A versatile approach to processing of high active area pillar coral- and sponge-like Pt-nanostructures. Application to electrocatalysis

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A facile electrochemical processing method for Pt-based nanostructures with high surface area and a broad range of possible applications is proposed, based on sacrificial ZnO nanostructures. At first, ZnO-nanorods and nanobelts were grown on a TiO₂ terminated steel substrate via a fast wet chemical method and subsequently sputter coated with an ultra-thin gold film to ensure electrical contact. These nanostructured substrates were used as electrodes for Pt electrodeposition. It is shown that ZnO was dissolved while Pt-nanoparticles nucleated and grew, replicating the ZnO nanostructure morphology. In this way we could process closed Pt-nanorods with morphologies reminiscent to pillar coral, and Pt-nanobelts with a sponge-like topology. In comparison to commercial catalysts like Pt/C30, the nanostructures obtained are characterized by higher real surfaces, higher efficiency for methanol electrooxidation and higher resistance to poisoning by carbonaceous species, and so should be promising as electrodes in direct methanol oxidation fuel cells.

1. Introduction

Platinum and platinum-based materials are critical to many essential industrial processes such as hydrogenation, dehydrogenation and partial oxidation of a variety of important molecules.1 In recent years, the development of low temperature proton exchange membrane fuel cells (PEMFC), that use alternative energy sources and so reduce our dependence on fossil fuels, has stimulated a vigorous interest in Pt-based electrocatalysts.2 In all types of these fuel cells platinum-based nanolayers or nanoparticles (Pt-NPs) are used as electrodes where electrochemical reduction and oxidation take place.34 Research has been focusing on the synthesis of novel Pt-NSs to maximize their surface-to-volume ratio and catalytic performance, and minimize costs.5,6,7 Existing chemical and electrochemical methods for the synthesis of Pt-NSs and their applications are summarized in the review articles by Rao and Trivedi and Chen and Holt-Hindle.6,7

To achieve a high surface-to-volume ratio of electrodes in PEMFC, synthesized Pt-NPs are usually dispersed on carbon supports such as carbon black,8 carbon nanotubes (CNTs),8 graphene nanosheets,9 polystyrene spheres10 or other substrates like porous membranes.11 Despite the high surface-to-volume ratio of electrodes based on carbon black supports, present FC technology suffers from their limited electrochemical stability.3 In comparison, nanostructured carbon materials with graphitic structure, like CNTs and carbon fibers, show better mechanical and chemical stability properties.12,13

More recently, various metal oxide nanorods and gold nanotubes were used as supports for Pt-based catalysts in the form of nanoparticles or thin film.14–19 Template-based synthesis20 of Pt, Pt–Cu alloy nanotube arrays,21,22 and porous nanostructures were also proposed.23,24 However, most of these methods require handling of fragile alumina (AAO) or polymeric templates23 and performing lots of other different necessary steps for nanostructure processing as electrode sputtering, electrodeposition, galvanic exchange reactions or delaying, and finally dissolving of the AAO or polymer template to expose NSs. The last step can be particularly critical for preserving the character of the nanostructure; usually high aspect ratios tend to promote collapsing of the nanotubes, nanorods and nanowires thus leading to the loss of active surface area. Further, it should prove difficult to process large area electrodes using porous template methods, exactly because of the reasons outlined above.

In recent years, 1,2,3-dimensional ZnO-nanostructures (ZnO-NSs) with different morphologies as rods, wires, belts, tubes and flowers have attracted a wide interest due to their unique properties and facile synthesis methods.25–28 One-dimensional ZnO-NSs also possess a large surface-to-volume ratio13 that is of critical importance to various applications, especially in catalysis. Some new approaches were developed to decorate basically ZnO nanorods (ZnO-NRs) or wires with noble metal NSs. In general electrolytic or electrophoretic deposition methods were used.29,30 A potential catalytic membrane of closed hexagonal Au tubes with tower-like structure was recently prepared on ZnO-NRs by electrolytic gold plating followed by ZnO removal in a hydrochloric acid solution.31
In the present work a facile, fast and effective electrochemical method for preparing closed Pt-nanotubes and nanobelts using ZnO-NSs as a sacrificial template is reported. Via judicious choice of electrolyte and deposition conditions it was possible to dissolve ZnO while depositing Pt-NPs. This method works also for other noble metals, and a proof of concept was demonstrated in a preliminary work on Pd-NSs deposition. Moreover, inherent advantages of the deposition method allow large area coating of any substrate, including soft materials, and any geometry. In our case a stainless-steel substrate, pre-coated with a TiO$_2$ buffer layer, was used for growing the ZnO-NSs and subsequent electrochemical Pt-NPs deposition. As one possible application, we explore the electrochemical activity of the so processed Pt-NSs towards methanol electro-oxidation.

2. Experimental section

Reagents

Hexamethylenetetramine (HTMA), zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O), polyethyleneimine (PEI), hexachloroplatinum(iv) acid (H$_2$PtCl$_6$), urea (CO(NH$_2$)$_2$) were purchased from Sigma-Aldrich, Germany. Methanol (CH$_3$OH), Ti(IV)-isopropoxide (C$_{12}$H$_{28}$O$_4$Ti), acetylacetone (C$_{5}$H$_{8}$O$_2$) were obtained from Fluka, Germany. Ammonium hydroxide (NH$_4$OH) and sulfuric acid (H$_2$SO$_4$) were supplied by Roth, Germany. All chemicals were of analytical grade purity. All solutions were degassed with nitrogen (N$_2$) before each experiment. A Pt mesh and Ag/AgCl (in saturated KCl) electrode were used as counter and reference electrodes, respectively. All potentials in this study were referred to the standard hydrogen electrode (SHE). The substrates (with ZnO templates sputter coated with Au) were used as working electrodes. To form a desirable geometrical surface area ($S_p$) of the electrode and to avoid Pt deposition on the back and lateral steel surface, the steel sheet was masked with a nonconductive black prior to electrodeposition. Pt electrodeposition was performed potentiostatically at 0.2 V from a 20 mM H$_2$PtCl$_6$ aqueous solution for 200 s. After deposition, the working electrode was removed from the electrolyte and thoroughly rinsed with deionized water.

The real surface area ($S_p$) of the catalyst was estimated from the hydrogen adsorption range. For this purpose, potential was cycled between 0 and +1.5 V at 50 mV s$^{-1}$ in 0.5 M H$_2$SO$_4$ aqueous solution. The electrocatalytic activity of Pt-NSs for methanol electro-oxidation was evaluated using cyclic voltammetry (CV) in an aqueous solution containing 0.5 M CH$_3$OH and 0.5 M H$_2$SO$_4$. The potential was swept between 0 and 1.4 V at a rate of 50 mV s$^{-1}$. All CV measurements were performed for multiple cycles until obtaining a stable curve. The chronoamperometric (current–time) measurements of the electrocatalytic performance of the Pt-electrode were made in an identical electrolyte of 0.5 M CH$_3$OH and 0.5 M H$_2$SO$_4$ at 0.7 V. The change in current was recorded for 1800 s. The current ($i$) in all electrochemical measurements was normalized with respect to the geometrical surface area of electrodes.

Characterization of microstructure

The samples were investigated by X-ray diffraction (XRD) (X'Pert Pro, PANalytical, Holland) in grazing incidence diffraction geometry with constant $\theta = 1^\circ$ using monochromatic Cu K$\alpha$ radiation with $\lambda = 1.5418$ Å and a scanning range of 20–90° 2$\theta$.

A high-resolution scanning electron microscope (Ultra Plus, ZEISS, Germany), equipped with an energy dispersive spectroscopy (EDS) package (Oxford, UK) was used to investigate microstructure and morphology of samples, and to verify elemental composition.

3. Results and discussions

The procedure steps for the synthesis of Pt-NSs are schematically displayed in Fig. 1.

Numbers in boxes indicate corresponding process steps. We have found that pre-coating the steel substrate with a thin TiO$_2$ layer ensured a homogeneous and very dense coating with ZnO-NSs, making a ZnO seed layer superfluous. Fig. 2 shows scanning electron microscopy (SEM) images of arrays of ZnO-NSs (a) and ZnO-NBs (b), respectively.

The Pt-NSs are electrodeposited on the ZnO-supported Au-film via reduction of the Pt(IV) complex by flow of cathodic current, according to Reaction (1):

$$[\text{PtCl}_6]^{2-} + 4e^- \rightarrow \text{Pt} + 6\text{Cl}^-$$ (1)

Electrochemical deposition of Pt and methanol electrooxidation study

Pt deposition and electrochemical measurements were carried out at room temperature in a standard three-electrode cell using an electrochemical workstation (IM6e, ZAHNER, Germany). All solutions were degassed with nitrogen (N$_2$) before each experiment. A Pt mesh and Ag/AgCl (in saturated KCl) electrode were used as counter and reference electrodes, respectively. All potentials in this study were referred to the standard hydrogen electrode (SHE). The substrates (with ZnO templates sputter coated with Au) were used as working electrodes. To form a desirable geometrical surface area ($S_p$) of the electrode and to avoid Pt deposition on the back and lateral steel surface, the steel sheet was masked with a nonconductive black prior to electrodeposition. Pt electrodeposition was performed potentiostatically at 0.2 V from a 20 mM H$_2$PtCl$_6$ aqueous solution for 200 s. After deposition, the working electrode was removed from the electrolyte and thoroughly rinsed with deionized water.
The standard potential of this half reaction is 0.74 V vs. SHE.\textsuperscript{41} We first explored the effect of deposition time on the Pt-NSs obtained using ZnO-NRs as a template. Fig. 3 and 4 show Pt-NRs obtained after 60 and 200 s, respectively. A short deposition time of 60 s had lead to porous, closed Au–Pt-nanotubes with a wall thickness <20 nm and a fairly smooth surface morphology (Fig. 3).

EDS-analysis of these Pt-NRs array displayed in Fig. 5 was devoid of all Zn peaks, at least within the sensitivity of the method, and indicated that whole ZnO was dissolved during electrodeposition. This dissolution should have taken place sometime at the beginning of electrodeposition, but slow enough to permit the ZnO-NRs to support the growing Pt-NSs and so to prevent their mechanical collapse. A longer deposition time of 200 s resulted in more rough nanostructures that exactly replicated the morphology of the zinc oxide templates (Fig. 4 and 6).

The morphology of Pt-NRs (Fig. 4) is reminiscent to pillar corals (\textit{Dendrogyra cylindricus}), while the Pt-NBs (Fig. 6) rather exhibit a sponge-like, porous nanostructure. On close examination of the SEM-micrographs it can be seen that both Pt-NSs consist of an assemblage of Pt-NPs that probably had grown on top of each other. Further, the Pt-NRs consist of smaller particles in the range ≈20 nm in comparison to approximately 40 nm for Pt-NBs (compare Fig. 4d with 6c).

More EDS analyses on both, Pt-NRs and Pt-NBs, confirmed the absence of ZnO and replicated the spectra shown in Fig. 5. Further confirmation of the absence of ZnO from the final Pt-NSs could be gained from XRD investigations.

The XRD patterns obtained at the individual processing steps (depicted in Fig. 1) are shown in Fig. 7. Tick marks denote reflex positions of a phase appearing after each step (TiO\textsubscript{2}, ZnO, Au). At steps 2 and 3 characteristic reflexes corresponding to the wurtzite hexagonal structure with preferred orientation along the pseudo-cubic direction [002] are obtained for ZnO-NRs. In the case of ZnO-NBs, the pattern was identical, but without preferred orientation.

After Pt-electrodeposition (step 5) all reflexes belonging to ZnO had disappeared and only Pt reflexes, in addition to those of...
Au and steel, were obtained. The presence of all fcc peaks indicates the random crystalline nature of the Pt-NSs thus processed. Hence, both EDS and XRD confirm the complete removing of the ZnO template and show that the final nanostructures obtained consist only of Au and on top of it Pt-NPs that in their assemblage had replicated the vanished ZnO-NSs. Because Pt-NPs heterogeneously nucleated and grew on the ultra-thin Au-film, and because the gold film decorated the whole ZnO-NSs, closed hollow Pt-NRs and NBs were likely to form as no ZnO was left after Pt electrodeposition.

We intentionally damaged small areas of Pt-NRs in order to gain insight into wall thickness and foster that the whole NRs are composed of Pt. Fig. 4d clearly shows that Pt-NRs indeed represent closed nanotubes with a wall thickness of approximately 30 nm and Pt particle size smaller than 20 nm.

Dissolution of ZnO during electrodeposition under the adapted conditions may be explained in the following terms: at the plating potential, \( E = +0.2 \) V, the local accumulation of \( \text{H}^+ \) ions and the favorable reduction of the \([\text{PtCl}_6]^{2-}\) complex take place at the cathode (our working electrode). The accumulation of \( \text{H}^+ \) ions close to the cathode surface is thought to lead to a local pH drop that could induce fast chemical ZnO dissolution according to reaction (2):

\[
\text{ZnO} + 2\text{H}^+ \rightarrow \text{Zn}^{2+} + \text{H}_2\text{O},
\]

a phenomenon that is more slow without current flow. An indirect support of the proposed mechanism was obtained by electrodeposition experiments at \( E = -0.7 \) V at which simultaneous reduction of both ions, \( \text{H}^+ \) and \([\text{PtCl}_6]^{2-}\), takes place.

EDS analysis of this sample had shown the presence of Zn peaks (spectra are not shown). It should be pointed out that electrochemical dissolution of ZnO is possible only at potentials higher than 0.88 V.\(^{42}\) So, based on the microstructural investigations depicted above, we may state the formation of closed Pt-NRs and Pt-NBs via electrodeposition on corresponding sacrificial ZnO-NS templates.

This is a facile and high throughput method that also allows large areas to be uniformly coated. It is also interesting to note that the wall thickness achieved imparted mechanical stability to the Pt-NRs array at increasing resolution (a–c) after 200 s deposition time. Notice the very small Pt-NPs on the surface of the NRs. The appearance of the Pt-NRs is reminiscent of pillar corals. (d) SEM micrograph of damaged Pt-NRs where again the hollow character of the Pt-NRs is displayed. Notice also that the wall thickness has increased in comparison to Fig. 3d.

Fig. 6 SEM images at increasing resolution of Pt-NBs replicated on ZnO-NBs shown above. The Pt-NBs are composed of an assemblage of approximately 40 nm Pt-NPs.

Fig. 5 EDS spectrum of Pt-NRs. The substrate peaks, including those of stainless steel (Fe, Ni, Cr), TiO\(_2\) and gold layers are present but none of the Zn peaks can be seen.
our Pt-NSs and that by no means mechanical collapse was observed. As outlined above, we surmise a gradual dissolution of the supporting ZnO-NSs while Pt-NPs first nucleated and grew, initially on the ultra-thin Au-film and later on the already formed Pt-NPs, according to reaction (1).

Among the many application possibilities of Pt-NSs, we explored the electrocatalytic activity of ours. Fig. 8a shows CVs of Pt-NRs and Pt-NBs in N₂ saturated 0.5 M H₂SO₄ aqueous solution. In the potential range 0 < E < 0.35 V all curves in forward and reverse scans show large broad peaks corresponding to H adsorption/desorption, accompanied with bisulfate adsorption/desorption. The shape of these peaks differs from that of bulk Pt that shows two separated peaks in cathodic and anodic sweeps in acid solution in this potential range. Peak profiles observed presently for H adsorption/desorption point to some possible structure perturbation from the Au substrate and randomly oriented Pt crystal surfaces.º¹ºº,º¹º²

Catalysts are characterized by their real surface area (Sₐ, cm²) that, among other properties, determines the efficiency of the catalyst surface. The higher the ratio of Sₐ to Sₐ (geometrical surface) the better are the catalytic properties. Sₐ was obtained from the broad hydrogen adsorption peak using eqn (3):

\[ Sₐ = Q_H/v_c, \]  

where \( Q_H \) denotes the integration area of the broad hydrogen adsorption peak between 0.05 and 0.35 V (in V A), \( v \) is the scan rate (in V s⁻¹) and \( c = 210 \mu C \) cm⁻² is the charge density corresponding to the adsorption of a monolayer of hydrogen on polycrystalline Pt.º³º⁴ Table 1 summarizes the geometrical and electrochemical (discussed below) values obtained for both Pt-NRs and Pt-NBs after 200 s deposition. Electrochemical characteristics of a commercial Pt-NP based catalyst, Pt/C30, obtained under similar conditions to ours were taken from literature.º³ In order to allow for direct comparison of our results with those reported for Pt/C30 an estimation of the specific electrochemical active surface areas (SESA = Sₐ/mₚt) is necessary. The Pt-loading, mₚt, from eqn (4):

\[ mₚt = Q_{dep}M/zF, \]  

Fig. 7 XRD patterns obtained after each process step depicted in Fig. 1. The patterns are shifted vertically for clarity. Tick marks denote reflection positions for (from down to the top) TiO₂, ZnO and Au. Stars represent reflections of the steel substrate. Notice that the patterns corresponding to step 5 contain no reflections corresponding to ZnO.

Fig. 8 Cyclic voltammograms of Pt-NRs (solid line for 200 s and dotted line for 60 s deposition time) and Pt-NBs (dashed line) at a scan rate of 50 mV s⁻¹ in 0.5 M H₂SO₄ (a) and 0.5 M H₂SO₄ + 0.5 M CH₃OH (b). In (a) the broad peak at small voltages in the reverse scan (hydrogen adsorption) was used for determining the real surface area, Sₐ. In (b) the peak current densities for forward, f, and backward, b, scans during methanol electro-oxidation are shown.
The long-term performance of Pt-NRs and Pt-NBs for room temperature methanol electrooxidation was also investigated via recording of \( j-t \) curves (CA) at 0.72 V in the same electrolyte described above. Fig. 9 shows that \( j \) decays with \( t \) for both nanostructures due to accumulation of carbonaceous species and reaches values of 3.25 and 1.5 mA cm\(^{-2}\) at 1800 s for Pt-NBs and NRs, respectively. However, none of the Pt-NSs had yet reached a steady state. It also appears that Pt-NBs are characterized by a higher (~twice) catalytic activity in comparison to Pt-NRs. This difference can be explained on the one hand by the higher roughness factor obtained for Pt-NBs (approximately 40% higher than that of Pt-NRs), and on the other hand by the bigger particle size observed for Pt-NBs (see above) that should account for their better electrocatalytic activity, and also for the better resistance against poisoning.\(^{49}\) It goes without saying that we have checked the Pt-NSs after repeated electrochemical experiments (CVs and CA) and found that neither their morphologies nor their adhesion to the TiO\(_2\) film were altered.

The processing method described in the present work uses ZnO-NSs as sacrificial moulds for Pt-NSs, with the advantage that ZnO is dissolved during electrodeposition. However, it is legitimate to argue that the same Pt-NSs could be easily obtained via Pt-sputtering and subsequent dissolution of ZnO. We conducted experiments in this sense, and the results are shown in the ESI† (Fig. S1 and S2). We found a rather smooth Pt morphology and poor electrocatalytic properties. These results

<table>
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<th>Electrode</th>
<th>( S_g / \text{cm}^2 )</th>
<th>( S_R / \text{cm}^2 )</th>
<th>( S_R / S_g )</th>
<th>SESA/m(^2) per ( g_{Pt} )</th>
<th>Peak current density, ( j ) (( \text{mA cm}^{-2} ))</th>
<th>( j / j_b )</th>
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<tr>
<td>Pt-NRs</td>
<td>1.19</td>
<td>68.6</td>
<td>57.65</td>
<td>11.26</td>
<td>31</td>
<td>0.81</td>
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<tr>
<td>Pt-NBs</td>
<td>1.19</td>
<td>96</td>
<td>96</td>
<td>13.57</td>
<td>38.73</td>
<td>0.97</td>
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<tr>
<td>Pt/C30 catalyst(^a)</td>
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<td>1.87</td>
<td></td>
<td>53.3</td>
<td>12.02</td>
<td>0.76</td>
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\(^a\) Data taken from Liu et al.\(^{24}\)
stress the role of particulate nucleation and growth obtained in the electrodeposition process for achieving surfaces with higher activity.

4. Conclusions

A facile electrochemical approach to fabrication of large area nanostructured Pt-films using wet chemically processed ZnO-NRs and ZnO-NBs as a soluble template was demonstrated. The formation of Pt-NPs on gold terminated ZnO-NSs simultaneously occurs with chemical dissolution of ZnO. Latter probably takes place because of pH drop due to H⁺ evolution at the vicinity of the electrode surface. The Pt-NSs processed in this way replicated the ZnO-NSs but were shown by means of both XRD and EDS analyses to be hollow. The electrocatalytic activity of these Pt-NSs was exemplary demonstrated on the electro-oxidation of methanol. It appeared that Pt-NPs had better properties both in terms of performance and long-term viability in comparison to Pt-NRs and the data reported for a commercial Pt-catalyst. The method reported should possess a high potential for the fabrication of different nanostructures of noble metals, and their alloys, for a wide range of catalytic applications.

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References