Supporting Information

Single-Atom Molybdenum Immobilized on Photoactive Carbon Nitride as Efficient Photocatalysts for Ambient Nitrogen Fixation in Pure Water

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Figure S7. PXRD patterns of PCN, 1-, 2- and 3-Mo-PCN, the weak diffraction peaks around 13° corresponding to the diffraction of in-plane repeating heptazine units, and a dominant peak at 27.7° related to (002) interlayer reflection of a graphitic structure.



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Figure S14. FT-EXAFS fitting curves of a) 1-Mo-PCN and b) 2-Mo-PCN at Mo K-edge.



Figure S15. a) N K-edge and b) C K-edge XANES spectra of Mo-PCN. In N K-edge spectrum, the peak A at 397.1 eV and peak B at 400.0 eV were mainly due to pyridinic π^* and graphitic π^* transitions. The peak C at 406.2 eV suggests the formation of C-N-C or C-N σ^* bond. In the C K-edge spectrum of Mo-PCN, peak A (ca. 286.6 eV) derived from C-C π^* (ring) excitations, and peak C (ca. 292.5 eV) originated from C-C σ^* (ring) transitions. These results suggest that the graphitization happens during the urea pyrolysis process. With increasing the Mo contents, the intensity of peak A in N and C K-edge spectra (at 397.1 eV and 286.6 eV, respectively) decreases obviously as the reduction in number of π^* bond. This result confirms that the introduction Mo centers can also locally alter the electronic structure of PCN matrix.



Figure S16. N 1s XPS spectra of the 1- and 2-Mo-PCN.



Figure S17. Structural model of Mo-PCN.



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Figure S20. H_2 or N_2H_4 was negligible in the product of photocatalytic N_2 fixation with 3-Mo-PCN as photocatalyst.



Figure S21. ¹H NMR spectra of both NH_4^+ and ${}^{15}NH_4^+$ produced from the N₂ reduction experiments using N₂ and ${}^{15}N_2$ as the feeding gases, respectively. The ¹H NMR spectrum of solution in N₂ shows a nearly 1:1:1 triplet pattern with the coupling constant of $J_{N-H} = 52$ Hz. When ${}^{15}N_2$ was used as the feeding gas, a doublet pattern with the coupling constant of $J_{N-H} = 72$ Hz can be detected. Both of these agree with the standard solution of NH₄Cl with ${}^{15}N$ enrichment of 10%.



Figure S22. Time course of photocatalytic NH_3 evolution with N_2 or Ar in pure water over 3-Mo-PCN.



Figure S23. HRTEM images of 3-Mo-PCN after photocatalytic reaction.



Figure S24. Element mapping images of 3-Mo-PCN after photocatalytic reaction.



Figure S25. PL spectra of PCN, 1-, 2- and 3-Mo-PCN at 298 K.



Figure S26. Temperature-programmed N_2 desorption profiles on PCN and 3-Mo-PCN. The temperature-programmed desorption (TPD) measurements were further performed to understand N_2 adsorption on the surface of 3-Mo-PCN. As result, it can be obviously observed that the peak for desorption of physically adsorbed N_2 were observed at about 125 °C for both PCN and 3-Mo-PCN. However, the desorption peak at 275 °C related to the chemisorbed N_2 was only observed on the Mo-PCN SAC.



Figure S27. Free energy diagrams for N_2 reduction catalyzed by Mo-PCN through distal (a) and alternating (b) mechanisms.



Figure S28. Optimized N₂ adsorption model on pure PCN and Mo-PCN.



Figure S29. Schematic depiction of distal (blue) and alternating (red) reaction pathways for N₂ reduction to NH₃ catalyzed by Mo-PCN SAC.



Figure S30. Optimized structures of the intermediates in N_2 reduction catalyzed by Mo-PCN SAC.



Figure S31. The pictures for chromogenic reaction of Nessler's reagent in pure water (pH 5) extracted from the photocatalytic N_2 fixation system at 0, 4, 8 and 12 h (from left to right), respectively. To make sure that the absorbance for each solution is within the linear range of the calibration curve, the filtrate after the photocatalytic reaction was diluted five times with double distilled water.



Figure S32. Calibration curves for NH₃ assay using a) Nessler's reagent and b) ion chromatography methods.



Figure S33. Kubelka–Munk plot (a, b, c) and XPS valence band spectra (d, e, f) for these Mo-SACs. Kubelka–Munk plot demonstrates that the optical band gaps are about 2.97 eV for these for Mo-PCN catalysts. XPS valence band spectra shows the VB maximum edge of 1-Mo-PCN, 2-Mo-PCN and 3-Mo-PCN to be located at 2.47 eV, 2.40 eV and 2.41 eV, respectively.

2. Supplementary Tables

Catalysis	Reaction medium	Scavenge r	Light source	$ NH_3 evlotion rate (µmol gcat-1 h-1) $	Reference	
3-Mo-	H ₂ O (l)	No	300 W Xenon	50.9	This work	
PCN	20 °C	ethanol	lamp	830		
Fe-doped g-C ₃ N ₄	H ₂ O (l) 30 °C	ethanol	250 W high- pressure sodium lamp, 400-800 nm	300	<i>Appl. Catal. B,</i> 2017, 201 , 58	
JRC-TIO- 6(rutile)	H ₂ O (l) 25 °C	No	300 W high- pressure Hg lamp, $\lambda > 280$ nm	0.73	J. Am. Chem. Soc., 2017, 139 , 10929	
Cu-CN	H ₂ O (l) ambient temperatur e	ethanol	300 W Xenon lamp, $\lambda > 420$ nm	186	<i>Sci China Chem.</i> , 2018, 61 , 1187	
CuCr-NS	H ₂ O (1) 25 °C	No	300 W Xenon lamp, $\lambda > 400$ nm	57.1	<i>Adv. Mater.</i> , 2017, 29 , 1703828	
MWO-1	H ₂ O (l) room temperatur e	No	300 W Xenon	61.9	J. Am. Chem.	
		Na ₂ SO ₃	lamp	195.5	<i>Soc.</i> , 2018, 140 , 9434	
Bi ₅ O ₇ Br	H ₂ O (1) 25 °C	No	300 W Xenon lamp, $\lambda > 400$ nm	1380	<i>Adv. Mater.</i> , 2017, 29 , 1701774	
BiOBr	H ₂ O (1) 25 °C	No	300 W Xenon lamp, $\lambda > 420$ nm	223.3	J. Am. Chem. Soc., 2015, 137 , 6393	
AuRu0.3 1	$\begin{array}{c} H_2O(l),\\ N_2(2)\\ atm), room\\ temperatur\\ e \end{array}$	No	400 mW cm ⁻²	101.4	J. Am. Chem. Soc., 2019, 141 , 7807	
TR-0.1	H ₂ O (l) 25 °C	ethanol	300 W high pressure xenon lamp	3.31	ACS Sustainable Chem. Eng., 2019, 7, 6813	

Table S1. Comparison of various photocatalysts for N_2 reduction to NH_3 .

sample	Scattering pair	CN	R(Å)	$\sigma^2(10^{-3} \text{ Å}^2)$
1 Ma DCN	Mo-N	2.2	1.75	3.3
1-1v10-FCIN	Mo-O	1.3	2.17	2.5
$2 M_{\odot} DCN$	Mo-N	2.1	1.75	3.6
2-1010-FCIN	Mo-O	1.0	2.15	2.9
2 Ma DCN	Mo-N	2.1	1.74	3.4
3-100-FCIN	Mo-O	0.8	2.16	2.0
Ma fail	Mo-Mo	8*	2.73	4.4
WIO IOII	Mo-Mo	6*	3.17	4.4
Ma	Mo-C	6*	2.08	4.1
WI0 ₂ C	Mo-Mo	12*	2.98	6.1

Table S2. Structural parameters extracted from Mo K-edge EXAFS fitting.

CN is the coordination number; R is interatomic distance (representing the bond length between Mo center and surrounding coordination atoms); σ^2 is Debye-Waller factor (a measure of thermal and static disorder in absorber-scatterer distances). Error bounds (accuracies) were estimated as CN, ±10%; Bond length, ±1%; σ^2 , ±10%. * is fixed coordination number according to the standard crystal structure.

Catalyst	Ammonia production rate (μ mol g _{cat} ⁻¹ h ⁻¹)			
Catalyst	Nessler's reagent	Ion chromatography		
3-Mo-PCN	52.4	50.9		
2-Mo-PCN	37.1	33.5		
1-Mo-PCN	16.2	15.9		

 Table S3. The calculated ammonia production rates based on different detection methods.

Table S4. Results for photocatalytic N_2 reduction to NH_3 in 6 mL pH = 5 pure water with 3 mg catalyst under the irradiation of 300 W Xenon lamp for 12 h.

Entry	catalyst	light	water	ethanol (mL)	N ₂	$\frac{\rm NH_3}{(\mu mol} \\ \rm g_{cat}^{-1})$	${ m H}_2 (\mu { m mol}\ { m g_{cat}}^{-1})$
1	PCN	+	+	-	+	< 0.1	-
2	1-Mo-PCN	+	+	-	+	190.7	
3	2-Mo-PCN	+	+	-	+	402.8	
4	3-Mo-PCN	+	+	-	+	611.2	
5		-	+	-	+	< 0.1	0
6		+	-	-	+	< 0.1	
7		+	+	-	-	< 0.1	
8		+	+	0.5	+	9954.8	