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Synthesis of Hollow Bimetal Particles Based on Silver and Gold

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Abstract—A pioneering procedure is presented for the photochemical synthesis of aqueous solutions of hollow bimetal silver-gold nanoparticles in the presence of poly-*N*-vinylpyrrolidone. The structure and properties of synthesized nanocages were studied by the methods of high-resolution transmission electron microscopy, UV visible spectroscopy, and energy-dispersive X-ray structural analysis. The mechanism of the formation of AgAu nanocages was suggested on the basis of the experimental data.

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The presence of plasmon absorption bands in the visible region of spectrum is responsible for a wide application of copper, silver, and gold particles of nanometer size in optics and medicine. The frequency of plasmon vibrations in particles depends on the dielectric permittivity of the medium and on the morphology, shape, and size of the particles. For practical purposes it is important to shift the plasmon surface resonance to the low-frequency region, in this case silver and/or gold systems are the most promising. It can be made by using particles of aspheric shapes: nanowire [1], cubes [2], triangular nanoprisms [3], and also hollow structures: nanoshells [4], nanocages [5], and nanorattles [6]. Conversion of solid metal nanostructures to hollow structures improves their properties and makes them attractive for practical applications, as their density becomes less, and the surface area essentially increases as compared to bulk analogs. The preparation of nanocages is based on the reaction of galvanic substitution, the essence of which consists in the interaction of atoms of a metal (template) particle with a lower value of the standard electrode potential and metal ions with a higher potential. In this way hollow monometallic nanoparticle of gold [7] and palladium [8] were obtained. The most spread templates are silver particles, which in combination with the use of gold and palladium halide complexes provide a side product, a crystalline silver halide as a coarse dispersion. To prevent its formation, either process solutions with a concentration lower than the solubility product of silver halide $\sqrt{\mathrm{SP}}$ are used or the galvanic substitution reaction is carried out on heating. The result of the first strategy is the preparation of colloids of low concentration, which hampers the study of samples; and in the second case the preparation procedure resulted in dispersions polluted with a silver halide. Furthermore, to synthesize hollow bimetal AgAu particles, toxic organic solvents (for example, toluene [9]) are often applied, which limits further use of such colloids for biomedical purposes.

The aim of the present study was the development of a pollution-free procedure of the synthesis of highly concentrated aqueous solutions of bimetal silver-gold nanocages with a narrow size distribution.

To obtain hollow bimetal nanoparticles of AgAu composition, we developed a three-stage procedure of the synthesis based on (1) the photochemical reduction of silver(I) ions up to nanoparticles from aqueous solutions of silver nitrate, (2) the galvanic substitution of gold atoms for silver atoms in particles, and (3) the photochemical reduction of silver ions, which have passed into a solution in the second stage.

The first stage of the synthesis is aimed at obtaining silver nanoparticles serving further as a template. Dynamics of the absorption spectrum of a silver colloid obtained upon UV irradiation of silver nitrate aqueous solution with a concentration of 5×10^{-4} within 150 min is shown in Fig. 1. It is seen that the band of surface plasmon resonance with a maximum at 414 nm characteristic of metal silver nanoparticles dominates in the spectrum. Intensity of the band increases in the

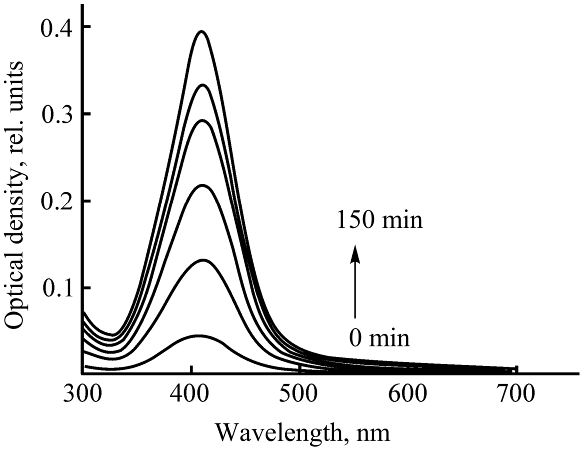

Fig. 1. Dynamics of the absorption spectrum of a silver colloid obtained upon 150 min UV irradiation of silver nitrate aqueous solution with a concentration of 5×10^{-4} M containing 1.5% PVP-40. Thickness of the photolyte layer 0.2 cm.

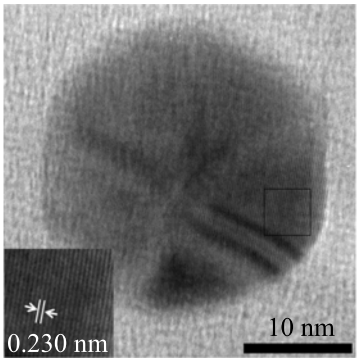

Fig. 2. The TEM image of a silver nanoparticle with twinning defects. A magnified image of a crystal lattice with average interplanar space of 0.230 nm is shown in the insert.

irradiation course, the position of the maximum remaining unchanged, which is caused by the formation of particles of presumably the same size. The plasmon absorption appears after an induction period of 8 min. The induction period corresponds to the formation and accumulation of nuclei of particles, clusters [10] characterized by absorption in the ultraviolet spectral region. The acceleration of the formation of particles after the induction period is caused by the increase in the surface area of nuclei at their growth and, as a consequence, proportional increase in the diffusion field expansion. As the irradiation time increases (τ > 250 min), the concentration of Ag(I) ions in the vicinity of nuclei decreases as a result of their consumption, and the growth of silver particles changes to a diffusion mode. The plateau on the kinetic curve corresponds to this process. The colloid phase formation is accompanied by a change in the photolyte color, which varies from lemon-yellow up to yellow-green depending on irradiation time.

Starting from known initial concentration of silver nitrate and assuming that all Ag(I) ions were reduced in the course of the photolysis, we have calculated the extinction coefficient ε_1 related to the concentration of metal atoms on the basis of optical density of a plateau height. The value of the extinction coefficient at the wavelength of 414 nm was 1.5×10^4 l mol^{-1} cm^{-1}, which agrees well with ε values for silver colloids obtained by radiolysis ($1.5–2.8\times10^4$ l mol^{-1} cm^{-1}) [11].

The weakly expressed band with a maximum at 612 nm in the optical spectrum of a silver colloid presented in Fig. 1 can be assigned to the absorption of the chain agglomerates of nanoparticles. The formation of agglomerates must not be ruled out at the use of poly-*N*-vinylpyrrolidone with a high molecular weight, which can give rise to a growth of several contacting metal particles along a long polymer chain. The observed low-intensive absorption band along with the main maximum at 414 nm is characteristic of the obtained silver colloids, as they are present in all optical spectra recorded for analogous samples.

The data of transmission electron microscopy (TEM) have shown (Fig. 2) that silver particles are of the polyhedral shape. The inhomogeneity of the image contrast present in the photograph as the alternation of light and dark sectors in a separate particle points to the pentagonal symmetry of the arrangement of twinning boundaries and to the presence of twinning defects. The interplanar space in the crystal lattice of the obtained silver nanoparticles measured by the data of high-resolution TEM was 0.230 nm, which corresponds to the Ag (111) plane [12, 13]. Particles with a similar symmetry are realized in the form of tenfold twinning decahedral and twentyfold twinning icosahedron structures. These structures are characterized by the least surface energy attained due to dense packing of the surface atoms [14, 15], and they predominate among particles of the obtained samples of colloid silver. The granulometric composition of the colloid based on measuring diameter of an arbitrary sample of 190 particles is presented as a bar graph in Fig. 3. The average diameter of particles appeared to be 33 nm at a standard deviation σ_a of 10%.

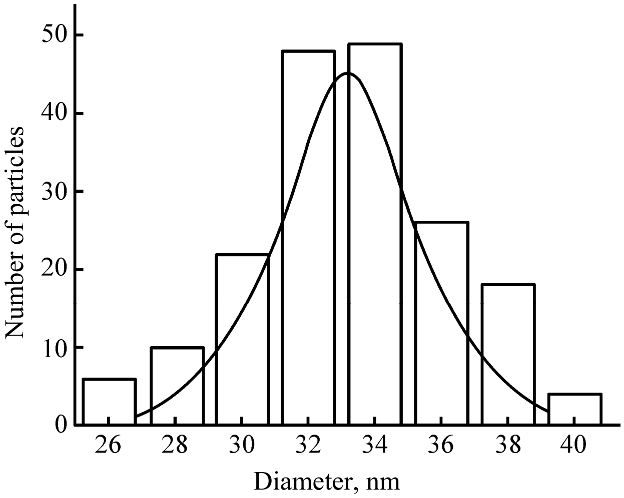

Fig. 3. Bar graph of silver nanoparticles obtained photochemically. *d* 3 nm, σ 10%.

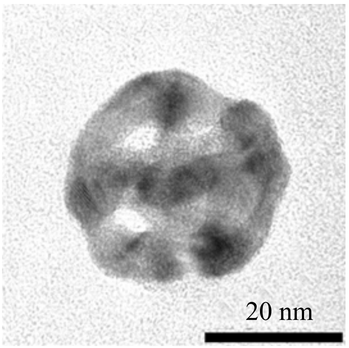

Fig. 4. The TEM image of a hollow bimetal AgAu nanoparticle after a dark reaction of galvanic substitution.

The value of the extinction coefficient ε_2 related to the concentration of silver particles was calculated on the basis of the high-resolution TEM images allowing particle size and their morphology to be revealed. At the initial concentration of Ag(I) ions in photolyte of 5.0×10^{-4} M, assuming that their reduction is complete, the concentration of silver particles was 4×10^{-10} M, and the extinction coefficient, 1.3×10^{9} l mol^{-1} cm^{-1}. This value agrees well with the values of extinction coefficients of silver colloids obtained by a chemical reduction [16].

Photochemically synthesized silver particles were used further as templates for the formation of a gold shell. For this purpose an aqueous solution of $HAuCl_4$ was added to silver dispersions in the 3:1 proportion of Ag:Au atomic concentrations. The process can be represented by the following scheme.

$$3Ag^0_{particle} + AuCl^-_{4sol} \rightarrow Au^0_{particle} + 3Ag^+_{sol} + 4Cl^-_{sol}.$$

The difference in the standard electrode potentials of the pairs of gold $E^0(AuCl_4^-/Au^0 + 4Cl^-)$ 0.99 V and silver $E^0(Ag^+/Ag^0)$ 0.79 V predetermines spontaneous passing of the galvanic substitution reaction between silver particles and Au(III) ions added to the dispersion.

When a solution of $HAuCl_4$ is added to a silver colloid the color of the reaction mixture varies from green through brown to intensively dark blue. The band of plasmon surface resonance of the dispersion shifts to 890 nm. This value does not correspond to absorption bands of solid monometallic silver and gold nanoparticles, for which the maxima of plasmon surface resonance bands fall to 400–420 and 520–530 nm, respectively. The characteristic absorption bands of solid bimetallic AgAu nanoparticles with the alloy structure fall on the interval between plasmon surface resonance bands of separate components with maxima not exceeding 500 nm [17]. Wide bands in the near infrared region were assigned [7] to porous gold shells of various width. The data of TEM confirm the hollow structure of forming particles (Fig. 4).

Using simple calculations (reaction scheme), we can determine a stoichiometric ratio of silver and gold atoms (3:1), which corresponds to the formation of monometallic gold shells as a result of a galvanic substitution reaction. It is possible on condition that all Au(III) ions have entered the substitution reaction. In practice silver can be detected in shells, which is caused, first, by gradual consumption of Au(III) ions in the vicinity of particles, therefore after a certain time the precipitation of gold changes to a diffusion mode; second, by the formation of Au(I) species, which do not participate in the subsequent sorption on the surface of silver particles; and third, by screening surface of silver particles by a layer of gold hampering diffusion of Ag(I) ions in solution.

Working concentrations of substances entered in a substitution reaction exceed 10^{-4} M that defines the precipitation of Ag(I) ions formed according to the scheme in the form of silver chloride AgCl (SP_{AgCl} 1.8×10^{-10}). The proper light sensitivity of AgCl promotes silver regeneration, therefore, to synthesize bimetal AgAu nanocages with an adjustable silver content and controlled shift of plasmon surface resonance band to the longwave spectral region, and

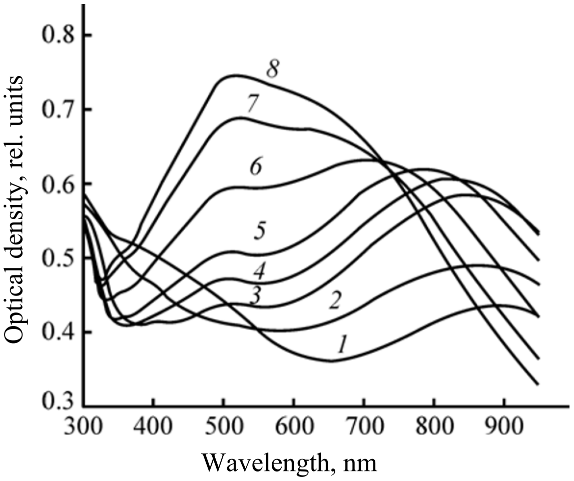

Fig. 5. Dynamics of the plasmon absorption spectrum of a bimetallic AgAu colloid in the course of irradiation by UV light within: (*1*) 0, (*2*) 1, (*3*) 10, (*4*) 20, (*5*) 30, (*6*) 40, (*7*) 50, (*8*) 80 min. Thickness of the photolyte layer 0.5 cm.

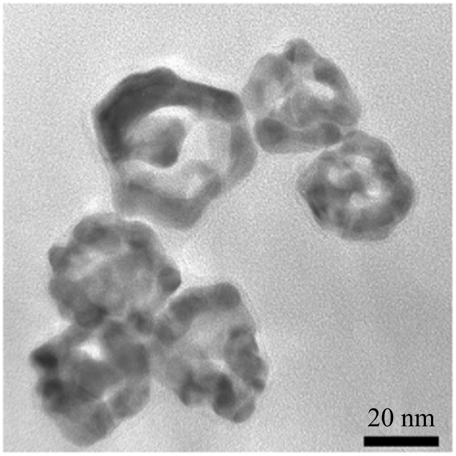

Fig. 6. The TEM image of bimetallic AgAu nanoparticles.

also to prevent silver losses, we used a secondary irradiation of the dispersion by UV light after the galvanic substitution reaction. The advantage of such approach is the possibility to use concentrated solutions of silver and gold precursors and, as a consequence, to obtain highly concentrated dispersions.

We have determined experimentally that the optimal time of the secondary irradiation is 80 min (Fig. 5). Exposure of samples of dispersions to UV light is accompanied by the following spectral changes: displacement of the maximum of plasmon surface resonance of particles to the short-wave region; growth of the intensity of plasmon surface resonance bands; appearance of a minimum at 320 nm in the spectrum. By virtue of special features of silver optical characteristics [10], bands of plasmon surface resonance of its particles are displaced to the short-wave region (380–500 nm), are highly intensive (surpass the intensity of bands of colloid gold of analogous concentration by two orders of magnitude), and have a minimum at 320 nm, which makes it possible to identify them easily in spectra of mixtures with gold particles. Hence the observed changes can be assigned to the photochemical reduction of Ag(I) ions passed into solution as a result of the galvanic substitution reaction and to the formation of bimetal colloids of the AgAu composition.

The data on the geometry and size of synthesized nanoparticles are presented in Fig. 6. It is seen from the TEM image that the shape of the obtained particles is close to the initial decahedron. Their central part is practically “transparent” for a transmitting electron beam, which can be interpreted as the presence of hollows. It is seen from the microphotographs that the particles have characteristic spherical “knots” on apexes of decahedron templates connected by thin “isthmuses.”

It is seen from the bar graph in Fig. 7 that the effective diameter of nanocages is 39 nm. The average size of hollows inside the obtained structures is 25 nm, which is slightly less than the average initial diameter of silver nanoparticles. A similar discordance in sizes between a concavity of a final bimetallic particle and an initial nucleus is caused by a mutual diffusion between gold and silver ions/atoms, i.e. silver diffuses from a template surface, whereas gold penetrates into it.

The analysis of high-resolution microphotograph (Fig. 8) has shown that hollow nanoparticles have a crystal structure, however it does not allow us to prove unambiguously the bimetallic nature of the product, as the calculated values of interplanar spaces d in the crystal lattice appear practically equal and identical to the interplanar space (111) in the initial silver nanoparticles. This result is natural owing to a similarity of parameters of gold and silver crystal lattices. At the same time the calculated values of interplanar spaces show that the surface of particles is free from silver chloride, the $d_{(111)}$ value of which is 0.318 nm [19].

Singular elemental analysis for the determination of qualitative and quantitative composition by means of energy-dispersive X-ray spectral analysis has shown (Fig. 9) that the peaks of gold Mα (2.1 keV), Lα

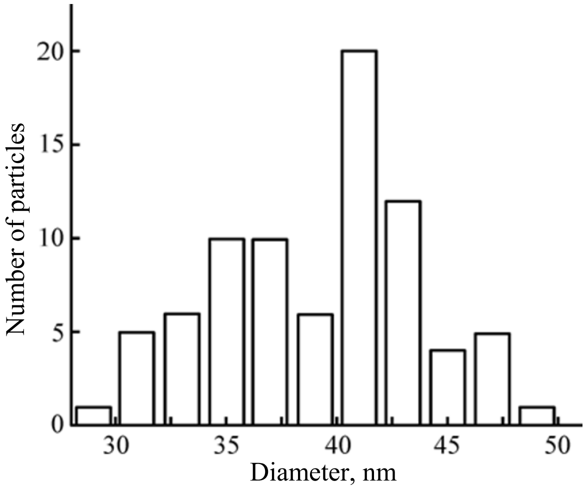

Fig. 7. Bar graph of bimetallic AgAu nanocages. *d* 38.9 nm, σ 12%.

(9.7 keV), and Lβ (11.4 keV), and also characteristic peaks of silver Lα and Lβ at 2.9 and 3.15 keV, respectively, are present in the spectra, which confirms the presence of both metals in each separate particle under study. Quantitative analysis of nanoparticle for the content of the metals has shown that the Ag:Au ratio is equal to 2:1 (at %). The high content of silver points to the photochemical reduction of Ag(I) ions on the surface of nanocages. Therewith it is necessary to point out that peaks characteristic of chlorine are absent from the spectra.

The experimental data set allows us a conclusion that the sequential synthesis results in the formation of hollow bimetallic particles of the composition AgAu, and the developed procedure makes it possible to obtain high-purity particles with a ratio of atoms necessary for practical use and with controlled adjustment of the plasmon resonance over the range from 515 up to 900 nm. It is mentioned in the literature that samples with a gold content less than 15% and an effective diameter of particles of 50 nm [5] were obtained without using UV radiation as a driving force in the case of the preparation of true bimetallic colloids. The developed procedure allows us to prepare aqueous dispersions of hollow silver-gold nanoparticles of a smaller size with a gold content of ~33% providing absorption in the near IR region, which is more promising for their practical use. Furthermore, the photolysis essentially reduces losses of silver precipitated in the form of chloride, which are imminent in chemical methods of the synthesis.

The formation of bimetallic nanocages is a complicated multistage process, which can be presented as follows on the basis of the experimental data (Fig. 10). The substitution reaction begins at crystal sites with a high energy. For silver particles faceted by planes (111) (Fig. 10a) such sits are the junctions of facets, apexes and edges. The TEM data have confirmed (Fig. 10b) a preferential metal precipitation in the vicinity of apexes of decahedrons, and then also of edges (Fig. 10c). Therewith the TEM analysis has shown that hollows preferentially start to be formed and then progress on the (111) planes of silver particles.

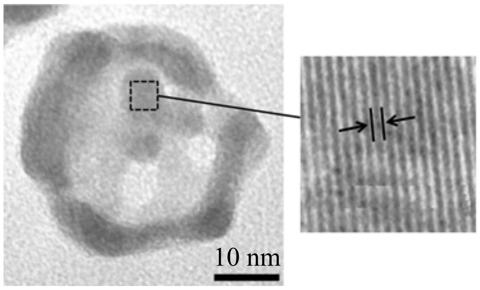

Fig. 8. Microphotographs of a bimetallic AgAu nanocell. A magnified image of a crystal lattice with average interplanar space of 0.230 nm is shown in an insert.

According to the reactions scheme, Au(III) ions diffusing to a silver particle are reduced either up to Au(I) or Au(0). The Au(0) atoms are precipitated on a silver nucleus, replicating its morphology due to the fact that gold and silver have the face-centered cubic packing with constants of lattices close in values. In turn, silver in the form of Ag(I) ions leaves particle surface preferentially from the (111) plane free from gold. Vacancies formed on the (111) silver facet become active sites for further substitution reaction. Silver atoms diffuse from the volume to a reaction place and react with Au(III), forming gold atoms precipitated on the silver template surface.

Simultaneously with the substitution reaction the formation of the Ag/Au alloy on the silver-gold boundary defined by the presence of vacancy defects is possible. According to the reaction stoichiometry, three silver atoms are consumed for the formation of one gold atom, which leaves a huge amount of vacancies in the template. These latter promote the mutual migration of silver and gold atoms and their alloying. The vacancies remaining upon the migration of silver and gold diffuse and coalesce through Ostwald ripening, counteracting an increase in the total surface energy. It results in broadening hollows on the particle surface and shortening edges between them. In this stage nanocages with porous sides are formed from each silver particle (Fig. 10d).

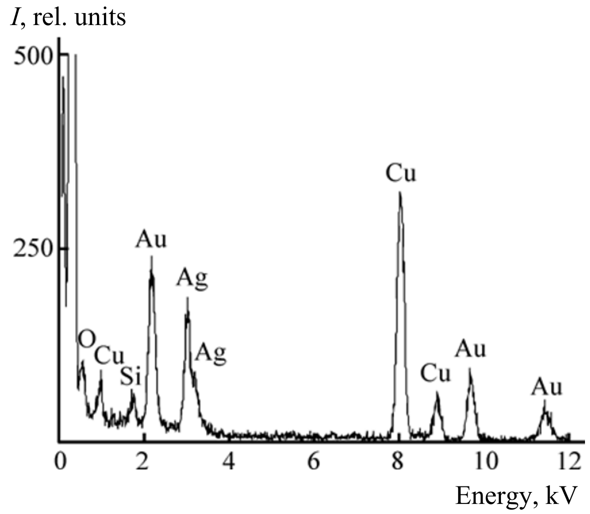

Fig. 9. Representative energy-dispersive X-ray spectrum of a bimetallic nanocage AgAu.

The UV irradiation of a dispersion results in the reduction of Au(I) and Ag(I) ions available in a solution up to atoms, which form a shell of bimetallic nanoparticles. As a whole, the system represents the hollow nucleus – gold-silver shell structure (Fig. 10e).

Thus, it is expedient to use the procedure of three-stage chemical/photochemical synthesis for the synthesis of hollow bimetal nanoparticles of the pentagonal symmetry (nanocages) with a silver-gold composition. The use of the galvanic substitution reaction in combination with the photolysis makes it possible to regulate purposefully the content of metals in nanocages and to realize controlled adjustment of plasmon resonance within the range of 415–900 nm. The nanocages are characterized by a high purity confirmed by the energy-dispersive X-ray structure analysis data and by the stability within three years of storage in air.

EXPERIMENTAL

The following reagents were used for the synthesis of silver-gold bimetallic nanoparticles: hydrogen tetrachloroaurate(III) trihydrate $HAuCl_4{\cdot}3H_2O$ (analytically-pure grade Acros organics, >99%; "P.L.Voikov Open Society Chemicals plant") and silver nitrate $AgNO_3$ (analytically-pure grade Fisher Sci., > 99%; Reakhim). As a stabilizer of metal nanoparticles we applied PVP-40 (MM 40000, Sigma-Aldrich). The reagents were used without additional refining. Nanoparticles were synthesized in aqueous solutions, deionized water (resistance of 18×10^6 Ω cm) was used in all experiments. Process solutions for the photochemical synthesis of nanoparticles of mono-metals were prepared by the addition of weighted samples of silver(I) and gold (III) compounds providing their concentration of 5×10^{-4} M in 0.5–2% aqueous solutions of poly-*N*-vinylpyrrolidone.

We used for irradiation a monochromatic light of an RPR-100 photoreactor consisting of 15 mercury

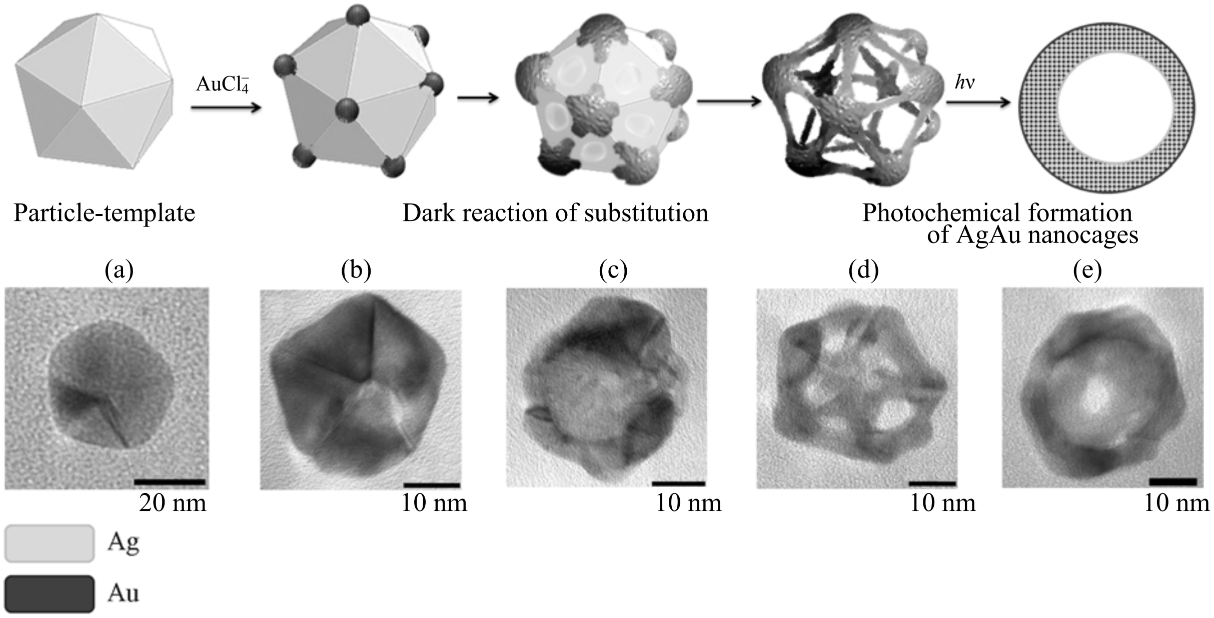

Fig. 10. Scheme of the mechanism of formation of AgAu bimetallic nanocages. See notations in the text.

lamps, each of 35 W power. The excitate wave length was 254 nm. The intensity of incident light of the monochromatic source was 1.7×10^{16} quantum/(cm^2 s). Light flux intensity was determined with a standard ferrioxalate actinometer [20]. Directly before carrying out an experiment a photolyte was deaerated by passing through nitrogen.

To obtain dispersions, solutions of metal compounds were irradiated in quartz cells K10 with the length of optical path 10 mm (OJSC LOMO, St. Petersburg). Absorption spectra of samples of colloids were recorded on a Varian Cary 50 Bio spectrophotometer within the range of 300–1000 nm in 0.2 nm steps of measuring. Elemental composition of the prepared mono- and bimetallic colloids was determined by the method of energy-dispersive X-ray structure analysis of separate nanoparticles, which was carried out using a Thermo Electron attachment and Noran System SIX software coupled with TEM. The morphology of mono- and bimetallic nanoparticles was studied with the help of transmission electron microscopes Jeol SX-100 (accelerating voltage of 100 kV) and Jeol JEM-2010 (accelerating voltage of 200 kV). Samples for TEM were prepared by a four-fold centrifuging of colloids and separating of a precipitate, their redispersing in methanol, subsequent depositing several drops of an alcohol dispersion on a copper net covered by a thin layer of amorphous carbon (200 mesh, Ted Pella, Inc., USA), and drying in air. Domination of energy lines of copper in the recorded spectra is caused by the substrate nature. An indistinct signal at 1.7 keV characteristic of silicon is an artifact, but it is present in all samples. It is connected with the fact that silicon is contained in the composition of grease for rubber rings on a microscope holder, which leads to a negligible contamination of substrates with samples of nanoparticles.

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