



# Gold–nickel/titania nanotubes as electrocatalysts for hydrazine oxidation



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## HIGHLIGHTS

- Self-ordered titania nanotubes as a support for catalysts.
- Electrocatalysts for the oxidation of hydrazine.
- Fabrication of catalysts by galvanic displacement of Ni layer by Au enables growth of nano-sized metal particles.
- Au(Ni)/TiO<sub>2</sub>-NTs are efficient electrocatalysts for hydrazine oxidation.

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## ABSTRACT

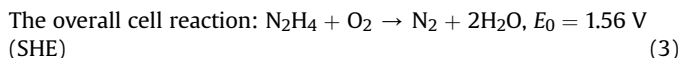
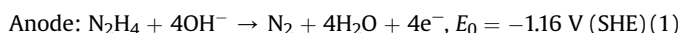
This work is focused on the study of self-ordered titania nanotube arrayed electrodes for preparation of efficient gold–nickel/titania nanotubes electrocatalysts (denoted as Au(Ni)/TiO<sub>2</sub>-NTs) for the oxidation of hydrazine in an alkaline medium. The Au(Ni)/TiO<sub>2</sub>-NTs catalysts were prepared by partial galvanic displacement of an electroless Ni layer, deposited on the self-ordered titania, by Au nanoparticles from the gold-containing solution. The morphology, structure and composition of the prepared nano-structured catalysts were examined by Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive X-ray Analysis (EDAX), X-ray diffraction (XRD) and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The electrocatalytic activity of the prepared catalysts was investigated towards the oxidation of hydrazine in an alkaline medium by means of cyclic voltammetry and chronoamperometry. It was found that the prepared Au(Ni)/TiO<sub>2</sub>-NTs catalysts with low Au loadings possess more than ten–twenty times higher electrocatalytic activity towards the oxidation of hydrazine in an alkaline medium as compared to that of Au electrodeposited on TiO<sub>2</sub>-NTs and Ni/TiO<sub>2</sub>-NTs, presumably due to formation of Au nanoparticles of high dispersivity as well as formation of Ni solid solution in gold.

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## 1. Introduction

Low-temperature fuel cells operating on hydrazine fuel comprise a promising class of new, non-conventional sources of energy [1]. Although hydrazine is highly toxic, it is an ideal fuel for direct liquid-feed fuel cells given that hydrazine oxidation only generates environmentally friendly nitrogen and water (Eq. (1)) and does not produce species which can poison the electrocatalysts [1,2]. The theoretical energy of a hydrazine/air fuel is 5.36 Wh g<sup>−1</sup>. Moreover, the theoretical voltage of 1.56 V (Eq. (3)) is much higher for direct hydrazine fuel cells than that for other fuel cells using

hydrogen (1.24 V) or methanol (1.19 V) as a fuel. The electrode reactions in an alkaline medium are as follows:



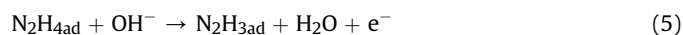
The oxidation of hydrazine in an alkaline medium has been investigated on various catalytic materials including Au [3–10], Pt [4,5,8,11–19], Pd [4,5,14,17,20–25], Ag [3,8,14,26–29], Ni [4,8,14,30–32] and some other metals. It was found that electro-oxidation of hydrazine on these mentioned metals may occur by two different mechanisms: either hydrazine is directly oxidized or

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it catalytically decomposes into hydrogen and other related compounds, the decomposed hydrogen being oxidized [4,20]. The reaction schemes of the anodic oxidation of hydrazine may be as follows:



or



followed by.



and



Notably, the anodic oxidation of hydrazine on the nickel, nickel–phosphorus, palladium and gold electrodes was found to proceed through the formation of intermediate radicals according to Eq. (5) and be followed by the reactions (6) and (7) [4,20].

It has been determined that noble metals are highly active for the oxidation of hydrazine, but the use of them as an electrode material in direct hydrazine fuel cells is limited by their high price. One of the ways to reduce the amount of noble metals is to disperse metal nanoparticles on a technologically relevant substrate. Recently, titania nanotube arrays (denoted as TiO<sub>2</sub>-NTs) have been used as a substrate for loading of metal nanoparticles with the aim to create high performance catalysts due to their easy preparation, high orientation, large surface area, high uniformity, non-toxicity, chemical stability and low production cost [33–35]. Platinum or palladium modified titania nanotubes composites (Pt/TiO<sub>2</sub>-NTs or Pd/TiO<sub>2</sub>-NTs) prepared by a simple reduction method using TiO<sub>2</sub>-NTs as a support have shown a high electrocatalytic activity towards the oxidation of hydrazine as compared with that of unsupported Pt or Pd particles [19,22]. Au nanoparticles dispersed over a self-organized nanotubular TiO<sub>2</sub> matrix have been used as a highly efficient catalyst system for the electrochemical oxygen reduction [36], electrochemical oxidation of glucose [33,37], water-gas shift reaction [34], degradation of dyes [35,38,39], oxidation of CO [40–44], borohydride [45,46], hydrazine [47] and others.

A variety of methods are used for loading of metal nanoparticles onto the TiO<sub>2</sub>-NTs surface. This work is focused on the study of efficient gold–nickel/titania nanotubes electrocatalysts (denoted as Au(Ni)/TiO<sub>2</sub>-NTs) for the oxidation of hydrazine in an alkaline medium prepared via a simple and low-cost galvanic displacement technique [48–59]. The electrocatalytic activity of the prepared catalysts was investigated towards the oxidation of hydrazine in an alkaline medium by means of cyclic voltammetry and chronoamperometry. The morphology, structure and composition of the prepared nanostructured catalysts were examined by Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive X-ray Analysis (EDAX), X-ray diffraction (XRD) and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES).

## 2. Experimental

### 2.1. Chemicals

Titanium foil (99.7% purity and 0.127 mm thickness), hydrazine hydrate (55%) and HAuCl<sub>4</sub> were purchased from Sigma–Aldrich Supply. H<sub>2</sub>SO<sub>4</sub> (96%), NH<sub>4</sub>F (97%), NaOH (98.8%) and ethanol were

purchased from Chempur Company. All chemicals were of analytical grade. Deionized water with the resistivity of 18.2 MΩ cm<sup>−1</sup> was used to prepare all the solutions.

### 2.2. Fabrication of catalysts

The self-ordered TiO<sub>2</sub> nanotube arrays in this study were prepared by anodic oxidation of Ti foil surface [46]. Briefly, prior to anodization, titanium sheets (1 cm × 1 cm) were degreased with ethanol, rinsed with deionized water and dried in an Ar stream. Titanium sheets were anodized in a 0.24 M H<sub>2</sub>SO<sub>4</sub> solution with 0.5 wt.% NH<sub>4</sub>F at a constant potential of 20 V at room temperature for 1 h. Two sheets of Pt were used as counter electrodes. The Au(Ni) catalysts were deposited on the TiO<sub>2</sub> nanotube arrayed surface according to the following procedures: a) immersion of the TiO<sub>2</sub> nanotube arrayed surface in a 0.5 g l<sup>−1</sup> PdCl<sub>2</sub> solution for 1 min with the aim to form catalytically active Pd centers on the substrate for further electroless nickel deposition; b) subsequent rinsing of the activated surface with deionized water; c) followed by immersion of the activated samples into an electroless nickel bath for 60 s. The electroless plating bath consisted of 0.1 M nickel sulfate, 0.4 M glycine, 0.25 M sodium hyphosphite and 0.1 M disodium malonate. The bath operated at pH 9 and a temperature of 85 ± 2 °C. Then the prepared Ni/TiO<sub>2</sub>-NTs electrodes were immersed in a 1 mM HAuCl<sub>4</sub> + 0.1 M HCl solution at 25 °C for 0.5, 1 and 5 min. The surface-to-volume ratio was 1.3 dm<sup>2</sup> l<sup>−1</sup>. 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 hydrazine electro-oxidation measurements without any further treatment.

For comparison, the Au/TiO<sub>2</sub>-NTs electrode was fabricated by direct electroplating of Au on the TiO<sub>2</sub> nanotubes in a 1 mM HAuCl<sub>4</sub> + 0.1 M HCl solution at a current density of 10 mA cm<sup>−2</sup> for 5 min.

### 2.3. Characterization of catalysts

The morphology and composition of the fabricated catalysts were characterized using a SEM/FIB workstation Helios Nanolab 650 with an energy dispersive X-ray (EDX) spectrometer INCA Energy 350 X-Max 20.

XRD patterns of the Ni and Au–Ni deposited on the titania nanotubed surface were measured using an X-ray diffractometer D8 Advance (Bruker) equipped with an X-ray tube with a Cu anode. The grazing incidence (GIXRD) method was used in the 2θ range 35–70°. The angle, α between the parallel beam of X-rays and the specimen surface was adjusted to 0.5°.

Chemical composition of samples was determined by X-ray fluorescence spectrometer with wave dispersion (WDXRF) Axios mAX (Panalytical) equipped with an 4 kW X-ray tube with a Rh anode. Omnian software for standard-less quantitative analysis was used for quantification of elements present in samples.

The Au metal loading was estimated from ICP-OES measurements. The ICP optical emission spectra were recorded using an ICP optical emission spectrometer Optima 7000DV (Perkin Elmer).

### 2.4. Electrochemical measurements

A conventional three-electrode electrochemical cell was used for electrochemical measurements. The Au(Ni)/TiO<sub>2</sub>-NTs, Ni/TiO<sub>2</sub>-NTs and Au/TiO<sub>2</sub>-NTs catalysts with a geometric area of 2 cm<sup>2</sup> were employed as working electrodes, a Pt sheet located in a separate glass-fritted compartment was used as a counter electrode and an Ag/AgCl/KCl (3 M KCl) electrode via a Lugin capillary with a salt bridge was used as a reference electrode. Due to the high mobility

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