

ELECTROCHEMICAL PREPARATION OF NANO SILVER BY COMBINING HIGH DC VOLTAGE WITH ANODIC PLASMA

Nguyen Duc Hung^{1,*}, Vu Nang Nam¹, Le Van Trung², Tran Thi Ngoc Dung¹

¹*Institute for Environmental Technology, VAST, 18 Hoang Quoc Viet, Cau Giay, Ha Noi*

²*Quy Nhon University, 170 An Duong Vuong, Quy Nhon City, Binh Dinh*

*Email: nguyenduchung1946@gmail.com

Received: 22 May 2018; Accepted for publication: 21 January 2019

Abstract. Silver nanoparticles (AgPNs) were prepared by high-voltage electrochemical methods using silver anode to produce silver ions and hydrogen gas at the cathode from electrolysis of distilled water as solvents. The electrolyte solution resulting from the obtained AgPNs product does not contain ions of the electrolyte solution such as conventional chemical or electrochemical methods. Silver anode dissolution process would provide Ag⁺ and disperse it into distilled water. The H₂ generated from the electrolysis of H₂O disperses into distilled water and escapes upward towards the anode due to the arrangement of the electrolytic vaporizer vertically above the anode and the cathode below. Ag⁺ and H₂'s encountered in the aqueous solution would take the oxidation-reduction reaction to form AgPNs. Due to the high-voltage DC electrolytic processes that generate gas on the electrodes, both high-voltage and high magnetic fields, as well as high water-distillation resistance, could increase the solution temperature as favorable conditions to form an electrochemical plasma on the electrodes. The plasma electrode process that separates water into H₂ and O₂ can occur simultaneously by electrochemical reactions that contribute to the supply of large amounts of gas to participate in oxidative reactions - reducing the formation of AgPNs. The properties of the AgPNs solution prepared by high-voltage DC lines were determined by UV-Vis, electrical conductivity, TEM, zeta potential, particle size distribution as well as content determined by weight lost method, Faraday's law and AAS analysis. Anodic plasma can be generated by stable high voltage mode to decompose water that supports electrochemical reactions to form AgPNs with structural and physicochemical properties as well as comparable constituents be with the current methods.

Keywords: AgPNs, high voltage DC, dissolved silver anode, anodic plasma, cathodic hydrogen.

Classification numbers: 2.4; 2.5.1; 2.10.2.

1. INTRODUCTION

Silver nanoparticles (AgPNs) are prepared by a variety of methods such as wetting the AgNO₃ solution [1-2] with reducing agents [3-4] or by using the physical effects [5-6]. Common electrochemical methods are also used to dissolve silver anode in electrolyte solution [7-8] and

deposition on cathode [9-10] or in combination with [11-12] to disperse the precipitate into AgPNs solution. The high DC voltage electrolytic method uses silver electrodes as anode dissolved in distilled water [13-14] but does not use electrolyte solution [15-16]. Therefore, NO_3^- ions are present in the solution of AgPNs. - as well as chemicals that are reducing agents, electrolyte solutions, stabilizers such as conventional chemical, biological, physical, or electrochemical methods [17-18]. With high-voltage DC currents, electrochemical reactions such as the silver electrolyte anode dissolution provide the Ag^+ ion as well as the cathode disassociation process that produces H_2 gas and then disperses it into distilled water and escapes to the anode. Make the following reactions:



The process of precipitating silver from ion silver on the cathode simultaneously with hydrogen gas is very strong, so it is difficult to form a metal film that is easy to disperse the nanoscale granules into the solution. On the other hand, H_2 gas escapes from cathode charge encountered with Ag^+ in the aqueous solution, which will carry out the oxidation-reduction process to form AgPNs. Simultaneously, the electrochemical process is equal to the high-voltage DC current that creates the gases on the electrodes, while heating the water due to the resistance of the distilled water increases the temperature of the reaction medium. In the space near gas-filled electrodes, both high-voltage and high-magnetic field environments, as well as increased solution temperatures, are favorable conditions for formation of electrochemical plasma on electrodes [19] as:

At the bottom cathode with H_2 gas, there is cathodic electrochemical plasma:



At the above anode with O_2 gas has an anodic electrochemical plasma:



The plasma process on the electrodes separates the water into H_2 , O_2 and H_2O_2 that do not follow the Faraday law [20-21]. It can occur simultaneously with Faraday electrochemical processes and electrochemical plasma processes that contribute to the large amount of dispersed gas in the solution to participate in the reaction for formation of AgPNs as [10]:



Thus, the major products of the electrode process in water with high voltage DC currents with electrochemical plasma are just AgPNs and do not contain ions from salts, reducing agents and electrolyte solutions.

The high-voltage DC generator can set a stable value to regulate and control the anode plasma to study the generation of AgPNs as well as the properties of the AgPNs solution formed as the content of this article.

2. EXPERIMENTAL METHODS

Figure 1 shows the high voltage DC remote control box device with features:

- Display and control the DC voltage from 0 to 20 kV, and stabilize the voltage,
- Display and control infinitely variable currents from 0 to 500 mA and stabilize the current,
- Record and display the amount of power (mAh) used to perform the reaction,
- Set automatically the reaction time,

the status light of the reaction mode, the automatic shut-off to protect equipment against over-voltage, over-current or power failure and failure.

The negative electrode of the device was connected to the silver electrode at the bottom of the electrochemical reactor as cathode and the positive electrode of the device was connected to the silver electrode mounted on the top of the reactor as anode.

The 750 mL volumetric flask was made of double-ended thermal insulated glass with 29 mm standard abrasive bottom for watertight and had cooling layer for circulating water. Cooling water with determined volume and temperature was pumped from under the flask and circulated to in cooling layer to the container.

The reaction product was received from the valve at the bottom of the flask, and the gas escapes through the valve at the top of flask.

Silver with 99.99 % purity was made into a cylindrical bar of diameter: Φ : 6 mm and molded with epoxy in glassy to form the cross-sectional area of electrodes in contact with properly distilled water of the electrodes and suitable for the anode and cathode of the glass flask to ensure tightness for water in bottom and air in top. The distance between the two electrodes is 500 mm.

Waters distilled twice and once with the respective electrical conductivity: 1.4 μS and 3.4 μS , respectively, were used as solvents for carrying out high-voltage electrochemical reactions.

Parameters of the reaction processes are: high voltage, current, time, power consumption, weight loss of anode, temperature variation of distilled water and cooling water.

The characteristics of the reaction product were investigated using UV-Vis spectra by UH 5300, Japanese Hitachi, at Institute of Environmental Technology, VAST; conductivity by Multi-Range Conductivity Meter: HANNA HI 8733. Singapore; TEM imaging with JEOL JEMOL equipment, Japan at Pasteur Institute; particle size distribution by Horiba, Laser Scattering Particle Distribution Analyzer LA-950V2, Japan at Institute of Chemistry and Materials; and zeta potentials using a mobile device with Zetasizer-Nano ZS from Malvern - UK at the Institute of Materials Science, VAST.



Figure 1. The functions of DC control box.

The concentration of AgPNs was calculated according to Faraday's law and the weight loss of anode, as determined by the AAS with the American Perkinelmer 3300 at the Institute of Chemistry, VAST.

3. RESULTS AND DISCUSSION

3.1. Plasma at anode

Figure 2 shows the reaction time with the difference of current through the electrochemical system (+)Ag / H₂O (distilled water) /Ag(-) using the high voltage stabilized voltage.

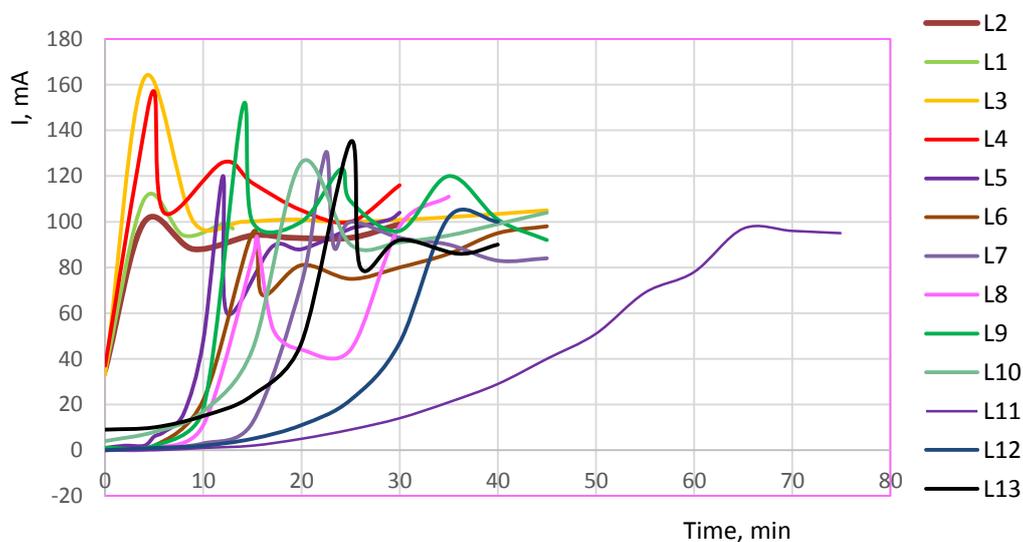


Figure 2. The dependence of current on the reaction time at silver electrodes by stabilized values of high voltage.

From Figure 2 it can be seen that by high constant voltage the reaction current increases through the electrochemical reaction reflects on three-stage: initial rise slowly, then jump to high value and oscillate with high value as time goes on. By close monitoring and video inspection can be seen at the value of the soaring line will appear anodic plasma. The time of occurrence of the plasma at the anode depends on the reaction parameters such as: electrode diameter, DC potential and conductivity of distilled water. Figure 3 shows the color changes of distilled water in the reaction flask and the appearance of plasma at anode. In the early time when there was no gas on the electrode, the reaction vessel had a clear color of distilled water (Figure 3a). Gas occurred in the form of tiny bubbles dispersed into distilled water and transferred up to the anode, the water color of the reactor flask turned white silver of the dispersed bubbles. By the time of the yellowish appearance of the anodized plasma, the aqueous solution near the anode begun to turn yellowish (Figure 3b) of AgPNs. From the time of the appearance of the plasma at anode, the coloring solution spread to the cathode and the color of the solution became darker (Figure 3c). The longer the retention time of plasma at anode is, the darker the color of the AgPNs, and the greater the width of the AgPNs formed zone (Figure 3d) in the top-down direction. This is in contrast to the process of generating high-voltage AgPNs without anodic plasma [14].

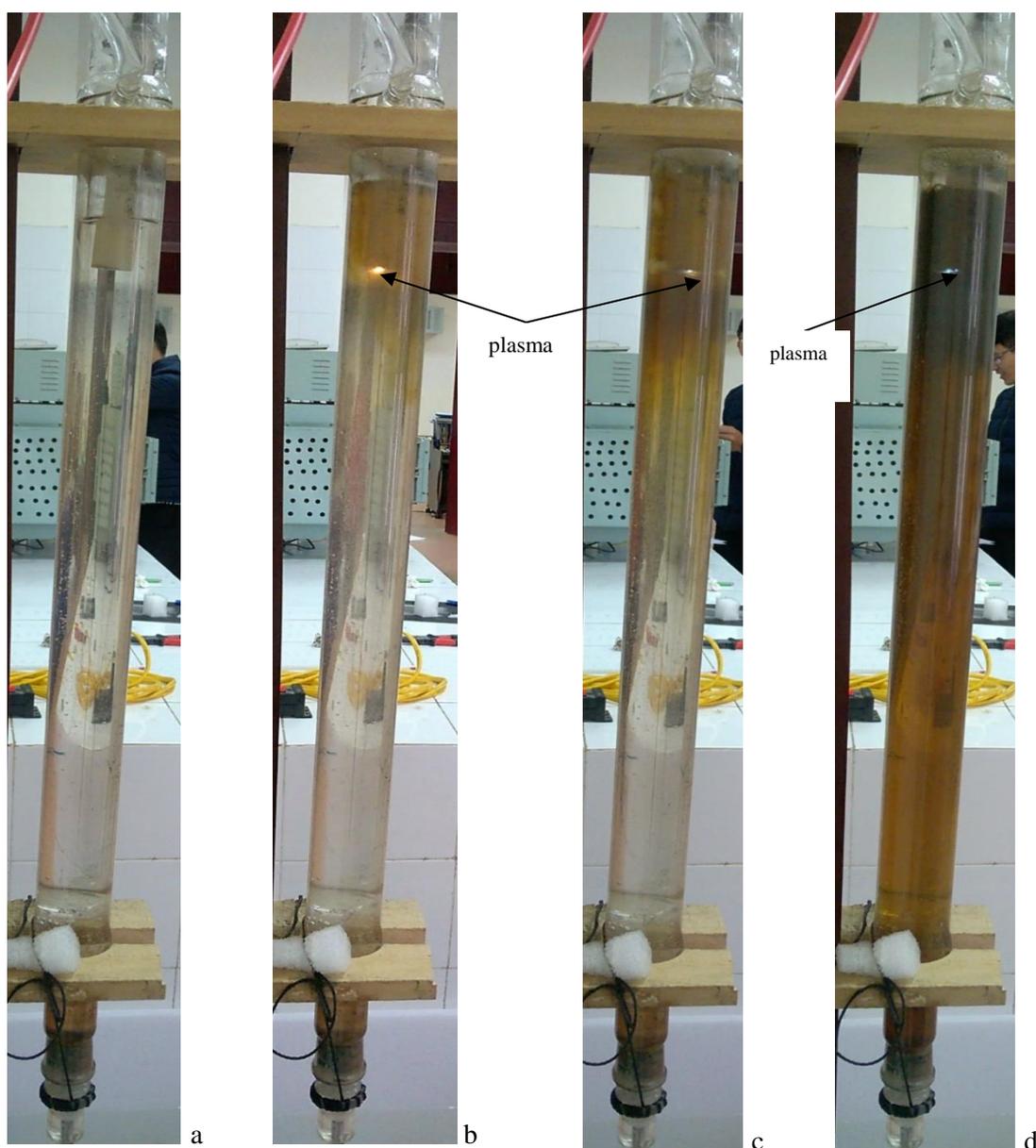


Figure 3. Video image from the color change of reaction flask and the formation of the plasma at anode (b, c, d).

Figure 4 shows the color of AgPNs solutions prepared under different conditions at different anodic plasma time from 13 min to 75 min in comparison with M7 prepared by chemical way.

Figure 4 indicates that the color difference of AgPNs solutions prepared under different conditions would be related to the concentration as well as the particle size of AgPNs similarly to what reported in the literature [11, 12].



M1: 3,2 min M2: 15.3 min M3: 2.4 min M4: 14.3 min M5: 67.2 min M6: 40 min M7: Chem.
Figure 4. Color of AgPNs solutions at different reaction conditions: M1. coal black, M2. brown black, M3. gray black, M4. dark black, M5. brown, M6. dark brown, M7. light brown.

3.2. UV-Vis spectra

Figure 5. depicts UV-Vis spectrum of AgPNs products prepared at different anodic plasma conditions.

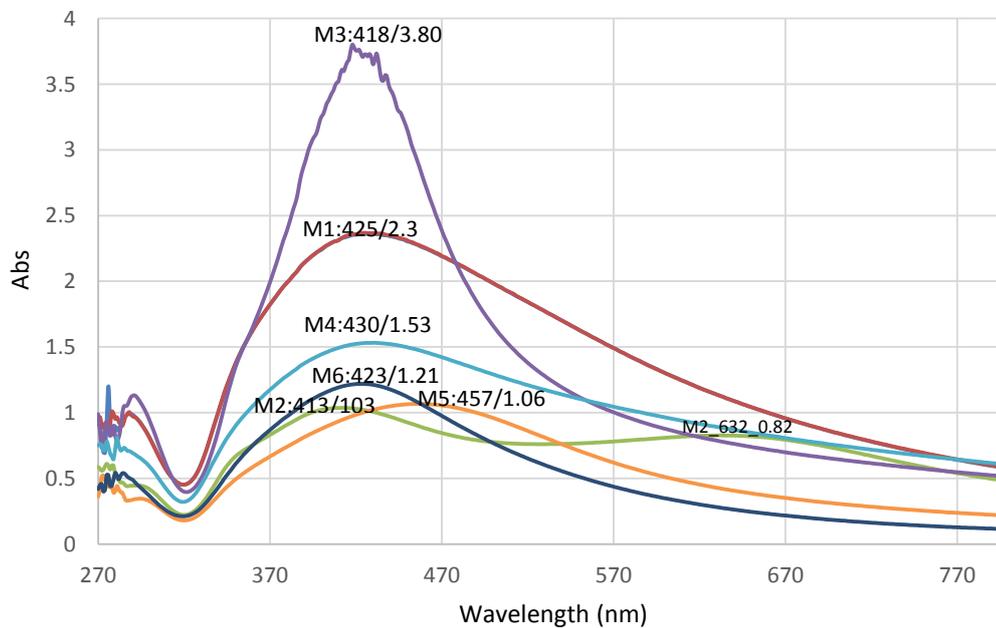


Figure 5. UV-Vis spectrum of AgPNs products prepared at different anodic plasma time during:
M1: 3.22 min, M2: 15.3 min, M3: 2.36 min, M4: 14.3 min, M5: 67.18 min, M6: 40.0 min.

Table 1 presents the wavelength values λ , typical characteristic for AgPNs and the absorption spectrum height at different reaction conditions.

Table 1. The values of UV-Vis spectra at different reaction conditions.

No.	λ , nm	Abs.	E, kV	I, mA	t, min.	Q, mAh	$C_{\Delta m}$, ppm	$C_{Far.}$, ppm	C_{AAS} , ppm	χ , μS	$t_{plas.}$, min.
M1	425	2.368	10/6	86	30	48	120.40	346.55	84.81	39.30	3.22
M2	413	1.037	10/6	63.91	45	49	243.38	386.29	107.97	23.47	15.30
	632	0.837									
M3	418	3.801	8/5	67.31	45	44	114.46	406.83	172.37	25.80	2.36
M4	430	1.532	10/5	84.33	45	60	340.70	509.74	59.46	29.99	14.30
M5	457	1.067	6/6	37.94	50	75	218.55	318.50	127.32	31.87	67.18
M6	423	1.219	10/10	32.22	40	21	47.60	115.42	36.31	27.15	40.0

From the results in Table 1 it can be seen that, with the appearance time of early anodic plasma, about 2.36 to 3.22 minutes, the UV value λ of the UV-Vis spectrum was less than 430 nm and the time of plasma period was about from 14.3 to 15.3 minutes the λ value would be greater than 430 nm. When the time of plasma appears longer, λ can be as large as 457 nm.

3.3. Size and distribution of AgPNs

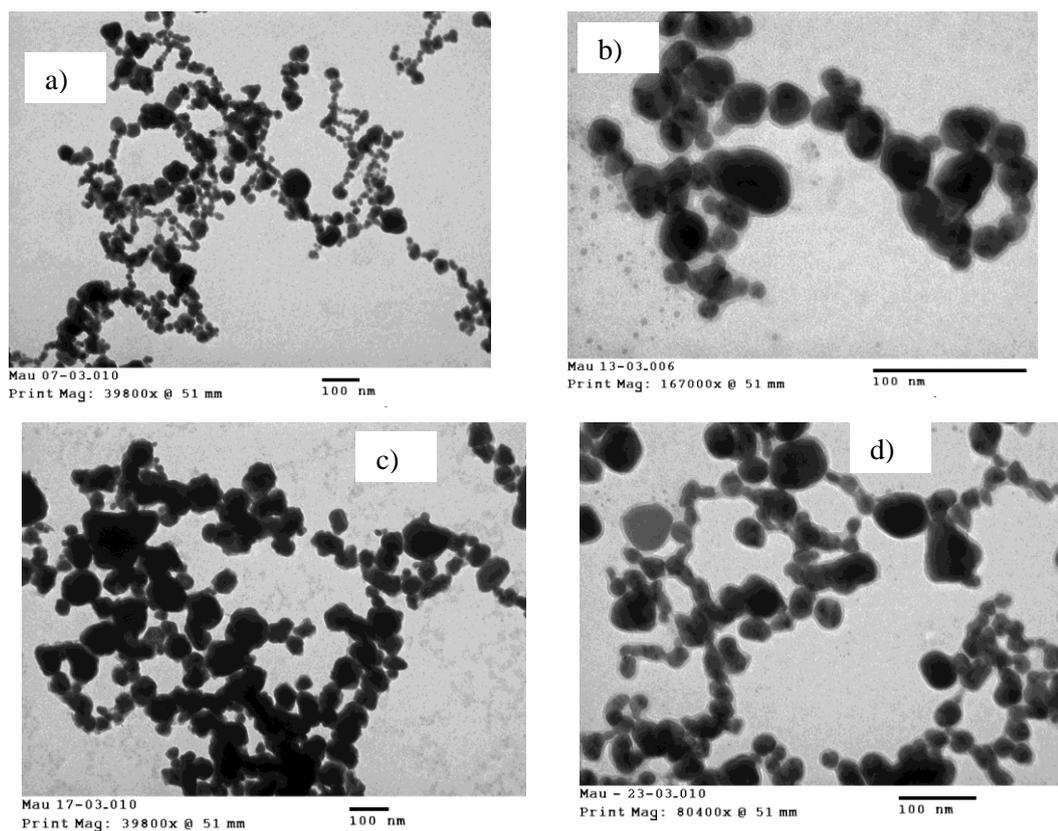


Figure 6. TEM images of AgPNs solutions under different reaction conditions: a. M1, b.M3, c. M5, d. M6.

From Figure 6 it can be seen that all AgPNs are spherical or near spherical with diameter smaller than 100 nm, but the size is not distributed evenly and sticky.

Figure 7 presents the granular size distribution patterns of AgPNs solutions prepared under different conditions.

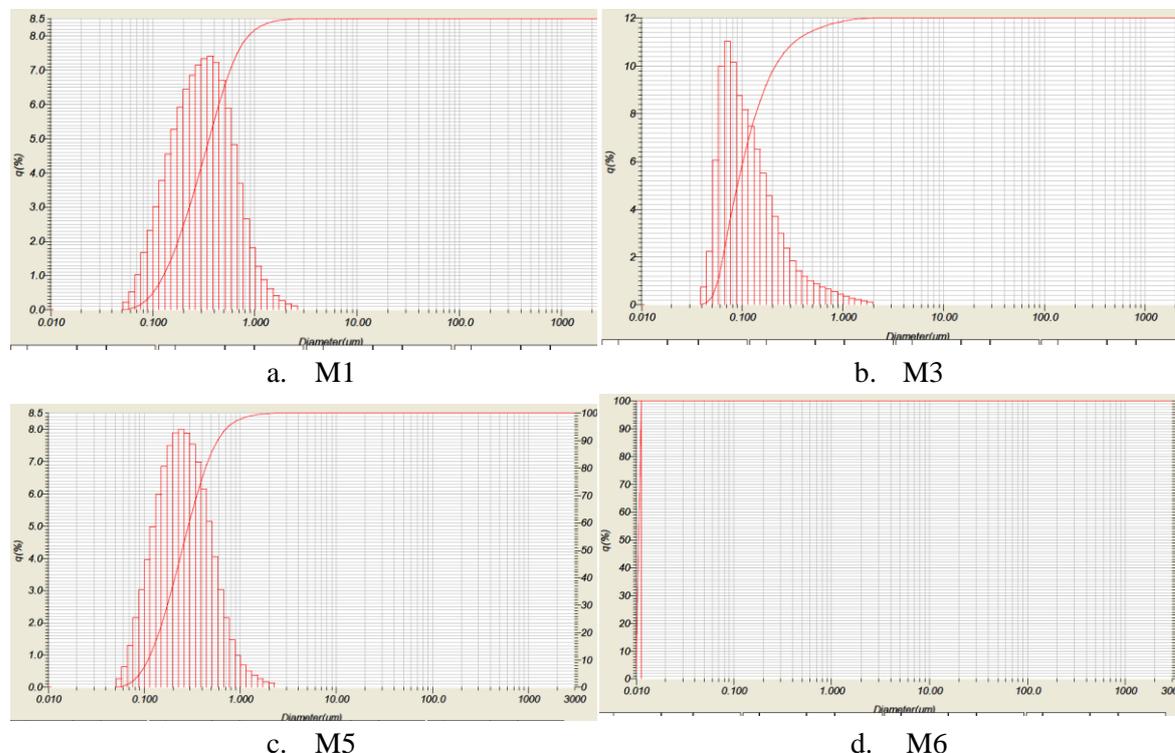


Figure 7. The grain size distribution of AgPNs solutions at different reaction conditions: a. M1, b. M3, c. M5, d. M6.

Table 2 presents the results of determining the particle size distribution from Figure 7. Results from Table 2 show that the average AgPNs size of the high-voltage electrochemical method with plasma at anodes ranging from 11 nm to 376 nm varied widely across AgPNs prepared by chemical methods with average value of 62 nm. AgPNs, which can be formed with the size of 11 nm from sample M6 through the appearance of the delayed anodic plasma are smaller than those prepared by chemical methods.

Table 2. Ratios of different grain sizes in nm under different reaction conditions.

Date	Sample	10 %	50 %	90 %	Average	Geo. Average
07/03	M1	> 0.119	> 0.303	> 0.717	0.303	0.230
13/03	M2	> 0.134	> 0.371	> 0.817	0.376	0.351
14/03	M3	> 0.059	> 0.102	> 0.293	0.102	0.118
15/03	M4	> 0.103	> 0.214	> 0.456	0.214	0.217
17/03	M5	> 0.109	> 0.248	> 0.579	0.248	0.252
23/03	M6	> 0.010	> 0.011	> 0.011	0.011	0.011
	Chemical	> 0.043	> 0.062	> 0.108	0.062	0.065

3.4. Zeta potentials

The results of zeta potential measurements of AgPNs solutions prepared under various conditions are shown in Figure 8.

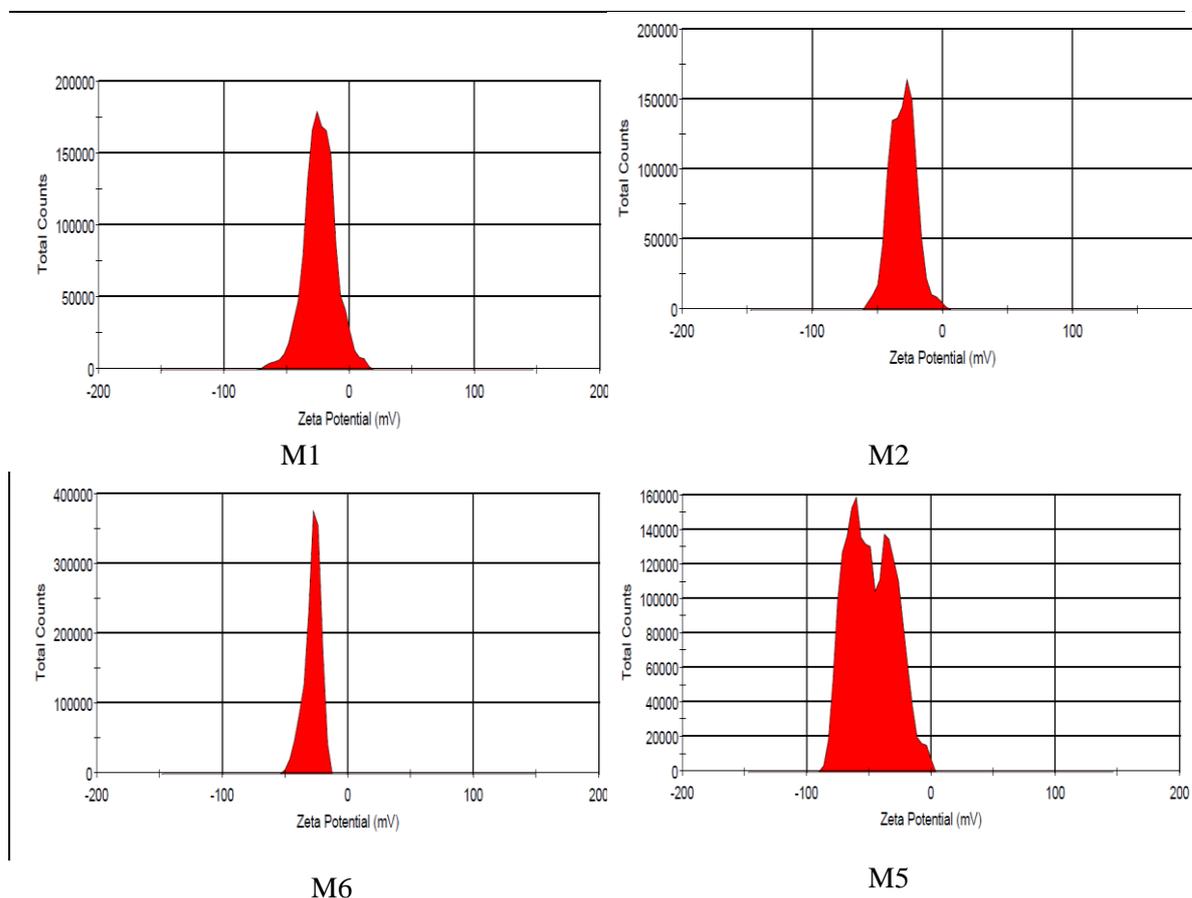


Figure 8. Distribution of colloidal particles and the zeta potential of the nanosilver solutions at different reaction conditions: a. M1, b.M3, c. M5, d. M6.

From Figure 8, it can be seen that the distribution of silver colloidal silver is modulated by high voltage DC current with negative value and quite concentrated with 1 peak. In the case of the long anodic plasma, there are two peaks.

Table 3. Zeta potential value, area and width of the high voltage electrodeposited AgPNs.

Sample	Potential of peak, mV	Area, %	Width of peak, mV	Conductivity, ms/cm
M1	- 23.5	100	12.50	0.0324
M2	- 30.6	100	9.93	0.0282
M3	- 28.2	100	12.40	0.0294
M5	- 61.4	56.5	10.10	0.0274
	- 30.8	43.5	10.20	
M6	- 28.2	100	6.51	0.0183

Table 3 presents the values of the peaks of zeta potentials, the area such as the amplitude of zeta potentials from the AgPNs glue layer, which is modulated by high voltage DC current. The magnitude of the zeta potentials value from -23.5 mV to -61.4 mV indicates that the glue system in the region is relatively stable even in the absence of a stabilizer. The peak intensity of the peaks from 6.51 mV to 10.2 mV indicates that the size of the glue particles is fluctuated too.

3.5. Concentration of AgPNs

The concentration of AgPNs is determined and calculated according to different methods such as the weight loss of anode, according to Faraday's law and analysing per AAS. The results are presented in Table 4. From the results in Table 4, we can see that the trend of AgPNs change from three different methods is the same. However, AgPNs concentration values of the same sample were determined in three different ways, but in the order of:

$$c_{\text{Far.}} > c_{\Delta\text{m}} > c_{\text{AAS}}$$

Table 4. Concentrations of AgPNs determined by the weight loss, Faraday's law calculation and AAS analysis.

Date	Sample	$c_{\Delta\text{m}}$	$c_{\text{Far.}}$	c_{AAS}	$c_{\text{Far.}}/c_{\Delta\text{m}}$	$c_{\Delta\text{m}}/c_{\text{AAS}}$
07/03	M1	120.40	346.55	84.81	2.88	1.42
13/03	M2	243.38	386.29	107.97	1.59	2.25
14/03	M3	172.37	406.83	114.46	2.36	1.55
15/03	M4	340.70	509.74	59.46	1.50	5.72
17/03	M5	218.55	318.50	98.21	1.46	2.23
23/03	M6	47.60	115.42	36.31	2.42	1.31

That's due to the following reasons: the concentration $c_{\text{Far.}}$ calculated according to Faraday's Law from the real anode current, it also includes the electric current of the electrolyse of water and the anodic plasma, which results in the greatest value. The concentration $c_{\Delta\text{m}}$ determined from weight loss of dissolved anode is usually smaller than $c_{\text{Far.}}$ from 1.46 to 2.88 times. The greater the difference, the greater the current for electrolysis of water and for anodic plasma in the dissolved anode. The concentration c_{AAS} obtained from the AAS analysis is the smallest as the result of the formation of AgPNs that is attached to the device wall of flask so that the amount in solution is less than that of the dissolved silver electrode.

4. CONCLUSION

At high DC voltage after the electrochemical reaction in distilled water, the plasma at the silver anode appears at different times depending on the voltage value. The intensity of the electrochemical reaction increases with time initially, and when the plasma appears on the anode, it fluctuates and is unstable due to the amount of gas formed and released on the strong electrodes.

The generation of AgPNs from electrolytic dissolved silver at the anode and hydrogen atom discharged from the cathode and from the plasma was detected by the color change of the reaction solution. Characteristics of the AgPNs solution prepared by high-voltage electrolysis combined with anodic plasma have UV-Vis spectrophotometer range from 413 nm to 457 nm

depending on the size and concentration of AgPNs. AgPNs particles are, by SEM imaging, spheres with size less than 100 nm, but due to clustering, the size distribution is only 10% below 100 nm and the average value ranging from 11 nm to more than 300 nm. The zeta potentials of AgPNs prepared by high voltage method combined with anodic plasma values was from -23.5 mV to -61.4 mV, indicating that durable glue does not need to use stabilizer.

The concentrations of AgPNs can be determined by three methods: calculated according to Faraday' law ($c_{\text{Far.}}$), weight loss of silver anode ($c_{\Delta m}$) and AAS analyse (c_{AAS}). Because the anode current includes both the current from water electrolyse and from anodic plasma, the concentration $c_{\text{Far.}}$ from calculations were the largest, while the concentration from the AAS analysis did not include AgPNs that were stucked to the reactor wall and the containers would have the smallest value.

Acknowledgments: This research is funded by VAST under grant number VAST.SXTN.03/16-17.

REFERENCES

1. Natalia L. Pacioni, Claudio D. Borsarelli, Valentina Rey and Alicia V. Veglia - Synthetic Routes for the Preparation of Silver Nanoparticles, in E.I. Alarcon et al. (eds.), *Silver Nanoparticle Applications*, Engineering Materials, Springer International Publishing, Switzerland, 2015.
2. Guangyu Zhang, Yan Liu, Xiaoliang Gao and Yuyue Chen - Synthesis of silver nanoparticles and antibacterial property of silk fabrics treated by silver nanoparticles, *Nanoscale Research Letters* **9** (2014) 216.
3. Lei Wang, Chong-Chong Liu, Yi-Yan Wang, Hui Xu, Hongyan Su, Xianhao Cheng - Antibacterial activities of the novel silver nanoparticles biosynthesized using *Cordyceps militaris* extract, *Current Applied Physics* **16** (2016) 969-973.
4. Sadhan Kumar Chaudhuri, Shivani Chandela, Lalit Malodia - Plant Mediated Green Synthesis of Silver Nanoparticles Using *Tecomella undulata* Leaf Extract and Their Characterization, *Nano Biomed En.* **8** (1) (2016) 1-8.
5. Kholoud M. M. Abou El-Nour, Ala'a Eftaiha, Abdulrhman Al-Warthan, Reda A. A. Ammar - Synthesis and applications of silver nanoparticles, *Arabian Journal of Chemistry* **3** (2010) 135-140.
6. Dang Van Phu, Bui Duy Du, Nguyen Ngoc Duy, Nguyen Tue Anh, Nguyen Thi Kim Lan, Vo Thi Kim Lang, Nguyen Quoc Hien - The effect of pH and molecular weight of chitosan on silver nanoparticles synthesized by γ -irradiation, *Vietnam Journal of Science and Technology* **47** (6) (2009) 47-52 (in Vietnamese).
7. Nicoleta Dobre, Aurora Petică, Mihai Buda, Liana Anicăi, Teodor Vișan - Electrochemical synthesis of silver nanoparticles in aqueous electrolytes, *U.P.B. Sci. Bull., Series B* **76** (4) (2014) 127-136.
8. Rodríguez-Sánchez L., Blanco M. C., and López-Quintela M. A., Rodríguez-Sánchez L., - Electrochemical Synthesis of Silver Nanoparticles, *J. Phys. Chem., B.* **104** (2000) 9683-9688.
9. Virginia Roldán M., Nora Pellegrini, and Oscar de Sanctis. - Electrochemical Method for Ag-PEG Nanoparticles Synthesis, *Journal of Nanoparticles* **2013**, ID 524150 (2013) 7 pages.

10. Rade Surudžič, Željka Jovanović, Nataša Bibić, Branislav Nikolić and Vesna Mišković-Stanković - Electrochemical synthesis of silver nanoparticles in poly(vinyl alcohol) solution, *J. Serb. Chem. Soc.* **78** (12) (2013) 2087–2098.
UDC 66.091+544.6:546.57:539.12: JSCS–4552.
11. Kuo-Hsiung Tseng, Yu-Chun Chen, Jing-Jong Shyue - Continuous synthesis of colloidal silver nanoparticles by electrochemical discharge in aqueous solutions, *J. Nanopart Res.* (2010) 8.
12. Carolyn Richmonds and R. Mohan Sankaran - Plasma-liquid electrochemistry: Rapid synthesis of colloidal metal nanoparticles by microplasma reduction of aqueous cations, *Applied Physics Letters* **93** 131501 (2008) 1-3.
13. Nguyen Duc Hung, Nguyen Minh Thuy, Mai Van Phuoc, Nguyen Nhi Tru. - Preparation of Nanosilver Colloidal Solution by Anodic Dissolution under High DC Voltage, *Electrochemistry* **81** (6) (2013) 454459, 10 pp.
14. Nguyen Duc Hung, Nguyen Minh Thuy, Nguyen Nhi Tru - Characteristics and mechanism of nanosilver formed by anodic dissolution with DC voltage, *The Eur. Phys. Jour. Appl.*, **63** (2013) 201402 10 pp.
15. Luisa Rodríguez-Sánchez M., José Rodríguez M., Carmen Blanco M., José Rivas, and Arturo López-Quintela M. - Kinetics and Mechanism of the Formation of Ag Nanoparticles by Electrochemical Techniques: A Plasmon and Cluster Time-Resolved Spectroscopic Study, *J. Phys. Chem. B* **109** (3) (2000) 1183–1191.
16. Gulnaz R. Naretdinova, Rezeda R. Fazleeva, Rezeda K. Mukhitova, Irek R. Nizameev, Marsil K. Kadirov, Albina Y. Ziganshina, Vitaliy V. Yanilkin - Electrochemical synthesis of silver nanoparticles in solution, *Electrochemistry Communication* **50** (2015) pp. 69-72.
17. Maria Starowicz, Barbara Stypuła, Jacek Banas - Electrochemical synthesis of silver nanoparticles, *Electrochemistry Communications* **8** (2006) 227–230.
18. Lucas Blandón, Mario V. Vázquez, Dora M. Benjumeab and Gelmy Cirob Lucas Blandón, Mario V. Vázquez, Dora M. Benjumeab and Gelmy Cirob - Electrochemical Synthesis of Silver Nanoparticles and their Potential Use as Antimicrobial Agent: a Case Study on Escherichia Coli, *Port. Electrochim. Acta* **30** (2) (2012) 135-154.
19. Rashid A. Khaydarov, Renat R. Khaydarov, Olga Gapurova, Yuri Estrin, Thomas Scheper - Electrochemical method for the synthesis of silver nanoparticles, *J. Nanopart. Res.* **11** (2009) 1193-1200.
20. Yu Toriyabe, Seiichi Watanabe, Shigeo Yatsu, and Tamaki Shibayama, Tadahiko Mizuno - Controlled formation of metallic nanoballs during plasma electrolysis Controlled formation of metallic nanoballs during plasma electrolysis, *Applied Physics Letters* **91** (2007) 1-3.
21. Tadahiko Mizuno, Tadashi Akimoto and Tadayoshi Ohmori - Confirmation of anomalous hydrogen generation by plasma electrolysis, in 4th Meeting of Japan CF Research Society, Iwate, Japan: Iwate University, 2003.