

Enhancement of the Electrocatalytic Activity of Gold Nanoparticles Towards Methanol Oxidation

Ying Chen · Achim Walter Hassel · Andreas Erbe

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Abstract By citrate reduction of HAuCl_4 , Au nanoparticles with a diameter of 15 nm and low polydispersity were synthesized. By deposition and subsequent dissolution of PbO_2 in an alkaline medium, the particles were cleaned from their organic capping agents. The electrocatalytic behavior towards methanol oxidation under alkaline condition of these particles was found to be substantially enhanced by the cleaning procedure. The origin of the enhancement was studied by comparing the voltammetric profiles of the cleaned nanoparticles prior and after treatment with diluted nitric acid. The reason for the enhancement is mainly the removal of the organic shell. No hints of contributions of residual Pb and/or PbO_2 from the cleaning process on the particle's surface to the enhancement were found.

Keywords Gold nanoparticles · Electrocatalysis · Methanol oxidation · Underpotential deposition (UPD) · Gold colloids

Introduction

Electrocatalytic properties are amongst the most important properties of metallic nanomaterials. Many real and potential applications in devices such as sensors and fuel cells are depending on the electrocatalytic properties of the used particles [1–10]. Thus, the investigation of electrocatalytic behavior of nanomaterials has been an important topic, and much research has been devoted to improve their electrocatalytic activities [2, 7, 11–13]. The majority of works on electrocatalysts for fuel cells are based on Pt or Pt-based materials because of their excellent electrocatalytic properties for many reactions, such as oxygen reduction and alcohol oxidation [2–5, 7, 8, 14]. Because of the high price of Pt, there is an ongoing search for cheap and efficient alternatives. For example, nitrogen-doped carbon nanotubes were proposed as excellent and stable electrocatalysts for the oxygen reduction reaction [15]. Likewise, polyhedral 50–facet Cu_2O microcrystals with high-index facets were found to be very active for CO oxidation [6].

Gold is generally regarded as an inert metal showing a low electrocatalytic activity. However, the benefit of gold as electrocatalyst is that no poisoning intermediates are formed [16, 17]. Recently, it was found that gold in the form of nano-sized particles exhibits an unusually high electrocatalytic activity [12, 13, 16, 18–23]. Initial results showed that gold could be a promising candidate for some applications, such as electrocatalytic oxidation of methanol and glucose [18, 24]. For example, the synthesis of gold nanoflowers and their applications in methanol oxidation and oxygen reduction reactions was reported [22]. Furthermore, the synthesis of Au nanobelts with either {111} or {110}

Y. Chen · A. W. Hassel · A. Erbe
Max-Planck-Institut für Eisenforschung GmbH,
Max-Planck-Str. 1, 40237 Düsseldorf, Germany

Y. Chen (✉)
Center for Electrochemical Sciences (CES),
Analytische Chemie, Ruhr-Universität Bochum,
44801 Bochum, Germany
e-mail: y.chen@mpie.de, chenying135@gmail.com

A. W. Hassel
Institute for Chemical Technology of Inorganic Materials
Johannes Kepler University, Linz Altenberger Str. 69,
4040 Linz, Austria

surfaces and their applications in methanol oxidation was described [13, 18, 25].

To date, the vast majority of gold nanoparticles (NPs) was synthesized by reduction of a gold precursor with a reduction agent in a solution with or without the presence of a capping agent [1, 3, 9, 26]. Because of the nature of the synthetic method, the surface of the as-prepared nanoparticles is always covered by organic layers. However, since the high electrocatalytic activity of metal nanocrystals are mainly originating from high energy surfaces or surface regions, e.g. atomic steps, edges, and kinks, the surface conditions of the catalysts are of vital importance for the catalytic efficiency [7, 12, 16]. The electrocatalytic activity of the gold nanoparticles can be significantly decreased by adsorbed organic layers [1, 11, 13]. Thus, much research has been devoted to clean the surface, hence improving the electrocatalytic activity of the Au NPs [12, 13, 16, 19]. There are two common ways to clean metallic nanoparticles. The first one is an electrochemical method. By repeated potential sweeping cycles in acidic or alkaline media with an upper potential higher than the potential for oxide formation [27, 28], organic species can be eliminated. The second strategy is a thermal decomposition of organic molecules due to heat treatment [29]. However, because of the small size and specific shapes of the nanocrystals, the melting temperature and the stability of the nanocrystals are much lower than that of the bulk materials [3]. The surface structure of the nanoparticles can be easily changed at high potentials or high temperature, decreasing the fraction of the catalytically active high energy parts. Thus, the reactivity can be changed dramatically, which is one of the disadvantages of these methods [13, 30]. Therefore, cleaning the metal nanoparticles' surface without surface reconstruction still remains a challenge. Recently, a new method involved the cycling of the Au NPs electrode in Pb^{2+} -containing alkaline electrolyte to clean the surface of Au NPs was proposed [30, 31]. During scanning in anodic direction, PbO_2 is deposited on the electrode. Organic species on the surface of the Au NPs are removed by the strong electrocatalytic oxidation activity of PbO_2 . The deposition potential of PbO_2 is relatively low (ca. 0.75 V). In addition, the surface of the Au NPs is covered by a layer of PbO_2 , hindering the oxidation of gold [13, 30, 31]. During the scans in cathodic direction, PbO_2 is dissolved, thus releasing the original surface. With this method, the surface of Au NPs can be easily cleaned without surface reconstructions [13, 30, 31]. So, it is highly promising and desirable, to extend this method to clean Au NPs prepared by different methods.

It was previously reported that the electrocatalytic ability of gold nanobelts prepared by directional eutectoid decomposition towards methanol oxidation can be much enhanced by the PbO_2 deposition cleaning method [13]. Unfortunately, the exact reason for this enhancement was not clear. Two possible reasons for the enhancement can be suggested. The first one is the cleaning effect. The surface of the nanobelts was cleaned from organic contaminants by the deposition/dissolution of PbO_2 . Meanwhile, it is also well known that electrode modification with a monolayer/multilayer of foreign metallic atoms was widely used to enhance the electrocatalytic abilities of the sample [2, 5, 32, 33]. During the deposition/dissolution of PbO_2 films in the cleaning process, tiny amount of Pb and/or PbO_2 could be retained on the surface of the Au nanobelts, especially on kinks and steps. That means there is a possibility that the remaining Pb/ PbO_2 is the reason for the enhancement of electrocatalytic activity, and not the removal of organic species. In this work, these two alternatives are investigated. Furthermore, the cleaning method is applied to gold nanoparticles synthesized by other methods, and the change in their electrocatalytic activity by this cleaning process is investigated.

While there are some examples in this work using gold nanobelts prepared by directional eutectoid decomposition, this work mainly deals with Au NPs synthesized by the reduction of HAuCl_4 with trisodium citrate (Na_3Ct), one classical and convenient method [34–36]. The as-synthesized Au NPs are used to test the effect of the cleaning procedure on the electrocatalytic behavior. The deposition/dissolution of PbO_2 in alkaline media is used to remove the citrate coating from the Au NPs. The methanol electrooxidation is investigated in the presence of the as-synthesized Au NPs, the particles after the cleaning procedure, and after a further treatment with nitric acid. The morphological changes were recorded by scanning electron microscopy. The changes in composition were studied by energy dispersive X-ray spectroscopy (EDX).

Experiments

Citrate coated gold nanoparticles were prepared according to Turkevich and Frens with slight modifications [34–36]. Typically, an aqueous solution of HAuCl_4 (2.5 mM and 50 mL) in a three-neck flask equipped with a reflux condenser was heated to boil while being stirred. Then, 0.3 mL 5 wt. % aqueous solution of Na_3Ct

was added to the solution. The reaction was allowed to run until the solution reached a wine red color, indicating the reaction was completed.

The morphology of the gold NPs was characterized by field emission scanning electron microscopy (FE–SEM; LEO 1550VP, GEMINI) equipped with energy dispersive X-ray spectroscopy (EDX, Oxford). The sample for FE–SEM characterization was prepared by dripping a drop of the gold colloid solution onto a glassy carbon electrode.

Gold nanobelts were synthesized by directional solid-state decomposition of an Fe–Au eutectoid followed by a phase-selective dissolution process [37, 38]. The preparation, morphology, electrochemical characterization and methanol oxidation of the Au nanobelts has been described in detail elsewhere [13, 18, 39, 40].

The cleaning of the Au NPs was achieved by cycling the electrode in 0.1 M NaOH + 10^{-3} M $\text{Pb}(\text{NO}_3)_2$ solution [30, 31, 41]. Three cycles of PbO_2 deposition/dissolution were performed in the Pb^{2+} containing alkaline solution from -0.73 to 0.72 V. The underpotential deposition (UPD) of lead in this solution was studied by cycling between -0.75 and 0 V, as an indicator for the surface structure.

A mixed aqueous solution of 0.1 M NaOH and 1.5 M CH_3OH was used as the electrolyte to characterize the electrocatalytic activity of the Au NPs for the methanol oxidation reaction. To investigate the reason of the enhancement of the electrocatalytic activity of the Au NPs, the electrode with nanoparticles after the electrocatalytic reaction was dipped in 1.0 M HNO_3 for 10 min. Thus, possible residues of Pb/PbO_2 originating from the cleaning process should be completely dissolved. After that, the electrode was transferred to the electrochemical cell again for further electrocatalytic experiments.

The electrode for electrochemical reactions was prepared by depositing a drop of Au NP solution onto a Teflon-surrounded glassy carbon electrode (Metrohm AG) with a diameter of 3 mm, which was pre-polished by silica till $0.1 \mu\text{m}$. The electrolytes for all of the electrochemical reactions were deaerated by bubbling with high-purity Ar for 15 min before each measurement. All of the glassware was cleaned by freshly prepared Piranha solution (concentrated H_2SO_4 : 30% H_2O_2 = 3:1, v/v). All electrochemical experiments were performed in a classical three-electrode cell, with an IviumStat potentiostat (Ivium Technologies B.V., The Netherlands) at room temperature (22 – 23°C). The counter electrode was a pure gold plate, and the reference electrode is Ag/AgCl in 3 M KCl (Metrohm AG, 208 mV versus the standard hydrogen electrode (SHE)). All the potentials indicated here are versus SHE.

Results and Discussion

Physical Characterization of the Gold Nanoparticles

The morphology of the Au NPs was characterized by field emission scanning electron microscopy (FE–SEM), as shown in Fig. 1. According to Ji et al. [36], the molar ratio of $\text{Na}_3\text{Ct}:\text{HAuCl}_4$ is of vital importance in determining the size of the obtained Au NPs. In this work, the molar ratio was kept at 4, the average size is about 10–15 nm, consistent with [36]. Over a large area, the particle size is homogeneous, indicating the successful preparation of monodisperse Au NPs. However, it should be pointed out that, because the nanoparticles were prepared in the presence of Na_3Ct and not washed at all for the FE–SEM characterization, the surface of the particles was inevitably covered by a thick organic layer (Na_3Ct or H_3Ct). One can clearly see from Fig. 1 that the top of some closed packed nanoparticles are covered with a layer. Furthermore,

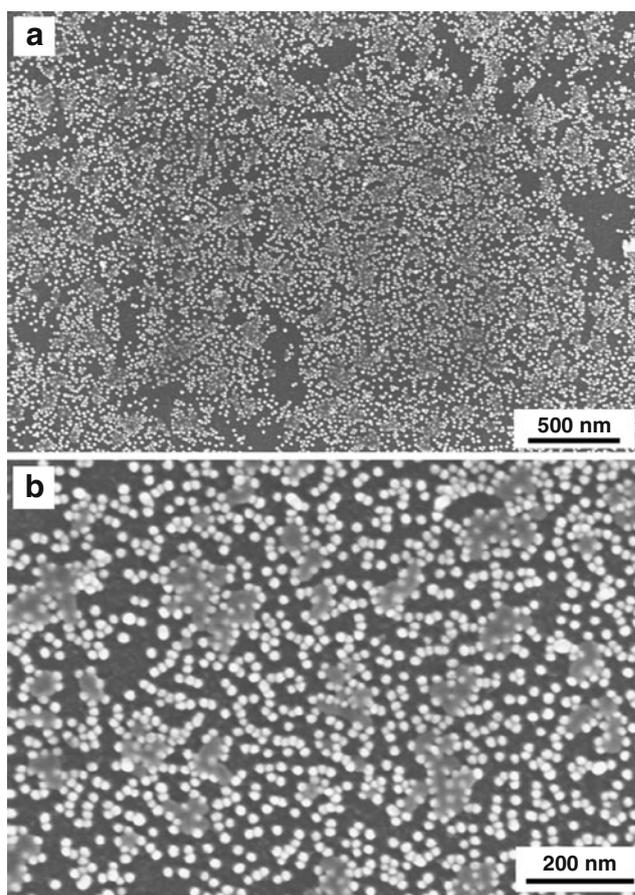


Fig. 1 FE–SEM images of the as synthesized gold nanoparticles. An organic film on the top of the nanoparticles can be found in some regions

Table 1 EDX analysis results for gold nanoparticles synthesized by citrate reduction before cleaning, after cleaning and after further treatment with HNO₃

	Before cleaning at. %	After cleaning at. %	After HNO ₃ at. %
C	35.0	25.0	20.7
Na	2.9	0	0
Cl	2.2	0	0
Au	59.9	71.0	79.3
Pb	0	4.0	0

the presence of sodium is found in the EDX results. The EDX results are shown in Table 1 (second column, before cleaning): 59.9 at.% Au, 2.9 at.% Na, and 2.1 at.% Cl, the latter originating from the gold precursor HAuCl₄. The large fraction of carbon is due to the supporting glassy carbon electrode and the adherent organic molecules.

The preparation of gold NPs by reduction through Na₃Ct is a classical preparation method [34–36]. This method is convenient, cheap and can be easily scaled up for industrial applications. However, it was already seen that the surface of the nanoparticles was covered by a thick organic layer, which may hinder the electrocatalytic abilities a lot. In fact, this is a common practical problem for most of the metallic nanoparticles synthesized by solution method [1, 9, 11, 13, 29].

Electrochemical Cleaning and Voltammetric Characterization

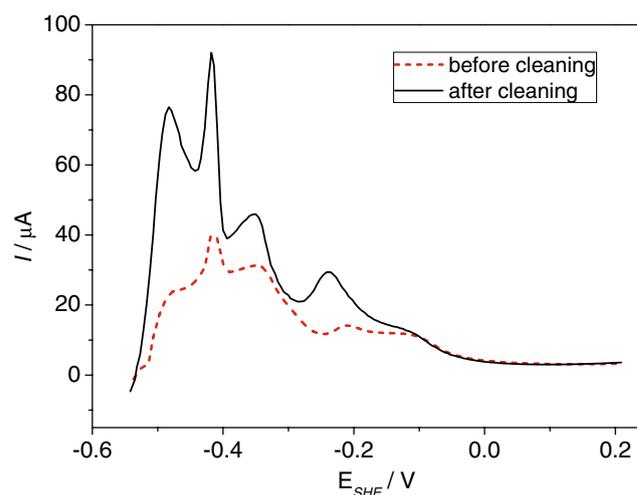
Because the surface of the solution synthesized Au NPs is most likely covered by organic layers, and the electrocatalytic properties of the electrocatalysts are mainly determined by their surface conditions [7, 11, 13, 18], Au NPs with surface free of organic materials are highly desired from the view point of electrocatalysts. By a recently introduced method using deposition and dissolution of PbO₂ in an alkaline medium, organic layers on the surface of gold nanoparticles can be easily removed without surface reconstruction [13, 27–30]. Furthermore, an additional advantage is that the surface features of the Au NPs can be accessed by studying the underpotential deposition (UPD) of lead, which is extremely sensitive to the surface structures of electrodes [13, 30, 41].

UPD of lead on gold single-, poly- and nanocrystals in alkaline media have been discussed in detail [30, 31, 41–48]. Obvious variations in the cyclic voltammograms (CVs) were observed for different electrode surfaces or crystallographic orientations. After cleaning the sur-

face of the nanoparticles by deposition/dissolution of PbO₂, the UPD of Pb was studied in the same solution within a lower potential range. The stripping peaks are generally used to assign the crystallographic orientations of the electrode [13, 31, 42]. Figure 2 shows a clear difference of the stripping voltammograms of lead from the Au NPs before and after the cleaning procedure. Compared with single- and poly-crystalline macroscopic gold electrodes as well as gold nanobelts [13], one obvious difference is that the stripping peaks at the most cathodic potentials are much stronger. The most negative stripping peak can be assigned to the dissolution of lead atoms from the kinks and steps of the electrode [13, 30]. For single crystalline gold electrodes, the surface is much smoother than for poly- and nanocrystals. This roughness explains the presence of the most negative peak on poly- and nanocrystals but not for gold single crystals [30]. In the present case, the size of the nanoparticles is about 10–15 nm, and the surface of these nanoparticles is supposed to be full of steps and kinks, explaining the strong stripping peaks at less than –0.38 V.

Moreover, the stripping peak intensity also changed a lot after the cleaning process. Before cleaning, the intensity of the peaks was relatively low and not clearly separated from each other. The intensity of these peaks, however, became much stronger and split into five separated peaks after cleaning, and all of these features can be clearly seen from Fig. 2. The assignment of these peaks for Au nanobelts has been discussed in detail elsewhere [13].

Overall, the cleaning method by deposition/dissolution of PbO₂ in alkaline medium can also be

**Fig. 2** Comparison of the stripping voltammograms for the lead UPD on the Au NPs in 0.1 M NaOH + 10^{−3} M Pb(NO₃)₂ before and after the deposition/dissolution of PbO₂. Scan rate: 20 mV/s

applied for citrate gold NPs. It may also be possible to clean other metallic particles as well.

Electrocatalytic Behavior Towards Methanol Oxidation

Previous results indicate that both gold electrodes with rough surfaces and gold nanostructures, including nanoflowers and nanobelts, showed higher electrocatalytic activity towards methanol oxidation in alkaline media compared with smooth gold electrodes, such as single crystals [11–13, 16–25, 49]. The high electrocatalytic activity was supposed to be induced by the crystallographic orientation of the surface of the particles on the electrode. Gold nanobelts with unique {110} surface indeed show a much higher electrocatalytic activity towards methanol oxidation [13, 18]. Typically, the electrocatalytic activity can be further enhanced by the cleaning procedure. The main objective of the present investigation is to examine the reason for the enhancement. First, the electrocatalytic behavior of the citrate gold NPs was investigated. Figure 3 shows the voltammetric profiles for the Au NPs deposited onto a glassy carbon electrode in 1.5 M CH₃OH + 0.1 M NaOH solution. To avoid surface reconstruction, the gold oxidation was avoided by setting the upper potential limit to 0.82 V. The details of the oxidation peaks have been discussed extensively [11–13, 16–25, 49]. Here the focus is on the changes for Au NPs before and after the cleaning process. Figure 3 shows that, compared with the electrode before deposition/dissolution of PbO₂, the oxidation peak for the electrode after such

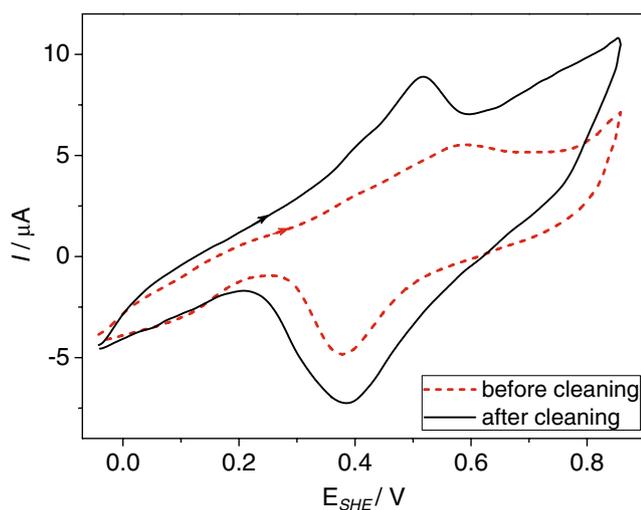


Fig. 3 CVs of the Au NPs before and after the deposition/dissolution of PbO₂ s in 0.1 M NaOH + 1.5 M CH₃OH. Both scans were done on the same surface. Scan rate: 20 mV/s

treatment has been shifted to cathodic direction by ca. 60 mV. Moreover, the relative peak intensity, i.e., the oxidation peak current, was increased by a factor of 1.5.

This result (Fig. 3) is exactly the same phenomenon as described earlier for gold nanobelts [13]. This indicates that the deposition/dissolution of PbO₂ can not only clean the surface of Au NPs from residual contaminants, but also remove the stabilizing layer in the case of citrate-stabilized gold nanoparticles. In both cases, the removal of organic species leads to an enhanced electrocatalytic activity of the NPs.

Origin of the Enhancement

Electrode modification with a monolayer of foreign metallic atoms were frequently used to enhance the electrocatalytic activities of different surfaces [2, 5, 32, 33]. For example, the deposition of a Pt monolayer onto AuNi_{0.5}Fe nanoparticles was shown to enhance the electrocatalytic activity towards the oxygen reduction reaction [5]. In the present work, the gold NPs were cleaned by the deposition/dissolution of PbO₂ in alkaline medium. During this cleaning process, an amount of Pb and/or PbO₂ could be retained on the surface of the gold NPs, especially on kinks and steps. So, there is a possibility that the remaining Pb/PbO₂ is the reason for the enhancement of electrocatalytic ability, and not the removal of organic species. In order to find out whether Pb/PbO₂ exists on the surface of the gold NPs, as well as the gold nanobelts (see [13]), a lower negative potential limit was applied during the study of methanol oxidation in alkaline solution. If there was

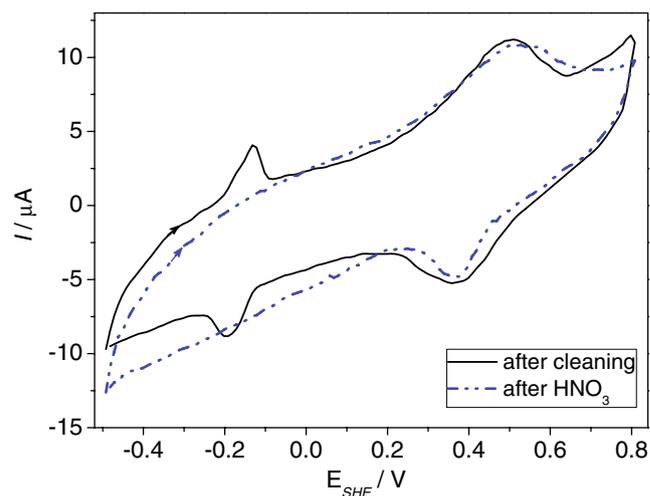


Fig. 4 CVs of the Au NPs in 0.1 M NaOH + 1.5 M CH₃OH after the deposition/ dissolution of PbO₂, and after further treatment in HNO₃. Both scans were done on the same surface. Scan rate: 20 mV/s

any lead present, the UPD of Pb should be observed on the surface of the Au NPs at potentials between -0.55 to 0.05 V since the methanol oxidation was also studied in alkaline solution. As shown in Fig. 4, Pb deposition/dissolution peaks were found for the sample after cleaning, which proved the existence of Pb/PbO₂ on the electrode surface. In addition, the presence of Pb was confirmed by EDX analysis. Table 1 (the third column, after cleaning) shows the EDX analysis and gives about 4 at.% of Pb. This amount corresponds to a substantial amount on the surface, though it must be pointed out that part of this Pb may be present on the supporting electrode surface as well, not only on the Au particles.

To further distinguish the enhancement effects from the removal of organic species and from the deposited Pb/PbO₂ films, the sample (after cleaning process and the previous electrocatalytic reaction) was taken out from the methanol solution and dipped in 1.0 M HNO₃ for 10 min (abbreviated as “after HNO₃”) to dissolve the retained Pb/PbO₂ from the surface of the Au

NPs. As shown in Fig. 4, the current peaks of deposition/dissolution of Pb disappeared after the treatment in HNO₃. At the same time, the peak corresponding to methanol oxidation remains almost unchanged. Figure 5 shows the FE-SEM images of the Au NPs after the deposition/dissolution of PbO₂ and further treatment with HNO₃. It is obvious that the organic layers on the surface of the Au NPs, which were observed before the cleaning procedure (see Fig. 1), were removed completely, and a clear image can be obtained. In the meantime, the morphology and the size of the Au NPs remains unchanged. As shown in Table 1 (the fourth column, after HNO₃), EDX analysis shows that the concentration of Pb/PbO₂ after the acid treatment is below the detection limit of EDX. While a remaining of traces of Pb on the surface cannot be excluded in the current experiments, the fact that the currents in the methanol oxidation experiments remain practically unchanged makes it reasonable to conclude that the enhancement of electrocatalytic activity of the Au NPs for methanol oxidation was achieved mainly by the cleaned surface, and not by deposition of Pb/PbO₂ films.

The nanoparticles synthesized here are about 10–15 nm in diameter, and considering their nearly spherical shape, there should be plenty of steps and kinks on the surface. However, because the nanoparticles were synthesized and stabilized by Na₃Ct, the particle surface is initially covered by citrate ions [35, 36, 50]. Adsorbed organic layer on the surface, do, however, block the surface, and hinder the ability of the

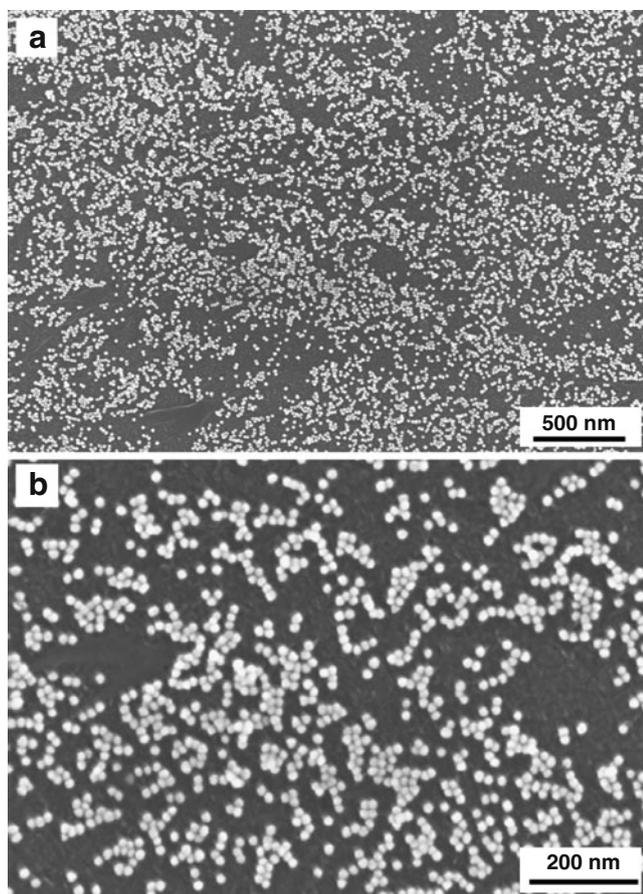


Fig. 5 FE-SEM images of the Au NPs after the deposition/dissolution of PbO₂ and further treatment in 1.0 M HNO₃

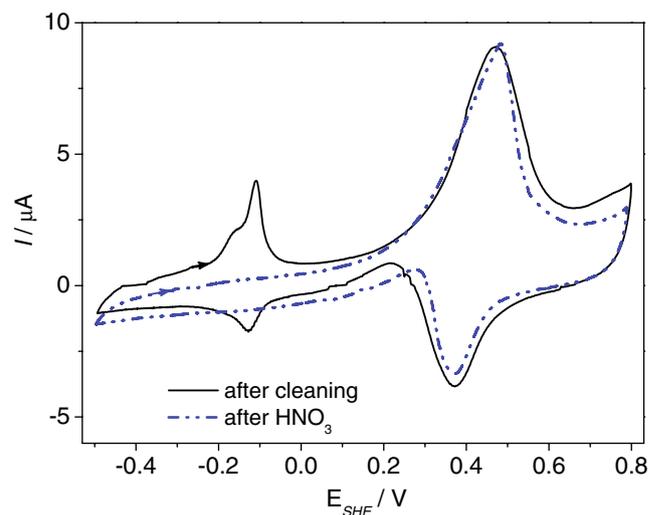


Fig. 6 CVs of the Au nanobelts in 0.1 M NaOH + 1.5 M CH₃OH after the deposition/dissolution of PbO₂, and after further treatment in 1.0 M HNO₃. Both scans were done on the same surface. Scan rate: 20 mV/s. See text for details

particle to act as catalysts or electrocatalysts. Because the deposition/dissolution of PbO₂ can remove most of the organic molecules from the surface of the particles without changing the surface structure, the steps and kinks on the nanoparticle surface are more accessible to reactants from solution after the cleaning procedure. Therefore, after the cleaning process, more surface atoms contribute to the overall reactivity of the electrode.

A similar experiment was done for the methanol oxidation on {110} gold nanobelts [13]. Gold nanobelts have been cleaned by deposition/dissolution of PbO₂ in alkaline solution, were treated in 1.0 M HNO₃, and their electrocatalytic behavior for methanol oxidation was studied. As shown in Fig. 6, the peak for Pb deposition and dissolution can also be found for the sample after cleaning. However, these peaks completely disappear after the treatment with HNO₃. At the same time, the current peaks for methanol oxidation remain unchanged by the treatment.

Conclusions

The increased electrocatalytic activity of gold nanoparticles after PbO₂ deposition and subsequent dissolution in alkaline medium is a strong hint that the stabilizing citrate layer in gold nanoparticles synthesized by citrate reduction of HAuCl₄ can be removed by the aforementioned treatment. This result means a successful extension of the PbO₂ deposition/dissolution method to clean gold nanoparticles obtained by reduction of a gold precursor. The electrocatalytic behavior towards methanol oxidation was investigated by CVs. After the treatment, the ability of the particles to act as catalysts for the methanol electrooxidation is enhanced. Combining the results from CVs with information on the chemical composition of the surface obtained by EDX and morphological information obtained by FE-SEM leads to the conclusion that the increase in electrocatalytic activity is due to the removal of organic material from the surface, and not due to an incomplete dissolution of the deposited Pb/PbO₂. The complete removal of the lead species can only be achieved by treatment with HNO₃. The results show that the cleaning method could be used for gold nanoparticles prepared by different strategies, making larger classes of gold particles potentially available as electrocatalysts. The method may be useful for other metal particles as well.

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