

Online Supporting Materials

I. Materials, instruments and methods:

A. Materials:

All solutions were prepared with Millipore water (18M Ω ·cm, Millipore Milli-Q). Ruthenium(III) chloride (Aldrich), perchloric acid (Aldrich, HClO₄ redistilled 99.999% HClO₄ content 69.0-72.0%) and hydrochloric acid (Mallinckrodt Baker, 36.5-38.0%, ACS grade) were used as received. Carbon monoxide (CP grade) was obtained from Matheson Air Products. Gold wire (Goodfellow, diameter 0.25mm, purity 99.99+%) was used.

The Pt(111) electrode was prepared according to Clavilier's method (Clavilier, J.; Faure, R.; Guinet, G.; Durand, R. *J. Electroanal. Chem.* **1980**, 107, 205). Prior to each experiment the electrode was flame-annealed for 30s, after which it was quenched in Millipore water before transferring to the electrochemical cell. The electrolyte used in all experiments was 0.1M HClO₄. For deposition of ruthenium, 1mM solutions of Ru(III) chloride in 0.1M HClO₄ were employed. For the adsorption of CO, CO saturated solutions in 0.1M HClO₄ were used. A RHE electrode was employed as a reference electrode in all experiments.

B. Instruments:

Electrochemical scanning tunneling microscopy (EC-STM) was carried out under a N₂ environment using a Nanoscope E controller (Veeco), and a Molecular Imaging 10 μ m scanner. The STM head was placed inside a Molecular Imaging PicoIC isolation chamber.

The STM tip morphology was studied by scanning electron microscopy (SEM) using a LEO-1550 Field Emission SEM (FE-SEM).

C. Methods:

1. STM tip (Ru-decorated Au tip) preparation procedure:

- 1) Electrochemical etching, at 30V, was carried out in hydrochloric acid solution (1:1 volume ratio) until breakage of the Au wire, typically 3 minutes

- 2) Annealing of the gold tip on a quartz plate for 2 minutes in the dark (so as to be able to visually assess wire temperature)
- 3) Re-etching at 5V in the hydrochloric solution (1:1 volume ratio) for 3 seconds
- 4) Surface masking of the Au tip with Apiezon wax leaving only a few microns exposed at the end of the tip
- 5) Electrochemical deposition of Ru on the Au tip in 1mM RuCl₃ and 0.1M HClO₄ solution by holding the potential at -0.05V (vs. RHE) for 15 minutes.

2. General procedures of the EC-STM experiment

- 1) Prepare Ru tip and Pt(111) substrate
- 2) Align the tip and the substrate, assemble the cell
- 3) Purge with N₂ for half an hour to replace the atmosphere
- 4) Inject CO saturated 0.1M HClO₄ solution, turn down N₂ flow
- 5) Record the I-V curve of the tip (taken as background)
- 6) Set the potentials of the tip and substrate so that the leakage current of the tip will be less than 10 pA.
- 7) Set a bias voltage (e.g., 10 mV) and a setpoint current (e.g., 2 nA), engage the tip to the substrate
- 8) Acquire STM image over a wide range, then center the tip over a large terrace, let the tip scan slowly over a small area (e.g., 5 nm × 5 nm)
- 9) Switch the STM to constant height mode
- 10) Set all gains to zero, turn off all plane-fitting functions
- 11) Zero the bias voltage
- 12) Record the I-V curve of the tip, repeat to determine the stability of the signal
- 13) Disengage the tip from the substrate
- 14) Record the I-V curve of the tip, compare it with the original background

3. DFT calculation

DFT calculations were performed using the DACAPO code (<http://www.fysik.dtu.dk/CAMPOS>) with calculating parameters chosen to be sufficient for the convergence in energy while of relatively less computational effort. A three-layer Ru(001) slab and a three-layer Pt(111) slab were constructed and separated by a given

distance. OH and CO were allowed to adsorb, with a 1/4 monolayer (ML) coverage, on the facing surfaces of the Ru slab and the Pt slab, respectively. Adsorbates and metal atoms in the surface layer of the substrates were allowed to relax. The surface Brillouin zone was sampled at 6×6 special Chadi-Cohen k -points. The Kohn-Sham one-electron valence states were expanded in a basis of plane waves with kinetic energies up to 25 Ry, and ionic cores were described by ultrasoft pseudopotentials. The exchange-correlation potential and energy were described self-consistently using the GGA-PW91 functional.

At a given surface-to-surface distance, e.g., 4.0 Å, all possible combinations of the adsorption sites of OH and CO were calculated. The molecular dynamic process was terminated only when the stress on each atom was less than 0.05 eV/Å.

II. Supplemental figures:

Figure S1 Representative SEM images of a Au tip before and after surface masking with Apiezon wax.

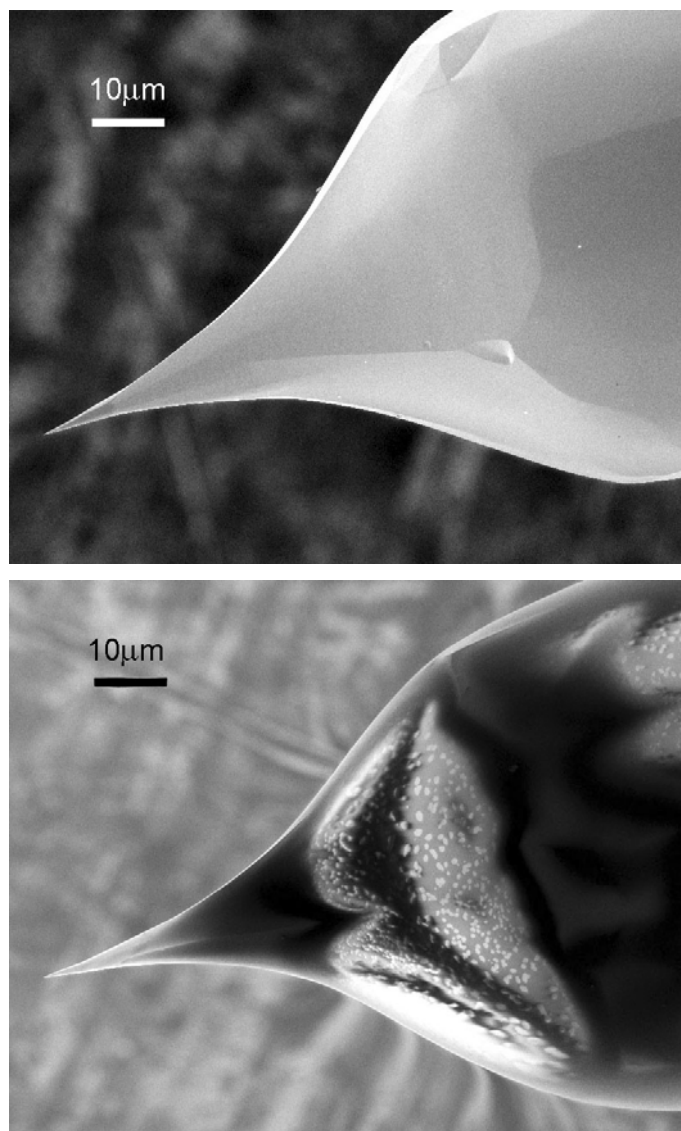


Figure S1

III. Further discussion on the observed Faradaic current density:

The Faradaic current observed upon engaging the Ru tip onto the Pt(111) substrate is on the order of 0.1 nA. If the reactive area of the Ru tip is taken to be 1 nm², the current density will turn out to be on the order of 10⁴ A/cm², which appears very large. However, on the basis of the follow considerations, such a Faradaic current density is not beyond either the theoretical maximum or the surface diffusion limit:

(a) From a physical viewpoint, an STM tip can stand a current as high as 5 nA.

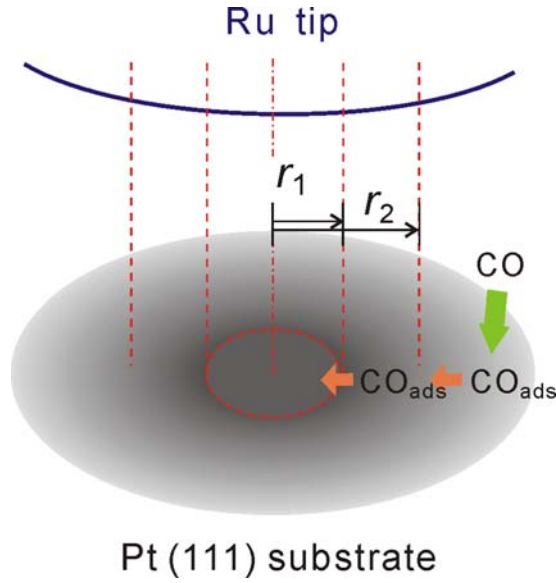
(b) From an electrochemical standpoint, the upper limit of current density (i_{\max}) can be estimated from the charge of stripping a full monolayer ($\sim 10^{-9}$ mol/cm²) of CO on Pt(111) surface and the time scale approximated by the vibrational lifetime of the bond (tens to hundreds of picosecond regime; 10^{-10} s). This estimation would lead to a maximal current density of 10⁶A/cm².

(c) The surface diffusion limiting current of CO oxidation, i_L , can be estimated (see next section for the derivation) by:

$$i_L = 2\pi\theta_0FD/\ln\frac{r_2}{r_1}$$

where θ_0 is the coverage of a full monolayer of CO (on the order of 10⁻⁹ mol/cm²), F is Faraday's constant, D is the surface diffusion coefficient of CO on Pt (111) and taken as 10⁻⁶ cm²/s (E. G. Seebauer, C. E. Allen, *Prog. Surf. Sci.* **1995**, 49, 265), r_1 is the radius of the reactive area and r_2 is the radius of a surrounding area where surface diffusion is the dominant mode of CO transport. Considering r_2 should be close to r_1 since the solution was saturated with CO, the surface diffusion limiting current (i_L) would be beyond 1 nA at $r_2/r_1 < 2$.

IV. Derivation of equation for estimating the surface diffusion limiting current



Above is a simplified model depicting the situation around the reactive area, the radius of which is r_1 . Surrounding the reactive area is a transient area with a radius r_2 , where surface diffusion is the dominant mode of CO transport. The surface diffusion limiting flux (J) through any concentric perimeter in this region is

$$J = \frac{i_L}{F2\pi r} = D \frac{d\theta}{dr}$$

where i_L stands for the surface diffusion limiting current, F is Faraday's constant, D is the surface diffusion coefficient of CO on Pt (111), r is the distance from the center of the reactive area, and θ is the surface coverage of CO. Taking the following boundary conditions: $\theta = 0$ ($r \leq r_1$) and $\theta = \theta_0$ ($r \geq r_2$), where θ_0 is the saturation coverage of CO, this differential equation can be solved as:

$$i_L = 2\pi\theta_0 FD / \ln \frac{r_2}{r_1}$$

Taking $D = 10^{-6} \text{ cm}^2/\text{s}$ (E. G. Seebauer, C. E. Allen, *Prog. Surf. Sci.* **1995**, 49, 265) and considering r_2 should be close to r_1 since the solution was saturated with CO, the surface diffusion limiting current (i_L) would be beyond 1 nA at $r_2/r_1 < 2$.