Formation of Porous Cerium Oxide Membrane by Anodization

Supplemental Information

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Figures referenced in the communication.

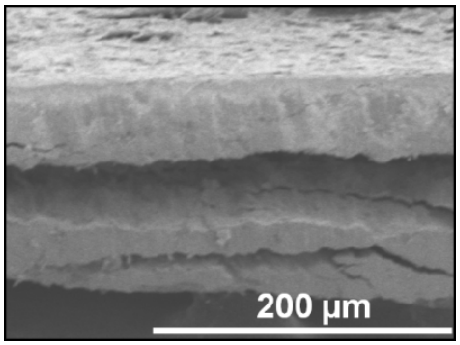

Figure SI-1 Cross-sectional SEM image of a ceria porous membrane after calcination at 400 ˚C.

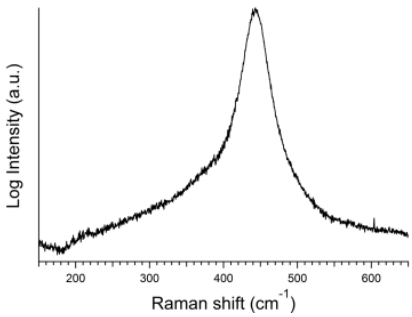

Figure SI-2 Raman scattering spectrum of an anodized ceria membrane calcined at 400 ˚C.

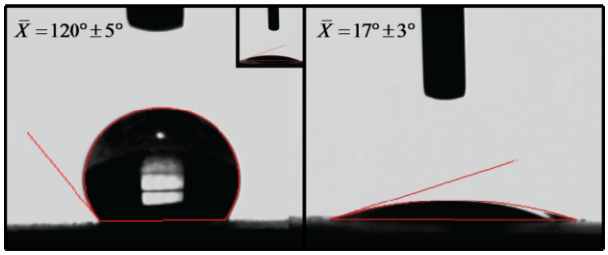

Figure SI-3 Optical images showing water contact angle measurements on (left) an anodized porous ceria membrane and (right) an cerium oxide surface formed on a piece of cerium metal oxidized under ambient conditions. (Inset) Water contact angle measurement on an anodized porous ceria membrane with its "ribbon-like" structures destroyed by sonication in ethanol. The measured water contact angle on this surface is 31 ± 3˚.

Experimental details

Materials:

All water used in this experiment was Ultrapure water (Millipore Corporation, Billerica, MA) of > 18 MΩ resistivity and filtered with 0.22 μm membranes. Cerium metal foils (0.25 mm thick, 99.9%) for the anodization experiment were purchased from Alfa Aesar, Ward Hill, MA). These foils were polished with 1-μm diamond grit (BUEHLER, Lake Bluff, IL) before use. Ethylene glycol (99.5 % Sigma Aldrich, Milwaukee, WI) and ammonium hydroxide (29.56 % aqueous solution, FisherScientific, Fair Lawn, NJ) were used in the preparation of the electrolytes.

Synthetic method:

Cerium metal foil was first cut into 1 cm x 1cm squares and polished with 1-μm diamond grit until a mirror-like finish was achieved. The samples were sonicated in acetone for 15 min. to remove any remaining diamond grit particles, and then dried with nitrogen. The dry samples were anodized in a two-electrode cell with the cerium foil as the anode and a 1 cm × 1 cm platinum foil as the cathode. To prevent the alligator clips holding the cerium anode from contacting the electrolyte, a piece of bent w-shaped platinum (Pt) foil was used to protect the cerium metal foil. The electrolyte solution was composed of ethylene glycol, ammonium hydroxide and water in ratios adjusted for each set of experimental conditions. The anodization was accomplished by applying a constant current of 100 μA with a source meter (Keithley 2410, Keithley Instruments Inc. Cleveland, OH) for 160 h. The membrane was considered to be fully anodized once the applied potential at 100 μA reached the limit of the source meter (1000 V). The membrane was then rinsed thoroughly with ethanol, dried under a nitrogen stream and immersed in a 100 mL ethanol bath for 12 h. The ethanol bath was gently stirred to facilitate the removal of remaining traces of electrolyte from the membrane structures. Afterwards, the sample was dried in a gentle stream of dry nitrogen. Conversion of the as-anodized membrane samples into cerium (IV) oxide was achieved by calcination at 400 °C for 2 h. under a flow of 100 SCCM dry air inside a 1" quartz tube vacuum furnace at 0.12 Torr. The temperature of the furnace was increased at a rate of 0.5 °C/min. so as to control the calcination rate of the structures and to promote gentle evaporation of any remaining solvent.

Sample characterization method:

The morphology of the processed samples was investigated by field emission scanning electron microscopy (FE-SEM, Hitachi S4700, Hitachi High Technologies America, Inc., Pleasanton, CA). The crystal structures of the samples were studied by Rigaku D/Max-B diffractometer equipped with Cu Kα X-ray source of average wavelength 1.544 Å (Rigaku America, The Woodlands, TX). Confocal Raman microscopy on the samples was performed with a HR800 confocal Raman microscope (Horiba Scientific, Kyoto Japan, LabRAM) using a 20 mW 632.8 nm He-Ne laser. Water contact angle measurements on the samples were performed using 0.25-μL droplets of Ultrapure water with a video contact angle analysis equipment (VCA Optima, AST Products, Inc., Billerica, MA). The AST software was used for the contact angle measurements in the recorded optical images.

The calculation of the surface area fractions from top view SEM images of the porous ceria membranes was accomplished using the NIH software package Image-J.[1] For a typical top view SEM image of a porous ceria membrane (Figure SI-4a), the ridges between the pores are shown as the light shaded areas whereas the pores (cavities) are shown as the dark shaded areas. When a water droplet is

dispensed on the porous membrane, the portion of surface area in contact with the water is composed of the ridges and upper portions of the pore structures. The Image-J software allows setting of a relative threshold brightness ratio between the structures with different shades in the SEM images (Figure SI-4b) and converts all the apparent pore area to appear as white and the rest as black. The process was automated using Image-J's built in scripting language as illustrated in Program 1 for our contact surface area estimation (See below). Following the conversion of the image into white areas (non-contact pore) and black areas (possible water contact surface area), Image-J calculates and reports these two apparent surface areas. The mean surface area fraction which describes the fraction of apparent surface area possibly in contact with a water droplet is estimated to be 0.51 ± 0.03. Owing to the irregularity of the ceria membrane surface structures, this mean surface area fraction is likely to be underestimated using this apparent surface area estimation method. Nonetheless, visual inspection appears to match this estimated value.

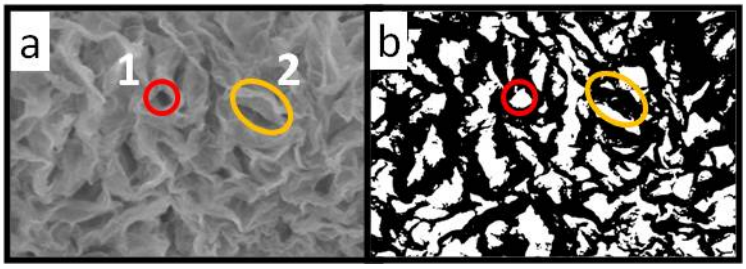

Figure SI-4 (a) Top view SEM image of ribbon-like nanostructures as imaged. Circle1 (red) is an example of a pore. Ellipsoid 2 (yellow) is a model ridge of the ribbon-like structures. (b) Processed SEM image with Image-J. The pores are represented by the white areas whereas the ridges between the pores are represented by the black areas.

Program 1 – Calculate the area on nanoribbons

```
// "Calculate the area on Nanoribbons"
//
// This script will batch process the .tif images in a given folder and subfolders
// and will calculate the ratio of the area of the ribbon edges to the area of the pore.
// This is accomplished by converting the image to binary (black and white) and reporting
// the percentage of the area that is above the threshold for conversion to black.
// the threshold level can be set manually if the contrast of the original image is too low.
//
// This macro batch processes all the files in a folder and any
// subfolders in that folder.

  requires("1.33s");
  dir = getDirectory("Choose a Directory ");
  sav = getDirectory("Choose a Save Directory ");
  setBatchMode(true);
  count = 0;
  countFiles(dir);
  n = 0;
  processFiles(dir);
  print(count+" files processed");
```

```
    function countFiles(dir) {
      list = getFileList(dir);
      for (i=0; i<list.length; i++) {
        if (endsWith(list[i], "/"))
          countFiles(""+dir+list[i]);
        else
          count++;
      }
    }
    function processFiles(dir) {
      list = getFileList(dir);
      for (i=0; i<list.length; i++) {
        if (endsWith(list[i], "/"))
          processFiles(""+dir+list[i]);
        else {
          showProgress(n++, count);
          path = dir+list[i];
          processFile(path);
        }
      }
    }
    function processFile(path) {
      if (endsWith(path, ".tif")) {
  //main function
        open(path);
          run("Make Binary");
          run("Analyze Particles...", "size=0-Infinity circularity=0.00-1.00 show=Masks display
clear summarize");
          done = sav+"done_"+list[i];
          saveAs("Tiff", done);
      }
    }
```

Reference

1. W. S. Rasband, U.S. NIH http://rsb.info.nih.gov/ij/.