Novel techniques for modifying microtube surface with various periodic structures ranging from nano to micro scale

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Rolled-up nanotechnology¹ has been rapidly developed and widely applied to obtain versatile micro/nano structures, such as nanospring, nanotube, nanowrinkle. In this work, we have successfully incorporated periodic structures, ranging from nano to micro scale, onto outer surface of microtubes through the combination of the electrochemical anodization and nanoimprint with the rolled-up nanotechnology. Compared with ordinary rolled-up microtubes with smooth tube wall, these specially designed and finely fabricated microtubes will have unique electrical, optical or mechanical properties, and thus even wider applications in miro/nano-optic, electronic and microfluidic devices and systems, etc.

Figure 1(a) schematically illustrates the process of fabricating a microtube with nanopillared surface. A low-cost porous alumina was first made under the voltage of 40 V in 0.5 M oxalic acid as a template. Then an ultrathin layer (~5nm) of HfO₂ was deposited on the surface of porous alumina by atomic layer deposition (ALD) technique, followed by the deposition of 10 nm Ti and 10 nm Cr onto textured HfO₂ thin film via E-beam evaporation. After rinsing the asdeposited sample in 1 M KOH for several minutes to selectively remove the porous alumina, the strained membranes were released from the substrate and self-assembled into microtube with nanostructured pillar array on the tube wall, generating a combined 3-D structure as shown in Figure 1(b).

Figure 2(a) shows another technique combing nanoimprinting with rolled-up nanotechnology to assemble hybrid structures of microtubes with micro/nano structures. Nanostructured membranes were obtained after the deposition of 20 nm Au onto a imprinted P(VDF-TrFE) polymer via E-beam evaporation and subsequently rolled up into microtubes with specific periodic structures depending on the pattern transferred from embossed polymer and other parameters, like aspect ratio, thickness, etc. Figures 2(b) - (d) and Figure 3 present the various morphologies of the hybrid microtubes fabricated with such technique.

In summary, we have developed two novel techniques for the incorporation of micro/nano periodic structures onto microtubes by rolling up structured membranes from porous alumina template and nanoimprinted polymer, respectively. Moreover, the sizes of periodic structures on the tubewalls are ranging from nano to micro scale and initially controlled by the parameters of asanodized porous alumina template and imprinted pattern and further tuned in the subsequent deposition processes. Such complex 3-D microtubes with well defined

¹ Mei Y. F., Huang G. S., Solovev A. A., et al. Advanced Materials. 20: 4085, 2008.

nanostructured surfaces are expected to have specific electrical, optical and mechanical characteristics and find broad applications in micro/nano electronics, mechanics, optics and fluidics, such as supercapacitors, microsprings and metamaterials, etc.



Figure 1. (a) The fabrication *flow:* HfO₂ was deposited onto the alumina template with highly ordered pores (i) by ALD technique (ii). 10 nm Ti and 10 nm Cr were evaporated via Ebeam evaporation (iii). After rinsed in KOH solution for several minutes, the stacked layers will be released from the substrate and roll into microtube (iiii). (b) The SEM images: The image clearly shows the nanotube array on the outer surface of microtube. The inset magnified the microtube wall to present the nanotube array. The scale bar in the inset is 200 nm.

Figure 2. (a) *The fabrication process:* After pattern transferred from imprint template, 20 nm Au was deposited and then rolled into microtube using acetone to selectively remove the polymer. Microtubes with different periodic structures are shown in (b), (c), (d). The scale bars are 20 µm.

Figure 3. The SEM images of wrinkling surface, resulting from incomplete rolling process, with dot array (a) and rolled up tube with pore array (b) on the tube-wall.