**Supplementary Information**

**Unveiling the electrochemical CO oxidation activity on support-free porous PdM (M = Fe, Co, Ni) foam-like nanocrystals over a wide pH range**

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2The two authors have the same contribution to this study.

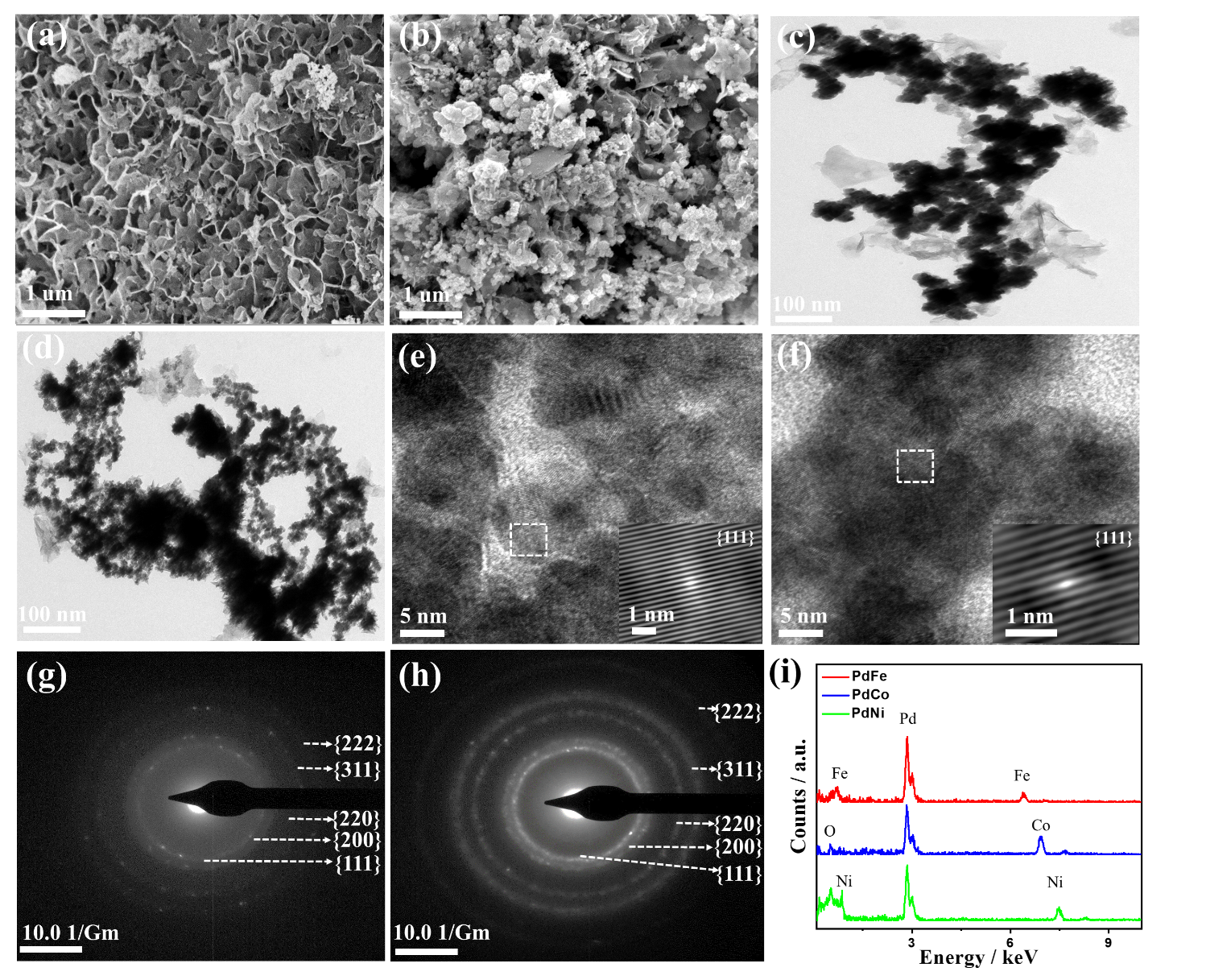


Fig. S1. (a,b) SEM, (c,d) TEM, (e,f) HRTEM with Fourier-transform of marked area for {111} facet of Pd, (g,h) SAED and (i) EDX of PdCo and PdNi nanocrystals.

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Fig. S2. Nanoparticle sizes distribution of (a) PdFe,(b) PdCo, and (c) PdNi nanocrystals

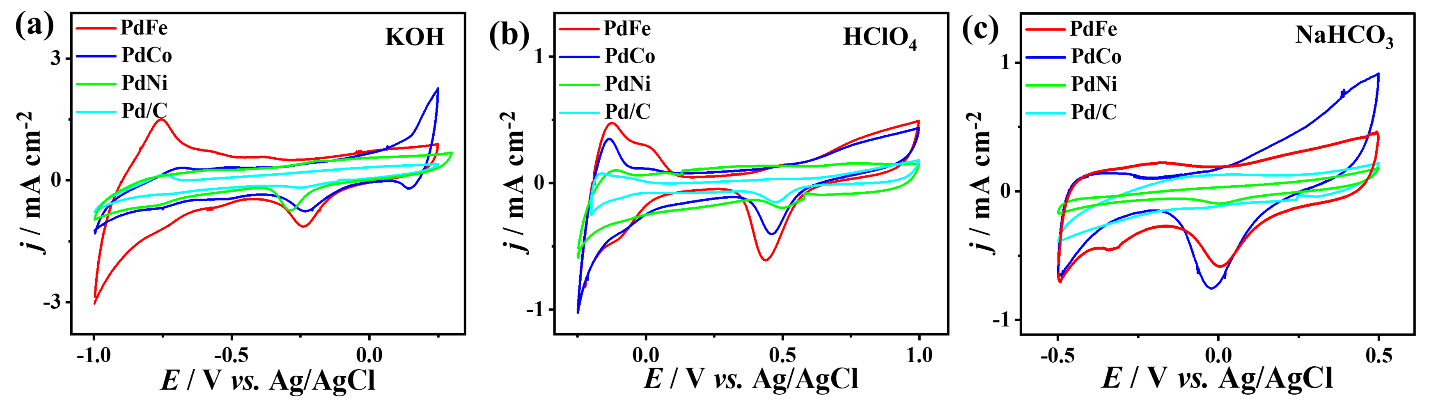


Fig. S3. CV curves of the binary PdM nanocrystals at 50 mV/s in N2-purged (a) 0.1 M KOH, (b) 0.1 M HClO4, and (c) 0.5 M NaHCO3

Table S1. Elemental composition of the binary PdM nanocrystals with EDX, XPS, and ICP-OES analysis.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Materials | EDX analysis (At%)  Pd M | | XPS analysis (At%)  Pd M | | ICP-OES analysis (At%)  Pd M | |
| PdFe | 71.18 | 28.82 (Fe) | 9.57 | 90.43 (Fe) | 83.46 | 16.54 (Fe) |
| PdCo | 56.10 | 43.90 (Co) | 43.87 | 56.13 (Co) | 54.09 | 45.91 (Co) |
| PdNi | 56.85 | 43.15 (Ni) | 69.05 | 30.95 (Ni) | 63.05 | 36.95 (Ni) |

Table S2. Binding energies of the PdM from the XPS analysis.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Catalysts | Pd 3d5/2 (eV) | | Pd 3d3/2 (eV) | | d-band center (eV) |
|  | Pd0 | Pd2+ | Pd0 | Pd2+ |  |
| PdFe | 334.92 | 337.83 | 340.31 | 346.17 | -1.71 |
| PdCo | 334.76 | 336.63 | 340.25 | 343.61 | -2.23 |
| PdNi | 334.90 | 336.95 | 339.45 | 343.53 | -1.95 |

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Fig. S4. ECSA of the binary PdM nanocrystals and Pd/C before and after stability test (a) 0.1 M KOH, (b) 0.1 M HClO4, and (c) 0.5 M NaHCO3

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Fig. S5. TEM of the (a) PdFe, (b) PdCo, and (c) PdNi after the stability test

Table S3. The electrochemical COOxid activity of Pd-based nanostructures compared with previously reported data in the literature.

|  |  |  |  |
| --- | --- | --- | --- |
| Electrocatalysts | Medium / Scan rate (mV/s)  / Reference electrode | Maximum Current  (mA/cm2) / Voltage (V) | Refs. |
| Pt{110}–Ru  Pt-NbOx | 0.5 M H2SO4 / 100 / RHE  0.5 M H2SO4 / 20 / RHE | 0.025 / 0.50  0.500 / 0.75 | [1] |
| Well-ordered Pt{111} | 0.1 M NaOH / 50 / RHE | 0.500 / 0.80 | [2] |
| PtRu (1:1) | 0.1 M HClO4 / 50 / Ag/AgCl | 0.120 / 0.25 | [3] |
| Pt/SnOx | 1.0 M HClO4 / 20 / RHE | 0.870 / 0.70 | [4] |
| Pt(FAM) | 0.1 M H2SO4 / 50 / RHE | 0.320 / 0.72 | [5] |
| Pt DEN | * 1. M HClO4 / 50 / Hg/Hg2SO4 | 0.200 / 0.30 | [6] |
| Polycrystalline Pd | 0.5 M H2SO4 / 20 / RHE | 0.175 / 0.90 | [7] |
| PdAg/C | 0.5 M KOH/ 20 / RHE | 0.944 / 0.60 | [8] |
| PtPd nanodendrites | 1.0 M KOH / 50 / Ag/AgCl | 5.100 / -0.15 | [9] |
| 60 wt. % Pt/C | 0.5 M H2SO4 / 10 / SHE | 0.200 / 0.64 | [10] |
| PtRu@h-BN/C | 0.1 M H2SO4 / 20 / RHE | 1.250 / 0.60 | [11] |
| PtNi multicubes | 1.0 M KOH / 50 / RHE | 0.580 / 0.65 | [12] |
| Pt PSS | 0.5 M H2SO4 / 50 / RHE | 0.300 / 0.80 | [13] |
| PtPd(50%) nanodendrites | 0.5 M H2SO4 / 20 / SCE | ⁓3.000 / ⁓0.60 | [14] |
| Pd/CMK-3-R8-1500-10 | 0.5 M H2SO4 / 20 / RHE | ⁓ 0.145 / ⁓ 0.90 | [15] |
| Pd-Pd(4:1)/C | 1.0 M KOH / 50 / Hg/HgO | ⁓ 0.175 / ⁓ -0.10 | [16] |
| Pd/Ti3C2Tx | 0.1 M HClO4 / 50 / Ag/AgCl | 0.318 / ⁓0.90 | [17] |
| Pd/Ni-MOF/PC | 0.1 M NaHCO3/ 50 / RHE | 1.220 / 0.83 | [18] |
| Pd/ZIF-67/C | 0.1 M NaHCO3/ 50 / RHE | 1.497 / 0.85 | [19] |
| AuPd/C | 0.5 M H2SO4/ 20 / Ag/AgCl | 0.567 / ⁓ 0.90 | [20] |
| PdNiO-CeO2/OLC | 0.1 M HClO4 /50 / RHE | 2.500 / 1.10 | [21] |
| PdNiO-CeO2/CB | 0.1 M HClO4 /50 / RHE | 2.650 / 1.05 | [22] |
| Pd nanocube  Pd nanosponge | 0.1 M H2SO4/ 50 / Ag/AgCl | 5.920 / 0.76  4.000 / 0.72 | [23] |
| PdCu | 0.1 M KOH / 50 / RHE | 3.610 / 0.94 | [24] |
| PdNi | 0.1 M HClO4 /50 / Ag/AgCl | 0.344 / 0.654 | This work |
| 0.1 M KOH / 50 / Ag/AgCl | 0.800 / -0.105 |
| 0.5 M NaHCO3 / 50 / Ag/AgCl | 0.222 / 0.196 |
| PdCo | 0.1 M HClO4 /50 / Ag/AgCl | 0.676 / 0.688 | This work |
| 0.1 M KOH / 50 / Ag/AgCl | 2.150 / -0.104 |
| 0.5 M NaHCO3 / 50 / Ag/AgCl | 1.590 / 0.274 |
| PdFe | 0.1 M HClO4 / 50 / Ag/AgCl | 1.480 / 0.770 | This work |
| 0.1 M KOH / 50 / Ag/AgCl | 5.220 / -0.104 |
| 0.5 M NaHCO3 / 50 / Ag/AgCl | 1.450 / 0.266 |

Dendrimer-encapsulated nanoparticles (DEN), polyhedron with smooth surfaces (PSS), unsupported Pt nanoparticles (Pt(FAM)), graphitized ordered mesoporous carbons (CMK-3), metal-organic framework derived porous carbon (MOF/PC), zeolitic imidazolate framework (ZIF-67), onion-like carbon (OLC), carbon black (CB).

Table S4: EIS data analysis for the PdFe, PdCo, PdNi, and Pd/C in 0.1 M KOH saturated by CO.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Catalysts | *R*s / Ω | *R*ct / kΩ | CPE / μS.s(1-n) | n |
| PdFe | 86.30 ± 6.7 | 4.60 ± 0.92 | 166.60 ± 9.6 | 0.88 |
| PdCo | 129.30 ± 17.5 | 5.84 ± 0.15 | 96.99 ± 1.04 | 0.88 |
| PdNi | 147.40 ± 11.4 | 7.10 ± 0.21 | 30.34 ± 2.12 | 0.89 |
| Pd/C | 84.70 ± 0.75 | 6.78 ± 3.78 | 72.25 ± 5.8 | 0.84 |

Table S5: EIS data analysis for the PdFe, PdCo, PdNi, and Pd/C in 0.1 M HClO4 saturated by CO.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Catalysts | *R*s / Ω | *R*ct / kΩ | CPE / μS.s(1-n) | n |
| PdFe | 61.41 ± 0. | 3.94 ± 0.58 | 43.1 ± 1.2 | 0.85 |
| PdCo | 128.2 ± 2.79 | 5.06 ± 0.908 | 25.21 ± 1.2 | 0.90 |
| PdNi | 115.9 ± 1.97 | 53.13 ± 0.482 | 18.83 ± 0.48 | 0.88 |
| Pd/C | 144.70 ± 0.75 | 107.60 ± 3.78 | 24.01 ± 2.22 | 0.90 |

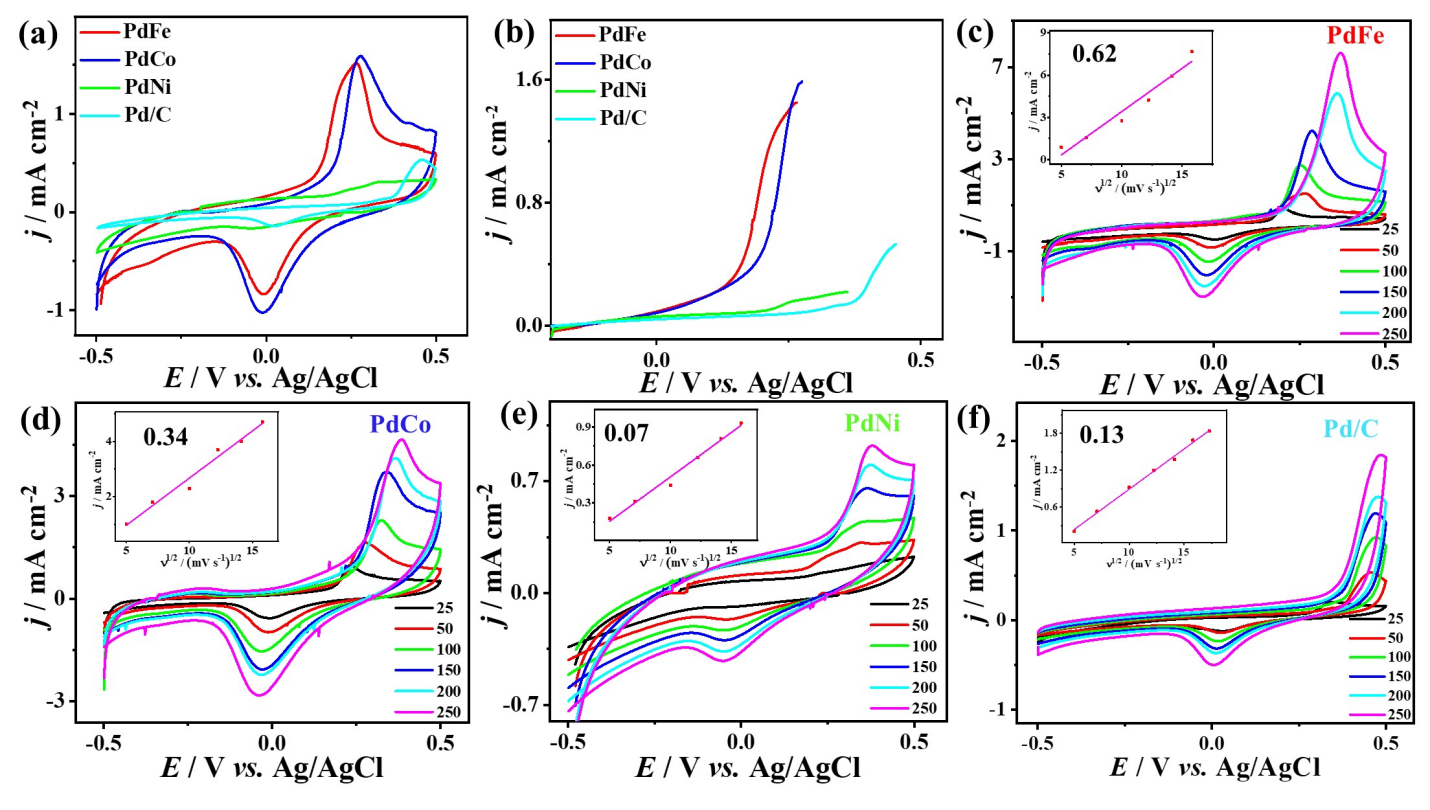


Fig. S6. (a) CV curves, (b) LSV curves at 50 mV/s, and (c-f) scan rate studies of PdFe, PdCo, PdNi, and Pd/C in CO-saturated 0.5 M NaHCO3

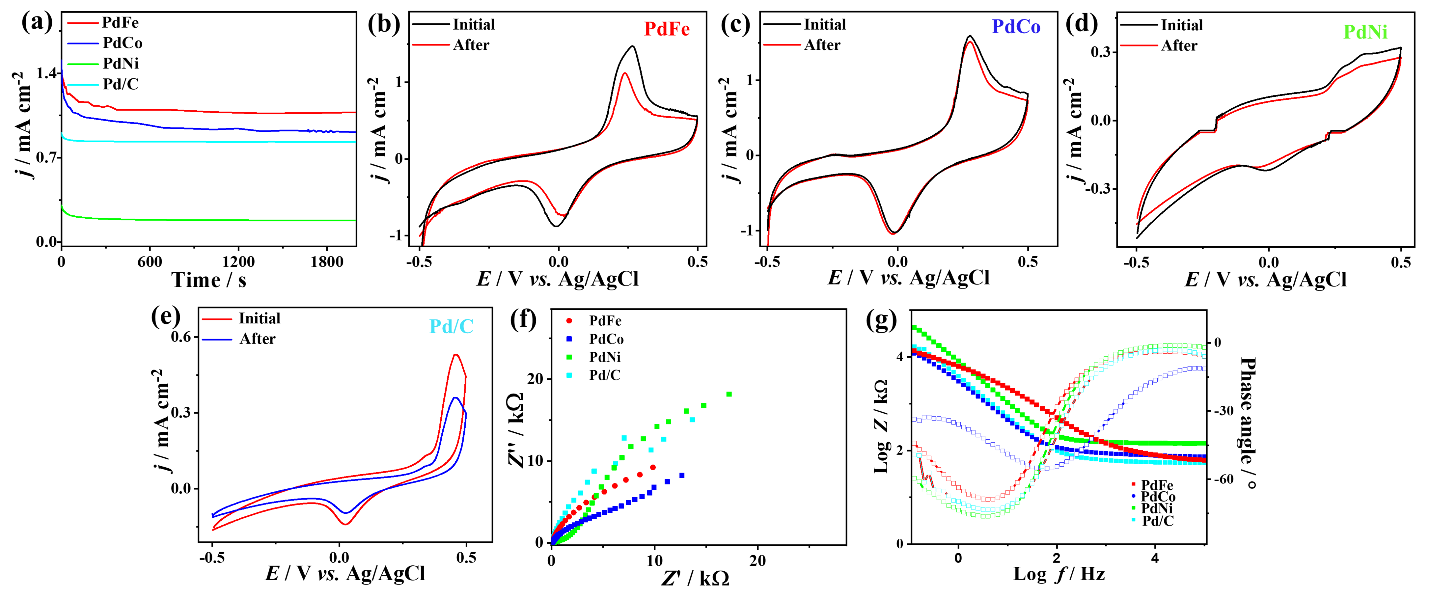


Fig. S7. (a) CA curves, (b-e) CV curves at initial and 1000 cycles, (f) Nyquist plots, and (g) Bode plots of PdFe, PdCo, PdNi, and Pd/C in CO-saturated 0.5 M NaHCO3

Table S6: EIS data analysis for the PdFe, PdCo, PdNi, and Pd/C in 0.5 M NaHCO3 saturated by CO.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Catalysts | *R*s / Ω | *R*ct / kΩ | CPE / μS.s(1-n) | n |
| PdCo | 82.98 ± 5.4 | 6.1 ± 0.5 | 88.07 ± 0.01 | 0.738 |
| PdFe | 93.62 ± 2.8 | 12.46 ± 1.1 | 60.22 ± 1.7 | 0.883 |
| PdNi | 95.00 ± 0.59 | 24.43 ± 1.66 | 25.74 ± 0.26 | 0.92 |
| Pd/C | 94.02 ± 1.13 | 19.03 ± 0.72 | 32.1 ± 2.39 | 0.886 |

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