2008 ECS Summer Fellowship Reports

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The 2008 Edward G. Weston Summer Research Fellowship — Summary Report

Leveling the Gap: An Electrochemical Approach to Nanowire Topology Control

by Matthew Banholzer

The topography of metal structures in general is of significant importance in a variety of areas relevant to chemistry, physics, and nanoscience, including electrochemical response, monolayer assembly, electrical contact quality, light scattering, and plasmonics.[1-3] While many methods to modify the topology of bulk or thin-film metal surfaces exist, methods for smoothing the topography of nanorod surfaces on the nanometer length scale do not exist, especially the segment ends where many of the interesting properties of the nanorod are significantly influenced. The lack of this capability is surprising considering hundreds of papers are published each year on such structures.

Many nanowires are grown by templated-growth electrochemical methods where electrodeposition is carried out in nanoscale pores.[4,5] Because such nanowire growth is typically dominated by diffusion processes (due to the fact that the usually 50 µm long pores are only 350 nm or less in diameter), by studying the deposition/diffusion processes underlying nanorod growth, it is possible to identify and optimize conditions that lead to smoother

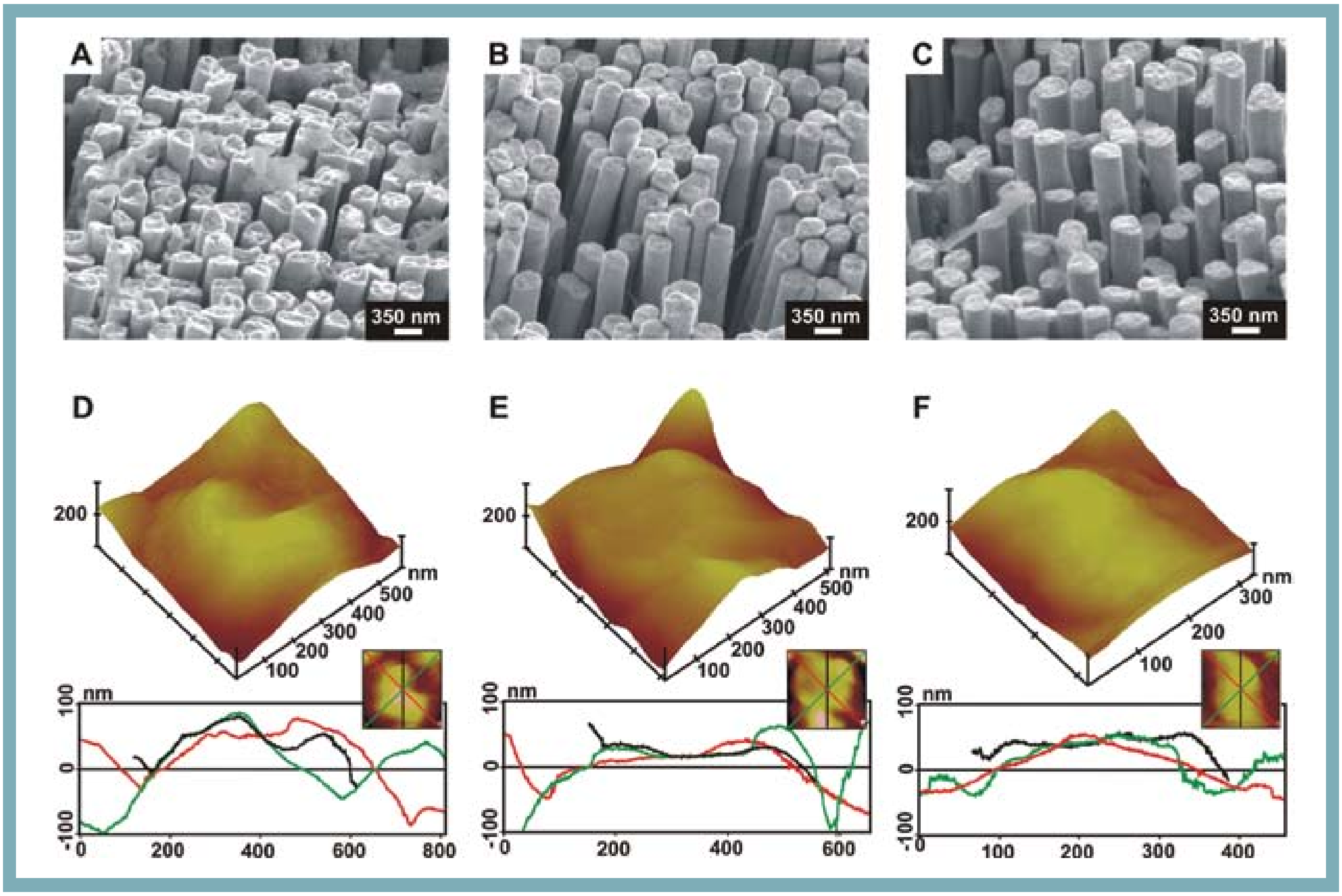

Fig. 1. *SEM (top) and AFM images (bottom) of as-made (A, D), partially smoothed (B, E), and fully smoothed (C, F) nanorods. Under each AFM image are 2D profiles of "slices" taken to give a better sense of the topology of the surface; the color of each trace corresponds to the path indicated in the insert. Note the scale changes in the x axis in (F) are meant to emphasize the smoother features.*

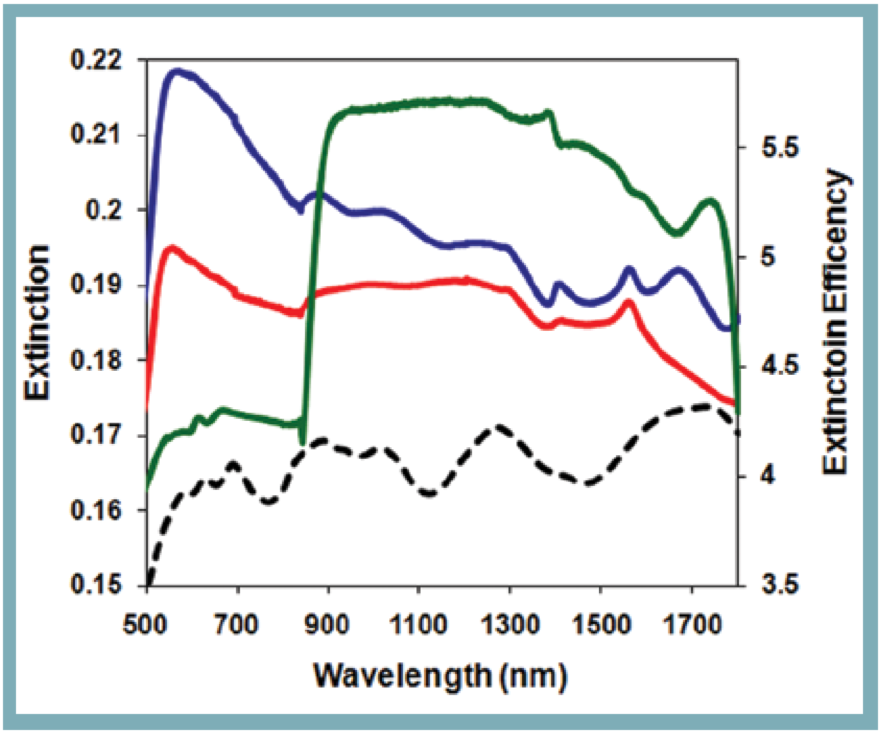

Fig. 2. *Extinction spectra of smoothed and unsmoothed 350 nm-diameter nanorods in solution. Blue line: 1.5 µm-long smoothed Au rods; red line: 1.5 µm-long as-made Au rods; green line: smoothed 3 µm Au rods. Dashed black line is the calculated extinction spectrum of a perfect 1.5 µm-long Au rod. Spectra artificially offset for clarity.*

interfaces. Indeed, over the past summer electrochemical conditions for smoothing the end surfaces of Au nanorods *in situ* were identified. A two-step procedure, using relatively simple and widely accessible growth solutions and pulse sequences was developed.[6] The first step is a reductive one aimed at controlling the diffusion and migration of metal ions (*e.g.* Au$^+$) to the growing nanorod surface by adjusting the applied potential and concentration of the metal ions in the growth solution. It was found that a pulsed deposition (pulse width approx. 1 s) designed to avoid depletion of metal ions at the metal surface aided in preventing the growth of rough features as the nanorod was formed. A second oxidative smoothing step, based in part on the energetic differences between topologically rough and smooth surfaces was used to further smooth the nanorods. It has been shown that surface free energy makes a repulsive contribution (the strength of which increases as the radius of curvature of the surface decreases) to the electrochemical potential, making rough structures easier to oxidize relative to smoother regions.[7] In this step, a mild oxidation potential selectively removed metal atoms from the topologically high points on the nanorod.

After this two step process, nanorods with initial end (root-mean squared) roughness of greater than 35 nm were smoothed to less than 5 nm (Fig. 1). This led to marked shifts in the optical properties of these nanorods; one example can be found in the UV-vis-NIR extinction spectra of these nanostructures (Fig. 2). While typical nanorods with unsmoothed ends have relatively low, ill-defined intensity plasmon resonances (collective oscillations of the surface electronics on the nanostructure), the smoothed rods exhibited more distinct and well defined plasmon resonances. Because some emerging biodetection assays are based on the proper identification of these resonances, any technology that allows for clearer, more easily read resonances could potentially improve the sensitivity of these assays.

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References

1. J. L. Conyers and H. S. White, *Anal. Chem.*, **72**, 4441 (2000).
2. H. Raether, *Surface Plasmons on Smoother and Rough Surfaces and on Gratings*, Springer, (1988).
3. E. A. Weiss, R. C. Chiechi, G. K. Kaufman, J. K. Kriebel, Z Li, M. Duati, Ma. A.Rampi, and G. M. Whitesides, *J. Am. Chem. Soc.*, **129**, 4336 (2007).
4. C. R. Martin, *Science,* **266**, 1961 (1994).
5. D. Routkevitch, T. Bigioni, M. Moskovits, and J. M. Xu, *J. Phys. Chem.*, **100**, 14037 (1996).
6. M. J. Banholzer, S. Li, J. B. Ketter, D. I. Rozkiewicz, G. C. Schatz, and C. A. Mirkin, *J. Phys. Chem. C.*, **112**, 15729 (2008).
7. X. Zhang, E. M. Hicks, J. Zhao, G. C. Schatz, and R. P. Van Duyne, *Nano Lett.*, **5**, 1503 (2005).