Supplementary information

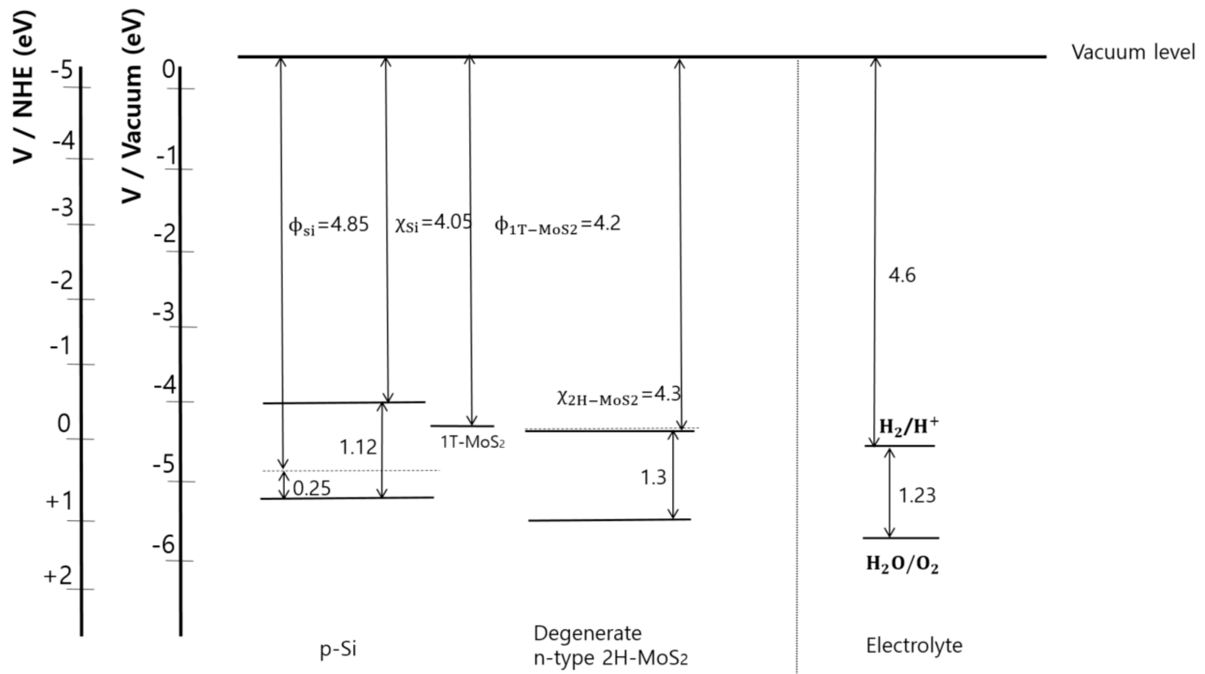

Figure S1. Schematic energy level diagram of the band alignment at *p*-Si/MoS_2 interface in terms of vacuum level and normal hydrogen electrode level in electrolyte of pH = 0.3. The *p*-Si doping level is ~$1.6\times \mathbf{10^{15}}$ cm^{-3}.

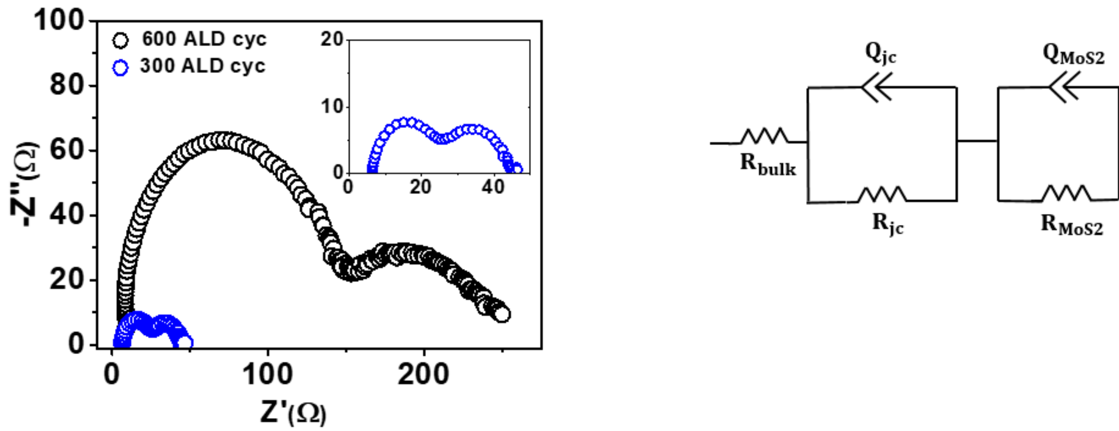

Figure S2. (a) Nyquist plot of 700–ALD-cycles and 300-ALD-cycles on *p*-Si photocathode under 1sun illumination at 0 bias. (b) Equivalent circuit corresponding to the EIS measurement. R_{bulk} is bulk resistance of the silicon, Q_{jc} is constant phase element (CPE) of *p*-Si/MoS_2 junction along with junction resistance R_{jc}, CPE of MoS_2/electrolyte interface is denoted as $QMoS_2$ and the resistance of R_{Mos2}.

Table S1. Measured charge transfer resistances.

Condition	R_{bulk} (Ωcm^2) Back contact/p-Si	R_{jc} (Ωcm^2) p-Si/SiOx/MoS_2	R_{MoS2} (Ωcm^2) MoS_2/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	$1.6 \times 10^{15} cm^{-3}$
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 MoS_2	10^{13} cm^{-3}
n_0	Electron concentration in p-Si at dark equilibrium	66,000 cm^{-3}
p_0	Hole concentration in n-MoS_2 at dark equilibrium	10^{13} cm^{-3}
n_s^0	Surface electron concentration across the electrode/electrolyte interface at light	cm^{-3}
n_s	Surface electron concentration across the Electrode/electrolyte interface at dark equilibrium	cm^{-3}
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-MoS_2 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	$1.38 \times 10^{-23} JK^{-1}$
q	Charge of an electron	$1.6 \times 10^{-19} C$
ε_r	Relative permittivity	Fm^{-1}
ε_0	Vacuum permittivity	Fm^{-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
V_o	band bending of silicon	V
ϕ_B	Barrier height	eV
ϕ_w	Work function	eV
J_{ph}	Saturated photocurrent density	$mA \cdot cm^{-2}$
J_{sc}	Photocurrent density at 0 V vs RHE	$mA \cdot cm^{-2}$
T	Temperature	T
C	Capacitance	Fcm^{-2}
R_s	Series resistance	Ωcm^2
F_p	Quasi-Fermi level in p-Si	eV
F_n	Quasi-Fermi level in n-MoS_2	eV
g_{op}	Optical generation rate	$cm^{-3}s^{-1}$