Self-ordered titania nanotubes and flat surfaces as a support for the deposition of nanostructured Au–Ni catalyst: Enhanced electrocatalytic oxidation of borohydride

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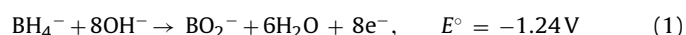
ABSTRACT

Gold aggregates with particle size of a few nanometers have been fabricated on the anodized titania nanotube arrays and flat surfaces by a two-step process which involves nickel electroless deposition followed by spontaneous galvanic displacement of Ni by Au from its chloro-complex solution. The structure, morphology and composition of the fabricated catalysts have been characterized using scanning electron microscopy and energy dispersive X-ray analysis. The catalytic activities of the nanostructured Au(Ni) catalysts preformed on the TiO_2 nanotube arrays and flat surfaces have been investigated towards borohydride oxidation in an alkaline medium by cyclic voltammetry and chrono-techniques. The nanostructured Au(Ni) catalysts on the titania nanotube arrays and flat surfaces exhibit enhanced electrochemical activity and stability towards oxidation of BH_4^- ions in an alkaline medium as compared to that of bulk Au.
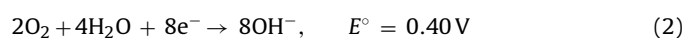
1. Introduction

Fuel cells allow direct conversion of chemical energy to electric energy. One type of the fuel cell, a direct borohydride fuel cell (DBFC), has recently been investigated as a potential candidate for portable and mobile applications due to its high energy density and the ease with which borohydride can be stored and transported [1–4]. The DBFC is based on borohydride oxidation:

$$BH_4^- + 8OH^- \rightarrow BO_2^- + 6H_2O + 8e^-, \qquad E^\circ = -1.24\,V \qquad (1)$$

and oxygen reduction:

$$2O_2 + 4H_2O + 8e^- \rightarrow 8OH^-, \qquad E^\circ = 0.40\,V \qquad (2)$$

The overall reaction:

$$BH_4^- + 2O_2 \rightarrow BO_2^- + 2H_2O, \qquad E^\circ = 1.64\,V \qquad (3)$$

Since borohydride is used as fuel, the development of low-cost, stable and highly active electrocatalysts towards borohydride oxidation is of considerable interest. It is well known that gold is an effective electrocatalyst for the oxidation of BH_4^- ions [5–10], however, the use of a noble metal as an electrode material is limited by its high price. One of the ways to reduce amount of Au is to disperse small Au particles (in order of a few nanometers) on a

technologically relevant substrate. A variety of nanostructured conducting materials like mesoporous carbon, carbon nanotubes and nanofibers were used as supports for Au catalysts to minimize the use of the precious metal.

This work is focused on the study of self-ordered titania nanotube arrayed (denoted as TiO_2-NTs) and flat (denoted as TiO_2-flat) surfaces as a support for loading of gold particles with the aim to fabricate a highly efficient nano-Au(Ni)/TiO_2-NTs and nano-Au(Ni)/TiO_2-flat electrocatalysts for the oxidation of BH_4^- ions in an alkaline medium. Anodized titania nanotube arrays and flat surfaces as a substrate for the fabrication of catalysts were applied here due to their easy preparation, high orientation, large surface area, high uniformity, non-toxicity, chemical and electrochemical stability and low production costs, which makes them valuable functional materials in many areas [11–17]. Self-ordered titania nanotubed surfaces are an ideal choice of supporting materials for high performance catalysts. Au nanoparticles dispersed over a self-organized nanotubular TiO_2 matrix have been used as a highly efficient catalyst system for the electrochemical oxygen reduction in aqueous solutions [18], electrochemical oxidation of glucose [19,20], water-gas shift reaction [21], degradation of dyes [22,23], CO oxidation [24–27] and others. The Au-modified TiO_2 nanotube arrays also provide excellent matrices for the immobilization of bio molecules in enzyme-attached electrode fabrication [13–15] or for the fabrication of H_2O_2 biosensors [16,17]. Ponce-de-Léon et al. [28] applied the TiO_2 nanotubes as a support for a gold-based electrocatalyst for borohydride oxidation. A variety of methods

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are used for the metal nanoparticles loading onto the TiO_2-NTs surface. One possibility is that Au/TiO_2-NTs electrodes are prepared by a two-step process of anodization of titanium followed by cathodic electrodeposition of gold on resulted TiO_2 [19,29], by ion-exchange adsorption followed by chemical reduction [28], by an argon plasma technique [16,17]. Another way for fabricating electrodes is focused on the deposition-precipitation methods that were used to load nanoparticles of different metals on the surface of mesoporous titanate nanotubes produced by alkali hydrothermal treatment of TiO_2 [30–33]. These methods are either complex and complicated or high-priced. So, less complicated and simpler methods for the fabrication of catalyst are desirable.

In this work we have successfully fabricated adherent gold-coated nickel films, Au(Ni), with particle size of a few nanometers on anodized titania nanotube arrayed and flat surfaces by a two-step process which involves nickel electroless deposition followed by spontaneous galvanic displacement of Ni by Au from its chloro-complex solution. This simple procedure is based on an electrochemical process, during which the deposition of a noble metal occurs by the oxidation of a precursor metal adlayer deposited on the substrate at the open-circuit potential [34–40]. In this study, the spontaneous oxidation of a Ni adlayer by $AuCl_4^-$ ions has been used to produce Au particles on the self-ordered titania nanotubes arrayed and flat surfaces. The electrocatalytic activity of the prepared catalysts was examined towards borohydride oxidation by cyclic voltammetry (CV), chronoamperometry (CA) and chronopotentiometry (CP). The structure, morphology and composition of the fabricated catalysts were characterized using scanning electron microscopy (SEM) and energy dispersive X-ray (EDAX) analysis.

2. Experimental details

2.1. Chemicals

Titanium foil (99.7% purity of 0.127 mm thickness), $NaBH_4$ and $HAuCl_4$ were purchased from Sigma–Aldrich Supply. H_2SO_4 (96%), NH_4F (97%), NaOH (98.8%), ethanol and acetone were purchased from Chempur Company. All chemicals were of analytical grade. Deionized water was used to prepare all the solutions.

2.2. Fabrication of catalysts

The self-ordered TiO_2 nanotube arrays in this study were prepared by anodic oxidation of Ti foil surface [41]. Briefly, prior to anodization, titanium sheets (1 cm × 1 cm) were degreased with ethanol, rinsed with deionised water and dried in an Ar stream. Titanium sheets were anodized in a 0.24 M H_2SO_4 solution with 0.5 wt.% NH_4F at a constant potential of 20 V at room temperature for 1 h. Two sheets of Pt were used as counter electrodes.

For comparison, flat TiO_2 electrodes were also grown as reference samples by anodizing Ti in (fluoride free) 0.24 M H_2SO_4 at 20 V for 10 min.

To deposit the Au(Ni) catalyst on the TiO_2 nanotube arrayed and flat surfaces, at first, a thin layer of electroless Ni was deposited on them by the following procedures: (a) activation of the TiO_2 nanotube arrayed and flat surfaces in a $0.5\,g\,l^{-1}$ $PdCl_2$ solution for 60 s; (b) subsequent rinsing of the activated surfaces with deionized water; (c) followed by the immersion of the activated samples into an electroless nickel bath for 60 s. The electroless plating bath consists of 0.1 M nickel sulfate, 0.4 M glycine, 0.25 M sodium hyphophosphite and 0.1 M disodium malonate. The bath operated at pH 9 and a temperature of $85 \pm 2\,°C$. Then the prepared Ni/TiO_2-NTs and Ni/TiO_2-flat electrodes were immersed in a 1 mM $HAuCl_4$ solution (pH 1.8) at room temperature for 60 s. The surface-to-volume ratio was $1.3\,dm^2\,l^{-1}$. After plating, the samples were

taken out, thoroughly rinsed with deionized water and air dried at room temperature. Then, the prepared catalysts were used for borohydride electro-oxidation measurements without any further treatment.

2.3. Characterization of catalysts

The surface morphology and composition of the samples were characterized using a Scanning Electron Microscope EVO-50 EP (Carl Zeiss SMT AG, Germany) with Energy Dispersive and Wave dispersion X-ray Spectrometers (Oxford, UK). Metal loading was estimated using STRATAGEM software and EDS K-ratios for Ni, P, Ti and O K alpha lines and Au L alpha lines.

2.4. Electrochemical measurements

A conventional three-electrode electrochemical cell was used for electrochemical measurements. The nano-Au(Ni)/TiO_2-NTs, nano-Au(Ni)/TiO_2-flat, Ni/TiO_2-NTs, TiO_2-NTs catalysts with a geometric area of $2\,cm^2$ were employed as working electrodes, an Ag/AgCl/KCl electrode was used as a reference electrode and a Pt sheet located in a separate glass-fritted compartment was used as a counter electrode. The electroactive surface area of the counter electrode calculated from the hydrogen adsorption was $7\,cm^2$. An Au-sputtered quartz crystal with a geometric area of $0.636\,cm^2$ was used as a bulk gold electrode. Cyclic voltammetry, chronoamperometry and chronopotentiometry experiments were made with a Metrohm Autolab potentiostat (PGSTAT100) using Electrochemical Software (Nova 1.6.013). The presented current densities are normalized with respect to the geometric area of catalysts.

3. Results and discussion

3.1. Physical characterization

Self-ordered TiO_2 nanotube arrays (Fig. 1a) in this study were prepared by anodic oxidation of Ti surface in an aqueous sulfuric acid solution containing NH_4F. The average tube diameter was about 100 nm and the thickness of titania layers was ~350 nm. The electroless Ni–P layer with the thickness of about 300 nm was deposited on the titania nanotube surface, which produces a layer of granular nickel particles about 200 nm in size, as Fig. 1b testifies. It is clearly seen, that immersion of Ni/TiO_2-NTs electrode into the gold-containing solution results in the formation of numerous gold particles on the Ni surface. The Au aggregates appear as bright spots and a statistical analysis of the observed granules indicated they had an average diameter of about 10–30 nm for 1 min Ni/TiO_2-NTs electrode immersion in the gold-containing solution. They are quite uniform in size and well separated. Fig. 1c and d shows SEM micrographs of the TiO_2-flat and nano-Au(Ni)/TiO_2-flat electrodes, respectively. The Au particles in size of 10–30 nm were also detected.

The presence of Au and Ni was confirmed by Energy dispersive X-ray analysis. According to the data of EDAX analysis presented in Table 1 a significant quantity of deposited nickel and a much lower amount of Au on both catalysts surfaces were detected, furthermore, lower amounts of both Ni and Au were deposited on the flat TiO_2 surface.

Also the Au loading in the fabricated catalysts was estimated using STRATAGEM software and EDS K-ratios for Ni, P, Ti and O K alpha lines and Au L alpha lines. It has been determined that after sonication of Ni/TiO_2-flat and Ni/TiO_2-NTs in a gold-containing solution for 1 min, the nano-Au(Ni)/TiO_2-flat and nano-Au(Ni)/TiO_2-NTs catalysts contained the Au loadings of 1.28 and $3.07\,\mu g\,Au\,cm^{-2}$, respectively.