
4 Experimental

In this chapter, the experimental details of the synthesis of different nanowires and nanowire assemblies using the ion track template electrodeposition method are described. In particular, attention is paid to specification of template fabrication and nanowire growth process. The obtained nanostructures were physically characterized by a number of methods including electron microscopy, X-ray diffraction, and energy dispersive X-ray analysis. In addition, cyclic voltammetry was employed to determine the electrochemical active surface area and to investigate the electrocatalytic performance.

4.1 Nanowire synthesis

Different kinds of nanowire assemblies and unconnected nanowires were synthesized. All nanowire structures were fabricated using the ion track template electrodeposition method, which involves two main process steps: template fabrication and electrodeposition.

4.1.1 Template fabrication

To produce appropriate templates for nanostructure synthesis, polymer membranes were irradiated with swift heavy ions. Subsequent chemical etching completed the template formation by creating nanochannels with a desired diameter. Depending on the required nanowire structures, the template fabrication was performed applying different irradiation protocols and various etching conditions. The exact procedures are described in the following.

Ion irradiation

Ion irradiation experiments were performed at the GSI Helmholtzzentrum für Schwerionenforschung GmbH (GSI) located in Darmstadt. GSI operates a large accelerator facility for heavy-ion beams. The accelerator system is capable of preparing ion beams of all elements from hydrogen to uranium in any state of electric charge. The facility consists of the UNILAC, a 120 m long linear accelerator, which accelerates the ions generated by three ion sources up to 15 % of the speed of light (11.4 MeV/u) and a heavy-ion synchrotron (SIS, Figure 4.1). In the SIS, ions are further accelerated up to 1.3 GeV/u corresponding to about 90 % of the speed of light. Subsequently, the experimental storage ring ESR allows the storage of the previously accelerated ions.

In this thesis, polymer membranes with a thickness of 10 – 100 μm were irradiated with swift heavy ions, provided by the linear accelerator, at the cave X0 (Figure 4.2a). The UNILAC was operated with a frequency of 10 – 50 Hz and a pulse length of 0.5 – 3 ms. Ions from heavy elements such as Au, Pb, and U were used. After passing a three-foil detector, necessary for online beam diagnostics, the kinetic energy of the ions is decreased to approximately 11 MeV/u. The beam was defocused and aligned to enable homogeneous conditions all over the sample area with an ion flux not exceeding 2×10^8 ions/cm² s in order to avoid excessive heating. After adjusting the beam parameters, the existing sample exchange system was employed to automatically irradiate up to 20 samples with maximum dimensions of 5 x 5 cm² (Figure 4.2b).

Templates for nanowires and nanowire arrays

In the case of template production for nanowires and nanowire arrays, polymer membranes with a thickness of 30 – 100 μm were irradiated under normal incidence. The fluence was adjusted to

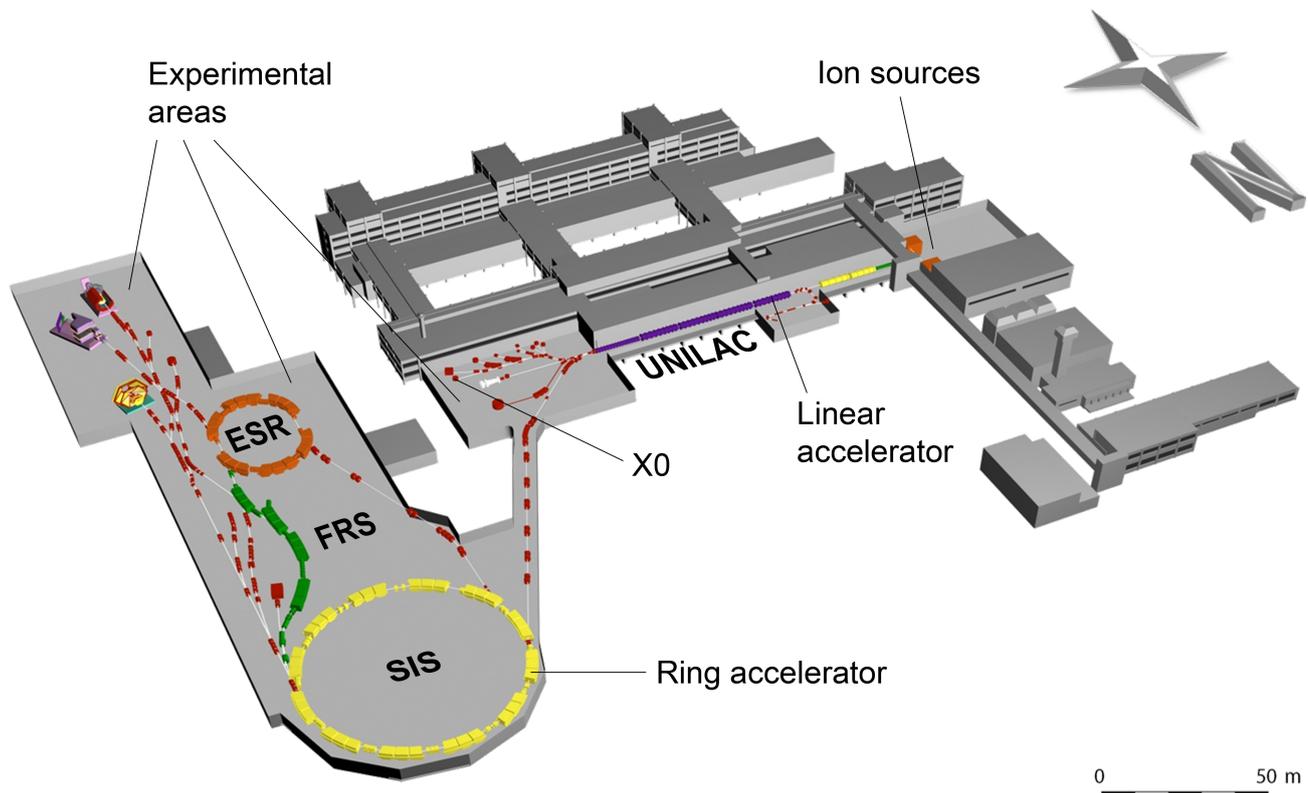


Figure 4.1: Scheme of the GSI heavy-ion accelerator facility

$1 \times 10^4 - 5 \times 10^9$ ions/cm².

Nanowire arrays, stabilized between two metal layers, were to some extent fabricated using specifically designed templates. Therefore, different masks had to be applied during template irradiation, in particular for the growth of very small arrays with lateral dimensions in the range of 50 μm to 1 mm. The fluence was $1 \times 10^7 - 1 \times 10^9$ ions/cm².

Templates for nanowire networks and hierarchical nanowire structures

For nanowire network templates, polycarbonate membranes with a thickness of 10 – 60 μm were irradiated in several steps, applying total fluences of $1.4 \times 10^9 - 3 \times 10^{10}$ ions/cm². According to the desired branching geometries, the templates were irradiated various times from different directions. In a typical irradiation experiment, the polymer membrane was first irradiated at an angle of 45° to the surface. After the first irradiation step, the membrane was turned in plane by 90° and irradiated again at an angle of 45° to the surface. This procedure was repeated twice until the membrane was irradiated 4 times from 4 different directions.

For more complex hierarchical nanowire structures, different template fabrication methods were combined. To achieve assemblies of nanowires with more than one wire diameter, several irradiation and etching steps were performed. Depending on the requirements, the templates were irradiated from both sides with an adjusted ion range that was shorter than the template thickness.

Chemical etching

UV light irradiation of both sides of the PC foils with UV fluorescent tubes (T-30 M, VILBER LOURMAT) for 60 min was applied as pre-etching treatment in the majority of cases, since this process was reported to decrease the pore size distribution.^{138,139} However, the effect is debatable and not relevant for many

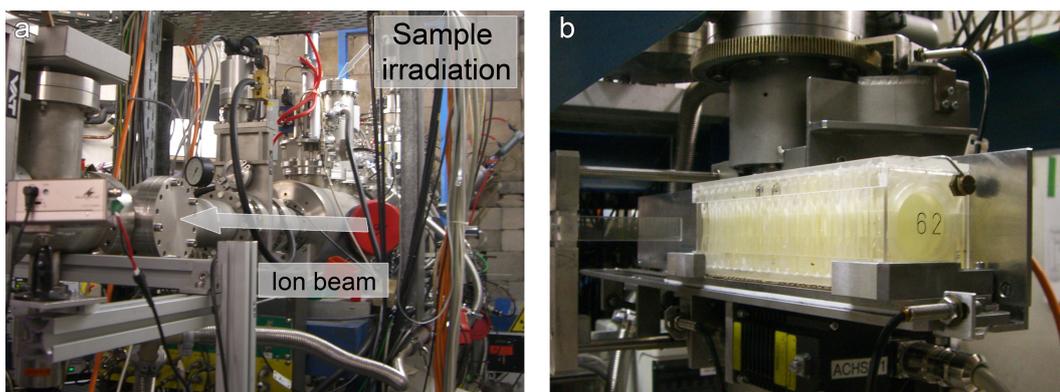


Figure 4.2: Irradiation at the cave X0: (a) Beam line in the cave. (b) The sample exchange system allows the irradiation of up to 20 sample holders by remote control.

experiments. Consequently, the author did not retain this procedure throughout the thesis, after observing no beneficial effect in comparison to untreated samples. Prior to chemical etching, the surface of the polymer membranes was cleaned with isopropanol to remove impurities and assure contact with the etching solution. The ion tracks were etched to nanochannels of the desired diameter in a 6 mol/L NaOH solution at 50 °C as described in previous works.^{27,140} Finally, the nanoporous template was immersed in deionized water to stop the etching process. Afterwards, the membrane was washed, dried, and stored until needed as template for nanowire synthesis.

4.1.2 Electrochemical deposition

All electrodeposition steps were performed in an electrochemical cell schematically shown in Figure 4.3. With the appropriate electrode configuration and electrolyte filling, the cell design allows electrodeposition at either side of the template. In Figure 4.3b, the cell configuration is schematically shown for Pt nanowire growth. Usually a two-electrode setup was used for deposition. In special cases, a three-electrode setup was employed to precisely control the composition during fabrication of composite and multilayer nanostructures.

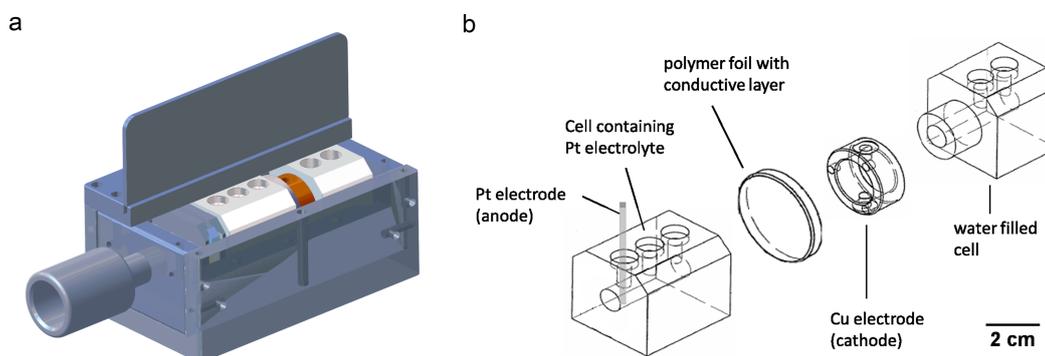


Figure 4.3: Experimental setup for nanowire deposition. (a) Scheme of the electrochemical cell used for electrodeposition of the Cu backlayer and the nanowires. (b) Exploded assembly drawing of the cell showing the two-electrode configuration employed for nanowire synthesis. Adopted from a previous work.¹⁹

Prior to electrodeposition of nanowires, a thin Au layer of ≈ 50 nm thickness was sputter-deposited on one side of the template and reinforced electrochemically by Cu serving subsequently as a cathode. Electrochemical deposition into the nanochannel templates was performed from different electrolyte solutions. Most frequently used for Pt nanostructure synthesis was Platin-OH (Metakem), an alkaline commercial electrolyte bath containing sodium hexahydroxyplatinate(IV) ($\text{Na}_2\text{Pt}(\text{OH})_6$) as Pt species, at temperatures ranging from room temperature to 65°C applying dc or various pulse electrodeposition methods. Au nanowires were grown from two different electrolytes, Au-SF and Au-CN containing ammonium sulfite gold(I) and potassium dicyanoaurate(I), respectively. Exact deposition conditions are described in the following or in chapters 5-6.

Nanowire arrays

Arrays of cylindrical metal nanowires were grown from different Au and Pt electrolytes applying a wide range of electrodeposition parameters to control the wire structure.

Structured nanowires

Segmented single-element nanowires: Segmented all-platinum nanowires were produced by PR electrodeposition into nanochannels at 65°C from Platin-OH electrolyte. The cathodic pulse was applied at a potential $U_c = -1.3$ V for different pulse durations t_c ranging from 1 to 20 s. The anodic pulse was invariably timed to $t_a = 1$ s at $U_a = +0.4$ V.

Multilayered nanowires: Multilayered CoPt nanowires were grown by modifying a previously reported method.³⁶ A single electrolyte consisting of 0.3 mol/L CoSO_4 , 0.3 mol/L K_2PtCl_6 , and 0.485 mol/L H_3BO_3 was used for pulse deposition with a three-electrode setup including a Ag/AgCl reference electrode. Pt segments formed at $U_1 = -0.4$ V applied for $t_1 = 10$ s, while Co-rich segments were deposited at $U_2 = -1.0$ V for $t_2 = 5$ s.

Closed nanowire arrays

The fabrication of closed Pt nanowire arrays was performed by pulse deposition techniques applying short deposition pulses at $U_c = -1.3$ V for $t_c \leq 100$ ms from the alkaline Pt electrolyte solution (Platin-OH). The time, during which no potential was applied (t_{off}), took at least 300 ms, but usually much longer. Eventually, reverse pulses were additionally applied at $U_a = +0.4$ V following the deposition pulse. The deposition was continued until caps, growing on top of the nanowires, coalesced and formed a stable metal layer. This continuous film could be enforced by another metal layer. To create monolithic closed nanowire arrays, electrodeposition was also performed at the initial starting point of the nanowires, in the opposite growth direction, after the cathode layer had been selectively removed. To precisely define the lateral array dimensions templates, which had been irradiated with a mask, were employed.

Nanowire Networks (NWNs)

Nanowire networks (and more complex hierarchical structures) consisting of different metals were produced under conditions comparable to those during formation of nanowire arrays of the same material. CdTe NWNs were deposited adapting a procedure described previously by Ohgai et al.¹⁴¹ Various structured NWNs, such as multilayer and single-element segmented network structures, could be synthesized by following procedures that were successfully applied for the growth of structured nanowire arrays (as mentioned above).

4.2 Analytical methods

For characterization by various methods the prepared nanowire structures were prepared in different ways. According to requirements, the Cu/Au layer, which served as cathode, was removed after electrodeposi-

tion by nitric acid and an aqueous solution of KI and I₂, respectively. The polymer template was dissolved in dichloromethane for methods such as electron microscopy and electrochemical investigations. The obtained nanowires could be purified by exchanging the solvent repeatedly and washing with ethanol. In addition, to remove all polymer residues and other impurities, the nanostructures were treated with 1 mol/L NaOH at 50 °C for 30 minutes and washed several times with deionized water. This cleaning procedure is important for certain characterization methods, especially for surface area measurements.

4.2.1 Electron microscopy

Scanning electron microscopy

Field-emission scanning electron microscopy (FESEM) was employed to investigate the structure of nanowires and nanowire assemblies using a JSM-7401 microscope (JEOL) operated at 1-30 kV. The electron beam is emitted by a field emission gun (cold-cathode type). For imaging, the sample's surface was scanned with the primary electron beam and signals produced by secondary electrons (SE) or back-scattered electrons (BSE) were detected. If not explicitly mentioned, the shown images were recorded in secondary electron imaging (SEI).

The microscope was equipped with a detector (XFlash 5030, Bruker) for energy dispersive X-ray spectroscopy (EDX) allowing the determination of the atomic composition of the samples. In addition, a detector (JEOL) measuring the transmission was used to perform scanning transmission electron microscopy (STEM).

Transmission electron microscopy

To analyze nanostructures in detail and crystallites of the nanowires, transmission electron microscopy (TEM, 400FX, JEOL, 400 kV) at the Max Planck Institute (Stuttgart) and at Xi'an University (China, JEM-3010, JEOL, 300 kV) was employed.

4.2.2 X-ray diffraction

X-ray diffraction (XRD) was performed using a STOE four-circle diffractometer with Co K_α radiation at the Department of Material- and Geo-Sciences of the TU Darmstadt. In addition, measurements were made with a HZG-4 goniometer in combination with a Seifert X-ray generator providing Cu K_α radiation at the GSI Helmholtzzentrum für Schwerionenforschung GmbH. For Co anodes, the wavelength of the generated X-rays are K_{α1} (λ = 178.8965 pm), K_{α2} (λ = 179.285 pm) and K_{α1} (λ = 154.060 pm), K_{α2} (λ = 154.443 pm) for Cu anodes.

Nanowires were investigated by XRD, while the nanostructures were still embedded in the polymer membrane. Samples were loaded on a silicon substrate for XRD measurements. The X-ray intensity was recorded as a function of 2Θ angle in Θ-2Θ geometry as illustrated in Figure 4.4. Consequently, Bragg diffraction is observed on planes that are aligned perpendicular to the wire axis. All diffraction patterns were prepared as step-scans. The detector is moved by an angle of 2Θ, while the sample is tilted by an angle Θ with reference to the incoming beam.

Texture

The crystallographic orientations of the crystallites were determined by the intensity distributions. Texture coefficients $T C_{hkl}$ were calculated for the different hkl reflections by:

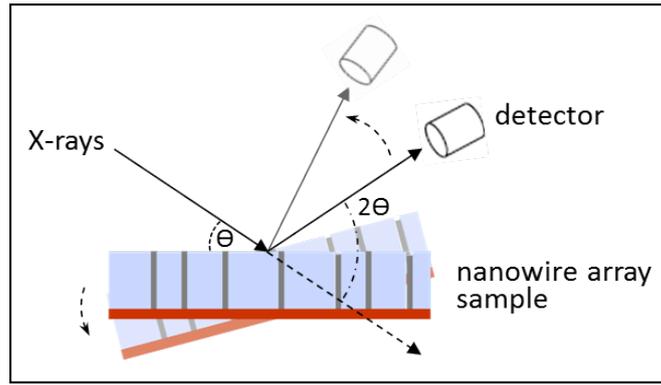


Figure 4.4: Experimental setup for X-ray diffraction on nanowire array samples

$$TC(h_i k_i l_i) = \frac{I(h_i k_i l_i)/I_0(h_i k_i l_i)}{(1/n) \sum_{j=1}^n (I(h_j k_j l_j)/I_0(h_j k_j l_j))} \quad (4.1)$$

with $I_0(h_i k_i l_i)$ = intensities of the $(h_i k_i l_i)$ lattice planes of a standard Pt powder sample
 $I(h_i k_i l_i)$ = intensities of the $(h_i k_i l_i)$ lattice planes under analysis
 n = total number of diffraction planes taken into account for calculations

The maximum value of the texture coefficient is represented by n . For $TC((h_i k_i l_i)) > 1$ there exists a preferred crystallographic orientation perpendicular to the $(h_i k_i l_i)$ planes. The texture often changes with the thickness of a electrodeposited material. It is not trivial to investigate gradients in the texture by XRD, since different depths are measured. Particularly in the case of nanowire arrays, a great volume of the sample contributes to the signal because large parts of the wires, which may be comparable to the total wire dimensions, are often analyzed.

Grain size

Grain sizes D were calculated by means of the Scherrer equation:

$$D = \frac{k \lambda}{\Delta H(2\Theta) \cos \Theta} \quad (4.2)$$

with k = grain shape specific constant
 λ = radiation wavelength
 $\Delta H(2\Theta)$ = increase in full width of half maximum (FWHM)

The unit of $H(2\Theta)$ is radian. The constant k is dimensionless. It is 0.94 for fcc lattices, but varies with the actual shape of the crystallite between 0.89 and 1.39.

It has to be considered that $\Delta H(2\Theta)$ is only the increase in FWHM. The measured FWHM $H(2\Theta)$ of the diffraction peak at 2Θ is the result of both, $\Delta H(2\Theta)$ and the influence originating from the experimental setup $H_{Exp}(2\Theta)$. $\Delta H(2\Theta)$ can be calculated with:

$$H(2\Theta)^2 = H_{Exp}(2\Theta)^2 + \Delta H(2\Theta)^2 \quad (4.3)$$

4.2.3 Electrochemical measurements

Experimental setup

The cyclic voltammetry (CV) studies were performed in a conventional three-electrode cell at room temperature using a Reference 600 potentiostat (Gamry Instruments). A schematic of the experimental setup is shown in Figure 4.5. A platinized titanium mesh was employed as counter electrode (CE). All potentials were measured with a Hg/HgSO₄ reference electrode (RE), but are given with respect to the reversible hydrogen electrode (RHE) in this work. As working electrode (WE) different nanowire samples were investigated and benchmarked against commercially available state-of-the-art nanoparticle catalysts.

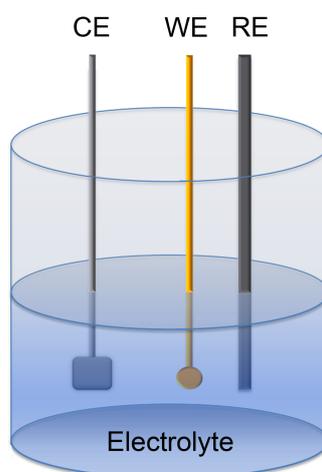


Figure 4.5: Schematic illustration of the three-electrode cell used for CV measurements

Electrode preparation

Pt nanowire networks on simple Au wire electrodes and commercial Pt catalysts, including platinum black (PtB, Alfa Aesar, 28.1 m²/g Pt) and platinum nanoparticles on a high surface area carbon support (Pt/C, HiSPEC 3000, Sigma-Aldrich, 20 wt. % Pt), on glassy carbon electrodes were employed as working electrodes. Figure 4.6 illustrates the preparation method of the glassy carbon catalyst electrodes, which was adopted and modified from previous reports.^{114,142–144} In brief, aqueous suspensions containing 5 mg_{catalyst}/ml for PtB and 2 mg_{catalyst}/ml for Pt/C were produced by ultrasonic mixing for 20 minutes to obtain the catalyst ink. Before serving as a support for the catalysts, glassy carbon electrodes (GCE, 0.25 cm², SPI Supplies) were cleaned and polished. A defined volume of catalyst ink was pipette on the GCE, leading to loads of 0.1 – 1 mg Pt/cm² for PtB and 0.1 – 0.6 mg Pt/cm² for Pt/C. After drying in air to eliminate solvent, the catalyst layer was covered with 20 μl of a 0.125% Nafion solution diluted from an initial 5 wt. % Nafion stock solution (Sigma-Aldrich). Subsequently, the electrodes were dried in an oven at 80 °C for about 30 minutes.

Determination of ECSA by CV

For the determination of the electrochemical active surface area (ECSA) the potential was cycled between 0 and 1.3 V versus RHE in nitrogen purged 0.5 mol/L H₂SO₄ solution with a scan rate of 50 mV/s. The area of hydrogen adsorption/desorption between 0 - 0.4 V has been frequently used to

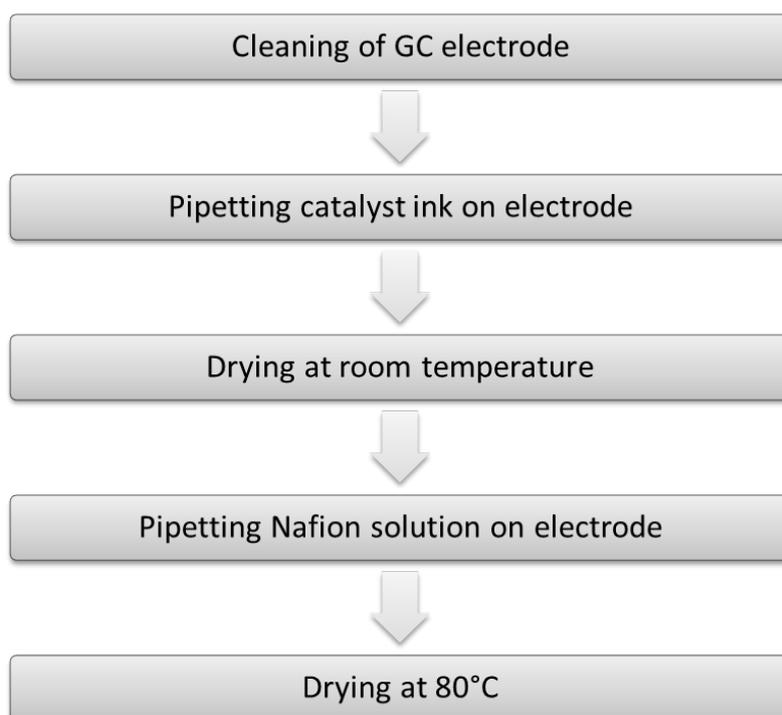


Figure 4.6: Schematic illustration of the GC catalyst electrode preparation.

estimate the ECSA of Pt-based catalysts.^{143–145}

In this study, the charge for hydrogen desorption $Q_{H,d}$ was used to calculate the ECSA by means of equation 4.4. The charges associated with hydrogen adsorption/desorption were obtained from CV curves by integrating the corresponding peaks and subtracting the charge arising from double layer charging. A typical CV scan of a Pt electrode in acidic solution, highlighting the areas of interest, is depicted in Figure 4.7.

$$ECSA = \frac{Q_{H,d}}{m \cdot c} \quad (4.4)$$

with $Q_{H,d}$ = charge for hydrogen desorption (mC/cm²)
 m = Pt loading (mg/cm²)
 c = charge required to oxidize a monolayer of hydrogen (0.210 mC/cm² on Pt)

The ECSA standard deviation was calculated by equation 4.5:

$$\Delta ECSA = \left| \frac{\Delta Q_{H,d}}{[Pt] \cdot 0.21} \right| + \left| \frac{\Delta [Pt] Q_{H,d}}{[Pt]^2 \cdot 0.21} \right| \quad (4.5)$$

ΔQ was estimated from the difference in charges from hydrogen desorption $Q_{H,d}$ and adsorption $Q_{H,a}$.

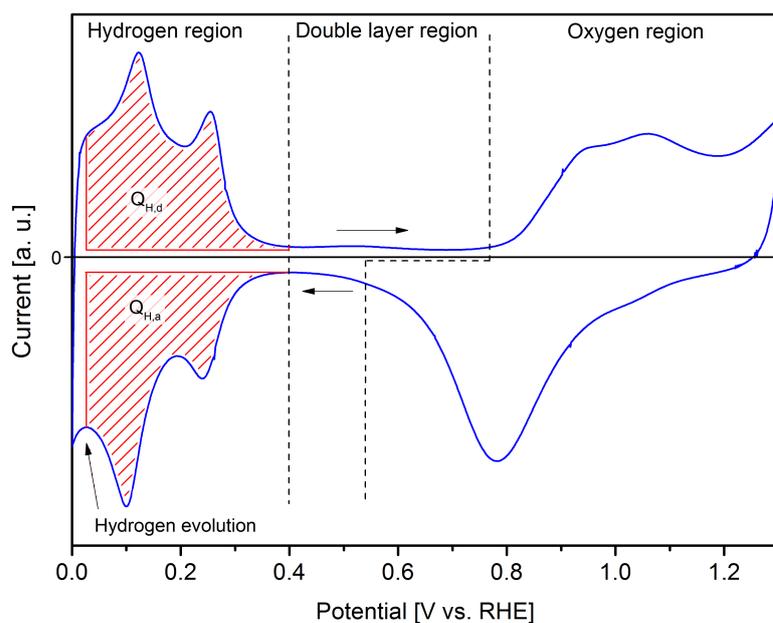


Figure 4.7: Cyclic voltammetric current potential curve for a platinum electrode in 0.5 mol/L H_2SO_4 solution. The charge contributions for hydrogen adsorption $Q_{\text{H},a}$ and desorption $Q_{\text{H},d}$ are indicated in the hydrogen region.

4.2.4 Electrocatalytic activity

In the methanol oxidation reaction (MOR) studies, CV curves were recorded between 0 and 1.3 V versus RHE in a nitrogen purged solution containing 0.5 mol/L CH_3OH and 0.5 mol/L H_2SO_4 . The scan rate was 50 mV/s. The obtained curves were evaluated with respect to peak current densities of the forward and backward scan (I_f and I_b , respectively).

Before recording CVs of the MOR, the samples (working electrode) were cycled several times in an aqueous solution containing only 0.5 mol/L H_2SO_4 to determine the ECSA. In addition, surface area measurements were conducted subsequent to the MOR studies.

4.2.5 Electrical transport properties

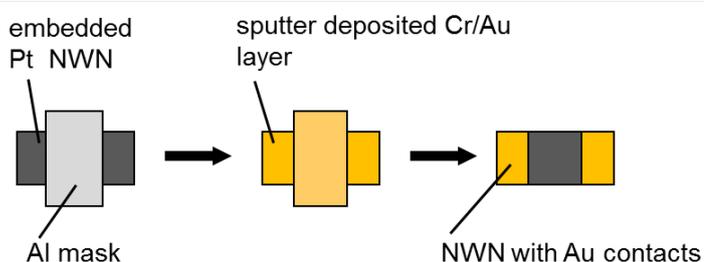


Figure 4.8: Scheme illustrating the deposition of electrical contacts on a NWN sample required for the measurement of electrical transport processes. The use of a mask during the deposition process allows the subsequent investigation of the network area between the Au contacts with respect to its electrical properties.

To measure the electrical transport properties of nanowires and complex assemblies the nanostructures had to be connected to macroscopic electrical contacts. Sample preparations for single nanowires can be found in a previous report.⁴⁵

NWNs were contacted while being embedded in the polymer matrix. The cathode layer had been completely removed, before contacting. During sputter deposition of a Cr/Au contact layer (10/200 nm) a mask was used to cover the network area of interest as schematically demonstrated in Figure 4.8. The as-prepared network sample was transferred to a silicon wafer and contacted with Au wires and Ag conductive varnish at both Au contacts.

Measurements were performed by H. Reith at University of Applied Sciences Wiesbaden (Rüsselsheim).

4.2.6 Determination of nanowire mass

During the deposition current-time curves were recorded. Assuming an efficiency of the deposition reaction of 100%, the total mass of the nanostructures can be calculated from the employed charge Q by the Faraday law:

$$m = \frac{M \cdot Q}{z \cdot F} \quad (4.6)$$

with m = total mass of the deposited material
 M = molar mass of the deposited material
 Q = electric charge employed during deposition
 z = ion charge state
 F = Faraday constant

In the case of mechanically stable Pt nanowire assemblies, the mass was also quantified by using a microbalance (AT20, Mettler Toledo).

4.3 Materials

The substances used within this thesis were purchased from companies as stated below and used as received:

Chemicals

Acetone (98%)	L-S Labor Service GmbH
Boric acid (H_3BO_3 , 99.8%)	L-S Labor Service GmbH
Cadmiumsulfate hydrate ($3 \text{ CdSO}_4 \cdot 8 \text{ H}_2\text{O}$, 98-102%)	Merck KGaA
Cobalt(II) sulfate heptahydrate ($\text{CoSO}_4 \cdot 7 \text{ H}_2\text{O}$, p. a.)	Merck KGaA
Copper(II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5 \text{ H}_2\text{O}$, p. a.)	Merck KGaA
Dichloromethane (CH_2Cl_2 , 99.5%)	L-S Labor Service GmbH
Ethanol (EtOH, 99.5%)	Carl Roth GmbH
Hydrochloric acid (HCl, 36.5-38.0%)	Carl Roth GmbH
Iodine (I_2 , 99.999%)	Merck KGaA
Isopropanol (99.9%)	Carl Roth GmbH
Methanol (MeOH, 99.8%)	L-S Labor Service GmbH
Nafion solution (5 wt. %)	Sigma Aldrich
Nitric acid (HNO_3 , 65%, p. a.)	L-S Labor Service GmbH

Potassium hexachloroplatinate(IV) (K_2PtCl_6 , 99.9+%)	Sigma Aldrich
Potassium iodide (KI, 99.5%)	L-S Labor Service GmbH
Sodium hydroxide pellets (NaOH, 97%)	L-S Labor Service GmbH
Sodium hydroxide standard solution (NaOH, 1 N)	Carl Roth GmbH
Tellurium dioxide (TeO_2 , 99.5+%)	Merck KGaA
Tetrahydrofuran (THF, 99.5%)	Merck KGaA
Trichloromethane (CH_3Cl , p. a.)	Carl Roth GmbH

Commercial electrolytes

Cu bright	Riedel
Platin-OH (10 g Pt/l)	Metakem GmbH
Platin DNP (10 g Pt/l)	Metakem GmbH
Platin DNS (10 g Pt/l)	Metakem GmbH
Au-SF (15 g Au/l)	Metakem GmbH
Au-CN (10 g Au/l)	Metakem GmbH

Catalysts and electrode materials

Au wire (d = 0.5 mm)	Allgemeine Gold- und Silberscheideanstalt AG
Glassy carbon electrodes (GCE)	SPI Supplies
Carbon supported Pt (Pt/C, 20 wt. % Pt, HiSPEC 3000)	Alfa Aesar
Platinum black (PtB)	Alfa Aesar

Template material

Polycarbonate foils (Makrofol N, Bayer) were employed as template material. This amorphous polymer has been frequently used for nanochannel template production and shows smooth channel surfaces.^{146,147}

