

GREEN SYNTHESIS OF SILVER NANOPARTICLES USING ENVIRONMENTALLY FRIENDLY REDUCING AGENTS

Dong Thi Linh, Cao Xuan Duong, Nguyen Van Truong*

TNU - University of Technology

| ARTICLE INFO | ABSTRACT |
|-------------------------------|---|
| Received: 28/4/2025 | In this study, silver nanoparticles were synthesized via a green electrochemical method using three environmentally friendly reducing agents: sodium citrate, oleic acid, and an extract of <i>Houttuynia cordata</i> . The synthesis employed high-purity silver electrodes in aqueous solutions, avoiding toxic chemical precursors. The resulting were comprehensively characterized using UV-Vis spectroscopy, X-ray diffraction, scanning electron microscopy, dynamic light scattering (DLS), and zeta potential analysis. UV-Vis and X-ray confirmed successful nanoparticle formation with a face-centered cubic structure. Silver nanoparticles synthesized using Oleic acid exhibited the highest crystallinity, while those synthesized with <i>Houttuynia cordata</i> showed the largest average particle size due to the influence of plant-derived organic compounds. The sample synthesized using sodium citrate demonstrated the greatest colloidal stability, with a zeta potential of -21.2 mV, attributed to efficient surface capping by citrate ions. These findings highlight the significant role of reducing agent selection in tuning the physicochemical properties of nano particles and support the potential of green electrochemical synthesis for scalable, sustainable nanomaterial production. |
| Revised: 30/5/2025 | |
| Published: 30/5/2025 | |
| KEYWORDS | |
| Green synthesis | |
| Silver nanoparticles | |
| Electrochemically synthesized | |
| Friendly reducing agents | |
| Zeta potential | |

TỔNG HỢP HẠT NANO KIM LOẠI BẠC BẰNG PHƯƠNG PHÁP HÓA HỌC XANH SỬ DỤNG MỘT SỐ CHẤT KHỬ THÂN THIỆN VỚI MÔI TRƯỜNG

Đông Thị Linh, Cao Xuân Dương, Nguyễn Văn Trường*

Trường Đại học Kỹ thuật Công nghiệp - ĐH Thái Nguyên

| THÔNG TIN BÀI BÁO | TÓM TẮT |
|----------------------------|--|
| Ngày nhận bài: 28/4/2025 | Trong nghiên cứu này, các hạt nano bạc đã được tổng hợp bằng phương pháp điện hóa xanh sử dụng ba tác nhân khử thân thiện với môi trường: natri citrate, axit oleic và dịch chiết từ cây diếp cá (<i>Houttuynia cordata</i>). Quá trình tổng hợp sử dụng điện cực bạc tinh khiết trong môi trường nước, không cần đến các tiền chất hóa học độc hại. Các hạt nano bạc thu được đã được đặc trưng bằng phổ UV-Vis, nhiễu xạ tia X, hiển vi điện tử quét, tán xạ ánh sáng động và đo thế zeta. Kết quả UV-Vis và nhiễu xạ tia X xác nhận sự hình thành thành công của các hạt nano bạc có cấu trúc lập phương tâm mặt. Mẫu nano bạc tổng hợp từ axit Oleic có độ kết tinh cao nhất, trong khi mẫu nano bạc tổng hợp từ dịch chiết diếp cá có kích thước trung bình lớn nhất do ảnh hưởng từ các hợp chất hữu cơ có trong dịch chiết thực vật. Mẫu nano bạc sử dụng natri citrate làm chất khử cho thấy độ ổn định keo tốt nhất với thế zeta $-21,2$ mV, nhờ khả năng tạo màng bảo vệ hiệu quả từ các ion citrate. Kết quả này cho thấy tác nhân khử có ảnh hưởng đáng kể đến đặc tính vật lý - hóa học của hạt nano bạc và khẳng định tiềm năng của phương pháp điện hóa xanh trong tổng hợp vật liệu nano quy mô lớn, bền vững. |
| Ngày hoàn thiện: 30/5/2025 | |
| Ngày đăng: 30/5/2025 | |
| TỪ KHÓA | |
| Tổng hợp xanh | |
| Hạt nano bạc | |
| Tổng hợp điện hoá | |
| Chất khử thân thiện | |
| Thế Zeta | |

DOI: <https://doi.org/10.34238/tnu-jst.12691>

* Corresponding author. Email: vtnguyen@tnut.edu.vn

1. Introduction

Nanotechnology has made significant breakthroughs across numerous scientific disciplines, including materials science, biotechnology, pharmaceuticals, and environmental science [1]. Accompanying these extensive applications is a considerable demand for nanoparticle supply. However, physical synthesis methods such as high-energy ball milling, sputtering, or physical vapor deposition typically consume substantial energy and require lengthy processing times, rendering them suitable primarily for laboratory-scale production [2]. Conversely, chemical synthesis methods often utilize toxic and expensive chemicals, potentially generating hazardous by-products contributing to environmental pollution [3], [4].

Green synthesis methods for nanomaterials have been researched extensively as solutions to these challenges, facilitating safe, environmentally friendly, and scalable nanoparticle production [5]. Silver nanoparticles (AgNPs) represent one of the most significant nanomaterials due to their widespread applications in catalysis, drug delivery, antimicrobial treatments, and environmental remediation, among others [6]. These applications necessitate safe silver nanoparticles, free from toxic chemical residues, and environmentally benign. In recent years, green synthesis methods employing eco-friendly reducing agents have been developed to meet these stringent requirements [7] – [9]. Non-toxic reducing agents reported for green synthesis of AgNPs include sodium citrate (a food additive labeled E331), oleic acid (a beneficial fatty acid known as omega-9), ascorbic acid (vitamin C), and extracts derived from plants, fungi, algae, bacteria, and other microorganisms [10], [11].

Nevertheless, recent studies have predominantly employed silver nitrate (AgNO_3) as a precursor in the synthesis of AgNPs [12]. While silver nitrate is approved and commonly utilized for specific medical and antimicrobial applications, it poses substantial health risks due to its highly reactive and corrosive nature. Direct contact with silver nitrate can result in severe skin burns, corneal damage leading to opacity, and potential blindness upon exposure to the eyes [13]. Furthermore, inhalation of AgNO_3 vapors or particles can lead to significant adverse health effects, including headaches, respiratory distress, nausea, vomiting, and in severe cases, respiratory failure. Beyond the human health implications, silver nitrate also presents considerable environmental hazards. Discharges of AgNO_3 into aquatic and terrestrial ecosystems can adversely impact biodiversity, notably affecting aquatic life forms by altering physiological processes, reducing reproductive viability, and potentially leading to bioaccumulation and biomagnification within ecological food webs [12], [14].

In this study, we propose a method to synthesize AgNPs from bulk silver material via an electrochemical approach, employing three distinct green and environmentally friendly reducing agents, completely eliminating toxic chemical residues during synthesis. Three variants of AgNPs were prepared: C-AgNPs reduced by sodium citrate, O-AgNPs reduced by oleic acid, and Bio-AgNPs reduced by extracts from *Houttuynia cordata*. The synthesized nanoparticles were characterized for size, morphology, and crystallinity through ultraviolet-visible spectroscopy (UV-Vis), X-ray diffraction analysis (XRD), scanning electron microscopy (SEM), and dynamic light scattering (DLS). Furthermore, the impact of surface electronegativity was discussed based on zeta potential measurements.

2. Materials and Methods

2.1. Materials

Sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$, 99.9%) and oleic acid ($\text{C}_{18}\text{H}_{34}\text{O}_2$, 99.9%) were purchased from Sigma Aldrich Chemical Company (Vietnam branch). Silver bars (99% purity) with dimensions of 100 mm \times 5 mm \times 0.5 mm were procured from a local silver store.

Fresh *Houttuynia cordata* leaves were sourced from local markets in Thai Nguyen province, thoroughly rinsed with distilled water, and subsequently dried in shade. The dried leaves were

finely chopped and immersed in double-distilled water at a ratio of 100 g leaves to 300 mL water. The mixture was heated on a magnetic stirrer and maintained at a constant temperature of 70 °C for 60 minutes. The resulting *Houttuynia cordata* extract was filtered twice through Whatman filter paper and stored in a refrigerator at 4 °C for further synthesis.

2.2. Green synthesis method for silver nanoparticles (AgNPs)

The colloidal silver nanoparticles (AgNPs) were synthesized via a green electrochemical approach, utilizing two high-purity silver bars as both working electrodes and the metallic source for nanoparticle generation. To ensure the integrity and environmental compatibility of the synthesis process, the silver electrodes were first mechanically polished to remove surface contaminants, then immersed in a 10% dilute hydrochloric acid (HCl) solution to eliminate surface oxides, and finally rinsed twice with double-distilled water to ensure complete purification.

Following the cleaning procedure, the electrodes were mounted on a fixed holder and immersed to a depth of 100 mm in a 200 mL glass beaker containing the prepared electrolyte solution, as the schematic illustrated in Figure 1. The inter-electrode distance was maintained at 30 mm throughout all experimental runs to ensure consistency. The electrochemical synthesis was conducted under an applied potential of 12 V between the silver electrodes for a duration of 60 minutes. AgNPs were synthesized by using three distinct types of electrolyte solutions were prepared: 200 mL of each solution - (i) sodium citrate named as C-AgNPs; (ii) oleic acid named as O-AgNPs - were prepared at the concentration of 6×10^{-4} M; (iii) for the bio-based electrolyte, 20 mL of *Houttuynia cordata* extract was mixed with 180 mL DI water named as Bio-AgNPs.

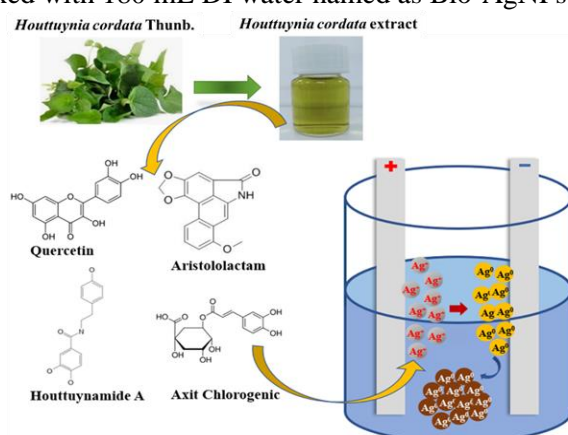


Figure 1. Schematic illustration of the green synthesis process of e-AgNPs

2.3. Characterization methods

The absorption spectra were recorded using a UV–Visible spectrophotometer (JENWAY 6850 dual-beam spectrophotometer) with quartz cuvettes over the wavelength range of 300 to 600 nm. The crystalline structure of the samples was analyzed by X-ray diffraction (XRD) using a Bruker D5005 diffractometer equipped with Cu-K α radiation ($\lambda = 0.154056$ nm), operated at an accelerating voltage of 40 kV and a current of 30 mA. The morphological features of the AgNPs were examined using scanning electron microscopy (SEM, Hitachi S-4800) operated at an accelerating voltage of 5 kV. Particle size distribution and colloidal stability were evaluated by dynamic light scattering (DLS) and zeta potential measurements, performed using a Horiba SZ-100 nanoparticle analyzer.

3. Results and Discussions

Figure 2 shows the UV–Vis spectra and XRD pattern of three synthesized AgNP colloidal solutions. All samples exhibited characteristic surface plasmon resonance (SPR) absorption peaks

(λ_{max}) in proximity to 400 nm, consistent with the optical signature typically associated with silver nanoparticles. As displayed in Figure 2a, the specific absorption maxima were observed at 435 nm for C-AgNPs, 415 nm for O-AgNPs, and 426 nm for Bio-AgNPs. The spectra of C-AgNPs and O-AgNPs displayed sharp and intense SPR peaks, indicating a narrow size distribution and high degree of colloidal stability. In contrast, the absorption peak corresponding to Bio-AgNPs was broader and exhibited lower intensity, which may be attributed to the complex composition of the plant extract used in their synthesis. While sodium citrate and oleic acid are high-purity chemical reagents, the *Houttuynia cordata* extract comprises a mixture of biomolecules that can influence both the reduction and stabilization processes, potentially leading to polydispersity in particle size and optical behavior [15], [16]. Furthermore, based on the spectral features, it can be inferred that C-AgNPs and O-AgNPs possess smaller and more uniform particle sizes in comparison to Bio-AgNPs. The relatively broad and subdued SPR peak of Bio-AgNPs suggests possible encapsulation within a thicker organic matrix derived from the plant extract, which may also affect their optical and colloidal properties.

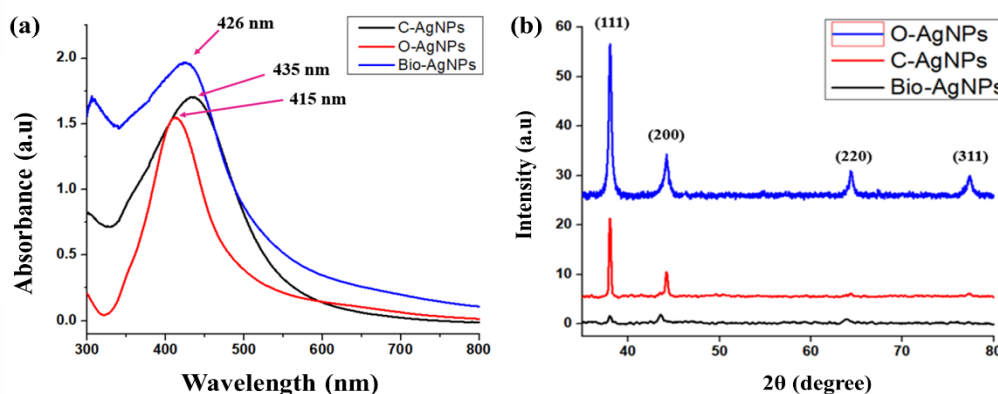


Figure 2. UV-Vis spectra (a), and XRD pattern (b) of the AgNPs samples

Figure 2b shows the XRD pattern of AgNPs samples synthesized via a green electrochemical approach. A face-centered cubic (FCC) structure was observed. Distinct diffraction peaks were observed at 2θ angles of 38.10° , 44.30° , 64.50° , and 77.30° , corresponding to the (111), (200), (220), and (311) crystallographic planes, respectively, as referenced by the JCPDS standard card No. 00-004-0783. Among the analyzed samples, the O-AgNPs exhibited the most intense and well-resolved diffraction peaks, indicating a higher degree of crystallinity relative to the C-AgNPs and Bio-AgNPs. Both O-AgNPs and C-AgNPs showed no additional peaks attributable to secondary phases or impurities, suggesting excellent phase purity and successful reduction of silver ions without the presence of undesired by-products. In contrast, the Bio-AgNPs sample displayed a notably weaker and less defined diffraction peak corresponding to the (311) plane, along with generally lower overall peak intensities. These features are indicative of a lower crystallinity in the Bio-AgNPs. The diminished crystallinity observed in the Bio-AgNPs is likely due to the complex organic matrix present in the *Houttuynia cordata* extract. The multitude of biomolecules in the plant extract may hinder the orderly nucleation and growth of silver crystals, thereby impeding the formation of well-defined crystalline domains during nanoparticle synthesis.

The SEM images presented in Figure 3 provide clear morphological evidence that the synthesized AgNPs predominantly exhibit spherical shapes with relatively uniform distribution. While the SEM images of O-AgNPs and C-AgNPs reveal nanoparticles with well-defined and distinct boundaries, the Bio-AgNPs exhibit a more diffuse and less sharply defined outer edge. Notably, the Bio-AgNPs sample displayed larger apparent particle sizes in comparison to the C-AgNPs and O-AgNPs. This increase in size is attributed to the presence of a thick organic coating surrounding the nanoparticles, originating from the complex mixture of biomolecules present in

the *Houttuynia cordata* extract. Such biomolecular layers likely contribute to increased particle dimensions observed in the SEM images, as they can form a stabilizing shell around the nanoparticle cores. The morphological distinctions observed among the samples further corroborate the differences in the surface chemistry and synthesis media used in the green electrochemical process.

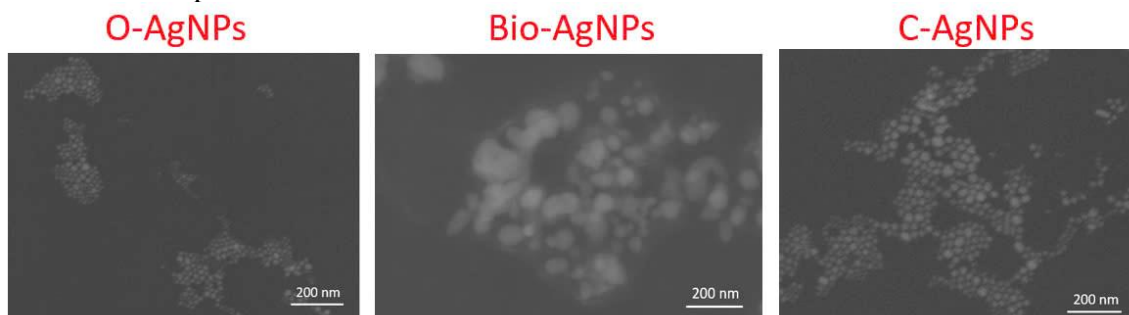


Figure 3. SEM images of AgNPs

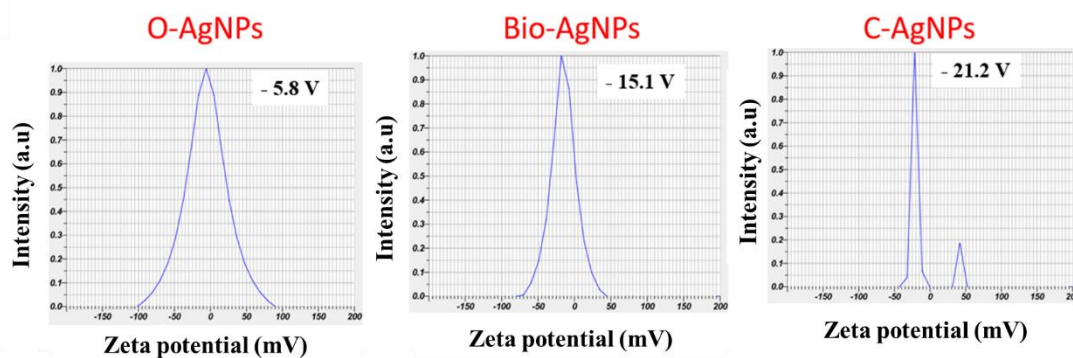


Figure 4. Zeta potential of AgNPs

The Zeta potential of AgNPs samples was exhibited in Figure 4. Citrate ions, as tricarboxylic acid derivatives, possess three negatively charged carboxylate groups ($-\text{COO}^-$) that are pivotal for both the reduction and stabilization of silver nanoparticles (AgNPs). During C-AgNP synthesis, two carboxylate groups typically coordinate to the nanoparticle surface through electrostatic interactions, while the third projects outward into the aqueous phase, thereby promoting hydrophilicity and colloidal dispersion. The accumulation of surface negative charges forms a stable electrical double layer, resulting in a zeta potential of -21.2 mV, indicative of strong electrostatic repulsion and excellent dispersion stability. For Bio-AgNPs, the reducing and capping agents originate from *Houttuynia cordata* extract, rich in phenolic acids, flavonoids, and hydroxylated compounds (Figure 1). These biomolecules adsorb onto the nanoparticle surface, imparting a net negative charge and yielding a zeta potential of -15.1 mV. Although the value is slightly lower than C-AgNPs, it still supports moderate colloidal stability, potentially affected by the heterogeneous composition of the extract. In contrast, O-AgNPs stabilized by oleic acid exhibit a markedly lower zeta potential of -5.8 mV. Oleic acid molecules form bilayers around the nanoparticles, with carboxyl groups binding the surface and hydrophobic alkyl tails projecting outward. Interactions between adjacent C=C bonds further disrupt surface charge distribution, leading to reduced electrostatic repulsion and increased susceptibility to agglomeration in aqueous media [17]. The average particle size in DLS measurements was calculated according to formula (1):

$$D_z = \frac{k_B T}{3\pi\eta D_t} \quad (1)$$

Where:

D_z is the average particle size (nm)

D_t is the average translational diffusion coefficient (m^2/s)

k_B is the Boltzmann constant

T is the absolute temperature (K)

η is the dynamic viscosity of the solution ($Pa \cdot s$)

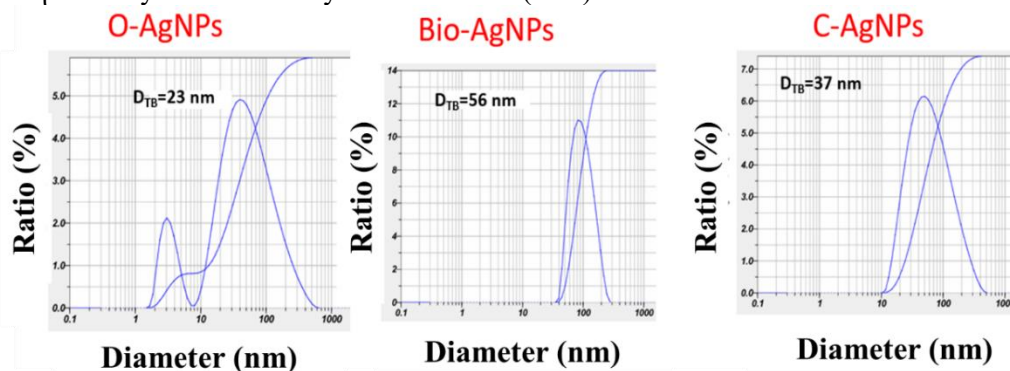


Figure 5. DLS size distribution profiles of AgNPs

The particle size distribution profiles of the three AgNPs samples, as determined by dynamic light scattering (DLS), are shown in Figure 5. The analysis revealed average hydrodynamic diameters of approximately 23 nm for O-AgNPs, 37 nm for C-AgNPs, and 56 nm for Bio-AgNPs. These hydrodynamic diameters represent the effective size of the particles in suspension, taking into account not only the core size of the nanoparticles but also the presence of a surrounding solvation layer and any potential agglomeration behavior within the colloidal system. It is noteworthy that the particle sizes obtained from DLS measurements are consistently larger than those observed in scanning electron microscopy (SEM) images. This variation arises from the fundamental difference in measurement principles between the two techniques. While SEM provides direct visualization of the dried and isolated nanoparticles on a substrate, DLS captures the behavior of particles dispersed in liquid media. In such environments, nanoparticles are prone to forming dynamic aggregates or clusters due to Brownian motion and interparticle interactions. Consequently, DLS reports the hydrodynamic diameter of these aggregates, which encompasses the physical core of the nanoparticle along with its solvation shell and any loosely bound surrounding species. This distinction is particularly relevant in the case of Bio-AgNPs, where the complex mixture of biomolecules from the *Houttuynia cordata* extract may promote greater steric and electrostatic stabilization, leading to the formation of larger hydrated clusters. Therefore, the higher average size measured for Bio-AgNPs may not reflect individual nanoparticle dimensions, but rather the combined structure of the core particle and its organic capping layers in solution.

Recent studies have also indicated that silver nanoparticles synthesized with *Houttuynia cordata* extract exhibit particle sizes smaller than 100 nm; however, these studies employed silver nitrate ($AgNO_3$) as the precursor [18], [19]. In contrast, the present study utilizes a green electrochemical approach with high-purity silver electrodes, thereby eliminating the need for salt-based precursors. This difference in synthetic route not only enhances the environmental sustainability of the process but may also influence nanoparticle characteristics such as size, morphology, and surface chemistry.

4. Conclusion

This study successfully demonstrated the green electrochemical synthesis of silver nanoparticles (AgNPs) using two high-purity silver electrodes and a selection of environmentally benign, biocompatible reducing agents. The electrochemical method employed enables the direct generation of silver ions from metallic silver, thereby eliminating the need for hazardous chemical precursors such as silver nitrate. Three types of AgNPs were synthesized using sodium citrate, oleic acid, and *Houttuynia cordata* extract as stabilizing and reducing agents, respectively. The synthesized AgNPs were found to possess predominantly spherical morphology, as confirmed by SEM analysis, and exhibited good colloidal stability in aqueous environments. The particles demonstrated average hydrodynamic diameters below 50 nm, with slight variations depending on the nature of the capping agent. UV–Vis spectroscopy confirmed the presence of surface plasmon resonance peaks characteristic of AgNPs, while XRD analysis verified their face-centered cubic crystalline structure. Further characterization through DLS and zeta potential measurements highlighted differences in surface charge and dispersion stability, particularly between chemically and biologically derived nanoparticles. The methodology presented offers a facile, scalable, and eco-friendly route for AgNP synthesis, with potential for large-scale production. Given their favorable physicochemical properties, biocompatibility, and synthesis sustainability, the AgNPs produced through this approach show significant promise for practical applications in diverse domains, including biomedicine, healthcare, food preservation, and environmental remediation. The combination of safety, cost-effectiveness, and functionality underscores the relevance of this green synthesis strategy for future nanomaterial development.

Acknowledgement

This research was supported by Thai Nguyen University of Technology with Grant number T2024-NCS21.

REFERENCES

- [1] N. K. Tolochko, "History of Nanotechnology - Encyclopedia of Life Support Systems (EOLSS)," *Nanoscience and Nanotechnologies*, vol. 1, pp. 1–18, 2018.
- [2] N. Kumar and S. Kumbhat, *Essentials in nanoscience and nanotechnology*. John Wiley & Sons, 2016.
- [3] H. T. M. Le, V. H. Nguyen, L. T. Tran, P. T. Nguyen, N. V. H. Phan, and H. V. T. Le, "Fabrication of Al/Al₂O₃/Ag SERS substrate by the corrosion method to detect ketoprofen," *Sci. Technol. Dev. Journal-Natural Sci.*, vol. 5, no. 3, pp. 1401–1409, 2021.
- [4] Z. Yang, C. Ma, W. Wang, M. Zhang, X. Hao, and S. Chen, "Fabrication of Cu₂O-Ag nanocomposites with enhanced durability and bactericidal activity," *J. Colloid Interface Sci.*, vol. 557, pp. 156–167, 2019.
- [5] A. M. E. Shafey, "Green synthesis of metal and metal oxide nanoparticles from plant leaf extracts and their applications: A review," *Green Processing and Synthesis*, vol. 9, no. 1, pp. 304–339, 2020.
- [6] L. Mogole, W. Omwoyo, E. Viljoen, and M. Moloto, "Green synthesis of silver nanoparticles using aqueous extract of Citrus sinensis peels and evaluation of their antibacterial efficacy," *Green Process. Synth.*, vol. 10, no. 1, pp. 851–859, 2021.
- [7] L. Xu, Y.-Y. Wang, J. Huang, C.-Y. Chen, Z.-X. Wang, and H. Xie, "Silver nanoparticles: Synthesis, medical applications and biosafety," *Theranostics*, vol. 10, no. 20, 2020, Art. no. 8996.
- [8] D. Zhang, X. L. Ma, Y. Gu, H. Huang, and G. W. Zhang, "Green Synthesis of Metallic Nanoparticles and Their Potential Applications to Treat Cancer," *Frontiers in Chemistry*, vol. 8, 2020, doi: 10.3389/fchem.2020.00799.
- [9] C. Vanlalveni, S. Lallianrawna, A. Biswas, M. Selvaraj, B. Changmai, and S. L. Rokhum, "Green synthesis of silver nanoparticles using plant extracts and their antimicrobial activities: A review of recent literature," *RSC Adv.*, vol. 11, no. 5, pp. 2804–2837, 2021.
- [10] T. V. T. Do, W. Suhartini, C. U. Phan, Z. Zhang, G. Goksen, and J. M. Lorenzo, "Nutritional value, phytochemistry, health benefits, and potential food applications of Pouteria campechiana (Kunth) Baehni: A comprehensive review," *J. Funct. Foods*, vol. 103, 2023, Art. no. 105481.

-
- [11] A.-T. Le *et al.*, "Synthesis of oleic acid-stabilized silver nanoparticles and analysis of their antibacterial activity," *Mater. Sci. Eng. C*, vol. 30, no. 6, pp. 910–916, 2010.
- [12] H. Jiang, M. Li, F. Chang, W. Li, and L. Yin, "Physiological analysis of silver nanoparticles and AgNO₃ toxicity to *Spirodela polyrhiza*," *Environ. Toxicol. Chem.*, vol. 31, no. 8, pp. 1880–1886, 2012.
- [13] M. Diez-Ortiz *et al.*, "Short-term soil bioassays may not reveal the full toxicity potential for nanomaterials; bioavailability and toxicity of silver ions (AgNO₃) and silver nanoparticles to earthworm *Eisenia fetida* in long-term aged soils," *Environ. Pollut.*, vol. 203, pp. 191–198, 2015.
- [14] A. Tripathi *et al.*, "Differential phytotoxic responses of silver nitrate (AgNO₃) and silver nanoparticle (AgNps) in *Cucumis sativus* L.," *Plant Gene*, vol. 11, pp. 255–264, 2017.
- [15] W. Cai *et al.*, "Phenolic contents and antioxidant activities of different parts of *Houttuynia cordata* Thunb.," *J. Med. Plants Res.*, vol. 6, no. 6, pp. 1035–1040, 2012.
- [16] Z. Wu *et al.*, "Houttuynia cordata Thunb: an ethnopharmacological review," *Front Pharmacol*, vol. 12, 2021, Art. no. 714694.
- [17] I. Ivanišević, "The role of silver nanoparticles in electrochemical sensors for aquatic environmental analysis," *Sensors*, vol. 23, no. 7, 2023, Art. no. 3692.
- [18] L. Kikon *et al.*, "Green synthesis and characterization of silver nanoparticles using aqueous extract of *houltuynia cordata*," *Biochem. Cell. Arch.*, vol. 24, no. 1, pp. 361 - 365, 2024.
- [19] X. Maimaiti *et al.*, "Green synthesis of silver nanoparticles using *Houttuynia cordata* Thunb rhizome extracts and their antibacterial potential against common foodborne pathogens," *Int. J. Food Sci. Technol.*, vol. 59, no. 5, pp. 3283–3296, 2024.