

## Supporting Information

# **Capping Polymer-Enhanced Electrocatalytic Activity on Pt Nanoparticles: A Combined Electrochemical and in situ IR Spectroelectrochemical Study**

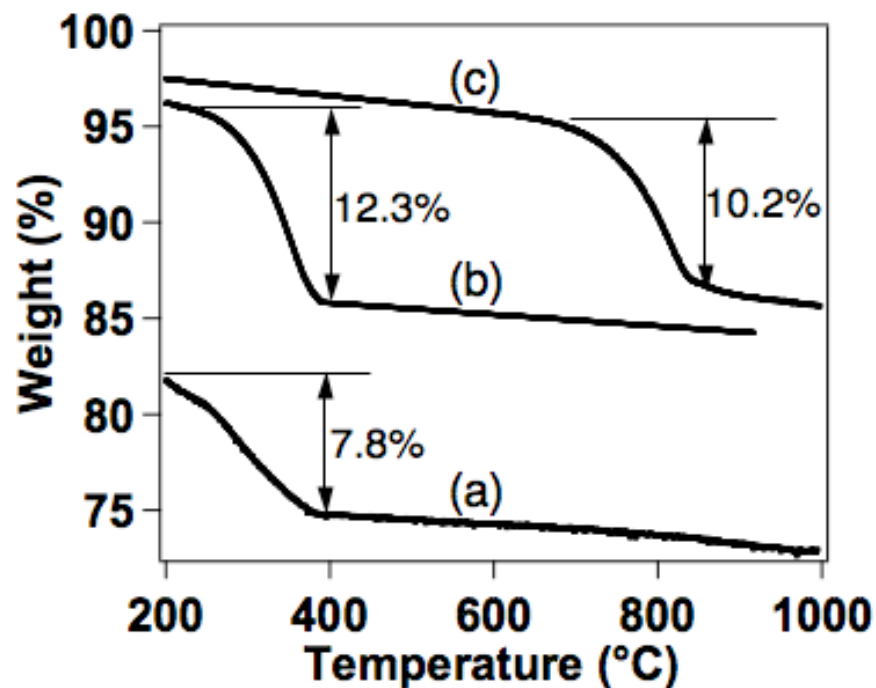
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**Figure S1:** TGA data of Pt-PVP12 (a), Pt-PVP24 (b), and Pt-PVP24-UV (c) catalyst samples. The part of the curves before 200°C is not shown since it corresponds to the loss of the residual solvents.

**Table S1:** Comparison of MeOH electro-oxidation activities of Pt black/PVP samples in (a) 0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.5 M MeOH and (b) 0.1 M HClO<sub>4</sub> + 0.5 M MeOH. The CAs were measured at 0.1 V vs Ag/AgCl.

(a)

	Peak Current of CV			Steady-State Current of CA	
	E/V vs RHE	mA/cm <sup>2</sup>	mA/mg Pt	μA/cm <sup>2</sup>	μA/mg Pt
Pt black	0.95	0.52	196.66	0.02	7.56
Pt-PVP12	0.90	0.77	210.33	0.05	13.66
Pt-PVP24	0.90	1.86	264.20	0.11	15.62

(b)

	Peak Current of CV			Steady-State Current of CA	
	E/V vs RHE	mA/cm <sup>2</sup>	mA/mg Pt	μA/cm <sup>2</sup>	μA/mg Pt
Pt black	1.14	1.38	828.00	0.05	30.00
Pt-PVP12	0.87	2.47	1012.16	0.13	53.27
Pt-PVP24	1.03	4.97	988.35	0.30	59.66

**Table S2:** Comparison of formic acid electro-oxidation CVs of Pt black/PVP samples in (a) 0.1 M  $\text{H}_2\text{SO}_4$  + 0.1 M  $\text{HCOOH}$ . The explanations for the peaks are in the text. (b) Comparison of the steady-state currents of formic acid electro-oxidation CAs at 60 min. The measurements were conducted in 0.1 M  $\text{H}_2\text{SO}_4$  + 0.1 M  $\text{HCOOH}$  at 0.42 V vs RHE.

(a)

	Pt black			PVP/Pt:12			PVP/Pt:24		
	E/V vs RHE	$\text{mA}/\text{cm}^2$	$\text{mA}/\text{mg Pt}$	E/V vs RHE	$\text{mA}/\text{cm}^2$	$\text{mA}/\text{mg Pt}$	E/V vs RHE	$\text{mA}/\text{cm}^2$	$\text{mA}/\text{mg Pt}$
Peak I	0.62	0.07	34.05	0.64	0.24	88.75	0.63	0.37	90.82
Peak II	0.85	0.12	58.38	0.91	0.35	129.42	0.90	0.55	135.00
Peak III	1.47	0.11	53.52	1.48	0.26	96.14	1.45	0.34	83.45
Peak IV	0.57	0.07	34.05	0.66	0.31	114.63	0.57	0.84	206.18

(b)

	$\mu\text{A}/\text{cm}^2$	$\mu\text{A}/\text{mg Pt}$
Pt black	0.16	77.84
PVP/Pt:12	0.54	199.68
PVP/Pt:24	0.90	220.91

**Table S3:** Comparison of formic acid electro-oxidation CVs of Pt black/PVP samples in (a) 0.1 M HClO<sub>4</sub> + 0.1 M HCOOH. (b) Comparison of the steady-state currents of formic acid electro-oxidation CAs at 60 min. The measurements were conducted in 0.1 M HClO<sub>4</sub> + 0.1 M HCOOH at 0.39 V vs RHE.

(a)

	Pt black			Pt-PVP12			Pt-PVP24		
	E/V vs RHE	mA/cm <sup>2</sup>	mA/mg Pt	E/V vs RHE	mA/cm <sup>2</sup>	mA/mg Pt	E/V vs RHE	mA/cm <sup>2</sup>	mA/mg Pt
Peak I	0.53	0.06	36.00	0.60	0.32	131.09	0.57	0.25	49.72
Peak II	0.82	0.15	90.00	0.85	0.45	184.40	0.87	0.78	155.11
Peak III	1.45	0.14	84.00	1.40	0.37	151.62	1.44	0.41	81.53
Peak IV	0.47	0.05	30.00	0.65	0.40	79.54	0.67	1.61	320.17

(b)

	μA/cm <sup>2</sup>	μA/mg Pt
Pt black	0.20	120.00
Pt-PVP12	0.90	368.80
Pt-PVP24	1.58	314.20