

Pivovarov O. A.  
Skiba M. I.  
Makarova A. K.

*Ukrainian State University  
of Chemical Technology*

Vorobyova V. I.

*National Technical  
University of Ukraine  
«Igor Sikorsky Kyiv  
Polytechnic Institute»*

Півоваров О. А.  
д.т.н., професор

Скиба М. І.  
к.т.н., асистент

Макарова А. К.  
аспірант

*Український державний  
хіміко-технологічний  
університет*

Воробйова В. І.  
к.т.н., асистент

*Київський  
політехнічний  
інститут імені Ігоря  
Сікорського*

**UDC 621.357:533+661.43+66.088;  
621.357:533; 661.8+66.067.8.081.3**

## **OBTAINING OF BIMETALLIC NANOPARTICLES BY USING PLASMA DISCHARGE**

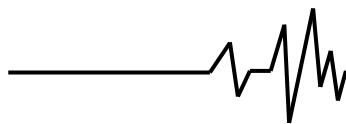
*Bimetallic silver and gold nanoparticles have been prepared using low-temperature contact non-equilibrium plasma in one and two steps. Gold-coated silver (Au/Ag) and silver-coated gold (Ag/Au) composite nanoparticles are prepared in two step by a seeding growth method. The absorption spectra of bimetallic nanoparticles prepared in two steps suggested the formation of core-shell structure. The one step plasma chemical synthesis of Au–Ag alloy of bimetallic particles was obtained. For Au–Ag alloy of bimetallic particles the surface plasmon absorption maxima appeared in between the peaks corresponding to pure silver and pure gold. The surface plasmon absorption maxima for bimetallic nanoparticles changes linearly with increasing of gold content in the alloy.*

**Key words:** nanoparticles, composite, bimetallic, obtaining, plasma discharge.

**Introduction.** Metallic and bimetallic nanoparticles are being become increasingly interesting in nanoscience and technology due to their unique optical, electrical and catalytic properties [1]. Nanoparticles can be categorized based on single or multiple materials into simple and core/shell or composite nanoparticles [2]. In general, simple nanoparticles are made from a single material; whereas, as the name implies, composite and core/shell particles are composed of two or more materials. The core/shell type nanoparticles can be broadly defined as comprising a core (inner material) and a shell (outer layer material). These can consist of a wide range of different combinations in close interaction, including inorganic/inorganic, inorganic/organic, organic/inorganic, and organic/organic materials. The choice of shell material of the core/shell nanoparticle is generally strongly dependent on the end application and use. Metallic and bimetallic nanoparticles are

widely used in different applications such as biomedical and pharmaceutical applications, catalysis, electronics, enhancing photoluminescence, creating photonic crystals, etc. In particular in the biomedical field, the majority of these particles are used for bioimaging, control of drug release, targeted drug delivery and cell labeling, and tissue engineering applications. Thus, the development of new methods aimed at obtaining of stable solutions of bimetallic nanoparticles is currently relevant.

**Analysis of research and publications.** Many methods have been reported for the preparation of metallic and bimetallic nanoparticles, such as laser irradiation [3], sonochemical deposition [4, 5], photochemical reduction [6], electrochemical method [7] and chemical reduction of metal salts. More recently, stable generation of plasmas at atmospheric pressure [5–7] has given the opportunity to explore a new range of approaches for nanomaterials



synthesis and various configurations have been reported to synthesize bimetallic nanoparticles directly in liquids (e.g. plasma generated by electrodes immersed in liquids [8], gas–liquid interfacial low-pressure plasmas [9], atmospheric pressure plasma interfacing with liquid).

Among plasmachemical discharges, a contactless non-equilibrium low-temperature plasma (NPC) is perspective in terms of practical application. The contact non-equilibrium plasma offers enhanced opportunities over solution chemistry for synthesis of new nanomaterials and tailoring their functional properties. In previous works, the authors demonstrated the effectiveness of using low-temperature contact non-equilibrium plasma (NPC) to obtain nanoparticles of silver and gold from aqueous solutions of metal salt in a single technological step without the use of additional reagents-reducing agents [6, 7]. Scientific and practical interest is represented in the study of plasma-chemical obtaining of bimetallic nanoparticles.

The aim of the work is an investigation of obtaining of bimetal nanoparticles of precious metals using contact non-equilibrium low temperature plasma.

**Experimental part.** The studies were carried out in a model gas-liquid plasma reactor of batch operation. Barrel-type reactor with inner diameter of 45 mm in height was used. Cooling of reaction mixture was provided by continuous circulation of cold water in outer jacket. Electrodes were made of stainless steel; one of the electrodes (diameter 4 mm) was placed in the lower part of the reactor and the other one (diameter 2, 4 mm) was placed at a distance of 10 mm above the solution surface. To get plasma discharge, voltage of 500–1000 V was applied to electrodes. Pressure in the reactor was held constant by

vacuum pump. The time of plasma treatment of sodium chloride solutions was being varied within the range from 1 to 12min. The volume of the solution in the reactor was 50 ml.

For the preparation of colloids of bimetallic nanoparticles, silver nitrate, hydrogen tetrachloroaurate (III) hydrate and sodium alginate were used as a metal salt precursor and a stabilizing agent, respectively. Ag–Au alloy nanoparticles were synthesized with varying initial Au/Ag molar ratios (0:1, 0,25:0,75, 0,5:0,5, 0,75:0,25, and 1:0, respectively). This synthesis was performed by reducing  $\text{HAuCl}_4$  and  $\text{AgNO}_3$  in the presence of sodium alginate by CNP. Au-core/Ag-shell nanoparticles were prepared using the following seed colloid technique. Obtained colloidal solution in the presence of the stabilizer (in accordance to techniques [6, 7]) was mixing with precursors Au–Ag, in accordance to structures planned to obtain with next plasma treatment. The prepared Au–Ag, Ag–Au NPs were controlled by spectrophotometer method in UV-spectroscopy by spectrophotometer model UV-5800PC in the wavelength range from 190 to 700 nm.

**Results and Discussion.** The interaction of small metal particles with an external electromagnetic field induced by light results in coherent oscillations of the conduction (free electron is mainly within the surface), called surface plasmon resonance (SPR). This surface plasmon resonance mainly depends on the particle size and shape, and its surrounding environment. The evaluation of the surface plasmon band for the core–shell bimetallic nanoparticles can be described by considering the polarizability of a core–shell particle with radius  $R$  as follows [12]:

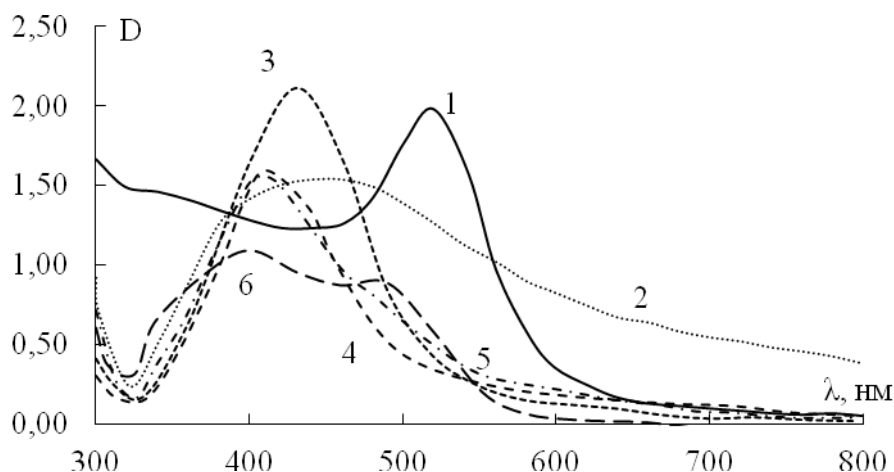
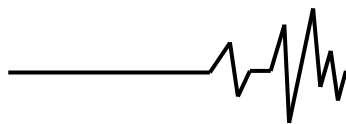
$$\alpha = R^3 \frac{(\varepsilon_s + \varepsilon_m)(\varepsilon_c + 2\varepsilon_s) + (1-g)(\varepsilon_s - \varepsilon_c)(2\varepsilon_s + \varepsilon_m)}{(\varepsilon_s + 2\varepsilon_m)(\varepsilon_c + 2\varepsilon_s) + (1-g)(\varepsilon_c - \varepsilon_s)(2\varepsilon_s - \varepsilon_m)}$$
$$g = 1 - \frac{R_1^3}{R_2^3}$$

where  $\varepsilon_m$  is the dielectric constant of the matrix,

$\varepsilon_c$  and  $\varepsilon_s$  are the dielectric functions of the core and shell materials, respectively, and  $g$  is the volume fraction of the shell layer. The radii of the

total composite particle and its core are  $R_2$  and  $R_1$ , respectively.

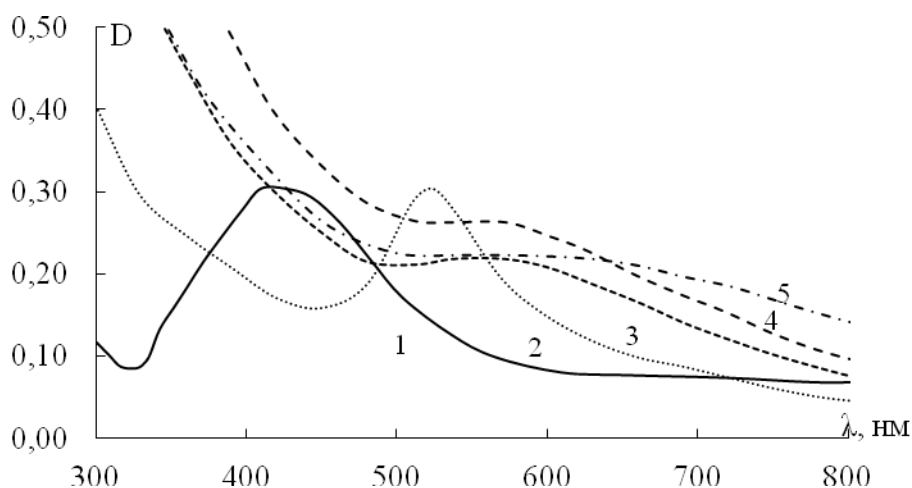
Fig. 1 shows ultraviolet (UV)–visible absorbance spectra of Au and Ag-coated Au colloids.



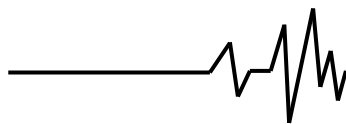
**Fig. 1. UV-vis absorbance spectra of (1) Au seed and (2–6) Au–Ag composite nanoparticles prepared with different Au seed volumes: (2) 0,4 ml, (3) 1 ml, (4) 2 ml, (5) 5 ml and (6) 40 ml**

The gold colloids exhibit absorbance band at around 520 nm. When the molar ratio (MR) of Ag/Au is around 1 (spectrum 6), two SPR bands located at 390 and 500 nm can be observed, which indicate the partial coverage of gold by silver nanoparticles or the formation of independent particles [11]. With the continual decrease of the Au seed volume, only a plasmon band appears between 400 and 460 nm. This can be exclusively attributed to plasmon resonance of Ag particles. The appearance of only one absorbance band corresponding to silver nanoparticles indicates that homogeneously mixed colloidal particles of the two metals are formed without significant formation of independent particles. The plasmon band gradually red-shifts as the seed concentration is decreased, suggesting the formation of composite particles

with larger diameter [12, 13]. The changes of plasmon band with seed volume are consistent with the calculated tendency, according to Eq., that the plasmon band red-shifts with increasing thickness of the Ag shell. From the UV-vis absorbance spectra, we can reasonably infer that the reduction of Ag salt alone occurs on the preformed Au core surface rather than forming more nucleation sites, and the core-shell structure of Au–Ag composite nanoparticles is formed [12–14]. Thus, it is not surprising that the optical properties of composite nanoparticles are dominated by the Ag shell, and the plasmon band of the composite nanoparticles red-shifts when the Ag shell gradually becomes thicker as the seed concentration is decreased. Fig. 2 shows the absorbance spectra of Ag and Ag–Au composite colloids.

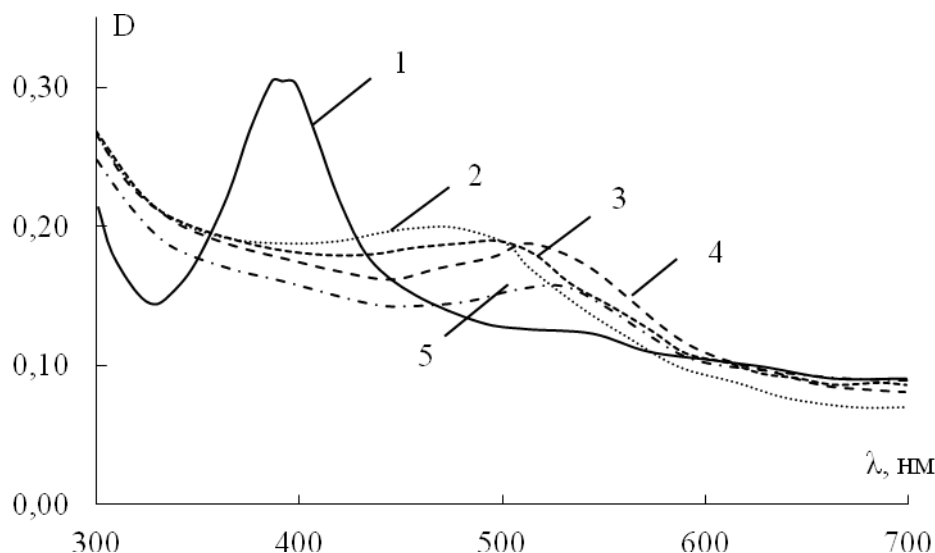


**Fig. 2. UV-vis absorbance spectra of (1) Ag seed and (2–5) Ag–Au composite nanoparticles prepared with different Ag seed volumes: (2) 1 ml, (3) 4 ml, (4) 12 ml, (5) 24 ml**



The Ag seed colloids exhibit one SPR band around 410 nm. After the addition of  $\text{HAuCl}_4$  solution, the colloid exhibits an Au-like SPR band, which indicates that optical properties of composite nanoparticles are dominated by gold shell. With the increase of Ag seed volume, their SPR bands red-shift. If Au–Ag alloy nanoparticles or individual Au and Ag mixed colloids were formed, the SPR band would blue-shift with increasing Ag seed volume [14]. As a result, the core–shell structure of Au–Ag composite

nanoparticles is formed, which has also been confirmed by comparing the experimental absorbance spectra of Au–Ag core–shell nanoparticles with their calculated spectra [13] according to the equation given by Hao [15]. Thus, it is not surprising that the optical properties of composite nanoparticles are dominated by the Au shell, and the plasmon band of the composite nanoparticles red-shifts when the Au shell gradually becomes thinner as the seed concentration is increased.



**Fig. 3. UV/Vis absorption spectra of Ag–Au alloy nanoparticles with varying gold mole fraction  $X_{Au}$ : (1) 0, (2) 25, (3) 50, (4) 75, (5) 100**

Fig. 3 shows the absorption spectra for gold, silver, and a series of gold–silver alloy nanoparticles with varying gold concentration. The absorption peaks at 520 and 410 nm belong to surface plasmon absorption of Au and Ag nanoparticles, respectively. If gold and silver ions are reduced simultaneously by sodium borohydride in the same solution, then gold–silver alloy particles are formed. The alloy formation is concluded from the fact that the optical absorption spectrum shows only one plasmon band and the wavelength at which maximum absorbance occurred. Calculation of the extinction spectra of Au–Ag nanoparticles, based on Mie theory, supports our results. Thus, nanoparticles are alloys rather than core–shell structures [17, 18]. The divergence of absorbance between Au, Ag, and Au–Ag alloy is due to the difference of extinction coefficients at the plasmon maximum.

### References

1. Anghuman Pal, Sunil Shah & Surekha Devi. Synthesis of Au, Ag and Au–Ag alloy

nanoparticles in aqueous polymer solution // Colloids and Surfaces A: Physicochem. Eng. Aspects, Vol. 302, 2007, pp. 51–57.

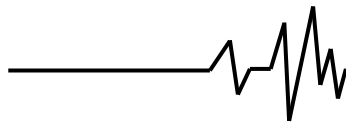
2. Ghosh Chaudhuri R., Paria S. Core/shell nanoparticles: classes, properties, synthesis mechanisms, characterization, and applications // Chemical reviews, 2011, Vol. 112, pp. 2373–2433.

3. J.P. Abid, A.W. Wark, P.F. Brevet, H.H. Girault. Preparation of silver nanoparticles in solution from a silver salt by laser irradiation // Chem. Commun., No. 7, 2002, pp. 792–793.

4. V.G. Pol, D.N. Srivastava, V. Palchik, M.A. Slifkin, A.M. Weiss, A. Gedanken. Sonochemical deposition of silver nanoparticles on silica spheres // Langmuir, Vol. 18, 2002, pp. 3352–3357.

5. R.M. Stiger, S. Gorer, B. Craft, P.M. Penner. Investigations of Electrochemical Silver Nanocrystal Growth on Hydrogen-Terminated Silicon (100) // Langmuir, Vol. 15, 1999, pp. 790–798.

6. H. Malune, J.Y. Kohon, Y. Takeda, T. Kondow. Structure and Stability of Silver



Nanoparticles in Aqueous Solution Produced by Laser Ablation // J. Phys. Chem. B, No. 104, 2000, pp. 8333-8337.

7. H.H. Hunng, X.P. Ni, G.L. Loy, C.H. Chew, K.L. Tan, H.C. Loh, J.H. Deng, G.Q. Xu. Photochemical Formation of Silver Nanoparticles in Poly (N-vinylpyrrolidone) // Langmuir, no. 12, 1996 pp. 909-912.

8. J.J. Zhu, S.W. Liu, O. Palchik, T. Koltypin, A. Gedanken. Shape-Controlled Synthesis of Silver Nanoparticles by Pulse Sonochemical Methods // Langmuir, no.16, 2000, pp.6396-6399.

9. O. Pasenko, M. Skiba, A. Makarova, V. Vorobyova, A. Pivovarov. Obtaining Solution with nanoscale particles of silver by plasmachemical method // Voprosy Khimii i Khimicheskoi Tekhnologii, Vol. 4, 2016. pp. 93 – 97.

10. Synthesis of gold nanoparticles from aqueous solutions of hydrogen tetrachloroate (III) by plasma // East-Ukrainian National University by Volodymyr Dahl, Vol. 4, 2014, pp. 39-44.

11. S. Pande, S.K. Ghosh, S. Praharaj, S. Panigrahi, S. Basu, S. Jana, A. Pal, T. Tsukuda, T. Pal. Synthesis of Normal and Inverted Gold–Silver Core–Shell Architectures in  $\beta$ -Cyclodextrin and Their Applications in SERS // Phys. Chem. C, no. 111, 2007, pp.10806-10813.

12. M. Moskovits, I.S. Sloufova, B. Vlckova. Bimetallic Ag–Au nanoparticles: Extracting meaningful optical constants from the surface-plasmon extinction spectrum // J. Chem. Phys., no.116, 2002, pp. 10435.

13. Lu L. et al. Seed-mediated growth of large, monodisperse core–shell gold–silver nanoparticles with Ag-like optical properties // Chemical Communications, Vol. 2, 2002, pp. 144-145.

14. N.R. Jana, L. Gearheart, C.J. Murphy. Evidence for Seed-Mediated Nucleation in the Chemical Reduction of Gold Salts to Gold Nanoparticles // Chem. Mater., Vol. 13, 2001, pp. 2313-2322.

15. E. Hao, G.C. Schatz. Electromagnetic fields around silver nanoparticles and dimers // J. Chem. Phys. Vol. 120, 2004, pp. 357-366.

16. S.T. He, S.S. Xie, J.N. Yao, H.J. Gao, S.J. Pang. Self-assembled two-dimensional superlattice of Au-Ag alloy nanocrystals // Appl. Phys. Lett., Vol. 81, 2002, pp. 150-152.

17. K.L. Kelly, T.R. Jensen, A.A. Lazaridis, G.C. Schatz, in: D.L.

18. Feldheim, C.A. Foss Jr (Eds.), Metal Nanoparticles: Synthesis, Characterization and Applications, Marcel Dekker, New York, 2002.

19. Kimberly Dick, T. Dhanasekaran, Zhenyuan Zhang, and Dan Meisel. Size-Dependent Melting of Silica-Encapsulated Gold Nanoparticles // J. Am. Chem. Soc., Vol. 124, 2002, pp. 2312-2317.

#### ОДЕРЖАННЯ БІМЕТАЛІЧНИХ НАНОЧАСТОК ЗА ДОПОМОГОЮ РОЗРЯДУ ПЛАЗМИ

**Анотація.** В роботі було одержано наночастки золота та срібла в одну технологічну стадію із застосуванням контактної нерівноважної низькотемпературної плазми. Композитні наночастки золота покриті сріблом (Au/Ag) та срібла покриті золотом (Ag/Au) було одержано у два етапи з попереднім формуванням ядра композитних наночасток. Також в одну технологічну стадію одержано сплав структури Au–Ag. Для сплаву біметалічних часток Au–Ag поверхневий максимум поглинання візуалізується між піками, що відповідають пікам чистого срібла та золота. Встановлено, що поверхневий максимум поглинання для біметалічних наночасток змінюється лінійно з збільшенням вмісту золота в сплаві.

**Ключові слова:** наночастки, композитні, біметалічні, одержання, розряд плазми.

#### ПОЛУЧЕНИЕ БИМЕТАЛЛИЧЕСКИХ ЧАСТИЦ С ПОМОЩЬЮ РАЗРЯДА ПЛАЗМЫ

**Аннотация.** В работе были получены наночастицы золота и серебра в одну технологическую стадию с помощью контактной неравновесной низкотемпературной плазмы. Композитные наночастицы золота покрытые серебром (Au/Ag) и серебра покрытые золотом (Ag/Au) были получены в два этапа с первичным формированием ядра композитных наночастиц. Так же в одну технологическую стадию был получен сплав структуры Au–Ag. Для сплава биметаллических частиц Au–Ag поверхностный максимум поглощения между пиками, которые соответствуют пикам чистого серебра и золота. Установлено, что поверхностный максимум поглощения для биметаллических наночастиц изменяется линейно с увеличением содержания золота в сплаве.

**Ключевые слова:** наночастицы, композитные, биметаллические, получение, разряд плазмы.