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CAPPING AGENT-FREE AQUEOUS GOLD NANOPARTICLES GENERATED BY AN ENVIRONMENTALLY FRIENDLY PLASMA-LIQUID METHOD

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This study investigates a simple approach for synthesizing gold nanoparticles (Au NPs) using atmospheric pressure plasma without the need for reducing agents, additives, or capping agents. The size, morphology, optical properties, and aggregation stability of the synthesized Au NPs were characterized using scanning electron microscopy, UV-vis spectroscopy, and zeta potential analysis. The UV-vis absorption spectra of the gold nanoparticles, obtained at various Au^{3+} concentrations and treatment durations with anode plasma discharge, were analyzed. The UV-vis spectra revealed a surface plasmon resonance absorption band between 530−600 nm, indicative of Au NP formation. Results demonstrated that the size of Au NPs can be tuned within the range of 30−75 nm by adjusting the gold salt precursor concentration from 0.3 to 2.5 mmol/L. It was found that plasma treatment for 3−10 minutes, at different Au^{3+} concentrations, resulted in the formation of Au NPs with varying sizes and morphologies. The study showed that particles with different shapes − spherical, hexagonal, and triangular − were formed depending on the initial concentration of Au^{3+}. The plasma-chemically synthesized nanoparticles at an Au^{3+} concentration of 0.06 mmol/L were predominantly spherical and exhibited the highest stability (lasting 12−24 hours), with a zeta potential of −20 to −22 mV, compared to samples with Au^{3+} concentrations ranging from 0.3 to 2.5 mmol/L.

Keywords: gold, nanoparticles, discharged anode plasma, average size, different shapes, stability.

Introduction

Nanomaterials of various structural organizations are among the most researched materials in the modern world due to their unique combination of physicochemical characteristics and prospects for comprehensive practical application. A separate category among nanomaterials consists of nanoparticles (NPs) of noble metals (gold and silver NPs), which, as a rule, are obtained in the form of dispersions of nanoparticles [1,2]. Noble metal nanoparticles are used in a variety of sectors due to their unique qualities and exceptional properties, including photosensitivity, catalysis, photoelectronics, and information storage. Among noble metals, the global gold nanoparticles market revenue was 6,641.1 million USD in 2022 and is expected to grow at a compound annual growth rate of 22.3% from 2023 to 2030 [3]. Analysts predict that the market for the manufacturing and commercialization of nanogold will expand dramatically by 2030 as metal nanoparticles of gold are increasingly used in medicine [2−4]. One of the requirements of the medical field of application of gold nanoparticles is the minimization of the components in the obtained nanoparticle dispersions, namely reducers, stabilizers, and other impurities that regulate the functionality of nanoparticles [4]. Despite the development of numerous methods, producing high-quality metallic nanoparticles with controllable features in a simple, cost-effective, and environmentally friendly manner remains a challenge [5,6]. Thus, the research, development, and improvement of synthesis methods, that minimize

the use of reducing reagents and eliminate the requirement for the selection of «reducing/stabilizing» reagent combinations for the controlled synthesis of stable dispersions of gold nanoparticles, are particularly relevant in view of the predictions of an increase in the practical consumption of gold nanoparticles in the medical field [4−6].

In the synthesis and surface engineering of nanomaterials, nonequilibrium air pressure plasma and the interaction phase of plasma and liquid have proven to be incredibly effective [7,8]. A considerable number of articles indicate that when interacting with water, a high density of gas-phase plasma electrons becomes solvated in the liquid, resulting in a fast chain reaction of transient nonlinear chemical processes and extremely reactive radicals. Solvated electrons and/or reactive species successfully take part in creating different nanomaterials such as monoparticle Au NPs, Ag NPs, and alloy NPs such as Au_xAg_{1-x} in aqueous solutions [7−11]. Despite the results of basic and practical research on plasma discharges that are already available, the conditions of their creation and application vary according to a large number of criteria, which are known to have a substantial impact on the traits and features of the produced nanosystems.

The atmospheric anodic type of plasma is one of the plasma discharge forms that can formed over a liquid [7−11]. In previous studies [12−14], we have demonstrated the effectiveness of this type of plasma discharge for the synthesis of silver nanodispersions both without a stabilizer and with the use of various types of ionic/non-ionic stabilizers. It was shown that the presence of stabilizers of different types, as well as the variation of technological parameters such as initial precursor concentration, the amount of stabilizer (precursor/capping agent ratio), and the duration of nanoparticle synthesis, allow controlling the dimensional parameters and properties of nanoparticles in dispersions [14].

The work objective is to study the usage of anode-type plasma discharge to obtain colloidal solutions of gold nanoparticles without using any reducing, additives, or capping agents.

Materials and methods

A one-pot plasma technique was used for the immediate synthesis of Au NPs. The experiments were carried out in a batch-operated model gas-liquid plasma reactor [12−14]. Electrodes were made of stainless steel; one of the electrodes (cathode) was placed in the lower part of the reactor and the other one (anode with a diameter of 2.4 mm) was placed at a distance of 10 mm above the solution surface. Upon the application of high-voltage (500−1000 V) to the electrodes, a discharge was ignited between the cathode and the solution surface. Pressure in the reactor was held constant by vacuum pump. The volume of the solution in the reactor was 50 ml.

The solutions of precursors were prepared by dissolving salt $HAuCl_4 \cdot 4H_2O$ samples of p.a. grade purity in flasks with distilled water. In a typical experiment, 40 ml of precursor solution of different concentrations were placed in the reactor and treated with a plasma discharge at different intervals of time. The reaction mixture after treatment was examined using spectrophotometry to characterize the gold nanoparticles produced. Spectra of colloidal solutions were acquired using quartz cuvettes and a spectrophotometer UV-5800PC in the wavelength range of 190−700 nm. The zeta potential of colloidal solutions was determined using the Zetasizer Nano-25 (Malvern Instruments Ltd., Malvern, England) zeta potential and particle size analyzer. Microphotographs of nanoparticles and particle sizes were taken using a JEOL JSM-6510LV scanning microscope (JEOL, Tokyo, Japan). For each sample, the measurement was performed three times.

Results and discussion

The main regularities and influences of the conditions for the gold ion reduction under the action of a plasma discharge on the synthesis of metal nanodispersions of gold, as well as the characteristics of the resulting nanoparticles, were investigated. Earlier [11], it was demonstrated a considerable influence of the precursor concentration on the size of the produced nanoparticles while employing the plasma-chemical technique of synthesis during the synthesis of silver. The plasma-chemical synthesis of Au NPs at different initial concentrations of the Au^{3+} precursor and various times of treatment plasma discharge on the solution without the use of stabilizer reagents was investigated. The UV-Vis spectra of Au NPs recorded for different concentrations of precursor as a function of time of synthesis by plasma discharge are shown in Fig. 1.

It is known [7−11] that the surface plasmon absorption peaks typically occur for gold nanoparticles at 520−580 nm, and the positions of these peaks vary with the size and morphology of the gold nanoparticles. Thus, the size, structure, and aggregation characteristics of gold nanoparticles can be analyzed through the study of the surface plasmon resonance absorption band. Due to the excitation of surface plasmon resonance (SPR) in the Au NPs, UV-vis spectroscopy provides a quick and accurate method for analyzing the optical characteristics of Au NPs. We assume that the abundance of gold nanoparticles is proportional to the absorption intensity. Based on the relationship between the optical characteristics of Au NP (surface
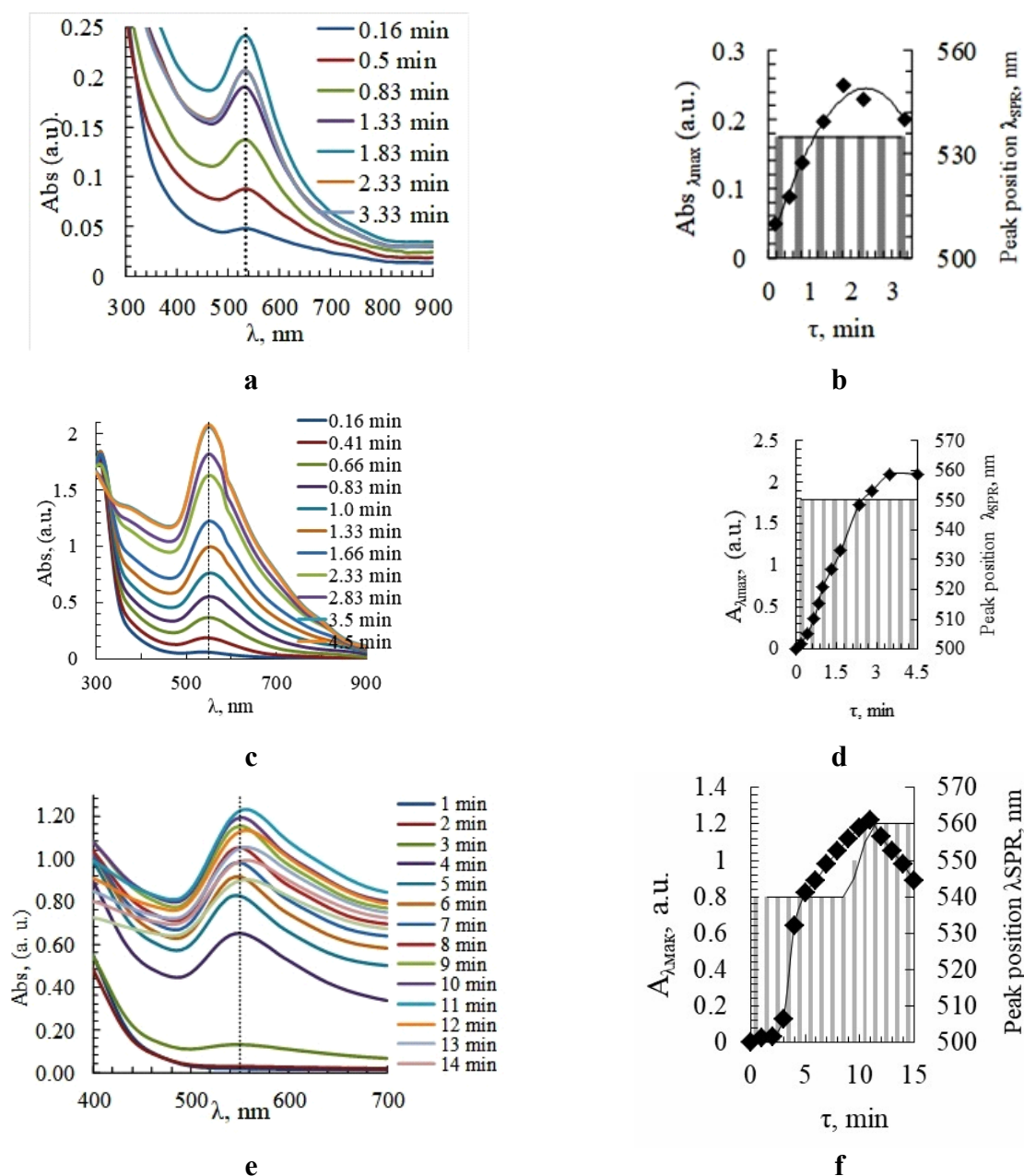
M.I. Skiba, I.L. Kovalenko, Y.M. Skyba, V.I. Vorobyova

Fig. 1. The UV-Vis spectra of Au NPs recorded as a function of time of synthesis by plasma discharge (I=120 mA, P=0.08 MPa) for different concentrations of Au³⁺: a and b − 0.06 mmol/L; c and d − 0.3 mmol/L; i and f − 2.5 mmol/L

plasmon resonance (SPR, absorbance)) (Fig. 1) and the size distribution of NPs (Fig. 2), a number of conclusions about the formation, growth, and characteristics of NPs during plasma chemical synthesis were drawn.

The production of non-stabilized dispersion of Au NPs via the plasma treatment of water solutions of precursors is characterized by a number of established patterns. Hence, for different time intervals of plasma discharge treatment, gold nanodispersions are formed, in which the metal is in a nanosized metallic state with absorption maxima in the range of λ=530−630 nm (A=0.05−2.0 a.u.), which indicates the spherical shape of the formed NPs (approximately 30−80 nm (Fig. 1). It can be seen that increasing the initial concentration of the treated solution from 0.06 mmol/l to 2.5 mmol/l necessitates increasing the length of plasma discharge treatment of the solution from 3.5 min to 10.0 min to obtain pronounced peaks. Furthermore, as the matching starting
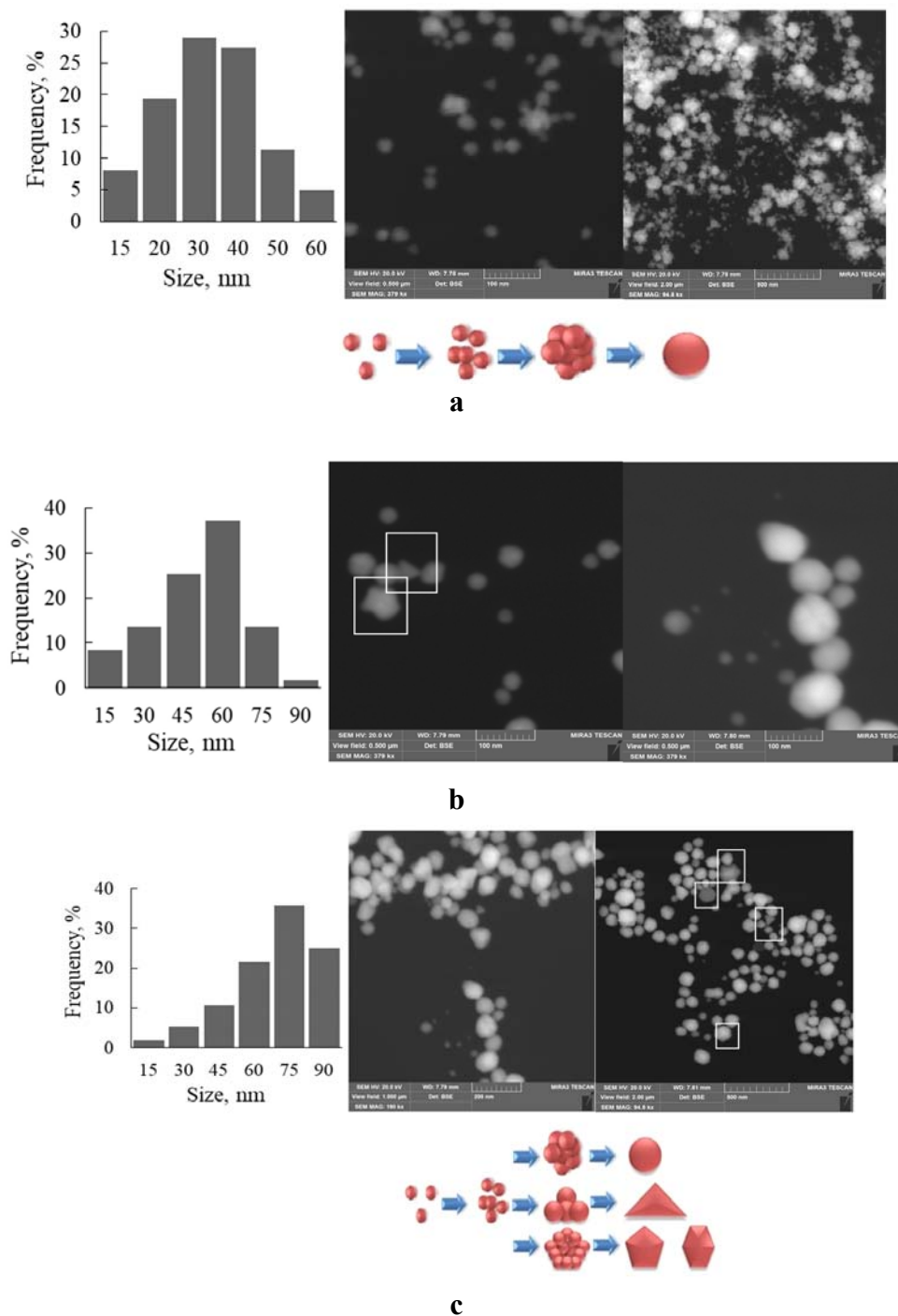
Fig. 2. SEM images and particle size distributions in the dispersion of nanoparticles after the action of the plasma discharge for different concentrations of Au^{3+}: a − 0.06 mmol/L (τ=3.33 min, U=800 V); b − 0.3 mmol/L (τ=4.5 min, U=800 V); and c − 2.5 mmol/L (τ=11.0 min, U=800 V)

concentration of the precursor increases, the produced peaks shift from 530 nm to 540−555 nm and broaden, indicating an increase in the average size of nanoparticles and size distribution. In particular, investigation of the size distribution of NPs in prepared samples with different initial concentrations of precursors by SEM analysis showed that the precursor concentration could be used to control the size of the synthesized Au NPs (Fig. 2). The physical and chemical properties of Au NPs are strongly influenced by their

M.I. Skiba, I.L. Kovalenko, Y.M. Skyba, V.I. Vorobyova

form. SEM analysis results were also used to determine particle shape distributions. According to the literature, the size and form of metal nanoparticles in solutions are determined by competition between nucleation and growth at distinct facets. All of the particles are spherical at low molar concentrations (0.06 mmol/l). The particle shape distribution of Au NPs contains many shapes such as spherical, hexagonal, and triangular for medium molar concentrations (0.3 mM). In the samples obtained at higher molar concentrations (2.5 mM), the formation of spherical or hexagonal gold nanoparticles is mainly observed. The prevalence of certain forms at varying concentrations could indicate that reduction of the gold precursor is initiated differently under different conditions.

Low concentrations (0.06 mmol/l) may allow reduction to largely take place in bulk solution, reducing the ions of precursor molecules to Au^0 atoms. As a result, reduced atom aggregation is isotropic, resulting in spherical particles. The possibility of partially reduced $HAuCl_4$ interacting with growing NPs increases as the precursor concentration increases (0.6−2.5 mmo/l), leading to reduction on the surface of existing nucleated seeds (or small particles). The surface energy of the various crystal facets will be a factor in surface-assisted reduction, which could result in non-spherical forms.

According to the kinetic curves of the intensity of the absorption maximum of the spectra and its position, the staged mechanism of nucleation and growth of nanoparticles under conditions of homogeneous nucleation is observed, typical of dispersion of nanoparticles (Fig. 3). In general, the observed nature of the intense increase in absorbance in the first minutes of synthesis at λ_{max} (530−600 nm) and the simultaneous decrease of λAu^{3+} indicates rapid nucleation and growth of NPs, which, as is known, provides all the prerequisites for the formation of small-sized NPs.

As is well known, the creation of gold nanoparticles under homogeneous nucleation circumstances is a complex and multistage process accompanied by phase transitions in the system. The following main stages of this process are usually distinguished in the corresponding system: nucleation (chemical reduction of metal ions to atoms, which is accompanied by the formation of unstable polyatomic clusters and/or ions; formation of particle nuclei) and autocatalytic growth of the formed nuclei. According to various estimates, the production of stable gold clusters might be considered an intermediate step in the process of nucleation via various methods of homogeneous metal particle nucleation. However, it should be highlighted that, from the standpoint of
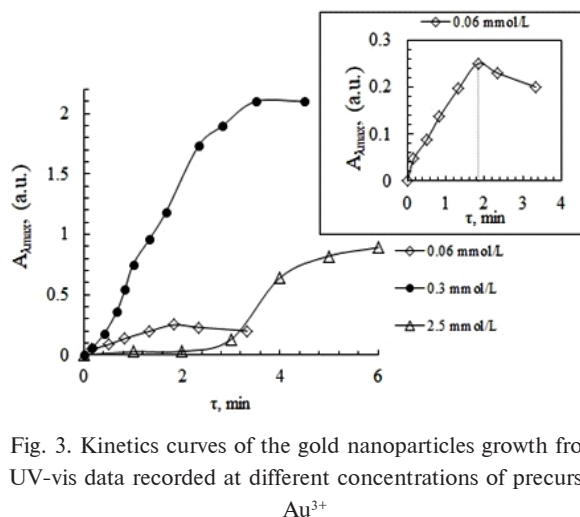

Fig. 3. Kinetics curves of the gold nanoparticles growth from UV-vis data recorded at different concentrations of precursor Au^{3+}

instrumental research, studying the stage of cluster formation is now problematic. As a result, only distinct stages of nanoparticle production were considered, as shown by the kinetic dependences of the change in absorbance. Therefore, the first stage after nucleation is characterized by an intense linear increase in the absorbance in the samples, which corresponds to the growth of NPs in the system to the critical time of formation τ_{kr}. After this time of synthesis, as a rule, stabilization of the formed solutions occurs and there are no changes in both the absorbance and the position of the SPR for samples with 0.06−0.3 mmol/l. When treating solutions with a concentration of more than 2.5 mmol/l after this synthesis time, the formation of larger aggregates of nanoparticles is observed and is characterized by the absence of a decrease in absorbance and a shift of the SPR peak to the long-wavelength zone up to 560 nm.

Particle size in the early stage of the synthesis of gold nanoparticles was investigated (Fig. 4). Thus, plasma chemical treatment for up to ~5 seconds causes the formation of dispersions of gold nanoparticles with an average size of NPs of $d_{av}=2−10$ nm and an IPD index of 0.2−0.3, which characterizes the monodisperse composition of nanoparticles in the medium. An increase in the duration of the synthesis to a conditionally «critical» time ($k_{cr}=0.8−3.0$ min) causes their further controlled growth with the formation of nanoparticles with $d_{av}=35−73$ nm with an IPD=0.41−0.65 and has a characteristic corresponding to SPR=530−600 nm without rapid aggregation. It should be noted that rapid aggregation is observed during the plasma-chemical synthesis of silver nanoparticles in a short period of time.

The stability of Au NPs in solution has always been a concern for several applications. The stability of gold nanoparticles in water dispersion synthesized

via the plasma-chemical method was investigated (Fig. 5).

Plasma-chemically obtained gold NPs, synthesized without a stabilizer, are aggregatively stable for up to 48 hours with a zeta potential value of −18.8...−22.0 mV. It should be noted that the comparison of the obtained samples shows that the dispersions of nanoparticles obtained at a low concentration of the precursor are the most stable. Therefore, these dispersions are stable to aggregation within 24−36 hours and are characterized by the highest value of zeta potential of about −22.0 mV.

It was shown [9−12] that the synthesis of Au NPs as a result of the reduction of Au^{3+} from the $HAuCl_4$ precursor in an aqueous solution is possible through the action of various oxidizing compounds which are present in different ratios, depending on the type of plasma discharge (plasma electrons, hydrogen radicals in liquid, hydrated e^-_{aq} electrons and hydrogen peroxide) according to the reactions given in Table.

Significant reactions generated by e_{aq}, H, OH, and H_2O_2 radicals, as well as their reduction potential values

Reaction	E_0, V
$AuCl_4^-+3e^-_{aq}\rightarrow Au^0+Cl^-$	1.0
$2AuCl_4^-+3H_2O_2\rightarrow 2Au^0+3O_2+6H^++8Cl^-$	0.31
$2H^++2e^-_{aq}\rightarrow H_2$	0
$H_2O_2+2H^++2e^-_{aq}\rightarrow 2H_2O$	1.76
$H_2O+e^-_{aq}\rightarrow H+OH^-$	−2.93
$AuCl_4^-+3H\rightarrow Au^0+3HCl+Cl^-$	−
$Au(OH)_4^-+3H\rightarrow Au^0+3H_2O+OH^-$	−
$AuCl_4^-+3/2H_2O_2+Au_m\rightarrow Au_{m+1}+3/2O_2+3HCl+Cl^-$	−

In this model, positive discharge ions, mainly $(H_2O^+)_g$ generated in the gas layer, but additionally air ions such as N_2^+ and O_2^+, bombard the surface of a liquid and have enough energy to collide with the water molecules, generating $(H_2O^+)_{aq}$ and a solvated electron (e^-_{aq}). These solvated electrons react with H^+_{aq} cations to produce the hydrogen radical НЧ. These radicals, according to hypothesis, migrate into the gas phase to form $(H)_g$. They are ionized in the discharge by electron impact ionization. This results in a free electron in the discharge phase $(e^-)_g$ derived from $(H)_{aq}$, and the ensuing $(H^+)_g$ dissolves back into solution. Reduction reactions at the solution's submerged cathode then ensure that electrons are replenished in the solution. However, the vast majority of scientists are currently inclined toward the opinion about the dominant effect of the hydrated electrons and the additional effect of H_2O_2 (which, as it was demonstrated, is eliminated in the preparation of nanosilver).

In contrast to the synthesis of nanosilver, when meeting with hydrated electrons e^-_{aq}, hydrogen peroxide can have an additional reducing effect during the formation of gold NPs as a result of the effect of a plasma discharge on $[AuCl_x(OH)_{4-x}]^-$ according to the following equation [9−12]:

$$3H_2O_2+3OH^-+Au^{3+}\rightarrow Au^0+3HO_2+3H_2O,$$

$$AuCl_4^-+3/2H_2O_2\rightarrow Au^0+3/2O_2+3H^++4Cl^-.$$
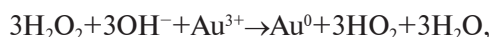
Conclusions

In this article, we have discussed the approaches for the synthesis of gold nanoparticles using atmospheric pressure plasma without any reducing
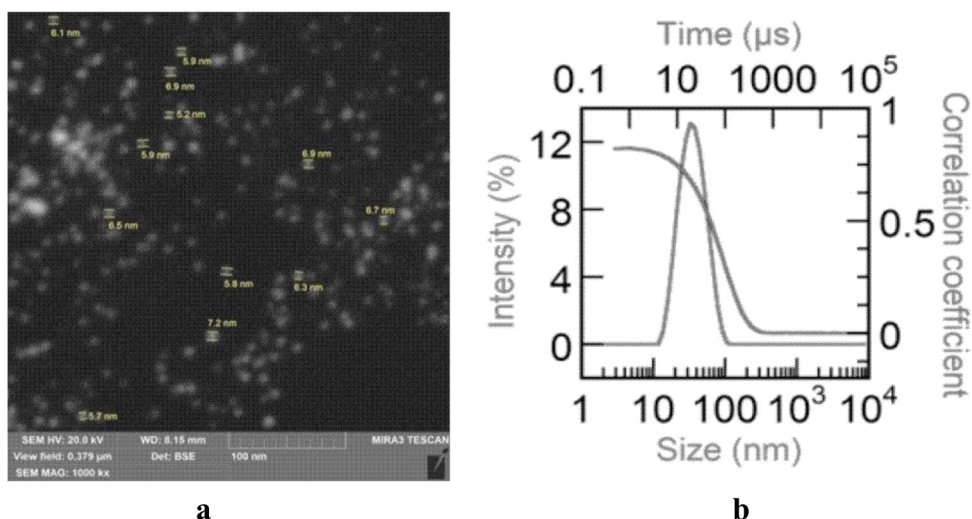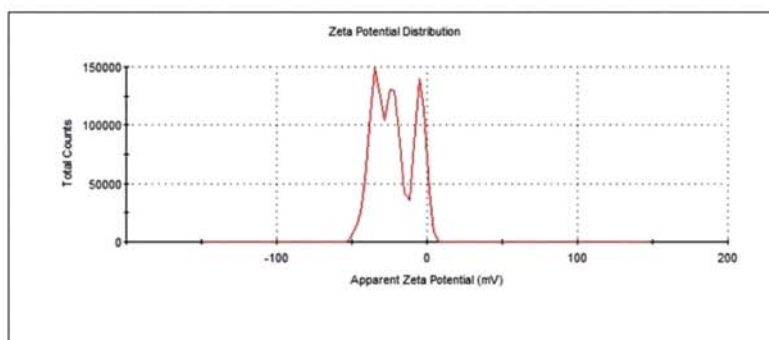

Fig. 4. SEM-image (a) and size distribution (b) of NPs synthesized by the plasma chemical method after a 5-second treatment of plasma discharge

M.I. Skiba, I.L. Kovalenko, Y.M. Skyba, V.I. Vorobyova

	Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV): -21,7	Peak 1: -34,6	37,8	5,03
Zeta Deviation (mV): 13,3	Peak 2: -21,8	34,3	4,72
Conductivity (mS/cm): 0,563	Peak 3: -4,64	27,8	3,80

a

	Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV): -20,6	Peak 1: -31,4	41,4	4,77
Zeta Deviation (mV): 12,4	Peak 2: -19,5	36,9	4,91
Conductivity (mS/cm): 0,552	Peak 3: -2,49	21,7	4,00
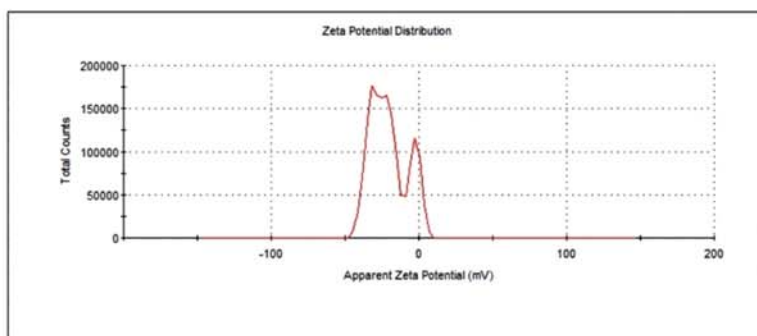
b

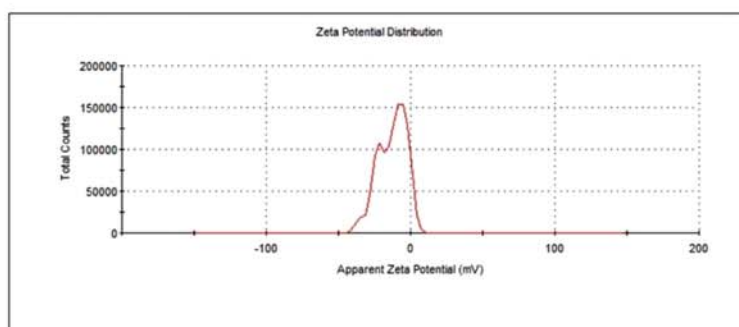|	Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV): -12,9	Peak 1: -8,25	68,4	6,23
Zeta Deviation (mV): 9,78	Peak 2: -24,2	31,6	5,32
Conductivity (mS/cm): 0,406	Peak 3: 0,00	0,0	0,00

c

Fig. 5. Zeta potential distribution of Au NPs synthesized by the plasma chemical method at different concentrations of Au^{3+}: a − 0.06 mmol/L; b − 0.3 mmol/L; and c − 2.5 mmol/L

agents. The UV-vis spectroscopy showed that the solution products possessed the absorption light from 530 nm to 550 nm associated with the gold nanoparticle formation in each collected sample. The results showed that by varying the concentration of the gold salt precursor (0.06−2.5 mmol/l), the size of the Au NPs can be controlled between ~30 and ~75 nm, with the surface plasmon resonance occurring between 530 and 600 nm without adjusting the pH of the solution. The observed kinetic curves of the intensity of the absorption maximum of the spectra and its position indicate that the nucleation and growth of nanoparticles under conditions of homogeneous nucleation are observed, typical of the dispersion of nanoparticles. The findings demonstrated that, depending on the precursor's initial concentration, varying numbers of particles with varied shapes (spherical, hexagonal, and triangular) formed in the samples. Nanoparticles formed with a low Au^{3+} concentration of 0.06 mmol/l, compared with other samples, are mostly spherical with d_{av}=35−38 nm and stable in aqueous solution for 12−24 hours, having a characteristic zeta potential of −20...−22 mV.

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M.I. Skiba, I.L. Kovalenko, Y.M. Skyba, V.I. Vorobyova

ДИСПЕРСІЇ НАНОЧАСТИНОК ЗОЛОТА, ЩО НЕ МІСТЯТЬ СТАБІЛІЗУЮЧОГО АГЕНТА, ОДЕРЖАНІ ЕКОЛОГІЧНО ЧИСТИМ ПЛАЗМОВО-РІДИННИМ МЕТОДОМ

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У цьому дослідженні реалізовано простий підхід для синтезу наночастинок Au (Au НЧ) за допомогою плазми атмосферного тиску без використання будь-яких відновлювачів, добавок чи блокуючих агентів. Розмір, морфологія, оптичні характеристики та агрегаційна стійкість синтезованих наночастинок золота були охарактеризовані за допомогою скануючої електронної мікроскопії, УФ-спектроскопії та вимірювання дзета-потенціалу. Досліджено спектральні характеристики поглинання в УФ-видимому діапазоні наночастинок золота, одержаних за різних значеннях концентрації Au^{3+} і тривалості оброблення анодним плазмовим розрядом. УФ-спектри Au НЧ виявили смугу поверхневого плазмонного поглинання між 530−600 нм, яка є результатом сформованих AuНЧ. Встановлено, що розмір Au НЧ можна регулювати в діапазоні 30−75 нм шляхом зміни концентрації прекурсора солі золота в діапазоні 0,3−2,5 ммоль/л. Встановлено, що для досліджуваних концентрацій Au^{3+} оброблення плазмою протягом 3−10 хв приводить до утворення НЧ Au різного розміру та морфології. Результати показали утворення в зразках різної кількості частинок різної форми: сферичної, гексагональної та трикутної, залежно від початкової концентрації Au^{3+}. Плазмохімічно одержані наночастинки у дисперсіях, утворені при концентрації Au^{3+} 0,06 ммоль/л, порівняно з іншими зразками з Au^{3+} 0,3−2,5 ммоль/л, є, переважно, сферичними та стабільними протягом 12−24 годин із дзета-потенціалом, рівним −20...−22 мВ.

Ключові слова: золото, наночастинки, розряджена анодна плазма, середній розмір, різні форми, стабільність.

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This study investigates a simple approach for synthesizing gold nanoparticles (Au NPs) using atmospheric pressure plasma without the need for reducing agents, additives, or capping agents. The size, morphology, optical properties, and aggregation stability of the synthesized Au NPs were characterized using scanning electron microscopy, UV-vis spectroscopy, and zeta potential analysis. The UV-vis absorption spectra of the gold nanoparticles, obtained at various Au^{3+} concentrations and treatment durations with anode plasma discharge, were analyzed. The UV-vis spectra revealed a surface plasmon resonance absorption band between 530−600 nm, indicative of Au NP formation. Results demonstrated that the size of Au NPs can be tuned within the range of 30−75 nm by adjusting the gold salt precursor concentration from 0.3 to 2.5 mmol/L. It was found that plasma treatment for 3−10 minutes, at different Au^{3+} concentrations, resulted in the formation of Au NPs with varying sizes and morphologies. The study showed that particles with different shapes − spherical, hexagonal, and triangular − were formed depending on the initial concentration of Au^{3+}. The plasma-chemically synthesized nanoparticles at an Au^{3+} concentration of 0.06 mmol/L were predominantly spherical and exhibited the highest stability (lasting 12−24 hours), with a zeta potential of −20 to −22 mV, compared to samples with Au^{3+} concentrations ranging from 0.3 to 2.5 mmol/L.

Keywords: gold; nanoparticles; discharged anode plasma; average size; different shapes; stability.

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