

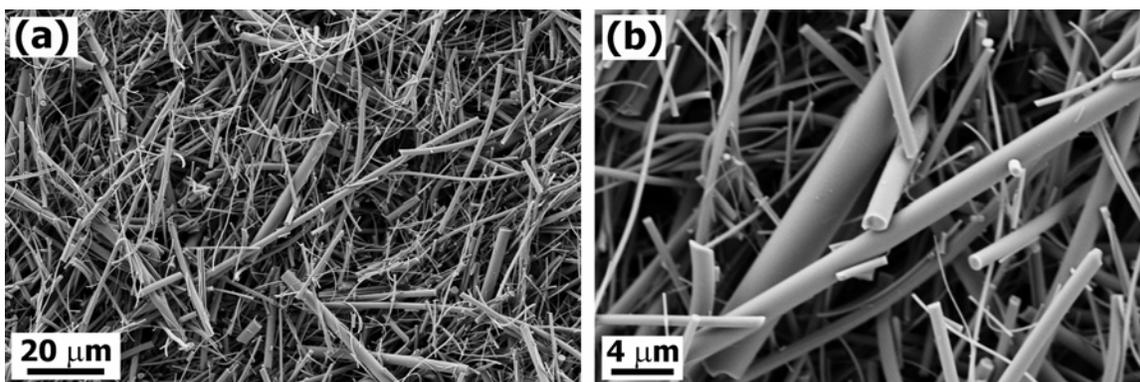
# Making the most of a scarce platinum-group metal: Conductive ruthenia nanoskins on insulating silica paper

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## Supporting Online Information

### Materials and Methods

Lightweight, flexible electrodes were prepared by sub-ambient temperature deposition of ruthenia onto silica fiber paper substrates (Pallflex tissuquartz, Pall Life Sciences). The SiO<sub>2</sub>-fiber substrate, used commercially as a filter for sampling aerosols and acidic gases, Figure S1, has a thickness of ~0.4 mm and is composed of submicron-to-micron diameter fibers of fused SiO<sub>2</sub>. The macroporous voids (100s of nanometers to several micrometers) between the fibers offer ample headspace for facile infiltration by fluids and the deposition of nanoscopic RuO<sub>2</sub> solution-based synthesis.



**Figure S1.** Scanning electron micrographs of as-received SiO<sub>2</sub> fiber paper imaged at different magnification.

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To prepare the precursor solution, two 15-mL aliquots of petroleum ether (Fisher Scientific), pre-chilled for 1 min in a dry ice/acetone bath, are used to extract RuO<sub>4</sub> from a 10-mL aqueous solution pre-chilled to T < 5 °C (0.5 wt% solution, Strem Chemicals). **Hazard warning:** RuO<sub>4</sub> is volatile and rapidly oxidizes skin—handle in a fume hood with standard protective gear. The phase transfer is carried out in ~1 min in order to minimize thermal decomposition of RuO<sub>4</sub>, however a small amount of black RuO<sub>2</sub> precipitate generally forms and is preferentially retained in the aqueous phase. The majority of RuO<sub>4</sub> is transferred into the petroleum ether concurrent with a color change of the organic phase from clear to dark yellow. The equilibration temperature of the petroleum ether–RuO<sub>4</sub> precursor solution with the SiO<sub>2</sub> fiber-paper substrate has been varied resulting in two subambient synthetic strategies: dry ice/acetone bath (subzero) vs aqueous ice bath (sub-ambient). Both methods successfully deposit nanoskins of RuO<sub>2</sub> with nominally similar weight loadings, morphology, and physical properties; however the sub-ambient technique shows greater repeatability than the subzero protocol.

**Sub-ambient synthesis:** After phase transfer, each aliquot of the nonaqueous precursor solution is rapidly mixed with a few mg of MgSO<sub>4</sub> (to remove water), passed through a coarse filter, and collected in a flask held in a dry ice/acetone bath. The nonaqueous solution (from the combined aliquots) is then thermally equilibrated in an aqueous ice bath and decanted into a pre-chilled (aqueous ice bath) glass vial containing a rectangular strip of SiO<sub>2</sub> paper (4.5 cm × 3 cm, ~70 mg) immersed in ~10 mL of petroleum ether. The capped vial is then removed from the bath and held at room temperature overnight (~15 h).

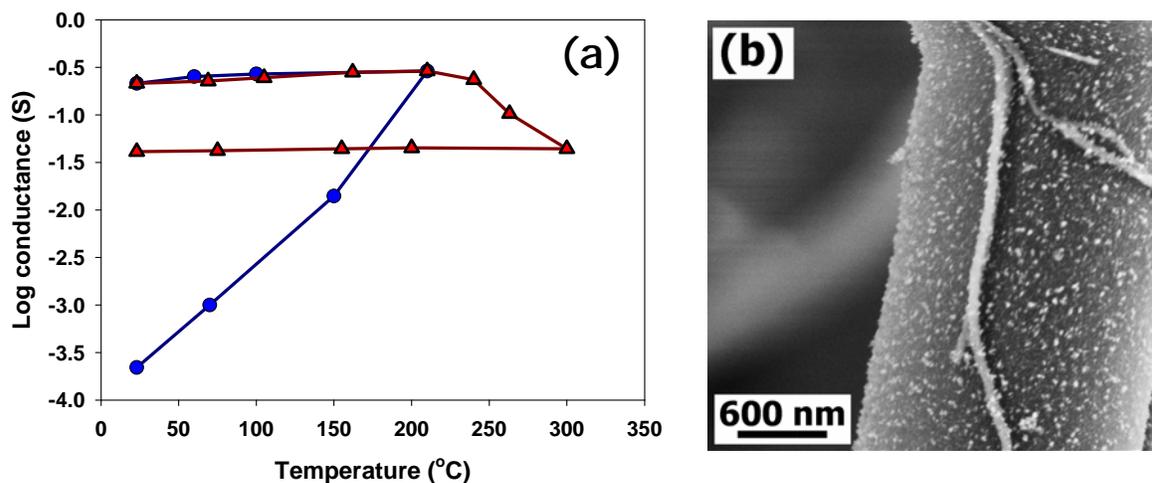
**Subzero synthesis:** The nonaqueous precursor solution is collected in a flask held in a dry ice/acetone bath to allow any transferred water to freeze and settle out of solution. The nonaqueous solution is then decanted into a pre-chilled (dry ice/acetone) glass vial containing a rectangular strip of SiO<sub>2</sub> paper (4.5 cm × 3 cm, ~70 mg) immersed in ~10 mL of petroleum ether. The capped vial is chilled in the dry ice/acetone bath for 45 min allowing RuO<sub>4</sub> to equilibrate with the SiO<sub>2</sub> fibers, and then removed from the bath and held at room temperature overnight (~15 h).

For both methods, decomposition of RuO<sub>4</sub> to RuO<sub>2</sub> occurs slowly after removal from the respective bath leading to an opaque, black solution within 20 to 30 min. After ~15 h at room temperature, the petroleum ether and precipitated RuO<sub>2</sub> are decanted off, and the resultant

$\text{RuO}_2(\text{SiO}_2)$  paper is washed with copious amounts of petroleum ether followed by sonication in petroleum ether for 5 min. The  $\text{RuO}_2(\text{SiO}_2)$  paper is then air dried for 1 to 2 h and dried under vacuum overnight.

## Conductivity

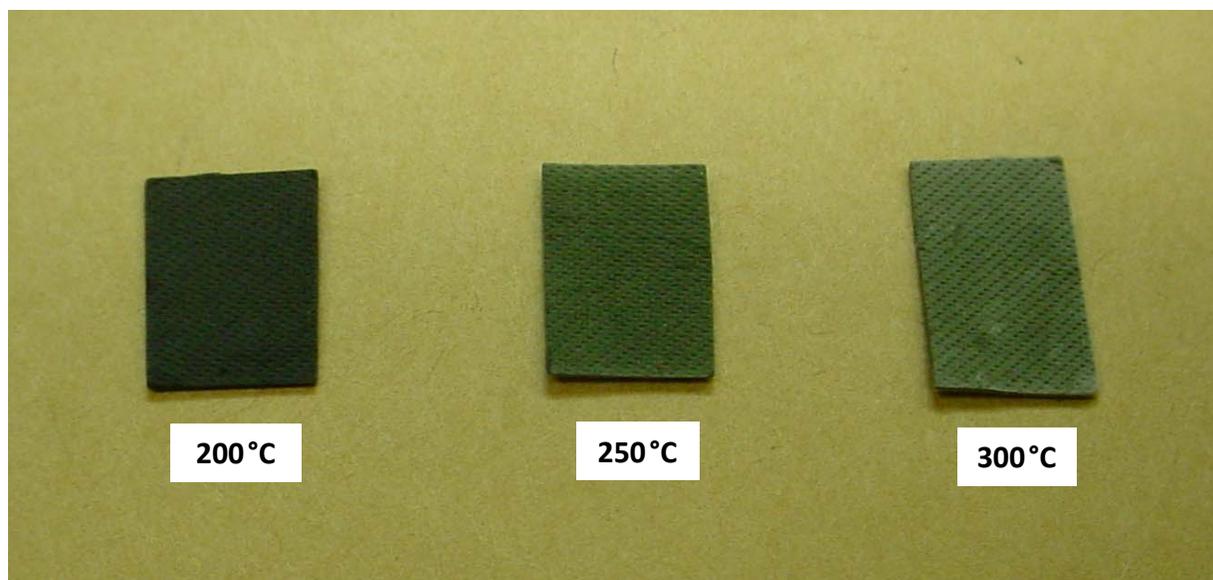
The *in-situ* electrical resistance of an as-prepared  $\text{RuO}_2(\text{SiO}_2)$  electrode was measured in air as a function of temperature from 25 to 200°C in a two-probe cell. A 0.7 cm × 0.7 cm strip of  $\text{RuO}_2(\text{SiO}_2)$  paper was sandwiched between two spring-loaded gold foil electrodes inside a quartz tube and heated with resistive tape powered by a Barnet Company temperature controller. The Au contact leads were welded to the Au foil electrodes and fed to the instrument leads. A thermocouple placed next to the sample regulated the power supply thereby ensuring accurate temperature control at the sample. The resistance of the Au/ $\text{RuO}_2(\text{SiO}_2)$ /Au sandwich was measured with a voltmeter at 25°C intervals after the sample was held for 15 min at each temperature with the exception of 200°C (2-h dwell). The sample was cooled to room temperature after measuring the resistance at 200°C to verify that the increased conductivity achieved upon crystallization is maintained upon cooling.



**Figure S2.** (a) Log conductance vs temperature as measured *in-situ* by a 4-point probe technique for the heating and cooling of an as-prepared  $\text{RuO}_2(\text{SiO}_2)$  paper. Resistance measurements were made 15 min after the sample reached each temperature except for 200 and 300°C, which were held for 2 h and 30 min, respectively. (b) Scanning electron micrograph of a  $\text{RuO}_2(\text{SiO}_2)$  paper calcined to 300°C for 2h. Dewiring of the  $\text{RuO}_2$  nanoskin results in the formation of discrete particles on the  $\text{SiO}_2$  surface with a concomitant thousand-fold loss in electron conductivity.

Additionally, the *in-situ* electrical resistance of an as-prepared  $\text{RuO}_2(\text{SiO}_2)$  electrode was measured in air as a function of temperature from 25 to 300 °C by the four-terminal method of van der Pauw (characteristic data are shown in Figure S2). A rectangular-shaped sample was mounted to a glass slide with cement (Aremco Ultra-temp 516) and copper wire leads were connected to the four corners of the sample with silver conductive epoxy (CW2400, Circuit Works). The slide was placed on a hot plate and a flat-mounted thermocouple was placed next to the  $\text{RuO}_2(\text{SiO}_2)$  to measure the temperature. Current was applied with a Solartron SI1286 Electrochemical Interface and potential was measured with a voltmeter after the sample was held for 15 min at each temperature with the exception of 200 °C (2-h dwell). The sample was cooled to room temperature after measuring the resistance at 200 and 300 °C to verify that the change in conductivity with heating is maintained upon cooling.

At calcination temperatures >250 °C, the  $\text{RuO}_2(\text{SiO}_2)$  papers bleach to a pale green, indicating sufficient particle growth to isolate particles thereby quantum confining the conduction electrons in the localized particles, Figure S3.

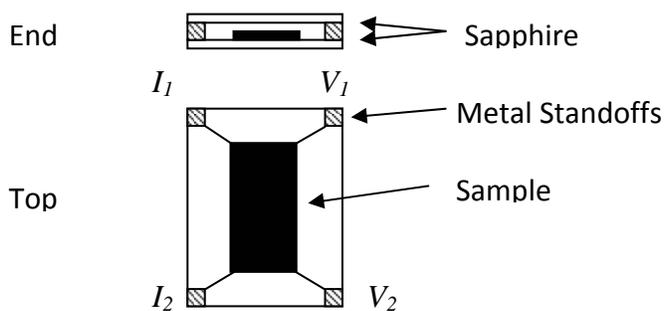


**Figure S3.** Optical images of  $\text{RuO}_2(\text{SiO}_2)$  paper calcined to 200, 250, and 300 °C in air. The observed “bleaching” from black at 200 °C to pale green by 300 °C is a result of  $\text{RuO}_2$  particle growth leading to isolated particles and localization of electrons.

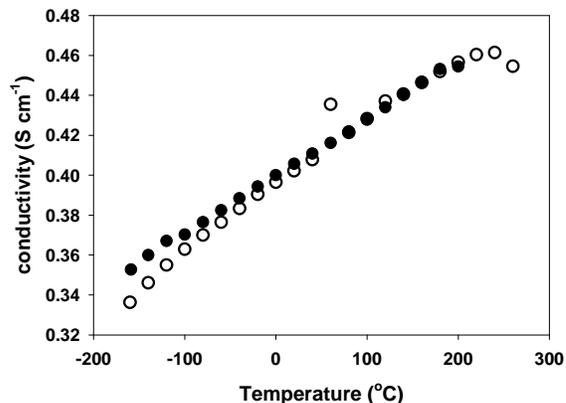
The geometric-factor-normalized resistances at room temperature in air of  $\text{RuO}_2(\text{SiO}_2)$  electrodes heated in air to  $200^\circ\text{C}$  for 2 h were determined by the four-point probe method of van der Pauw. The electrodes were cut into strips  $\sim 1\text{ cm} \times 0.7\text{ cm}$  and connected to copper wire leads with silver conductive epoxy. Current was applied with a Solartron SI1286 Electrochemical Interface and potential was measured with a voltmeter.

The conductivity as a function of temperature from  $-160$  to  $260^\circ\text{C}$  (see Figure S4) was measured using a four-terminal technique in a sapphire cell as shown in Figure S5. Each sapphire plate was  $\sim 1\text{-mm}$  thick. The sample was thinner than the gap between the sapphire plates, *i.e.*, thinner than the metal standoffs, so that the sample is free-standing. Each corner of the sample was attached to a metal standoff using conductive epoxy. Long, thin copper leads were attached to each of the metal standoffs.

The configuration shown in Figure S5 was mounted between the plates of a Novocontrol BDS 1200 sample holder. The long, thin copper electrical leads attached to the metal standoffs of the sample holder were run across the seal at the top of the BDS 1200. The four-terminal electrical measurements were carried out using a Keithley 181 Constant Current Source and a Keithley 224 Nanovoltmeter. Measurements of the voltage were made at an applied current of



**Figure S5.** Sample cell used to make four-terminal electrical measurements from  $260$  to  $-160^\circ\text{C}$ .



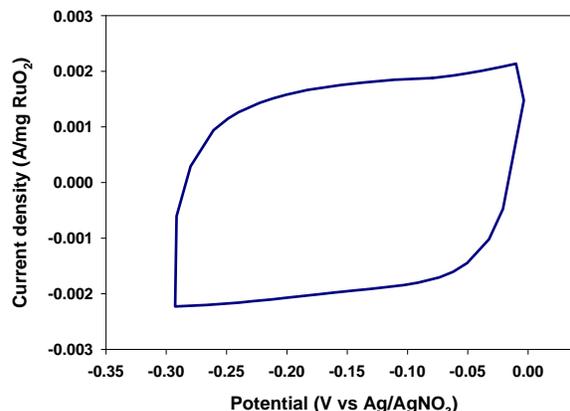
**Figure S4.** Conductivity vs temperature measured *in situ* by a four-point probe technique for  $200^\circ\text{C}$ -calcined  $\text{RuO}_2(\text{SiO}_2)$  paper. Resistance was measured from high to low temperature: initially from (●)  $200$  to  $-160^\circ\text{C}$  and (○) then from  $260$  to  $-160^\circ\text{C}$ .

$0.1\text{ mA}$  and  $0.2\text{ mA}$  to check for linearity. The temperature was controlled using a Novocontrol Quatro Cryocontrol temperature controller. Measurements were carried out in flowing nitrogen gas. The sample was allowed to equilibrate for  $\sim 15\text{ min}$  between temperatures.

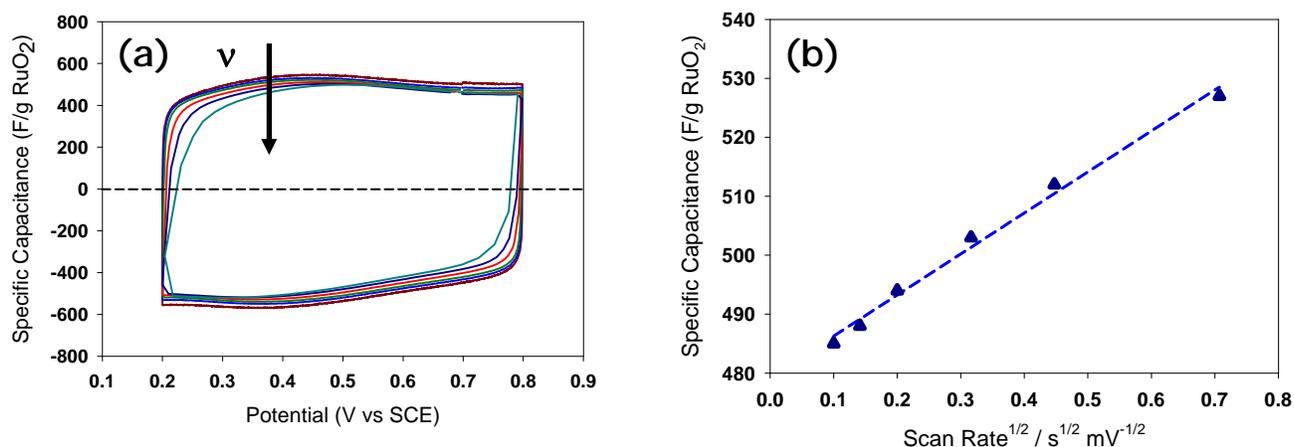
The resistance,  $R$ , was calculated by dividing the voltage by the current. The conductivity was calculated using:  $\sigma = \frac{l}{RA}$ , where  $l$  and  $A$  are the length and cross-sectional area of the sample, respectively. The absolute uncertainty in the conductivity is estimated to be  $\sim 10\%$  though the precision (reproducibility and variation with temperature) is much better than that.

## Electrochemistry

All electrochemical measurements were made using a Solartron SI 1286 potentiostat on  $\text{RuO}_2(\text{SiO}_2)$  papers calcined to  $200^\circ\text{C}$ . A gold foil with a gold wire welded to it was used as the electrical contact/support and a Pt mesh was used as the auxiliary electrode. The  $\text{RuO}_2(\text{SiO}_2)$  papers were attached to the gold foil with either an all-plastic paper clip (physical contact) or carbon epoxied to a gold wire. Measurements were conducted in a three-neck flask (purged with Ar for  $\sim 30$  min before the experiment) with Ar flowing over the electrolyte solution during measurements. The cyclic voltammetric response of  $\text{RuO}_2(\text{SiO}_2)$  paper was measured at ambient temperature in  $0.5\text{ M H}_2\text{SO}_4$  at  $2\text{ mV s}^{-1}$  versus an SCE (saturated calomel) reference electrode. The response of a  $\text{RuO}_2(\text{SiO}_2)$  electrode for the ferricyanide redox couple was measured in  $1\text{ M KNO}_3$  with  $5\text{ mM K}_3\text{FeCN}_6$  at  $5\text{ mV s}^{-1}$  with a SCE reference electrode. Measurement of the double-layer capacitance was made in acetonitrile with  $0.1\text{ M}$  tetrabutylammonium perchlorate using a  $\text{Ag}/\text{AgNO}_3$  reference electrode at  $25\text{ mV s}^{-1}$  (Figure S6). In this case, the  $\text{RuO}_2(\text{SiO}_2)$  was attached to a Pt wire contact with the all-plastic paper clip. The dependence of the electrochemical capacitance on potential scan rate ( $\nu$ ) for a  $200^\circ\text{C}$ -calcined  $\text{RuO}_2(\text{SiO}_2)$  paper was measured from  $2$  to  $100\text{ mV s}^{-1}$  in  $0.5\text{ M H}_2\text{SO}_4$  (see Figure S7). The linear dependence of capacitance with  $\nu^{-1/2}$  was obtained to extrapolate the fraction of the total capacitance associated with the “outer” surface of the electrode. The capacitance was determined for each scan rate by averaging the positive scan data from  $400$  to  $800\text{ mV vs SCE}$ . Extrapolation of these



**Figure S6.** Cyclic voltammogram of a  $200^\circ\text{C}$ -calcined  $\text{RuO}_2(\text{SiO}_2)$  paper in  $0.1\text{ M}$  tetrabutylammonium phosphate in acetonitrile at  $25\text{ mV s}^{-1}$  vs  $\text{Ag}/\text{AgNO}_3$  reference electrode.



**Figure S7.** The dependence of electrochemical capacitance on potential scan rate. **(a)** Cyclic voltammograms of a 200 °C-calcined RuO<sub>2</sub>(SiO<sub>2</sub>) paper in 0.5 M H<sub>2</sub>SO<sub>4</sub> as a function of scan rate ( $v$ ) from 2 to 100 mV s<sup>-1</sup>. **(b)** The linear dependence of capacitance and  $v^{-1/2}$  (capacitance averaged from the positive scan data from 400 to 800 mV vs SCE).

capacitance–scan rate data to infinite  $v$  establishes the “outer” surface (fast-kinetics proton exchange) pseudocapacitance; the ratio of this capacitance to the total capacitance obtained at slow scan rate (2 mV s<sup>-1</sup> in this study) provides an estimate of the percentage of RuO<sub>2</sub> at the surface of the monoparticulate nanoskin.

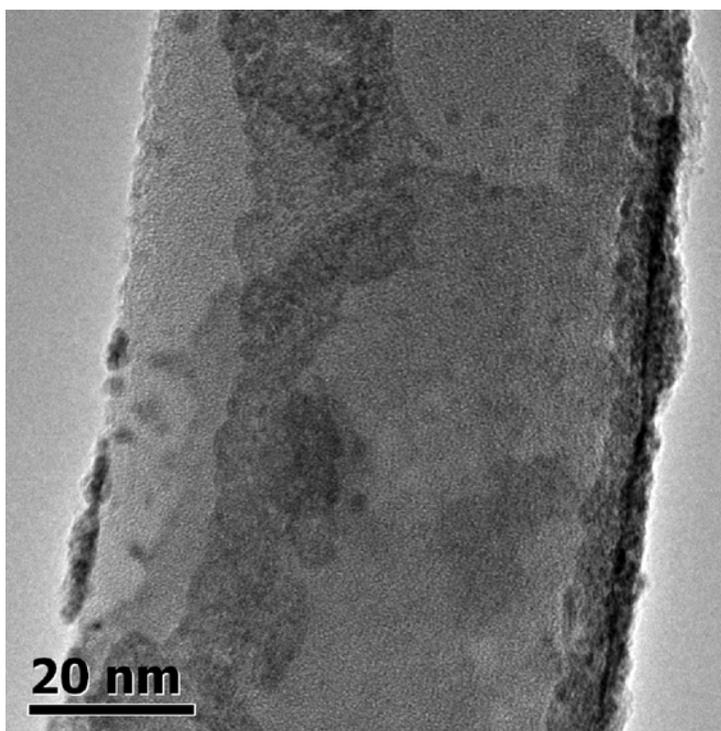
## Microscopy

Scanning electron microscopy (SEM; Carl Zeiss Supra 55 microscope) was used to characterize the nanoscale RuO<sub>2</sub> coating on SiO<sub>2</sub> fibers in the paper. The specimens were prepared for analysis by attaching a small portion of the paper to an aluminum stub with conductive carbon tape.

A JEOL 2200FS transmission electron microscopy (TEM) equipped with a Gatan CCD camera and Noran System Six EDS was used to characterize the fiber morphologies, confirm particle size and the nature of the coating, image lattice fringes, and perform elemental identification. For analysis, the specimens were prepared by dry-grinding then brushing the fibers/dust onto holey-carbon support Cu grids.

Multiple TEM images at higher resolution of the core-shell structure were analyzed to confirm the thickness of the RuO<sub>2</sub> nanoskin on the SiO<sub>2</sub> nanowires. The thickness was determined by measuring the difference between the crystalline edge of the RuO<sub>2</sub> and the amorphous edge of the SiO<sub>2</sub>, by noting the change in intensity due to crystalline material diffracting electrons more strongly than amorphous material. Figure S8 clearly shows that the thickness of the shell ranges from ~2 nm to ~5 nm with an average thickness of ~3 nm observed.

**Figure S8.** Transmission electron micrograph of a 200°C-calcined RuO<sub>2</sub>(SiO<sub>2</sub>) fiber imaged to illustrate the thickness of the RuO<sub>2</sub> shell. The nanoscale texture of the RuO<sub>2</sub> film is observed with particle sizes on the order of 2 to 3 nm.



## Nitrogen Porosimetry

The surface area of bulk cryogenerated RuO<sub>2</sub> harvested from the cryogenic synthetic route and then calcined to 200°C was determined by nitrogen physisorption using a Micromeritics ASAP2010 accelerated surface area and porosimetry analyzer. The sample was degassed at 100°C for 24 h prior to characterization. Elemental analysis of a 200°C-calcined RuO<sub>2</sub>(SiO<sub>2</sub>) paper was measured by ICP-AES (inductively coupled plasma-atomic emission spectroscopy) by Galbraith Laboratories, Knoxville, TN to confirm weight loadings of RuO<sub>2</sub> established using a Sartorius CPA26P microbalance.