

## Supplementary Information

### **Pd homogeneous junction enables remarkable CO<sub>2</sub> electroreduction**

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## **Experimental section**

### **Chemicals and materials**

Palladium chloride ( $\text{PdCl}_2$ , 99.0%) was purchased from Energy Chemical, Potassium Bicarbonate ( $\text{KHCO}_3$ ,  $\geq 99.0\%$ ), Sodium borohydride ( $\text{NaBH}_4$ ,  $\geq 99.0\%$ ), Sodium hydroxide ( $\text{NaOH}$ ,  $\geq 99.0\%$ ), and poly(vinylpyrrolidone) (PVP,  $M_w \approx 55000$ ) were all obtained from Sigma-Aldrich. Hydrochloric acid ( $\text{HCl}$ , 36.5% ~ 38.0%) was purchased from Sinopharm Chemical Reagent Co. Ltd.. All the chemicals were used as received. All experiments used Deionized (DI) water with a resistivity of  $18.2 \text{ M}\Omega \cdot \text{cm}$ .

### **Synthesis of Pd nanoparticles**

The Pd nanoparticles were synthesized according to previous work with some modification<sup>2</sup>. In a typical synthesis, 60 mg PVP dissolved in 20 ml deionized water and stirred vigorously for 30 min. Then, 0.5 mmol  $\text{PdCl}_2$  (dissolved in 0.1 M  $\text{HCl}$  solution) was added, 2.5 mL of 0.1 M  $\text{NaBH}_4$  solution was added into the suspension dropwise under vigorous stirring at room temperature. After the suspension was stirred for 2 h, the black precipitate was collected by centrifugation, washed several times with water and acetone for further use. The resulting Pd nanoparticles was named Pd-0.

### **Synthesis of Pd aerogels**

The as-synthesized Pd nanoparticles were evenly dispersed in the mixture of water and ethanol. An appropriate amount of solid sodium hydroxide is weighed and placed in a 25 mL beaker, puttered it in the muffle furnace, heated from room temperature to  $350 \text{ }^\circ\text{C}$  with a heating rate of  $10 \text{ }^\circ\text{C}/\text{min}$ , and then the dispersed Pd nanoparticles were slowly added into the molten sodium hydroxide and kept for 2 min. The beaker was removed and the centrifuged solids were washed until neutral. The content of sodium hydroxide is controlled to produce Pd-x aerogels (where x is the mass of sodium hydroxide).

### **Materials characterizations**

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were carried out on JEOL JEM-F200 microscope at 200 KV. XRD patterns were performed

on a SmartLab X-ray diffraction system (40 KV, 150 mA, Cu K $\alpha$  radiation). The specific surface area was obtained by the Brunauer-Emmett-Teller (BET) method and measured by using a Micromeritics ASAP 2020 with the samples degassing in vacuum at 110 °C for 10 h and then measuring at 77 K. The CO<sub>2</sub> temperature-programmed desorption (CO<sub>2</sub>-TPD) measurements were carried out on Micromeritics AutoChem 2920 Version. In situ diffuse Fourier transform infrared (DRIFT) spectroscopy was captured using a Nicolet iS50 FT-IR spectrometer equipped with a MCT detector. The flow rate of CO<sub>2</sub> in this experiment was controlled at 20 mL/min.

## **Electrochemical measurements**

In order to complete the electrochemical reduction of CO<sub>2</sub>, the electrochemical measurements were carried out in an H-cell system, which was separated by Nafion 115 membrane. The working electrode was the carbon fiber cloth coated with a catalyst, with a size of 1 cm  $\times$  2 cm. The Pt and the Ag/AgCl electrodes were used as the counter electrode and the reference electrode, respectively. During the test, all potentials were measured against the Ag/AgCl reference electrode. The potentials were controlled by an Autolab potentiostat/galvanostat (CHI660e). EIS measurements were carried out at -0.78 V vs. RHE and 5 mV amplitude in a frequency range from 10000 to 0.01 Hz. At room temperature under atmospheric pressure, the electrocatalytic reduction of CO<sub>2</sub> was carried out in a 0.5 M KHCO<sub>3</sub> solution saturated with CO<sub>2</sub>. After blowing CO<sub>2</sub> into the KHCO<sub>3</sub> solution for at least 30 minutes to remove residual air in the reservoir, controlled potential electrolysis was performed at each potential for 30 minutes. The gas products of electrocatalytic CO<sub>2</sub> reduction were monitored by gas chromatography (Agilent GC 8860). The CO standard curve was obtained by inject different volumes of CO standard gas into the gas chromatography. The peak area of CO standard gas with different volumes can be obtained by the gas chromatograph. The liquid products were quantified by nuclear magnetic resonance (NMR) (Bruker AVANCE AV III 400) spectroscopy, in which 0.5 mL electrolyte was mixed with 0.1 mL D<sub>2</sub>O and 0.01 mL dimethyl sulfoxide (DMSO, Sigma, 99.99%) was added as an internal standard. The HCOOH standard curve can be acquire through detecting the peak area of H in the

mixture (0.5 mL HCOOH standard solutions with different concentration, 0.1 mL D<sub>2</sub>O and 0.01 mL dimethyl sulfoxide) by NMR.

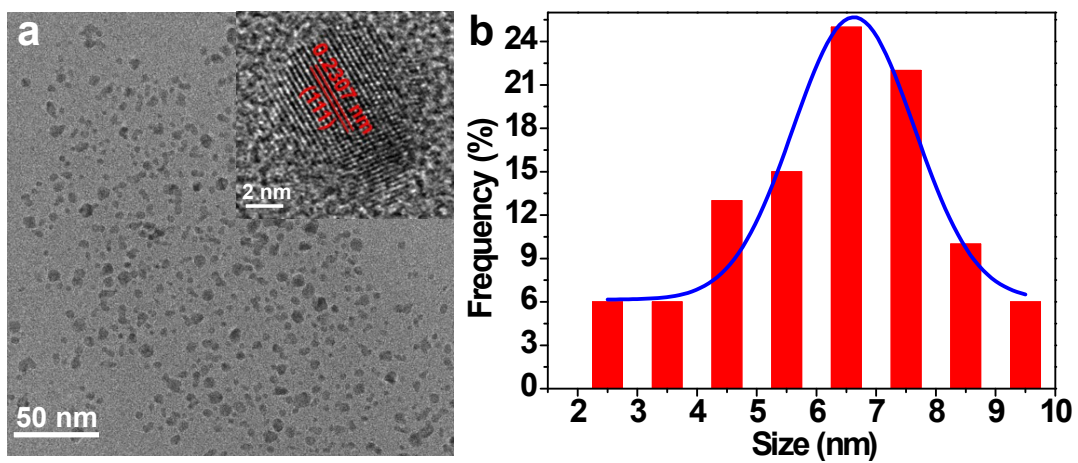
## **CO stripping**

The CO adsorption process in the measurement of the CO stripping voltammogram was accomplished by polarizing the electrode at 0.14 V and bubbling a 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte solution with CO for 10 min. Subsequently, the Ar was bubbled for another 30 min to remove excess CO in the solution. Then, the cyclic voltammogram was measured from 0.65 to 1.2 V vs. Ag/AgCl at a scan rate of 10 mV/s.

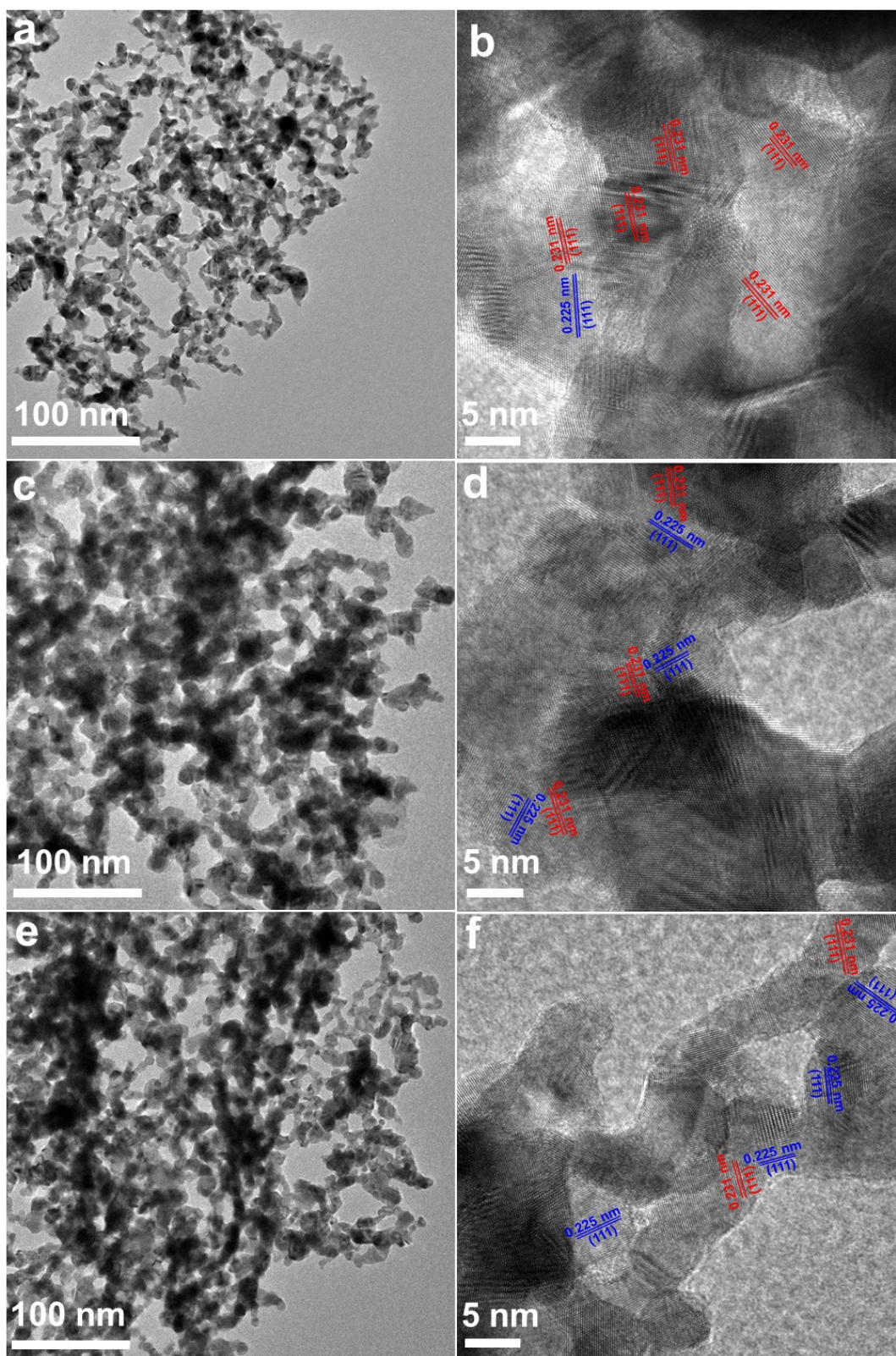
We used the stripped charge of the saturated CO adsorption layer on the catalyst to determine the electrochemically active surface area of the catalyst. It can be seen from previous studies that CO adsorption takes place in the range between 0.65 and 1.2 V (vs. Ag/AgCl). Then, the net Faraday charge for oxidation of the saturated CO adsorption layer is determined by the difference between the integral of 0.65 and 1.2 V (vs. Ag/AgCl) CV with and without CO adsorption divided by the scan rate. The ECSA of the Pd catalysts were evaluated by the following formula:

$$\text{ECSA} = Q / (Q_{\text{ref}} G),$$

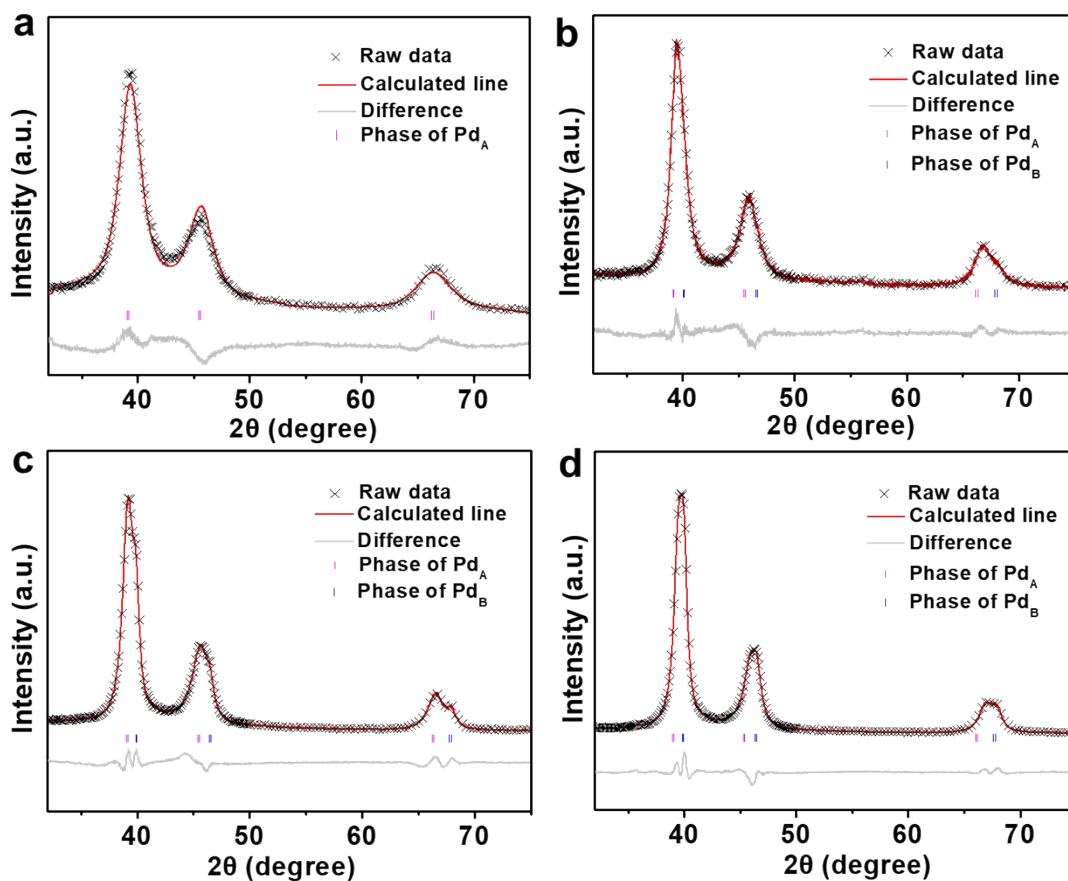
where  $Q$  is the coulombic charges (mC) of the Pd oxides reduction,  $Q_{\text{ref}}$  is a conversion coefficient of 424  $\mu\text{C cm}^{-2}$  and  $G$  is the total mass of Pd on the electrode, respectively<sup>13</sup>. The ECSA is calculated to correct the partial current density for CO production.



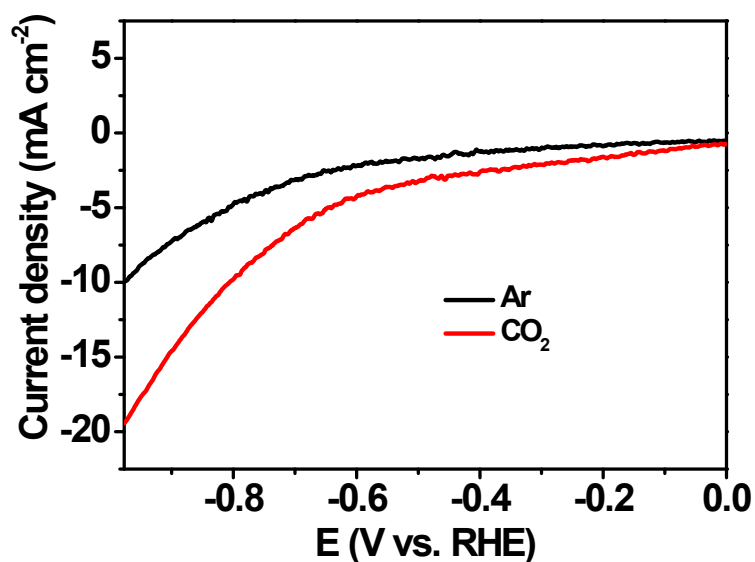
**Fig. S1** (a) TEM image of the Pd-0. (b) Size distribution of the Pd-0. The inset in panel (a) shows the HRTEM image of the Pd-0.



**Fig. S2** TEM (a, c, e) and corresponding HRTEM (b, d, f) images of the Pd-1, Pd-2 and Pd-4, respectively.

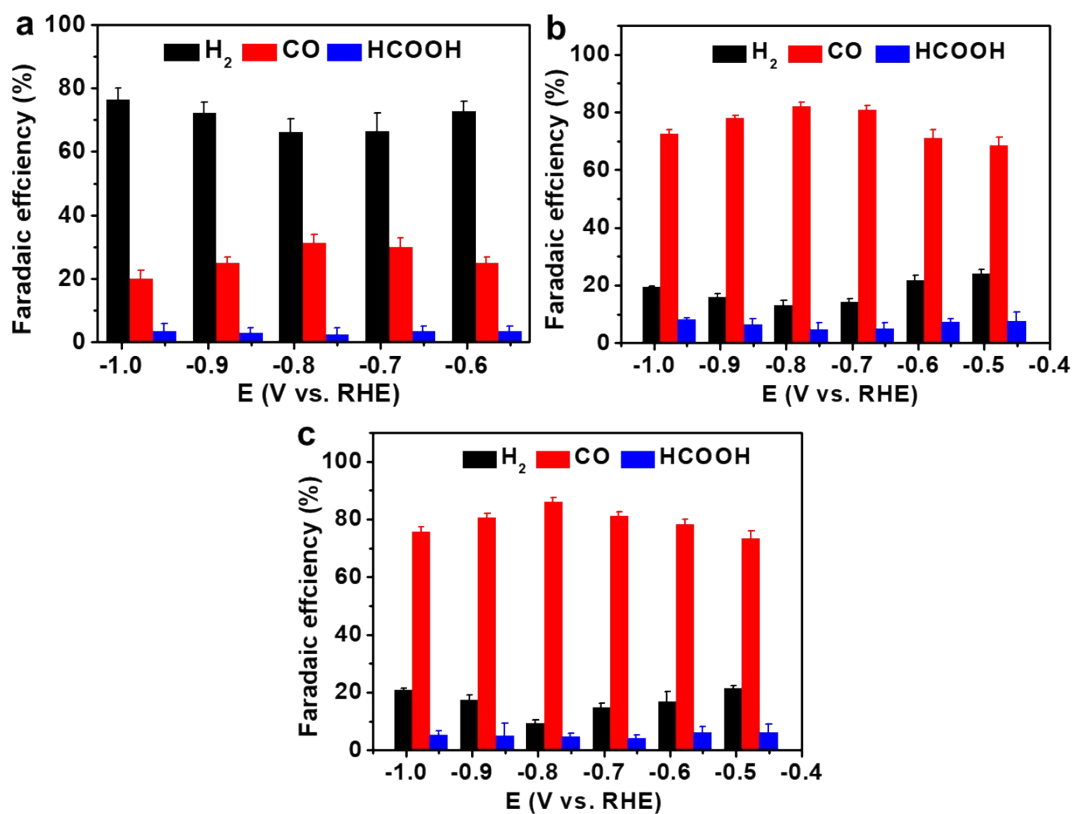


**Fig. S3** Refined XRD patterns of the (a) Pd-0, (b) Pd-1, (c) Pd-2 and (d) Pd-4.

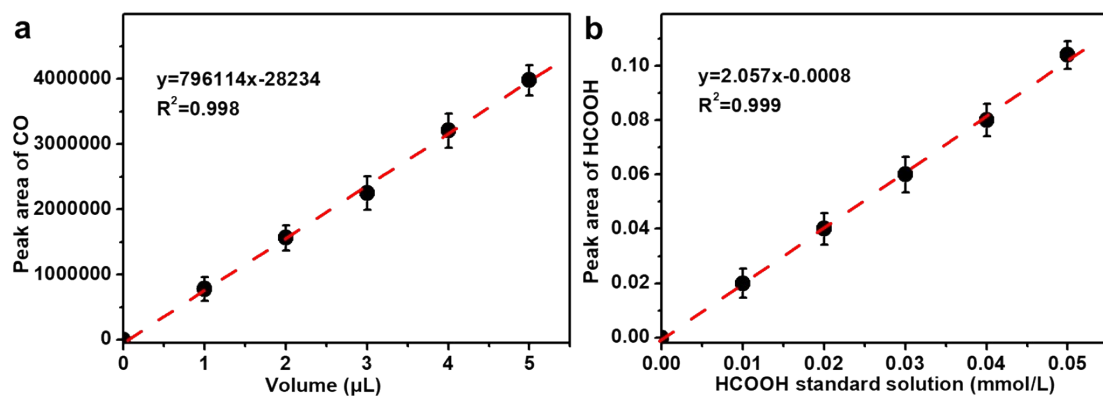


**Fig. S4** Polarization curve of Pd-2 in Ar- or CO<sub>2</sub>-saturated 0.5 M KHCO<sub>3</sub> solution.

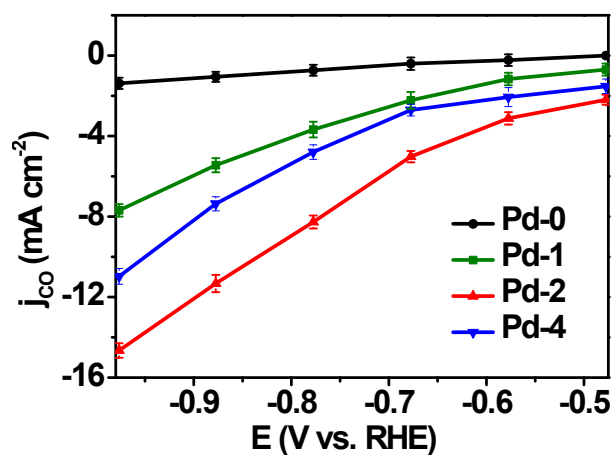




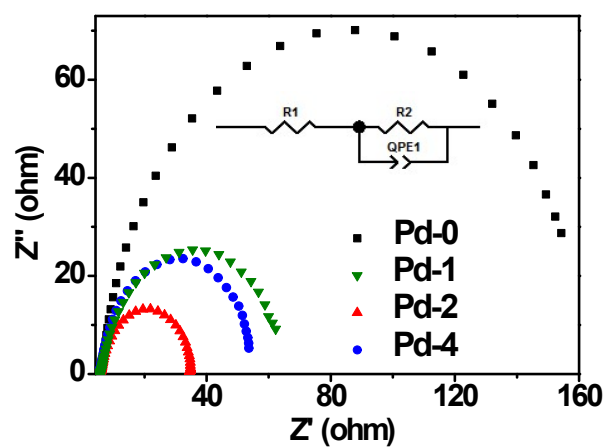
**Fig. S5** Faraday efficiency of the (a) Pd-0, (b) Pd-1 and (c) Pd-4.



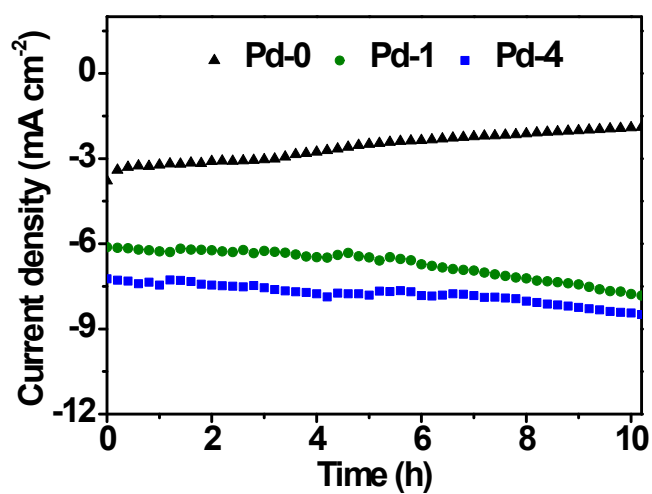
**Fig. S6** The standard curve for the detection of (a) CO and (b) HCOOH products.



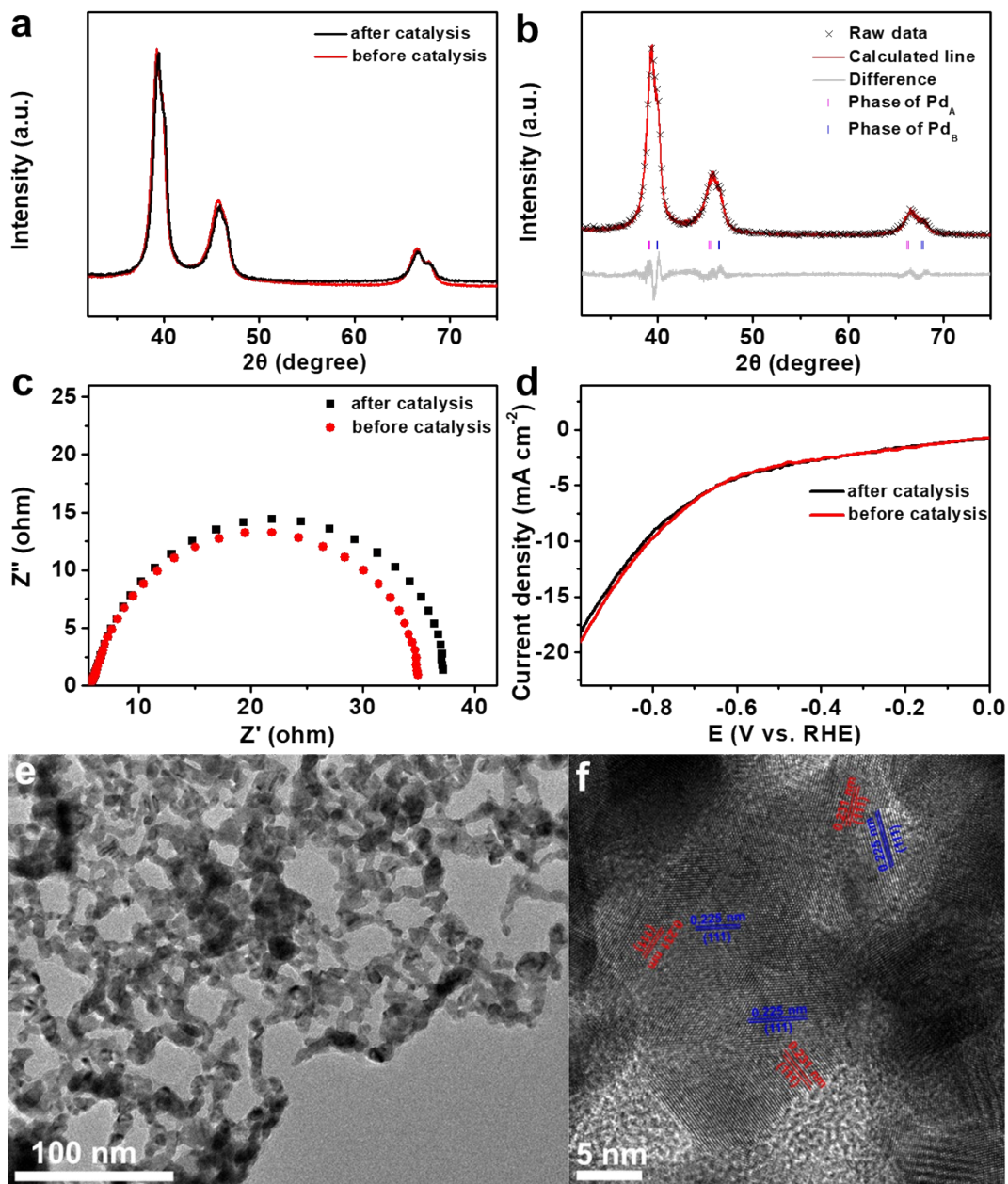
**Fig. S7** Current density of different Pd catalysts for CO production.



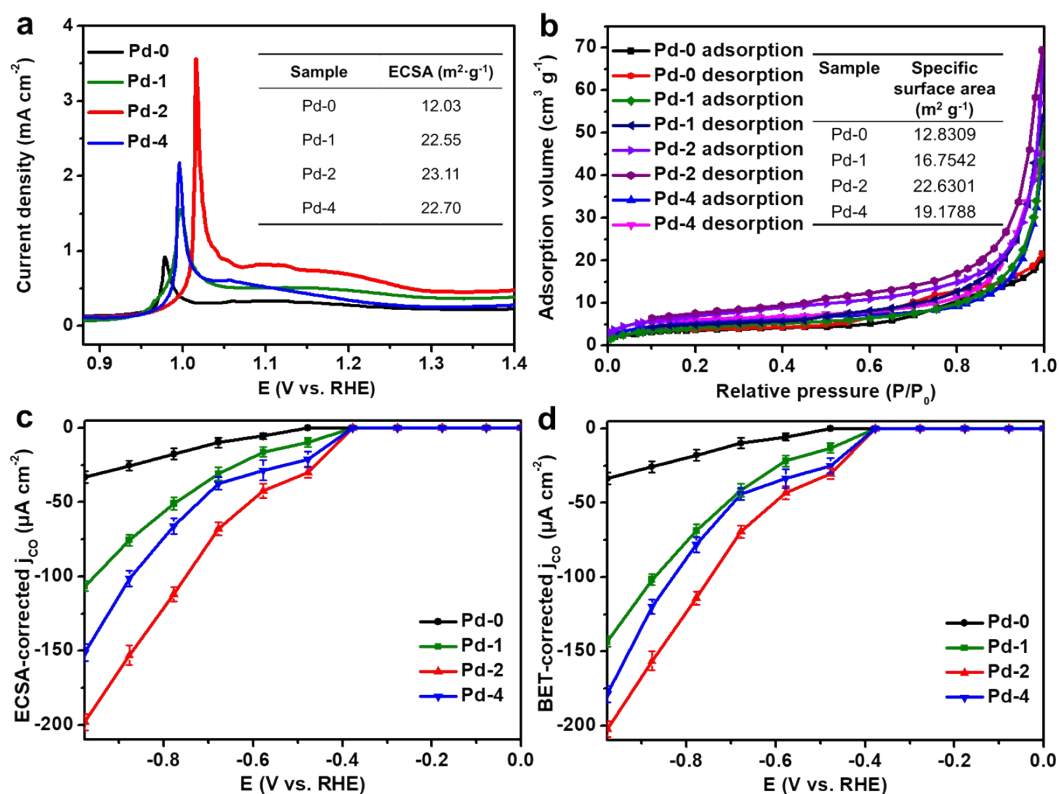
**Fig. S8** Electrochemical impedance spectra of different Pd catalysts.



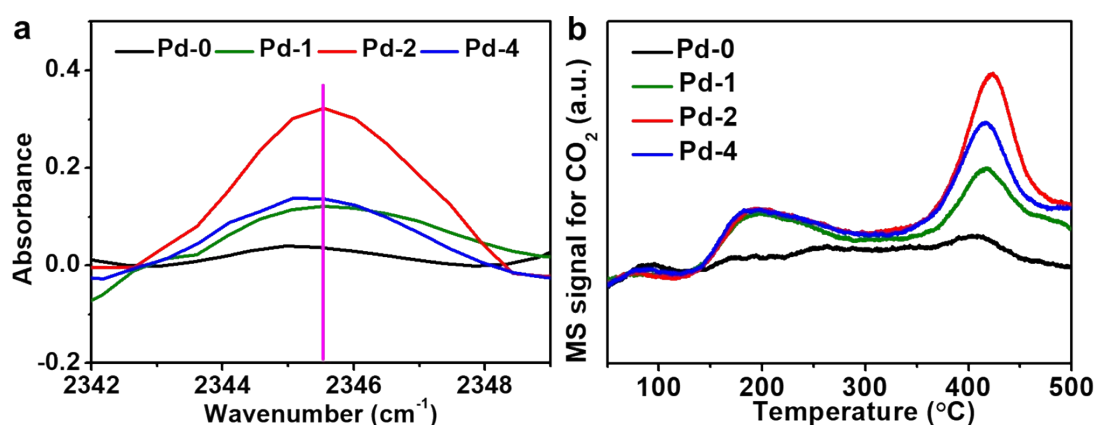
**Fig. S9** Electrochemical stability measured at -0.78 V vs. RHE.



**Fig. S10** (a) The XRD patterns, (b) Refined XRD pattern, (c) EIS, (d) LSV curves, (e) TEM and (f) its corresponding HRTEM image of Pd-2 after electrolysis.



**Fig. S11** (a) CO stripping voltammetry, (b) N<sub>2</sub> adsorption-desorption curves, (c) ECSA-corrected and (d) BET-corrected the CO partial current density of the Pd-0, Pd-1, Pd-2 and Pd-4 catalysts.



**Fig. S12** (a) *In situ* DRIFT of CO<sub>2</sub>-saturated adsorption. (b) CO<sub>2</sub>-TPD spectra of the Pd-0, Pd-1, Pd-2 and Pd-4, respectively.

**Table S1.** The obtained parameters in XRD refinement.

Sample	Atom	Space group	Pd <sub>A</sub>	Pd <sub>B</sub>	Ratio of Pd <sub>A</sub>	Ratio of Pd <sub>B</sub>	2Pd <sub>x</sub> (X=A, B)	R <sub>wp</sub>	R <sub>p</sub>	χ <sup>2</sup>
Pd-0	Pd0	Fm-3m	3.998	/	100.0%	0	0	6.34%	5.39%	6.899
Pd-1	Pd0	Fm-3m	3.994	3.904	75.33%	24.67%	49.34%	7.08%	5.61%	2.648
Pd-2	Pd0	Fm-3m	3.987	3.906	61.04%	38.96%	77.92%	6.42%	4.78%	8.282
Pd-4	Pd0	Fm-3m	3.996	3.911	29.93%	70.07%	59.86%	5.88%	4.63%	7.956
Pd-2 after catalysis	Pd0	Fm-3m	3.987	3.906	61.14%	38.86%	77.72%	9.78%	7.67%	1.762

**Table S2.** Comparison of the catalytic performance of as-prepared Pd catalysts and other previously reported catalysts for electrochemical CO<sub>2</sub>RR.

Catalyst	Media	Current density at maximum FE <sub>CO</sub> (mA cm <sup>-2</sup> )	Maximum FE <sub>CO</sub> (%)	Ref.
Pd/C	0.5 M NaHCO <sub>3</sub>	-0.7	60	[1]
6.2 nm Pd NPs	0.1 M KHCO <sub>3</sub>	-1.7	65	[2]
Te-Pd NCs/C	0.1 M KHCO <sub>3</sub>	-0.6	95.8	[3]
Pd-NC	0.5 M NaHCO <sub>3</sub>	-0.65	55	[4]
Pd Octahedra	0.5 M NaHCO <sub>3</sub>	-17	94	[5]
10% Pd/TaC	0.5 M NaHCO <sub>3</sub>	-0.5	50	[6]
Pd/VN	0.5 M NaHCO <sub>3</sub>	-0.2	77	[7]
Pd-50	0.1 M KHCO <sub>3</sub>	-25	93	[8]
Pd <sub>2</sub> DAC	0.5 M KHCO <sub>3</sub>	-17.7	98.2	[9]
Pd/PANI-CP(I)	0.1 M KCl	-16	84.1	[10]
Pd@UiO-67	1 M KOH	-12	78.3	[11]
Au@Pd CCs	0.5 M KHCO <sub>3</sub>	-6	87	[12]
Pd-2	0.5 M KHCO <sub>3</sub>	-8.3	92	This work

**Table S3.** Electrochemically active surface area of the Pd catalysts.

<b>Sample</b>	<b>ECSA (F·cm<sup>-2</sup>)</b>	<b>ECSA (m<sup>2</sup>·g<sup>-1</sup>)</b>
Pd-0	0.0093	12.03
Pd-1	0.0161	22.55
Pd-2	0.0165	23.11
Pd-4	0.0162	22.70

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