Preparation of Graded Materials by Laterally Controlled Template Synthesis

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Abstract

Preparation of graded materials displaying gradients of properties (e.g., roughness, composition, reactivity, porosity) is potentially important for obtaining materials of unusual characteristics, 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 lateral potential drop on the working electrode during the electrochemical synthesis.

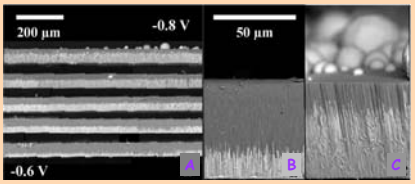
The method is demonstrated with three examples: (i) Thickness gradients of a metal (**Cu**) are obtained by electrodeposition (or electrodissolution) of **Cu** in the NAM template using a lateral voltage drop on the working electrode. (ii) Thickness gradients of a conductive polymer (**polyaniline** (**PANi**)) are obtained by electrochemical oxidation of the monomer to form a polymer deposit using a lateral voltage drop. (iii) Compositional gradients are achieved by electrochemical co-deposition of **Au** and **Pd** in the membrane template under a lateral voltage drop, to form an alloy showing a continuous lateral change of the **Au**:**Pd** ratio.

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 spectrometry (EDS) and X-ray diffraction (XRD) measurements were carried out as well, primarily for analyzing the alloy compositional gradients.

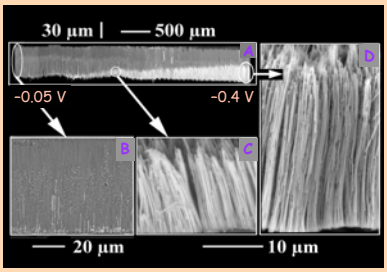
The approach shown here opens possibilities for obtaining graded materials showing gradients of structural, magnetic, optical, conductive, or catalytic properties on the micrometer scale. Changing the lateral potential drop by varying the geometry of the gradient-inducing electrodes (e.g., to circular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

Thickness Gradients

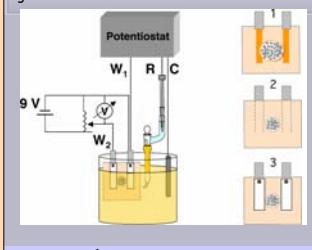
Cu

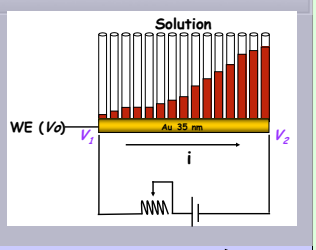


(*A*) Bottom-left to top-right: SEM image showing the entire cross-section (ca. 4 mm) of a NAM, filled with **Cu** electrodeposited using a lateral potential gradient of −0.6 V to −0.8 V (vs. K_2SO_4-saturated Hg/Hg_2SO_4). (*B*, *C*). SEM images showing the edge sections of a **Cu**-filled membrane. Deposition solution: 0.3 M $CuSO_4$ + 0.1 M H_2SO_4.

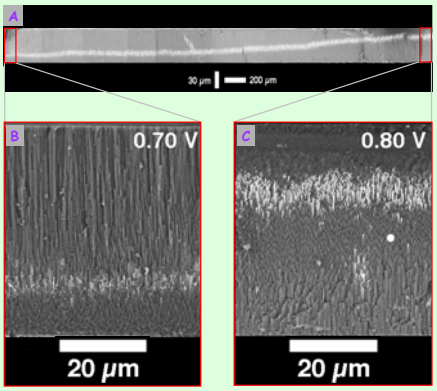


(*A*) SEM image showing the entire cross-section of a **Cu**-filled NAM. **Cu** was first deposited at −0.8 V (vs. K_2SO_4-saturated Hg/Hg_2SO_4) and then partly dissolved using a lateral potential gradient of −0.4 V to −0.05 V. Note the different x and y scales. (*B*) SEM image showing the edge section 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).





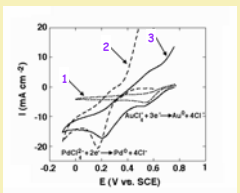
Polyaniline



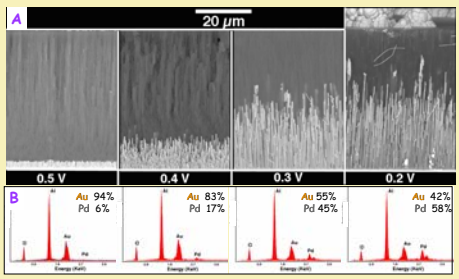
(*A*) ESEM image showing the entire cross-section (ca. 4 mm) of a NAM, filled with **PANi** and **Cu**. The structure was obtained using a lateral potential gradient of +0.7 V to +0.8 V (vs. SCE) for **PANi** deposition, followed by uniform **Cu** electrodeposition at −0.6 V (vs. K_2SO_4-saturated Hg/Hg_2SO_4). (*B*, *C*) Higher magnification ESEM images showing the edge sections of the **PANi**-**Cu** filled membrane. Solutions: (i) **PANi** deposition: 0.2 M ANi + 1.0 M $HClO_4$. (ii) **Cu** deposition: 0.3 M $CuSO_4$ + 0.1 M H_2SO_4.

Compositional Gradients

Au-Pd alloy

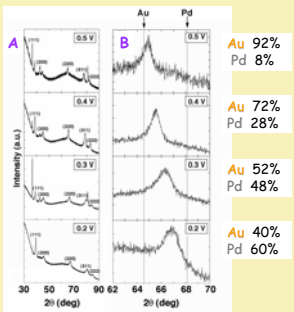


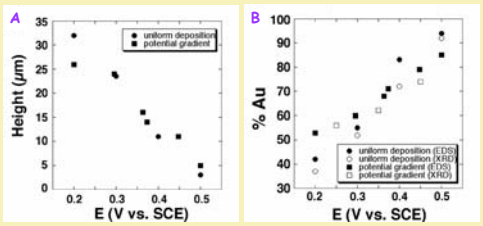
Cyclic voltammograms (first scan) recorded in (1) 10 mM $HAuCl_4$ + 0.5 M HCl, (2) 25 mM H_2PdCl_4 + 0.5 M HCl, and (3) 10 mM $HAuCl_4$ + 25 mM H_2PdCl_4 + 0.5 M HCl solutions. The working electrode: 35 nm Au film evaporated on a NAM. Scan rate: 50 mV/sec. All scans started in the negative direction.



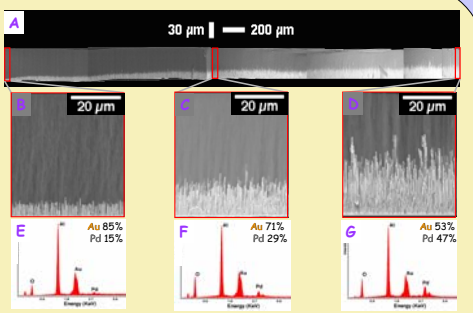
(*A*) ESEM images showing cross-sections of NAMs filled with **Au**-**Pd** alloy following **uniform** electrodeposition for 1 h at different potentials (vs. SCE, indicated). (*B*) Corresponding EDS spectra and calculated alloy compositions (atomic %). Deposition solution: 10 mM $HAuCl_4$ + 25 mM H_2PdCl_4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





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.



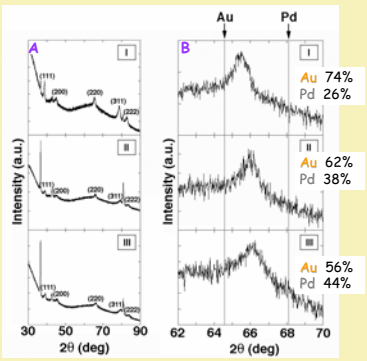
(*A*) ESEM image showing the entire cross-section of a NAM filled with **Au**-**Pd** alloy, obtained using a lateral potential gradient of +0.2 V to +0.5 V (vs. SCE). Note the different x and y scales. (*B*-*D*) Higher magnification ESEM images of different parts of the membrane (indicated). (*E*-*G*)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

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 gradients 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.

References

- Sehayek, T.; Vaskevich, A.; Rubinstein, I. *J. Am. Chem. Soc.* **125**, 2003, 4718-4719.
- Sehayek, T.; Bendikov, T.; Vaskevich, A.; Rubinstein, I. *Adv. Funct. Mater.* **16**, 2006, 693-698.



(*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.