Synthesis and characterization of branched gold nanoparticles

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In this paper we demonstrate obtaining and properties of gold nanostars and nanoflowers with average size in the range of 50 to 70 nm and the size dispersion <20 %. Transmission electron microscopy and photoelectron spectroscopy were used to study the composition and structure obtained Au nanoparticles, optical properties their colloidal solutions were studied.

Keywords: gold nanostars, gold nanoflowers, optical properties.

Приведены результаты по получению и изучению свойств нанозвезд и наноцветов золота со средним размером в диапазоне от 50 до 70 нм и дисперсией по размерам <20 %. Методами просвечивающей электронной микроскопии, фотоэлектронной спектроскопии исследованы состав и структура полученных наночастиц Au, изучены оптические свойства их коллоидных растворов.

Отримання та характеризація розгалужених наночастинок золота. *Т.Г.Бейник, Н.А.Матвєєвська, М.В.Добротворська, О.С.Гарбуз, Д.Ю.Косьянов, В.І.Вовна, А.А. Ворновських С.І.Богатиренко.*

Наведено результати з отримання та вивчення властивостей нанозірок і наноквітів золота із середнім розміром у діапазоні від 50 до 70 нм і дисперсією за розмірами <20 %. Методами просвічуваючої електронної мікроскопії, фотоелектронної спектроскопії досліджено склад і структуру отриманих наночастинок Au, вивчено оптичні властивості їх колоїдних розчинів.

1. Introduction

The search of new nanostructured materials for creating selective biological and chemical sensors, new optical and nonlinear optical devices is an actual problem of modern materials science. Materials based on monodisperse metal nanoparticle (NP) ensembles (gold, silver, platinum, copper) are widely used in many fields, including nanomedicine [1], surface-enhanced Raman spectroscopy (SERS) [2, 3], biotechnology

[4], catalysis [5, 6], electronics [7], non-linear optics [8].

Materials based on Au NPs are widely used as SERS substrates for determining trace concentrations of various substances [9]. SERS intensity of molecules adsorbed on metal surface strongly depends on metal surface morphology. When substrates based on gold nanostars (Au NSs) and nanoflowers (Au NFs) are used, there is significant SERS-signal enhancing [3] due to the local increasing of electromagnetic field on the ends of sharp tips [10], strongly depending on shape and size of Au NPs. There is a great deal of current interest in the development of new methods for different Au NPs synthesis (nanorods [11], nanostars [10], nanoprisms [12], nanocubes [13]) that would enable to control precisely the morphology and size of the NPs. The most common method of producing non-spherical Au NPs is method of colloidal synthesis [14], wherein various surfactants [13] and polymers [14] are used to stabilize Au NPs. For example, toxic surfactant cetyltrime thylammonium bromide (CTAB) is used for Au NSs and NRs obtaining [11]. It makes impossible to use obtained Au NPs in biomedical applications and SERS without further purification procedures. Therefore design of techniques for Au NPs producing with precise control of the NPs morphology and size without using of surfactants and polymers is relevant.

In this paper we demonstrated the possibility of Au NSs and NFs obtaining with <20 % variance in size in the absence of surfactant and polymer. Materials based on the obtained Au NPs are promising for use as SERS-substrates.

2. Experimental

For the AuS_S and NF_s synthesis of gold nanostars were used chloroauric acid $HAuCl_4 \cdot 3H_2O \geq 99.9\%$, sodium citrate $Na_3C_6H_5O_7 \geq 98 \%$, hydrochloric acid aqueous solution $HCl \geq 38 \%$, silver nitrate $AgNO_3 \geq 99.8 \%$, ascorbic acid $C_6H_8O_6 \geq 99 \%$ without further purification.

Colloidal aqueous solutions of $AuNS_S$ and NF_s were obtained using seed-mediated growth method [10]. The seed solution was prepared by adding 1.5 ml of 1 % citrate solution to 10 ml of boiling 1 mM $HAuCl_4$ solution under vigorous stirring. After 15 min of boiling while keeping the solution volume stable, the solution was cooled in air.

For synthesis of $AuNS_S$ and NFs gold nanostars and nanoflowers with different size 0.1 ml of the above citrate-stabilized seed solution was added to 10 ml of 0.25 mM $HAuCl_4$ solution (pH = 3) at room temperature under vigorous stirring. Quickly, 2, 4 or 6 µl of 0.05 M $AgNO_3$ solution and 0.5 ml of 0.01 M ascorbic acid were added. The solution was stirred for 1 min, its colour rapidly turned from light red to green-blue or blue.

Morphology and structure of Au NPs was characterized using transmission electronic microscope TEM-125 with an accelerating voltage of 100 kV. The X-ray photoelectron spectra (XPS) of samples surface were measured with MXPS XP high vacuum double-chamber system (Omicron, Germany) with a hemispherical electrostatic analyser (vacuum in camera was 10^{-7} Pa, the radiation energy was 1253.6 eV (MgK_α), the accuracy of the binding energy determination is 0.2 eV). Absorption spectra of gold nanoparticles were measured with a PerkinElmer Lambda-35 spectrophotometer within the range 400–900 nm with 0.1 nm measurement accuracy.

3. Results and discussion

Colloidal Au NSs and NFs aqueous solutions were obtained using seed-mediated growth method which allowed to control NPs size and shape.

At the first, reduction of chloroauric acid with sodium citrate at a temperature of 100°C was carried out, spherical Au NPs with average size of 12 nm were obtained. These spherical Au NPs served as seeds for the Au NSs controlled growth process. Au NSs and NFs were obtained by reduction of chloroauric acid with ascorbic acid on seeds in the presence of silver ions. The presence of silver ions is a necessary condition for the formation of non-spherical Au NPs, i.e., formation and growth of gold sharp branches along certain crystallographic facets of citrate-capped gold seeds. Silver is adsorbed on the Au surface facets with the highest surface energy, forms a monolayer or submonolayer [11, 15], selectively stabilizes {110}, {310}, {720} Au facets [16] and prevents further Au growth on the surface of these facets. Consequently, anisotropic Au NPs 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, and Au branches in this direction are formed.
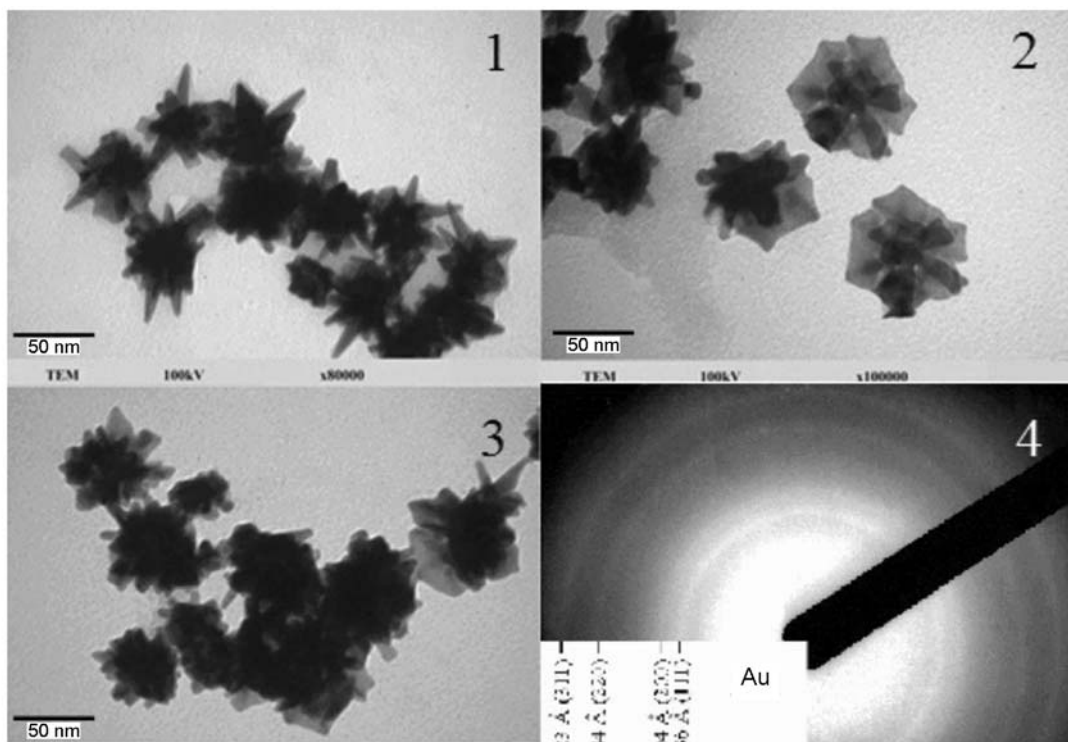
Fig. 1. Au NSs and NFs electron microscopic images depending on the synthesis conditions: 1) — [Ag$^+$] = 10 µM; 2) — [Ag$^+$] = 20 µM; 3) — [Ag$^+$] = 30 µM; 4) — Au NPs electronic microdiffraction.

NSs and NFs with average size 53, 61 and 68 nm (size distribution is less than 20 % for each sample) (Fig. 1.) were obtained by varying the concentration of silver ions in the growth solution. With the increasing Ag$^+$ concentration number of Au branches increases, shape changes from NSs to NFs. For example, when Ag$^+$ concentration in the growth solution is 10 µM, NSs are formed (Fig. 1.1), branches are sharp, narrow and long. When Ag$^+$ concentration is increased to 30 µM, number of branches and their length decreases, ends of the branches become more rounded and NFs are formed (Fig.1. 3).

Obtained Au NPs 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. 1.4).

The X-ray photoelectron spectroscopy (XPS) was used to study the composition of obtained NPs. XPS spectra of Au 4f, Ag 3d from NPs' surfaces are presented in the Fig. 2. It was found that binding energy of Au 4$f_{7/2}$ — line for all samples was (84.0±0.2) eV, which corresponds to gold in metal state. Binding energy of Ag 3$d_{5/2}$ was (367.9±0.2) eV. Because silver line doesn't have a sufficient chemical shift, i.e. for most silver compounds Ag 3d binding energy differs from one for metal not more than 0.2 eV [17], it's impossible to find out the chemical state of silver. However, since we didn't see chlorine lines from HCl and HAuCl$_4$ in XPS spectra and silver oxide formation during synthesis is improbable from the chemical point of view, we can suppose that silver also has metal state.

Study of optical properties of colloidal solutions showed that the morphology and size of Au NPs significantly affect to their optical properties. Absorption spectra Au NPs colloidal solutions were studied. For colloidal solutions of spherical Au NPs with a diameter of 12 nm maximum of absorption (surface plasmon resonance (SPR)) is in the region of 525 nm, Au NSs and NFs absorption peaks shift to longer wave region in absorption spectrum (Fig. 3) comparing with spherical Au NPs.

The SPR position of Au NSs and NFs doesn't depend on the particle size significantly and it is determined by their shape (the number of branches and their length). So, for Au NSs with 53 and 61 nm size SPR position is observed at 660 and 673 nm, respectively, for Au NFs with 68 nm size — 685 nm, i.e. with increasing NP size by
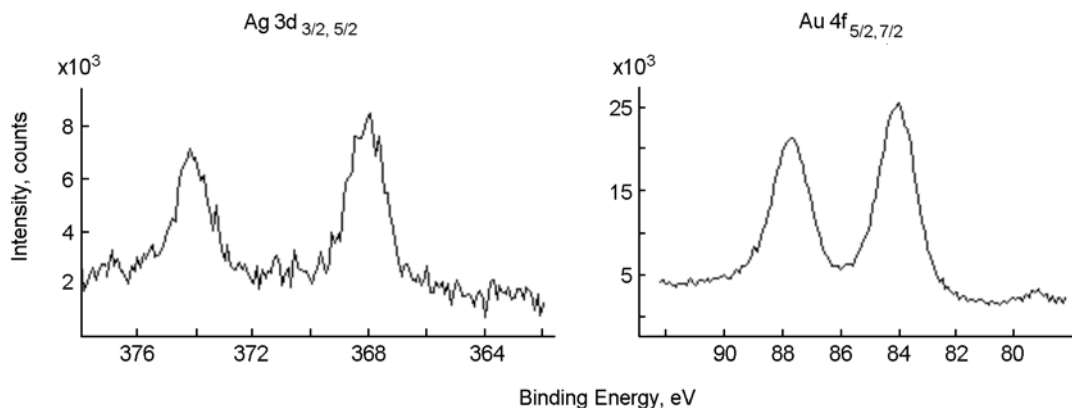
Fig. 2. X-ray photoelectron spectra of Au 4*f*, Ag 3*d* — core levels from Au NPs surface.

15 nm SPR maximum is shifted by 25 nm in the absorption spectra.

For non-spherical particles (nanorods, nanostars, nanocubes) different particle orientations with respect to the incident light are unequal. Regions of positive and negative charge formed near the NPs surface as a result of displacement of the conductivity electrons induce the polarization of the surrounding medium in which metal particle exists. This polarization leads to reduce the magnitude and frequency of the induced dipole oscillation and, consequently, leads to SPR shift in longer wave region. These effects are more pronounced the greater the ability of the environment to the polarization [18, 19].

It was shown [10] that Au NSs maximum position and its intensity determined by the ratio "number of branches/their length". As with the increase of number of branches their length decreases, according to theoretical calculations, the SPR maximum is shifted to longer wave region.

Also, there is a SPR maximum broadening for Au NSs and NFs colloidal solutions comparing with spherical NPs, which is associated with a greater size distribution of obtained Au NSs and NFs.

4. Conclusions

In this paper results of obtaining Au NPs with different morphologies are demonstrated. Stable NFs and nanoflowers colloidal solutions are prepared, average size obtained NFs is in the range of 50 to 70 nm, size dispersion is less than 20 %. The effect of silver ions on the Au NSs formation and growth is studied. It is shown that when concentration ratio Ag^+/Au^{3+} in the reaction mixture increases, number of branches and the average size of Au NPs increases, shape
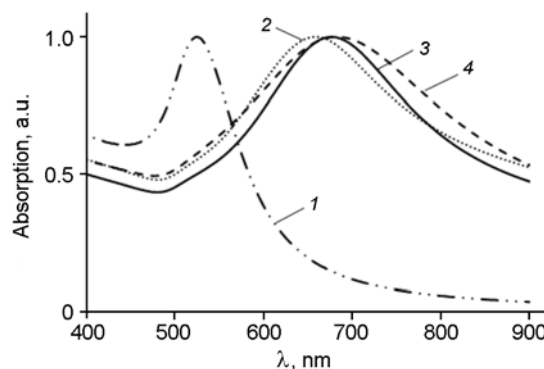

Fig. 3. Absorption spectra (plasmon resonance) colloidal solutions of Au NPs of different shapes and sizes: *1* — spherical NPs with 12 nm average size; *2, 3, 4* — NSs and NFs with 53, 61 and 68 nm average size, respectively.

changes from NPs to NFs. It was established that changing the shape of Au NPs from spherical to NSs and NFs in their colloidal solutions leads to SPR shift to 660–685 nm region in the absorption spectra. Materials based on such branched structures are promising candidates for using in surface-enhanced Raman spectroscopy as substrates.

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