Supporting Information for

Stable CdTe Photoanodes with Energetics Matching Those of a Coating Intermediate Band

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1 Experimental Methods

Preparation of CdS and CdTe Films

The CdS/CdTe heterojunctions were synthesized according to the previous publication.¹ The CdS window layer was first deposited by radio-frequency (RF) sputtering on a SnO₂:F/SnO₂ transparent conducting oxide (TCO) layer at room temperature using a hot-pressed CdS target and then the CdS layer was annealed at 600 °C for 5 min in a 4% O₂-in-Ar mixture. A CdTe layer was grown on top of the CdS layer by using a close-spaced sublimation (CSS) method, with the source and substrate temperatures held at 660 and 600 °C, respectively. Vapor-phase CdCl₂ annealing was subsequently performed in a CSS configuration at 430 °C for 10 min. Copper (Cu) was introduced through a wet 0.1 mM CuCl₂ (aq) solution treatment, followed by annealing.

For fabricating the CdS/CdTe solar cells, Au back contacts were coated by electron-beam evaporation at room temperature without intentional substrate heating. For the CdTe photoanode fabrication, a bromine/methanol etching treatment for CdTe was performed prior to coating TiO₂ by atomic layer deposition (ALD). The CdTe sample was dipped in a freshly made bromine/methanol (0.1% by volume ratio) solution for 30 s, followed by rinsing with copious amounts of methanol and then dried in a stream of N₂. An alternative Ar⁺ sputtering surface treatment was tried, in which an ion gun was used to sputter-etch the sample surface with 500-eV Ar⁺ ions for 5 min.

ALD TiO₂ Stabilization Coating

TiO₂ stabilization layers were coated onto the CdTe (CdTe/CdS/SnO₂/SnO₂:F layered stack), Si, and SnO₂:F substrates at 150 °C using an Ultratech Fiji G2 ALD system. Both the Si and SnO₂:F substrates were cleaned with deionized water, acetone, and ethanol in sequence and loaded immediately into the ALD chamber. Prior to ALD TiO₂, the surface of CdTe in the CdS/CdTe films stack was prepared by bromine/methanol etching as described above. Each ALD cycle consisted of a 0.06 s pulse of H₂O, followed by a 0.25 s pulse of tetrakis-dimethylamido-titanium (TDMAT, Sigma-Aldrich, 99.999%). A constant flow of Ar (99.9997%) gas purged the reactor between each precursor pulse. TiO₂ coatings of ~110-nm thickness were conformally deposited on the surfaces of the substrates, with the cycle number for the thickness calculated according to a planar growth rate of 0.47 Å per cycle.²

Deposition of Ni/NiOx Films

Ni metal films of ~50-nm thickness were deposited onto the surfaces of ALD TiO₂ layers using a thermal evaporation system (MBraun, MB-EcoVap) with Ni pellets (Kurt J. Lesker Corp., 99.995%) as the source material. The background pressure was kept at 1×10^{-6} Pa. The evaporation rate was controlled at a constant of 0.03 nm s⁻¹. The Ni surfaces become Ni/NiO_x during PEC water oxidation, so we denote Ni/NiO_x as the OER electrocatalyst.

Materials Characterizations

X-ray diffraction (XRD, Rigaku SmartLab) was used to identify the crystal structure of the CdTe films after film growth and post-growth treatment. The XRD instrument employs a Cu Ka source with a beam energy of 8.04 keV, which corresponds to an X-ray wavelength of 1.5406 Å. Optical absorption properties were measured using an Ultraviolet-visible (UV-vis) spectrophotometer (UV-2600, SHIMADZU) under a diffused reflectance spectroscopy (DRS) configuration. The light was incident from the TCO side and the light absorption of CdTe based photoanodes could be calculated by Absorption (%) = 100% – Reflection (%) – Transmission (%). To characterize the film morphology, scanning electron microscope (SEM) was performed using a Hitachi SU8230 UHR system. Energy dispersive X-ray spectroscopy (EDX, Bruker QUANTAX FlatQUAD) attached to this SEM system was conducted to observe the elemental distribution of the film. Xray photoelectron spectroscopy (XPS, PHI VersaProbeII) was used to investigate the elemental composition and the oxidation state of the as-prepared films. Steady-state photoluminescence (PL) measurements were performed using a Raman spectrometer (HORIBA Scientific) under room temperature. The excitation wavelength was set at 528 nm by using a tunable filter to pick the output light of 10-nm bandwidth from a supercontinuum laser (NKT photonics). A 570 nm longpass filter was used to filter and block the 528-nm excitation light. Time-resolved photoluminescence (TRPL) was acquired using time-correlated single-photon counting (PicoHarp 300), with a 528-nm pulsed laser for optical excitation and a monochromator set at a center wavelength of 840 nm for PL decay detection. The PL intensity decay was fit by a single exponential equation, and the decay time constant was obtained as an indicator for surface recombination. Microscope (OLYMPUS BX51) was used to obtain the dark field images to exam the morphology of CdS/CdTe/TiO₂/Ni/NiO_x photoanodes after stability testing.

Photoelectrochemical (PEC) Performance Characterization

All PEC measurements for CdTe photoanodes were conducted using a Bio-Logic S200 potentiostat in a three-electrode PEC cell, with the photoanode as the working electrode, a Ag/AgCl electrode as the reference electrode, and a Pt wire as the counter electrode. A porous glass plate separates the working and the counter electrodes. The light source was produced from a Xe lamp (Newport, 300 W) with an AM 1.5G filter. The illumination intensity was calibrated by placing a Si photodiode (FDS100, Thor Labs) in the electrolyte-containing electrochemical cell in the same location as the photoelectrode during PEC performance measurements.

For the PEC measurements, the electrolyte used was 1.0 M KOH (pH = 14). The applied bias vs Ag/AgCl was converted into a reversible hydrogen electrode (RHE) according to the equation (1) below:³

$$E_{RHE} = E_{Aq/AqCl} + 0.059 \times pH + 0.1976 \quad (1)$$

The current density vs potential (J-E) measurements, including cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were conducted with a scan rate of 20 mV s⁻¹. The solution resistance loss was corrected according to equation (2):^{4, 5}

$$E_{corr} = E_{meas} - iR_s \quad (2)$$

, where Rs represents the solution resistance, which is extracted from impedance measurement.

During the stability test, the photocurrent vs time (*I-t*) curve was recorded under a bias voltage of 2.0 V vs RHE, at which potential the photocurrent reached a light-limited value. Incident photon-to-current-efficiency (IPCE) measurements were performed under different wavelengths. The light source (at a 10-nm bandwidth and chopped at 27 Hz) was generated from a computer-controlled monochromator (Newport Corp.). A chopping frequency of 27 Hz was reasonable considering that the response time constant was less than milliseconds for the CdTe photoelectrode if it is given a step potential. Monochromated light, obtained by passing through a long-pass filter to remove higher-order diffractions, was focused to a spot size that under-fill the photoelectrode active area. The incident light intensity at each wavelength was calibrated using a silicon photodiode (FDS100-CAL, Thor Labs) of known quantum yields. Therefore, the IPCE value could be calculated according to the following equation:

$$IPCE = 1240 \times \frac{J_{\lambda}}{\lambda P_{\lambda}} \quad (3)$$

, where J_{λ} is the photocurrent density (mA cm⁻²) under illumination of wavelength λ (nm), and P_{λ} is the power intensity of the incident monochromatic light. The applied potential was set at three

increasing values of 1.5 V, 1.7 V and 2.0 V vs RHE, to make sure the full extraction of photogenerated carriers in the photoanode at 1.5 V vs RHE.

Electrochemical Impedance Spectroscopy (EIS) Analysis

To study the liquid interfacial energetics of TiO₂-coated CdTe photoanodes immersed in aqueous electrolytes, Mott-Schottky differential capacitance-potential analysis was derived from EIS measurements. The measurements were conducted in an aqueous solution of $Fe(CN)_6^{3-/4-}$ redox couple [50 mM K₃Fe(CN)₆ and 350 mM K₄Fe(CN)₆] in the complete dark. The frequency ranged from 5 MHz to 1 Hz and the waiting time for each potential step was 5 s. A 50-nm TiO₂ layer was coated on SnO₂:F for Mott–Schottky analysis. The differential capacitance of the space charge region was calculated by fitting the data with a Randles circuit in which a constant phase element (CPE) and a resistor in parallel were connected in series with another resistor.

The solution resistance (R_s) was also obtained by EIS measurements in 1.0 M KOH(aq) in the dark. The R_s value was extracted by fitting the data with a Randles circuit, in which the series resistance component was defined as R_s .

Solid-State Electrical Measurements

For both CdS/CdTe/Ni/NiO_x and CdS/CdTe/Au devices, the front and back electrical ohmic contacts were connected through the SnO₂:F/SnO₂ and the Ni/NiO_x(Au) films, respectively. This device was held by a chip carrier, and the back electrical ohmic contact for the CdS/CdTe/TiO₂/Ni/NiO_x(Au) structure was formed by bonding Ni(Au) contact pads with Al wires. Solid-state current vs voltage (*J*–*V*) measurements were performed using a two-electrode setup, with the working electrode connected to Ni/NiO_x(Au), and with the counter and reference electrodes shorted and electrically wired to In dots that are soldered onto SnO₂:F/SnO₂. The illumination was calibrated to a simulated solar light (AM 1.5G, 100 mW cm⁻²).

2 Supplementary Discussions

Structural Characterizations of CdS/CdTe/TiO₂/Ni/NiO_x Multilayers

SEM images showed that the CdS polycrystalline film with a thickness of 100 nm was uniformly coated on the TCO layer. No diffraction peaks from this CdS window layer were observed obviously due to its thickness as thin as 100 nm. Instead, CdS was detected by SEM and EDX mapping. A ~3.5- μ m thick CdTe film was densely grown on the top of CdS (**Figure S2**, **Figure S3a**). The small crystallites (100 nm in size) that existed at the grain boundaries of CdTe were produced during annealing in a CdCl₂ atmosphere, which was designed to eliminate the boundary defects or pinhole defects of CdTe.⁶ It will be elucidated later that the post-growth CdCl₂ annealing procedure further improved CdTe density, thereby reducing pinhole density and enhancing stability. The CdS/CdTe films were then conformally coated with ~110-nm thick ALD-grown TiO₂, followed by ~50 nm thermal evaporated Ni/NiO_x (**Figure S3b, Figure S3c and Figure S4**). Only Ni element present in combination of Ni/NiO_x was detected by investigating the XPS spectra (**Figure S5**), further confirming that the uniform TiO₂/Ni/NiO_x coatings fully covered the top of CdS/CdTe structure.^{7, 8}

Oxidation State of p-Type CdTe Surface

XPS measurements were performed to characterize the Te oxidation state of p-type CdTe surfaces. The Multipak software was used to quantify the surface elemental composition of CdTe. As shown in **Figure S10**, the atom concentrations of C, O, Cd, and Te were 57.39%, 21.54%, 11.80% and 9.29%, respectively. Note that except for CdTe compounds, there were also surface tellurium oxides, which would seriously inhibit the charge transfer at the interface as a tunnel barrier. The tellurium oxide would also cause the recombination of photogenerated carriers, thus leading to a low photovoltage.⁹ After Ar⁺ sputter-etching treatment for CdTe, C was completely removed. The atomic composition ratio of O, Cd, and Te was 0.22 to 1.21 to 1, revealing that the surface oxidation layer was effectively removed (**Figure S11**). Additionally, bromine/methanol (0.1% by volume ratio) etching of CdTe for 30 s not only removed the tellurium oxidation layer, but also created a Te-rich surface (atomic ratio of Cd to Te = 0.73:1) according to the previous publication.¹⁰ It has been reported that the formation of small valence band offset between CdTe and Te could facilitate photogenerated holes transfer from CdTe to Te layer.^{11, 12}

Band-Edge Energetics Determination by Mott-Schottky Analysis

According to Mott–Schottky analysis, the inverse square of the differential capacitance (C⁻²) vs potential (*E* vs RHE) was plotted for the SnO₂:F/TiO₂ electrode. The flat-band potential, which is the Fermi level (E_f) with respect to the solution when the electronic bands of TiO₂ become flat across the film-thickness direction, could be represented by a linear fit of C^{-2} vs *E*.¹³

According to Figure S15, we obtained the space charge density by the following equation:¹⁴

$$\frac{1}{C^2} = \frac{2}{\varepsilon \varepsilon_0 q N_D} \left(E - E_{FB} - \frac{kT}{q} \right) \quad (4)$$

where *C* represents the differential capacitance; ε (=130) is the dielectric constant of TiO₂; ε_0 is the vacuum dielectric constant (8.854×10⁻¹⁴ F cm⁻¹); *q* is the absolute charge of an electron; *N_D* is the space charge density (in typical semiconductors, it means the doping concentration because the semiconductor is depleted with); *E* is the applied potential; *E_{FB}* is the flat band potential; *k* is the Boltzmann constant; and *T* is the temperature.

Conventionally, N_D , the space charge density, is used to approximate the free carrier concentration, but it is not true for intermediate-band oxides. According to a slope of $5.1 \times 10^9 \text{ F}^{-2}$ cm⁴ V⁻¹ for the Mott–Schottky plot, the fixed positive space charge density of this ALD TiO₂ was calculated to be 2.1×10^{20} cm⁻³. Typically, the space charge density equals to the doping density and free carrier concentration. However, the free carrier concentration, in "leaky" TiO₂, should not equal to the space charge density, which is due to oxygen vacancy. The spatial density of electron trap states due to Ti^{3+} defects is also on the order of 10^{20} cm⁻³. Therefore, it is considered that the free carriers are trapped, resulting in a unique observation of a high space charge density and a low free carrier concentration. The respective E_f is lowered to the Ti³⁺-defect band edge, 0.4 eV below the TiO₂ conduction band (CB) edge. The E_f value for SnO₂:F/TiO₂ was -0.8 V vs Ag/AgCl in $Fe(CN)_6^{3-/4-}$ (pH 8.5). Valence band (VB) XPS data in our previous study showed a valence band maximum (VBM) of 2.94 eV below the Ef for this "leaky" TiO2. Therefore, the VBM position was 2.14 V vs Ag/AgCl in water. According to the bandgap of 3.34 eV for TiO₂, the CB position lies at -1.2 V vs Ag/AgCl. The position of the defect band for TiO₂, with a density-of-state maximum at 0.94 eV \pm 0.03 eV below the E_f and a full width at half-maximum (FWHM) of 0.88 eV \pm 0.10 eV, was calculated to locate at the range of -0.30 V - +0.58 V vs Ag/AgCl.¹⁵

Many publications have reported the band alignment between TiO_2 and CdTe.¹⁶⁻²¹ They can form a type-II staggered band structure for charge separation and transfer according to the E_f

alignment. For example, K. Ernst *et al.* reported that the CdTe CB lies approximately 0.6 eV above the TiO₂ conduction band.¹⁶⁻¹⁸ Tiefenbacher *et al.* demonstrated a CB offset of 0.7 eV at the CdTe/TiO₂ interface.¹⁹ Brus *et al.* also reported an experimental CB discontinuity (ΔE_c) value of 0.7 eV.^{20, 21} Considering that our similar surface preparation and carrier concentration of CdTe with that reported by Brus *et al.*, herein we adopted a CB offset of 0.7 eV. Then CdTe, with a bandgap of 1.5 eV, exhibits the CB and VB positions at -1.9 V vs Ag/AgCl and -0.4 V vs Ag/AgCl, respectively. These values are shown in **Figure 3** for the band alignment near the CdTe/TiO₂ interface. Therefore, the CdTe VBM of -0.4 V vs Ag/AgCl aligns with the TiO₂ intermediate band of -0.3 V - +0.58 V vs Ag/AgCl (FWHM). This alignment explains the ohmic electrical conduction from CdTe VB to the Ni/NiO_x electrocatalysts through the Ti³⁺-defect band.¹⁵ Still, the interfacial layer and chemical property at the CdTe/TiO₂ interface have not yet been dertermined as cautiously represented with a dashed box, and the interfacial band energetics may not be flat.

We derive that the VBM of p-type CdTe aligned well with the intermediate band of "leaky" TiO₂, indicating a low resistance contact, which favors the interfacial charge transport. It is known that the band alignment at the interface of two semiconductors is affected by the E_f , doping concentration, interfacial reaction, surface states, etc.²² Therefore, it is reasonable that two semiconductors could generate different band alignments. For example, Tiefenbacher *et al.* reported a VB offset of 2.6 eV, a CB offset of 0.7 eV at the CdTe/TiO₂ interface.²⁰ In their study, the TiO₂/CdTe heterointerfaces were prepared inside the ultrahigh vacuum (UHV) chamber which avoids most detrimental cleaning procedures. The TiO₂ film is heavily n-type doped and CdTe is weakly p-doped, with a E_f of 0.5 eV above the VBM. K. Ernst *et al.* also reported a TiO₂/CdTe heterojunction, in which the TiO₂ CB locates at about the mid-gap of CdTe.^{16,17} Additionally, the Type II CdTe/TiO₂ heterojunctions as those observed in this study were reported.^{23,24}

Long-Term Stress Testing and Corrosion Analysis

The CdS/CdTe/TiO₂/Ni/NiO_x photoanodes were tested under 100 mW cm⁻² simulated solar illumination with the potential of the SnO₂:F TCO layer held constant at 2.0 V vs. RHE. During the long-term stress testing, the instability of the CdS/CdTe/TiO₂/Ni/NiO_x photoanode mainly arises from CdS. Bright spots in dark-field optical images showed the corroded CdS pits that scattered light strongly (**Figure S16**). Accordingly, the photocurrent eventually decreased to ~35% of the original photocurrent level (**Figure S17**) due to the weak points in CdS layers (**Figure S16**).

In an extreme case of 350-hour stability testing, a portion of TiO₂ coatings got lifted-off, thereby exposing the CdTe underneath the TiO₂ coating (**Figure S18**), leading to accelerated CdTe photocorrosion and passivation. Plan-view SEM images indicated that the corroded CdTe crystallites, i.e., CdTeO_x, were re-deposited onto the electrode surface (**Figure S19**), and the corresponding EDX element mappings (**Figure S20**) also supported the re-deposition of CdTeO_x particles. These results indicated the corrosion of both CdS and CdTe layers. But the CdS layers that are covered underneath the CdTe layers took more severe corrosion, and became the weak point of the CdTe photoanodes. XPS analysis revealed that the Ni element presents in Ni(OH)₂, and the Cd and Te elements were also observed and found to exist at their highest oxidation state, i.e., Cd(II) and Te(IV), respectively (**Figure S21**).



Figure S1. XRD patterns of the as-prepared CdS/CdTe layers, in which the CdTe film exhibited a cubic zincblend structure and a strong preferred orientation along the {111}-type planes. The CdS diffraction peaks were not detected obviously because it was too thin (~110-nm thick).



Figure S2. Cross-sectional SEM image of as-prepared CdS/CdTe films.



Figure S3. Plane-view SEM images of (a) CdS/CdTe, (b) CdS/CdTe/TiO₂ (110 nm) and (c) CdS/CdTe/TiO₂ (110 nm)/Ni/NiO_x (50 nm) multilayer stacks.



Figure S4. Cross-sectional SEM image of Si/TiO₂/Ni/NiO_x, with the same growth parameters of TiO₂ and Ni/NiO_x as CdS/CdTe. Herein, the ALD cycles of TiO₂ was kept 2200 and the growth rate of TiO₂ film was about 0.5 Å per cycle.



Figure S5. (a) XPS survey scan of CdS/CdTe/TiO₂/Ni/NiO_x film. Neither Cd nor Te signal was detected, suggesting that the TiO₂/Ni/NiO_x species have covered the CdTe surface completely. (b) Core-level XPS spectra of Ni 2p peaks, consisting of metallic Ni and NiO_x.



Figure S6. (a) Tauc plot of the CdS/CdTe layers acquired from its UV-vis DRS absorption property (black line in the inset). The band gap of CdTe was calculated to be ~1.45 eV. The absorption property curve of the CdS/CdTe/TiO₂/Ni/NiO_x film was also shown in the inset (red line). The improved light absorption at wavelength >850 nm with Ni metallic back contacts was due to increased light scattering, which was supported by the reduced reflected (b) and transmitted (c) light.



Figure S7. Solid-state J-V curve of the CdS/CdTe/TiO₂/Ni/NiO_x device under simulated 1-sun illumination, in which the open-circuit voltage (V_{oc}) was 780±20 mV and the short-circuit photocurrent density (J_{sc}) was 24.5±0.5 mA cm⁻².



Figure S8. Solid-state J–V curve of the CdTe solar cell (CdS/CdTe/Au) under simulated 1-sun illumination, in which the V_{oc} was 830±10 mV and the J_{sc} was 25.5 ± 0.1 mA cm⁻².



Figure S9. Intrinsic energy-conversion property of the CdS/CdTe/TiO₂/Ni/NiO_x photoanode. (a) Effective *I-V* energy-conversion behavior of the CdTe photoanode by comparing the photoanode behavior with a dark SnO_2 :F/TiO₂/Ni/NiO_x anode using the same Ni/NiO_x catalysts, and (b) the measured *J*–*E* characteristics of CdS/CdTe/TiO₂/Ni/NiO_x photoanode before (dashed red line) and after (solid red line) correction for solution series resistance losses, and the electrocatalytic behavior of a SnO_2 :F/TiO₂/Ni/NiO_x anode (solid black line). The R_s value was calculated to be 12±1 ohm according to the EIS analysis.



Figure S10. XPS spectra of element (a) C, (b) O, (c) Cd and (d) Te for as-prepared CdS/CdTe films.



Figure S11. XPS spectra of element (a) C, (b) O, (c) Cd and (d) Te for CdTe after Ar⁺ sputter-etching.



Figure S12. *J*–*E* behavior of CdS/CdTe/TiO₂/Ni/NiO_x photoanode in 1.0 M KOH under illumination. CdTe was etched by Ar^+ sputter prior to deposition of TiO₂. It was noted that the onset potential was ~1.03 V vs RHE.



Figure S13. *J*–*E* behavior of CdS/CdTe/TiO₂/Ni/NiO_x photoanode in 1.0 M KOH under illumination. CdTe was coated by TiO₂ directly without any etching treatment beyond cleaning with CH₃OH. The onset potential was \sim 1.18 V vs RHE.



Figure S14. (a) Steady-state PL spectra of CdTe films before and after bromine/methanol etching treatment and (b) the corresponding TRPL measurements. Herein, single exponential data analysis model $(y = y_0 + Ae^{\frac{-t}{\tau}})$ was adopted to fit the PL decay. The calculated τ values for the CdTe films before and after etching treatment were 127 ps and 171 ps, respectively, indicating that surface etched by bromine/methanol made a modest improvement to the minority carrier lifetime of CdTe.



Figure S15. Mott–Schottky analysis of the SnO_2 :F/TiO₂ electrode. Electrolyte: $Fe(CN)_6^{3-/4-}$ redox couple (pH 8.5).



Figure S16. Dark-field images from TCO side of the CdS/CdTe/TiO₂/Ni/NiO_x photoanode before (a) and after (b) 350-hour stability test. The bright nanoparticles in the right figure were caused by corrosion of CdS nanoparticles.



Figure S17. Stability test of CdS/CdTe/TiO₂/Ni/NiO_x photoanode during long term PEC reaction. The photocurrent decreased \sim 35% of original photocurrent level after 350-hour operation.



Figure S18. (a) SEM of the CdS/CdTe/TiO₂/Ni/NiO_x photoanode after 350-hour stability test; (b)-(f) Corresponding EDX elemental mappings of Ni, Ti, Cd, Te and O. Note that the TiO₂ protective layer lifted off, exposing CdTe.



Figure S19. SEM images of CdS/CdTe/TiO₂/Ni/NiO_x photoanodes before (a) and after (b) 350-hour stability test operation.



Figure S20. SEM of CdS/CdTe/TiO₂/Ni/NiO_x photoanode after 350-hour stability test (a) and the corresponding EDX elemental mappings of (b) Ni, (c) Ti, (d) Cd, (e) Te and (f) O, indicating that the oxidized species (CdTeO_x) were re-deposited onto the electrode surface.



Figure S21. (a) XPS survey scan of CdS/CdTe/TiO₂/Ni/NiO_x photoanode after 350-hour stability test and the corresponding core-level XPS spectra of (b) Cd, (c) Te and (d) Ni. The element Te has been oxidized into TeO₂ completely and element Ni existed in the form of Ni(OH)₂.

Layer	SnO ₂	CdS	CdTe	TiO ₂
Bandgap (eV)	3.6	2.4	1.5	3.34
Electron affinity (eV)	4.7	4.5	4.4	4.4
VBM to vacuum (eV)	8.4	6.9	5.9	7.74
Work function (eV)	4.7	4.61	5.64	4.8

Table S1. Energetic parameters of the various layer components. ^{15, 25}

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