Supporting Information

Self-Standing Pd-Based Nanostructures for Electrocatalytic CO Oxidation: Do Nanocatalyst Shape and Electrolyte pH Matter?

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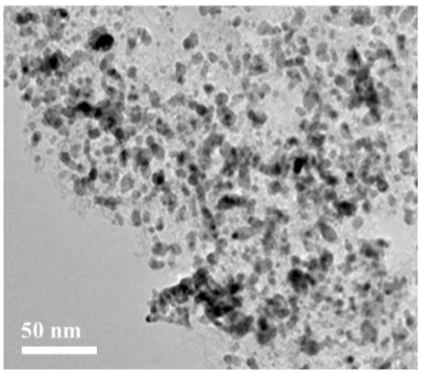

Figure S1. TEM of the Pd/C.

Table S1. Binding energies of Pd 3d in Pd nanocube, Pd nanosponge, and Pd/C catalysts.

Catalyst	Pd $3d_{5/2}$		Pd $3d_{3/2}$	
	Pd^0	Pd^{2+}	Pd^0	Pd^{2+}
Pd nanocube	333.52	335.43	338.93	342.49
Pd nanosponge	333.73	335.62	338.94	341.34

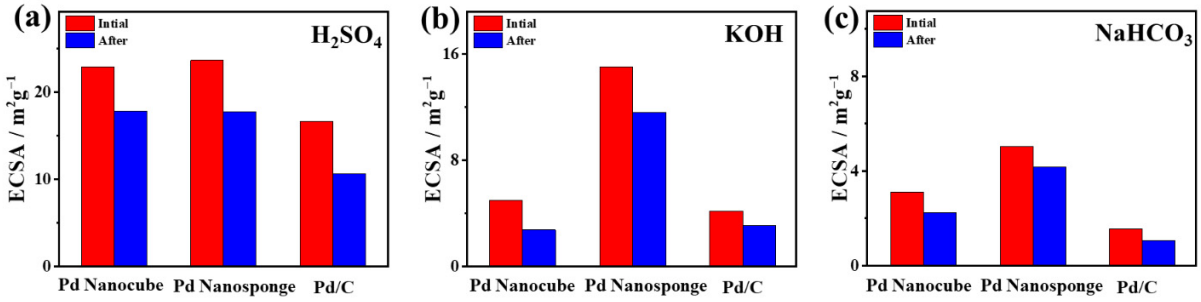

Figure S2. The ECSA before and after electrochemical CO oxidation stability (a) 0.1 M H_2SO_4, (b) 0.1 M KOH and (c) 0.5 M $NaHCO_3$.

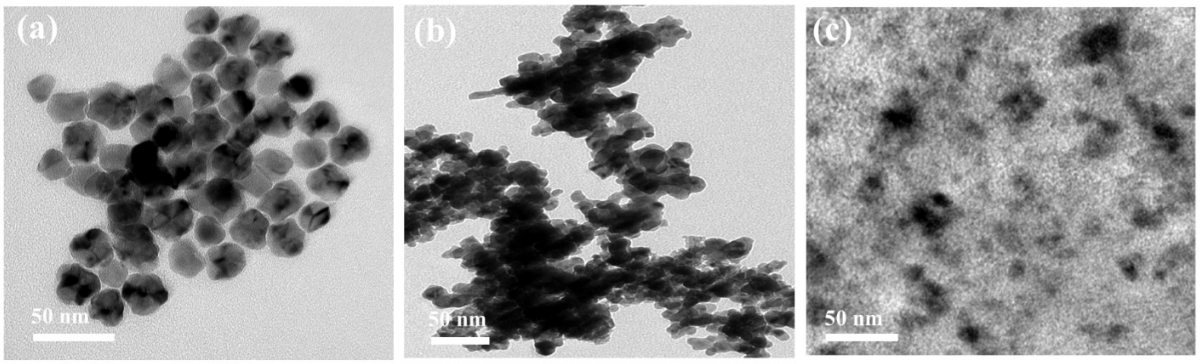

Figure S3. TEM of the catalyst after the stability test in 0.1 M H_2SO_4 (a) Pd nanocube, (b) Pd nanosponge, and (c) Pd/C.

Table S2. Electrochemical activity comparison of our prepared catalysts related to the previously reported works.

Catalyst	**Medium/ scan rate/ Reference electrode**	**Maximum current (mA cm^{-2}) density/voltage (V)**	**Ref.**
Pd nanocube Pd nanosponge	0.1M H_2SO_4 50mV/s Ag/AgCl	5.92 / 0.755 4.0 / 0.715	Our work
PtPd Nanodendrites	1 M KOH 50 mV/s Ag/AgCl	5.1 / -0.15	[1]
Pd/$Ti_3C_2T_x$	0.1 M $HClO_4$ 50 mV/s Ag/AgCl	0.32 / ~0.9	[2]
PtNi multicubes	0.1M KOH 50 mV/s RHE	0.580 / 0.65	[3]
Pt DEN	0.1M $HClO_4$ 50 mV/s Hg/Hg_2SO_4	0.200 / 0.30	[4]
PdAg/C	0.5 KOH 20 mV/s RHE	0.944 / 0.60	[5]
Polycrystalline Pd	0.5 M H_2SO_4 20mV/s RHE	0.18 / 0.9	[6]
Pd/CMK-3-R8-1500-10	0.5 M H_2SO_4 20 mV/s RHE	~ 0.15 / ~ 0.9	[7]
PdNiO/OLC	0.1M H_2SO_4 50mV/s RHE	1.44 / 1.16	[8]

PtPd(50%) nanodendrites	0.5 M H_2SO_4 20 mV/s SCE	~3 / ~0.6	[9]
PdNiO-CeO_2/OLC	0.1M H_2SO_4 50mV/s RHE	2.5 / 1.1	[8]
PdAu/C	0.5 M H_2SO_4 20 mV/s Ag/AgCl	0.57 / ~ 0.9	[10]
Pd-Pd(4:1)/C	1.0 M KOH 50 mV/s Hg/HgO	~ 0.18 / ~ -0.1	[11]
Pt/SnO_x	1 M $HClO_4$ 20 mV/s RHE	0.870 / 0.70	[12]

Table S3. EIS analysis of the catalysts measured in 0.1 M H_2SO_4.

Catalyst	R_s **(Ω)**	R_{ct} **(kΩ)**	**CPE (μF.s$^{(1-\alpha)}$)**	α
Pd nanocube	96.90 ± 0.65	30.0 ± 1.36	55.25 ± 0.63	0.757
Pd nanosponge	99.40 ± 0.78	47.5 ± 2.8	42.00 ± 0.01	0.817
Pd/C	146.20 ± 0.11	74.3 ± 1.2	25.30 ± 2.20	0.911

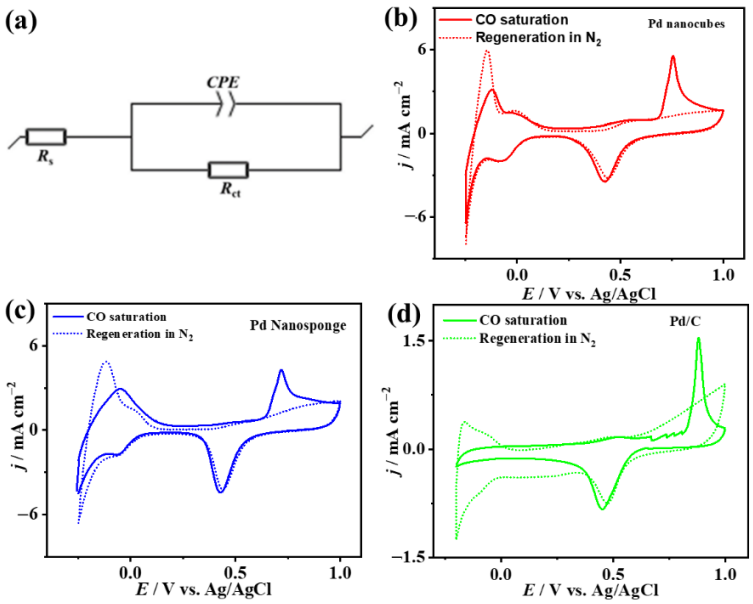

Figure S4. Voigt electrical equivalent circuit (a) and regeneration of the Pd catalysts after CO gas was switched to N_2 for 1 h (b-d).

Table S4. EIS analysis of the catalysts measured in 0.1 M KOH.

Catalyst	R_s (Ω)	R_{ct} (kΩ)	CPE (μF.s$^{(1-\alpha)}$)	α
Pd nanocube	96.87 ± 0.65	30.17 ± 1.3	38.25 ± 0.63	0.817
Pd nanosponge	93.34 ± 0.54	40.49 ± 2.8	15.82 ± 1.90	0.757
Pd/C	99.40 ± 0.79	47.49 ± 2.8	40.50 ± 1.30	0.821

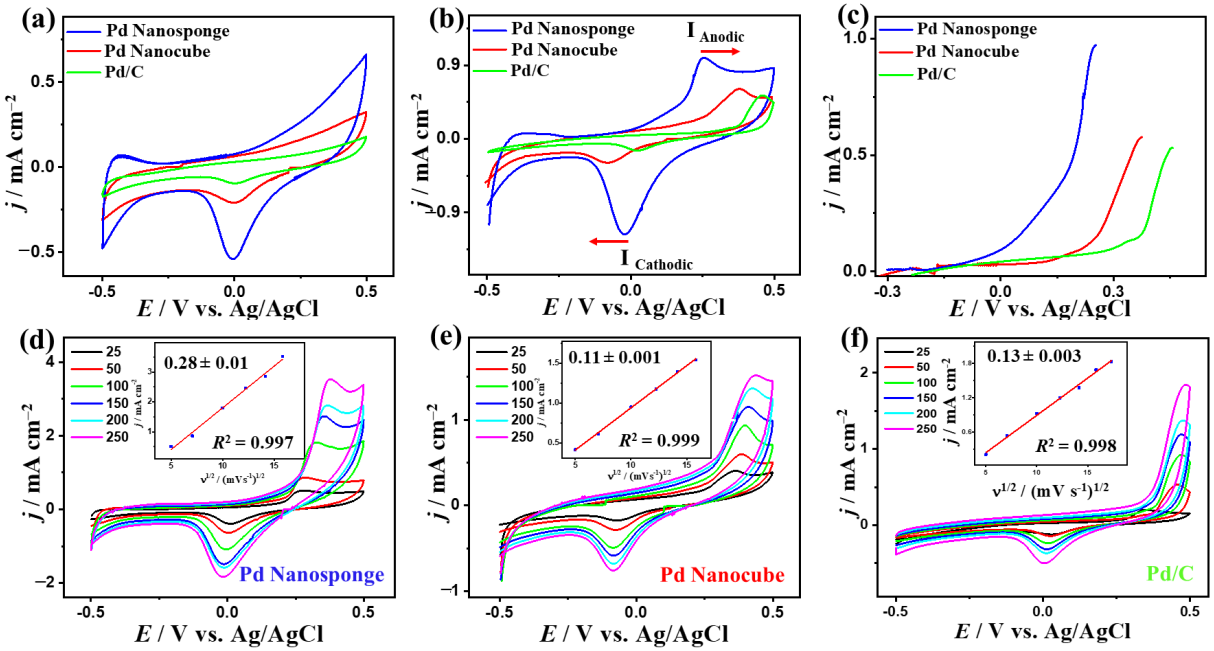

Figure S5. CV curves in N_2-saturated 0.5 M $NaHCO_3$ (a), CO-saturated 0.5 M $NaHCO_3$ at 50 mV/s (b), LSV at 50 mV/s (c), CV curves at different scan rates and their related plots of I_f *vs.* $v^{1/2}$ of Pd nanosponge, Pd nanocube, and Pd/C (d-f), in CO-saturated 0.5 M $NaHCO_3$.

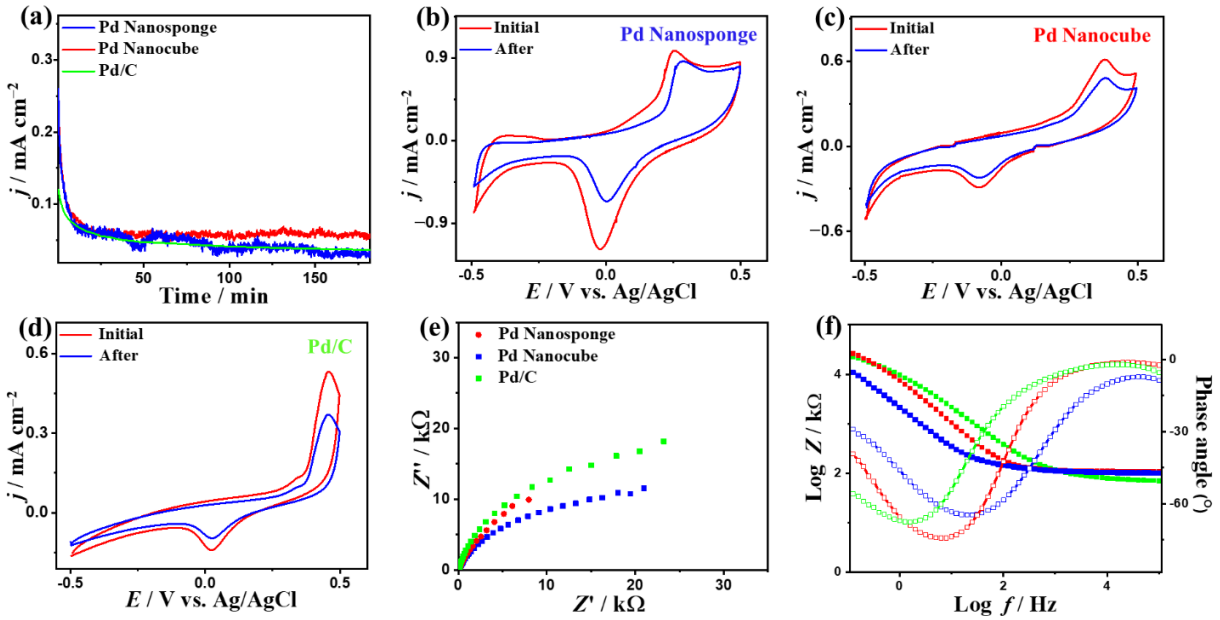

Figure S6. CA tests measured in CO-saturated 0.5 M $NaHCO_3$ (a), CV curves measured after CA (b-d), EIS (e), and Bode plots (f) of Pd nanosponge, Pd nanocube, and Pd/C.

Table S5. EIS analysis of the catalysts measured in 0.5 M $NaHCO_3$.

Catalyst	R_s (Ω)	R_{ct} (Ω)	CPE ($\mu F.s^{(1-\alpha)}$)	α
Pd nanosponge	74.34 ± 0.56	21.00 ± 0.746	82.26 ± 1.5	0.771
Pd nanocube	108.80 ± 0.87	74.86 ± 0.11	18.93 ± 0.35	0.848
Pd/C	120.1 ± 0.22	81.16 ± 0.01	16.03 ± 0.13	0.878

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