

Review Article

Green Plasma Electrochemical Synthesized Colloidal Silver Nanoparticles and Their Antibacterial Activity

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Nanosilver solutions of colloidal silver nanoparticles at reasonable price, good quality, and availability are increasingly demanded for the application in agriculture and aquaculture for the prevention and treatment of diseases. In this paper, we have applied a new simple and environmental-friendly fabrication method based on a plasma electrochemical procedure, where silver nanoparticles are directly formed in the plasma environment from silver ions generated by the electrochemical process from the silver anode. The electrode dissolution rate, the formation percentage, and quality of the silver nanoparticles were examined and evaluated using atomic absorption spectroscopy, electrode mass change, transmission electron microscopy, and UV-Vis absorption spectroscopy. The silver nanoparticle formation was found of nearly 100% with the rate of about 3.3 mg per minute. Spherical nanoparticles are found in quite homogenous size distribution around about 9.7 nm in the solution. The solution of the plasma synthesized nanosilvers shows better antibacterial property in comparison to that of AgNO₃ of the same molar concentration on both normal and antibiotics resistant *E. coli* strains.

1. Introduction

Silver is known as the chemical element with the most powerful antibacterial properties, which are significantly enhanced when the material is in the dimensions in nanometer scale, namely, in the form of nanoparticles [1]. Silver nanoparticles (AgNPs) are widely used in agriculture and aquaculture for the prevention and treatment of diseases [1, 2] as well as in many other areas [3–8]. However, accessing to appropriately high-quality silver nanoparticle products is still a challenge for quite a number of farmers. High price due to expensive and complicated manufacture procedure is also a big barrier. In Vietnam, in accordance with the restructure and transition of the agricultural production to successfully adapt to the more and more apparent climate and environment changing conditions and also to essential improve the agriproduct quality to meet the high standard

of export markets much attentions are paid to the application of new, advanced technologies and materials, among which antibacterially active metal nanoparticles and materials are highly demanded.

AgNPs have been synthesized by various physical [9–11], chemical [12, 13], and biological methods [14, 15] targeting at different application purposes [16]. They all show also diverse advantages and disadvantages with respect to the fabrication cost and time consumptions, the stability, the size distribution, the purity, and other properties. One of the most commonly used methods is the chemical reduction owing to the convenient procedure and simple and easily available equipment needed [17, 18]. However, the chemical method is the most environment-unfriendly and expensive with rather low purity synthesized AgNPs. In contrast, biological methods using naturally reducing agents, such as microorganism (bacteria or fungi) or plant extracts to obtain

AgNPs from appropriate silver salts, are environment-friendly and quite cost effective [19, 20]. Nonetheless, a major disadvantage of these methods is that the produced AgNP solutions only reach low concentrations and uncontrollable particle size distributions [16]. In comparison to these, the physical approaches have approved the ability to produce large quantities of high-purity AgNPs by different routes. It is even quite convenient to fabricate large quantity of AgNPs with well-homogeneous particle size distribution from bulk silver in just a single process [9–11]. Several groups have successfully produced good quality AgNP solutions using the plasma liquid interaction techniques [21]. Thuy [22] used two pure silver metal electrodes, one of them is submerged in the solution, and the other touched the surface of the solution. With this configuration, it is possible to produce a fairly pure AgNP solution. However, the resulting solution is still dilute (concentration was lower than 300 ppm) with rather wide particle size distribution.

In this work, we apply a plasma electrochemical method using the plasma-in-liquid configuration with both discharging electrodes from bulk silver metal submerged in the solution for the green synthesis of colloidal AgNPs. The experimental results have revealed that this low-cost fabrication method could provide high concentration and high-quality colloidal AgNP solution with high antibacterial effectiveness in a single process.

2. Materials and Experimental Methods

2.1. The Plasma Electrochemical Fabrication of the Colloidal AgNP Solution. The plasma electrochemical system for the synthesis of the colloidal AgNP solution consists of two electrodes submerged into the solution confined in a glass container and a pulsed DC high voltage up to 6 kV power source with the repetition rate of 25 Hz and the duty cycle of 50% as is shown in Figure 1. Both electrodes were covered by a Teflon tube with only a small uncovered tip part directly exposed to the solution. The cathode was a sharpened molybdenum rod placed oppositely polarized to the anode in the distance of about 2 mm. The anode was a bulk silver rod (99.999% purity) with diameter of 6 mm purchased from a domestic jewelry company in Hanoi, Vietnam.

Large amount of the synthetic conditions has been investigated including pH, supply voltage, peak plasma current as well as distance between electrodes. In this present work, we perform only the best condition with pH 7, 6 kV supply voltage, 1.4 A peak plasma current, and 2 mm electrode distance. We examine only the synthesis duration and the properties of synthesised AgNPs.

The principle of AgNP formation in the plasma electrochemical system can be described with 3 stages as follows.

Stage 1. Electrolysis

At the beginning of a cycle, the system acts as an electrolysis cell. The cathodic reaction is an electrolysis of water that produces hydrogen gas in the form of bubbles:

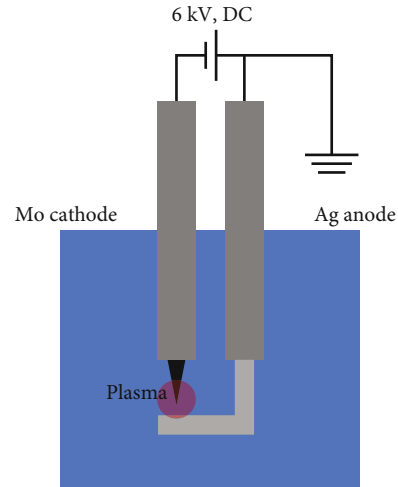
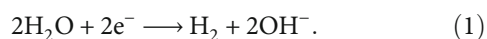


FIGURE 1: Plasma electrochemical system for the colloidal AgNP synthesis.

Meanwhile, on the anode side, silver is electrolyzed, releasing the Ag^+ ions into the solution:



When the amount of generated hydrogen is large enough to cover the surface of the cathode and the voltage increases sufficiently (about 2 kV), the continuous electric discharge will occur; the reaction system moves to stage 2.

Stage 2. Plasma and particle formation

After the electric field between the cathode and the anode was broken down, the plasma arc was formed between the two electrodes. The original plasma was the plasma of the ionic species of hydrogen and water vapor mixture. However, the steam plasma will then prevail. During this stage, the space between the two electrodes is divided into three regions as shown in Figure 2:

- (i) Electrolytic region, adjection to the anode, where Ag^+ ions continuously are released from the anode and moving towards the cathode
- (ii) The reduction region, where the Ag^+ ions were reduced to silver atom Ag^0 by atomic hydrogen and electrons
- (iii) Nucleation and growth region, where the silver nanonucleus were formed and grown into nanoparticles

Stage 3. Extinguishing and electrolysis

When the voltage drops to about 400 V, the plasma was no longer maintained, and the system returned to an electrolysis cell.

2.2. Estimation of the AgNP Formation Rate. Every two minutes, the anode was weighed to determine the Ag^+ release rate. Meanwhile, the AgNP solution was centrifuged to collect the generated AgNPs, and the silver content was determined by the atomic absorption spectroscopy.

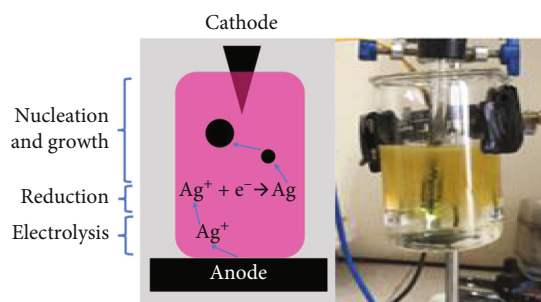


FIGURE 2: Structure of a plasma electrochemical system for the AgNP formation.

2.3. Characterizations of AgNPs. The morphology and particle size of AgNPs were examined by the transmission electron microscopy (TEM using the JEM 1010, JEOL system) at 80 kV. The UV–visible absorption was measured using the UV–near IR spectrometer of the type V-570 (Jasco).

2.4. Antibacterial Assays. Two bacterial strains, namely, normal and antibiotic-resistant *Escherichia coli* (ATCC 25923), were provided by the Genome Research Institute, Vietnam Academy of Science and Technology, Vietnam. The disc-diffusion technique (the so-called modified Kirby–Bauer technique) was applied to examine the antibacterial activity of AgNPs. Plastic Petri dishes were first filled with Luria–Bertani (LB) agar and then inoculated separately with two bacterial strains, respectively, of normal and antibiotic-resistant *E. coli*. Bacterial concentrations of the order of 10^8 colony-forming unit (cfu)/ml were used. Each LB agar dish was punched with four holes of 5 mm diameter. Two of these holes on each disk were filled with the AgNO_3 solutions and the others with the AgNP solutions of the same concentrations. Six values of concentrations of 250 ppm, 160 ppm, 80 ppm, 40 ppm, 20 ppm, and 10 ppm were examined. Zones of inhibition were determined after 24 h of incubation at temperature of 37°C .

3. Results and Discussion

Initially, the solution was colorless, then gradually turned yellow due to the formation of silver nanoparticles. The longer the plasma processing time is, the darker the solution becomes.

As can be seen in Figure 3, the measured UV–vis spectra show the spectral characteristics of silver NPs with a maximum surface plasmon resonance corresponding to a wavelength of 408 nm. The UV–vis spectra provided strong evidence of the formation of the surface-plasmon-resonance band of spherical AgNPs.

Figure 4 shows that most of the as-synthesized AgNPs are of spherical shape and homogeneous in both size and shape distribution. Particle sizes range mainly from 8 nm to 11 nm, with an average size of 9.7 nm. The AgNP distribution is not sharply homogenous, since the AgNPs formed in the plasma region can leave the region and stop their growth but others can stay or some from outside plasma region can reenter and continue to grow further.

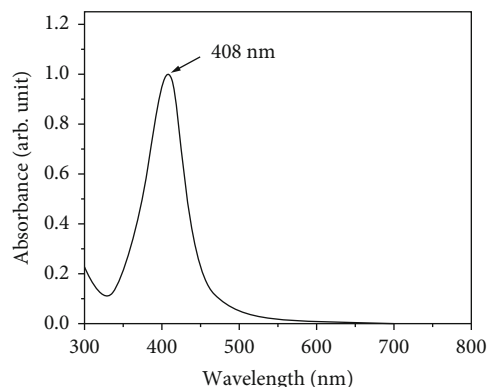


FIGURE 3: UV–vis spectra of the solution diluted 140 times from the 14 minutes plasma processing with the batch of 40 ml.

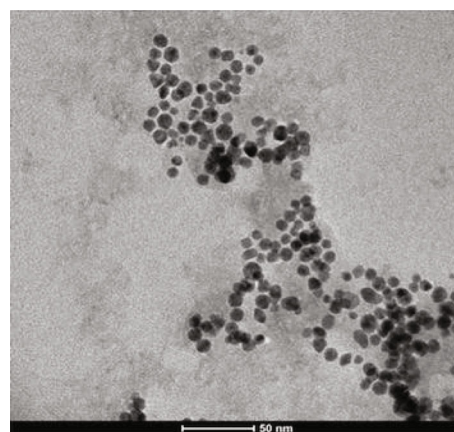


FIGURE 4: Transmission electron microscopy (TEM) image of silver nanoparticles in solution.

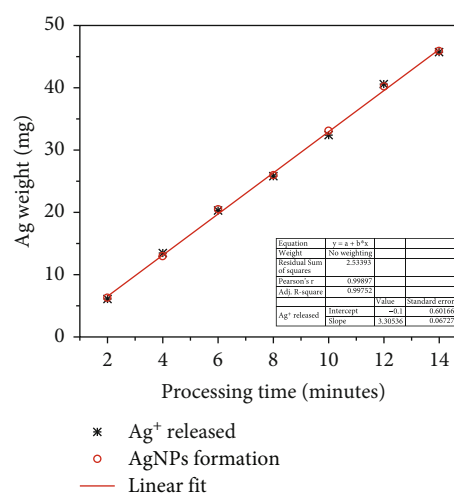


FIGURE 5: Ag^+ release and AgNP formation.

The measured weight decrease of the Ag electrode with the plasma processing time is shown in Figure 5. As estimated from this weight decrease, the Ag^+ release during

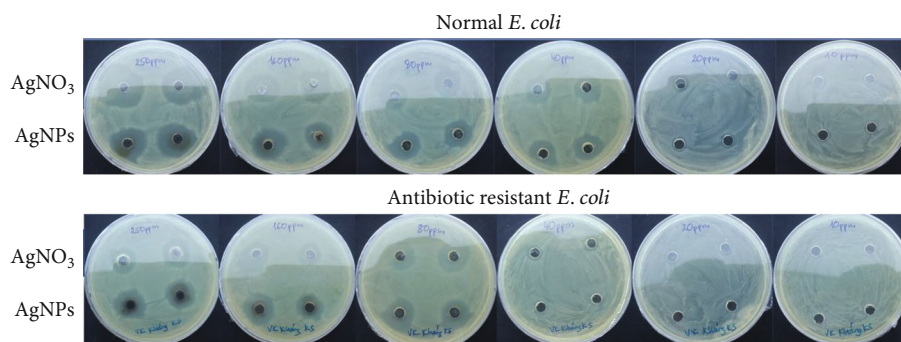


FIGURE 6: Comparison in the bactericidal properties of the AgNP solution produced by the plasma electrochemical technique and those of the AgNO_3 solution on normal and antibiotic-resistant *E. coli*.

the processing is about 3.3 mg/min. The nanoparticle formation rate estimated from the results of atomic absorption spectroscopy, thus, also gives the same rate which indicates a 100% nanoformation. In order to confirm this, ascorbic acid was introduced into the as-synthesized solutions. The UV-vis absorption spectra before and after the ascorbic acid introduction were found to remain identical. There should be no free Ag^+ in the plasma electrochemical AgNP solutions. Using the AgNP formation rate, the concentration of the AgNPs for a batch of 40 ml solution after 14 minutes processing could be estimated as 1150 ppm.

The observed results show that both the AgNO_3 solution and the AgNP solution are capable of killing the *E. coli*, even at low concentrations (20 ppm). However, with the antibiotic-resistant *E. coli*, a higher concentration (80 ppm) of the sterile ring is clearly observed. We can see that the inhibition zone created by the plasma electrochemical AgNPs is mostly larger than the inhibition one produced by the nano-silver obtained on the market with the same concentration. In particular, with the antibiotic-resistant bacteria, this difference is even more pronounced, demonstrating the outstanding bactericidal properties of the silver nanoparticles created by the plasma electrochemical method (Figure 6).

4. Conclusions

This work has demonstrated a low-cost green synthesis of colloidal AgNPs in a single process utilizing the plasma electrochemical method. Results have shown that the as-synthesized AgNPs are spherical in shape and homogeneous in size averaged with 9.7 nm diameter. The colloidal AgNP solutions show high antibacterial effectiveness against both normal and antibiotic-resistant bacteria. The advantages of the above described fabrication method have revealed to be a simple high yield preparation technique, which is very promising for the synthesis of colloidal AgNPs of with high homogeneity purity and antibacterial activity for different applications.

Data Availability

No data were used to support this study.

Conflicts of Interest

The authors declare that they have no conflicts of interest regarding the publication of this paper.

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References

- [1] L. Q. Kha, N. H. Chau, and H. T. Lua, "The Tendency of Nanotechnology Application in Plants and Aqueous Products Farming, Center of Science and Technology Information and Statistics, Department of Science and Technology of HCM City," in *Trends of application of nanotechnology in crop and aquaculture farming*, Center for Science and Technology Information and Statistics, Ho Chi Minh City Department of Science and Technology, 2016.
- [2] H. C. Nguyen, T. T. Nguyen, T. H. Dao, Q. B. Ngo, H. L. Pham, and T. B. Nguyen, "Preparation of Ag/SiO₂nanocomposite and assessment of its antifungal effect on soybean plant (a Vietnamese species DT-26)," *Advances in Natural Sciences: Nanoscience and Nanotechnology*, vol. 7, no. 4, article 045014, 2016.
- [3] A. Hebeish, M. H. El-Rafie, M. A. El-Sheikh, A. A. Seleem, and M. E. El-Naggar, "Antimicrobial wound dressing and anti-inflammatory efficacy of silver nanoparticles," *International Journal of Biological Macromolecules*, vol. 65, pp. 509–515, 2014.
- [4] D. Roe, B. Karandikar, N. Bonn-Savage, B. Gibbins, and J. B. Roulet, "Antimicrobial surface functionalization of plastic catheters by silver nanoparticles," *The Journal of Antimicrobial Chemotherapy*, vol. 61, no. 4, pp. 869–876, 2008.
- [5] EPA, *EPA/600/R-10/081F*, U.S. Environmental Protection Agency, Washington, DC, 2012.
- [6] Y. Echegoyen and C. Nerin, "Nanoparticle release from nano-silver antimicrobial food containers," *Food and Chemical Toxicology*, vol. 62, pp. 16–22, 2013.
- [7] A. Kumar, P. K. Vemula, P. M. Ajayan, and G. John, "Silver-nanoparticle-embedded antimicrobial paints based on vegetable oil," *Nature Materials*, vol. 7, no. 3, pp. 236–241, 2008.

- [8] F. Zhang, X. Wu, Y. Chen, and H. Lin, "Application of silver nanoparticles to cotton fabric as an antibacterial textile finish," *Fibers and Polymers*, vol. 10, no. 4, pp. 496–501, 2009.
- [9] K.-H. Tseng, Y.-C. Chen, and J.-J. Shyue, "Continuous synthesis of colloidal silver nanoparticles by electrochemical discharge in aqueous solutions," *Journal of Nanoparticle Research*, vol. 13, no. 5, pp. 1865–1872, 2011.
- [10] M. N. Nadagouda, T. F. Speth, and R. S. Varma, "Microwave-assisted green synthesis of silver nanostructures," *Accounts of Chemical Research*, vol. 44, no. 7, pp. 469–478, 2011.
- [11] F. Mafuné, J. Y. Kohno, Y. Takeda, T. Kondow, and H. Sawabe, "Formation and size control of silver nanoparticles by laser ablation in aqueous solution," *The Journal of Physical Chemistry. B*, vol. 104, no. 39, pp. 9111–9117, 2000.
- [12] C. Ortiz, R. Torres, and D. Paredes, "Synthesis, characterization, and evaluation of antibacterial effect of Ag nanoparticles against *Escherichia coli* O157:H7 and methicillin-resistant *Staphylococcus aureus* (MRSA)," *International Journal of Nanomedicine*, vol. 9, pp. 1717–1729, 2014.
- [13] A. Panacek and L. Kvitek, "Silver colloid nanoparticles: synthesis, characterization, and their antibacterial activity," *The Journal of Physical Chemistry. B*, vol. 110, no. 33, pp. 16248–16253, 2006.
- [14] J. L. López-Miranda, M. Vázquez, N. Fletes, R. Esparza, and G. Rosas, "Biosynthesis of silver nanoparticles using a *Tamarix gallica* leaf extract and their antibacterial activity," *Materials Letters*, vol. 176, pp. 285–289, 2016.
- [15] S. Gurunathan, K. Kalishwaralal, R. Vaidyanathan et al., "Biosynthesis, purification and characterization of silver nanoparticles using *Escherichia coli*," *Colloids and Surfaces B: Biointerfaces*, vol. 74, no. 1, pp. 328–335, 2009.
- [16] Q. H. Tran, V. Q. Nguyen, and A. T. Le, "Silver nanoparticles: synthesis, properties, toxicology, applications and perspectives," *Advances in Natural Sciences: Nanoscience and Nanotechnology*, vol. 4, no. 3, article 033001, 2013.
- [17] H. Wang, X. Qiao, J. Chen, and S. Ding, "Preparation of silver nanoparticles by chemical reduction method," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 256, no. 2-3, pp. 111–115, 2005.
- [18] M. G. M. Guzmán, J. Dille, and S. Godet, "Synthesis of silver nanoparticles by chemical reduction method and their antibacterial activity," *International Journal of Chemical and Biomolecular Engineering*, vol. 2, pp. 104–111, 2009.
- [19] S. Ahmed, M. Ahmad, B. L. Swami, and S. Ikram, "A review on plants extract mediated synthesis of silver nanoparticles for antimicrobial applications: a green expertise," *Journal of Advanced Research*, vol. 7, no. 1, pp. 17–28, 2016.
- [20] S. Jain and M. S. Mehata, "Medicinal plant leaf extract and pure flavonoid mediated green synthesis of silver nanoparticles and their enhanced antibacterial property," *Scientific Reports*, vol. 7, no. 1, p. 15867, 2017.
- [21] V. S. Santosh, K. Kondeti, U. Gangal, S. Yatom, and P. J. Bruggeman, "Ag+reduction and silver nanoparticle synthesis at the plasma-liquid interface by an RF driven atmospheric pressure plasma jet: Mechanisms and the effect of surfactant," *Journal of Vacuum Science and Technology A*, vol. 35, no. 6, article 061302, 2017.
- [22] N. M. Thuy, *Research on the Anaerobic Dissociation of the Anode to Generate Silver Nanoparticles Using High Voltage*, [Ph.D. thesis], Vietnam Academy of Science and Technology, 2015.