

Electrochemistry of metal nanoparticles: the effect of substrate

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Abstract It is shown that nanoparticles localized on a foreign solid electrode may display two opposite shifts of dissolution potential, namely, a shift toward either more positive or more negative values as compared with the equilibrium potential of M^{n+}/M^0 or the potential of bulk metal electrooxidation. The observed phenomena are interpreted in view of three energy states of substance, which are realized depending on contribution of the surface Gibbs free energy (ΔG°) to the energy of the system. Literature data concerning different metal-substrate pairs and specially conducted experimental investigations of electrooxidation of gold nanoparticles (radius equal to 10 and 150 nm), which are localized on the surface of glassy carbon, bulk gold, and platinum electrodes are presented and discussed. A shift of maximum current potential of small nanoparticles oxidation toward more positive values is observed in this series. The oxidation potential of large nanoparticles is not affected by the nature of the substrate. In all cases, electrooxidation of gold nanoparticles occurs at the more negative potentials than those of the bulk gold electrooxidation. It is shown that depending on the nature of the substrate and nanoparticle size, the dominating effect is either interaction of nanoparticles with the substrate ($\Delta G^\circ < 0$) and

electrochemical potential shifts toward positive values or impact of surface Gibbs free energy of nanoparticles ($\Delta G^\circ > 0$) into energy of the system and electrochemical potential shifts toward negative values. The validity of the proposed assumptions is confirmed by good correlation of literature and our experimental data with calculated ones.

Keywords Gold nanoparticles · Electrooxidation · Effect of substrate · Size-dependent effect

Introduction

Electrochemical behavior of metal nanoparticles, which are localized on the solid substrate, has been investigated in a number of papers, which stated the different behavior of nanoparticles, localized on different substrates. The potential of nanoparticles electrooxidation shifts toward more positive as well as more negative values in comparison with the equilibrium potential of M^{n+}/M^0 or the potential of bulk metal electrooxidation. In particular, the authors of [1–7] have analyzed electrooxidation of nanoparticles localized on the solid surface, which occurs, as a rule, at potentials with more negative values than the values of the potential of electrooxidation of the corresponding bulk metal. Meanwhile, the authors of [8–12] have argued that electrooxidation of metal nanoparticles occurs at a potential with a more positive value than the equilibrium potential of M^{n+}/M^0 or the potential of bulk metal electrooxidation. For example, it has been demonstrated in [8] that the potential of single gold nanoparticle, localized on the platinum nanoelectrode, shifts toward more positive values relative to the potential of the bulk gold electrode oxidation if the particle becomes smaller. The authors explain the observed phenomenon by specific stability of nanoparticles compared with bulk metal.

“Our best regards to Nina Zacharchuk, our friend and recognized person in Electrochemistry and our best wishes to her for many years to come”.

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This statement can hardly be agreed with. The findings given in [8–12] suggest that the substrate (electrode) affects the energy state of nanoparticles, and in certain cases, there may be an interaction, similar to that observed during underpotential deposition (UPD), formation of intermetallic compounds or alloys.

The classic works devoted to initial stages of electrocrystallization [13] where crystallization overpotential is discussed from thermodynamic point of view, and data concerning UPD [14, 15], were used in the concept of three energy states of the metal on the electrode surface [16]. The later provides the possibility to include the electrodisolution processes into consideration. This approach, in our opinion, can be prospective in the description of the regularities, observed in ready-made nanoparticles, localized on the solid electrode electrooxidation. This approach is illustrated by the diagram, given below [16], where M_I , M_{II} , and M_{III} are the metal in the first, second, and third energy state, ΔG° —surface Gibbs free energy:

M_I	M_{II}	M_{III}
$\Delta G^\circ < 0$	$\Delta G^\circ \approx 0$	$\Delta G^\circ > 0$

It is obvious that the left part of the diagram describes UPD processes, while the right one—electrooxidation of nanoparticles [17].

The shifts of oxidation potentials of nanoparticles localized on a foreign solid electrode in two opposite directions can be explained as follows: the potential of nanoparticles electrooxidation shifts toward negative values when the substrate is inert to the particles, and toward positive values when metal nanoparticles interact with the substrate.

For rigorous description of the phenomena, it is necessary to take into account different energies of different

crystal planes, but it is not clear how to take it into account considering nanoparticles, for example, how to evaluate what is more essential in this case; difference in crystallography or impact of broken links on the surface. That is why we think that that approach proposed is suitable as the first step in understanding of the problem.

Theoretical considerations

Returning to the aforementioned diagram and the results presented in [16, 17], it is expected that the transition from the systems where electrooxidation of nanoparticles occurs at potentials more negative than those of the bulk metal electrooxidation, to the systems that are experiencing the opposite phenomenon, depends on the magnitude of the surface Gibbs Free energy of nanoparticles itself and Gibbs free energy of interaction of metal–substrate interaction. The latter is associated with the difference in work functions ($\Delta\Phi$) between metal nanoparticles and the substrate [16], possibility of formation of alloys and/or intermetallic compounds in the system metal–substrate.

Table 1 compares the above-mentioned quantities ($\Delta\Phi$) and potential shifts (ΔE) of electrooxidation of metal nanoparticles localized on different substrates, given in some publications.

The table shows that between the magnitude of $\Delta\Phi$, the nature of interactions in the nanoparticle metal–electrode and the oxidation potential of nanoparticles there is an interrelationship.

Thus, if $\Delta G^\circ > 0$, the metal does not interact with the substrate material, and the maximum current potential of nanoparticles oxidation is reduced compared with the corresponding value for bulk metal. The magnitude of the shift of the oxidation potential toward negative values is

Table 1 Comparison of work functions and potential shift values in different systems

System	$\Delta\Phi = (\Phi_m - \Phi_s)$, eV	Type of interaction in system [16]	Particle diameter, nm	ΔE , V	Reference
Au/C	0.28	No interaction	20 300	−0.252 ^a −0.101 ^a	[3]
Ag/C	−0.37	No interaction	0.4–1.0	+0.500 ^b	[11]
Bi/C	−0.66	No interaction	106	−0.149 ^a	[4]
Au/Pt	−0.24	Solid solution	14 20	+0.040 ^a +0.013 ^a	[8]
Cu/Au	−0.47	Intermetallic compounds	<1	+0.200 ^a	[10]

Average electron work functions are taken from [22]

Φ_m electron work function of nanoparticle metal (electronvolt), Φ_s electron work function of substrate (electronvolt)

^a $\Delta E = E_m(\text{nps}) - E_m(\text{bulk})$

^b $\Delta E = E_m(\text{nps}) - E_{\text{eq}}(M^{r+}/M^0)$

affected by particle size. These data are consistent with the views expressed in [17]. If $\Delta G^\circ < 0$, the metal, as a rule, interacts with the substrate material, and the maximum current potential of nanoparticles oxidation shifts toward positive values relative to the corresponding values for bulk metal. The exception is Bi/C system, which is likely to be the result of two factors: lack of interaction between Bi and carbon and quite a large size of the investigated nanoparticles.

The approach developed by Plieth [18, 19] implies that standard redox potential of metal nanoparticles shifts toward more negative values compared with the potential of the bulk metal. This value is dependent on the radius of particles. The approach can be viewed as part of more general considerations [16], since the shift E° is defined as function of surface tension, i.e., value of surface Gibbs free energy.

Thus, it should be recognized that potential of nanoparticles oxidation is the result of two countervailing factors, and the reason for the voltammogram shift toward positive potential values lies in the interaction of nanoparticles with the substrate, the formation of intermetallic compounds or alloys, rather than in stability of nanoparticles. The shift in the potential of nanoparticles electrooxidation can serve as an indication of greater particle stability only when nanoparticles are initially produced as alloys or intermetallic compounds and applied to inert, not interacting with them substrate. This conclusion is supported, in particular, by the findings described by Ivanova [20].

These data allow us to give consideration to the following:

1. The stronger interaction in the metal–electrode system, the more positive potential should be for oxidation of the same nanoparticles. Thus, electrooxidation of gold nanoparticles, which are localized on the surface of the glassy carbon electrode (GC), should be observed at potentials with more negative values than in Au/Pt system.
2. The smaller the particle size, the stronger interaction effect in a system and shift of oxidation potential toward positive values. However, smaller particle size will lead to greater contribution of surface Gibbs free energy of nanoparticles itself to thermodynamics of the process, which, in turn, should lead to a shift of oxidation potential toward more negative values. Thus, depending on the nature and size of nanoparticles and substrate, the dominant effect could be either interaction of nanoparticles with the substrate (a shift toward positive potentials), or an impact of the surface Gibbs free energy of nanoparticles in the energy of the system (a shift toward negative potentials).
3. As the size of the particles grows, both effects will reduce and the oxidation potential will be close to the potential of the bulk metal oxidation.

Further, we present the results of experimental studies and calculations in order to support these considerations.

Methods of calculations and the choice of parameters

We used two approaches to take into account the effect of interaction in the “metal nanoparticle–electrode” system based on:

- the ratio between the difference in maximum current potentials in voltammograms (ΔE) and the difference of the electron work functions ($\Delta\Phi$) of metal electrode, which is proposed by Gerisher et al. [14]

$$\Delta E = \alpha \Delta\Phi \quad (1)$$

where $\alpha = 0.5 \text{ V/eV}$,

model and calculation equations proposed earlier in [17]. The value of ΔG° was found taking into account relation $E^\circ = \Delta G^\circ / zF$ [21] and Eq. 1. It follows from them a simple relationship,

$$\Delta G_1^\circ = \alpha F \Delta\Phi \quad (2)$$

It is believed that the surface Gibbs free energy of the system can be presented as an algebraic sum of its parts. Thus,

$$\Delta G^\circ = \sum (\Delta G_1^\circ + \Delta G_2^\circ) \quad (3)$$

where ΔG° —surface Gibbs free energy of metal–electrode interaction ($\Delta G_1^\circ \leq 0$), ΔG_2° —surface Gibbs free energy of nanoparticles ($\Delta G_2^\circ \geq 0$). $\Delta G_2^\circ = \sigma \times S$, where σ —surface tension of nanoparticle metal, S —mole surface of nanoparticles. Equation 3 will further be used for calculating voltammograms. The problem is that the range of published values of electron work function is broad [22], however, trends are likely to be observed.

Initial data for calculations are given in Table 2. We used the average quantities of surface tension and electron work function for Au and Pt as the most probable.

The correctness of the approach and the choice of values for $\Delta\Phi$ are illustrated in Fig. 1 which shows the curves calculated for different ΔG_1° , corresponding to different values of electron work functions chosen within the range of published values [22]. The resulting set of voltammograms “covers” the experimental curve. The latest one is close enough to the curve corresponding to the mean value of $\Delta\Phi = -0.24 \text{ eV}$, which is used in the further calculations.

Experimental section

Chemical reagents and instruments. Procedures.

Reagents (high purity and extra high purity grade): acids: HCl (Reachim, Russia) and HNO₃ (Chimreaktivsnab, Russia); sodium citrate (Na–cit) (Labtech, Russia), HAuCl₄. All solutions were prepared with deionized water with a

Table 2 Parameters for calculating voltammograms of gold nanoparticles electrooxidation

Parameter	Value
M —molar mass of gold	197 g mol ⁻¹
ρ —density of gold	19.3 g cm ⁻³
σ —surface tension of gold on the boundary with air (at 700 °C)	1,200 dyne cm ⁻¹ [24]
n —number of electrons involved in the electrode process	1
δ —fraction of particles of a particular size	Relative units
E° —standard electrode potential for the process $\text{Au} + \text{Cl}^- \rightarrow \text{AuCl} + \bar{e}$	0.95 V [25]
k_s —constant of the electrode process rate	3×10^{-8} cm s ⁻¹ [3]
ΔG°_2 —surface Gibbs free energy of particles:	J mol ⁻¹
10 nm Au nps	3,675
150 nm Au ps	245
1,000 nm (Au bulk)	37
Φ —average electron work functions of elements:	eV
Au	5.29 [22]
Pt	5.53 [22]
$\Delta\Phi(\text{Au}/\text{Pt})$ —difference of electron work functions between nps metal (Φ_{Au}) and the substrate (Φ_{Pt})	-0.24 eV
ΔG°_1 —Gibbs free energy of metal–electrode interaction (Au/Pt)	-7,903 J mol ⁻¹

resistivity of no less than 18 M Ω cm, obtained with the membrane system DVS-M/1NA (18)-N (Russia).

Electrochemical behavior of gold nanoparticles localized on different substrates was examined with potentiodynamic voltammetry, by using IVA-5 (Russia), a semiautomatic inverse voltammetric analyzer, and a three-electrode electrochemical cell. A glassy carbon rod was used as auxiliary electrode; a saturated silver/silver chloride electrode (SCE) ($E=0.22$ V vs NHE)—as reference electrode. GC (Metrohm, Switzerland), disk Pt (Metrohm, Switzerland), and gold-sputtered (hereafter “bulk”) electrodes ex situ modified with gold nanoparticles (Au nps) were used as working electrodes. The working surface area of GC and Pt was 0.07 cm². The gold electrode (Au_{bulk}) which served as bulk one was produced by vacuum metal sputtering from the wire surface ($d=0.2$ mm, 99.99 % pure gold) onto polyethylene-terephthalate strip (0.25 mm) by VUP-4 [3]. The deposited gold layer was 0.5–1.0 μm thick. Cementit 3172 glue was applied to isolate the working area of the electrodes.

Au nps were synthesized by chemical reduction of aqueous solution of H₂AuCl₄ with sodium citrate [3]. Gold sol containing smaller particles (red sol) was obtained at $C(\text{AuCl}_4^-)/C(\text{Na-cit})=1:5$, while sol containing larger particles (blue sol) was obtained at $C(\text{AuCl}_4^-)/C(\text{Na-cit})=1:1$. The magnetic stirrer with controlled heating IKA RCT basic (Germany) was used for synthesis of gold nanoparticles.

Gold sols with varying concentrations were prepared by diluting either the initial solution of H₂AuCl₄ or concentrated sol. All synthesized sols were stored at +4 °C in the dark.

Before immobilization of gold particles, the surfaces of Pt and GC were polished with aluminum powder (0.3 μm). Then they were thoroughly washed with deionized water and the voltammograms were recorded using 0.1 M HCl as background electrolyte. Immobilization of gold nanoparticles on the electrode surface was carried out by dropping a few microliters of sol to the working area of the electrode and left at room temperature in the open air until completely dry. The number of Au nps on the electrode surface was varied by applying different amounts of solutions with different concentrations, using micropipettes with variable volume dosage of 0.5–10 μl (Lenpipet, Russia). The results of studies of the electrode surface modified with red and blue sols by scanning electron microscopy (Leo 982, Germany) are described in [3]. On the electrode surface modified with red gold sol, the predominant particle radius (r_0) was 10 nm; with blue sol—150 nm. Research carried out by optical microscopy showed that the surface of the bulk gold electrode has a granular structure. In the calculations, the radius of the grains was taken as 1 μm , assuming that the properties of the particles of that size do not differ from the properties of bulk metal.

Voltammograms of gold were recorded at a linear potential sweep in the range from 0.5 to 1.4 V at a scan rate 0.05 Vs⁻¹ using 0.1 M HCl as a background electrolyte. The peak of gold oxidation potential (E_m , volts), the maximum current (I_m , microamperes), and quantity of electricity (Q_0 , microcoulombs) which corresponded to the quantity of substance participating in the electrochemical process, were measured. Q_0 was determined by graphical integration of

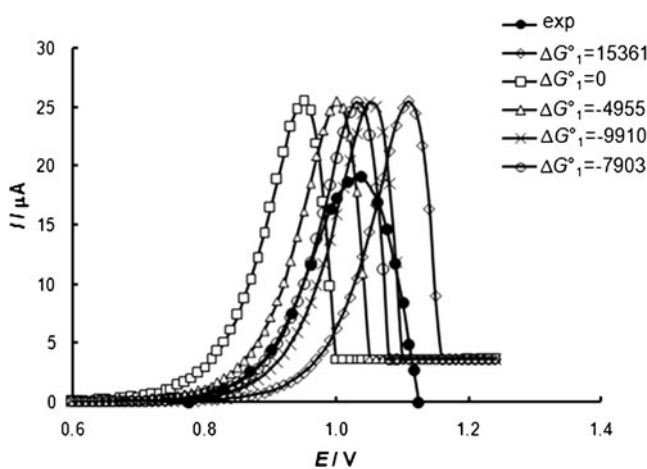


Fig. 1 Voltammograms of gold nanoparticles electrooxidation calculated for different Φ_{Au} , and experimental one. Parameters for calculations are given in Table 2. Experimental conditions were the following: gold nanoparticles ($r_0=10$ nm) were localized on Pt electrode, 0.1 M HCl was used as background solution, $v=0.05$ V s⁻¹

the area under the voltammograms of gold oxidation. All potentials are given relative to SCE.

Data and discussions

Figure 2 shows the voltammograms of electrooxidation of Au nps ($r_0=10$ nm) localized on the surface of GC (Fig. 2a, curve 1), bulk Pt (Fig. 2a, curve 2), and Au electrodes (Fig. 2b). The measured values of the parameters for voltammograms are given in Table 3. It is apparent that in this series gold nanoparticles, localized to GC, are first to oxidize, while those localized on Pt are the last to oxidize. In the first case, the peak potential of nanoparticles oxidation is by 129 mV (curve 1) more negative than in the second (curve 2). However, in both cases, electrooxidation of Au nps occurs at potentials more negative than electrooxidation of Au_{bulk} ($E_m=1.186$ V).

Figure 3 presents voltammograms for oxidation of larger gold particles ($r_0=150$ nm) localized on the surface of GC (curve 1) and Pt (curve 2). In this case, the gold particles localized on the surface of the GC and Pt electrodes are oxidized at the same potential of ~ 1.09 V. This implies that an increase in nanoparticle size effect of the substrate decreases.

Comparison of the data presented in Figs. 2 and 3 and Table 3 also shows that with increasing size of gold particles, regardless of the substrate material (GC or Pt), the peak potential of gold oxidation increases in the row E_m (10 nm Au nps) $< E_m$ (150 nm Au nps) $< E_m$ (Au_{bulk}). The latter again confirms the manifestation of the size effect in nanoparticle electrochemistry, which we stated earlier while studying electrooxidation of gold [3], bismuth [4], and silver [5] nanoparticles on the surface of thick-film carbon (screen-printed) electrode. Thus, as expected, the gold nanoparticles localized on graphite screen-printed electrode and GC are oxidized at nearly the same potential.

The observed results can be easily interpreted within the framework of the considerations described above. The shift of the peak potential of oxidation of small gold particles, localized on Pt, toward more positive values as compared with GC, occurs apparently due to the interaction of gold nanoparticles with Pt surface (Table 1). For Au/GC, interaction is not observant, that is why the oxidation potential is affected by the size of particles only. A slight shift (25 mV) of the oxidation potential toward more positive values during electrooxidation of gold nanoparticles on Au_{bulk} surface might be related to different orientation of crystallographic planes of nanoparticles and bulk gold. This statement is consistent with the data [22], which show that work function can change for crystalline elements based upon the orientation. For example, for Au, work function varies from 5.1 to 5.47 depending on the orientation of crystallographic faces

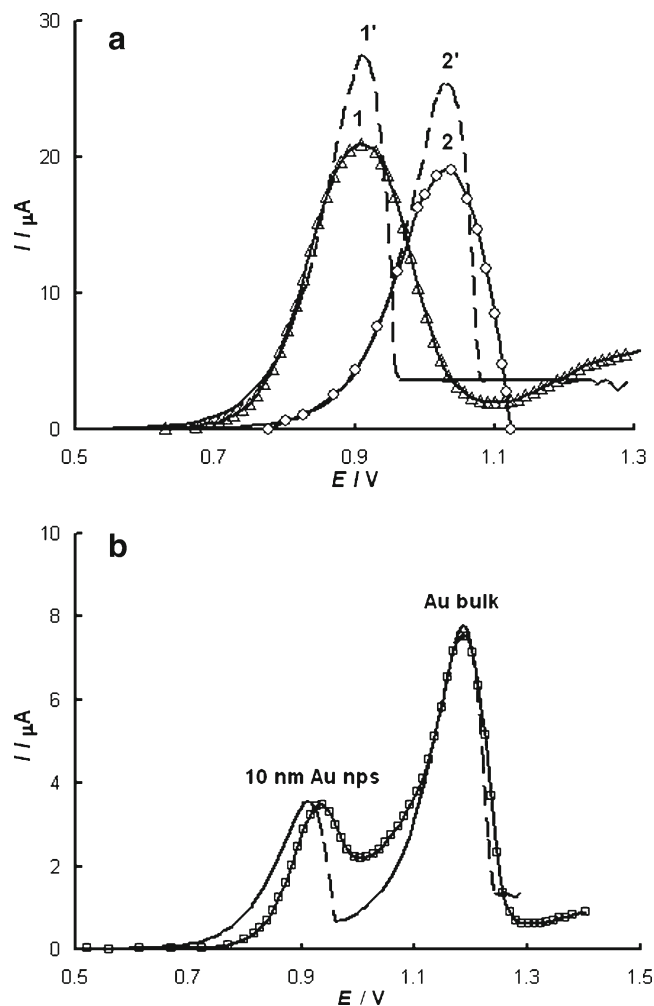


Fig. 2 Experimental ($I-2$) and calculated ($I'-2'$) voltammograms of electrooxidation of gold nanoparticles ($r_0=10$ nm), localized on: **a** GC (1), Pt (2); **b** Au_{bulk} (squares) (background is subtracted), calculated voltammograms (dashed). Background: 0.1 M HCl, $\nu=0.05$ V s⁻¹. Parameters for calculations are the following: $\Delta G^\circ_1=-7,903$ J mol⁻¹ (Pt); $\Delta G^\circ_2=3,675$ J mol⁻¹ (GC, Au_{bulk}), $\delta=0.5$ (b), other parameters: as given in Table 2

on the surface. In Figs. 2 and 3, the dashed line is used for calculated (Eq. 1) voltammograms of electrooxidation of gold particles ($r_0=10$ and 150 nm), which are localized on different electrodes. In this case, the calculations were based on the proposed model [17], where ΔG° was calculated from Eq. 3. Table 3 compares the parameters of the experimental and calculated voltammograms. Presented in Figs. 2 and 3 and Table 3 data demonstrate an agreement between the experimental and calculated results, which confirms the validity of assumptions. Significant discrepancy between the calculated and experimental data is observed only when describing electrooxidation of large gold nanoparticles ($r_0=150$ nm) localized on Pt. This results, as it will be shown further, from the fact that an increase in particle size leads to a significant reduction of area of particle contact with electrode surface. Consequently, contribution of the “metal–

Table 3 Parameters for calculated and experimental voltammograms of gold nanoparticles electrooxidation

Electrode	Au _{bulk}	Gold nanoparticles localized on the surface of				
		GC	Au _{bulk}	Pt		
Au nps radius, nm	1000	10	150	10	10	150
E_m , V experimental	1.186	0.909	1.090	0.934	1.038	1.086
ΔE_m , V calculated (Eq. 1)	1.190	0.910	1.090	0.910	1.030	1.170
$\Delta E_m = E_m(\text{bulk}) - E_m(\text{nps})$ experimental	–	0.277	0.096	0.252	0.148	0.100
$\Delta E_m = E_m(\text{bulk}) - E_m(\text{nps})$ calculated (model [17])	–	0.280	0.100	0.280	0.160	0.020
I_m , μA experimental	7.36	20.95	37.96	3.48	19.03	21.36
I_m , μA calculated	7.32	27.41	34.77	3.47	25.40	24.90
Q_0 , μC	8.46	66.45	85.06	17.85	61.88	60.71

Experimental conditions are the following: background electrolyte—0.1 M HCl, $v=0.05 \text{ V s}^{-1}$

electrode” interaction energy to the energy of the system becomes less significant and results in a shift of the peak potential of the experimental curve toward more negative values as compared with the calculated curve.

Below is given calculation of the ratio of the areas of contact between nanoparticles with radius equal to 10 and 150 nm with a flat electrode. The calculations are based on the concept of static pressing of a ball to flat surface when the “contact patch” is [23]:

$$d = [0.75fD(\eta_1 - \eta_2)]^{\frac{1}{3}} \quad (4)$$

where d —diameter of the “contact patch”; $D=2 \times r_0$ —diameter of the particle; f —force which presses a ball to the supporting surface; η_1, η_2 —coefficients reflecting strength properties of the ball substance and supporting surface. The number of nanoparticles in the same amount of substance (total charge Q_0) is in inverse proportion to r_0^3 . Thus, the total contact area

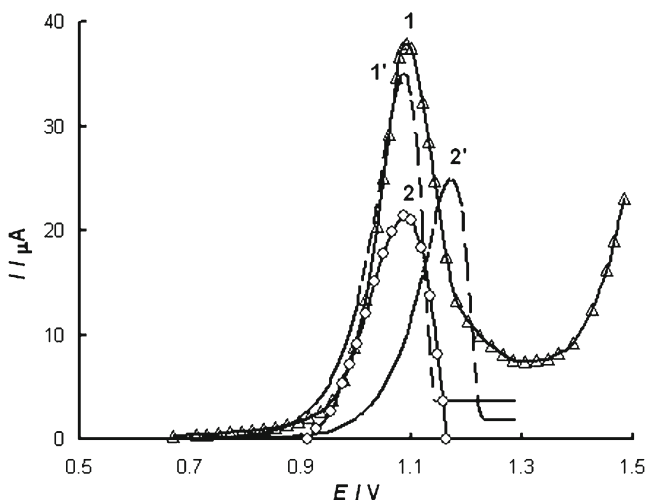


Fig. 3 Experimental ($I-2$) and calculated ($I'-2'$) voltammograms of electrooxidation of gold nanoparticles ($r_0=150 \text{ nm}$), localized on GC (1) or Pt (2) (background is subtracted), calculated voltammograms (dashed). Background: 0.1 M HCl, $v=0.05 \text{ V s}^{-1}$. Parameters for calculations are the following: $\Delta G^{\circ}_1=-7,903 \text{ J mol}^{-1}$ (Pt), $\Delta G^{\circ}_2=245 \text{ J mol}^{-1}$ (GC). Other parameters: as given in Table 2

of an ensemble of nanoparticles with the surface of the electrode under otherwise equal conditions is inversely proportional to particle radius to the power 7/3. It can be assumed that the intensity of interaction of particles of variable sizes with the electrode surface is determined by the total contact area, i.e.

$$\frac{\Delta G_1}{\Delta G_2} \approx \left[\frac{r_2}{r_1} \right]^{\frac{7}{3}} \quad (5)$$

This approach allows excluding unknown parameters from Eq. 4 from our consideration.

This implies that the total contact area of particles with $r_0=10 \text{ nm}$, with a surface electrode is $(150/10)^{7/3}=555$ times larger than the corresponding quantity for particles with $r_0=150 \text{ nm}$ (at the same amount of gold on the electrode surface). These estimates are illustrated in Fig. 4, which demonstrates the ratio of the total areas of “contact patches” for particles with variable sizes. Particles with $r_0=1,000 \text{ nm}$ were chosen as the basis for comparison.

The given data explain the observed lower effect of substrate when particle size increases. This results from a

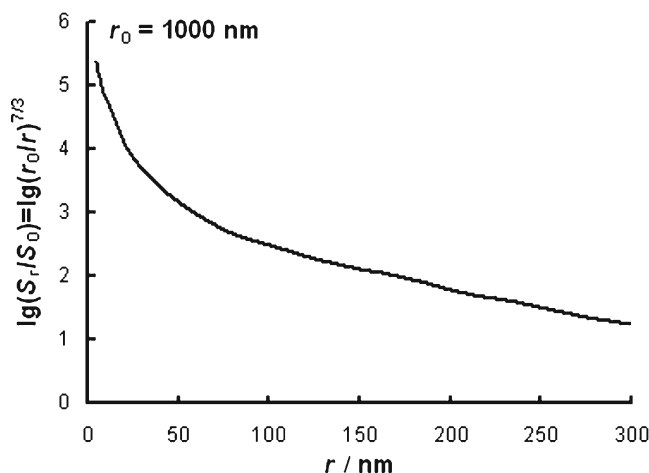


Fig. 4 The dependence of the total area of “contact points” on the particle size

decrease in the relative surface contact area of larger particles with the electrode surface as compared with smaller particles.

Conclusion

Phenomena described above fit into the scheme proposed by us earlier [16]. The position of voltammograms of nanoparticles oxidation on the potential axis is determined by the nature of interactions which are observed in the “metal–electrode” system: in the presence of strong interactions (large difference between electron work functions of the metal and the electrode, formation of solid solution or intermetallic compounds) voltammograms of metal oxidation shift toward more positive values as compared with voltammograms of bulk metal electrooxidation. Electrooxidation of nanoparticles, localized on the particle–inert surface, occurs at potentials with more negative values than the oxidation potential of bulk metal. Thus, two countervailing factors are present in the “nanoparticle–substrate” system. The predominance of one of them is determined by the ratio of the Gibbs free energy of nanoparticles and the energy of metal interaction with the substrate [2]. The latter can be characterized by ΔG°_1 which is determined by the difference $\Phi_m - \Phi_s$, where Φ_m —electron work function of nanoparticle metal; Φ_s —electron work function of the substrate material.

In practice extreme as well as intermediate cases can exist. A shift of peak current potential in the system Au/GC to negative values as compared with the peak current potential of oxidation of the bulk metal indicates a greater contribution of surface Gibbs free energy of nanoparticles to the energy of the system relative to the energy of interaction between metal and electrode. The shift of peak current potential to positive values in the system Au/Pt indicates a greater contribution of Gibbs free energy of metal–substrate interaction to the system energy.

Consequently, speaking about manifestation of some enhanced stability of nanoparticles relative to bulk metal requires a high degree of caution, and only when it comes to oxidation of pre-formed nanoparticles of alloys or intermetallic compounds, but then it is not the studied metal but the other object.

The data presented in this paper clearly indicate that the nature of voltammograms of metal nanoparticles oxidation and, in particular, their position on the potential axis are determined by interactions within the metal nanoparticle–electrode system.

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