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Electronic Supplementary Information

for

Isotopic Effect on Electrochemical CO_2 Reduction Activity and Selectivity in H_2O- and D_2O-based Electrolytes over Palladium

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A. Supplementary Methods

Preparation of Electrolyte

All reagents were purchased from Sigma Aldrich. 0.1M alkali-ion bicarbonate ($AHCO_3$, A=Na or K) in deionized (DI) water was prepared by bubbling CO_2 gas for 12 h into 0.05M alkali-ion carbonate in DI water. The D_2O-based electrolytes (0.1M $NaDCO_3$ and $KDCO_3$ in D_2O) were prepared by the same way with using D_2O. The pH values of these solutions were ~6.8 after the full saturation of CO_2, which is attributed to a negligible difference (~3.3 mM) in the solubility of CO_2 in D_2O and H_2O.[1]

Preparation and Characterization of Working Electrode

The commercial carbon-supported Pd (Pd/C) with Pd loading of 10 wt% was purchased from E-TEK. For the preparation of working electrode, the Pd/C catalyst was first dispersed in the mixture of deionized water and isopropanol solution (*v*:*v*=1:1) containing 0.05 wt% Nafion with a concentration of 2 mg mL^{-1}. After sonication for 20 min, the ink was dropped on water-proofed carbon paper (10%, Toray, TGP-H-060) and dried overnight. The catalyst ink was cast on both sides of carbon paper to avoid, if any, the contribution of carbon paper on CO_2RR. The areal mass loading was fixed to be 200 μg cm^{-2}.

Synchrotron X-ray diffraction profiles were obtained on the 17-BM beamline at Advanced Photon Source (APS) with a detector distance of 300 mm. Pd/C powder was loaded into capillary tubes (Polyimide, Cole-Parmer, Model: 95820-90), followed by plugging the ends with rubber clay. An amorphous silicon detector (Perkin-Elmer) was used. The 2D ring patterns were integrated and converted into 1D diffraction patterns using GSAS-II software.[2]

To analyze the particle size distribution before and after CO_2 electrolysis, transmission electron microscopy (TEM, JEOL, Model: JEM2100F) analysis was used. After long-term CO_2 electrolysis, the spent catalyst was collected by sonicating the working electrode in an ethanol-containing vial, followed by TEM analyses.

Electrochemical Measurements

A saturated calomel electrode (SCE) and graphite paper were used as reference and counter electrodes, respectively. The CO_2-saturated 0.1M $AHCO_3$ or $ADCO_3$ solutions ($A=Na^+$ or K^+) were utilized as an electrolyte. The reference electrode was calibrated before each electrolysis experiment by using a hydrogen electrode (HydroFlex, ET-070, EDAQ).

A typical air-tight two-compartment cell was filled with CO_2-saturated solution. In each compartment, 18 mL of the electrolyte was filled, leaving ~13 mL of empty head space. A proton exchange membrane (Nafion 117) was used to separate catholyte and anolyte. The working electrode was placed together with a reference electrode in the air-tight cathodic compartment. The counter electrode was located in the anodic compartment.

The electrochemical measurements were carried out using a Biologic potentiostat (SP-150). The applied potential (V) was controlled by *i*R-compensation (80%) and converted to the reversible hydrogen electrode by using the following Supplementary Equation (1):

$$V = V_{SCE} + 0.248 + 0.059 \times pH \quad (1)$$

Thus, all of the potentials in this study are written based on the reversible hydrogen electrode potential.

In order to achieve stable electrochemical CO_2 reduction data, 5 cyclic voltammetry (CV) scans were first performed with a scan rate of 100 mV s^{-1} from 0.1 to 1.2 V. After that, the electrode was scanned three times from 0 to -1.2 V by using the linear scanning voltammetry (LSV) technique. Then, two additional CV scans were used to get rid of the products from the previous LSV step under CO_2 purging. After additional CO_2 bubbling for 10 min, the electrochemical CO_2RR performance was evaluated by using the chronoamperometry (CA) method at each constant potential for 20 min. Vigorous magnetic stirring was applied during the electrolysis to help mitigate the mass transport limitation of the dissolved CO_2 in the electrolyte. The gaseous product distribution was analyzed by using gas chromatography (GC, Agilent, Agilent 7890B). Once each CA was completed for CO_2RR, 100 μL of gas in the empty head space at the cathodic compartment was collected and injected into GC to quantify the gaseous products. The liquid products were analyzed by using ^{1}H NMR with an Avance III spectrometer (Bruker) operating at 400 MHz. The ^{1}H NMR spectra were obtained in the water suppression mode. The small peak corresponding to formate ($HCOO^-$) was detected at a chemical shift of ~8.4 ppm. But, due to its negligible amount (~10^{-5} M) in the electrolyte, it was difficult to conduct a reliable quantitative analysis.

In-situ XAFS Measurements and Analyses

A lab-made acryl kit was used for the *in-situ* X-ray measurements. The areal mass loading of the working electrode was ~5 mg cm^{-2} in order to achieve sufficient XAFS signal. During the measurements, CO_2 gas was continuously bubbled into the electrolyte. The other conditions were the same as in the electrochemical measurements. The potential range was determined after confirming the potential range sufficient for phase transition of Pd-to-Pd hydride (PdH) or Pd deuteride (PdD).

In-situ XAFS measurements were conducted in the 7-BM beamline (QAS) at National Synchrotron Light Source-II (NSLS-II) at Brookhaven National Laboratory. Both transmission and fluorescent signals were detected from 0.3 V to -0.8 V with a 0.1 V interval. Each potential was held for 1 min before measurement and for an additional 10 min using CA technique during each XAFS measurement. The typical duration for a single spectrum was 1 min and ten spectra were merged to get high signal-to-noise spectrum at each potential. During all of the XAFS measurements, the spectrum of reference Pd foil was simultaneously recorded, and was further used for calibrating the edge energy (E_0) of the sample under analysis.

The obtained spectra were processed using the ATHENA and ARTEMIS software in IFFEFIT package.[3-5] The procedure which was described in B. Ravel *et al.,* was followed during the data process.[3] EXAFS analyses were conducted by using the ARTEMIS software. The EXAFS spectrum ($\chi(k)$) was weighted with k^2 value to intensify the signal in the high k-regime. The Hanning window was utilized for the Fourier-transform. All of the EXAFS fittings were done in the R-space. The goodness of fitting was evaluated based on the reliable factor (*R*-factor) and reduced chi-square (reduced χ^2). The fitted spectra at the initial and final potentials are shown in Supplementary Figure 3. The fitting results are tabulated in Supplementary Table 1.

The typical Pd crystal structure (Space group=Fm-3m, lattice constant=3.90 Å) was utilized as a fitting model. All of the data were co-refined using this model. A single scattering path between Pd and its first neighbor Pd was taken into consideration for all EXAFS fitting.

Faradaic Efficiency (FE) and Partial Current Density Calculations [6-7]

The FE for CO (FE(CO)) was calculated by using the following Supplementary Equations (2)-(5):

N_{CO} (in gaseous phase) = C_{CO} [%]×13 (mL)/22.4 (L mol^{-1}) (2)

N_{CO} (dissolved in electrolyte) = (K_{CO})×18 (mL)×1 (g/mL)/18 (g mol^{-1}) × C_{CO} [%] (3)

N_{CO} (total) = N_{CO} (in gaseous phase) + N_{CO} (dissolved in electrolyte) (4)

$$\mathrm{FE(CO)}\ [\%] = \frac{2\ \times 96485\ (C\ mol^{-1}) \times N_{CO}(total)}{\int_0^t idt} \times 100 \qquad (5)$$

Where N_{CO} (in gaseous phase) is the amount of CO in the empty head space (13 mL) in the cathodic compartment of the cell. N_{CO} (dissolved in the electrolyte) is the amount of CO dissolved in the catholyte, estimated using Henry's law. The constant (K_{CO}=1.774×10^{-5}) is the molar solubility of CO in water at CO partial pressure of 1 bar and room temperature. C_{CO} is the concentration (%) of CO in the empty head space, which is determined from GC analysis. For FE(CO) calculations, the Faraday constant (96485 C mol^{-1}) and the number of the electron (2) for a single CO production were used. i and t are the current (Ampere) and electrolysis time (seconds) measured by the potentiostat, respectively. The same procedure was used for calculating FE for H_2 (FE(H_2)) except for its different molar solubility in water (*i.e.*, K_{H2}=1.411×10^{-5}).

The partial current densities of CO (J(CO)) and H_2 (J(H_2)) and total current density (J(total)) were calculated based on the following Supplementary Equations (6)-(8):

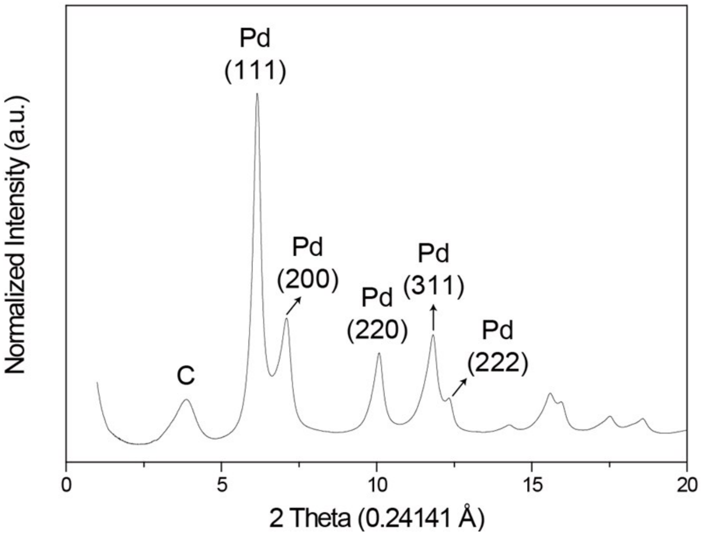
$$J(CO)\ [\mathrm{mA\ cm^{-2}}] = FE(CO) \times \frac{\int_0^t i dt}{A} \div 100 \qquad (6)$$

$$J(H_2)\ [\mathrm{mA\ cm^{-2}}] = FE(H_2) \times \frac{\int_0^t i dt}{A} \div 100 \qquad (7)$$

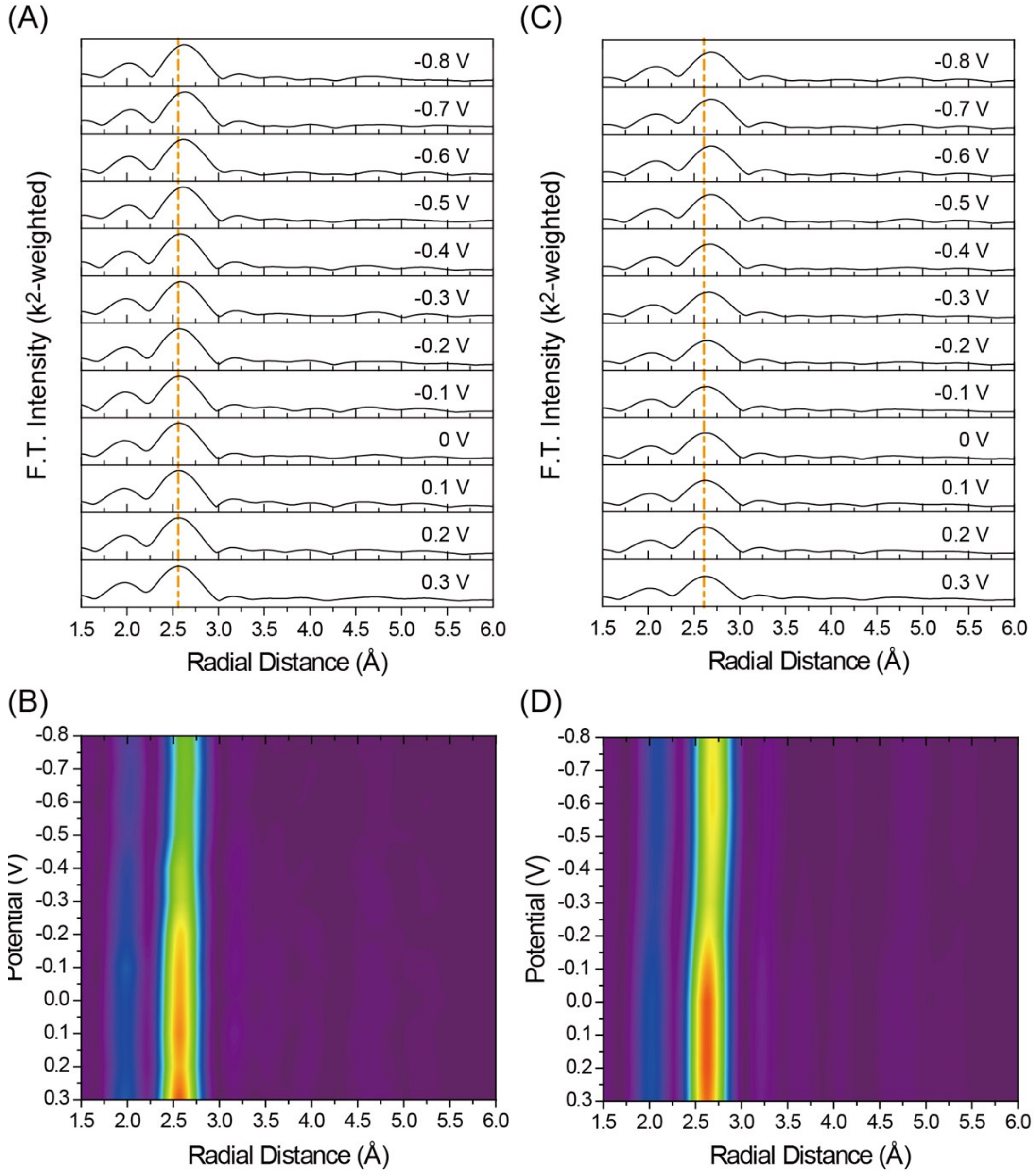
$$J(\mathrm{total})\ [\mathrm{mA\ cm^{-2}}] = \frac{\int_0^t i dt}{A} \div 100 \qquad (8)$$

A is the geometric area of the working electrode. The error bars in FE and J calculations were obtained from repeated gas analyses using GC.

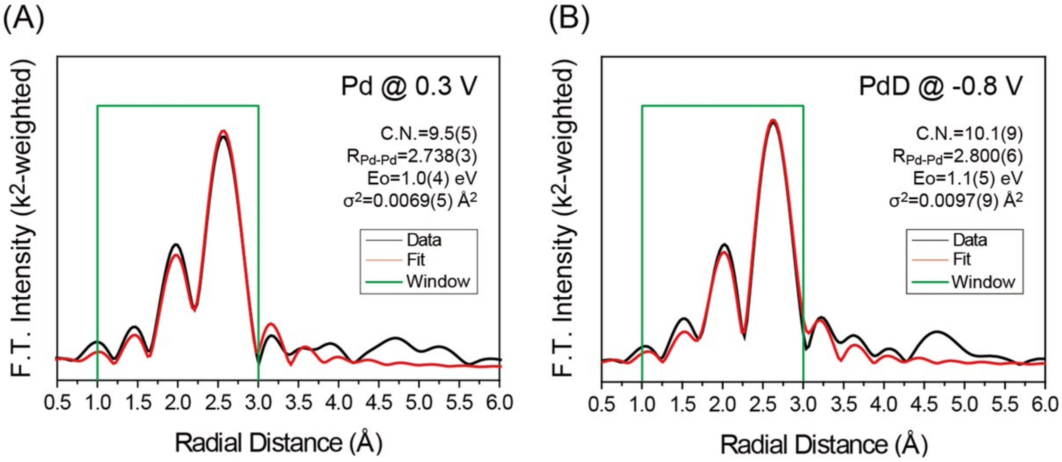
B. Supplementary Figures and Table



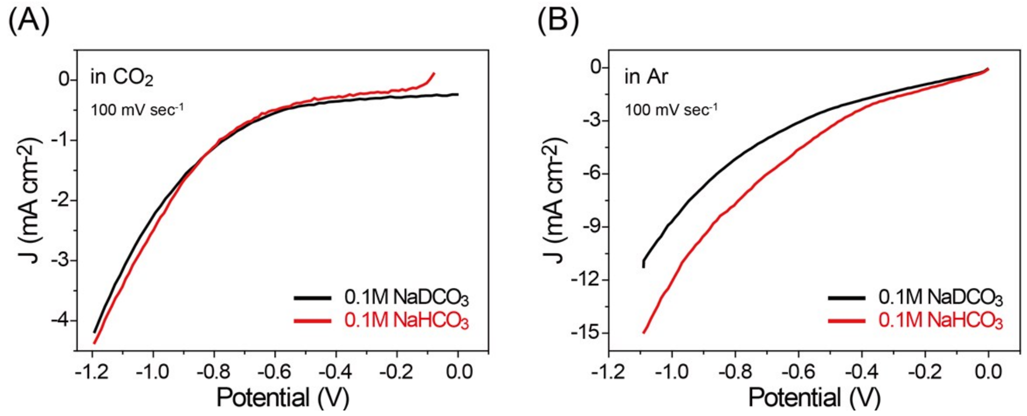
Supplementary Figure 1. Synchrotron X-ray diffraction pattern of Pd/C used in this study.



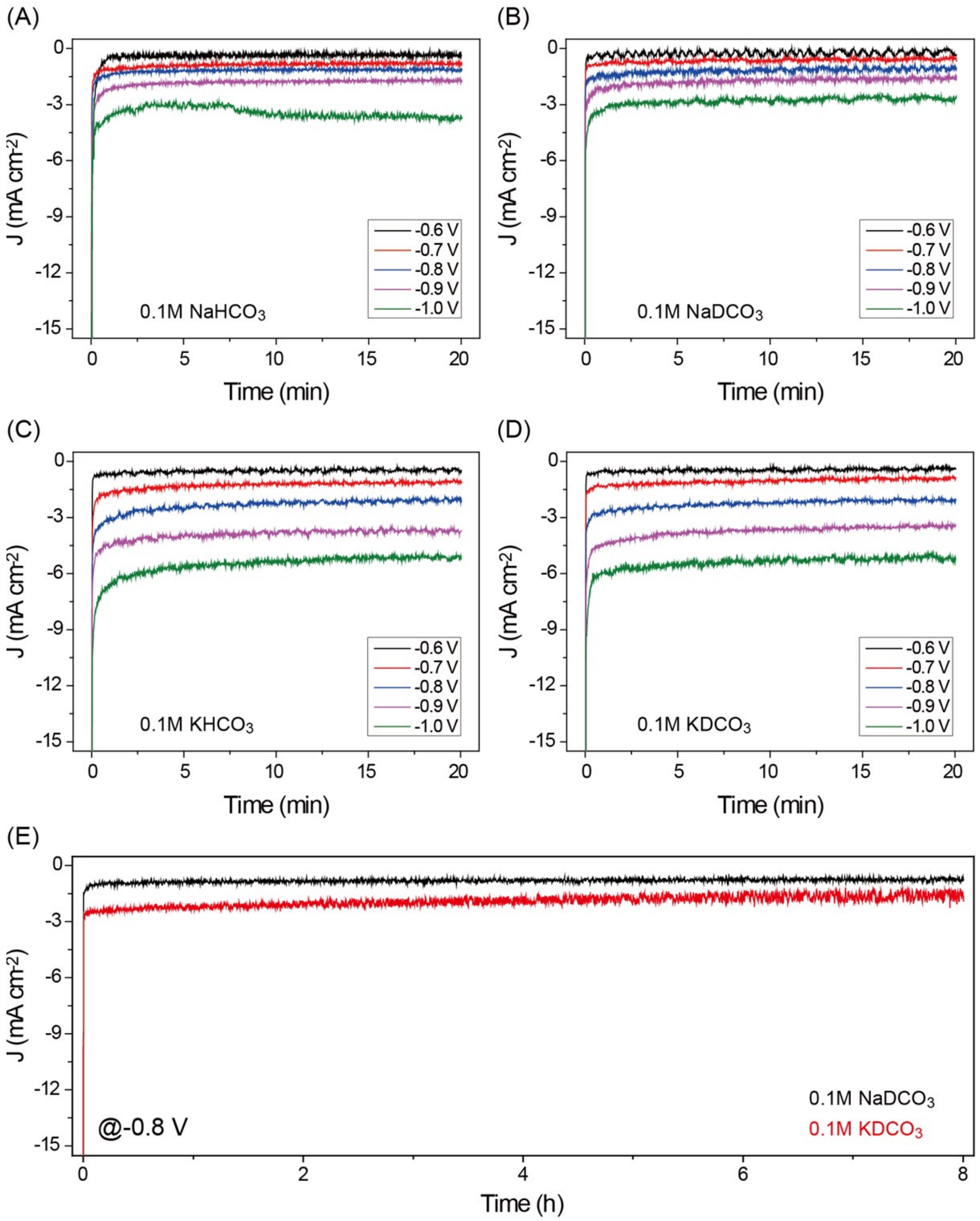
Supplementary Figure 2. *In-situ* EXAFS analysis measured at Pd K-edge. (A) *In-situ* EXAFS profiles for Pd/C in 0.1M $NaDCO_3$ solution. (B) The contour map of EXAFS profiles in (A). (C-D) The same construction for Pd/C in 0.1M $NaHCO_3$ solution. The orange lines in (A) and (C) are vertical lines to visualize the peak shift upon the progress of PdD and PdH formation, respectively.



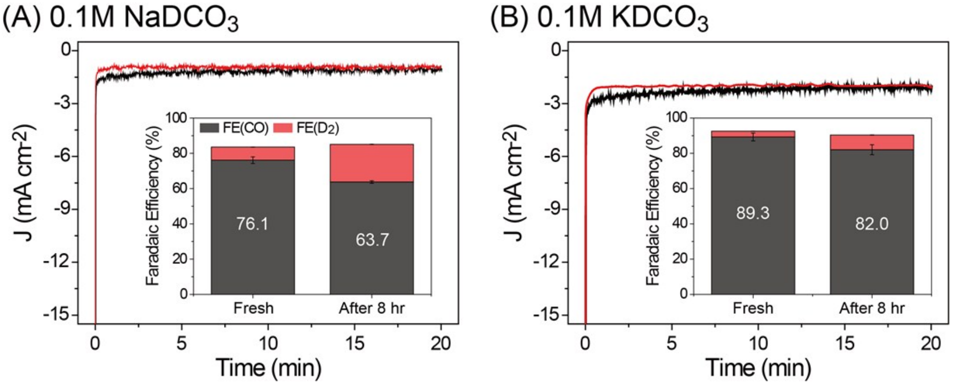
Supplementary Figure 3. Typical EXAFS fitting of Pd/C measured at (A) 0.3 V and (B) -0.8 V in 0.1M $NaDCO_3$ solution. Black, red, and green lines indicate the data, fitted curve, and fitting window, respectively.



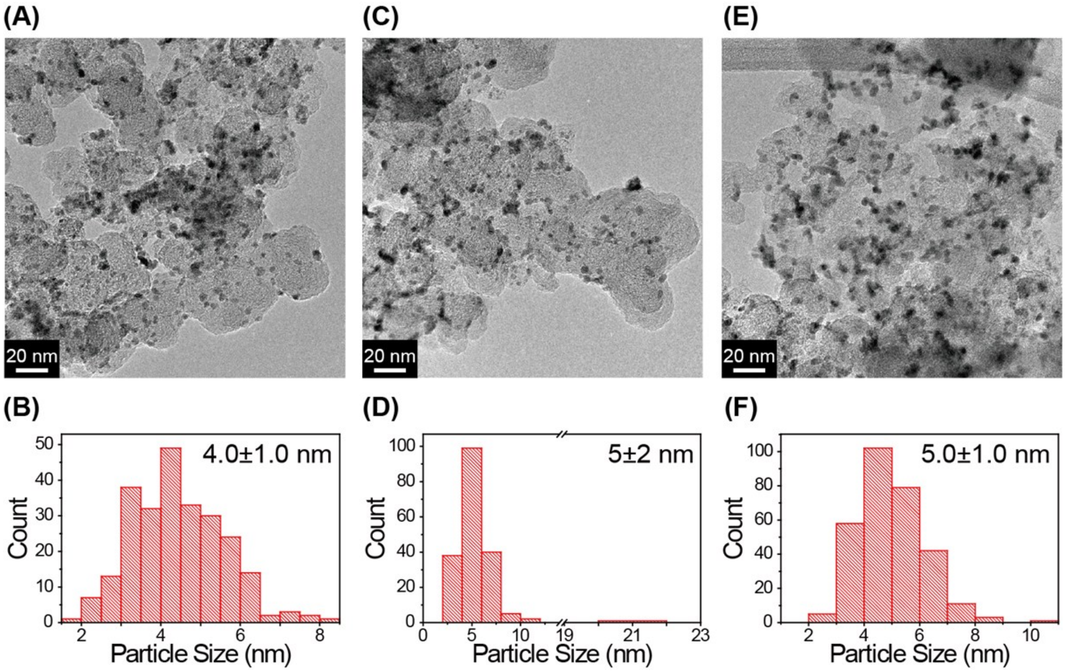
Supplementary Figure 4. The linear scanning voltammetry curves of Pd/C in 0.1M $NaHCO_3$ and $NaDCO_3$ electrolytes with (A) CO_2- and (B) Ar-saturated conditions.



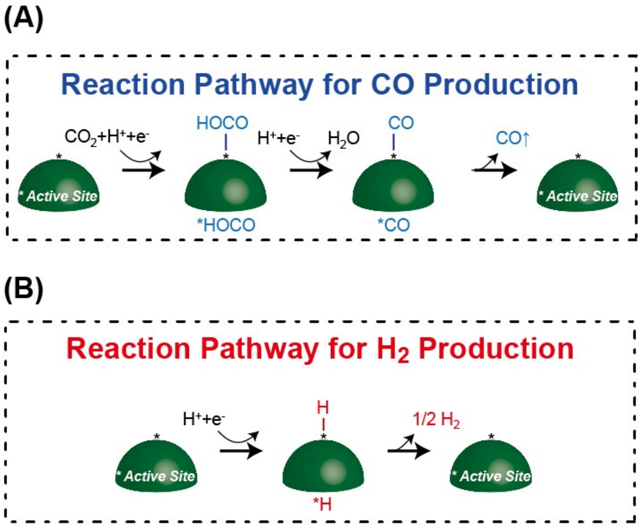
Supplementary Figure 5. The chronoamperometry measurement in different potentials. (A-D) chronoamperometry curves in 0.1M (A) NaHCO$_3$, (B) NaDCO$_3$, (C) KHCO$_3$, and (D) KDCO$_3$. (E) A long-term stability test measured at -0.8 V in D$_2$O-based electrolytes.



Supplementary Figure 6. The chronoamperometry curves before (black) and after (red) 8 hr CO_2 electrolysis at -0.8 V in 0.1M (A) $NaDCO_3$ and (B) $KDCO_3$ electrolytes. The insets are the comparison of the Faradaic efficiencies of CO and D_2 production.



Supplementary Figure 7. Particle size distribution analysis. (A) TEM images for Pd/C and (B) its particle size distribution analysis. (C-F) The same analyses after CO_2 electrolysis for 8 hr in (C-D) 0.1M $NaDCO_3$ and (E-F) 0.1M $KDCO_3$.



Supplementary Figure 8. Schematic illustration for reaction pathways of (A) CO and (B) H_2 production.

Supplementary Table S1. EXAFS fitting results.

Parameter	Entry	
	Pd in 0.1M $NaDCO_3$	Pd in 0.1M $NaHCO_3$
Independent Points	117	116.25
Number of Variables	48	48
Chi-square	1503.342232	18117.7363928
Reduced Chi-square	21.7875686	265.4613391
R-factor	0.0076402	0.0045766
k-range	2.568 – 10.400	2.470 – 10.251
R-range	1 – 3	1 – 3
Number of Data Set	12	12
Structure Model		
Chemical Formula	Pd	
Space Group	Fm-3m	
Lattice Constant	3.900 Å	

C. Supplementary References.

[1] Hazelton et al, *J. Am. Soc. Chem.*, **1938**, 60, 2771.

[2] B.H. Toby et al, *J. Appl. Crystall.*, **2013**, 46, 544.

[3] B. Ravel et al., *Methods Soil Anal.*, **2008**, 5, 387.

[4] M. Newville et al., *J. Synchrotron Radiat.*, **2005**, 12, 537.

[5] R. C. Albers et al., *Rev. Mod. Phys.*, **2000**, 72, 621.

[6] J. G. Chen et al., *Energy Environ. Sci.*, **2017**, 10, 1180.

[7] J. G. Chen et al., *Adv. Funct. Mater.*, **2018**, 28, 1804762.