

# Exotemplate-based Fabrication of 1-dimensional Hybrid Nanostructures for Catalysis and Sensing

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**Abstract** – For the fabrication of 1-dimensional nanostructures, such as nanowires and nanotubes, and networks thereof, ion-track etched polymer foils can serve as exotemplates. They are formed by ion irradiation of polymer foils of several  $\mu\text{m}$  thickness and chemically etching the straight damage tracks into nanochannels, with diameters in the sub- $\mu\text{m}$  range, down to 20 nm. The high-aspect ratio nanochannels were filled up either electrochemically with a metal, forming metallic nanowires, or by coating the nanochannel walls by electroless chemical deposition, thus forming nanotubes, either from metals or oxides. When the nanochannels were formed from crossed ion tracks, nanowire and –tube networks were obtained. The synthesis of 2-metal nanostructures based on Ni/Pd, Bi/Pd, and Ni/NiCo-hydroxide is shown. The nanostructures were used as catalysts for methanol oxidation and for glucose sensing.

**Keywords:** nanotechnology, exotemplate synthesis, nanowires, nanotubes, sensing, catalysis

## 1. Introduction

1-dimensional (1D) nanostructures, such as nanowires, nanotubes, and networks thereof, show large surface area, high surface-to-volume ratio, porosity with enhanced mass transfer, good electron conduction, and a high density of (electro)chemically active sites. That renders them particularly suitable for catalysis and sensing applications. The 1D nanostructures discussed in the following with their micro/nano-architecture have been used as electrode materials for electrochemical applications [1, 2, 3, 4]. They are fabricated by depositing the metallic or oxidic material inside polymeric exotemplates. Those are nanochannels, either parallel or intersected, formed by the ion-track etching method [5, 6, 7]. Polymer foils, mostly polycarbonate (PC) or polyethyleneterephthalate (PET), of typically 10 to 30  $\mu\text{m}$  thickness were irradiated with highly energetic ions of medium to heavy elements, such as Ar and Au, from an ion accelerator. When the ions pass through the polymer templates, they induce chemical bond breaking. The cylindrical damage cores with a diameter of typically a few nanometers, showing a lower density, are preferentially chemically etched, forming nanochannels. The number of these nanochannels per unit area can be chosen over a wide range, typically from  $10^5$  to  $10^8$  per  $\text{cm}^2$ . At larger areal densities, an increasing number of undesired overlaps of the stochastically distributed ion tracks is found and needs to be avoided. The mostly cylindrical nanochannels with diameters from typically 20 nm up to the sub- $\mu\text{m}$  range are either filled up electrochemically by depositing metal into it, providing nanowires [8,9], or their walls are coated by an electroless chemical method thus forming nanotubes [1]. When the polymer is removed by a solvent, the 1D nanostructures are set free. Combination of the deposition methods leads to multielement structures, either as alloys or as hybrid materials, such as metal coatings on nanowires, forming two-element core-shell nanowires, or in combination with 0D or 2D nanostructures, yielding nanoparticle- or nanosheet-decorated nanowires or nanotubes. As mentioned before, the crossing of the ion tracks leads to nanonetworks, the 3D arrangement of the 1D nanoobjects [10]. In the following, several examples of such nanostructures and their applications are shown.

## 2. Fabrication and application of 1D nanostructures

1D nanostructures, both from metals and oxides, were used for different types of catalysis. Nanotubes of titanium oxide formed by electroless deposition of titania and heat treatment were used as photocatalysts. They showed a large activity towards photochemical degradation of the dye methylene blue under low power UV light irradiation, due to synergistic action of a phase mixture of rutile and anatase [11]. Using  $\text{TiO}_2$  nanotubes as a carrier for Platinum nanoparticles gave an effective electrocatalyst for fuel cells operating with ethanol and formic acid [12].

A fuel cell type with a large application potential is the Direct Methanol Fuel Cell. As an electrocatalyst for methanol, Palladium-containing nickel nanowires were fabricated [13]. Fig. 1 shows schematically the multi-step procedure. Thus, free-standing nickel carrier nanowire networks doped with catalytically active Pd nanoparticles on the nanowire surface were obtained. With this approach, the disadvantage of shielding active precious metal in the nanowire interior was overcome. In addition, the agglomeration of the catalyst nanoparticles was hindered due to their stable location on the nickel nanowires.

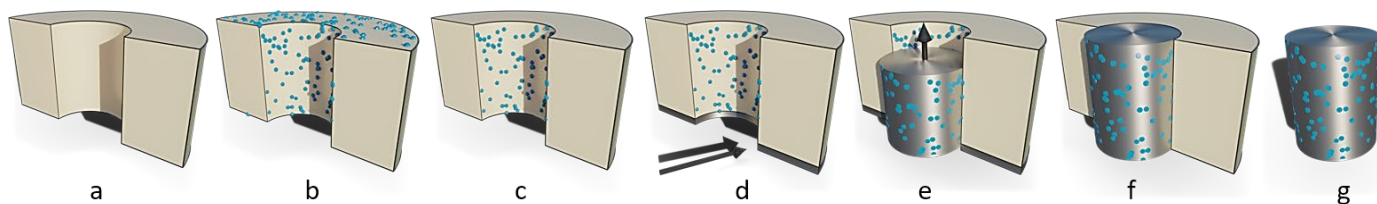


Fig. 1: Formation of carrier nanowires, doped at their surface with a catalytically active metal, a: ion track etching of ion damage track of polymer foil into nanochannel, b: deposition of nanodots of catalytically active metal (in blue) on nanochannel wall by swelling-activating the nanochannel walls, c: chemomechanical removal of dots on top, d: deposition of metal thin film by sputtering, as a cathode, e: electrochemical deposition of metal nanowire inside the nanochannel, f: filling of exotemplate with carrier metal nanowire, chemomechanical removal of the back electrode after stopping the electrodeposition process, g: free-standing nanowire with catalyst nanoparticles on the surface after removal of polymer template by chemical dissolution.

Fig. 2 shows an SEM micrograph and current-voltage (I-V) curves from anodic half-cell cyclic voltammetric measurements, demonstrating the high activity with large oxidation currents, for different methanol concentrations. In comparison to a state-of-the-art commercial type carbon-supported palladium nanoparticle catalyst, the system showed a better long-term stability and turned out to be able to handle larger concentrations of the fuel [13].

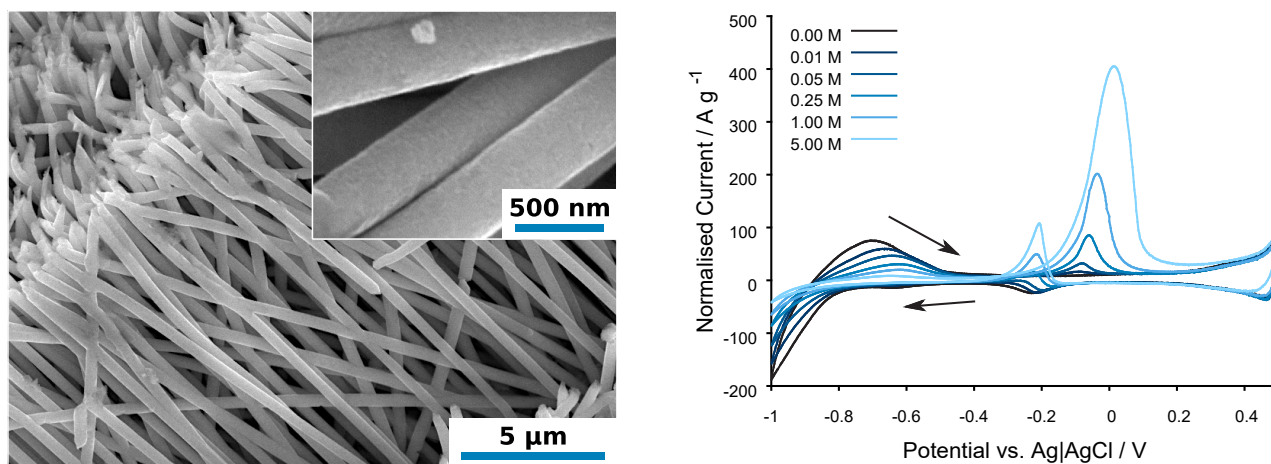


Fig. 2: Left: SEM of Nickel nanowires with Palladium nanoparticles on top, right: Cyclic voltammetry curves of Pd-doped Ni nanowires with different concentrations of methanol; the arrows show the voltage scan directions.

A similar technique was applied to fabricate Palladium-Bismuth nanowires [14]. Here, the deposition of a thin Palladium film onto/into the polycarbonate membrane template (channel areal density  $1.5 \times 10^8 \text{ cm}^{-2}$ , 400 nm channel diameter) was combined with electroless deposition of a Bismuth film on top of the Pd layer, forming a double-layered nanotube. The plating bath consisted of Bi-EDTA as the Bi source and dimethylamino borane as reducing agent. Fig. 3 shows TEM cross-

sections through the nanotube, with the outer Pd nanolayer and the nanocrystallites of the Bi nanotube. It can be seen that the Bi layer consists of slightly elongated particles in the range of 20 – 50 nm with very small Pd particles on top. The high porosity of the layer increases its active surface area and thus is desirable for many electrochemical applications.

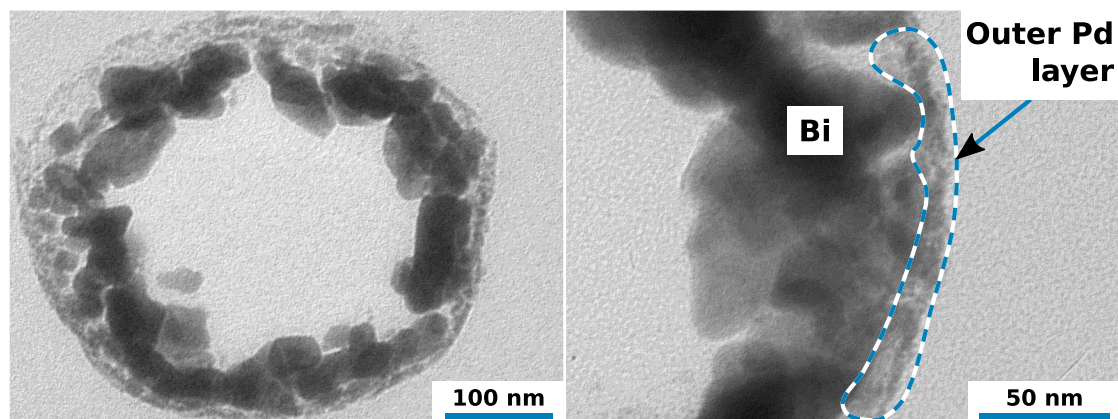


Fig. 3: TEM image of cross-section of Bismuth nanotube with an outer Palladium layer.

Chemical sensor application of Bi nanotube membranes was demonstrated for determining the toxic heavy metal Pb in water by means of square-wave anodic stripping voltammetry with a preconcentration step at a certain potential, followed by measuring the dissolution current in the stripping step. Pb concentrations from  $\sim 5 \mu\text{M}$  up to  $\sim 50 \mu\text{M}$  could be detected by analyzing the maximum current of the stripping peak [15].

Apart from sensing chemical elements, also organic molecules of low concentrations can be detected. Core-shell metal and metal oxide nanotubes of Cu with copper oxide and with nickel have been used for glucose sensing [16].

In a new development for glucose sensing, Nickel nanotube networks loaded with Nickel Cobalt Layered Double Hydroxide (NiCo-LDH) nanosheets, a recently evolved material with a large electrocatalytic activity, have been fabricated by combining electroless plating of polycarbonate membrane templates with 200 and 400 nm channel diameter and electrodeposition of an LDH layer [17]. Fig. 4 shows SEM images of the Ni-nanotube network before and after the electrodeposition of NiCo hydroxide nanosheets onto the inner and outer walls.

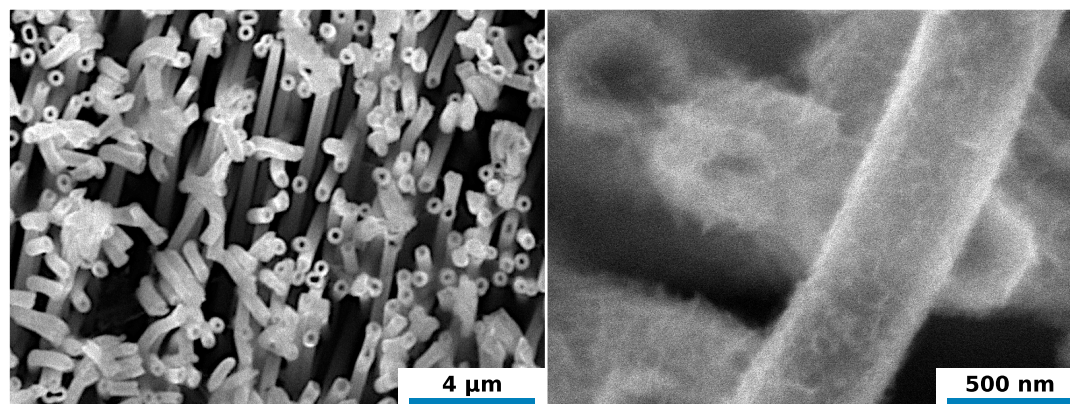


Fig. 4: SEM micrographs of nickel nanotube networks (left-hand side) and NiCo-LDH nanosheets on them (right-hand side).

These nickel nanotube-based architectures proved high redox activity in alkaline medium due to the transitions between metal hydroxide and oxyhydroxide types in case of nickel and even the oxide upon insertion of cobalt. Moreover, such architectures offer large active surface areas which represents a crucial property in electrochemical applications. Their

performance has been evaluated for glucose sensing which plays a role e.g. in medical diagnosis and food industry. Fig. 5 shows the chronoamperometric response of the two materials in comparison. The approach shown here is a non-enzymatic one, thus avoiding the cost of enzyme production and also the limited storage stability of such types of sensors.

The comparison of the two materials revealed that the best performance was achieved for the surface-area- and activity-optimized NiCo-LDH nanosheet-decorated nickel nanotube networks. It showed high sensitivity, fast response time, and low detection limit, cp. Table 1 [17]. The previously mentioned paradigms offer a tunable route for the improvement of electrode systems by integrating different active materials that fit different applications.

Table 1: Comparison of sensing performance of nickel nanotube networks and nickel-cobalt hydroxide nanosheet-decorated nickel nanotube networks

Material	Limit of detection / $\mu\text{M}$	Response time / s
Ni nanotubes	0.69	6.4
Ni/NiCo-LDH	0.20	5.3

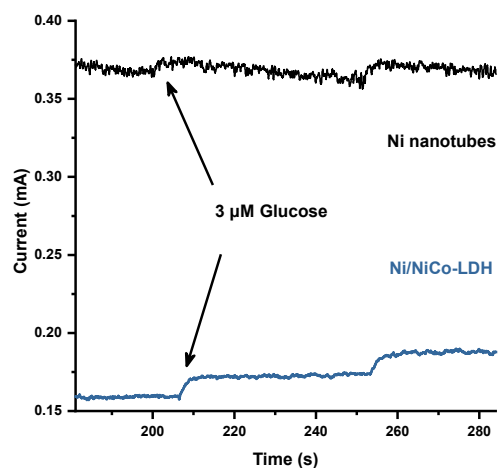


Fig. 5: Amperometric glucose sensing curves with stepwise addition of  $3 \mu\text{M}$  of glucose for nanowire networks of nickel and NiCo layered double hydroxide (adapted from ref [17]).

### 3. Conclusion

Nanowires and nanotubes, either freestanding or mechanically stabilized as networks, with the combination of oxides/hydroxides and metals (Ni/NiCo-hydroxide) or of two metals (Ni/Pd, Bi/Pd) have been synthesized and characterized by electron microscopy (SEM, TEM) for their microstructure, surface topography, and local element composition. Cyclovoltammetry and chronoamperometry demonstrated their favorable performance in (electro)catalysis and sensing, namely for methanol oxidation for direct methanol fuel cells and sensing of metals and organic molecules in aqueous media for environmental analysis and medical diagnostics.

The examples shown have demonstrated that the use of ion-track-etched polymeric nanochannel exotemplates in combination with electrochemical and electroless deposition of metals and oxides, as well as alloys and metal/oxide combinations, is a powerful technique for fabricating micro-nano-architected hybrid materials that show a large potential for various applications fields, including sensorics, chemical element and (bio) molecule analysis and energy conversion.

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