

Multifunctional Noble Metal Phosphide Electrocatalysts for the Organic Molecule Electro-Oxidation

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Supporting Figures

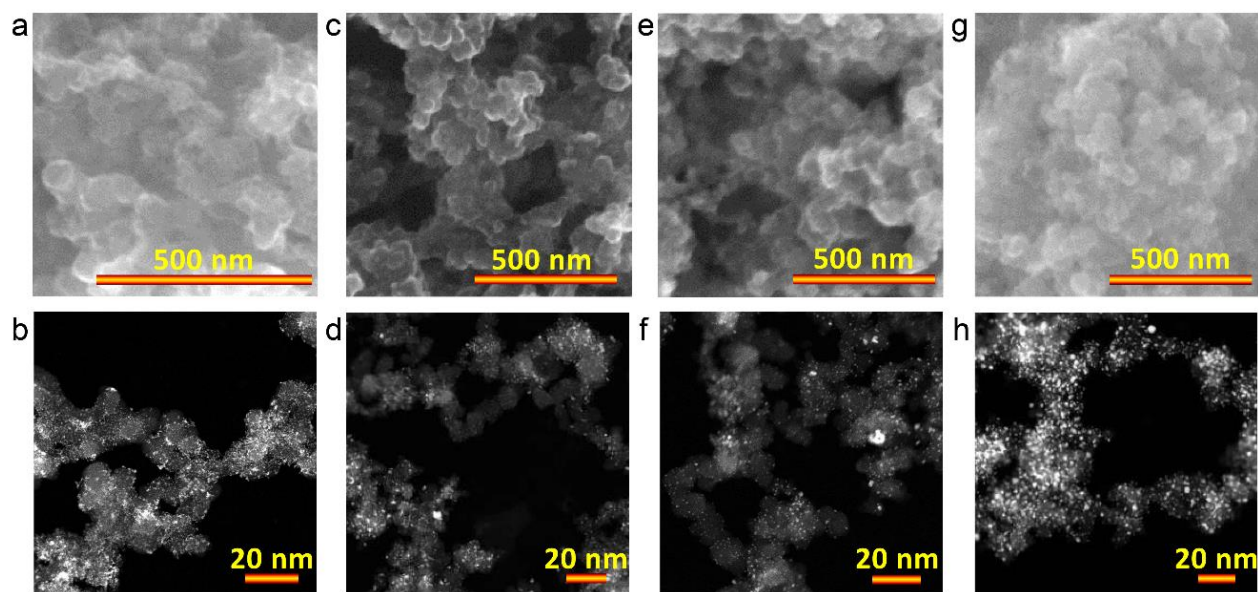


Figure S1. SEM and low-magnification HAADF-STEM images of (a-b) commercial Pd/C, (c-d) PdP₂/C, (e-f) PdP₂-Pd/C and (g-h) Pd₅P₂-Pd/C catalysts derived from the simple one-step phosphorization.

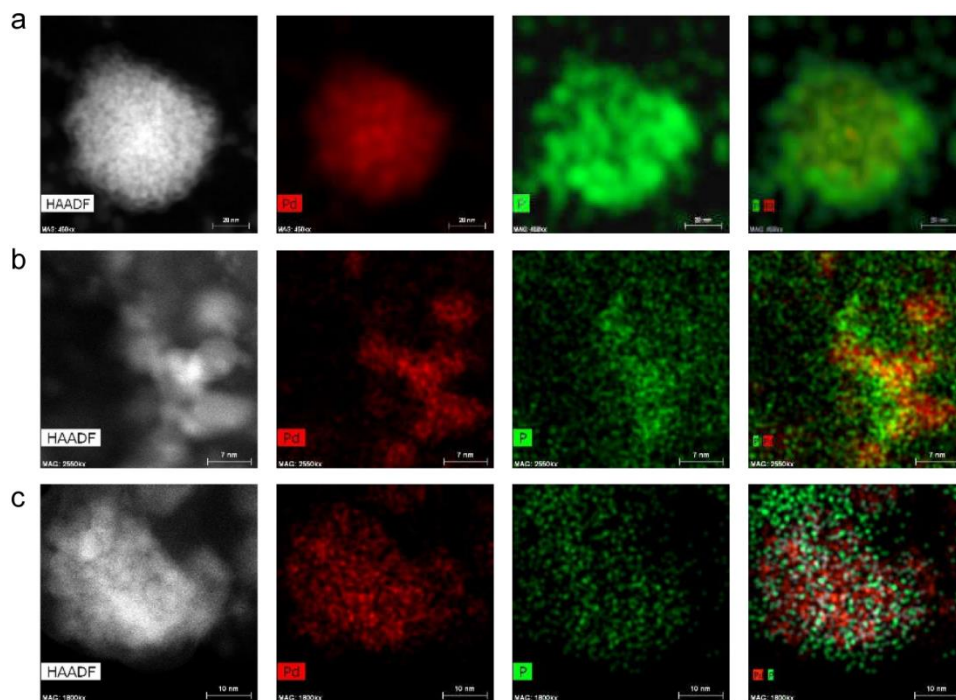


Figure S2. HAADF-STEM image of (a) PdP₂/C, (b) PdP₂-Pd/C and (c) Pd₅P₂-Pd/C and the corresponding elemental maps of Pd, P and their overlay.

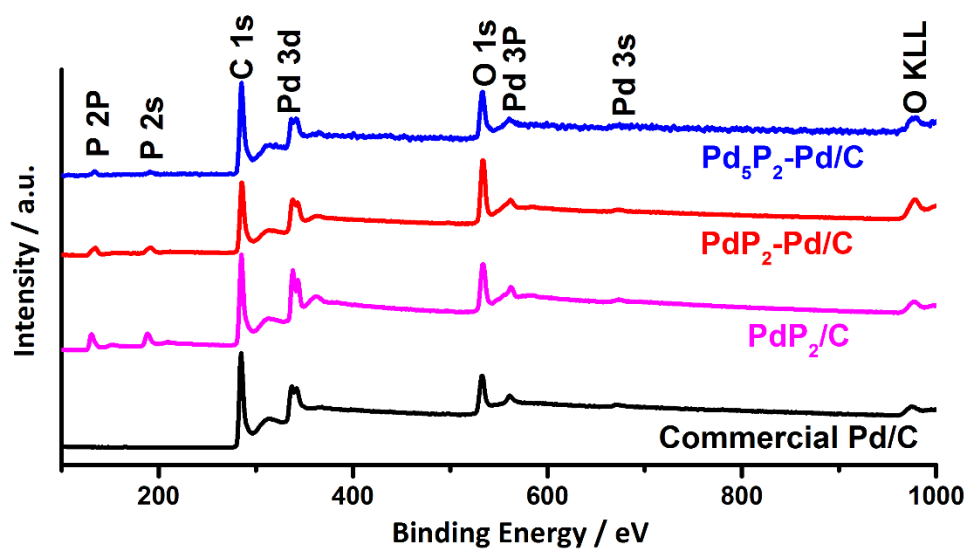


Figure S3. XPS survey spectra of commercial Pd/C, PdP₂/C, PdP₂-Pd/C and Pd₅P₂-Pd/C catalysts.

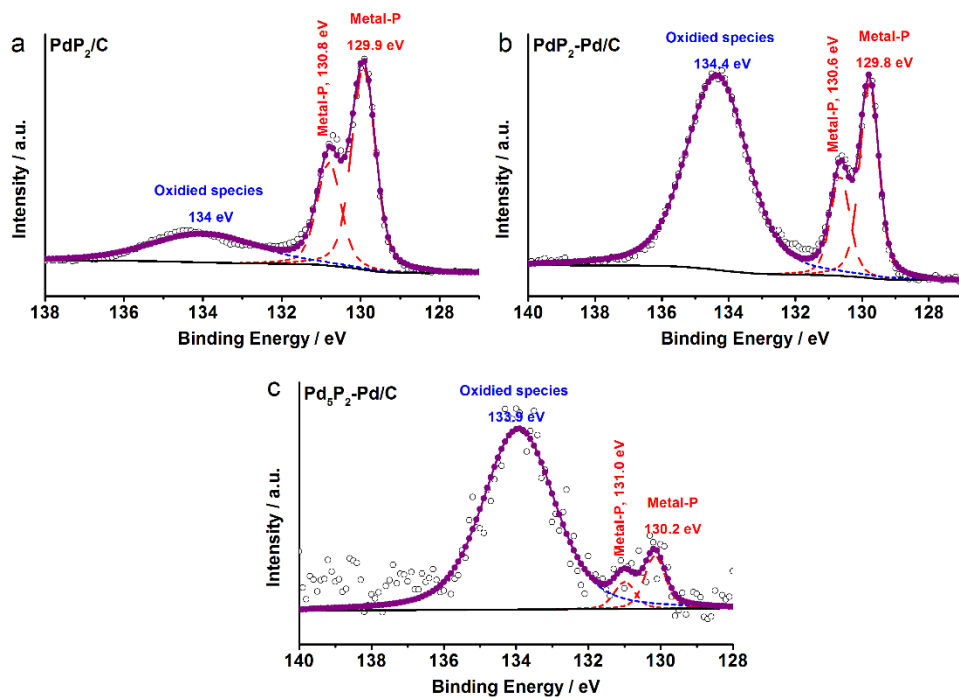


Figure S4. High-resolution P 2p XPS spectra of (a) PdP₂/C, (b) PdP₂-Pd/C and (c) Pd₅P₂-Pd/C catalysts.

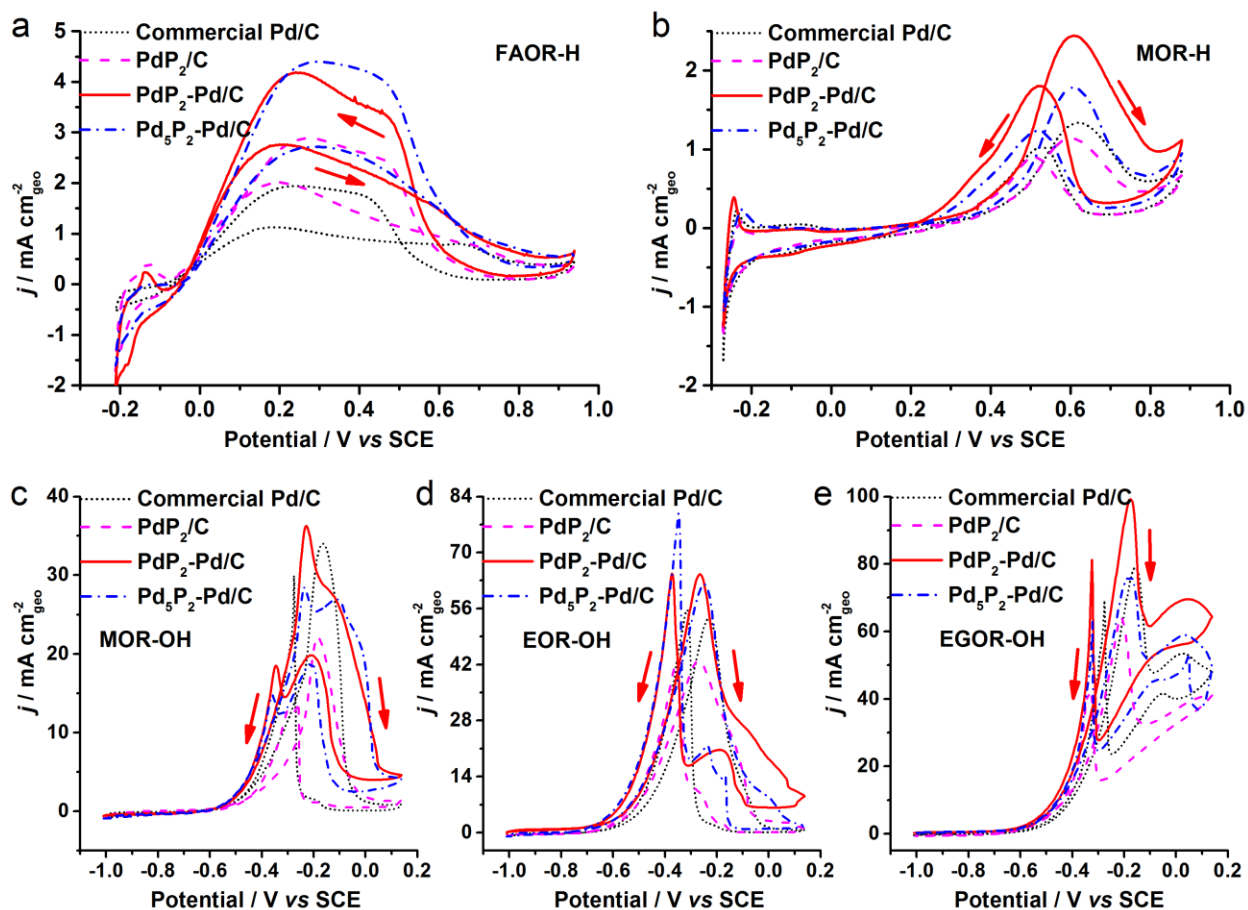


Figure S5. Electrocatalytic performance of commercial Pd/C, PdP₂/C, PdP₂-Pd/C and Pd₅P₂-Pd/C catalysts toward different OMEO reactions. (a) FAOR-H recorded in 0.5 M HCOOH + 1.0 M HClO₄. (b) MOR-H recorded in 0.5 M CH₃OH + 0.1 M HClO₄. (c) MOR-OH recorded in 1.0 M CH₃OH + 1.0 M KOH. (d) EOR-OH recorded in 1.0 M CH₃CH₂OH + 1.0 M KOH. (e) EGOR-OH recorded in 1.0 M EG + 1.0 M KOH. All CV curves were recorded at 20 mV s⁻¹.

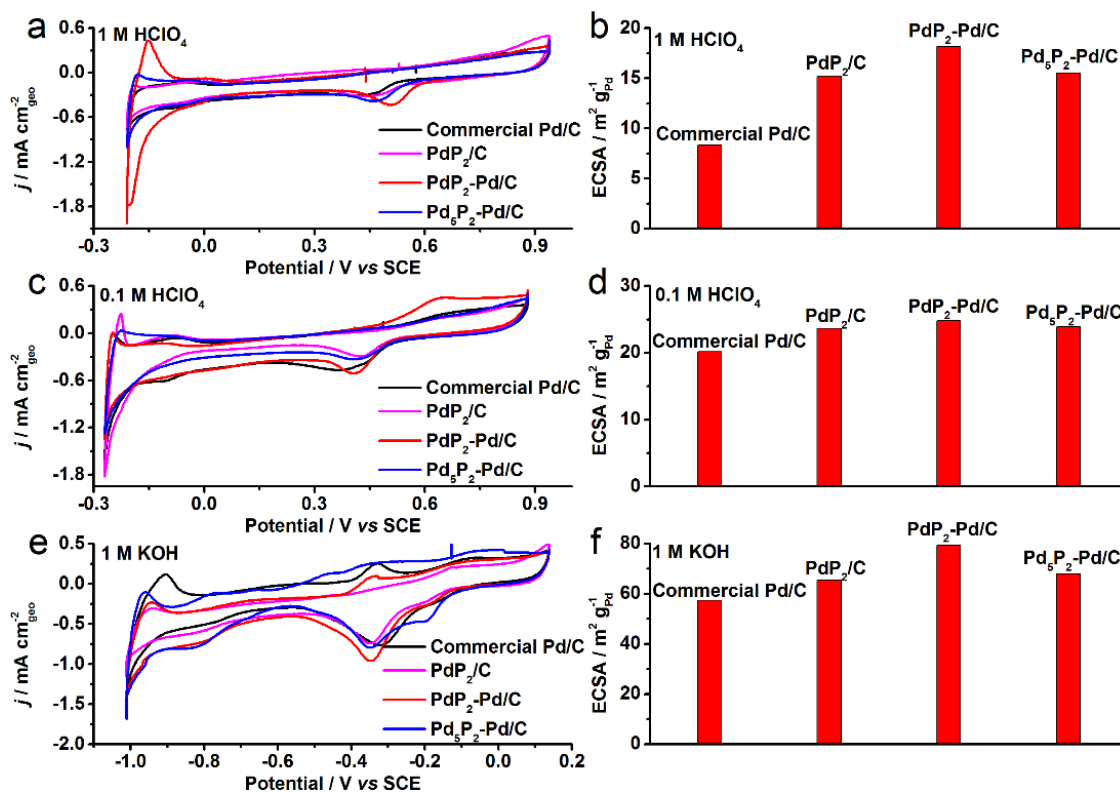


Figure S6. Electrochemical CV curves of commercial Pd/C, PdP₂/C, PdP₂-Pd/C and Pd₅P₂-Pd/C catalysts recorded at a scan rates of 20 mV s⁻¹ in N₂-purged (a) 1.0 M HClO₄, (c) 0.1 M HClO₄ and (e) 1.0 M KOH. ECSAs of all Pd-based catalysts calculated from the CV curves recorded in (b) 1.0 M HClO₄, (d) 0.1 M HClO₄ and (f) 1.0 M KOH.

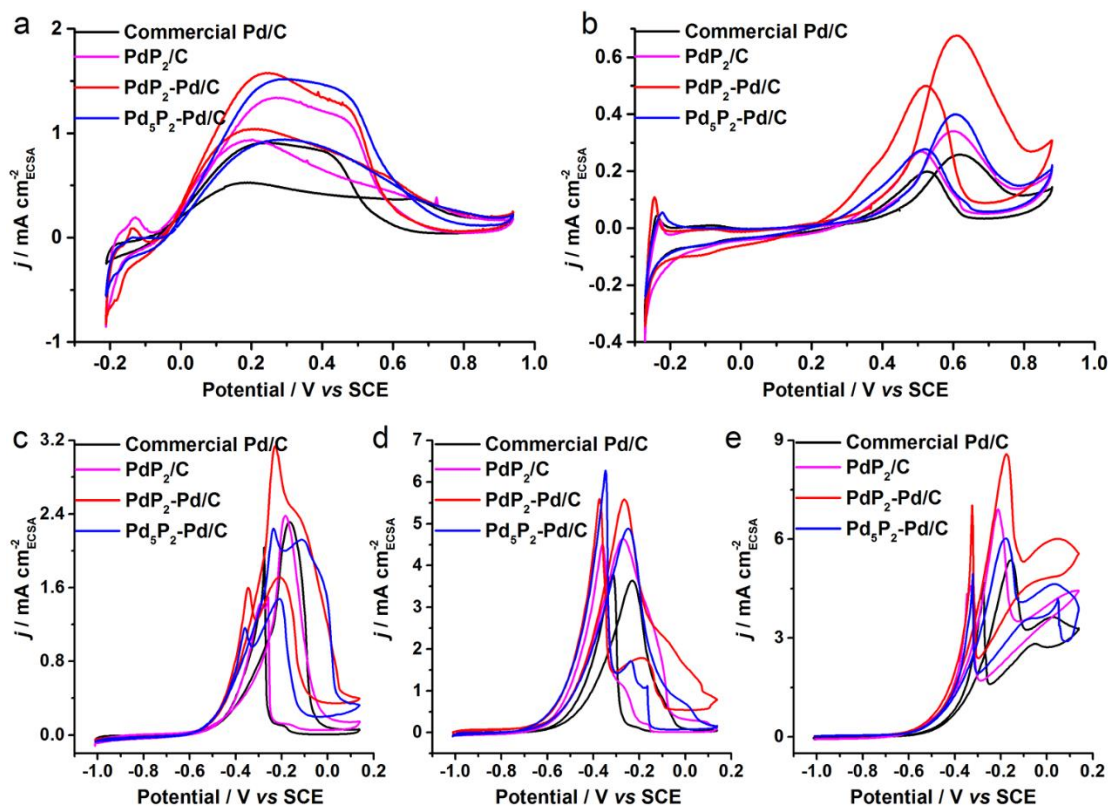


Figure S7. Specific activities of commercial Pd/C, PdP₂/C, PdP₂-Pd/C and Pd₅P₂-Pd/C catalysts for different catalytic reactions. (a) FAOR-H recorded in 0.5 M HCOOH + 1.0 M HClO₄. (b) MOR-H recorded in 0.5 M CH₃OH + 0.1 M HClO₄. (c) MOR-OH recorded in 1.0 M CH₃OH + 1.0 M KOH. (d) EOR-OH recorded in 1.0 M CH₃CH₂OH + 1.0 M KOH. (e) EGOR-OH recorded in 1.0 M EG + 1.0 M KOH. All CV curves were acquired at 20 mV s⁻¹.

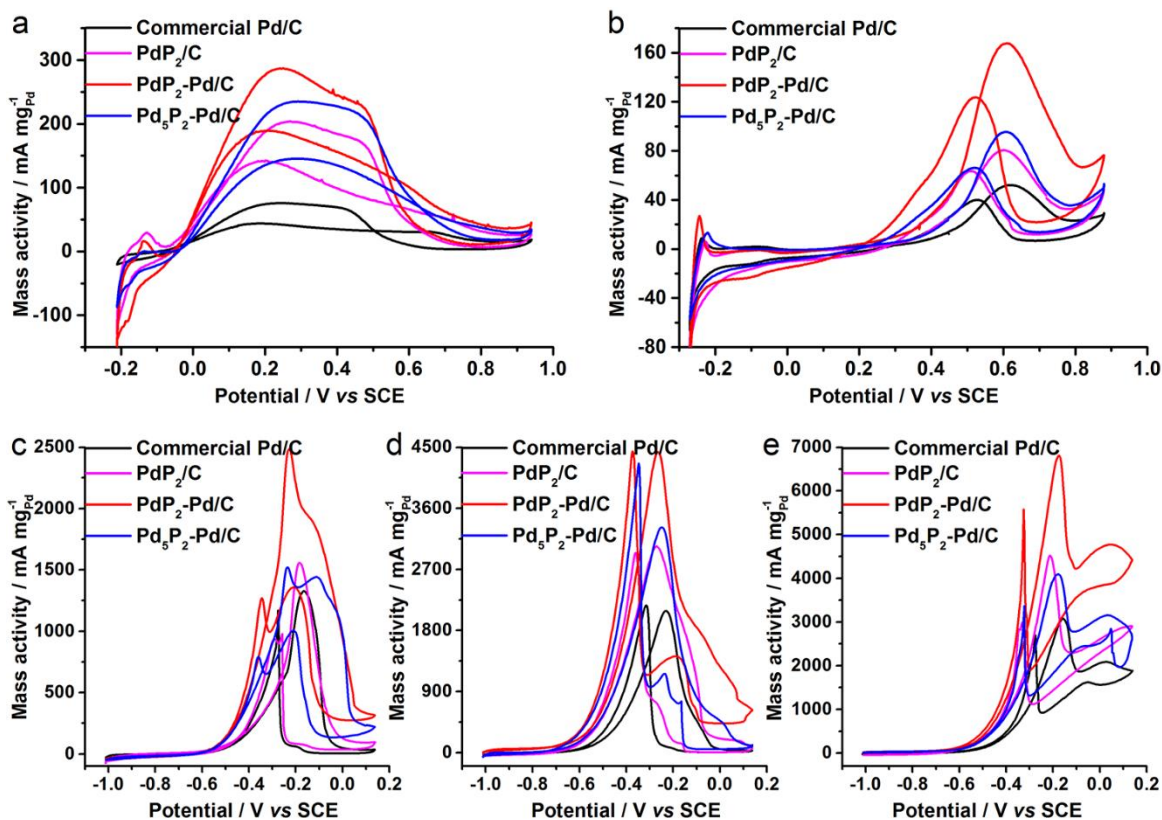


Figure S8. Mass activities of commercial Pd/C, PdP₂/C, PdP₂-Pd/C and Pd₅P₂-Pd/C catalysts for different catalytic reactions. (a) FAOR-H recorded in 0.5 M HCOOH + 1.0 M HClO₄. (b) MOR-H recorded in 0.5 M CH₃OH + 0.1 M HClO₄. (c) MOR-OH recorded in 1.0 M CH₃OH + 1.0 M KOH. (d) EOR-OH recorded in 1.0 M CH₃CH₂OH + 1.0 M KOH. (e) EGOR-OH recorded in 1.0 M EG + 1.0 M KOH. All CV curves were acquired at 20 mV s⁻¹.

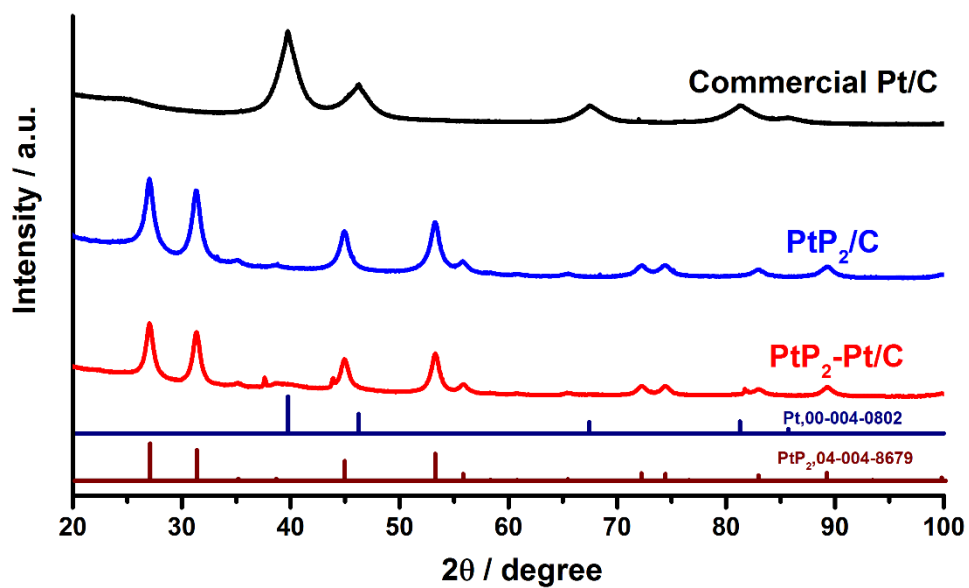


Figure S9. XRD patterns of commercial Pt/C, PtP₂/C, PtP₂-Pt/C catalysts.

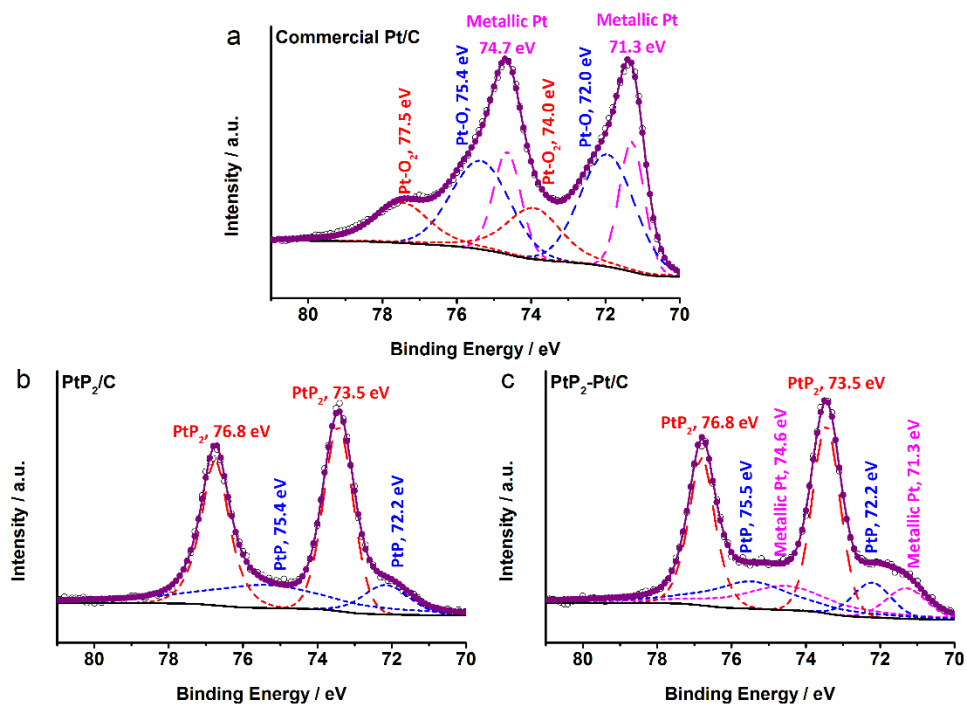


Figure S10. High resolution Pt 4f XPS spectra of (a) commercial Pt/C, (b) PtP₂/C, (c) PtP₂-Pt/C.

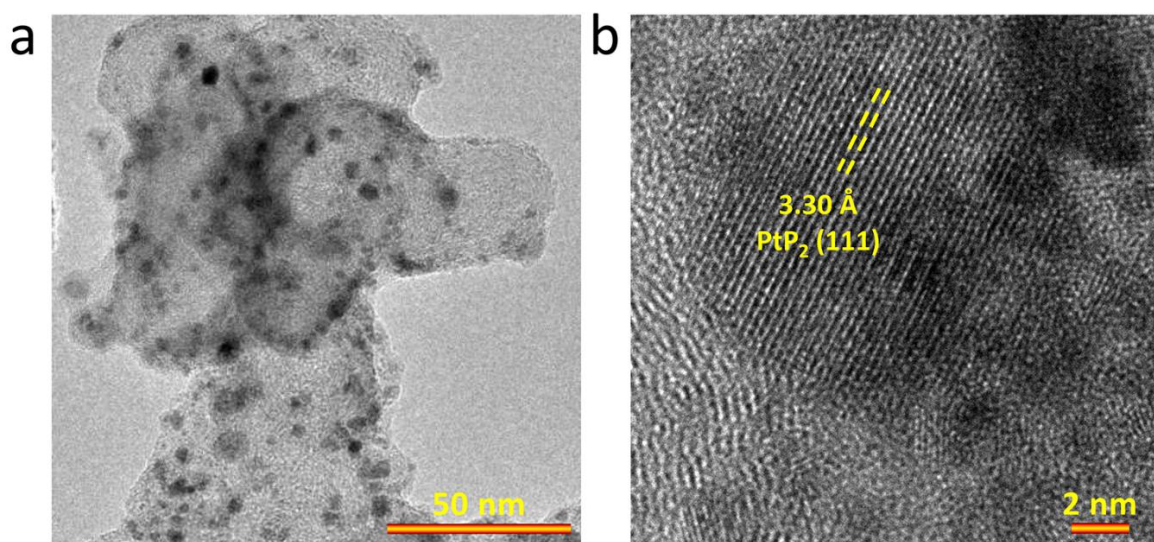


Figure S11. TEM characterization of PtP₂/C catalysts. (a) Low-magnification TEM image, (b) HRTEM image.

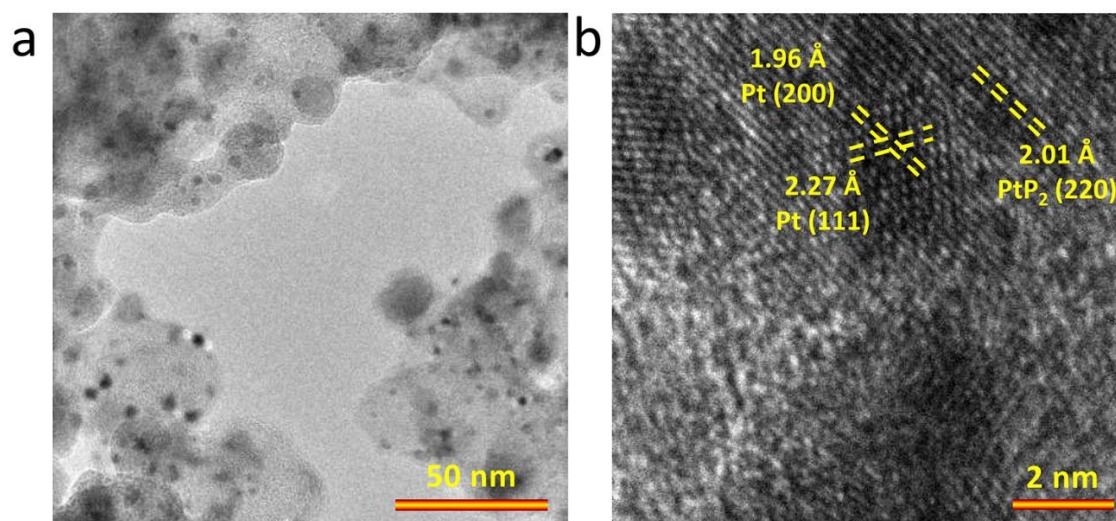


Figure S12. TEM characterization of PtP₂-Pt/C catalysts. (a) Low-magnification TEM image, (b) HRTEM image.

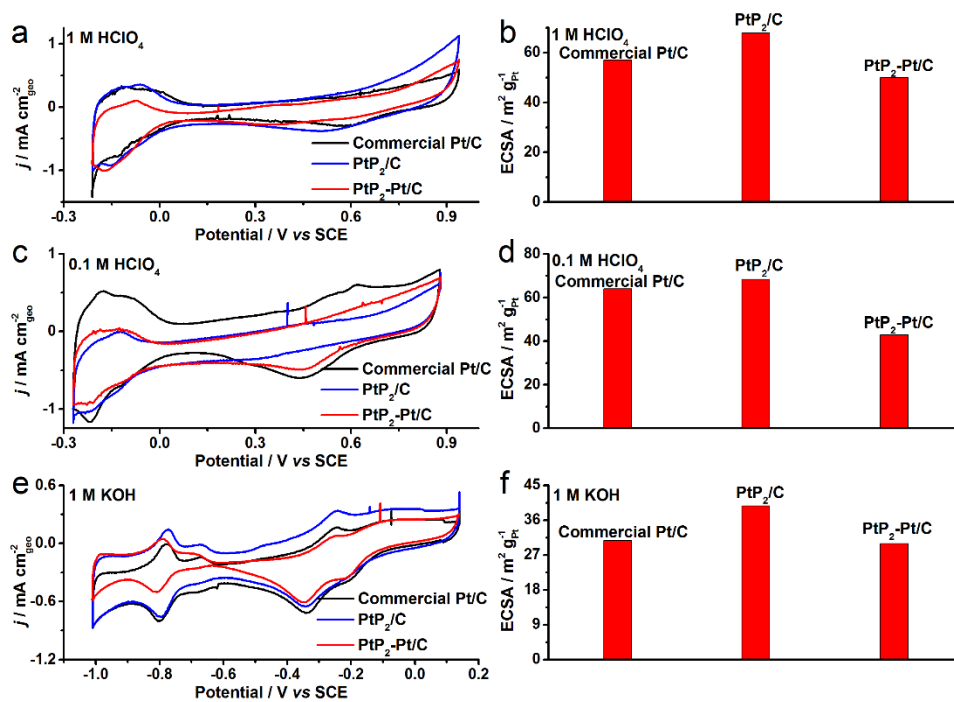


Figure S13. Electrochemical CV curves of commercial Pt/C, PtP₂/C, PtP₂-Pt/C catalysts recorded at a scan rates of 20 mV s⁻¹ in N₂-purged (a) 1.0 M HClO₄, (c) 0.1 M HClO₄ and (e) 1.0 M KOH. ECSAs of all Pt-based catalysts calculated from the CV curves recorded in (b) 1.0 M HClO₄, (d) 0.1 M HClO₄ and (f) 1.0 M KOH.

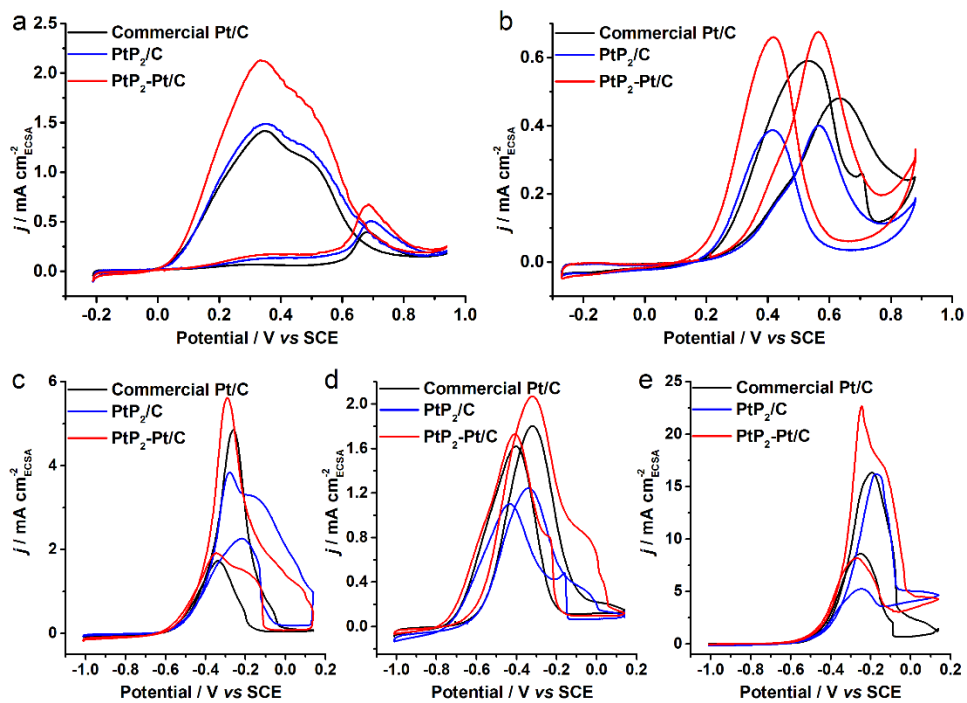


Figure S14. Specific activities and mass activities of commercial Pt/C, PtP₂/C, PtP₂-Pt/C catalysts for different catalytic reactions. (a) FAOR-H recorded in 0.5 M HCOOH + 1.0 M HClO₄. (b) MOR-H recorded in 0.5 M CH₃OH + 0.1 M HClO₄. (c) MOR-OH recorded in 1.0 M CH₃OH + 1.0 M KOH. (d) EOR-OH recorded in 1.0 M CH₃CH₂OH + 1.0 M KOH. (e) EGOR-OH recorded in 1.0 M EG + 1.0 M KOH. All CV curves were acquired at 20 mV s⁻¹.

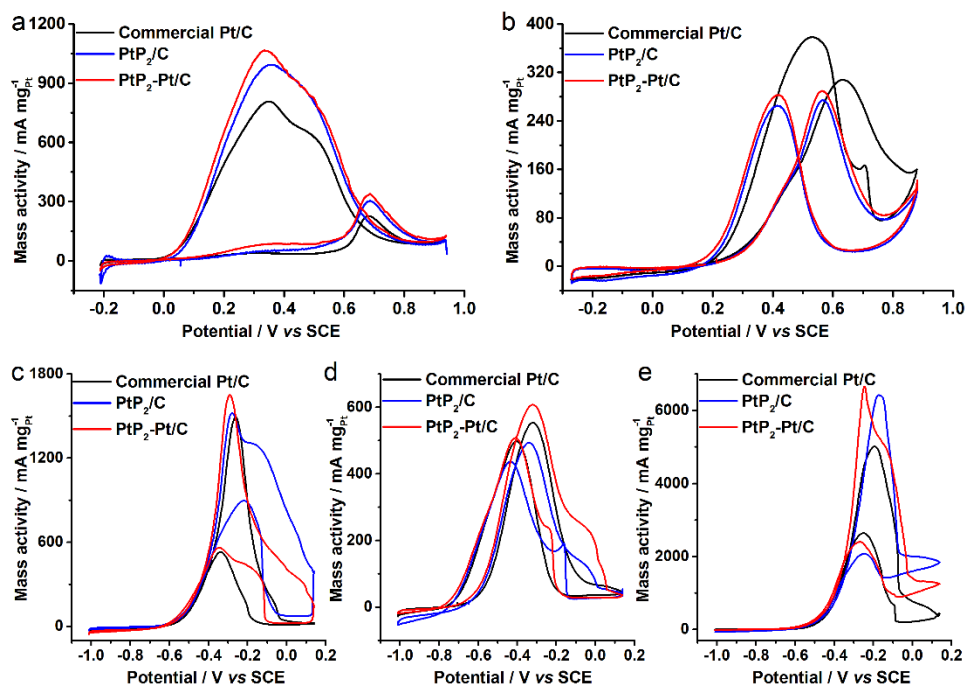


Figure S15. Mass activities of commercial Pt/C, PtP₂/C, PtP₂-Pt/C catalysts for different catalytic reactions. (a) FAOR-H recorded in 0.5 M HCOOH + 1.0 M HClO₄. (b) MOR-H recorded in 0.5 M CH₃OH + 0.1 M HClO₄. (c) MOR-OH recorded in 1.0 M CH₃OH + 1.0 M KOH. (d) EOR-OH recorded in 1.0 M CH₃CH₂OH + 1.0 M KOH. (e) EGOR-OH recorded in 1.0 M EG + 1.0 M KOH. All CV curves were acquired at 20 mV s⁻¹.

Table S1. Onset potential and current densities at low potentials of different catalysts toward the OMEO reactions of investigation.

Catalyst \ Reaction		FAOR-H	MOR-H	MOR-OH	EOR-OH	EGOH-OH
Onset potential (potential V vs. SCE at 0.5 mA cm ⁻²)	Pd/C	0.01	0.49	-0.55	-0.65	-0.63
	PdP ₂ /C	-0.01	0.49	-0.49	-0.67	-0.65
	PdP ₂ -Pd/C	-0.01	0.42	-0.57	-0.80	-0.82
	Pd ₅ P ₂ -Pd/C	0.01	0.46	-0.56	-0.72	-0.82
Current density at low potentials (mA cm ⁻² , 0.05 V for FAOR-H; 0.17 V for MOR-H; -0.60 V for MOR-OH, EOR-OH and EGOR-OH)	Pd/C	0.71	0.02	0.12	1.19	0.70
	PdP ₂ /C	1.22	0.01	0.04	1.94	1.45
	PdP ₂ -Pd/C	1.63	0.04	0.19	3.27	1.64
	Pd ₅ P ₂ -Pd/C	1.10	0.03	0.17	3.09	1.59

Table S2. Comparison of the poisoning tolerance for PdP₂-Pd/C and PtP₂-Pt/C toward all reactions under investigation with respect to the commercial Pd/C and Pt/C catalysts.

Catalysts	R	FAOR-H	MOR-H	MOR-OH	EOR-OH	EGOR-OH
Commercial Pd/C	I _f /I _b	0.60	1.33	1.13	0.96	1.13
PdP ₂ -Pd/C	I _f /I _b	0.68	1.40	1.97	1.00	1.22
Commercial Pt/C	I _f /I _b	0.28	0.82	2.81	1.12	1.90
PtP ₂ -Pt/C	I _f /I _b	0.32	1.02	2.94	1.20	2.77