**Supplementary information**



Figure S1. Schematic energy level diagram of the band alignment at *p-*Si/MoS2 interface in terms of vacuum level and normal hydrogen electrode level in electrolyte of pH = 0.3. The *p*-Si doping level is ~1.6$×10^{15}$cm-3.



Figure S2. (a) Nyquist plot of 700–ALD-cycles and 300-ALD-cycles on *p*-Si photocathode under 1sun illumination at 0 bias. (b) Equivalent circuit corresponding to the EIS measurement. Rbulk is bulk resistance of the silicon, Qjc is constant phase element (CPE) of *p-*Si/MoS2 junction along with junction resistance Rjc, CPE of MoS2/electrolyte interface is denoted as QMoS2 and the resistance of RMos2.

**Table S1.** Measured charge transfer resistances.

|  |  |  |  |
| --- | --- | --- | --- |
| **Condition** | **Rbulk (Ωcm2)****Back contact/p-Si** | **Rjc (Ωcm2)****p-Si/SiOx/MoS2** | **RMoS2 (Ωcm2)****MoS2/electrolyte** |
| **Dark (500)** | 5.94 | 702.5 | 9517 |
| **600** | 5.514 | 77.98 | 157.4 |
| **500** | 4.974 | 27.38 | 22.38 |
| **300** | 4.642 | 22.26 | 16.95 |
| **100** | 4.108 | 83.11 | 77.1 |

**List of symbols with values and Units**

$N\_{a} $ Acceptor density 1.6 x$10^{15}cm^{-3}$

$N\_{d}$ Donor density $10^{19} cm^{-3}$

$n\_{i\\_Si}$ Intrinsic carrier density of p-silicon $10^{10} cm^{-3}$

$n\_{i\\_MoS\_{2}}$ Intrinsic carrier density of MoS2 $10^{13} cm^{-3}$

$n\_{0}$ Electron concentration in p-Si at dark equilibrium 66,000 $cm^{-3}$

$p\_{0}$ Hole concentration in n-MoS2 at dark equilibrium $10^{13} cm^{-3}$

$n\_{s}^{0}$ Surface electron concentration across the cm-3

 electrode/electrolyte interface at light

$n\_{s}$ Surface electron concentration across the cm-3

 Electrode/electrolyte interface at dark equilibrium

W Depletion width cm

$χ\_{p}$ Electron negativity of p-Si eV

$χ\_{n}$ Electron negativity of MoS2 eV

$x\_{p}$ Interface to p-Si depletion width cm

$x\_{n}$ Interface to n-MoS2 depletion width cm

$L\_{n}$ Minority carrier diffusion length in p-Si cm

$L\_{p}$ Minority carrier diffusion length in MoS2 cm

$N\_{c}$ Density of states in the conduction band $cm^{-3}$

$N\_{v}$ Density of states in the valence band $cm^{-3}$

k Boltzmann’s constant 1.38$×10^{-23}JK^{-1}$

q Charge of an electron 1.6$×10^{-19}$C

$ε\_{r}$ Relative permittivity F$m^{-1}$

$ε\_{0}$ Vacuum permittivity F$m^{-1}$

$V\_{ph}$ Photovoltage V

$V\_{on}$ On-Set voltage V

$V\_{bi}$ Built-in potential V

$V\_{fb}$ Flatband potential V

$V\_{A}$ Applied voltage V

$V\_{0}$ The maximum restriction of photovoltage V

*Vo* band bending of silicon V

$ϕ\_{B}$ Barrier height eV

$ϕ\_{w}$ Work function eV

*Jph*Saturated photocurrent density mA·cm-2

*Jsc* Photocurrent density at 0 V vs RHE mA·cm-2

T Temperature T

C Capacitance F$cm^{-2}$

$R\_{s}$ Series resistance $Ω$cm2

$F\_{p}$ Quasi-Fermi level in p-Si eV

$F\_{n}$ Quasi-Fermi level in n-MoS2 eV

$g\_{op}$ Optical generation rate $cm^{-3}s^{-1}$