



Investigation into parameters affecting the synthesis of hybrid gold nanoparticle/nitrogen-doped carbon dot colloids

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Abstract

This study reports a two-step synthesis method for producing hybrid nanoparticles composed of gold nanoparticles (AuNPs) and nitrogen-doped carbon dots (CDs). Initially, we employed hydrothermal synthesis to fabricate CDs derived from mangosteen peel extract, which exhibits green light emission. Subsequently, the hybrid AuNPs/CDs were synthesized by inducing plasma in a solution containing CDs and a gold precursor, namely gold(III) chloride trihydrate. Our primary aim was to investigate the key parameters influencing the synthesis process. We assessed the colloidal properties of the AuNPs/CDs by introducing a stabilizer, specifically sodium alginate, and examined how factors such as the presence of sodium alginate, CD concentration, and plasma discharge time influenced the colloidal properties of the synthesized AuNPs/CDs, thereby enabling precise control over the synthesis process. Furthermore, incorporating AuNPs with CDs led to a noticeable blue shift in luminescence compared to pure CDs. This study presents significant insights into the controlled synthesis of AuNPs/CDs, underscoring the importance of adjusting experimental conditions to achieve desired characteristics. The findings also hold implications for various materials science and nanotechnology applications, emphasizing the need for tailored synthesis approaches to meet specific requirements.

1. Introduction

The synthesis of hybrid nanoparticles has garnered considerable interest in recent years due to their unique and tunable properties, which arise from the synergistic effects of their constituent materials. Among these, the combination of gold nanoparticles (AuNPs) and carbon dots (CDs) represents a promising class of nanocomposites with potential applications in areas such as biomedicine and catalysis [1-4]. AuNPs are well-known for their excellent biocompatibility, distinct optical properties, and catalytic activity [5], while CDs are valued for their strong photoluminescence, low toxicity, and versatility in surface functionalization [6]. Integrating AuNPs with nitrogen-doped CDs offers a compelling pathway to create hybrid materials with enhanced and novel functionalities. CDs, derived from natural sources like mangosteen peel extract, provide a green and sustainable approach to nanoparticle synthesis. These CDs exhibit intrinsic photoluminescent properties, which can be tailored through doping and surface modifications, making them suitable for various applications, including bioimaging, sensing, and energy conversion.

This study explores a two-step synthesis method to fabricate hybrid AuNPs/CDs colloids. The first step involves the hydrothermal synthesis of nitrogen-doped CDs, hereafter called CDs, from mangosteen peel extract as a carbon source and ethylenediamine as a nitrogen source, a process known for its simplicity, environmental friendliness, and ability to produce CDs with strong luminescence [7]. The second step utilizes plasma-induced synthesis in a liquid medium called 'Solution Plasma Process (SPP)' to create AuNPs in the presence of the preformed

aqueous solution of CDs and a gold precursor, *i.e.*, gold(III) chloride trihydrate. Specifically, the SPP can induce AuNP formation by generating active species in the gold precursor solution and reducing Au³⁺ to Au⁰ [8]. The advantage of using this method is reducing chemical usage and processing time.

The primary objective of this research is to investigate the feasibility of the proposed synthesis method and to determine the key parameters affecting the synthesis and colloidal properties of the AuNPs/CDs. Specifically, we examine the role of sodium alginate as a stabilizer, the concentration of CDs, and the plasma discharge time. These parameters are critical for achieving stable colloids with desired optical and structural characteristics. Additionally, we explore the luminescence properties of the hybrid AuNPs/CDs, comparing them to those of the neat CDs. We aim to provide valuable insights into the controlled synthesis of AuNPs/CDs, highlighting the importance of optimizing experimental conditions to tailor the properties of hybrid nanoparticles. The findings from this study are expected to contribute to the advancement of material science and nanotechnology, demonstrating the potential of hybrid nanoparticles in developing innovative solutions for various technological challenges.

2. Experimental

2.1 Materials

Gold(III) chloride trihydrate (HAuCl₄·3H₂O, ≥99.9% trace metals basis) was purchased from Sigma-Aldrich and used as the gold

precursor. Mangosteen peel powder was obtained from Popaya herb (Bangkok, Thailand). Ethylenediamine (EDA, purity > 99%) was supplied by Fluka (Bangkok, Thailand). Sodium alginate (viscosity of 1% in water at 25°C = 5.0 cps to 40.0 cps) was used as a stabilizer and purchased from Sigma-Aldrich. Distilled water was used for all tests and sample preparation. All reagents were of analytical grade and used without further purification.

2.2 Synthesis of carbon dots (CDs)

Approximately 0.5 g of mangosteen peel powder (MPP) was dissolved in 100 mL of deionized water with stirring. The mixture was centrifuged at 5,000 rpm for 15 min to separate the MPP from the suspension, serving as the CD precursor. Nitrogen doping of the CDs was achieved by adding ethylenediamine (1 mL) in 29 mL of the CDs solution in a Teflon container, which was then put into a stainless-steel autoclave and hydrothermally processed at 180°C for 12 h, followed by cooling to room temperature. The resulting solution was filtered through a 0.22 µm syringe filter before further use.

2.3 Synthesis of hybrid AuNPs/CDs colloids

Figure 1 presents a schematic illustration of the SPP experimental setup and the anticipated reaction process. A 100 mL glass beaker served as the reactor. Tungsten rods (99.9% purity, Nilaco Corp., Japan) with a diameter of 1 mm were used as electrodes. Each electrode was covered with a ceramic tube, inserted into a silicone stopper, and positioned in the SPP reactor. The distance between the tips of the electrodes was set to 0.5 mm. The study was divided into two parts:

2.3.1 Study on the effect of adding a stabilizer (sodium alginate).

A 100 mL of HAuCl₄·3H₂O precursor (0.2 mM in water) was added to the reactor. Subsequently, 2.0 mL of the as-prepared CD solution was introduced. Plasma was generated at atmospheric pressure and room temperature using a bipolar pulse power supply (Kurita, Japan) with a frequency of 15 kHz and a pulse width of 0.9 µs. The plasma treatment was carried out for 5 min. The solutions were continuously stirred at 400 rpm to ensure homogeneity throughout the process. A 1.0% w/v sodium alginate aqueous solution was used in place of water to study the effect of the sodium alginate stabilizer.

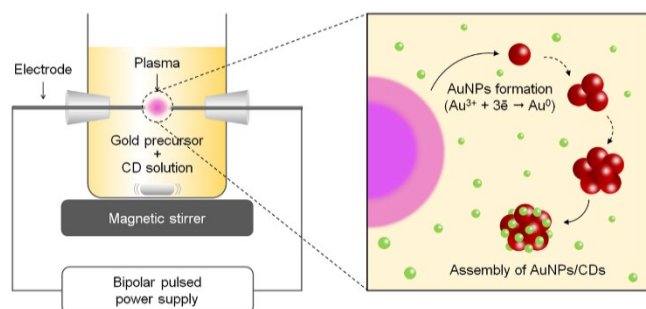


Figure 1. Schematic illustration of the SPP experimental setup and the anticipated reaction process.

2.3.2 Study on the effect of the plasma discharge time and CD content.

The experiment was conducted as described in Part 2.3.1, using a 1.0% w/v sodium alginate aqueous solution as the medium. The volume of the CD solution was varied to 2.0, 1.8, 1.6, and 1.4 mL, and the SPP treatment time was adjusted from 0 min to 30 min in 5 min intervals.

2.4 Material characterizations

The formation of CDs can be visually observed under 365 nm UV light (blacklight). Their photoluminescence properties were analyzed using a FluoroMax® 4 spectrofluorometer (Horiba Scientific), with a slit width of 3 nm for both excitation and emission. The formation of AuNPs can be visually observed by the change in color of the solution from pale yellow to purple to red, indicating the successful reduction of the gold precursor to gold nanoparticles. The zeta potential was measured with a Malvern Zetasizer Nano ZS instrument, with the temperature set to 25°C and an equilibration time of 120 sec. The morphology and elemental composition of the samples were characterized using a field emission transmission electron equipped with energy-dispersive X-ray spectroscopy (FE-TEM, JEOL JEM-3100F).

3. Results and discussion

3.1 The formation of CDs and the effect of the addition of sodium alginate on AuNPs/CDs' colloidal stability

Figure 2(a) shows the resulting CDs under daylight and UV 365 nm light. The green fluorescence under UV light confirms the successful synthesis of CDs.

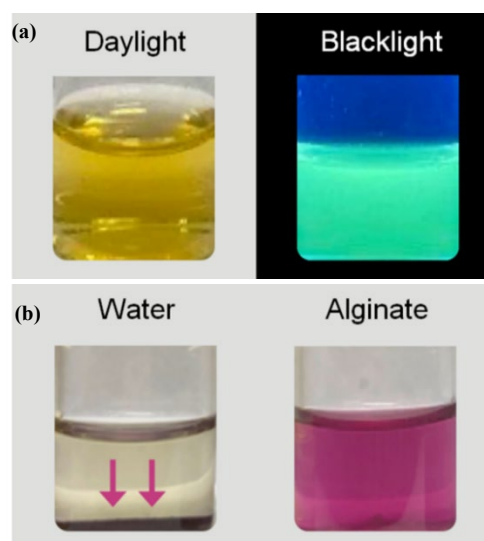


Figure 2. (a) CDs under daylight and UV 365 nm light. (b) AuNPs/CDs synthesized via SPP (5 min treatment) in water and sodium alginate aqueous solution, observed after synthesis for one week.

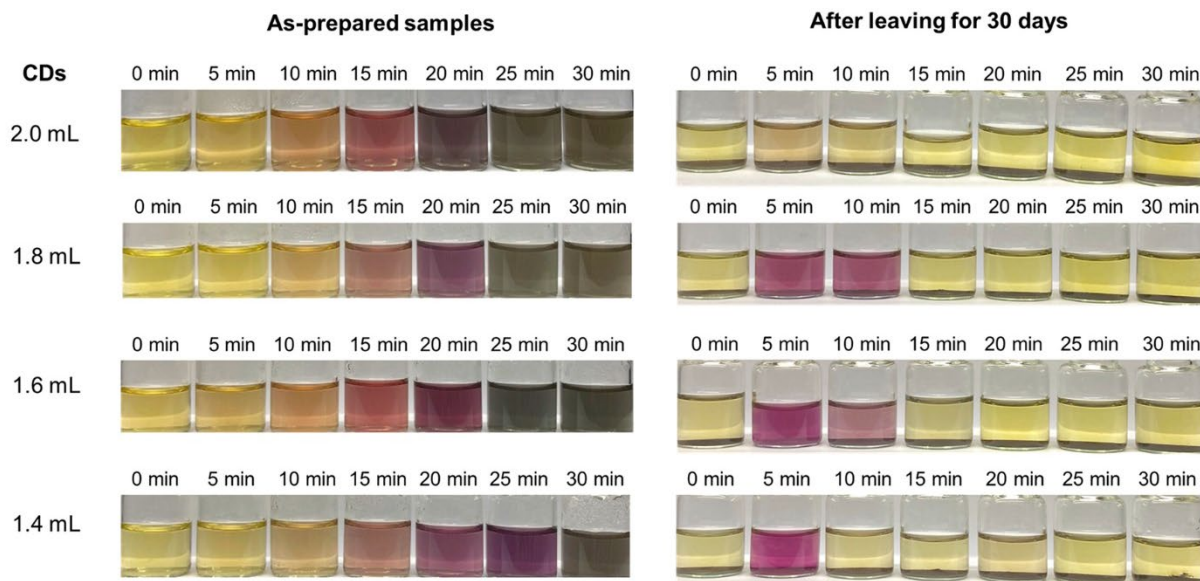


Figure 3. Images of the AuNPs/CDs colloids synthesized in alginate aqueous solutions using varying CD contents and plasma discharge times. The photographs were captured under daylight immediately after discharge and after the samples were allowed to stand for 30 days.

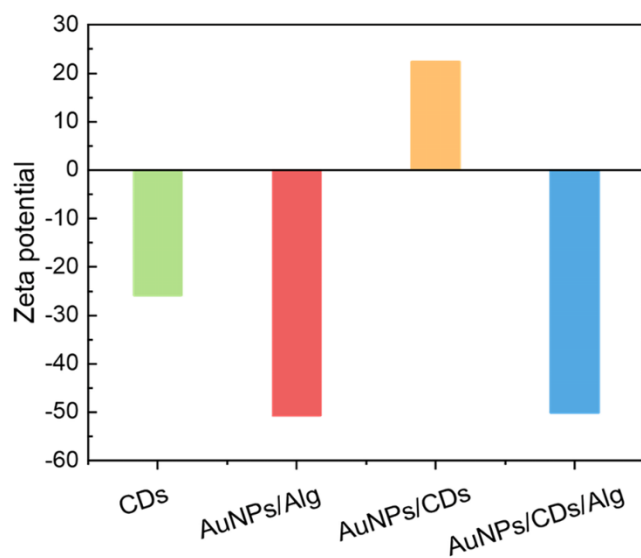


Figure 4. Zeta potential values of the CD solution, AuNPs/Alg, AuNPs/CDs, and AuNPs/CDs/Alg colloids. The properties of the colloids were measured immediately after plasma discharge.

Figure 2(b) depicts the AuNPs/CDs synthesized through the SPP in water and sodium alginate aqueous solution, observed after synthesis for one week. The characteristic purple color indicates successful AuNP formation. It can be observed that while the AuNPs/CDs synthesized in water precipitated, those synthesized in sodium alginate remained a stable colloid. This result demonstrates the necessity of sodium alginate as a stabilizer for synthesizing stable AuNPs/CDs colloids through the proposed method. Therefore, we synthesized hybrid AuNPs/CDs in an alginate solution in the subsequent experiment.

3.2 Effect of the plasma discharge time and CDs content

Based on the findings from the previous section, higher quantities of CDs and longer discharge times increase the likelihood of AuNPs/

CDs precipitation. Subsequently, we investigated the impact of CD dosage and plasma treatment duration on the formation of stable AuNPs/CDs colloids. Results are shown in Figure 3.

The results indicate that a plasma discharge time of 5 min produced stable AuNPs/CDs colloids with a maximum CD loading capacity of 1.8 mL, making this formulation ideal for further analysis. Integrating CDs and AuNPs through SPP, even with sodium alginate as a stabilizer, led to agglomeration. This observation is likely due to the opposite surface charges of Au ions and CDs, which promote the assembly of larger particles. This hypothesis is supported by zeta potential measurements showing that CDs have a negative charge (Figure 4). The negative charge of the CDs likely originates from functional groups, such as hydroxyl (OH^-) and carboxylate (COO^-), on their surface. Upon assembly with positively charged Au ions (Au^{3+}), the surface charge of the resulting AuNPs/CDs in water shifted to positive. This suggests that the positive charge contribution from Au ions outweighs the negative charge contribution from the CDs. Further, when alginate was added, AuNPs/Alg and AuNPs/CDs/Alg had negative surface charges because the negatively charged alginate ($-\text{COO}^-$ functional group) wrapped around the particles. Results also indicate that extended plasma exposure intensified flocculation, possibly due to heightened reactive species encouraging bonding between AuNPs and CDs, leading to larger hybrid AuNPs/CDs and diminished colloidal stability.

3.3 TEM images and EDS mapping

As previously noted, a plasma discharge time of 5 min yields stable AuNPs/CDs/Alg colloids with a maximum CD loading capacity of 1.8 mL. Consequently, we used this condition for further investigation, examining the morphology and size with a TEM equipped with EDS to identify the chemical elements present and their specific locations in the sample. As evidenced in Figure 5, the AuNPs/CDs synthesized in the alginate solution are nearly spherical, with the AuNPs as a central particle covered with the CDs decorated on the AuNP surface. Each particle has an average size ~ 20 nm.

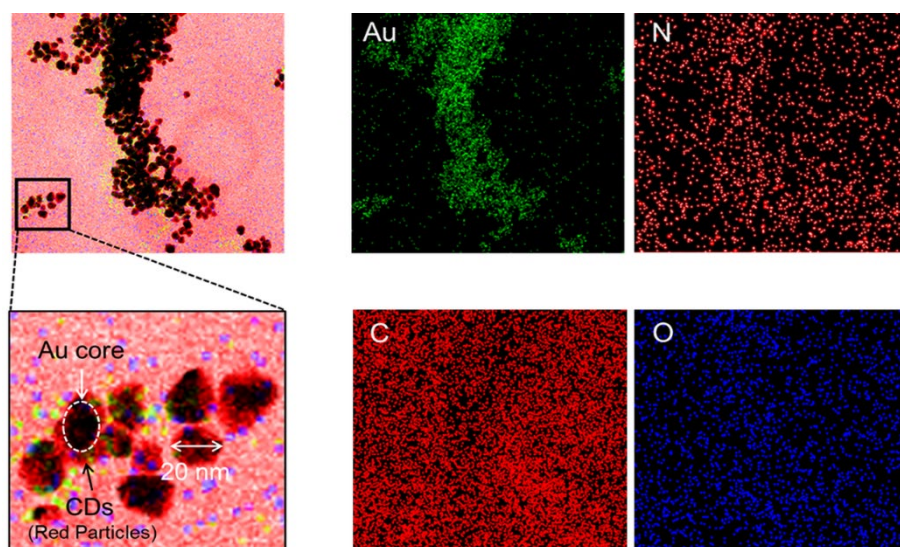


Figure 5. TEM-EDS images of the AuNPs/CDs synthesized in the alginate solution using a plasma discharge time of 5 min. The precursor solution contains 100 mL of 0.2 mM $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ in 1.0% w/v sodium alginate aqueous solution and 1.8 mL of the as-prepared CD solution.

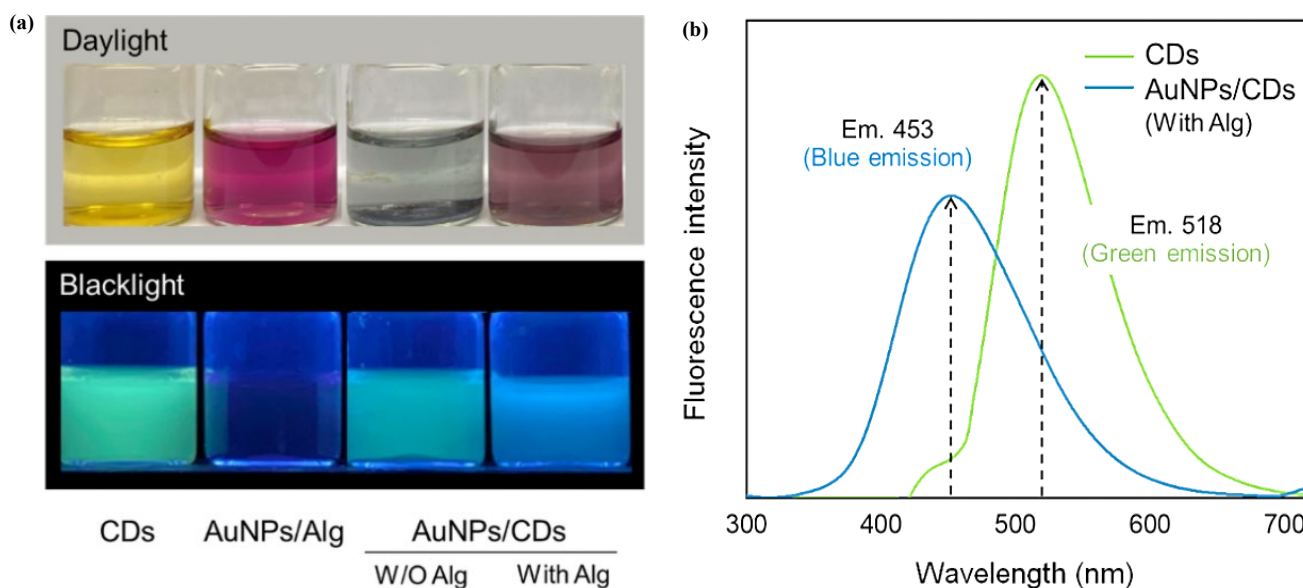


Figure 6. (a) Photographs of CDs, AuNPs/Alg, AuNPs/CDs, and AuNPs/CDs/Alg under daylight and UV 365 nm light, (b) Fluorescence emission spectra of CDs and AuNPs/CDs/Alg at their maximum excitation wavelength, *i.e.*, 400 nm.

3.4 Optical properties

Finally, the optical properties of the resulting colloids were investigated. Figure 6(a) displays photographs of CDs, AuNPs/Alg, AuNPs/CDs, and AuNPs/CDs/Alg under daylight and UV 365 nm light. Notably, while the CDs exhibited luminescence under UV light, the AuNPs/Alg did not. However, when AuNPs were combined with CDs, the resulting colloids retained their luminescent behavior: AuNPs/CDs emitted a green glow, and AuNPs/CDs/Alg emitted a blue glow. However, the green luminescence of AuNPs/CDs in water was due to the CDs dispersed in the solution, as the AuNPs/CDs had already precipitated.

The fluorescence emission spectra of the CDs and AuNPs/CDs/Alg at their maximum excitation wavelength (400 nm) are shown in Figure 6(b). The results align with the observed luminescence colors:

the emission wavelengths of CDs and AuNPs/CDs/Alg are 518 nm and 453 nm, corresponding to green and blue emissions, respectively. This finding indicates that incorporating AuNPs with CDs resulted in a noticeable blue shift in luminescence.

The observed blue shift in the emission spectrum of AuNPs/CDs/Alg can be attributed to changes in the energy levels of the CDs upon interaction with AuNPs. Specifically, the incorporation of AuNPs with CDs likely alters the surface states and electronic transitions of the CDs, increasing the energy gap (ΔE) between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). This increase in ΔE corresponds to a shorter emission wavelength, as reflected in the shift from green (518 nm) to blue (453 nm) luminescence. The interaction between the AuNPs and CDs, possibly through charge transfer or surface plasmon effects, contributes to these modifications in the electronic structure of the CDs.

4. Conclusions

This study presents a two-step synthesis method for producing hybrid AuNPs/CDs colloids. First, hydrothermal synthesis synthesized CDs from mangosteen peel extract in water, resulting in green luminescent CDs. Next, hybrid AuNPs/CDs were created by generating plasma in a solution containing the as-prepared CDs and a gold precursor. The results indicate that several factors influence the colloidal properties of the synthesized AuNPs/CDs: (1) the presence of sodium alginate as a stabilizer, (2) the ratio between the gold precursor and CDs, and (3) the plasma discharge time. Specifically, sodium alginate is essential for synthesizing stable AuNPs/CDs colloids using this method. Higher quantities of CDs and longer discharge times increase the likelihood of AuNPs/CD precipitation. Additionally, when AuNPs are combined with CDs, the resulting colloids maintain their luminescent behavior, with a noticeable blue shift in luminescence. These findings provide a foundation for further exploration and optimization of hybrid nanoparticle synthesis for potential applications in bioimaging, sensing, and photonic devices.

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References

- [1] T. Nozaki, T. Kakuda, Y. B. Pottathara, and H. Kawasaki, "A nanocomposite of N-doped carbon dots with gold nanoparticles for visible light active photosensitisers," *Photochemical & Photobiological Sciences*, vol. 18, no. 5, pp. 1235-1241, 2019.
- [2] S. Pawar, H. Duadi, Y. Flegler, and D. Fixler, "Design and use of a gold nanoparticle-carbon dot hybrid for a flim-based implication nano logic gate," *ACS Omega*, vol. 7, no. 26, pp. 22818-22824, 2022.
- [3] Y. Zhu, J. Du, Q. Peng, F. Wang, J. Hu, Y. Luo, A. A. Alshehri, K. A. Alzahrani, B. Zheng, X. Sun, and D. Xiao, "The synthesis of highly active carbon dot-coated gold nanoparticles via the room-temperature in situ carbonization of organic ligands for 4-nitrophenol reduction," *RSC Advances*, vol. 10, no. 33, pp. 19419-19424, 2020.
- [4] S. Ghosh, S. S. Satapathy, K. Ghosh, S. Jauhari, S. K. Panda, and S. Si, "Carbon dots assisted synthesis of gold nanoparticles and their catalytic activity in 4-nitrophenol reduction," *Chemistry Select*, vol. 4, no. 12, pp. 3416-3422, 2019.
- [5] I. Hammami, N. M. Alabdallah, A. A. jomaa, and M. kamoun, "Gold nanoparticles: Synthesis properties and applications," *Journal of King Saud University - Science*, vol. 33, no. 7, p. 101560, 2021.
- [6] J. Liu, R. Li, and B. Yang, "Carbon Dots: A new type of carbon-based nanomaterial with wide applications," *ACS Central Science*, vol. 6, no. 12, pp. 2179-2195, 2020.
- [7] H. Ferjani, S. Abdalla, O. A. Oyewo, and D. C. Onwudiwe, "Facile synthesis of carbon dots by the hydrothermal carbonization of avocado peels and evaluation of the photocatalytic property," *Inorganic Chemistry Communications*, vol. 160, p. 111866, 2024.
- [8] N. Treesukkasem, C. Chokradjaroen, S. Theeramunkong, N. Saito, and A. Watthanaphanit, "Synthesis of Au nanoparticles in natural matrices by liquid-phase plasma: effects on cytotoxic activity against normal and cancer cell lines," *ACS Applied Nano Materials*, vol. 2, no. 12, pp. 8051-8062, 2019.