

## Formation of monolayer ensembles of branched gold nanoparticles

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Monolayer film structures based on branched gold nanoparticles (Au NPs) with  $(80\pm 20)$  nm average NPs size were synthesized using template synthesis on functionalized glass substrates. The obtained materials have a high distribution uniformity of isolated Au NPs in a monolayer. The study of the surface profile of monolayer ensembles showed that NPs have a three-dimensional shape, the average roughness of the films surface is 20–30 nm, which corresponds to the length of the sharp NP branches  $(25\pm 5)$  nm). The optical properties of Au NPs monolayer ensembles were studied.

**Keywords:** branched gold nanoparticle, monolayer, film, optical properties.

Методом темплатного синтеза на функционализированных стеклянных подложках получены стабильные монослойные пленочные структуры на основе разветвленных наночастиц золота со средним размером наночастиц  $(80\pm 20)$  нм. Полученные материалы обладают высокой однородностью распределения изолированных наночастиц золота в монослое. Изучение профиля поверхности монослойных ансамблей показало, что наночастицы имеют объемную форму, средняя шероховатость пленок составляет 20–30 нм, что соответствует значению длины острых ответвлений наночастиц  $(25\pm 5)$  нм). Исследованы оптические свойства монослойных ансамблей наночастиц золота.

**Отримання моношарових ансамблів розгалужених наночастинок золота.**

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Методом темплатного синтезу на функціоналізованих скляних підкладках отримані стабільні моношарові плівкові структури на основі розгалужених наночастинок золота з середнім розміром наночастинок  $(80\pm 20)$  нм. Отримані матеріали мають високу однорідність розподілу ізолюваних наночастинок золота в моношарі. Вивчення профілю поверхні моношарових ансамблів показало, що наночастинки мають об'ємну форму, середня шорсткість плівок становить 20–30 нм, що відповідає значенню довжини гострих відгалужень наночастинок  $(25\pm 5)$  нм). Досліджено оптичні властивості моношарових ансамблів наночастинок золота.

## 1. Introduction

In recent decades branched Au NPs have been increasingly used in many fields, including catalysis [1, 2], Raman spectroscopy and analytical chemistry [2–4], etc. due to the presence of NPs sharp branches where significant electric field strength increase is observed caused by the excitation of delocalized electrons of Au NPs by the electromagnetic wave [5].

Since using colloidal solutions of branched Au NPs is limited with their aggregative instability, more attention is paid to the creation of stable materials based on gold nanoparticles in the form of films. The main requirements for film structures are: monodispersity of NPs with the ability of controlling their size and morphology; homogeneity of NP distribution over the substrate surface; NP isolation, absence of aggregated fraction; film insensitivity to the environment.

The most common methods of forming film structures are the self-assembly method (SAM) [6, 7], layer-by-layer assembly (l-b-l method) [8–10], and also the template method [11, 12]. There is also a number of the films formation methods based on the destruction of the crystal lattice of metallic gold under high-voltage current action [5], the vacuum deposition method [6]. The main disadvantage of this method is the size and shape NPs distribution in the film structure, which leads to the film surface inhomogeneity. Therefore, to obtain monodisperse NPs of given morphology, condensation (chemical) methods are often used. The SAM [7, 8] and l-b-l method [9–11] are based on the adsorption of NPs, formed in a colloidal solution, onto the surface of functionalized substrate. The substrate immersion into colloidal solution can lead to NPs coagulation and, as a result, to the formation of an inhomogeneous film with the fraction of aggregated NPs.

Previously, we obtained film structures based on branched Au NPs by SAM [7] and l-b-l method [9]. The prepared films have framework (arched) structure, large number of pores, fraction of aggregated NPs, which narrows their application field a lot. Concerning this, it becomes necessary to develop method of films formation that would ensure NPs monodispersity, isolation and homogeneous distribution in the ensemble formed on the substrate surface. As opposed to SAM and l-b-l method, the template method assumes the realization of a controlled nucleation process and the subsequent growth of NPs directly on the surface of

the functionalized substrate (template), which avoids substrate immersing into the colloidal solution, ensures high NPs size homogeneity and allows controlling the filling density of the substrate surface [13].

For today, the problem of obtaining monolayer films based on metal NPs using template synthesis method is little studied, the aspects of material science of the Au NPs ensembles formation are insufficiently studied, thus the aim of this work was to obtain stable homogeneous branched Au NPs monolayer ensembles with preservation of NPs individual properties, as well as to study the optical properties of the obtained materials.

## 2. Experimental

Commercial chloroauric acid  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  ( $\geq 99.9\%$ ); silver nitrate  $\text{AgNO}_3$  ( $\geq 99.8\%$ ); ascorbic acid  $\text{C}_6\text{H}_8\text{O}_6$  ( $\geq 99.0\%$ ); (3-aminopropyl)triethoxysilane (APTES)  $\text{C}_9\text{H}_{23}\text{NO}_3\text{Si}$  ( $\sim 98.0\%$ ), sulfuric acid  $\text{H}_2\text{SO}_4$  ( $\sim 98.0\%$ ); hydrogen peroxide  $\text{H}_2\text{O}_2$  ( $\sim 38.0\%$ ), ethyl alcohol  $\text{C}_2\text{H}_6\text{O}$  ( $\sim 96\%$ ) were used as received without further purification.

Monolayer ensembles of branched Au NPs were formed by the method of template synthesis. The formation of ensembles was carried out on a surface of  $1 \times 1 \text{ cm}^2$  glass slides.

At the first stage, the surface of glass substrates was modified by APTES molecules, which interact with the silanol groups of the glass and due to the presence of positively charged amino groups, form the active layer, which ensures Au precursor adsorption from the solution [11]. Glass slides were cleaned by piranha solution (30 %  $\text{H}_2\text{O}_2$  : 98 %  $\text{H}_2\text{SO}_4 = 1:10$ , v:v) at  $25^\circ\text{C}$  for 8 hours to remove the adsorbed impurities, then the slides were sonicated in bidistilled water several times. (Caution: piranha solution is a powerful oxidizing agent). Modification of glass surface was carried out using APTES. The slides were immersed into 5 % (v/v) APTES solution in ethanol, the solution was heated and boiled during 90 minutes keeping the solution volume stable. Modified glass slides were sonicated in ethanol and bidistilled water several times.

Adsorption of the tetrachloroaurate (III) ions on glass occurs due to the electrostatic interaction between negatively charged  $\text{AuCl}_4^-$  ions and positively charged  $\text{NH}_3^+$  groups of the modified substrate surface. Modified glass slides were subsequently immersed into  $2 \cdot 10^{-4} \text{ M}$   $\text{HAuCl}_4$  solution (20 mL), 0.008 mL of 0.05 M  $\text{AgNO}_3$  was

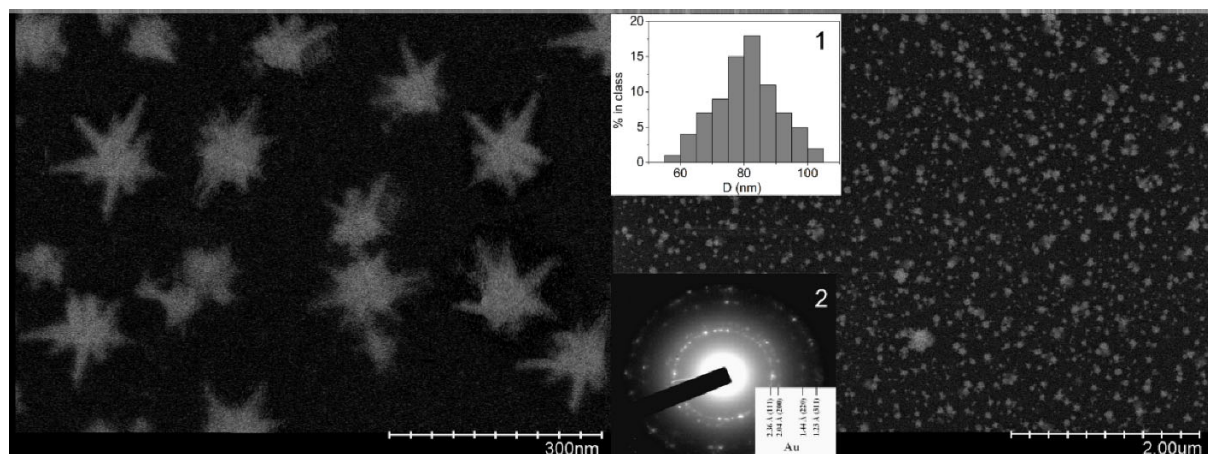


Fig. 1. SEM images of monolayer films surface with  $L = 100$  nm thickness at different magnification, insert 1 — NPs size distribution in the monolayer, insert 2 — Au NP electron microdiffraction in the ensemble.

added under stirring, the solution was vigorously stirred for 10 minutes, then 0.8 mL of 0.01 M ascorbic acid was added. The solution was stirred for 1 hour, then substrates were kept in Au NPs colloidal solution for 1, 2, 3 and 5 hours, then washed with water several times to remove Au NPs adsorbed from the solution. To further fill the substrates surface, the 2<sup>nd</sup> and the 3<sup>rd</sup> cycles were performed similarly.

The formation of nonspherical Au NPs occurs due to the realization of the underpotential deposition of silver atoms on the Au NPs surface [2, 14–17]. At the first stage of nonspherical Au NPs growth on the modified substrate surface  $\text{AuCl}_4^-$  ions are reduced by ascorbic acid, since  $\text{AuCl}_4^-/\text{Au}^0$  reduction potential is higher than  $\text{Ag}^+/\text{Ag}^0$  potential. After the formation of Au NPs on the substrate surface, which are the centers of nucleation,  $\text{Ag}^+$  ions are reduced by ascorbic acid on the Au NPs crystal faces surface at a potential value less than the  $\text{Ag}^+/\text{Ag}^0$  standard reduction potential [14]. In the result, silver atoms are adsorbed on the Au seed surface facets with the highest surface energy, forms monolayers, selectively stabilizes  $\{110\}$ ,  $\{310\}$ ,  $\{720\}$  Au facets [2, 15–17]. Anisotropic Au NP growth leads to the formation of lateral branches, which are grown on other facets with lower surface energy. After stabilization  $\{110\}$  facets Au adsorbs on  $\{111\}$  facets, which leads to Au branches formation [17].

Morphology and structure of the films based on Au NPs were studied by means of ultra-high resolution scanning electron microscopy (UHR FE-SEM) (Hitachi S-5500, Hitachi High-Technologies Corp., Japan), and scanning probe microscopy (SPM)

(SPM-9600, Shimadzu Corp., Japan) in the non-contact mode at a frequency of 0.2 Hz using cantilever PPP-NCHR. The film thickness was determined using the "step method" based on measuring the difference between the artificially formed groove and the film. The roughness analysis was carried out along a horizontal line along the center of the SPM image with an area of  $10 \times 10 \mu\text{m}^2$ . The size distribution of NPs in films was obtained by the linear intercept method. The room temperature absorption spectra were measured over a range from 0.4 to 1.1  $\mu\text{m}$  with a Lambda-35 spectrophotometer (Perkin-Elmer, USA).

### 3. Results and discussion

Monolayer ensembles of branched Au NPs were obtained directly on the substrate surface by the template method. A study of the morphology of the film surface showed that the average NP size determined from SEM images (Fig. 1) is  $(80 \pm 20)$  nm, the average number of branches is  $(9 \pm 2)$ , and their length is  $(25 \pm 5)$  nm, NPs are evenly distributed over the substrate surface without significant aggregation. The represented histogram (Fig. 1, insert 1) indicates to monomodal distribution of NPs size in the ensemble. Au NPs in ensemble are crystalline, the diffraction rings in electron diffraction pattern corresponding to the  $\{111\}$ ,  $\{200\}$ ,  $\{220\}$ ,  $\{311\}$  facets can be indexed to the face centered cubic unit cell structure of Au NPs (Fig. 1, insert 2).

Surface investigations of Au NPs ensembles by the SPM method showed that the average film thickness ( $L$ ) after the 1<sup>st</sup> cycle (Fig. 1) is 100 nm, surface roughness ( $R_a$ ) at a base length  $l = 15 \mu\text{m}$  is 20 nm

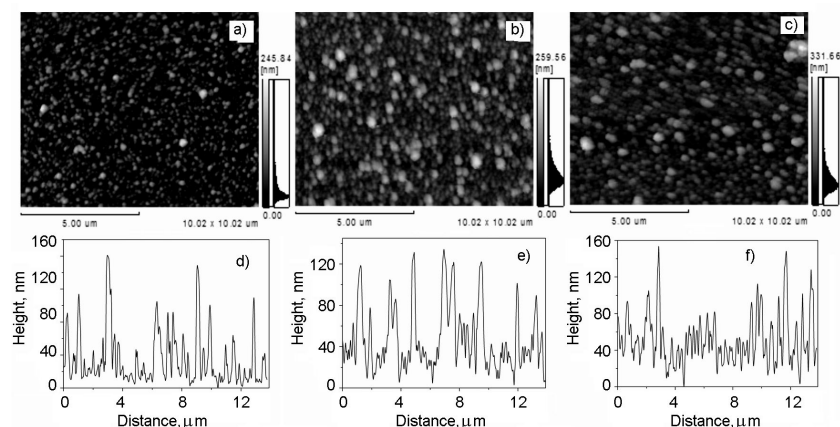


Fig. 2 SPM images of films after the 1<sup>st</sup> ( $L = 100$  nm), 2<sup>nd</sup> ( $L = 120$  nm) and 3<sup>rd</sup> ( $L = 120$  nm) cycles (a-c) and surface profile of the monolayer ensembles (d-f).

(Fig. 2a). Since the average film thickness  $L$  is close to the average NP size value, it can be concluded that NPs monolayer is formed on the substrate surface. Further filling of substrate surface by Au NPs leads to increasing of the films thickness  $L$  (Fig. 2b, c) and their roughness  $Ra$  (Fig. 2e, f), the average roughness  $Ra$  for  $L = 120$  nm films thickness is 30 nm.

The fact that the surface profile of monolayer ensembles deviates by 20–30 nm within the basic length  $l = 15$   $\mu\text{m}$  can indicate that Au NPs have a three-dimensional shape, rather than a planar, since the average length of the sharp branches (Fig. 1) corresponds to the surface roughness ( $Ra$ ) value of branched Au NPs monolayer ensembles.

The optical properties of the formed monolayer ensembles of branched Au NPs were investigated. In the absorption spectra of monolayer ensembles two maxima are observed, which correspond to the longitudinal (900–1010 nm) and transverse (580–620 nm) peaks of localized plasmon resonance (LPR), (Fig. 3a). The LPR peak in the region of 620 nm for films with  $L = 100$  nm thickness can be associated with the delocalized electrons (plasmons) excitation of Au NP core, and its position depends on the core size [14]. The maximum at 900–1000 nm refers to the oscillations of electrons on NPs sharp branches and its position is determined by the number and length of Au NPs sharp branches [1, 2, 14]. Both LPR bands are broadened, which is due to the branched structure of NPs and their size distribution. When film thickness increases to  $L = 120$  nm, the LPR maximum shifts to the shortwave region of the spectrum (from 620 to 583 nm), which can be related to the contacts of closely located NPs in the monolayer [18].

The presence of a maximum in the long-wave region is a distinctive feature for NPs with long and sharp branches. For example, for branched Au NPs colloidal solutions with a smaller length of NP branches (branch length is  $(13.1 \pm 5.0)$  nm, NPs size is  $(50 \pm 24)$  nm, [19] there is one maximum in the region of 600 nm, representing the superposition of LPR of NP core and branches. It should also be noted that the LPR maximum position is affected by the shape of the branches: the sharper and longer are NP branches, the more LPR maximum is shifted to the longwave region of the spectrum [2].

Varying the time, during which the substrates are in a NPs colloidal solution, in the range of 1 to 5 hours has shown that the intensity of the lines in the absorption spectra changes insignificantly (Fig. 3b). This suggests that the monolayer films formation occurs due to the realization of the nucleation process and the further growth of branched NPs directly on the substrate surface, and not due to the adsorption of NPs formed in the colloidal solution to the substrate surface. The study of absorption spectra in time has shown that the position and intensity of the LPR maxima don't change for 4 months, which indicates the stability of Au NPs monolayer ensembles to the environment.

The obtained Au NPs monolayer ensembles are promising as substrates for enhancement of fluorescence and Raman scattering spectra [18] due to the excitation of NP localized plasmons, as well as the formation of so-called "hot zones" or "hot spots", which are a superposition of electromagnetic fields of closely located NPs. In contrast to films based on planar gold structures, for example, flat nanoprisms [13], in which "hot zones" can be formed near inho-

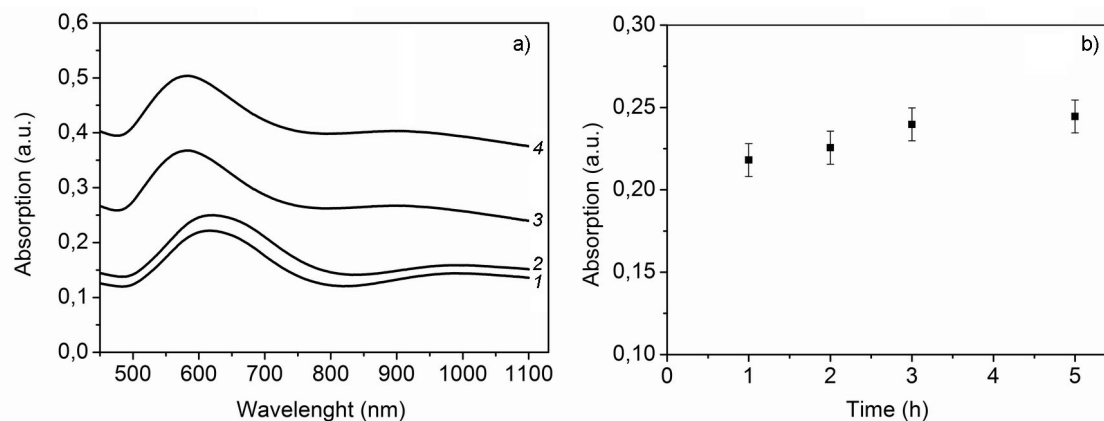


Fig. 3. (a) Absorption spectra of monolayer ensembles of branched Au NPs after (1) the 1<sup>st</sup> cycle and aging during 1 hour, (2) the 1<sup>st</sup> cycle and aging during 5 hours, (3) the 2<sup>nd</sup> cycle and aging during 1 hour, (4) the 3<sup>rd</sup> cycle and aging during 1 hour; (b) the dependence of the maximum intensity in plasmon resonance spectra on the time of substrates aging in the colloidal solution.

mogeneities of NP surface (sharp ends of nanoprisms), in the case of branched Au NPs on the substrate surface formation of "hot zone" near each sharp branch is possible, which is confirmed by theoretical calculations of the electromagnetic field distribution near the branched Au NP [19].

#### 4. Conclusions

The possibility of obtaining monolayer ensembles of branched Au NPs by the template method with 80 nm average NPs size on glass substrates is demonstrated. Parameters that allow to obtain ensembles of isolated NPs directly on the substrate surface and to avoid the NPs aggregated fraction have been established. It is shown that the formation of sharp branches occurs in all growth directions. In the absorption spectra (plasmon resonance) of monolayer ensembles 2 maxima in the region of 580–620 nm and 900–1000 nm are observed.

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