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Supporting Information

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Adsorbed Carbon Monoxide-Enabled Self-Terminated Au-Grafting on Pt_6 Nanoclusters for Enhanced Methanol Electrooxidation

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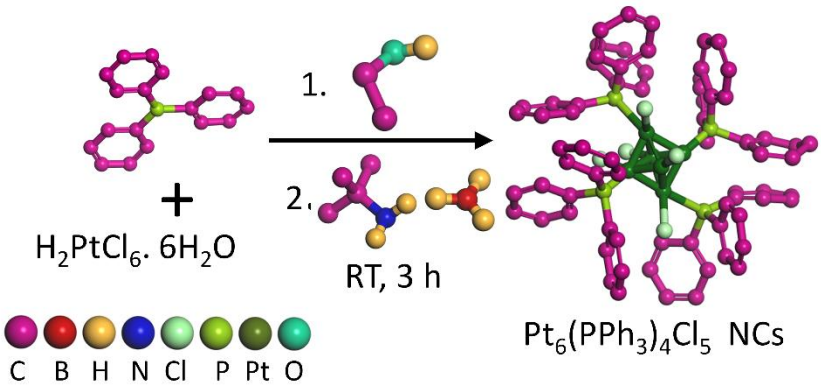

Figure S1: Scheme for the synthesis of $Pt_6(PPh_3)_4Cl_5$.

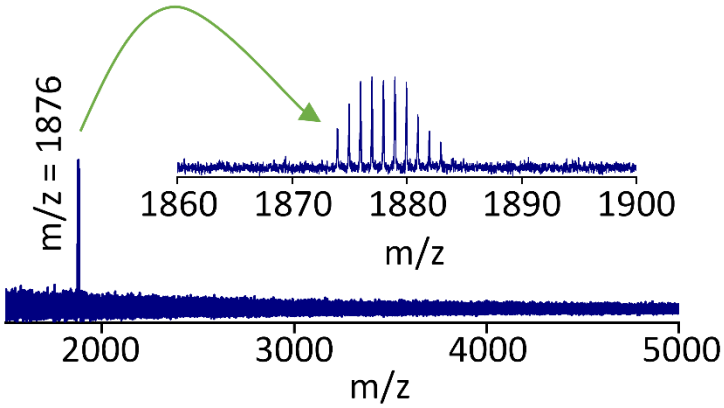

Figure S2: The MALDI-TOF mass spectrum of $Pt_6(PPh_3)_4Cl_5$ and an enlarged view of the molecular ion peak is given in the inset.

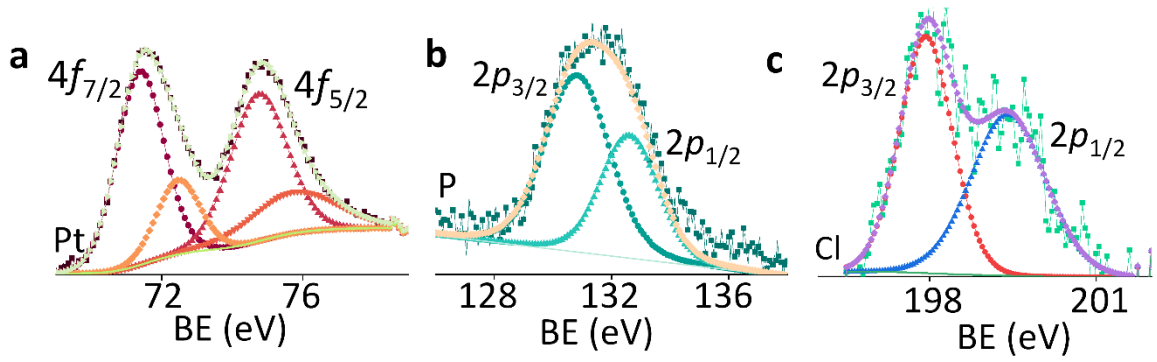

Figure S3: XPS of (a) Pt, (b) P, and (c) Au of Pt_6 NC/C.

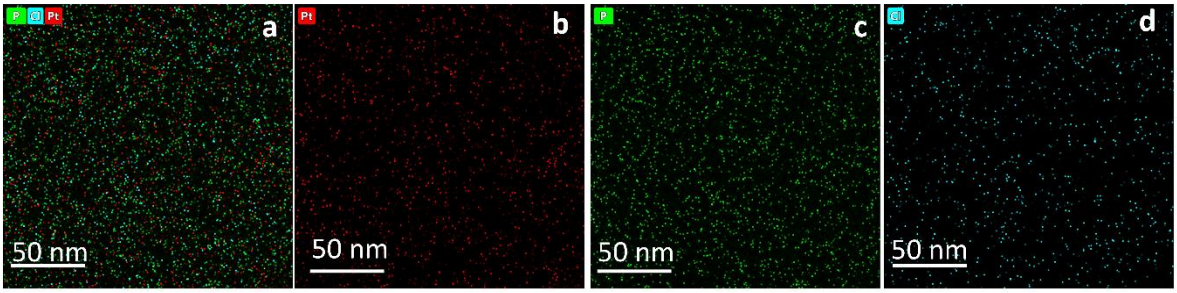

Figure S4: Element maps of Pt_6 NC showing distributions of Pt (red), P (green), and Cl (turquoise), respectively.

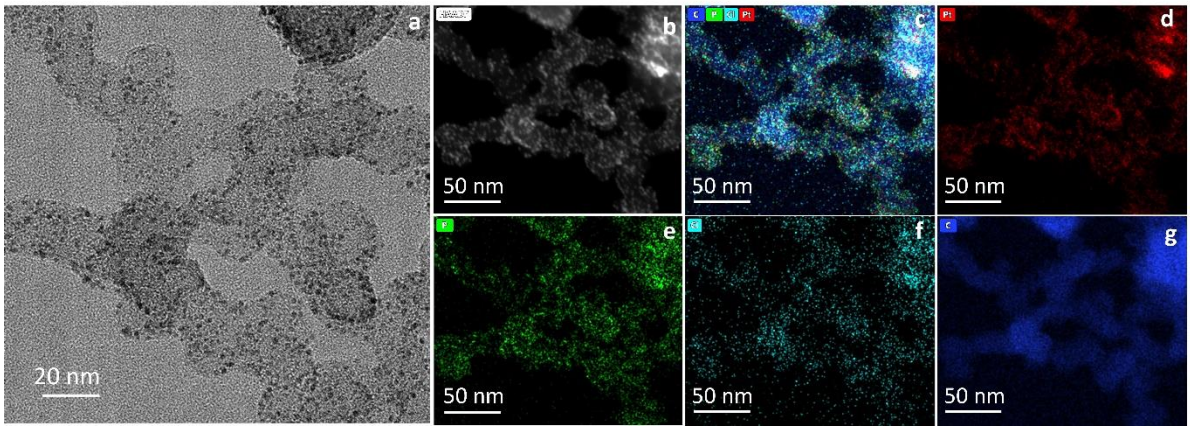

Figure S5: (a) HR-TEM (b) HAADF-STEM, and corresponding element maps of Pt_6 NC/C showing distributions of Pt (red), P (green), Cl (turquoise), and C (blue), respectively.

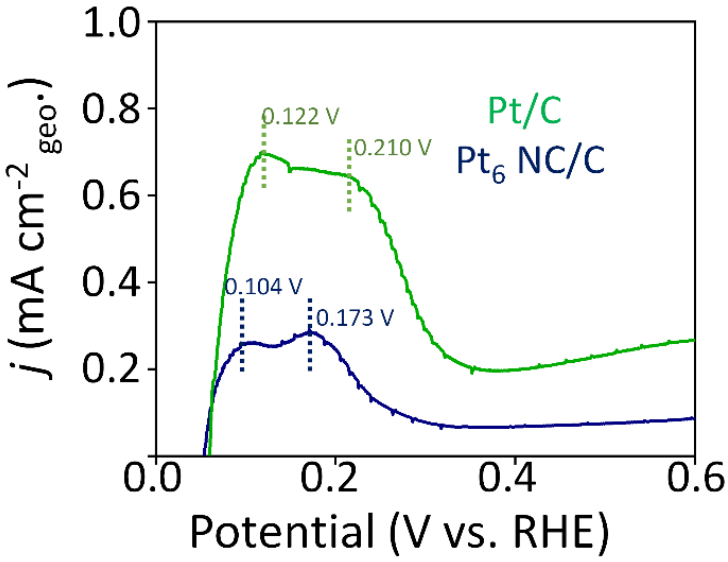

Figure S6: CV curves of Pt_6 NC/C and Pt/C in 0.1 M H_2SO_4 at 100 mV s^{-1} showing the hydrogen desorption region.

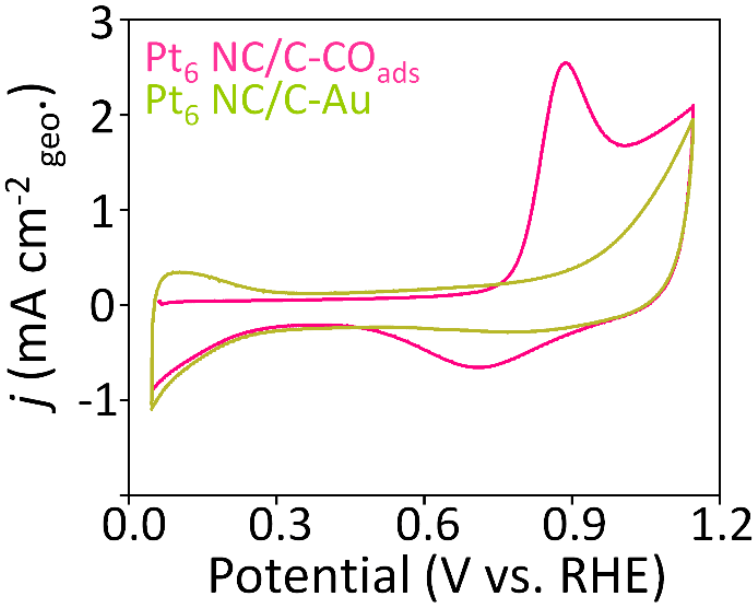

Figure S7. CO-stripping curves of Pt_6 NC/C in deaerated 0.1 M H_2SO_4 at 50 mV s^{-1} before and after Au decoration.

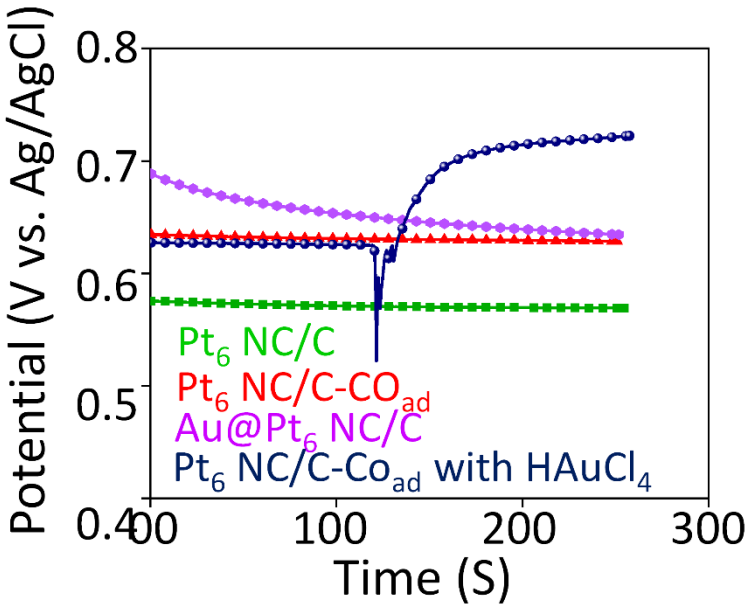

Figure S8. The OCV of Pt_6 NC/C, Pt_6 NC/C-CO_{ads}, Au@Pt_6 NC/C, and Pt_6 NC/C-CO_{ads}.

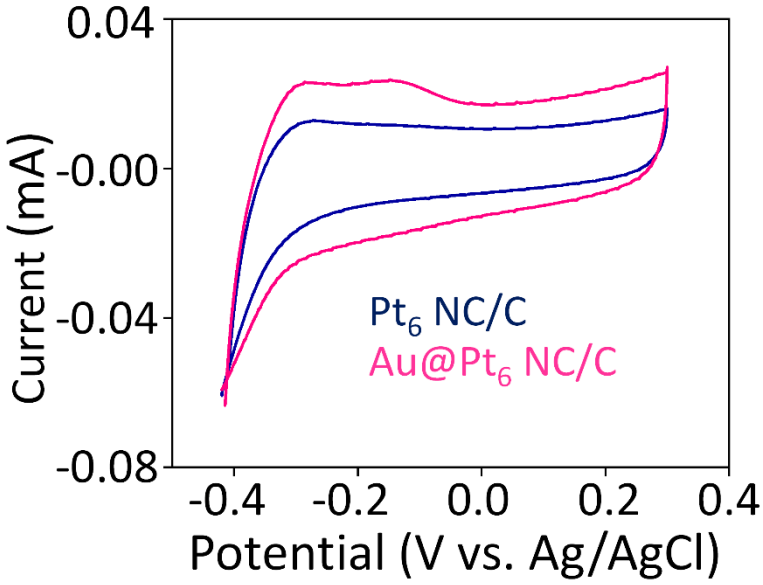

Figure S9. CV curves of Pb-UPD of Pt_6 NC/C and Au@Pt_6 NC/C at 20 mV s^{-1}.

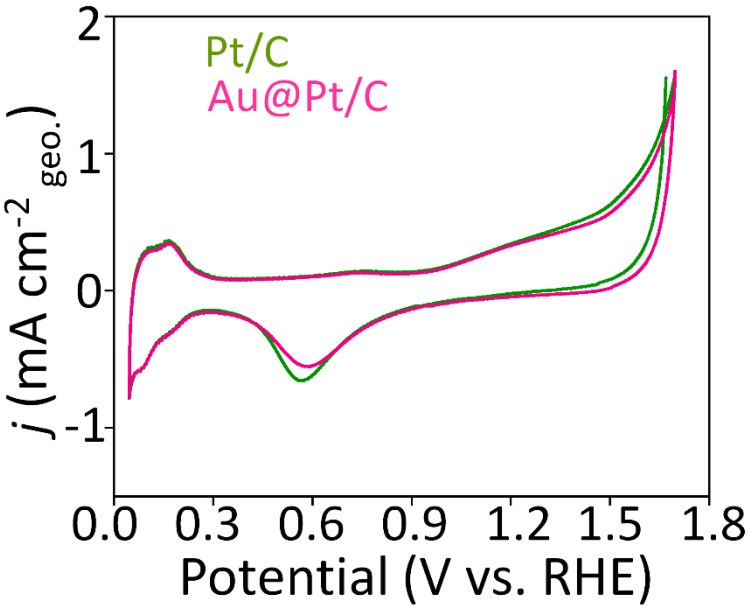

Figure S10. CV curves of Pt/C and Au@Pt/C in 0.1 M H_2SO_4 at a scan rate of 100 mV s^{-1} from 0.00 to 1.45 V_{RHE}.

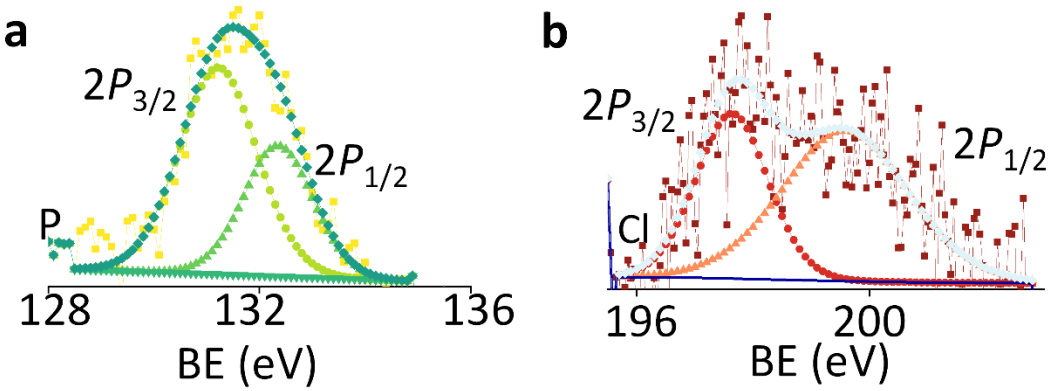

Figure S11. The XPS of (a) P 2*p* and (b) Cl 2*p* of Au@Pt_6 NC/C.

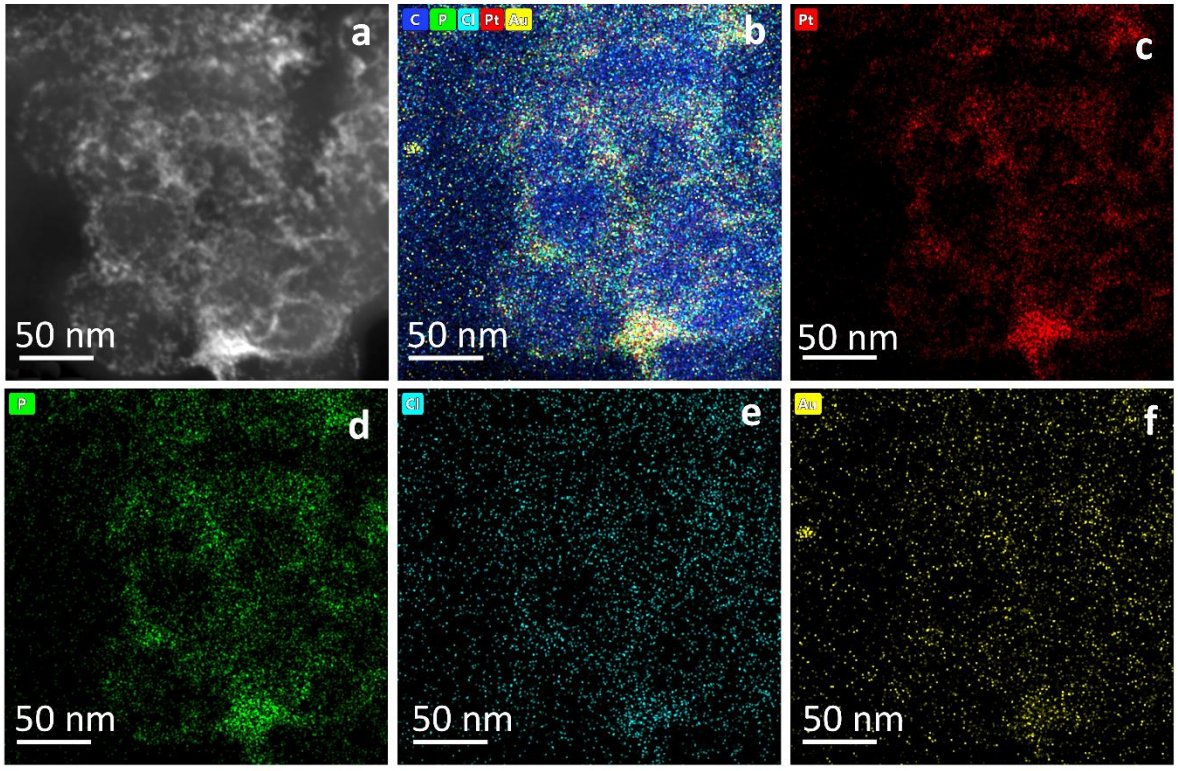

Figure S12: (a) HAADF-STEM and STEM-EDS mapping of the Au@Pt_6 NC/C shows the presence of (c) Pt, (d) P, (e) Cl, and (f) Au.

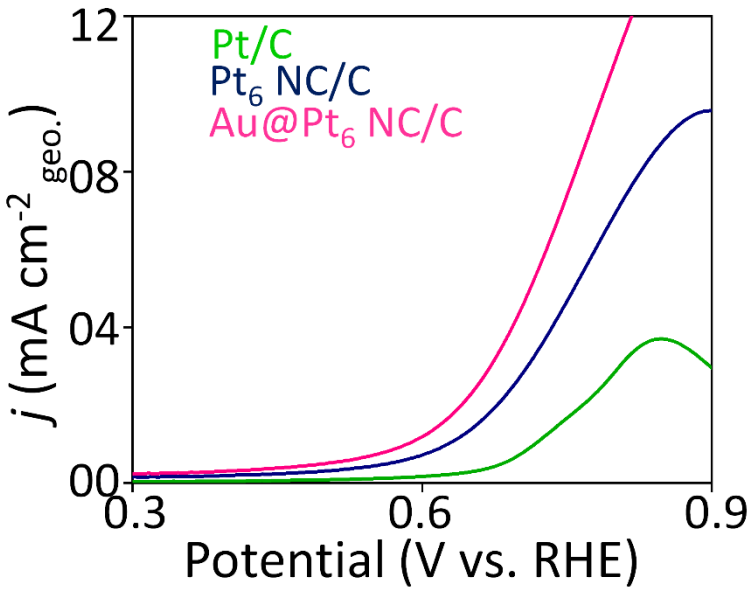

Figure S13. CV of Pt/C, Pt_6 NC/C, and Au@Pt_6 NC/C showing the MOR onset potential region.

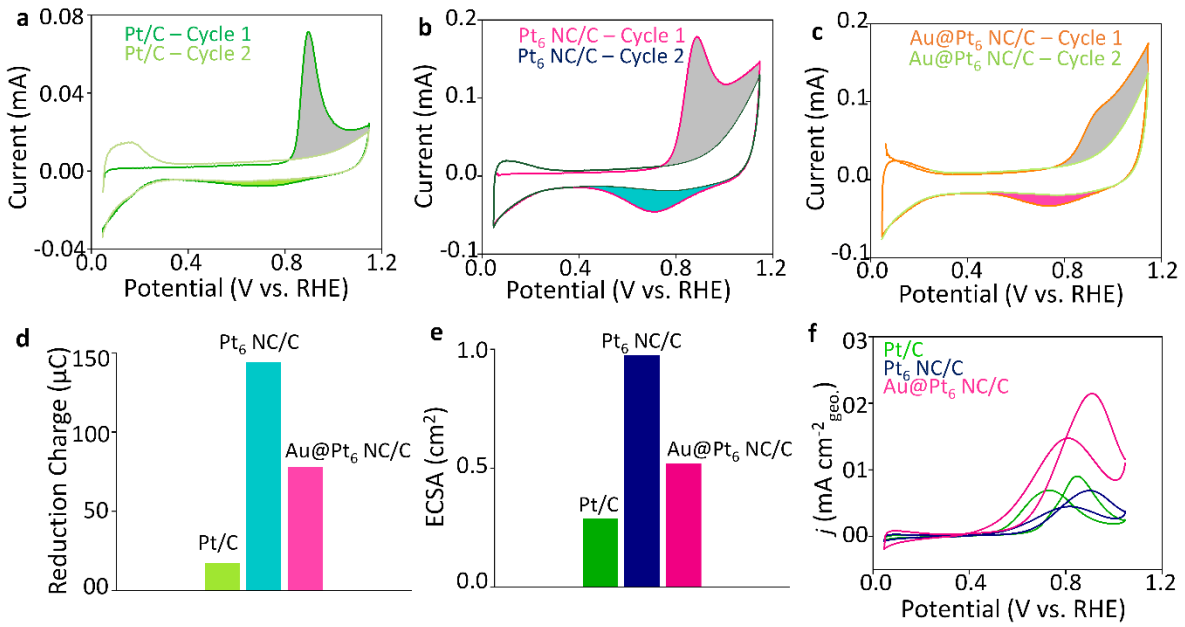

Figure S14: (a-c) CO-stripping curves of Pt/C, Pt_6 NC/C, and Pt_6 NC/C-Au in deaerated 0.1 M H_2SO_4 at 50 mV s^{-1}. Histogram representing (d) charge corresponding to oxide reduction and (e) ECSA of the Pt/C, Pt_6 NC/C, and Au@Pt_6 NC/C. (f) *iR*-corrected and ECSA normalized MOR curves of the Pt/C, Pt_6 NC/C, and Au@Pt_6 NC/C in 0.1 M H_2SO_4 at 50 mV s^{-1}.

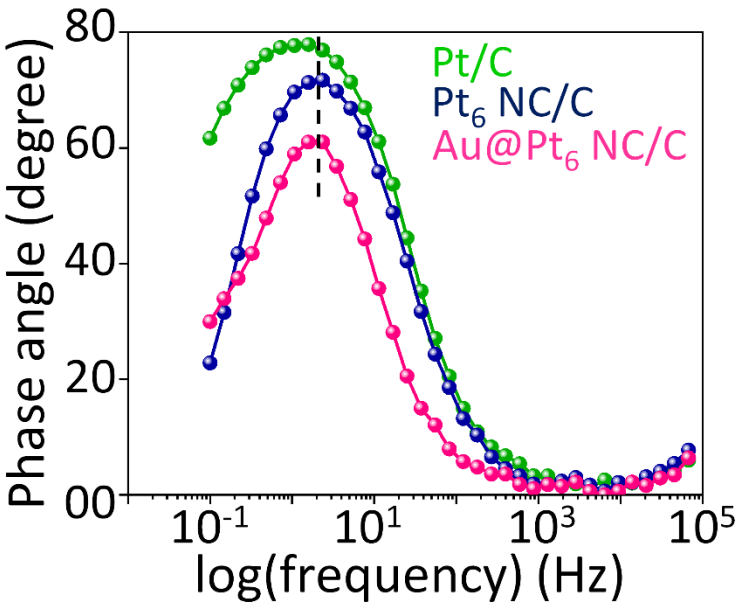

Figure S15. EIS Bode plot of Pt/C, Pt_6 NC/C, and Au@Pt_6 NC/C at 0.40 $V_{Ag/AgCl}$

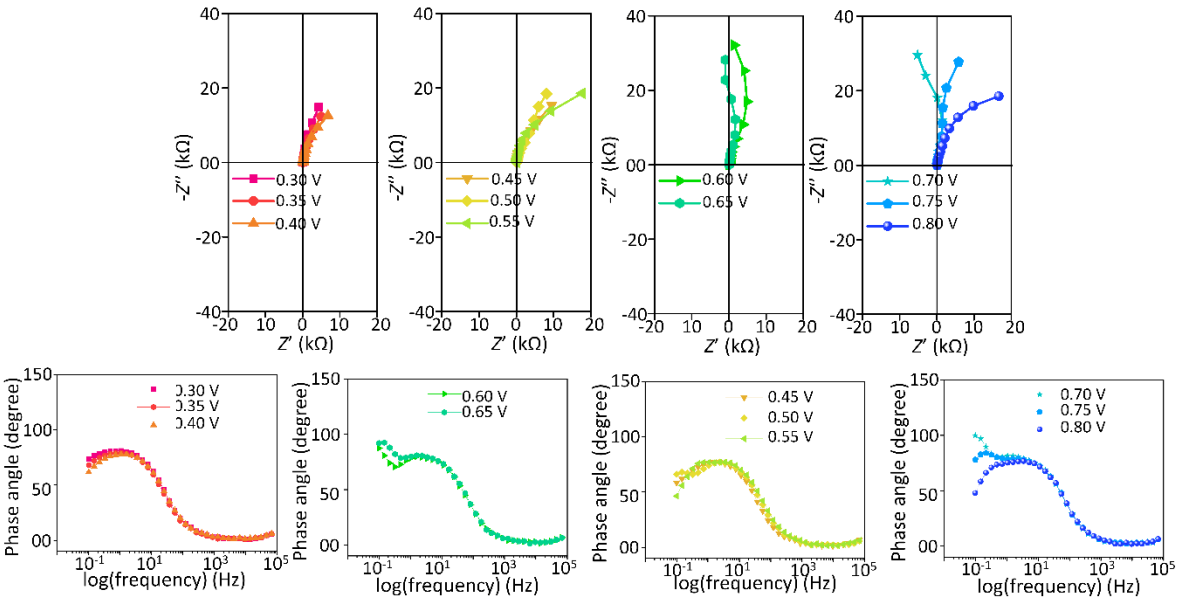

Figure S16. EIS Nyquist plot and Bode plot of Pt/C in 0.1 M H_2SO_4 and 0.1 M methanol.

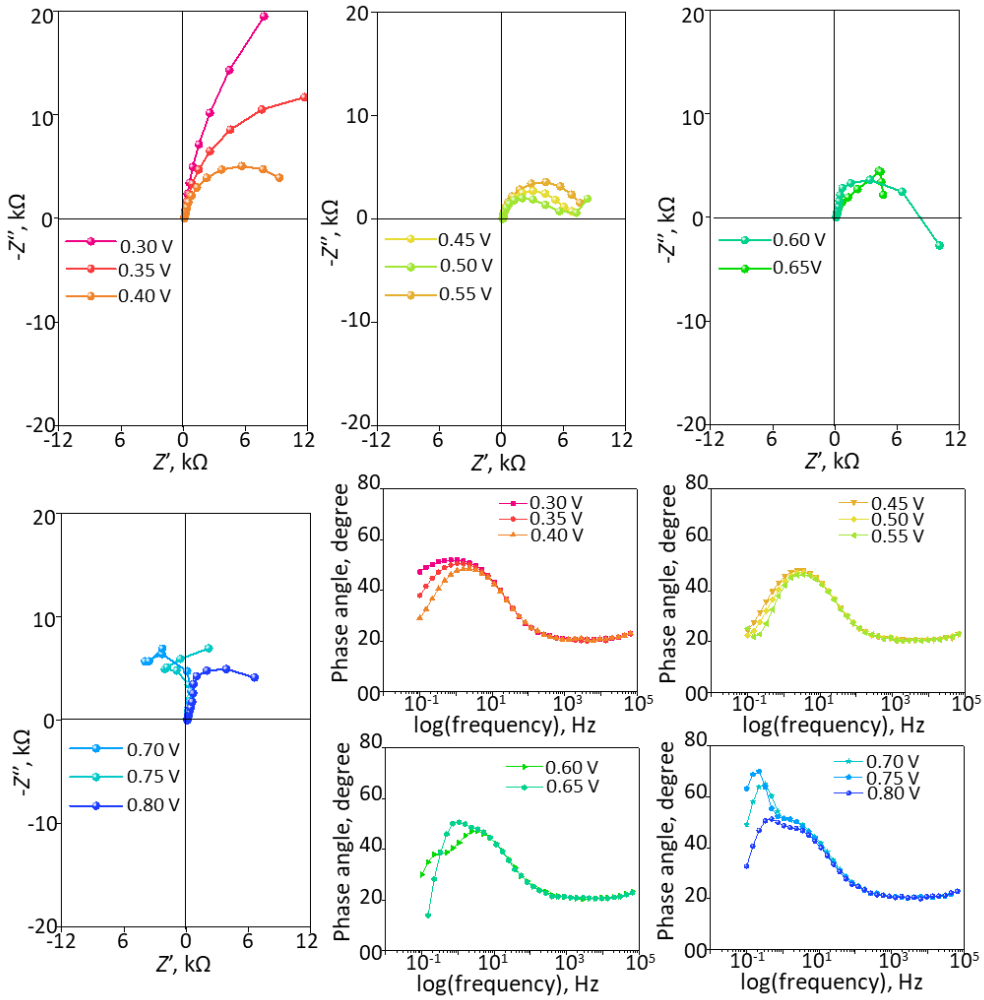

Figure S17. EIS Nyquist plot and Bode plot of Pt_6 NC/C in 0.1 M H_2SO_4 and 0.1 M methanol.

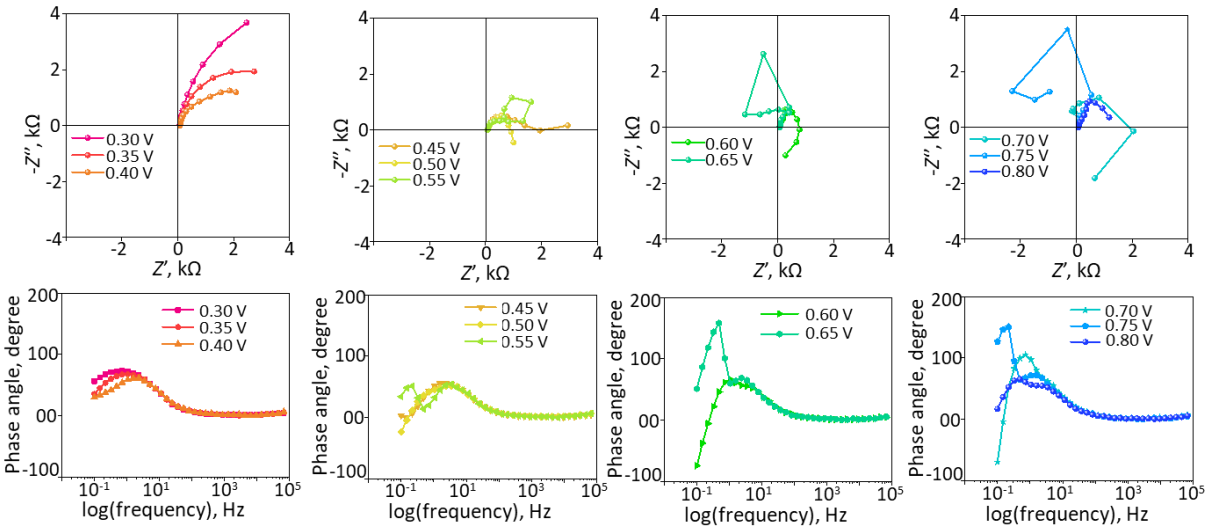

Figure S18. EIS Nyquist plot and Bode plot of Au@Pt_6 NC/C in 0.1 M H_2SO_4 and 0.1 M methanol.

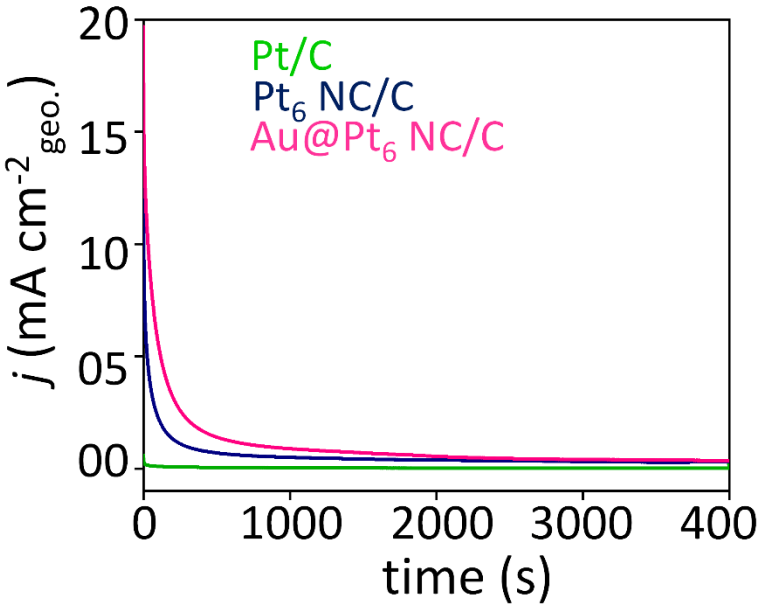

Figure S19. The CA MOR was conducted at 0.65 $V_{Ag/AgCl}$ under quiescent conditions for 4000 s.

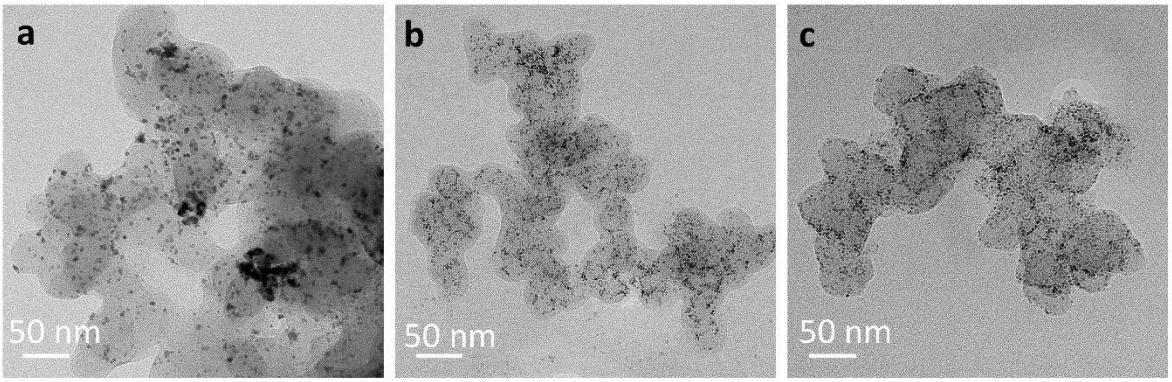

Figure S20. TEM of (a) Pt/C, (b) Pt_6 NC/C, and (c) Au@Pt_6 NC/C after CA test.

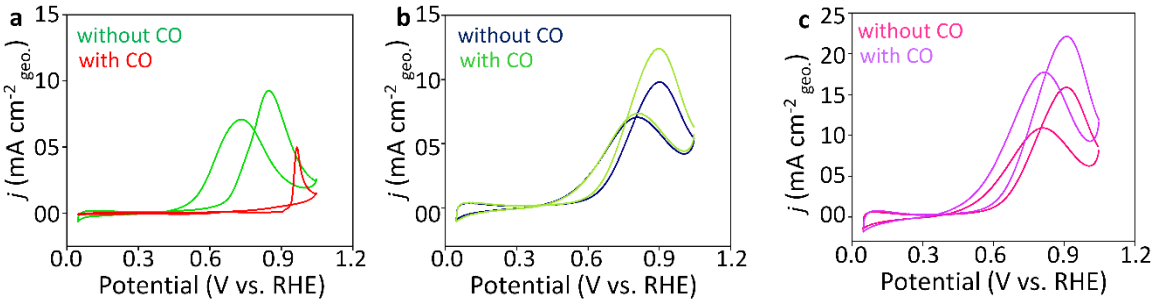

Figure S21. MOR curves of (a) Pt/C, (b) Pt_6 NC/C, and (c) Au@Pt_6 NC with CO and without CO.

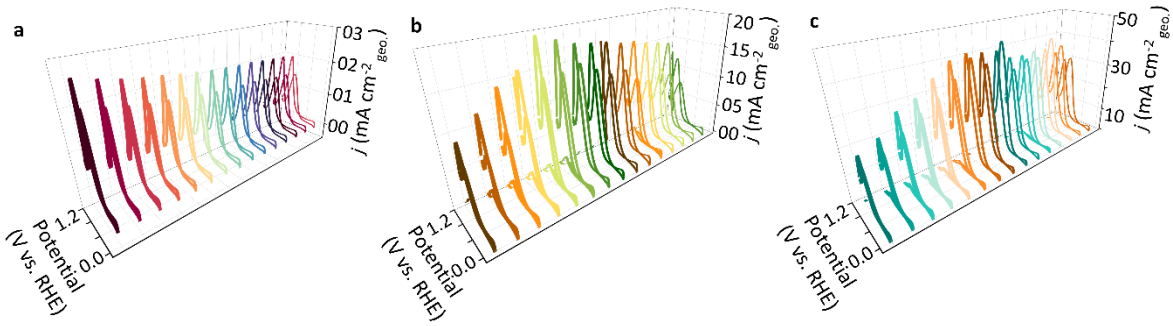

Figure S22. MOR curves of (a) Pt/C, (b) Pt_6 NC/C, and (c) Au@Pt_6 NC/C after each activation cycle.

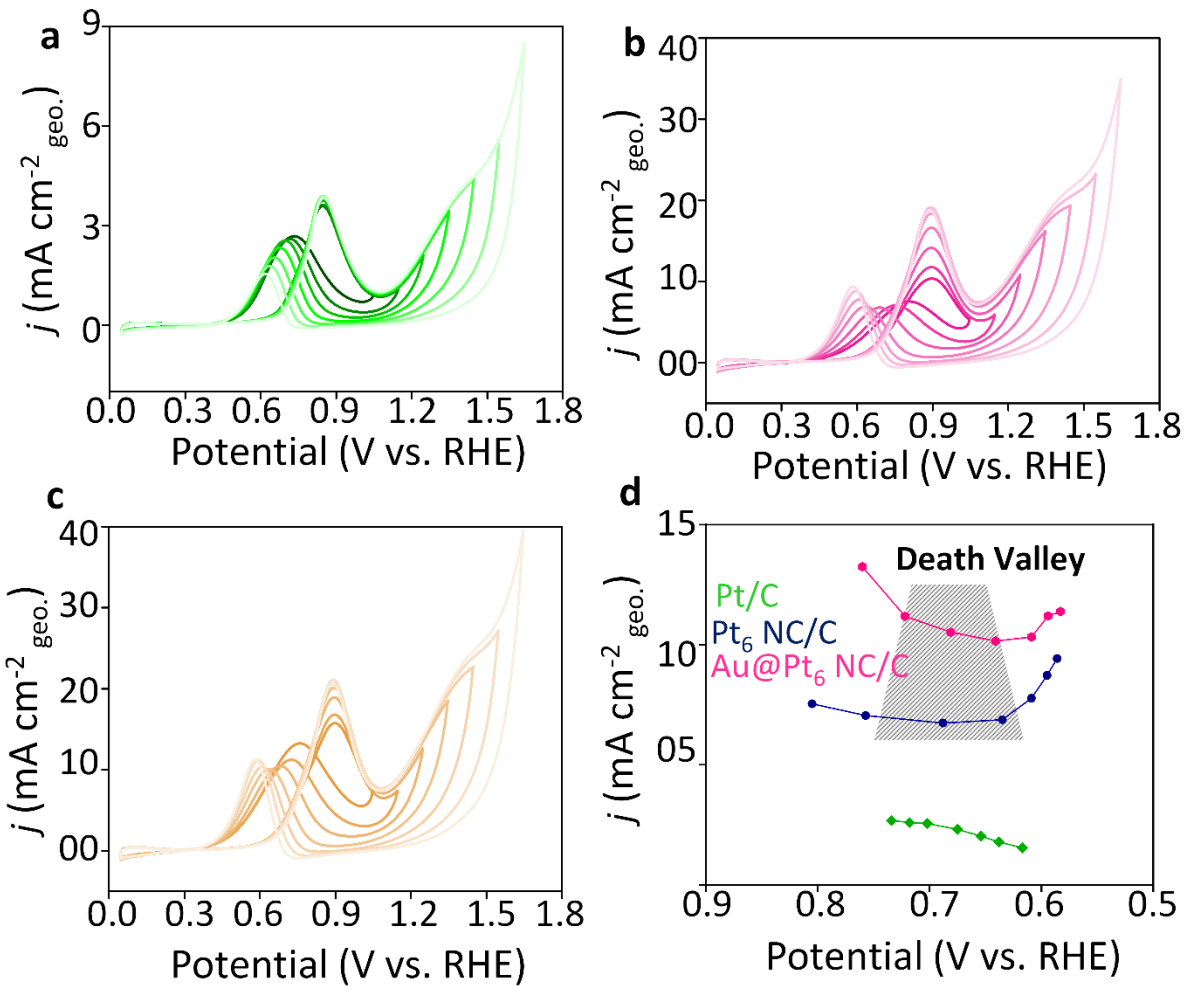

Figure S23. MOR curves of (a) Pt/C, (b) Pt_6 NC/C, and (c) Au@Pt_6 NC/C with different anodic limit potentials. (d) The plot of MOR peak current density values as a function of cathodic sweep peak potential.

Sample	Element	Orbital	Peak Area	RSF	Corrected Area	Total Corrected Area
Au@Pt_6 NCs	Pt	$4f_{7/2}$	115056.83	8.65	13301.37	29315.05
		$4f_{5/2}$	109053.14	6.81	16013.68	
	Au	$4f_{7/2}$	22133.19	9.58	2310.35	5106.50
		$4f_{5/2}$	21082.97	7.54	2796.15	
Total	Pt+Au	-	-	-	34421.55	Pt (85.16%) Au (14.84%)

Table S1: Calculation of atomic composition of Pt and Au of Au@P_6 NC/C from XPS data.

Catalyst	Oxidation Charge (Q_{ox}, μC)	Oxide reduction Charge (Q_{red}, μC)	CO-Stripping Charge (Q_{CO}, μC)	Charge (Qs, μC cm^{-2})	ECSA (cm^2)
Pt/C	137.6	17.94	119.66	420	0.2849
Pt_6 NC/C	553.8	144.2	409.6	420	0.9752
Au@Pt_6 NC/C	295.8	78	217.8	420	0.5185

Table S2: Calculation of ECSA of Pt/C, Pt_6 NC/C, and Au@Pt_6 NC/C.