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Shape-Controlled CO₂ Electrochemical Reduction on Nanosized Pd Hydride Cubes and Octahedra

Wenlei Zhu, Shyam Kattel, Feng Jiao, and Jingguang G. Chen*

Electrochemical CO₂ reduction reaction (CO₂RR) provides a potential pathway to mitigate challenges related to CO₂ emissions. Pd nanoparticles have shown interesting properties as CO₂RR electrocatalysts, while how different facets of Pd affect its performance in CO₂ reduction to synthesis gas with controlled H₂ to CO ratios has not been understood. Herein, nanosized Pd cubes and octahedra particles dominated by Pd(100) and Pd(111) facets are, respectively, synthesized. The Pd octahedra particles show higher CO selectivity (up to 95%) and better activity than Pd cubes and commercial particles. For both Pd octahedra and cubes, the ratio of H₂/CO products is tunable between 1 and 2, a desirable ratio for methanol synthesis and the Fischer–Tropsch processes. Further studies of Pd octahedra in a 25 cm² flow cell show that a total CO current of 5.47 A is achieved at a potential of 3.4 V, corresponding to a CO partial current density of 220 mA cm⁻². In situ X-ray absorption spectroscopy studies show that regardless of facet Pd is transformed into Pd hydride (PdH) under reaction conditions. Density functional theory calculations show that the reduced binding energies of CO and HOCO intermediates on PdH(111) are key parameters to the high current density and Faradaic efficiency in CO₂ to CO conversion.

1. Introduction

Fossil fuel utilization over the past few decades caused a rapid increase of CO₂ concentration in atmosphere. Powered by renewable electricity, electrochemical CO₂ reduction reaction (CO₂RR) could be a promising method to both reduce CO₂ emission and produce valuable chemicals. A variety of metallic catalysts have been identified as potential candidates for electrocatalytic conversion of CO₂ to CO. We recently showed that carbon supported Pd catalysts can simultaneously produce CO and H₂ in CO₂RR with an adjustable H₂ to CO ratio between 1 and 2, which is a highly desired ratio for thermochemical synthesis of methanol and Fischer–Tropsch processes. Due to the heterogeneous structure of the Pd/C catalysts, it was unclear regarding the preferred facets, such as Pd(111) or Pd(100), that would optimize the H₂/CO ratios. By comparing the well-characterized Pd cubes and octahedra in the current study, it would allow one to directly determine the effect of crystalline facets, a key step to understand design principles for using shape-controlled Pt NPs to optimize H₂/CO (or CO/H₂) ratios for the electrochemical reduction of CO₂. Although a recent study has reported CO₂RR activity over Pd(100) and Pd(111) surfaces, Pd was considered as the active sites in that study. In the current work, the in situ synchrotron-based X-ray absorption fine structure (EXAFS) measurements revealed the transformation of Pd to Pd-H under the CO₂RR conditions. This in turn allowed us to perform density functional theory (DFT) calculations on the Pd-H sites. The combined in situ and DFT results identified the importance of Pd-H formation in modifying the binding energies (BEs) of key intermediates, such as H, HOCO, and CO, which consequently modified the activity and selectivity (CO/H₂ ratio) for the CO₂RR.

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The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/aenm.201802840.

DOI: 10.1002/aenm.201802840
2. Results and Discussion

Herein, we synthesized two different types of monodispersed Pd NPs, Pd cubes and Pd octahedra with dominant Pd(100) and Pd(111) facets, respectively. The synthesis procedures for Pd NPs were based on a solution method using polyvinylpyrrolidone (PVP) as a stabilizing agent and l-ascorbic acid as a reductive agent. KBr was also added as a capping agent to assist the selective formation of Pd cubes. In the case of Pd octahedra, formaldehyde was used as a mild reducing agent to grow octahedra from Pd cube seeds. By doing so, Pd atoms could deposit on the (100) facet, leading to the transformation of Pd cubes into octahedra dominated by the (111) facet. Transmission electron microscopy (TEM) images at low magnifications (Figure 1a,c) show that Pd cubic particles have an average size of 18.4 ± 2.1 nm, whereas Pd octahedral particles have an average dimension of 29.3 ± 3.1 nm. We examined many areas of the Pd samples and concluded that both samples have a narrow size distribution (Figure S1, Supporting Information). To check the crystal nature of Pd particles, high-resolution TEM (HRTEM) analysis was performed and the results (Figure 1b,d) show clearly lattice fringes, suggesting a high crystalline nature of both Pd samples. The distances between two neighboring fringes for the Pd cubic and octahedral particles are 0.20 and 0.22 nm, corresponding to Pd(100) and Pd(111) facets, respectively. Therefore, the Pd cubes were dominated by the Pd(100) facet, whereas the Pd octahedra were dominated by the Pd(111) facet. Powder X-ray diffraction spectra (Figure S2, Supporting Information) also showed a preferential crystal growth along the (100) direction for the Pd cubes and the (111) direction for the Pd octahedra, which are in good agreement with the HRTEM results.

To investigate the phase transition from Pd to Pd hydride (PdH) in both cubes and octahedra during the CO₂RR, we performed in situ X-ray absorption spectroscopic (XAS) measurements in a CO₂-saturated 0.5 M NaHCO₃ electrolyte. The Pd K-edge X-ray absorption near-edge spectroscopy (XANES) results at various applied potentials are shown in Figure 2. Increasing the overpotential resulted in a clear shift of both peaks to lower energy, suggesting the formation of PdH. Peak A showed dipole allowed transition from Pd 1s to the 4d5p hybridized unoccupied states, and Peak B corresponded to the transition from Pd 1s to 4f state. The energy shift of Peak A was attributed to the mix of Pd antibonding bands with the unoccupied s and p orbitals of absorbed H atoms. The Pd K-edge EXAFS spectra are fitted to illustrate the Pd structural change during the CO₂RR (Figures S3 and S4, Supporting Information). The Pd–Pd bond length remains unchanged above −0.4 V at 2.731 Å. When the potential decreases to below −0.4 V, Pd–Pd bond length gradually increased to ≈2.740 Å and then quickly increased to ≈2.830 Å for both cubic and octahedral particles, indicating the formation of PdH at approximately −0.5 V. The phase transition from Pd to PdH clearly caused a lattice expansion in the Pd-based catalysts. Based on existing literature, underpotential deposition of H on Pd could occur at potentials around 0 V (vs RHE). However, our XAS results reveal that well-defined PdH phase is not formed until a potential of lower than −0.5 (vs RHE), suggesting the presence of other structures.
of surface hydrogen and/or amorphous PdH in the potential range between 0 and −0.5 V (vs RHE). On Pd(111), our DFT calculations show that H adsorption on the surface is thermodynamically more favorable by 0.33 eV compared to subsurface H adsorption. Furthermore, previous DFT calculations have shown that the energy barrier for H migration from surface to subsurface on Pd(111) is ≈0.4 eV. This suggests that surface H could potentially migrate to the subsurface and form bulk PdH phase at high negative potential in agreement with the experimental observations.

The electrocatalytic properties of Pd particles were first evaluated in a two-compartment three-electrode batch cell. A commercial Pd NP sample was also studied for comparison (structural characterization data are shown in Figures S2 and S5, Supporting Information). The electrodes were made by drop-casting a solution containing a certain concentration of Pd NPs, isopropanol and Nafion on gas diffusion layer. The CO₂ electrolysis experiments were performed in a CO₂-saturated high purity 0.5 M sodium bicarbonate (NaHCO₃) electrolyte under ambient conditions. The gas products were analyzed using a gas chromatography and the liquid products were measured by ¹H nuclear magnetic resonance spectroscopy. Figure 3a shows both CO and H₂ FEs under a variety of applied potentials. Among all the three Pd catalysts, the Pd octahedra catalyst exhibited the highest CO selectivity of 94% at an applied voltage of −0.7 V versus RHE (all the voltages are on the RHE scale unless stated otherwise), which is comparable to current state-of-the-art Pd catalysts reported in the literature (Table S1, Supporting Information). At potentials more negative than −0.7 V, CO FE decreased significantly and H₂ production increased substantially, which could be caused by the mass transport of CO₂ to active sites. At very negative potentials, H₂ and CO were the dominant products for all Pd catalysts, while a significant amount of formate was detected at potentials high than −0.5 V (Figure S6, Supporting Information), which can be attributed to the active phase switched from Pd to β-PdH at relatively negative potentials. More detailed studies on the presence of different PdH phases at different potential regions have been reported by Gao et al. A relative low current density was observed for commercial Pd/C catalyst, which was likely due to the strong CO adsorption on edge and corner sites in the sample.

CO partial current densities at various potentials are showed in Figure 3b (current density profiles can be found in Figure S7, Supporting Information), where Pd octahedra exhibited a much higher CO partial current density (≈41 mA cm⁻² at −0.9 V) than that of Pd cubes (≈15 mA cm⁻²). We also calculated current densities based on the estimated Pd surface areas using their loadings and sizes (Figure S8 and Table S2, Supporting Information). The Pd octahedra exhibited a more than three times higher CO partial current density than Pd cubes, suggesting that the Pd(111) surface is more active than the Pd(100) surface in CO₂RR. The plateau of maximum CO partial current density for the Pd octahedra was caused by CO₂ transport issues due to the low CO₂ solubility in aqueous bicarbonate electrolyte. In comparison to Pd cubes and octahedra, the commercial Pd catalyst showed a much lower CO FE (<60%) and an extremely low current density (<3 mA cm⁻²) under test conditions. We suspect that it may be due to the fact that the commercial Pd particles have a rough surface populated with low coordinated sites that unfavorably bind to intermediates for CO formation. The H₂ to CO products ratio for Pd cubes and octahedra at different applied potentials are shown in Figure 3c. At relatively negative potentials (i.e., high current densities), the H₂ to CO ratios for both Pd cubes and octahedra fall into the desired ratios of synthesis gas for Fischer–Tropsch process and methanol synthesis. The stability of Pd octahedra and cubes was examined using TEM and the results (Figure S8, Supporting Information) showed no obvious morphology change to the catalysts.

The transport limitation of CO₂ in the batch cell could be circumvented by using a flow cell system, where gaseous CO₂ is fed directly to the catalyst surface. Because Pd octahedral catalyst exhibited the best performance in the batch cell tests, we chose it for the flow cell investigation. Pd octahedral particles were first sprayed onto a 25 cm² gas-diffusion layer (i.e., a porous carbon support) with a Pd loading of 0.3 mg cm⁻².

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**Figure 2.** In situ structural characterization of Pd/C catalyst under the CO₂RR conditions using XAS. In situ XANES spectra of Pd K-edge for a) Pd octahedra and b) Pd cubes.
which served as the cathode. IrO₂ (loading: 1 mg cm⁻²) was used as the anode and 1 M KOH was used as the anolyte. A schematic diagram of the whole flow cell setup is shown in Figure S9 in the Supporting Information. Remarkably, a CO partial current densities up to 220 mA cm⁻² (corresponding to a total CO current of 5.5 A) together with a CO FE of ≈92% was achieved at a cell potential of 3.2 V (Figure S10, Supporting Information).

DFT calculations were performed to gain further insights into the CO selectivity of Pd(111) and Pd(100) surfaces. Table 1 summarizes the DFT calculated BEs (optimized configurations are shown in Figure S11, Supporting Information) of reaction intermediates involved in CO₂RR and HER on Pd/PdH(111) and Pd/PdH(100) surfaces. The BEs of *H and *CO are similar on both Pd(111) and Pd(100). *CO binds strongly on Pd(111) and Pd(100), thus its desorption is predicted to be difficult at electrochemical conditions. In contrast, all intermediates bind much more strongly on PdH(100) compared to PdH(111). The change in Gibbs free energy (ΔG) for CO₂RR along the carboxyl (*HOCO) and formate (*HCOO) pathways and HER at a potential (U) = 0 V were calculated (see Computational Methods for details) and presented in Figure 4 and Figure S12 in the Supporting Information. As shown in Figure 4a, the HER activity of Pd(111) and Pd(100) is limited by *H desorption whereas *H adsorption is the limiting step on the PdH(111) and PdH(100) surfaces. Thus the HER is predicted to be downhill in energy at applied negative potential of U = −0.34 V and U = −0.12 V on PdH(111) and PdH(100), respectively. It is found that the CO₂RR via the *HOCO pathway is energetically more favorable over *HCOO pathway on Pd(111), Pd(100) and PdH(111), while the *HCOO pathway is slightly favorable over *HOCO pathway on PdH(100) (Figure S12, Supporting Information). Figure 4b shows that *HOCO/*HCOO is stabilized on Pd(111) and Pd(100). However, *CO is strongly bound, which makes *CO desorption uphill in energy by 1.51 and 1.44 eV and Pd/PdH(100) surfaces.

**Table 1.** DFT calculated binding energies (in eV) of H, CO and HOCO on Pd and PdH surfaces.

<table>
<thead>
<tr>
<th>Species</th>
<th>Pd(111)</th>
<th>Pd(100)</th>
<th>PdH(111)</th>
<th>PdH(100)</th>
</tr>
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<tbody>
<tr>
<td>H</td>
<td>−0.58</td>
<td>−0.49</td>
<td>0.12</td>
<td>−0.10</td>
</tr>
<tr>
<td>CO</td>
<td>−2.03</td>
<td>−1.96</td>
<td>−0.50</td>
<td>−1.29</td>
</tr>
<tr>
<td>HOCO</td>
<td>−2.21</td>
<td>−2.50</td>
<td>−1.73</td>
<td>−2.16</td>
</tr>
</tbody>
</table>

Figure 3. Electrocatalytic CO₂ reduction results for Pd octahedra and cubes in a batch cell: a) FEs, b) CO partial current densities (normalized to electrode areas), and c) H₂ to CO ratios. Results for commercial Pd were also shown for comparison. Flow cell test results for Pd octahedra catalyst were shown in d). All the batch experiments were performed in CO₂-saturated 0.5 M NaHCO₃ electrolytes (pH = 7.2).
on Pd(111) and Pd(100), respectively. Thus, CO desorption is the rate-limiting step on both Pd(111) and Pd(100) surfaces. In comparison, on PdH(111), Figure 4b shows that CO desorption is the most difficult step and is uphill in energy by 0.77 eV. In contrast, it is noted that CO desorption is thermoneutral on PdH(111) and no longer a rate-limiting step. As a result, CO desorption should be much more facile on PdH(111) compared to PdH(100). Therefore, the DFT results are in agreement with the experimental findings of higher CO selectivity on PdH(111) (Pd octahedra) than PdH(100) (Pd cubes) due to the facile desorption of CO from the PdH(111) surface.

3. Conclusions

In summary, we showed that both Pd cubic and octahedral NPs have been successfully synthesized and investigated as potential electrocatalysts for CO2RR. The PdH(111) surface of Pd octahedra exhibited higher CO FE and CO partial current density than the Pd(100) surface in Pd cubes. In situ XAS studies confirmed the phase transition from Pd to PdH at about -0.5 V. DFT calculations unraveled the origin of high CO selectivity and activity to the weaker CO BE on PdH. Therefore, tuning the relative adsorption strength of CO, HOCO, and H on NPs with controlled morphology could offer opportunities to increase synthesis gas production rate and tune H2 to CO products ratio.

4. Experimental Section

Synthesis and Characterization of Pd NPs: Pd cubic NPs were synthesized according to a previously published method. Typically, 8.0 mL of an aqueous solution containing KBr (600 mg), PVP (105 mg), and L-ascorbic acid (60 mg) was added into an 11 mL vial. This vial was heated in air under magnetic stirring at 80 °C in an oil bath for 10 min. Subsequently, 3.0 mL of an aqueous solution of Na2PdCl4 (57 mg) was added with a pipette. After the vial had been loosely capped, the reaction could proceed at 80 °C in an oil bath for 3 h. The products were collected by centrifuging in water for three times (10 000 RPM, 10 min). Precipitates were resuspended in 11 mL water. Pd octahedral NPs were synthesized according to literature. Typically, 3.0 mL of an aqueous solution containing 14.5 mg of Na2PdCl4 was introduced into 7.7 mL of a mixture containing AA (60 mg), PVP (105 mg), KBr (300 mg), and 0.3 mL of the 18 nm Pd seeds, which had been heated at 60 °C for 5 min under magnetic stirring. The product was collected by centrifugation, washed ten times (10 000 RPM, 10 min) with water to remove surfactant, and resuspended in ethanol for further process.

The as-synthesized Pd catalysts were characterized using TEM (JEOL JEM-3010) and powder XRD (Bruker DB). In situ X-ray absorption spectroscopy (XAS) measurements were performed at the 5-BM-D beamline at Argonne National Laboratory. Electrochemical CO2 Reduction Test: A Princeton Applied Research VersaSTAT 3 potentiostat was used for all CO2 reduction experiments. A carbon rod was used as the counter electrode. The electrolyte was 0.5 M NaHCO3 saturated with CO2 with pH of 7.2. All potentials were measured against an Ag/AgCl reference electrode (3.0 m KCl, BASI), iR corrected and converted to RHE. Electrosynthesis was performed under room temperature in a gas-tight two-compartment electrochemical cell with two halves separated and connected with a piece of Nafton 117 membrane. Before each experiment, the electrolyte was purged again with CO2 gas for at least 30 min and the headspace for at least 20 min. Gas products were analyzed every 30 min using a gas chromatograph (SHIMADZU GC-2014) equipped with PLOT MolSieve SA and Q-bond PLOT columns, whereas liquid products were analyzed on a Bruker AVIII 600 MHz NMR spectrometer. FE calculation was based on methods described in previous papers.

For the flow cell tests, the experiments were performed in a two-channel flow cell with channels of dimension 5 × 5 × 0.15 cm3. The gas flow rate into the flow cell was controlled at 100 sccm via a Brooks GF40 mass flow controller. The cathode and anode were separated via a Sustainain anion exchange membrane.

DFT Calculations: Spin polarized DFT calculations were performed at the GGA level within the PAW-PW91 formalism using the Vienna Ab-Initio Simulation Package (VASP) code. The Brillouin zone integration was performed using a 3 × 3 × 1 Monkhorst-Pack grid and a plane wave cut-off energy of 400 eV was used for the total energy calculations. The Pd(111) and Pd(100) surfaces were modeled using six layer 3 × 3 surface slabs. Similarly, the H-terminated PdH(111) (using the NaCl crystal structure for bulk PdH) and PdH(100) surfaces were modeled using six bilayers (a bilayer contains a unit of one Pd layer and one H layer) 3 × 3 surface slabs. A vacuum layer of ~14 Å thick was added in the slab cell along the direction perpendicular to the surface in order to minimize the artificial interactions between the surface and its periodic images. During geometry optimization, atoms in the top three layers were allowed to relax while atoms in the bottom three layers were fixed until the Hellman–Feynman force on each ion was smaller than 0.01 eV Å−1. The BE of an adsorbate was calculated as:

![Figure 4. DFT calculated free energy diagrams: a) HER and b) CO2RR on Pd(111), Pd(100), PdH(111), and PdH(100).](image-url)
BE(adsorbate) = E(slab + adsorbate) – E(slab) – E(adsorbate)

where E(slab + adsorbate), E(slab), and E(adsorbate) are the total energy of slab with adsorbate, the energy of clean slab, and the energy of adsorbate in the gas phase, respectively. E(H) is taken as one-half the total energy of the H₂ molecule during the calculation of hydrogen BE. The Gibbs free energy (G) of a species is calculated as:

\[ G = E + ZPE - TS \]

Here, E is the total energy of a species obtained from DFT calculations, ZPE and S are the zero-point energy and entropy of a species respectively, and T = 298.15 K.

The free energy diagram of CO₂ RR to CO has been calculated by considering the following sequential steps:[3]

\[ \text{CO}_2 + (\text{H}^+ + \text{e}^-)^+ \rightarrow \text{HOCO} \]

\[ \text{HOCO} + (\text{H}^+ + \text{e}^-) \rightarrow \text{CO} + \text{H}_2 \text{O} \]

\[ \text{CO} \rightarrow \text{CO}^+ \]

In aqueous electrolytes, the HER inevitably takes place via the following sequential steps,[30] and competes with the CO₂ RR:

\[ \text{H}^+ + \text{e}^- + \rightarrow \text{H}(\text{Volmer step}) \]

\[ \text{H}^+ + \text{e}^- \rightarrow \text{H}_2^+ \text{e}^- \] (Heyrovsky step)

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

W.Z. and S.K. contributed equally to this work. Authors from Columbia University are partially supported by the US Department of Energy, Catalysis Program (DE-FC02-13ER16381). Authors at University of Delaware thank the financial support from the Department of Energy under Award Number DE-FE0029868. The authors also thank the National Science Foundation Faculty Early Career Development program (Award No. CBET-1350911). This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. The DFT calculations were performed using computational resources at the Center for Functional Nanomaterials, a user facility at Brookhaven National Laboratory.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

CO₂ reduction, density functional theory, free energy, Pd nanocrystals, syngas ratio

Received: September 11, 2018
Revised: December 10, 2018
Published online: January 9, 2019