Synthesis of (Au)Ag core-shell nanocomposite in the water-ethanol mixture and its optical properties

A V Abakshonok¹, A Yu Panarin², V E Agabekov¹, A N Eryomin¹ and S N Terekhov²
¹ Institute of Chemistry of New Materials of NAS of Belarus, F. Skarina Street 36, 220141, Minsk, Belarus
² B.I. Stepanov Institute of Physics of NAS of Belarus, Nezalezhnasti Avenue 68, 220072, Minsk, Belarus

E-mail: nura2007@tut.by

Abstract. The technique of synthesis of (Au)Ag core-shell bimetallic nanocomposite was developed. Gold seed nanoparticles (NPs) were obtained by HauCl₄ reduction with sodium citrate at ultrasonic treatment during 3 hours in a mixture of water - ethanol (1:1). Then, the surface of gold NPs was modified by silver. In the presence of polyvinylpyrrolidone (PVP) K30 (Mw ~ 24000) and K90 (Mw ~ 360000) the core-shell (Au)Ag NPs of spherical shape were formed. They are characterized by aggregate stability and well-defined absorption maximum at 400-514 nm. Composite (Au)Ag, prepared in the solution without a polymer or in the presence of carboxymethylcellulose (CMC), sodium polystyrene sulfonate (PSS), dextran T100 and T500, had a broad band plasmon resonance in the whole range of visible spectrum. The ability to use the (Au)Ag core-shell nanoparticles in absorption nanospectroscopy based on the phenomenon of plasmon resonance energy transfer (PRET) was evaluated. In the presence of 0.1-2.0 μM of water-soluble cationic Cu (II) -5,10,15,20-tetrakis (4-N-methyl pyridinium) porphyrin (CuTMPyP4) distinct dips due to plasmon quenching matched the absorption maximum of CuTMPyP4 were detected in the resonant scattering spectrum of (Au)Ag solution.

1. Introduction
Gold, silver and their composite nanoparticles are characterized by intense absorption and scattering due to surface plasmon resonance. The size- and shape-dependent unusual optical characteristics allow to use these particles in the various analytical methods [1-3]. The techniques can be based on shift of the plasmon resonance maximum depending on dielectric properties of environment, change the resonance light scattering in the dark-field microscopy as well as on the appearance of dips in the NPs resonant scattering spectra at a wavelength coinciding with optical absorption maximum of the test compound (the phenomenon of plasmon resonance energy transfer - PRET). Optical absorption spectroscopy requires relatively high concentrations of the compounds and has a low spatial resolution. In the case of PRET-based absorption nanospectroscopy, resonance energy migration is caused by a direct transfer, so PRET spectra can be recorded at lower concentrations of defined molecules [2, 3].
The purpose of the study is the development of a method for the synthesis of (Au)Ag bimetallic core-shell NPs for their usage in absorption spectroscopy based on PRET.

2. Experimental section
Hydrogen tetrachloroaurate (HAuCl₄) and the polymers from Aldrich carboxymethylcellulose (CMC; ~ 250 kD), sodium polystyrene sulfonate (PSS; 70 kD), polyvinylpyrrolidone (PVP) K30 (Mw ~ 24000) and K90 (Mw ~ 36000), also dextrans T110 (Fluka, Switzerland) and T500 (Loba-Chemie, Austria) were used. Chemicals AgNO₃, NaHCO₃, sodium citrate, glucose and hydrogen peroxide (‘Reahim’, Russia), cationic Cu(II)-5,10,15,20-tetrakis (4-N-methyl pyridinium) porphyrin (CuTMPyP4) and anionic Fe tetra (sulfonatophenyl) porphyrin (FeTPPS) were of analytical grade and were used as received.

The ultrasonic bath Elmasonic S 30 H (Germany) with a frequency of 37 kHz, the effective power of 60 W and a maximum peak power of 240 watts was used throughout the experiments. Extinction spectra were recorded with a spectrofluorimeter CM2203 («SOLAR», Belarus). Diameter of gold NPs was calculated by the equation

\[ d \text{ (nm)} = 2.02X - 23.1, \ X = \frac{\lambda_{\text{max}} \text{ (nm)}}{500} \geq 20 \]  

[4].

The size and shape of the gold NPs and composite (Au)Ag were assessed by transmission electron microscopy («JIM/100SX», Japan). The zeta potential and the z-Average size of the particles were determined using a Zetasizer Nano («Malvern Instruments», UK).

Resonant scattering spectra of gold NPs and the composite (Au)Ag colloidal solutions were recorded with a hand-made experimental setup [5]. To minimize the effect of reabsorption of the scattered light on spectra strongly diluted solutions were used. The optical path length of the exciting light was 5 mm. Also, the beam passed about 1 mm near the wall of the cell. 90 ° scattering geometry was used. In this case, the reflected light did not enter into the detector system, and only scattered radiation was recorded.

Composite (Au)Ag was fabricated in two steps: at first seed gold NPs were obtained, and then they were modified with silver. Gold core NPs were synthesized in a mixture of water-ethanol (1:1) containing 0.4 mM HAuCl₄, 1.0 mM sodium citrate and 0.15 mg/ml PVP. Gold NPs were coated with silver by adding to the colloidal gold solution (the final dilution of gold NP 1.33 times) aliquots 10.0 mM NaHCO₃, 50.0 mM glucose, 5.0 mM hydrogen peroxide and 0.25 mM AgNO₃. Seed gold NPs and silver shell were synthesized at ultrasonic treatment during 3 hours at the temperature varied from 16 to 62 °C.

3. Results and discussion
Number of seed gold NPs rises proportionally to an increase of HAuCl₄ concentration, reaching a maximum at 0.4 mM (table 1). Size of gold NPs depends on the ratio of [sodium citrate] / [HAuCl₄]. It is well known that the concentration of sodium citrate influences on the size of gold NPs: the higher it is, the smaller the particles are formed [6]. This regularity is consistent with the obtained our data only for a concentration of HAuCl₄ no more than 0.2 mM. The probability of formation of smaller particles increases at a higher degree of supersaturation of the solution with HAuCl₄ and relatively low rate of germs condensation of the new phase. Gold sol prepared in a solution with 0.4 mM HAuCl₄ had the highest intensity of resonant light scattering. Therefore, the further synthesis of seed gold NPs was performed in an aqueous solution containing 0.4 mM HAuCl₄ and 1.0 mM sodium citrate. Gold NPs synthesized under these conditions had a spherical shape and formed aggregates about 40-60 nm (figure 1A).

The size of gold seeds and their tendency to agglomerate is influenced by the admixture of polymers in the reaction solution. In the presence of CMC gold NPs with diameter of 22-27 nm are obtained (figure 1B). In the case of PVP K30 (or K90) addition seeds of 7-10 nm occur (figure 1C). Gold sol formed both in the absence and in the presence of the aforementioned polymers, was characterized by colloidal stability and pronounced absorption maximum (figure 2). In the presence of
dextran T110 (or T 500) a gray-violet gold sol was obtained, in which agglomeration of gold NPs was found. Its absorption spectrum did not show distinct bands of surface plasmon resonance (figure 2, spectrum 4). Furthermore, gold sols containing dextran (0.15 mg / ml) were unstable due to the poor solubility of these polymers in water–ethanol mixture.

Table 1. Characteristics of gold NPs obtained at different concentrations of HAuCl₄ in water-ethanol solution (1:1).

| [HAuCl₄] | λ_max, nm | D_max, nm |
|----------|-----------|-----------|
| 0.05     | 553       | 0.24      |
| 0.10     | 562       | 0.36      |
| 0.15     | 575       | 0.61      |
| 0.20     | 581       | 0.88      |
| 0.30     | 563       | 1.20      |
| 0.40     | 547       | 1.68      |

Figure 1. TEM micrographs of the gold NPs (A-D), synthesized in the absence of the polymer (A) and in the presence of CMC (B), PVP K30 (C), dextran T110 (D) and the composite (Au)Ag (E-H), prepared in medium without the polymeric additive (E), in the presence of CMC (F), PVP K30 (G), dextran T110 (H). Magnification is 100 000 times.

The surface of gold NPs was coated with silver in aqueous solution of 10 mM NaHCO₃, using glucose for the gradual reduction of AgNO₃, and also hydrogen peroxide to dissolve small clusters of silver. In the absence of polymer additives composite (Au)Ag is formed, which shows a broad absorption in the whole range of visible spectrum (300-1100 nm) without well-defined plasmon resonance band (figure 3, spectrum 1). Sol has a gray-violet color. It consists of the rod-shaped particles (figure 1E). Moreover, the particles agglomerate to form a ribbon like structures. Absorption of the composite increases in direct proportion to the concentration of AgNO₃ in the reaction solution. The (Au)Ag composite, obtained in a medium with 0.2 and 0.3 mM AgNO₃, had the highest intensity of light scattering.
Figure 2. The absorption spectra of gold NPs synthesized in the medium without polymer (1) and in the presence of CMC (2), PVP K90 (3), dextran T110 (4) and PSS (5).

Figure 3. Absorption spectra of the composite (Au)Ag, synthesized in the medium without polymer (1) and in the presence of CMC (2), PVP K90 (3), dextran T110 (4) and PSS (5).

Ribbon like structures are formed in the presence in the reaction solution of CMC (figure 1F), PSS and dextran (figure 1H). Composite (Au)Ag prepared in the presence of these polymers has a low colloidal stability and is characterized by a broad absorption band in the visible region (figure 3, spectrum 2, 4 and 5). Only in the presence of PVP K30 or PVP K90 (0.11 mg / mL) spherical shape composite (Au)Ag is formed with particles size 20-26 nm (figure 1G). It is stable and has well-defined maximum of absorption (figure 3, spectrum 3). Increasing diameter of the composite particles as compared with germinal gold NPs and broad absorption band at 400 nm are indication of strong silver component in the composite (Au)Ag, which determines its optical properties.

Table 2. The hydrodynamic characteristics of the composite (Au)Ag, synthesized in the presence of different polymers (0.11 mg / ml).

| Polymer          | Zeta-potential, mV | Conductivity, mS/cm | Z-Average size, nm | Polydispersity |
|------------------|--------------------|---------------------|--------------------|---------------|
| Without polymer  | -15.1              | 0.021               | 767                | 0.392         |
| CMC              | -39.1              | 0.213               | 161                | 0.274         |
| PVP K30          | -33.8              | 0.117               | 88                 | 0.262         |
| PVP K90          | -21.6              | 0.239               | 73                 | 0.365         |
| Dextran T110     | -11.9              | 0.269               | 285                | 0.248         |
| Dextran T500     | -7.9               | 0.218               | 260                | 0.334         |
| PSS              | -29.2              | 0.285               | 237                | 0.297         |
The zeta potential and the hydrodynamic size of the composite substantially depend on the presence of polymer in the reaction medium (table 2, figure 4). In general, the polymers reduce the hydrodynamic radius of the composite (Au)Ag. The largest size of the particles is inherent to the composite obtained in the medium without the polymeric additive and the least - in cases of PVP. This weak cationic polyelectrolyte does not reduce, but rather increases the zeta potential of the composite (Au)Ag as compared with the particles synthesized in a medium without the polymer (table 2).

Apparently, in the presence of PVP structures [PVP-(Au)Ag] are formed, in which polymer molecule forms the core, while negatively charged (Au)Ag particles – the sheath. Such kind of structure is very compact and has a well-defined surface plasmon resonance band at 400-514 nm caused by gold and silver components. Concentration of PVP equal to 0.15-0.20 mg / ml is optimal for the formation of [PVP-(Au)Ag]. The most intense spectrum of light scattering was observed for the composite (Au)Ag, prepared in the presence of PVP with a mass of 360 kDa.

To evaluate the usefulness of the (Au)Ag core-shell nanoparticles in absorption nanospectroscopy, based on PRET resonant scattering spectra of their mixture with cationic/anionic water-soluble porphyrins were measured. Cationic Cu (II) -5,10,15,20-tetrakis (4-N-methyl pyridinium) porphyrin (CuTMPyP4) has a maximum extinction in the visible region at 550 nm (figure 5, spectrum 1), which satisfactorily overlaps with peak scattering of composite (Au)Ag (figure 5, spectrum 2) obtained in the medium with PVP (~ 360 kDa). Decrease in the intensity of band scattering at 530 nm and a dips at ~ 560 nm are detected for sol (Au)Ag depending on the concentration of porphyrin (figure 5). This behaviour is caused by the transfer of energy plasmon resonance to CuTMPyP4 molecules. After addition of FeTPPS in the composite sol (Au)Ag, synthesized in the presence of 0.11-0.15 mg / ml PVP of molecular weight ~ 360 kD, dip in the scattering spectrum at 413-415 nm, where porphyrin has an intensive Soret band [7], is found.

Apparently, the differences of light scattering spectra are due to various binding of these two porphyrins with [PVP-(Au) Ag]. Composite (Au)Ag, due to the odd negative charge (table 2), effectively binds cationic CuTMPyP4, but not anionic FeTPPS. Last one predominantly interacts with the cationic PVP, forming the core of [PVP-(Au) Ag], and only indirectly with the particles (Au)Ag, surrounding this core polymer.
Figure 5. Absorption spectrum of CuTMPyP4 (1) and the scattering spectra of composite (Au)Ag (2), its complex with 0.1 (3), 0.4 (4) and 2.0 (5) μM CuTMPyP4.

Figure 6. Absorption spectrum of 5 μM FeTPPS (1) and the scattering spectra of composite (Au)Ag (2), its complex with 1 (3), 10 (4) and 100 (5) μM FeTPPS.

4. Conclusion
In the water-ethanol mixture (1:1) (Au)Ag core-shell composite was synthesized in two steps, suitable for use in absorption spectroscopy, based on the effect of plasmon resonance energy transfer. For the course of synthesis of (Au)Ag the presence in the reaction solution of the polymer additive is important. It was established that the PVP - is the most effective additive, which not only promotes the formation (Au)Ag, but the structure [PVP-(Au)Ag], comprising a cationic polymer PVP and negatively charged nanoparticles (Au)Ag.

Colloidal solution of composite [PVP -(Au)Ag], comprising PVP having a molecular weight of ~ 360 kDa , is characterized by intense scattering of light in the 400-800 nm. With increasing concentration of the cationic CuTMPyP4 dip appears in the band of the light scattering, indicating that the porphyrin is directly bound with (Au)Ag. In the case of anionic FeTPPS - in the shortwave minimum of light scattering spectrum reflecting that the FeTPPS is directly bound with cationic PVP.

5. References
[1] Wang J, Kong L, Guo Z, Xua J and Liua J 2010 Synthesis of novel decorated one-dimensional gold nanoparticle and its application in ultrasensitive detection of insecticide J. Mater. Chem. 20 5271–79
[2] Choi Y, Park Y, Kang T and Lee L P 2009 Selective and sensitive detection of metal ions by plasmonic resonance energy transfer-based nanospectroscopy Nature nanotechnology 4 742–46
[3] Liu G L, Long Y, Choi Y, Kang T and Lee L P 2007 Quantized plasmon quenching dips nanospectroscopy via plasmon resonance energy transfer Nat Method 4 1015-17
[4] Khlebtsov N G, Bogatyrev V A, Dykman L A and Khlebtsov B N 2007 Gold plasmon resonant nanostructures for biomedical applications Russian Nanotechnologies 2 69-86
[5] Eryomin A N, Abakshonok A V, Agabekov V E, Zhavnerko G K, Panarin A Yu and Terekhov S N 2013 Spectra of resonant light scattering of gold nanoparticles Proceedings of the academy of sciences of Belarus. Series of chemical sciences 55-62
[6] Frens G 1973 Controlled nucleation for the regulation of the particle size in monodisperse gold suspensions Nature Phys. Sci. 241 20-22
[7] Fleischer E B, Palmer J M, Srivastava T S and Chatterjee A 1971 Thermodynamic and Kinetic Properties of an Iron-Porphyrin System J. Am. Chem Soc. 93 3162-67