Redox-Active Phenanthrenequinone as Molecular Electron Bridge for Ultrastable Pd-Catalyzed Formic Acid Electrooxidation

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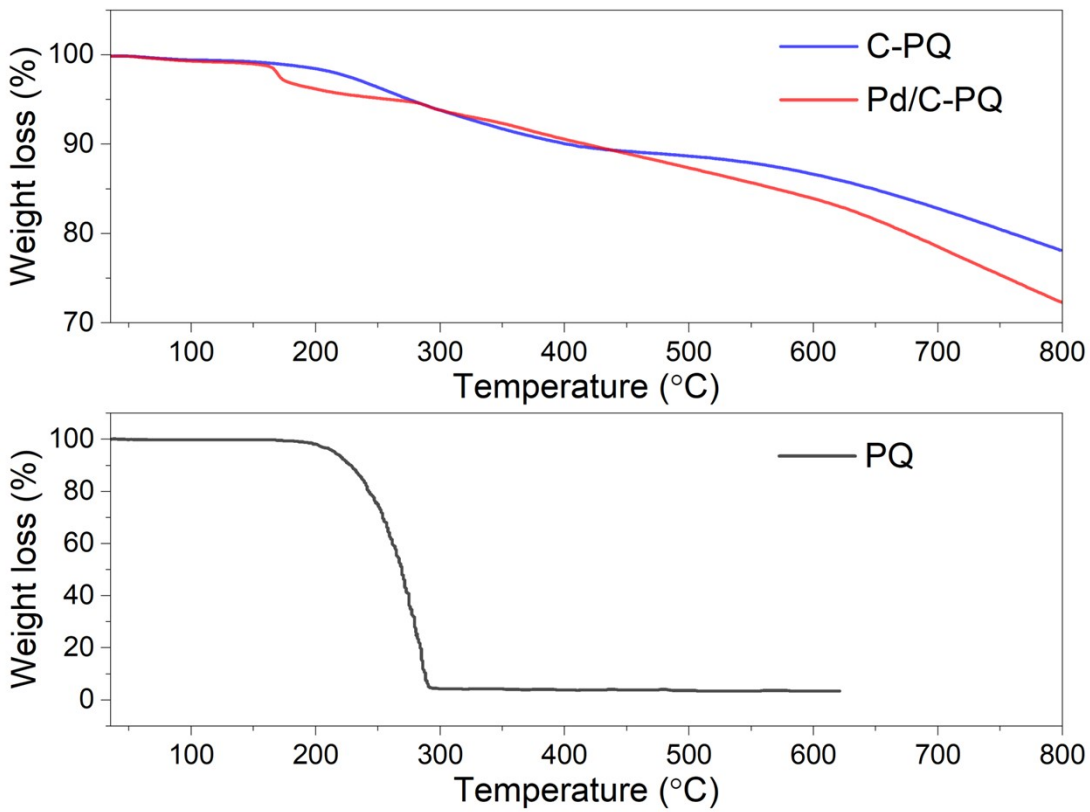

Figure S1 TGA curves of C-PQ, Pd/C-PQ and PQ at the rate of 5 ℃ min^{-1} in nitrogen atmosphere.

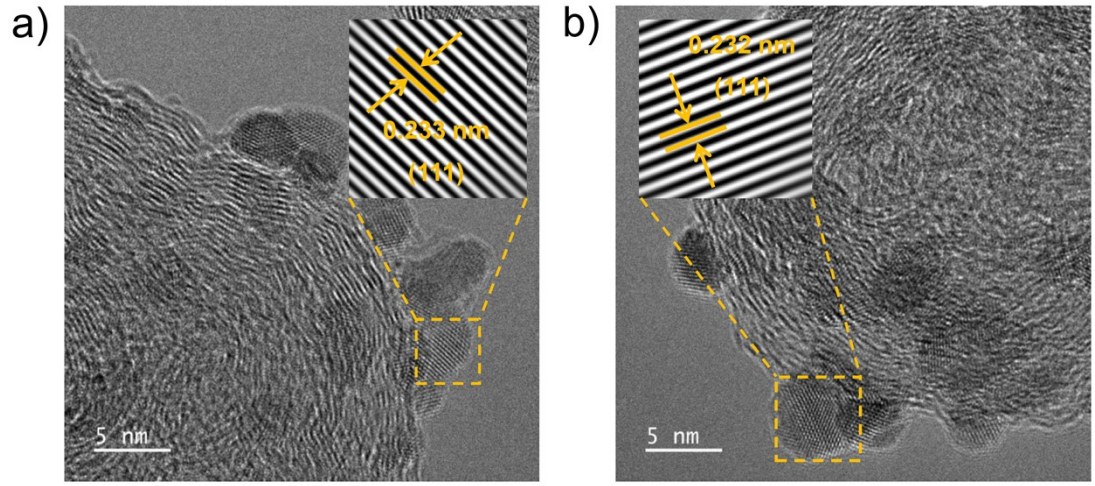

Figure S2 HR-TEM images of Pd/C-PQ (a) and Pd/C (b) catalysts.

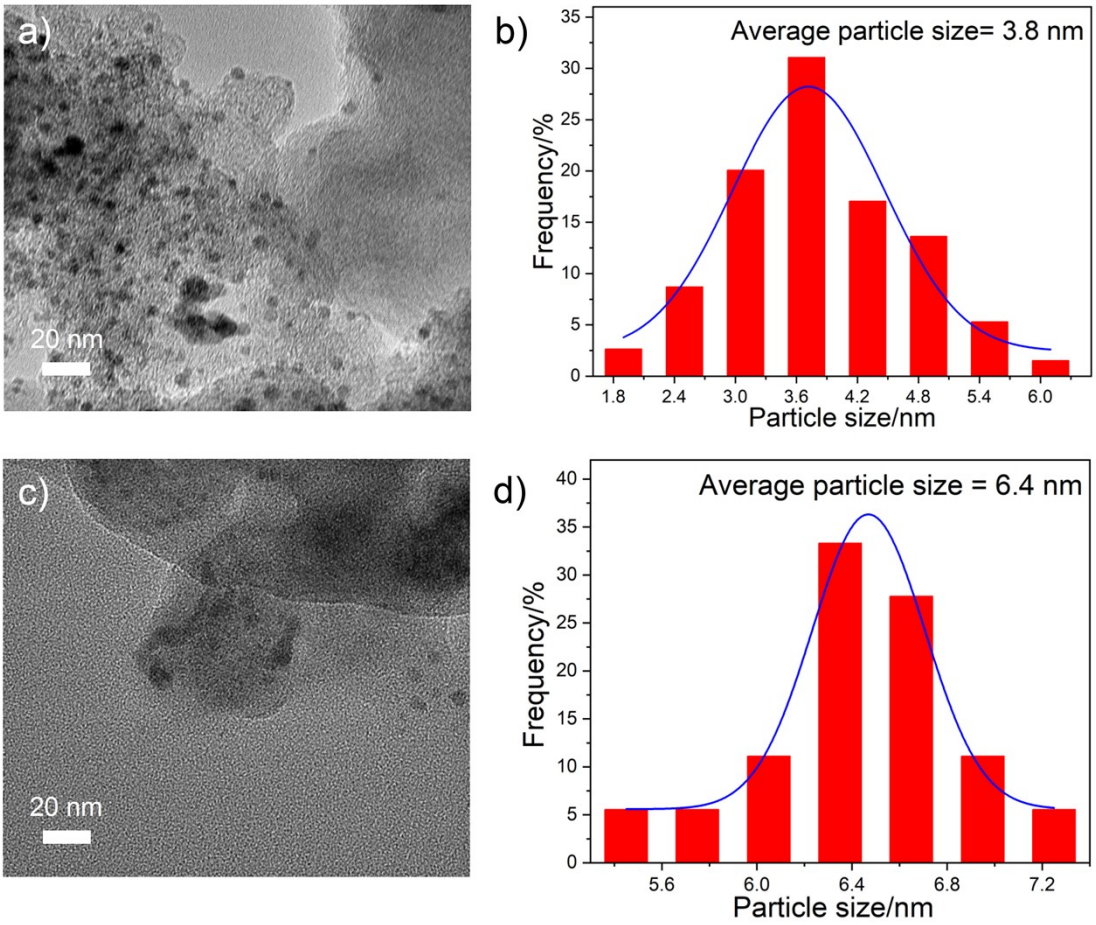

Figure S3 TEM images and corresponding particle size histograms of Pd/C-PQ (a-b) and Pd/C catalysts (c-d) after 50 cycles of CV measurements.

Table S1 Binding energy and relative peak percentages of fitted Pd 3*d* for Pd/C and Pd/C-PQ catalysts.

element	index	Pd/C		Pd/C-PQ	
		Pd(0)	Pd(II)	Pd(0)	Pd(II)
Pd $3d_{5/2}$	binding energy/eV	334.6	336.6	334.9	336.7
	atom/%	33.2	27.6	43.2	17.7
Pd $3d_{3/2}$	binding energy/eV	339.8	341.7	340.1	341.8
	atom/%	18.3	20.9	26.2	12.9

Table S2 Peak position and relative peak percentages of fitted C 1*s* and O 1*s* for Pd/C and Pd/C-PQ catalysts.

element	functional group	Pd/C		Pd/C-PQ	
		binding energy/eV	atom/%	binding energy/eV	atom/%
C 1*s*	C-C	284.8	58.7	284.7	59.3
C 1*s*	C-OH/C-O-C	285.8	22.8	285.6	24.0
C 1*s*	C=O	287.0	8.4	286.9	9.0
C 1*s*	COO	289.2	10.1	289.1	7.7
O 1*s*	C=O	531.6	20.1	531.5	21.3
O 1*s*	C-OH	532.8	35.1	532.7	38.7
O 1*s*	C-O-C	534.1	30.0	534.0	25.0
O 1*s*	H_2O	535.4	14.8	535.3	15.0

Table S3 Comparison of the reported performances of Pd-based anode catalysts for formic acid oxidation.

Materials	Mass activity ($mA\ mg^{-1}$)	Specific activity ($A\ m^{-2}$)	Electrolyte	Reference
Pd/C-PQ	712	13.5	0.5 M HCOOH + 0.5 M H_2SO_4	This work
Pd/N-doped graphene-CNT	630	/	0.5 M HCOOH + 0.5 M H_2SO_4	[1]
Pd/graphene	273	/		
Pd/CNT	170	/		
PdNi/RGO	604	/	0.5 M HCOOH + 0.5 M H_2SO_4	[2]
Pd/RGO	308	/		
Pd/rGO	697	/	0.5 M HCOOH + 0.1M $HClO_4$	[3]
Pd_6Ga_4/rGO	762	7.4	1 M HCOOH + 0.5 M H_2SO_4	[4]
AuCore-PdShell/RGO	620	1.9	0.5 M HCOOH + 0.5 M H_2SO_4	[5]
Pd@N-carbon	362	/	0.1 M HCOOH + 0.1M$HClO_4$	[6]
Pd_1Ni_1/N-doped graphene	709	/	1 M HCOOH + 0.5 M H_2SO_4	[7]
Pd/RGO	648	/	0.5 M HCOOH + 0.5 M H_2SO_4	[8]
Pd/CNT	516	/		

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