

Supporting Information

Pd/CuO-Ni(OH)₂/C as highly efficient and stable catalyst for electrocatalytic oxidation of ethanol

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Supporting Information

***In-situ* FTIR:** Electrochemical *in-situ* Fourier transform infrared (FTIR) reflection spectroscopy was used by a Nicolet-8700 spectrometer included with a liquid-nitrogen-cooled MCT-A detector. The configurations and characteristics of IR cell was described in previous work. The absorbed species and dissolved species could be detected by IR passed through the thin solution layer formed by the working electrode and CaF₂ windows. A Pt foil and a SCE were used as counter and reference electrodes, respectively. The catalysts (2.0mg) were dispersed in 1.0 mL of mixed solution (ethanol: water = 1:1) and ultrasoniced 30 mins. The working electrode was deposited 10 μ L ink and added 5 μ L 0.25wt% Nafion solution after ink dried. The working electrode was electrochemically cleaned until stable in N₂-saturated 1.0 M KOH solution, and electrochemical *in-situ* FTIR measured in 1.0 M KOH + 1.0 M ethanol solution. Multi-stepped FTIR spectroscopy (MS-FTIR) was used to collect spectra from -0.857 V to 0.143 V (vs.SCE) at 0.1 V intervals. The FTIR spectra were recorded from 1000 cm⁻¹ to 4000 cm⁻¹ with a spectral resolution of 8 cm⁻¹. The spectra were reported as the relative change in reflectivity ($\Delta R/R$), calculated by the following equation:

$$\frac{\Delta R}{R} = \frac{R(E_S) - R(E_R)}{R(E_R)}$$

(1)

$R(E_S)$ and $R(E_R)$ represent the single-beam spectra recorded at the sample potential E_S and the reference potential E_R , respectively. The downward bands and upward bands in the resulting spectra indicate the formation of products and the consumption of reactants. The E_R was fixed at -0.757 V.

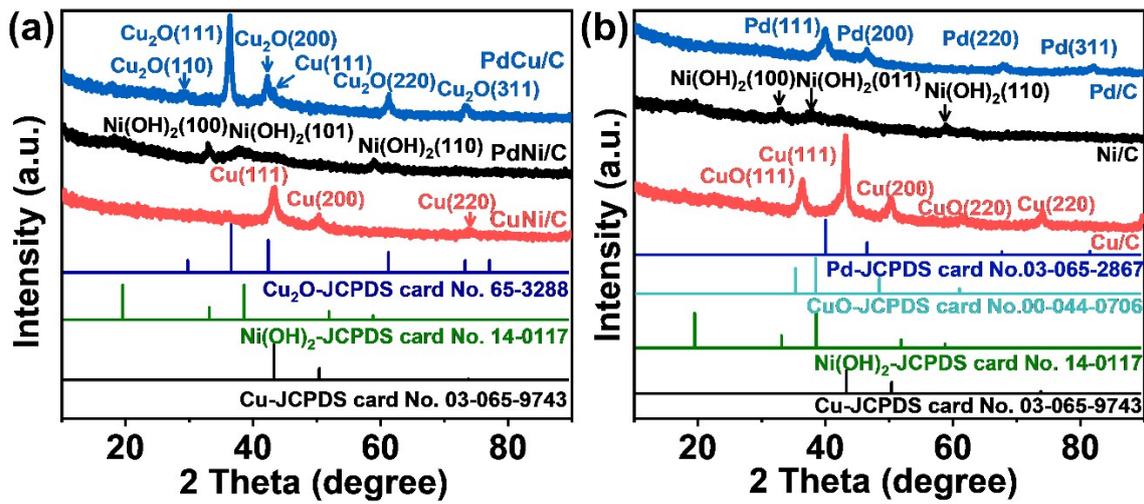


Fig. S1. XRD patterns of (a) PdNi/C, PdCu/C, CuNi/C and (b) Pd/C, Ni/C, Cu/C.

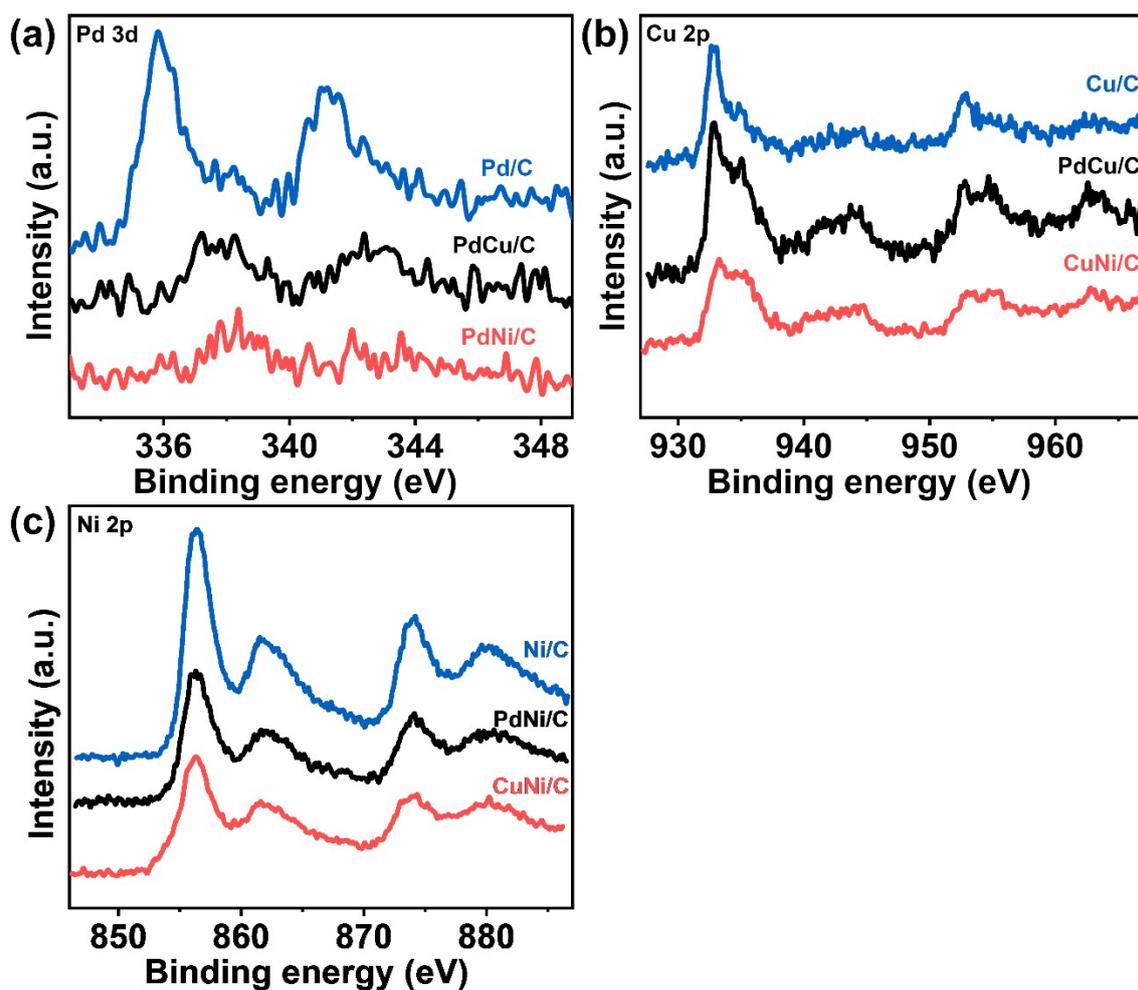


Fig. S2. (a) Pd 3d XPS spectra of PdNi/C, PdCu/C and Pd/C, (b) Cu 2p XPS spectra of PdCu/C, CuNi/C and Cu/C, (c) Ni 2p XPS spectra of PdNi/C, CuNi/C and Ni/C.

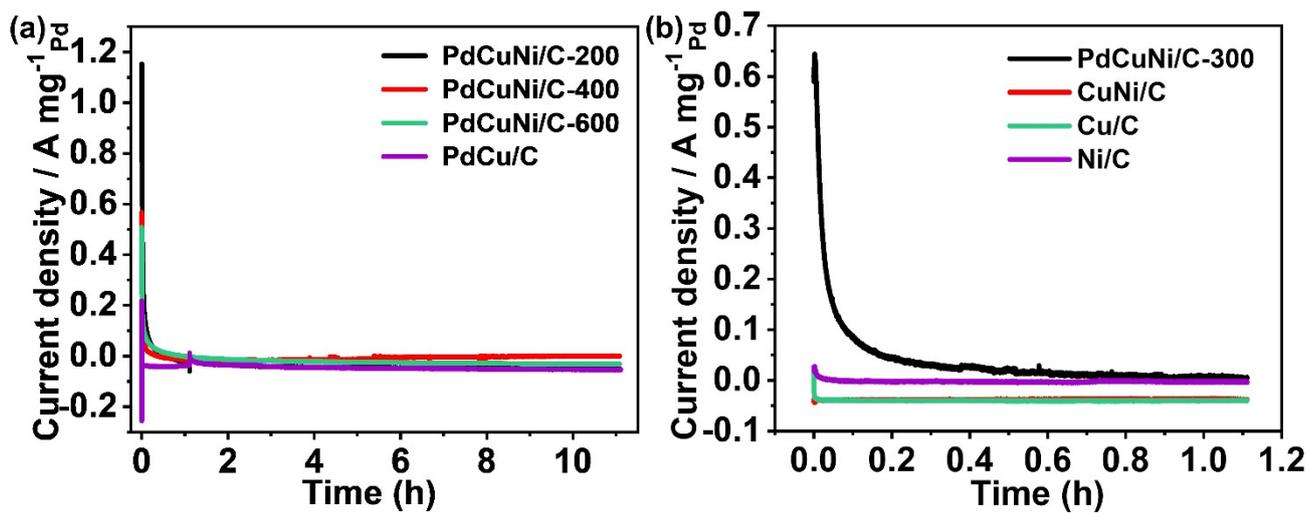


Fig. S3. (a) CA curves of electrocatalytic ethanol oxidation over PdCuNi/C-200, PdCuNi/C-400, PdCuNi/C-600 and PdCu/C catalysts at -0.3 V in 1.0 M KOH+1.0 M C₂H₅OH for lasting 11 h. (b) CA curves of electrocatalytic ethanol oxidation over PdCuNi/C-300, CuNi/C, Cu/C and Ni/C catalysts at -0.3 V in 1.0 M KOH+1.0 M C₂H₅OH for lasting 1h.

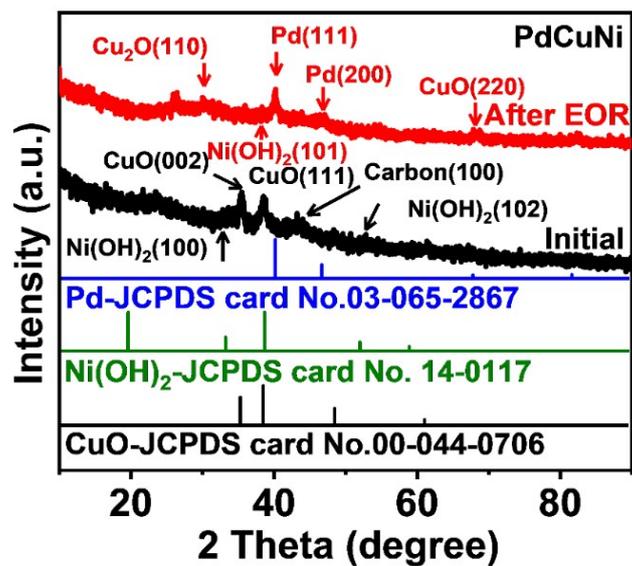


Fig. S4. The comparison of the XRD patterns of the PdCuNi/C catalyst before and after chronoamperograms.

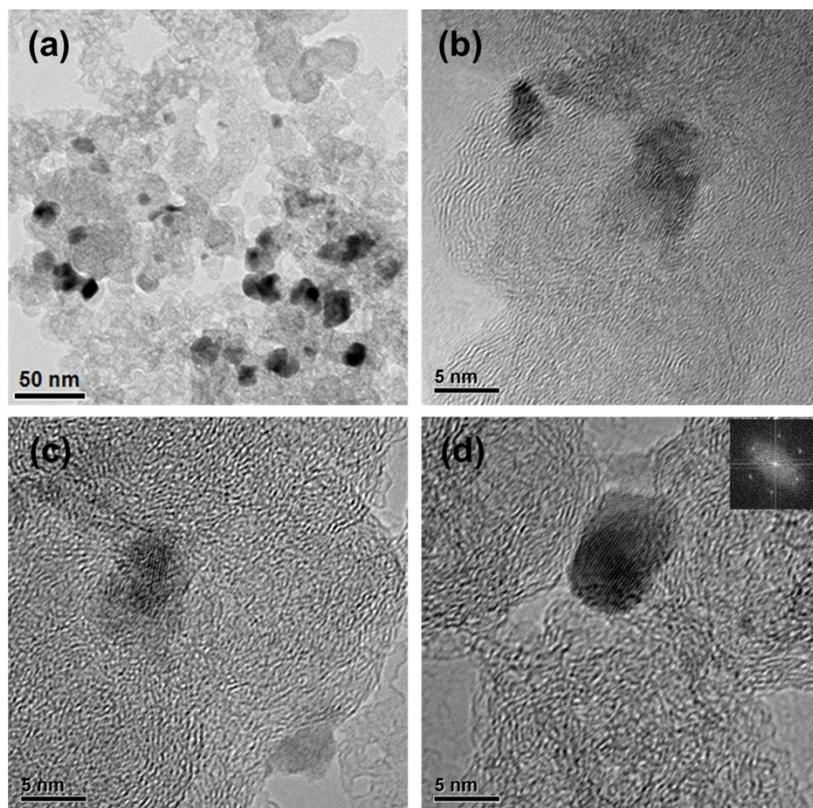


Fig. S5. (a-c) TEM images of PdCuNi/C with different magnifications and (d) HRTEM image of PdCuNi/C after Chronoamperograms, inset-patterns of FFT (fast Fourier transform).

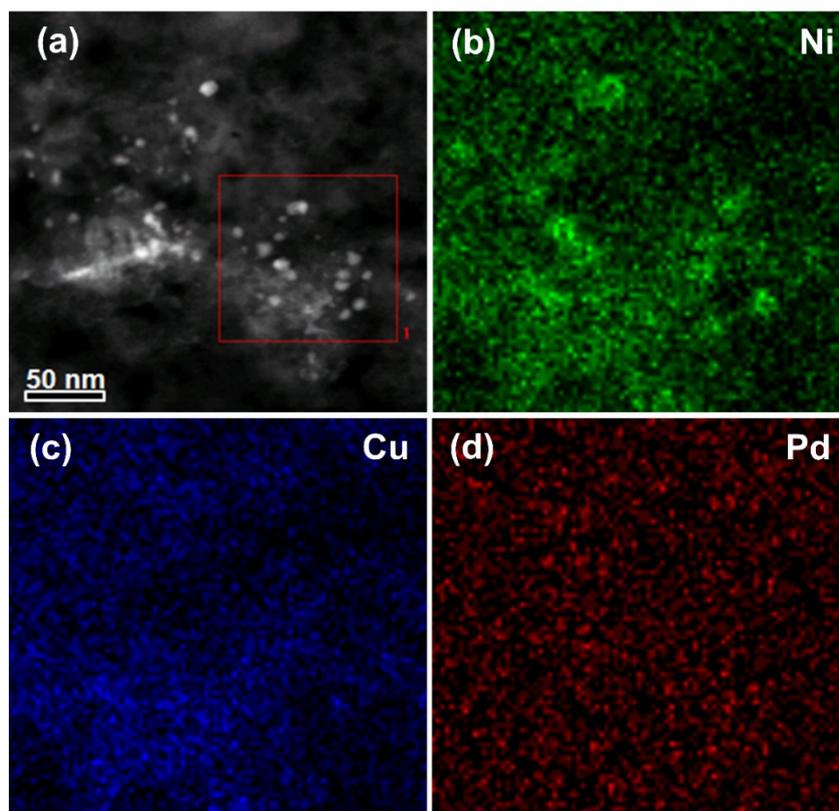


Fig. S6. (a) HAADF-STEM image of PdCuNi/C after Chronoamperograms, STEM-EDS elemental mapping of PdCuNi/C (b) Ni (green), (c) Cu (blue) and (d) Pd (red).

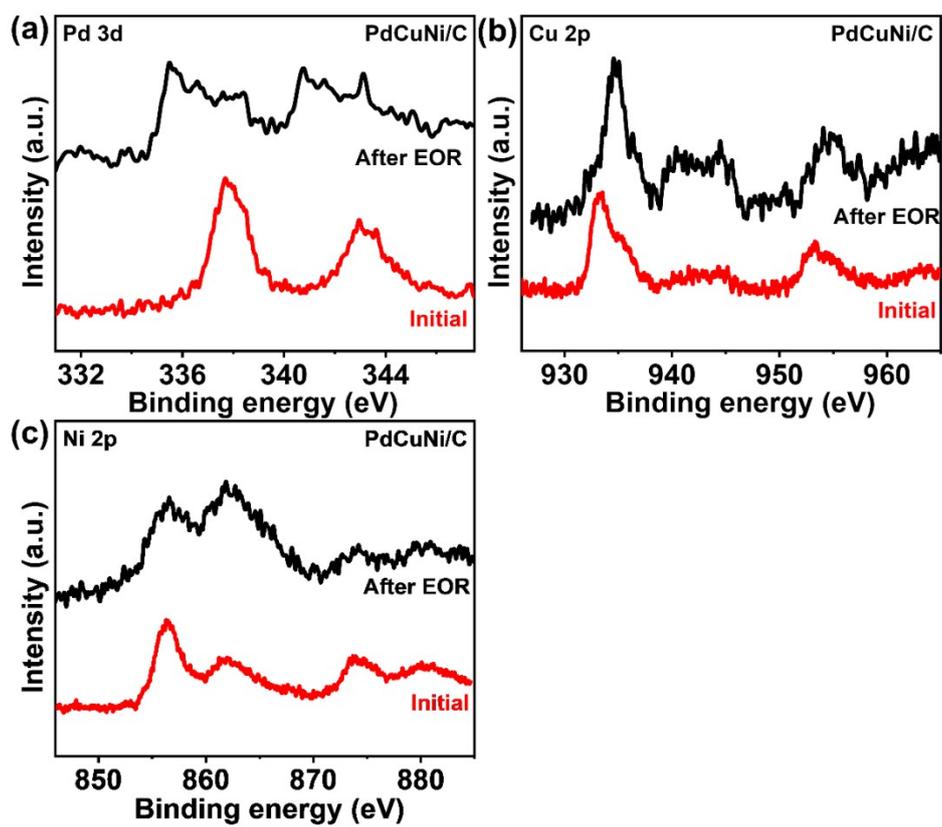


Fig. S7. (a) Pd 3d, (b) Cu 2p, (c) Ni 2p XPS spectra of PdCuNi/C before and after Chronoamperograms.

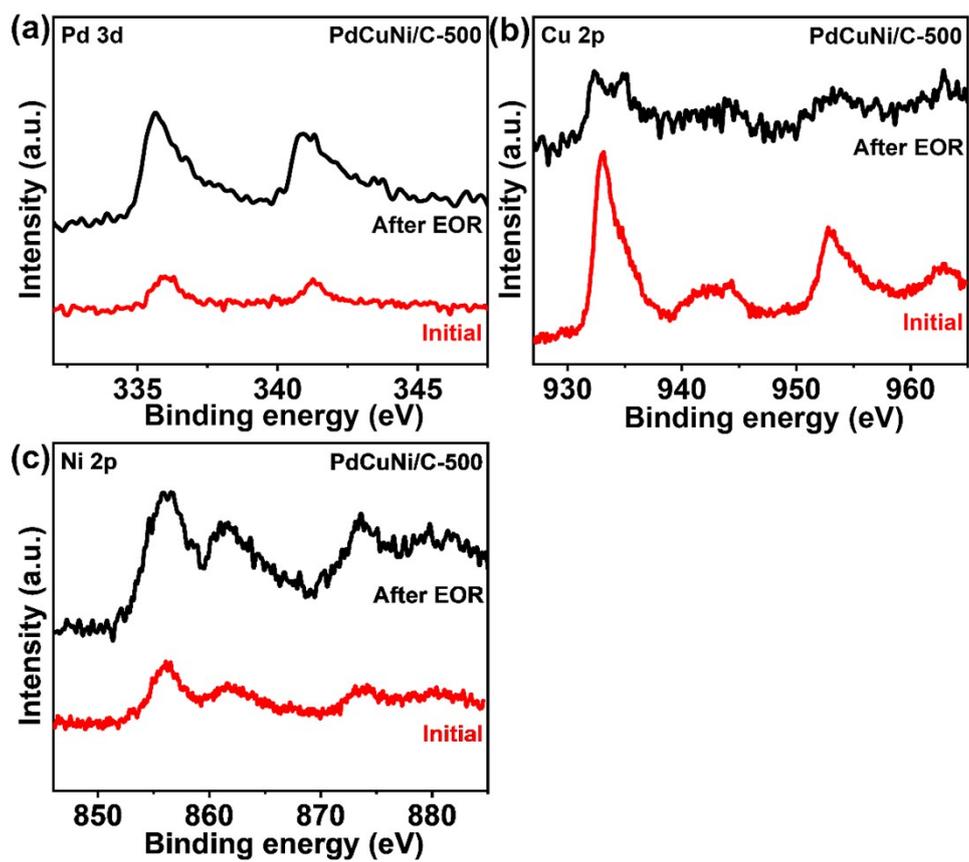


Fig. S8. (a) Pd 3d, (b) Cu 2p, (c) Ni 2p XPS spectra of PdCuNi/C-500 before and after Chronoamperograms.

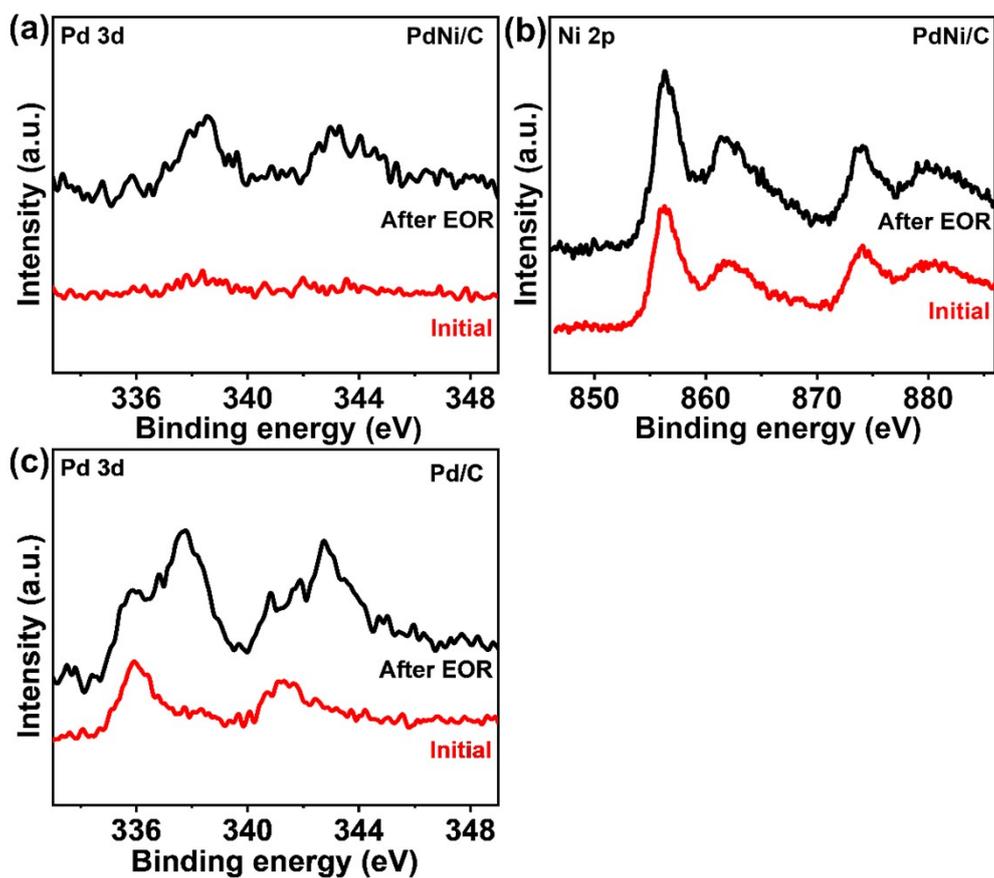


Fig. S9. (a) Pd 3d, (b) Ni 2p XPS spectra of PdNi/C before and after Chronoamperograms, (c) Pd 3d XPS spectrum of Pd/C before and after Chronoamperograms.

Table S1. Comparison of EOR activity between PdCuNi/C and other prepared catalysts before and after chronoamperometry.

Electrocatalysts	E _b	I _b	E _a	I _a	Time
	V	A/mg _{pd}	V	A/mg _{pd}	h
PdCuNi/C	0.84	3.72	0.80	3.08	22
PdCuNi/C-200	0.80	2.84	0.84	2.88	11
PdCuNi/C-300	0.90	2.28	0.89	0.84	1
PdCuNi/C-400	0.78	1.09	0.79	0.88	11
PdCuNi/C-500	0.86	1.23	0.80	0.89	22
PdCuNi/C-600	0.78	1.46	0.78	1.40	11
PdNi/C	0.81	0.14	0.78	0.08	22
PdCu/C	0.86	0.09	0.82	0.84	11
CuNi/C	0.85	0.13	0.80	0.08	1
Ni/C	0.94	0.04	0.94	0.04	1
Cu/C	0.86	0.13	0.87	0.07	1
Pd/C	0.85	1.20	0.80	1.15	22

Table S2. Comparison of EOR activities between PdCuNi/C and other as-prepared catalysts.

Electrocatalysts	E_f	I_f	E_b	I_b	I_f/I_b
	V	A/mg _{pd}	V	A/mg _{pd}	-
PdCuNi/C	0.84	3.72	0.73	5.59	0.67
PdCuNi/C-200	0.80	2.84	0.71	5.26	0.54
PdCuNi/C-300	0.90	2.28	0.75	2.60	0.88
PdCuNi/C-400	0.78	1.09	0.69	2.46	0.23
PdCuNi/C-500	0.86	1.23	0.74	1.80	0.68
PdCuNi/C-600	0.78	1.46	0.68	3.01	0.48
PdCu/C	0.81	0.14	0.68	0.25	0.56
PdNi/C	0.86	0.08	0.68	0.08	1
CuNi/C	0.85	0.13	-	-	-
Cu/C	0.94	0.04	-	-	-
Ni/C	0.86	0.13	-	-	-
Pd/C	0.85	1.20	0.75	1.45	0.83
Pd/C-JM	0.86	0.19	0.72	0.36	0.52

Table S3. Comparison of EOR activities between PdCuNi/C and reported electrocatalysts.

Electrocatalysts	Electrolyte	E_r (V vs RHE)	Mass activity (A mg _{metal} ⁻¹)	References
PdCuNi/C	1 M KOH + 1 M C ₂ H ₅ OH	0.84	3.72	This work
PdCuNi/C-200	1 M KOH + 1 M C ₂ H ₅ OH	0.80	2.84	This work
PdCuNi/C-300	1 M KOH + 1 M C ₂ H ₅ OH	0.90	2.28	This work
0.2SnO ₂ -Rh NSs/C	0.1 M KOH + 0.5 M C ₂ H ₅ OH	0.78	0.21	Adv. Mater. (2020) 2005767
8nm Pd ₃ Pb/C	0.5 M KOH + 0.5 M C ₂ H ₅ OH	0.83	2.50	Chem. Mater. 32 (2020) 2044–2052
AlPdNiCuMo	0.1 M KOH + 0.5 M C ₂ H ₅ OH	0.87	2.67	Adv. Funct. Mater. (2020) 2007129
100-Ni(OH) ₂ @Pd/GD	1 M KOH + 1 M C ₂ H ₅ OH	0.73	1.44	Appl. Surf. Sci. 420 (2017) 214–221
Au@Pt ₁ -Pd ₁ H-Ss	1 M KOH + 1 M C ₂ H ₅ OH	0.95	3.17	Adv. Mater. (2021) 2100713
Pt/MoS ₂ /GNS	0.1 M H ₂ SO ₄ + 0.1 M C ₂ H ₅ OH	1.61	0.85	Appl. Catal. B: Environ, 259 (2019) 118060
PtSn-350°C	0.5 M H ₂ SO ₄ + 1 M C ₂ H ₅ OH	1.74	0.36	Nano Energy 70 (2020) 104565

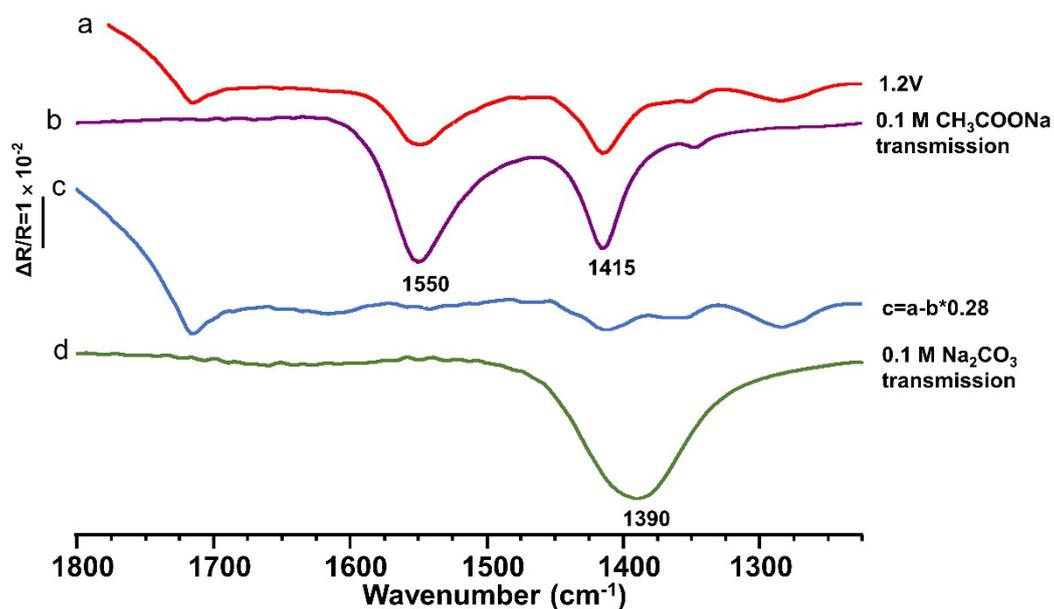


Fig. S10. (a) Identification of carbonate as the product of ethanol electrocatalytic oxidation. *In-situ* FTIR spectrum of the electrooxidation of 0.1 M ethanol at 1.20 V. Transmission IR spectra of (b) 0.1 M CH_3COONa and (d) 0.1 M Na_2CO_3 . (c) The resulting spectrum of $a - b \cdot 0.28$. The band at 1415 cm^{-1} and 1550 cm^{-1} can be assigned to CH_3COO^- as compared with spectrum b. And the band at 1390 cm^{-1} can be assigned to CO_3^{2-} as compared with spectrum d.