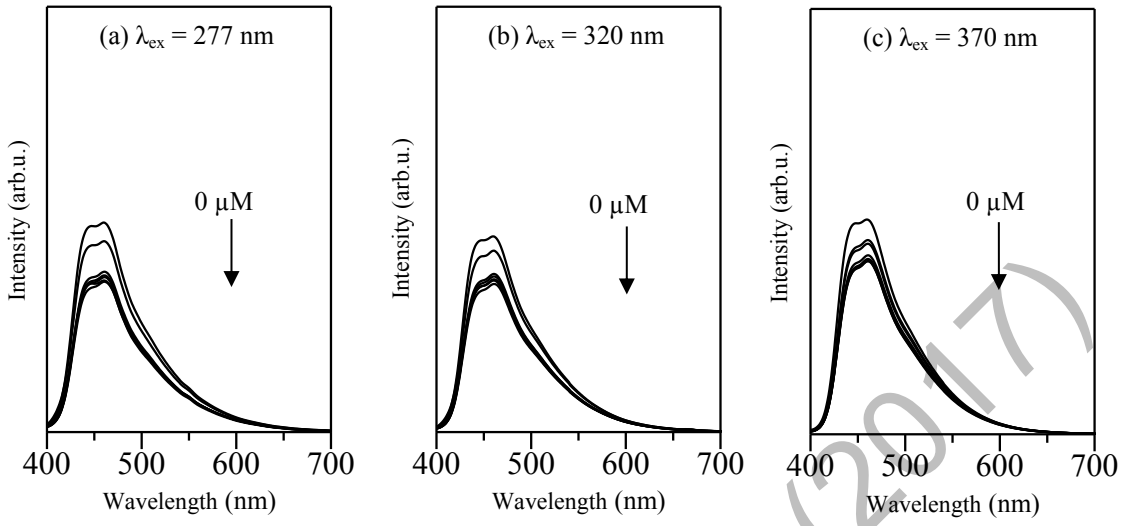


Figure 8. Emission spectra of Cu *(0.5)*/CN in the absence and presence of NO_3^- with various concentrations, monitored at excitation wavelength of (a) 277, (b) 320 and (c) 370 nm

In order to determine the most sensitive sensing sites on the CN and its composites, quenching efficiencies at each sensing sites of the samples need to be calculated. The quenching efficiencies of the sensor can be determined by the relationship between the reduced intensity and the added concentration of NO_3^-, which is reflected by the Stern-Volmer equation:

$$I_0/I = K_{SV}[Q] + 1 \quad (1)$$

where I_0 is the fluorescence intensity of sensor in the absence of quencher (NO_3^-) and I is the fluorescence intensity of sensor in the presence of quencher (NO_3^-), K_{SV} is the Stern-Volmer constant which measures the efficiency of quenching and [Q] is the concentration of NO_3^-.

Among the three sensing sites of the CN and its composites, which are C=N, C=O and C-N terminal groups, the C=N showed the strongest interaction between the samples and the NO_3^- ion. The Stern-Volmer plots of the CN and Cu*(x)*/CN composites for the C=N sites monitored at excitation wavelength of 277 nm are shown in Figure 9. The CN gave almost linear plot to sense NO_3^- ion up to 1800 μM. On the other hand, the Cu *(0.1)*/CN composite and the Cu(*0.5*)/CN composites gave a linear plot up to 1500 and 900 μM, respectively. When the added concentration was higher than these concentration levels, saturation was observed and this was more prominently observed on the Cu(*0.5*)/CN. The addition of Cu was found to give lower concentration range detection, which may be caused by the blocking of the sensing sites by the added Cu species. However, it is clear that the addition of Cu improved the quenching efficiency of the CN. The calculated K_{SV} values of CN, Cu(*0.1*)/CN and Cu(*0.5*)/CN composites at excitation wavelength of 277 nm were 2.11×10^{-4}, 2.50×10^{-4} and 5.27×10^{-4} μM^{-1}, respectively, as summarized in Figure 10. Although detection range on the Cu(*0.5*)/CN composite was lower, obviously the Cu(*0.5*)/CN composite showed almost twofold higher K_{SV} value as compared to the unmodified CN. It is revealed that the presence of copper species improved the performance of CN for the detection of NO_3^- ion. Therefore, it can be concluded that Cu(*x*)/CN composites were potential to be used as a fluorescence sensor for detection of NO_3^- ion.

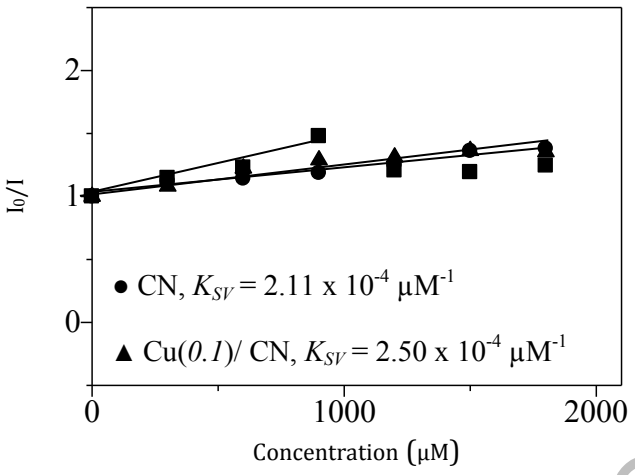


Figure 9. Stern-Volmer plots between the relative emission intensity of CN and Cu(*x*)/CN and the concentration of NO_3^-, monitored at excitation wavelength of C=N sites (277 nm)

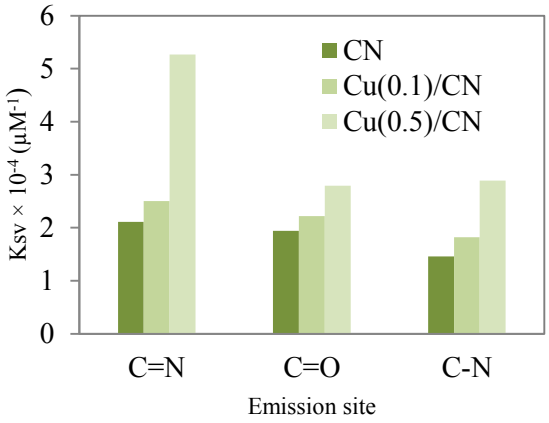


Figure 10. The K_{SV} values for CN and Cu(*x*)/ CN for all the emission sites

Conclusion

The CN was successfully synthesized via a thermal polymerization technique, while the Cu*(x)*/CN composites were prepared by impregnation of copper species, followed by thermal reduction process. XRD patterns and FTIR spectra did not show any changes, suggesting that the structural properties of CN were not influenced by the addition of copper species onto CN. On the other hand, the DR UV-Vis spectra showed the presence of copper species in the composites in the area below 350 nm, which was due to the LMCT between the copper species and CN. The CN and Cu*(x)*/CN composites exhibited three emission sites, which are C=N, C=O and C-N sites. Among all these emission sites, the C=N site showed the most favorable sensing site for detection of NO_3^- ion. The quenching efficiencies were represented by the K_{SV} values, which values for CN, Cu*(0.1)*/CN and Cu*(0.5)*/CN composites were 2.11×10^{-4}, 2.50×10^{-4} and 5.27×10^{-4} μM^{-1}, respectively. Modification with copper species (0.5 mol%) onto the CN improved the quenching efficiency up to two times higher than the unmodified CN. This work clearly demonstrated that the Cu*(x)*/CN composites can be used as a potential fluorescence sensor for detection of NO_3^- ion.

Acknowledgements

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References

1. Aravamudhan, S. and Bhansali, S. (2008). Development of micro-fluidic nitrate-selective sensor based on doped-polypyrrole nanowires. *Sensors and Actuators B*, 132: 623 – 630.
2. Guadagnini, L. and Tonelli, D. (2008). Carbon electrodes unmodified and decorated with silver nanoparticles for the determination of nitrite, nitrate and iodate. *Sensors and Actuators B,* 188: 806 –814.
3. Ogata, F., Imai, D. and Kawasaki, N. (2015). Adsorption of nitrate and nitrite ions onto carbonaceous material produced from soybean in binary solution system. *Journal of Environmental Chemical Engineering*, 3: 155 – 161.
4. Kim, D., Goldberg, I. B. and Judy, J. W. (2009). Microfabricated electrochemical nitrate sensor using double-potential-step chronocoulometry. *Sensor and Actuators B*, 135: 618 – 624.
5. Trikas, D. (2007). Analysis of nitrite and nitrate in biological fluids by assays based on the Griess Reaction: Appraisal of the Griess Reaction in the L-arginine/nitric oxide area of research. *Journal of Chromatography B*, 851: 51 – 70.
6. Wang, S., Lin, K., Chen, N., Yuan, D. and Ma, J. (2016). Automated determination of nitrate plus nitrite in aqueous samples with flow injection analysis using vanadium (III) chloride as reductant. *Talanta,* 146: 744 – 748.
7. Lee, M., Lee, Y., Soltermann, F. and Gunten, U. V. (2013). Analysis of *N*-nitrosamines and other nitro(so) compounds in water by high-performance liquid chromatography with post-column UV photolysis/Griess reaction. *Water Research,* 47: 4893 – 4903.
8. Ridnour, L. A., Sim, J. E., Hayward, M. A., Wink, D. A., Martin, S. M., Buettner, G. R. and Spitz. D. R. (2000). A spectrophotometric method for the direct detection and quantification of nitric oxide, nitrite and nitrate in cell culture media. *Analytical Biochemistry*, 281: 223 – 229.
9. Bryan, N. S. and Grisham. M. B. (2007). Methods to detect nitric oxide and its metabolites in biological samples. *Free Radical Biology and Medicine*, 43(5): 645 – 657.
10. Kumar, V. V. and Anthony, S. P. (2014). Highly selective silver nanoparticles based label free colorimetric sensor for nitrite anions. *Analytica Chimica Acta,* 842: 57 – 62.
11. Hernandez-Torres, J., Gutierrez-Franco, A., Gonzalez, P. G., Garcia-Gonzalez, L., Hernandez-Quiroz, T., Zamora-Peredo, L., Mendez-Garcia, V. H. and Cisneros-de la Rosa. A. (2016). Photoluminescence and raman spectroscopy studies of carbon nitride films. *Journal of Spectroscopy*, 2016: 1 – 8 .
12. Chai, B., Peng, T., Mao, J., Li, K. and Zan, L. (2012). Graphitic carbon nitride ($g\text{-}C_3N_4$)-Pt-TiO_2 nanocomposite as an efficient photocatalyst for hydrogen production under visible light irradiation. *Physical Chemistry Chemical Physics,* 14: 16745 – 16752.
13. Yang, S., Gong, Y., Zhang, J., Zhan, L., Ma, L., Fang, Z., Vajtai, R., Wang, X. and Ajayan, P. M. (2013). Exfoliated graphitic carbon nitride nanosheets as efficient catalyst for hydrogen evolution under visible light. *Advanced Material*, 25: 2452 – 2456.
14. Thomas, A. Fischer, A. Goettmann, F. Antonietti, M. Muler, J-O. Schlogl, R. and Carlsson, J. M. (2008). Graphitic carbon nitride materials: Variation of structure and morphology and their use as metal-free catalysts. *Journal of Material Chemistry*, 18: 4893 – 4908.
15. Xia, B., Chu, M., Wang, S, Wang, W., Yang, S., Liu, C. and Luo, S. (2015). Graphene oxide amplified electrochemiluminescence of graphitic carbon nitride and its application in ultrasensitive sensing for Cu^{2+}. *Analytical Chemica Acta*, 9: 891:113 - 119.
16. Zhao, Z., Sun, Y. and Dong, F. (2015). Graphitic carbon nitride based nanocomposites: A review. *Nanoscale*, 7: 15 – 37.
17. Lee, E. Z., Jun, Y-S., Hong, W. H., Thomas, A. and Jin, M. M. (2010). Cubic mesoporous graphitic carbon(iv) nitride: an all-in-one chemosensor for selective optical sensing of metal ions. *Angewandte Chemie International Edition,* 49: 9706 – 9710.

18. Tian, J., Liu, Q., Asiri, A. M., Al-Youbi, A. O. and Sun, X. (2013). Ultrathin graphitic carbon nitride nanosheet: A highly efficient fluorosensor for rapid, ultrasensitive detection of Cu^{2+}. *Analytical Chemistry,* 85: 5595 – 5599.
19. Zhang, S., Li, J., Zeng, M., Xu, J., Wang, X. and Hu, W. (2014). Polymer nanodots of graphitic carbon nitride as effective fluorescent probes for the detection of Fe^{3+} and Cu^{2+} Ions. *Nanoscale*, 6: 4157 – 4162.
20. Sam, M. S., Lintang, H. O., Sanagi, M. M., Lee, S. L. and Yuliati, L. (2014). Mesoporous carbon nitride for adsorption and fluorescence sensor of *n*-nitrosopyrrolidine. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 124: 357 – 364.
21. Mane, G. P. Dhawale, D. S. Anand, C. Ariga, K. Ji, Q. Wahab, M. A. Mori, T. and Vinu, A. (2013). Selective sensing performance of mesoporous carbon nitride with a highly ordered porous structure prepared from 3-amino-1,2,4-triazine. *Journal of Materials Chemistry A*, 1: 2913 – 2920.
22. Wang, Q., Wang, W., Lei, J., Xu, N., Gaul, F. and Ju, H. (2013). Fluorescence quenching of carbon nitride nanosheet through its interaction with DNA for versatile fluorescence sensing. *Analytical Chemistry*. 85: 12182 – 12188.
23. Alim, N. S. Lintang, H. O. and Yuliati, L. (2015). Fabricated metal-free carbon nitride characterizations for fluorescence chemical sensor of nitrate ions. *Journal Teknologi*, 76(13): 1 – 6.
24. Wang, N., Han, Z., Fan, H. and Ai, S. (2015). Copper nanoparticles modified graphitic carbon nitride nanosheets as a peroxidase mimetic for glucose detection. *RSC Advances*, 5: 91302 – 91307.
25. Lee, S. C., Lintang, H. O. and Yuliati, L. (2012). A urea precursor to synthesize carbon nitride with mesoporosity for enhanced activity in the photocatalytic removal of phenol. *Chemistry-An Asian Journal*, 7: 2139 – 2144.
26. Cheng, S-L. and Chen, M-F. (2012). Fabrication, characterization, and kinetic study of vertical single-crystalline CuO nanowires on Si substrates. *Nanoscale Research Letters*, 7:119 – 126.
27. Zhu, J., Xiao, P., Li, H. and Carabineiro, S. A. C. (2014). Graphitic carbon nitride: synthesis, properties and application in catalysis. *Applied Materials & Interfaces*, 6: 16449 – 16465.
28. Dong, G., Zhang, Y., Pan, Q. and Qiu, J. (2014). A fantastic graphitic carbon nitride (g-C_3N_4) material: Electronic structure, photocatalytic and photoelectronic properties. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, 20: 33 – 50.
29. Cui, Y., Tang, Y. and Wang, X. (2015). Template-free synthesis of graphitic carbon nitride hollow spheres for photocatalytic degradation of organic pollutant. *Materials Letters*, 161: 197 – 200.
30. Dai, H., Gao, X., Liu, E., Yang, Y., Hou, W., Kang, L. and Fan, J. (2013). Synthesis and characterization of graphitic carbon nitride submicrospheres using microwave method under mild condition. *Diamond and Related Materials*, 38: 109 – 117.
31. Tiong, P., Lintang, H. O., Endud, S. and Yuliati, L. (2015). Improved interfacial charge transfer and visible light activity of reduced graphene oxide-graphitic carbon nitride photocatalysts. *RSC Advances*, 5: 94029 – 94039.
32. Jasman, S. M., Lintang, H. O. and Yuliati, L. (2017). Enhanced detection of nitrite ions over copper acetylacetonate/polymeric carbon nitride composites. *Macromolecular Symposia*, 371: 84 – 93.
33. Ding, Z., Chen, X., Antonietti, M. and Wang, X. (2011). Synthesis of transition metal-modified carbon nitride polymers for selective hydrocarbon oxidation. *ChemSusChem,* 4: 274 – 281.
34. Luo, J., Cui, Z-C. and Zang, G-K. (2013). Mesoporous metal-containing carbon nitrides for improved photocatalytic activities. *Journal of Chemistry*, 2013: 1 – 6.
35. Mu, T., Huang, J., Liu, Z., Han, B., Li, Z., Wang, Y., Jiang, T. and Gao, H. (2004). Synthesis and characterization of polyester structure carbon nitride. *Journal of Material Research*, 19(6): 1736 – 1741.
36. Liu, J., Zhang, T., Wang, Z. Dawson, G. Chen, W. (2011). Simple Pyrolysis of Urea into Graphitic Carbon Nitride with Recyclable Adsorption and Photocatalytic Activity. *Journal of Materials Chemistry*, 21: 14398 – 14401.
37. Derrien, G., Charnay, C., Zajac, J., Jones, D. J. and Roziere, J. (2008). Copper-containing monodisperse mesoporous silica nanospheres by a smart one-step approach. *Chemistry Communication*, 27: 3118 – 3120.
38. Tang, I. H., Sundari, R., Lintang, H. O. and Yuliati, L. (2016). Polyvinylpyrolidone as a new fluorescent sensor for nitrate ion. *Malaysia Journal of Analytical Sciences*, 20(2): 288 – 295.