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Carbon Dots Synthesis from Soybean with Urea Doped As Sensitive Fe (II) Ion Detection

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Abstract

Synthesis of carbon dots from soybeans with urea doped (N-CDs) has been successfully conducted using the bottom-up approach via the hydrothermal method. The N-CDs showed a dark brown solution, indicating the carbon dots formed. This study analyzed the effect of optical properties before and after Fe (II) ions addition on the sensitivity of N-CDs. N-CDs characterizations were analyzed using UV-Vis Spectrophotometer and Photoluminescence Spectroscopy (PL). The results showed that the absorbance spectrum range is from 200 to 600 nm, with its absorbance peak at 290 nm. The band gap energy obtained is 3.32 eV, which indicates that N-CDs are semiconductors. The N-CDs solution resulted in good fluorescence when observed under ultraviolet light (395 nm) and emitted a bright green color. N-CDs' sensitivity when sensing Fe (II) ions with a minimum Limit of Detection (LOD) is as low as 5.7 nM. Thus, N-CDs can be used as biosensors with an easy and environmentally friendly method.

Keywords: N-CDs,Urea, Soybean, Hydrothermal, Fe(II), Fluorescence

INTRODUCTION

In recent years the increase of industrialization and population has led to urbanization and an increase in air, water and soil pollution (Nurhadini, & Silalahi, 2017). The supply of clean water is increasingly difficult due to industrialization, and the world is facing a shortage of clean water, especially in developing countries (Kiamah et al., 2018). Water contaminants in the form of organic matter, bacteria, viruses, dyes, and heavy metal ions derived from the remaining production of the printing industry, chemical factories, textiles, pharmaceuticals and electronics (Firnanelty et al., 2022) with non-biodegradable properties that pose a major risk to human health (Baby, Saifullah, & Hussein, 2019). One of the most common heavy metal wastes is Fe (II), often found in the textile, metallurgical, agrochemical, and mining industries (Altalhi et al., 2021). Fe (II) ions can be very dangerous if they accumulate excessively in the body and damage the liver (Harimu et al., 2020), kidneys and other organ systems. Fe (II) ion waste can cause turbidity and corrosion, which harms the environmental ecosystem (Song et al., 2017).

Identification and prevention are the best steps for environmental protection, so an accurate, fast and affordable method is needed to detect Fe (II) ions. Currently the detection of Fe (II) can be carried out using different analytical methods such as atomic absorption spectroscopy (AAS), mass spectroscopy, coupled plasma spectroscopy, electrochemistry, spectrophotometry, colorimetry, electron paramagnetic resonance (EPR) (Mohammed & Omer, 2020). However, the main disadvantage of this technique is that the sample pretreatment procedure is lengthy and thus requires complex instrumentation and is not easily accessible (Iqbal et al., 2016).

The optical detection method using the fluorescence technique based on Carbon-dots (CDs) nanomaterials is one of the most promising methods; having superior electronic and optical properties and can be reproduced on a large scale from natural bio-resources made CDs have become very popular. (Tejwan et al., 2021). CDs are also considered environmentally friendly due to their easy availability, low cost, high biocompatibility, and high renewability. (Liu, Chen, Li, & Huang, 2019). Numerous reports have shown that CDs display fully-colour-tunable fluorescence emission from the blue to the near-infrared region (Chen et al., 2016). The different structural defects introduce different energy levels in CDs; thus, emitting light varies the excitation energy. Generally, the synthesis temperature controls structural defects changed further modified prepared CDs with ethylenediamine (Jing, Tian, Wang, & Zhang, 2019) urea (Devi et al., 2019). This also proved that N-defects such as C-N and N-H defects are finely tuned by substituting for partial O defects. Due to the high sensitivity and desirable selectivity, CDs synthesized were successfully used to selectively recognisee^{3+} (Fang et al., 2016). CDs are zero-dimensional (0D) materials with size smaller than 10 nm with bright fluorescence (Jani, Arcos-Pareja, & Ni, 2020). CDs consist of sp^2/sp^3 carbon skeleton and the surface of CDs are generally consist of functional groups/polymer chains, such as carboxyl, hydroxyl, and amine (Xia et al., 2019) It's properties which are non-toxic, high sensitivity, selectivity, and rapid detection (Das, Ngashangva, & Goswami, 2021) have made it used in various fields such as cell imaging, in vivo imaging, drug delivery, fluorescence sensing, photocatalysis, production of multicolor light-emitting diode (LED), energy conversion and storage, etc. (Fang et al., 2016).

CDs can be synthesized by top-down and bottom-up methods (Sugiarti & Darmawan, 2015). The bottom-up method is a synthesis method for the formation of CDs from precursor molecules built into CDs. Some of the methods are: hydrothermal, solvothermal, supported synthesized, and microwave methods. The top-down method is a synthesis method in which the larger carbon bond structure is broken down to form CDs particles including arc discharge, laser ablation, and electrochemical oxidation (Yu et al., 2021).

The hydrothermal method, considered as "green technology" or the most environmentally friendly, this method has been used to produce CDs from biomass source including glucose, sucrose, citric acid, chitosan, orange juice, grass, soybeans (Shabbir et al., 2021). Therefore in this study a soybean was used as CDs source with carbon rich element and low cost. In addition soybeans contain 5.6% higher Nitrogen compared to other biomass. Several modifications has been attempted to improve the functionality and properties of CDs, mostly involve doping or surface functionalization. CDs modifications are very useful to overcome the drawback especially if CDs has limited water solubility and aggregation (Ng, Lim, & Leo, 2021).

Among several different types of dopant, nitrogen is one of the most effective dopant because it's atomic size that is not much different from carbon, it electronegativity properties, has five valence electrons for chemical bonds and lone pairs of electrons that are easily transferred to the π -orbital sp^2 of carbon structure, thus N-CDs have different electronic structures, photophysical properties, and photoluminescence (PL) (Park et al., 2020).

Urea is one of the most popular fertilizers used for nitrogen sources, easily obtain, harmless and relatively cheap compared to other nitrogen source chemicals. In this study, CDs were synthesized with N-doping. In this study, the synthesis of N-CDs was carried out using the hydrothermal method and characterization using PL Spectroscopy and UV-Vis was carried out for further analysis of Fe (II) detection tests.

METHODOLOGY

Materials and Instrumentals

Materials used in this study are soybean, distilled water, urea (CH_4N_2O), NaOH (Smart Lab), $Fe(SO_4).7H_2O$ (Smart Lab), Whatman filter paper no. 41, dialysis membranes, pH strips. Tools used in this study are 2000 mL, 500mL and 250mL beakers, 40-200 µL & 100-1000 µL micropipette, blender, 50 mesh sieve, 100mL autoclave vessel, oven, 1.5 mL microtube, centrifuge, glass rod, magnetic bar, hot plate, ultrasonic, analytical balance (Metler AE 163), UV-Vis spectrophotometer (Jenway 7315 spectrophotometer) and Photoluminescence spectrometer (Ocean optics USB 2000+).

CDs Preparation

The soybean was washed until the skin peeled after that the soybeans dried in the oven at 60℃for 2h. Dried soybeans were blended and grinded into fine powders then sieved through 50 mesh sieve remove the larger particle. Soybean powders amount 5 g was dispersed into 60 mL and 0.2 M NaOH. Next, the suspension was being ultrasonication then transferred into Teflon-lined autoclave and heated in the oven at 200 ℃ for 5 h then cooled down to room temperature. The solutions were centrifuged at 13,000 rpm for 10 m and the supernatant were filtered through filter paper (Whatman Filter Paper 125 mm). For further purification the solutions was dialyzed for 24 h until it reached neutral pH. Then, the supernatant heated at 85 ℃ for 24 h until dry powder was obtained.

N-CDs Preparation

Similar to the procedure before, the addition of 2 g urea in aqueous solution was conducted. Next, the suspension was being ultrasonication then transferred into Teflon-lined autoclave and heated in the oven at 200℃ for 5 h then cooled down to room temperature. The solutions were centrifuged at 13,000 rpm for 10 m and the supernatant were filtered through filter paper (Whatman Filter Paper 125 mm). For further purification the solutions were dialyzed for 24 h after that the pH was observed until it reached neutral pH.

Then the supernatant was heated at 85 °C for 24 h until dry powder obtained.

Detection of Fe (II) Ion Test

One milligram (1 mg) N-CDs was dispersed in 10 mL aqueous solution then dispersed $FeSO_4{\cdot}7H_2O$ on different concentration 1 µM-5 µM with interval 0.5 µM in aqueous solution. The N-CDs solution with the same concentration dissolved in $FeSO_4{\cdot}7H_2O$ at different concentration. Then the N-CDs were characterized using UV-Vis spectrophotometer (Jenway 7315 spectrophotometer) and Photoluminescence spectrometer (Ocean optics USB 2000+).

RESULTS AND DISCUSSION

UV-Vis spectrophotometer was used to determine the absorbance of N-CDs. For reference CDs and N-CDs was characterized at the same concentration to confirm that CDs with urea dope was success. The absorbance spectrum in the UV region is related to the presence of conjugated compounds in the N-CDs structure and the light absorbance in that region indicates an electronic transitıon mechanism in the aromatic orbitals π (Qu et al. 2012).

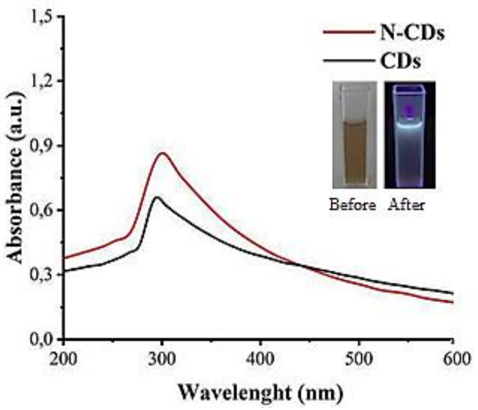

Figure 1. Absorbance spectra of N-CDs and CDs

Figure 1 show the N-CDs and CDs absorbance spectra range observed from 200 nm to 600 nm. N-CDs peak 0.906 at 290 nm wavelength. It showed that N-CDs have large absorbance spectra in the UV region. Compared to CDs without N doped, N-CDs show higher absorbance at around 300 nm. Wang et al has shown that N-doped CDs increase in UV-Vis peak at 300 nm indicating N-doping was successfully incorporated into CDs (Wang et al., 2016). The insets show the photographs of N-CDs in aqueous solution. Before irradiation with UV lamp, the N-CDs solution has dark brown color and after irradiation with UV lamp (395 nm) the N-CDs solution emitted a bright green color and energy excitation of the N-CDs.

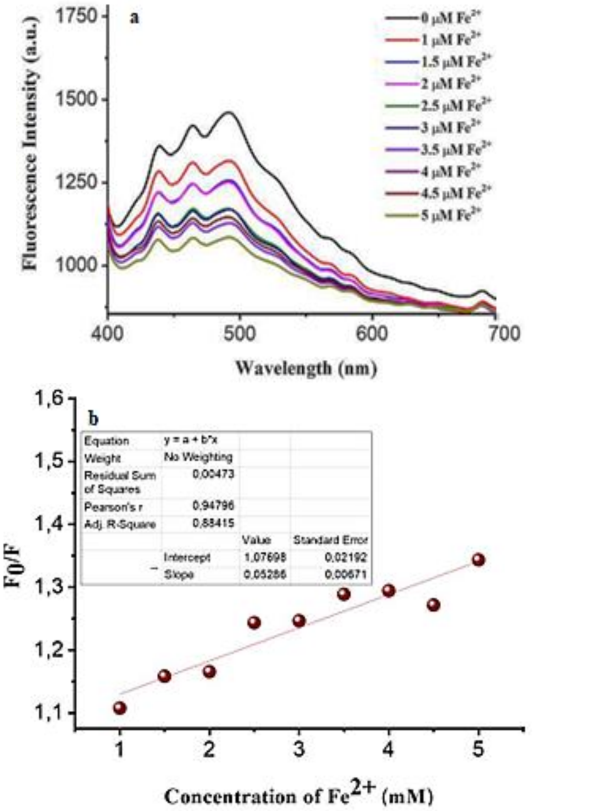

Figure 2. a) Fluorescent intensity spectra of N-CDs with various concentrations of Fe (II). b) Linear relationship between the relative fluorescence intensity (F_0/F) of N-CDs and the concentration of Fe (II)

The next characterization was conducted Photoluminescence spectrometer to determine the photoluminescence spectra with various concentration of $FeSO_4{\cdot}7H_2O$ from 1 μM-5 μM with 0.5 μM interval in aqueous solution of N-CDs. Figure 2a shown the photoluminescence characterization of N-CDs from 400 nm to 700 nm wavelengths. It showed that N-CDs before Fe (II) addition has the highest fluorescence intensity. As the increase of Fe (II) concentration, the fluorescence intensity of N-CDs gradually reduces and the lowest fluorescence intensity was indicated when the Fe (II) concentration reached 5 μM.

To show the linear regression value for Fe (II) ions was used the Stern-Volmer Equation 1.

$$F_0/F = 1 + K_{sv}\,[C] \qquad (1)$$

Where K_{sv} is the Stern–Volmer quenching constant, C is the concentration of Fe (II), F_0 and F are fluorescent intensity of N-CDs at 491 nm before and after Fe (II) addition (Reshma et al., 2018) of various concentrations of Fe (II). The linear regression value obtained is F_0/F = 1+0.004 [Fe (II)] with a correlation coefficient (R^2) of 0.9479 (Figure 1b).

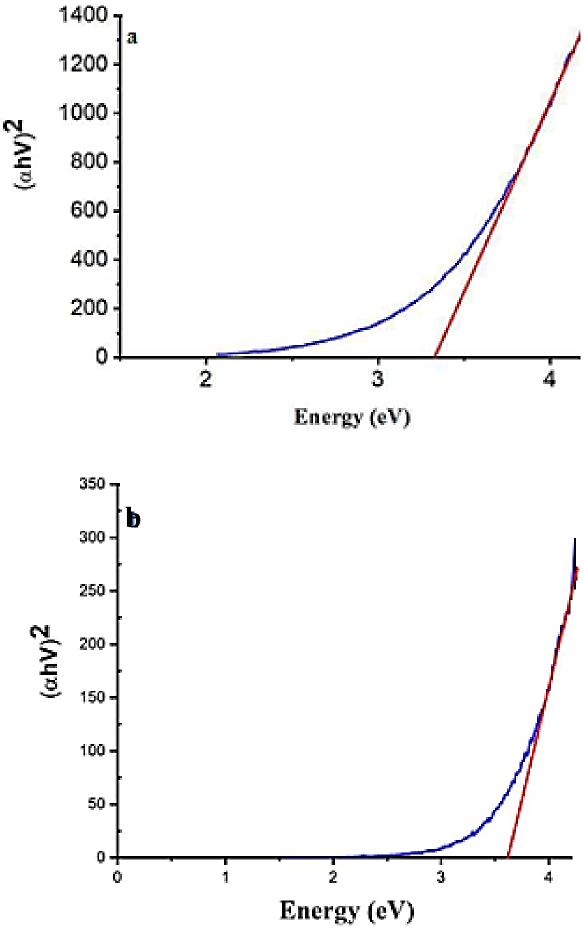

Figure 3. Curve band gap energy of a) N-CDs. b) CDs

Figure 3 show the band gap energy of N-CDs and CDs was obtained by using the Tauc Plot method based on the absorbance spectra of the UV-Vis spectrometer. The equation that used to determine the band gap energy is equation 2.

$$(\alpha h\nu)^2 = B(h\nu - Eg) \quad (2)$$

Where, α is the absorption coefficient, $h\nu$ is the photon energy, B is the constant and Eg is the band gap energy. Then, on the curve of $(\alpha h\nu)^2$ was regression as a function of $h\nu$ (Efa & Imae, 2018). The band gap energy of N-CDs found at 3.32 eV and CDs at 3.52 eV. It proves that the N doping was successfully incorporated into CDs matrix. In the previous studies, the band gap energy obtained 3.87 eV (Yu et al., 2021), this indicates that N-CDs have low excitation and emission energies are semiconductor.

The limit of detection of the Fe (II) ion was obtained as low as 5.7 nM based on the Equation 3.

$$LOD = 3.33 \frac{Sy}{S} \quad (3)$$

Where, Sy is the standard deviation of the blank signal and S is the linear slope. From previous research, it was found that the limit of detection of CDs made from soybeans was 21 nM (Fang et al., 2016), 95 Nm (Deng et al., 2021), 797 nM (Li et al., 2021), which is higher than the limit of detection value in this experiments for Fe (II) detection. These results show that N-CDs have highly sensitivity to sense Fe (II) ions.

CONCLUSION

In this study, carbon dots from soybean doped with N has been successfully prepared via hydrothermal approach. The N-CDs solution showed dark brown solution under visible light and emitted a bright green color when observed under UV light (395 nm) and higher absorption at around 300 nm shown that N doping was successfully incorporated into CDs. The absorbance spectrum range was observed from 200 to 600 nm and its absorbance peak observed at 290.86 nm. The bandgap energy obtained 3.32 eV, which indicates that N-CDs are semiconductor. Based on our finding, the photoluminescence intensity of CDs decreased when Fe (II) concentration increasing at 1 μm until 5 μm, which implied that N-CDs has good sensitivity. In addition, Limit of Detection (LOD) of N-CDs from soybean was 5.7 nM. Thus revealing the potential of N-CDs for Fe (II) detection.

REFERENCES

Altalhi, T. A., Ibrahim, M. M., Mersal, G. A. M., Alsawat, M., Mahmoud, M. H. H., Kumeria, T., El-Bindary, M. A. (2021). Mesopores Silica Nanotubes-Based Sensors for the Highly Selective and Rapid Detection of Fe^{2+} Ions In Wastewater, Boiler System Units and Biological Samples. *Analytica Chimica Acta*, *1180*, 338860.

Baby, R., Saifullah, B., & Hussein, M. Z. (2019). Carbon Nanomaterials for the Treatment of Heavy Metal-Contaminated Water and Environmental Remediation. *Nanoscale Research Letters*, *14*(1), 341.

Chen, B. bin, Liu, Z. X., Deng, W. C., Zhan, L., Liu, M. L., & Huang, C. Z. (2016). A Large-Scale Synthesis of Photoluminescent Carbon Quantum

Dots: A Self-Exothermic Reaction Driving The Formation of The Nanocrystalline Core At Room Temperature. *Green Chemistry, 18*(19), 5127–5132.

Das, S., Ngashangva, L., & Goswami, P. (2021). Carbon Dots: An Emerging Smart Material for Analytical Applications. *Micromachines*, *12*(84), 1-36.

Deng, J., Hu, J., Zhao, J., An, N., Liang, K., Wang, Q., Zhang, F. (2021). Eco Friendly Synthesis of Fluorescent Carbon Dots for The Sensitive Detection of Ferric Ions and Cell Imaging. *Arabian Journal of Chemistry*, *14*(7), 103195.

Devi, J. S. A., Aparna, R. S., Aswathy, B., Nebu, J., Aswathy, A. O., & George, S. (2019). Understanding the Citric Acid-Urea Co-Directed Microwave Assisted Synthesis and Ferric Ion Modulation of Fluorescent Nitrogen Doped Carbon Dots: A Turn On Assay for Ascorbic Acid. *ChemistrySelect*, *4*(3), 816–824.

Efa, M. T., & Imae, T. (2018). Hybridization of carbon-dots with ZnO nanoparticles of different sizes. *Journal of the Taiwan Institute of Chemical Engineers*, *92*, 112–117.

Fang, L., Xu, Q., Zheng, X., Zhang, W., Zheng, J., Wu, M., & Wu, W. (2016a). Soy Flour-Derived Carbon Dots: Facile Preparation, Fluorescence Enhancement, And Sensitive Fe^{3+} Detection. *Journal of Nanoparticle Research*, *18*(8), 224.

Firnanelty, F., Chadijah, S., Adawiah, S.R., Firdaus, F. and Dyan, M.I.D.N.I.. (2022). Analysis of the Heavy Metal Levels (Cd, Fe, Hg and Pb) at Losari Beach Tourism Reclamation of Makassar. *Indo. J. Chem. Res.*, *10(2)*, 97-101.

Harimu, L., Haetami, A., Sari, C.P., Haeruddin, H. and Nurlansi, N. (2020). Comparison of Spray Aeration Ability (Spray) with Adsorption Method Using Adsorbent Powder Cocoa Rind to Reduce Iron and Manganese Levels in Dug Well Water. *Indo. J. Chem. Res.*, *8(2)*, 137-143.

Iqbal, A., Tian, Y., Wang, X., Gong, D., Guo, Y., Iqbal, K., … Qin, W. (2016). Carbon Dots Prepared By Solid State Method Via Citric Acid and 1,10-Phenanthroline for Selective and Sensing Detection of Fe^{2+} and Fe^{3+}. *Sensors and Actuators B: Chemical*, *237*, 408–415.

Jani, M., Arcos-Pareja, J. A., & Ni, M. (2020). Engineered Zero-Dimensional Fullerene/Carbon Dots-Polymer Based Nanocomposite Membranes for Wastewater Treatment. *Molecules*, *25*(21), 4934.

Jing, N., Tian, M., Wang, Y., & Zhang, Y. (2019). Nitrogen-Doped Carbon Dots Synthesized From Acrylic Acid and Ethylenediamine for Simple and Selective Determination of Cobalt Ions In Aqueous Media. *Journal of Luminescence*, *206*, 169–175.

Kiamah Fathirizki A, Kamarati, Marlon Ivanhoe A, & M. Sumaryono. (2018). Heavy Metal Content Iron (Fe), Lead (Pb) and Manganesee (Mn) in The Water of The Santan River. *Jurnal Penelitian Ekosistem Dipterokarpa*, *4*(1), 49-56.

Li, Y., Chen, J., Wang, Y., Li, H., Yin, J., Li, M., … Chen, L. (2021). Large-Scale Direct Pyrolysis Synthesis of Excitation-Independent Carbon Dots and Analysis Of Ferric (III) Ion Sensing Mechanism. *Applied Surface Science*, *538*, 148151.

Liu, M. L., Chen, B. bin, Li, C. M., & Huang, C. Z. (2019). Carbon Dots: Synthesis, Formation Mechanism, Fluorescence Origin and Sensing Applications. *Green Chemistry*, *21*(3), 449–471.

Mohammed, L. J., & Omer, K. M. (2020). Dual Functional Highly Luminescence B, N Co-Doped Carbon Nanodots as Nanothermometer and Fe^{3+}/Fe^{2+} Sensor. *Scientific Reports*, *10*(1), 3028.

Ng, H. K. M., Lim, G. K., & Leo, C. P. (2021). Comparison Between Hydrothermal And Microwave-Assisted Synthesis of Carbon Dots From Biowaste And Chemical For Heavy Metal Detection: A Review. *Microchemical Journal*, *165*, 106116.

Nurhadini, N. and Silalahi, I.H. (2017). Adsorption of Hg (II) by UsingSargassum crassifoliumWith Presence of Pb (II), Cu (II), And Fe (II). *Indo. J. Chem. Res.*, *5*(1), 7-11.

Park, Y., Kim, Y., Chang, H., Won, S., Kim, H., & Kwon, W. (2020). Biocompatible Nitrogen-Doped Carbon Dots: Synthesis, Characterization, and Application. *Journal of Materials Chemistry B*, *8*(39), 8935–8951.

Reshma, Vaishnav, S. K., Karbhal, I., Satnami, M. L., & Ghosh, K. K. (2018). Spectroscopic Studies on In Vitro Molecular Interaction of Highly Fluorescent Carbon Dots With Different Serum Albumins. *Journal of Molecular Liquids*, *255*, 279–287.

Shabbir, H., Tokarski, T., Ungor, D., & Wojnicki, M. (2021). Eco Friendly Synthesis of Carbon Dot by Hydrothermal Method for Metal Ions Salt Identification. *Materials*, *14*(24), 7604.

Song, P., Zhang, L., Long, H., Meng, M., Liu, T., Yin, Y., & Xi, R. (2017). A Multianalyte Fluorescent Carbon Dots Sensing System

Constructed Based on Specific Recognition of Fe(III) Ions. *RSC Advances*, *7*(46), 28637-28646.

Sugiarti, S., & Darmawan, N. (2015). Synthesis of Fluorescence Carbon Nanoparticles from Ascorbic Acid. *Indonesian Journal of Chemistry*, *15*(2), 141–145.

Tejwan, N., Sharma, A., Thakur, S., & Das, J. (2021). Green Synthesis of A Novel Carbon Dots from Red Korean Ginseng and Its Application for Fe^{2+} sensing and preparation of nanocatalyst. *Inorganic Chemistry Communications*, *134*, 108985.

Wang, H., Sun, P., Cong, S., Wu, J., Gao, L., Wang, Y., Dai, X., Yi, Q., & Zou, G. (2016). Nitrogen-Doped Carbon Dots for "Green" Quantum Dot Solar Cells. *Nanoscale research letters*, *11*(1), 1-6.

Xia, C., Zhu, S., Feng, T., Yang, M., & Yang, B. (2019). Evolution and Synthesis of Carbon Dots: From Carbon Dots to Carbonized Polymer Dots. *Advanced Science*, *6*(23), 1901316.

Yu, J., Song, H., Li, X., Tang, L., Tang, Z., Yang, B., & Lu, S. (2021). Computational Studies on Carbon Dots Electrocatalysis: A Review. *Advanced Functional Materials*, *31*(49), 2107196.