Supporting information

Fig. S1 SEM images of MoS$_2$/WS$_2$ catalyst with different Mo:W ratios. (a) and (d) Mo:W=2:1; (b) and (e) Mo:W=2:1; (c) and (f) Mo:W=2:1

Fig. S2 Raman spectra of MoS$_2$/WS$_2$ (1:1)

Fig. S2 Raman spectra of MoS$_2$/WS$_2$ (1:1)
Fig. S3 The band gap of the MoS$_2$, WS$_2$, and MoS$_2$/WS$_2$ catalyst with different Mo:W mole ratios

The optical band gap (E$_g$) of the samples was calculated using the Tauc’s method. [1] According to this method, the plot of $[a(hv)^n]$ against $hv$ shows a linear region just above the optical absorption edge, where $n = 2$ is used for the direct allowed transition, $n = 1/2$ for the indirect allowed transition, and $hv$ is the photon energy (eV). Bulk or fewer 2H-MoS$_2$ is a semiconductor with an indirect band gap of $\sim$1.2 eV, and the nature of the band gap changes from indirect to direct when thickness is reduced to be a single layer ($\sim$1.9 eV). [2] We estimated the band gap using $n = 1/2$ for the indirect allowed transition, which was fitted for the fewer layer MoS$_2$ or WS$_2$ nanosheets. Hence, in the Tauc plot shown in Figure S3, $n = 1/2$ was employed, which clearly yields a satisfactory linearity for all the WS$_2$, MoS$_2$ and MoS$_2$/WS$_2$ samples. The band gap E$_g$ is derived from the intercept of this straight line with the photon energy axis at $[a(hv)]^{1/2}$=0. The resulting E$_g$ values for WS$_2$, MoS$_2$ and MoS$_2$/WS$_2$ are shown in Fig. S3. In this context, both WS$_2$ and MoS$_2$ exhibit a small increase in the band gap. The increase in the band gap is properly attributed to the effect of the E$_g$ of In$_2$S$_3$ ($\sim$2.4 eV) derived of ITO under hydrothermal condition.
Fig.S4 XRD patterns of the pristine WS$_2$ and MoS$_2$ grown on ITO under hydrothermal condition.

Fig.S5 I-t plot for stability testing of the nanostructured MoS$_2$, WS$_2$ and MoS$_2$/WS$_2$ of different mole ratio at 0.372 V (vs RHE). Light source: Xenon lamp (300W) (0.50M H$_2$SO$_4$)
Fig. S6  J-V curves of cathodic polarization of MoS$_2$/WS$_2$ catalysts on ITO and MoS$_2$/WS$_2$ catalysts on Ti in dark and under simulated solar light (0.5M H$_2$SO$_4$)

Fig. S7 Tafel plots of as prepared photoelectrocatalysts
Fig. S8 Electrochemical double-layer capacitance (EDLC) measurements and the corresponding current density-scan rates curve of several electrocatalysts. (a) and (d) MoS$_2$; (b) and (e) WS$_2$; (c) and (f) MoS$_2$/WS$_2$ (1:1), respectively.

The electrochemical double-layer capacitance (EDLC) is determined by the following equation: $i_c = \nu \cdot CDL$; where $i_c$ represents the capacitive current, $\nu$ is the product of the scan rate, and CDL is the electrochemical double-layer capacitance. The electrochemical double-layer capacitance is obtained by the slope of a straight line extracted from the capacitive current as a function of scan rate. [3-5]

Fig. S9 Mott-Schottky plot of photoelectrodes (a) MoS$_2$; (b) WS$_2$; (c) MoS$_2$/WS$_2$ (1:1), respectively.
Fig.S10 HRTEM image of MoS$_2$/WS$_2$ (1/1) with its corresponding fast Fourier transform (FFT), highlighting the ordered and random orientation of individual building blocks (evidenced by FFT ring pattern)

From the structural viewpoint for HER catalysis, the strongly disordered structure is beneficial to offer more active sites. [6] However, fast interdomain electron transport due to the 2D electron conjugation along the basal surface will be significantly blocked by the disordered structure,[7] and thus leads to poor overall conductivity and further restrict the HER process. Hence, a moderate degree of disorder with a certain periodic arrangement of nanodomains should be adjusted to compromise the contradictory relation between active sites and conductivity. In this special hierarchical structure, controllable disorder of nanostructure can be achieved by W-doping MoS$_2$ hybrid, which offers the opportunity to tune the active site numbers. During reaction, W probably located on substitutional sites, will tend to migrate toward the free surfaces and edges of the MoS$_2$, which changes on the rotated surface interlayers.

Actually, for MoS$_2$/WS$_2$ (1/1) sample, ordered and disordered domains coexisted in the atomic arranging manners. The coexistence of ordered and disordered domains were confirmed by HRTEM image (SI Fig.S10). As shown in above HRTEM image (SI
Fig. S10), both disordered and ordered nanodomain are observed, as indicated by the red and blue boxes, respectively.

As shown in Fig. S10, some nanodomain are observed as the rotation of overlapped hexagonal networks between individual MoS$_2$ layers,[7] which is a kind of disordered structure. In order to directly estimate the extent of disorder for the MoS$_2$/WS$_2$ sample, fast Fourier transform (FFT) was applied to show splitting whose angle corresponds to the degrees of rotation, thus reflecting the degrees of disorder[8-12] In addition, the degree of disorder can be evaluated by the angle determined by a diffraction arc length and the central spot,[5] and the different diffraction arc length indicates the different periodic arrangements of nanodomains.

As shown in the upper right of Fig. S10, the FFT patterns (enclosed by red box) showed a set of concentric rings instead of sharp spots as a result of the strongly disordered arrangement of nanodomains. Furthermore, the image obtained with the other part of the sample, enclosed by blue box, FFT pattern, shown in the lower right of Fig. S10, is observed to possess six diffraction arcs with little arc length, indicating an almost single layer of nanodomains with a good periodic arrangement. Additionally, WS$_2$ has been verified to be highly crystallized as compared with MoS$_2$. [13] In this work, the XRD spectrum clearly shows that the highly crystallized WS$_2$ and poorly crystallized MoS$_2$ coexist in the hybrid. It is inferred that the as-obtained MoS$_2$/WS$_2$ nanosheet of mole ratio of 1/1 possesses simultaneously intrinsic conductivity and defects, hence being anticipated to have enhanced electrocatalytic activity for HER process.
In a typical photocatalytic experiment, MoS$_2$/WS$_2$ grown uniformly on 8 cm$^2$ area of the ITO substrate was suspended in 20 ml 0.50 M H$_2$SO$_4$ solution. The thickness of the MoS$_2$/WS$_2$ layer is ~223.1 nm (Fig.S11). The opening of the reactor was sealed with a silicone rubber septum. Bubbling N$_2$ gas is required to remove air in the reactant mixture and to ensure the anaerobic conditions of the reaction system. And then, the reaction system was irradiated by a 300-W Xe lamp with a cutoff filter of 420 nm for H$_2$ evolution. The amount of hydrogen evolution was measured using gas chromatography (GC- 7920, TCD detector), and the hydrogen production rate is 0.049 ml h$^{-1}$. For comparison with the previous studies, we have to convert it to $\mu$mol g$^{-1}$ h$^{-1}$, a customary unit used for hydrogen production rate. The hydrogen production rate is determined by the following equation:

$$\nu (H_2) = \frac{n}{tm} (1); \quad m=S_{MoS_2/WS_2} \times h \times \rho_{MoS_2} (2); \quad \nu = \frac{M}{\rho} n (3)$$

where $\nu(H_2)$ represents the hydrogen production rate /$\mu$mol g$^{-1}$ h$^{-1}$, t is the operation time (hour), m is the mass weight of the MoS$_2$/WS$_2$ which is estimated by equation (2) wherein, $S_{MoS_2/WS_2}$ is the surface areas of MoS$_2$/WS$_2$/ITO(8 cm$^2$), h represent the thickness of the MoS$_2$/WS$_2$ layer(223×10$^{-4}$ cm), and $\rho_{MoS_2}$ is the density of MoS$_2$ (4.8 g cm$^{-3}$) (the density of MoS$_2$ is used in the equation (2) since the amount of WS$_2$ in
hybrid is so small that it can be ignored. \( n \) is the moles of the produced \( \text{H}_2 \) which is calculated from the equation (3), \( V \) is hydrogen gas volume (0.049 ml h\(^{-1}\)), \( M \) is the molar mass of \( \text{H}_2 \) (2), \( \rho \) is the density of the \( \text{H}_2 \) (0.899 g cm\(^{-3}\)). Noteworthy is, the estimated mass of MoS\(_2\)/WS\(_2\) is greater than the actual mass because the MoS\(_2\)/WS\(_2\) structure is hierarchical rather than solid, thus leading to the lowest estimate for \( \text{H}_2 \) evolution production.

Table S1 Comparison of Hydrogen Evolution Data of WS\(_2\)/MoS\(_2\) Composites
Compared with Few of the Literature Reports

<table>
<thead>
<tr>
<th>catalyst</th>
<th>activity (( \mu )mol h(^{-1}) g(^{-1}))</th>
<th>reaction conditions</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>WS(_2)/MoS(_2)/Au</td>
<td>1.819</td>
<td>0.5 M H(_2)SO(_4) (a 300 W Xe lamp; ( \lambda \geq 420) nm)</td>
<td>14 (2016)</td>
</tr>
<tr>
<td>CdS/WS(_2)</td>
<td>373.41</td>
<td>Na(_2)SO(_4) aqueous solution (0.5 M) (300 W Xe lamp; ( \lambda \geq 420) nm)</td>
<td>15 (2016)</td>
</tr>
<tr>
<td>g-C(_3)N(_4)/WS(_2)</td>
<td>101</td>
<td>Methanol: water (1:3) (300 W xenon arc lamp; ( \lambda \geq 420) nm)</td>
<td>16 (2015)</td>
</tr>
<tr>
<td>MoS(_2@)Cu(_2)O</td>
<td>562.5</td>
<td>methanol/water (1:3) 350 W Xe arc lamp (( \lambda \geq 420) nm) at a bias of (-0.1) V vs. SCE</td>
<td>17 (2014)</td>
</tr>
<tr>
<td>Material</td>
<td>Reaction Conditions</td>
<td>Reference</td>
<td></td>
</tr>
<tr>
<td>-------------------</td>
<td>--------------------------------------------------------------------------------------</td>
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<tr>
<td>MoS₂ QDs</td>
<td>10% (v/v) triethanolamine (TEOA) aqueous solution (300 W xenon arc lamp; λ≥420 nm)</td>
<td>18 (2017)</td>
<td></td>
</tr>
<tr>
<td>TiO₂/1T-WS₂</td>
<td>methanol/water(1:3) (300 W xenon arc lamp)</td>
<td>19 (2014)</td>
<td></td>
</tr>
<tr>
<td>AgInZnS/MoS₂</td>
<td>aqueous solution containing 10% lactic acid(300 W xenon arc lamp; λ≥420 nm)</td>
<td>20 (2017)</td>
<td></td>
</tr>
<tr>
<td>WS₂/MoS₂</td>
<td>0.50 M H₂SO₄/lactic acid solution(300 W xenon arc lamp; λ≥420 nm)</td>
<td>This work</td>
<td></td>
</tr>
</tbody>
</table>


15. Y. Zhong, G. Zhao, F. Ma, Y. Wu and X. Hao, Applied Catalysis B: Environmental, 2016, 199, 466-472.


18. X. Hao, Z. Jin, H. Yang, G. Lu and Y. Bi, Applied Catalysis B: Environmental, 2017, 210, 45-56.
