Supporting Information

2D PtS nanorectangles/g-C₃N₄ nanosheets with metal sulfide-support

interaction effect for high-efficiency photocatalytic H₂ evolution

Bo Lin,^{+a} Yao Zhou,^{+b} Baorong Xu,^c Chao Zhu,^d Wu Tang,^e Yingchun Niu,^f Jun Di,^d Pin Song,^d Jiadong Zhou,^d Xiao Luo,^a Lixing Kang,^d Ruihuan Duan,^d Qundong Fu,^d Haishi Liu,^a Ronghua Jin,^c Chao Xue,^g Qiang Chen,^h Guidong Yang,^c Kalman Varga,ⁱ Quan Xu,^{*f} Yonghui Li,^{*j} Zheng Liu^{*d} and Fucai Liu^{*a}

^aSchool of Optoelectronic Science and Engineering, University of Electronic Science and Technology of China, Chengdu 611731, China, E-mail: fucailiu@uestc.edu.cn

^bSchool of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore

°XJTU-Oxford International Joint Laboratory for Catalysis, School of Chemical Engineering and Technology, Xi'an Jiaotong University, Xi'an 710049, China

^dSchool of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore, E-mail: z.liu@ntu.edu.sg

eSchool of Materials and Energy, University of Electronic Science and Technology of China, Chengdu 611731, China

^fState Key Laboratory of Heavy Oil Processing, China University of Petroleum-Beijing, Beijing 102249, China, Email: xuquan@cup.edu.cn

^gState Centre for International Cooperation on Designer Low-carbon and Environmental Materials (CDLCEM), School of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450001, China

^hSchool of Chemical Engineering and Technology, Sun Yat-sen University (Zhuhai Campus), Zhuhai 519082, China

ⁱDepartment of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee 37235, USA

^jDepartment of Physics and Tianjin Key Laboratory of Low Dimensional Materials Physics and Preparing Technology, School of Science, Tianjin University, Tianjin 300350, China, Email: yonghui.li@tju.edu.cn

⁺ Bo Lin and Yao Zhou contributed equally to this work.

1. Experimental Procedures

1.1 Material synthesis

Synthesis of $g-C_3N_4$ nanosheets: 2 g of melamine was directly calcined at 550 °C for 4 h in a forming atmosphere (20% H₂ + 80% Ar) with a heating rate of 5 °C min⁻¹ to obtain bulk $g-C_3N_4$. Then 0.5 g of synthetic bulk $g-C_3N_4$ was heated at 500 °C for 2 h in air atmosphere with a heating rate of 10 °C min⁻¹ to obtain $g-C_3N_4$ nanosheet.

Synthesis of 2D PtS nanorectangles/g-C₃N₄ nanosheets: 2D PtS nanorectangles/g-C₃N₄ nanosheets sample was obtained by a novel in-situ vapor-phase (ISVP) growth method: 0.5 g of synthetic g-C₃N₄ nanosheet was ultrasonically dispersed in 40 mL of deionized water, then a certain amount of H₂PtCl₆ aqueous solution was added dropwise to the above dispersion solution with a Pt loading of 5 wt%, and vigorously stirred for 6 h at room temperature. The precipitate was collected, dried at 70 °C for 24 h and ground into powder. Subsequently, an aluminium boat containing precipitate powder and another aluminium boat containing sulfur powder were placed on the center and upstream (upwind) of the tube furnace, respectively. The above tube furnace was heated at 500 °C with a heating rate of 50 °C/min in Ar atmosphere, and then continually heated to 550 °C at same heating rate in a mixed atmosphere (10% H₂ + 90% Ar). After 0.5 h reaction at 550 °C in above mixed atmosphere, the tube furnace was cooled to room temperature in Ar atmosphere to obtain 2D PtS nanorectangles/g-C₃N₄ nanosheets. As a reference, Pt/g-C₃N₄ nanosheets sample (a Pt loading of 5 wt%) was synthesized under the above similar conditions, and the only difference is the lack of sulfur powder.

1.2 Characterization

The crystalline phase of samples was recorded by a powder X-ray diffractometer (Shimadzu XRD-6000). X-ray photoelectron spectroscopy (XPS) was obtained by an ESCALAB 250 spectrometer (Thermo ElectronCorporation). The morphologies and structures of prepared samples were collected by a transmission electron microscopy (JEOL JEM-2100F). Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were collected by a JEM-ARM200F operated at 60 kV. UV-Vis diffuse reflectance spectra (DRS) of products were recorded on a UV-vis spectrophotometer (Shimadzu UV-2450). Photoluminescence spectra (PL) were performed on a Varian Cary Eclipse spectrometer (USA). The Brunauer-Emmett-Teller (BET) specific surface areas were obtained by using a Surface Area and Porosity Analyzer (TriStar II 3020). The GIXRD measurements were carried out at the BL14B1 beamline of Shanghai Synchrotron Radiation Facility (SSRF) with X-ray at a wavelength of 1.24 Å. The 2D GIXRD patterns were obtained via the FIT2D software and displayed in scattering vector q coordinates with an equation of $q=4\pi sin\theta/\lambda$, where θ represents a half of the diffraction angle and λ represents the wavelength of incident X-ray.

1.3 Photocatalytic activity measurement

Photocatalytic H₂ evolution reaction was conducted in gas-closed system with a Pyrex reaction cell. Typically, 30 mg of photocatalyst was suspended in 50 mL of aqueous solution containing 10 vol% of triethanolamine as the hole-scavenger. The reaction vessel was deaerated by bubbling purity N₂ to remove air. Subsequently, the above reaction vessel was irradiated by a 300 W Xenon-lamp (NbeT, HSX-F300) with a 420 nm UV cutoff filter. The generated H₂ was quantified using a gas chromatograph (Beifen-Ruili, SP-2100A) coupled with a thermal conductive detector (TCD) and 5 Å molecular sieve column. The apparent quantum efficiency (AQE) of photocatalysts was measured under same reaction conditions except by replacing the above 420 UV-cutoff filter with the band-pass interference filters centered at 420, 450, 500, 550 and 600 nm. The average hydrogen evolution rate was tested after illumination for 3 h. The AQE was evaluated by the following

equation:

$$AQE (\%) = \frac{2 \times \text{number of evolved hydrogen molecules}}{\text{number of incident photons}}$$
(1)

1.4 Photoelectrochemical measurement

The transient photocurrent response and electrochemical impedance spectroscopy were performed by using a conventional electrochemical analyzer (AMETEK, PMC-1000/DC) coupled with a three-electrode system, where 1 M of Na₂SO₄ aqueous solution was elected as the electrolyte. In the system, a platinum wire and an Ag/AgCl (3 M KCl) electrode were used as the counter electrode and the reference electrode, respectively. The glassy carbon electrodes coated with obtained samples were served as the working electrodes.

1.5 DFT Calculations

Density Functional Theory (DFT) was used as the many-body approximation to describe the electronic behavior. The simulation software is the Vienna ab initio Simulation Package (VASP).¹ We choose the Perdue-Burke-Ernzerhof functional as the exchange-correlation potential for its performance and accuracy.² The adhesive behavior in our model is corrected by the van der Waals interaction using the empirical Grimme method (DFT-D3).³ The simulations are done on the supercomputers from XSEDE.⁴ The PtS quantum dots are located on multiple zones of the g-C₃N₄ substrate. Therefore, it is impossible to treat the quantum dot as the bulk material. Without the periodic boundary condition, the dimension of the box of the simulation is 28.4Å×24.6Å×20.0Å. The g-C₃N₄ nanosheet is fixed at the z=0 plane with frozen carbon and nitrogen atoms. The size of PtS quantum dot is about $15Å\times15Å\times10Å$, which is comparable to the experimental quantum dot. The thickness of the vacuum layer in z direction is about 10Å. The energy cutoff in the simulation is 450 eV. The convergence criterions for the electronic energy and forces are 10^{-5} eV

and 0.01 eV/Å, respectively.

2. Results



Fig. S1 a-c) HAADF-STEM images of PtS/CN.



Fig. S2 EDX image of PtS/CN. The Cu signal peak is due to the carbon-supported copper net used to load the samples in the Mapping tests.



Fig. S3 XPS spectra of CN in the regions of a) C 1s and b) N 1s.



Fig. S4 XPS spectra of PtS in the regions of a) S 2p and b) Pt 4f.



Fig. S5 Time-dependent photocatalytic H₂ evolution for PtS/CN with different Pt-loading amounts under visiblelight irradiation (λ >420 nm). The PtS/CN with a Pt-loading amount of 5 wt% shows the optimal photocatalytic hydrogen-evolution rate.



Fig. S6 XRD patterns of fresh PtS/CN and recycled PtS/CN. Fresh PtS/CN and recycled PtS/CN show similar XRD trends.



Fig. S7 TEM image of PtS/CN after 10 cycling tests. The TEM image indicates that PtS remains the intact 2D rectangle-like sheet structure supported by $g-C_3N_4$ nanosheet in the PtS/CN sample after 10 cycling tests.



Fig. S8 Optimized geometric structure of PtS/CN. Silver and green spheres represent C and N atoms, respectively. Purple and orange spheres represent Pt and S atoms, respectively.



Fig. S9 The side view of total charge density for the assembly of $PtS/g-C_3N_4$. Blue region represents the electron cloud. The diagram was obtained by fixing g-C₃N₄ and only allowing PtS to move in the Z-axis direction.



Fig. S10 The calculated distance between N atom in $g-C_3N_4$ and Pt atom in PtS. The regular triangle geometry is used in the structure of PtS to match with the structure of $g-C_3N_4$. The black circle indicates the bonding position. According to the distance trend between Pt atom and N atom by DFT calculations, the $Pt(\delta^+)-N(\delta^-)$ bonding state may be constructed.



Fig. S11 Band structure and DOS of the bulk PtS crystal. (Images adopted from "Materials Project"⁵)



Fig. S12 The top view of overall charge density difference for PtS/CN. Blue and yellow regions represent the electron accumulation and depletion, respectively.



Fig. S13 a) Nitrogen adsorption-desorption isotherms for CN and PtS/CN. b) Pore-size (radius) distributions of CN and PtS/CN using the BJH method.

The N₂ adsorption-desorption isotherms of CN and PtS/CN were measured. As shown in Fig. S13a, both samples show the IV adsorption-desorption isotherm of N₂ with the H3-type hysteresis loop, indicating the presence of mesopores. As displayed in Fig. S13b, a pore-size (radius) distribution in the region of 2-60 nm is presented in CN and PtS/CN, strongly supporting the presence of mesopores. Notably, a sharp peak at about 4.5 nm can be found in the pore-size distribution curve of PtS/CN, which is due to the introduction of mesopores with the smaller size along with the construction of 2D PtS nanorectangles/g-C₃N₄ nanosheets.

Table S1 Comparisons of reaction conditions and photocatalytic H_2 evolution activity with g-C₃N₄ based photocatalysts using Pt as the cocatalyst.

Photocatalysts	Light	Reaction	AQE	Ref.
	sources	conditions		
PtS/CN	Xe lamp	Band-pass	45.7%	This
		interference filter		work
		centered at 420 nm		
Pt/CCTs	Xe lamp	Band-pass	10.94%	6
		interference filter		
		centered at 420 nm		
Pt/V-CN ₁₀₀	Xe lamp	Band-pass	12.7%	7
		interference filter		
		centered at 420 nm		
Pt/Au	Xe lamp	Band-pass	9.1%	8
NR769/CNNT650		interference filter		
		centered at 420 nm		
Pt/CCNNSs	LED lamp	Band-pass	8.57%	9
		interference filter		
		centered at 420 nm		
Pt/few-layer C ₃ N ₄	Xe lamp	Band-pass	9.8%	10
		interference filter		
		centered at 420 nm		
Pt/CNA2	Xe lamp	Band-pass	5.07	11
		interference filter		
		centered at 420 nm		
Pt/HCNS-1	Xe lamp	Band-pass	7.5%	12
		interference filter		
		centered at 420.5		
		nm		
Pt/HC-CN	Xe lamp	Band-pass	6.17%	13
		interference filter		
		centered at 420 nm		

Table S2 Specific surface areas and pore volumes of PtS/CN and CN. PtS/CN shows a reduced specific surface area and pore volume in comparison with CN, indicating that the growth of PtS on the surface of $g-C_3N_4$ may block some pores existed in the $g-C_3N_4$.

Samples	S _{BET} (m² g-¹)	Pore volume (cm ³ g ⁻¹)
CN	23.54	0.17
PtS/CN	13.73	0.10

References

- 1 G. Kresse and J. Furthmiiller, Comp. Mater. Sci., 1996, 6, 15-50.
- 2 J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., 1996, 77, 3865-3868.
- 3 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, J. Chem. Phys., 2010, 132, 154104.
- J. Towns, T. Cockerill, M. Dahan, I. Foster, K. Gaither, A. Grimshaw, V. Hazlewood, S. Lathrop, D. Lifka,
 G. D. Peterson, R. Roskies, J. R. Scott and N. W. Diehr, *Comput. Sci. Eng.*, 2014, 16, 62-74.
- 5 A. Jain, S. P. Ong, G. Hautier, W. Chen, W. D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder and K. A. Persson, *APL Mater.*, 2013, 1, 011002.
- 6 Y. Wang, X. Liu, J. Liu, B. Han, X. Hu, F. Yang, Z. Xu, Y. Li, S. Jia, Z. Li and Y. Zhao, Angew. Chem. Int. Ed., 2018, 57, 5765-5771.
- 7 Y. Zhang, L. Wu, X. Zhao, Y. Zhao, H. Tan, X. Zhao, Y. Ma, Z. Zhao, S. Song, Y. Wang and Y. Li, *Adv. Energy Mater.*, 2018, 8, 1801139.
- 8 L. Zhang, N. Ding, L. Lou, K. Iwasaki, H. Wu, Y. Luo, D. Li, K. Nakata, A. Fujishima and Q. Meng, *Adv. Funct. Mater.*, 2018, 29, 1806774.
- 9 H. Ou, L. Lin, Y. Zheng, P. Yang, Y. Fang and X. Wang, Adv. Mater., 2017, 29, 1700008.
- Y. Xiao, G. Tian, W. Li, Y. Xie, B. Jiang, C. Tian, D. Zhao and H. Fu, J. Am. Chem. Soc., 2019, 141, 2508-2515.
- 11 B. Lin, G. Yang and L. Wang, Angew. Chem. Int. Ed., 2019, 58, 4587-4591.
- 12 J. Sun, J. Zhang, M. Zhang, M. Antonietti, X. Fu and X. Wang, *Nat. Commun.*, 2012, 3, 1139.
- 13 W. Xing, W. Tu, Z. Han, Y. Hu, Q. Meng and G. Chen, *ACS Energy Lett.*, 2018, **3**, 514-519.