Alloying promotion of Pd-based metallenes in electrocatalytic hydrogenation of functionalized nitroarenes

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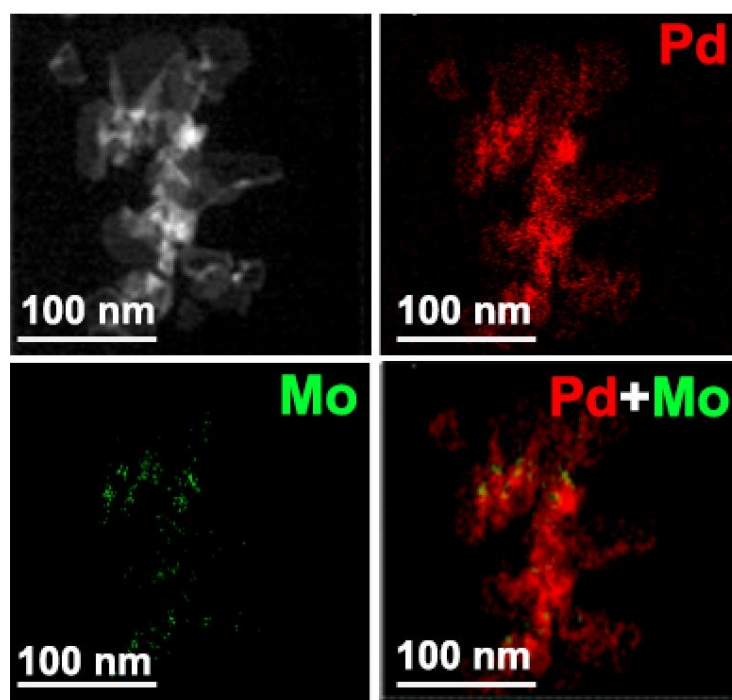

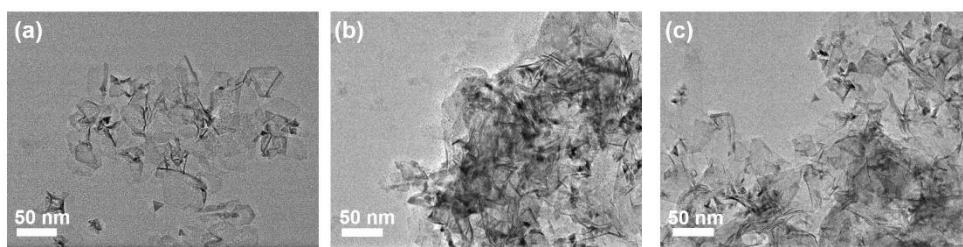**Fig. S1** EDS elemental mapping of Pd and Mo in Pd-Mo metallene.

Fig. S2 TEM images of Pd-Mo metallenes obtained after varying the feeding content of $Mo(CO)_6$ (a: 2 mg, b: 10 mg, c: 15 mg.) along with the fixed one of $Pd(ac)_2$ (12 mg).
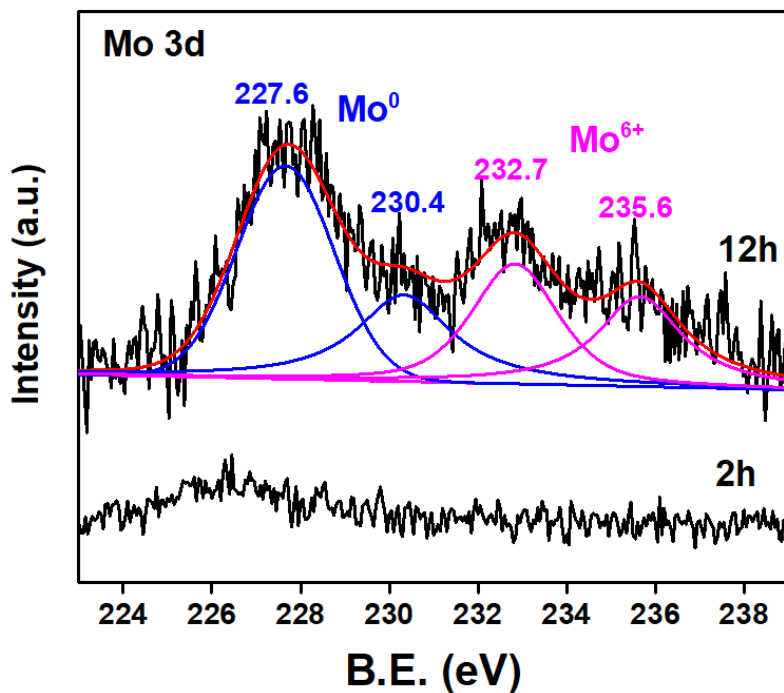

Fig. S3 Mo 3d XPS of Pd-Mo metallene received at different time during preparation. The presence of Mo^{6+} is due to the slight surface oxidation when the sample is exposed to air.
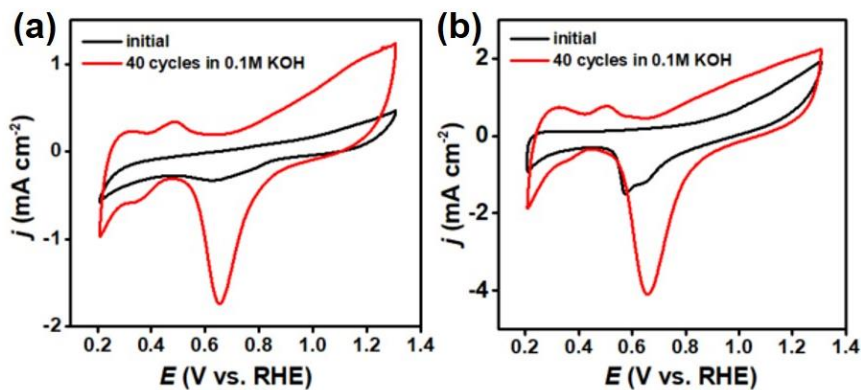

Fig. S4 CVs of (a) Pd and (b) Pd-Mo metallenes before and after surface cleaning by repeated CVs in 0.1 M KOH.
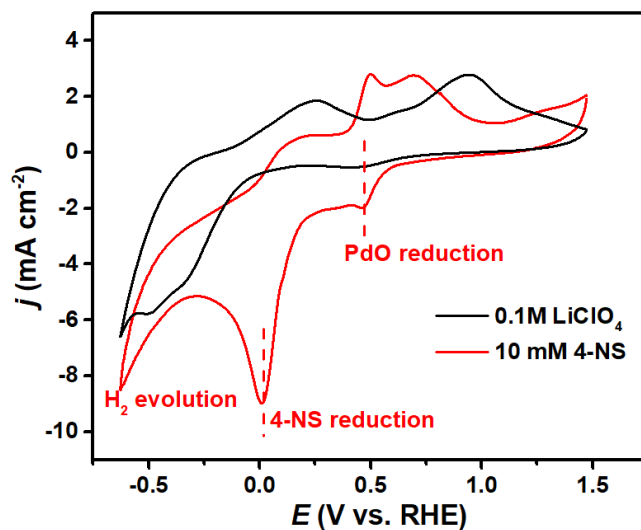
Fig. S5 CV curves of Pd-Mo in 0.1 M LiClO$_4$ (pH 6.8) before and after introducing 4-NS (10 mM). For this test, Pd-Mo metallene was dropped onto a glassy carbon electrode.
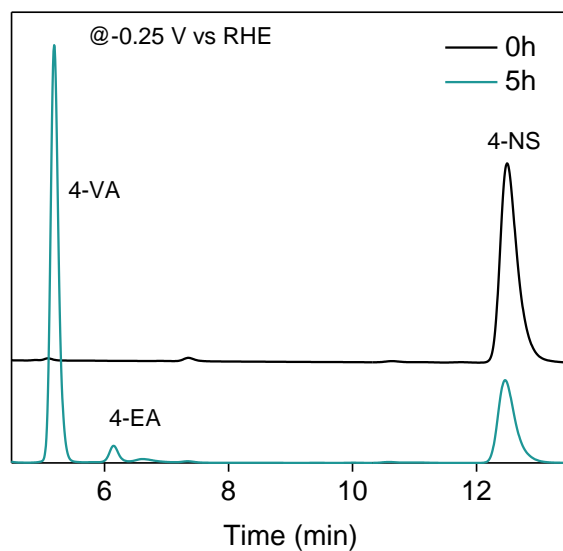

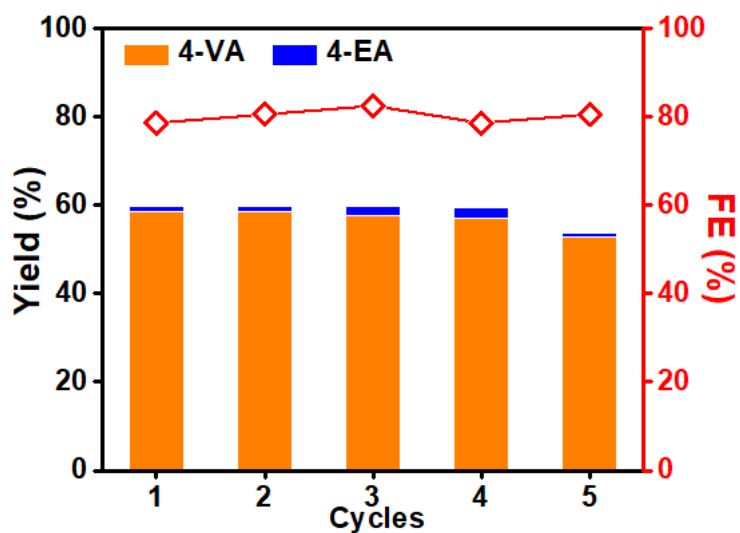**Fig S6** HPLC profiles of liquid products received after the ECH.

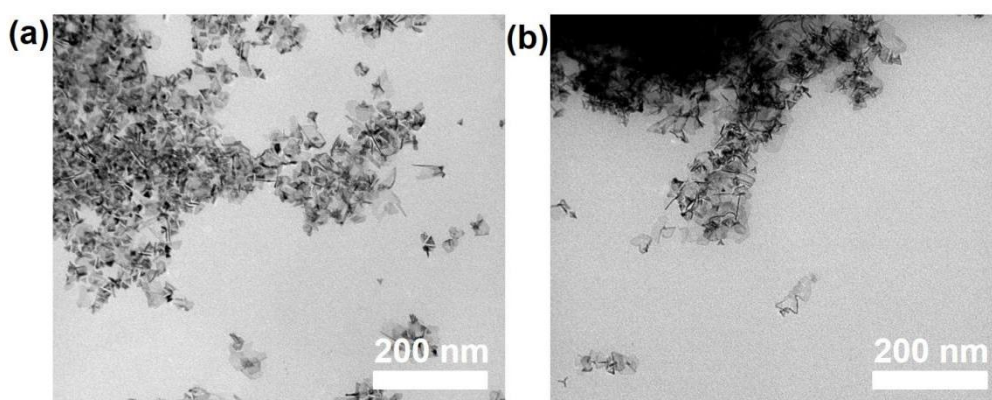**Fig. S7** Cycle test for the ECH of 4-NS over Pd-Mo metallene at −0.25 V vs. RHE.

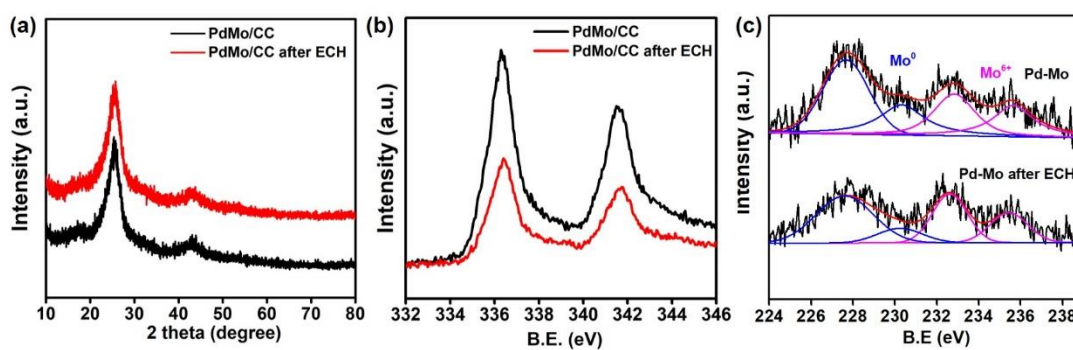**Fig. S8** TEM images of Pd-Mo metallene (a) before and (c) after the ECH test.

Fig. S9 (a) XRD patterns, and (b) Pd 3d and (c) Mo 3d XPS profiles of Pd-Mo metallene before and after the ECH test.
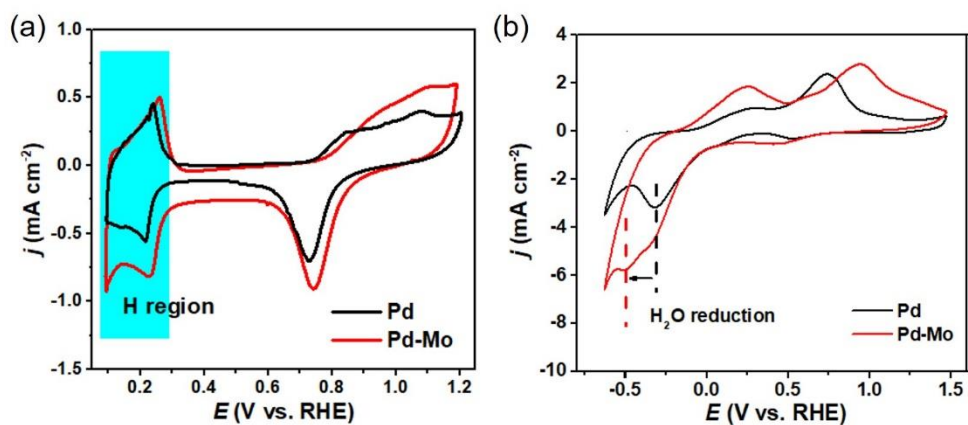
Fig. S10 CVs of Pd and Pd-Mo metallene in (a) 0.05 M H_2SO_4 and (b) 0.1 M $LiClO_4$.
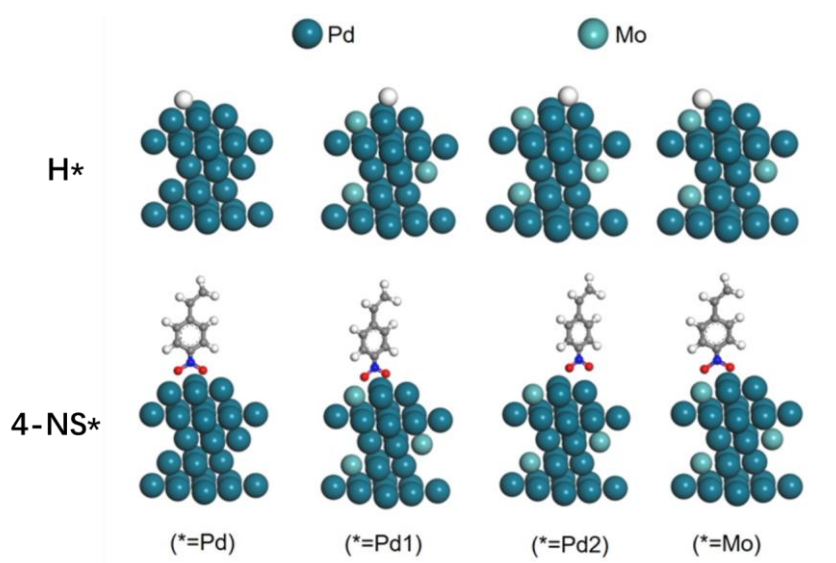

Fig. S11 Adsorption configurations of H* and 4-NS* on Pd and Pd-Mo.
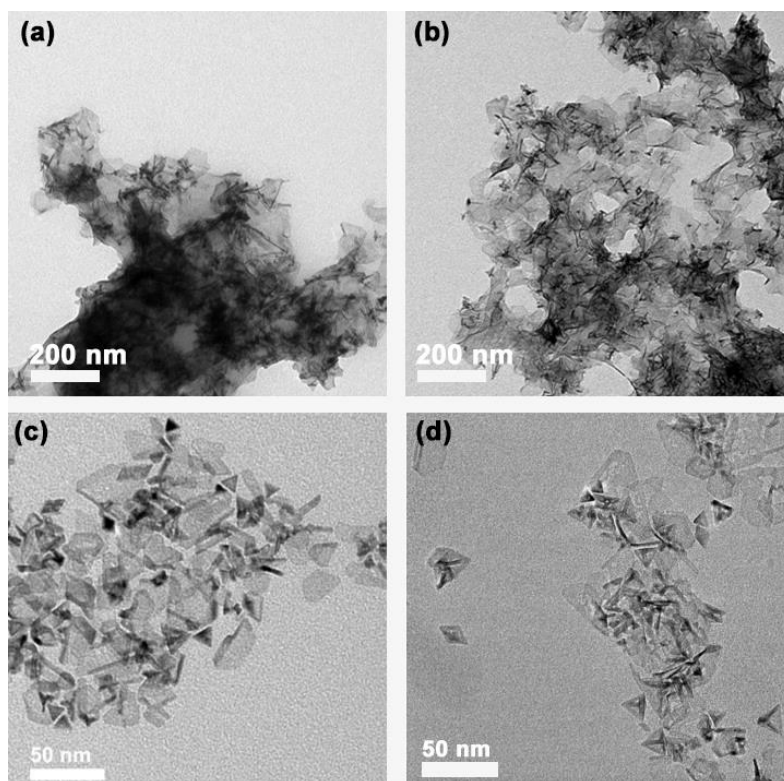
Fig. S12 TEM images of (a) Pd-Cr, (b) Pd, (c) Pd-Mo and (d)Pd-W metallenes.
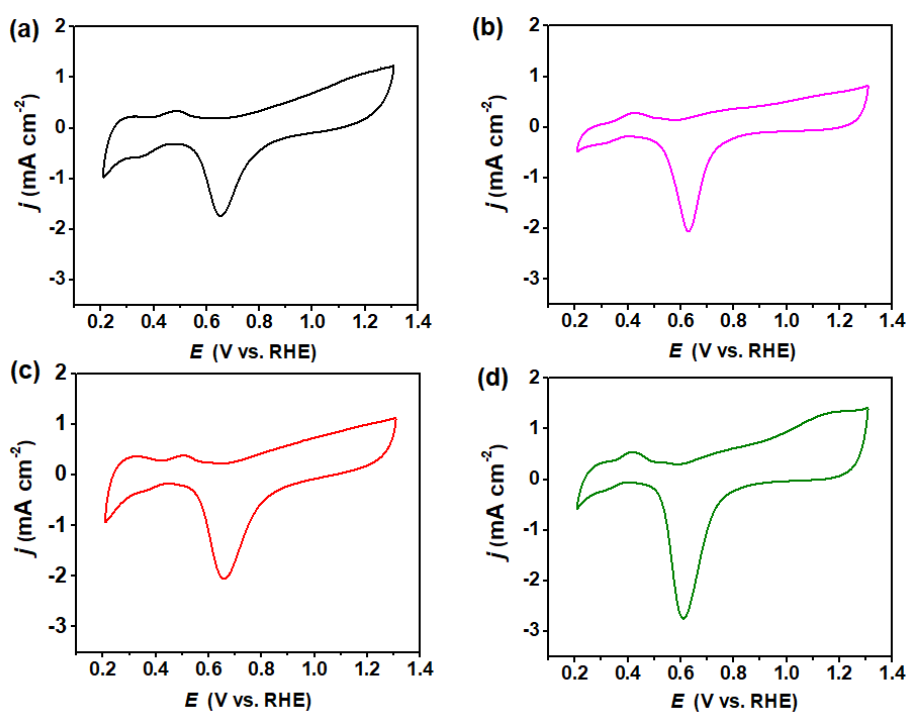
Fig. S13 CVs of (a) Pd-Cr, (b) Pd, (c) Pd-Mo and (d) Pd-W metallenes in 0.1 M KOH. For this test, the samples were loaded onto a glassy carbon electrode with a mass loading of 0.15 mg cm^{-2}.
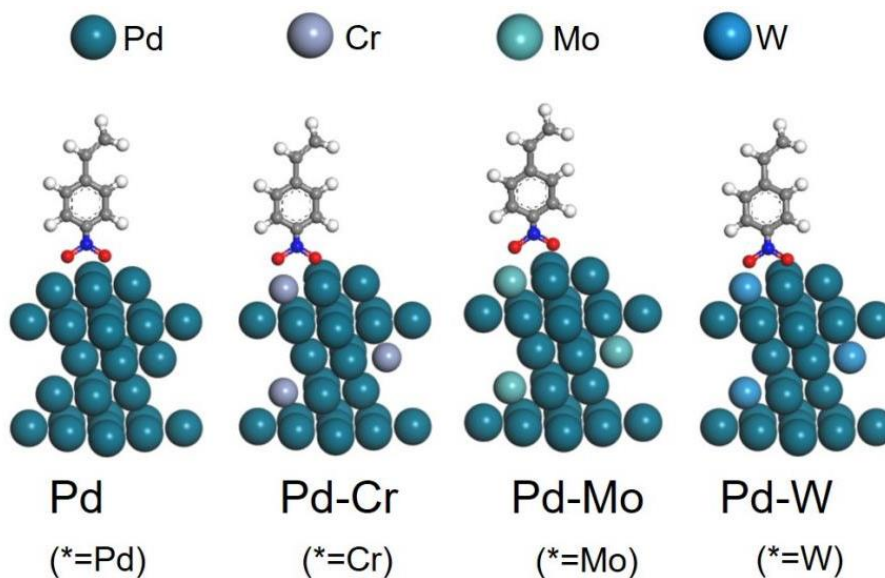
Fig. S14 Adsorption configuration of 4-NS* on Pd and Pd-M (M=Cr, Mo, W).

Table S1 Composition of Pd-Mo with different concentration of Mo precusor.

feeding Mo(CO)$_6$ (mg)	Pd (wt%)	Mo (wt%)	molar Mo/Pd
2	97.1	2.9	0.03
4	96.9	3.1	0.04
10	96.2	3.8	0.04
15	97.6	2.4	0.03

Table S2 Composition of Pd-M.

	Pd (wt%)	Cr/Mo/W (wt%)
Pd	>99.9	/
PdCr	97.7	2.3
PdMo	96.9	3.1
PdW	97.3	2.7

Table S3 Comparison of ECH performance (4-NS to 4-VA) for Pd-Mo metallene with other works.

Catalyst	Time/Q	solution	Driven condition	F.E.	Sel.	Yield	Ref.
Pd-Mo metallene	5 h/~216 C			84%	93%	63%	
Pd metallene	5 h	0.1 M LiClO$_4$ (pH 6.8)	-0.25 V vs RHE	68%	96%	59%	**This work**
Pd-Cr metallene	5 h			77%	96%	51%	
Pd-W metallene	5 h			82%	97%	76%	
CuCo$_2$O$_4$/NF	300 C	1M KOH	-1.0V vs SHE	~89%	~99%	93%	[1]
Co$_3$S$_{4-x}$	6 h	1M KOH	-1.0V vs Hg/HgO	-	96%	~86%	[2]
CoP	6 h	1M KOH	-1.2 V vs Ag/AgCl	-	92%	~86%	[3]

Table S4 ECSA and specific rate of 4-NS reduction of Pd and Pd-M metallenes (in initial 1h).

	Pd	Pd-Cr	Pd-Mo	Pd-W
ECSA (cm^2 mg^{-1})	111.60	100.41	123.46	129.71
$r_{4\text{-NS}}$ ($\times 10^{-2}$ mmol h^{-1})	5.94	5.76	11.76	10.68
$r_{4\text{-NS,ECSA}}$ ($\times 10^{-5}$ mmol h^{-1} cm$_{ECSA}^{-2}$)	53.23	57.36	95.25	82.34

Reference

[1] ACS Catal. 2022, 12, 58

[2] CCS Chem., 2021, 3(1): 507-515.

[3] Nat. Sci. Rev., 2020, 7(2): 285-295.