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On the preferential crystallographic orientation of Au nanoparticles: Effect of electrodeposition time

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ABSTRACT

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Keywords: Electrodeposition Preferential orientation ORR Nanostructures Electron back scatter diffraction (EBSD) The crystallographic orientation of Au nanoparticles electrodeposited at glassy carbon (nano-Au/GC) electrodes (prepared by potential step electrolysis) is markedly influenced by the width of the potential step. The oxygen reduction reaction (ORR) and the reductive desorption of cysteine have been studied on nano-Au/GC electrodes. Furthermore, electron backscatter diffraction (EBSD) technique has been used to probe the crystallographic orientation of the electrodeposited Au nanoparticles. That is, Au nanoparticles prepared in short time (5-60 s) have been found rich in the Au(1 1 1) facet orientation and are characterized by a relatively small particle size (ca. 10–50 nm) as well as high particle density (number of particles per unit area) as revealed by SEM images. Whereas Au nanoparticles prepared by longer electrolysis time (>60 s) are found to be much enriched in the Au(1 0 0) and Au(1 1 0) facets and are characterized by a relatively large particle size (>100 nm). EBSD patterns provided definitive information about the crystal orientations mapping of Au nanoparticles prepared at various deposition times.

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1. Introduction

Nanometer-scale materials are continuously attracting considerable attention due to their unusual and fascinating properties [1–5]. The decrease of the size of materials down to the nanometer range leads to a tremendous change of their surface, electronic and optoelectronic properties compared with their bulk metal counterparts [6,7]. The use of gold nanoparticles has been rapidly extended to several applications in electronics, optoelectronics, electroanalysis [8,9] as well as chemical and electrochemical catalysis [4,10–13]. In this regard, the preparation of tailored design nanostructures in terms of size and crystallographic structure is a subject of unequivocal importance [14–17].

Electrodeposition is among the most familiar binder-free technique used for the preparation of nanoparticles. It is a facile technique which results in the direct attachment of the nanoparticles to the substrate in addition to the facile control of the characteristics of the metal (or metal oxide) (e.g., size, crystallographic orientation, mass, thickness and morphology of the nanostructured materials) by adjusting the operating conditions and bath chemistry [17–21] in contrast to other techniques which require several steps and consume relatively longer time, such as sol–gel [22,23], micelle-based cluster generation [24,25] and metal vapor synthesis routes [26,27]. This paper addresses the influence of the electrodeposition time on the crystallographic orientation of Au nanoparticles deposited on glassy carbon (nano-Au/GC) electrodes. SEM, XRD and electron backscatter diffraction (EBSD) techniques are used to characterize the electrodeposited Au nanoparticles in terms of size and preferential facet orientation. Furthermore, the reductive desorption of cysteine and the oxygen reduction reactions in alkaline medium are used as probing electrochemical reactions to monitor the variation of the crystallographic orientation of the electrodeposited Au nanoparticles with time.

2. Experimental

The working electrode was a GC rod of 3.0 mm diameter sealed in a Teflon jacket leaving an exposed geometric surface area of 0.07 cm^2 . A spiral Pt wire and an Ag/AgCl/KCl (sat) were the counter and the reference electrodes, respectively. Prior to the electrodeposition of Au nanoparticles, the GC electrode was polished with aqueous slurries of alumina powder (particle size down to $0.06 \,\mu\text{m}$) with the help of a polishing microcloth then sonicated for 10 min in Milli-Q water. Au nanoparticles were electrodeposited from 0.5 M H₂SO₄ + 1.0 mM Na[AuCl₄] solution by applying potential step electrolysis from 1.1 to $0.0 \,\text{V}$ vs. Ag/AgCl/KCl(sat) [20,28]. The duration of the potential step electrolysis was varied from 5 to 900s to obtain Au deposits with different characteristics (cf. Table 1). The thus-prepared Au nanoparticles-electrodeposited GC electrodes were characterized electrochemically in a deoxygenated (i.e., N₂saturated) 0.5 M H₂SO₄ solution (cf. Fig. 1). The self-assembled

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Fig. 1. SEM micrographs of Au nanoparticles electrodeposited onto GC electrodes from 0.5 M H₂SO₄ containing 1.0 mM Na[AuCl₄] by applying potential step electrolysis from 1.1 to 0 V vs. Ag/AgCl/KCl(sat) with a step width of (a) 5, (b) 10, (c,c') 60, (d,d') 300, (e,e') 900 s. Note that images c'-e' are taken at an inclination of 70° of the sample.

monolayer (SAM) of cysteine [HS-CH₂-CH(NH₂)-COOH] was prepared by immersing the nano-Au/GC electrodes into an aqueous solution of 1.0 mM cysteine for 20 min. The reductive desorption experiments were carried out in a deoxygenated 0.5 M KOH solution. For the oxygen reduction measurements, O_2 gas was bubbled directly into the cell containing 0.5 M KOH to obtain an O_2 -saturated solution and during the measurements O_2 gas was flushed over the cell solution. Electrochemical measurements were performed in a three-electrode cell using EG&G potentiostat (model 273A) at room temperature. The current densities were calculated on the

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Variation of O _{Au(111}) of Au	nanoparticles with electrode	position time $(t_{\rm s})$. T	he nano-Au/GC electro	odes were prepared a	is described in the car	ption of Fig. 1.
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t _d (s)	Amount of deposited Au nanoparticles ^a ($\mu g cm^{-2}$)	Equivalent film thickness ^b (nm)	$Q_{Au(111)}^{c}$ (%)	Particle size range (nm)	Particle density ^d
5	1.53	0.79	90	5-20	~100
10	1.94	1.01	85	10-50	~75
30	3.11	1.61	75	15-60	~ 70
60	5.37	2.78	55	20-80	~55
120	8.12	4.21	48	50-120	~55
300	18.26	9.46	35	50-200	~ 50
900	43.12	22.91	30	100–500	~30

^a Calculated from the Q-t curves during the potential step electrolysis.

^b The thickness of a homogeneous Au film that covers the entire surface area of GC electrode and with the same Au loading as that of electrodeposited Au nanoparticles.

 c $Q_{Au(111)}$ represent the ratio of the amount of charge consumed during the reductive desorption of cysteine SAMs from the Au(111) and Au(100)+Au(110) surface domains, respectively at -700 and -1000 mV vs. Ag/AgCl/KCl(sat)) [33-37].

 $^d\,$ The number of particles per 1 $\mu m^2.$

basis of the geometric surface areas of the electrodes. All chemicals used in this study were of analytical grade and were used without further purification. XRD measurements were performed on PANalytical X'Pert PRO MRD X-ray Diffractometer, using Cu K α_1 radiation (λ = 1.54056 Å) with a Ni filter working at 45 kV and 40 mA. Scanning electron microscopy (SEM) and electron backscatter diffraction analyses of the Au nanoparticles electrodeposited onto GC electrodes were carried out using an JSM-6500F scanning electron microscope (JEOL Optical Laboratory, Japan) equipped with a backscatter camera.

3. Results and discussion

3.1. Morphological characterization of Au nanoparticles

Fig. 1 shows typical SEM images of Au nanoparticles electrodeposited onto GC (nano-Au/GC) for different times. Images c'-e' are obtained at an inclined angle of 70° of the sample to allow for the observation of the height and morphology of the electrodeposited Au nanoparticles. These images show an approximately hemispherical shapes of the electrodeposited Au nanoparticles similarly to those in the previous reports [20,29,30]. Particle size distribution and the particle density of the Au nanoparticles electrodeposited on GC electrodes were estimated based on the data in Fig. 1 and the



Fig. 2. Current transient recorded during a potential step from 1.1 to 0V vs. Ag/AgCl/KCl(sat) for a GC electrode in 0.5 M H₂SO₄ + 1.0 mM Na[AuCl₄].

results are given in Table 1. This table shows that, Au nanoparticles with different sizes are present: the size of Au particles increases with increasing electrodeposition time (t_d). At long t_d , a noticeable decrease in particle density is observed which is attributed to the growth and coalescence of the neighboring Au particles. Generally, the first step of metal deposition is the formation of nuclei of the depositing metal. Subsequently, two processes take place, i.e., the growth of the initially formed nuclei and progressive nucleation [31]. The characteristics of the deposit (e.g., granularity, thickness, preferential crystallographic orientation) are determined by several parameters including the overpotential, concentration of active species and the electrodeposition time [20]. For the sake of simplicity, the electrodeposition of Au nanoclusters has been carried out from a solution of $0.5 \text{ M H}_2\text{SO}_4 + 1.0 \text{ mM Na}[\text{AuCl}_4]$ and one value of overpotential has been used (the potential was stepped from 1.1 to 0 V vs. Ag/AgCl/KCl(sat), corresponding to an overpotential (η) of -800 mV [20], and the electrodeposition time is the only parameter that is being tested.

Fig. 2 represents a current transient recorded during the electrodeposition of Au nanoparticles by applying a potential step from 1.1 to 0 V vs. Ag/AgCl/KCl(sat). The initial sharp high current is due



Fig. 3. CVs measured at 100 mV s^{-1} for the various nano-Au/GC electrodes in 0.5 M H₂SO₄. The nano-Au/GC electrodes have been prepared as described in the caption of Fig. 1 with a step width of (a) 5, (b) 10, (c) 30, (d) 60, (e) 300 and (f) 900 s.



Fig. 4. CVs measured at 50 mV s^{-1} for the reductive desorption of cysteine-SAM formed at various nano-Au/GC electrodes in N₂-saturated 0.5 M KOH. The nano-Au/GC electrodes are prepared as described in the caption of Fig. 1 with a step width of (a) 5, (b) 10, (c) 30, (d) 60, (e) 120, (f) 300 and (g) 900 s.

to the charging of the double layer. A current decay is observed which is linear with $t^{-1/2}$ indicating a planar diffusion regime which arises due to the overlapping of the growing hemispherical diffusion layers which provide mass transport for nanocrystal growth [20,32].



Fig. 5. CVs measured at 100 mV s^{-1} for the oxygen reduction at (a) bare GC, (b–d) nano-Au/GC and (e) bare polycrystalline Au electrodes in O₂-saturated 0.5 M KOH. The nano-Au/GC electrodes are prepared as described in the caption of Fig. 1 with a step width of (b) 60, (c) 300 and (d) 900 s.



Fig. 6. XRD patterns of nano-Au/GC electrodes prepared in the same way as in Fig. 1 with a step width of (a) 60, (b) 300 and (c) 900 s.

3.2. Electrochemical characterization of Au nanoparticles

3.2.1. Characteristic CVs

Fig. 3 shows cyclic voltammetric (CV) curves of the various nano-Au/GC electrodes in 0.5 M H_2SO_4 solution at a potential scan rate of 100 mV s⁻¹. This figure shows that the peak current at around 0.9 V (corresponding to the reduction of the Au-oxide monolayer formed during the positive-going potential scan) increases with t_d reflecting the increase of the Au surface area. Table 1 summarizes the loading and surface characteristics of the Au nanoparticles electrodeposited on GC electrodes for different t_d . The appearance of different patterns (positive to 1.1 V) for the formation of the gold oxide layer indicates a difference of the compositional ratios of the different facets covering the Au nanoparticles at each case. However, no quantitative estimation for each facet can be given.

3.2.2. Reductive desorption of cysteine

It has been reported that the polycrystalline Au surfaces are composed, mainly, of three facets of low index crystallographic orientations, i.e., domains of Au(111), Au(100) and Au(110) orientations [33,34]. Each single crystalline domain exhibits different binding strength towards an attached thiol. For instance, for a short chain thiol species like cysteine, a multiple reductive desorption CV pattern was observed at potentials of -700, -1000 and -1100 mV vs. Ag/AgCl/KCl(sat) [33,34], corresponding to the reductive desorption of cysteine from the (QAu(111)), Au(100) and Au(110) domains of a polycrystalline Au electrode [33–37]. The ratio of the peak current intensities reflects the proportion of the low index facets. In order to assess the ratio of the different Au facets, the reductive desorption of cysteine was followed at various nano-Au/GC electrodes.

Fig. 4 shows the CV patterns, measured in 0.5 M KOH solution at potential scan rate of 50 mV s⁻¹, for the reductive desorption of cysteine-SAM formed at the various nano-Au/GC electrodes. This figure shows the existence of multiple reductive desorption peaks at each electrode with different heights depending on t_d . Table 1 summarizes the variation of the ratio of the amount of charge consumed during the reductive desorption of cysteine from the Au(111), Au(100) and Au(111) surface domains (QAu(111)). It reveals two points:



Fig. 7. Electron backscatter diffraction (EBSD) patterns of Au nanoparticles electrodeposited onto GC electrodes (at magnification factor of 80k, *S* = 500 nm). Electrodeposition time: (A) 60, (B) 300 and (C) 900 s. (D) is a color coding to identify the crystallographic orientation of Au nanoparticles (Colour online: blue = 1 1 1, red = 0 0 1 and green = 1 0 1 facets).

- (i) Au nanoparticles electrodeposited at short time are enriched in the Au(111) facet orientation (cf. Fig. 7A). It is worth to mention here that the Au(111) facet is thermodynamically more stable than the Au(100) and Au(110) ones of Au [31].
- (ii) The percentage of $Q_{Au(111)}$ decreases with t_d and reaches about 30% for Au nanoparticles electrodeposited for 900 s (close to the natural ratio obtained at the polycrystalline Au electrodes (25 %) [17]). This reflects the polycrystalline nature of the Au nanoparticles electrodeposited at longer t_d (cf. Fig. 7C).

3.2.3. Oxygen reduction

The oxygen reduction reaction (ORR) was taken as a probing reaction to further assign the facets of the prepared nano-Au/GC electrodes. This reaction has been extensively studied at Au single crystal electrodes [38,39], Au nanoparticles-based electrodes [11,40–42] as well as on thin Au films coated carbon substrates [13,43]. The ORR is well known to depend on the crystallographic orientation of the Au surface in alkaline media [33,38]. Fig. 5 shows CVs measured in O₂-saturated 0.5 M KOH at (a) bare GC, (b–d) nano-Au/GC and (e) bulk Au electrodes. Inspection of this figure reveals some interesting points:

(i) The ORR proceeds quasi-reversibly at the nano-Au/GC electrode prepared at 60 s (curve b) This behavior is similar to that obtained at Au(111) single crystal electrode [33], indicating the enrichment of this nano-Au/GC electrode with Au(111). Furthermore, the peak current density of the ORR at this electrode (curve b) is very close to that obtained at the bare GC (curve a). The latter is know to support a two-electron reduction pathway of O_2 to hydrogen peroxide in alkaline media [40,44,45] and similarly electrode marked b supports the two electron reduction of O_2 as well [33,40].

(ii) The ORR proceeds irreversibly at the nano-Au/GC electrodes (curves c and d) prepared for 300 and 900s with about 1.7 times higher peak current density compared with electrode marked b. The increase in the peak current density is attributed to the increase in the number of exchanged electron during the course of the ORR [33,17]. The behavior of electrodes marked c and d is similar to that observed at the polycrystalline Au electrode (curve e) reflecting the polycrystalline nature of the Au nanoparticles electrodeposited at longer deposition time.

It is worthy to mention here that each nano-Au/GC electrode is considered as a micro disk array-type electrode at which the diffusion layers at individual Au nanoparticles overlap each other to form a linearly expanding diffusion region as can be expected by comparison of the diffusion layer thickness ($\delta = \sqrt{(\pi D_{0_2} t)} \approx 0.021$ cm; D_{0_2} is the diffusion coefficient of O₂ in alkaline aqueous medium ($\approx 10^{-5}$ cm² s⁻¹) and *t* is the electrolysis time (s)) and the average distance between Au nanoparticles ($\approx 50-200$ nm). As can be readily seen that δ is much larger than the average distance between the Au nanoparticles prepared in all cases. Thus, the particle size is of insignificant role towards the ORR and the crystallographic orientation of the Au nanoparticles is believed to play the primary role in determining the electrocatalytic activity towards the ORR.

3.3. XRD and electron backscatter diffraction (EBSD) patterns

The determination of microstructure of Au nanoparticles is important because it determines many of their physical and electrocatalytic properties. Fig. 6 shows the XRD patterns of the Au nanoparticles electrodeposited onto GC electrodes for various durations. The diffraction peaks located at 2θ values of ca. 45 and 80° are attributed to the (011) and (110) planes of the carbon substrate, respectively [46]. This figure reveals the existence of two peaks at 2θ

Table 2

Variation of the total fraction of the (001), (101) and (111) facet domains for the Au nanoparticles electrodeposited for various durations.

<i>t</i> _d (s)	Total fractio	Total fraction			
	(001)	(101)	(111)		
60	0.010	0.026	0.030	45	
300	0.055	0.097	0.069	31	
900	0.089	0.210	0.108	26	

of $\approx 38^{\circ}$ and 64° corresponding to the Au(111) and Au(220) facet domains of the Au nanoparticles, respectively [47]. For the present case, the substrate is glassy carbon, which is of less ordered surface structure and the quantitative estimation of the preferential crystallographic orientation of Au nanoparticles is difficult due to the noisy background of the XRD patterns caused by the interference from the GC substrate.

EBSD is a powerful technique which advantageously allows for obtaining crystallographic information (i.e., crystal orientation mapping) of samples (e.g., particles, clusters, aggregates). Fig. 7 shows typical crystal orientation maps obtained for the same samples in Fig. 1(c-e). Note that particles of the similar orientations are in similar colors. Black regions of the mapping image represent areas undetected by electron backscattering due to roughness of the GC substrate [48]. This figure reveals the following points: (i) Au nanoparticles electrodeposited at short time (60 s, image A) are rich in the (111) orientation (as indicated from the predominance of the blue color) and (ii) longer electrodeposition time (\geq 300s) leads to enrichment of Au nanoparticles with the (100) and (110)orientations as reflected from the high intensity of the red and green colors of images B and C consistently with the observations of the electrochemical measurements (Fig. 4). This observation is consistent with the theoretical studies of the equilibrium and growth forms of three-dimensional crystals, in which the growth forms of three-dimensional crystals contain closely packed crystallographic orientation (the most thermodynamically stable facet, i.e., the (111) facet for Au) at the early stage of electrodeposition [31]. On the other hand, at longer electrodeposition times the percentage of (100) and (110) increases probably due to the more complex mechanism of growth and coalescence of the neighboring Au nanoclusters [31]. The fractions for the (001), (101) and (111) orientations corresponding to the three samples are given in Table 2. The total fraction of a specific facet is the percentage of a specific orientation relative to the total area of the analyzed region of the surface [49]. This table shows that the increase of $t_{\rm d}$ resulted in: (i) increase in the total fraction of the three low index facets of Au nanoparticles and (ii) a decrease in the percent of the (111) orientation. It should be mentioned here that the analysis of the EBSD images (given in Table 2) provided the relative percentage of the three low index facet orientations of the electrodeposited Au nanoparticles and cannot be used to estimate the total surface coverage of GC.

4. Conclusions

In this study, the influence of the electrodeposition time on the preferential crystallographic orientation of Au nanoparticles is followed by electrochemical and EBSD techniques. Au nanoparticles electrodeposited at relatively short potential step width (5–60 s) are

found rich in the Au(111) facet orientation. At longer deposition time (>60 s), the Au nanoparticle's surface consist more Au(100) and Au(110) with a relatively big particle size (>100 nm) and low particle density (number of particles per unit area) as depicted from the SEM images.

References

- A. Wieckowski, E.R. Savinova, C.G. Vayenas (Eds.), Catalysis and Electrocatalysis at Nanoparticle Surfaces, Marcel Dekker, Inc., New York, 2003.
- [2] G. Ozin, A. Arsenault, Nanochemistry: A Chemistry Approach to Nanomaterials, Springer Verlag, New York, 2005.
- [3] M.-C. Daniel, D. Astruc, Chem. Rev. 104 (2004) 293.
- [4] D.M. Kolb, F.C. Simeone, Electrochim. Acta 50 (2005 2989).
- [5] F.M. Bayoumi, B.G. Ateya, Electrochem. Commun. 8 (2006) 38.
- [6] R.E. Cavicchi, R.H. Silsbe, Phys. Rev. Lett. 52 (1984) 16.
 [7] P. Ball, G. Li, Nature 761 (1992) 355.
- [8] R. Raj, T. Okajima, T. Ohsaka, J. Electroanal. Chem. 543 (2003) 127.
- [9] C.M. Welch, R.G. Compton, Anal. Bioanal. Chem. 384 (2006) 601.
- [10] M.S. El-Deab, T. Ohsaka, Electrochem. Commun. 4 (2002) 288.
- [11] N. Alexeyeva, T. Laaksonen, K. Kontturi, F. Mirkhalaf, D.J. Schiffrin, K. Tammeveski, Electrochem. Commun. 8 (2006) 1475.
- [12] M. Haruta, Catal. Today 72 (1997) 63.
- [13] A. Sarapuu, M. Nurmik, H. Mander, A. Rosental, T. Laaksonen, K. Kontturi, D.J. Schiffrin, K. Tammeveski, J. Electroanal. Chem. 612 (2008) 78.
- [14] D.L. Feldheim, C.A. Foss, Metal Nanoparticles; Synthesis, Characterization and Applications, Marcel Dekker, New York, 2002.
- [15] J. Rockenberger, E.C. Scher, A.P. Alivisatos, J. Am. Chem. Soc. 121 (1999) 11595.
 [16] Q. Song, Z.J. Zhang, J. Am. Chem. Soc. 126 (2004) 6164.
- [17] M.S. El-Deab, T. Sotomura, T. Ohsaka, J. Electrochem. Soc. 152 (2005) C1.
- [18] D.-L. Lu, K.-I. Tanaka, J. Phys. Chem. 100 (1996 1833).
- [19] H. Huang, X. Yang, Colloids Surf. A: Physicochem. Eng. Aspects 255 (2005) 11.
- [20] M.O. Finot, G.D. Braybrook, M.T. McDermott, J. Electranal. Chem. 466 (1999) 234.
- [21] V. Srinivasan, J.W. Weidner, J. Electrochem. Soc. 144 (1997) L210.
- [22] H.Y. Lee, S.W. Kim, H.Y. Lee, Electrochem. Solid-State Lett. 4 (2001) A19.
- [23] M.S. Hong, S.H. Lee, S.W. Kim, Electrochem. Solid-State Lett. 5 (2002) A227.
 - [24] J. Spatz, S. Mossmer, M. Moller, Chem. Eur. J. 2 (1996) 1552.
 - [25] R. Glass, M. Moller, J.P. Spatz, Nanotechnology 14 (2003) 1153.
 - [26] M. Magnusson, K. Deppet, J.-O. Malm, J.-O. Bovin, L. Samuelson, Nanostruct. Mater. 12 (1999) 45.
 - [27] P.J. Collier, J.A. Iggo, R. Whyman, J. Mol. Catal. A: Chem. 146 (1999) 149.
 - [28] M.S. El-Deab, T. Okajima, T. Ohsaka, J. Electrochem. Soc. 150 (2003) A851.
 - [29] L. Komsiyska, G. Staikov, Electrochim. Acta 54 (2008) 168.
 - [30] M.S. El-Deab, T. Okajima, T. Ohsaka, J. Electrochem. Soc. 153 (2006) E201.
 - [31] E. Budevski, G. Staikov, W.J. Lorenz, Electrochemical Phase Formation and Growth, VCH, Weinheim, 1996 (Chapter 4).
 - [32] G. Gunawardena, G. Hills, I. Montenegro, B. Scarifker, J. Electroanal. Chem. 138 (1982) 225.
 - [33] M.S. El-Deab, K. Arihara, T. Ohsaka, J. Electrochem. Soc. 151 (2004) E213.
 - [34] K. Arihara, T. Ariga, N. Takashima, K. Arihara, T. Okajima, F. Kitamura, K. Tokuda,
 - T. Ohsaka, Phys. Chem. Chem. Phys. 5 (2003) 3758. [35] M.M. Walczak, C.A. Alves, B.D. Lamp, M.D. Porter, J. Electroanal. Chem. 396
 - (1995) 103.
 - [36] C.-J. Zhong, J. Zak, M.D. Porter, J. Electroanal. Chem. 421 (1997) 9.
 - [37] D.-F. Yang, C.P. Wilde, M. Morin, Langmuir 12 (1996) 6570.
 - [38] S. Strbac, R. Adzic, Electrochim. Acta 41 (1996) 2903.
 - [39] C. Paliteiro, N. Martins, Electrochim, Acta 44 (1998) 1359.
 - [40] M.S. El-Deab, T. Sotomura, T. Ohsaka, Electrochem, Commun, 7 (2005) 29.
 - [41] F. Gao, M.S. El-Deab, T. Okajima, T. Ohsaka, J. Electrochem. Soc. 152 (2005) A1226.
 - [42] M.S. El-Deab, T. Ohsaka, Electrochim. Acta 52 (2007) 2166.
 - [43] A. Sarapuu, K. Tammeveski, T.T. Tenno, V. Sammelselg, K. Kontturi, D.J. Schiffrin,
 - Electrochem. Commun. 3 (2001) 446. [44] A. Sarapuu, K. Vaik, D.J. Schiffrin, K. Tammeveski, J. Electroanal. Chem. 541 (2003) 23.
 - [45] K. Vaik, A. Sarapuu, K. Tammeveski, F. Mirkhalaf, D.J. Schiffrin, J. Electroanal. Chem. 564 (2004) 159.
 - [46] W.F. McClune (Ed.), Powder Diffraction File, International Centre for Diffraction Data (ICDD), USA, 2003.
 - [47] T. Kinoshita, S. Seino, K. Okitsu, T. Nakayama, T. Nakagawa, T.A. Yamamoto, J. Alloys Compd. 359 (2003) 46.
 - [48] K. Nogita, A.K. Dahle, Mater. Charact. 46 (2001) 305.
 - [49] A.K. Veneva, M.R. Koblischka, Mater. Sci. Eng. B 151 (2008) 60.