# Preparation of Graded Materials by Laterally Controlled Template Synthesis

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Preparation of graded materials displaying gradients of desired properties (roughness,[1] composition,[2,3] reactivity,[4] porosity,[5] etc.) is one of the less-developed areas in materials chemistry. Here we present a new approach to the fabrication of gradient structures by electrodeposition in insulating templates. The method is demonstrated using deposition of Cu gradients in nanoporous alumina membranes (NAMs).

Template synthesis is a common method for producing defined nanostructures. NAMs are widely used as templates for the deposition of nanocylindrical materials[6] (e.g., nanorods, nanotubes) comprising polymers,[7] metals,[8] semiconductors,[6b] carbon,[9] etc. Nanomaterials prepared in such templates present an assembly of geometrically and chemically uniform objects, in terms of diameter, length, and composition. Here we show control of template electrodeposition in the pores of NAMs in both the vertical and the lateral directions, thus producing a graded material. While vertical control of template-synthesized nanomaterials is relatively simple to achieve (e.g., by varying the deposition time), to our knowledge lateral control of template synthesis has not been demonstrated to date.

NAMs (Whatman, Anodisc 0.02 $\mu$m) were treated with 3-mercaptopropyl trimethoxysilane,[10] which serves as an adhesive layer, and coated on one side with evaporated Au (35 or 100 nm thick).[11] The membranes were then used as templates for Cu electrodeposition in the pores, with the Au serving as the cathode. Cu was potentiostatically electrodeposited in the membrane pores from 0.3 M $CuSO_4$ + 0.1 M $H_2SO_4$ solution. A standard electrochemical cell was used with a $K_2SO_4$-saturated $Hg/Hg_2SO_4$ reference electrode and a Pt counter electrode. The potential was chosen between −0.36 V (the measured Nernst potential) and −0.8 V. The deposition time was chosen in the range 10−200 min. The deposited Cu was imaged in a cross-sectional view, using a scanning electron microscope (SEM) (JEOL JSEM 6400, JEOL Ltd., Tokyo, Japan) in the energy dispersive spectrometer (EDS) and backscattered electron (BSE) modes.

Control of the electrodeposition in the vertical direction is done by controlling the amount of charge passed. Figure 1 shows cross-sectional views of partially filled membranes. The electrodeposition was carried out at −0.8 V for different time periods using a 100-nm evaporated Au cathode. The copper-filled volume (bright) increases with time of deposition. Cu wires grow inside the membrane pores from the Au cathode, forming an array of rather uniform Cu wires. When some wires reach the pore end the deposition is accelerated due to enhanced mass transport, and Cu "mushrooms" start to form, as seen in Figure 1c. Prior to mushroom deposition the height of the Cu wires is linearly correlated with the charge passed during electrodeposition. X-ray diffraction of the deposited Cu (see Supporting Information) shows preferred growth of an assembly of (111) oriented Cu wires.

Lateral control of electrochemical reactions was demonstrated recently by Bohn and co-workers[2] using potential gradients applied to a thin Au working electrode displaying a low longitudinal
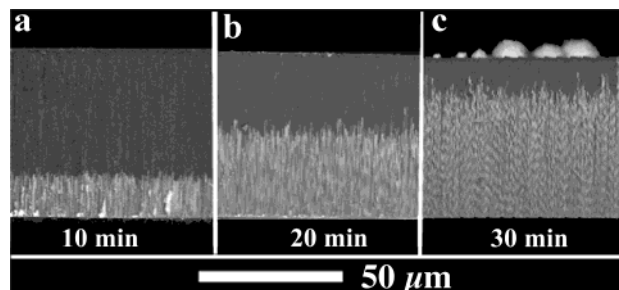


**Figure 1.** SEM images showing cross-sections of Cu-filled NAMs following uniform Cu electrodeposition for several time periods (indicated). Electrodeposition was carried out at −0.8 V. The current density (calculated using the total pore area) increased during deposition from ca. 10 to ca. 20 mA cm$^{-2}$.
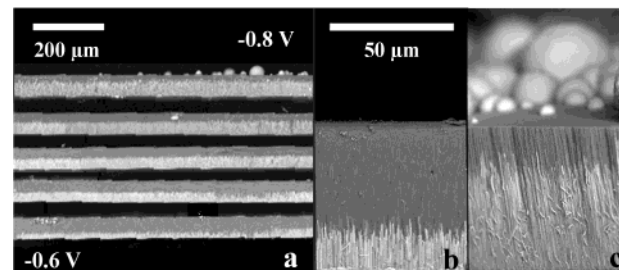


**Figure 2.** (a) Bottom-left to top-right: SEM image showing the entire cross-section (ca. 4 mm) of a NAM, filled with Cu electrodeposited using a lateral potential gradient of −0.6 to −0.8 V. (b, c) SEM images showing the edge sections of the Cu-filled membrane.

conductivity. This basic approach is exploited here for obtaining lateral control of template deposition. A thin Au film (35 nm thick) was evaporated on the membrane and used as the cathode for Cu deposition, as shown above. An in-plane potential distribution over the electrode length, $V(x)$, was maintained by applying different potential values to the Au at the two membrane ends. To image the height gradient of the deposited Cu, the samples were cut along the line where the potential gradient was applied, to expose the membrane cross-section for SEM imaging.

Cu gradients were obtained in NAMs by applying potential gradients for different time periods at several set potentials. Figure 2 shows an example of a metal gradient, deposited at −0.8 V (applied to one side of the membrane) to −0.6 V (applied to other side of the membrane). The images were taken in different regions of the membrane along the potential gradient, sampling the entire distance of 4 mm between the electrodes (Figure 2a). The height of the electrodeposited Cu varies gradually from ca. 16 $\mu$m at one edge (Figure 2b) to ca. 45 $\mu$m at the other edge (Figure 2c).

A blank experiment with a bare Au electrode of the same thickness and conductivity was carried out by mounting the substrate in the cell with the bare Au side (i.e., not the membrane side) exposed to the solution. On the bare Au a potential (and metal) gradient can be obtained only in the early stages of the process,
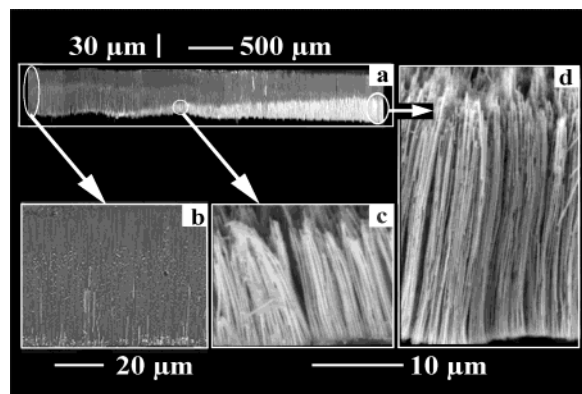
**Figure 3.** (a) SEM image showing the entire cross-section of a Cu-filled NAM. Cu was first deposited uniformly at −0.8 V and then partly dissolved using a lateral potential gradient of −0.4 to −0.05 V. Note the different $x$ and $y$ scales. (b) SEM image showing the edge section of the membrane corresponding to Cu dissolution at −0.05 V. (c, d) SEM images of Cu "nano-brushes" obtained after uniform Cu deposition, gradient Cu dissolution, and alumina membrane dissolution, imaged at different parts of the membrane (indicated).

where the Cu thickness is very small (<1 $\mu$m). Continued Cu deposition decreases the lateral resistivity dramatically, eliminating the possibility of maintaining a lateral potential drop and hence of depositing a metal gradient. On the other hand, Cu deposition in the membrane does not influence the resistivity of the fraction of Au film on the insulating part between the pores, thereby enabling formation of substantial Cu gradients, as shown in Figure 2.

Cu gradients in NAMs were also obtained by uniform deposition followed by gradient dissolution. In the example shown in Figure 3, Cu was first uniformly electrodeposited (ca. 30 $\mu$m height) by applying −0.8 V for 20 min, as in Figure 1. An oxidation potential gradient was then introduced by applying −0.4 V to one side of the membrane and −0.05 V to the other side, such that the Cu dissolution rate, hence the Cu height, varied along the line of potential gradient. Figure 3a shows a cross-sectional view of the membrane along the line of potential gradient (4 mm in length). The height of Cu wires varies gradually between the two sides from ca. 30 $\mu$m (the originally deposited height) to no Cu. Three areas are seen in the image: Bright and dark areas show the Cu-filled volume and the unfilled alumina, respectively. The gray area contains traces of Cu, left after dissolution due to formation of electrical discontinuities.

A Cu "nano-brush" is obtained by dissolving the alumina membrane after Cu deposition and gradient dissolution, using 1.0 M NaOH. Figure 3, c and d show Cu "nano-brushes" prepared from two areas along the gradient (marked in the figure) after membrane dissolution. The Cu traces in the gray area (Figure 3, a and b), disconnected from the Cu wires, are no longer seen after membrane dissolution.

In conclusion, electrodeposition and electrodissolution provide the possibility to form gradients of conducting deposits in nanoporous alumina membranes (NAMs) as well as in other insulating templates. Formation of sizable metal gradients in the insulating membranes is shown to occur under conditions where essentially no gradient is formed on similar bare electrodes. The latter is attributed to the permanent resistivity of the thin Au film between the pores, which does not disappear upon metal deposition as it does when bare electrodes are used.

The system demonstrated here opens various possibilities for obtaining graded structures with gradients of structural, compositional, magnetic, optical, or conductive properties on the $\mu$m scale, using a variety of materials (e.g., conductive polymers, magnetic metals). Alloy gradients can be obtained by co-deposition of two metals with different reduction potentials. Changing the geometry of the gradient-inducing electrodes (e.g., to circular geometry) enables obtaining various 2-D gradient depositions. Such experiments are currently underway.

**Supporting Information Available:** X-ray diffraction pattern of Cu electrodeposited in a NAM (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) 0.02 $\mu$m Whatman membranes have pores of ca. 0.22 $\mu$m diameter (determined by cross-sectional E-SEM imaging) throughout the entire membrane thickness, branching at one end to thinner ones of ca. 0.02 $\mu$m diameter. The Au was deposited on the 0.02 $\mu$m side.

JA029877J