Nanoreactors

DOI: 10.1002/anie.200802954

A Chip-Sized Nanoscale Monolithic Chemical Reactor**

*Alexander Popp and Jörg J. Schneider**

Central to the general concept of a lab-on-a-chip is the idea of scaling down single- or multiple-step processes in a miniaturized device with an area of several square centimeters or millimeters. Outstanding heat- and mass-transfer capabilities of fluidic microdevices such as micromixers, micro heat exchangers, and microreactors have been the driving force for the continuous scale-down of thermal and chemical processes in recent years. As only small amounts of fluids are required, microreactors have gained importance in the testing of chemical reactions and catalysts, handling of potentially hazardous reactants, and screening of pharmaceuticals and diagnostics for biological use.[1–3]

The surface-to-volume ratio, the key parameter in microreactors, is currently limited to the range of 1×10^4 to $5\times10^4\,\mathrm{m^2m^3}$. Decreasing linear dimensions further into the nanometer regime would certainly result in significantly higher heat-transfer coefficients and improved mass transport, facilitating isothermal reaction conditions. This in turn enables better control of chemical process parameters.

The large surface areas in microreactors are a consequence of their drastically reduced reaction channels which are in the size range of 50–500 μm. These channels are typically fabricated by photolithography or mechanical micromachining techniques.[1,4] However, when such top-down methods are applied for fabrication, structuring is generally limited either by the wavelength of the radiation used for the photolithographic process or the size of the micromachining tools used to create the reaction channels.

Herein, we report on a bottom-up approach to build a mechanically stable, flexible, and monolithic porous carbon nanotube structure with macroscopic dimensions, and we demonstrate its use as a nanostructured chemical reactor. Our new reactor design exhibits a dramatically increased surface-to-volume ratio of 5×10^6 to $2\times10^7\,\mathrm{m^2m^3}$, which exceeds that of state-of-the-art microreactors by at least two orders of magnitude. Continuous flow around the individual tubes is accomplished which makes it possible to perform catalytically driven chemical reactions on a sub-μm to nm scale.

Porous alumina produced by electrochemical oxidation is well known for its properties as a template in nanocasting;[5] it features parallel, hexagonally arranged, cylindrical pores ranging from 10 to 200 nm in diameter[6] (Figure 1a). As a result of its variable porosity and a template height that can be adjusted from a few to several hundreds of micrometers, porous alumina is a highly adaptable material. In addition it offers a high thermal stability.

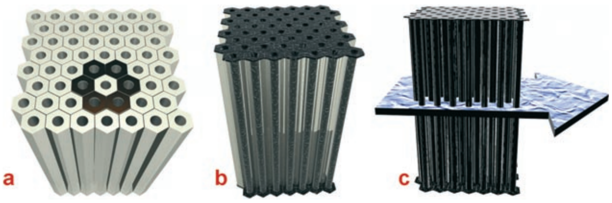

Figure 1. a) A porous alumina template with hexagonally arranged pores. b) An alumina/carbon composite structure with carbon nanotubes interconnecting carbon top and bottom layers. c) Open CNT structure as carbon negative copy of (a) obtained after removal of alumina; the arrow indicates a possible flow of reactants which can pass along the outside of the tubes.

In a chemical vapor deposition (CVD) process, propylene was used to form a carbon layer inside the pores and at the same time on top and bottom of the porous alumina (Figure 1b). After removal of the alumina template by chemical wet etching, a carbon negative copy was obtained as a self-supporting and flexible monolithic structure consisting of a top and bottom carbon layer connected by multi-walled carbon nanotubes (Figure 1c). The remaining alumina amounted to approximately 0.4 atom% (EDAX) indicating almost complete removal of the template.

The resulting 3D structure formed is built up by nanotubes arranged in macroscopic dimensions of up to 3 cm² and a height H of 50 μm. It can be handled easily with tweezers (Figure 2b); it shows remarkable mechanical stability but is still flexible and bendable.

The top and bottom carbon layer of the structure is not separated from the tubes, but both tubes and layers merge into each other. We consider this unique structural feature to be essential for the structural stability as well as for the mechanical flexibility of the structure. The distribution of tube diameters is narrow and controlled by the pore size of the alumina template. Besides the degree of graphitization, the tube wall thickness as well as the thickness of the top and bottom carbon layers can be tailored by adjusting the CVD reaction conditions. Depending on the synthesis parameters, the top and bottom layer can be produced either as an impermeable layer (completely closed surface) or as a porous film with open pores such that the interior of the carbon nanotubes is still accessible.

An important feature of CNTs is their extraordinary heat conductivity;[7] they are perfectly suited to minimize temperature gradients when used, for example, in a microreactor

---

[*] Dipl.-Ing. A. Popp, Prof. Dr. J. J. Schneider
Fachbereich Chemie
Eduard-Zintl-Institut für Anorganische und Physikalische Chemie
Technische Universität Darmstadt
64287 Darmstadt, Petersenstrasse 18 (Germany)
Fax: (+49) 6151-163-470
E-mail: joerg.schneider@ac.chemie.tu-darmstadt.de

[**] We thank Dr. M. an der Heiden, TU Darmstadt for GC measurements.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200802954.

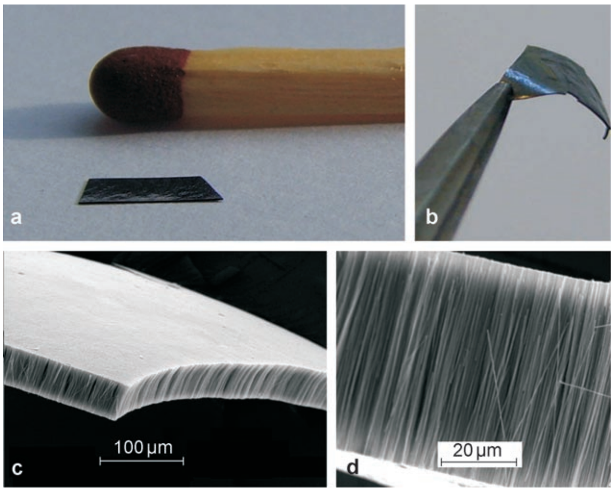

Figure 2. a) Nanostructured reactor with dimensions on the macroscopic scale. b) The skinlike, flexible, all-carbon structure can be handled with tweezers. c) SEM view of the top carbon layer. The tubes are embedded between top and bottom layers. d) A close-up side view of the structure showing the straight and parallel tubes in a three-dimensional array.

device. Aside from offering the possibility to disperse catalyst particles on the outside surface, an arrangement of nanotubes permits a drastic increase of the specific surface. An improvement of reaction performance by using carbon nanotubes inside channels of a microreactor has been proven already.[8]

Our monolithic carbon structure represents the reactor itself, in which parallel aligned CNTs are sandwiched between bottom and top carbon layers. Thus, the smooth transition from tubes to top and bottom layer may not only provide for a better heat transfer but also offers the possibility for measuring electric conductivity across ordered CNT bundles within the reactor. This could lead to valuable analytical information on reactants and reaction kinetics, and could furthermore allow for feedback control of the reactor. Work in this area is currently in progress.

From a synthetic point of view the aligned nanotubes can not only be functionalized on the outer surface: It is also possible to utilize the interior of the tubes which is still accessible through the open carbon top and bottom layers. This may help to establish a flow inside the tubes[9] as an additional cross flow or to further reinforce the structure by the introduction of other materials into the tubes.

To examine the enormous gain in active surface area, we calculated the theoretical surface-to-volume ratio of the structure. The number of nanotubes N in a given area A_T of diameter d_T can be evaluated if the porosity ε and the average pore diameter $\bar{d}$ of the original template is known, for example from BET or image analysis. The porosity ε is generally defined as ratio of void volume V_V to total volume V_T [Eq. (1)].

$$\varepsilon = \frac{V_V}{V_T} = \frac{N\frac{\bar{d}^2\pi}{4}H}{A_T H} = \frac{\bar{d}^2 N}{d_T^2} \tag{1}$$

Since the final carbon structure is a negative copy of the template, the pore diameter corresponds to the outer tube diameter and the height of the template corresponds to the height of the tubes. The surface-to-volume ratio of the final structure is hence the ratio of the outer surface of all CNTs in a given area and the surface of the top and bottom layer divided by the volume of the structure [Eq. (2)].

$$\frac{S}{V} = \frac{N\overbrace{\bar{d}\pi H}^{\text{outer surface of one tube}} + \overbrace{\frac{1}{2}d_T^2\pi(1-\varepsilon)}^{\text{surface of top and bottom layers}}}{\underbrace{\frac{d_T^2}{4}\pi H}_{\text{total volume}}} = \frac{\frac{\varepsilon}{\bar{d}}4H + 2(1-\varepsilon)}{H} \tag{2}$$

The surface calculated here takes into account only the surface available if a flow around the nanotubes parallel to the top and bottom layer is considered according to Figure 1c. The real surface of the structure is, however, almost twice as large if the inner surface of the tubes is also taken into account. The nanotubes formed by our process take up the void volume of the template, hence a volume fraction of $(1-\varepsilon)V_T$ is provided for the flow.

Decreasing the tube diameters below values of 400 nm leads to a surface-to-volume ratio of more than $1\times10^6\ \mathrm{m^2\,m^3}$ (Figure 3), with even better ratios possible at higher porosities and lower template heights. Generally, the porosity[10] of porous alumina is 0.1, but it can be increased by methods such as selective pore widening by chemical etching.[11]

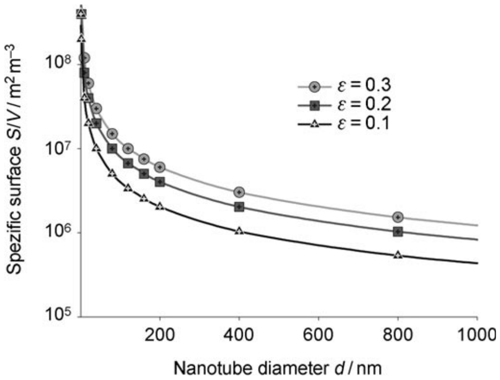

Figure 3. Surface-to-volume ratio S/V as a function of tube diameter d for different porosities ε and a fixed tube length of 50 μm. The surface drastically increases with decreasing tube diameter.

For our prototype nanostructured reactor a template with average pore diameter of 161 nm, porosity of 0.22, and a template height of 50 μm was used. This corresponds to a surface-to-volume ratio of $5.5\times10^6\ \mathrm{m^2\,m^3}$ which is hundred times higher than that of state-of-the-art microstructured reactors.

Since the side walls of the carbon structure (Figure 2c) have to be contained to provide a closed integrated reactor geometry and in order to connect an reactor inlet and outlet for continuous flow, we designed two prototypes of a nanostructured reactor. For prototype I the structure was embedded in a solid poly(methyl methacrylate) (PMMA) block (Figure 4a). To access the structure two small holes were drilled through the PMMA block into the upper and lower

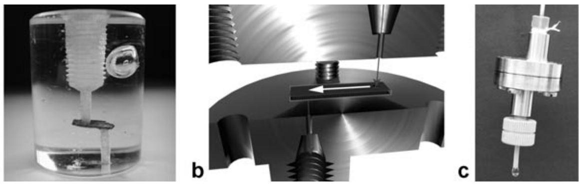

Figure 4. a) Prototype I in which the structure is embedded in a solid PMMA block; the screw thread on top is used to connect the HPLC pump b) Representation of prototype II in which the structure is fixed between two steel plates. Access to the CNT structure is obtained by piercing holes into the top and bottom layers; then flow around the individual tubes through the structure can be established. c) Reactor prototype II in action (see also the Supporting Information).

carbon layer of the structure with lateral displacement (Figure 4a and Figure S2 in the Supporting Information). Thereby, the carbon structure has a localized opening, allowing the flow of reactants to enter through the top carbon layer (inlet). The flow of reactants around the tubes can thus pass through the structure and finally leaves through the hole in the bottom carbon layer (outlet).

For prototype II the carbon structure was fixed between two metal plates with excentric nozzles by using an acrylate polymer that locks the structure into position inside the metal jacket and serves as a gasket (Figure 4b). The reactant inlet and outlet was again realized by piercing the top and bottom carbon layer. In both cases screw threads were used to connect an HPLC pump to the reactor for continuous reactant feed.

For both reactor prototypes (Figure 4) the carbon/alumina samples were embedded in a uniform parylene[12] film, then the local openings of the polymer were made, and the alumina was dissolved. The parylene polymer sheath is advantageous in further stabilizing the final carbon structure for multiple handling operations.

To finally test the two reactor geometries, the palladium-catalyzed transfer hydrogenation[13] of *p*-chloronitrobenzene to *p*-chloroaniline was chosen as a first test reaction to test the loading of the CNT structure with metal nanoparticles as catalyst and to test our nanoscale reactor concept. The palladium catalyst particles were generated by impregnating the carbon structure with a methanolic Pd^{2+} solution followed by subsequent reduction with hydrazine hydrate to give Pd^0 particles. The reactants in methanol were then continuously pumped through the structure using an HPLC pump (see the video in the Supporting Information). The pressure drop was stable for a test run (> 10 min), indicating no change of the internal carbon structure during operation. The flow at the outlet was collected and analyzed by gas chromatography (GC). At a flow rate of $0.6\,\mathrm{mL\,min^{-1}}$ and a distance of 4 mm between inlet and outlet, the pressure amounted to 27 ± 2.8 bar. The unoptimized yield of *p*-chloroaniline was 2.6%.

We have described the formation of a novel flexible, nano/macro-integrated all-carbon monolithic structure consisting of parallel carbon nanotubes sandwiched between a top and bottom carbon layer. The whole structure is assembled in a one-step catalyst-free CVD/CVI process using porous alumina as the template and propylene as the precursor gas. When packaged in a suitable housing (prototype I or II) the structure can serve as a nanostructured reactor with a surface-to-volume ratio two orders of magnitude higher than that of state-of-the-art microreactors. This represents a significant step further towards miniaturization and integration of nanostructures into macrodevices.

Experimental Section

The deposition of carbon was carried out in a CVD reactor at 750°C for 10 min. Induction heating with a template holder made of carbon was used and a temperature ramp of 20 min was applied until the reactor reached the final temperature. Propylene (C_3H_6) was chosen as the carbon source and argon as the carrier gas. Porous alumina membranes were used as templates (Whatman Anodisc). After carbon deposition, they were dissolved using hydrofluoric acid (HF). The average diameter of the pores and the porosity of the structure were determined by counting more than 500 pore diameters in images.

For the test reaction, the nanostructured reactor was connected to an HPLC pump. The synthesis and deposition of palladium nanoparticles was carried out by infiltration of the carbon structure with a methanolic sodium tetrachloropalladate(II) solution ($Na_2[PdCl_4]$) using the HPLC pump. The impregnated palladium complex was subsequently reduced using hydrazine hydrate (N_2H_5OH) prior to washing the structure with methanol (CH_3OH). *p*-Chloronitrobenzene ($ClC_6H_4NO_2$) and ammonium formiate ($HCOONH_4$) dissolved in methanol were pumped through the structure as the reaction feedstock.

Received: June 20, 2008
Revised: July 31, 2008

Keywords: carbon nanotubes · catalysis · fluidics · nanoreactors · template synthesis

---

[1] K. Jähnisch, V. Hessel, H. Löwe, M. Baerns, *Angew. Chem.* **2004**, *116*, 410–451; *Angew. Chem. Int. Ed.* **2004**, *43*, 406–446.
[2] P. D. I. Fletcher, S. J. Haswell, E. Pombo-Villar, B. H. Warrington, P. Watts, S. Y. F. Wong, X. Zhang, *Tetrahedron* **2002**, *58*, 4735–4757.
[3] J. Köhler, T. Henkel, *Appl. Microbiol. Biotechnol.* **2005**, *69*, 113–125.
[4] W. Ehrfeld, V. Hessel, H. Löwe, *Microreactors: New Technology for Modern Chemistry*, Wiley-VCH, Weinheim, **2000**, 7.
[5] a) C. R. Martin, *Chem. Mater.* **1996**, *8*, 1739–1746; b) A.-H. Lui, F. Schüth, *Adv. Mater.* **2006**, *18*, 1793–1805; c) J. J. Schneider, J. Engstler, *Eur. J. Inorg. Chem.* **2006**, 1723–1736.
[6] J. H. Yuan, F. Y. He, D. C. Sun, X. H. Xia, *Chem. Mater.* **2004**, *16*, 1841–1844.
[7] P. Kim, L. Shi, A. Majumdar, P. L. McEuen, *Phys. Rev. Lett.* **2001**, *87*, 215502.
[8] N. Ishigami, H. Ago, Y. Motoyama, M. Takasaki, M. Shinagawa, K. Takahashi, T. Ikuta, M. Tsuji, *Chem. Commun.* **2007**, 1626–1628.
[9] M. Whitby, N. Quirke, *Nat. Nanotechnol.* **2007**, *2*, 87–94.
[10] K. Nielsch, J. Choi, K. Schwirn, R. B. Wehrspohn, U. Gösele, *Nano Lett.* **2002**, *2*, 677–680.
[11] J. J. Schneider, J. Engstler, K. P. Budna, S. Franzka, C. Teichert, *Eur. J. Inorg. Chem.* **2005**, 2352–2359.
[12] W. F. Gorham, *J. Polym. Sci. Pol. Chem.* **1966**, ***4***, 3027–3039.
[13] R. A. W. Johnstone, A. H. Wilby, *Chem. Rev.* **1985**, *85*, 129–170.