**Supplementary information**

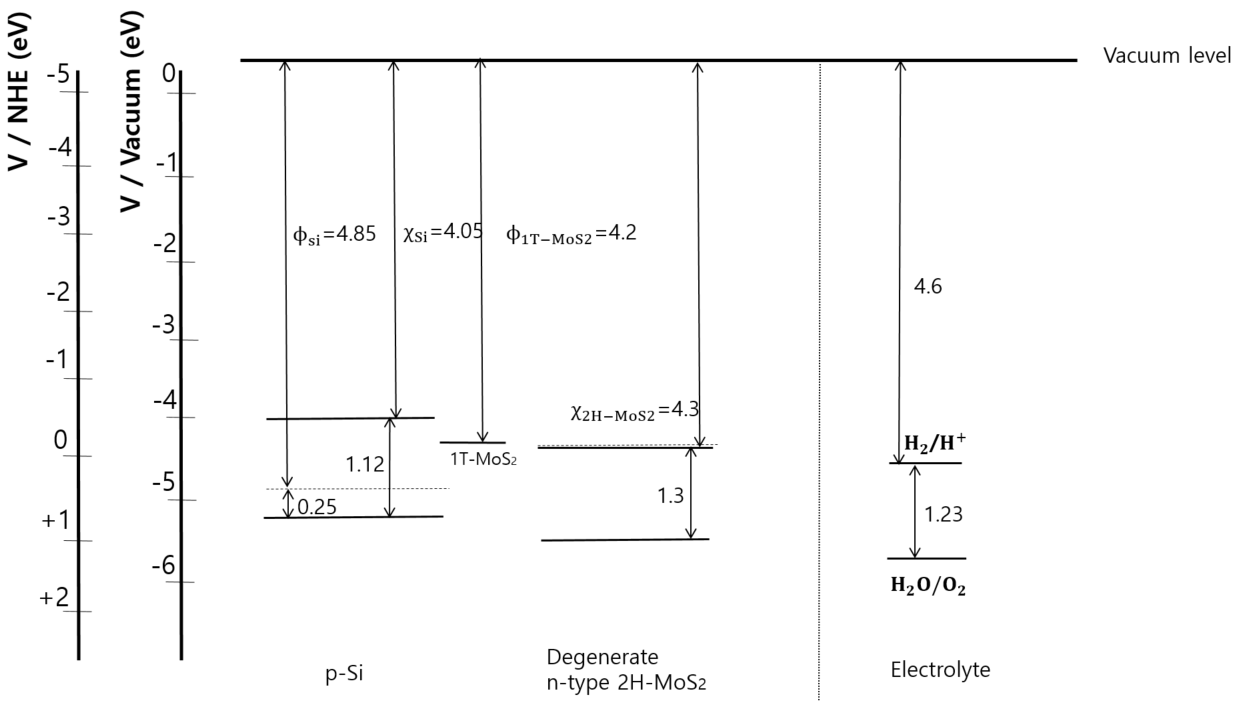


Figure S1. Schematic energy level diagram of the band alignment at *p-*Si/MoS2 interface in terms of vacuum level and normal hydrogen electrode level in electrolyte of pH = 0.3. The *p*-Si doping level is ~1.6cm-3.

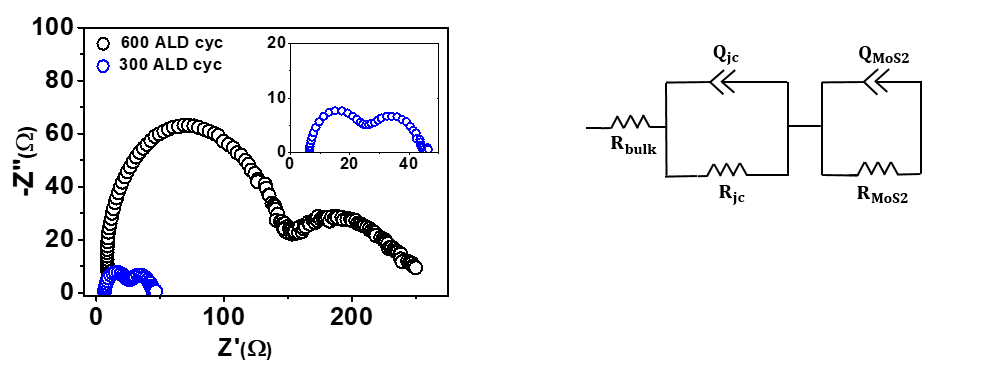


Figure S2. (a) Nyquist plot of 700–ALD-cycles and 300-ALD-cycles on *p*-Si photocathode under 1sun illumination at 0 bias. (b) Equivalent circuit corresponding to the EIS measurement. Rbulk is bulk resistance of the silicon, Qjc is constant phase element (CPE) of *p-*Si/MoS2 junction along with junction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

Acceptor density 1.6 x

Donor density

Intrinsic carrier density of p-silicon

Intrinsic carrier density of MoS2

Electron concentration in p-Si at dark equilibrium 66,000

Hole concentration in n-MoS2 at dark equilibrium

Surface electron concentration across the cm-3

electrode/electrolyte interface at light

Surface electron concentration across the cm-3

Electrode/electrolyte interface at dark equilibrium

W Depletion width cm

Electron negativity of p-Si eV

Electron negativity of MoS2 eV

Interface to p-Si depletion width cm

Interface to n-MoS2 depletion width cm

Minority carrier diffusion length in p-Si cm

Minority carrier diffusion length in MoS2 cm

Density of states in the conduction band

Density of states in the valence band

k Boltzmann’s constant 1.38

q Charge of an electron 1.6C

Relative permittivity F

Vacuum permittivity F

Photovoltage V

On-Set voltage V

Built-in potential V

Flatband potential V

Applied voltage V

The maximum restriction of photovoltage V

*Vo* band bending of silicon V

Barrier height eV

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

Series resistance cm2

Quasi-Fermi level in p-Si eV

Quasi-Fermi level in n-MoS2 eV

Optical generation rate