



News & Views

Newly developed two-dimensional materials for efficient photocatalytic hydrogen evolution

Xueying Zhan^a, Fengmei Wang^a, Zhongzhou Cheng^a, Zhenxing Wang^{a,b}, Jun He^{a,b,*}

^a Chinese Academy of Sciences (CAS) Center for Excellence in Nanoscience, CAS Key Laboratory of Nanosystem and Hierarchical Fabrication, National Center for Nanoscience and Technology, Beijing 100190, China

^b Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China

Due to the increasing environmental and energy issues, hydrogen, as a clean and non-carbon energy source, has received more and more attention in the past decades. Photocatalysis has been known as a promising approach for hydrogen generation and a key measure in solving serious environmental problems. Different from traditional catalysts, such as ZnO and TiO₂, two-dimensional (2D) materials display unique advantages to hydrogen production due to their large specific surface area, high charge migration rate, tunable electronic structure and ultra-lightweight [1]. Especially, 2D materials show short migration distance for the generated electrons and holes, leading to the reduction of electron-hole recombination, which is one of the key factors affecting photocatalytic efficiency [2–4]. MoS₂ [5], 1T-WS₂ and 2H-WS₂ nanosheets [6] have been reported as efficient co-catalysis for hydrogen evolution, which means the integration of 2D nanosheets with other catalysts such as TiO₂ is still needed. Therefore, developing new photocatalysts is a pressing need for efficient hydrogen generation.

Layered metal phosphorous trichalcogenides (MPX₃, M = Ni, Fe, Cd, Mn, Cu, Zn, etc; X = S, Se, Te) is a new type 2D material with tunable composition and electronic structure. Recently, layered MPX₃ has been considered as a promising candidate for efficient hydrogen evolution due to their suitable band gaps range from 1.77 to 3.94 eV [7]. The calculated locations of valence band maximum (VBM) and conduction band minimum (CBM) of MPX₃ monolayer indicate that most of MPX₃ are suitable for photocatalytic hydrogen generation (Fig. 1a) [7]. Most of MPX₃ (MnPS₃, FePS₃, CoPS₃, NiPS₃, ZnPS₃, CdPS₃, SnPS₃) have been synthesized by chemical vapor transport (CVT), and exhibit superior magnetic and electrochemical properties [8]. Later, FePS₃ nanosheets with good photocatalytic activity and photostability are synthesized by a sulfurphosphidation method [9]. However, monolayered MPX₃ is still difficult to obtain. Recently, we reported that monolayered FePS₃ quantum sheets with diameters range from 4 to 8 nm can be obtained via exfoliation of the corresponding bulk materials in hydrazine solution (Fig. 1b) [10]. These monolayered FePS₃ quantum sheets exhibit a bandgap of 2.18 eV. Due to the

monolayer feature, FePS₃ quantum sheets display a photocatalytic H₂ generation rate of 290 μmol h⁻¹ g⁻¹, three times higher than the corresponding bulk materials. This study presents a facile approach of producing uniform monolayer FePS₃ quantum sheets and provides a new way to designing other photocatalysis based on monolayered MPX₃.

The band structures near Fermi level for MPX₃ were also calculated. MnPSe₃ monolayer is calculated as a direct band gap semiconductor and has strong absorption in the visible-light region [7]. The high carrier mobility of MnPSe₃ monolayer could be comparable to or even higher than those of many other 2D materials, indicating that the transfer of carriers to reactive sites would be easier in the photocatalytic process. Few layer MnPS₃ photodetectors have been reported to have high photo-responsivity (288 A W⁻¹) and photogain at a wavelength of 365 nm [11]. All these indicate that MnPX₃ is a promising photohydrolytic catalyst with great visible-light absorption and high carrier mobility. Exfoliated layered MnPX₃ has also been studied as electrocatalysts for hydrogen evolution [12]. However, compared with the CVT method, chemical vapor deposition (CVD) is more suitable and easily to obtain the large-scale MPX₃. Here we report a designed novel way of synthesizing layered MnPX₃. MnPS₃ and MnPSe₃ nanosheets are successfully grown on flexible carbon cloth substrate through a two-steps CVD method (Fig. 1c). Two growth routes were carried out, and the desired MnPX₃ can be obtained by temperature regulation. After the theoretically speculated photocatalytic activity of direct band gap MnPX₃ nanosheets, sunlight-driven catalytic activity is measured. Both MnPSe₃ and MnPS₃ exhibit promising photocatalytic activities of H₂ production with a rate of 6.5 and 3.1 μmol h⁻¹, respectively [13]. This work demonstrates that MnPX₃ monolayer would be a promising photocatalyst for water splitting under visible light.

In summary, metal trichalcogenophosphite (MPX₃) layered materials were considered a promising candidate for efficient hydrogen evolution. Among these layered materials, we reported the synthesis of monolayered FePS₃ quantum sheets. And then, a more facile CVD growth method for layered MnPX₃ was developed. All of these materials show great photocatalytic activity for hydrogen evolution, providing a significant step in exploring new photocatalysts for efficient hydrogen generation.

* Corresponding author.

E-mail address: hej@nanoctr.cn (J. He).

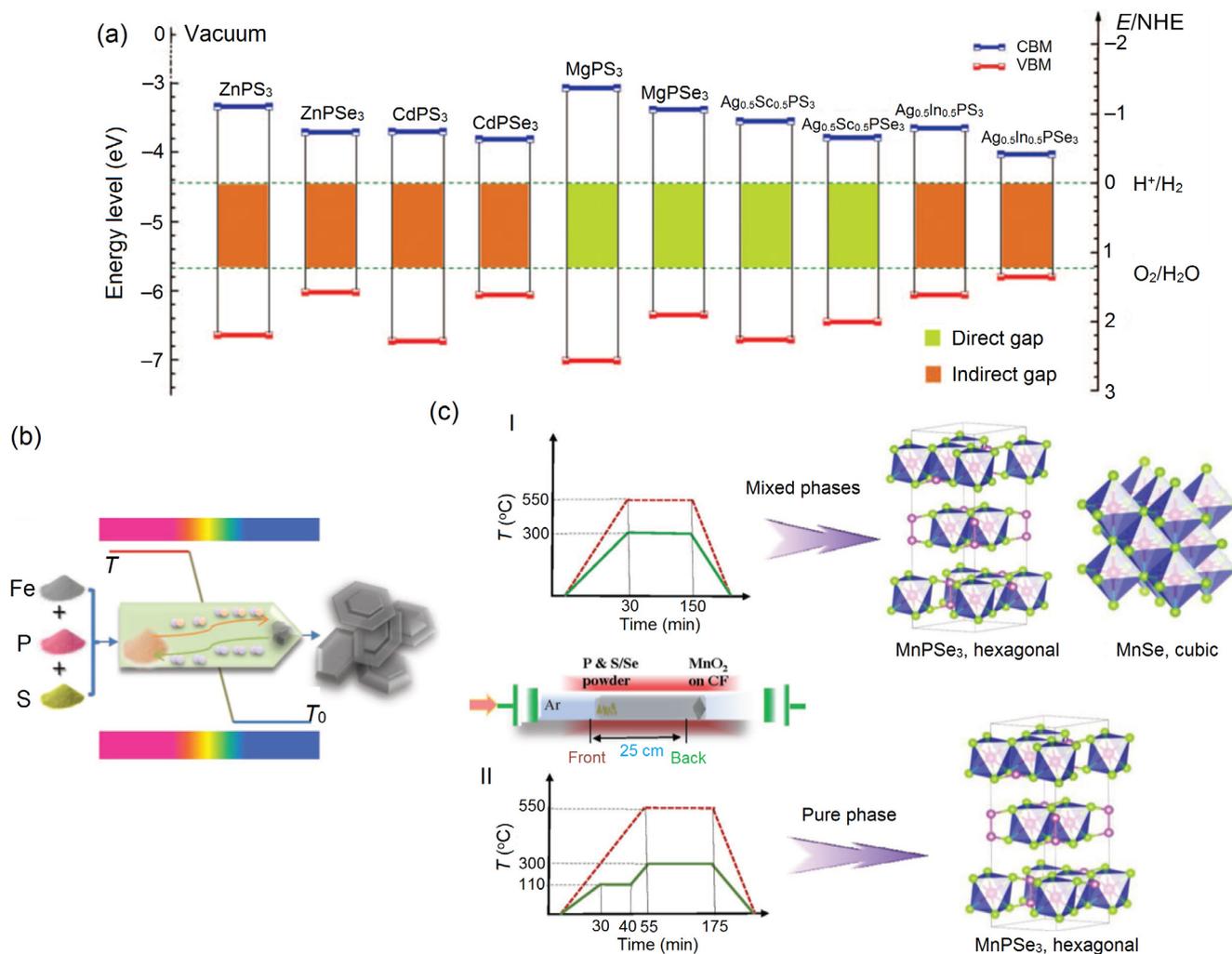


Fig. 1. (Color online) (a) The locations of VBM and CBM of MPX₃ monolayer [7]. (b) The schematic of CVT method [10]. (c) Temperature profiles of chemical vapor deposition routes leading to mixed phase (route-I) and pure phase (route-II) products along with schematic of their chemical structures [13].

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (61625401, 61474033, and 61574050), the Ministry of Science and Technology of China (2016YFA0200700), Strategic Priority Research Program of the Chinese Academy of Sciences (XDA09040201), and CAS Key Laboratory of Nanosystem and Hierarchical Fabrication. The authors also gratefully acknowledge the support of Youth Innovation Promotion Association CAS.

References

- [1] Voiry D, Shin HS, Loh KP, et al. Low-dimensional catalysts for hydrogen evolution and CO₂ reduction. *Nat Rev Chem* 2018;2:0105.
- [2] Guo JM, Wen RM, Zhai JY, et al. Enhanced NO₂ gas sensing of a single-layer MoS₂ by photogating and piezo-phototronic effects. *Sci Bull* 2019;64:128–35.
- [3] Guo Y, Liu JW, Xu YT, et al. In situ redox growth of mesoporous Pd-Cu₂O nanoheterostructures for improved glucose oxidation electrocatalysis. *Sci Bull* 2019;64:764–73.
- [4] Di J, Yan C, Handoko AD, et al. Ultrathin two-dimensional materials for photo- and electrocatalytic hydrogen evolution. *Mater Today* 2018;21:749–70.
- [5] Min SX, Lu GX. Sites for high efficient photocatalytic hydrogen evolution on a limited-layered MoS₂ cocatalyst confined on graphene sheets—the role of graphene. *J Phys Chem C* 2012;116:25415–24.
- [6] Mahler R, Hoepfner V, Liao K, et al. Colloidal synthesis of 1T-WSe₂ and 2H-WSe₂ nanosheets: applications for photocatalytic hydrogen evolution. *J Am Chem Soc* 2014;136:14121–7.
- [7] Liu J, Li X, Wang D, et al. Diverse and tunable electronic structures of single-layer metal phosphorus trichalcogenides for photocatalytic water splitting. *J Chem Phys* 2014;140:054707.
- [8] Mayorga-Martinez CC, Sofer Z, Sedmidubsky D, et al. Layered metal thiophosphite materials: magnetic, electrochemical, and electronic properties. *ACS Appl Mater Interfaces* 2017;9:12563–73.
- [9] Zhang J, Feng F, Pu Y, et al. Tailoring the porosity in iron phosphosulfide nanosheets to improve performance of photocatalytic hydrogen evolution. *ChemSusChem* 2019. <https://doi.org/10.1002/cssc.201900789>.
- [10] Cheng ZZ, Shifa TA, Wang F, et al. High-yield production of monolayer FePS₃ quantum sheets via chemical exfoliation for efficient photocatalytic hydrogen evolution. *Adv Mater* 2018;30:1707433.
- [11] Kumar R, Jenjeti RN, Austeria MP, et al. Bulk and few-layer MnPS₃: a new candidate for field effect transistors and UV photodetectors. *J Mater Chem C* 2019;7:324–9.
- [12] Gusmão R, Sofer Z, Pumera M, et al. Exfoliated layered manganese trichalcogenide phosphite (MnPX₃, X = S, Se) as electrocatalytic van der Waals materials for hydrogen evolution. *Adv Funct Mater* 2019;29:1805975.
- [13] Shifa TA, Wang FM, Cheng Z, et al. High crystal quality 2D manganese phosphorus trichalcogenide nanosheets and their photocatalytic activity. *Adv Funct Mater* 2018;28:1800548.



Xueying Zhan received her B.S. degree at Huazhong University of Science and Technology (HUST), China in 2010. Then she obtained her Master degree of Optoelectronic Engineering from College of Optoelectronic Science and Engineering, HUST, China in 2013. From then on, she worked as an engineer at National Center for Nanoscience and Technology, Chinese Academy of Sciences. Her major research interests include controllable synthesis and applications of 1D and composite nanomaterials in the area of optoelectronics and photocatalysis.



Jun He received his Ph.D. degree in Semiconductor Physics from the Institute of Semiconductors, Chinese Academy of Sciences (CAS) in 2003. Then he worked successively at Applied Physics Department of Technische Universiteit Eindhoven, Netherlands, Material Department of University of California, Santa Barbara, and California NanoSystem Institute, University of California, Los Angeles, USA. He joined the “100-Talents” Program of CAS in 2010 and became a Full Professor of the National Center for Nanoscience and Technology since then. His main research interest is the synthesis, characterization, and devices of low dimensional semiconductor materials.