

Fabrication of Gold Microtubes and Microwires in High Aspect Ratio Capillary Arrays

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In this communication, we describe the sequential deposition of materials in capillaries to produce self-assembled three-dimensional (3-D) gold microtubes (μ -tubes), hollow gold microwires (μ -wires), and μ -tube and μ -wire arrays with unprecedented aspect ratios. The fabrication of these structures is of interest in chemistry, biology, and medicine for their possible use in microanalytical, microfluidic, microelectromechanical, and neuroprosthetic devices.

Traditionally, photolithography,¹ microcontact printing,² micro-machining,³ and micromanipulation⁴ have been employed to produce μ -wires and μ -wire arrays with two-dimensional and low aspect ratio 3-D relief. The fabrication of arrays *in situ* using electrochemical⁵ and electroless⁶ deposition in a porous template has proven to be a superior option for preparing more complex, higher aspect ratio 3-D μ -tube and μ -wire arrays. Electrochemical and electroless deposition techniques typically involve diffusion of the plating solutions through template pores, an inherently time-consuming process for high aspect ratio features. Thus, electrochemical and electroless deposition is usually limited to thin substrates ($\sim 100 \mu\text{m}$), or else deposition must be conducted over long periods of time (days).

Recently, Kenis et al.^{7,8} employed small-diameter capillaries as reaction vessels to perform rapid spatially controlled microfabrication. Small-diameter capillaries have characteristically low Reynolds numbers, corresponding to highly laminar flow. Under laminar flow conditions, two liquid streams injected side-by-side at the head of a capillary mix by diffusion only and maintain a high degree of separation throughout the capillary's length, even if the capillary is nonlinear. This phenomenon was used to form single μ -wires in the center of the capillaries⁸ from two simultaneously injected reagents. Fluid flow moved the reagent solutions axially through the capillary, and diffusion transported the reagents radially to the reaction zone at the interface of the two liquids in the capillary. This technique would be difficult to apply to fabricate arrays of μ -wires, as each capillary in the array would require multiple reagent ports.

An alternative approach to the simultaneous flow of reagents through capillaries is to use sequential flow, where each reagent deposits a layer on the inside surface of the capillary. Sequential flow is advantageous, as it still employs axial transport of solution through the capillary, but simplifies plumbing and facilitates the fabrication of ensembles and arrays; a single reagent source can supply any number of parallel capillaries. When used in conjunction with electroless deposition procedures, the bulk transport of solution through capillaries nearly eliminates previous diffusional limitations and facilitates the fabrication of high aspect ratio features in a short amount of time.

Sequential flow is capable of producing μ -tubes and μ -wires with macroscopic to submicrometer diameters and very high aspect ratios. Mechanical constraints aside, the diameters and lengths achievable using the technique are primarily limited by reagent depletion axially in the capillary, which is a function of deposition rate for a continuous process. If the rate of deposition is too fast,

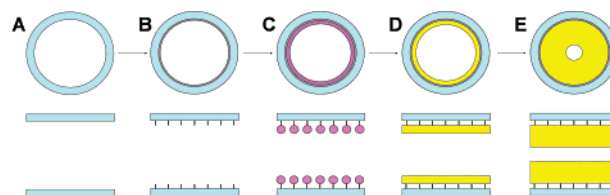


Figure 1. Fabrication of a gold μ -tube in a single silica capillary (end and side views). Cleaned silica capillaries (A) are modified with a monolayer of bifunctional silane (B), which is used to deposit a monolayer of colloidal gold on the surface of the capillary (C). Deposition of bulk gold from solution increases the size of the gold colloid, eventually forming a uniform layer (D). As deposition progresses, the gold thickness approaches the radius of the capillary (E).

occlusion at the orifice of the capillary can occur, thereby precluding the formation of long wires. The deposition rate can often be controlled by the choice of flow rate, temperature, and deposition chemistry. We have found the conditions delineated below to be sufficient to enable gold deposition in at least 2.5-cm long capillary arrays containing 631 11- μm diameter capillaries.

Figure 1 demonstrates the sequential deposition process for fabricating a gold μ -tube within a single silica capillary. The capillary (A) is first treated with a bifunctional silane, which forms a monolayer on the inside of the capillary⁹ (B). Next, a solution of colloidal gold is flowed through the capillary, depositing a monolayer of gold nanoparticles¹⁰ on the functionalized capillary surface (C). Finally, these seed particles are grown by electroless deposition of bulk gold from solution¹¹ (D). The dimensions of the resulting deposited gold are determined by the concentration of the plating solution, deposition rate of the gold, and residence time of the deposition solution in the capillary. At shorter times, the capillary contains a μ -tube, while at longer times, the thickness of the gold tube wall approaches the radius of the capillary (E). As a final treatment, the capillary may be subjected to deposition without flow, thereby sealing the ends of the μ -tube completely to form a hollow μ -wire (not shown).

As a simple demonstration of this technique, Tygon tubing was used to connect a cylindrical capillary array to a syringe, which was used to deliver pressurized fluids into the lumen of the capillaries. Fluid flow was generated manually by applying pressure to the syringe plunger. This method enabled the fabrication of μ -wires inside 2.2-mm diameter cylindrical capillary arrays containing 631 hexagonally packed 11- μm diameter silica capillaries on a 41- μm pitch (Figure 2). Each of the deposition steps outlined above, with the exception of silanization, produced a visible change in the array: untreated or silane-treated arrays appeared translucent when viewed from the side (Figure 2A,B, left); colloidal gold-modified arrays appeared blue to purple, a result of the surface plasmon effect (not shown); electroless gold-deposited arrays appeared light gold from the formation of thin μ -tubes at short deposition times (Figure 2A,B, center) and dark gold as their thickness increased at longer deposition times (Figure 2A,B, right).

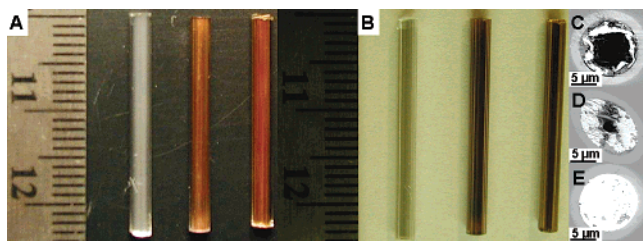


Figure 2. (A) Pieces of capillary array 2.2-mm in diameter and \sim 2.2-cm in length (optical distortion makes the capillary portion of the array appear to fill the bundle, but it only occupies 1 mm in the center of the 2.2-mm diameter bundle). (Left) untreated, (center) after colloidal gold treatment and brief bulk deposition, and (right) after colloidal gold treatment and long bulk deposition. (B) The same arrays on a white background show the characteristic color and reflectivity of gold. SEM images of: (C) A single thin gold μ -tube (the gold was deformed by the polishing process), (D) a single thick gold μ -tube, and (E) a single gold μ -wire.

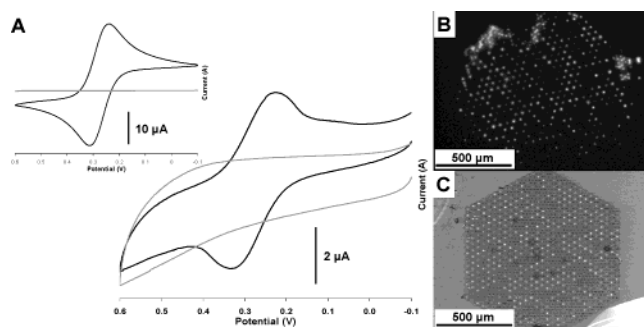


Figure 3. (A) CVs of 10 mM $\text{K}_3\text{Fe}(\text{CN})_6$ in 1 M KCl (dark trace) and 1 M KCl (light trace) using a polished μ -wire array show classic large electrode CV behavior resulting from overlap of individual diffusion volumes. Inset: CVs of 10 mM $\text{K}_3\text{Fe}(\text{CN})_6$ (dark trace) in 1 M KCl and 1 M KCl (light trace) using a 1-mm gold disk electrode. 100 mV/s scan rate vs Ag/AgCl, Pt CE. (B) Microscopic image of ECL induced using a polished μ -wire array (spaces with no apparent ECL contain capillaries plugged with silica), 1 mM $\text{Ru}(\text{bpy})_3^{2+}$ /0.1 M tripropylamine/0.15 M phosphate buffer (pH 7), $E_{\text{app}} = 1.3$ V vs Ag/AgCl, Pt CE $5\times$ objective, 1 s integration, no filters. (C) SEM image of the polished μ -wire array used in ECL imaging. Gold μ -wires appear as light-colored circles in the darker-colored silica matrix.

The deposition process could be observed via SEM imaging as well; a thin μ -tube, a thicker μ -tube, and a μ -wire are shown in Figure 2, parts C, D, and E, respectively. The silica arrays could be dissolved in HF, leaving behind the individual gold μ -tubes or μ -wires, although the dissolution process resulted in the distortion and breakage of many of them. Despite the simplicity of the fabrication technique, more than 70% of the available capillaries were filled.

The electrical nature of the arrays is characteristic of bulk conductive μ -tubes and μ -wires: the resistance across the 2.2-cm long array pictured at right in Figure 2A is 11 Ω . The μ -wire arrays can be used as working electrodes by polishing one end and using silver paint on the other to establish electrical connectivity. Cyclic voltammograms (CVs) obtained using such an array (Figure 3A) show the expected overlap of the diffusion zones between active μ -wires (electrodes) with a signal similar to that of a large electrode CV (Figure 3A, inset), a result of the interelectrode center-to-center spacing to electrode radius ratio of 7.5.¹² The large background current is likely the effect of solution seeping into gaps between the μ -wires and the capillary walls and residual unfilled capillaries,

as the array was not subjected to a sealing treatment prior to electrochemical use.¹³ Electrogenerated chemiluminescence¹⁴ (ECL) (Figure 3B) further demonstrates the conductivity of individual μ -wires in the array (Figure 3C). Many of the spaces in Figure 3B with no ECL and the darker spaces in Figure 3C correspond to capillaries that are plugged with silica during the fiber manufacturing process. Approximately 90 of the 631 capillaries were plugged in this manner.

In conclusion, we have demonstrated a technique to fabricate gold μ -tubes, μ -wires, and μ -tube and μ -wire arrays using sequential flow of reagents by fabricating an array of 11- μm diameter gold μ -wires inside a 2.2-cm-long capillary array. The capillary diameter, length, and shape presented do not represent the physical limits of this technique; much narrower, longer, and more irregular features are possible. It is also possible to produce structures composed of materials other than gold or to modify the hollow gold μ -tubes with other chemistries. Ultimately, these μ -tube and μ -wire arrays may be useful in many applications, including electrochemistry, microfluidics, and sensing. Present research is focused on improving the fabrication technique and examining their potential uses.

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Supporting Information Available: Related instrumentation and procedures (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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