Electronic Supplementary Material

Electric field and photoelectrical effect bi-enhanced hydrogen evolution reaction

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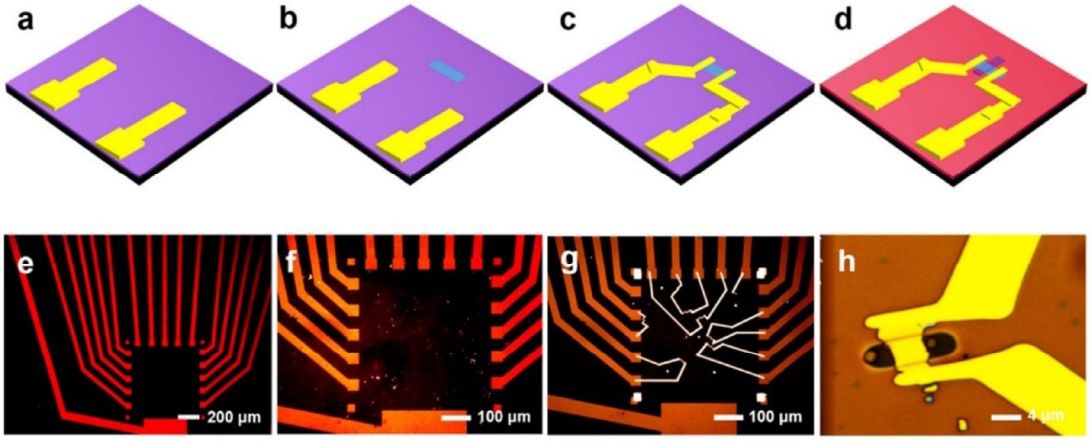

Figure S1 The assembly process of HER device based on individual MoS_2 nanosheet is schematically illustrated. Step 1, a suitable size silicon substrate (with 300-nm-thick insulation layer) is ultrasonic cleaned and spined with photoresist, then patterned by ultraviolet lithography and deposited Cr and Au through physical vapor deposition (PVD) to form the pattern of Cr/Au (5 nm/50 nm) on the silicon substrate as the outer electrode. Step 2, transferring MoS_2 nanosheets on silicon substrate with outer electrode by micromechanical exfoliation. Step 3, utilizing electron beam lithography and PVD to make two metal nanowires which is composed of Cr/Au and contacted with individual MoS_2 nanosheet as the inner electrode. Step 4, a layer PMMA is spin-coated as an insulating layer and then a part of individual MoS_2 nanosheet is exposed to make the nanosheet in contact with the electrolyte as work electrode. (a-d) The schematic diagram of the assembly process. (e-f) The optical image of the assembly process.

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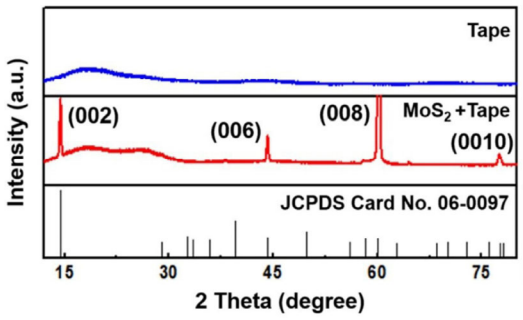

Figure S2 The XRD patterns of tape and the exfoliated MoS_2 on the tape. These diffraction peaks demonstrate the MoS_2 which has been used is single-structure.

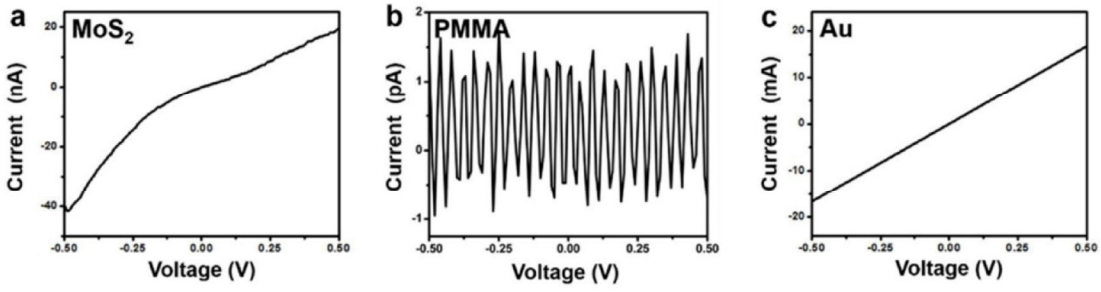

Figure S3 I–V curves of **a.** MoS_2 nanosheet, **b.** PMMA and **c.** Au, which are measured by probe station and semiconductor device analyzer. The conductivity of Au is far greater than that of MoS_2 and PMMA is far less conductive than MoS_2. Therefore, it is necessary to spin-coat PMMA photoresist onto Si/SiO_2 wafer to eliminate the impact of Au.

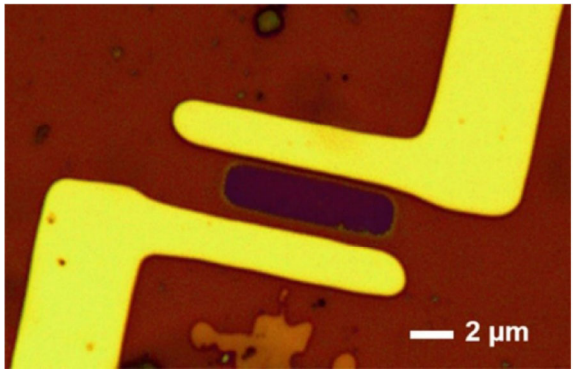

Figure S4 The optical image of the blank sample. No MoS_2 nanosheet can be found between two inner electrodes, which are insulated by PMMA layer.

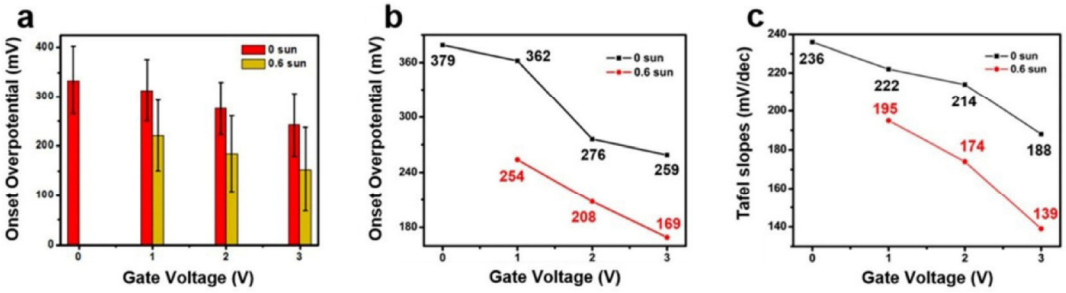

Figure S5 (a) The influence of different gate voltages and sunlight illumination on onset overpotentials in four different samples. (b-c) The values of onset overpotentials and Tafel slopes of the 9-nm-thick MoS_2 nanosheet, which decrease with back gate voltage increasing from 0 to 3 V and sunlight illumination applying. These values are obtained by measuring LSV curves at a scan rate of 5 mV/s.

Potential conversion from SCE to RHE

The potential conversion from SCE to RHE can been described as follows [1]:

$$E_{RHE} = E_{SCE} + 0.059\text{V*pH} + 0.24\text{V}; \text{pH} = -\text{Log}[\text{H}^+]$$

The electrolyte we used is 0.5 M H_2SO_4, in which the concentration of H^+ is 1 M, thus the value of pH is 0. The potential conversion between SCE and RHE can be simplified as follow:

$$E_{RHE} = E_{SCE} + 0.24\text{ V}(298\text{ K})$$

Relationship between between 60 mW/cm² and 0.6 sun

$$10\text{ mV/cm}^2 = 1\text{ sum};$$

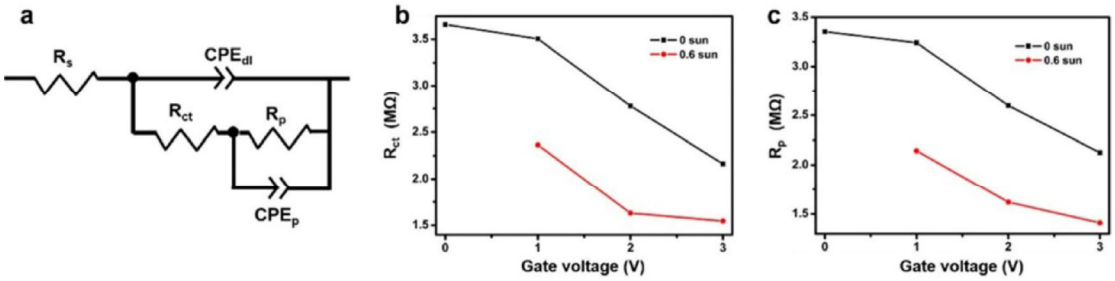

Figure S6 (a) A two-time constant equivalent circuit for fitting data. (b-c) The variation tendency of the corresponding R_{ct} and R_p under different back gate voltage and light illumination. The changes of R_{ct} and R_p are perfectly consistent with Tafel slopes in Fig. S3b. Thus, an accelerated kinetic process is able to be explained by the enhancement of conductivity.

In this measurement, the frequency ranged from 100 kHz to 100 Hz and the DC potential was set at -0.12 V *vs.* RHE.

Time constant (τ) calculation

A two-time constant equivalent circuit is adopted shown in Fig. S5a, R_s is the uncompensated electrolyte resistance. R_{ct} and CPE_{dl} refer to charge transfer resistance and double layer capacitance respectively, which are related to the high frequency time constant (τ_1). The low frequency time constant (τ_2) is connected with hydrogen adsorption include the Faradaic resistance for the electrodesorption and/or recombination reactions (R_p) and adsorption pseudocapacitance (CPE_p) [1, 2].

The constant phase element impedance (Z_{CPE}) is calculated by:

$$Z_{CPEdl} = \frac{1}{Q_1(\text{iw})^k}, \quad Z_{CPEp} = \frac{1}{Q_2(\text{iw})^k}$$

where Q_1 and Q_2 are the frequency-independent parameter in high and low frequency, respectively. i = √-1, ω is the angular frequency of the AC voltage and *k* is a dimensionless parameter related to the constant phase angle which has a range from 0 to 1.

The time constant (τ) value is calculated by:

$$\tau_1 = \frac{1}{\omega^*} = R_{ct}Q_1, \quad \tau_2 = \frac{1}{\omega^*} = R_pQ_2$$

where ω^* is characteristic angular frequency, R_{ct} and R_p are charge transfer resistance and the Faradaic resistance for the electrodesorption and/or recombination reactions, respectively.

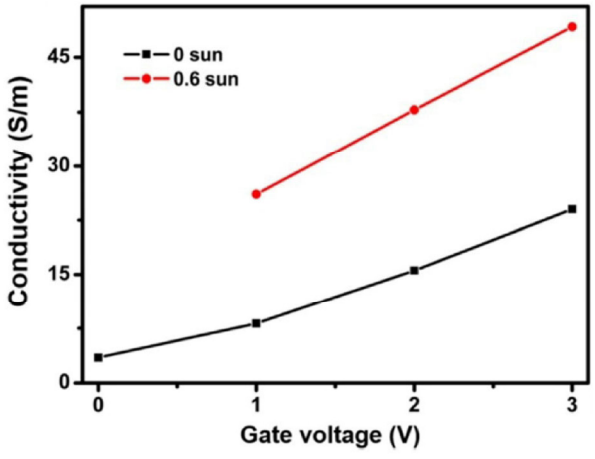

Figure S7 The conductivity of individual MoS_2 nanosheet is enhanced with the back gate voltage changing from 0 to 3 V and light illumination applying.

Table S1 The values of onset overpotentials in four samples under different back gate voltages increasing from 0 to 3 V and with/without sunlight illumination. The electrochemical property is related to MoS_2 structure like the number of MoS_2 layers [3]. Besides, the electrical property of MoS_2 nanosheets is influence by MoS_2/metal contact resistance, defects and so on [4], which may result in the difference in electrochemical property. All these factors cause that different samples have different electrochemical data.

	1	2	3	4	average
0 sun, 0V (mV)	379	347	233	375	334
0 sun, 1V (mV)	362	335	221	336	314
0 sun, 2V (mV)	276	322	202	306	277
0 sun, 3V (mV)	259	306	155	251	243
0.6 sun, 1V (mV)	254	295	127	211	222
0.6 sun, 2V (mV)	208	283	113	136	185
0.6 sun, 3V (mV)	169	266	89	89	153

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