

Supporting Information

Enhanced Catalytic Activity of Palladium Nanoparticles Confined inside Porous Carbon in Methanol Electro-Oxidation

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S1. X-ray Photoelectron Spectroscopy (XPS)

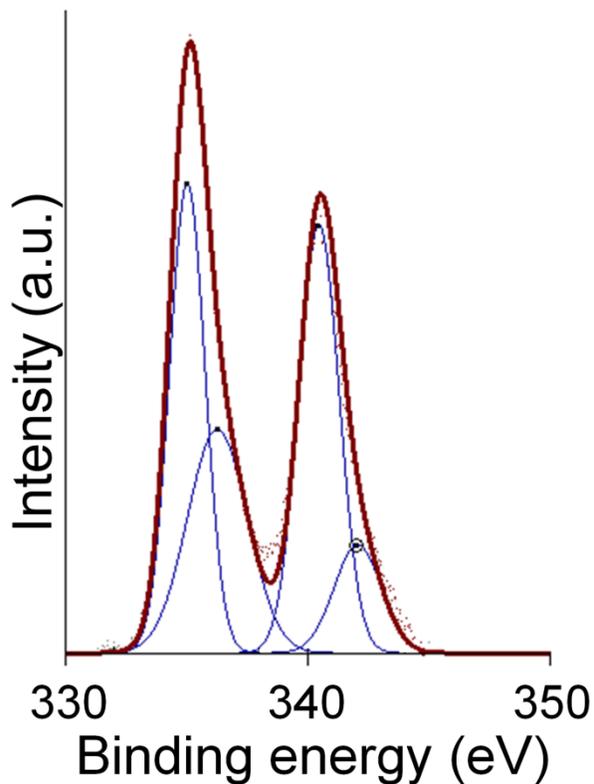


Figure S1: Pd *3d* XPS spectrum of Pd@C1.

XPS analysis of the Pd *3d* core level in Pd@C1 shows the presence of 35% Pd²⁺ species. The Pd *3d* peaks are resolved into two sets of spin-orbit doublets. Pd ($3d_{5/2, 3/2}$) peaks observed at 335.1 and 340.4 eV are due to the presence of Pd⁰ state and the peaks at 336.2 and 342.03 eV are assigned to Pd²⁺.

S2. Cyclic Voltammograms (CVs) without catalyst (blank) and only mesoporous carbon (without Pd NPs)

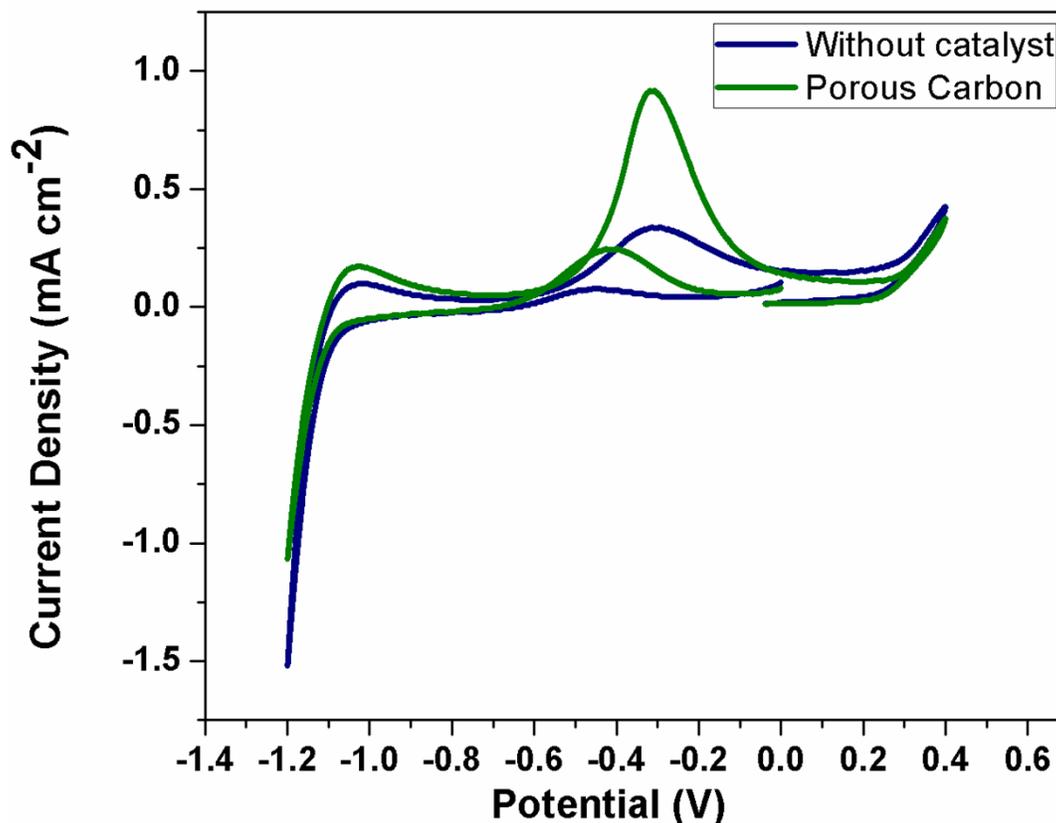


Figure S2: CVs for MeOH EOx without catalyst and with mesoporous carbon having no metal loading.

The blank reaction without any catalyst showed negligible peak current density (0.3 mA/cm^2) with very low ECSA of 1.23 cm^2 at potential -0.03 V . On the other hand the electrooxidation reaction using mesoporous carbon without Pd NP loading showed a peak current density 0.9 mA/cm^2 . The ECSA was observed to be $1.71 \text{ cm}^2/\text{mg}_{\text{Carbon}}$. The catalytic activity of mesoporous carbon can result from the active defect sites, which are high in number.

Table S3: Recyclability of Pd@C1, Pd@C2 and Pd/C catalysts. All measurements were performed with 0.5 M MeOH and 0.5 M KOH)

Catalyst	Cycles	Reaction Condition (Stirring)	Potential (V)	Peak Current density (mAcm ⁻²)	Mass-specific current density Peak (A/mg _{Pd})	Electrochemically active surface area (ECSA) (cm ² /mg _{Pd})
Pd@C1	1	Without	0.45	141	801	613
		With	-0.29	142	815	626
	100	Without	0.45	125	722	491
		With	-0.28	128	735	516
	200	Without	0.46	100	512	386
		With	-0.33	100	570	404
	300	Without	0.49	12	95	91
		With	-0.28	29	163	139
Pd@C2	1	Without	0.50	120	265	191
		With	-0.30	100	286	234
	100	Without	0.49	91	210	175
		With	-0.30	85	240	202
	200	Without	0.47	69	72	159
		With	-0.33	72	200	176
	300	Without	0.46	6	12	14
		With	-0.3	10	27	22
Pd/C	1	Without	0.56	108	185	189
		With	-0.25	70	121	162
	100	Without	0.53	13	79	46
		With	-0.27	41	110	95
	200	Without	--	--	4	5.2
		With	-0.30	3	9	7.6
	300	Without	--	--	1	1.3
		With	-0.3	1	2	2.2

Table S4: Effect of alkali concentration on methanol electro-oxidation. All measurements were performed with 0.5 M MeOH using Pd@C1 catalyst.

Concentration of KOH (M)	Reaction Condition (Stirring)	Potential (V)	Peak Current density (mAcm ⁻²)	Mass-specific Current density Peak (A/mg _{Pd})	Electrochemically active surface area (ECSA) (cm ² /mg _{Pd})
0.1	Without	0.45	80	425	322
	With	-0.3	70	412	297
0.2	Without	0.47	101	560	401
	With	-0.3	97	543	472
0.5	Without	0.45	141	801	613
	With	-0.29	142	815	626
1.0	Without	0.45	139	780	589
	With	-0.29	135	785	607

Table S5: Effect of methanol concentration on its electro-oxidation. All measurements were performed with 0.5 M KOH using Pd@C1 catalyst.

Concentration of MeOH (M)	Reaction Condition (Stirring)	Potential (V)	Peak Current density (mAcm ⁻²)	Mass-specific Current density Peak (A/mg _{Pd})	Electrochemically active surface area (ECSA) (cm ² /mg _{Pd})
0.1	Without	0.5	103	465	378
	With	-0.3	76	426	357
0.2	Without	0.49	122	556	462
	With	-0.3	92	517	437
0.5	Without	0.45	141	801	613
	With	-0.29	142	815	626
1.0	Without	0.45	133	726	603
	With	-0.28	120	700	591