CHEMIJA. 2006. Vol. 17. No. 4. P. 13–19
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Electrocatalytic properties of gold nanoparticles in oxidation reactions of reducing agents

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The glassy carbon (GC) electrodes modified by Au nanoparticles (200–900 ng cm^{-2} Au) from colloid solutions formed by Au(III) reduction with Sn(II) were found to be electrocatalysts for hydrazine, borohydride and dimethylamine borane (DMAB) oxidation in alkaline solutions. The activity of Au particles formed in acidic and alkaline solutions does not differ significantly, except hydrazine oxidation when particles prepared in an acidic medium are more active. The presence of SnO_2 (40–70 mol%) does not diminish the catalytic activity of Au particles or even enhances it. The GC electrode becomes electrocatalytically active after immersion in Au(III) solution due to a spontaneous metallic Au formation in gold ions interacting with carbon.

Key words: gold nanoparticles, tin(II), glassy carbon, hydrazine, borohydride, dimethylamine borane, anodic oxidation

INTRODUCTION

The strong reducing agents hydrazine, borohydride and dimethylamine borane (DMAB) find various important practical applications, such as solutions for electroless metal deposition and fuel cells. The oxidation of these compounds was investigated both in homogeneous and heterogeneous systems, including metallic catalysts.

One of the main steps of an electroless metal deposition process is the anodic oxidation of a reducing agent. The general mechanism of the anodic process of various compounds including borohydride, DMAB and hydrazine, based on the formation of adsorbed atomic hydrogen as the first step was proposed in [1]. According to this mechanism, DMAB and borohydride are expected to produce three-coordinated borane radicals, $\times BH_2(OH)^-$, $\times BH(OH)_2^-$ and $\times B(OH)_3^-$, and hydrazine – $\times N_2H_3$, N_2H_3OH.

In a study of the catalytic DMAB oxidation reaction by an ab initio molecular orbital method, the five-coordinated borane intermediate was suggested to play a key role in the catalytic process [2–4].

The kinetic studies of the anodic reaction of hydrazine and DMAB on various metals including gold, showed the existence of unique substrate/reducing agent interactions [5]. The role of active Au surface oxides in the overall oxidation of DMAB was described in [6–8]. A study of the adsorption-desorption phenomena at DMAB oxidation on gold led to suggesting two borane-containing reactive intermediates during the formation and reduction of surface gold oxides. The kinetic parameters for DMAB oxidation in an alkaline solution were determined [9]. The oxidation at gold microelectrodes was observed to occur in two three-electron waves, the first wave was further resolved into three one-electron steps.

Although Au is an active electrocatalyst in the anodic oxidation of hydrazine, this process on the Au electrode has not been studied very extensively. The electrochemical behaviour of hydrazine on several metals including Au was investigated in alkaline [10–14], acidic media [14–16], and on Au electrodes modified by cobalt hexacyanoferrate [17]. The rate-controlling process in the hydrazine oxidation at gold electrodes is either a two-electron reaction with the participation of hydroxide ions or a chemical volume or a surface reaction of the product of a one-electron reversible oxidation [10]. The anodic oxidation may proceed through the formation of intermediate radicals such as N_2H_{4ad} or N_2H_{3ad}, [10–12]:

$$N_2H_{4ad} + OH^- \rightarrow N_2H_{3ad} + H_2O + e^-, \quad (1)$$

$$N_2H_{3ad} \rightarrow N_2 + 3H_a, \quad (2)$$

$$H_{ad} + OH^- \rightarrow H_2O + e^-. \quad (3)$$

The complicated electrode reaction of borohydride oxidation on the gold electrode was studied by cyclic voltammetry and by scanning electrochemical microscopy [18, 19]. These investigations led to the conclusion that the total irreversibility of BH_4^- oxidation on Au is the result of the presence of very unstable intermediates forming in a two-electron process, e.g. BH_3 or B_2H_6,

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which diffuse in the solution and participate in a rapid homogeneous chemical reaction. The kinetic parameters for borohydride oxidation on the Au electrode such as the diffusion coefficient, apparent rate constant, Tafel slope, Levich slope, the number of electrons exchanged and the reaction order [20–22] have been determined.

Borohydrides are potential fuels for fuel cells due to their high energy and power density. The electrochemistry of borohydride oxidation in an alkaline medium on various gold electrocatalysts [23–28] including Pt-Au alloys [26, 27], colloidal Au [27], nanodispersed gold on high-surface area carbon silk [23] and carbon blacks [28] was investigated. Not only the electrochemical behaviour, but also the performance of borohydride fuel cells has been studied in an effort to develop suitable electrode materials for borohydride-fueled cells.

In this work, the electrocatalytic activity of the Au nanoparticles prepared by Au(III) reduction with Sn(II) were studied in the anodic oxidation of hydrazine, borohydride and DMAB in alkaline solutions. Recently, the silver nanoparticles obtained by a similar method have shown a high electrocatalytic activity in formaldehyde oxidation [29].

EXPERIMENTAL

Gold colloid preparation and characterization

The gold colloid solutions were prepared by the procedure described in [30]. The Au(III) and Sn(II) solutions were mixed by adding tin salt to gold(III), then the mixture was shaked intensively for 0.5–1 min. The Au(III) solution was prepared by dissolving $HAuCl_4$ in water, the tin(II) solution was prepared by dissolving $SnCl_2 \times 2H_2O$ in concentrated HCl under heating and then diluting by distilled water; the freshly prepared tin salt solution was always used to minimize the effects of tin(II) oxidation by atmospheric oxygen and other side reactions. Au(III) concentration in all cases was 0.5 mmol l^{-1}.

Au colloid solutions of two types – acidic and alkaline – were prepared. The alkaline colloid solution was obtained after transforming $HAuCl_4$ to $KAuO_2$ by adding K_2CO_3.

The obtained colloid solutions were characterized by light absorption spectra, using a Perkin–Elmer Lambda 35 UV/VIS spectrometer.

Electrochemical measurements

Cyclic voltammetric curves (CV) were obtained by using standard electrochemical equipment (a programming potentiostat PI-50-1.1, a sweep generator PR-8, two digital voltmeters B7-46/1 connected to a PC through the IEEE 488 interface and a three-electrode electrochemical cell). A glassy carbon (SU-1200) working electrode (apparent surface area 0.636 cm^2), a Pt-wire counter-electrode and $Ag/AgCl/KCl_{sat}$ reference electrode were used. All potentials are given versus the SHE.

Before every measurement, the glassy carbon surface was refreshed by polishing it with diamond paste (1 μm particle size). The final cleaning of the electrode was performed in acetone solution.

Prior to the measurements, the glassy carbon electrode was modified (activated) in Au colloid or Au(III) solution for 5 min and then rinsed twice with distilled water. Three different types of gold solutions were used (Table 1).

Table 1. **Gold solutions used for electrode surface modification**

No.	Solution type	Reagents, mmol l^{-1}				pH
		$HAuCl_4$	$SnCl_2$	HCl	K_2CO_3	
1	ionic, Au(III)	0.5	–	–	–	3.0
2	Au colloid, acidic	0.5	0.9	65.0	–	2.2
3	Au colloid, alkaline	0.5	0.9	10.0	14.5	8.5

The amount of gold on the glassy carbon electrode was determined by anodic stripping voltammetry according to the procedure described in [31]. The voltammograms were measured in a mixture of acids: 0.1 mol l^{-1} HCl and 0.32 mol l^{-1} HNO_3, at a potential scan rate 200 mV s^{-1}.

The electrochemical experiments of the anodic oxidation were carried out in 0.1 mol l^{-1} NaOH containing various reducing agents at a concentration of 0.05 mol l^{-1}. The potential scan rate was 10 mV s^{-1}.

Analytical grade chemicals and triply distilled water were used to prepare the solutions. All solutions were purged by Ar. Sodium borohydride ($NaBH_4$), hydrazine monohydrate ($H_2NNH_2 \cdot H_2O$, 64% of N_2H_4), DMAB ($(CH_3)_2NHH \cdot BH_3$), dimethylamine borane complex, 97% (Aldrich Chemical Company, Inc.) were used.

RESULTS AND DISCUSSION

The glassy carbon electrodes are inactive for anodic oxidation of DMAB, borohydride and hydrazine, no anodic current is observed almost in all potential ranges of GC stability up to the positive potential values of 0.5–1.0 V. The modification of the GC electrode surface by gold species gives rise to the electrocatalytic activity of the electrode in these processes. The activation effect was observed after the modification of the surface in various gold solutions, both ionic and colloid ones (Table 1).

The used Au colloid solutions are comparatively stable. The colloid particles were shown by X-ray diffraction measurements [30] to contain metallic Au phase alongside SnO_2. The size of Au particles for both colloid types in Table 1 – acidic and alkaline – is similar, 5–6 nm, while Au content is different: 63 and 27 mol%

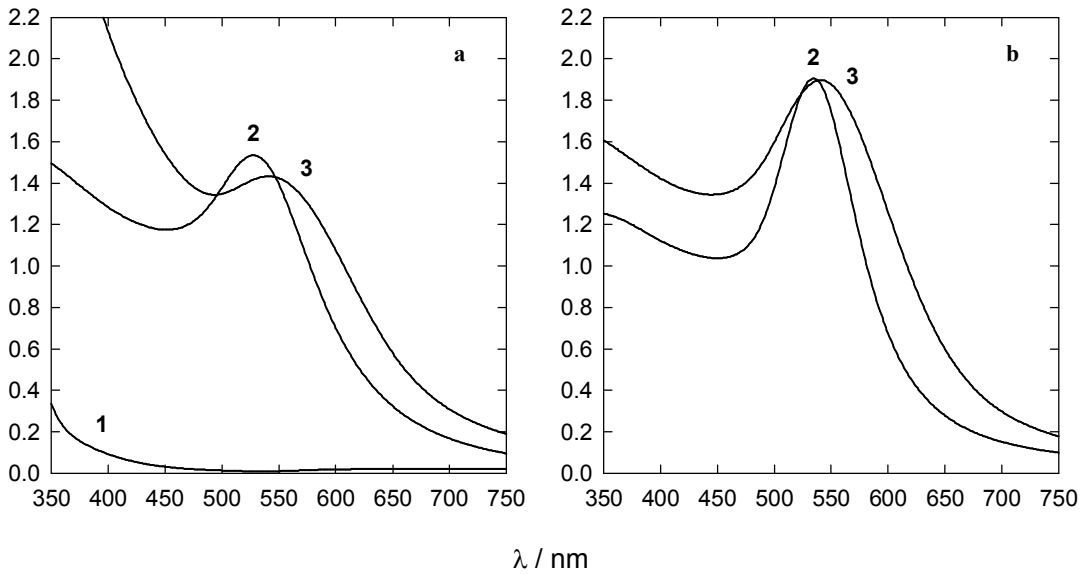

Fig. 1. Light absorption spectra of Au(III) and Au colloid solutions: 1 – 0.5 mM $HAuCl_4$, 2 – acidic (pH 1.1) colloid; 3 – alkaline (pH 9.1) colloid; *a* – 6 h, *b* – 5 days after preparation

for the nanoparticles obtained in acidic and alkaline solutions, respectively [30].

The gold colloid solutions have characteristic light absorption spectra (Fig. 1). A rather high absorbance is observed in a wide wavelengths interval from UV region to ca. 600 nm (curves 2 and 3 in Fig. 1) in contrast to the Au(III) solution spectrum with only slight rise in the absorbance close to UV region (curve 1 in Fig. 1a). The spectra of Au colloid solutions have light absorption maxima at 530–550 nm typical of small gold particles. These absorbance maxima increase with colloid aging (compare curves 2 and 3 in Figs. 1a and 1b) indicating changes in Au particles.

The Au particles adsorbed on non-catalytic surfaces of dielectrics or GC from the acidic colloid 2–3 h after its preparation, catalyse the oxidation of the reducing agents and electroless copper plating. Later (6 h after colloid preparation) the activity of Au particles rises – the induction period of electroless Cu deposition decreases. After 5–6 days, a considerable fall in colloid activity is observed, and in the subsequent two days its sedimentation begins.

In alkaline solutions the colloid formation and changes are slower: the absorbance maximum arises after several hours from the mixing of Au(III) and Sn(II), and it becomes clear only the next day. The activity of Au nanoparticles from the alkaline colloid solution, according to the induction period of electroless plating, increases with time in a similar way as the light absorption spectra, the highest activity is reached after two or three days and remains stable for a long time.

The amount of metallic gold on the glassy carbon electrodes modified with Au species was determined immediately after the modification or voltammetric measurements and rinsing with water using anodic stripping voltammetry in the acidic mixture (HCl + HNO_3). This determination was successful for the surfaces treated in

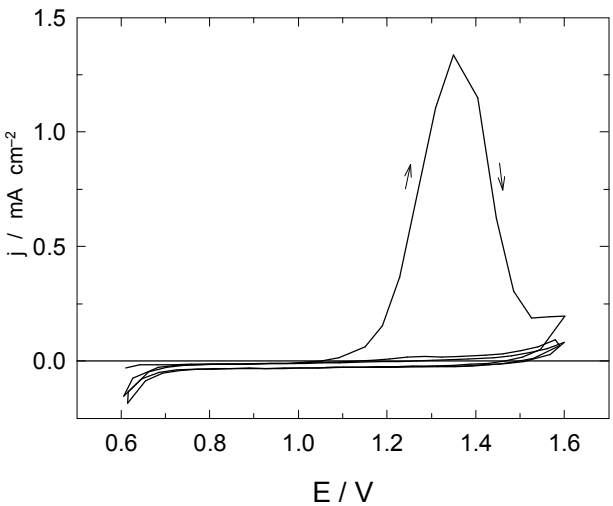

Fig. 2. A typical voltammogram for Au-modified GC electrode in 0.1 mol l^{-1} HCl + 0.32 mol l^{-1} HNO_3. Potential scan rate 200 mV s^{-1}; 20 °C. The GC was activated in acidic Au colloid solution

acidic colloid and ionic Au(III) solutions (a typical voltammogram for the Au-modified GC electrode is shown in Fig. 2). In the case of the GC electrode modified by the alkaline Au colloid, practically no anodic current was observed at anodic stripping experiments, as no metallic Au would have been present on the surface. Evidently, gold surface in these colloid particles is not accessible for the anodic dissolution reaction due to a high content of SnO_2 (over 70 mol%). Nevertheless, the blocking effect of tin species is not seen clearly in the electrocatalytic processes of anodic oxidation and electroless plating.

The amount of Au adsorbed on the GC surface from acidic Au colloid solution depended on the colloid age and solution temperature. At 25 °C, for Au colloid solution prepared before 5 h, ca. 900 ng cm^{-2} Au were

found, and after 1 day considerably less gold – ca. 550 ng cm^{-2} was adsorbed. At lower temperature, 16 °C, the changes in Au amount adsorbed are slower: from 830 ng cm^{-2} at 1 day after the colloid preparation, it decreased to 340 and 140 ng cm^{-2} after 2 and 3 days, respectively.

The metallic gold was found also on the GC electrode treated with the non-colloidal Au(III) solution: ca. 1320 ng cm^{-2} was adsorbed on the electrode after 5 min in 0.5 mmol l^{-1} $HAuCl_4$. Evidently, gold ions are reduced to metal on the electrode surface by carbon. A similar reduction of silver ions by carbon is described in [32].

The anodic oxidation of three reducing agents – hydrazine, borohydride and dimethylamine-borane was studied on the GC electrode activated (modified) with Au species (Table 1, the colloid solutions were of 1 day age), using cyclic voltammetry. Electrode potential was scanned to more positive values gradually increasing the positive potential limit.

The electrochemical responses of a bare (non-modified) GC (dashed curves) and Au-modified GC (solid curves) electrodes in 0.1 mol l^{-1} NaOH solution of 0.05 mol l^{-1} reducing agent are demonstrated in Figs. 3–5. At the bare GC electrode no anodic oxidation of these reducing agents was observed in a wide potential range up to 0.8 V, with some exception for hydrazine – small anodic current is measured beginning from 0.5 V (Fig. 4). On the GC electrode modified in three Au solutions, considerable anodic currents are observed with no cathodic currents at the subsequent negative-going scan, indicating an irreversible oxidation of these reducing agents.

The open-circuit potential of the modified GC electrodes depends to some extent on the modification type, and its values are most negative in DMAB solutions, around –0.6 V, for borohydride and hydrazine they are ca. –0.43 and –0.18 V, respectively (Table 2). The difference between Au species used for the electrode surface treatment are observed only for DMAB solutions where acidic Au colloid leads to more negative potential values indicting a higher electrocatalytic activity of these Au nanoparticles. The oxidation of these compounds at an appreciable rate begins at more positive potentials: ca. –0.4, –0.2 and 0.0 V, respectively for DMAB, BH_4^- and N_2H_4.

The CVs measured in borohydride and hydrazine solutions are of similar form for all GC electrodes (Figs. 3 and 4). At a positive-going potential scan an almost linear rise of the anodic current in a wide potential range is observed, the current reached at the positive potential limit, 0.8 V, is slightly larger for borohydride oxidation (ca. 5.5 mA cm^{-2}), while the maximum current of hydrazine oxidation is about 4.5 mA cm^{-2}. The CV curves are fairly well reproduced at the successive scans showing the absence of irreversible changes of the electrode surface state.

Somewhat different picture was observed for DMAB oxidation: the anodic current at the successive scans progressively decreased (Fig. 5) indicating a fall in the electrocatalytic activity of the surface. This can be explained by the adsorbed intermediates, and the products of DMAB oxidation block the electrode surface, and inhibiting the anodic process.

Table 2. **Open-circuit potentials of GC electrode modified by Au species, in solutions of reducing agents**

Au source	E_{oc}, V		
	DMAB	$NaBH_4$	N_2H_4
$HAuCl_4$ solution	–0.59	–0.42	–0.17
Acidic colloid solution	–0.64	–0.44	–0.18
Alkaline colloid solution	–0.57	–0.45	–0.18

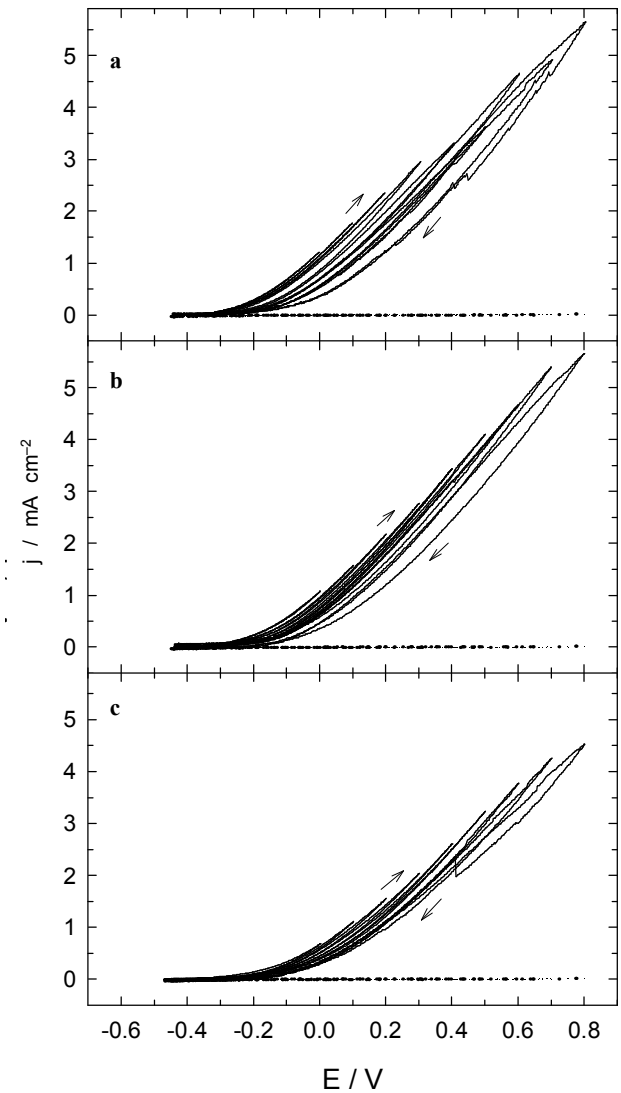

Fig. 3. CVs of the bare GC (dashed lines) and the GC modified by Au (solid lines) in alkaline borohydride solution containing (mol l^{-1}): $NaBH_4$ – 0.05; NaOH – 0.1. The GC electrode modified in solutions: Au(III) solution (*a*), acidic Au colloid (*b*), alkaline Au colloid (*c*). Potential scan rate 10 mV s^{-1}

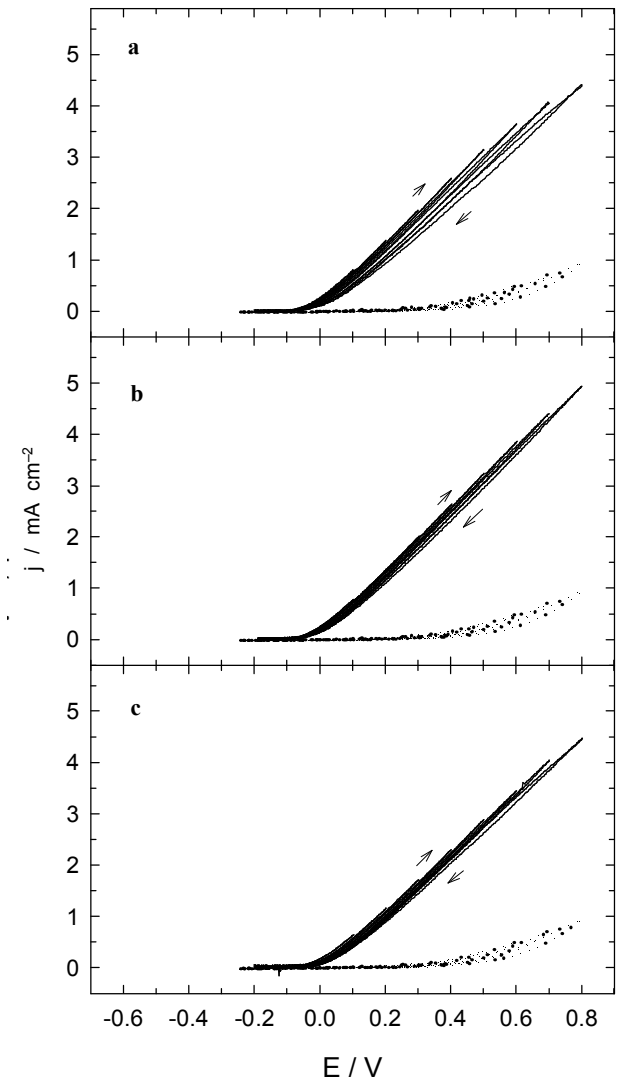

Fig. 4. CVs of the bare GC (dashed lines) and the GC modified by Au (solid lines) in alkaline hydrazine solution containing (mol l^{-1}): N_2H_4 – 0.05; NaOH – 0.1. The GC electrode modified in solutions: Au(III) (*a*), acidic Au colloid (*b*), alkaline Au colloid (*c*). Potential scan rate 10 mV s^{-1}

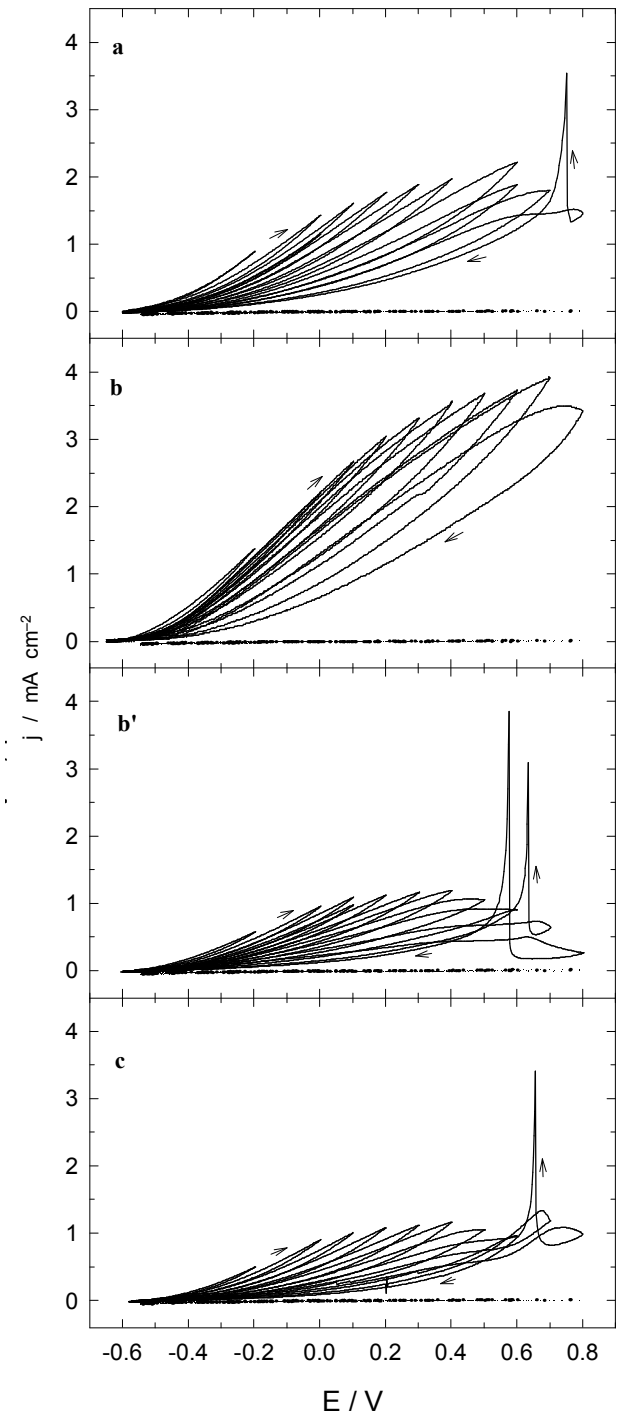

Fig. 5. CVs of the bare GC (dashed lines) and the GC modified by Au (solid lines) in alkaline DMAB solution containing (mol l^{-1}): DMAB – 0.05; NaOH – 0.1. The GC electrode modified in solutions: Au(III) (*a*), acidic Au colloid (*b*, *b'*), (*b'*) two days after colloid preparation; alkaline Au colloid (*c*). Potential scan rate 10 mV s^{-1}

Higher anodic currents for the oxidation of DMAB are obtained on the GC modified with acidic Au colloid compared to the other Au sources (compare *b* and *a*, *c* in Fig. 5). But the catalytic activity of this Au colloid decreases in time, and the electrode activated in this solution is similar to the other ones (Fig. 5 *b*) after one more day. Unusual high peaks of anodic current were observed at the reverse scan in a highly positive potential region (Fig. 5 *a*, *b* and *c*). The similar anodic peak for DMAB-gold system were described in [6, 7], there the formation was explained by the reactivation of gold surface during the reduction of oxide layer and the participation of the reactive intermediates of DMAB oxidation.

The electrocatalytic activity of Au nanoparticles depends on the age of colloid (Fig. 6). The Au particles formed in the acidic medium are more active in hydrazine oxidation as compared to those from the alkaline solution, but the period of activity lasts only several days (Fig. 6a), while the Au particles in the alkaline colloid solution remain active for more than 20 days (Fig. 6*b*).

The difference between the two types of Au colloid solutions is obviously related to the different SnO_2

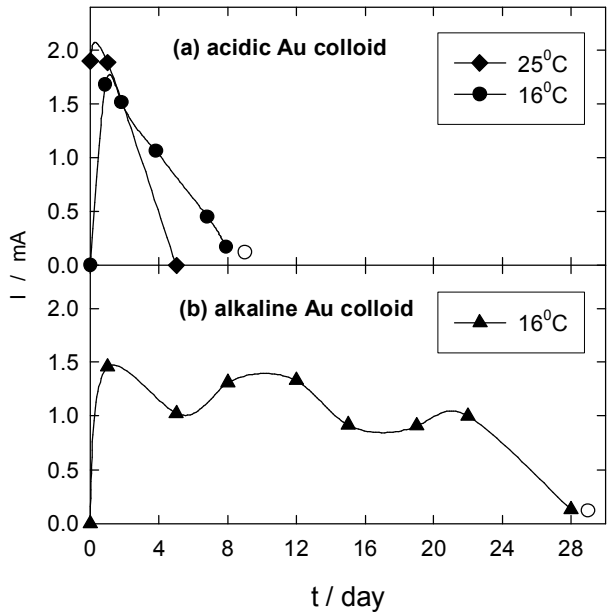

Fig. 6. Dependence of anodic current density on the Au-modified GC electrode at 0.4 V in hydrazine solution on Au colloid age. The solution contained (mol l^{-1}): N_2H_4 – 0.05, NaOH – 0.1. The GC surface was modified in Au colloid solutions: (*a*) acidic, (*b*) alkaline (Table 1). The current values were taken from CVs, positive potential limit 0.4 V

content in the colloid particles. The higher amount of tin(IV) oxide in the Au nanoparticles prepared in alkaline solutions leads to a slower change in the colloid (also to a slower particle formation) age, to a lower catalytic activity due to a higher degree of Au surface shielding. The rate of changes in Au particles and the period of Au colloid solution stability depend also on temperature, therefore, the period of colloid activity becomes considerably longer when the colloid solution is kept at 16 °C instead of 25 °C (Fig. 6*a*). At 25 °C the acidic Au colloid becomes active soon after its preparation, and after 5 h the highest activity of Au particles is achieved, while for the solution kept at 16 °C, the similar activity is observed only after 1 day.

CONCLUSIONS

1. The Au nanoparticles obtained by Au(III) reduction with Sn(II) are electrocatalysts for the anodic oxidation of hydrazine, borohydride and DMAB in alkaline solutions when adsorbed on the GC electrode surface from Au colloid solutions (the surface coverage 200–900 ng cm^{-2} Au).

2. The electrocatalytic activity of the Au particles formed in acidic and alkaline solutions does not differ significantly except for the hydrazine oxidation when the particles prepared in the acidic medium are more active.

3. The presence of SnO_2 (40–70 mol%) does not diminish the catalytic activity of Au particles or even enhances it.

4. The GC electrode becomes electrocatalytically active after immersion in Au(III) solution due to a spontaneous metallic Au formation in gold ions interaction with carbon on the GC surface.

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AUKSO NANODALELIŲ ELEKTROKATALIZINĖS SAVYBĖS REDUKTORIŲ OKSIDACIJOS REAKCIJOSE

S a n t r a u k a

Stiklo anglies elektrodas buvo modifikuotas Au nanodalelėmis (200 μg – 900 ng cm^{-2}), naudojant koloidinius tirpalus, gautus redukuojant AU(III) tirpalą Sn(II) chloridu. Taip modifikuotas stiklo anglies elektrodas katalizina hidrazino, borhidrido ir dimetilaminoborano oksidacijos reakcijas. Stiklo anglies elektrodo paviršiaus, modifikuoto Au nanodalelėmis, tiek rūgštiniame, tiek šarminiame Au koloiduose, aktyvumas beveik nesiskiria, išskyrus hidrazino oksidacijos atvėjį, kai paviršius, modifikuotas rūgštiniame Au koloide, yra aktyvesnis.