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<th>MoS2/TiO2 Edge-On Heterostructure for Efficient Photocatalytic Hydrogen Evolution</th>
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Converting solar energy into chemical fuels has been considered as one of the major strategies to solve the energy crisis. In 1972, Fujishima and Honda firstly split water on TiO\textsubscript{2} electrodes, marking a new era in photocatalysis. Generally, photocatalysts are composed by semiconductor and co-catalyst. 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. 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.

Recently, the low-cost layered molybdenum disulfide (MoS\textsubscript{2}) has been extensively investigated as a potential electrocatalyst for hydrogen evolution, with the goal to replace the costly noble metals. Moreover, several reports demonstrated that MoS\textsubscript{2} could also be used as a potential co-catalysts for
photocatalytic hydrogen evolution.\textsuperscript{12,15} For instance, the photocatalytic activity of CdS can be improved by loading MoS\textsubscript{2} as cocatalyst.\textsuperscript{15,16} Liu et al. reported that integration of a certain quantity of MoS\textsubscript{2} with TiO\textsubscript{2} can effectively enhance the photocatalytic hydrogen production.\textsuperscript{17} The catalytic efficiency of the systems decorated with MoS\textsubscript{2} as a co-catalyst, however, is still not comparable with those loaded with noble metals.

The low efficiency of such MoS\textsubscript{2} co-catalyst systems may own to the unoptimized geometrical configuration of MoS\textsubscript{2} on the semiconductor surface. It is commonly believed that layered MoS\textsubscript{2} 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.\textsuperscript{18-20} Furthermore, in such lay-down configuration of MoS\textsubscript{2} flakes, the photoexcited electrons in the semiconductor have to hop through each layer to reach the active edge sites in the MoS\textsubscript{2} flakes, resulting in a much higher electron resistance (~2200 times higher than the electron moving in the same layer).\textsuperscript{21,22} According to the fact that edges of MoS\textsubscript{2} is more conductive than its basal plane,\textsuperscript{13,21,23,24} making MoS\textsubscript{2} standing on the semiconductor surface, e.g., connecting the edges of few-layered MoS\textsubscript{2} 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 MoS\textsubscript{2} on the semiconductor surface, such as TiO\textsubscript{2}, in large scale.

Herein, we demonstrate a strategy to control the contact facets between the layered co-catalyst MoS\textsubscript{2} and TiO\textsubscript{2}, whereby manipulating the nucleation and growth process. Solid edge-on junctions, which seamlessly connect TiO\textsubscript{2} and few-layered MoS\textsubscript{2}, 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 TiO\textsubscript{2} and thus the photocatalytic activity is dramatically enhanced.

Previous studies reported that MoS\textsubscript{2} preferred to lie flat on TiO\textsubscript{2} to minimize surface energy (Figure 1a and Figure S1).\textsuperscript{19,25} In such cases, the MoS\textsubscript{2} plates are connected with TiO\textsubscript{2} along basal
planes (named TiO$_2$/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 TiO$_2$/MoS$_2$ (E) in the remaining text). First, MoO$_2$ nanoparticles were decorated on TiO$_2$ surface (named TiO$_2$/MoO$_2$, Figure S2). TiO$_2$/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).

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 TiO$_2$/MoS$_2$ (E) are shown in Figure 2. Figure 2a and b display the scanning electron microscopy (SEM) image of MoS$_2$/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 TiO$_2$/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 TiO$_2$/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 TiO$_2$/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 (M$_3$-edge), S at 165 eV (L$_{2,3}$-edge), Ti at 460 eV(L$_2$L$_3$ 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 TiO$_2$/MoS$_2$(E) heterostructures (Figure S5).

X-ray measurements were carried out to characterize the TiO$_2$/MoS$_2$ (E) heterostructure (shown in Figure S6). The XRD patterns of the as-prepared TiO$_2$ nanorods and post-treated TiO$_2$/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 Eg(1),B1g(1), A 1g +B1g(2), and Eg(2) modes of anatase TiO$_2$ respectively (Figure S7). However, it is challenging to identify peaks belonging to MoS$_2$ in XRD patterns and Raman spectra, owing to the low content of MoS$_2$. 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 TiO$_2$/MoS$_2$ (E) exhibits clear absorption bands centered at at 423 nm and 605 nm which could be attributed to few layer MoS$_2$.

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$_2$.

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$_2$, MoS$_2$/TiO$_2$(E)3% and MoS$_2$/TiO$_2$(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 MoS$_2$/TiO$_2$(E)3% is much lower than that of others, which is attributed to the higher electron-hole separation efficiency of MoS$_2$/TiO$_2$(E)3%. Additionally, results of photocurrent are in line with the PL spectra (Figure 5b). MoS$_2$/TiO$_2$(E)3% exhibits a highest photocurrent, because of the enhanced electron-hole separation efficiency. Both the results of PL and photocurrent measurement elucidate that MoS$_2$/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 μmol h⁻¹ 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 μmol h⁻¹ 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 decreases 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. 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. 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 TiO$_2$/MoS$_2$(B) structures. Second, the photoexcited electrons can diffuse along each basal plane of the few-layer MoS$_2$ separately rather than traverse layer-by-layer in the TiO$_2$/MoS$_2$(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 MoS$_2$ basal plane is 2200 times higher than that in parallel with basal plane.$^{19}$ Therefore, a higher photocatalytic activity is observed in the TiO$_2$/MoS$_2$(E) structure, which presumably results from the aforementioned factors that improve the electron-hole separation by facilitating the electron transport from TiO$_2$ to MoS$_2$.

In conclusion, by controlling the MoS$_2$ growth process, TiO$_2$/MoS$_2$(E) catalysts with fast electron transport were synthesized. The TiO$_2$/MoS$_2$(E) photocatalysts showed high photocatalytic hydrogen evolution activity with a rate as high as 4300 μmolh$^{-1}$g$^{-1}$ for the sample with 3% MoS$_2$ loading, 36 times higher than pure TiO$_2$. It is believed that high conductivity of MoS$_2$ 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 TiO$_2$, which facilitates photoexcited electron transfer to active site on MoS$_2$. 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 MoO$_2$ nanoparticles and TiO$_2$ nanorods:* MoO$_2$ 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 H$_2$O and CH$_3$CH$_2$OH= 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 MoO$_2$ were diluted into 1 mg/L. TiO$_2$ nanofibers were prepared using a hydrothermal method similar to that described by Dongjiang Yang et al.$^{35}$ Generally, 6 g of TiO$_2$ 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 $\text{H}_2\text{SO}_4$ 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 TiO$_2$/MoS$_2$ (E)*: Certain weight of MoO$_2$ 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 MoO$_2$/TiO$_2$ was put in center of quartz-tube furnace and sulfur powder was placed in upstream. The MoS$_2$/TiO$_2$(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 MoS$_2$/TiO$_2$(E) 3% is about 2.97% determined by inductively coupled plasma optical emission spectrometer (ICP-OES, ICAP 6300, Thermo Scientific).

*Synthesis of TiO$_2$/MoS$_2$ (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 MoS$_2$/TiO$_2$(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 Cu Kα line of 0.1541 nm. X-ray photoelectron spectroscopy (XPS) measurement was performed on a Thermo Scientific Theta probe XPS with a monochromatized Al Kα (hv = 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 $H_2$ Production: The photocatalytic $H_2$ 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.

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Figure 1. Schematic illustration of preparing TiO$_2$/MoS$_2$ composite. a) Wet chemical method for preparing TiO$_2$/MoO$_2$ /B composite, where MoS$_2$ nanoplates contact with TiO$_2$ surface along (B) basal planes; b) CVD strategy to prepare TiO$_2$/MoS$_2$(E) composite, where MoS$_2$ nanoplates contact with TiO$_2$ surface along high conductive (E) planes.
Figure 2. Morphologies of TiO$_2$/MoS$_2$(E) heterostructures. a) and b) SEM images of as-prepared TiO$_2$/MoS$_2$(E)3%; c) TEM image of TiO$_2$/MoS$_2$(E)20%, d) TEM image of TiO$_2$/MoS$_2$(E)3%, showing few-layer MoS$_2$ nanoplate erects on TiO$_2$ surface; e) enlarged TEM image of TiO$_2$/MoS$_2$(E)3%. It is clear that MoS$_2$ nanoplate connects 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 TiO$_2$/MoS$_2$(E) with basal planes of MoS$_2$ perpendicular to the viewing direction. Insertions in upper right corner and bottom right corner are atomic model along the zone axis of TiO$_2$ and MoS$_2$ respectively. b) The FFT image taken from ear 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 TiO$_2$ and 2H MoS$_2$; d) FFT image of MoS$_2$ marked with green square corresponding to 2H-type MoS$_2$. 
Figure 4. High resolution ADF-STEM and EELS analysis of TiO_2/MoS_2(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 TiO$_2$, TiO$_2$/MoS$_2$(E)3% and TiO$_2$/MoS$_2$(B)3%, exited at 330 nm; b) photocurrent density–time curves of TiO$_2$, TiO$_2$/MoS$_2$(E)3% and TiO$_2$/MoS$_2$(B)3% (bias: 0 V vs Ag/AgCl, 0.1 M Na$_2$SO$_4$, light irradiation: ≤400 nm); c) the rate of H$_2$ evolution over TiO$_2$/MoS$_2$(E) loaded with different amount of MoS$_2$; d) comparison of H$_2$ evolution rate on TiO$_2$, TiO$_2$/MoS$_2$(E)3% and TiO$_2$/MoS$_2$(B)3%; e) recycling photocatalytic H$_2$ evolution test of TiO$_2$/MoS$_2$(E)3%; f) schematic illustration of photo excited electrons transport pathway on TiO$_2$/MoS$_2$(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. MoS$_2$/TiO$_2$ edge-on heterostructures result in high conductive MoS$_2$/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

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MoS$_2$/TiO$_2$ Edge-On Heterostructure for Efficient Photocatalytic Hydrogen Evolution