Electronic Supplementary Material (ESI) for Energy Advances.

Supporting Information

Boost Interlayer Charge Transfer in Polymeric Carbon Nitride by Mo Ion for Efficient Photocatalytic H_2 evolution

Feng Liu‡, Wencheng Li‡, Xi Rao, Shaohui Zheng, and Yongping Zhang**

School of Materials and Energy, Southwest University, Chongqing 400715, China

*Corresponding authors, E-mail: shaohuizheng@swu.edu.cn (S. Zheng),

zhangyyping6@swu.edu.cn (Y. Zhang)

‡These authors contributed equally to this work.

Table S1 Comparison of the hydrogen evolution rate (HER) of Mo doped g-C_3N_4 photocatalysts from different literatures.

Photocatalyst (Mo/g-C_3N_4 precursors)	HER rate [μmol/(h▪g)]	Light source	Reaction conditions	Reference
Sodium molybdate Urea	1666	500 W Xe lamp, λ > 420 nm	3 wt% Pt 17 vol% TEOA	This work
Ammonium molybdate Melamine	800	300 W Xe lamp, λ > 420 nm	3 wt% Pt 10 vol% TEOA	[1]
Ammonium molybdate Melamine	2008	300 W Xe lamp, λ >420 nm	3 wt% Pt 10 vol% TEOA	[2]
Ammonium molybdate Melamine	887	300 W Xe lamp, λ > 380 nm	3 wt% Pt 17 vol% TEOA	[3]
Sodium molybdate Melamine	641	300 W Xe lamp, λ > 380 nm	3 wt% Pt 17 vol% TEOA	[4]
Ammonium tetrathiom-olybdat Urea	773	300 W Xe lamp, λ > 420 nm	1 wt% Pt 10 vol% TEOA	[5]
Sodium molybdate Dicyandiamide	1124	300 W Xe lamp, λ ≥ 400 nm	3 wt% Pt 20 vol% TEOA	[6]
Ammonium molybdate Melamine	955	300 W Xe lamp, λ ≥ 400 nm	3 wt% Pt 20 vol% TEOA	[7]

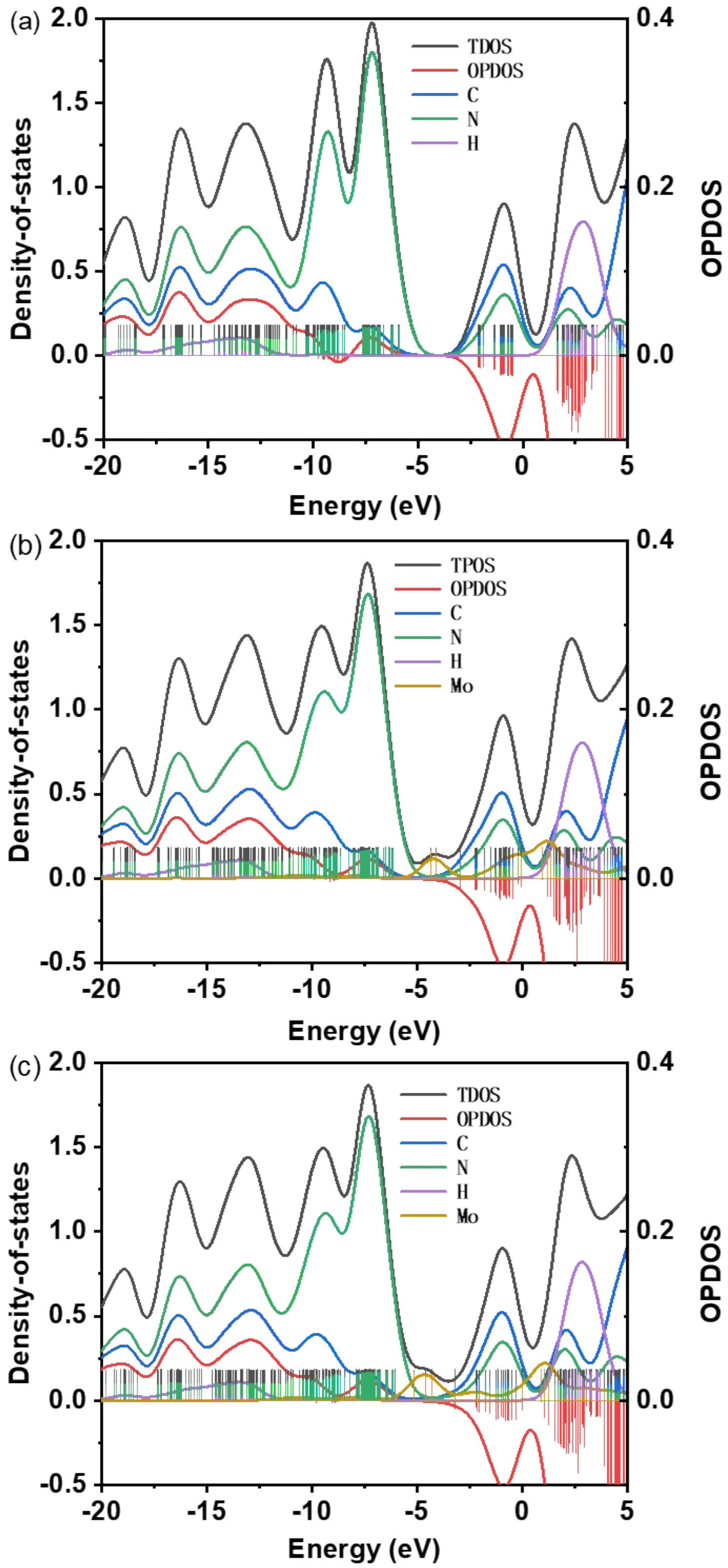

Figure S2 Calculated total density of states and partial density of states of (a) pure CN, (b) Mo^{6+}-CN, (c) Mo^{4+}-CN.

The calculated density of states (DOS) is shown in Figure S2, and the density of states of pure phase g-C_3N_4 is shown in Fig, It is mainly the aromatic ring structure with C–N as the skeleton. As shown in Figure S2 (b) and (c), the orange curve (Mo) is obviously positive in the range of - 5 eV to 5 eV, indicating that Mo mainly contributes to the g-C_3N_4 conduction band, thus changing the electronic structure of g-C_3N_4.

References

[1] H. Che, C. K. Ngaw, P. Hu, J. Wang, Y. Li, X. Wang, W. Teng, Fabrication of molybdenum doped carbon nitride nanosheets for efficiently photocatalytic water splitting, *J. Alloys Compd* **2020**, *849*.

[2] Y. Wang, Y. Zhang, S. Zhao, Z. Huang, W. Chen, Y. Zhou, X. Lv, S. Yuan, Bio-template synthesis of Mo-doped polymer carbon nitride for photocatalytic hydrogen evolution, *Appl. Catal.B* **2019**, *248*, 44-53.

[3] Y. Wang, Y. Xu, Y. Wang, H. Qin, X. Li, Y. Zuo, S. Kang, L. Cui, Synthesis of Mo-doped graphitic carbon nitride catalysts and their photocatalytic activity in the reduction of CO_2 with H2O, *Catal. Commun* **2016**, *74*, 75-79.

[4] X.-W. Guo, S.-M. Chen, H.-J. Wang, Z.-M. Zhang, H. Lin, L. Song, T.-B. Lu, Single-atom molybdenum immobilized on photoactive carbon nitride as efficient photocatalysts for ambient nitrogen fixation in pure water, *J. Mater. Chem. A* **2019**, *7*, 19831-19837.

[5] H. Zhao, S. Sun, Y. Wu, P. Jiang, Y. Dong, Z. J. Xu, Ternary graphitic carbon nitride/red phosphorus/molybdenum disulfide heterostructure: An efficient and low cost photocatalyst for visible-light-driven H_2 evolution from water, *Carbon* **2017**, *119*, 56-61.

[6] J. Sun, S. Yang, Z. Liang, X. Liu, P. Qiu, H. Cui, J. Tian, Two-dimensional/one-dimensional molybdenum sulfide (MoS_2) nanoflake/graphitic carbon nitride (g-C_3N_4) hollow nanotube photocatalyst for enhanced photocatalytic hydrogen production activity, *J Colloid Interface Sci* **2020**, *567*, 300-307.

[7] J. Dong, Y. Shi, C. Huang, Q. Wu, T. Zeng, W. Yao, A New and stable Mo-Mo_2C modified g-C_3N_4 photocatalyst for efficient visible light photocatalytic H_2 production, *Appl. Catal. B* **2019**, *243*, 27-35.