



Electroless synthesis of nanostructured nickel and nickel–boron tubes and their performance as unsupported ethanol electrooxidation catalysts

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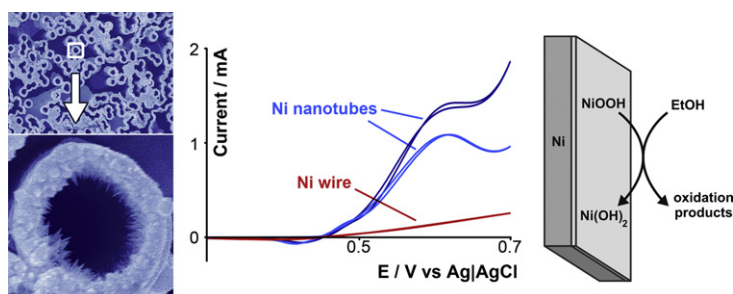
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HIGHLIGHTS

- ▶ New electroless plating bath allows fabrication of pure Ni nanomaterials.
- ▶ Tubular Ni and Ni–B nanomaterials are obtained by metalization of hard templates.
- ▶ 1D Ni catalysts show clearly improved activities in ethanol electrooxidation.
- ▶ The presence of boron does not hamper the electrocatalytic activity.

GRAPHICAL ABSTRACT



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ABSTRACT

Considering the low abundance of platinum group metals and the high catalytic performance of nickel for the oxidation of small organic molecules, nickel catalysts are promising substitutional materials for direct alcohol fuel cells. Despite the simplicity, good scalability and flexibility of electroless plating, reports on the fabrication of nickel-based catalysts with this method are rare, in particular regarding the deposition of pure nickel. To expand the existing synthetic repertoire, we developed an electroless plating bath allowing the homogeneous deposition of spiky nickel films on very complex shaped substrates. Nanostructured nickel and nickel–boron tubes were obtained by combination of the new and a borane-based plating reaction polymer templates, respectively. The composition, morphology and crystallinity of the products was comprehensively investigated with X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD). Finally, the nickel and nickel–boron tubes were applied as unsupported electrocatalysts for the oxidation of ethanol (EtOH) in alkaline environment. Compared to a macroscopic reference, both of the nanostructured catalysts showed improved utilization of high EtOH concentrations and considerably increased oxidation activities, rendering the applied deposition reactions promising routes towards novel catalysts for direct alcohol fuel cells.

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1. Introduction

Lately, there is a rising need for cost-efficient energy storage and conversion solutions and a desire to redesign economic processes towards increased sustainability and independence from rare materials. In the course of these developments, common

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metals are attracting considerable interest as substitutes for expensive catalyst systems. For instance, Fe was used to efficiently generate hydrogen from formic acid [1], Cu was implemented in a room temperature operated borane fuel cell [2], and Ni was applied in the oxidation of small organic molecules such as methanol [3], EtOH [4–7] and glucose [8]. Due to the sluggish alcohol electrooxidation kinetics in acidic electrolytes, much research has been performed on the development of fuel cell setups and novel catalyst systems for the operation in alkaline environment [9,10]. In this reaction type, Ni is an interesting substitutional material for noble metals such as Pt [10].

Nanostructured metal catalysts provide enhanced surface area [2,4,7] and often exhibit improved performance compared to the bulk materials [8]. Among the different classes of metal catalysts, unsupported, highly anisotropic structures such as nanotubes (NTs) or nanowires recently attracted special attention due to their enhanced properties [11–14]. While conventional catalyst designs such as carbon black decorated with metal nanoparticles often suffer from moderate electron transfer and corrosion, one-dimensional metal nanostructures can exhibit excellent conductivity [11,14] and aging resistance [11–13]. Also, NTs have a large and well accessible surface [11–13], allowing excellent mass transport of chemical species between the surrounding medium and the catalyst. Finally, high metal loadings which are needed e.g. for direct alcohol or high performance fuel cells can be effectively obtained with unsupported nanostructures [11,14].

However, special synthetic routes are required to create metal NTs, mostly involving hard [13–17] or sacrificial templates [12] which enforce the uncommon morphology by spatial confinement. In combination with template methods, electroless plating is often used to fabricate complex, arbitrary shaped metal nanostructures [18] and metal NTs [15–17]. This versatile yet surprisingly simple class of wet-chemical metal depositions is based on the autocatalytic, surface-selective reduction of metal precursor solutions. The electrons for reduction are provided by a dissolved chemical agent [15–20], and the reactions can be easily scaled up. No complicated instrumentation is necessary to initiate the continuous metal deposition. A suitable work piece only has to be immersed in an electroless plating bath. The substrates do not need to be conductive, and can be shaped very irregularly [15–18]. However, for the preparation of nanomaterials with this technique, sufficient reaction control and deposition homogeneity are required [21].

Despite the outstanding catalytic performance of tubular metal nanocatalysts [11–13,21] and the effectiveness of Ni catalysts for the electrooxidation of EtOH [4–7] as an important fuel cell reaction for upcoming portable energy applications, Ni NTs have not been tested in alcohol oxidation to date. In addition, there are only very few reports on electroless plating procedures with sufficient nanoscale control to fabricate Ni NTs in porous templates [15,16], and they rely on hypophosphite or aminoboranes as the reducing agents. The insertion of heteroatoms (P, B) by these conventional reducing agents [15,16,22,23] can be detrimental to the properties of the resulting materials. For instance, the presence of boron clearly reduces the ductility of Ni [19] as well as its catalytic performance in hydrogenation reactions [22].

In this work, we present a route to overcome the lack of electroless plating protocols suitable for the fabrication of pure Ni nanomaterials with complex morphologies. Ni NTs were synthesized with a newly developed plating bath based on the clean reducing agent, hydrazine, and the previously reported dimethylaminoborane (DMAB) [23]. To the best knowledge of the authors, this is the first report of the synthesis of tubular structures in porous hard templates consisting of pure Ni. Finally, the two Ni NT catalyst types were applied in the electrooxidation of EtOH to

evaluate their catalytic potential in dependence on their nanostructure and composition.

2. Experimental

2.1. General, chemicals

Glassware was cleaned with nitric acid prior to use. All solutions were freshly prepared. Milli-Q water ($>18\text{ M}\Omega$) was employed in all procedures. The following chemicals were applied without further purification: 2-chlorophenol (Aldrich, 98%); AgNO_3 (Grüssing, p.a.); CH_2Cl_2 (Sigma Aldrich, puriss. p.a.); borane dimethylamine complex (Fluka, purum); EtOH (Labor Service GmbH, p.a.); iminodiacetic acid (Fluka, purum); methanol (Aldrich, 99.8%); NaOH solution 32% in water (Fluka, puriss. p.a.); Ni wire (Aldrich, $\geq 99.9\%$ trace metal basis); $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (Sigma–Aldrich, puriss. p.a.); $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ solution 80% in water (Merck, for synthesis); NH_3 solution 33% in water (Merck, puriss.); $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (Sigma–Aldrich, ACS reagent); sodium citrate tribasic dihydrate (Sigma–Aldrich, puriss. p.a.); trifluoroacetic acid (Riedel-de Haën, $>99\%$).

2.2. Fabrication of Ni nanostructures

The synthetic steps involved in the Ni NTs fabrication are summarized in Fig. 1, beginning with the template preparation. At first, polycarbonate (PC, Makrofol[®] from Bayer Material Science AG) and polyethylene terephthalate (PET, Hostaphan[®] from Hoechst) foils (nominal thickness: PC 30 μm , PET 36 μm) were irradiated with Au ions (energy = 11 MeV per nucleon, fluence = 1×10^8 ions cm^{-2}) at the GSI Helmholtz Centre for Heavy Ion Research. The PET foil was irradiated with UV light (Privileg UVA lamp, 105 W, 1 h irradiation per side) to improve etchability. Subsequently, the polymer foils were etched in stirred NaOH solutions (50 °C, PC: 6 mol L^{-1} NaOH, PET: 4.8 mol L^{-1} NaOH), leading to the selective removal of the ion tracks and the formation of cylindrical channels inside the foils. The diameter of the channels was adjusted by variation of the etching time [24]. The as-prepared templates were washed with water and dried. Prior to electroless plating, the templates were activated with a thin layer of Ag nanoparticles which act as nuclei to initiate the metal deposition

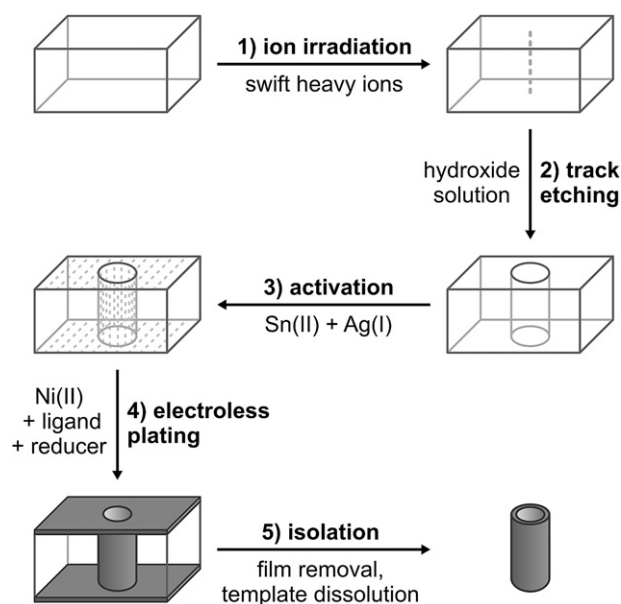


Fig. 1. Sketch of the synthetic steps involved in the fabrication of metal NTs by combining electroless deposition with ion track etched polymer templates.

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