Supporting information

Multisegmented Nanotubes by Surface-Selective Atomic Layer Deposition

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Experimental details

Electrochemical anodization: The first cylindrical pores were produced by a two-step anodization method. High purity aluminum foils (99.999% Goodfellow, UK) were degreased by sonication in acetone followed by ethanol. The samples were polished electrochemically with a mixture of perchloric acid/ethanol (1 : 3 vol. %). The foils were first anodized at 195 V in 0.1 wt. % phosphoric acid solutions at 0.5 °C for 16 h. Then, the anodized layers were removed in a mixture of 6 wt. % H$_2$CrO$_4$ and 1.8 wt. % H$_3$PO$_4$ in water at 45 °C for 48 h. The second anodization was done in the same conditions as the first one for a desired time. The pore widening was proceeded in 10 wt. % phosphoric acid solutions at 45 °C, when needed for barrier layer thinning. Upon the growth of organic or inorganic overlayers, the continuous anodization processes used the same conditions.

Self-assembled monolayers: n-octadecyltrichlorosilane (OTS, 98%, Aldrich) was commercially available and was used without further purification. The porous templates with or without the overlayers were plunged into a vessel of anhydrous toluene solutions containing OTS molecules (1 vol. %). These molecules formed SAMs on the entire areas of the hydroxylated surfaces in the following reactions: 
\[
\text{RSiCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{RSi(OH)}_3 + 3\text{HCl}; \\
\text{RSi(OH)}_3 + 3(\text{MSOH}) \rightarrow 3(\text{MSO})\text{SiR} + 3\text{H}_2\text{O},
\]
where R = CH$_3$(CH$_2$)$_{17}$, and MS represents surface metal.

Atomic layer deposition: Amorphous TiO$_2$ and ZrO$_2$, and polycrystalline ZnO were deposited at 120 °C where titanium(IV)isopropoxide (99%, Aldrich), tetrakis(ethylmethylamino)zirconium(IV) (99%, STREM, US), and diethylzinc (99%, STREM, US) were used as metal containing reactants preheated at 70, 80, and 25 °C, respectively. Water vapor was used as oxygen source. Dried N$_2$ was used as carrier and purging gas. In typical ALD reactions, an exposure-mode protocol was applied where a full ALD cycle is consisting of 2 s pulse, 20 s waiting, and 60 s purging using commercial ALD reactors (SAVANNAH 100, Cambridge NanoTech Inc. USA for TiO$_2$ and ZnO, and TFS 200, Beneq, Finland for ZrO$_2$). The reactions respectively for TiO$_2$, ZrO$_2$, and ZnO are as followings: 
\[
\text{Ti(OPr)}_4 + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{OPrOH}; \\
\text{Zr(EnMe)}_{4+} + 2\text{H}_2\text{O} \rightarrow \text{ZrO}_2 + 4\text{HNMeEt}; \\
\text{ZnEt}_2 + \text{H}_2\text{O} \rightarrow \text{ZnO} + 2\text{EtH}.
\]
Scheme S1. Full schematic depiction of fabrication procedures for realizing multisegmented nanotubes/nanopores by sequential surface modification through nanopores. Clockwise, a) anodized cylindrical nanopores on aluminium, b) formation of octadecyltrichlorosilane self-assembled monolayers (OTS-SAMs) on alumina surfaces, c) further anodization of the underlying Al, d) atomic layer deposition (ALD) of desired inorganic layers such as TiO$_2$, ZnO and ZrO$_2$, e) anodization, f) coating of OTS-SAMs, g) anodization, h) ALD, i) anodization, and j) ashing of organic layers. Light gray (porous alumina), dark gray (aluminium), pink (OTS-SAMs), and blue (ALD layers), where 100% transparency in pink onto blue segments is rendered in order to reveal the underlying layers.
**Figure S1.** Cross-sectional SEM images of ~12 nm-thick TiO$_2$-coated alumina templates (a) before and (b) after carrying out additional anodization processes in 0.1 wt. % phosphoric acid solutions at 195 V for ~1 h, which are the same experimental conditions used for the template fabrication and expected to grow the pores following the original ones up to ~3.5 micrometers. The results show that no anodization took place, by demonstrating the increased incubation time by a factor of more than 10 (typical value for phosphoric acid anodization, several minutes), and that the sample is in the nucleation stage at the growing front as marked as yellow arrows.

**Figure S2.** Cross-sectional SEM of the resulting structures (equivalent to Scheme 1e in the main text) when employed thick ALD layers e.g. ~12 nm-thick TiO$_2$. The composite layers consisting of 12 nm-thick TiO$_2$ and 180 nm-thick Al$_2$O$_3$ increased their dielectric strength for electrochemical breakdown compared to that of alumina itself, leading to the formation of several localized nuclei per pore at their growing front with boosted incubation time as explained in Fig. S1, and to multiple-branched growth along each pore (around middle parts in the above micrograph).
Figure S3. Another route to beat the thickness limit for inorganic segments. The dielectric strength of the composite TiO$_2$ + Al$_2$O$_3$ layers could be reduced even by increasing the thickness of TiO$_2$ from 7 nm up to 20 nm at decreased Al$_2$O$_3$ thickness from 180 nm down to 100 nm, for example. Upon anodization across the composite layers, the resulting structures and the continuity of pores were visualized by coating with 5 nm ZrO$_2$ and dissolving the templates: (a) low- and (b) high-magnification SEM of ZrO$_2$ core - TiO$_2$ sheath segmented tubes. The widening processes for thinning the barrier layers also resulted in the changes in the diameter of segmented nanotubes, as distinguishable between bright and dark segments.

Figure S4. Low-magnification SEM of OTS-SAMs/TiO$_2$/OTS-SAMs/TiO$_2$ segmented nanotubes/pores.
Figure S5. (a) Quantitative energy dispersive x-ray (EDX) elemental analysis of OTS-SAMs/TiO$_2$/OTS-SAMs/TiO$_2$ segmented nanotubes/pores in the area of Fig. 3c (also the right-side panel, bright-field TEM). (b) Their EDX maps: left – a scanning tunneling electron micrograph; right – each color respectively indicates the presence of titanium (red spots), aluminum (green spots), and oxygen (blue spots) elements, as depicted in the central illustration. The results are in an excellent agreement as expected, indicative of the good site-selectivity for TiO$_2$ ALD during the entire segmentation processes.
Figure S6. (a) Low- and (b) high-magnification SEM of ZrO$_2$/TiO$_2$/ZrO$_2$ segmented nanotubes, having ~200 nm-long TiO$_2$ nanotubes as the middle segments, one of the smallest segments prepared to date in our laboratory.