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Strain Effects on the Oxidation of CO and HCOOH on Au–Pd Core–Shell Nanoparticles

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Supporting Information

ABSTRACT: The mechanism of CO and HCOOH electrooxidation in an acidic solution on carbon-supported Au–Pd core–shell nanoparticles was investigated by differential electrochemical mass spectrometry and in situ Fourier transform infrared (FTIR) spectroscopy. Analysis performed in nanostructures with 1.3 ± 0.1 nm (CS1) and 9.9 ± 1.1 nm (CS10) Pd shells provides compelling evidence that the mechanism of adsorbed CO (COads) oxidation is affected by structural and electronic effects introduced by the Au cores. In the case of CS10, a band associated with adsorbed OH species (OHads) is observed in the potential range of CO oxidation. This feature is not detected in the case of CS1, suggesting that the reaction follows an alternative mechanism involving COOHads species. The faradaic charge associated with COads oxidation as well as the Stark slope measured from FTIR indicates that the overall affinity and orbital coupling of CO to Pd are weaker for CS1 shells. FTIR spectroscopy also revealed the presence of HCOOads intermediate species only in the case of CS1. This observation allowed us to conclude that the higher activity of CS10 toward this reaction is due to a fast HCOOads oxidation step, probably involving OHads, to generate CO2. Density functional theory calculations are used to estimate the contributions of the so-called ligand and strain effects on the local density of states of the Pd d-band. The calculations strongly suggest that the key parameter contributing to the change in mechanism is the effective lattice strain.

KEYWORDS: formic acid, Au–Pd core–shells, DEMS, in situ FTIR, strain effect

INTRODUCTION

The catalytic activity of bimetallic structures can be significantly different from that of the individual components and can be tuned through the controlled growth of thin films on foreign supports.1,2 The reactivity of this type of system can be rationalized in terms of electronic and geometric (so-called strain) effects, which can alter the position of the d-band center.3,4 Pd overlayers on Au substrates have received a significant amount of attention for a variety of catalytic reactions, particularly in the context of the hydrogen evolution–oxidation reactions and formic acid oxidation, where it has been shown that the underlying Au substrate can alter the electrocatalytic activity of the Pd layers.5–11 The generation of complex Pd-based nanostructures has also provided a rich variety of structures and compositions with interesting catalytic properties.12–15

A strong dependence on the Au substrate structure has been experimentally demonstrated for the oxidation of adsorbed CO (COads) on Pd overlayers.16,17 Density functional theory (DFT) calculations concluded that the COads binding energy at pseudomorphic Pd overlayers on Au (111) surfaces goes through a maximal value for two overlayers,18 although it is not
clear how the computed strain of the relaxation mechanism compared with experimental values. The effective strain of Pd nanoshells on Au cores in the range of 1–10 nm can be described by the generation of edge dislocation with Burgers vectors of $\langle 110 \rangle$ in the $(111)$ plane.\textsuperscript{19,20} The Pd strain relaxation manifests as an increase in the charge associated with the oxidation of CO$_{\text{ads}}$ corrected by changes in the mean particle surface roughness.

The oxidation of HCOOH at Pd surfaces, contrary to the case of Pt, is commonly associated with the so-called direct mechanism in which no CO$_{\text{ads}}$ intermediate is generated.\textsuperscript{21,22,25,26} It is proposed that the reaction rate is controlled by the oxidation of adsorbed formate (HCOO$_{\text{ads}}$) intermediates.\textsuperscript{25,27} Although the catalytic activity of HCOOH has been investigated as a function of the Pd content, the rationale for the experimental trends has not been clarified.

In this paper, the electrooxidation of CO$_{\text{ads}}$ and HCOOH on Au–Pd core–shell nanoparticles, supported on Vulcan XC-72R, is studied by in situ Fourier transform infrared (FTIR) spectroscopy and differential electrochemical mass spectrometry (DEMS). The experimental data provide conclusive evidence that the surface binding of key intermediates is strongly affected by the Pd thickness. In particular, we show that CO$_{\text{ads}}$ oxidation at CS10 particles undergoes a reaction with adsorbed OH (OH$_{\text{ads}}$) species, while no evidence of this intermediate was obtained in the case of CS1. CO Stark slopes obtained from FTIR spectra also show a significantly weaker orbital interaction with strained Pd shells. The Au-like features characterizing CS1 are further demonstrated by the detection of HCOO$_{\text{ads}}$ intermediate species during the oxidation of HCOOH, an intermediate not observed in the case of CS10. We further rationalize the contrast in electrocatalytic activity by employing DFT calculations for model structures, assessing the role of ligand and strain (geometric) effects. Analysis of the Pd d-band local density of states strongly suggests that the contrast in electrocatalytic properties is primarily linked to strain in the Pd lattice.

## RESULTS AND DISCUSSION

Characteristic transmission electron microscopy (TEM) images of 20 nm Au nanoparticles coated with 1.3 ± 0.1 nm (CS1) and 9.9 ± 1.1 nm (CS10) thick layers of Pd are illustrated in Figure 1. High-resolution imaging of the core–shell boundary shows lattice fringes extending from the Au core into the thin Pd layer in CS1 (Figure 1a), consistent with “quasi” epitaxial growth. Figure 1b shows a narrow size distribution, which is preserved upon dispersion over the carbon support (Figure 1c). Figure 1d shows high-resolution TEM images of a CS10 particle in which the contrast between the Pd shell and the Au core is visible under bright field mode. The dark field image in Figure 1e does provide a stronger contrast between the 10 nm Pd shell and the Au core, while Figure 1f also demonstrates a good dispersion of the particles once deposited onto the carbon support. EDX line-scan analysis in Figure S1 further confirms the core–shell configuration of these nanostructures, which is consistent with the low-temperature method used for depositing the Pd layer onto the Au cores.\textsuperscript{10–22,26} Indeed, previous electron diffraction studies performed on particles obtained by this method also reveal diffraction spots associated with the Au and Pd lattices, which allowed the effective strain of the shell to be estimated.\textsuperscript{19,26} The mean shell thickness was estimated as the difference between the average diameter of the core–shell and core nanoparticles based on the statistics of >200 particles from each composition (Table S1). The mean shell thickness correlates well with analysis of individual particles employing STEM–EDX line-scan analysis (Figure S1). Consequently, the structure–activity relationships described below are based on the most representative particle dimensions, as opposed to a small selection of particles imaged by electron microscopy.

Figure 2 shows typical cyclic voltammograms for the oxidation of a monolayer of adsorbed CO on CS1 and CS10 catalysts in 0.5 M H$_2$SO$_4$. The data are magnified in the potential range in which CO oxidation occurs, while voltammograms across the whole potential range can be found in Figure S2. Both catalysts exhibit a CO$_{\text{ads}}$ oxidation peak at around 0.9 V, although CS10 is characterized by a significantly sharper response. CS10 also exhibits a prepeak that has been assigned to the oxidation of CO$_{\text{ads}}$ at defect sites, which is consistent with the fact that these particles exhibit a degree of surface roughness.\textsuperscript{16,21} The dashed lines in both voltammograms correspond to the responses recorded during the second potential cycle. The second cycle corresponds to a CO-free Pd surface; thus, the difference in faradaic charges recorded in the first and second forward sweep is effectively proportional to the population of adsorbed CO. Calculations of effective surface areas are nontrivial, which we have tackled by quantifying several independent surface sensitive probes, including hydrogen adsorption, hydrogen absorption, oxide reduction, and oxidation of adsorbed CO.\textsuperscript{20,21} This multi-parameter approach allows a self-consistent analysis of the effective surface area regardless of uncertainties in particle loading, the amount of catalyst layer deposited on the electrode, the particle size, and the mean nanoparticle surface roughness. For example, the charge associated with CO$_{\text{ads}}$ oxidation at CS10 particles (0.31 mC cm$^{-2}$) is very close to the values reported for bulk Pd, while the corresponding charge for CS1

![Figure 1](https://example.com/figure1.jpg)
(0.16 mC cm$^{-2}$) approaches values observed at pseudomorphic Pd monolayers on Au(111) surfaces.$^{21}$ It should be mentioned that comparisons with pure Pd nanoparticles on carbon supports are not straightforward because of the influence of a variety of parameters such as particle size and functional groups on the carbon support.$^{21,28}$

The oxidation of CO$_{ads}$ is commonly associated with a surface bimolecular reaction involving adsorbed OH species (OH$_{ads}$), which is not linked to any clear voltammetric feature. Consequently, the shape of the voltammogram does not provide direct evidence of the oxidation mechanism or the CO binding energy. We shall address some of these issues employing in situ FTIR.

Figure 3 shows FTIR spectra obtained in the range of 0.2−1.2 V versus a reversible hydrogen electrode (RHE) in the presence of an adsorbed CO monolayer at CS1 (a and c) and CS10 (b and d). The spectrum at 0.20 V ($E_{ref}$), corresponding to the maximal CO coverage, was used as a reference. The emergence of positive bands at a given potential ($E$) indicates a decrease in the population of species responsible for the IR absorption with respect to the population at $E_{ref}$. Initially, a bipolar signal is observed in both samples at 1970−1920 cm$^{-1}$, which is ascribed to bridge-adsorbed CO (CO B).$^{29}$ As the potential is increased from 0.90 to 1.2 V, this band becomes positive, indicating that CO$_{ads}$ is being oxidized. The negative band at 2343 cm$^{-1}$ corresponds to CO$_2$. The onset potential for the CO$_2$ band is 0.50 V for CS10 and 0.70 V for CS1. This result indicates that the onset potential for CO$_{ads}$ oxidation is more negative in the case of CS10.

A close inspection of the spectral range between 3800 and 3600 cm$^{-1}$ (Figure 3c,d) shows the development of a negative band at approximately 3700 cm$^{-1}$ in the case of CS10. This band is associated with OH$_{ads}$ stretching,$^{30,31}$ the population of which decreases as the applied potential increases. The fact that the 3700 cm$^{-1}$ feature is absent in the case of CS1 has very interesting implications for the mechanism of adsorbed CO oxidation as summarized in Scheme 1. In the case of CS10, CO$_{ads}$ electrooxidation is promoted by OH$_{ads}$ species generated from water molecules interacting with the Pd surface to generate CO$_2$, a process previously established for bulk Pd.$^{32}$ In contrast, this reaction undergoes an alternative pathway at the surface of CS1 particles, most likely involving adsorbed carboxylate species (COOH$_{ads}$) formed by a direct reaction between CO$_{ads}$ and water. This adsorbate is not stable and rapidly decomposes to CO$_2$, as proposed in previous studies.$^{37,38}$ The short lifetime and low coverage of this intermediate could justify the fact that it cannot be detected spectroscopically.$^{27}$
Figure 4 illustrates the integral of the band intensities assigned to CO\textsubscript{B} and CO\textsubscript{2} at each electrode potential employing the method developed by Iwasita and Nart\textsuperscript{29}. Integration of the CO\textsubscript{2} band was easily performed for the spectra presented in Figure 3. However, it was not possible to directly integrate the CO\textsubscript{B} band because of its bipolar character. Consequently, the reference spectrum was changed to one at which no adsorbed CO\textsubscript{B} was present on the surface, to obtain monopolar bands. In this case, the spectrum acquired at 1.10 V was taken as a reference for the calculation of the FTIR spectra and the whole series was replotted as shown in Figure S3. For both electrodes, the CO\textsubscript{B} band intensity remains constant in the potential region prior to the onset of CO\textsubscript{B} oxidation and decreases as the formation of CO\textsubscript{2} occurs. The data show that the onset of CO\textsubscript{2} formation is approximately 150 mV more negative at CS\textsubscript{10} than at CS\textsubscript{1}.

The potential dependence of the CO\textsubscript{B} band center (obtained from the spectra in Figure S3) is displayed in Figure 5. The upshift of the band center with increasing applied potentials can be linked to (i) metal-induced changes in the population of the CO antibonding orbital (back-bonding effect), (ii) perturbations of the vibration frequency due to the static double-layer electric field (Stark effect), and (iii) lateral interactions between adsorbed molecules\textsuperscript{34,35}. Firstly, it can be observed that the CO\textsubscript{B} stretching frequency at 0.20 V is similar for both catalysts (1951 and 1948 cm\textsuperscript{-1} for CS\textsubscript{1} and CS\textsubscript{10}, respectively). However, there are significant differences with regard to the change in the wavenumber with potential (i.e., dv/dE, commonly known as the Stark slope). It is observed that between 0.20 and 0.45 V the Stark slope for CS\textsubscript{1} is 22 cm\textsuperscript{-1} V\textsuperscript{-1} while CS\textsubscript{10} shows a value of 48 cm\textsuperscript{-1} V\textsuperscript{-1}. The Stark slope of CS\textsubscript{10} is close to the values reported for bulk Pd crystals and Pd adlayers at Pt surfaces,\textsuperscript{36–38} suggesting strong binding of CO to the relaxed Pd shell. On the other hand, the shallower Stark slope in CS\textsubscript{1} reveals a weaker back-donating effect and, consequently, weaker CO bonding. This trend is consistent with the view that strained Pd shells adopt catalytic behavior similar to that of the Au core, which is characterized by weak CO bonding in acidic media\textsuperscript{33,39,40}. It is interesting to see a decrease in the Stark slope of CS\textsubscript{10} to values close to CS\textsubscript{1} in the potential range of CO\textsubscript{ads} oxidation (between 0.45 and 0.70 V), suggesting a weakening of CO binding. This observation is yet to be fully rationalized, although it suggests a nontrivial link between CO coverage and binding strength.

Figure 6 shows the cyclic voltammograms (black line) and the simultaneously recorded mass spectrometric cyclic voltammograms (MSCVs, red lines) for m/z 44 (corresponding to CO\textsubscript{2}) for CS\textsubscript{1} and CS\textsubscript{10} in 0.1 M HCOOH and 0.5 M H\textsubscript{2}SO\textsubscript{4}. In both cases, the CO\textsubscript{2} mass signals follow the corresponding voltammetric profile of formic acid oxidation, albeit with a slight offset because of the lag time between the formation and detection of CO\textsubscript{2}. Via calculation of the current efficiency (ε\textsubscript{CO\textsubscript{2}}) as described in the Supporting Information, values of approximately 100% were estimated, confirming CO\textsubscript{2} as the only product in formic acid oxidation. The differences between the currents in the CVs and the Faradaic currents calculated from the MSCVs could be due to the contribution of double-layer charging and OH adsorption—desorption processes to the current in the CVs\textsuperscript{41}.
Figure 6. Faradaic currents associated with the oxidation of HCOOH obtained from CV (black) and MSCV (red). The MSCV signal was calculated from m/z 44 (CO₂). The electrolyte solution contained 0.1 M HCOOH and 0.5 M H₂SO₄. The electrode potential was scanned at 1 mV s⁻¹.

Figure 7 shows the FTIR spectra recorded during formic acid electrooxidation as the potential is increased from 0.05 V (reference potential) to 1.20 V. The spectra exhibit three positive bands around 1200, 1620, and 1700 cm⁻¹, which correspond to bisulfate/sulfate anions, water bending, and carbonyl vibration from HCOOH, respectively.²⁹,³⁹,⁴¹ The negative band located at 2343 cm⁻¹ is attributed to the formation of CO₂ during oxidation. The strong response from water (1620 cm⁻¹) introduces some complexity into the spectral analysis around this frequency range. However, it is clear that the sharp features associated with CO₉ads are absent in the spectral responses at CS1 and CS10, indicating that oxidation of HCOOH to CO₂ proceeds through the direct pathway.²¹,²⁵,⁴² A negative band at 1290 cm⁻¹ assigned to HCOO₉ads is observed as the potential is made more positive in the case of CS1 (Figure 7c), but not on the CS10 catalyst (Figure 7d). This observation strongly suggests that the lifetime of HCOO₉ads intermediates is significantly shorter on CS10 than on CS1.

As in the case of CO, the contrast in reactivity (current) and the presence of HCOO₉ads as an intermediate species in CS1 strongly suggest a Au-like behavior at the strained Pd shells, promoting a different pathway as summarized in Scheme 2. Indeed, an in situ surface-enhanced Raman spectroscopy (SERS) study by Beltramo and co-workers identified HCOO₉ads as the intermediate species in the oxidation of HCOOH at Au electrodes, in addition to little dependence of the oxidation current on the HCOOH concentration, concluding that HCOO₉ads oxidation is the rate-determining step.⁴⁰ At platinum electrodes, HCOO₉ads has previously been reported to act as a site-blocking spectator in the oxidation of formic acid.⁴³ Consequently, the weaker activity of CS1 toward the HCOOH can be linked to the formation of stable HCOO₉ads. On the other hand, the fast oxidation of HCOO₉ads at CS10 could be linked to either a weaker HCOO₉ads binding to the
relaxed Pd shell or a fast bimolecular reaction involving OH$_{ads}$ species (as shown in the spectral features in Figure 3). Given that we have no direct evidence of strain-dependent HCOO$_{ads}$ binding strength, we postulate the bimolecular reaction pathway (Scheme 2) as the most likely process promoting the fast HCOOH oxidation at CS10 particles.

The contrast in CO affinity and mechanism for formic acid oxidation provides a clear indication of changes in the electronic structure of the Pd shells as a function of thickness. However, whether these changes are exclusively related to strain or whether ligand effects do play a role it is yet to be clarified. To address this point, we have performed DFT calculations to estimate the local density of d states (LDOS), employing the effective strain relaxation parameters observed experimentally as shown in Table 1. Details of the methods of calculation can be found in Section 1 of the Supporting Information. The strategy implemented in these calculations is inspired by the work by Quaino et al.$^{44}$ contrasting the electronic structure of the CS1 Pd shells in the presence and absence (denoted as artificial structure) of the Au core. To reduce computational cost, CS1 is modeled as a Pd monolayer (as opposed to the three atomic layers corresponding to a mean thickness of 1.3 nm), although the 3.4% tensile strain observed experimentally was maintained.$^{20}$ We have also computed the electronic structure of the CS1 Pd shells in the presence and absence (denoted as artificial strain) of the Au-like behavior of the Au core. To this end, the calculated contributions from ligand effects are most likely to be negligible in comparison with the estimated 200 meV shift introduced by the strain effects.

Finally, it is interesting to place these findings in the context of our previous studies of CO$_2$ reduction.$^{23,45}$ The experimental evidence shows that the primary product in CS1 particles is CO, while CS10 will produce formate at low overpotentials. The studies presented here show that an effective tensile strain of 3.5% characteristic of CS1$^{20}$ weakens binding of CO to the Pd layer, which is consistent with CO being the main product of CO$_2$ reduction. On the other hand, fully relaxed Pd CS10 leads to a strong CO binding that promotes the formation of not only HCOO$^-$ but also methane and ethane.

### CONCLUSIONS

FTIR and DEMS studies of carbon-supported Pd–Au core–shell nanoparticles reveal significant changes in the reactivity and mechanism of CO$_2$ and HCOOH oxidation reactions as a function of Pd strain. Investigations were focused on Pd shells featuring thicknesses of 1.3 $\pm$ 0.1 nm (CS1) and 9.9 $\pm$ 1.1 nm (CS10), which are characterized by tensile strain values of 3.5 and 1%, respectively.$^{20}$ FTIR studies show evidence of the formation of OH$_{ads}$ at CS10, which reacts with adsorbed CO through a bimolecular surface reaction. No OH$_{ads}$ intermediates are detected in the case of CS1, suggesting that the reaction follows a different path involving the formation of the carboxylic species COOH$_{ads}$ as a short-lived intermediate. Furthermore, a significantly shallower Stark slope was observed in the case of CS1, suggesting CO orbital coupling with the strained Pd layer.

DEMS and FTIR studies showed that formic acid oxidation is characterized by a 100% conversion to CO$_2$ in the absence of CO intermediates at both catalysts, confirming the so-called “direct mechanism”.$^{21,25,42}$ However, FTIR responses show the presence of HCOO$_{ads}$ only in the case of CS1. This behavior suggests that HCOO$_{ads}$ has a very short lifetime at CS10, probably because of the presence of OH$_{ads}$ which can promote the fast oxidation to CO$_2$. The stronger interaction between HCOO$_{ads}$ and CS1 further confirms the Au-like behavior of the strain Pd shells, which manifests itself by a lower activity toward HCOOH oxidation. DFT calculations showed that the center of the d-band is upshifted by $>$0.26 eV with an increase in the lattice strain of the Pd shell from 1.0% (CS10) to 3.5% (CS1). The d-band shift is slightly less pronounced (by no more than 50 meV) if we include electronic effects arising from the Au core, indicating that the variations in mechanism and activity

#### Table 1. Pd d-Band Center ($\varepsilon_d$) as a Function of the Mean Pd Shell Thickness and Effective Lattice Constant ($a_0$)

| Shell Thickness | Model | $a_0$ (Å) | $\varepsilon_d$ (eV) |
|-----------------|-------|-----------|---------------------|
| CS10            | 9.9   | 3.9159    | -2.0066             |
| CS5             | 5.1   | 3.9499    | -1.9211             |
| CS1 (artificial)| 1.3   | 4.027     | -1.7424             |
| CS1             | 1.3   | 4.027     | -1.7972             |

$^a$Shell thickness of CS5 taken from ref 19. $^b$Data obtained from selected area electron diffraction reported in ref 19.
between CS1 and CS10 are mainly determined by strain effects. Finally, it should be mentioned that a direct link between the electronic structure of thin Pd layer and reaction pathways does require DFT calculations involving intermediate species and solvation effects, as recently illustrated by Schmickler and co-workers in relation to the oxygen reduction reaction.36 Arce et al. have also shown that OH adsorption at Pt strongly influences the metal surface electronic structure, even at low coverages.37 We conclude that, although a strong correlation between reaction pathways experimentally determined and the calculated strain effect on the Pd d-band center is demonstrated in this work, fundamental mechanistic insights remain to be fully rationalized.

### EXPERIMENTAL SECTION

**FTIR and Cyclic Voltammetry Measurements.** Electrochemical experiments were performed in a three-electrode electrochemical cell connected to an Autolab PGSTAT302N instrument. A large-surface area carbon rod was used as a counter electrode, and a RHE in the supporting electrolyte was employed as a reference electrode. All potentials in the text are referenced to this electrode. The working electrode was prepared by ultrasonically dispersing 2 mg of the electrocatalysts in 0.5 mL of pure water (Millipore) and 15 μL of Nafion. An aliquot of the dispersed suspension was drop-cast onto the top of the working electrode and dried at ambient temperature. The working electrode supports were glassy carbon electrodes for CO\textsubscript{ads} oxidation (7.0 mm diameter) and a gold disk for Fourier transform infrared spectroscopy (10 mm diameter). The experiments were performed in a 0.5 M sulfuric acid (Merck p.a.) solution prepared with Milli-Q water (Millipore). Fourier transform infrared spectroscopy experiments were performed with a Bruker Vector 22 spectrometer (Millipore). FTIR spectra were acquired from the average of 128 scans, obtained with 8 cm\textsuperscript{-1} resolution at selected potentials, by applying 0.05 V single-potential steps from a reference potential, in the positive direction. The reflectance ratio R/R\textsubscript{0} was calculated, where R and R\textsubscript{0} are the reflectance values measured at the sample and the reference potential, respectively. In this way, positive and negative bands represent the loss and gain of species at the sampling potential, respectively.

**DEMS Setup.** The gaseous and volatile species produced on the electroactive surface can be followed online by DEMS. The experiments were conducted in a three-electrode electrochemical cell made of Plexiglass, at room temperature and atmospheric pressure. The counter electrode was a large-surface area carbon rod, and the reference electrode was a RHE placed inside a Luggin capillary. The working electrode was fixed between a PTFE membrane (Scimat) and a glassy carbon rod, connected to an Au wire that served as the electrical contact. The experimental setup allows the simultaneous acquisition of mass spectrometric cyclic voltammograms (MSCVs) for selected m/z (mass to charge) ratios and conventional cyclic voltammograms (CVs). Details of the setup calibration are given in the Supporting Information and in previous publications.38 Electrocatalysts were deposited onto gas diffusion electrodes (GDEs) that were 7 mm in diameter following previously established procedures.39 Briefly, a microporous layer was prepared by mixing Vulcan XC-72R, ultrapure water, isopropanol (Merck, p.a.), and a PTFE dispersion (60 wt %, Dyneon) and painted onto one side of a carbon cloth until a final loading of 0.8 mg cm\textsuperscript{-2} was achieved. To fix this layer, the carbon cloth was treated at 280 °C for 0.5 h and at 350 °C for 0.5 h. Electrocatalyst inks were prepared by mixing the respective electrocatalysts with a Nafion dispersion (5 wt %, Sigma-Aldrich) and ultrapure water [1:5:10 (w/w)] and deposited onto the GDE. The final metal loading of the working electrodes was 0.7 mg of metal cm\textsuperscript{-2}.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.6b03237.

Experimental methods associated with synthesis, characterization, DEMS calibration, and DFT calculations; STEM–EDX mapping of CS1 and CS10; full CO\textsubscript{ads} oxidation voltammograms and FTIR spectroelectrochemistry of CO\textsubscript{ads} oxidation (PDF)

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**Notes**

The authors declare no competing financial interest.

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