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Reactivity of Gold Nanobelts with Unique {110} Facets

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Gold nanobelts were synthesized by directional solidification of the Fe–Au eutectoid followed by selective phase dissolution. Cleaning from organic molecules was performed in alkaline solution by PbO₂ deposition/dissolution to avoid surface reconstruction. The electrochemical behaviour of the Au nanobelts was determined by structure sensitive electrochemical reactions, and the findings confirm the results obtained by selected area electron diffraction (SAED). The

underpotential deposition (UPD) of lead under alkaline conditions and cyclic voltammograms (CVs) in sulphuric acid revealed an unusual large amount of {110} domains (> 65 %). At last, it was found the Au nanobelts after cleaning showed a higher and stable electro-catalytic behaviour toward methanol oxidation in alkaline media. The possible mechanism and the potential applications of the Au nanobelts were discussed.

Introduction

Nanostructured metals, especially those consisting of noble metals, such as Au, Ag and Cu, have been in the research focus for the last two decades giving kudos to the wide range of applications [1-5]. Heterogeneous catalysis is one of them which is of particular practical relevance in fuel cells, gas diffusion electrodes and synthesis, which was achieved by using their high surface area as compared with that of bulk materials [2, 3, 6-8]. For these reactions, the roles of both, the size and the shape (the surface structure) of the nanostructures are of vital importance. Although the size effect has been extensively studied [8], the influence of surface structure of nanostructures as electrocatalysts is still in the focus of investigations [9-11]. Different crystal surfaces or directions may exhibit different physical and chemical properties due to the anisotropic properties of crystals. For example, the {111}, {110} and {100} surfaces of a face centred cubic (fcc) metal, such as gold, show differences not only in the surface atom density, but also in the electronic structures and the resulting chemical reactivity [2,12]. Jana et al. described that gold nano-spheroids and nanorods show different chemical reactivities for persulfate and cyanide [13]; Carbó-Argibay et al. reported a chemical sharpening process of gold nanorods [14]; and Xiang et al. reported that modifying the morphology of Au nanorods is possible by switching the growth of {110} facets from restriction to preference, thus turning Au nanorods with {110} facets into arrow-headed Au nanorods and Au nano-octahedra [15]. The synthesis and characterization of nanomaterials has been the subject of incalculable studies, and nanostructures with various shapes and exposed surfaces were reported by chemical, physical and even biological procedures [1-4, 15]. However, the characterization of crystalline surface of nanostructures is limited to a few ex-situ techniques, such as high resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED) and scanning probe microscopy (SPM). These techniques require

a high experimental effort and are time consuming. Moreover, only a limited number of particles can be analyzed, which may not be representative of the overall surface crystalline structure of the sample. Since most of the electrocatalytic reactions are very sensitive to surface structure [17-20], it is necessary to find a potent and convenient way to 'see' the surface structures of the nanostructures.

Surface structure sensitive reactions, which have been extensively studied [18-28], are the method of choice for this purpose. Within the scope of electrochemistry, the well known underpotential deposition (UPD), by electrodepositing metal monolayer(s) on a foreign metal substrate at potentials that can be significantly less negative than that for deposition on the same metal surface as the adsorbate, which were usually performed on single crystal electrodes, could allow the detection of the surface structure of the sample [21,23,24]. Recently, Hernández et al. reported on the surface structure sensitive reaction by Pb UPD on single crystals and nanostructures of gold under alkaline conditions [6, 19-21]. These are less common as compared to acidic conditions [23-28]. Besides the surface structure sensitivity, this method has another advantage. Since most of the Au nanoparticles were synthesized in the presence of surfactants or organic molecules, it is inevitable that these organic molecules will be absorbed chemically or physically on the surface of the particles. It should be emphasized that for applications in electrocatalysis the surface condition of the catalysts is of vital

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importance for its efficiency [6, 7, 30]. Thus, before any electrochemical study, the nanoparticles have to be cleaned to remove the organic species, but without changing the surface construction. This is a crucial point, as it always happened when the nanoparticles were cleaned by repeated cycling in basic or acidic solution that the range of metal oxide films are formed [20]. Hernández et al. [20] developed a new method for this purpose; it consists of cycling the gold nanoparticles electrode in a Pb^{2+} containing alkaline solution to a high potential. At high potentials, a PbO_2 film is deposited and the well known electrocatalytic oxidation properties could be used to remove the adsorbed organic species from the surface of the Au nanoparticles.

Gold is generally considered as a very inert metal toward methanol oxidation [30-32], but an advantage of gold as the catalyst is that the poisoning intermediates are not formed, and recent studies [6, 7, 9-11, 30-32] discovered that Au could exhibit an unusual high electrocatalytic activity. The electrocatalytic activity was attributed to the size and shape; the initial results showed that gold could be a promising candidate for the electrocatalytic oxidation of methanol. Among various morphologies, nanostructures could be a better choice. Very recently, Jena reported the synthesis of Au nanoflowers and their applications in methanol oxidation and oxygen reduction reactions [7], whereas Zhao described the synthesis of Au nanobelts and their applications in methanol oxidation [9].

Thus, the idea of this work was to find a proper way of characterizing the surface structure using structure sensitive reactions, and to study the electrocatalytic properties toward methanol oxidation. As compared with 'normal' Au nanobelts or other nanostructures with the more stable and therefore predominant $\{111\}$ surface this is the first study on Au nanobelts with preferential $\{110\}$ crystalline facets. This became only possible with a completely different synthesis route which was developed very recently.

Lead UPD in alkaline solutions and CVs under acidic conditions have been carried out to obtain the information about the surface structure of the Au nanobelts; and the results were compared with that from SAED. Moreover, the electrocatalytic activities toward methanol oxidation have been investigated to demonstrate potential applications of the obtained Au nanobelts.

Results and Discussion

3.1 Physicochemical characterization of Au nanobelts

The Au nanobelts have been comprehensively characterized by FE-SEM, HRTEM and SAED (Figure 1). It is seen that most of the products possess belt type morphology, although some 'short' nanobelts, or nanoparticles, can be found. The appearance of these shorter structures results from the ultrasonication process, which can break longer nanobelts with their extremely high aspect ratio of more than 2,000 due to the high oscillatory energy induced. As described before [35], these Au nanobelts have an average thickness and width of 25-30 nm and 250 nm, respectively. The average length is about 20 μm . SAED performed on a single Au nanobelt shows the characteristic pattern of $\{110\}$ planes, which is in agreement with the results obtained by Electron Backscattered Diffraction (EBSD) technique [36]. This is different from the all reported results for the Au nanobelts synthesized by wet chemical method [9, 37, 38].

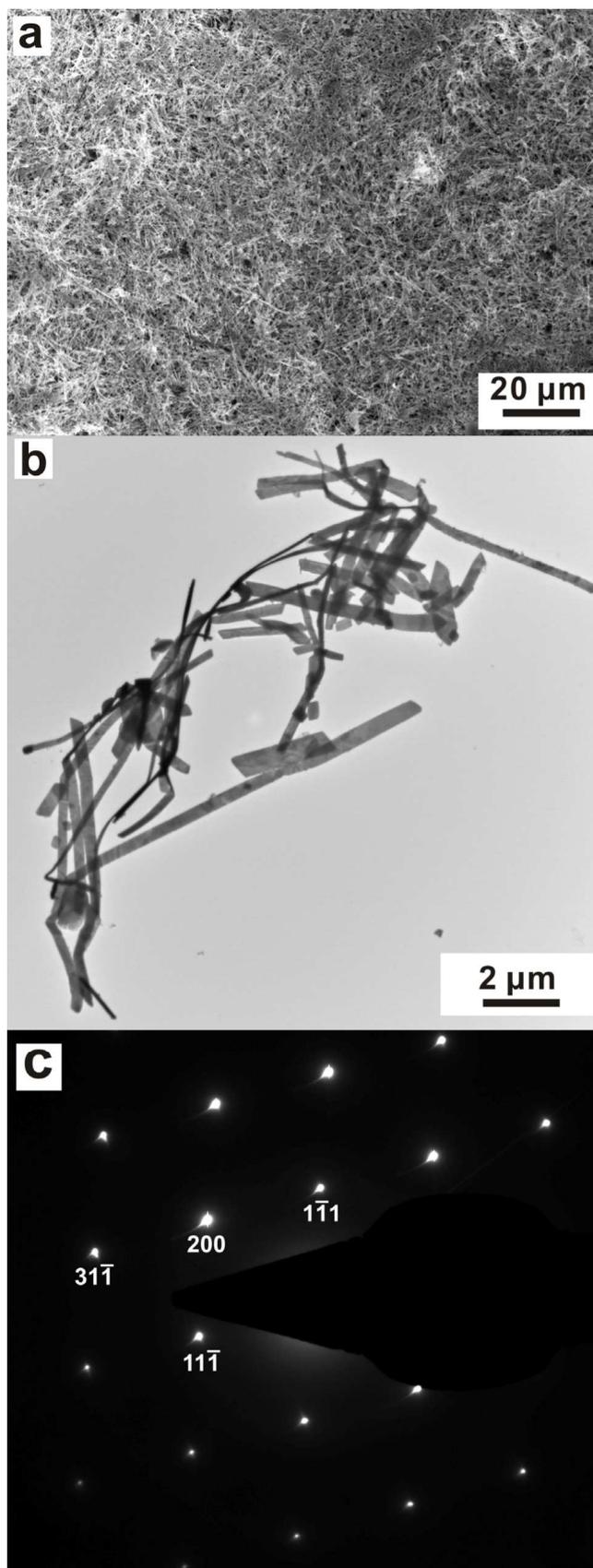


Figure 1. TEM (a) and FE-SEM (b) images of Au nanobelts, with its corresponding SAED pattern (c).

The SAED patterns are essentially identical over the entire belt, which proved the single crystalline and structurally uniform nature

of the nanobelts. However, this tests the crystallographic information only from single nanobelts. Overall crystallographic information needs further characterization to prove the predominant appearance of {110} surfaces for gold, considering an industrial applications.

2 Cleaning and voltammetric characterization of Au nanobelts in alkaline and acidic media

Electrochemical reactions are usually very sensitive to the surface conditions of the electrode [18-21], minute structural changes or tiny amount of contaminations can change the characteristic of the reactions drastically. Although the Au nanobelts prepared in the present case are surfactant free, an organic compound, a chelating agent, *o*-phen, was used during the selective etching process to reduce the risk of Fe ion hydrolysis. It might be adsorbed on the surface of Au nanobelts since the interaction between Au and N atoms is quite strong. This can in turn block the surface active sites of Au nanobelts and further modify their electrochemical behaviour, such as characteristics in structure sensitive reactions and electrocatalytic properties. So, it is very necessary to remove this organic layer before any electrochemical analysis to ensure that the reactivity is representative for the real crystallographic properties of {110} Au nanobelts. According to Hernández et al. [6, 20, 22], by cycling the Au nanoparticles electrode in a Pb^{2+} containing alkaline solution, gold nanoparticles could be well cleaned because of the electrocatalytic properties of PbO_2 for the oxidation of organic species. Three cycles were carried out to clean the surface of Au nanobelts in the present case, and the electrochemical characteristics of both before and after the cleaning were examined.

For Pb UPD on Au single crystals, the deposition and dissolution potential depends on the surface symmetry, different current peaks in the CVs correspond to deposition/dissolution on the different crystal faces of Au, each crystal face may produce separate peaks associated with different orientations, important changes in the CVs were observed for different crystallographic orientations in acidic [19, 23-28] and alkaline media [20, 22]. After the cleaning process, the lead UPD process was studied in the same solution. Fig. 2 shows the lead UPD curves for Au nanobelts deposited on glassy carbon electrode before (a), and after (b) the cleaning process. The difference can be clearly seen. Before the deposition/dissolution of PbO_2 film, there are no characteristic peaks for the lead UPD on gold for different sites, only a very broad peak at ca. -0.2 V representing a possible deposition of lead. This curve indicates coverage of the Au nanobelts surface with organic molecules. However, as for the same sample, after cleaning process by deposition/dissolution of PbO_2 film, the current peak splits into several peaks for the deposition and stripping of lead ad-layer.

Alongside the results of Hernández et al. [20, 22] an assignment of different peaks to different crystallographic surfaces having different symmetries and atomic densities can be conducted. The same assignment is possible for a polycrystalline Au electrode (abbreviated as poly-Au). An assignment of the stripping peaks according to the literature [20-29] is straightforward for both acidic and basic media. The peak at -0.34 V corresponds to the contributions of the {111} terrace sites, the shoulder peak at -0.27 V could be assigned to that of {100} facets, and the strong, broad peak at -0.17 V corresponds to the {110} facets. Comparing the UPD voltammetric profiles obtained in this work with those from

the literature for Au spherical nanoparticles [22] and nanocubes [19], important differences can be observed. First of all, the prominent peak at -0.42 V was not assigned as it is not related to any of the low index surfaces, but it is often observed on polycrystalline Au and Au nanostructures [22, 25]. In acidic condition, Hamelin [22] assigned it to a change in structure of the adsorbed atoms, allowing for the accommodation of more lead on the gold surface. Hernández et al. [22] deemed that this is associated with the dissolution of the lead from steps or kinks under these experimental conditions since the current in this potential region on the basal planes are very small. Here the latter explanation seems more reasonable because the charge consumed during the sweeps is rather small and a decent amount of steps and kinks can be expected from the simple fact that the nanobelts side planes may have a different surface orientation. The interface energy of these surfaces is significantly larger as it is only formed due to the limited solid state diffusion length. The information in the literature on the reconstruction of lead adlayers on {110} gold surfaces in alkaline solutions is scarce.

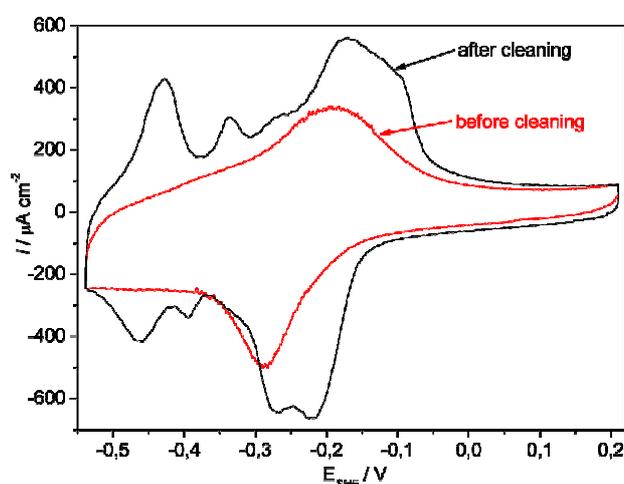


Fig. 2 CVs of Au nanobelts in 0.1 M NaOH + 10^{-3} M $\text{Pb}(\text{NO}_3)_2$ before (a), and after (b) the deposition/dissolution of PbO_2 film. Scan rate: 20 mV/s.

Such defects and edges can be the origin of the steps or kinks which conclude in the formation of the current peak at -0.42 V for the stripping of lead. The second difference is that the relative intensity of the peak at -0.34 V, corresponding to {111} surface, is quite low. At the same time, the peak at -0.17 V, corresponding to the contributions from the {110} surface is much stronger than that of {111} surface, accompanied by a weak shoulder peak at -0.27 V for the {100} surface. The relative charge (or the height) of different peaks can be compared to estimate the relative area for different facets of Au nanobelts [22]. The low peak intensity at -0.34 V corresponds to a small contribution for the lead stripping from the {111} surface. The strong peak at -0.17 V on the other hand can be understood as a high contribution from the {110} surface. Computing the charge of the voltage scans yields a 65% contribution from the {110} surface. This is much higher than that of {111} and {100} facets and it implies that the area of {110} facets is accordingly larger than that of the {111} and {100} facets. This is in good agreement with the results from the SAED pattern. So, the characteristic peaks of the lead UPD on Au nanobelts indicate that the major part of the Au nanobelts is {110} terminated.

For comparison a polycrystalline Au electrode was studied in the same solution as that for the selective etching of iron for 30 min; the organic molecules could be adsorbed on the surface of poly-Au. After that, the lead UPD profile was obtained before and after the deposition/dissolution of PbO_2 film. As can be seen from Fig. 3, the same as for Au nanobelts, there are obvious differences after the cleaning process. The assignment of the peaks for gold poly-electrode under the same conditions has been discussed in detail by Hernández et al. [22], the only difference is that the peak corresponding to $\{111\}$ facets was not split. Whether this difference is a result of a small difference in surface condition or that of a contamination can not be decided here. A similar result was obtained when the gold electrode was dipped into Piranha solution, the strongly oxidising agent can eliminate all organics. This treatment clearly causes a different reaction since the relatively weak peak corresponding to the $\{100\}$ surface completely disappeared (data was not shown here). This behaviour is however not surprising since the conditions are strikingly different. Not only that the environment is strongly oxidising but also highly acidic, thus it would be no wonder if the mechanism is different. From this result, one can see that the deposition/dissolution of PbO_2 film can be an effective way to clean the electrode; and more importantly, without changing the surface structures of the electrode.

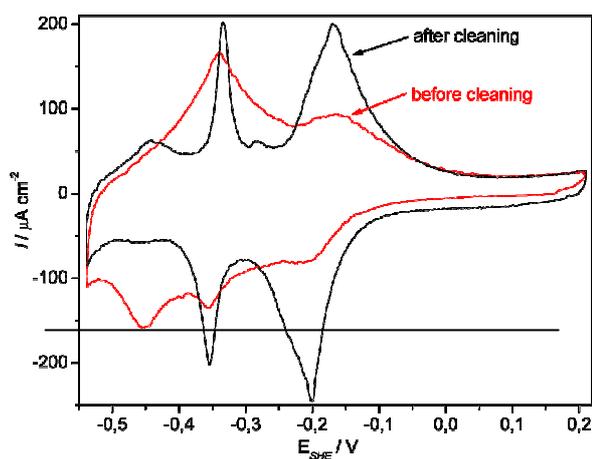


Fig. 3 CVs of poly-Au electrode in 0.1 M NaOH + 10^{-3} M $\text{Pb}(\text{NO}_3)_2$ before (a), and after (b) the deposition/dissolution of PbO_2 film. Scan rate: 20 mV/s.

When physically well-defined clean gold faces are used, the analysis of the obtained CVs can provide a lot of information [18]. The topic of the 'finger print' of the gold face in various electrolytes was intensively studied [18, 39, 40]. The behaviour of gold electrodes in CVs is significantly influenced by the superficial structure of the gold faces. For example the three low-index facets $\{111\}$, $\{110\}$ and $\{100\}$ show different characteristics in acidic solutions not only in the electrochemical double layer region, but also in the region of surface oxidation/reduction [18, 39, 40]. Fig. 4 shows the CVs of Au nanobelts on glassy carbon electrode in 0.01 M H_2SO_4 before and after the cleaning process for the same sample. It is seen that the electrode behaviour prior to cleaning is more like a polycrystalline gold electrode with a single current peak at ca. 1.27 V. After cleaning however the behaviour in this region changes dramatically while other regions remain unaffected. The current intensity of the main peak at 1.28 V was much increased in this region accompanied by the growth of a shoulder peak at ca. 1.38 V. These findings are in

agreement with results from the literature [18] in which gold $\{110\}$ single crystal electrodes show a main peak at 1.28 V with a shoulder peak 100 mV more positive in diluted H_2SO_4 . The coincidence with cleaned nanobelts is seen in Fig. 4. For comparison a polycrystalline gold electrode was subjected to the same procedure. It turned out that the current intensity in this region after the cleaning process was also improved (Fig. 5), but without appearance of a shoulder peak. All these results prove that the synthesized Au nanobelts are single crystals with a predominant $\{110\}$ facet. The less stable $\{110\}$ surface is prone to be used in chemical reactions, catalysts or electro-catalysts taking advantage of its active specialities.

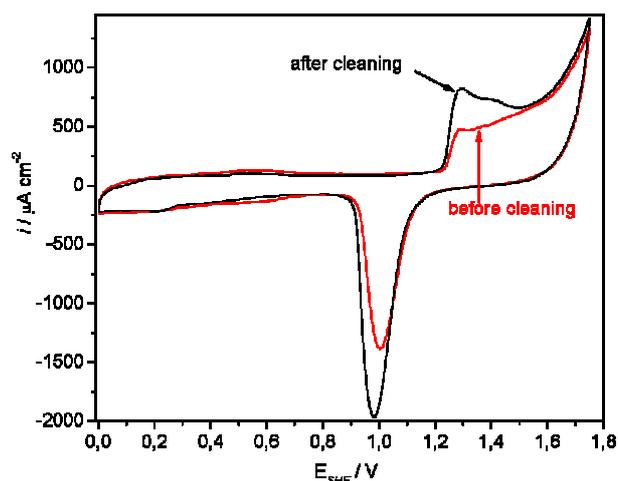


Fig. 4 CVs of Au nanobelts in 0.01 M H_2SO_4 before (a), and after (b) the deposition/dissolution of PbO_2 film. Scan rate: 20 mV/s.

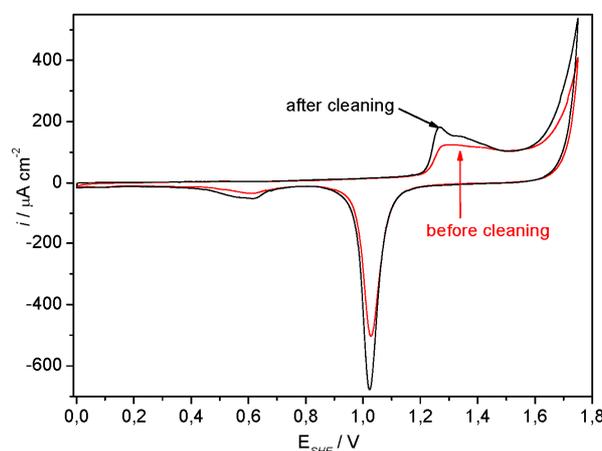


Fig. 5 CVs of Au polycrystalline electrode in 0.01 M H_2SO_4 before (a), and after (b) the deposition/dissolution of PbO_2 film. Scan rate: 20 mV/s.

3.3 Electrocatalytic activity toward methanol oxidation

Gold has been attracted more and more interest as an electrocatalyst as it is considered to be less sensitive to poisoning by intermediates in methanol oxidation [6, 7, 9-11, 24, 30, 32]. According to reported results [9], Au nanobelts with $\{111\}$ facets could show considerably higher electrocatalytic activity than normal polycrystalline gold electrode. The $\{111\}$ facet is the most stable surface for gold and should show the lowest electrocatalytic activity. In comparison, the Au nanobelts with predominant $\{110\}$ facets in the study presented here should

show a higher electrocatalytic activity. The electrocatalytic properties of Au nanobelts for the methanol oxidation were investigated by studying the CVs of Au nanobelts on glassy carbon electrode in alkaline solution being composed of 1.5 M MeOH in 0.1 M aqueous NaOH solution. The typical CVs of Au nanobelts electrode before and after the cleaning process and the polished poly-Au electrode after the cleaning, normalized to the surface area are shown in Fig. 6. The surface area of the Au nanobelts electrode was calculated by the apparent area of the supporting glassy carbon electrode. In order to reserve the structure of Au nanobelts, the oxidation of the surface has been avoided by setting the upper potential below 0.8 V. The oxidation of methanol to formats as the final product through a four electron transfer reaction [9, 31, 41] on the Au nanobelts after the cleaning process occurs in the potential region from 0.0 to 0.6 V with a current maximum at 0.44 V. This is well before the formation of Au oxide species and should not alter the surface. This result is in accordance with the results reported for Au nanoparticles [6, 20], nanoporous Au electrode [10, 11], Au nanoflowers [7] and Au nanobelts with {111} facets [9].

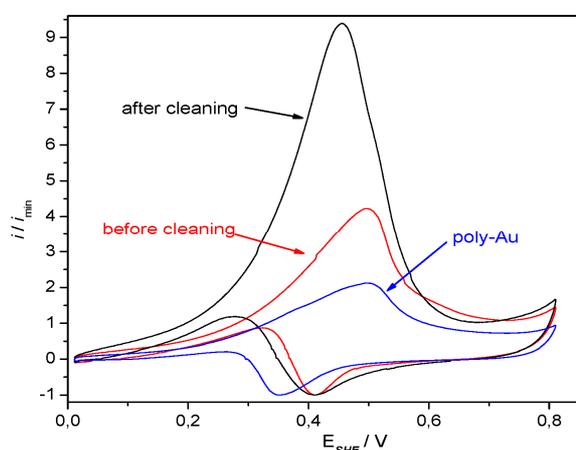


Fig. 6 CVs of poly-Au electrode (a), Au nanobelts before (a), and after (b) the deposition/dissolution of PbO_2 film in 0.1 M NaOH + 1.5 M CH_3OH . Scan rate: 20 mV/s.

Comparing the current peaks of methanol oxidation for Au nanobelts before and after oxidation with the poly-Au electrode, it is seen that for Au nanobelts without cleaning, the maximum is only slightly shifted negative as compared with that of poly-Au electrode, but with a much stronger current intensity. The large surface area and the special morphology of the nested Au nanobelts electrode should be the reason for this behaviour. However, after the cleaning process, the intensity of the current maximum is much stronger; and more importantly, it is shifted 50 mV negative. Obviously the cleaning process plays a crucial role for the surface condition, since the deposition/dissolution of PbO_2 eliminates most of the organic molecules on the surface of Au nanobelts without changing the surface structure. Subsequent to the cleaning process the reactivated surface atoms contribute to the overall reactivity of the electrode. According to the results from lead UPD and SAED, the surface of Au nanobelts is preferentially {110} oriented and a lot of surface atoms are at the steps and kinks, they provide plenty of active sites for electrocatalytic reactions. So, in this case, not only the surface area increases resulting in an increase of current; but also the

number of active sites increases as compared with the non-cleaned sample.

Summarizing, the stability of Au nanobelts electrode toward methanol oxidation was studied and it was found that the electrocatalytic activity is very stable upon repetitive cycling in this potential region as long as the gold oxide formation is prevented. Since Au nanobelts at present case were prepared by directional solidification of an Fe–Au eutectoid followed by a phase selective etching, an up-scaling is easily possible. It was recently shown that such material can be produced in the laboratory in gram amount [42, 43]. This route is suitable for mass production which is an advantage over synthesis via chemical reduction of HAuCl_4 for which it is not possible or not that straightforward [9, 36, 37]. These Au nanobelts are potential candidates for real applications with their high and stable electrochemical catalytic activity.

Conclusion

Gold nanobelts, with less common {110} crystalline surface have been prepared by a combination of directional solid state decomposition of an Fe–Au eutectoid followed by a phase selective dissolution process. FE-SEM and TEM investigations revealed that the majority of the product consists of single crystalline nanobelts with an average thickness of 25 nm and width of 250 nm. The average length can exceed 20 μm . These Au nanobelts were well cleaned by deposition/dissolution of PbO_2 film in Pb^{2+} containing alkaline media. Lead UPD in alkaline solution, as well as the CVs in sulphuric acid, revealed that the majority of surface domains are {110}, which was in full agreement with the SAED result. These Au nanobelts show high electrocatalytic activity toward methanol oxidation. Methanol oxidation in basic solution occurs at ca. 0.44 V, which is more than 50 mV lower than for a polycrystalline gold electrode. Besides, the current intensity is significantly increased. The fabrication procedure of Au nanobelts is straightforward and suitable for mass production. Based on their uncommon {110} surface they could be also used in other fields, such as electrochemical sensing, bio sensing or for specific nanodevices that make use of the interesting shape and structure.

Experimental Section

Gold nanobelts have been synthesized by a combination of directional solid state decomposition of an Fe–Au eutectoid followed by a phase selective dissolution process, which was described in detail recently [33-36]. Briefly, pre-alloys were prepared using 99.999% Au and high purity Fe, which was 5 times zone refined in house, by induction melting under inert atmosphere and drop casting into a cylindrical copper mould. Subsequently, the as-cast ingots were inserted into alumina crucibles and processed in a Bridgman type crystal growing facility. The selective etching of the α -Fe phase in the alloy was achieved by dissolving the sample into an aqueous solution containing 1.0 M HNO_3 and 0.05 M o-phenanthroline (o-phen) as a chelating agent to prevent the possible hydrolysis of Fe ions during the dissolution process. After complete dissolution, the samples were first separated by centrifugation, then washed with water in an ultrasonic bath and repeated several times until the pH value of the final suspension was 7.0; eventually it was dispersed in water.

The morphology and the crystallographic structure of the Au nanobelts were characterized by Field Emission Scanning Electron Microscopy (FE-SEM, LEO 1550VP, GEMINI), High Resolution

Transmission Electron Microscopy (HRTEM, Tecnai F20 G2, supertwin) and Selected-Area Electron Diffraction (SAED).

The electrodes were prepared by depositing the nanobelt suspension onto a Teflon surrounded glassy carbon electrode (Metrohm AG) with a diameter of 3 mm, which was pre-polished by alumina till 0.1 μm . One small droplet (2 μl , containing ca. 1.2 μg of gold) of the nanobelts suspension was placed on the surface of the electrode, and dried in an Ar stream. Before any electrochemical experiment, the Au nanobelts have to be cleaned due to the possible adsorption of o-phen molecules on the surface. This was achieved by the strong electrocatalytic properties of PbO_2 for the oxidation of organic species, as described by Hernández et al. [6, 20, 22, 24]. In summary, three cycles of PbO_2 deposition/desorption were performed in 0.1 M NaOH + 10^{-3} M $\text{Pb}(\text{NO}_3)_2$ solution from -0.73 to 0.72 V. A further advantage of this method is that the lead UPD itself provides an indicator for the surface structure. A clean Au electrode with the same diameter as that of glassy carbon electrode was used as reference sample. It was immersed in the same solution as for the dissolution of Fe–Au eutectoid for ca. 30 min, and three cleaning cycles were performed to prove that the organic molecules can be eliminated.

Two different structure sensitive reactions were carried out; the first one being the Pb UPD in alkaline media, the same electrolyte as that of the cleaning process, at a lower potential range, from -0.75 to 0 V; the second one is the voltammetric behaviour in 0.01 M H_2SO_4 .

A mixed solution of 0.1 M NaOH + 1.5 M CH_3OH was used as the electrolyte to characterize the electrocatalytic activity of Au nanobelts samples for methanol oxidation reactions.

The electrolytes for electrochemical reactions were deaerated by bubbling with high-purity Ar for 20 min before each measurement. All of the glassware was cleaned by freshly prepared Piranha solution. All electrochemical experiments were performed in a three-electrode cell, with PAR Potentiostat/Galvanostat model 283 at room temperature (22 $^\circ\text{C}$), the counter electrode is pure gold plate, the reference electrode is Ag/AgCl in saturated KCl (Metrohm AG), and all the potentials used in this article are given versus Standard Hydrogen Electrode (SHE.).

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Keywords: Au nanobelts, {110} facets, structure sensitive reactions, underpotential deposition (UPD), methanol oxidation

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