

Synthesis of Nitrogen-Doped Carbon Dots from Nanocrystalline Cellulose by Pyrolysis Method as Hg²⁺ Detector

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Abstract. The synthesis of modified carbon dots (N-CDs) from nanocrystalline cellulose, as the carbon source, with the combination of urea and ethylenediamine, as nitrogen dopant agents, was successfully carried out by pyrolysis at 300 °C. The N-CDs dispersed in both ethanol and distilled water generated bright blue fluorescent color under a UV lamp at 365 nm wavelength with a 29% quantum yield value. FTIR analysis confirmed that the surfaces of carbon dots were modified by amine and N-doped groups on the carbon ring structure and the data from the UV-VIS spectrum also showed that assumption. Produced N-CDs had a size distribution of 2-5 nm with an average diameter of around 3.4 nm. The ability of N-CDs as a detector was explored from the fluorescence quenching by Hg²⁺ ions, in which it reached 40%. The determination of Hg²⁺ could be completed in 10 min with a wide linearity range from 0-100 µM and a detection limit of 59 µM by the static quenching process.

Keywords: Carbon dots; Metal ion sensor; Nanocrystalline cellulose; N-dopant agent; Static quenching

1. Introduction

Mercury (II) ion (Hg²⁺) is one of the heavy metals commonly utilized in industrial processes related to pesticides, catalysts, batteries, and gold mining. Due to its high toxicity, the presence of this metal has caused serious environmental pollution that badly affected human health (Liu *et al.*, 2013). Instrumental methods, such as atomic absorption spectrometry (AAS) and inductively coupled plasma mass spectrometry (ICP-MS), are generally more preferred to detect metal ions. They have high selectivity and sensitivity, even at a very low or trace concentration (Zhou *et al.*, 2019). However, these techniques have some drawbacks, where their analysis requires skillful operators, is time-consuming and high-cost, and with equipment that is difficult to carry (Ju *et al.*, 2011). Meanwhile, fluorescent chemosensors are promising techniques, providing qualitative and quantitative

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and quantitative metal ion detection that are cost-efficient with high selectivity and sensitivity, simple sample preparation, and no requirement of reference solutions, real-time monitoring, and fast response time (Kaur, Kaur, and Kumar, 2018; Ju *et al.*, 2011).

Carbon dots (CDs), one of the carbon materials with attractive optical properties and sizes smaller than 10 nm, have drawn great attention into nanotechnology owing to their wide range of applications in chemical biosensors, biomedical applications – including biomedical imaging, drug delivery, clinical diagnosis, and optoelectronics (Kusrini *et al.*, 2020; Devi *et al.*, 2018; Wang *et al.*, 2017). Quantum dots were studied to be used as fluorescent labels to substitute toxic synthetic dyes in biomedical imaging and it turned out that they were more stable than organic dyes (Lim *et al.*, 2021; Goreham *et al.*, 2019). The attractive optical properties, such as adjustable photoluminescence and multiple emission with dependent excitation, were obtained from the effect of quantum confinement or the existence of conjugated π -domain (Zu *et al.*, 2017). CDs are superior to the other conventional fluorescent detectors with their excess photobleaching resistance, neglectable toxicity, chemical inertness, good biocompatibility, inexpensive charge, water-soluble, and facile synthesis (Zuo *et al.*, 2015). They can be used as detectors based on their interaction with the substances and confirmed by the decreasing fluorescence intensity, also known as the quenching effect. High quenching effect shows that CDs have excellent detection capability of various metal ions, such as Fe(III) (Cheng, Xing, and Wu 2019), Cu(II) (Liu *et al.*, 2017), Pb(II) (Wang *et al.*, 2015), Cr(VI) (Zhang *et al.*, 2017), As(III) (Gupta *et al.*, 2016), Ag(I) (Ahmed, Kumar, and Veerappan, 2016), and Hg(II) (Yan *et al.*, 2016). The sensing mechanism based on fluorescence quenching consists of static and dynamic types. Static quenching occurs when a non-fluorescent complex is formed from the interaction between the surface groups in carbon dots, such as –COOH, –OH, and –NH₂, and metal ions as quenchers (Sagbas and Sahiner, 2019), while dynamic quenching is dependent on the diffusive collision of excited fluorescence molecule with the quencher (Wu *et al.*, 2017).

The carbon sources for CDs have a great influence on their quantum yields and optical properties. Therefore, screening carbon sources with non-toxic characteristics, stability in composition, and extensively available is still the center of focus in the preparation of CDs. Cellulose is the most abundant biopolymer and accounts for fifty percent of the natural biomass. Cellulose consists of several hundred of 1,4-anhydrous-D-glucopyranose units arrange into a long linear chain (Trache *et al.*, 2017). Nanocrystal cellulose is a nanosized crystalline region in cellulose fibers obtained by acid hydrolysis. It has many advantageous properties, such as good biocompatibility, large surface area, unique morphology, and stable chemical properties. Moreover, it is renewable, environment-friendly, and non-toxic (Rochardjo *et al.*, 2021; Souza *et al.*, 2016). Furthermore, the molecules contain a lot of hydroxyl and ether groups, which could provide the elemental and basic structure in the formation of CDs.

The pyrolysis method is commonly used in CDs synthesis. This method is advantageous due to the directness, repeatability, and practicality of producing CDs (Wang *et al.*, 2017). However, most CDs prepared via biomass pyrolysis method usually have low fluorescence quantum yields, hence limiting their utilization. Souza *et al.* (2016) synthesized CDs from nanocrystal cellulose by pyrolytic process at 300-600°C and produced a 1.64% quantum yield (Souza *et al.*, 2016). Fluorescence quantum yield is greatly associated with the surface condition, especially with the presence of functional groups or heteroatom-doping that contain of O, N, and S elements. Nitrogen atoms can generate a new surface state (N-state). The electrons trapped in the N-state can produce a high yield of radiative recombination and depress non-radiative recombination. Therefore, improving the quantum yield of carbon dots can be achieved by modifying the surfaces. The preferred choices of dopants to

improve QY in CDs in the respective order are as follows: primary amine > secondary amine (while tertiary amine is hardly applied to produce CDs) and diamine > monoamine (Zhai *et al.*, 2012). Shen *et al.* (2016) improved the quantum yield of cellulose by up to 21.7 % by using urea as the N-doped source via the hydrothermal method (Shen *et al.*, 2016).

In this study, modified CDs with high quantum yield, low toxicity, good water-solubility and high photostability were prepared by the pyrolysis of nanocrystal cellulose as the carbon source, with the combination of urea and ethylenediamine as modified agents. Nanocrystal cellulose was isolated from the fibers of oil palm empty fruit bunches as an approach to utilize the waste from PT. Perkebunan Nusantara IV, Indonesia. The selectivity and sensitivity of Nitrogen-doped carbon dots (N-CDs) in various metal ions were determined. Produced carbon dots were applied as fluorescent probes to detect Hg^{2+} metal ions in water.

2. Materials and Methods

2.1. Materials

Ethylenediamine, ethanol absolute, urea, standard solution of $\text{Cd}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$, $\text{Cr}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_2$, $\text{Mn}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2$, $\text{Hg}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$, NaNO_3 , and H_3AsO_4 were purchased from Merck, Germany. Oil palm empty fruit bunches (OPEFB) were collected from the oil palm plantation developed by Adolina PT. Perkebunan Nusantara IV, Indonesia. Dialysis membrane was obtained from Biodesign Inc., New York. All chemical reagents were pro-analysis grade, and they were directly used untreated. Deionized water was used throughout the entire experiment.

2.2. Carbon dots synthesis

The nanocrystal cellulose (NCC) isolated from an oil palm empty fruit bunch was prepared based on the procedure described by Marpongahtun *et al.* (2018). The NCC (6 g) was soaked in 10 mL absolute ethanol and 6 g urea solution. The mixture was stirred at room temperature for 15 minutes. After that, 5.4 ml ethylenediamine was slowly dropped into the mixture while it was being stirred. Next, the mixture was put in porcelain glass and pyrolyzed in a furnace at 300°C for 2 hours in a nitrogen atmosphere. The carbon dots produced were grounded into powder with a ceramic mortar and immersed in two solvents, such as distilled water and ethanol, consecutively, overnight. The filtrate was dialyzed in a dialysis bag (MWCO =3500) for 72 hours. Finally, N-CDs in powder form were obtained by freeze-drying for further research. Figure 1 shows a schematic illustration of the N-CDs preparation and formation mechanism.

2.3. Characterization

UV-VIS absorption spectrum was analyzed by using Jenway 7305 spectrophotometers, and Photoluminescence PL Matrixes (EEM) were obtained from Duetta Horiba Fluorescence and Absorbance Spectrometer with Excitation Emission method. The morphology and mean diameter of N-CDs were characterized by using H9500 high-resolution TEM (HRTEM)-EDX operating at 200 kV. Fourier transform infrared spectroscopy (FTIR) was measured at wavenumbers ranging from 500-4000 cm^{-1} using a Shimadzu IR Prestige-21 spectrometer with a KBR disc. The fluorescent lifetime was analyzed by using Horiba FluoroMax Hybrid Fluorescence Spectroscopy steady State and Life Time System.

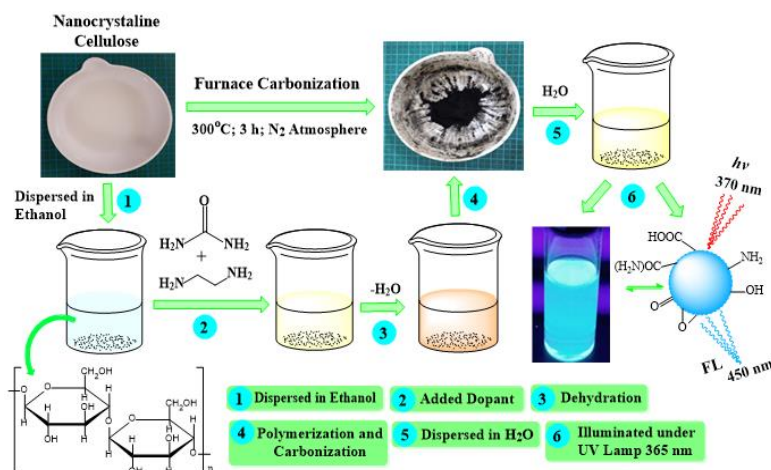


Figure 1 Schematic illustration of N-CDs preparation and formation mechanism.

2.4. Quantum yield measurement

The quantum yield of N-CDs was calculated based on the literature (Zhang and Chen, 2013) by using the following equation (1):

$$\phi_u = \phi_s (Y_u/Y_s)(A_s/A_u)(\eta_s/\eta_u)^2 \quad (1)$$

In brief, quinine sulfate (0.5 M H₂SO₄ as solvent) with QY of 54%, was chosen as a reference standard. The subscripts u and s indicated the values for N-CDs and quinine sulfate respectively, ϕ is the QY, Y is the integrated area of the fluorescence emission peak, A is the absorbance at 370 nm, and η is the refractive index ($\eta_s = 1.369$, $\eta_u = 1.332$).

2.5. Metal ion detection

The selectivity detection of Hg²⁺ was performed based on N-CDs fluorescence quenching with various metal ions. N-CDs dispersion (1 μ g/mL) was mixed with 100 μ M concentration of each metal ion, such as Cd²⁺, Pb²⁺, Cu²⁺, Cr²⁺, Mg²⁺, Fe²⁺, Mn²⁺, Ni²⁺, Co²⁺, Hg²⁺, and Zn²⁺ in an acidic solution. The sensitivity of Hg²⁺ ion detection was investigated by the addition N-CDs solution into different concentrations of Hg²⁺ ranging from 0.1 μ M to 100 μ M. All the experiments were carried out by 1:1 solution ratio (not only N-CDs: various metal ions, but also N-CDs: various concentrations of Hg²⁺), and each mixture was gently stirred for 15 minutes at room temperature before the fluorescence measurement was recorded at 370 nm.

3. Results and Discussion

3.1. Characterization of N-CDs

The surface modification by nitrogen-containing functional groups in carbon dots was confirmed by FTIR spectra. Figure 2 shows the FTIR spectra of nanocrystalline cellulose and N-CDs. Nanocrystalline cellulose (NCC) had a broad band at 3387 cm⁻¹ that could be assigned to O-H stretching vibrations and the peak at 2916 cm⁻¹ corresponded to C-H stretching vibrations. These were aligned with the previous study (Lu and Hsieh, 2010). The interaction between the hydrogen bond and absorbed water was detected at 1635 cm⁻¹, and the band at 1319 cm⁻¹ was related to the presence of the crystalline structure of cellulose (Yun-Fei, Maimaiti, and Bo, 2017). The absorption peaks at 1210 cm⁻¹ and 1056 cm⁻¹ were associated with C-O-C stretching of aromatic ether linkages, the peak at 1056 cm⁻¹ exhibited -CH₂- stretching vibration band, and the peak at 894 cm⁻¹ indicated β -glycosidic bond that connected glucose monomers in cellulose (Shanmugarajah *et al.*, 2015).

The absorption peaks of N-CDs at 3370 cm⁻¹, 1680 cm⁻¹, and 1635 cm⁻¹ corresponded to -OH/-NH, C=O and C=C stretching vibrations in respective orders (Nie *et al.*, 2014; Hsu

and Chang, 2012). The presence of nitrogen-containing functional groups in CDs was proven by the appearance of specific peaks at 1404 cm^{-1} and 1270 cm^{-1} , which were assigned to typical stretching modes of C-N-C heterocyclic and C-N bonds according to the previous research (Wu *et al.*, 2017). These results confirmed that nitrogen-containing functional groups were formed during the pyrolysis process with the combination of ethylenediamine, urea, and NCC. Nitrogen species were efficiently doped into the framework of CDs.

The morphological characteristic of N-CDs by using a High-Resolution Transmission Microscope (HRTEM) is shown in Figure 3. The particle size distribution and the lattice spacing of N-CDs were determined by using the *Image-J* application. N-CDs had a spheroidal shape, and the particles were evenly distributed without agglomeration (Figure 3a). The size distribution of N-CDs, as presented in the histogram (Figure 3c), was 2-5 nm with a mean diameter of 3.4 nm. Moreover, the inset in Figure 3a indicated that N-CDs had stripe-like structures with a lattice spacing of 0.206 nm, which was too close to the (100) diffraction facet of graphite carbon (Figure 3b).

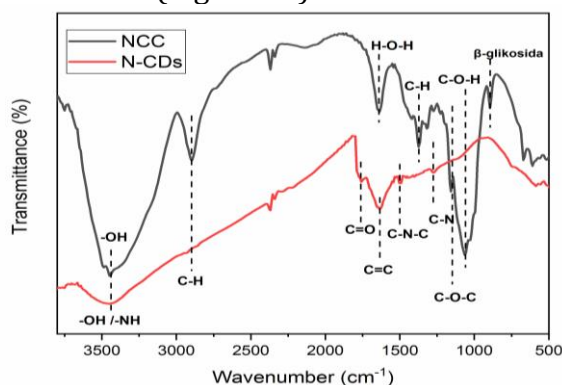


Figure 2 FTIR spectra of NCC and N-CDs

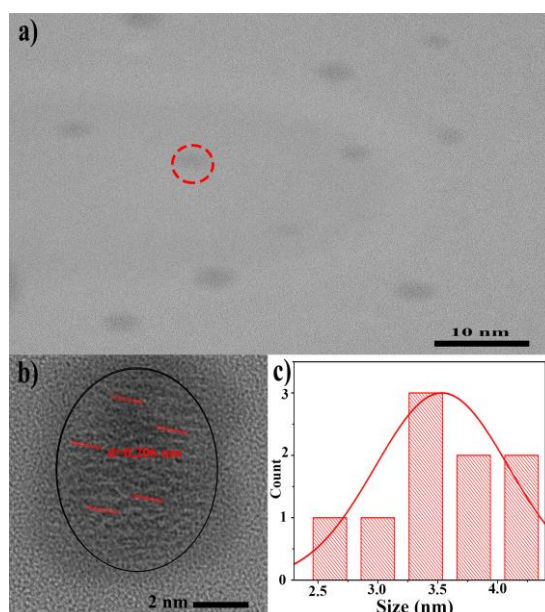


Figure 3 (a) HRTEM of N-CDs (b) Magnification image of HRTEM (c) Histogram of particle size distribution

3.2. Optical properties of N-CDs

The UV-VIS absorption spectrum of N-CDs showed two typical absorption peaks at 270 nm (π - π^* transition of C=C aromatic) and 340 nm (n - π^* transition of C=O/C=N bonds)

(Kumar *et al.*, 2017), as shown in Figure 4. The presence of nitrogen-containing functional groups in the surfaces of CDs was proven by the shift of absorption peaks to longer wavelengths, such as from 270 nm to 340 nm. Therefore, it was reasonable to assume that nitrogen-containing groups unshared electron pairs to become auxochromes and reacted with C=C aromatic as chromophores. From the photographic image (shown as an inset in Figure 4), the N-CDs dissolved in ethanol were yellowish under daylight. But, under UV lamp irradiation (365 nm), the modified carbon dots produced bright blue fluorescence. The strong fluorescence caused nitrogen atom in functional groups to not only generate chromophores on the surface but also to act as energy trap sites to trap excitons and induce transitions, thus emitting fluorescence (Yun-Fei, Maimaiti, and Bo, 2017). By using quinine sulfate as a reference, the quantum yield of N-CDs was 29% at 390 nm excitation wavelength. This result indicated that the amine functional group from the modified agent increased the QY to become much higher than in the previous study.

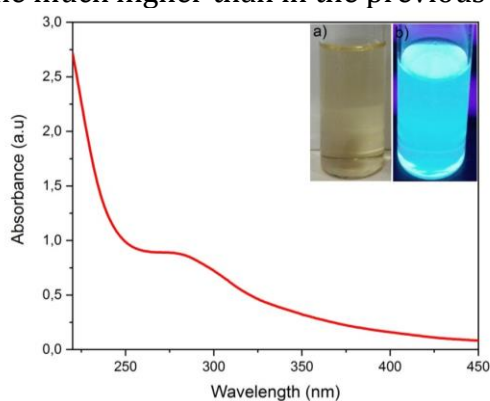


Figure 4 N-CDs UV-VIS absorption spectrum, the inset displays N-CDs under a) daylight b) UV lamp irradiation at 365 nm

Fluorescence emission spectra of N-CDs were obtained from the excitation wavelength ranging from 310 nm to 470 nm at different fluorescence intensities, as represented in Figure 5. When the excitation wavelength increased, the fluorescence intensity would initially increase but gradually decrease after that. The fluorescence spectra of N-CDs could be concluded that they depended on the excitation wavelength and had multiple excitations and emission spectral characteristics.

Carbon dots were synthesized by surface oxidation or passivation agent modification to emit fluorescence. Thus, they were generally hydrophilic in nature owing to the existence of oxygenated functionalities on their surfaces (Zhao and Zhu, 2018). Hydrophilic functional groups, such as -OH, -NH₂, and -COOH, could exist in carbon dots because nanocrystal cellulose (NCC) had rich -OH functional groups, while urea/ethylenediamine, as a modified agent, contained many amine functional groups. The structure of carbon dots with large carbon skeletons and the functional group could be formed by “Bottom-up” formation that involves the pyrolysis or carbonization of organic molecules. Condensation, polymerization, carbonization and passivation were common stages in the pyrolysis of organic molecules to produce carbon dots (Liu *et al.*, 2019).

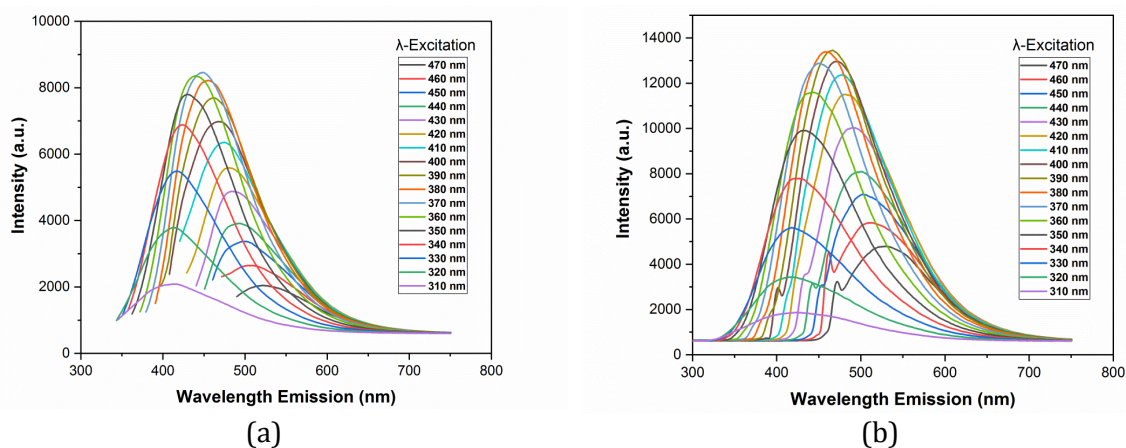


Figure 5 Photoluminescence spectra of N-CDs (a) in distilled water (b) in ethanol

In this study, we used two polar solvents (distilled water and ethanol) to extract/dissolve the N-CDs. The use of different solvents turned out to have affected the intensity of photoluminescence and the maximum emission wavelength of N-CDs. Carbon dots dissolved/extracted by ethanol had a maximum emission intensity at 470 nm wavelength when 390 nm excitation wavelength was given (Figure 5a). Meanwhile, carbon dots dissolved/extracted with distilled water had a maximum emission intensity at 450 nm wavelength when 370 nm excitation wavelength was given (Figure 5b). The carbon dots dispersed in ethanol had higher photoluminescence intensity than CDs in distilled water. This occurred because the presence of oxygenated species in carbon dots increased the density and electron transfer on the CDs, which affected the optical properties and luminescence produced. Good dispersibility of carbon dots in protic solvents could happen due to hydrogen bond interaction between the oxygenated functional groups and solvent. No precipitation indicated complete dispersion in carbon dots. Although carbon was hydrophobic, because the particle size was below 10 nm and it was supported by a plentiful of hydrophilic functional group, it could stabilize the carbon nanoparticles in an aqueous solution.

3.3. Mechanism fluorescence of N-CDs and their quenching process for Hg^{2+} detection

As depicted in Figure 1, nanocrystalline cellulose was used as the carbon source, while ethylenediamine and urea were used as the modification agents or N-dopant agents. The N-CDs obtained had strong fluorescence and high stability. The surface conditions, which were related to the functional groups and the degree of surface oxidation, determined the strong fluorescence emission of N-CDs (Liu *et al.*, 2019). During pyrolysis at 300°C under a nitrogen (N_2) atmosphere, NCC (precursor) underwent a degradation process involving several steps, such as decarboxylation, dehydration, condensation, and also aromatization (Supriadi *et al.*, 2017). When ethylenediamine and urea were presented to the reaction system, not only were some nitrogen-containing functional groups formed but N atoms were also introduced to the precursor carbon nuclear lattice through the high-temperature pyrolysis process. If the degree of surface oxidation increased, the surface defect would form greatly. The surface could yield defect sites when nitrogen with functional groups was introduced to it. These defect sites resulted in trapped fluorescence emission that emerged from the excitons radiative recombination (Yang *et al.*, 2012).

Fluorescence characteristic was used to determine the ability of N-CDs to detect Hg^{2+} metal ions. Figure 6 shows the photoluminescence intensity of N-CDs with the presence of various metal ions, such as Cd^{2+} , Co^{2+} , Cr^{3+} , Cu^{2+} , Fe^{2+} , As^{5+} , Hg^{2+} , Mg^{2+} , Mn^{2+} , Ni^{2+} , Pb^{2+} , and Zn^{2+} . The histogram of % quenching $(F_0 - F) / F_0$. F represented the fluorescence intensity of N-CDs with the addition of various metal ions at 370 nm excitation wavelength, whereas F_0

represented the fluorescence intensity of N-CDs without the presence of metal ions. Figure 6 (a) confirmed the carbon dots selectivity of Hg^{2+} was the largest quenched fluorescence intensity among other metal ions. The histogram in Figure 6 (b) shows that Hg^{2+} metal ion was quenched by the fluorescence intensity to up to 40 %, whereas the other ions only showed little effect in the sensing system. This indicated that the N-CDs were highly selective towards Hg^{2+} ions.

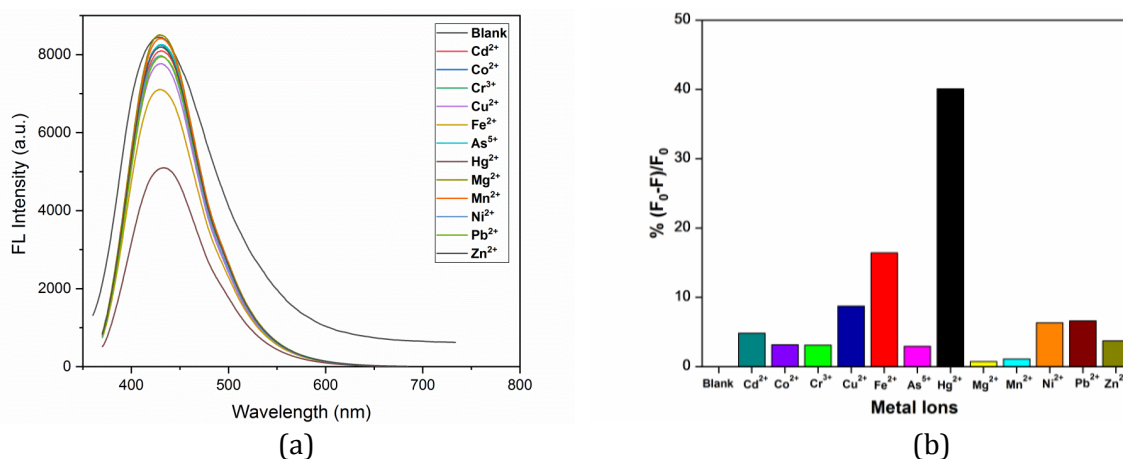


Figure 6 (a) Fluorescence emission spectra of N-CDs with the addition of various metal ions (b) Relative N-CDs fluorescence intensity in the presence of various metal ions at the concentration of $100\mu\text{M}$

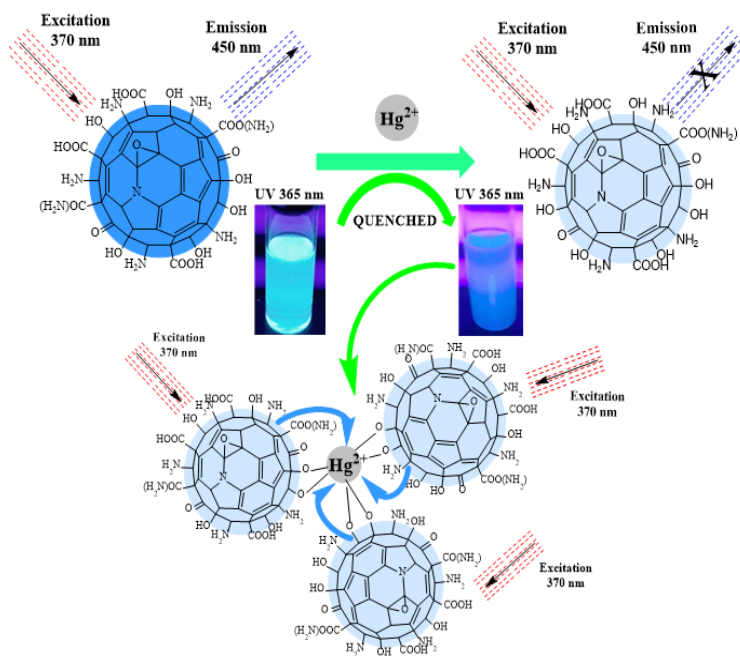


Figure 7 Schematic illustration quenching process

Figure 7 shows a schematic illustration of the fluorescence quenching mechanism of N-CDs in the presence of Hg^{2+} . The strong quenching fluorescence intensity of N-CDs by Hg^{2+} was related to the large affinity of nitrogen and oxygen on the surface of N-CDs (Atchudan *et al.*, 2017). The fluorescence quenching was caused by the complex compounds formed from the electron-rich functional groups in CDs to the vacant d-orbitals in Hg^{2+} . Higher binding affinity in the d-orbitals in Hg^{2+} ions on the surface of the carbon dots might be the main reason for the selective characteristics. Meanwhile, Fe^{2+} ions had only enough

fluorescence intensity quenching. Even though Fe^{2+} could react with electron donor groups in carbon dots, their electrophilic ability/electron capture was weaker than that of Hg^{2+} .

In order to explore the sensitivity of the resulting N-CDs, the fluorescence responses towards different concentrations of Hg^{2+} in the range of 0-100 μM were investigated. The fluorescence intensity gradually decreased with the increase in Hg^{2+} concentration (Figure 8). There was a good linear relationship between the fluorescence intensity and Hg^{2+} concentration from 0 to 100 μM ($R^2=0.9168$), with a detection limit of 59 μM (Figure 9).

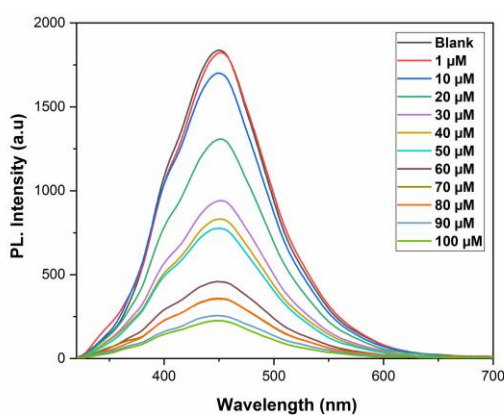


Figure 8 Emission spectra of N-CDs at Hg^{2+} concentration range of 0-100 μM

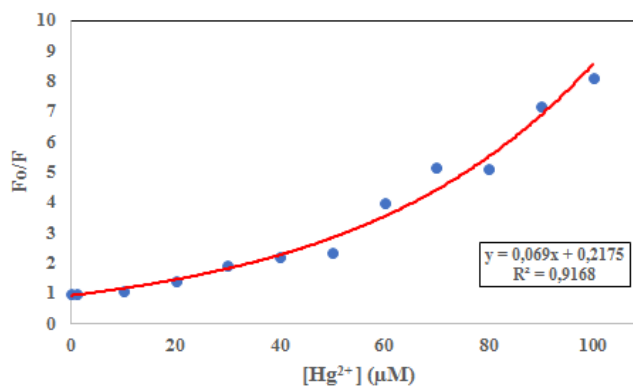


Figure 9 Stern-Volmer plots described the dependence of F_0/F the fluorescence intensity on the Hg^{2+} concentration (0-100 μM)

Normally, the mechanism of fluorescence quenching consists of static and dynamic quenching. In the static type, the quenching was activated by the production of ground state complexes, while in the dynamic type, the quenching was dependent on the collisions between the quencher and excited fluorescence molecules (Li *et al.*, 2021). Stern-Volmer plots could be used to distinguish between static and dynamic quenching. Linear F_0/F on $[Q]$ was observed previously as dynamic quenching (Lakowicz, 2006). But, as seen in Figure 9, the Stern-Volmer plots exhibited upward curvature or concave toward the y-axis. This indicated that the fluorescence quenching of N-CDs by Hg^{2+} was a static quenching type. Fluorescence lifetime was the preferred method to identify static or dynamic quenching for more accurate results. Fluorescent decay curves (Figure 10) were fitted by using a bi-exponential function as shown in equation 2 (Lakowicz, 2006):

$$R(t) = B_1 \exp(-t/\tau_1) + B_2 \exp(-t/\tau_2) \quad (2)$$

Where $R(t)$ was the intensity of decay as the amount of every single exponential decays, B_1 and B_2 were the pre-exponential factors, τ_1 and τ_2 were decay times.

The average lifetime of N-CDs (τ_{ave}) was determined by equation 3 as follows (Lakowicz, 2006):

$$\tau_{ave} = \frac{B_1\tau_1^2 + B_2\tau_2^2}{B_1\tau_1 + B_2\tau_2} \quad (3)$$

Based on the fitting results with a chi-square value (χ^2) of 1.17, two decay times were obtained, such as τ_1 of 13.8 ns (23.92%) and τ_2 of 4.3 ns (76.08%) and the average fluorescence lifetime of CDs was about 5.14 ns.

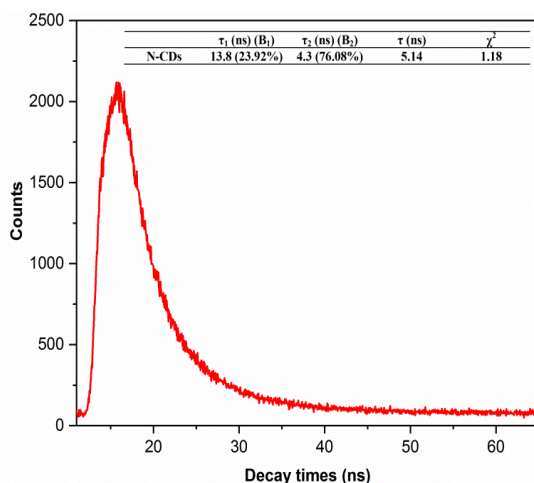


Figure 10 Fluorescence decay curves of N-CDs

4. Conclusions

High fluorescent N-CDs were successfully synthesized from cellulose in a one-step synthesis by pyrolysis; the ethylenediamine/urea was used as the nitrogen source, and ethanol was the solvent. The resulting N-CDs emitted strong blue fluorescence with QY value of 29% and could be considered as hydrophilic carbon dots owing to good dispersion in water and ethanol. Moreover, the N-CDs were spherical without having any agglomeration. The average diameter was 3.4 nm, and the lattice spacing was 0.206 nm. Functional groups in N-CDs were confirmed by FTIR analysis. Based on its excellent water solubility and persistently high fluorescence intensity, the N-CDs could be utilized as a fluorescent probe for sensitive and selective direct detection of Hg²⁺ in a concentration range of 0-100 μ M and detection limit of 59 μ M. The fluorescence quenching of N-CDs by Hg²⁺ was a static quenching type, where the Stern-Volmer diagram plot showed an upward curvature and the average lifetime of N-CDs was measured to be 5.14 ns.

Acknowledgments

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