6 Results on nanowire building block assemblies

This chapter highlights the fabrication of different kinds of nanowire building block assemblies extending from closed nanowire arrays to supportless nanowire networks and more complex hierarchical nanowire structures. The building block assemblies were characterized by various methods. Special attention is paid to general synthesis strategies generating nanowire arrangements of various connectivities. Finally, the combination of these methods with previously described structuring techniques is demonstrated.

6.1 Closed nanowire arrays

A possibility to create 3-D nanoscale building block assemblies is based on vertical integration of parallel aligned nanowires. The synthetic approach was already reported.[19] In brief, the deposition is continued until caps forming on top of each nanowire coalesce (6.1a). To achieve homogeneous growth and small size distribution of the caps, the concept of PR deposition is adopted to compensate for the slow diffusion driven transport in high-aspect materials. Finally, an additional metal layer can be deposited on the caps to increase the mechanical stability. Afterwards, the polymer matrix can be dissolved in dichloromethane to obtain a template-free closed nanowire array, e.g., a vertically aligned nanowire array between supporting layers (VANAS). In this "sandwich structure", two metal layers are interconnected by arrays of adjustable integration density. Figure 6.1a illustrates the fabrication process.

The mechanical stability of a closed nanowire array can be very high as evidenced impressively by Figure 6.1b. The cross-sectional view was created by cutting the sample after removing the polymer matrix and imaging by SEM. The nanowires are still parallel and are barely deformed.

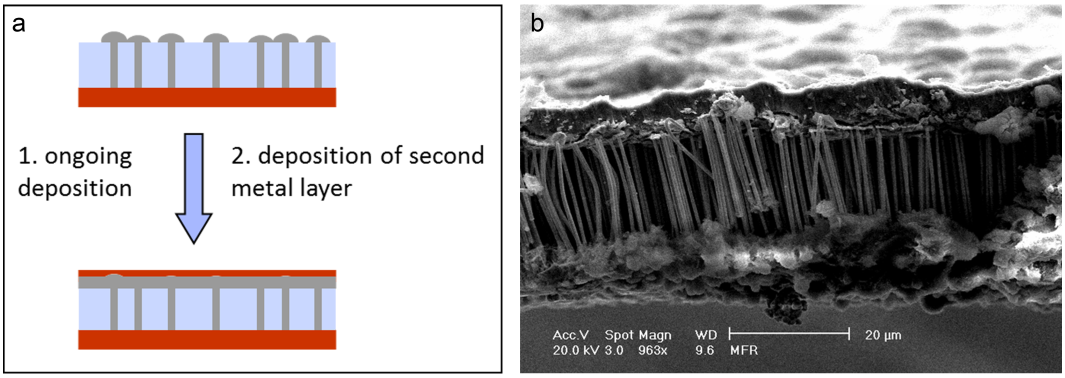

Figure 6.1: (a) Schematic showing the fabrication of closed nanowire arrays. A second metal layer is obtained by continuing the depostion process until caps growing on top of the nanowires coalesce. Consequently, a stable structure with vertically integrated nanowires is created. (b) SEM image of a closed nanowire array illustrating parallel aligned wires between two metal layers. Adopted from Rauber.[19]

The two metal layers are fundamental components since they not only interconnect the wires to an array, but also maintain their parallelism. Furthermore, as an essential structural element, the layers

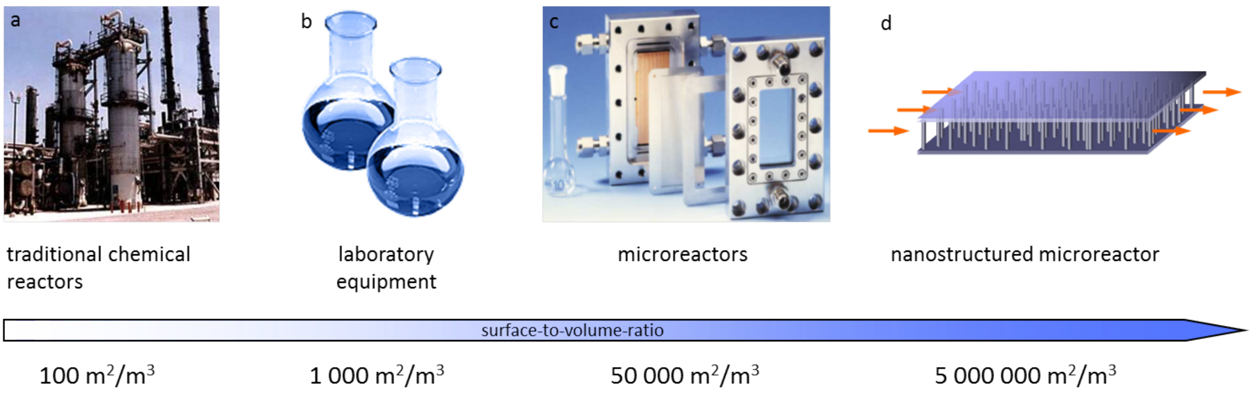

Figure 6.2: Surface-to-volume ratio of different reactor systems ranging from industrial reactors (a) to microreactors (c-d). Controlled nanostructuring by integration of nanowires can increase the specific surface area by two orders of magnitude. (c) Copyright 2004 Wiley-VCH Verlag GmbH & Co. KGaA. Reprinted with permission.[166]

represent a physical barrier, inhibiting effectively mass transport. A closed chamber, where reactions can take place, is consequently created. The closed nanowire array constitutes a very stable and easy to handle microreactor suitable for specific gas- and liquid-phase reactions. Moreover, the 3-D architecture with parallel aligned nanowires provides the integration as functional element in sensor systems.

Integrated parallel aligned 1-D nanostructures can be used to increase the surface area of microstructured reactors dramatically as demonstrated by Popp and Schneider, who fabricated a microreactor based on carbon nanotube arrays.[165]

Microreactors are reactors with typical inner dimensions between ten and a hundred micrometers. As a consequence, their surface-to-volume ratio is much larger than the ratio of conventional reactors.[166] Figure 6.2 illustrates different reactor systems with their typical surface-to-volume ratios ranging from industrial reactors to microreactors. State-of-the-art microreactors with channel dimensions of 50 µm exhibit specific surface areas of up to 50000 m^2/m^3, whereas conventional large scale industrial reactor systems typically have a value of 100 m^2/m^3.[166] The surface-to-volume ratio of laboratory equipment is about 1000 m^2/m^3.[167]

In microstructured reactors many processes proceed very efficiently, including heat and mass transport, due to the large specific surface area. Further increase of the surface-to-volume ratio may even result in improved properties. A very promising approach to reach this goal is the integration of nanowires.

A nanostructured microreactor could easily exceed the specific surface area of a current microreactor. A simple calculation can help to illustrate this concept. Closed arrays consisting of 30 µm long wires with an average diameter of 250 nm and an integration density of $1x10^8$ wires/cm^2 have a calculated surface-to-volume ratio of $8.5x10^5$ m^2/m^3. For arrays with a higher integration density of $5x10^9$ wires/cm^2 and a wire diameter of 40 nm, which readily were synthesized, the surface-to-volume ratio is $6.3x10^6$ m^2/m^3. It has to be considered that the values, calculated assuming a perfect cylindrical shape, are underestimated. Because of surface roughnesses, the real surface area is usually even much larger.

6.1.1 Nanowire microarrays

To avoid mechanical stress induced by cutting, the array can be shaped with respect to the lateral dimensions by using a mask during template irradiation. Figure 6.3 shows a scheme of the fabrication process. Because of the mask, heavy ions can hit the polymer foil only at the unmasked areas. Subsequently, nanochannels are generated in well-defined areas. It is possible to create monolithic closed nanowire arrays by growing metal layers, which consist of coalesced caps, on both sides of the wires. To

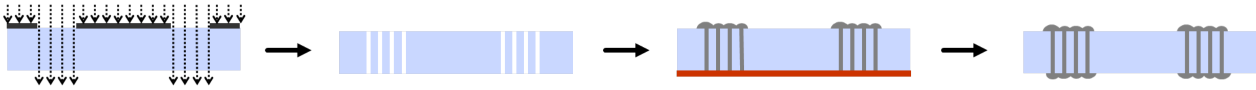

Figure 6.3: Schematic showing the nanowire microarray fabrication starting with the ion irradiation using a mask.

achieve this, caps are first grown according to the procedure described in section 6.1. The initial cathode layer has to be selectively removed, before a conductive metal film can be evaporated on the polymer side with the formed caps to serve as contact for a second deposition step. In this second deposition step, caps are also grown at the initial points of electrodeposition.

Figure 6.4 depicts SEM images of a representative Pt nanowire microarray, consisting of parallel aligned nanowires between two metal layers. For the irradiation process a mask with circular holes was used. The structure measures approximately 35 µm in height and has lateral dimensions of 50 µm (diameter). With an integration density of 10^8 wires/cm^2, roughly 2000 wires with an average radius of 110 nm are vertically integrated into the structure. Caps at both ends of the wires form continuous metal layers, which are rather thin (≈2 µm). Figure 6.4b reveals not only that the integrated wires of the monolithic structure are tightly attached to the caps, but also shows that most of the volume inside the microstructure is free volume (void space). The porosity is ≈96%.

To achieve homogeneous wire and cap growth, pulse electrodeposition was employed. The growth process is carried out at room temperature to minimize mechanical stress induced by thermal expansion. The average current density is decreased to maintain similar electrolyte concentrations everywhere at the electrode surface, leading to long deposition times. For instance, the total growth process for the array shown in Figure 6.4 took more than 24 h. A sequence of three pulses was repeatedly applied for the growth process (−1.3 V for 100 ms, −0.2 V for 2 ms, and −0.4 V for 200 ms).

In consideration of the high porosity and small thickness of the metal layers, the structure is remarkably robust. Hardly any defects arising from the polymer removal process are observed.

The fabrication of arrays with other geometries and dimensions is possible by using appropriate masks during template irradiation. The small arrays can be manipulated and integrated as functional elements into devices by microassembly techniques. Potential applications lie within the field of sensitive sensing.[168]

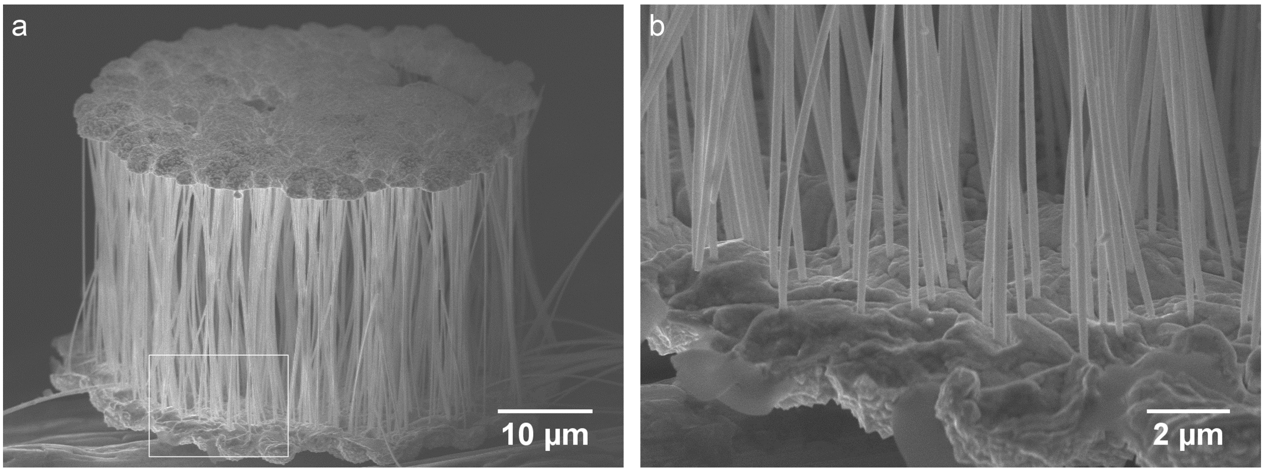

Figure 6.4: FESEM images of a nanowire microarray. (a) Closed nanowire array with microscopic dimensions (diameter is 50 μm, height is 35 μm). Approximately 2000 nanowires are integrated in the microstructure. (b) At higher magnification individual nanowires, which are tightly attached to the metal layer, can be identified. In addition, the high porosity inside the nanowire assembly is revealed.

6.1.2 Nanowire microarray arrays

The method described in the previous section (6.1.1) is very suitable for the production of numerous small arrays. Using the appropriate mask for template fabrication large quantities can be obtained. Figure 6.5a depicts an optical microscopy image of an array of 19x25 microarrays embedded in a polymer membrane. With the depicted density more than 5000 arrays can be grown in 1 cm^2. In Figure 6.5b a similar array is shown after template removal.

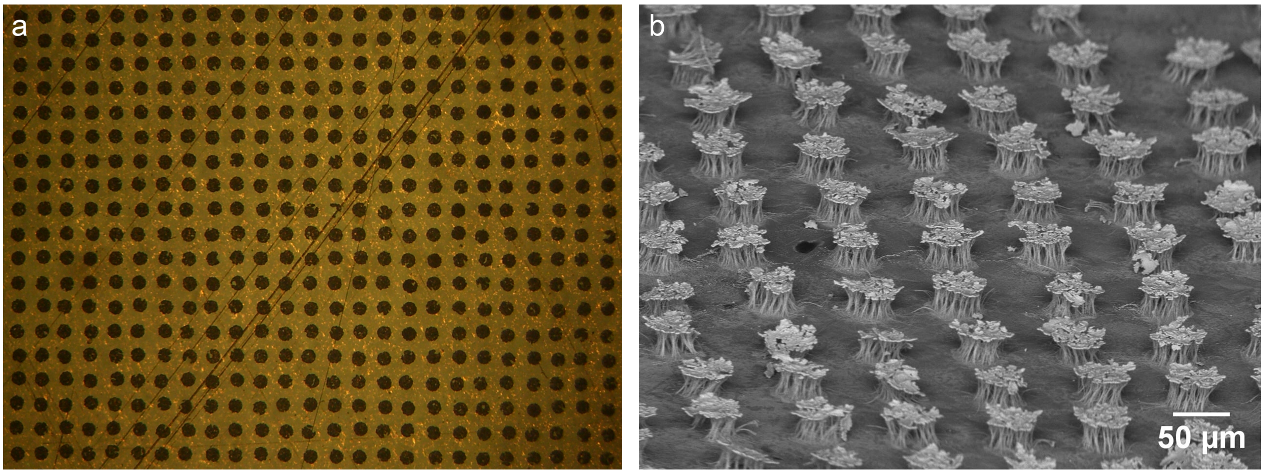

Figure 6.5: Images of nanowire microarray arrays. (a) Top view on microarrays embedded in a polymer membrane. The arrays shown as dark spots measure 50 μm in diameter. (b) FESEM analysis of microarrays connected to the cathode layer.

6.2 3-D nanowire networks

In this section, the direct synthesis of highly-ordered large-area nanowire networks by a hard-template based method using electrodeposition within nanochannels of track-etched polymer membranes is reported. Control over the complexity of the networks and the dimensions of the integrated nanostructures are achieved by a modified template fabrication. The networks exhibit high surface area and excellent transport properties turning them into a promising electrocatalyst material as demonstrated by cyclic voltammetry studies on platinum nanowire networks catalyzing methanol oxidation. The method opens up a new general route for interconnecting nanowires to stable macroscopic network structures of very high integration level that allow easy handling of nanowires while maintaining their connectivity.

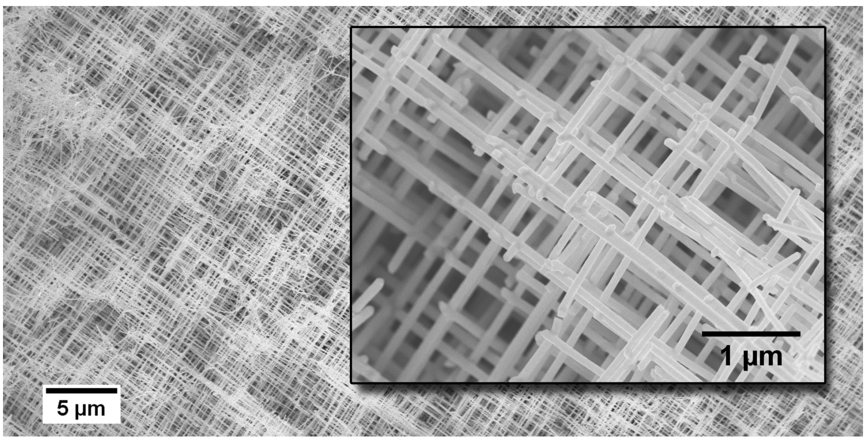

Figure 6.6: FESEM image showing a continuously organized 3-D architecture of interconnected platinum nanowires. The arrangement can be described as an open porous network structure exhibiting meso- and macropores.