Supplementary Information

Protein-Metal Ions Networks Coated Carbon Matrix as a Precursor: To Construct Carbon-Supported Mo-based Catalyst with Highly Exposed Active Site for Hydrogenation of Nitro Compounds

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Figures and tables

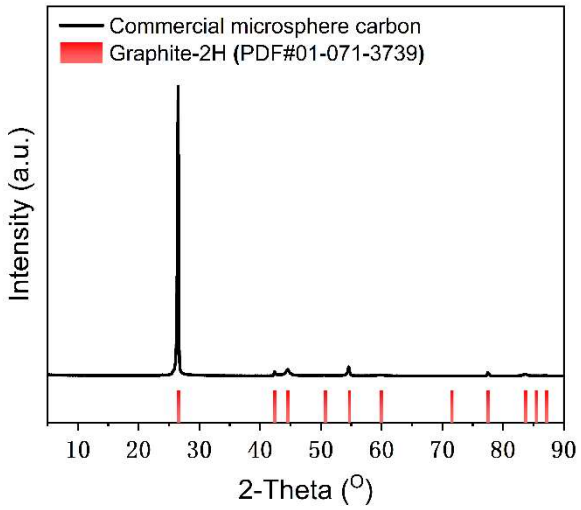


Fig. S1 XRD pattern of the pure commercial microsphere carbon (MC) support.

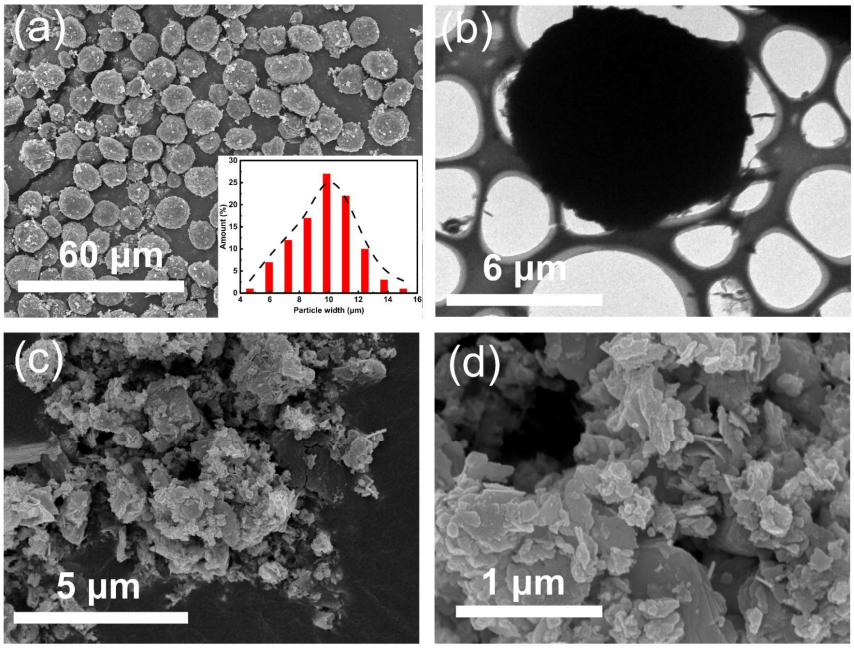


Fig. S2 SEM image and particle width distribution of commercial microsphere carbon support (a). TEM image of Mo@C/MC catalyst (b). SEM images of Mo@C catalysts(c,d).

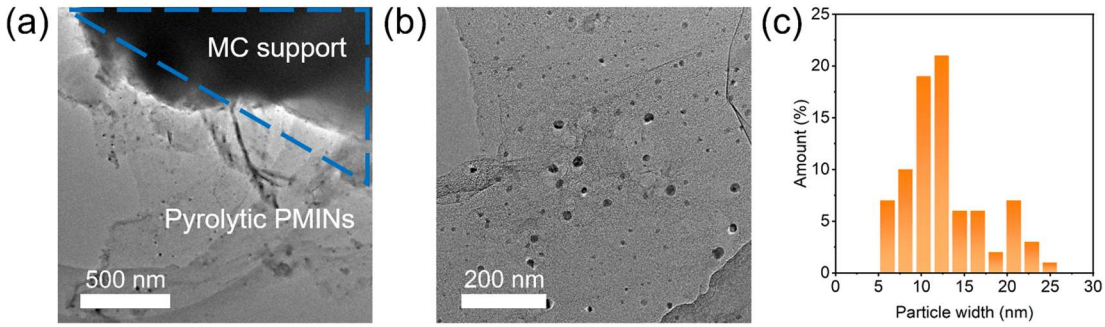


Fig. S3 TEM images of the edge of Mo@C/MC catalyst (a, b) and particle width distribution of Mo@C/MC catalysts (c).

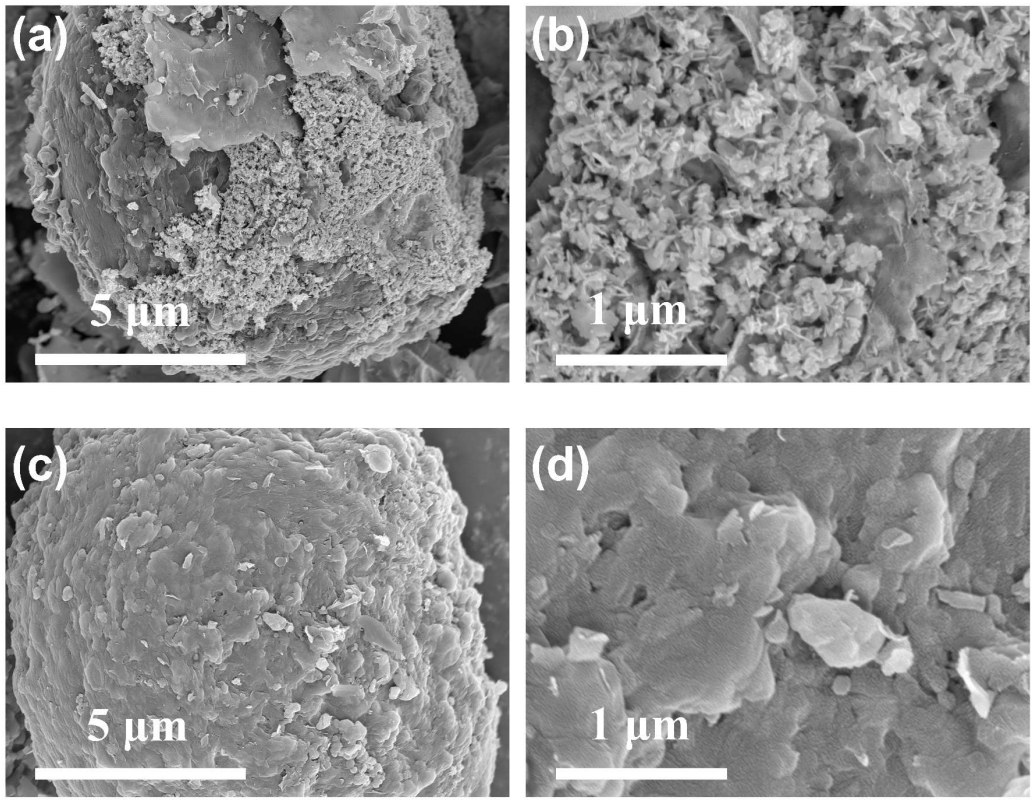


Fig. S4 SEM image of Mo@C/MC catalyst (a, b) and Mo/MC catalyst (c,d).

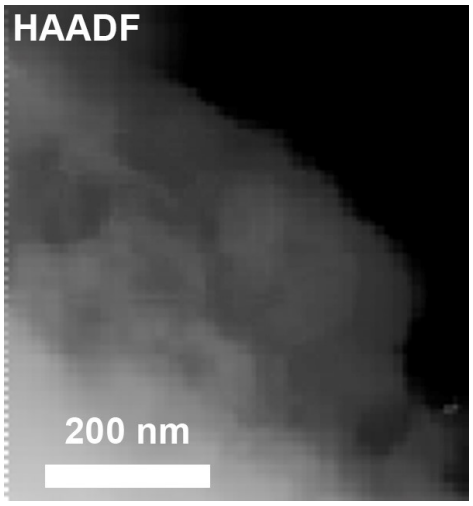


Fig. S5 HAADF image of Mo@C/MC catalyst.

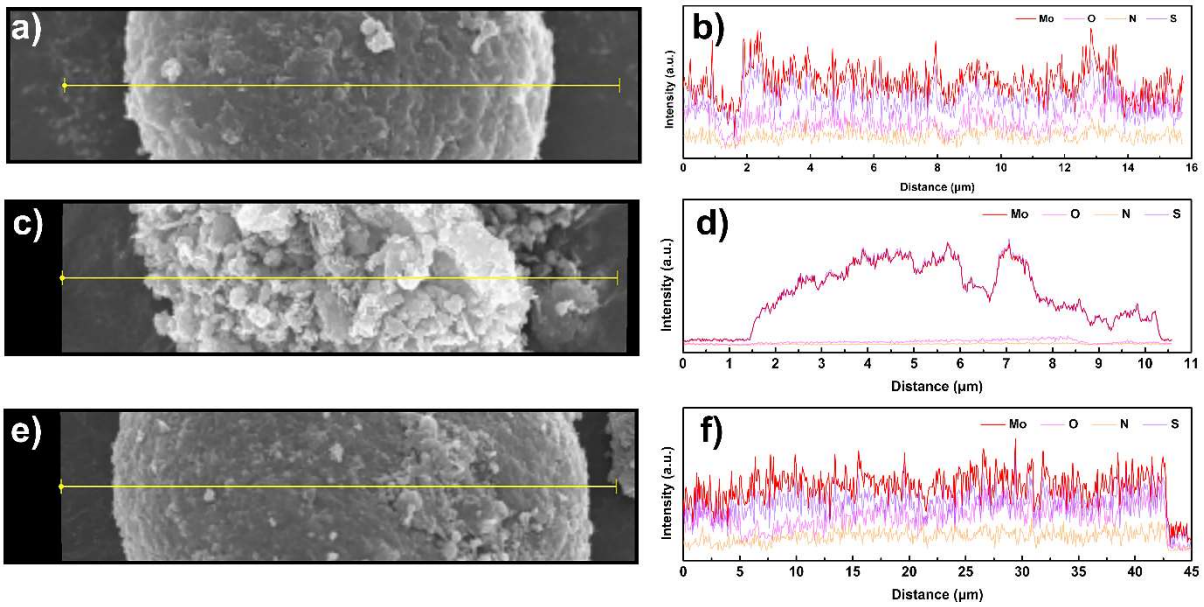


Fig. S6 Line scan EDS image of Mo@C/MC (a, b), Mo@C (c, d) and Mo/MC (e, f) catalysts.

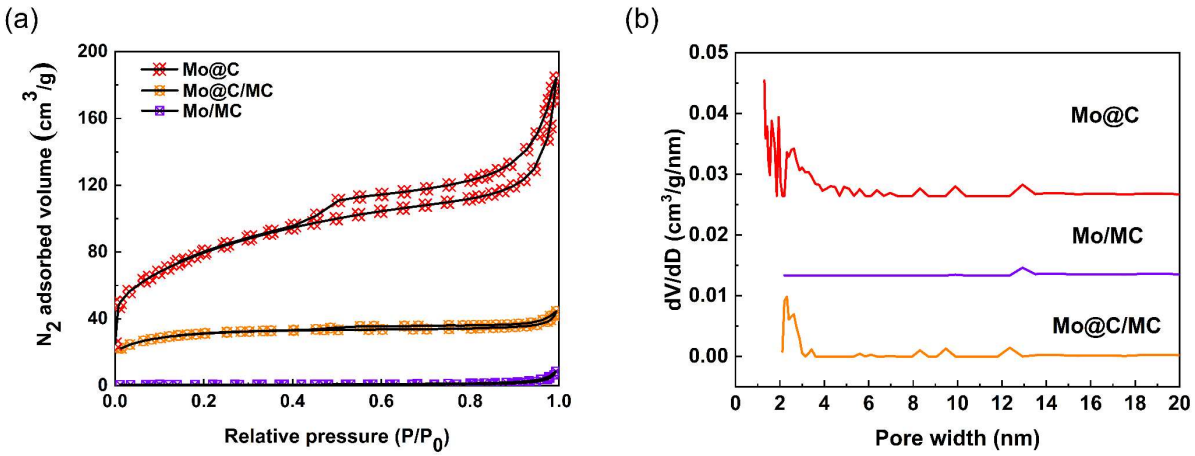


Fig. S7 Nitrogen adsorption and desorption isotherms (a) and pore size distribution (b) of three catalysts.

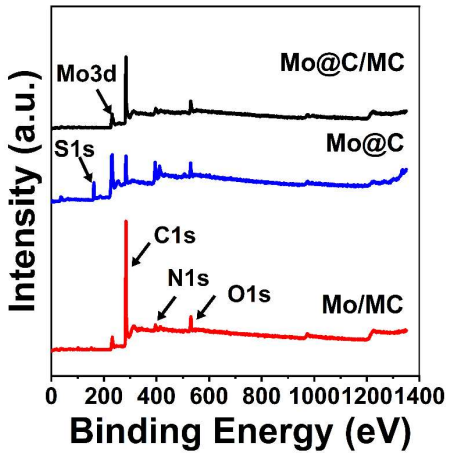


Fig. S8 XPS survey scan of Mo@C/MC, Mo@C and Mo/MC catalysts.

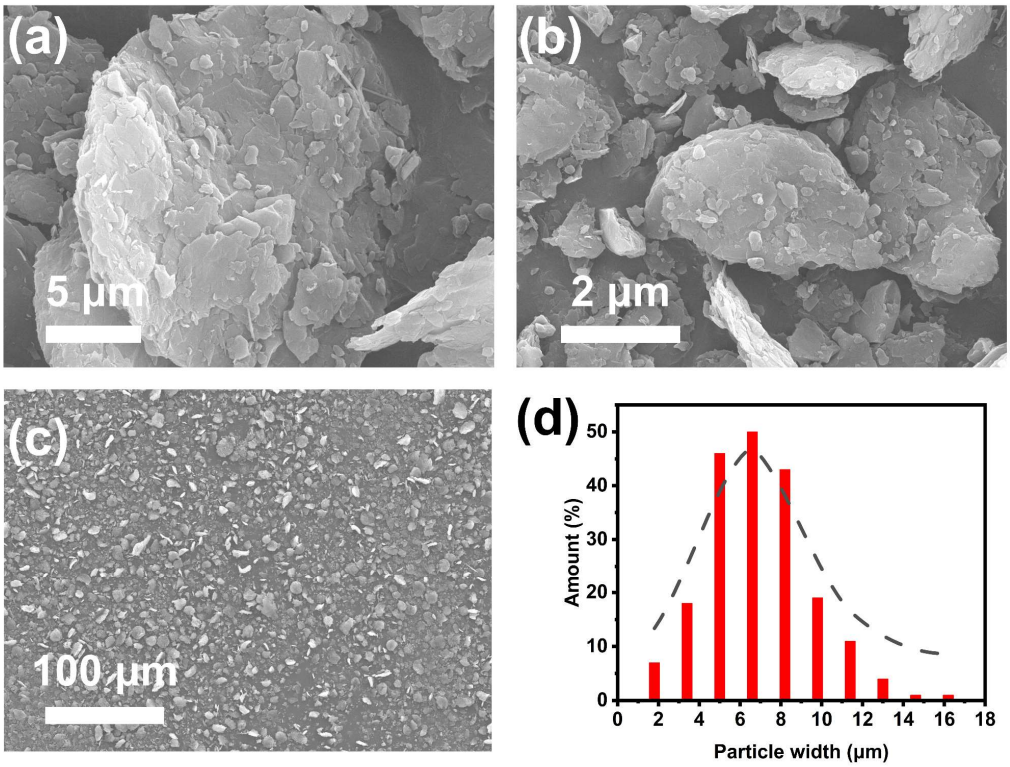


Fig. S9 SEM images of Mo@C/MC catalyst after ball milling (a, b and c) and its particle width distribution (d).

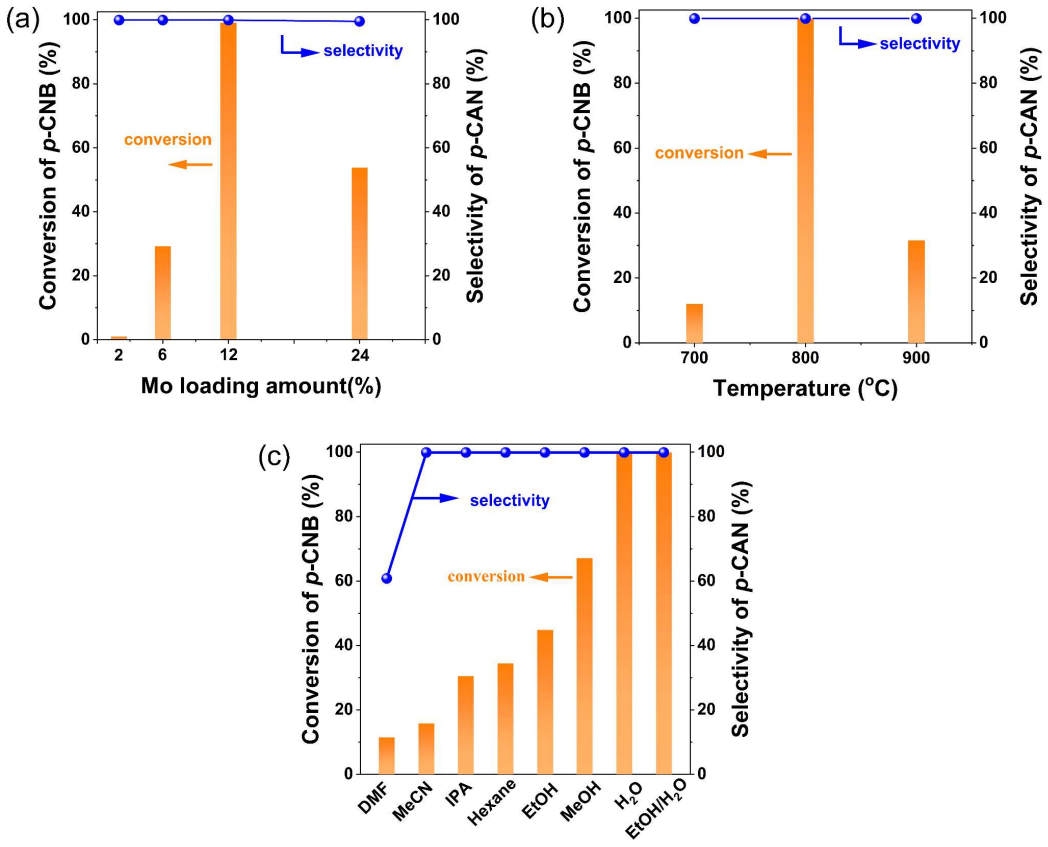


Fig. S10 Impact of Mo amount (a), calcination temperature (b) and solvent (c) on the hydrogenation of *p*-CNB. Reaction conditions: 0.25 mmol *p*-CNB in 5 mL ethanol/H_2O (V/V = 1:4) with 50 mg catalyst reacted at 100 °C, 5 bar H_2 for 3 h. The identity of the products was further determined by HPLC.

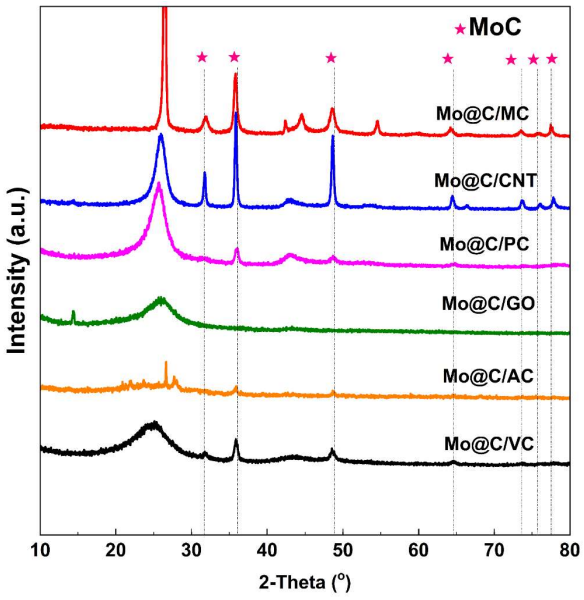


Fig. S11 XRD pattern of different types of protein-coated carbon matrices (including carbon

nanotubes (CNTs), graphite oxide (GO), porous carbon (PC), activated carbon (AC), and Vulcan XC72 (VC)). (MoC pattern PDF#03-065-6664)

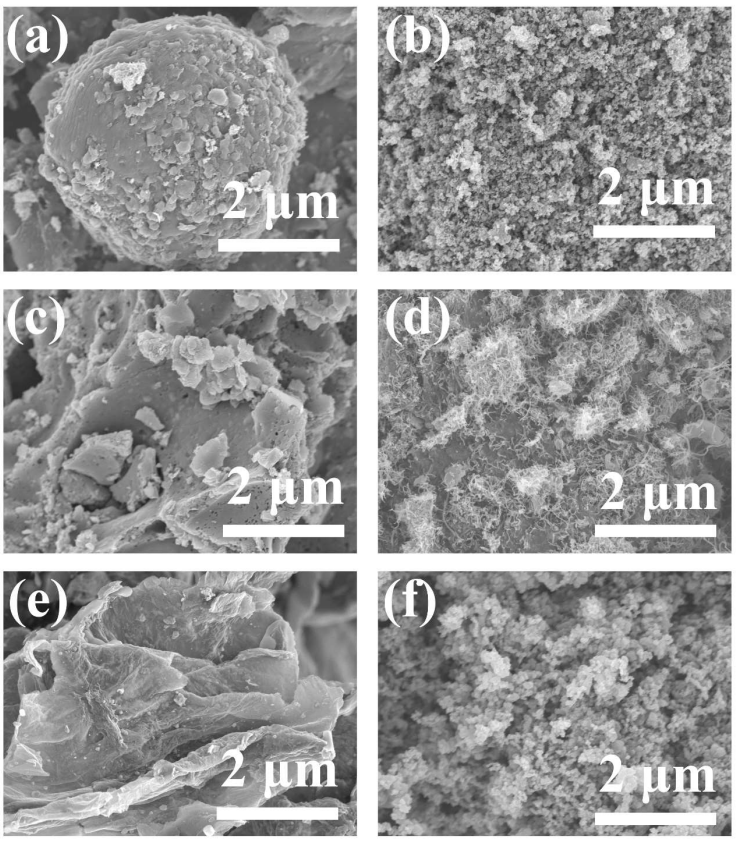


Fig. S12 SEM image of Mo@C/MC (a), Mo@C/VC (b), Mo@C/AC (c), Mo@C/CNTs (d), Mo@C/GO (e), Mo@C/PC (f) catalyst.

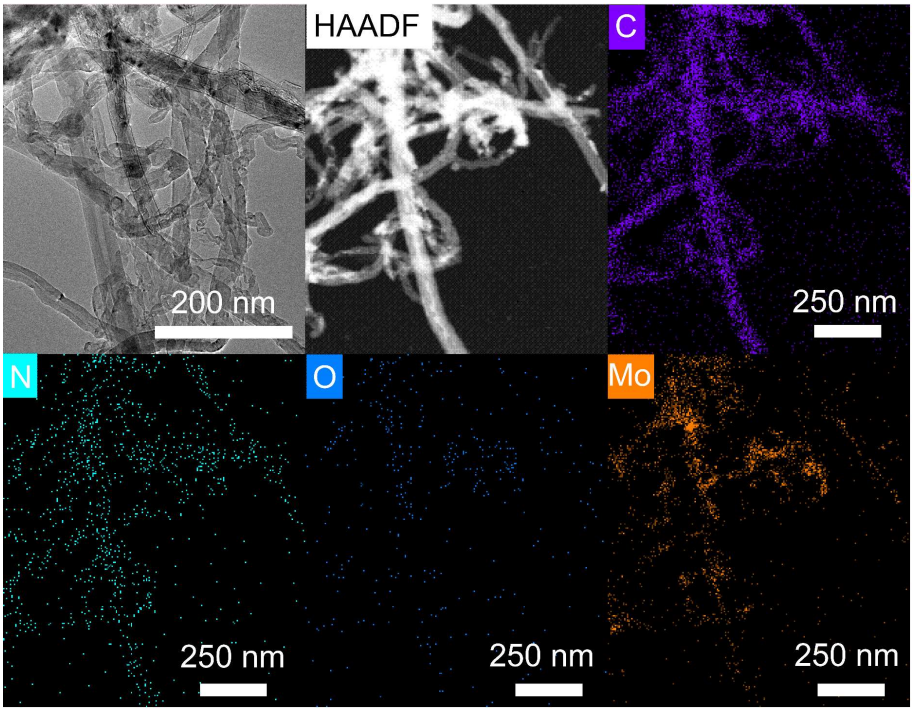


Fig. S13 TEM and mapping profiles of the Mo@C/CNTs catalyst.

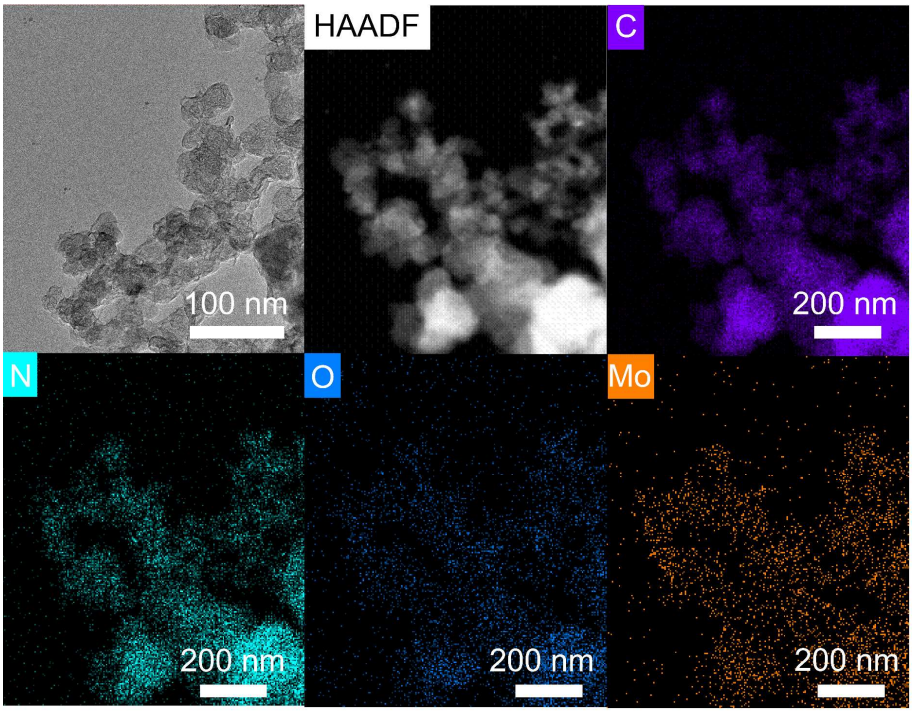


Fig. S14 TEM and mapping profiles of the Mo@C/PC catalyst

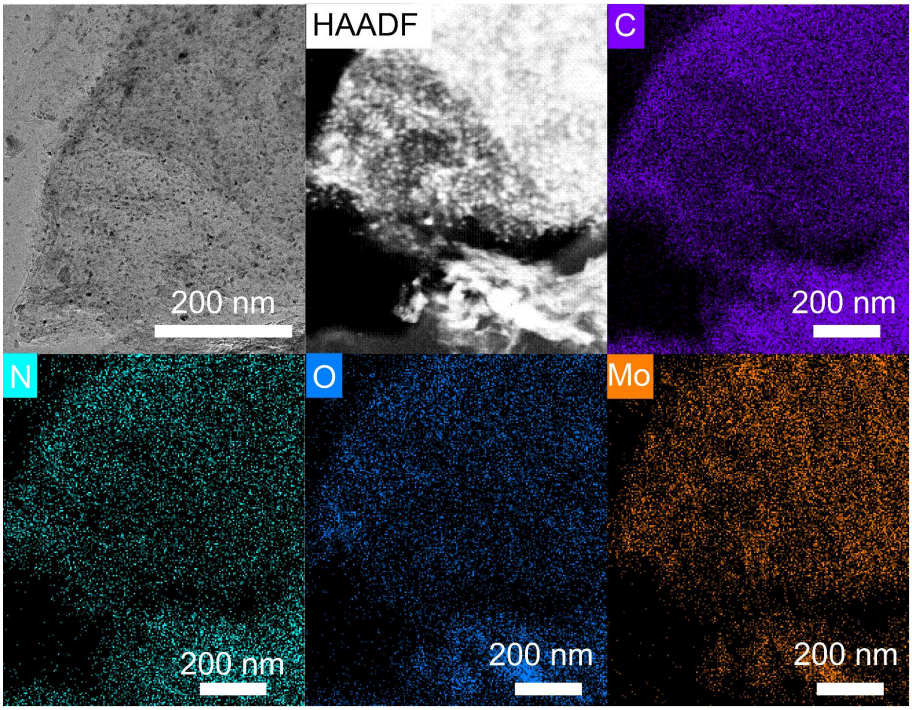


Fig. S15 TEM and mapping profiles of the Mo@C/GO catalyst

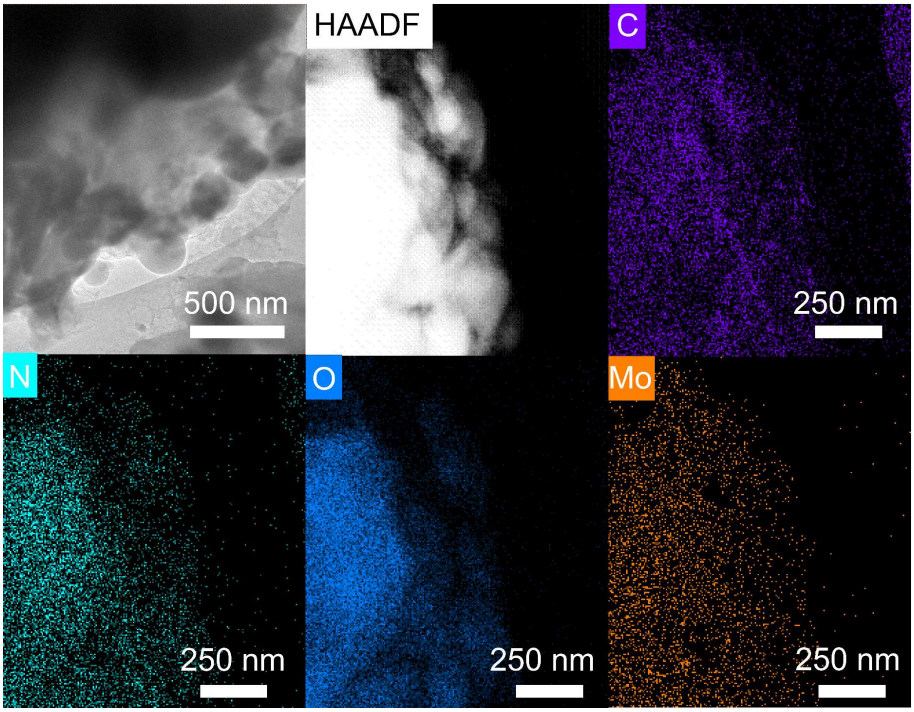


Fig. S16 TEM and mapping profiles of the Mo@C/AC catalyst

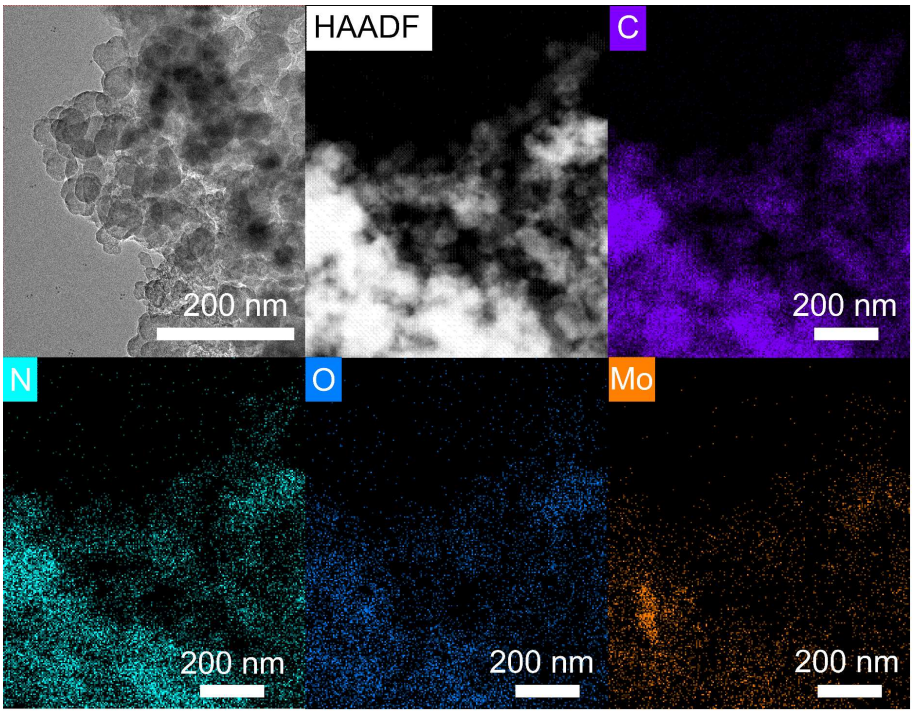


Fig. S17 TEM and mapping profiles of the Mo@C/VC catalyst

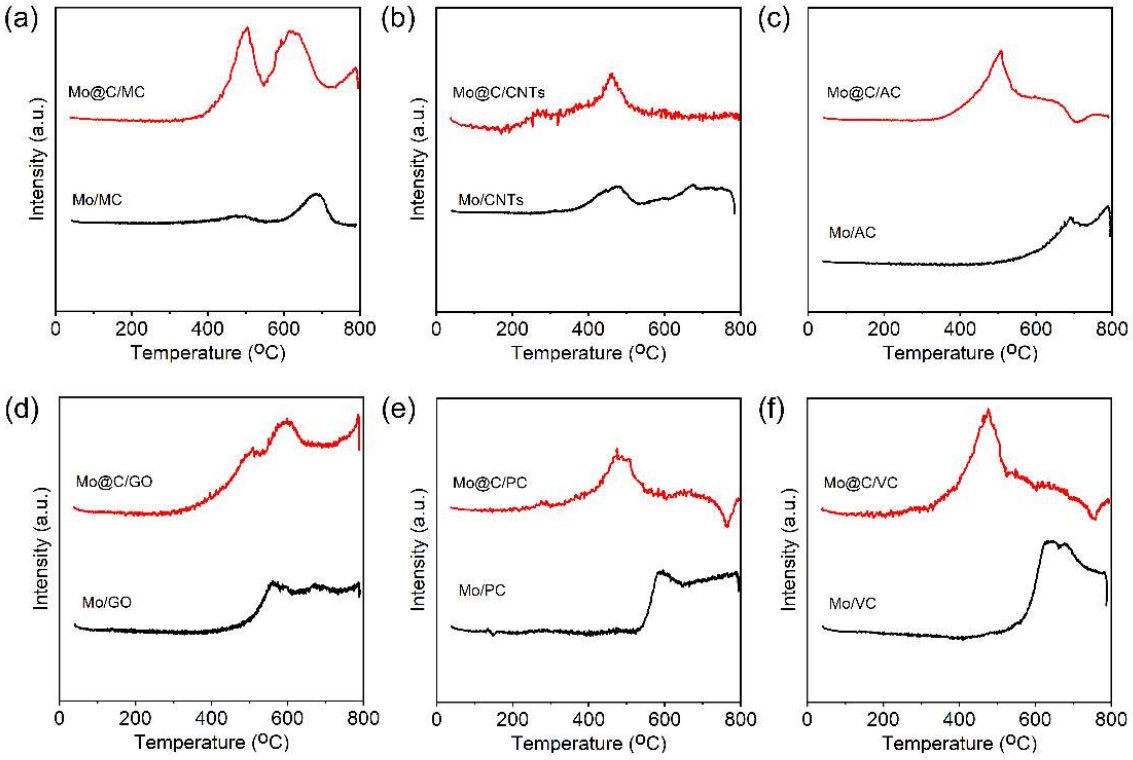


Fig. S18 H_2-TPR profiles of the catalysts containing different carbon matrices

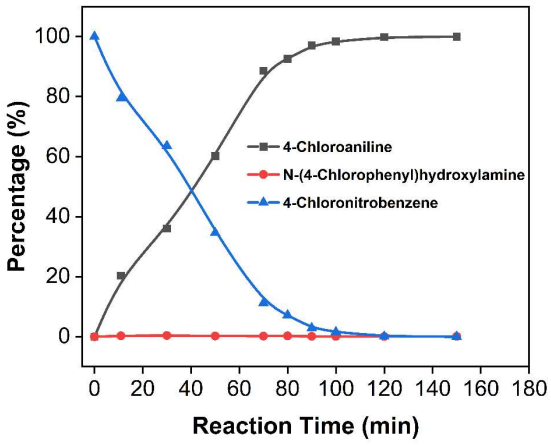


Fig. S19 The yields of *p*-CNB and *p*-CAN upon Mo@C/MC catalyst. Reaction conditions: 0.25 mmol *p*-CNB in 5 mL ethanol/H_2O (V/V = 1: 4) with 50 mg catalyst reacted at 100 °C, 5 bar H_2 for 3 h. The identity of the products was further determined by HPLC.

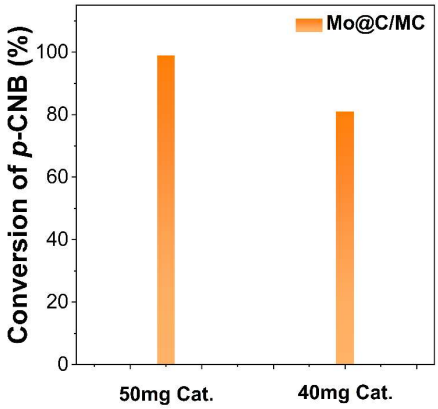


Fig. S20 Catalyst usage on Mo@C /MC. Reaction conditions: 0.25 mmol *p*-CNB in 5 mL ethanol/H_2O (V/V = 1:4) with catalyst reacted at 100 °C, 5 bar H_2 for 3 h. The identity of the products was further determined by HPLC.

Table S1 Properties of the catalysts.

Catalyst	S_{BET}/m^2 g^{-1}	V_{Total}/cm^3 g^{-1}	D_p/nm	V_{Micro}/cm^3 g^{-1}	V_{ultra}/cm^3 g^{-1}
Mo@C/MC	116	0.07	2.04	0.02	0.03
Mo@C	287	0.28	3.25	0.01	0.25
Mo/MC	3	0.01	7.98	0	0.01

Table S2 Element amount of the catalysts by XPS.

Catalyst	Atomic %				
	C	N	O	S	Mo
Mo@C/MC	86.87	5.05	6.51	0.23	1.34
Mo@C	49.39	11.35	33.97	1.66	3.64
Mo/MC	86.28	4.35	7.4	0.31	1.66

Table S3 The relative content of Mo species in the catalysts determined by XPS.

Catalyst	Mo^{4+}(area %)	Mo^{6+}(area %)
Mo@C/MC	83.5	16.5
Mo@C[a]	56.9	27.6
Mo/MC	26.2	73.8

[a] The total area of the Mo@C including 15.5% of S1s , 56.9% of Mo^{4+}, and 27.6% of Mo^{6+}.

Table S4 Investigation of Mo amount before and after ball milling treatment.

Catalyst	Total Mo amount [c] /%	Mo amount at surface [d]/%
Mo@C/MC	4.7[a] /4.6[b]	1.3[a] / 0.5 [b]
Mo@C	29.2[a] /30.8[b]	3.6[a] / 4.0[b]

[a] The data was measured using raw samples that have not been ball milled,
[b] The data was measured using processed samples with ball milling at the condition of 500 r/min and 8 h using a 50 mL agate jar by the Planetary Ball Mill instrument.
[c] The data was detected by ICP-OES.
[d] The data was detected by XPS.

Table S5 Investigation of surface Mo distribution before and after ball milling treatment.

Catalyst	Surface distribution [a]/%	
	Before ball milling	After ball milling
Mo@C/MC	27.7	10.9
Mo@C	12.3	13.0

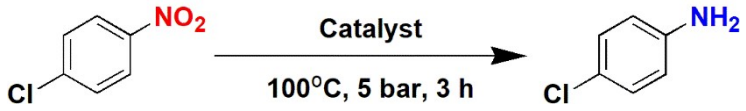
[a] Data was obtained using Mo amount detected from XPS result divided by that from ICP-OES result.

Table S6 Investigation of surface Mo dispersion before and after ball milling treatment by CO-pulse adsorption.

Catalyst	Metal dispersion /%	Metal surface area /m^2 g^{-1}	Average particle diameter /nm
Mo@C/MC	6.4[a]/6.3[b]	29.5[a]/28.9[b]	19.9[a]/20.3[b]
Mo@C	2.4[a]/2.7[b]	3.3[a]/3.7[b]	53.4[a]/47.1[b]

[a] The data was measured using raw samples that have not been ball milled
[b] The data was measured using processed samples with ball milling at 500 r/min for 8 h using a 50 mL agate jar by the Planetary Ball Mill instrument.

Table S7 Catalytic performance of *p*-CNB hydrogenation with different amount of protein-Mo networks[a]



Entry	Catalyst	*Conv.* (%)	*Sel.* (%)
1	Mo@C/MC	>99	>99
2	Mo@C/MC[b]	57.5	99
3	Mo@C	12	99

[a] Reaction conditions: 0.25 mmol *p*-CNB in 5 mL ethanol/H_2O (V/V = 1:4) with 50 mg catalyst reacted at 100 °C, 5 bar H_2 for 3 h.
[b] The catalyst was prepared by reducing the amount of protein-Mo networks ($Na_2MoO_4 \cdot 2H_2O$: 150 mg and egg white: 3.5 g).

Table S8 Properties of the catalysts with different types of protein-coated carbon matrices.

Catalyst	S_{BET}/m^2 g^{-1}	V_{Total}/cm^3 g^{-1}	D_p/nm
Mo@C/PC	90	0.23	5.39
Mo@C/VC	108	0.24	4.92
Mo@C/CNTs	58	0.30	12.8
Mo@C/GO	16	0.03	4.99
Mo@C/AC	41	0.06	5.63

Table S9 The carbon yield of catalysts [a].

Catalyst	Carbon yield/ %
Mo@C/MC	56.0%
Mo@C	26.7%

[a] Data was obtained using mass detected from the dry catalyst after pyrolysis divided by that from the fresh dry precursor.

Table S10 Investigation of Mo amount before and after reaction [a].

Catalyst	Total Mo amount/%	
	Before reaction	After reaction
Mo@C/MC	4.7%	4.1%

[a] The data was detected by ICP-OES.