Preparation of Graded Materials by Laterally Controlled Template Synthesis

Tali Sehayek, Tatyana Bendikov, Alexander Vaskevich and Israel Rubinstein

Department of Materials & Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel

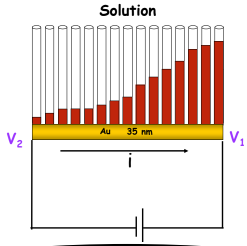
Abstract

Preparation of graded materials displaying gradients of properties (e.g., roughness, composition, reactivity, porosity) is potentially important for obtaining materials of unusual properties, which can be used as sensors, catalysts, or in other applications requiring spatially varying properties of the material. Here we present an approach to the fabrication of graded materials showing structural and compositional gradients, obtained by electrochemical template synthesis in nanoporous alumina membranes (NAMs), precoated on one side with a thin evaporated gold film used as the working electrode. A lateral gradient of the properties of a material deposited in the insulating membrane is achieved by applying a controlled lateral potential drop on the working electrode during the electrochemical synthesis. The method is demonstrated with three examples: (i) Thickness gradients of a metal (Cu) are obtained by electrodeposition (or electrodissolution) of Cu in the NAM template using a lateral voltage drop on the working electrode. (ii) Thickness gradients of a conductive polymer (polyaniline (PANi)) are obtained by electrochemical oxidation of the monomer using a lateral voltage drop. (iii) Compositional gradients are achieved by electrochemical co-deposition of Au and Pd alloy in the membrane template under a lateral voltage drop.

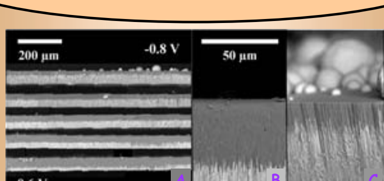
The gradients were characterized by scanning electron microscope (SEM) imaging of cross-sections along the line of the applied voltage gradient. Local elemental analysis by energy dispersive spectrometery (EDS) and X-ray diffraction (XRD) measurements were carried out as well, primarily for analyzing the alloy compositional gradients.

The approach shown here opens possibilities for obtaining graded materials showing gradients of structural, magnetic, optical, conductive, or catalytic properties on the micrometer scale. Changing the lateral potential drop by varying the geometry of the gradient-inducing electrodes (e.g., to circular geometry) will enable preparation of various 2D graded structures.

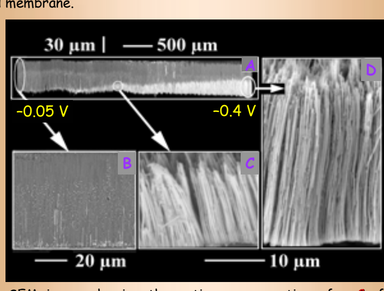
Solution



Cu

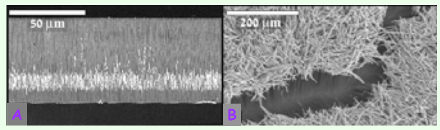


(A) Bottom-left to top-right: SEM image showing the entire cross-section (ca. 4 mm) of a NAM, filled with Cu electrodeposited using a lateral potential gradient of -0.6 V to -0.8 V vs. K_2SO_4-saturated Hg/Hg_2SO_4. (B, C). SEM images showing the edge sections of a Cu-filled membrane.

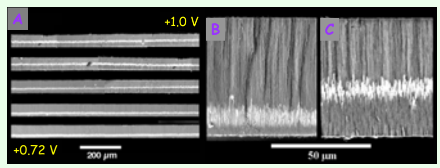


(A) SEM image showing the entire cross-section of a Cu-filled NAM. Cu was first deposited at −0.8 V vs. K_2SO_4-saturated Hg/Hg_2SO_4 and then partly dissolved using a lateral potential gradient of −0.4 V to −0.05 V vs. K_2SO_4-saturated Hg/Hg_2SO_4. Note the different x and y scales. (B) SEM image showing the edge section at −0.05 V. (C, D) SEM images of Cu "nano-brushes" obtained after uniform Cu deposition, gradient dissolution, and alumina membrane dissolution, imaged at different parts of the membrane (indicated).

Polyaniline

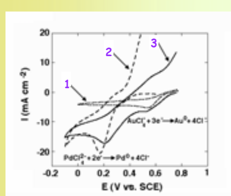


(A) SEM image showing a cross-section of PANi-Ag filled NAM, obtained by uniform PANi deposition (cyclic voltammetry, potential range: -0.05 to +0.95 V vs. Ag/AgCl, 125 cycles), followed by Ag deposition (0.1 M $AgNO_3$ and 1.0 M $HClO_4$ solution at +0.3 V vs. Ag/AgCl, for 3 minutes). (B) SEM image of a PANi-Ag 'nanobrush' obtained after membrane dissolution.

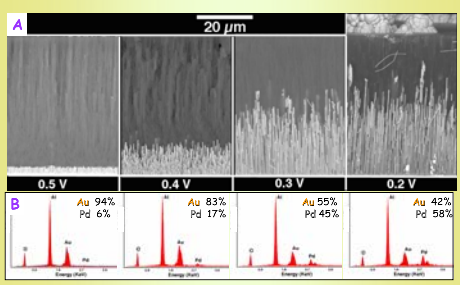


(A) Bottom-left to top-right: SEM image showing the entire cross-section (ca. 4 mm) of a NAM, filled with PANi and Cu. The structure was obtained using a lateral potential gradient of +0.72 V to +1.0 V vs. Ag/AgCl for PANi deposition, followed by uniform Cu electrodeposition at −0.8 V vs. K_2SO_4-saturated Hg/Hg_2SO_4. (B, C) SEM images showing the edge sections of the PANi-Cu filled membrane.

Au-Pd alloy

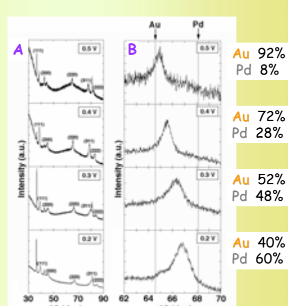


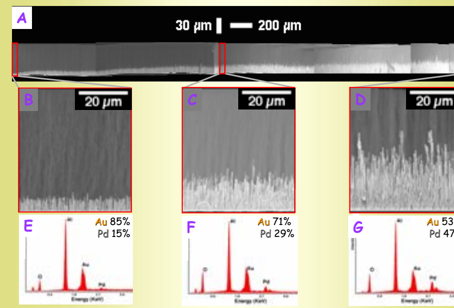
Cyclic voltammograms (first scan) recorded in (1) 10 mM $HAuCl_4$ + 0.5 M HCl, (2) 25 mM H_2PdCl_4 + 0.5 M HCl, and (3) 10 mM $HAuCl_4$ + 25 mM H_2PdCl_4 + 0.5 M HCl solutions. The working electrode: 35 nm Au film evaporated on a NAM. Scan rate: 50 mV/sec. All scans started in the negative direction.



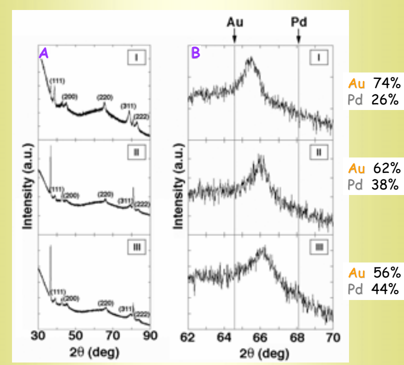
(A) ESEM images showing cross-sections of NAMs filled with Au-Pd alloy following uniform electrodeposition for 1 h at different potentials (vs. SCE, indicated). (B) Corresponding EDS spectra and calculated atomic %. Solution: 10 mM $HAuCl_4$ + 25 mM H_2PdCl_4 + 0.5 M HCl.

(A) XRD spectra and calculated atomic % of Au-Pd alloys deposited uniformly in NAMs at indicated potentials. Diffraction lines that originated from the glue are not assigned. (B) Magnification of the (220) diffraction peak; the vertical lines indicate peak positions for pure Au and Pd. Compositions derived using Vegard's law.

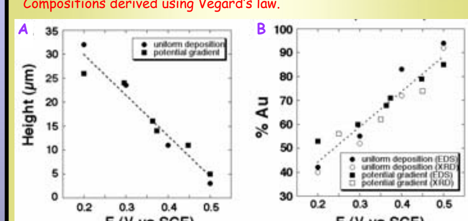




(A) ESEM image showing the entire cross-section of a NAM filled with Au-Pd alloy, obtained using a lateral potential gradient of +0.2 V to +0.5 V (vs. SCE). Note the different x and y scales. (B–D) Higher magnification ESEM images of different parts of the membrane (indicated). (E–G) Corresponding EDS spectra and calculated atomic %.



(A) XRD spectra and calculated atomic % of Au-Pd alloy deposited in a NAM under a potential gradient of 0.2 V to 0.5 V. I, II and III denote different parts of the sample. Diffraction lines that originated from the glue are not assigned.
(B) Magnification of the (220) diffraction peak; the vertical lines indicate peak positions for pure Au and Pd. Compositions derived using Vegard's law.



Height (A) and composition (B) of the Au-Pd nanowire alloys vs. deposition potential, for uniform and gradient depositions. The applied potential along the membrane during gradient deposition was assumed to vary linearly with distance along the lateral potential drop. The lines present linear regression fit of all the data. (sentence deleted)

References

Sehayek, T.; Vaskevich, A.; Rubinstein, I. *J. Am. Chem. Soc.* **2003**, *125*, 4718-4719.

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Conclusions

- A new approach to the synthesis of graded materials was developed, based on spatial control of electrodeposition (or electrodissolution) in insulating templates.
- The new method was demonstrated via formation of thickness gradients of Cu and polyaniline and compositional (as well as thickness) gradients of Au-Pd alloy , in nanoporous alumina membranes.
- The new method opens various possibilities for obtaining graded materials showing gtadients of structural, magnetic, optical, conductive, or catalytic properties on the micrometer scale.
- Graded materials of different shapes can be obtained by controlling the geometry of the applied potential drop.