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Heterogeneous Inorganic Acid/Organic Acid-salt Reaction inside Anodic Aluminum Oxide Templates

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Reaction of gaseous HCl with Eosin-Y disodium salt (Eosin-Y•2Na) nanorods nested inside anodic aluminum oxide templates (AAO), produced perforated Eosin-Y free acid (Eosin-Y-FA) nanorods with surface nanoholes on the order of 50 nm in diameter. Diffusion of different acids yielded different surface patterns with retention of the overall nanorod structure. Also, different pattern formation was observed for different templated organic acid salts/inorganic acid interactions.

We have shown that it is possible for one reactant 1,2,4,5-tetracyanobenzene (TCNB) to diffuse inside AAO-templated 9-methylanthracene (9-MA) nanorods to produce highly crystalline 1:1 cocrystals (TCNB/9-MA) with retention of nanorod morphology.[1] But, can we move beyond the solid nanorod morphology and design nanorods with nanopatterns on the surface via heterogeneous diffusion?[2] Formation of hole patterns on 200-nm diameter polymer nanotubes was previously observed when PMMA nanotubes embedded inside AAO templates were heated above their T_g.[3] A similar pseudo hole pattern formation was observed on inorganic silica nanotubes prepared by passing tetraethoxysilane sol through an AAO template.[4] This hole pattern formation contributed to Rayleigh instability inside the alumina nanopores. Hole patterns were also individually drilled on a single pentacene nanotube using FIB lithography.[5]

An interesting hole pattern formation was observed when AAO-templated nanorods of the organic salt compound Eosin-Y•2Na were allowed to react with HCl gas via a heterogeneous reaction (gas/solid reaction).[6,7] Strong acids such as HCl react with the Eosin-Y•2Na to protonate the oxide anion and yield Eosin-Y free acid (Eosin-Y-FA) and an inorganic ionic salt NaCl. The type of ionic salt produced depends on the inorganic acid/organic-salt reaction (Figure 1).

Eosin-Y•2Na nanorods were grown inside AAO templates with 200-nm pore diameter using solvent annealing.[8] It was previously shown that solvent-annealing organic compounds inside AAO templates yields crystalline molecular crystal nanorods.[8] After solvent annealing, cubic crystals of EosinY•2Na formed on the surface of the template. The surface crystals were polished off using fine sand paper (Supporting Information 1).[10] A sample of the polished template was crushed and viewed

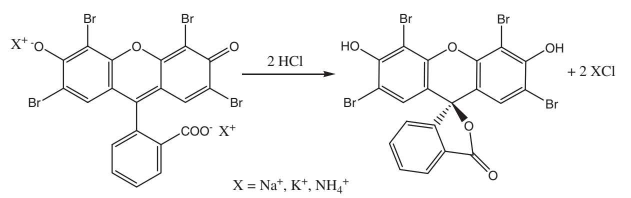

Figure 1. Chemical structure and general reaction of Eosin-Y•2Na.

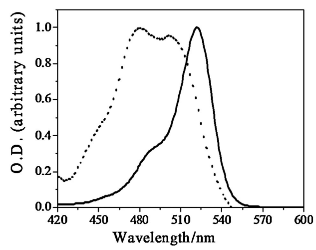

Figure 2. Normalized spectra of Eosin-Y•2Na (solid line) and Eosin-Y-FA (dotted line) in methanol.

under an SEM to reveal the presence of solid EosinY•2Na clogging the AAO nanopores (Figure S1a).[10] Gravimetric analysis of the loaded AAO template suggested full packing of the nanopores.

When templated Eosin-Y•2Na nanorods were suspended in an atmosphere of dry HCl gas, the acid slowly diffused inside the 55-µm thick template, from either end, converting the Eosin-Y•2Na to Eosin-Y-FA and NaCl. UV–vis absorption spectra of the material inside the template, in an appropriate solvent, confirmed the complete conversion of the Eosin-Y•2Na to Eosin-Y-FA as shown in Figure 2.

FTIR spectra of the before and after are shown in Figure S1b.[10] The conversion was monitored gravimetrically showing the absorption of two equivalents of HCl (±4%) per one equivalent of EosinY•2Na (Supporting Information 1).[10] The polished surface of the Eosin-Y•2Na-loaded template was observed under an SEM to reveal the formation of nanometer sized crystals of NaCl. Formation of NaCl crystals was similar to those formed on the surface of microcrystals of Eosin-Y•2Na after a brief exposure to HCl gas (Figure S2).[10] Washing the surface of the HCl-exposed Eosin-Y•2Na microcrystals with water resulted in a pitted surface with nanoholes replacing the dissolved NaCl crystals (Figure S3).[10] When the HCl-treated AAO template was dissolved with 50% H_3PO_4, Eosin-Y-FA nanorods were liberated. Upon closer inspection, the surface of these nanords was perforated with random sized elliptical holes on the order of 50–70 nm in diameter, as shown in Figure 3b (Figures S4a–S4e).[10] These holes were not deep or wide enough to cause the nanorod to fragment. Because the tips of the liberated nanorods were semitubular (Figure 3c), it was thought that the perforated nanorods were hollow along the whole nanorod length (bamboo flute). Porosity of the Eosin-Y-FA nanorods was tested by placing the water-washed template containing Eosin-Y-FA nanorods on a glass frit funnel. Suction was applied and water was added to the surface of the template. Not a single drop of water passed through, thus proving that the Eosin-Y-FA-perforated nanorods were not continuously hollow

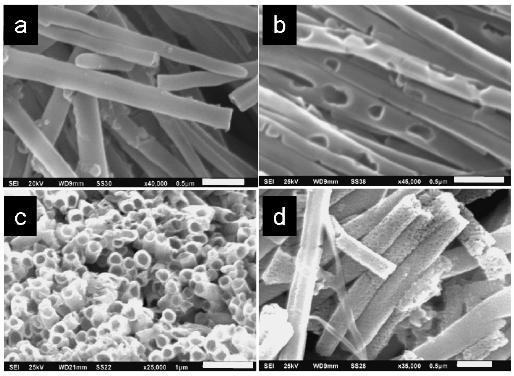

Figure 3. a) Eosin-Y-FA solvent-annealed nanorods. b) Perforated Eosin-Y-FA nanorods from HCl gas diffusion. c) Top view of Eosin-Y-FA nanorods with holes on top. d) Eosin-Y-FA nanorods from 50% H_3PO_4. Scale bar: $a = 0.5\,\mu m$, $b = 0.5\,\mu m$, $c = 1\,\mu m$, and $d = 0.5\,\mu m$.

all the way through. Similar but smaller holes (ca. 20 nm) were observed when HI gas was used instead. When concentrated aqueous HCl (38%) solution was used instead of HCl gas a similar result to HCl gas was observed. On the other hand, using dilute HCl (0.005 molar) the Eosin-Y•2Na diffused out of the template and precipitated in solution as the free acid form. Reacting templated Eosin-Y•2K nanorods with HCl gas (Figures S5a–S5c),[10] we noticed less perforation in the nanorods, and the surface was less smooth and segmented. We tested different acid interaction on the templated Eosin-Y•2Na nanorods. Allowing 50% aqueous H_3PO_4 to diffuse from one side while slowly etching out the alumina template, we observed the formation of smoother but brittle nanorods. Upon closer inspection we noticed that the tip of the nanorod starts smooth and gradually segments as shown in Figure 3d (Figures S6a–S6c).[10] Using concentrated H_2SO_4 (50%) yielded perforated nanorods much similar to those produced by HCl gas. We wanted to test whether Eosin-Y-FA will form solid nanorods using the typical solvent-annealing method or whether hole formation was an intrinsic property of Eosin-Y-FA nanorods. A sample of Eosin-Y-FA was solvent-annealed in THF at room temperature. Surface crystals were polished off and the template was suspended in dry HCl, then the template was etched out using 50% H_3PO_4. The results confirmed that solvent-annealed Eosin-Y-FA forms smooth nanorods as shown in Figure 3a (Figures S7a and S7b).[10]

A possible application of perforated Eosin-Y-FA might be in capturing drug nanoparticles of certain size inside the nanopores, thus forming a composite speckled nanorod. A more subtle application is in pH sensing of acid or base gases.[9] EosinY•2Na and Eosin-Y-FA are weakly fluorescent in the solid state. Instead, absorption spectrum of the nanorods was investigated under different conditions. When a suspension of porous Eosin-Y-FA nanorods in acidic water was passed over a peace of silanized glass, the hydrophobic glass surface was covered with a layer of Eosin-Y-FA nanorods.[4] The layer appears colorless and gives a broad absorption spectrum ($\lambda_{max} = 512$ nm). Upon exposing the slide to dry ammonia gas the layer becomes visibly red with the absorption spectrum doubling in intensity and shifting to the red ($\lambda_{max} = 573$ nm). This process can be reversed by adding HCl gas. The process can be cycled several times without any apparent fatigue (Figure S8b).[10] Upon closer inspection of the cycled nanorods, we notice the formation of a thin layer of NH_4Cl on top of the nanorod thus increasing its diameter by several folds (Figure S9).[10]

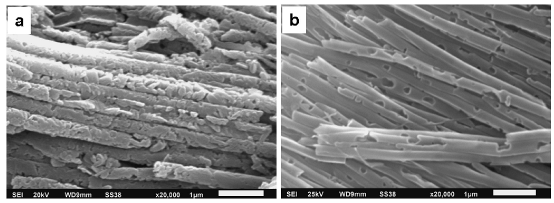

Figure 4. a) SEM of 9AC segmented nanorods. b) Perforated Eosin-Y-FA nanrods. Scale bar: $a = 1\,\mu m$ and $b = 1\,\mu m$.

To test whether the phenomena of nanorod pore formation can be repeated inside AAO templates with smaller pores, we solvent-annealed EosinY•2Na inside 80-nm pore AAO template. Exposure to HCl gas did not yield perforated nanorods, instead, shapeless fragments and slivers resulted after etching out the AAO template.

Heterogeneous HCl gas diffusion applies to other organic acid salts as well. Ammonium salt of 9-anthracenecarboxylate was solvent-annealed inside AAO templates using ethanol. Treatment with HCl resulted in segmented 9-anthracenecarboxylic acid (9AC) nanorods (Figure 4a) instead of the perforated morphology obtained for EsinY•2Na as shown in Figure 4b (Figures S10a and S10b).[10]

Reaction of a strong acid (HCl, HI, and H_3PO_4) with templated Eosin-Y•2Na nanorods causes phase separation between the organic Eosin-Y-FA and the inorganic salt. The mechanism of formation of the pores is still an open question. It is possible that the ionic character of the alumina can cause the NaCl crystals to migrate to the edges where they form seeds and then that these crystals are washed away with water leaving behind holes, similar to what was observed at the surface of the microcrystals. This technique can pave the way for new methods for texturing nanopatterns on nanowires, thus increasing the surface area of a nanostructure while retaining the overall nanorod form.

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10 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

