

Supplemental Information

Conformal coating of nanoscale features of microporous Anodisc™ membranes with zirconium and titanium oxides

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General considerations:

Zirconyl nitrate (35% wt. in dilute HNO₃) and dipotassium ethylenediaminetetraacetic acid were purchased from commercial sources and used without further purification. Polyethyleneimine (PEI) was purchased from BASF Corporation of Clifton, NJ and used without further purification. The titanium solution was prepared according to literature procedures.¹ Porous alumina membranes (Anodisc™) with a nominal pore diameter of 0.2 μm were obtained from Whatman™. All water was purified using a Milli-Q water treatment system. Ultrafiltration was carried out using Amicon stirred cells and 10000 molecular weight cut off flat cellulose filter disks (PM10) under 60 psi nitrogen pressure.

Metal analysis of solutions:

Metal analysis was conducted on a Varian Liberty 220 Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES), following the standard SW846 EPA (Environmental Protection Agency) Method 6010 procedure. Metal standards were matrix-matched to the sample type by adding

the appropriate buffer and polymer concentrations. Metal ion analyses were verified with a QC-19 quality control standards obtained from Plasma Chem.

Preparation of coating solution:

Dipotassium ethylenediaminetetraacetic acid (1.00 g, 2.47 mmole) was dissolved in 30 mL of water. Zirconyl nitrate (2.00 g, 3.02 mmole) followed by polyetheleneimine (1 g) were added and the reaction mixture stirred. The resulting solution was clear and had a pH of 8.0. This solution was placed in an Amicon filtration unit containing a PM10 filter designed to pass materials having a molecular weight < 10,000 g/mol and washed twice with water. The final viscosity of the solution was measured and found to be 5.3 mm²/s. The final concentration was found to be 250 mM in Zr. A second similar solution was prepared and concentrated further to give a 480 mM Zr solution.

The solution of metal bound polymer was placed as a drop on a glass slide. The AnodiscTM (0.2 µm membrane discs; 14 mm diameter) was then placed on the drop, allowing the solution to wet the membrane completely. Excess solution was removed by pulling the membrane across the glass slide. This was repeated after inverting the membrane. The AnodiscsTM were baked in a Thermolyne 48000 furnace by ramping to 120 °C at 1 °C/min, followed by a 30 min dwell, ramping to 350 °C at 2 °C/min, followed by a 30 min dwell, ramping to 450 °C at 2 °C/min, followed by a 360 min dwell, and finally stepping back to room temperature. All heating was done under an atmosphere of air.

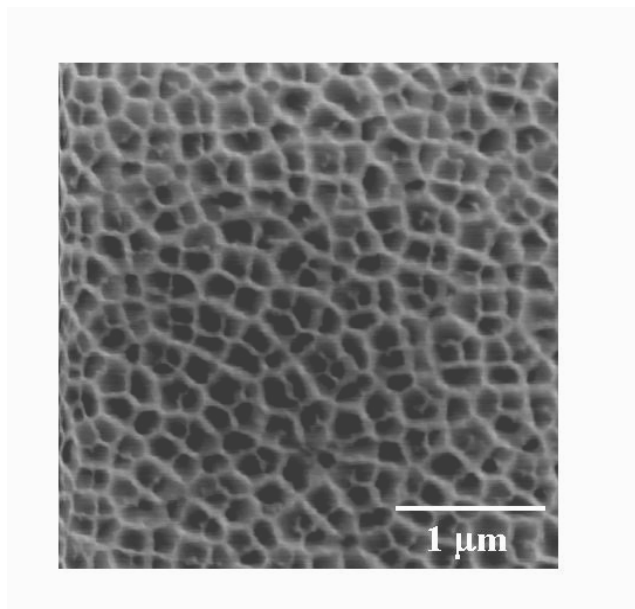
Micro X-Ray Fluorescence (MXRF) of Films:

X-ray excitation and detection were performed using either a Horiba Ltd. (Kyoto, Japan) micro X-ray fluorescence system or an EDAX Eagle II (EDAX, Mahwah, NJ), both of which have a Rh target excitation source and a Si detector. The Horiba has an X-ray source that is equipped with an X-ray guide tube enabling a 10 µm nominal X-ray spot size. X-ray tube operating conditions were maintained at 50 kV and 400 µA. The Eagle II has a polycapillary focusing optic which enables increased

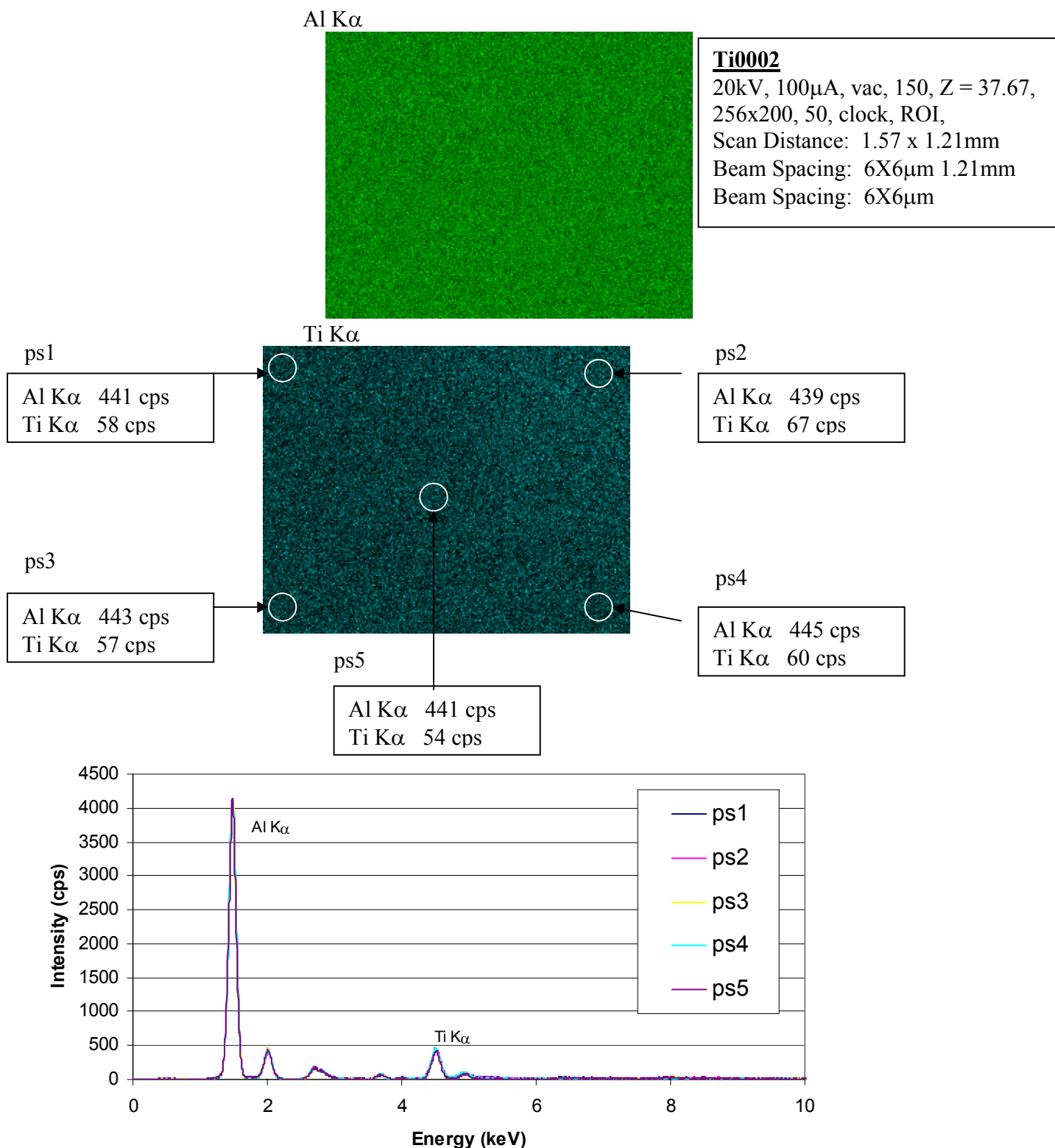
sensitivity but with a larger (50 μm) spot size. X-ray tube operating conditions were maintained at 20 kV and 100 μA . The sample was either analyzed as is (EDAX) or sandwiched between two pieces of tape and then cut to expose an internal surface of the membrane (Horiba). The membrane was then mounted perpendicular in the instrument. Confocal MXRF (XOS Inc. Greenbush, NY) was used to obtain a depth profile of the sample. This system has a Ag target excitation source and an EDS detector. Both the X-ray source and the detector were equipped with a polycapillary focusing optic having a 30 μm nominal X-ray spot size. The membrane was mounted horizontally in the instrument and a 1 mm^2 area analyzed.

SEM of Films:

The ZrO_2 and TiO_2 coated samples were analyzed by a Hitachi-800 Field-Emission Scanning Electron Microscope (SEM). The microscope was equipped with a PGT Energy Dispersive Spectroscopy (EDS) system for compositional analysis.

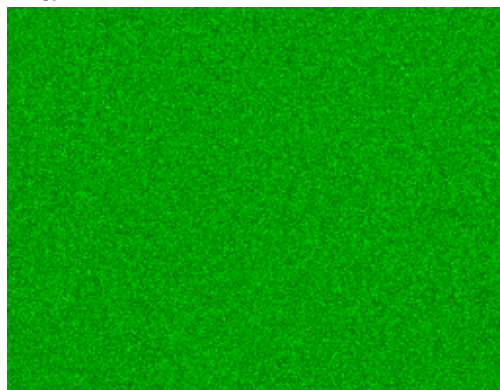


S1: SEM of membrane ZrO_2 coated twice from a 480 mM Zr solution.



S2: Top: MXRF of elemental aluminum spectral image of the Anodisc™. Middle: MXRF of elemental Ti (211 mM; 1 coat) spectral image of the Anodisc™. Bottom: Overlay of the MXRF spectrum from the five points from Ti coated membrane.

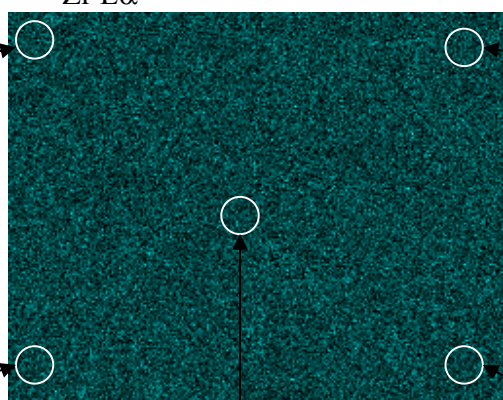
Al K α



Zr001 - Thin

40kV, 300 μ A, vac, 150, Z=37.67,
256x200, 50, clock, ROI,
Scan Distance: 1.57 x 1.21mm
Beam Spacing: 6X6 μ m 1.21mm
Beam Spacing: 6X6 μ m

Zr L α



ps1

ps2

Al K α 1574 cps
Zr L α 100 cps
Zr K α 64 cps

Al K α 1534 cps
Zr L α 103 cps
Zr K α 63 cps

ps3

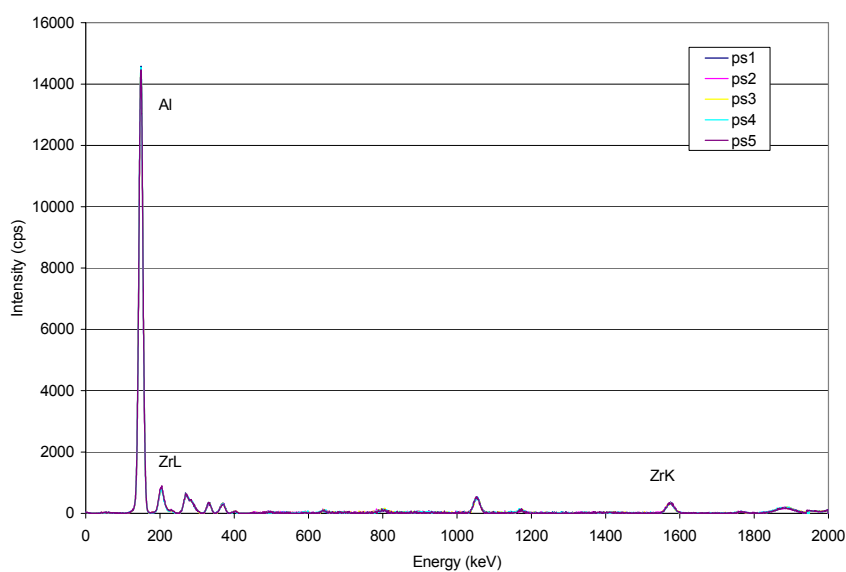
ps4

Al K α 1583 cps
Zr L α 96 cps
Zr K α 60 cps

Al K α 1583 cps
Zr L α 93 cps
Zr K α 58 cps

ps5

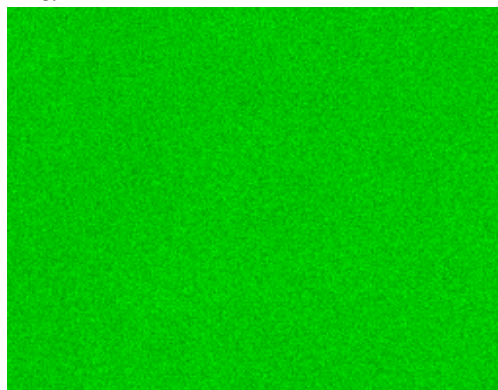
Al K α 1574 cps
Zr L α 105 cps
Zr K α 63 cps



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S3 (previous page): Top: MXRF of elemental aluminum spectral image of the Anodisc™. Middle: MXRF of elemental Zr (250 mM; 1 coat) spectral image of the Anodisc™. Bottom: Overlay of the MXRF spectrum from the five points from Zr coated membrane.

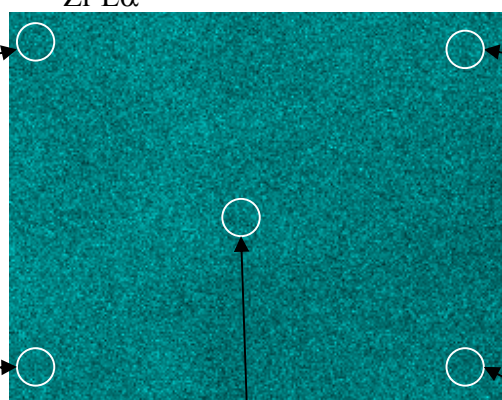
Al K α



Zr002 - Thick

40kV, 300 μ A, vac, 150, Z=37.67
256x200, 200, clock, ROI,
Scan Distance: 1.57 x 1.21mm
Beam Spacing: 6X6 μ m 1.21mm
Beam Spacing: 6X6 μ m

Zr L α



ps1

ps2

Al K α 1452 cps
Zr L α 169 cps
Zr K α 115 cps

Al K α 1450 cps
Zr L α 163 cps
Zr K α 112 cps

ps3

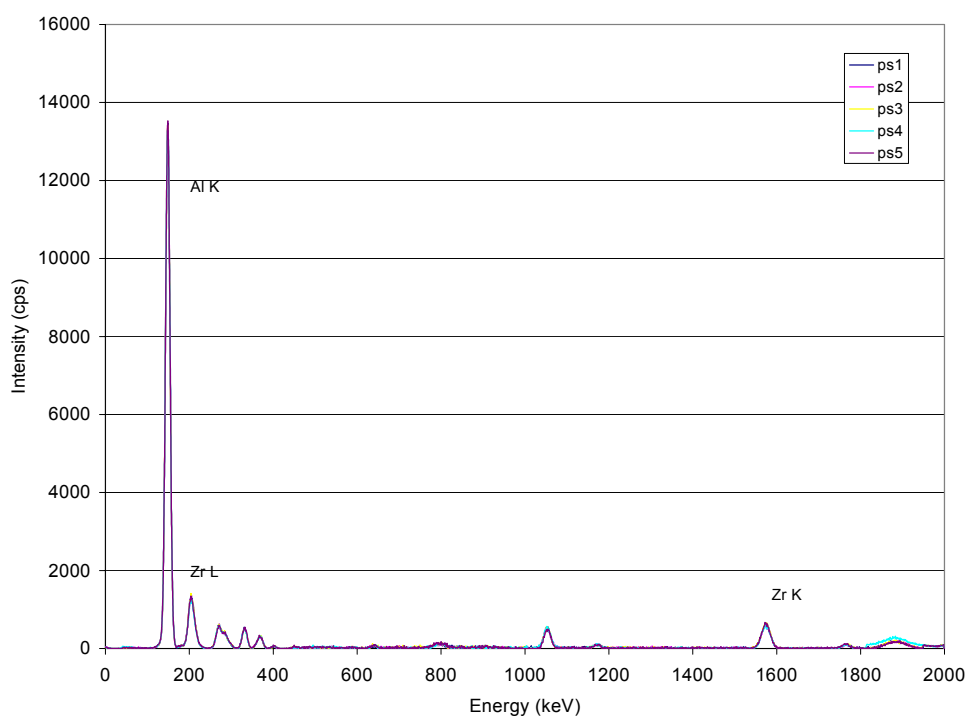
ps4

Al K α 1452 cps
Zr L α 165 cps
Zr K α 121 cps

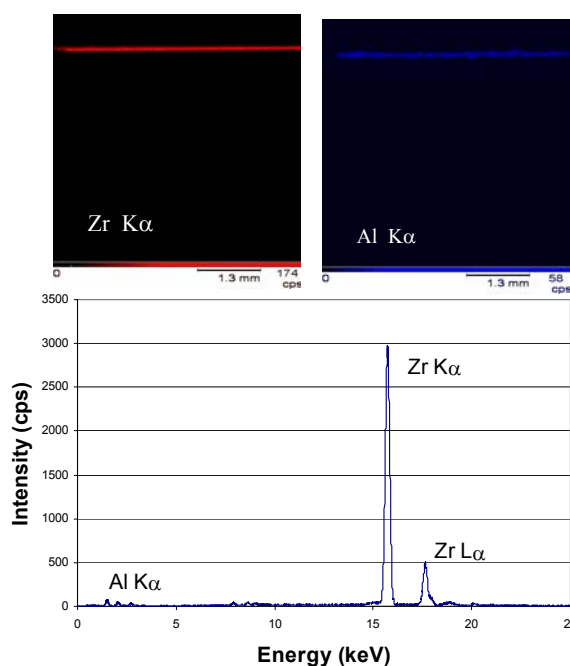
Al K α 1462 cps
Zr L α 155 cps
Zr K α 111 cps

ps5

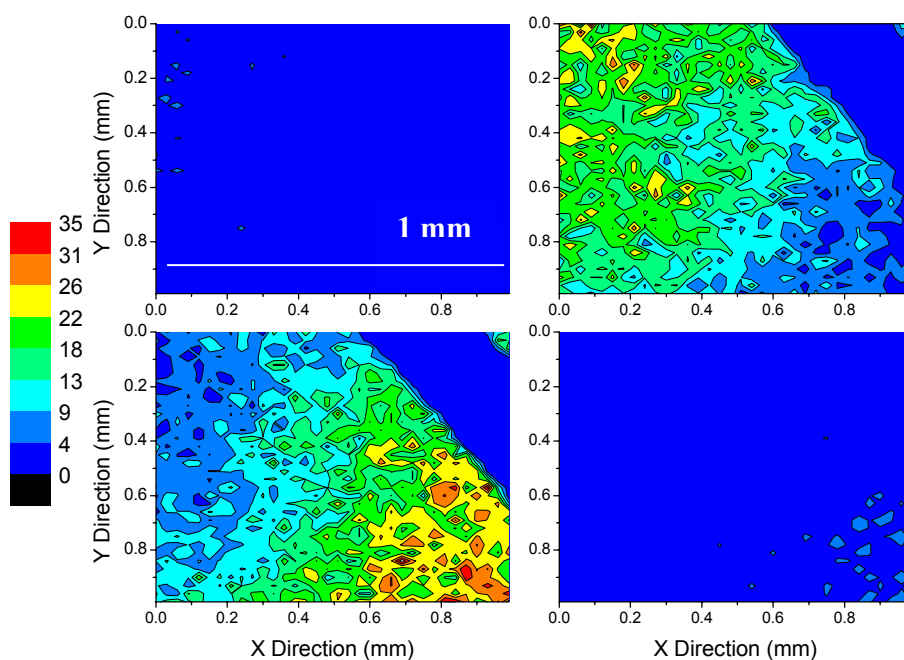
Al K α 1458 cps
Zr L α 163 cps
Zr K α 118 cps



S4 (previous page): Top: MXRF of elemental aluminum spectral image of the Anodisc™. Middle: MXRF of elemental Zr (480 mM; 2 coats) spectral image of the Anodisc™. Bottom: Overlay of the MXRF spectrum from the five points from Zr coated membrane.



S5: MXRF 2D analysis of membrane. 10 μm spot size, 50 kV, 0.4 mA, and integration time 100s.



S6: Confocal MXRF depth profile of Zr in the membrane. 30 μm spot size, 50 kV, 0.5 mA, 50 μm step.
Note: the drop in intensity across the scan at 50 μm and 100 μm is as a result of a bend in the membrane.

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Reference:

1. Jia, Q. X.; McCleskey, T. M.; Burrell, A. K.; Lin, Y.; Wang, H.; Li, A. D. Q.; Foltyn, S. R. *Nature Materials*, **2004**, *3*, 529-532.