

## Making the Most of a Scarce Metal

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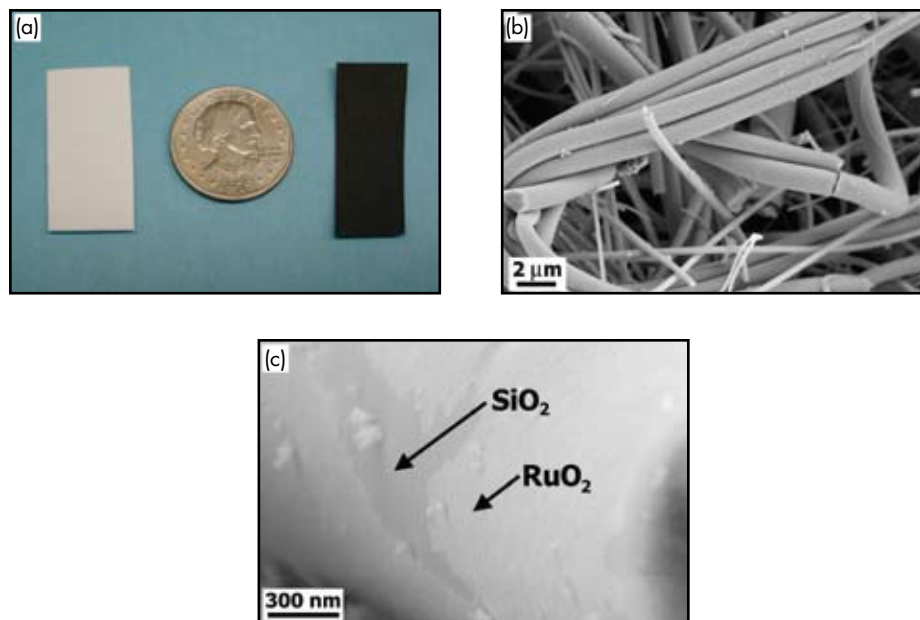
**Introduction:** Precious indeed are the platinum-group metals (PGMs): ruthenium, Ru; rhodium, Rh; palladium, Pd; osmium, Os; iridium, Ir; and platinum, Pt. The earthly scarcity and concomitant cost of PGMs have always tempered their adoption in the vast array of strategic and commercial technologies in which their inclusion would yield improved performance. We can now attain the impressive electronic and electrochemical properties of ruthenium oxide — high electronic conductivity, high capacitive charge storage for pulse power, and fast electron transfer for catalysis, analysis, or sensing — by distributing modest amounts of the material onto dirt-cheap, insulating substrates, namely paper made of silica fibers.

In the pursuit of a robust, flexible, and inexpensive electronic and catalytic substrate, we adapted our prior protocol for depositing 4-nanometer-high webs of ruthenium dioxide ( $\text{RuO}_2$ ) throughout the interior of silica ( $\text{SiO}_2$ ) nanoarchitectures.<sup>1</sup> Now, in place of specialty porous silica, commercially available silica filter paper is soaked in chilled solutions of  $\text{RuO}_4$  in petroleum ether; the  $\text{RuO}_4$  decomposes to  $\text{RuO}_2$  as the solution warms to room temperature. The initially white silica membrane turns black as nanoscale  $\text{RuO}_2$  nucleates on the fibers (Fig. 5(a)). The macroporous

voids between the fibers (hundreds of nanometers to several micrometers between the submicron- to micron-diameter silica fibers, Fig. 5(b)) offer ample headspace for deposition of nanoscopic  $\text{RuO}_2$  while retaining facile perfusion of fluids through the membrane. The time for equilibration and  $\text{RuO}_2$  deposition is less than one day and is carried out in ambient atmosphere without specialized reactors.

**Improved Properties on the Nanoscale:** The resistance of the as-prepared  $\text{RuO}_2||\text{SiO}_2$  composite decreases by four orders of magnitude upon heating in flowing oxygen to 200 °C. The marked increase in conductivity arises because the disordered, as-deposited oxide nanoparticles convert into a nanoscopic skin (Fig. 5(c)) of the more conductive, crystalline rutile form. The four-point probe-derived conductivity of the calcined  $\text{RuO}_2||\text{SiO}_2$  nanocomposite is  $0.5 \text{ S cm}^{-1}$  at room temperature in air with only  $\sim 300 \mu\text{g cm}^{-2}$  of  $\text{RuO}_2$  per geometric area of silica paper.<sup>2</sup>

The  $\text{RuO}_2||\text{SiO}_2$  fiber membranes express an electrochemical surface area of  $\sim 90 \text{ m}^2 \text{ g}^{-1}$  ( $\text{RuO}_2$ ), exhibit a thermopower consistent with metallic  $\text{RuO}_2$ , and support fast electron-transfer reactions in aqueous and nonaqueous electrolytes. The  $\text{RuO}_2||\text{SiO}_2$  composite retains the mechanical attributes of the  $\text{SiO}_2$  membrane, which is flexible, has a degree of compressibility (softness), and can be easily molded through pressure to form quality interfacial contact with uneven surfaces. All of these are important attributes in fabricat-



**FIGURE 5**

The morphology of  $\text{RuO}_2$  nanoskins on  $\text{SiO}_2$  fiber paper. (a)  $\text{SiO}_2$  paper before (white) and after sub-ambient temperature deposition of  $\text{RuO}_2$  (black). (b-c) Scanning electron micrographs of a 200 °C-calcined  $\text{RuO}_2||\text{SiO}_2$  composite: the morphology of the paper is unaltered by  $\text{RuO}_2$  deposition, which forms a through-connected nanoscale shell on the membrane fibers leaving only small islands of uncoated  $\text{SiO}_2$ .

ing practical devices that incorporate these conductive papers.

This inexpensive, practical manifestation on the macroscale of a metallic-like conductor on the nanoscale is accomplished at low ruthenia mass loadings (~5 weight %) and volume fraction (<0.1 volume %), thereby maximizing the utilization of this expensive platinum-group metal; the 2009 cost of materials runs less than \$0.20 USD per square centimeter of conductive composite. The conductivity we report is normalized using the geometric dimensions of the insulating silica paper, and so does not completely express the remarkable behavior of the conductive nanoskin. Contrast the density-normalized conductivity of RuO<sub>2</sub> in three forms:

Form of RuO <sub>2</sub>	Density-normalized electronic conductivity S cm <sup>2</sup> mg <sup>-1</sup>
RuO <sub>2</sub>   SiO <sub>2</sub> paper, calcined at 200 °C	50
Pressed pellet of RuO <sub>2</sub> powder harvested from the subambient synthesis, calcined at 200 °C	14
Polycrystalline RuO <sub>2</sub>	12

Expressing the same oxide as a nanoskin wrapped contiguously around a curved dielectric imparts a four-fold enhancement in the electron conductivity.

The 2- to 3-nanometer-thick coatings of RuO<sub>2</sub> that cover the convex walls of the silica fibers also exhibit atypically high specific capacitance for electron–proton charge storage — five times that — at crystalline RuO<sub>2</sub>. In acidic electrolyte, 90% of the total electron–proton charge is stored at the outer surface of the ruthenia phase in the RuO<sub>2</sub>||SiO<sub>2</sub> fiber membranes.<sup>2</sup> In a 2-nanometer spherical particle of rutile RuO<sub>2</sub>, more than 90% of the crystalline subunits are expressed at the surface of the particle. The electrochemical capacitive response we obtain indicates that the nanocrystalline RuO<sub>2</sub> shell can be considered to be equivalent to a single oxide layer stabilized by the supporting silica fiber. In analogy with graphene,<sup>3</sup> the ruthenia nanoskin on the silica fiber paper acts as an exfoliated layer of the conductor.

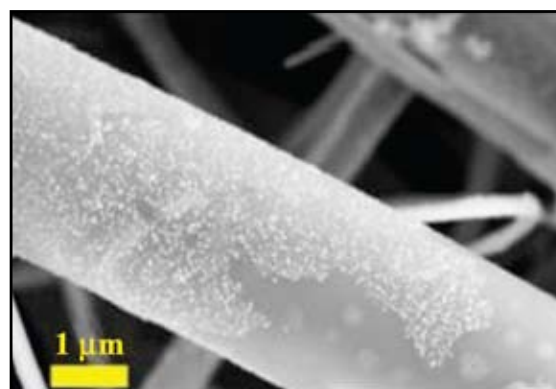
**Future Applications:** The ever-increasing energy and power demands of Navy and Marine Corps missions will require advancements in such portable power technologies as fuel cells. All of the features discussed above, including the ease and low expense

of the synthesis, make this new electrode structure a prime candidate as an electron–proton conductive, gas-diffusion electrode in which neither carbon nor ionomer will be required to form a fuel-cell electrode. We have preliminary evidence that Pt nanoparticles are readily electrolessly deposited only at the ruthenia nanoshell of the RuO<sub>2</sub>||SiO<sub>2</sub> membrane, as seen in Fig. 6. This advanced electrode structure wires protons and electrons along the electrically conductive nanoshell of RuO<sub>2</sub> and thereby removes two limiting components in fuel-cell electrodes: (i) carbon to support the metal electrocatalytic nanoparticles and provide an electron path through the electrode structure; and (ii) ionomer to transport protons to the proton-conducting solid membrane (e.g., Nafion™) that physically separates the anode from the cathode. The weight loadings of Pt should easily reach ≤100 μg cm<sup>-2</sup> for such paper-based electrode architectures, which would meet future Department of Energy targets for hydrogen-fed fuel cells.

[Sponsored by ONR]

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**FIGURE 6**

Scanning electron micrograph of a 200 °C-calcined RuO<sub>2</sub>||SiO<sub>2</sub> fiber membrane after electroless deposition of Pt from a 2 mM H<sub>2</sub>PtCl<sub>6</sub> solution in 0.5 M H<sub>2</sub>SO<sub>4</sub>. The Pt ions reduce at the electrified RuO<sub>2</sub> coating, forming nanoparticles associated with the through-networked nanoskin without forming electrically unaddressable Pt on bare SiO<sub>2</sub>.