MoS₂/TiO₂ Edge-On Heterostructure for Efficient Photocatalytic Hydrogen Evolution

He, Haiyong; Lin, Junhao; Fu, Wei; Wang, Xingli; Wang, Hong; Zeng, Qingsheng; Gu, Quan; Li, Yongmei; Yan, Cheng; Tay, Beng Kang; Xue, Can; Hu, Xiao; Pantelides, Sokrates T.; Zhou, Wu; Liu, Zheng

2016

He, H., Lin, J., Fu, W., Wang, X., Wang, H., Zeng, Q., et al. (2016). MoS₂/TiO₂ Edge-On Heterostructure for Efficient Photocatalytic Hydrogen Evolution. *Advanced Energy Materials*, 6(14), 1600464-.

<https://hdl.handle.net/10356/83215>

<https://doi.org/10.1002/aenm.201600464>

© 2016 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. This is the author created version of a work that has been peer reviewed and accepted for publication by *Advanced Energy Materials*, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. It incorporates referee's comments but changes resulting from the publishing process, such as copyediting, structural formatting, may not be reflected in this document. The published version is available at: [<http://dx.doi.org/10.1002/aenm.201600464>].

Downloaded on 26 Apr 2023 22:43:13 SGT

MoS₂/TiO₂ Edge-On Heterostructure for Efficient Photocatalytic Hydrogen Evolution

*Haiyong He, † Junhao Lin, † Wei Fu, Xingli Wang, Hong Wang, Qingsheng Zeng, Quan Gu, Yongmei Li, Cheng Yan, Beng Kang TAY, Can Xue, Xiao Hu, Sokrates T. Pantelides, Wu Zhou and Zheng Liu**

((Optional Dedication))

Dr. H. He, W. Fu, H. Wang, Q. Zeng, Q. Gu, Y. Li, C. Yan, Prof. Dr. C. Xue, X. Hu, Z. Liu
Center for Programmed Centre, School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore
E-mail: Z.Liu@ntu.edu.sg

Dr. J. Lin Prof. Dr. S. Pantelides, W. Zhou
Materials Science and Technology Division, Oak Ridge National Lab, Oak Ridge, Tennessee 37831, USA

Dr. J. Lin Prof. Dr. S. Pantelides, W. Zhou
Department of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee 37235, USA

Mr. X. Wang, Prof. Dr. B. Tay, Z. Liu
NOVITAS, Nanoelectronics Centre of Excellence, School of Electrical and Electronic Engineering, Nanyang Technological University, 639798, Singapore

[†] H. He and J. Lin contributed equally to this work.

Keywords: edge-on heterostructure, interfacial conductivity, electron transport pathway, water splitting, photocatalyst

Converting solar energy into chemical fuels has been considered as one of the major strategies to solve the energy crisis.¹⁻³ In 1972, Fujishima and Honda firstly split water on TiO₂ electrodes, marking a new era in photocatalysis.^{4,5} Generally, photocatalysts are composed by semiconductor and co-catalyst.⁶⁻⁸ Previous studies show that the hydrogen evolution, a key step in water splitting, depends on the properties of the cocatalysts and efficient charge transfer between the semiconductor and the co-catalysts. The co-catalysts not only assist in accelerating the separation of photoexcited electron-hole pairs in the semiconductors, but also supply active sites for hydrogen evolution.⁹⁻¹¹ It is well known that noble metal and its oxides are effective co-catalysts. However, they are costly. Therefore, it is valuable to explore alternative low-cost co-catalysts to replace the noble metals for such application.^{9,12}

Recently, the low-cost layered molybdenum disulfide (MoS₂) has been extensively investigated as a potential electrocatalyst for hydrogen evolution, with the goal to replace the costly noble metals.^{13,14} Moreover, several reports demonstrated that MoS₂ could also be used as a potential co-catalysts for

photocatalytic hydrogen evolution.^{12,15} For instance, the photocatalytic activity of CdS can be improved by loading MoS₂ as cocatalyst.^{15,16} Liu et al. reported that integration of a certain quantity of MoS₂ with TiO₂ can effectively enhance the photocatalytic hydrogen production.¹⁷ The catalytic efficiency of the systems decorated with MoS₂ as a co-catalyst, however, is still not comparable with those loaded with noble metals.

The low efficiency of such MoS₂ co-catalyst systems may own to the unoptimized geometrical configuration of MoS₂ on the semiconductor surface. It is commonly believed that layered MoS₂ prefers to grow along its basal plane on the semiconductor surface to minimize surface energy (surface energy at the edges is 100 time higher than basal plane). Such configuration leads to a low exposure of the active edge sites.¹⁸⁻²⁰ Furthermore, in such lay-down configuration of MoS₂ flakes, the photoexcited electrons in the semiconductor have to hop through each layer to reach the active edge sites in the MoS₂ flakes, resulting in a much higher electron resistance (~2200 times higher than the electron moving in the same layer).^{21,22} According to the fact that edges of MoS₂ is more conductive than its basal plane,^{13,21,23,24} making MoS₂ standing on the semiconductor surface, e.g., connecting the edges of few-layered MoS₂ flakes with the semiconductor, serves as a promising heterostructures for improving the efficiency of the hydrogen evolution, owing to a better electronic contact and an optimized the electron transport pathway. However, to the best of our knowledge, few strategies have been reported to realize such configuration of MoS₂ on the semiconductor surface, such as TiO₂, in large scale.

Herein, we demonstrate a strategy to control the contact facets between the layered co-catalyst MoS₂ and TiO₂, whereby manipulating the nucleation and growth process. Solid edge-on junctions, which seamlessly connect TiO₂ and few-layered MoS₂, are demonstrated. Such heterostructure can improve the interfacial conductivity and regulate the electron transportation pathway along the basal planes. Therefore, the photoexcited electrons are more effectively separated from TiO₂ and thus the photocatalytic activity is dramatically enhanced.

Previous studies reported that MoS₂ preferred to lie flat on TiO₂ to minimize surface energy (Figure 1a and Figure S1).^{19,25} In such cases, the MoS₂ plates are connected with TiO₂ along basal

planes (named $\text{TiO}_2/\text{MoS}_2$ (B) in the main text). In order to control the growth direction of MoS_2 on TiO_2 surface, we adopted a two-step strategy to synthesize the heterostructures with MoS_2 standing on TiO_2 along the edge (named $\text{TiO}_2/\text{MoS}_2$ (E) in the remaining text). First, MoO_2 nanoparticles were decorated on TiO_2 surface (named $\text{TiO}_2/\text{MoO}_2$, Figure S2). $\text{TiO}_2/\text{MoO}_2$ was then sulfurized in chemical vapor deposition (CVD) system (Figure 1b). During sulfurizing process, sulfur in gas phase diffused to the MoO_2 surface, and the sulfurization starts on the surface of MoO_2 (Figure S3). After that, the sulfur diffused furthermore from MoO_2 surface to interface. It was reported that the sulfur diffusion is faster parallel to the basal plane, because of the weak interaction between MoS_2 layers (Figure S3).²⁶ Therefore, the growth direction of MoS_2 nanoplates would be the same as that of sulfur diffusion, from MoO_2 surface to interface. Eventually, an interface between the standing MoS_2 nanoplates and TiO_2 connected along the edge of MoS_2 was achieved (Figure S3). Comparing to wet chemical methods, the affection of surface energy on growth process of MoS_2 is suppressed.

The morphologies of $\text{TiO}_2/\text{MoS}_2$ (E) are shown in Figure 2. Figure 2a and b display the scanning electron microscopy (SEM) image of $\text{MoS}_2/\text{TiO}_2$. The rod-like TiO_2 can be clearly observed. The diameter range of TiO_2 nanorods is from 20 ~ 60 nm, of which length is several tens of micrometers. The few-layered MoS_2 flakes are invisible under SEM due to their small size. In order to demonstrate the reliability of our method, the $\text{TiO}_2/\text{MoS}_2$ (E) containing 20% MoS_2 was measured by transmission electron microscopy (TEM) to get enough standing MoS_2 nanoplates in view. TEM images show that the size of the MoS_2 nanoplates are around 4 ~ 15 nm connecting to TiO_2 surface (Figure 2c). Almost all the MoS_2 nanoplates (marked by red color) stand on TiO_2 surface. High resolution TEM (HRTEM) images of $\text{TiO}_2/\text{MoS}_2$ (E) 3% (Figure 2d, e and Figure S4) demonstrate that the MoS_2 nanoplate is seamlessly bonded to TiO_2 surface along the edges. Fringes with lattice spacing of ca. 6.1 Å exhibited in Figure 2d corresponds to the (002) plane of hexagonal MoS_2 . The lattice spacing corresponding to TiO_2 , as extracted from the fast Fourier transform patterns (FFT) of selected area (marked by green frame) shown in the inset, are agreed to the anatase TiO_2 .

In order to examine the quality and the interface in the $\text{TiO}_2/\text{MoS}_2$ (E) heterostructure, annular dark-field scanning transmission electron microscopy (ADF-STEM) was employed to characterize the samples. Figure 3 shows us the view of edge-on junction from another direction, perpendicular to basal planes of MoS_2 . Figure 3 a displays the schematic and crystal structures of TiO_2 and MoS_2 , showing that our method can get high quality of MoS_2 without affecting the property of TiO_2 . The FFT image taken from the junction shows no any other diffraction spots, except from TiO_2 and MoS_2 , which confirms the complete sulfurization of MoS_2 (Figure 3 c). These results demonstrate that the MoS_2 nanoplates are bound to TiO_2 along edges, which is believed to improve the conductivity of heterojunction, thus enhancing the efficiency of electron-hole separation and photocatalytic performance. It should be noted that the distance between the two layers is ac. 1.8 nm, which is several times larger than lattice spacing of (002) plane of MoS_2 . It is thought that such large distance is caused by the size differences among layers. Figure 4a shows the atom-resolved hexagonal lattice structure of the standing few-layered MoS_2 along (001) which extended from the TiO_2 . The clean surface of MoS_2 indicates a complete sulfurization of MoO_2 nanoparticles and the resulting MoS_2 nanoplates are of high quality. Figure 4b presents the interface between MoS_2 and TiO_2 , suggesting a smooth interface between the edges of MoS_2 and the anatase TiO_2 (Figure 4b). However, the clear atomic bonding of the interface between MoS_2 and TiO_2 is not resolved on account of the thickness of TiO_2 . Electron energy loss spectrum (EELS) of the interface is shown in Figure 4c, revealing the characteristic peaks of Mo at 35 eV ($\text{M}_{3\text{-edge}}$), S at 165 eV ($\text{L}_{2,3\text{-edge}}$), Ti at 460 eV (L_2L_3 edge) and O at 532 eV.²⁷⁻²⁹ Elemental mapping results of Ti, S and Mo (the inset in Figure 4c) show the distribution of each element. The separation of Ti distribution area from Mo and S further proves that the MoS_2 does stand rather than coat on TiO_2 surface with little interfacial diffusion. Similar elemental distribution are consistently observed in the $\text{TiO}_2/\text{MoS}_2$ (E) heterostructures (Figure S5).

X-ray measurements were carried out to characterize the $\text{TiO}_2/\text{MoS}_2$ (E) heterostructure (shown in Figure S6). The XRD patterns of the as-prepared TiO_2 nanorods and post-treated $\text{TiO}_2/\text{MoS}_2$ (E) show similar peaks, which are indexed to the anatase phase (JCPDS file No. 21-1272)³⁰, suggesting the

sulfurization process did not affect the intrinsic properties of TiO_2 . In order to further confirm the structure of as-synthesized samples, Raman spectroscopy was employed to find out the photon vibration modes of MoS_2 and TiO_2 . The Raman spectra of samples show several peaks at 148, 399, 518, and 639 cm^{-1} , assigned to the $\text{Eg}(1)$, $\text{B1g}(1)$, $\text{A1g} + \text{B1g}(2)$, and $\text{Eg}(2)$ modes of anatase TiO_2 respectively (Figure S7).³¹ However, it is challenging to identify peaks belonging to MoS_2 in XRD patterns and Raman spectra, owing to the low content of MoS_2 .¹² The UV-vis absorption spectrum shown in Figure S8. The intense UV absorption band below 400 nm could be assigned to the intrinsic bandgap absorption of anatase TiO_2 (Eg: 3.2 eV). Compared with pure TiO_2 nanobers, the $\text{TiO}_2/\text{MoS}_2$ (E) exhibits clear absorption bands centered at 423 nm and 605 nm which could be attributed to few layer MoS_2 .^{32,33} More detailed information of the chemical states of MoS_2 and TiO_2 was investigated by X-ray photoelectron spectroscopy (XPS) analysis. The existence of 2H phase MoS_2 and TiO_2 is also confirmed by X-ray photoelectron spectroscopy (XPS) measurement (Figure S9). For XPS spectrum of Mo 3d, the peaks at 229.0 eV and 232.3 eV vindicate the 2H phase of MoS_2 .³⁴ The states of Ti, O and S are all in agreement with TiO_2 and MoS_2 , according to the XPS spectra.³¹

The efficiencies of electron-hole separation affecting the photocatalytic activity, were evaluated from photoluminescence (PL) spectra and photocurrent densities. Figure 5a shows the PL of TiO_2 , $\text{MoS}_2/\text{TiO}_2(\text{E})3\%$ and $\text{MoS}_2/\text{TiO}_2(\text{B})3\%$. We can find that TiO_2 has the highest PL intensity, indicating its good photoexcited electron hole recombination efficiency. The comparison of PL intensity demonstrates that the PL intensity of $\text{MoS}_2/\text{TiO}_2(\text{E})3\%$ is much lower than that of others, which is attributed to the higher electron-hole separation efficiency of $\text{MoS}_2/\text{TiO}_2(\text{E})3\%$. Additionally, results of photocurrent are in line with the PL spectra (Figure 5b). $\text{MoS}_2/\text{TiO}_2(\text{E})3\%$ exhibits a highest photocurrent, because of the enhanced electron-hole separation efficiency. Both the results of PL and photocurrent measurement elucidate that $\text{MoS}_2/\text{TiO}_2$ edge-on heterostructure displays a better electron-hole separation performance than that of heterostructure, where MoS_2 connects with TiO_2 via basal plane.

The photocatalytic activity for hydrogen evolution was evaluated under simulated sunlight irradiation using ethanol as a scavenger. Figure 5c shows the rate of hydrogen evolution over pure TiO₂ and TiO₂/MoS₂(E) catalysts with different MoS₂ loadings. Pure TiO₂ demonstrates photocatalytic activity in hydrogen evolution, but with low reaction rate around 120 $\mu\text{molh}^{-1}\text{g}^{-1}$. With only 0.5 wt% MoS₂ loading on TiO₂ nanorods, the rate of hydrogen evolution increases (almost 4 times higher). The activity of hydrogen evolution achieves its maximum rate when the loading of MoS₂ is increased to 3 wt%, which reaches to 4300 $\mu\text{molh}^{-1}\text{g}^{-1}$, nearly 36 times higher than pure TiO₂. As a control experiment, the photocatalytic activity remains much lower for the TiO₂/MoS₂(B) structures with the same MoS₂ loading (Figure 5d). However, the photocatalytic activity starts to decrease if we continue to increase the content of MoS₂ over 3 wt%. This may be ascribed to the increased coverage of MoS₂, which reduces the exposure area of TiO₂ to light and consequently lowers the rate of the generation of electron-hole pairs. To evaluate the stability, the reaction was proceeded for 12 h with intermittent evacuation (Figure 5e). The continuous H₂ evolution was evident at the beginning of reaction without noticeable degradation of active in the repeated run.

A mechanism was proposed to explain the high photocatalytic activity of TiO₂/MoS₂(E) samples, as illustrated in Figure 5f. Under the irradiation of UV light, the photoexcited electrons and holes are generated in the conduction band (CB) and valance band (VB), respectively. The photoexcited electrons then transport to MoS₂ and diffuse to the active sites. Previous studies have shown that, in such process, resistance of the junction and electron transport in cocatalyst would dramatically affect the electron-hole pair separation, leading to a significant change in photocatalytic activity of the hydrogen evolution.³² Our design of the TiO₂/MoS₂(E) heterostructure have two major advantages over the TiO₂/MoS₂(B) based on the electron-hole pair separation mechanism. First, the junction resistance of TiO₂/MoS₂(E) is significantly lower than TiO₂/MoS₂(B), owing to the directly bonding to the edges of MoS₂, which is more conductive than those bonding perpendicular to the basal plane.²³ Therefore, the remarkably high catalytic activity of TiO₂/MoS₂(E) benefits from such efficient electron transfer from TiO₂ to the edge of MoS₂, while the photoexcited electrons have to penetrate high potential barrier to reach active sites in

those TiO₂/MoS₂(B) structures. Second, the photoexcited electrons can diffuse along each basal plane of the few-layer MoS₂ separately rather than traverse layer-by-layer in the TiO₂/MoS₂(B) structures. Such change of the electron transport pathway increases the efficiency of electrons to reach the active sites, because the resistance perpendicular to the MoS₂ basal plane is 2200 times higher than that in parallel with basal plane.¹⁹ Therefore, a higher photocatalytic activity is observed in the TiO₂/MoS₂(E) structure, which presumably results from the aforementioned factors that improve the electron-hole separation by facilitating the electron transport from TiO₂ to MoS₂.

In conclusion, by controlling the MoS₂ growth process, TiO₂/MoS₂(E) catalysts with fast electron transport were synthesized. The TiO₂/MoS₂(E) photocatalysts showed high photocatalytic hydrogen evolution activity with a rate as high as 4300 $\mu\text{mol h}^{-1}\text{g}^{-1}$ for the sample with 3% MoS₂ loading, 36 times higher than pure TiO₂. It is believed that high conductivity of MoS₂ edge site can effectively improve the interfacial conductivity and suppress the electron-hole recombination. Additionally, our new design can regulate the electron transport along basal plane after separation from TiO₂, which facilitates photoexcited electron transfer to active site on MoS₂. Our findings provide a new avenue to understand and realize rationally designed electronic contact between TMD and semiconductor with specified crystal facets, which is of importance to the enhancement of charge separation and the obtainment of improved photocatalytic performance.

Experimental Section

Synthesis of MoO₂ nanoparticles and TiO₂ nanorods: MoO₂ was prepared by hydrothermal method. 0.1 g, 0.5 g PVP and 1 ml HCl solution (12 mol/L) were added to 30 ml solvent (volume ratio of H₂O and CH₃CH₂OH= 2:1) at room temperature. After stirring for 2 hours, the homogenous blue solution was transferred into 100 ml autoclave and held at 180°C for 12 hours. After that, black solution containing MoO₂ were diluted into 1 mg/L. TiO₂ nanofibers were prepared using a hydrothermal method similar to that described by Dongjiang Yang et al.³⁵ Generally, 6 g of TiO₂ powder was dispersed into 80 ml 10 M NaOH solution. The solution was stirred for 0.5 h followed by hydrothermal treatment at 180 °C for 48 h. After hydrothermal treatment, the precipitate was filtrated and washed with 0.1 M HCl solution and

DI water until the pH value of rinsing solution is ca 6 to obtain $\text{H}_2\text{Ti}_3\text{O}_7$. To coarse the surface of TiO_2 nanorod, 0.1 g of $\text{H}_2\text{Ti}_3\text{O}_7$ was dispersed into 40 ml H_2SO_4 solution (0.05 M) and maintained at 120 °C for 12 h. Finally, the product was annealed at 700 °C for 2 h.

Synthesis of $\text{TiO}_2/\text{MoS}_2(\text{E})$: Certain weight of MoO_3 and TiO_2 were dispersed into DI water and the solution was stirred at 60 °C for 12 h. The product was filtrated and dried at 80 °C under vacuum. The as-prepared $\text{MoO}_3/\text{TiO}_2$ was put in center of quartz-tube furnace and sulfur powder was placed in upstream. The $\text{MoS}_2/\text{TiO}_2(\text{E})$ sample was fabricated at 400 °C for 1h with heating rate of 30 °C min^{-1} under vacuum. The content of MoS_2 in $\text{MoS}_2/\text{TiO}_2(\text{E})$ 3% is about 2.97% determined by inductively coupled plasma optical emission spectrometer (ICP-OES, ICAP 6300, Thermo Scientific).

Synthesis of $\text{TiO}_2/\text{MoS}_2(\text{B})$: TiO_2 nanofibers were dispersed into DI water via ultrasonic treatment. And then hexaammonium molybdate and thioacetamide were added into TiO_2 nanofiber solution under vigorous stirring. The resulting solution was pour into autoclave and kept at 200 °C for 10 hours. After heat treatment, the products were filtrated and washed with DI water. The content of MoS_2 in $\text{MoS}_2/\text{TiO}_2(\text{B})$ 3% is about 3.1% determined by ICP-OES.

Characterization: X-ray diffraction (XRD) measurements were carried out by using the Shimadzu XRD-600 X-ray diffractometer with a $\text{Cu K}\alpha$ line of 0.1541 nm. X-ray photoelectron spectroscopy (XPS) measurement was performed on a Thermo Scientific Theta probe XPS with a monochromatized $\text{Al K}\alpha$ ($h\nu = 1486.7$ eV) source. Field emission scanning electron microscopy (FESEM; JSM-7600F) and transmission electron microscopy (TEM; JEOL JEM2100) were used to characterize the morphologies and structures of the samples. ADF-STEM imaging was performed on a Nion UltraSTEM-100, equipped with a 5th order aberration corrector, operated at 60 kV. The convergence angle is set to be ~ 30 mrad. All ADF-STEM images were acquired from the ~86 – 200 mrad range.

UV–vis diffuse reflectance spectroscopy (DRS) of the products was recorded on a Lambda 750 UV/vis/NIR spectrophotometer (Perkin-Elmer, USA).

Photocatalytic H₂ Production: The photocatalytic H₂ production tests were performed in a 50 mL quartz reactor. Typically, 10 mg of the photocatalysts was dispersed in 10 mL of mixed solution made of DI water and ethanol (8:2). This suspension of photocatalyst was sealed in the quartz reactor by a rubber plug and then bubbled with argon gas for half an hour to completely remove the dissolved air. Subsequently, the reactor was exposed under a 300 W Xe lamp (MAX-302, Asahi Spectra Co. Ltd.). The gas product composition from the upper space above the liquid in the quartz reactor was periodically analyzed by an Agilent 7890A gas chromatograph (GC) equipped with a thermal conductivity detector (TCD).

Supporting Information ((delete if not applicable))

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was supported by the National Research Foundation Singapore under NRF RF Award No. NRF-RF2013-08. This work was also supported by MOE2011-T2-2-147 and MOE2011-T3-1-005 from Ministry of Education, Singapore. Part of the electron microscopy characterizations were carried out at the Center for Electron Microscopy of Zhejiang University. W.L. and C.J. acknowledged financial support by the National Basic Research Program of China (2014CB932500 and 2015CB921000), the National Science Foundation of China (51222202, 51410305074 and 51472215), and the Program for Innovative Research Team in University of Ministry of Education of China (IRT13037) and the Fundamental Research Funds for the Central Universities (2014XZZX003-07). J.L. and S.T.P. thanks the supported from U.S. DOE grant DE-FG02-09ER46554. This research is supported in part by the U.S. Department of Energy, Office of Science, Basic Energy Science, Materials Sciences and Engineering Division (WZ), and through a user project at ORNL's Center for Nanophase Materials Sciences (CNMS), which is a DOE Office of Science User Facility.

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

[1] K. Maeda, K. Teramura, D. Lu, T. Takata, N. Saito, Y. Inoue, K. Domen, *Nature* **2006**, *440*, 295-295.

[2] X. Chen, S. Shen, L. Guo, S. S. Mao, *Chem. Rev.* **2010**, *110*, 6503-6570.

- [3] A. L. Linsebigler, G. Lu, J. T. Yates Jr, *Chem. Rev.* **1995**, 95, 735-758.
- [4] K. Hashimoto, H. Irie, A. Fujishima, *Jpn. J. Appl. Phys.* **2005**, 44, 8269-8285.
- [5] M. Ni, M. K. Leung, D. Y. Leung, K. Sumathy, *Renewable Sustainable Energy Rev.* **2007**, 11, 401-425.
- [6] H. Kato, A. Kudo, *J. Phys. Chem. B* **2001**, 105, 4285-4292.
- [7] M. Murdoch, G. Waterhouse, M. Nadeem, J. Metson, M. Keane, R. Howe, J. Llorca, H. Idriss, *Nat. Chem.* **2011**, 3, 489-492.
- [8] J. Yu, J. Ran, *Energy Environ. Sci.* **2011**, 4, 1364-1371.
- [9] C. Wang, R. L. Thompson, J. Baltrus, C. Matranga, *J. Phys. Chem. Lett.* **2009**, 1, 48-53.
- [10] W.-N. Wang, W.-J. An, B. Ramalingam, S. Mukherjee, D. M. Niedzwiedzki, S. Gangopadhyay, P. Biswas, *J. Am. Chem. Soc.* **2012**, 134, 11276-11281.
- [11] J. S. Jang, S. H. Choi, H. G. Kim, J. S. Lee, *J. Phys. Chem. C* **2008**, 112, 17200-17205.
- [12] Q. Xiang, J. Yu, M. Jaroniec, *J. Am. Chem. Soc.* **2012**, 134, 6575-6578.
- [13] Y. Li, H. Wang, L. Xie, Y. Liang, G. Hong, H. Dai, *J. Am. Chem. Soc.* **2011**, 133, 7296-7299.
- [14] J. Kibsgaard, Z. Chen, B. N. Reinecke, T. F. Jaramillo, *Nat. Mater.* **2012**, 11, 963-969.
- [15] J. Chen, X. J. Wu, L. Yin, B. Li, X. Hong, Z. Fan, B. Chen, C. Xue, H. Zhang, *Angew. Chem.* **2015**, 127, 1226-1230.
- [16] X. Zong, H. Yan, G. Wu, G. Ma, F. Wen, L. Wang, C. Li, *J. Am. Chem. Soc.* **2008**, 130, 7176.
- [17] Q. Liu, Z. Pu, A. M. Asiri, A. H. Qusti, A. O. Al-Youbi, X. Sun, *J. Nanopart. Res.* **2013**, 15, 1-7.
- [18] J. A. Spirko, M. L. Neiman, A. M. Oelker, K. Klier, *Surf. Sci.* **2003**, 542, 192-204.
- [19] H. Wang, D. Kong, P. Johanes, J.J. Cha, G. Zheng, K. Yan, N. Liu, Y. Cui, *Nano lett.* **2013**, 13(7), 3426-3433.
- [20] H. Wang, Z. Lu, S. Xu, D. Kong, J.J. Cha, G. Zheng, P.C. Hsu, K. Yan, D. Bradshaw, F.B. Prinz, Y. Cui, *PNAS.*, **2013**, 110(49), 19701-19706.
- [21] A. B. Laursen, S. Kegnæs, S. Dahl, I. Chorkendorff, *Energy Environ. Sci.* **2012**, 5, 5577-5591.

- [22] C. Liu, L. Wang, Y. Tang, S. Luo, Y. Liu, S. Zhang, Y. Zeng, Y. Xu, *Appl. Catal. B.*, **2015**, *164*, 1-9.
- [23] T. F. Jaramillo, K. P. Jørgensen, J. Bonde, J. H. Nielsen, S. Hørch, I. Chorkendorff, *science* **2007**, *317*, 100-102.
- [24] B. Hinnemann, P. G. Moses, J. Bonde, K. P. Jørgensen, J. H. Nielsen, S. Hørch, I. Chorkendorff, J. K. Nørskov, *J. Am. Chem. Soc.* **2005**, *127*, 5308-5309.
- [25] M.-X. Zhang, P. Kelly, M. Qian, J. Taylor, *Acta Mater.* **2005**, *53*, 3261-3270.
- [26] D. Kong, H. Wang, J. J. Cha, M. Pasta, K. J. Koski, J. Yao, Y. Cui, *Nano Lett.* **2013**, *13*, 1341-1347.
- [27] K. Griffin, M. Varela, S. J. Pennycook, A. Pakhomov, K. M. Krishnan, *J. Appl. Phys.* **2006**, *99*, 08M114.
- [28] C. Reza-San Germán, P. Santiago, J. Ascencio, U. Pal, M. Pérez-Alvarez, L. Rendon, D. Mendoza, *J. Phys. Chem. B* **2005**, *109*, 17488-1745.
- [29] T. Akita, M. Okumura, K. Tanaka, K. Ohkuma, M. Kohyama, T. Koyanagi, S. Tsubota, M. Haruta, *Surf. Interface Anal.* **2005**, *37*, 265-269.
- [30] H. G. Yang, C. H. Sun, S. Z. Qiao, J. Zou, G. Liu, S. C. Smith, H. M. Cheng, G. Q. Lu, *Nature* **2008**, *453*, 638-641.
- [31] M. Smirnov, R. Baddour-Hadjean, *J. Am. Chem. Soc.* **2004**, *121*, 2348-2355.
- [32] T. Wang, L. Liu, Z. Zhu, P. Papakonstantinou, J. Hu, H. Liu, M. Li, *Energy Environ. Sci.* **2013**, *6*, 625-633.
- [33] G. Eda, H. Yamaguchi, D. Voiry, T. Fujita, M. Chen, M. Chhowalla, *Nano lett.* **2011**, *11*, 5111-5116.
- [34] Y. H. Lee, X. Q. Zhang, W. Zhang, M. T. Chang, C. T. Lin, K. D. Chang, Y. C. Yu, J. T. W. Wang, C. S. Chang, L. J. Li, *Adv. Mater.* **2012**, *24*, 2320-2325.
- [35] J. Liu, H. Bai, Y. Wang, Z. Liu, X. Zhang, D. D. Sun, *Adv. Funct. Mater.* **2010**, *23*, 4175-4181.

Figure 1. Schematic illustration of preparing $\text{TiO}_2/\text{MoS}_2$ composite. a) Wet chemical method for preparing $\text{TiO}_2/\text{MoS}_2$ (B) composite, where MoS_2 nanoplates contact with TiO_2 surface along (B) basal planes; b) CVD strategy to prepare $\text{TiO}_2/\text{MoS}_2$ (E) composite, where MoS_2 nanoplates contact with TiO_2 surface along high conductive (E) planes.

Figure 2. Morphologies of $\text{TiO}_2/\text{MoS}_2(\text{E})$ heterostructures. a) and b) SEM images of as-prepared $\text{TiO}_2/\text{MoS}_2(\text{E})3\%$; c) TEM image of $\text{TiO}_2/\text{MoS}_2(\text{E})20\%$, d) TEM image of $\text{TiO}_2/\text{MoS}_2(\text{E})3\%$, showing few-layer MoS_2 nanoplates on TiO_2 surface; e) enlarged TEM image of $\text{TiO}_2/\text{MoS}_2(\text{E})3\%$. It is clear that MoS_2 nanoplates connect with TiO_2 via edge. Inset is fast Fourier transform (FFT) patterns of area marked by green rectangular box.

Figure 3. a) STEM image of TiO₂/MoS₂(E) with basal planes of MoS₂ perpendicular to the viewing direction. Insertions in upper right corner and bottom right corner are atomic model along the zone axis of TiO₂ and MoS₂ respectively. b) The FFT image taken from area marked with red square in figure a revealing the anatase structure; c) FFT image of junction indicated by yellow square showing the diffraction spots from anatase TiO₂ and 2H MoS₂; d) FFT image of MoS₂ marked with green square corresponding to 2H-type MoS₂.

Figure 4. High resolution ADF-STEM and EELS analysis of $\text{TiO}_2/\text{MoS}_2(\text{E})3\%$. a) ADF-STEM image of as-synthesized MoS_2 revealing atomic structure. A flat surface and hexagonal symmetry can be confirmed in image, indicating the high quality of MoS_2 . b) ADF-STEM image of interface between MoS_2 and TiO_2 . c) EELS spectra and elemental mapping of sample. The distribution area of Ti is separated from Mo and S.

Figure 5. a) PL spectra of TiO₂, TiO₂/MoS₂(E)3% and TiO₂/MoS₂(B)3%, excited at 330 nm; b) photocurrent density–time curves of TiO₂, TiO₂/MoS₂(E)3% and TiO₂/MoS₂(B)3% (bias: 0 V vs Ag/AgCl, 0.1 M Na₂SO₄, light irradiation: ≤400 nm); c) the rate of H₂ evolution over TiO₂/MoS₂(E) loaded with different amount of MoS₂; d) comparison of H₂ evolution rate on TiO₂, TiO₂/MoS₂(E)3% and TiO₂/MoS₂(B)3%; e) recycling photocatalytic H₂ evolution test of TiO₂/MoS₂(E)3%; f) schematic illustration of photo excited electrons transport pathway on TiO₂/MoS₂(E).

Via edge engineering, we demonstrate a facile two-step method that produces solid edge-on junctions between TiO_2 and few-layered MoS_2 in large scale. $\text{MoS}_2/\text{TiO}_2$ edge-on heterostructures result in high conductive $\text{MoS}_2/\text{TiO}_2$ interfaces and an optimized electron transport pathways which facilitate the electron-hole pair separation, leading to an efficient solar water splitting.

Keywords: edge-on heterostructure, interfacial conductivity, electron transport pathway, water splitting, photocatalyst

Haiyong He, † Junhao Lin, † Wei Fu, Xingli Wang, Hong Wang, Qingsheng Zeng, Quan Gu, Yongmei Li, Cheng Yan, Beng Kang TAY, Can Xue, Xiao Hu, Sokrates T. Pantelides, Wu Zhou and Zheng Liu*

$\text{MoS}_2/\text{TiO}_2$ Edge-On Heterostructure for Efficient Photocatalytic Hydrogen Evolution