Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Synergy between molybdenum nitride and gold leading to platinum-like activity for hydrogen evolution

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Table S1. Structural parameters obtained from EXAFS fittings and known structure of γ-Mo_2N				
Bond	**distance / Å**	**Coordination number, N**	**σ^2 / Å^2**	**ΔE_0 / eV**
Mo3/20/80-Z8FA-1050				
Mo-O	1.77 (3)	1.5	0.020 (4)	4.83
Mo-N	2.07 (2)	4.0	0.011 (2)	4.83
Mo-Mo	2.97 (2)	4.7	0.013 (2)	4.83
Mo-Mo	4.03 (2)	2.0	0.011 (2)	4.83
Mo6/20/80-Z8FA-1050 after 500 cycles (gold CE)				
Mo-O	1.73 (2)	2.0(3)	0.012 (3)	2.70
Mo-N	2.05 (3)	3.5(4)	0.016 (4)	2.70
Mo-Mo	3.08 (3)	4.2(6)	0.020 (3)	2.70
Mo-Mo	4.20 (3)	2.0(4)	0.020 (3)	2.70
γ-Mo_2N (expected interatomic distance and coordination numbers for bulk γ-Mo_2N with cell parameter 4.16 Å and having nitrogen atoms located in octahedral sites)				
Mo-N	2.08	3	--	--
Mo-Mo	2.94	12	--	--
Mo-Mo	4.16	6	--	--

Table S2. Results from the fitting of the XPS narrow scan spectra									
	Mo_{3d}			N_{1s}			O_{1s}		
	Mo^{δ}	Mo^{IV}	Mo^{VI}	Mo_2N & pyridinic	Pyrrolic	Oxidized	O^{2-} (MoO)	C=O	C-O-C
Mo3/20/80 - Z8FA -1050	**228.7** (46.4)	**229.9** (12.4)	**232.5** (41.2)	**398.8** (36.0)	**401.4** (47.4)	**402.8** (16.6)	**530.8** (42.2)	**532.7** (48.5)	**534.5** (9.3)
	1.2 at. %			2.6 at. %			4.7 at. %		
Mo6/20/80 -Z8FA-1050	**228.8** (43.4)	**230.1** (15.3)	**233.3** (41.3)	**398.4** (74.8)	**401.3** (22.2)	**402.7** (3.0)	**530.7** (59.5)	**532.6** (35.1)	**534.5** (5.4)
	3.3 at. %			3.0 at. %			5.1 at. %		
For each sample, the first row gives the binding energy, BE, (in bold) and relative % (in brackets) for each species, while the second row reports the absolute atomic percentage for each element in the sample. For the Mo_{3d} signal, the BE of the Mo $3d_{5/2}$ level is given while the relative percentage corresponds to that of the Mo species assigned to that BE.									

Table S3. Electrocatalytic activity for the HER in acid medium

Catalyst description	Electrolyte	Loading (all elements) / mg·cm^{-2}	E @ 1.0 mA·cm^{-2} / mV *vs.* RHE	Tafel slope / mV·dec^{-1}	Ref.
70 wt. % Pt/C	0.1 M $HClO_4$	0.47	+12 [(1)]	42	This work
MoS_2	0.5 M H_2SO_4	300 nm MoS_2 layer	-160	?	[13]
MoS_2/graphene (*ca* 35 wt. % Mo)	0.5 M H_2SO_4	0.28	-100	41	[17]
1T-MoS_2	0.5 M H_2SO_4	0.050 (pure MoS_2)	-160	40	[15]
chemically exfoliated 1T-MoS_2	0.5 M H_2SO_4	?	-140	43	[S1]
33 wt. % MoS_2/MWCNT	1.0 M H_2SO_4	0.51	-150	40	[16]
MoS_2/Au	0.5 M H_2SO_4	10^{-3} (excl. Au)	-150	69	[45]
30 wt. % Mo_2C/CNT	0.1 M $HClO_4$	2.0	-63	55	[19]
bulk Mo_2C	1.0 M H_2SO_4	1.4	-150	56	[18]
20 wt. % MoN/Vulcan	0.1 M $HClO_4$	0.25	-260	54	[21]
$(Ni_2Mo_3N)_{0.3}$+Mo_2N / Vulcan (20 wt. % metal on Vulcan)	0.1 M $HClO_4$	0.25	-150	36	[21]
δ-MoN/Vulcan (20 wt. % metal on Vulcan)	0.1 M $HClO_4$	0.25	-250	54	[21]
W_2C microspheres	1.0 M H_2SO_4	?	-60	118	[S2]
Mo3/20/80-Z8FA-1050	0.1 M H_2SO_4	0.80	-255 [(2)]	125	This work
Mo3/20/80-Z8FA-1050 / Au			-130 [(3)]	78	
Mo0/20/80-Z8FA-1050 / Au			-220 [(3)]	109	
Mo6/20/80-Z8FA-1050 / Au		0.80 (0.25 Au, estimated)	-20 [(3)]	67	

[(1)] positive due to the absence of H_2 in the electrolyte, shifting upward the H^+/H_2 equilibrium potential;
[(2)] Before and [(3)] after 1000 cycles at 100 mV·s^{-1} between -0.6 and +0.4 V *vs.* SCE.

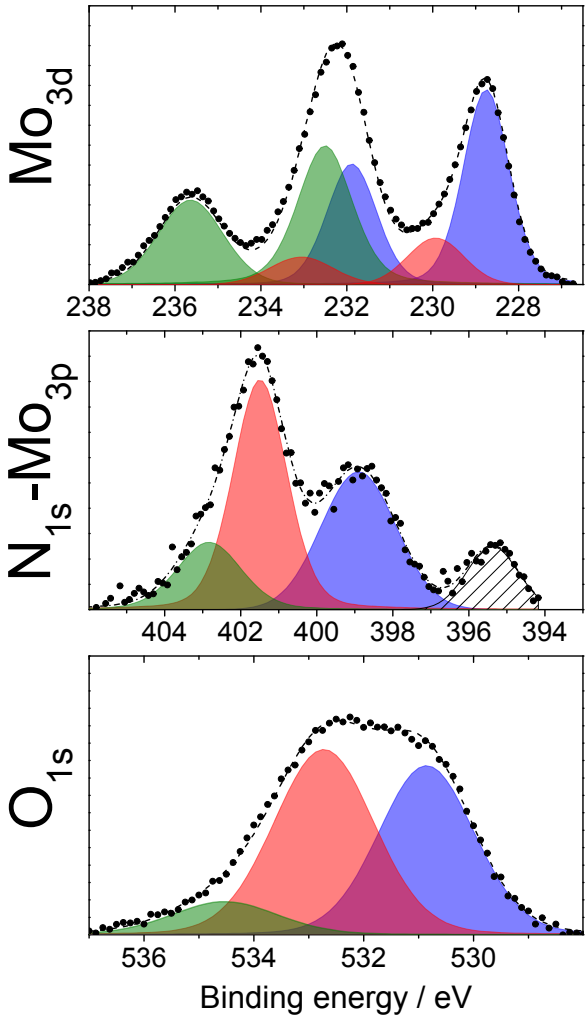

Figure S1. X-ray photoelectron spectroscopy narrow scan spectra for Mo_{3d}, N_{1s} and O_{1s} in Mo3/20/80-Z8FA-1050

The filled circles represent the experimental data points and the dotted line the fitting. The Mo_{3p} contribution to the N_{1s} region is indicated by the dashed area. For a given core level, each colour identifies one species, with increasing BE in the order: blue, red, green.

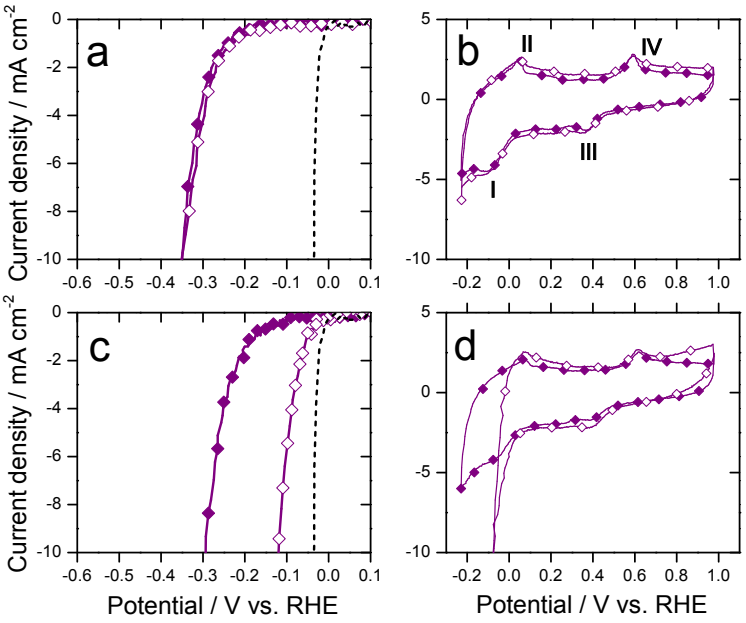

Figure S2. Effect of potential limits during cycling on the activation of Mo6/20/80-Z8FA-1050

Left. HER polarization curves before and after 1000 cycles at 100 $mV \cdot s^{-1}$ in the potential limits of **a)** +0.17 to +0.67 V *vs.* RHE, **c)** -0.33 to +0.67 V *vs.* RHE (scan rate 1 $mV \cdot s^{-1}$). **Right.** Cyclic voltammograms for Mo6/20/80-Z8FA-1050 before and after 1000 cycles at 100 $mV \cdot s^{-1}$ in the potential limits of **b)** +0.17 to +0.67 V *vs.* RHE, **d)** -0.33 to +0.67 V *vs.* RHE (scan rate 20 $mV \cdot s^{-1}$)

1.0 M H_2SO_4 solution, rotating speed 1500 rpm, catalyst loading 800 $\mu g_{Mo/N/C} \cdot cm^{-2}$. The dotted line corresponds to the Pt/C catalyst (328 $\mu g_{Pt} \cdot cm^{-2}$). Potential corrected for the iR drop. The peaks labelled I/II are assigned to electrochemical hydrogen adsorption/desorption on Mo_2N while peaks III/IV are assigned to the reduction/oxidation of the passivated Mo_2N surface.

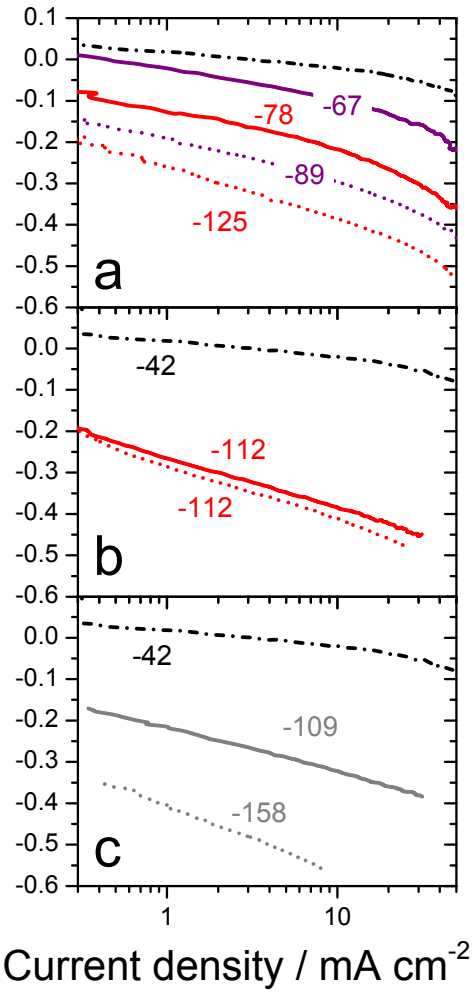

Figure S3. Tafel plots for the hydrogen evolution reaction on Mo-based catalysts (a, b) and N-doped carbon (c).

Same figure caption as Figure 3. The values of the Tafel slopes are indicated in mV·dec^{-1} in the graph. The current density is in absolute value, for a logarithmic-scale presentation.

Supplementary references

S1. M. A. Lukowski *et al*, *J. Am. Chem. Soc.*, 2013, **135,** 10274-10277.

S2. D. J. Ham, R. Ganesan and J. S. Lee, *Int. J. Hydrogen Energy*, 2008, **33,** 6865-6872.