Supporting Information

Tuning Pd-Catalyzed Electroreduction of CO\textsubscript{2} to CO with Reduced Overpotential

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Electrocatalytically active surface area (ECSA) and ECSA corrected-Tafel slope measurements. The values of ECSA were evaluated on the basis of the reduction charge of surface Pd(OH)\textsubscript{2} in the potential region of −0.25 to +1.2 V (vs. RHE) on the CVs in a deaerated 0.1 M HClO\textsubscript{4} solution with a scanning rate of 50 mV/s. We chose +1.2 V as the appropriate potential limit because +1.2 V is the upper limit for the formation of Pd(OH)\textsubscript{2} in a solution of pH = 1. The ECSA value can be determined by

\[
\text{ECSA} = \text{GSA} \times \left( \frac{Q_R}{Q_F} \right)
\]

(Eq. S1)

where GSA is the the geometric surface area, \(Q_R\) is the charge density for reduction of surface Pd(OH)\textsubscript{2} on work electrode and \(Q_F\) is the charge density for the formation a fully covered Pd(OH)\textsubscript{2} layer which was chosen to be 430 \(\mu\text{C cm}^{-2}\). ECSA-corrected Tafel slopes for CO production (that is, \(j_{\text{total}} \times \eta_{\text{CO/ECSA}}\)) were calculated from corresponding ECSA-corrected current densities for CO based on the linear sweep voltammetry curves and the CO Faradaic efficiency.

Number of active sites and turn over frequency (TOF) measurements. To further characterize the catalytic activities of 3% Pd/C, 3% Pd\_30% CeO\textsubscript{x}/C and 3% PdTe\_(0.15)_30% CeO\textsubscript{x}/C, we applied a roughness factor technique to determine the number of active edge sites of the catalysts. Roughness factor (\(R_f\)) was estimated by dividing the electrocatalytically active surface area to geometric surface area (0.19625 cm\textsuperscript{2} here).
\[ R_f = \frac{\text{ECSA/GAS}}{Q_R / Q_F} \quad \text{(Eq. S2)} \]

The calculated number of active sites for each catalyst was obtained using the equation:
\[
\text{Density of active sites for catalyst (sites/cm}^2\text{)} = \text{Density of active sites for standard sample (sites/cm}^2\text{)} \times R_f \quad \text{(Eq. S3)}
\]

We note that the chemical compositions of the Pd-based catalysts remained unchanged during electrochemical CO\textsubscript{2} reduction at applied potentials in the range of -0.6 to -1.2 V (vs. RHE), allowing for estimation of turnover frequency (TOF) in this potential range. The CO formation TOF of active sites for CO\textsubscript{2} reduction reaction was calculated at different overpotentials using Eq. S4:\
\[
\text{CO formation TOF (s}^{-1}\text{)} = i_0 (\text{A cm}^{-2}) \times \text{CO formation FE} / ([\text{active sites density (sites/cm}^2\text{)}] \times [1.602 \times 10^{-19} \text{ (C/e}^{-}) \text{]} \times [2\text{e}^{-}/\text{CO}_2]) \quad \text{(Eq. S4)}
\]

**Faradaic efficiency (FE) measurement.** The FE values of catalysts were calculated using \( E_{\text{Faradaic}} = \alpha nF/Q \), where \( \alpha \) is the number of electrons transferred (\( \alpha = 2 \) for CO and H\textsubscript{2} production), \( n \) the number of moles for a given product, \( F \) Faraday's constant (96,485 C mol\textsuperscript{-1}), \( Q \) all the charge passed throughout the electrolysis process (measured by calculating the curve area of current density vs. time plot). CO and H\textsubscript{2} mole fractions of injected samples were calculated using GC calibration curve.
Fig. S1  XRD patterns of 3 wt% Pd/C and 3 wt% Pd_30% CeO_x/C.

![Fig. S1 XRD patterns of 3 wt% Pd/C and 3 wt% Pd_30% CeO_x/C.](image)

Fig. S2 (a) Ce 3d XPS spectrum of 30% CeO_x/C, 3% Pd_30% CeO_x/C and 3% PdTe (0.15)_30% CeO_x/C. (b) The wide-survey XPS spectrum of 3% PdTe (0.15)_30% CeO_x/C.

![Fig. S2 XPS spectra of Ce 3d and wide-survey.](image)

Table S1 Charge of Pd and O atom in interface of Pd and CeO_2

<table>
<thead>
<tr>
<th>Atom</th>
<th>CeO_2</th>
<th>Pd/CeO_2</th>
<th>PdTe/CeO_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>-1.068</td>
<td>-1.128</td>
<td>-1.135</td>
</tr>
<tr>
<td>Pd</td>
<td>+0.303</td>
<td>+0.095</td>
<td></td>
</tr>
</tbody>
</table>

We proposed that electron transfer occurred from Pd to O through Pd1-O bond. Positive charge of Pd1 was found in Pd/CeO_2 and PdTe/CeO_2, while more negative charge of O was obtained in Pd/CeO_2 and PdTe/CeO_2 than that of CeO_2.
Fig. S3  Te 3d XPS spectrum of 3% PdTe(0.15)–30% CeOₓ/C.
Fig. S4 STEM and EDX characterization of 3% PdTe_30% CeO_x/C. (a)-(b) Low-magnification, (c)-(f) high-magnification, and (g) medium-magnification STEM images. (h) EDX spectrum, and (i)-(k) EDX mapping images of Pd, Te, and Ce, respectively, taken from the region shown in (g).
Fig. S5 Current–voltage curves on (a) 3% Pd/C, (b) 3% Pd_30% CeO₂/C, (c) 3% PdTe (0.15)_30% CeO₂/C, (d) 3% Te/C and (e) 30% CeO₂/C electrodes obtained from the LSV scans in CO₂- and N₂-saturated 0.1 M aqueous KHCO₃. (f) LSVs of 30% CeO₂/C, 3% Te/C, 3% Pd/C, 3% Pd_30% CeO₂/C, and 3% PdTe(0.15)_30% CeO₂/C electrodes in CO₂-saturated 0.1 M KHCO₃. Scan rate: 5 mV s⁻¹.
Fig. S6 (a) Faradaic efficiency for H₂ production of 30% CeOₓ/C, 3% Te/C, 3% Pd/C, 3% Pd_30% CeOₓ/C and 3% PdTe (0.15)_30% CeOₓ/C catalysts, and (b) partial current density of CO formation on 30% CeOₓ/C, 3% Te/C, 3% Pd/C, 3% Pd_30% CeOₓ/C and 3% PdTe (0.15)_30% CeOₓ/C catalysts at various applied potentials in 0.1 M aqueous KHCO₃.

Fig. S7 (a) Mass activities and FEs, and (b) partial current density and FEs on different CeOₓ mass loadings at various applied potentials in 0.1 M KHCO₃ electrolyte.
Fig. S8 (a) Mass activities and FEs, and (b) partial current densities and FEs of 3\% PdTe$_{30\%}$ CeO$_x$/C with different Te/Pd molar ratios [Te/Pd (mol/mol) = 0.05, 0.15, 0.3] at various applied potentials in 0.1 M aqueous KHCO$_3$.

Fig. S9 Representative CVs of 30\% CeO$_x$/C, 3\% Pd/C, 3\% Pd$_{30\%}$ CeO$_x$/C and 3\% PdTe (0.15)$_{30\%}$ CeO$_x$/C electrodes in a deaerated 0.1 M HClO$_4$ solution with a scanning rate of 50 mV/s with upper potential limits at 1.2 V vs. RHE.
Fig. S10 CO$_2$-TPD-MS spectra of 3% Pd/C and 3% Pd$_{30}$% CeO$_x$/C.

References