Supplementary Information for

Alkaline O$_2$ Reduction on Oxide-Derived Au:

High Activity and 4e^- Selectivity without (100) Facets

Xiaoquan Min, Yihong Chen, and Matthew W. Kanan*

*Correspondence to: mkanan@stanford.edu

This PDF file includes:

Materials and Methods

Materials

Gold foil (thickness 0.1 mm, 99.99%), gold wire (diam. 0.25 mm, 99.9%), gold(III) chloride trihydrate (≥99.9%), sodium borohydride (≥98.0%), cetyltrimethylammonium chloride (25 wt.% in H_2O), sodium bromide (≥99.5%), KI (≥99.5%), L-ascorbic acid (≥99.0%), potassium hydroxide (99.99%), Pt gauze (99.9%), Pt wire (99.9%), Na_2CO_3 (99.9999%, TraceSELECT®), and H_2SO_4 (≥95%, TraceSELECT®) were purchased from Sigma-Aldrich; gold disk (thickness 4 mm, diam. 5 mm, 99.99%) was purchased from Pine Research Instrumentation Inc.; oxygen (99.99%), and carbon dioxide (99.99%) was purchased from Praxair. Gold foil and wire were etched in fresh aqua regia for ~20 s, and then rinsed with deionized water thoroughly prior to experiments. All other chemicals were used without further purification. Electrolyte solutions were prepared with deionized water (Ricca Chemical, ASTM Type I). $NaHCO_3$ solution was prepared by vigorously bubbling CO_2 gas through Na_2CO_3 solutions.

Preparation of OD-Au on Gold Foil and Gold Disk

A piece of gold foil (~0.5 cm^2) was immersed in aqueous 0.5 M H_2SO_4 solution in an one-compartment electrochemical cell with a platinum gauze auxiliary electrode and a Hg/Hg_2SO_4 reference electrode (0.50 M H_2SO_4, CH Instruments). Symmetric 1 kHz square-wave pulses between 2.70 V and 0.70 V were applied for 5 min (300,000 cycles) with the use of a Gamry Reference 600 Potentiostat. After pulsed anodization, the foil was rinsed very gently with deionized water to remove remaining H_2SO_4 from the as-grown oxide layer. Then the foil was immersed in CO_2-saturated $NaHCO_3$ solution and held at −1.03 V vs Ag/AgCl reference electrode (3.0 M KCl, World Precision Instruments) for 5 min to fully reduce the gold oxide layer. The preparation of OD-Au on Au disk was the same as above except that a gold disk was used.

Syntheses of Shaped Au Nanoparticles (NPs)

The procedure was adapted from a two-step, seed-mediated method established in literature (refs 8 and 9 in the main text). The Au seed solution was prepared by injecting 0.45 mL of 0.02 M freshly prepared, ice-cooled $NaBH_4$ solution into 10 mL solution containing 0.25 mM $HAuCl_4$ and 0.1 M cetyltrimethylammonium chloride (CTAC) while stirring. The resulting solution was left undisturbed for 2 h to allow complete decomposition of excess $NaBH_4$.

Growth solution I and growth solution II were prepared with a different recipe for each type of polyhedral nanoparticles. Growth solution I was prepared by adding 0.01 mL of 0.01 M NaBr and 0.09 mL of 0.04 M ascorbic acid (cubes), or 0.01 mL of 0.01 M NaBr and 0.15 mL of 0.04 M ascorbic acid (dodecahedra), or 0.01 mL of 0.001 M KI and 0.22 mL of 0.04 M ascorbic acid (octahedra) into 10 mL of 0.25 mM $HAuCl_4$ and 0.1 M CTAC. Growth solution II was prepared with the same concentration as growth solution I but 20-fold higher volume. 0.025 mL Au seed solution was injected into the growth solution I while stirring. After ~20 s, 0.5 mL of the resulting pink solution from growth solution I was injected into growth solution II. After stirring for 1 min, the solution was left undisturbed for 2 h for growth. The nanoparticles were centrifuged and washed repeatedly with DI water. After washing, the nanoparticles were re-dispersed to ~ 2 mg/mL in DI water for electrode preparation experiments.

Electrochemical Measurements

A CH Instruments 760D Potentiostat or a Gamry Reference 600 Potentiostat was used for all oxygen reduction experiments. Experiments were performed at room temperature (20 °C). A piece of platinum gauze was used as the auxiliary electrode. All potentials were measured against an Hg/Hg_2Cl_2 reference electrode (satd. KCl, CH Instruments) or Ag/AgCl reference electrode (3.0 M KCl) and converted to the RHE reference scale using E (vs RHE) = E (vs Hg/Hg_2Cl_2) + 0.241 V + 0.0591 V × pH or E (vs RHE) = E (vs Ag/AgCl) + 0.21 V + 0.0591 V × pH.

For shaped Au NPs, the suspension was mixed with ~10 wt.% Nafion and 0.020 mL of the catalyst ink was drop-dried onto the glassy-carbon rotating disk electrode for electrochemical experiments.

Electrochemical Surface Area (ECSA) Measurement

The electrochemical surface area of the ODAu and shaped Au nanoparticle electrodes were determined by measuring the desorption charge associated with the stripping of the underpotential deposited Cu monolayer on Au (**Figure S2**). The experiments were conducted in 0.50 M H_2SO_4 solution with a piece of Pt gauze as the counter electrode and an Hg/Hg_2SO_4 electrode (0.50 M H_2SO_4, CH Instruments) as the reference electrode. The desorption peaks at ~ –0.1 V were integrated.

Pb-underpotential deposition (Pb-upd) Measurement

The Pb-upd measurements of ODAu and shaped Au nanoparticles were conducted in 0.1 M NaOH solution containing 1 mM $Pb(OAc)_2$ with a piece of Pt gauze as the counter electrode and an Ag/AgCl electrode (3.0 M KCl, World Precision Instruments) as the reference electrode. The scan rate was 50 mV/s.

Koutechy-Levich Kinetics and Determination of n Values

Koutecky-Levich Equation: $j^{-1} = j_k^{-1} + j_d^{-1}$

j : current density, $A \cdot cm^{-2}$

j_k : kinetic current density, $A \cdot cm^{-2}$

$j_d = 0.62nFD_0^{2/3}v^{-1/6}C_0\omega^{1/2}$, diffusion-limited current density, $A \cdot cm^{-2}$

F: Faraday's Constant, 96485 $C \cdot mol^{-1}$

D_0: diffusion coefficient of O_2 in 0.1 M KOH (1.93×10^{-5} $cm^2 \cdot s^{-1}$)[1],[2]

v: kinematic viscosity of the electrolyte, 0.1 M KOH, (1.09×10^{-2} $cm^2 \cdot s^{-1}$)[1],[2]

C_0: saturation concentration of O_2 in 0.1 M KOH at 1 atm O_2 pressure, (1.26×10^{-6} $mol \cdot cm^{-3}$)[1],[2]

ω: rotation rate, $rad \cdot s^{-1}$

$0.62FD_0^{2/3}v^{-1/6}C_0 = 1.152 \times 10^{-4}$ $A \cdot cm^{-2} \cdot s^{1/2} \cdot rad^{-1/2}$

Taking 0.8 V as an example, the linear fitting of the plot of j^{-1} vs $\omega^{-1/2}$ has a slope of 2195 $A^{-1} \cdot cm^2 \cdot s^{-1/2} \cdot rad^{1/2}$, which corresponds to $n = 3.95$.

Calculations of n in the literature often use the B factor, which is the slope of the i^{-1} vs $\omega^{-1/2}$ plot when i is the current in units of mA and ω is the rotation rate in units of rpm. In this treatment, $B = 0.62nFD_0^{2/3}v^{-1/6}C_0S_{geo}(2\pi/60)^{1/2}$, where $S_{geo} = 0.196$ cm^2 is the geometric area of the electrode used in our experiments. For a $4e^-$ reduction of O_2 in 0.1 M KOH with these electrodes, the theoretical value of $B = 2.92 \times 10^{-2}$ $mA \cdot rpm^{-0.5}$. Taking 0.8 V as an example, the linear fitting of the plot of i^{-1} vs $\omega^{-1/2}$ gives a slope of 3.46×10^4 $A^{-1} \cdot rpm^{0.5}$; therefore, the experimental value of B is 2.89×10^{-2} $mA \cdot rpm^{-0.5}$, which corresponds to $n = 3.96$.

[1] Blizanac, B.B.; Ross, P.N.; Markovic, N.M. *J Phys Chem B* **2006**, *110*, 4735.

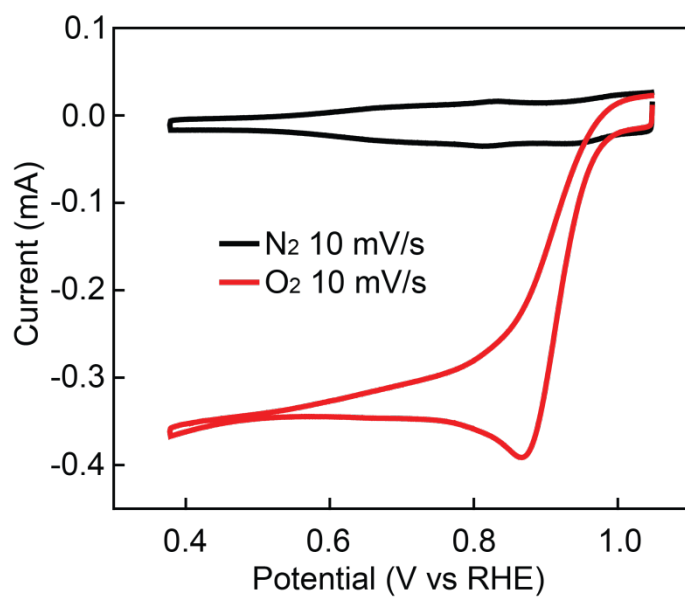[2] Singh, P.; Buttry, D.A. *J Phys Chem C* **2012**, *116*, 10656.

Figure S1

Cyclic voltammograms (CVs) of OD-Au in N_2-, and O_2-saturated 0.1 M KOH with a scan rate of 10 mV/s.

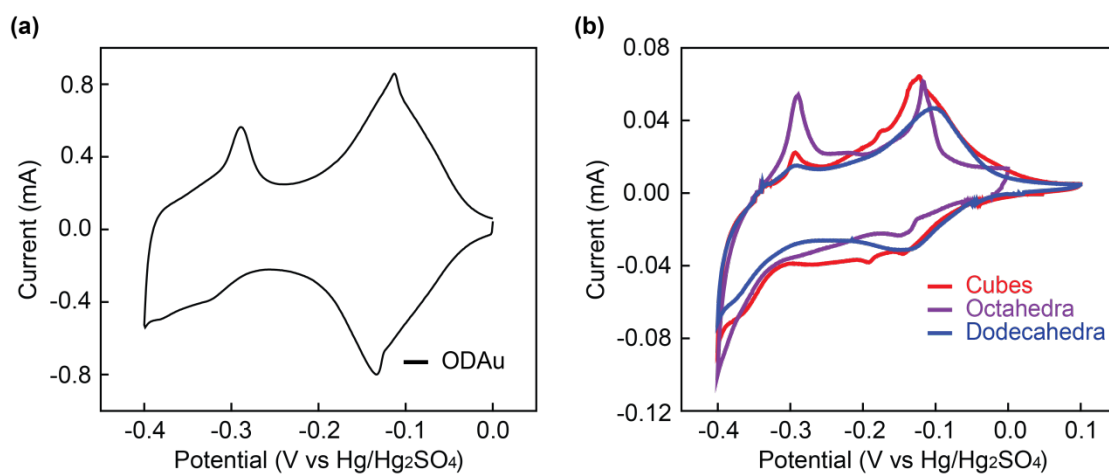**Figure S2**

Electrochemical surface area (ECSA) measurements of OD-Au and shaped Au NP electrodes using Cu-upd method. Scan rate: 50 mV/s.

	OD-Au	Au Cubes	Au Octahedra	Au Dodecahedra
Roughness Factor	47.7	4.3	1.2	2.9

Table S1
Roughness factor comparison between OD-Au and shaped Au nanoparticles

Potential V vs RHE	n
0.8	3.95
0.75	3.88
0.7	3.84
0.65	3.84
0.6	3.78
0.55	3.74
0.5	3.69
0.45	3.69

Table S2

n-values of OD-Au at different potentials determined from the slopes of the Koutecky-Levich plots.