

## Electronic Supplementary Information

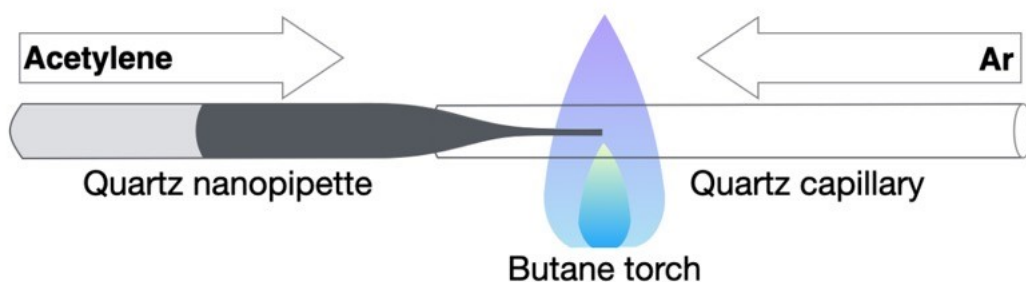
14 October, 2022

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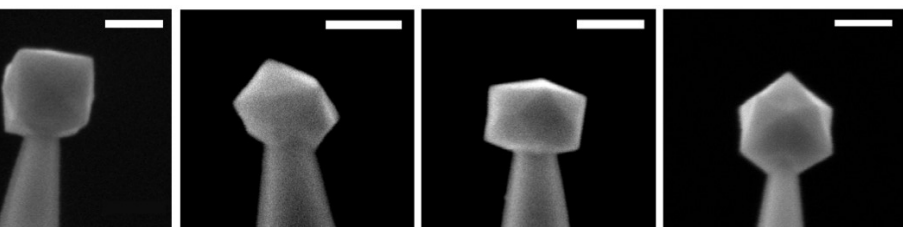
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**Preparation of carbon nanoelectrodes (CNEs).** Quartz nanopipettes were prepared using a P-2000 Laser Puller and quartz capillaries (1.0 mm O.D. and 0.7 mm I.D.), both from Sutter Instrument Company. Parameters for the laser puller were: HEAT 700, FIL 3, VEL 25, DEL 135, PUL 150. Carbon was then deposited onto the inside wall of the nanopipettes by pyrolyzing acetylene gas. Specifically, the larger end of each nanopipette was connected to an acetylene (dissolved in acetone) cylinder (Praxair), and it was then clamped horizontally and capped by a second quartz capillary (1.0 mm × 0.7 mm) connected to an Ar Cylinder (99.995%, Praxair). **Scheme S1** shows the general setup for carbon deposition within a nanopipette.



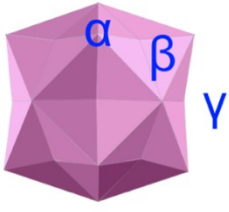
**Scheme S1.** Illustration for CNE preparation by pyrolyzing acetylene.

The flow rate of the Ar was precisely controlled by a flowmeter (Dwyer), and a gentle Ar flow between 60 to 70 sccm through the second capillary was used to protect the quartz nanopipette tip. The acetylene flow was controlled to be between 5.0 and 5.5 psi using a regulator (LP Gas). The flame of a butane torch (Dremel) was adjusted to be ~1020 °C, which was measured using a k-type thermal couple (Omega).



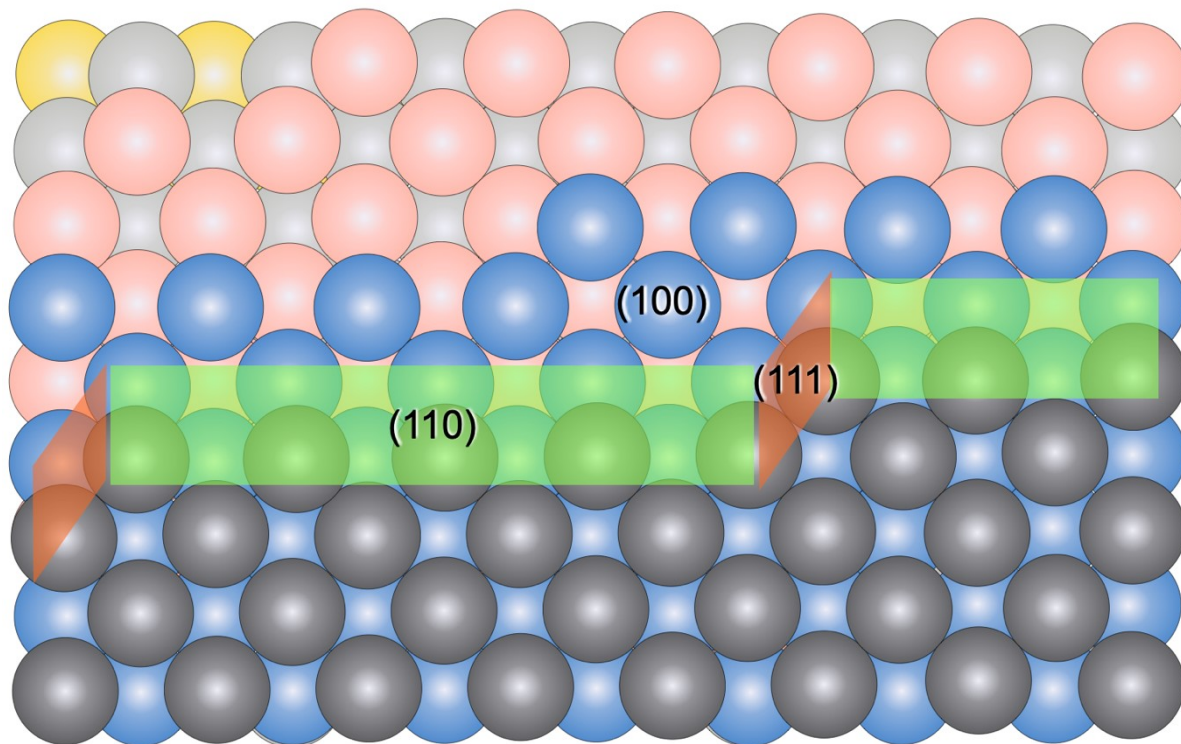
**Figure S1.** Five independently prepared HOH single Pt NPs. All scale bars are 200 nm.

**Table S1.** Equations for calculating theoretical projection angles for HOH Pt NPs.

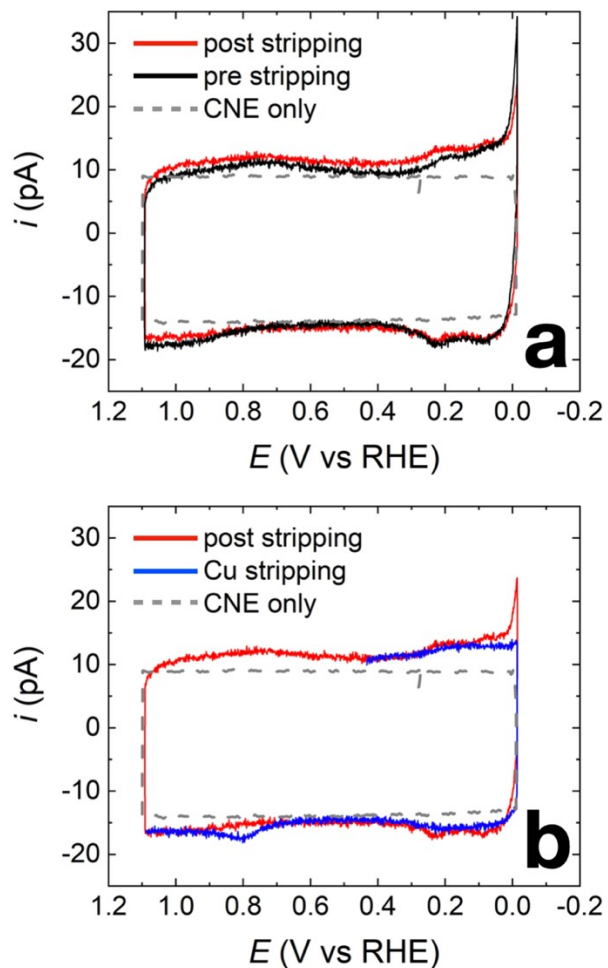
<u>Name</u>	<u>Projection Direction</u>	<u>Projection Image</u>	<u>Equations</u>
HOH {hkl}, h>k>l>0	[110]		$\alpha = 2 \tan^{-1} \left( \frac{\sqrt{2}h}{k-l} \right)$ $\beta = 90 - \left( \frac{\alpha + \gamma}{2} \right)$ $\gamma = 2 \tan^{-1} \left( \frac{h}{k} \right)$

**Table S2.** Comparison of experimentally measured projection angles and calculated values for different {hkl} combinations.

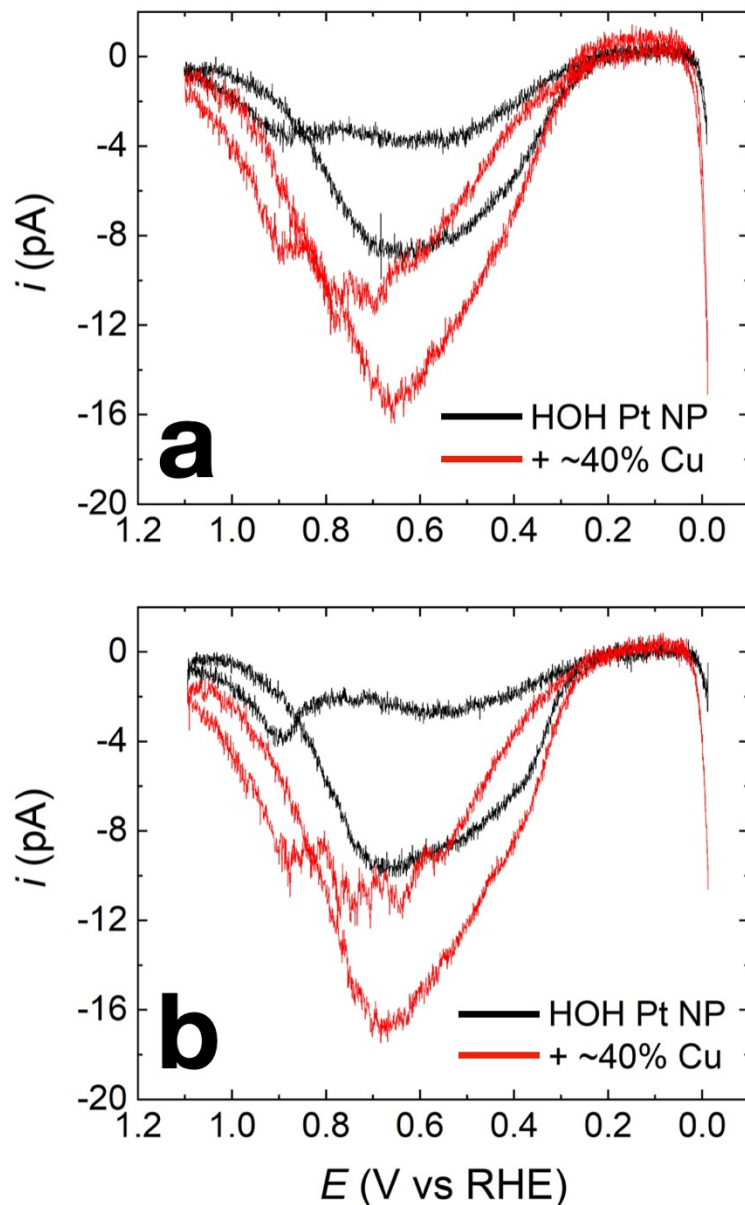
{hkl}	$\alpha$	$\beta$	$\gamma$
<b>Sample 1 (with Cu)</b>	149.4	98.7	168.7
<b>Sample 2 (with Cu)</b>	151.2	99.0	169.5
<b>Sample 3 (no Cu)</b>	150.4	98.6	171.3
<b>{11 5 1}</b>	151.2	99.4	169.9
<b>{10 5 1}</b>	148.4	100.4	169.6
<b>{8 4 1}</b>	150.3	98.1	166.6



**Figure S2.** An illustration of the atomic model of the  $\{11\ 5\ 1\}$  Pt surface facet, which is constructed of Pt(100) terraces that are separated by Pt(110) steps (highlighted in green) and Pt(111) kinks (highlighted in red). The different colors of balls represent different layers of Pt atoms.



**Figure S3.** (a) Cyclic voltammograms (CVs) obtained in 0.5 M  $\text{H}_2\text{SO}_4$  at a scan rate of 1.0 V/s on the same single Pt NP before (black) and after (red) Cu UPD and Cu-stripping.  $\sim 40\%$  of a Cu monolayer was first deposited and then stripped. The similarity of the CVs in (a) indicate that the electrochemical characteristics of the HOH Pt NP are essentially unchanged after deposition and removal of Cu. The red trace in (b) is the same as in (a) and the blue trace in (b) shows the Cu stripping voltammogram in 0.5 M  $\text{H}_2\text{SO}_4$  at a scan rate of 1.0 V/s after 240 s of Cu UPD at 0.42 V. The small peak at  $\sim 0.80$  V in (b) corresponds to the removal of Cu from the Pt surface. The dashed line corresponds to the current from the carbon nanotube electrode (CNE) only.



**Figure S4.** Comparison of CVs for the FAO reaction on HOH single Pt NPs (black) and HOH single Pt@Cu<sub>40%</sub> NPs (red). These CVs are replicates corresponding to Figure 3 in the main text. The similarity of the CVs shown here and in Figure 3 demonstrate the reproducibility of the fabrication methodology. The three pairs of CVs were obtained using independently prepared single Pt NPs. The CVs were recorded in freshly prepared solutions containing 0.50 M HCOOH and 0.50 M H<sub>2</sub>SO<sub>4</sub> at a scan rate of 0.10 V/s.

**Control experiments in NaOH solution.** The Cu adlayer on Pt, deposited via the UPD process, has been reported to be stable in alkaline solutions.<sup>1,2</sup> Moreover, distinct voltammetric features related to the oxidation and reduction of the Cu adlayer can be observed between 0.5 V and 1.2 V (vs. RHE) when scanning the Cu-decorated Pt surface between 0.0 V and 1.2 V in 0.1 M NaOH. Accordingly, we compared the voltammetric features of an HOH single Pt NP after Cu UPD and FAO treatment in 0.10 M NaOH.

This experiment was carried out as follows. (1) The single Pt NP was first cleaned in 0.50 M H<sub>2</sub>SO<sub>4</sub> by scanning between -0.01 V and 1.10 V for 7 cycles. (2) Three consecutive CVs were obtained by scanning the electrode potential between -0.01 V and 1.20 V in 0.10 M NaOH at 1.00 V/s. (3) Cu UPD was carried out in a solution containing 10.0 mM Cu(ClO<sub>4</sub>)<sub>2</sub> and 0.10 M HClO<sub>4</sub> by stepping the electrode potential to 0.42 V for 240 s. This leads to the formation of an HOH single Pt@Cu<sub>40%</sub> NP. (4) Three consecutive CVs of the HOH single Pt@Cu<sub>40%</sub> NP were then obtained by scanning in the same potential window as in step 2 in 0.10 M NaOH. (5) The same HOH single Pt@Cu<sub>40%</sub> NP was then scanned between -0.01 V and 1.10 V for 8 cycles in a solution containing 0.50 M HCOOH and 0.50 M H<sub>2</sub>SO<sub>4</sub>. (6) A final set of CVs was obtained by scanning the potential of the HOH single Pt@Cu<sub>40%</sub> NP between -0.01 V and 1.20 V in 0.10 M NaOH. The electrodes were gently rinsed in DI water between operations in different solutions. There is little difference between the second and third cycles of CV when scanning in 0.10 M NaOH. CVs presented below are the third cycles.

The CVs obtained in steps 2, 4, and 6 (as described above) are presented in **Figure 5** in the main text. Specifically, **Figure 5a** compares the CVs of the HOH single Pt NP (step 2, black) and its HOH single Pt@Cu<sub>40%</sub> counterpart (step 4, blue) immediately after Cu UPD. The blue trace in **Figure 5b** is the same as the

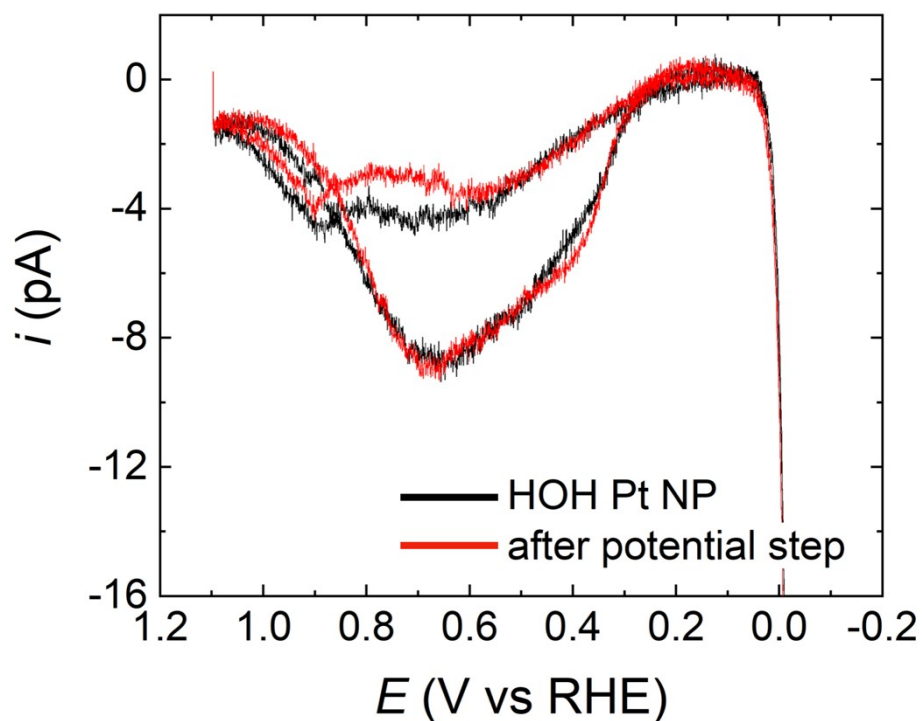


blue trace in **Figure 5a**, but here it is compared with a CV obtained using an HOH single Pt@Cu<sub>40%</sub> NP after FAO measurements (step 6, green).

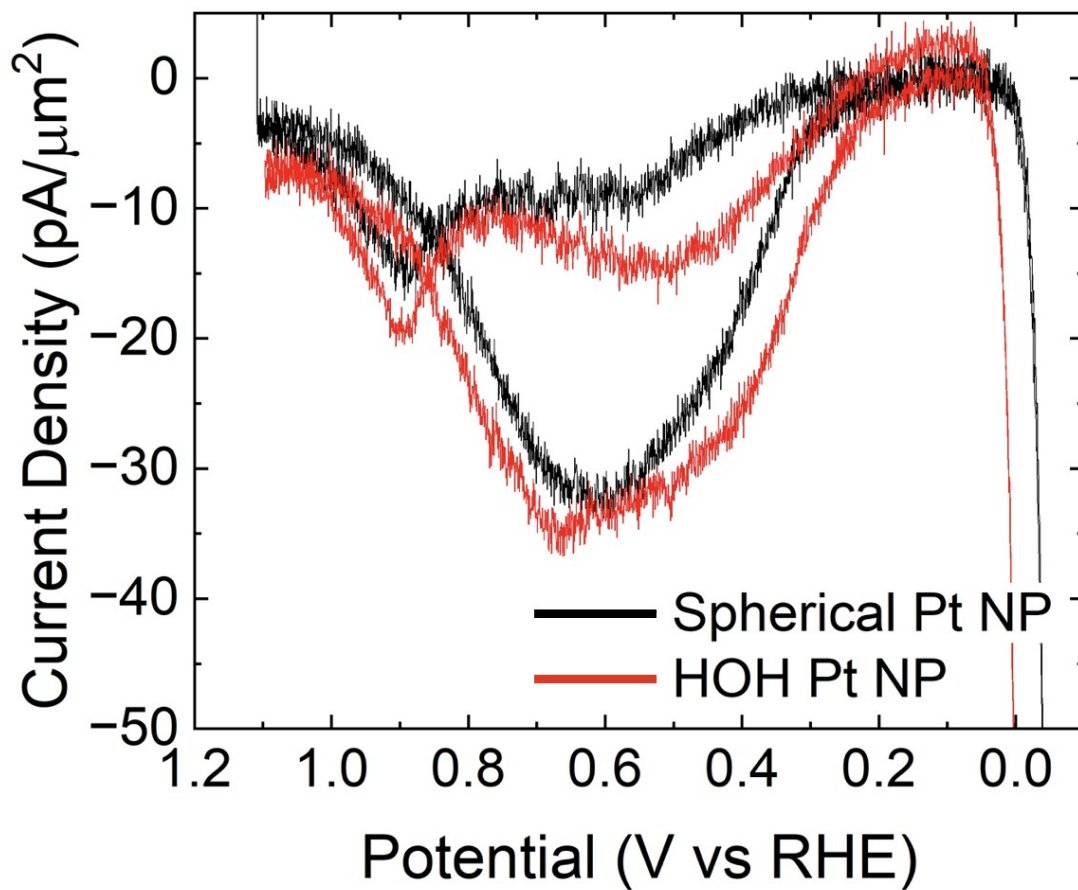
**Control experiments in the absence of Cu.** We have shown that the electrocatalytic activity of HOH single Pt NPs for the FAO reaction is enhanced by ~40% following Cu UPD. While this enhancement correlates with the presence of Cu, we performed a control experiment to ensure that Cu is responsible for this observation.

Specifically, an HOH single Pt NP was first cleaned in 0.50 M H<sub>2</sub>SO<sub>4</sub> by cycling its potential (6-8 times) between 0.0 V and 1.1 V. The cleaned single Pt NP was then used to obtain FAO CVs in a solution containing 0.50 M HCOOH and 0.50 M H<sub>2</sub>SO<sub>4</sub>. The FAO CVs were obtained by scanning the electrode between -0.01 V and 1.10 V five times. Next, the Pt-only NP was subject to a potential step from 0.90 V to 0.42 V for 240 s. This last step was intended to mimic the Cu UPD step, but it was carried out in the absence of Cu<sup>2+</sup>. Following these steps, the FAO CVs of the single NP were obtained again using the same parameters described above.

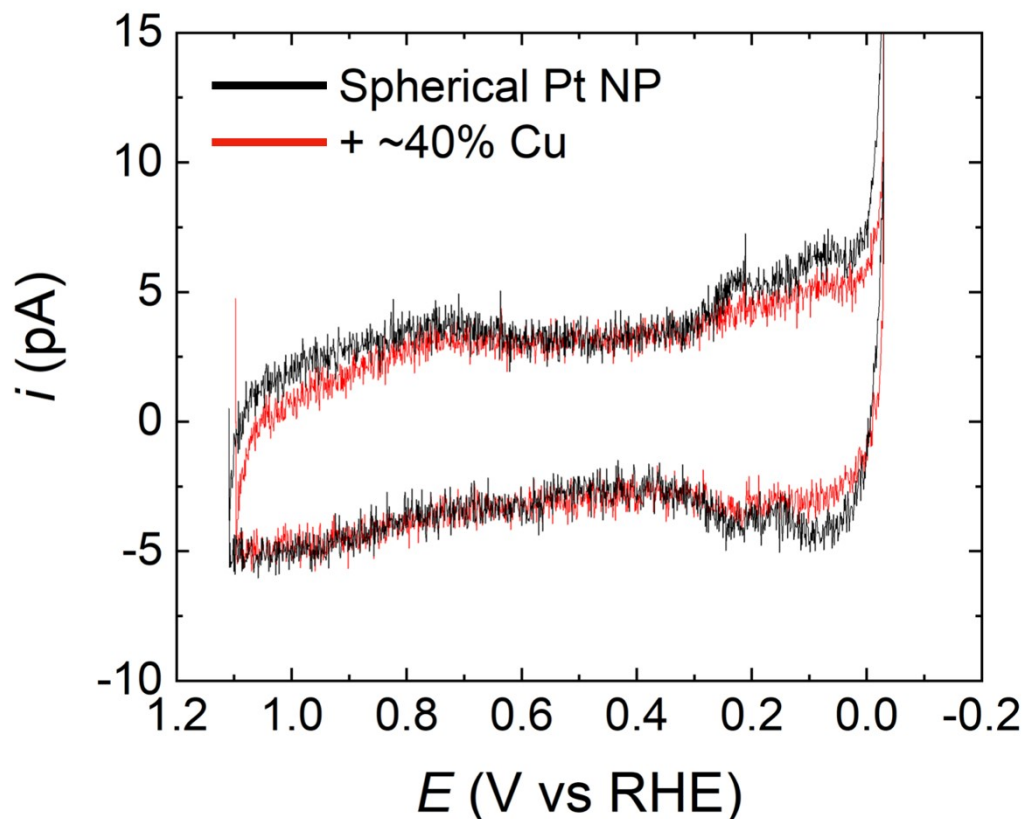
**Figure S5** shows a comparison of the FAO CVs before and after the potential step. The results indicate that there is almost no difference in the current, onset potentials, or peak positions in the two CVs. Because the only difference between this experiment and the procedure used to obtain the data in **Figure 3** (main text) was the presence of Cu<sup>2+</sup>, we conclude that the presence of Cu on the electrode surface causes the electrocatalytic activity enhancement for the FAO reaction on HOH single Pt NPs.



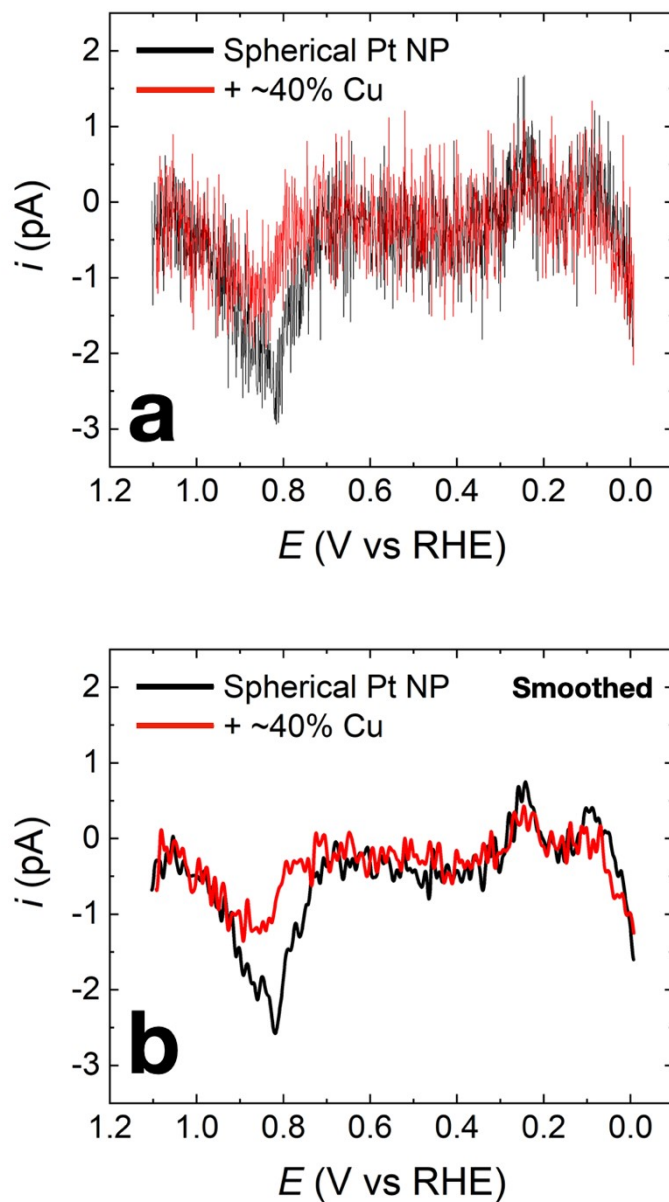
**Figure S5.** The black trace is the FAO CV that was obtained using an HOH single Pt NP immediately after electrochemical cleaning in 0.50 M  $\text{H}_2\text{SO}_4$ . The red trace is the FAO CV that was obtained using the same single NP but after a potential step from 0.90 V to 0.42 V for 240 s in a 0.10 M  $\text{HClO}_4$  solution. The result shows that the introduction of Cu is required for the enhancement of activity on HOH single Pt NPs for the FAO reaction.



**Figure S6.** FAO CV comparison between a spherical single Pt NP (black) and an HOH single Pt NP (red) prior to Cu modifications. The CVs were recorded in freshly prepared solutions containing 0.50 M HCOOH and 0.50 M H<sub>2</sub>SO<sub>4</sub> and obtained using a scan rate of 0.10 V/s.



**Figure S7.** CVs recorded in a 0.50 M  $\text{H}_2\text{SO}_4$  solution for a polycrystalline spherical single Pt NP (black) and the same NP with ~40% Cu surface coverage after FAO measurements (red). The scan rates are 1.0 V/s in both cases. This result shows that a significant amount of the original Pt surface is still covered by Cu after FAO measurements. This finding suggests that the submonolayer of Cu deposited on polycrystalline spherical Pt NP is stable during the FAO reaction.



**Figure S8.** (a) CO\*-stripping voltammograms of a polycrystalline spherical single Pt NP before (black) and after (red) Cu surface modification with ~40% Cu surface coverage. (b) The same data as in (a) but smoothed using a 5-pt FFT filter in Origin. The scan rate was 1.0 V/s and the electrolyte solution consisted of 0.50 M H<sub>2</sub>SO<sub>4</sub>. The result suggests that the submonolayer of Cu on spherical Pt NP surface blocks some active sites for CO\* binding and oxidation during the FAO reaction. This finding contrasts with the results for HOH single Pt NPs before and after Cu-modification.

## References

- (1) Luo, L.; Zhang, L.; Duan, Z.; Lapp, A. S.; Henkelman, G.; Crooks, R. M. Efficient CO Oxidation Using Dendrimer-Encapsulated Pt Nanoparticles Activated with <2% Cu Surface Atoms. *ACS Nano* **2016**, *10* (9), 8760–8769. <https://doi.org/10.1021/acsnano.6b04448>.
- (2) Borthen, P.; Hwang, B. J.; Strehblow, H. H.; Kolb, D. M. In Situ Observation of the Potential-Dependent Chemical State and Structure of a Cu Monolayer Deposited on the Surface of Carbon-Supported Platinum Clusters. *J. Phys. Chem. B* **2000**, *104* (21), 5078–5083. <https://doi.org/10.1021/jp993168j>.