

Electronic Supplementary Information (ESI)

**Enhancing reductive C-N coupling of nitrocompounds through
interfacial engineering of MoO₂ in thin carbon layers**

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1. Experimental

1.1. Chemicals

Ammonium heptamolybdenum tetrahydrate (AR, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$), Phosphomolybdic acid n-Hydrate (AR, $\text{H}_3\text{Mo}_{12}\text{O}_{40}\text{P}$), Molybdenyl acetylacetonate (AR, $\text{C}_{10}\text{H}_{14}\text{MoO}_6$), Sodium molybdate (AR, MoNa_2O_4) and Tetraethylorthosilicate (AR, TEOS) were purchased from Sinopharm Chemical Reagent Co., Ltd. Bromo-3-nitrobenzene, p-chloronitrobenzene, 5-Fluoro-2-nitroanisole, 2-Nitrofluorene, 4-Phenoxyphenylboronic acid, 4-(Phenylcarbonyl)phenylboronic acid, Phenylboric acid and 4-methoxy-phenylboric acid were purchased from Bidepharm. Dodecyl amine (DDA, $\geq 98\%$) was commercially obtained from Aladdin., Triphenylphosphine (PPh_3), ethanol anhydrous, aqueous ammonia, 3-Hydroxytyramine hydrochloride and methanol (gradient grade for HPLC) were purchased from Energy Chemical company. Toluene, Cyclopentyl anisole (CPME), dichloromethane (CH_2Cl_2) and acetonitrile were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were commercially available and utilized without further purification.

1.2. Synthesis of $\text{Mox}@\text{SiO}_2$ nanosphere

The typical preparation procedure was as follows: 5 mL of ammonia water was added to a beaker containing 100 mL of anhydrous ethanol and 30 mL of deionized water. The mixture was stirred for 5 min, and then 5 mL of tetraethyl orthosilicate (TEOS) was added and stirred for 1 hour to obtain solution A. In a separate beaker, 0.5 g of dopamine hydrochloride was added to 5 mL of anhydrous ethanol and 5 mL of deionized water. After thorough stirring, x mmol of molybdenum source ($x=0.6, 0.8, 1.0$; molybdenum sources: phosphomolybdate, sodium molybdate, ammonium molybdate, molybdenum acetylacetonate) was added to obtain solution B. Solution B was then slowly added drop by drop to solution A (over about 10 min) and stirred at room temperature for 36 hours. The resulting brown precipitates were obtained by centrifugation, followed by washing with ethanol and deionized water, and then drying. The samples were ground and placed in a tubular furnace with a quartz tube for programmed thermal treatment under a nitrogen atmosphere ($5\text{ }^\circ\text{C}/\text{min}$) at $600/700/800/900^\circ\text{C}$ for 3 h to obtain black powder. The corresponding products were

denoted as MoSm/C@SiO₂, MoAm/C@SiO₂, MoMa/C@SiO₂ (x=0.8, thermal treatment temperature is 700 °C), Mo_{0.6}/C@SiO₂, Mo_{0.8}/C@SiO₂, Mo_{1.0}/C@SiO₂ (thermal treatment temperature is 700 °C), Mo_{0.8}/C@SiO₂-600, Mo_{0.8}/C@SiO₂-700, Mo_{0.8}/C@SiO₂-800, and Mo_{0.8}/C@SiO₂-900, respectively. For Mo_{0.8}@SiO₂-O₂, the same synthesis method as Mo_{0.8}/C@SiO₂-700 was used, with the only difference being the annealing atmosphere changed to air.

1.3. Characterizations

Field Emission Scanning Electron Microscopy (SEM, Zeiss Germany) was used to study the morphology of the samples. Transmission electron microscopy (TEM) images were collected on a JEM-2010 EX microscope (JEOL, Tokyo, Japan) equipped with EDX. The wide-angle X-ray diffraction patterns were collected by XRD-6000X (Shimadzu Corporation, Tokyo, Japan) equipped with a rotating anode and Cu K α radiation ($\lambda = 0.154$ nm). Raman spectra were collected on a Spex 1877 D triplemate spectrograph with 2 cm⁻¹ resolution. The X-ray photoelectron spectra (XPS) were recorded on a PHI 5000 Versa Probe X-ray photoelectron spectrometer (ULVAC-PHI, Kanagawa, Japan) equipped with Al K α radiation (1486.6 eV). The C1s peak at 284.6 eV was used as the reference for binding energies. The structural properties of catalysts were measured by BELSORP -MAX volumetric adsorption analyzer (BEL Japan, Osaka, Japan). The surface area and pore volume were calculated by Brunauer-Emmett-Teller (BET) method, and the pore size was calculated by the BJH model. Electrochemical cyclic voltammetry curve (CV spectra, Chenhua CHI760E) was employed to study the electron transfer capacity. The working electrode was prepared by dispersing 4 mg of the catalyst in a mixed solution of 450 μ L of ethanol, 500 μ L of deionized water, and 50 μ L of Nafion solution. The dispersion process involved ultrasound treatment for 1 h to ensure thorough mixing of the catalyst in the solution. Subsequently, 5 μ L of the dispersed solution was dropped onto the surface of the glassy carbon electrode and allowed to dry in the air. A platinum foil was used as the counter electrode, and an Ag/AgCl electrode served as the reference electrode. The electrolyte solution used was 0.05 mol L⁻¹ Na₂SO₄.

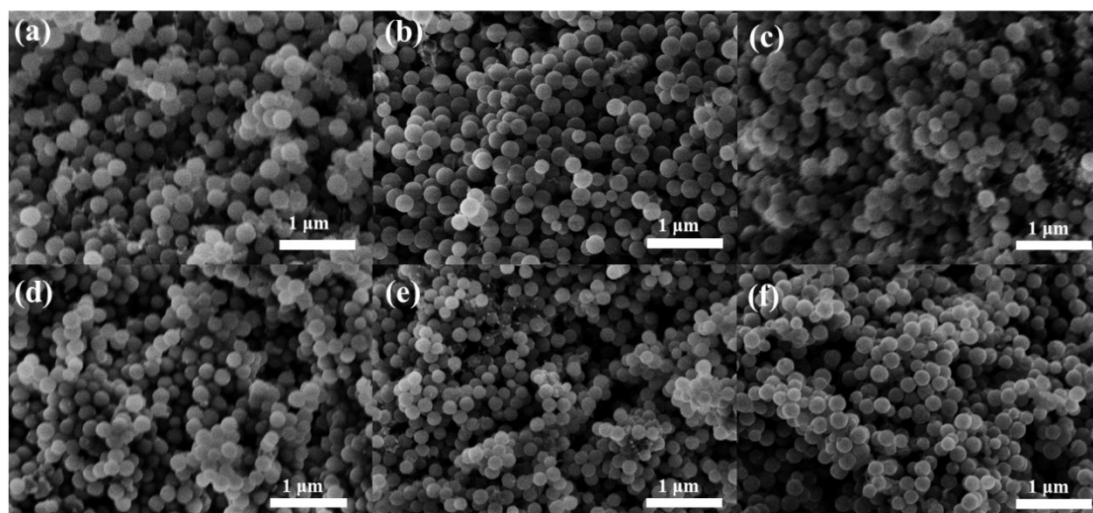


Fig. S1 Representative SEM images of $\text{Mo}_{0.8}/\text{C}@/\text{SiO}_2\text{-600}$ (a), $\text{Mo}_{0.8}/\text{C}@/\text{SiO}_2\text{-700}$ (b), $\text{Mo}_{0.8}/\text{C}@/\text{SiO}_2\text{-800}$ (c), $\text{Mo}_{0.8}/\text{C}@/\text{SiO}_2\text{-900}$ (d), $\text{Mo}_{0.6}/\text{C}@/\text{SiO}_2$ (e), $\text{Mo}_{1.0}/\text{C}@/\text{SiO}_2$ (f).

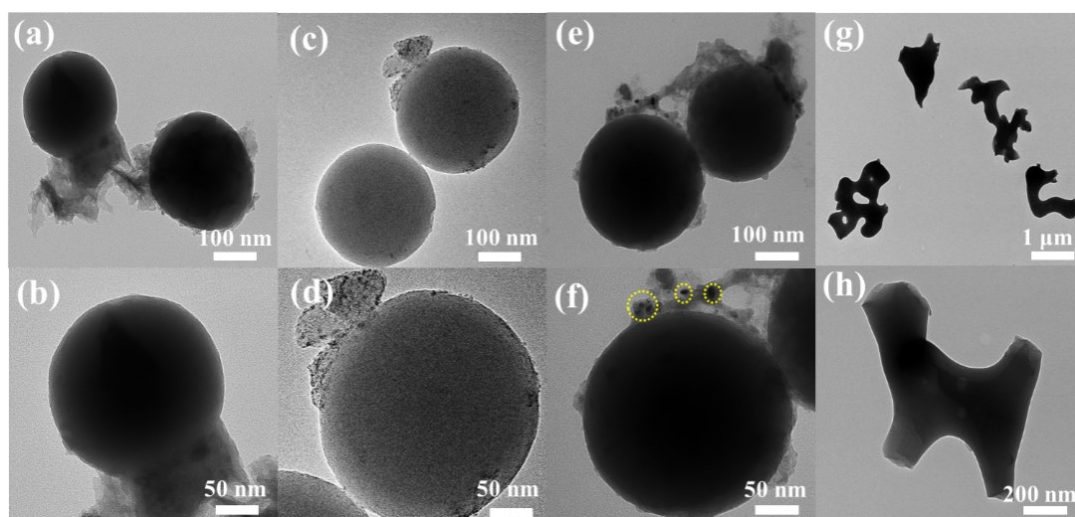


Fig. S2 Representative TEM images of $\text{Mo}_{0.8}/\text{C}@/\text{SiO}_2\text{-600}$ (a, b), $\text{Mo}_{0.8}/\text{C}@/\text{SiO}_2\text{-700}$ (c, d), $\text{Mo}_{0.8}/\text{C}@/\text{SiO}_2\text{-800}$ (e, f) and $\text{Mo}_{0.8}@/\text{SiO}_2\text{-O}_2$ (g, h).

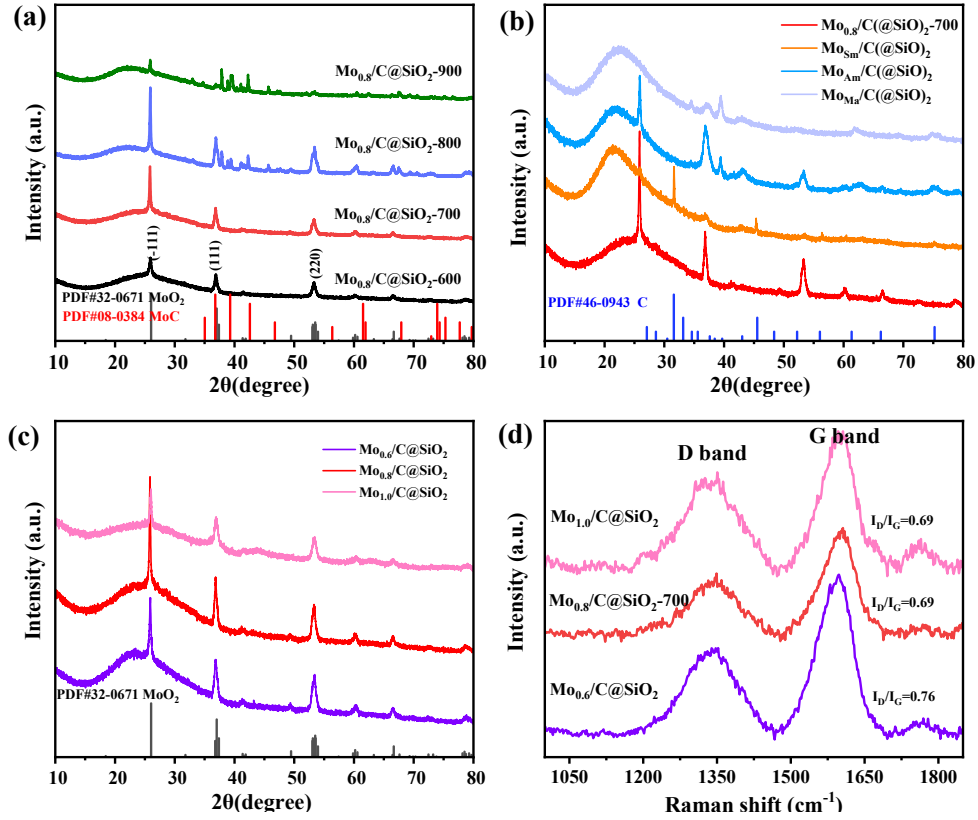


Fig. S3 Wide-angle XRD patterns of (a) $\text{Mo}_{0.8}/\text{C}@/\text{SiO}_2$ -600, $\text{Mo}_{0.8}/\text{C}@/\text{SiO}_2$ -700, $\text{Mo}_{0.8}/\text{C}@/\text{SiO}_2$ -800 and $\text{Mo}_{0.8}/\text{C}@/\text{SiO}_2$ -900, (b) $\text{Mo}_{0.8}/\text{C}@/\text{SiO}_2$ -700, $\text{Mo}_{\text{Sm}}/\text{C}@/\text{SiO}_2$, $\text{Mo}_{\text{Am}}/\text{C}@/\text{SiO}_2$, and $\text{Mo}_{\text{Ma}}/\text{C}@/\text{SiO}_2$, and (c) $\text{Mo}_{0.6}/\text{C}@/\text{SiO}_2$, $\text{Mo}_{0.8}/\text{C}@/\text{SiO}_2$, and $\text{Mo}_{1.0}/\text{C}@/\text{SiO}_2$. (d) Raman spectra of $\text{Mo}_{1.0}/\text{C}@/\text{SiO}_2$, $\text{Mo}_{0.8}/\text{C}@/\text{SiO}_2$ -700 and $\text{Mo}_{0.6}/\text{C}@/\text{SiO}_2$.

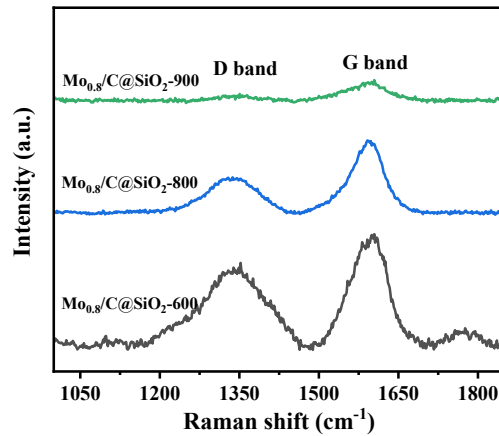


Fig. S4 Raman spectra of $\text{Mo}_{0.8}/\text{C}@/\text{SiO}_2$ -600, $\text{Mo}_{0.8}/\text{C}@/\text{SiO}_2$ -800 and $\text{Mo}_{0.8}/\text{C}@/\text{SiO}_2$ -900 samples.

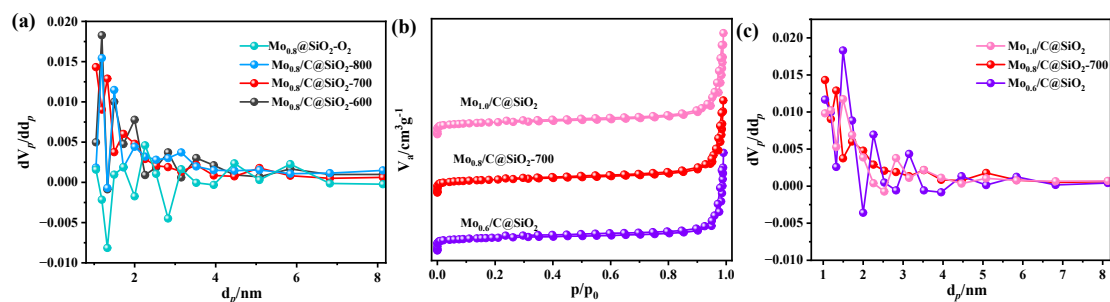


Fig. S5 (a) Pore diameter distribution of the different samples; (b) N_2 adsorption-desorption isotherm of the optimal and other comparative catalysts; (c) Pore diameter distribution of the different samples.

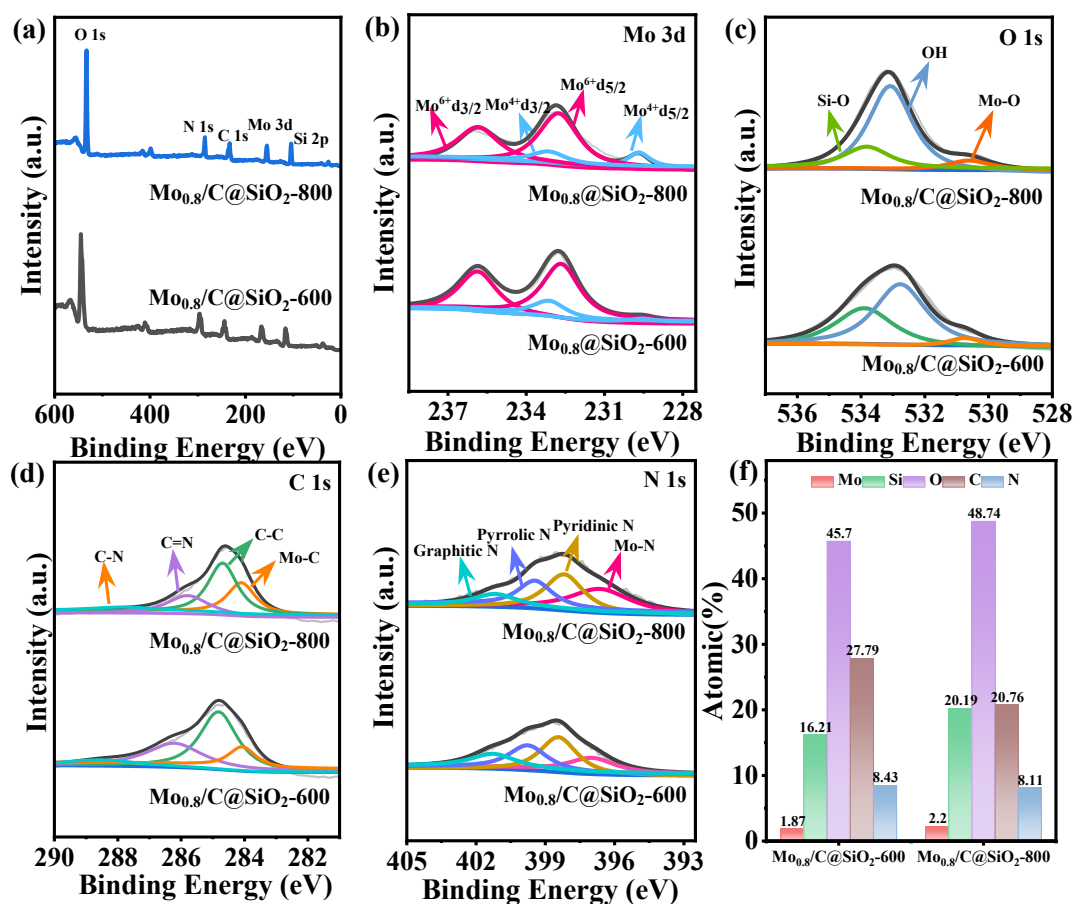


Fig. S6 XPS spectra of $\text{Mo}_{0.8}/\text{C}@/\text{SiO}_2\text{-700}$: (b) Mo 3d core level, (c) O 1s core level, (d) C 1s core level, (e) N 1s core level and (f) atomic ratio of the samples derived from XPS data.

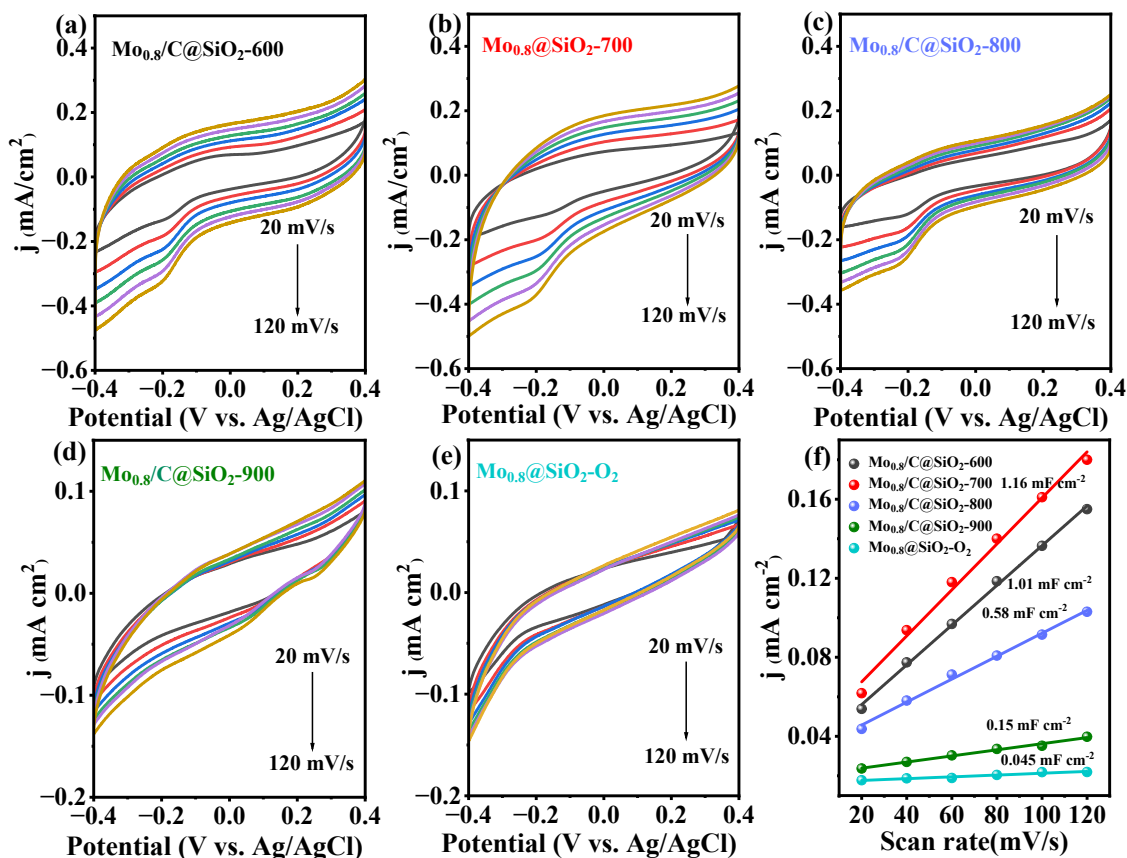


Fig. S7 CV curves of Mo_x/C@SiO₂ samples with scan rate from 20 mV/s to 120 mV/s (a-e); Linear fits of capacitive currents versus scan rates for the extraction of *C*_{dl} (f). $ECSA = (C_{dl} \cdot A) / C_s$ (*A* is the area of the working electrode; *C*_s = 0.04 mF cm⁻²)

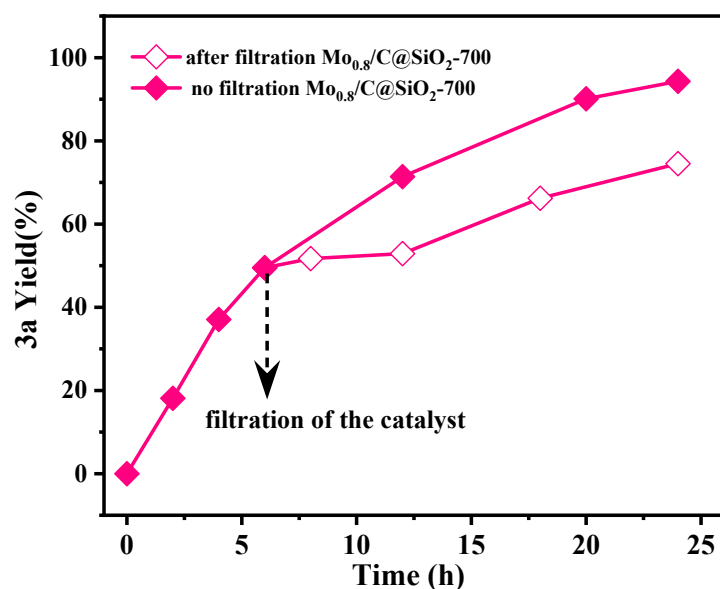


Fig. S8 Leaching experiments of Mo_{0.8}/C@SiO₂-700. Reaction conditions: Mo_{0.8}/C@SiO₂-700 was used as the catalyst, 1a (0.2 mmol), 1b (0.3 mmol), using toluene as solvent (2 mL), under N₂ atmosphere at 100 °C for 24 h.

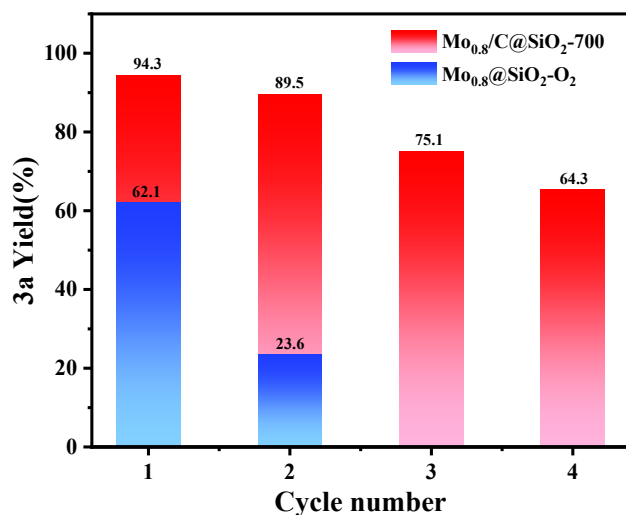


Fig. S9 Recycled coupling reaction tests of Mo_{0.8}@SiO₂-O₂ and Mo_{0.8}/C@SiO₂-700 for the synthesis of 3a product.

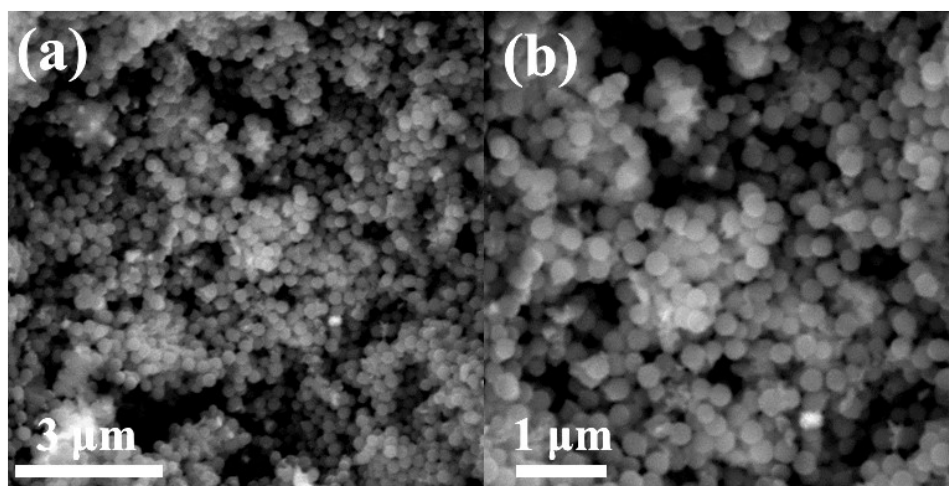


Fig. S10 The SEM images of spent Mo_{0.8}/C@SiO₂-700 for reductive C-N coupling.

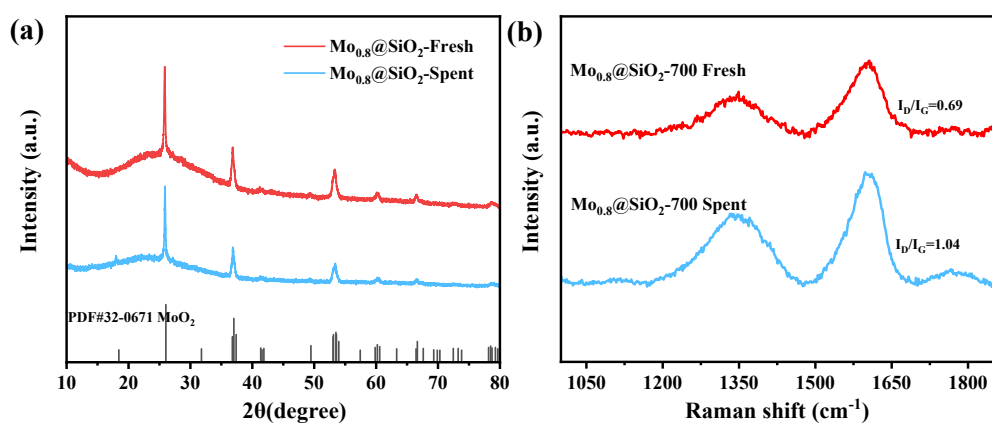


Fig. S11 XRD patterns and Raman spectra of fresh and spent Mo_{0.8}/C@SiO₂-700 for

reductive C-N coupling.

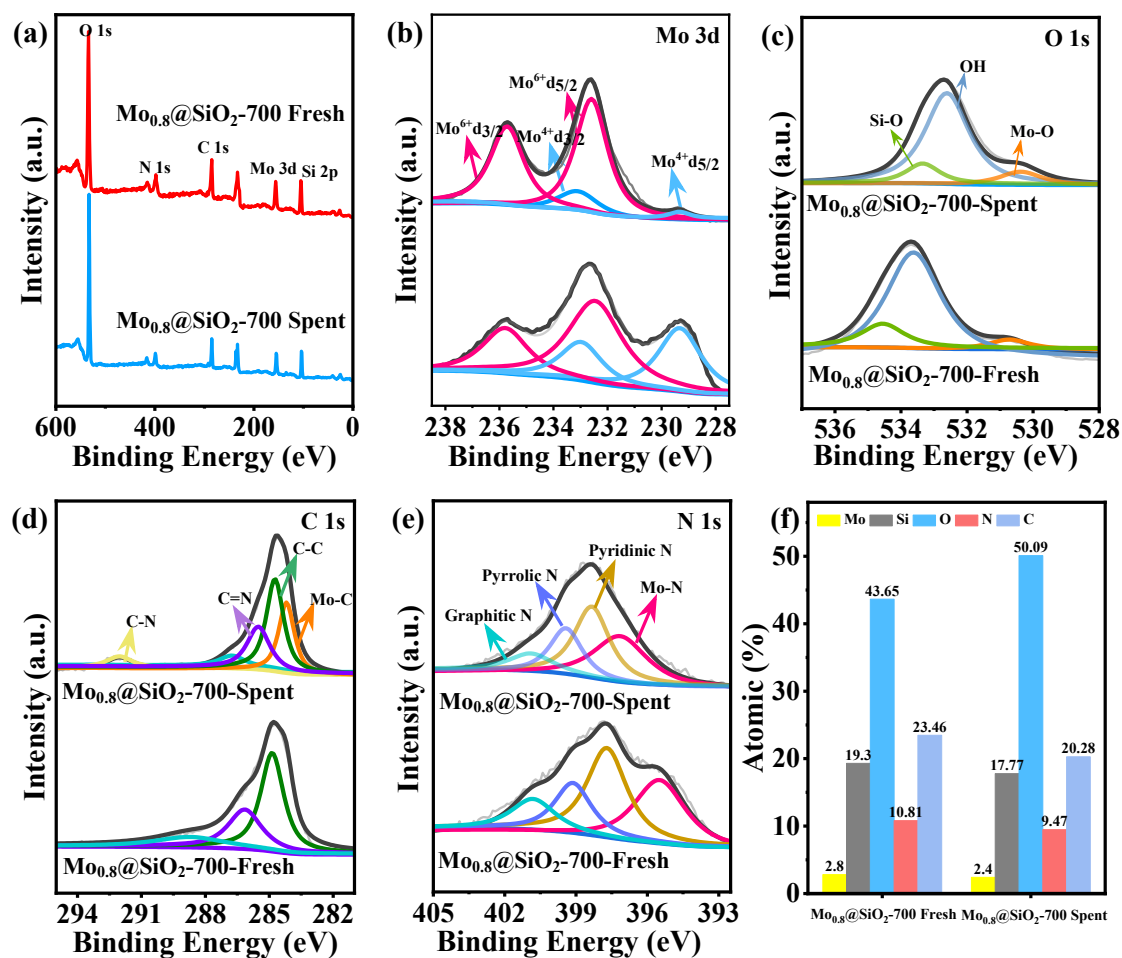
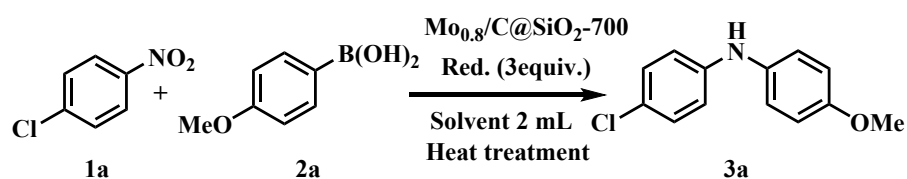


Fig. S12 High-resolution XPS spectra of fresh and spent $\text{Mo}_{0.8}/\text{C}@/\text{SiO}_2\text{-700}$ for reductive C-N coupling. (a) Survey spectra, (b) Mo3d, (c) O1s, (d) C1s, (e) N1s and (f) atomic ratio of the samples derived from XPS data.

Table S1 Textural properties of Mo/C@SiO₂.

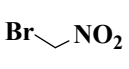
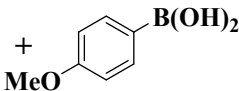
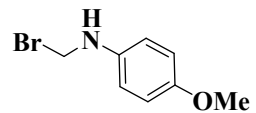
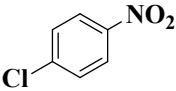
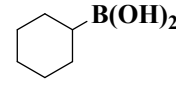
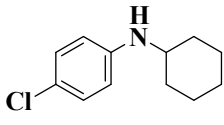
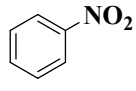
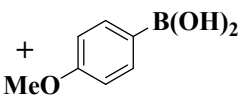
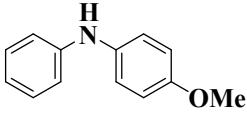
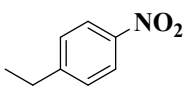
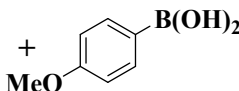
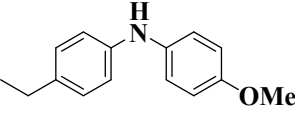
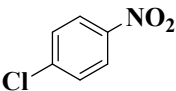
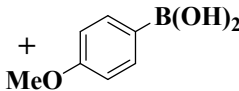
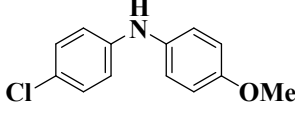
Samples	S _{BET} ^a (m ² g ⁻¹)	Average pore diameter (nm)	V _{total} ^b (cm ³ g ⁻¹)	Mo content ^c (wt%)
Mo _{0.8} /C@SiO ₂ -600	40.49	15.45	0.156	---
Mo _{0.8} /C@SiO ₂ -700	41.83	32.54	0.1228	31
Mo _{0.8} /C@SiO ₂ -800	32.24	17.79	0.143	---
Mo _{0.6} /C@SiO ₂	52.11	11.08	0.144	20
Mo _{1.0} /C@SiO ₂	49.08	12.54	0.154	44
Mo _{0.8} @SiO ₂ -O ₂	5.06	13.70	0.017	---

^aS_{BET} represents specific surface area derived from BET method; ^bV_{total} represents total pore volume; ^cmeasured by ICP-OES analysis.

Table S2. Optimization of reaction conditions for reductive C-N coupling.

Entry	T (°C)	Time (h)	Solvent	Catalyst (mg)	Yield (%)
1	100	24 h	Toluene	10	94.3 %
2	100	24 h	CPME	10	54.4 %
3	100	24 h	Acetonitrile	10	42.4 %
4	100	24 h	CH ₂ Cl ₂	10	38.2 %
5	100	24 h	Ethanol	10	12.6 %
6	100	12 h	Toluene	10	59.4 %
7	60	24 h	Toluene	10	20.8 %
8	80	24 h	Toluene	10	61.0 %
9	120	24 h	Toluene	10	95.1 %
10	100	24 h	Toluene	8	56.1 %
11	100	24 h	Toluene	12	89.2 %

Table S3 The substrate scope used $\text{Mo}_{0.8}/\text{C}@/\text{SiO}_2-700$ as the catalyst.

$\text{R}_1\text{-NO}_2$	+	$\text{R}_2\text{-B(OH)}_2$	$\xrightarrow[\text{Solvent 2 mL, 100 }^\circ\text{C}]{\text{Mo}_{0.8}/\text{C}@/\text{SiO}_2-700, \text{PPh}_3}$	$\text{R}_1\text{-N}^{\text{H}}\text{-R}_2$	Yield%
	+		\longrightarrow		98.3%
	+		\longrightarrow		72.1%
	+		\longrightarrow		84.3%
	+		\longrightarrow		34.0%
	+		\longrightarrow		94.3%

Reaction conditions: reactants: nitrocompounds (0.2 mmol), boric compounds (0.3 mmol), using toluene as solvent (2 mL), under N_2 atmosphere at $100\text{ }^\circ\text{C}$ for 24 h.