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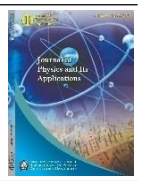

Optical Response of Various Heavy Metal Ions-Based Carbon Dots Photoluminescent Quenching Effect

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ABSTRACT

Carbon nanodots (Cdots) are a type of semiconductor carbon-based nanomaterial that is gaining popularity due to its excellent characteristics (e.g., biocompatibility, unique optical properties, low cost, eco-friendly, and high stability). In terms of physicochemical properties for an environmentally friendly sensor application, this material also has an excellent ability to detect heavy metal ions in the biosphere. In this study, we proposed a comprehensive optical characterization to examine the sensitivity of the Cdots probe for three heavy metal ions (i.e., Mn, Pb, and Cr ions) and compare the performance. The results of the experiment revealed that each heavy metal ion reacted differently to the physical properties of Cdots. With the addition of Cr, Mn, and Pb metal ions from the original Cdot solution, which is only 1.45 ns, the lifetime of quenched Cdots is 2.55 ns, 3.15 ns, and 2.15 ns, respectively, according to the TRPL experiments. With additional Cr, Mn, and Pb discovered, the intensity of PL dropped by 5.7%, 14.2%, and 21.4%, respectively. Among these various heavy metal ions, Pb ions show the most affected by the quenching effect in Cdots-based photoluminescence, FTIR, and ultraviolet-visible light absorption characterization. Based on the results of three heavy metal ion experiments, this study can be implemented as the heavy metal ion sensor-based luminescence quenching effect of Cdots.

1. Introduction

Over the last century, human and industrial activities have resulted in massive rises in environmental exposure to various heavy metals (e.g., Cr, Pb, Cd, and As) [1,2]. The accumulation of these heavy metals has a wide range of negative effects on various body tissues and organs, resulting in human poisonings. Heavy metal ions have been an essential issue due to their special chemical significance and difficulty detecting them [2]. Concerning those issues, an environmentally friendly, low-cost material-based sensor must be employed to detect those various heavy metals. Among various heavy metal ion detection-based optical sensors (fluorescence spectroscopy, infrared spectroscopy, colorimetric spectroscopy, chemiluminescence spectroscopy, Raman spectroscopy, and refractive index spectroscopy sensing), carbon-dot-based sensing is the most potential technique that is both safe for the body (biocompatible) and simple to develop [3].

Since its initial discovery in 2004, Cdots have been promoted as a composite material using simple techniques, such as the electrophoresis method for producing single-walled carbon nanotubes [4]. Furthermore, Cdots are increasingly being explored and used for a variety of applications due to their superior properties, such as high biocompatibility [5,6], strong luminescence properties [7,8], chemical inertness and non-toxicity [7], and good photostability [9]. Besides their excellent properties, Cdots are extremely simple to synthesize because any biomass containing carbon atoms can be used as precursors. Since they come from organic materials and are environmentally friendly, Cdots are widely applied in biomedical [9], cell imaging [10], photocatalysis [11], lighting, and sensors [12]. Cdot is the most intensively active material for sensors to replace conventional semiconductor quantum dots (QDs) as their detection probe. This strategy is reasonable because QDs are highly toxic and expensive. After all, it contains heavy metal ions such as CdS, CdSe, and ZnS [13,14] and toluene as the solution, which is very dangerous for our environment and living organisms. Concerning those considerations, Cdots are the best material to replace semiconductor quantum dots-based heavy metal ion sensors.

Heavy metal pollution of terrestrial and aquatic ecosystems is a significant ecological issue with adverse effects on human health. Most heavy metals are produced naturally, although some come from

artificial sources. High atomic mass and toxicity to living things are two traits that define heavy metals. Most heavy metals can harm humans and pollute the ecosystem and atmosphere. As heavy metals interact with various environmental components like water, soil, and air, as well as with people and other animals, they can become highly poisonous [15]. Heavy metal refers to a class of metals or metalloids with toxic effects even at low concentrations (parts per billion) and a higher density [16,17]. They are also poisonous at low concentrations. Therefore, heavymetal ion detection in liquid is important for our lives.

Cr is a naturally occurring heavy metal in industrial processes and can be found in the earth's crust and seawater [2]. Because of bioaccumulation in the human body, Cr can cause various diseases. This includes everything from dermal, renal, neurological, and gastrointestinal disorders to the development of cancers in the lungs, larynx, bladder, kidneys, testicles, bone, and thyroid [18]. Moreover, Pb exposure can cause neurological, pulmonary, urogenital, and cardiovascular diseases due to immune-modulating, oxidative, and inflammatory pathways. This material may also trigger inflammatory reactions in different organs and throw off the equilibrium of the oxidant-antioxidant system. The body's physiological processes can be altered by Pb exposure, and it has been linked to a number of illnesses [2,19-21]. The metabolization of amino acids, cholesterol, and carbohydrates all benefit from the presence of Mn. Male infertility, neurological abnormalities, birth disabilities, and bone malformations are just a few effects that higher Mn concentrations can have [22]. Overall, it is important to minimize exposure to these heavy metals and to follow proper safety precautions when working with them to protect our health.

In general, the detection mechanism of heavy metal ions based on Cdots emission intensity can occur through two interaction phenomena, i.e., turn-on and turn-off detection. Turn-on detection appears when the intensity of Cdots emission increases after interaction with heavy metal ions. On the contrary, turn-off detection, often called the quenching phenomenon, is the decreasing emission intensity of Cdots due to interaction with heavy metal ions [14].

There have been reports on various techniques to generate Cdots, extending from simple to relatively complex processes (i.e., capillary electrophoresis and microwave pyrolysis). Although capillary electrophoresis is a potential technique for scaling up the methods, microwave pyrolysis stands out from other procedures due to its advantages in terms of reaction timeframes, reaction conditions, energy consumption, stability, ease of reproducibility, and product efficiency. In contrast to alternative synthesis techniques, which are labor-intensive and necessitate the isolation of the desired red-emissive, microwave pyrolysis shows significant promise [23].

In this paper, we studied the characteristic changes of Cdots fabricated by the simple microwave pyrolysis technique after interacting with three types of heavy metal ions (Mn, Cr, and Pb) using various optical spectroscopic methods to investigate the quenching effect (a process that reduces the fluorescence intensity of an original substance). In this experiment, we present three methods of sensing detection using photoluminescence, absorbance, and time-resolved photoluminescence. All three methods that we used show similar trends. Here, the photoluminescence properties of Cdots appear because of the surface passivation process during the synthesis process. This passivation effect makes energy trap at the surface of Cdots so that they can attract other ions or substances. This passivation effect is significant for heavy metal ion detection. In the future, absorbance (using a UV-Vis spectrometer) and photoluminescence methods will be the fastest way to detect heavy metal ions since these methods are simple and cheaper.

2. Methods

2.1. Materials

The precursors that we used were citric acid ($C_6H_8O_7$) as a carbon source and urea (CH_4N_2O) as a passivation agent; both were purchased from local distributor, PT Pudak Scientific, Indonesia. All chemicals used in this research are technical-grade reagents; the solvent used in this study was distilled water.

2.2. Cdots preparation

The Cdots were prepared with the following procedure: 2 grams of citric acid ($HOC(CH_2CO_2H)_2$) were mixed with 3 grams of urea ($CO(NH_2)_2$). The mixed powders were transferred into 60 mL of distilled water and homogenized using a magnetic stirrer at 70 ^oC. The solution was irradiated using a microwave with 450-watt power for 10 minutes. A solid black powder was formed after the irradiation. Furthermore, the black powder was crushed using a crucible and weighed before it was dissolved in distilled water with a concentration of 100 ppm (see Figure 1 (a)). This solution was then characterized and analyzed for heavy metal ions sensing.

2.3. Characterization method for Cdots

The spectrometer MAYA Pro 2000 from Ocean Optics acquired absorption and emission spectra. The photoluminescence spectrum was obtained using excitation light from a laser diode wavelength of 420 nm. We used the FTIR (Thermoscientific Nicolet iS-10) technique to characterize the bond structure's arrangement. To obtain the lifetime data, we used the

time-resolved photoluminescence (TRPL) technique using a picosecond pulsed diode laser at wavelength 420 nm with photon counting detector PDM series and signal processor TimeHarp 260 from Picoquant.

[24]. The photoluminescence properties of Cdots appeared because of the surface passivation process during the synthesis process. This passivation effect makes energy trap at the surface of Cdots so that they

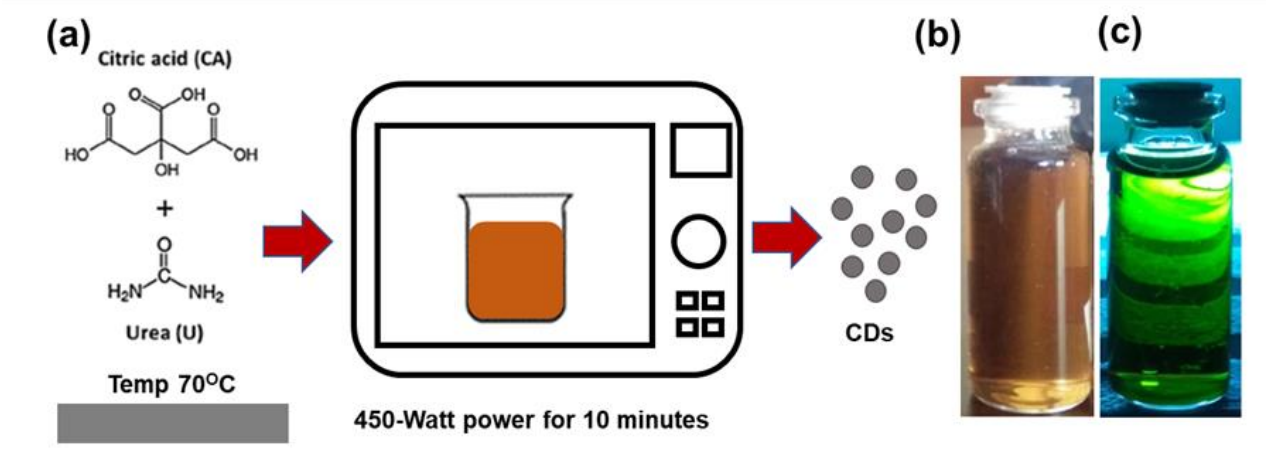

Fig. 1: (a). Synthesis of Cdots with microwave-assisted pyrolysis technique and the **(b).** Synthesized Cdots solution under ambient light. **(c).** Synthesized Cdots under UV-C light.

The pulse duration of the laser diode is less than 70 ps, with a maximum frequency of 40 MHz.

2.4. Sensing properties of three heavy metal ions

To investigate the sensing effect of Cdots, we used three different heavy metal ions, i.e., Cr, Mn, and Pb. The solution of Cr, Pb, and Mn with a concentration of 1 mM was added into Cdots solutions. In this experiment, we only make one ratio (9:1) of Cdot and heavy metal ions. We conducted a single ratio to specifically examine the selectivity of Cdots towards various heavy metal ions. This solution then observed the change in characteristics to evaluate the selectivity of Cdots as heavy metal ions sensors. In this paper, we did not conduct a sensitivity test.

3. Results and Discussion

3.1. Synthesized Cdots

Cdots from citric acid and urea were successfully synthesized using simple microwave irradiation methods where brown liquid samples were formed. To verify the formation of Cdots, we illuminated the treated samples using a UV-C lamp and emitting green emission (see Figure 1 (b) and (c)). During the UV-C irradiation procedure, the green emission (photoluminescence) of Cdots reveals that carbon was changed into quantum dimensional materials can attract other ions or substances. This passivation effect is significant for heavy metal ions detections. Surface passivation coats the Cdots surface using amine functional groups obtained from urea during microwave irradiation [25]. This process forms a thin insulating capping layer that can increase their photoluminescence properties.

3.2. Selectivity of three heavy metals ions

In the selectivity sensing experiment, Cdots liquid 9 mL was added with 1 mL of heavy metal ions. This mixture was then investigated to find the characteristics change after heavy metal ions addition. Figures 2(a) and (b) show the appearance of the Cdots production under ambient light using TEM (FEI TEM Tecnai G2 20 S-Twin 200kV) characterization [26]. Figure 2(a) shows the typical TEM image of the Cdots with an average size of 5.7 nm. Although the mixture has a different composition (i.e., Cr, Mn, and Pb), it can be seen that there was no significant difference in color when they were directly seen using the naked eye, as shown in Figures 2(c)-(e). Additionally, the TEM image indicates the size of the Cdots to be around 10 nm.

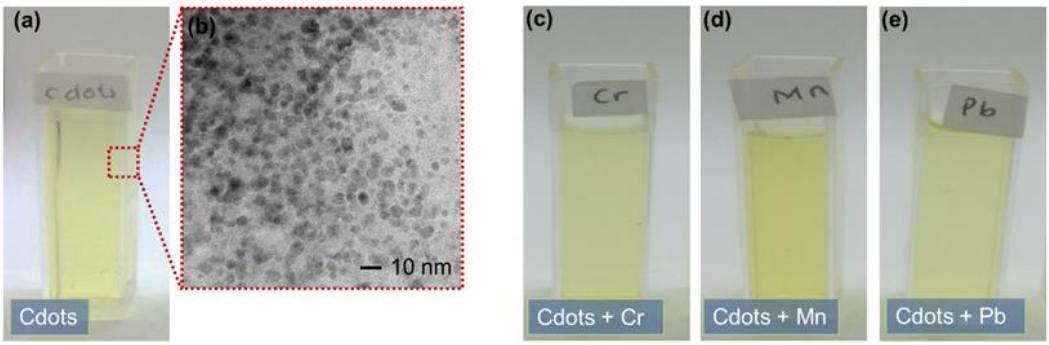

Fig. 2: (a). Original Cdots solution **(b)**. TEM image of the as-synthesized Cdots solution **(c)**. Cdots solution added with Cr **(d)**. Cdots solution added with Mn **(e)**. Cdots solution added with Pb.

Several optical and structural approaches were used to investigate the selectivity of CDots as a heavy metal ion detector. In this report, we investigated the selectivity of Cdots exclusively using the optical spectroscopy technique [25]. From the photoluminescence experiment using 420 nm wavelength excitation light, we can see that the emission peak of Cdots has predominance at 550 nm wavelength (see Figure 3 (a)). This result is appropriate with the green color shown by Cdots at the preliminary observation. With the addition of heavy metal ions, the intensity of Cdots emissions affected the first peak of Cdots. Moreover, the second peak for all the samples is located at a wavelength of 325 nm. According to several previous studies [28,29], this peak is a transition of π-π*, the peak of the C=C bonds. In general, the intensity has decreased with the addition of heavy metal ions results (see Figure 3(b)). The types of heavy metals that give various binding effects from weak to strong are Cr, Mn, and Pb, respectively. The peak at around 408 nm wavelength revealed the peak of n-π*, which is the absorbance peak of C=O bonds. Heavy metal ions that give a weak effect to a strong effect are Mn,

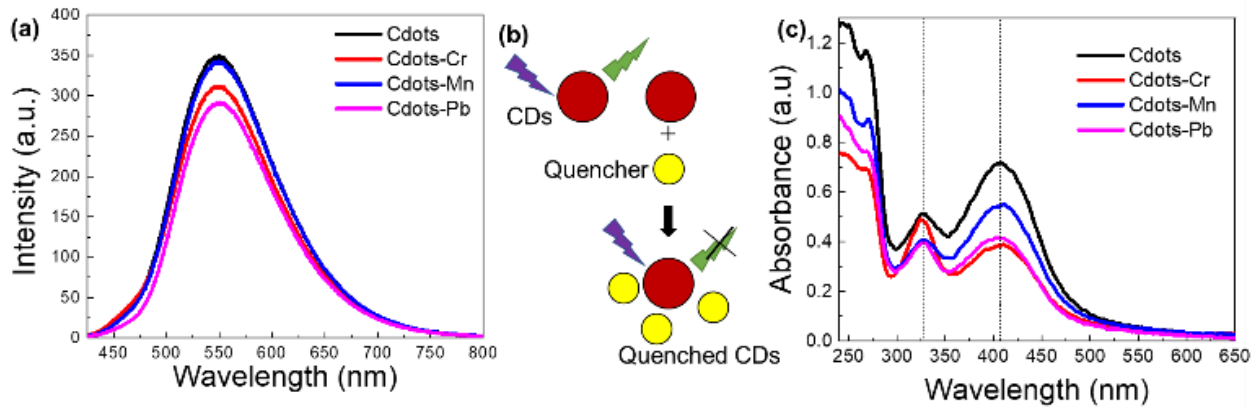

Fig. 3: (a). Photoluminescence **(b).** Quenching mechanisms of CDots **(c).** Absorption spectra of the various samples

was decreased due to the quenching effect. Once specific molecules or atoms are brought close to carbon nano-dots, the intensity of the light emitted by the dots decreases. The interaction between the illuminating carbon nano-dots and the quenchers (heavy metals ion) causes this effect. The degradation of intensity with additional Cr, Mn, and Pb was detected around 5.7%, 14.2%, and 21.4%, respectively. As the quenchers come into contact with the carbon nano-dots, they absorb the energy that causes the luminescence to decrease. Furthermore, the quenchers compete with the Cdots to release the excitation energy, decreasing the luminescence intensity (see Figure 3 (b)). Instead of being released as light, this absorbed energy might be lost as heat or through other non-luminescent pathways (static quenching effect). The hydroxyl and carboxyl groups, which we can see in the further FTIR spectra, can respond to this heavy metal selectivity. This interaction results in charge transfer and results in non-radiative exciton recombination. We can see three absorbance peaks from UV-vis characterization in each sample from the absorbance spectra results in Figure 3(c).

The first peak is at 250 nm, the absorbance peak of C=C from the core of Cdots [27]. However, this peak has decreased quite drastically with the addition of heavy metal ions. The heavy metal ions influencing the decreasing intensity peak most from the weakest are Mn, Pb, and Cr, respectively. This result proves that adding heavy metal ions strongly Pb, and Cr, respectively. Regarding the intensity level from the absorbance experiment, we can conclude that the shifting of intensity and wavelength of absorbance spectra can be used to indicate Cdots selectivity as heavy metal ions sensors.

Since the decreasing PL intensity was very obvious for Pb ions, followed by Cr and Mn, heavy metal ions Mn do not significantly quench the PL intensity. In addition, there was a change in FWHM due to the addition of heavy metal ions (see Figures 4 (a) and (b)). The most significant shifted parameter was reduced FWHM when heavy metals were added. From the experiment, Pb ions greatly reduced the Cdots FWHM, followed by Cr and Mn. These decreased results can be attributed to the number of surfaces that have functional groups influenced by the Pb ions. More reduction of FHWM means more Cdots functional groups that are affected by heavy metal ions. The PL and FWHM decline patterns are the same for Cr, Mn, and Pb. Although the trends differ, these results also support changes in the previous absorbance spectrum. From the results, we can conclude that Cdot is very responsive to Pb ions.

To obtain the lifetime properties of Cdots after interaction with heavy metal ions, time-resolve photoluminescence (TRPL) experiments were conducted. Previous studies have shown that observing changes in a lifetime using the TRPL method can increase the observed sensitivity of detecting heavy metal ions [30]. From the TRPL results, it can be seen that there is a change in decay

lifetime due to the addition of heavy metal ions. Lifetime decay is when an electron returns to its ground state after being excited (see Figure 5(a)). Nevertheless, the lifetime value was increased after addition of Cr, Mn, and Pb metal ions, the lifetime of quenched Cdots becomes 2.55 ns, 3.15 ns, and 2.15 ns, respectively. This is because the metal ions can form complexes with the surface functional groups of

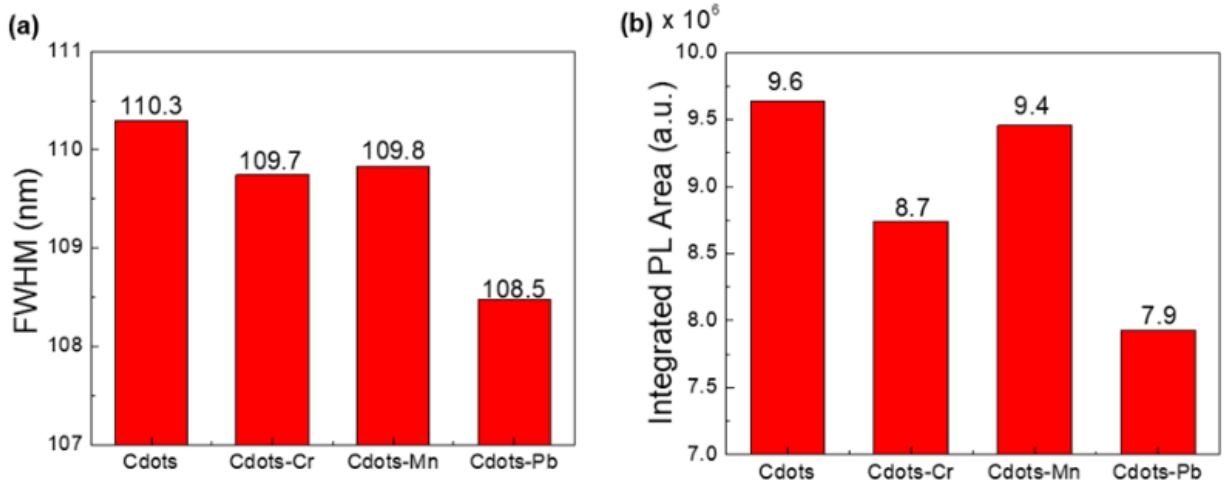

Fig. 4: (a). FWHM and **(b)**. The intensity of samples from PL spectra

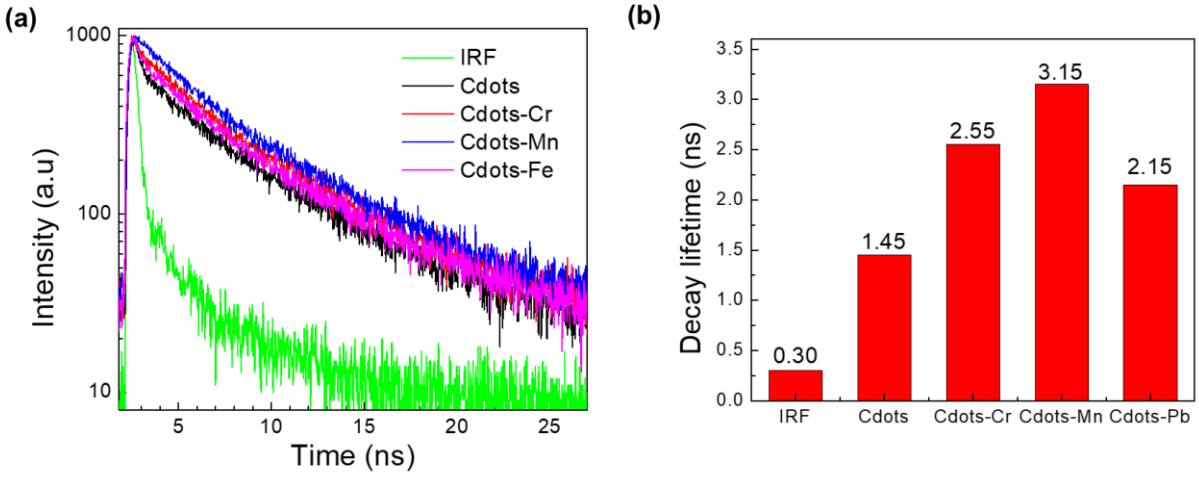

Fig. 5: (a). Lifetime spectra and **(b).** Lifetime calculation of samples.

adding heavy metal ions. This is due to changes in the surface energy level of the Cdots. The surface energy level can be changed into a radiative or non-radiative recombination center for electrons. From our results, we can assume that Pb and Cr ions make fewer changes in surface energy than Mn ions. The surface of Cdots is likely to be a non-radiative center when Pb and Cr ions are added. On the other hand, Mn ions tend to make fewer non-radiative centers at the surface of Cdots. This is why the photoluminescence and absorbance intensity of Cdot with Mn ions is higher than that of Cdots Pb and Cr ions. This change in a lifetime can also be used to indicate the selectivity of Cdots sensing heavy metal ions. The curve's lifetime decay (τ) was calculated using Eq.1.

$$\tau = \frac{(A_1\tau_1)^2+(A_2\tau_2)^2}{(A_1\tau_1)+(A_2\tau_2)} \qquad (1)$$

From the TRPL spectra above, we can see an increase in Cdots electron lifetime after adding various types of quenchers using equation (1). While Cdots solution only has a lifetime of around 1.45 ns. With the the carbon dots, which can, in turn, lead to a decrease in the non-radiative decay pathways and an increase in the radiative decay pathways (see Figure 5(b)).

Furthermore, we measure the FTIR spectra to determine if there is a change in functional group bonds on the Cdots after adding three different heavy metal ions (see Figure 6). FTIR spectra show that Cdots with or without heavy metal ions show transmitted bands at wavenumber 3400 cm^{-1} correspond to O-H bond, 1800 cm^{-1} correspond to C=C bonds, and 2200 cm^{-1} correspond to $C \equiv C$ bonds. These results follow the results obtained by previous researchers. With the addition of heavy metal ions, the transmitted bond of Cdots shows no significant differences. However, we can see a decrease in the intensity of each peak. Heavy metal Mn gives the least reduction in FTIR transmittance intensity, meaning that only a few functional groups are lost. Meanwhile, Pb and Cr are very dominant in reducing the FTIR transmittance of Cdots, meaning that many surfaces functional groups are missing.

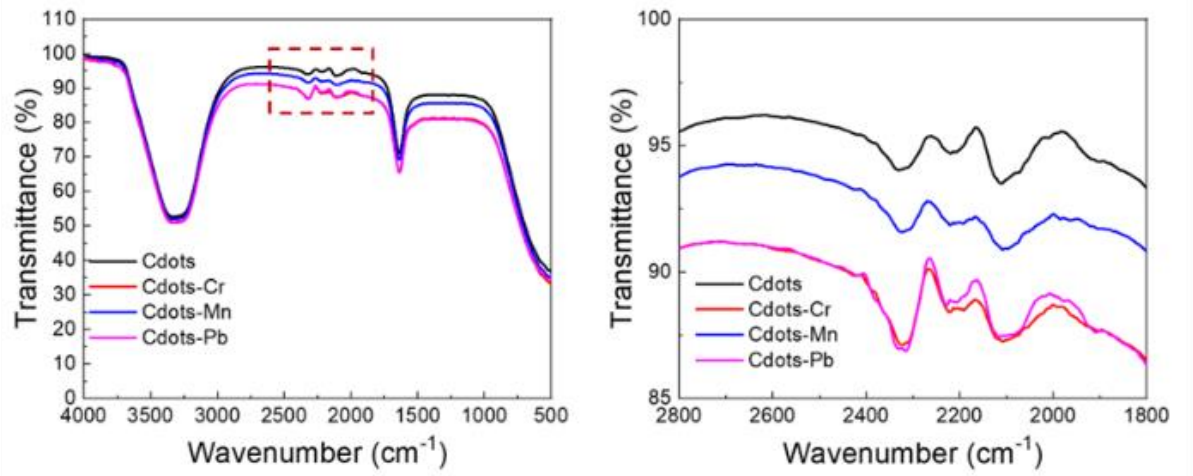

Fig. 6: FTIR spectra of samples.

These results correspond to the previous TRPL results.

The outcome of this study demonstrates Cdot's selectivity against a variety of well-known heavy metals. In a subsequent experiment, the nanomaterials will be combined with portable devices and biomaterial raw materials. According to measurement results, the quenching effect can reduce not only the PL intensity but also the time decay in TRPL. These two parameters could prove suitable for the heavy metal detection-based photoluminescence quenching effect of Cdot optical sensors.

4. Conclusion

Cdots synthesized from citric acid and urea were successfully synthesized and produced surface functional groups, which can be seen from the absorbance results. The addition of heavy metals Mn, Cr, and Pb greatly affected the absorbance and photoluminescence spectra. The addition of heavy metals also affects the lifetime value of Cdots, which can be seen in TRPL results. Furthermore, the intensity of FTIR was also decreased after the addition of heavy metal ions. This is because the heavy metals Mn, Cr, and Pb reduce the surface functional groups of Cdots by different mechanisms. Therefore, the results of this research can prove the selectivity of Cdot against heavy metals. However, it is necessary to carry out further testing for other types of metals and concentrations of other heavy metal ions.

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