Supporting Information

Increasing Stability and Activity of Core-shell Catalysts by Preferential Segregation of Oxide on Edges and Vertices: Oxygen Reduction on Ti-Au@Pt/C

Jue Hu ^{a,b}, Lijun Wu ^c, Kurian A. Kuttiyiel ^a, Kenneth R. Goodman ^d, Chengxu Zhang ^{b,*}, Yimei Zhu ^c, Miomir B. Vukmirovic ^a, Michael G. White ^{a,d}, Kotaro Sasaki ^a,
Radoslav R. Adzic ^{a,*}

^a Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973, USA

^b Institute of Plasma Physics, Chinese Academy of Sciences, P. O. Box 1126, 230031,
P. R. China

^c Department of Condensed Matter Physics and Materials Science, Brookhaven
National Laboratory, Upton, NY 11973, USA

^d Department of Chemistry, Stony Brook University, Stony Brook, NY 11794, USA

Corresponding Authors:

Dr. Radoslav R. Adzic

Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973, USA

Email: adzic@bnl.gov

Dr. Chengxu Zhang

Institute of Plasma Physics, Chinese Academy of Sciences, 230031, China

Email: chxzhang@ipp.ac.cn

Details of experimental procedure

Chemicals

Sodium tetrachloroaurate (III) dihydrate ($\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$, 99%), titanium (IV) isopropoxide ($\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$, 97%), potassium tetrachlorophatinate (II) (K_2PtCl_4 , 99.9%), copper (II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\geq 98\%$), Super-Hydride solution (1M lithium triethylborohydride solution in tetrahydrofuran, $\text{Li}(\text{C}_2\text{H}_5)_3\text{BH}$), and anhydrous ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$, $\geq 99.8\%$) were all purchased from Sigma-Aldrich. Trisodium citrate dihydrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$, 99%) was bought from Alfa Aesar. Perchloric acid (HClO_4 , 70%) and sulfuric acid (H_2SO_4 , 93-98%) were purchased from Fisher Scientific. Anhydrous ethyl alcohol (200 proof, ACS/USP grade) was bought from Pharmco-Aaper. All the chemicals were used as received without further purification. Milli-Q ultrapure deionized water (18.2 M Ω /cm) prepared through Milli-Q Advantage A10 water purification system was used in all experiments.

Synthesis

Carbon supported Ti oxide doped Au (Ti-Au) nanoparticles were prepared by first mixing Vulcan carbon XC72R with titanium isopropoxide in anhydrous ethyl alcohol. Later, trisodium citrate at a ratio of 3:1 with respect to Ti salt was mixed with the uniform carbon mixture. After ultrasonication the mixture for an hour under continuous Ar flow, Super-Hydride was added into the mixture while simultaneously purging the mixture with Ar. After 15 min of reaction time, the mixture was heated to 40 °C for half an hour to remove part of reductant. The 0.05 M NaAuCl_4 solution in

ethylene glycol was then added into this mixture and ultrasonicated for 1 h so as to obtain Ti-Au/C catalyst. The mixture was filtered and rinsed with Millipore water, and then dried. For comparison, Au nanoparticles were synthesized under the same condition and followed the same procedure. The only difference is no Ti salt added. Figure S5 shows the TEM image and the particles size distributions of the as synthesized Au nanoparticles. The particle size distribution shows that the mean particle size is 6.2 nm in diameter.

Electrochemical testing

Electrochemical measurements were carried out in a three-electrode test cell by using a Volta PGZ402 potentiostat (Voltalab, Radiometer Analytical). The catalyst ink was prepared by ultrasonic mixing of 4 mg of the catalyst with 2 ml MilliQ water, 2 ml iso-propanol and 8 μ l 5wt% Nafion solution until a uniform aqueous dispersion was obtained. A thin film of the catalyst was prepared on a glassy carbon RDE by placing 20 μ l of the obtained dispersion, and then dried in air at room temperature. We deposited Pt shell both on the prepared Au/C and Ti-Au/C nanoparticle surfaces using the galvanic displacement of Cu layer formed by Cu underpotential deposition (UPD)¹⁸. Because the Cu UPD process cannot occur on the metal oxide surface, so Pt layer can only cover Au surface facets. The Pt loadings for the Au@Pt/C and Ti-Au@Pt/C catalysts were 1.3 and 1.1 μ g cm⁻² respectively, whereas their Au loading were 18.3 and 8.4 μ g cm⁻² respectively, based on the geometric electrode area of 0.196 cm². The rotating disk electrode (RDE) with catalyst was mounted onto a rotator (Pine Research Instrumentation) as the working electrode. A Pt foil and Ag/AgCl (3M

NaCl) electrode were served as the counter electrode and reference electrode, respectively. The electrochemical surface area (ECSA) was determined by integrating the hydrogen underpotential deposition charge on the cyclic voltammetry (CV) curve in Ar-saturated 0.1 M HClO₄ solution with a scan rate of 50 mV s⁻¹. The oxygen reduction reaction (ORR) measurements were performed in an O₂-saturated 0.1 M HClO₄ solution at the scan rate of 10 mV s⁻¹ and rotation rates of 1600 rpm. The accelerate durability tests (ADTs) were carried out in air-saturated 0.1 M HClO₄ solution using potential cycling between 0.6 V and 1.0 V with the sweep rate of 50 mV s⁻¹ at room temperature. For comparison, commercial Pt/C (Tanaka Kikinzoku International Inc., 46.6 wt% Pt, Pt particle size 2.6 nm) was used as the baseline catalyst under the same measuring conditions. The electrochemical measurements were all performed at room temperature, and the potential were referenced to that of the reversible hydrogen electrode (RHE).

Characterization

High-resolution TEM, STEM images and chemical mapping were performed using the double aberration-corrected JEOL-ARM200F microscope with a cold-field emission gun and operated at 200 kV. The microscope is equipped with JEOL and Gatan HAADF detectors for incoherent HAADF (Z-contrast) imaging, Gatan GIF Quantum ER Energy Filter with dual EELS for EELS and Oxford Instruments SDD detector for EDS. X-ray photoelectron spectroscopy (XPS) was performed in a standard ultra-high vacuum (UHV) chamber, equipped with a hemispherical electron

energy analyzer (110 mm radius; ThermoFisher Scientific, Alpha 110) and an Al/Mg twin anode X-ray source (ThermoFisher Scientific, T352/NT). The sample was prepared by pressing the catalyst powder between two plates (10x10x1 mm) at a pressure around 2000 psi. One of the loaded plates was then clamped into a molybdenum holder. The XPS spectra were obtained using unmonochromatized Al K_{α} (1486.6 eV) radiation. All atom-specific core level spectra were taken at analyzer pass energy of 20 eV, with a step size of 0.2 eV, and dwell time of 0.1 s. Each region signal was averaged for 20 scans except for Ti and Au which were averaged over 40 and 25 scans respectfully, in order to improve the signal to noise ratio that was a result of the low metal concentrations in the samples. Analysis of the XPS spectra was performed using XPSPEAK version 4.1. The Au 4f (7/2) peak at 83.8 eV of the metallic Au was used to calibrate the energy scale to which all the measured binding energies were adjusted. A Shirley background was applied to the spectra which were then fit with an appropriate number of peaks. The fits were allowed to optimize without constraints as long as a reasonable FWHM (below 3 eV) and goodness of fit were obtained. In cases where a FWHM greater than 3 eV occurred, widths and/or known peak separations were fixed to one another, until an acceptable fit was achieved. The atomic sensitivity factors of 0.63 (O), 1.1 (Ti), 1.9 (Au), and 0.205 (C) were used to correct for differences in photoemission cross sections to obtain relative surface atomic compositions.

(a)

(b)

Figure S1 (a) TEM images and (b) particle size distribution of the Ti-Au nanoparticles.

Figure S2 (a) High resolution HAADF-STEM image of a Ti-Au nanoparticle viewed along $[110]$ direction, showing five twins and possible icosahedral shape. Truncations happen at some vertexes. A icosahedron is shown in the inset. (b,c) Signal intensity maps of (b) Ti L32 and (c) Au M54 edges from the 2D EELS spectrum image of the same particle, showing that Au is at core, while Ti distributes at the surface of the particles. (d) Color mixture from (c) and (b). (e) Another Ti-Au nanoparticle, also showing multiple facets and edges.

Figure S3 O 1s XPS spectrum of Ti-Au/C sample. Orange circle is the original data, dark cyan line is the fitted curve, blue line is the oxygen-metal bond fit, and red line is the O-H bond fit.

(a)

(b)

Figure S4 (a) TEM images and (b) particle size distribution of the Ti-Au@Pt nanoparticles.

Figure S5 (a) TEM images and (b) particle size distribution of the Au nanoparticles.

Figure S6 (a) Mass activities given as kinetic current densities normalized to the loading amount of Pt for Ti-Au@Pt/C, Au@Pt/C and commercial Pt/C catalysts. (b) The specific activities given as kinetic current densities normalized to the ECSA.

Figure S7 (a) The 10th cycle of cyclic voltammograms for Ti-Au@Pt/C catalyst in the accelerated durability test at room temperature. (b) Variations of peak potential for Ti-Au@Pt/C catalyst deducted from Figure S8a during 10,000 potential cycles between 0.6 and 1.0 V. The variations of the peak potential indicates that there is no obvious decline of activity for Ti-Au@Pt/C catalyst during 10,000 potential cycles, which is consistent with the CV and ORR behavior analyses in Figure 4.

Figure S8 ORR polarization curves and (inset) corresponding cyclic voltammograms of (a) commercial Pt/C catalyst, (b) Au@Pt/C catalyst before and after 10,000 potential cycles between 0.6 and 1.0 V. Pt loading for Au@Pt/C and commercial Pt/C catalysts were 1.3 and 9.7 $\mu\text{g cm}^{-2}$.