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This version (published 16.02.23) replaces the original version published on 02.02.17 which contained typographic text occlusion in the caption of Figure SA1, which should be correctly shown as "Figure SA1. A photographic image and schematic of the closed space sublimation apparatus".

Supplementary information

Photoelertochemical Hydrogen Evolution from Water on Surface Modified CdTe Thin Film Electrode under Simulated Sunlight

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Table S1. The thickness of CdTe layers deposited on FTO substrates using different CSS deposition times.

Deposition time of CdTe	3 min	6 min	12 min	18 min	24 min
Thickness of CdTe layer	500 nm	1.0 μm	2.0 μm	3.8 μm	5.2 μm

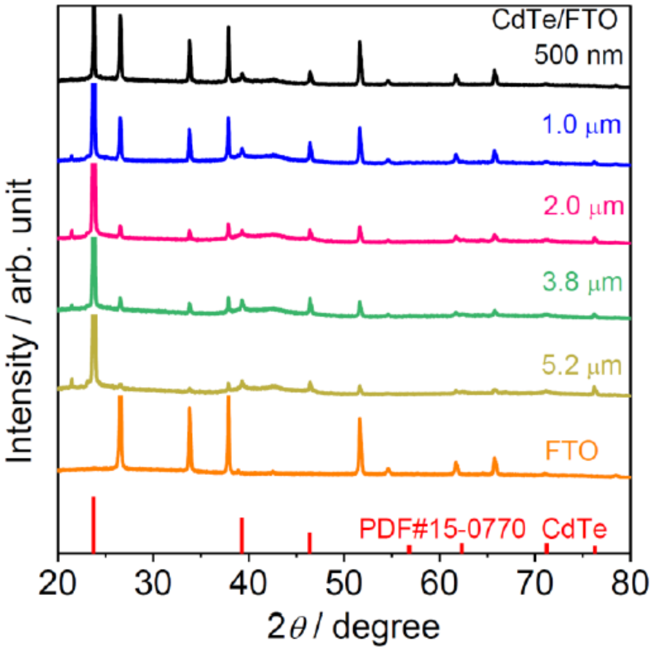

Figure S1. The XRD patterns were obtained from CdTe/fluorine-doped tin oxide (FTO) specimens with various thick CdTe layers.

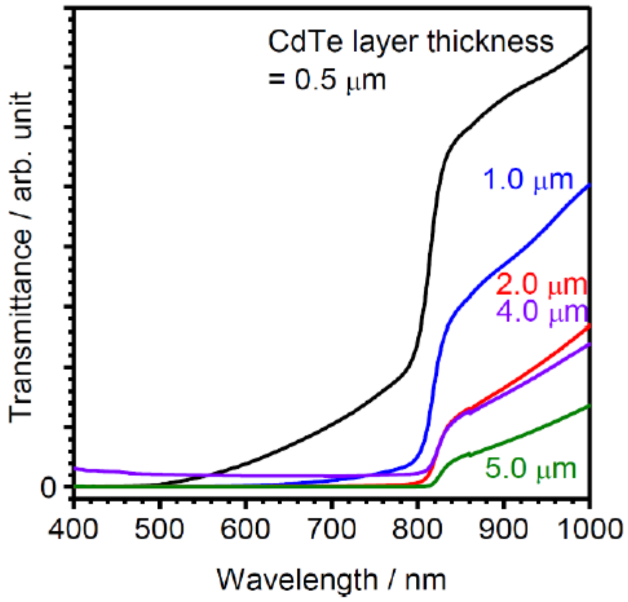

Figure S2. The UV-vis transmission spectra were obtained from CdTe/FTO specimens with various thick CdTe layers.

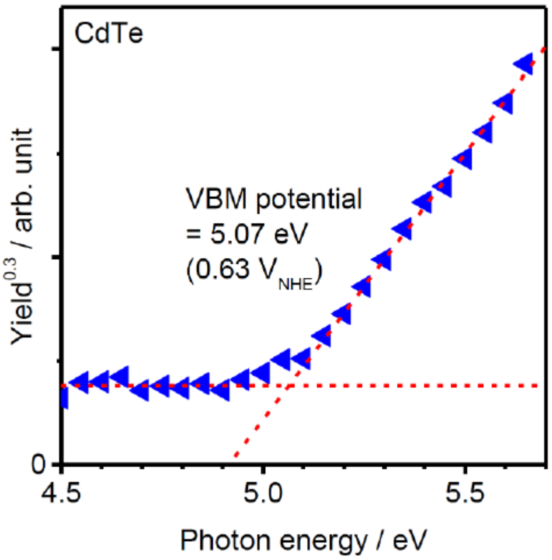

Figure S3. The PESA spectrum of a CdTe/FTO specimen. The valence band maximum (VBM) potential was determined to be 5.07 eV.

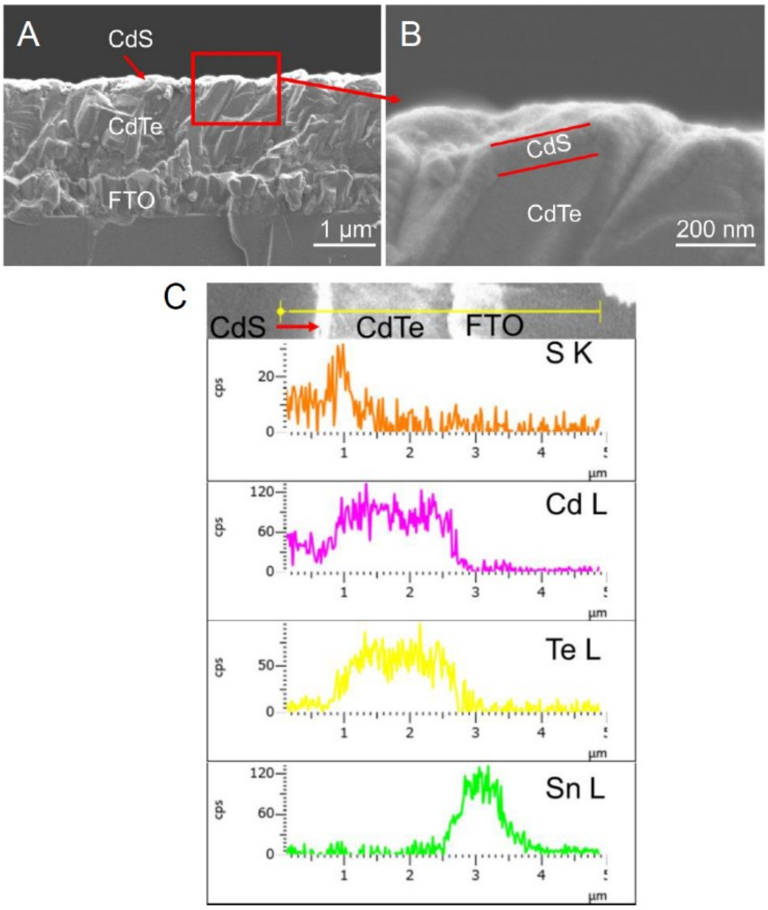

Figure S4. (A and B) Cross-sectional SEM images and (C) an EDX line analysis of a CdS/CdTe/FTO specimen fabricated using a CdS deposition time of 8 min.

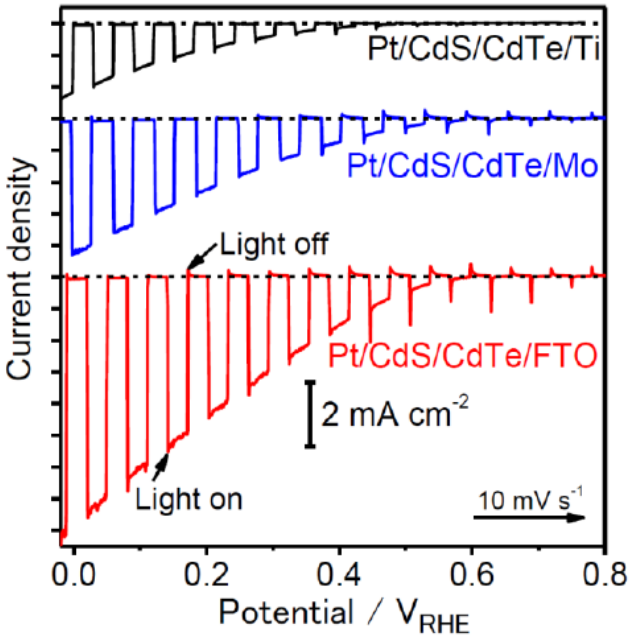

Figure S5. Current-potential curves for Pt/CdS/CdTe/Ti, Pt/CdS/CdTe/Mo, and Pt/CdS/CdTe/FTO specimens under chopped simulated sunlight in a 0.5 M aqueous KH_2PO_4 solution with pH adjusted to 8.

Table S2. Work functions of examined substrates.

Conductor layer	Work function
Ti	4.3
Mo	4.6
FTO	5.0

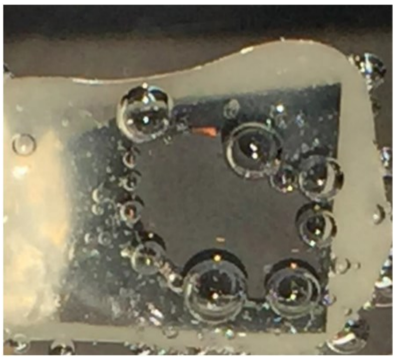

Figure S6. A photographic image of a Pt/CdS/CdTe/FTO photocathode during hydrogen evolution from water under simulated sunlight.

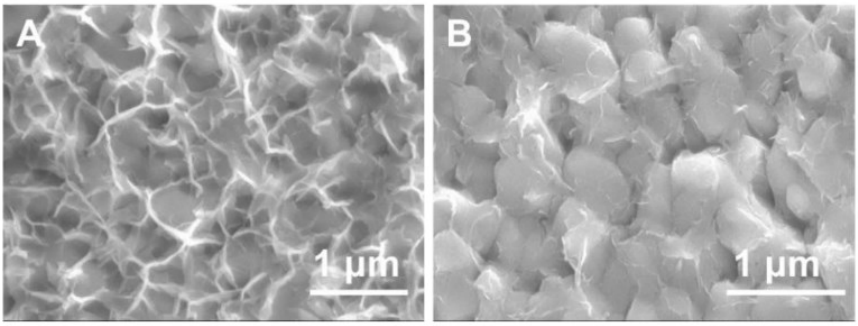

Figure S7. An SEM image of a Pt/CdS/CdTe/FTO photocathode surface (A) before and (B) after the durability test shown in Figure 8 of the main text. A networked CdS found on the surface of the specimen disappeared after the durability test.

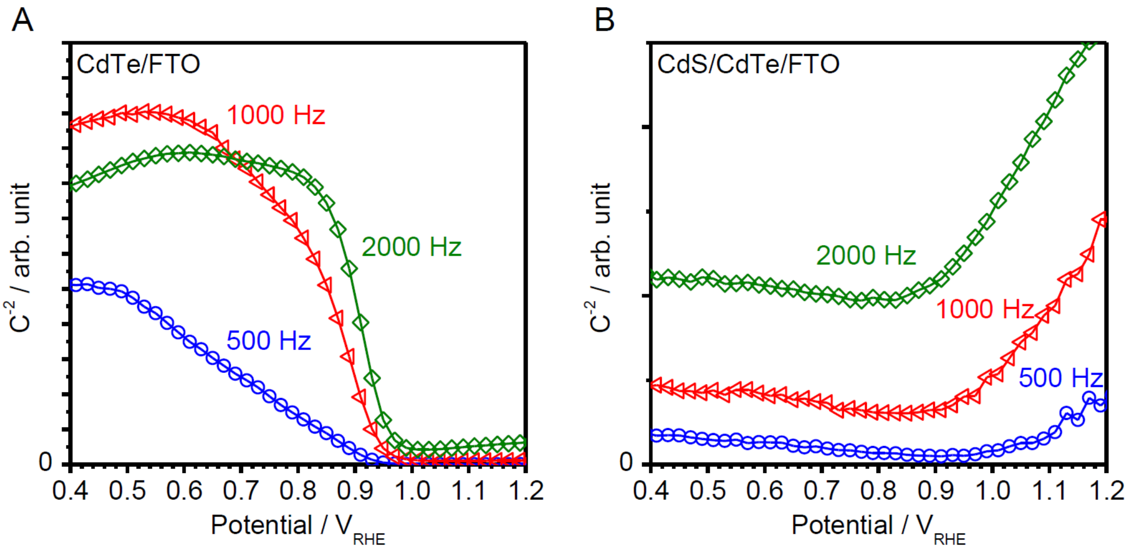

Figure S8. (A) Mott-Schottky (MS) plots of CdTe/FTO and (B) CdS/CdTe/FTO measured in 0.5 M KH_2PO_4 aqueous solution with pH adjusted to 8. A sinusoidal voltage perturbation with an amplitude of 10 mV and a frequency of 500-2000 Hz was superimposed on the potential applied by a potentiostat. An ideal RC series circuit was used as an equivalent circuit for analysis. The CdTe/FTO showed typical p-type behavior while CdS/CdTe/FTO showed V-shaped MS plots. The V-shaped MS plots indicate the existence of the n-type CdS layer on the p-type CdTe layer. At below 0.8-0.9 V_{RHE}, the electrolyte/CdS/CdTe interface was polarized cathodically and the depletion layer became thinner with increasing applied potential. On the other hand, the electrolyte/CdS interface was polarized anodically and the depletion layer became thicker with increasing the potential at above 0.8-0.9 V_{RHE}.

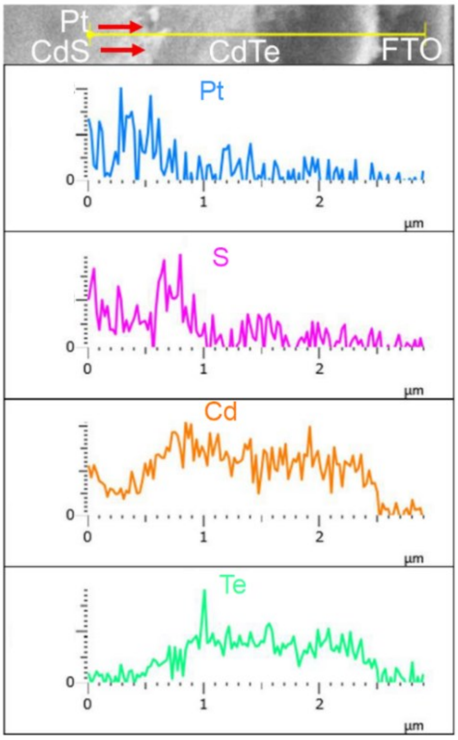

Figure S9. Results of EDX line analysis in cross-sectional SEM observation for Pt/CdS/CdTe/FTO.

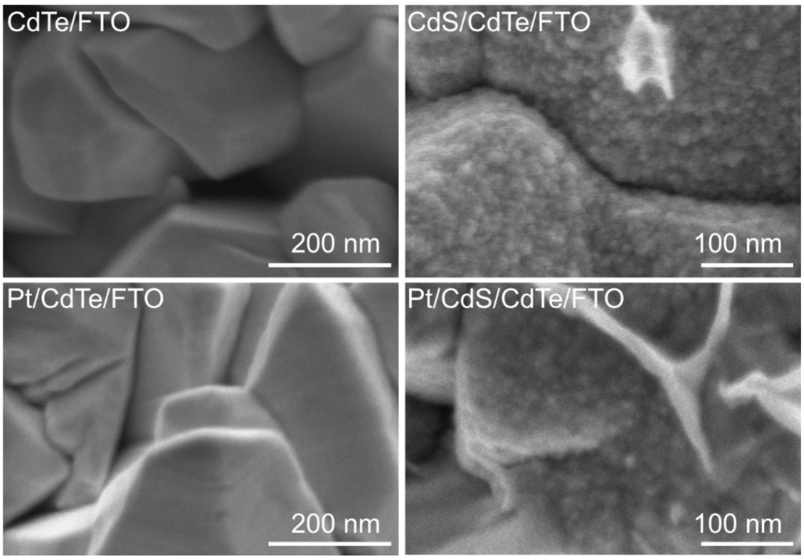

Figure S10. Top-view SEM images of CdTe/FTO, Pt/CdTe/FTO, CdS/CdTe/FTO and Pt/CdS/CdTe/FTO. 2 nm-Pt deposition didn’t change the surface morphology obviously. However, EDX analysis revealed the existence of Pt on Pt/CdTe/FTO and Pt/CdS/CdTe/FTO. The particle size of Pt should be less than 10 nm.

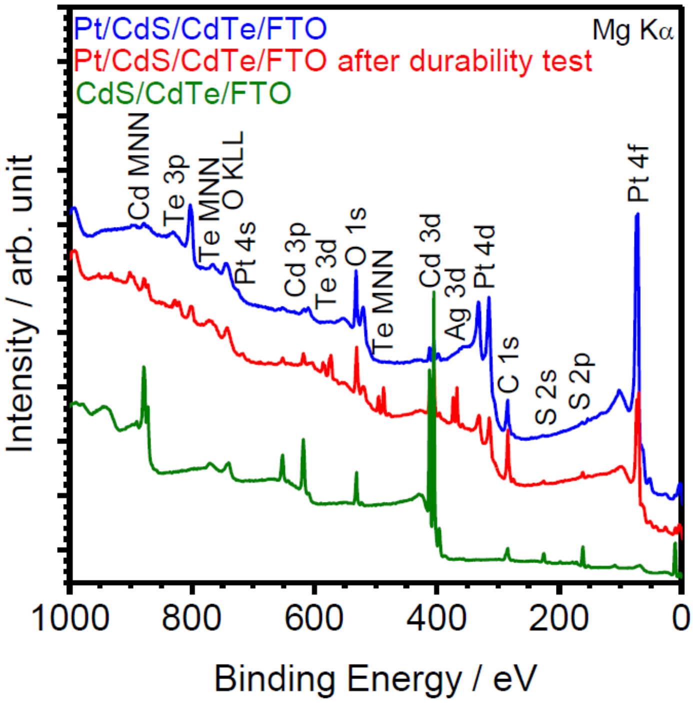

Figure S11. XPS spectra of Pt/CdS/CdTe/FTO before and after the durability test is shown in Figure 8, and of CdS/FTO. The surface compositional ratio of CdS/CdTe/FTO was found to be S/Cd = 0.72. The compositional ratios for Pt/CdS/CdTe before and after the durability test were difficult to determine because of the weak signals from both S 2s and S 2p due to the existence of the surface Pt layer and small ionization cross-section. The peak found at 803 eV is the ghost of the Pt 4f caused by the O Kα line from the oxidized X-ray source. Before the durability test, only Pt, C, Cd, S, and O were detected on the Pt/CdS/CdTe/FTO surface. After the durability test, Te and Ag appeared in addition to Pt, C, Cd, S and O. Ag was due to the reference electrode, Ag/AgCl. The variation indicates that Pt and CdS layers were partially removed during the durability test and the CdTe layer was exposed. The signals from Sn and Cu were due to the exposed surrounding region of FTO and sample stage, respectively.

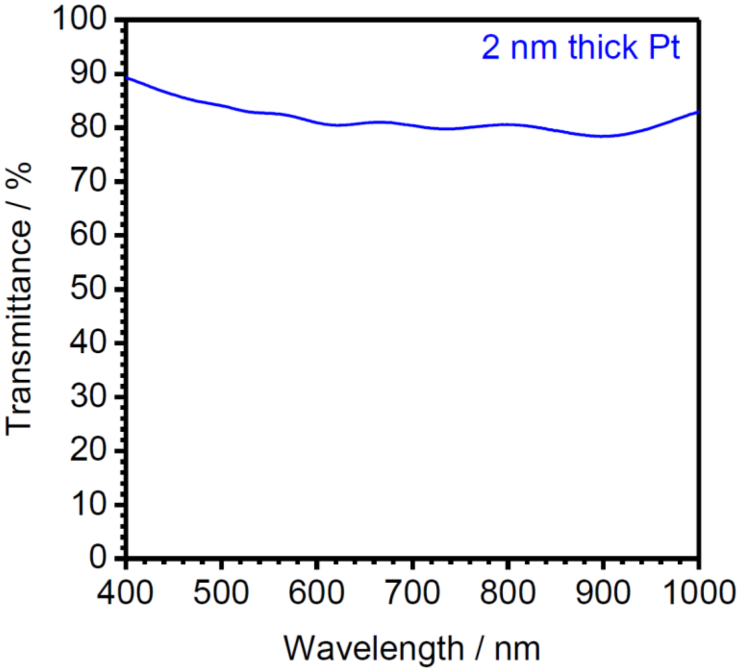

Figure S12. Optical transmittance of 2 nm thick Pt layer deposited on FTO substrate.

SA. Preparation of CdTe film by close-spaced sublimation (CSS) method

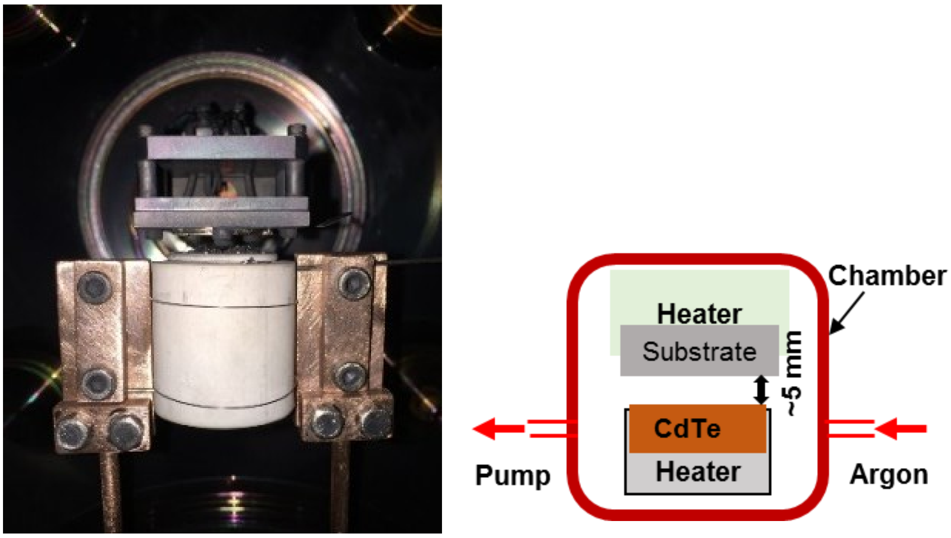

Figure SA1. A photographic image and schematic of the closed space sublimation apparatus.

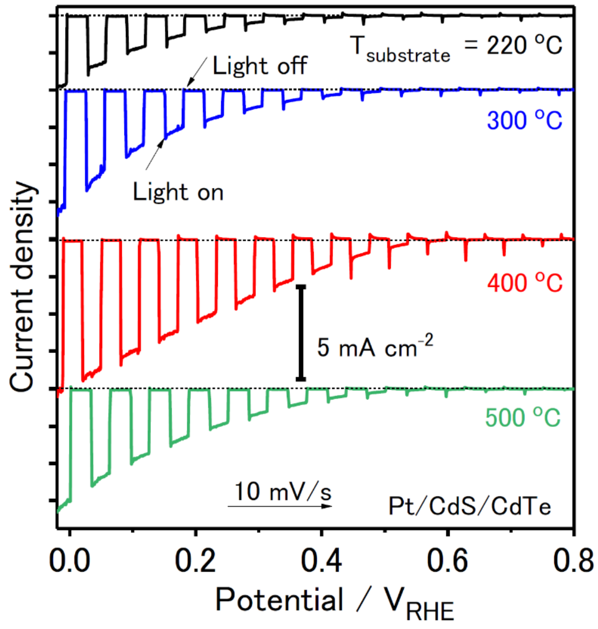

Figure SA2. Current-potential plots obtained from Pt/CdS/CdTe specimens prepared using various substrate temperatures under chopped simulated sunlight in a 0.5 M aqueous KH_2PO_4 solution with pH adjusted to 8. The CdTe and CdS layers in these specimens were 2 µm and approximately 80 nm thick, respectively. The optimal substrate temperature during CdTe deposition was determined to be 400 °C. The substrate temperature during the CdTe deposition was optimized to be 400°C.

SB. Calculation of band diagram

The band diagram at the solid–liquid interface was calculated by using Poisson's equation. The equations for CdS and CdTe layers are respectively given by

$$\frac{d^2\varphi}{\mathrm{d}x^2} = -\frac{qN_\mathrm{D}}{\varepsilon_r\varepsilon_0} \quad \text{(B1)}$$

$$\frac{d^2\varphi}{\mathrm{d}x^2} = \frac{qN_\mathrm{A}}{\varepsilon_r\varepsilon_0}, \quad \text{(B2)}$$

where φ, x, q, and ε_0 are the potential, position, elementary charge and vacuum permittivity, respectively. The dielectric constant (ε_r) of CdS and CdTe are 8.9 and 10.2, respectively.[1] The concentration of donors (N_D) in the CdS layer and acceptors (N_A) in the CdTe layer were assumed to be 10^{16} cm^{-3}. The difference between the Fermi level (E_F) and the conduction band minimum for CdS and that between E_F and the valence band maximum for CdTe were assumed to be 0.2 eV. The valence band maximum offset at the CdS/CdTe interfaces was 0.85 eV.[2] The flat-band potential for CdS and CdTe were set to −0.27 $\mathrm{V_{RHE}}$ and 0.56 $\mathrm{V_{RHE}}$.[3,4]

References

1. A. Morales-Acevedo, *Sol Energy*, 2006, 80, 675-681.
2. J. Fritsche, A. Thissen, A. Klein and W. Jaegermann, *Thin Solid Films*, 2001, 387, 158-160.
3. W. G. C. Kumarage, R. P. Wijesundera, V. A. Seneviratne, C. P. Jayalath and B. S. Dassanayake, *J Phys D Appl Phys*, 2016, 49.
4. X. Mathew, A. Bansal, J. A. Turner, R. Dhere, N. R. Mathews and P. J. Sebastian, *J New Mat Electr Sys*, 2002, 5, 149-154.