Supporting Information

Sol-gel synthesis of ruthenium oxide nanowires to enhance methanol oxidation in supported platinum nanoparticle catalysts

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Additional Details on the Development of a Two-Step Sol-Gel Technique for the Production of RuO$_2$ NWs

In prior reports, vacuum filtration was shown to be effective at filling the pores of the anodic alumina and polycarbonate filter membranes. Typically, the gelling agent is added to the precursor sol to initiate gelation before the template pores are impregnated. However, this standard approach led to the formation of a thin layer of bulk material on the surface of the template (Figure S1A) that was impossible to remove before annealing via washing the template (Figure S1B) or after annealing by polishing the template. Both of these approaches led to a loss of the desired one-dimensional, NW morphology.

To circumvent this challenge, a two-step protocol was developed to avoid the formation of a RuO$_2$ thin film. In the first step, the template was loaded with the ruthenium sol before gelation via vacuum impregnation. Loading the template with the precursor sol had two important benefits: a higher loading could be achieved inside of the pores due to the lower viscosity of the sol as compared with the sol-gel, and residues of the dry sol could be easily removed by polishing the surfaces of the template on a Whetstone. Since the polycarbonate membrane is unstable to direct contact with propylene oxide, we employed a modified glass-petri dish as a glass-reactor to expose the impregnated filter membrane to saturated propylene oxide vapors to complete the gelation directly inside of the pores. The progress of the reaction was tracked by the color change of the template from the reddish-brown color of the sol to the black color of the sol-gel. The reaction proceeded for 30 minutes to allow for complete gelation. In the final step, the template was annealed to simultaneously crystallize the gel into RuO$_2$ NWs and vaporize the template material.
Characterization and Electrochemical Measurements

Powder X-ray diffraction (XRD) studies were performed on a Bruker D2 Phaser equipped with a scintillation detector. To prepare the samples, a concentrated paste was prepared by dispersing the sample into a small amount of either ethanol or isopropyl alcohol. This slurry was then deposited, dropwise, onto a zero-background Si wafer holder. X-ray diffraction patterns were collected from 20° – 60° in 2 theta.

SEM studies were conducted on a Zeiss EVO MA-10 electron microscope equipped with a LaB₆ filament at an accelerating voltage of 15 kV. Energy dispersive X-ray spectroscopy (EDX) measurements were performed on an Oxford X-max spectrometer. The samples were prepared for imaging by first dispersing a small amount of the product into ethanol by vortex mixing. Sonication was avoided to ensure that the morphology of the nanowires was maintained. Following vortex mixing, a drop of the dispersion was placed onto a silicon wafer and allowed to air dry. HRTEM analysis was conducted on a FEI Talos F200X S/TEM at an accelerating voltage of 200 kV. To prepare the samples for HRTEM analysis, they were sonicated briefly in ethanol to produce a dilute slurry. Then ~ 100 µL of the slurry was deposited onto a 400 copper grid covered with a layer of holey carbon.

The precise Pt loading in the Pt NP/RuO₂ NW sample was determined by inductively coupled plasma mass spectrometry (ICPMS, ThermoElectron X Series) obtained from the catalyst dissolved in a 1:3 mixture of nitric acid and hydrochloric acid. The instrument was calibrated for Pt ion concentration using a Pt standard solution (Spex CertiPrep, 1 µg·mL⁻¹ Pt in 2% HCl) diluted in nitric acid (Fisher Scientific, Optima Grade). The Pt loading in the Pt NP/C sample was determined from thermogravimetric analysis (TGA, TA Instruments Q500). The
temperature was ramped at a rate of 20°C·min⁻¹ to 700°C in ultra-dry air until a stable mass of Pt was obtained. TGA was also performed on the RuO₂ NWs to determine their crystallinity. The temperature was ramped at a rate of 10°C·min⁻¹ to 800°C in ultra-dry air.

X-ray photoelectron spectroscopy on a PHI Quantera XPS instrument. The powders were supported on silicon wafers prior to analysis. The data was collected with monochromatic Al Kα radiation with a 25 W beam and a 100 µm spot size. Survey scans were collected at a 45° photoelectron takeoff angle with a 280 eV analyzer pass energy at 1.0 eV per step. High resolution scans for the platinum, ruthenium, and oxygen elements were referenced to the Si 2p (99.6 eV) of metallic Si peak of the substrate. We use the Si peak of the substrate as a reference since the carbon peaks, which are traditionally used as a reference, overlap with the peaks for ruthenium. Survey scans and fits the of the high resolution XPS data, peak positions, and peak assignments can be found in Figure S3 and Figure S4, respectively.

The as-prepared Pt NP/RuO₂ NW and Pt NP/C catalysts were dispersed into absolute ethanol with a concentration of 2 mg·mL⁻¹ to form catalyst inks. Glassy carbon rotating disk electrodes (GC-RDE, Pine Instruments, 5 mm) were polished with aluminum oxide pastes until a mirror finish was achieved. The catalysts were loaded onto the GC-RDE by adding a 5 µL aliquot of the catalyst to the electrode and allowing it to dry in air. To improve the dispersion of the catalyst, the GC-RDE was pre-modified with a thin layer of Vulcan carbon before depositing the Pt NP/RuO₂ NW catalysts. In both cases, the electrode was sealed by adding a 5 µL drop of Nafion, (0.025% in absolute ethanol) which was allowed to dry in air. The sealed electrodes were immersed into ultrapure water (18.2 MΩ-cm, Millipore Direct Q5) to remove residual impurities.

Electrochemical experiments were performed with a Pine Instruments WaveDriver20 bipotentiostat and a custom three electrode cell. An Ag/AgCl (3 M Cl⁻) reference electrode
housed in a double junction chamber supplied by BASi Instruments and a platinum counter electrode (Alfa Aesar, 3.0 cm² active area) served as the reference and counter electrodes respectively. Cyclic voltammograms were obtained in deoxygenated 0.1 M HClO₄ prepared by diluting the concentrated acid (Fisher Scientific, Optima grade) in ultrapure water. The methanol oxidation and formic acid oxidation performance was examined via linear sweep voltammetry and chronoamperometry in a deoxygenated solution of 0.1 M methanol or formic acid (Fisher Scientific, Optima grade) and 0.1 M HClO₄. Carbon monoxide stripping voltammetry was performed after immersing the electrode in a CO saturated solution for a period of 45 minutes. All potentials are reported with respect to the reversible hydrogen electrode (RHE). The electrochemically accessible surface area (ESA) of Pt was determined from the integrated hydrogen adsorption (H_ads) charge in the cyclic voltammogram, utilizing the conversion factor 0.21 mC·cm⁻². The capacitive contribution of the support material was removed during the integration of the H_ads peaks.
**Figure S1.** A) SEM image of a RuO$_2$ sample prepared using the traditional sol-gel method and then polishing the template. B) SEM image of a RuO$_2$ sample produced by washing the template with a small amount of ethanol to remove the sol-gel reaction from the surface of the template.
Figure S2. Histogram of Pt NP size on RuO$_2$ NWs.
Figure S3. Survey XPS spectra collected from Pt NP/C (A) and Pt NP/RuO₂ NWs (B).
Figure S4. High resolution scans including fits of the Ru 3d (A) and Pt 4f (B) regions for the Pt NP/RuO$_2$ NWs and the Pt 4f region of the Pt NP/C (C). Peak assignments and locations are presented in the corresponding tables.
Figure S5. MOR specific activity collected in 0.1 M methanol/0.1 M HClO₄ at a scan rate of 20 mV·s⁻¹.