

Optimization of the NH₂-UiO-66@MoS₂ Heterostructure for Enhanced Photocatalytic Hydrogen Evolution Performance

Zenghuan Ren,^b Xinghao Zhang,^a Xiaofan Shi,^a Di Yang,^a Mei-Hui Yu,^a Wenjun Zheng^{bc} and Jijie Zhang^{*a}

^a *School of Materials Science and Engineering, Tianjin Key Laboratory of Metal and Molecule-Based Material Chemistry, Nankai University, Tianjin 300350, China.*

^b *Department of Chemistry, Key Laboratory of Advanced Energy Materials Chemistry (MOE), TKL of Metal and Molecule-based Materials Chemistry, College of Chemistry, Nankai University, Tianjin 300071, P. R. China.*

^c *Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin 300071, P. R. China.*

^{*}Corresponding author. *E-mail address:* zhangjijie@nankai.edu.cn

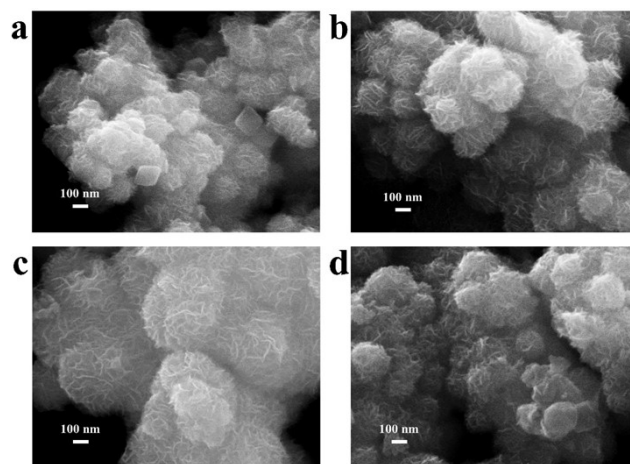


Figure S1. SEM images of (a) C-NUM-0.05; (b) C-NUM-0.1; (c) C-NUM-0.2 and (d) C-NUM-0.3.

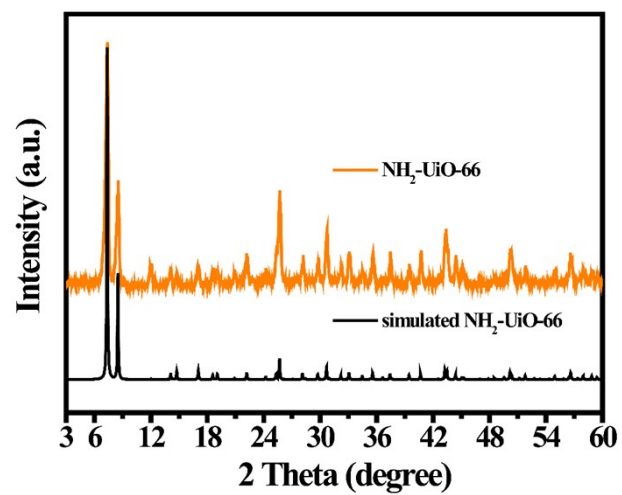


Figure S2. PXRD pattern of (a) NH₂-UiO-66 and (b) simulated NH₂-UiO-66.

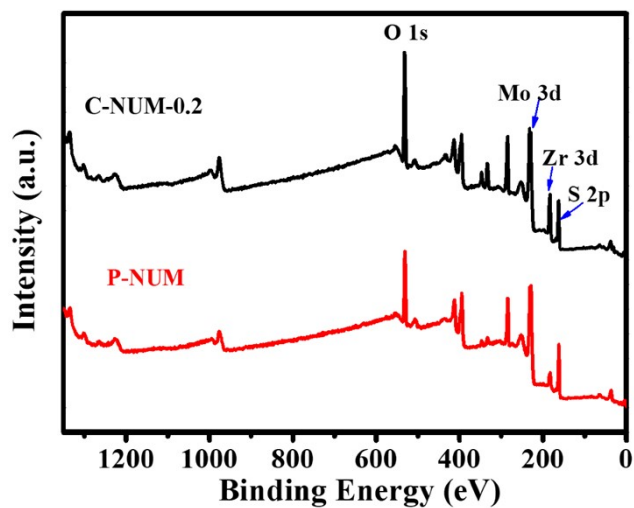


Fig. S3. Survey XPS spectra of C-NUM-0.2 and P-NUM

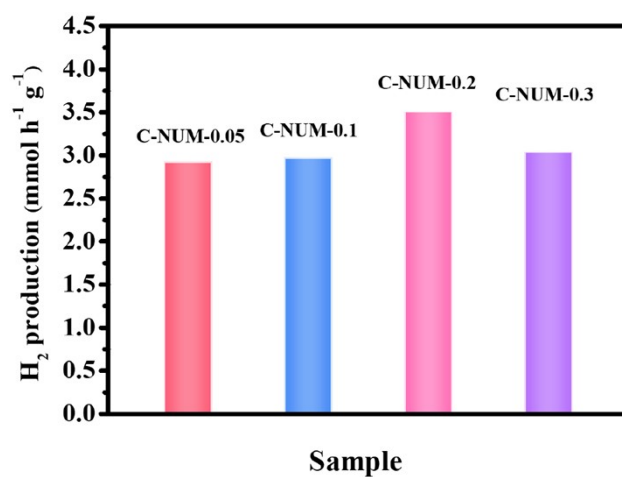


Figure S4. Hydrogen evolution performance of C-NUM-0.05; C-NUM-0.1; C-NUM-0.2 and C-NUM-0.3.

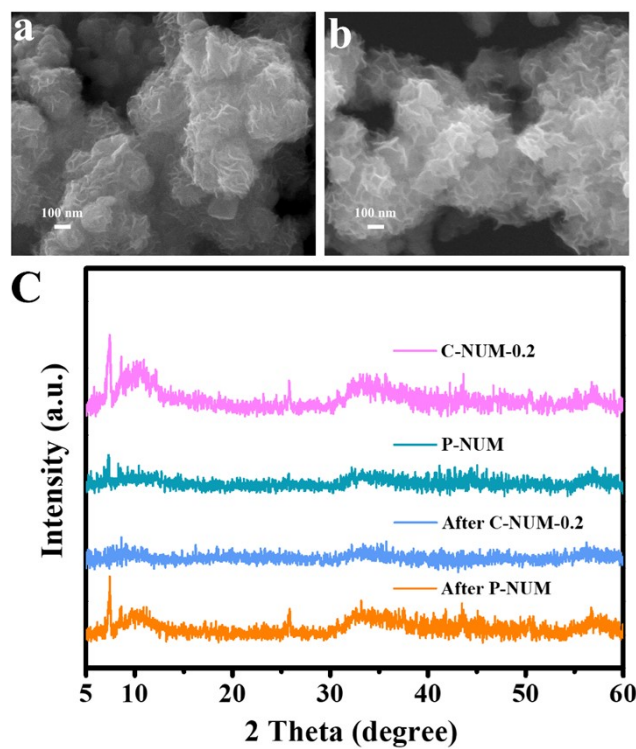


Figure S5. SEM image of (a) C-NUM-0.2 and (b) P-NUM after photocatalytic reaction; (c) PXRD pattern of C-NUM-0.2 and P-NUM before and after photocatalytic reaction.

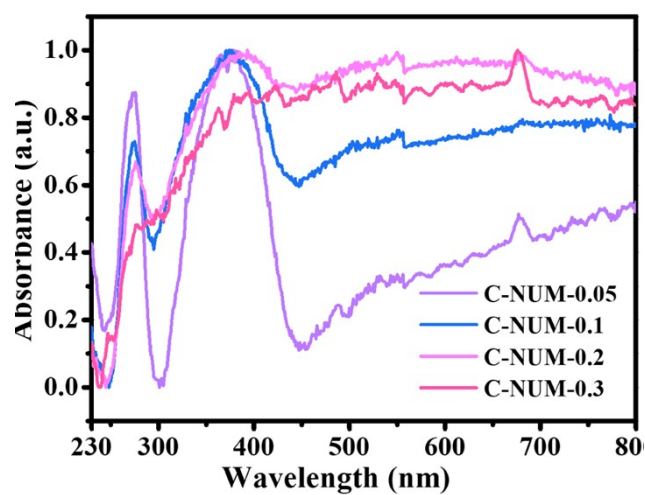


Figure S6. UV-vis spectra of C-NUM-0.05; C-NUM-0.1; C-NUM-0.2 and C-NUM-0.3.

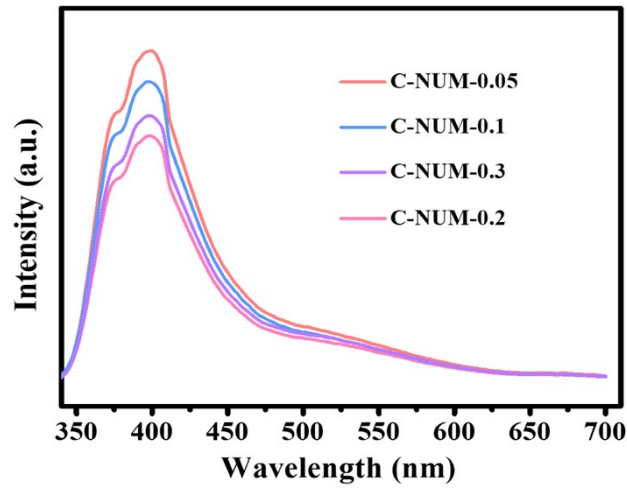


Figure S7. PL spectra of C-NUM-0.05; C-NUM-0.1; C-NUM-0.2 and C-NUM-0.3.

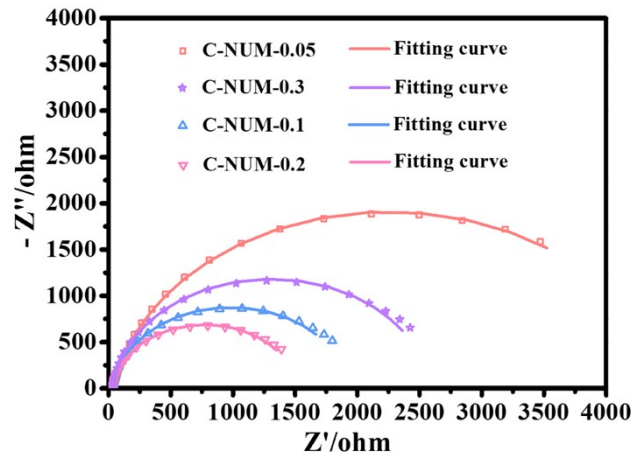


Figure S8. EIS plots of C-NUM-0.05; C-NUM-0.1; C-NUM-0.2 and C-NUM-0.3.

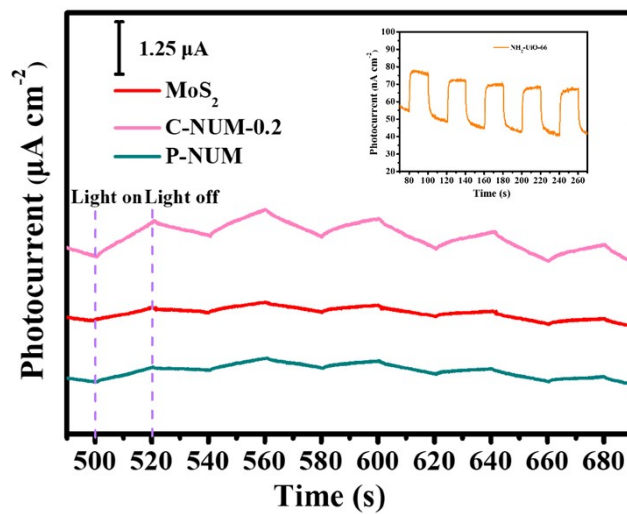


Figure S9. I-t curves of MoS₂; C-NUM-0.2; P-NUM and NH₂-UiO-66(inset).

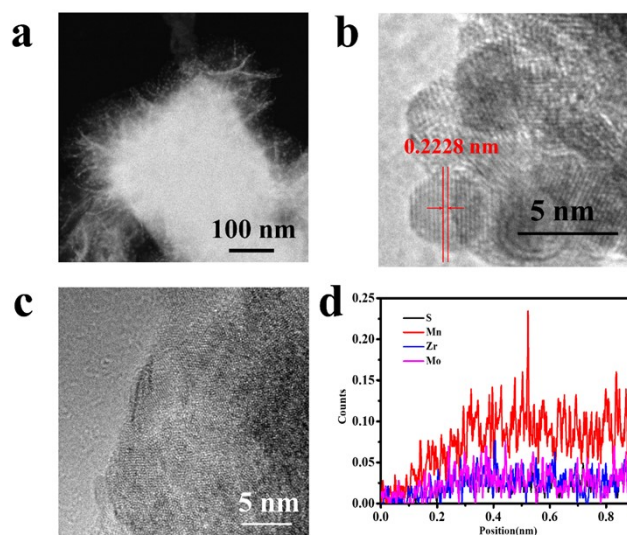


Figure S10. (a) TEM image of C-NUM-0.2/Pt, (b) HRTEM image of Pt nanoparticle, (c) TEM image of C-NUM-0.2/MnO_x, (d) EDS line scan result of C-NUM-0.2/MnO_x

Table S1. ICP-OES results for the contents of Zr and Mo.

Samples	Zr (wt %)	Mo (wt %)
C-NUM-0.05	10.96	28.15
C-NUM-0.1	6.70	34.36
C-NUM-0.2	3.71	38.53
P-NUM	3.91	38.01
C-NUM-0.3	2.72	36.39

Table S2. BJH results of NH₂-UiO-66, MoS₂, C-NUM-0.2 and P-NUM.

Samples	Adsorption (cm ³ /g)	Desorption (cm ³ /g)
NH ₂ -UiO-66	0.080	0.080
MoS ₂	0.144	0.145
C-NUM-0.2	0.077	0.077
P-NUM	0.079	0.081

Table S3. Similar reported photocatalyst

Sample	Test conditions	Light source	H ₂ production rate	Ref.
C-NUM-0.2	H ₂ O/Na ₂ S/Na ₂ SO ₃	Full spectrum	3.509 mmol g ⁻¹ h ⁻¹	This work
1T-MoS ₂ /HCN-4	TEOA	AM1.5G	2724.2 mmol g ⁻¹ h ⁻¹	[1]
CN/MoS ₂ -1	TEOA	λ ≥ 400 nm	441.3 μmol g ⁻¹ h ⁻¹	[2]
ac-MoS _x /TiO ₂	Ethanol/H ₂ O	365 nm LED	3.43 mmol h ⁻¹ g ⁻¹	[3]
1T-MoS ₂ /MIL-125-NH ₂	MeCN/TEA/H ₂ O	λ ≥ 420 nm	1454 μmol g ⁻¹ h ⁻¹	[4]
MoS ₂ -MoC@rGO/TiO ₂	CH ₃ OH/H ₂ O	UV light	575 μmol h ⁻¹ g ⁻¹	[5]
MoS ₂ /ZnO	H ₂ O/Na ₂ S/Na ₂ SO ₃	Visible light	235 μmol g ⁻¹ h ⁻¹	[6]
CdS/MoS ₂	H ₂ O/Na ₂ S/Na ₂ SO ₃	UV light	5587 μmol g ⁻¹ h ⁻¹	[7]
g-C ₃ N ₄ -MoS ₂ -ZnNi-ZIF	TEOA	λ ≥ 420 nm	77.8 μmol g ⁻¹ h ⁻¹	[8]

Table S4. Parameters of equivalent circuit for the impedance data of NH₂-UiO-66, MoS₂, C-NUM-0.2 and P-NUM.

Samples	R ₁ (Ω)	R ₂ (Ω)
NH ₂ -UiO-66	42.94	1.27*10 ⁷
MoS ₂	42.53	2456
C-NUM-0.2	35.27	1479
P-NUM	42.85	2343

Table S5. Parameters of equivalent circuit for the impedance data of C-NUM-0.05; C-NUM-0.1; C-NUM-0.2 and C-NUM-0.3

Samples	R ₁ (Ω)	R ₂ (Ω)
C-NUM-0.05	42.68	4434
C-NUM-0.1	35.29	1897
C-NUM-0.2	35.27	1479
C-NUM-0.3	38.63	2538

Reference

- [1] Y. Xiong, T. Liu, W. Liu, X. Wang, Y. Xue and J. Tian, *Int. J. Hydrogen Energy*, 2023, **48**, 7284-7293.
- [2] Y. Xu, J. Ouyang, L. Zhang, H. Long, Y. Song and Y. Cui, *Chem. Phys. Lett.*, 2023, **814**, 140331.
- [3] L. Li, D. Gao, F. Chen, X. Wang and H. Yu, *Appl. Surf. Sci.*, 2023, **608**, 155173.

- [4] T. Nguyen, S. Kampouri, B. Valizadeh, W. Luo, D. Ongari, O. Planes, A. Zuttel, B. Smit and K. Stylianou, *ACS Appl. Mater. Interfaces*, 2018, **10**, 30035-30039.
- [5] M. Pan, L. Gao, P. Wang, X. Wang and H. Yu, *J. Alloys Compd.*, 2023, **939**, 168721.
- [6] Y. Hunge, A. Yadav, S. Kang, S. Jun Lim and H. Kim, *J. Photochem. Photobiol., A*, 2023, **434**, 114250.
- [7] L. Lin, S. Huang, Y. Zhu, B. Du, Z. Zhang, C. Chen, X. Wang and N. Zhang, *Dalton Trans.*, 2019, **48**, 2715-2721.
- [8] N. Arif, Y. Z. Lin, K. Wang, Y. Dou, Y. Zhang, K. Li, S. Liu and F. T. Liu, *RSC Adv.*, 2021, **11**, 9048-9056.