

Gold colloids obtained by Au(III) reduction with Sn(II): preparation and characterization

Rima Tarozaitė,

Remigijus Juškėnas,

Marija Kurtinaitienė,

Aldona Jagminienė and

Algirdas Vaškėlis*

*Institute of Chemistry,
A. Goštauto 9, LT-01108 Vilnius,
Lithuania*

Gold colloid solutions were prepared by reduction of Au(III) by tin(II) in chloride solutions in both acidic (HCl) and alkaline (carbonate) media, and characterized by electron microscopy, X-ray diffraction and light absorption spectra. Depending on the colloid preparation conditions, metal particles 5–30 nm in size were obtained. Light absorption spectra of the Au colloid solutions contain absorption band at 500–600 nm, typical of small gold particles. According to XRD data, colloid particles contain metallic Au and SnO₂ phases and no metallic Sn. The colloid formation rate and colloid solution stability depend on solution pH; the alkaline colloid solutions form more slowly and are more stable. The gold nanoparticles adsorbed on dielectrics surface found to initiate the electroless copper deposition process.

Key words: gold colloid solutions, Au nanoparticles, tin(II)

INTRODUCTION

Gold colloid solutions and gold nanoparticles in general are important objects of contemporary chemistry, physics and materials science due to their chemical stability, specific optical and other physical properties [1–3]. Gold colloids were among the first widely investigated in the classical period of colloid chemistry in the second half of the 19th and early in the 20th century.

Noble metals such as palladium and silver, including their colloids, are widely used in the last decades as dielectric surface activators in the electroless plating of non-metallic substrates or as catalysts for other systems [4, 5]. Gold can also serve for the preparation of surface activators, particularly in the cases when palladium or silver is not desirable.

The gold colloid is a typical lyophobic sol; the system is thermodynamically unstable and inclined to a spontaneous coalescence of the nanoparticles. Such colloid solutions cannot be produced in the concentrated form, and they coagulate with a rise of temperature or with addition of electrolytes.

Gold colloid solutions can be prepared by chemical reduction of gold(III) with various substances: formaldehyde, borohydride, hydrazine, citrate, tartrate, tannine, etc. Formation of an intensively coloured product under the interaction of gold salt solution with tin(II) compounds was detected as long ago as in the 17 century: the substance obtained in that reaction was used for glass and ceramics coloration under the name of “Cassius purpur”. The long controversy on the nature of this substance between two different views – metal-

lic gold and gold (I) or (II) oxide (Berzelius described it as a chemical compound Au₂O₂·2SnO₂·H₂O) – lasted throughout the 19th century until R. Zsigmondy [6] proved colloidal gold particles to be the main component of “Cassius purpur” alongside tin compounds. Later these conclusions were supported by the X-ray diffraction data: the intensive lines of metallic gold and weak lines corresponding to SnO₂ were observed in the diffraction patterns of “Cassius purpur” [7].

The reaction with SnCl₂ has been proposed for both qualitative and quantitative determination of gold [8–10]. However, in the second case, when applying colorimetric or spectrophotometric techniques, difficulties arise due to the sensitivity of the colloid solution absorbance to various factors.

The reduction process of Au salts by Sn(II) has been studied mostly in relation with gold colloid application for gold analysis [10, 11], but there are no modern investigations of this process.

In this work, colloid gold solutions were prepared by a method employing reduction by tin(II). The main aim of this study was to find conditions for preparing stable enough systems suitable to serve as a source of gold nanoparticles for modifying various surfaces and to use them as catalysts. Recently, fairly stable silver colloid solutions with a rather high concentration of Ag particles have been obtained by a similar method [12]; silver nanoparticles showed a high electrocatalytic activity in formaldehyde oxidation.

EXPERIMENTAL

Au colloid solutions were prepared using two main stock solutions: 5 mM HAuCl₄ and 50 mM SnCl₂. The Au(III)

* Corresponding author. E-mail: vaskelis@ktl.mii.lt

solution was prepared by dissolving the gold complex in water. The tin(II) solution was prepared by dissolving $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in concentrated HCl under heating and then diluting with distilled water; a freshly prepared tin salt solution was always used to minimize the effects of tin(II) oxidation by atmospheric oxygen and other side reactions.

Analytical grade chemicals and triply distilled water were used to prepare the solutions. Au colloid solutions of two types – acidic and alkaline by adding HCl or K_2CO_3 to adjust solution pH – were prepared and studied. The Au(III) and Sn(II) solutions, diluted to the concentrations needed, were mixed by adding tin salt to gold(III) after adjusting pH, then the mixture was shaken intensively for 0.5–1 min. The solution changed its colour from reddish-brown to reddish-purple. Gold concentration in all colloid solutions was 0.5 mM.

The colloid solutions obtained were characterized by light absorption spectra using a Perkin–Elmer Lambda 35 UV/VIS spectrometer. Metal nanoparticles were studied by X-ray diffraction using D8 X-ray diffractometer (Bruker HXS) and by electron microscopy and using a JEOL electron microscope.

The catalytic activity of the Au nanoparticles was tested by their ability to initiate the electroless copper plating process on dielectrics surface modified by its treatment in Au colloid solution. The substrates of ABS plastic or glass were kept in the colloid solution for 5 min, rinsed with water, and immersed into electroless plating solution containing (mM): CuSO_4 – 28, KNa tartrate – 80, Na_2CO_3 – 20, NaOH – 110, CH_2O – 340 at 25 °C.

RESULTS AND DISCUSSION

Acidic Au colloid solutions

Au colloid formation using tin(II) was controlled by light absorption spectra. A light absorption band with a maximum at 520–550 nm wavelength was observed for the solutions under study (Fig. 1). The absorption band appeared at once after mixing the gold and tin salt solutions, indicating formation of Au nanoparticles in the solution. The spectra observed are similar in form and position to those calculated theoretically for small Au particles [13]. The absorbance of the colloid solutions changed in time and depended on the colloid preparation conditions. The light absorption maximum in some cases changed its position, showing changes in nanoparticle size. Therefore light absorption data not always can give quantitative information on gold particle concentration due to the poly-dispersion character of these colloids.

The location of the light absorption maximum depends on the initial HCl concentration in the colloid solution (Fig. 1a). When HCl concentration is 2.5 mM, the absorption maximum is observed at 520 nm. With increase in HCl concentration to 60 mM, the maximum shifts to the longer wavelengths and remains close to

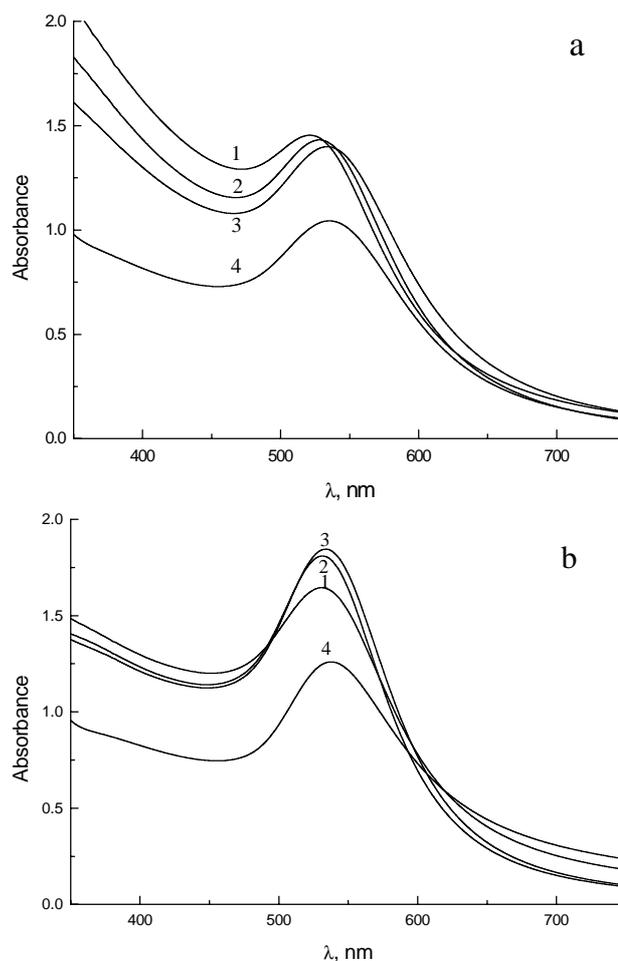


Fig. 1. Dependence of Au colloid light absorption on HCl concentration; **a** – colloid freshly prepared, **b** – after 25 h. The initial solutions contained (mM): Au(III) – 0.5; Sn(II) – 0.9; HCl: 1 – 2.5; 2 – 26; 3 – 62; 4 – 120

540 nm with a rise in solution acidity until 100 mM HCl. However, the further increase in HCl concentration leads to a lower light absorption (Fig. 1a, curve 4), and a steel-gray precipitate, probably Au_2O , is formed when HCl concentration exceeds 150 mM.

The rise of light absorption in the shorter wavelength region is probably related to tin(II) species in the solution. This absorbance decreases in time (Fig. 1a, b) simultaneously with the rise of absorption maximum at 540 nm, indicating the Au(III) reduction progress and a rising concentration of Au nanoparticles. However, the colloid solutions containing both the lowest and the highest HCl concentration are of a rather low stability and begin to coagulate 20–30 h following their preparation; therefore the light absorption maxima in these cases (Fig. 1b, curves 1 and 4) apparently don't reflect all Au particles in the system. Meanwhile, colloid solutions containing 25–60 mM HCl remain stable for 2–3 days.

The rate of Au colloid formation and its stability depend on the initial Sn(II) and Au(III) concentration ratio. When this ratio is close to 2:1, a medium-height maximum of light absorption at 540 nm is observed

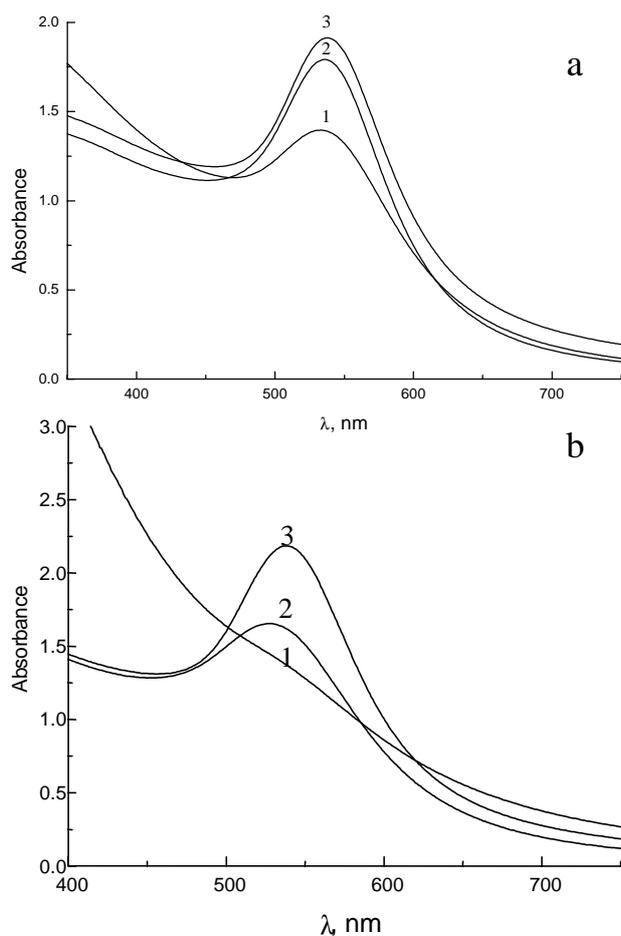


Fig. 2. Change of light absorption spectra of Au colloid solutions in time: 1 – as prepared, 2 – after 25 h, 3 – after 50 h. Initial concentrations (mM): Au(III) – 0.5; HCl – 20; Sn(II): **a** – 0.9; **b** – 1.8

soon after mixing the components (Fig. 2a); the maximum increases during the first 50 hours simultaneously with the decrease in light absorption at 350–450 nm. Electron microscope images (Fig. 3a and b) show the growth of Au nanoparticles in the first 20 hours, their shape being mostly spherical. At a longer time, formation of Au particle conglomerates induces coagulation of the colloid after approx. 3 days.

At the ratio Sn(II)/Au(III) being close to 4:1, the light absorption curve for freshly prepared colloid solution differs considerably from the curve discussed above: no light absorption maximum typical of Au nanoparticles is observed at a rather high absorbance in all wavelength interval from 350 to 600 nm (Fig. 2b, curve 1). The EM image in Fig. 3c shows only a little number of particles with a definite shape; apparently, the formation of Au particles at a higher concentration of the reducing agent – Sn(II) – is retarded, possibly due to formation of some intermediates. After some time the particles are formed (Fig. 3d) and light absorption maximum at 530 nm appears and increases (Fig. 2b). The particles of gold colloid prepared using a high concentration of Sn(II) are larger, therefore the stability of this colloid solution is lower, its sedimentation begins after 2–3 days.

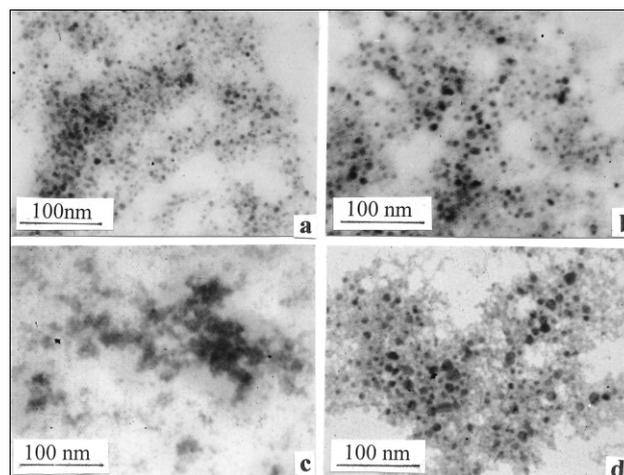


Fig. 3. Transmission electron micrograph of Au colloidal particles formed in solutions containing (mM): Au(III) – 0.5; HCl – 20; Sn(II): **a** and **b** – 0.9; **c** and **d** – 1.5. Freshly prepared **a** and **c**; after 20 h – **b** and **d**

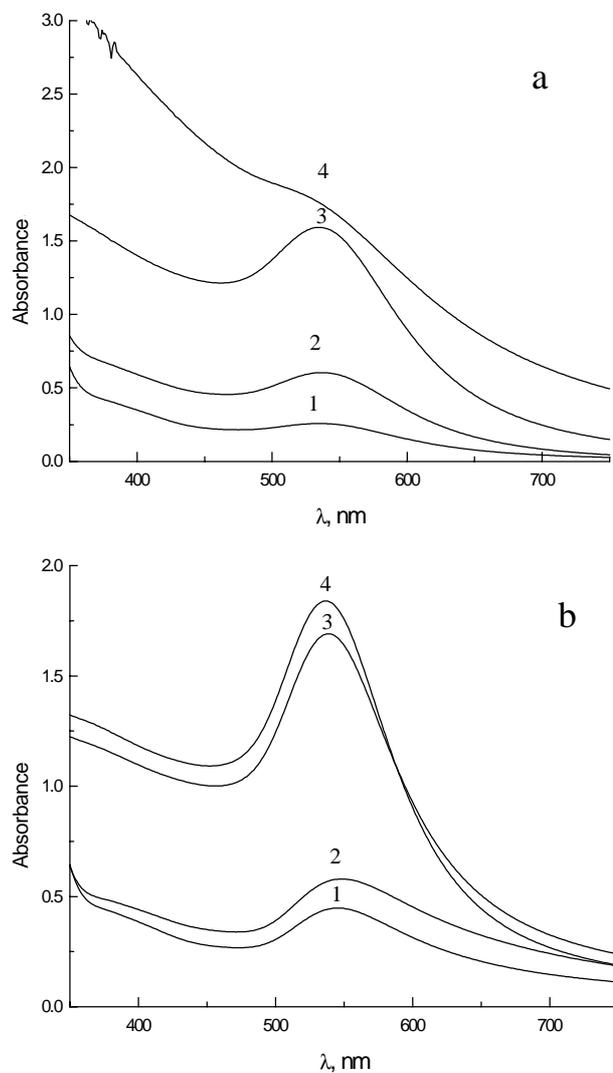


Fig. 4. Dependence of light absorption of Au colloid solutions on initial Sn(II) concentration when Sn(II):HCl = 1:60; **a** – as prepared, **b** – after 50 h. Initial concentrations (mM): Au(III) – 0.5; Sn(II): 1 – 0.25; 2 – 0.5; 3 – 1.0; 4 – 1.5

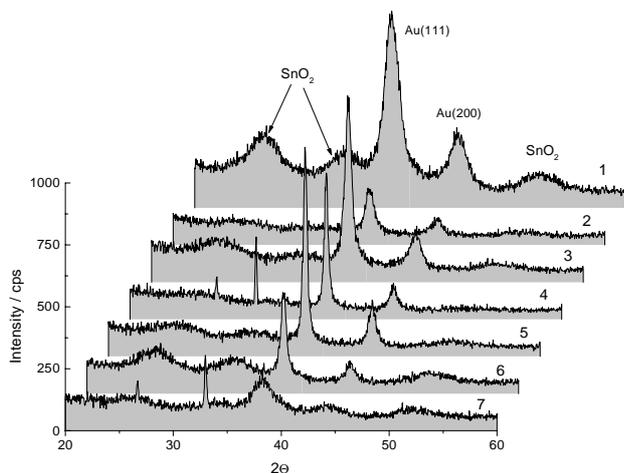
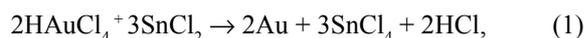


Fig. 5. XRD patterns of precipitated Au colloid particles. The colloids were prepared in solutions containing (mM): Au(III) – 0.5; Sn(II): 1–4 and 7 – 0.9; 5 – 0.45; 6 – 4.4; HCl: 1 – 2.5; 2 – 40; 3 – 62; 4 – 100; 5 – 40; 6 – 12; K_2CO_3 : 7 – 14

The light absorption spectra of freshly prepared colloid solutions with various Sn(II) concentrations in the initial solution at a constant Sn(II):HCl ratio have no distinct maxima (Fig. 4a); they appear later. These experiments show that the ratio Sn(II):Au(III) value close to 1:2 is the most favourable for the normal Au colloid formation (Fig. 4b).

X-ray diffraction measurements showed that Au colloidal particles (after sedimentation from the solutions) contain Au as a metallic phase, alongside with an Sn(IV) compound SnO_2 (Fig. 5). Probably, Sn(IV) ions formed in the reaction of Au(III) with $SnCl_2$ are hydrolyzed in diluted solutions with formation of α -stannic acid:



This compound is stable only in aqueous solution and may be also described as $mSnO_2 \cdot nH_2O$. This α -stannic acid is soluble in acids and in alkali. It can play an important role in colloid stability. Some facts indicate it being a cause of a poor colloid solution stability, e.g., in a case of the colloid prepared with a low con-

centration of HCl. On the other hand, a layer of adsorbed stannic acid could have a stabilizing function protecting gold particles from coalescence. However, it may transform to β -stannic acid insoluble in both acids and alkalis, and may destroy the colloid.

No other crystalloid species were found in the Au nanoparticles obtained in various conditions. No metallic Sn was detected, in contrast to palladium colloids obtained by a similar method. Tin(II) compounds were not found either; their adsorption ability may be lower as compared with tin(IV). By the composition, Au nanoparticles are most similar to Ag ones also containing two phases – metal and SnO_2 [12].

The results of X-ray diffraction show (Table) that precipitated Au colloid particles obtained in solutions with a moderate HCl:Sn(II) molar ratio (up to 50) contain more than 50 mol% of SnO_2 . It must be noted that these colloids are less stable compared with the colloids prepared with a higher HCl:Sn(II) ratio (except the cases when HCl excess may reduce Au(III) to Au_2O_3).

According to X-ray data, Au particles 5–30 nm in diameter were in the precipitate studied. The particle size changed depending on colloid preparation conditions. The largest particles were obtained at a high HCl:Sn(II) ratio – when it equaled 90–110 (Nos. 4 and 5 in Table). In these solutions Au particles grow slower than in other solutions, and there are possibilities to form a lower number but larger particles. The question can arise if Au nanoparticles in solution are of the same size as in the precipitate, or they may be even finer. If coagulation was caused by the coalescence of particles without recrystallizing, the X-ray data may reflect the solution's situation correctly enough.

Addition of a certain amount of HCl to the already prepared Au colloid solution protects it from fast sedimentation and increases its catalytic activity determined according to the test of dielectrics activation for electroless copper plating. The whole surface of the plastics was covered with copper after substrate modification by a not stabilized Au colloid within 10–15 min (two days after colloid preparation), meanwhile the identical surface activated in a colloid solution stabilized with HCl was covered by copper within 3–5 min even five days after preparation (colloid sedimentation in this

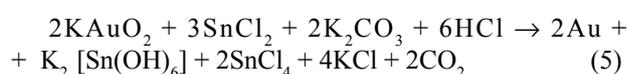
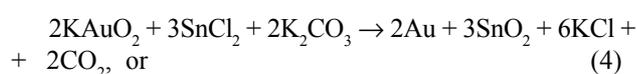
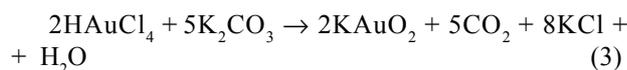
Table. Data of Au colloid X-ray diffraction measurements. Initial Au(III) concentration 0.5 mM

No.	Initial concentrations, mM		HCl:Sn(II)	$D_{Au(111)}$, nm	$D_{Au(200)}$, nm	Au, mol. %	SnO_2 , mol. %
1	Sn^{2+} 0.9	HCl 2.5	2.8	14	8.3	41	59
2	0.9	40	44	9.5	9.5	47	52
3	0.9	62	69	5.9	5.5	63	37
4	0.9	100	111	29.3	15.3	69	30
5	0.45	40	89	28.6	13.7	70	30
6	4.4	12	2.7	17.4	11.5	35	65
7	0.9	K_2CO_3 14	pH 9.1	4.8	5.5	27	73

case began after 10 days). It can be supposed that addition of HCl to the already formed Au colloid slows down changes of the Sn(IV) compounds present in colloid solution and increases their solubility. The addition of such HCl quantity at the colloid preparation leads to its precipitation.

Alkaline Au colloid solutions

Au colloids may be prepared also in alkaline media by reducing Au(III) with Sn(II), in a similar way as it was done using formaldehyde [14]. The Au(III) chloride complex is transformed to aurate by the addition of K_2CO_3 , after which aurate is reduced to Au:



Solution pH changes with colloid formation and ageing from 8.0–9.0 (depending on K_2CO_3 concentration) to 9.1–9.6. From this point of view, reaction (5) could better describe the Au(III) reduction process in weakly alkaline solutions.

Data of X-ray diffraction measurements showed that Au particles in a colloid prepared in this way are rather fine (their diameter is ca. 5 nm), and the precipitates contain also Au as a metallic phase and SnO_2 (Fig. 5, Table). The SnO_2 content in the particles is considerably higher compared to acid solutions (over 70%); this value exceeds the stoichiometric Sn(IV) content in Au(III) reduction products equal to 60%. Apparently, Sn(IV) forms also in reaction with air oxygen.

Light absorption spectra of these colloid solutions changes in time: the maximum at 520–540 nm, hardly visible after 1 h, slowly increases during several days (Fig. 6a, curves 1–4), and the spectra become typical of Au nanoparticles. As is seen in Fig. 7, colloidal particles in freshly prepared solutions are not sufficiently distinct, and they develop with time. The colloid ageing period depends on temperature and may be shortened by heating the prepared colloid solution (Fig. 6b): at 90 °C the formation of Au colloid characterized by a high light absorption maximum takes 10 min instead of 5 days at room temperature.

The alkaline Au colloid solution is rather stable. It shows catalytic activity according to the test of activated plastics surface covering by copper in electroless plating solution. The activity of alkaline Au colloids passes through a maximum with its ageing, however, it remains high enough much longer compared to the activity of acidic colloids (the plastics surface modified in alkaline Au colloid 20 days after preparation was covered with electroless copper within 10–15 min). The

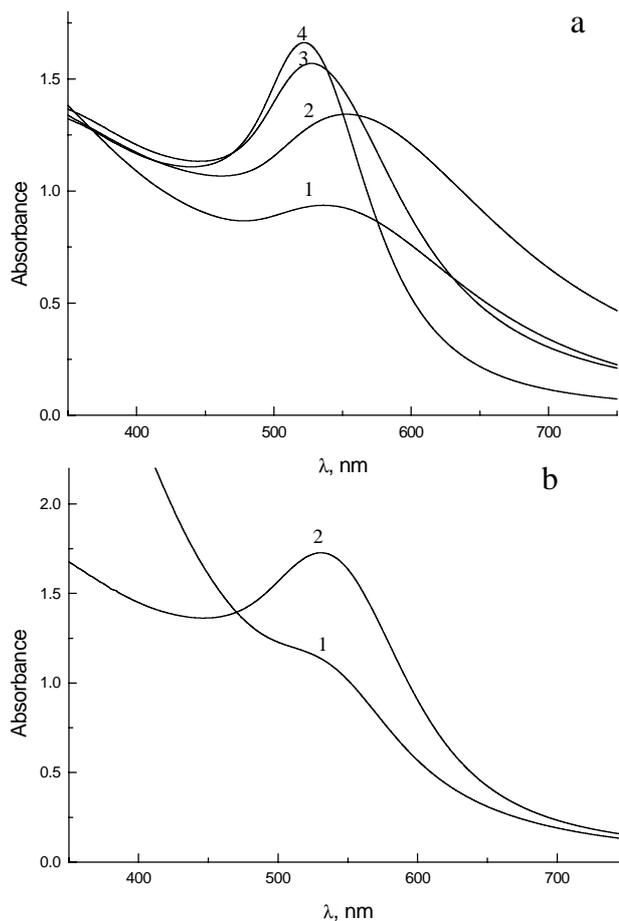


Fig. 6. Light absorption spectra of alkaline Au colloid solutions; **a** – effect of time after its preparation (h): 1 – 1; 2 – 25; 3 – 90; 4 – 160. **b** – effect of temperature: 1 – freshly prepared; 2 – after heating for 10 min at 90 °C. Initial concentrations (mM): Au(III) – 0.5; Sn(II) – 0.9; pH 9.5

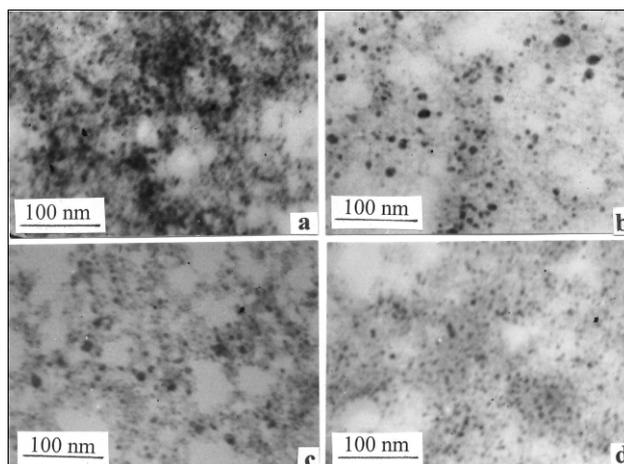


Fig. 7. Transmission electron micrographs of Au colloid particles prepared in alkaline solution: **a** and **b** – pH 8.5; **c** and **d** – pH 9.6; **a** and **c** – freshly prepared; **b** and **d** – after 160 h. Initial concentrations (mM): Au(III) – 0.5; Sn(II) – 0.9

activity of fresh Au colloid can be enhanced by increasing the temperature of Au(III) and Sn(II) solutions used for colloid preparation and by heating the prepared colloid solution.

CONCLUSIONS

1. Au colloid solutions obtained by reduction of Au(III) with Sn(II) may be prepared in both acidic and alkaline media. The colloid formation rate and colloid solution stability depend on solution pH; alkaline colloid solutions are more stable.

2. According to X-ray diffraction measurements, Au nanoparticles 5–30 nm in size were precipitated in colloid solutions. They contained two phases – metallic Au and SnO₂.

3. Au nanoparticles are catalytically active: adsorbed on dielectrics surface they initiate electroless copper plating. The particles' activity changes with colloid ageing.

Received 12 July 2006

Accepted 14 August 2006

References

1. G. Schmid, *Chem. Revs.*, **92**, 1709 (1992).
2. L. N. Lewis, *Chem. Revs.*, **93**, 2693 (1993).
3. T. Sugimoto (Ed.), *Fine Particles. Synthesis, Characterization, and Mechanisms of Growth*, Marcel Dekker, 2000.
4. M. Šalkauskas, A. Vaškelis, *Chemical Metallizing of Plastics*, Khimiya, Leningrad, 1985s (in Russian).
5. G. O. Mallory, J. B. Hajdu (eds.), *Electroless Plating. Fundamentals and Applications*, American Electroplaters and Surface Finishers Society, Orlando, 1990.
6. R. Zsigmondy, *Liebigs Ann.*, **301**, 29, 361 (1898).
7. A. Huber, *Physik. Z.*, **25**, 45 (1921).
8. R. N. Costeanu, *Z. Anal. Chem.*, **104**, 351 (1936).
9. C. G. Fink, G. L. Putnam, *Ind. Eng. Chem. Anal. Ed.*, **14**, 468 (1942).
10. A. I. Busev, V. M. Ivanov, *Analytical Chemistry of Elements. Au*, Moscow, Nauka, 1973 (in Russian).
11. E. Müller, R. Behnewitz, *Z. anorgan. allg. Chem.*, **179**, 113 (1929).
12. A. Vaškelis, A. Jagminienė, L. Tamašauskaitė Tamašiūnaitė, R. Juškėnas, *Electrochim. Acta*, **50**, 4586 (2005).
13. J. A. Creighton, D. G. Eadon, *J. Chem. Soc. Faraday Trans.*, **87**, 3881 (1991).
14. I. N. Putilova, *The handbook for practical proceedings in colloid chemistry*, Goschimizdat, 1948 (in Russian).

**Rima Tarozaitė, Remigijus Juškėnas,
Marija Kurtinaitienė, Aldona Jagminienė,
Algirdas Vaškelis**

AUKSO KOLOIDAI, GAUTI AU(III) REDUKAVUS ALAVU(II): GAMYBA IR APIBŪDINIMAS

S a n t r a u k a

Aukso koloidiniai tirpalai buvo gauti redukavus aukso(III) junginius alavo(II) chloridu rūgščioje (HCl) arba šarminėje (karbonatų) terpėje ir apibūdinti šviesos absorbcijos spektrais bei taikant rentgeno spindulių difrakciją ir elektroninę mikroskopiją. Priklausomai nuo koloido gavimo sąlygų susidaro 5–30 nm dydžio dalelės. Koloidinių tirpalų šviesos sugėrimo spektruose yra sugėrimo juosta ties 500–600 nm, būdinga mažoms aukso dalelėms. Rentgenografijos duomenimis, nusėdusios koloidinės dalelės yra sudėtos iš dviejų fazių – metalinio Au ir SnO₂, jose nėra metalinio Sn. Koloidų susidarymo greitis ir patvarumas priklauso nuo tirpalo pH; šarminiai koloidiniai tirpalai formuojasi lėčiau ir yra stabilesni. Aukso nanodalelės, adsorbuotos dielektrikų paviršiuje, katalizina cheminio variavimo procesą.