

Supporting Information for

Sub-10-nm PdNi@PtNi Core-Shell Nanoalloys for Efficient Ethanol Electrooxidation

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Chemicals. Platinum (II) acetylacetonate ($\text{Pt}(\text{C}_5\text{H}_7\text{O}_2)_2$, $\text{Pt}(\text{acac})_2$), Palladium (II) acetylacetonate ($\text{Pd}(\text{C}_5\text{H}_7\text{O}_2)_2$, $\text{Pd}(\text{acac})_2$), Nickel (II) acetylacetonate ($\text{Ni}(\text{C}_5\text{H}_7\text{O}_2)_2$, $\text{Ni}(\text{acac})_2$) were all purchased from SigmaAldrich. Polyvinyl pyrrolidone (($\text{C}_6\text{H}_9\text{NO}$) $_n$, PVP), Ascorbic acid ($\text{C}_6\text{H}_7\text{NO}_6$, AA), Potassium bromide, (KBr, >99%) and N,N-Dimethylformamide ($\text{C}_3\text{H}_7\text{NO}$, DMF) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All chemicals were used as they were received, and no further purification process was performed during the experiment. The commercial Pt/C catalysts (Vulcan XC-72R) used for comparison were purchased from the Sainergy company. The loading of Pt content was about 40 wt %. The water used in all experiments was ultrapure ($18.2 \text{ M}\Omega\cdot\text{cm}$).

CO-stripping measurements

For CO stripping measurements, a monolayer of CO was adsorbed on the working electrode through holding it at 0.1 V vs. RHE in N_2 -saturated 1 M KOH under a flow of CO. Then the dissolved CO in the solution was removed by bubbling N_2 for 15 min. Then, two CV curves were recorded between 0 V and 1.2 V vs. RHE in N_2 -saturated 1.0 M KOH solution at a scan rate of 50 mV s^{-1} .

The calculation methods

The ECSA ($\text{m}^2_{\text{gPt}}^{-1}$) of the catalysts is estimated according to the equation $\text{ECSA} = Q_{\text{H}}/(210 \times W_{\text{Pt}})$, where W_{Pt} represents the Pt loading ($\mu\text{g cm}^{-2}$) on the electrode, Q_{H} is the total charge (μC) for hydrogen desorption, and 210 represents the charge ($\mu\text{C cm}^{-2}_{\text{Pt}}$) required to oxidize a monolayer of hydrogen on a clean Pt surface. The area-specific activity is calculated as the ratio of current to the calculation of the active surface area of Pt by the adsorption/desorption peak of the hydrogen region, while the mass-specific activity is the ratio of current to the mass of the added catalyst.

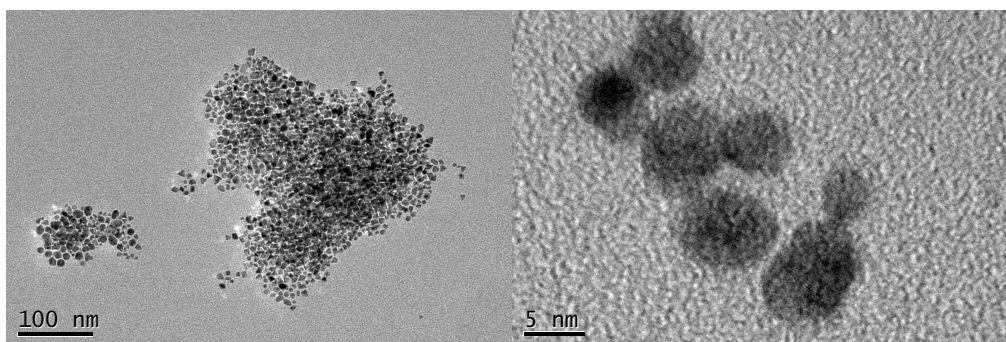


Figure S1. TEM images of PtNi NPs.

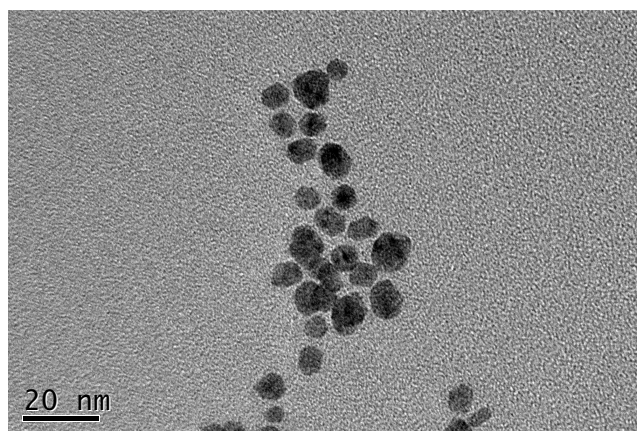


Figure S2. TEM image of PtPd NPs.

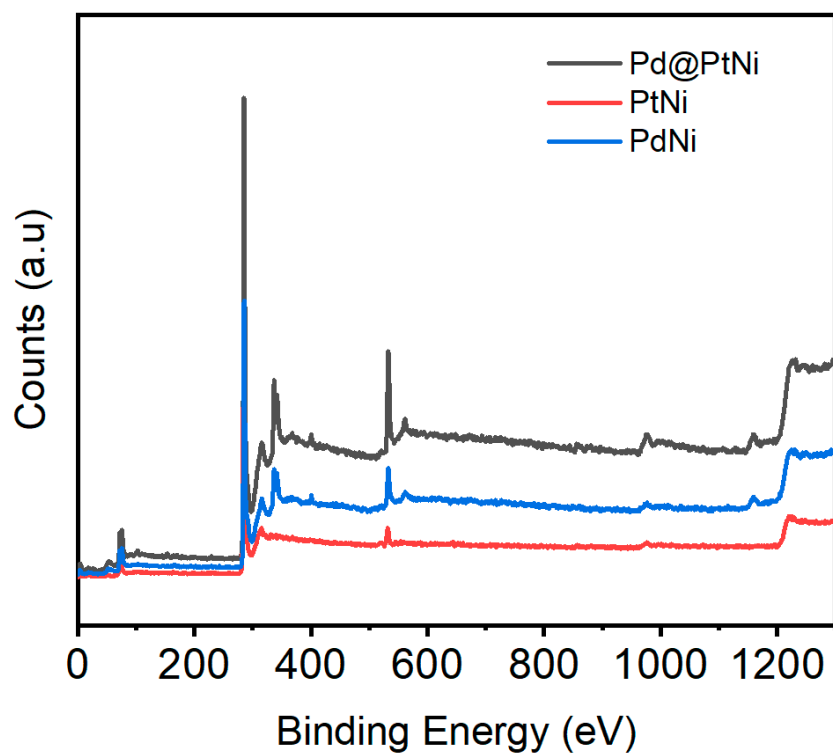


Figure S3. XPS spectra of PdNi@PtNi, PtNi and PtPd catalysts

Table S1. The contents of PdNi@PtNi NPs tested by ICP-OES

	Pt, %	Pd, %	Ni, %
PdNi@PtNi NPs	10.1	60.1	29.8
PtNi NPs	82.1	-	17.9
PtPd NPs	66.2-	33.7	

Table S2. The contents of PdNi@PtNi NPs tested by ICP-OES and XPS.

	Pt, %	Pd, %	Ni, %
ICP-OES	10.1	60.1	29.8
XPS	24.4	54.5	21.1

Table S3. The ECSA of PdNi@PtNi, PtNi and PtPd catalysts.

Catalysts	ECSA, m ² /g _{Pt}
PdNi@PtNi	229
PtPd	75.3
PtNi	26.4
Pt/C	45.7

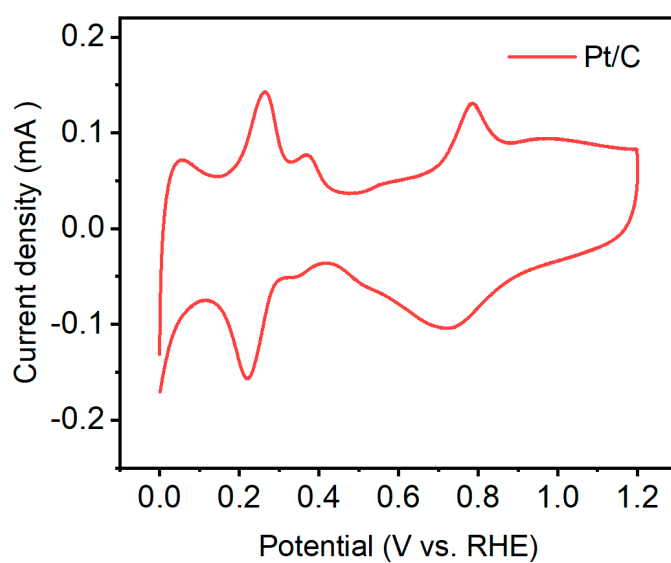


Figure S4. Cyclic voltammetry curves of Pt/C at a sweep rate of 50 mV s^{-1} in 1 M KOH.

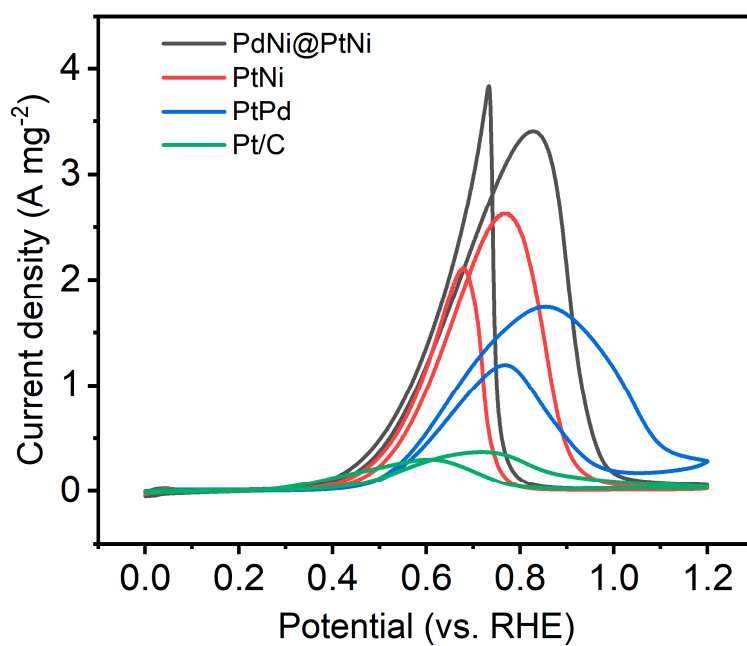


Figure S5. Mass current densities of PdNi@PtNi, PtNi and PtPd catalysts for EOR at a scanning speed of 50 mV/s.

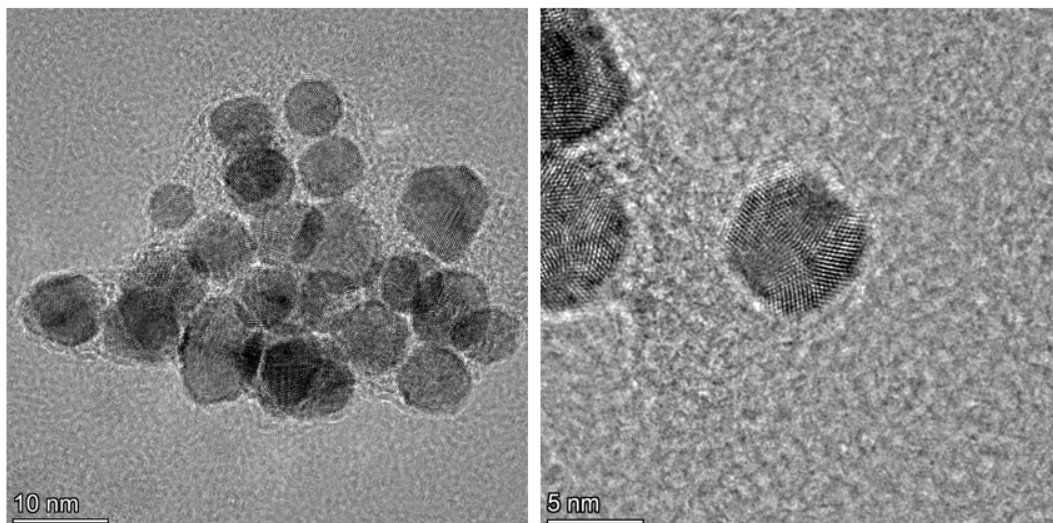


Figure S6. Mass current densities of PdNi@PtNi, PtNi and PtPd catalysts for EOR at a scanning speed of 50 mV/s.

Table S4. Electrocatalytic activities of prepared catalysts and other similar electrocatalysts for EOR in Alkaline medium from reported literatures.

Catalyst	Electrolyte	Specific Activity (mA cm ⁻²)	Mass activity (mA mg ⁻¹)	Ref
PdNi@PtNi NPs	1 M KOH + 1 M Ethanol	14.31	3350	This work
PtNi NPs	1 M KOH + 1 M Ethanol	12.05	2810	This work
PtPd NPs	1 M KOH + 1 M Ethanol	7.79	1730	This work
Pd-Au HNS/C	1 M KOH + 1 M Ethanol	11.5	-	[1]
FFT Pt-Ir NRs	1 M KOH + 1 M Ethanol	10.22	-	[2]
PdCu SMPs	1 M KOH + 1 M Ethanol	-	6090	[3]
a-PdCu	1 M KOH + 1 M Ethanol	-	152500	[4]
Au@PtIr/C	1 M KOH + 1 M Ethanol	-	8300	[5]
PdAgSn/PtBi HEA NPs	1M KOH + 1M Ethanol	-	3386	[6]
PdCo NTAs/CFC	1M KOH + 1M Ethanol	-	1491	[7]
Pd/PANI/Pd SNTAs	1M NaOH + 1M Ethanol	-	~350	[8]
<i>fcc</i> Pd ₃ Sn	1M KOH + 1M Ethanol	-	2450	[9]
c-Pd-Ni-P@a-Pd-Ni-P	1M NaOH + 1M Ethanol	-	3050	[10]
PdZn NSs	1M NaOH + 1M Ethanol	-	2730	[11]
Pt/ α -PtO _x /WO ₃	0.1 M NaOH + 0.5 M Ethanol	-	2760	[12]
Pt1Mo1/C	0.5 M KOH + 1 M Ethanol	-	500	[13]
Pt-CeO _{2-x} /GNS	1 M KOH + 1 M Ethanol	-	1300	[14]

Catalyst	Electrolyte	Specific Activity (mA cm ⁻²)	Mass activity (A mg ⁻¹)	Ref
PdNi@PtNi NPs	1 M KOH + 1 M Ethanol	14.31	3.35	This work
PtNi NPs	1 M KOH + 1 M Ethanol	12.05	2.81	This work
PtPd NPs	1 M KOH + 1 M Ethanol	7.79	1.73	This work
Pd/Ni(OH) ₂ @C/NF	1.0 M KOH+1.0 M Ethanol	-	1.3	[15]
mPdNi/Ni NTs	1.0 M KOH+1.0 M Ethanol	-	1.52	[16]
PdPtNi NPs	1.0 M KOH+1.0 M Ethanol	-	1.5	[17]
CuPdNiP NHs	1.0 M KOH+1.0 M Ethanol	-	1.19	[18]
NiO@C/CC	1.0 M KOH + 1.0 M Ethanol	119.1	1.985	[19]
Ni _x Co _{1-x} alloy	1.0 M KOH + 5.0 M Ethanol	142	-	[20]
Ni-B NTs	0.1 M NaOH + 0.5 M Ethanol	19.2	0.430	[21]
LDH@MnO ₂	1.0 M KOH+1.0 M Ethanol	~4.5	-	[22]
NGr-NiO/Pulse	0.5 M NaOH + 1.0 M Ethanol	2.3	-	[23]
NiFe/ZrO ₂ /n-Si	1.0 M KOH+1.0 M Ethanol	34.4	-	[24]
Pd ₈₀ Ni ₂₀ /C	1 M NaOH + 0.5 M Ethanol	-	0.456	[25]

Table S5. Electrocatalytic activities of prepared catalysts and other Ni-based electrocatalysts for EOR in Alkaline medium from reported literatures.

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