

Rare-earth oxides promoted Pd electrocatalyst for formic acid oxidation

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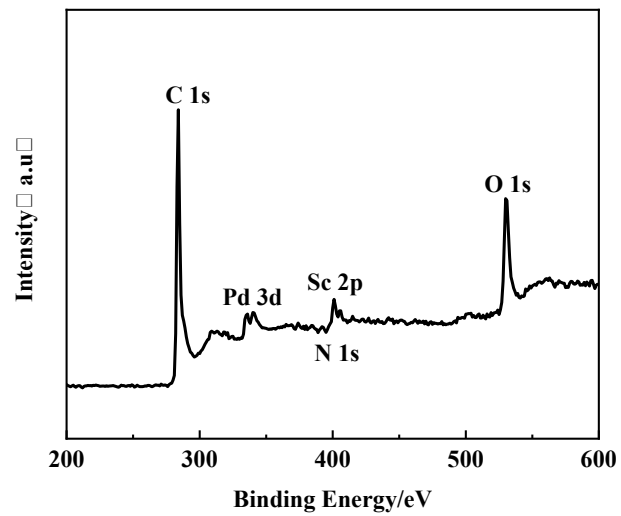


Figure S1. XPS survey spectrum of the Pd-Sc₂O₃/N-rGO-2/3.

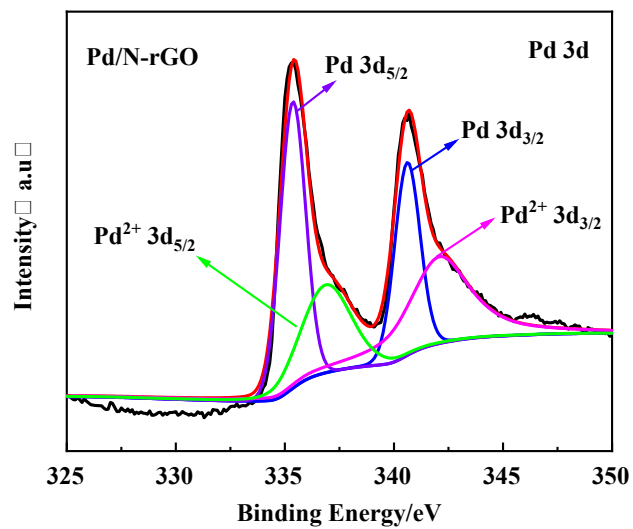


Figure S2. XPS spectrum of Pd 3d for Pd/N-rGO.

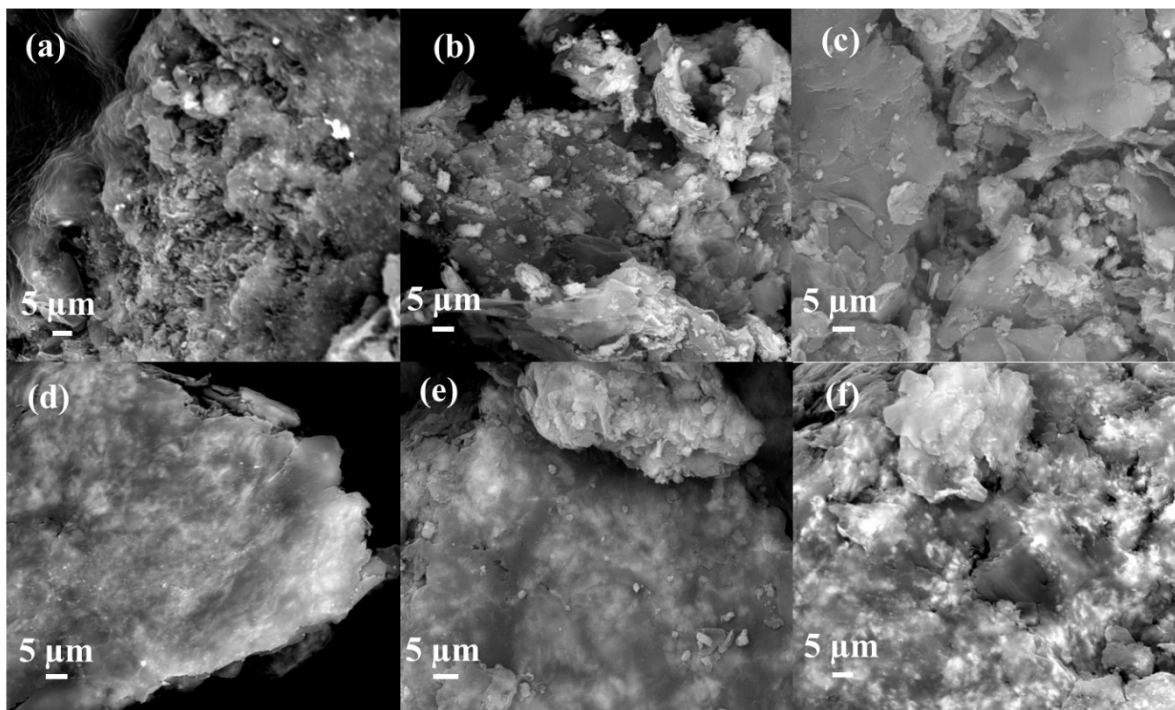


Figure S3. SEM images of (a) Pd/N-rGO and (b-f) Pd-Sc₂O₃/N-rGO-x. SEM images of (b) Pd-Sc₂O₃/N-rGO-1/3, (c) Pd-Sc₂O₃/N-rGO-1/2, (d) Pd-Sc₂O₃/N-rGO-2/3, (e) Pd-Sc₂O₃/N-rGO-1, (f) Pd-Sc₂O₃/N-rGO-3/2.

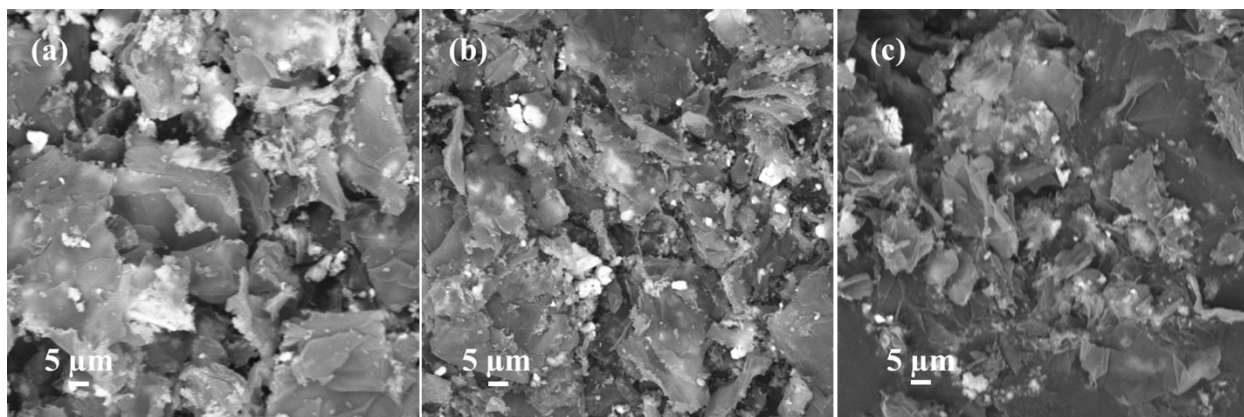


Figure S4. SEM images of (a) Pd-CeO₂/N-rGO, (b) Pd-La₂O₃/N-rGO, (c) Pd-Pr₂O₃/N-rGO.

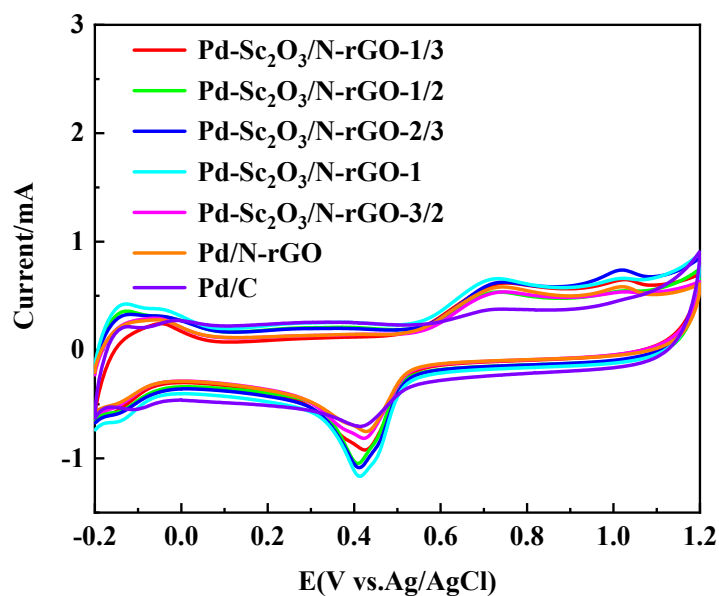


Figure S5. CV curves of Pd/C, Pd/N-rGO and Pd-Sc₂O₃/N-rGO-x in 0.5 M H₂SO₄ solution.

Supplementary Note 1

The electrochemically surface area (ECSA) is calculated from charges involved in the reduction of Pd oxide processes during the negative scan, according to the equation of $ECSA_{PdO} = Q / (C * Pd_m)$ in the potential range of 0.3-0.6 V, where Q is the integral of the peak from the reduction of Pd oxide, Pd_m is the load of Pd on the electrode, and C is the double-layer capacitance of 0.424 mC cm⁻² (Ref: *Electrochim. Acta*, 2019, 324, 134816). Based on the CVs, the ECSA_{PdO} of Pd-Sc₂O₃/N-rGO-2/3 is found to be 5.63 m² g⁻¹, Pd-Sc₂O₃/N-rGO-1/3 (4.59 m² g⁻¹), Pd-Sc₂O₃/N-rGO-1/2 (4.60 m² g⁻¹), Pd-Sc₂O₃/N-rGO-1 (5.61 m² g⁻¹), Pd-Sc₂O₃/N-rGO-3/2 (4.45 m² g⁻¹), Pd/N-rGO (4.09 m² g⁻¹) and Pd/C (3.52 m² g⁻¹).

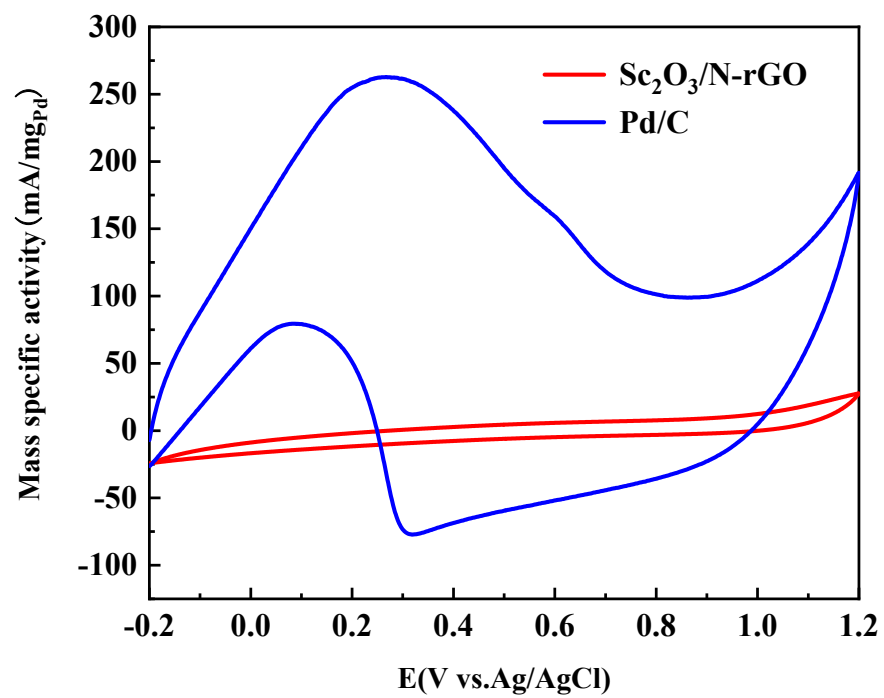


Figure S6 CV curves for Sc₂O₃/N-rGO and Pd/C catalyst in 0.5 M H₂SO₄ + 1.0 M HCOOH solutions.

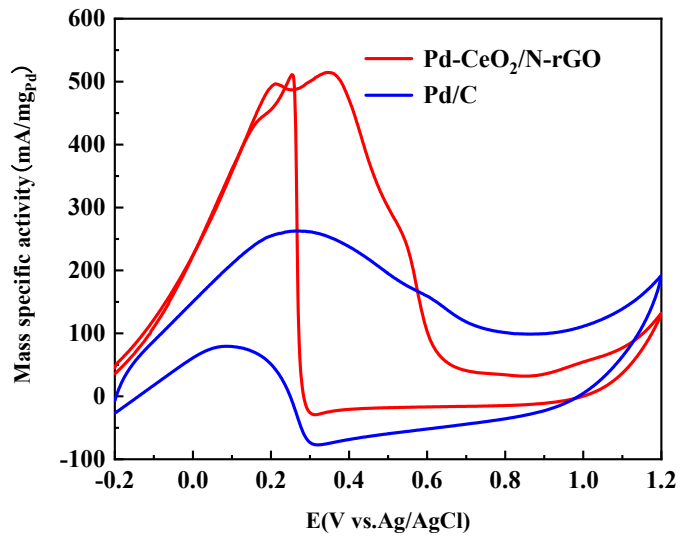


Figure S7 CV curves for Pd-CeO₂/N-rGO and Pd/C catalyst in 0.5 M H₂SO₄ + 1.0 M HCOOH solutions.

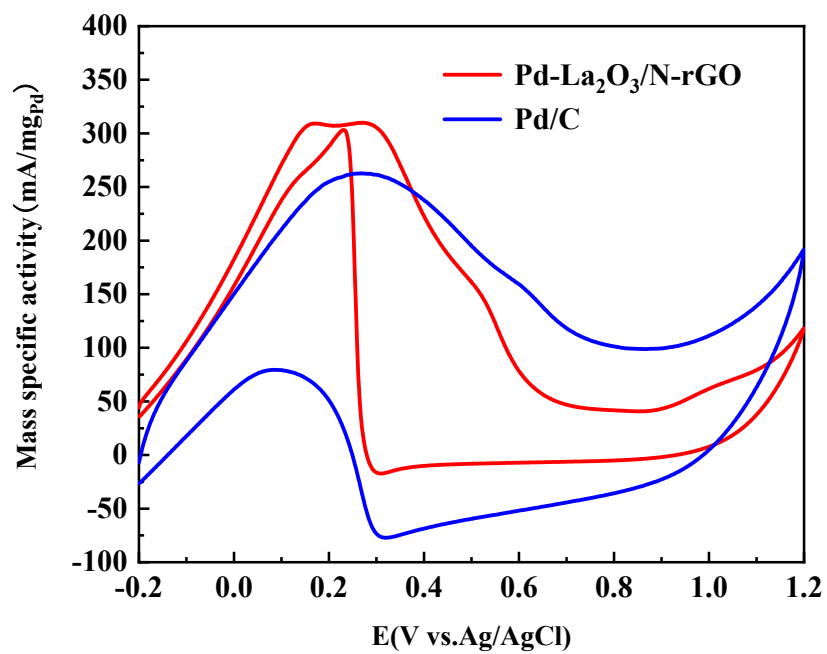


Figure S8 CV curves for Pd-La₂O₃/N-rGO and Pd/C catalyst in 0.5 M H₂SO₄ + 1.0 M HCOOH solutions.

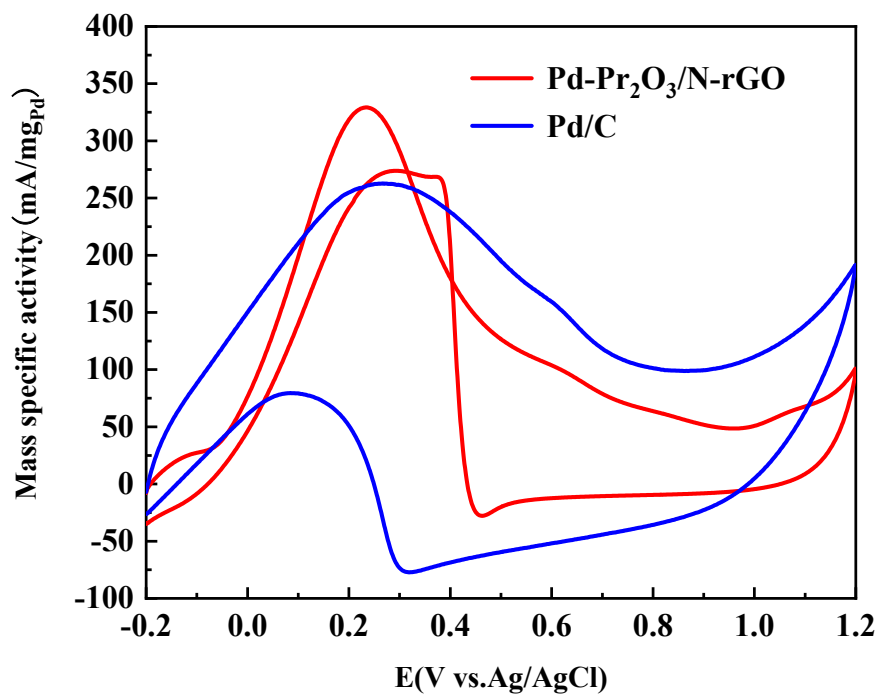


Figure S9 CV curves for Pd-Pr₂O₃/N-rGO and Pd/C catalyst in 0.5 M H₂SO₄ + 1.0 M HCOOH solutions.

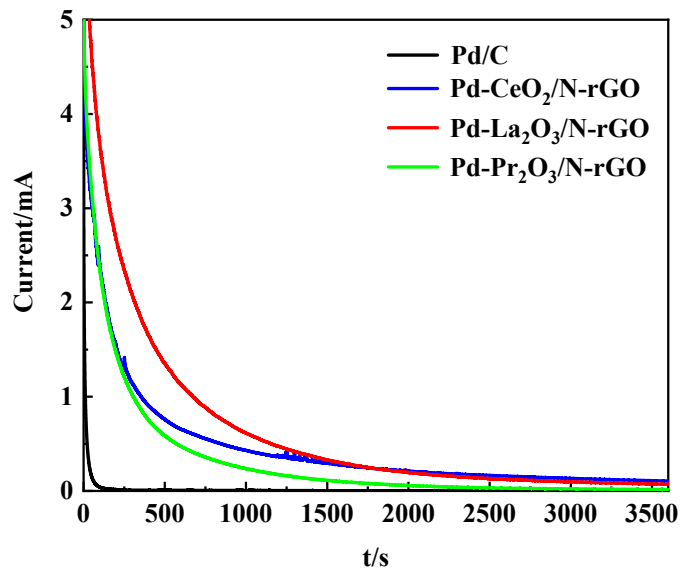


Figure S10 Chronoamperometric curves of Pd-CeO₂/N-rGO, Pd-La₂O₃/N-rGO, Pd-Pr₂O₃/N-rGO and Pd/C in 0.5 M H₂SO₄ + 1 M HCOOH solution.

Table S1. ICP-OES results of Pd-Sc₂O₃/N-rGO-x, Pd/N-rGO, Pd-CeO₂/N-rGO, Pd-La₂O₃/N-rGO and Pd-Pr₂O₃/N-rGO catalysts.

Samples	Pd (wt.%)
Pd-Sc ₂ O ₃ /N-rGO-1/3	8.89
Pd-Sc ₂ O ₃ /N-rGO-1/2	9.35
Pd-Sc ₂ O ₃ /N-rGO-2/3	8.27
Pd-Sc ₂ O ₃ /N-rGO-1	8.65
Pd-Sc ₂ O ₃ /N-rGO-3/2	9.13
Pd/N-rGO	9.08
Pd-CeO ₂ /N-rGO	9.47
Pd-La ₂ O ₃ /N-rGO	8.46
Pd-Pr ₂ O ₃ /N-rGO	8.30

Table S2. Binding energies and their shifts of Pd 3d for Pd/N-rGO and Pd-Sc₂O₃/N-rGO-2/3 catalysts.

Catalyst	Species	Binding Energy (eV)
Pd/N-rGO	Pd(0) 3d _{3/2}	340.6
	Pd(0) 3d _{5/2}	335.4
Pd-Sc ₂ O ₃ /N-rGO-2/3	Pd(0) 3d _{3/2}	340.3
	Pd(0) 3d _{5/2}	335.1

Table S3. Comparison of electrochemical performance of reported literature and the current work

Samples	^a E _f (V)	^b E _r (V)	^c J (A/m ²)	^d J (A/m ²)	^e I _f /I _b	Ref.
Pd ₃₀ La ₇₀ /rGO	0.66	0.56	694.5	627	1.11	1
Pd-CeO ₂ /C	0.13	0.15	350	300	1.16	2
Pd ₄ Sm ₆ /rGO	0.30	0.20	968	589	1.6	3
PdEuO _x /C	0.33	0.35	700	650	1.06	4
Pd ₆ Y ₄ /rGO	0.36	0.46	1066	1329.5	0.80	5
Pd/C	0.28	0.12	146	43	3.3	This work
Pd/N-rGO	0.05	0.1	162	99.5	1.62	This work
Pd-Sc ₂ O ₃ /N-rGO-2/3	0.36	0.43	449	546	0.82	This work

^a E_f = forward peak potential.

^b E_r = backward peak potential.

^c J = forward current density.

^d J = backward current density.

^e I_f/I_b = ratio of forward to backward oxidation peak.

References

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- [2] Y. Wang, S. Wang and X. Wang. *Solid-State Lett.*, 2009, **12**, 2009 B73.
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