

# Adjusting optical and structural properties of gold nanoparticles produced using direct current atmospheric pressure glow discharge operated in contact with a flowing liquid cathode under helium atmosphere

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**Abstract:** In this work, we show the influence of direct current atmospheric pressure glow discharge (dc-APGD) generated in contact with a flowing liquid cathode (FLC) working under helium atmosphere on the optical and structural properties of gold nanoparticles (AuNPs). Using statistical methods, *i.e.* design of experiments (DoE) followed by the response surface methodology (RSM), the operating conditions of the dc-APGD treatment for the production of size-defined AuNPs was assessed.

**Keywords:** cold atmospheric pressure plasma, nanomaterials, statistical analyses

## 1. Introduction

In recent years, there has been an increasing need for the production and usage of the nanomaterials due to their unique properties that differ compared to the same bulky materials. Among the many different types of nanomaterials, the most promising are the noble metal nanoparticles (NPs).

The popularity of noble metal nanostructures is associated with their wide range of applications including drug delivery systems [1], inactivation of pathogenic bacteria [2,3], and the catalytic decomposition of organic compounds [4]. Up to now, many methods of noble metal NPs synthesis have been developed and effectively improved [5]. These methods include chemical reduction methods [6], green synthesis methods [7], and so on. Alternatives to the above-listed method are the cold atmospheric pressure plasma (CAPP)-based methods, in which the production of inorganic nanostructures is supported by the reactive oxygen and nitrogen species (RONS), along with the hydrated electrons ( $e^-_{aq}$ ) and H radicals, generated during the CAPP operation.

Generally, for the production of noble metal NPs, the CAPP is operated in the stationary mode reaction-discharge systems [8-13]. In these non-flowing reaction-discharge systems, bulky liquids, serving as the NPs precursor solution, work as an anode or cathode [8-13]. Because uncontrolled reactions occur between the CAPP and NPs precursor solution in the above-mentioned stationary reaction-discharge systems, in our research group we have developed a CAPP-based method for the size – controlled synthesis of noble metal nanostructures such as gold nanoparticles (AuNPs) [14-17], silver nanoparticles (AgNPs) [16, 18, 19], platinum nanoparticles (PtNPs) [20], and gold-silver core-shell nanoparticles (Au@AgCSNPs) [16], in a continuous flow reaction-discharge systems [14-20]. In these reaction-discharge systems [14-20], as a source of CAPP we used direct current atmospheric pressure glow discharge (dc-APGD) [14-19] or pulse-modulated radio-frequency atmospheric pressure glow discharge (pm-rf-APGD) [20]. In addition, dc-APGD [14-19] or pm-rf-APGD [20] was operated between the surface of the flowing liquid electrode (FLE) and gaseous jet [14-16] or pin-type metallic electrode [17-

20]. The above-mentioned reaction-discharge systems provide a better control and safety over the course of the synthesis process as well as a better quality of the produced nanomaterials. In this case, the penetration of the surface of the FLE, containing NPs precursor solution, by RONS, hydrated electrons ( $e^-_{aq}$ ) and H radicals was highly reproducible.

Here, we have tailored the optical and structural properties of AuNPs obtained using the CAPP-based continuous flow synthesis reaction-discharge system developed in our research group. In addition, we have used statistical methods, *i.e.* the design of experiments (DoE) followed by the response surface methodology (RSM), to estimate the operating conditions under which the smallest AuNPs would be produced.

## 2. Materials and Methods

As a AuNPs precursor stock solution, a chloroauric acid tetrahydrate solution ( $\text{HAuCl}_4 \times 4\text{H}_2\text{O}$ , Avantor Performance Materials, Poland) of Au(III) ions at a concentration of  $1000 \text{ mg L}^{-1}$  was prepared as follow.  $0.05227 \text{ g}$  of  $\text{HAuCl}_4 \times 4\text{H}_2\text{O}$  was dissolved in  $250.00 \text{ mL}$  of re-distilled water in a volumetric flask. In order to obtain the diluted AuNPs precursor solution, the resultant stock solution was diluted 100, 9.52, and 5 times, to obtain solutions of 10, 105, and  $200 \text{ mg L}^{-1}$  of Au(III) ions. As a stabilizer, gelatine from bovine skin Type B (Sigma-Aldrich, Germany) was present in each of prepared solutions at a final concentration of 0.5 % (m/v).

To obtain the size-controlled gelatine-stabilized AuNPs, we used our existing dc-APGD-based reaction-discharge system (Fig. 1) [14-16]. Briefly, in the above-mentioned system, the dc-APGD was generated between the two electrodes. One of the electrodes was a gaseous jet (helium), while the other was a flowing liquid cathode (FLC) consisting of a AuNPs precursor solution enriched with gelatine. High-purity helium (99.999% He, Linde, Poland) was applied as a gaseous microjet. The flow rate of the proper discharge gas, in the range from 120 to 300 sccm (standard cubic centimeters per minute) was regulated by a Tylan General FC-2900 and RO-28 mass flow controller (MFC). The noble metal nanostructures precursor solution was introduced to the reaction-discharge

system at a flow rate in the range from 2.0 to 6.0 mL min<sup>-1</sup> using a Masterflex L/S peristaltic pump (Cole-Parmer, UK). A dc-HV generator (Dora Electronic Equipment, Poland) was used for applying a voltage of 1,100-1,500 V and discharge current in the range from 15 to 45 mA. Moreover, a 10 k $\Omega$  ballast resistor (Tyco, USA) was applied to stabilize the discharge current.

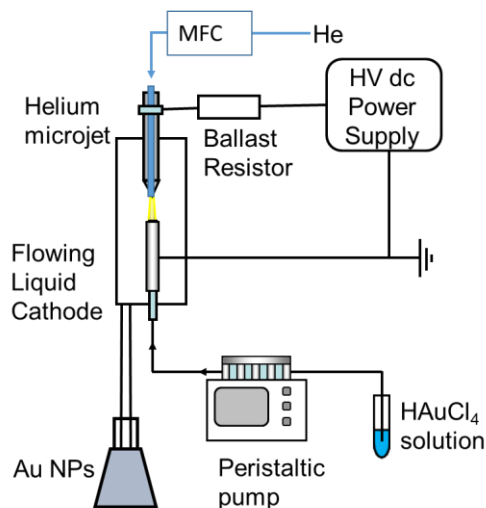


Fig. 1. The dc-APGD reaction-discharge system applied for the continuous synthesis of AuNPs.

Minitab 17 statistical software for Windows 7 was applied to find the optimal operating conditions under which the smallest AuNPs would be produced. The statistical analyses were performed based on the usage of the design of experiments (DoE) along with response surface methodology (RSM). For that reason, a Box-Behnken design (BBD) consisting of 3 central points and 27 randomized runs was created (see Table 1).

Based on the proposed BBD matrix, it was possible to examine not only the impact of one factor at time (OFAT) but the influence of 4 operating factors (*i.e.* concentration of Au(III) ions in the reaction mixture, the flow rate of the solution, the discharge current, and the flow rate of the helium discharge gas) on the localization of the  $\lambda_{\max}$  of the localized surface plasmon resonance (LSPR) absorption band in the UV/Vis absorption spectrum. The presence of the above-mentioned LSPR absorption band in the UV/Vis absorption spectra is related to Mie's light scattering theory [21]. For AuNPs, the LSPR absorption band typically occurs in the range from 520 to 570 nm [22]. For that reason, the dc-APGD treated solutions were gathered for further analyses including estimation of optical and structural properties of AuNPs produced under helium dc-APGD discharge atmosphere.

The UV/Vis absorption spectrophotometry (UV/Vis) was employed to reveal the optical properties of the resultant Au nanostructures formed under defined operating conditions (Table 1). To reach this goal, an Analytik Jena (Jena AG, Germany) spectrophotometer was

used. The UV/Vis absorption spectra were acquired in the range from 250-900 nm.

Table 1. BBD matrix with the levels of the examined factors. The parameters are named as follow: A: flow rate of the FLC (mL min<sup>-1</sup>), B: the concentration of the Au(III) ions in the AuNPs precursor solution (in mg L<sup>-1</sup>), C: the discharge current (in mA), and D: flow rate of the helium discharge gas (in sccm). The response is  $\lambda_{\max}$  of the localized surface plasmon resonance (LSPR) absorption band (in nm).

Run order	A	B	C	D	Response
1	4	105	30	210	541.0
2	4	105	45	120	535.0
3	4	10	30	300	524.0
4	4	105	30	210	537.5
5	6	200	30	210	547.5
6	4	10	45	210	527.0
7	6	105	30	120	545.5
8	2	10	30	210	534.0
9	6	105	30	300	544.5
10	4	105	45	300	536.0
11	6	10	30	210	510.5
12	2	105	15	210	541.5
13	4	105	15	120	557.0
14	4	200	15	210	540.0
15	6	105	15	210	556.5
16	2	105	30	120	536.5
17	2	200	30	210	537.7
18	4	10	15	210	535.0
19	4	10	30	120	530.5
20	4	200	30	120	542.0
21	4	200	30	300	537.0
22	6	105	45	210	535.0
23	4	105	30	210	535.0
24	4	105	15	300	542.0
25	2	105	30	300	537.0
26	2	105	45	210	537.0
27	4	200	45	210	540.0

The structural properties of AuNPs obtained under the optimal conditions in relation to the NPs size and shape were estimated by applying scanning electron microscopy (SEM). A Jeol JSM-6610LVnx instrument (JEOL USA, USA) was used to fulfil this need. To carry out the SEM measurements, one drop of AuNPs obtained under optimal operating conditions was placed on a carbon sticky tape and put on the stainless holder. Next, the so holder was introduced to the SEM chamber and evaporated under vacuum conditions. The pressure in the SEM chamber was changed in the range from 10 to 270 Pa, and the SEM micrographs were acquired at different magnifications.

### 3. Results and Discussion

It was found that after passing the AuNPs precursor solution through the dc-APGD reaction-discharge system working under helium atmosphere, the colloidal suspensions of AuNPs were produced in all of the examined experimental conditions (Table 1). These observations were based on the change in colour of the reaction mixture, *i.e.* from yellowish, characteristic for the AuNPs precursor solution, to ruby-red, associated with the formation of the AuNPs [14]. For that reason, the optical properties for all of the collected solutions were analyzed using UV/Vis absorption spectrophotometry.

The DoE and RSM was used to analyze the BBD matrix in order to find the settings of the reaction-discharge system that would result in the production of the smallest AuNPs obtained under helium atmosphere. Four experimental factors such as flow rate of the FLC (A), the concentration of the Au(III) ions in the reaction mixture (B), discharge current (C), and the flow rate of helium discharge gas (D) were selected as the main parameters that might impact the optical and structural properties of AuNPs. Based on the performed measurements, the following statistical model was calculated:

$$\lambda_{\max\text{LSPR}} = 567.7 + 0.31A + 0.0561B - 1.144C - 0.113D - 0.000754B^2 + 0.01241C^2 + 0.0438AB - 0.1417AC + 0.00296CD$$

According to the proposed statistical model, the concentration of the Au(III) ions, the flow rate of the FLC, and the discharge current were suggested as statistically significant parameters with p-values lower than 0.05. The flow rate of the helium discharge gas had no impact on the position of the  $\lambda_{\max}$  of the LSPR absorption band. The  $R^2$  value was 83.94%, showing that more than 83% of the variation of the  $\lambda_{\max}$  of the LSPR absorption band could be explained by the developed regression model. The adjusted and predicted  $R^2$  values were acceptably high, *i.e.* 75.43% and 49.75%, respectively.

Based on the suggested model, the optimal operating conditions for producing the smallest AuNPs colloidal suspension with the lowest position of the  $\lambda_{\max}$  of the LSPR absorption band (optical properties) was determined. To synthesize the smallest gelatine-stabilized AuNPs of the  $\lambda_{\max}$  of the LSPR absorption band of 530.5 nm, the following conditions should be maintained: the flow rate of the FLC: 6.0 mL min<sup>-1</sup>, the concentration of the Au(III) ions in AuNPs precursor solution: 10 mg L<sup>-1</sup>, and the discharge current: 45 mA.

The adequacy of the proposed statistical model was confirmed by performing AuNPs synthesis under defined operating conditions. Five independent experiments were made and dc-APGD treated solutions containing AuNPs produced in these conditions were analyzed by UV/Vis absorption spectrophotometry. Consequently, it was determined that the  $\lambda_{\max}$  of the LSPR absorption band of the obtained GEL-AuNPs was 531.0 ± 2.5 nm. As this result corresponded well with the predicted value, it was

concluded that the model was able to accurately predict the  $\lambda_{\max}$  of the LSPR absorption band.

Fig. 2 shows the morphology of AuNPs produced under the optimal operating conditions. As can be seen from Fig. 2, the synthesized AuNPs were mostly spherical in shape, with visible grain boundaries, and they were non-aggregated. The excellent stabilizing properties of GEL might be associated with its molecular weight >10<sup>4</sup> g mol<sup>-1</sup>, which provide steric stabilization associated with the spatial dimension of the molecular compounds commensurable with the range of the London's forces of attraction or even exceed them [23].

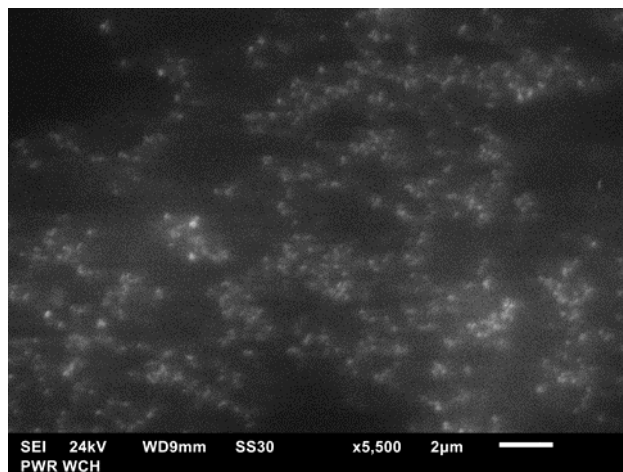


Fig. 2. Representative SEM photomicrograph of AuNPs obtained under optimal operating conditions of dc-APGD-based reaction-discharge system, working under helium atmosphere.

### 4. Conclusions

In this work, it was found that the use of a dc-APGD-based continuous-flow reaction-discharge system, working under helium atmosphere, can be successfully applied in the production of AuNPs. By changing the operating parameters such as flow rate of the FLC, concentration of the Au(III) ions in the reaction mixture, and the discharge current, it is possible to control the optical and structural properties of the synthesized Au nanostructures. We believe that the proposed method for NPs synthesis will be widely applied in many field of knowledge including medicine, catalysis, and cosmetology.

### 5. References

- [1] M. Rai, A. P. Ingle, I. Gupta, A. Brandelli, International journal of pharmaceutics, **496**, 159 (2015).
- [2] Q. H. Tran, A. T. Le, Advances in Natural Sciences: Nanoscience and Nanotechnology, **4**, 033001 (2013).
- [3] W. C. Huang, P. J. Tsai, Y. C. Chen, Future Medicine, **2**, 6 (2007).
- [4] P. Cyganowski, A. Lesniewicz, A. Dzimitrowicz, J. Wolska, P. Pohl, D. Jermakowicz-Bartkowiak, Journal of Colloid and Interface Science, **541**, 226 (2019).

- [5] K. Alagad, T. A. Saleh, *Journal of Environmental and Analytical Toxicology*, **6**, 4 (2016).
- [6] S. Eustis, M. A. El-Sayed, *Chemical Society Reviews*, **35**, 209 (2006).
- [7] V. Kumar, S. K. Yadav, *Journal of Chemical Technology and Biotechnology*, **84**, 151 (2009).
- [8] Q. Chen, T. Kaneko, R. Hatakeyama, *Chemical Physics Letters*, **521**, 113 (2012).
- [9] D. Mariotti, J. Patel, V. Svrcek, P. Maguire, *Plasma Processes and Polymers*, **9**, 1074 (2012).
- [10] C. Richmonds, R. M. Sankaran, *Applied Physics Letters A*, **93**, 131501 (2008).
- [11] J. Patel, L. Nemcova, P. Maguire, W. G. Graham, D. Mariotti, *Nanotechnology*, **24**, 245604 (2013).
- [12] N. Shirai, S. Uchida, F. Tochikubo, *Japanese Journal of Applied Physics*, **53**, 046202 (2014).
- [13] W. H. Chiang, C. Richmonds, R. M. Sankaran, *Plasma Sources Science and Technology*, **19**, 034011 (2010).
- [14] A. Dzimitrowicz, P. Jamroz, K. Greda, P. Nowak, M. Nyk, P. Pohl, *Journal of Nanoparticle Research*, **17**, 185 (2015).
- [15] A. Dzimitrowicz, T. Lesniewicz, K. Greda, P. Jamroz, M. Nyk, P. Pohl, *RSC Advances*, **5**, 90534 (2015).
- [16] A. Dzimitrowicz, P. Jamroz, M. Nyk, P. Pohl, *Materials*, **9**, 268 (2016).
- [17] A. Dzimitrowicz, K. Greda, T. Lesniewicz, P. Jamroz, M. Nyk, P. Pohl, *RSC Advances*, **6**, 80773 (2016).
- [18] A. Dzimitrowicz, P. Jamroz, D. Pogoda, M. Nyk, P. Pohl, *Plasma Processes and Polymers*, **14**, e1600251 (2017).
- [19] A. Dzimitrowicz, A. Bielawska-Pohl, G. C. diCenzo, P. Jamroz, J. Macioszczyk, A. Klimczak, P. Pohl, *Nanomaterials*, **8**, 398 (2018).
- [20] A. Dzimitrowicz, P. Cyganowski, P. Pohl, D. Jermakowicz-Bartkowiak, D. Terefinko, P. Jamroz, *Nanomaterials*, **8**, 619 (2018).
- [21] G. Mie, *Annals of Physics*, **25**, 377 (1908).
- [22] N. B. Pal, C. Kryschi, *Physical Chemistry Chemical Physics*, **17**, 21423 (2015).
- [23] A. D. Pomogailo, V. N. Kestelman. *Metallopolymer Nanocomposites*. Springer, New York, USA (2005).

## 6. Acknowledgements

This work was supported by the statutory activity subsidy from the Polish Ministry of Science and Higher Education for the Faculty of Chemistry of Wrocław University of Science and Technology and by the National Science Centre, Poland (UMO-2015/17/N/ST4/03804). Anna Dzimitrowicz is supported by the Foundation for Polish Science (FNP), program START 022.2018. Authors would like to thank M.Sc. Urszula Jablonska for technical support and to Dr. George diCenzo for proofreading the article.