Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting information

Two-Dimensional Functionalized Hexagonal Boron Nitride for Quantum Dot Photoelectrochemical Hydrogen Generation

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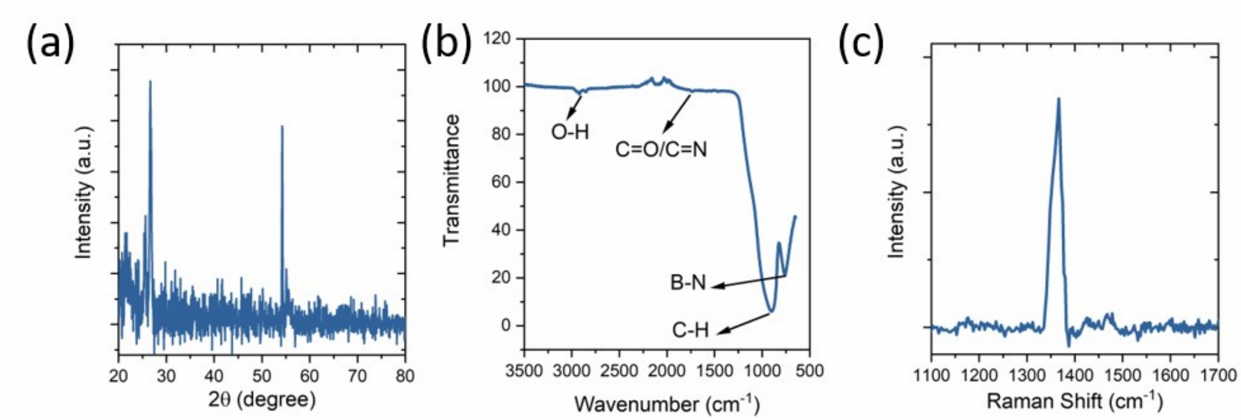

Figure S1 Structural characterizations of F-h-BN nanoflakes: (a) XRD; (b) FTIR; (c) Raman spectrum

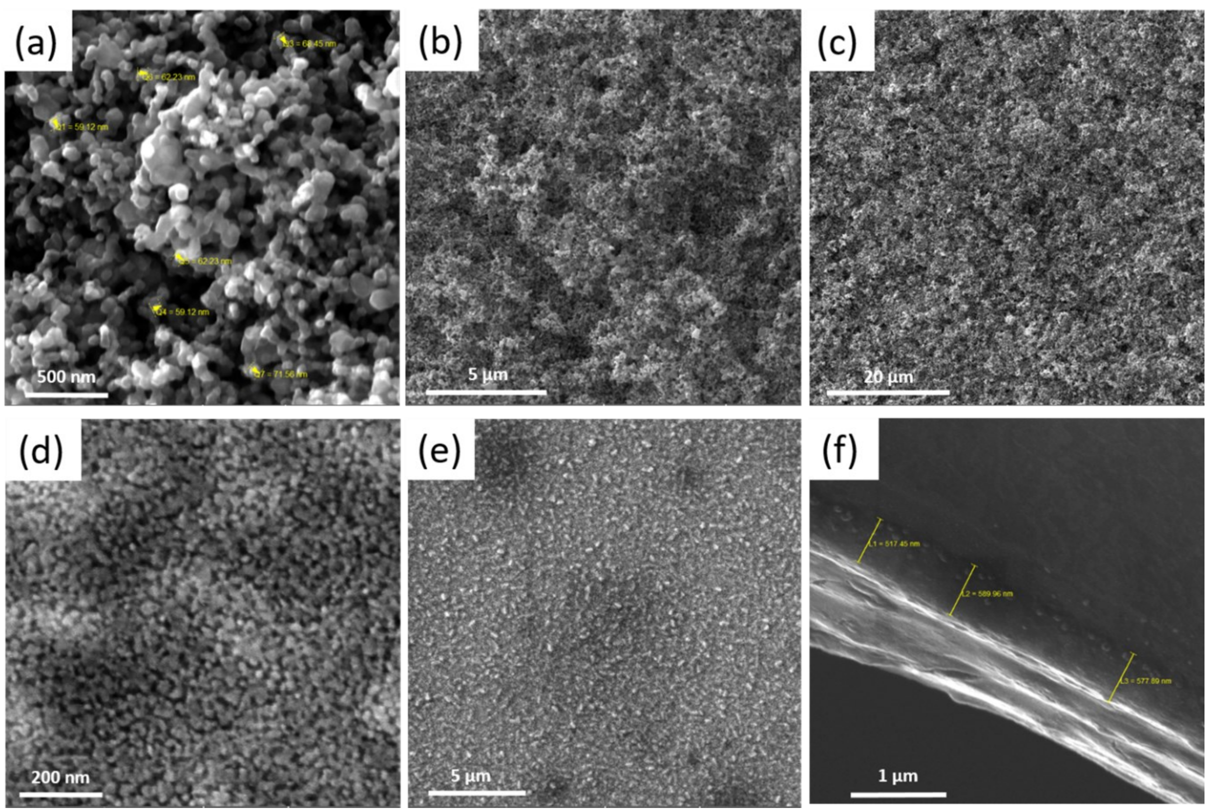

Figure S2 SEM images for (a) SnO_2 photoanode particle size (b) and (c) SnO_2 photoanode at lower magnification (d) and (e) SnO_2 blocking compact layer at high and low magnification (f) SnO_2 blocking layer thickness.

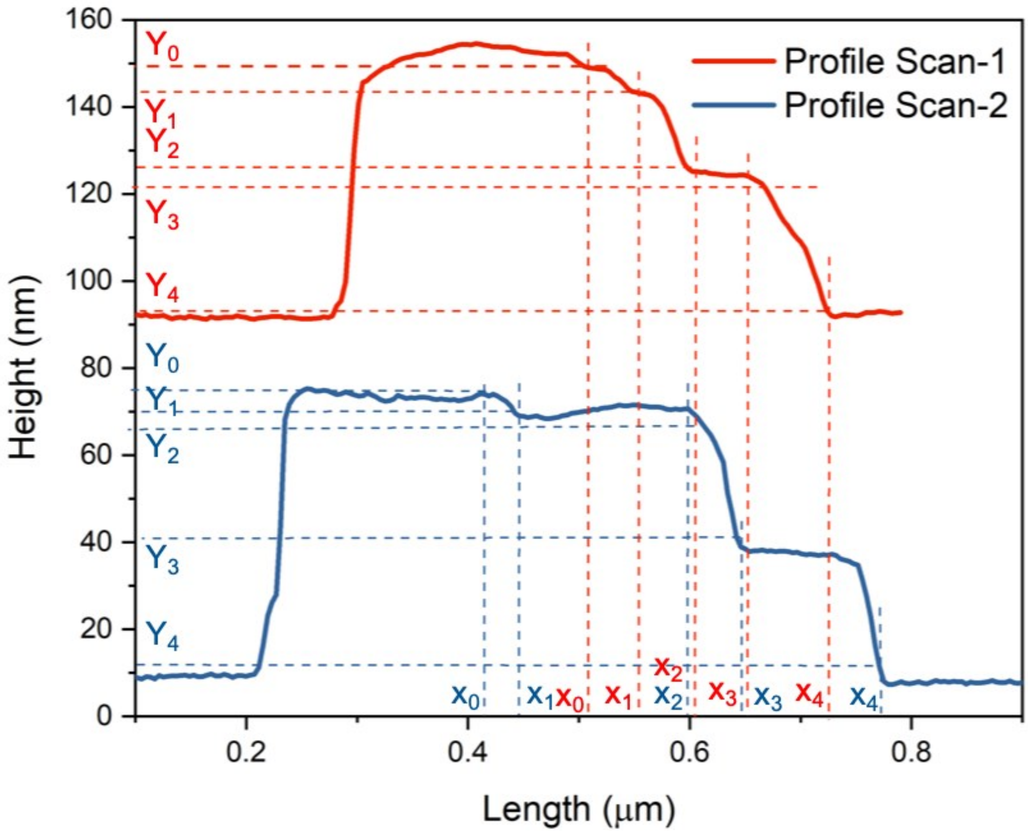

Figure S3 Thickness analysis of scanned F-h-BN nanoflakes: Profile 1 (red color line) and Profile 2 (Navy blue color line).

Table S1. Calculated thickness of F-h-BN nanoflakes from the AFM scan

Profile	Point X_i (μm) (i = 0 - 4)	Y_j (nm) (j = 0 - 4)	Length (nm)	Thickness (nm)	Angle (deg)
Profile-1	0.419	57.2			
	0.465	52.3	45	4.9	-6.14
	0.594	54.1	130	1.8	0.80
	0.657	21.6	63	32.6 (3-4 layers)	-27.53
	0.788	-8.8	131	30.3 (3-4 layers)	-13.03
Profile-2	0.484	53.5			
	0.514	50.2	29	3.3	-6.36
	0.554	44.6	41	5.6	-7.86
	0.606	26.6	52	18.1 (2-3 layers)	-19.16
	0.739	-6.3	133	32.9 (3-4 layers)	-13.94

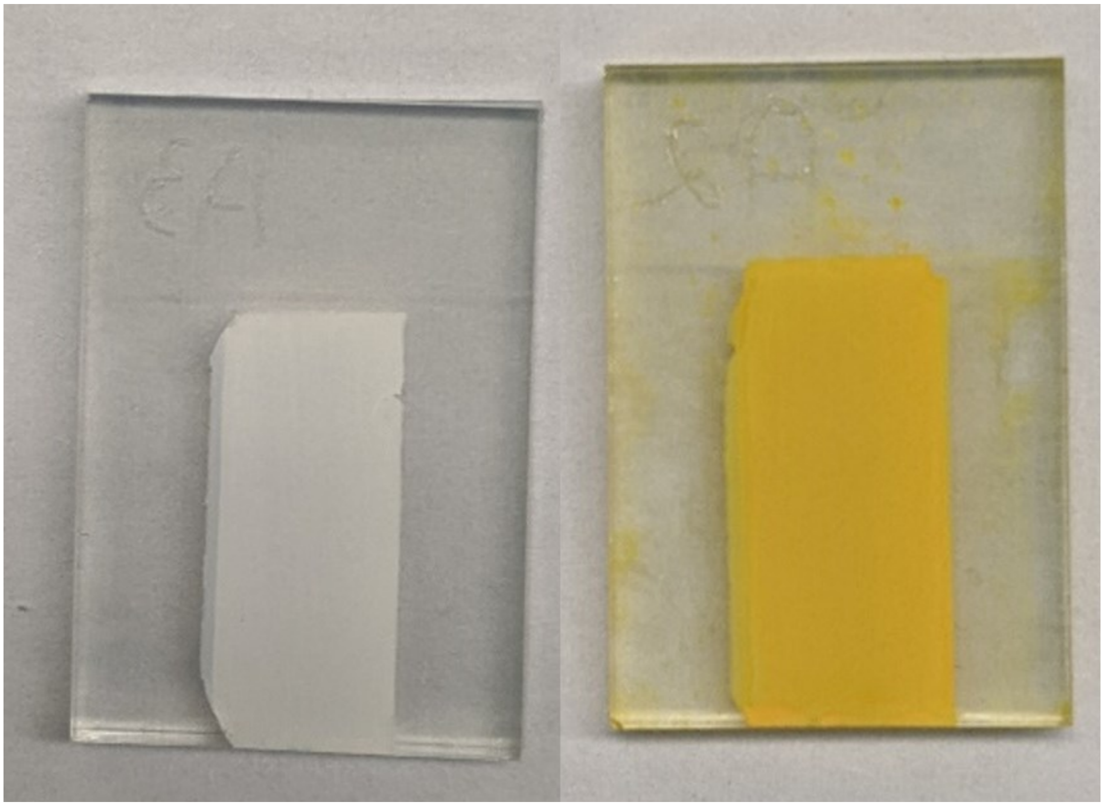

Figure S4 Visual inspection for SnO_2/TiO_2/F-h-BN photoanode before and after sensitization with CdS QDs using 7 cycles of SILAR method.

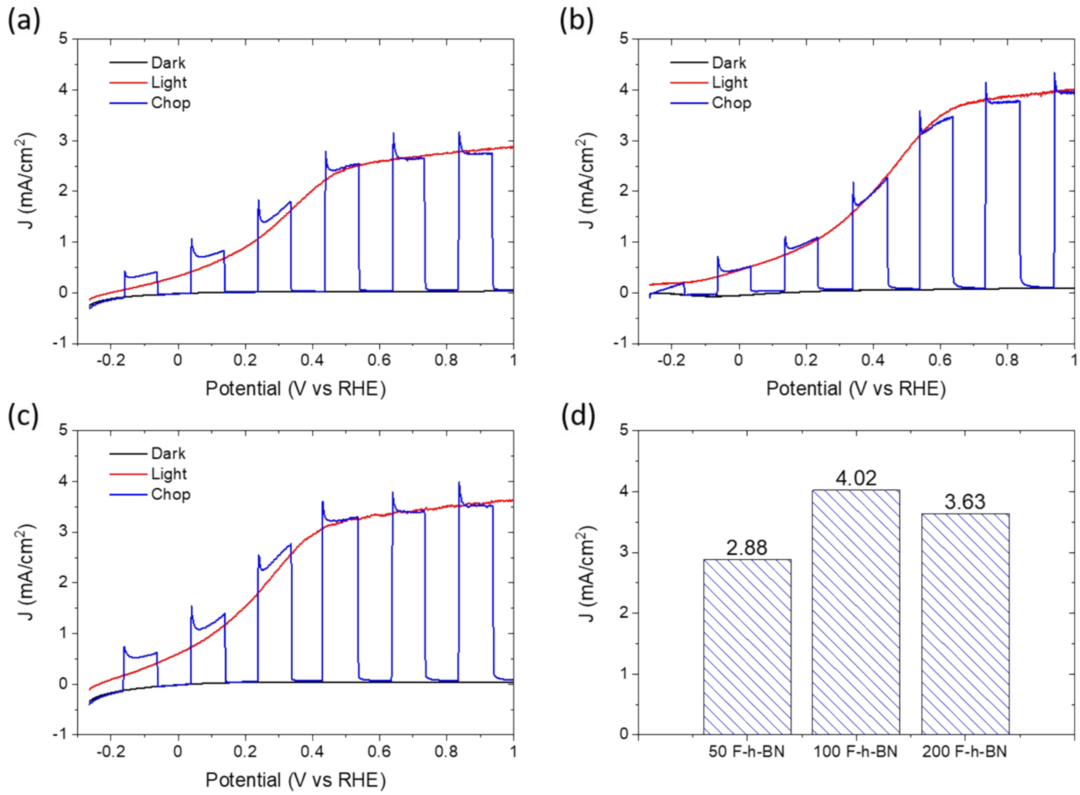

Figure S5 PEC performance under dark, light and chop for two-layer SnO_2/F-h-BN/CdS photoanode with different amounts of F-h-BN solution: (a) 50 µl; (b) 100 µl; (c) 200 µl. (d) Comparison of the saturated photocurrent density at 1.0 V vs RHE with different amounts of F-h-BN solution.

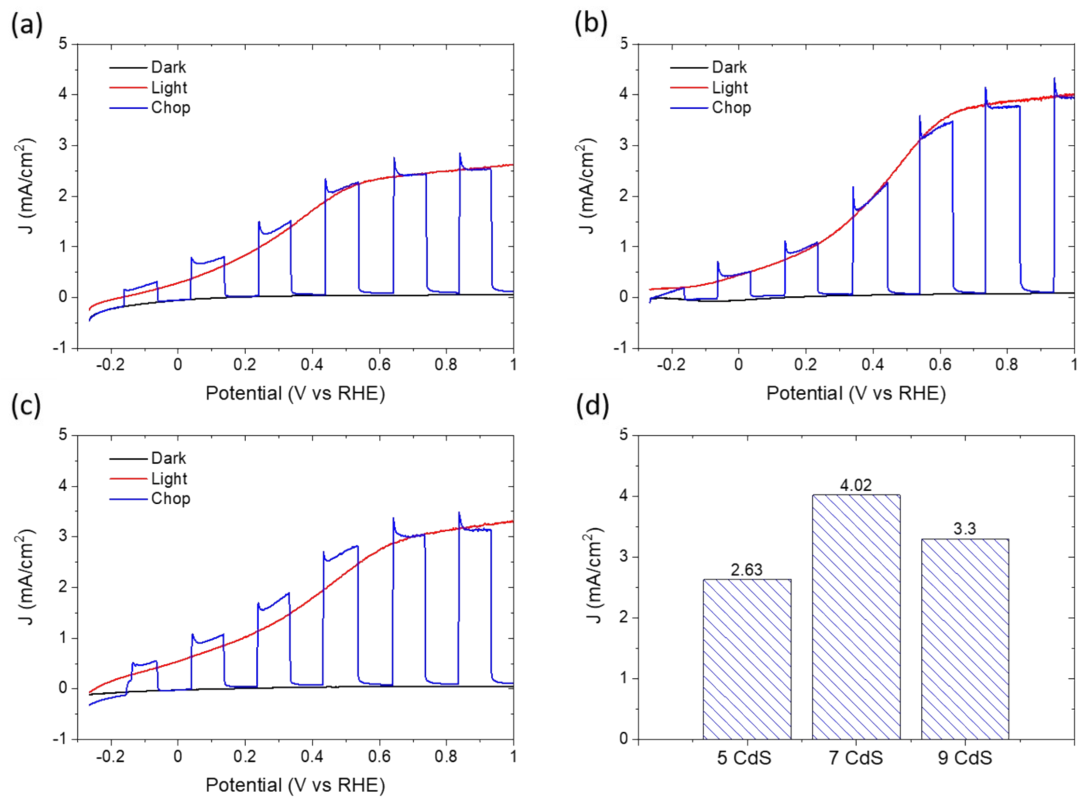

Figure S6 PEC performance under for two-layer SnO_2/100 µl F-h-BN/CdS photoanode with different numbers of CdS QDs SILAR cycles: (a) 5; (b) 7; (c) 9. (d) Comparison of the saturated photocurrent density at 1.0 V vs RHE with different numbers of CdS QDs SILAR cycles.

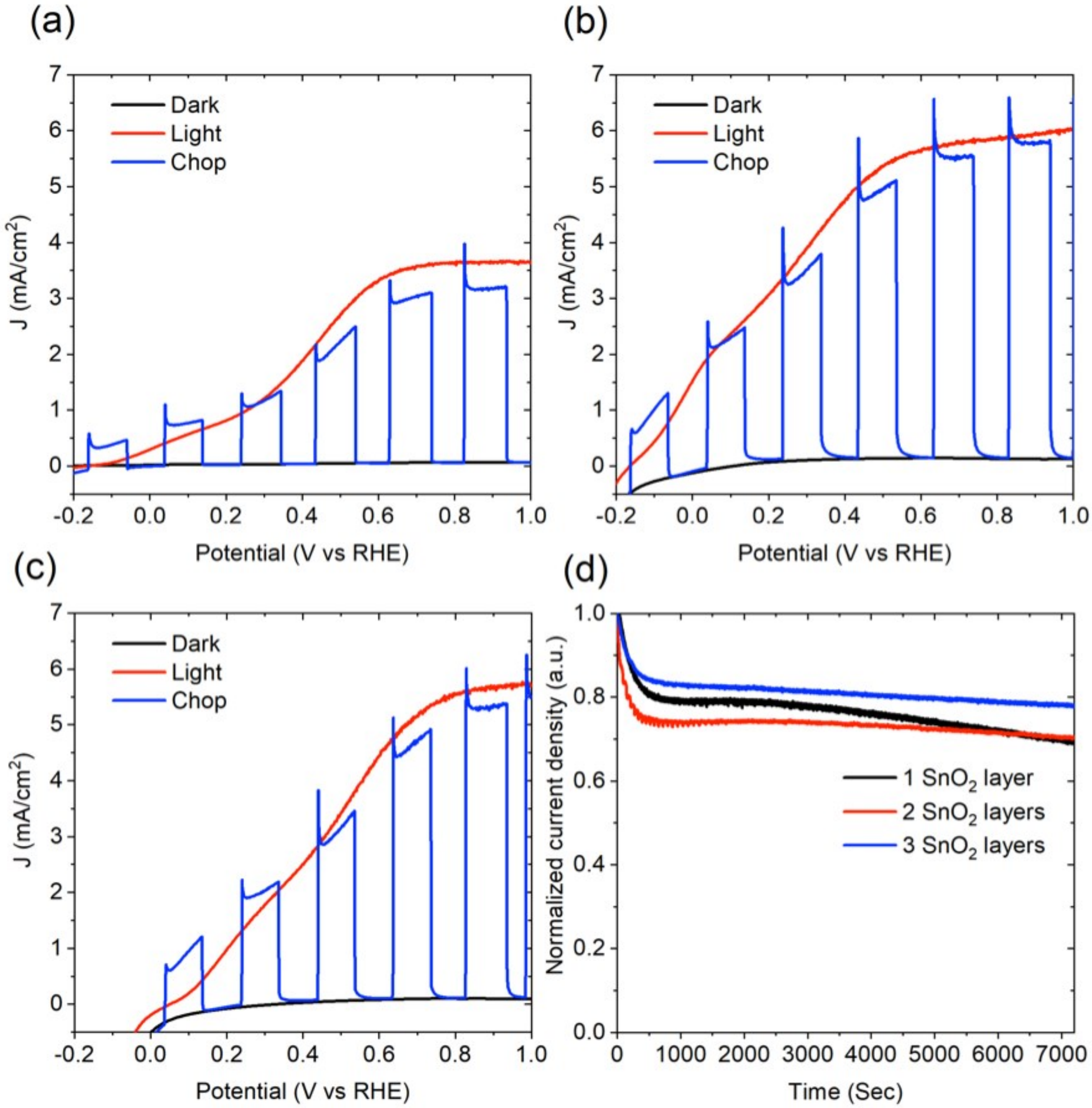

Figure S7 PEC performance under dark, light, and chop for SnO_2/F-h-BN/CdS/CdSe/ZnS photoanode with a different number of SnO_2 mesoporous film layers: (a) One layer; (b) Two layers; (c) Three layers of SnO_2. (d) Stability performance: Normalized current density vs time (sec).

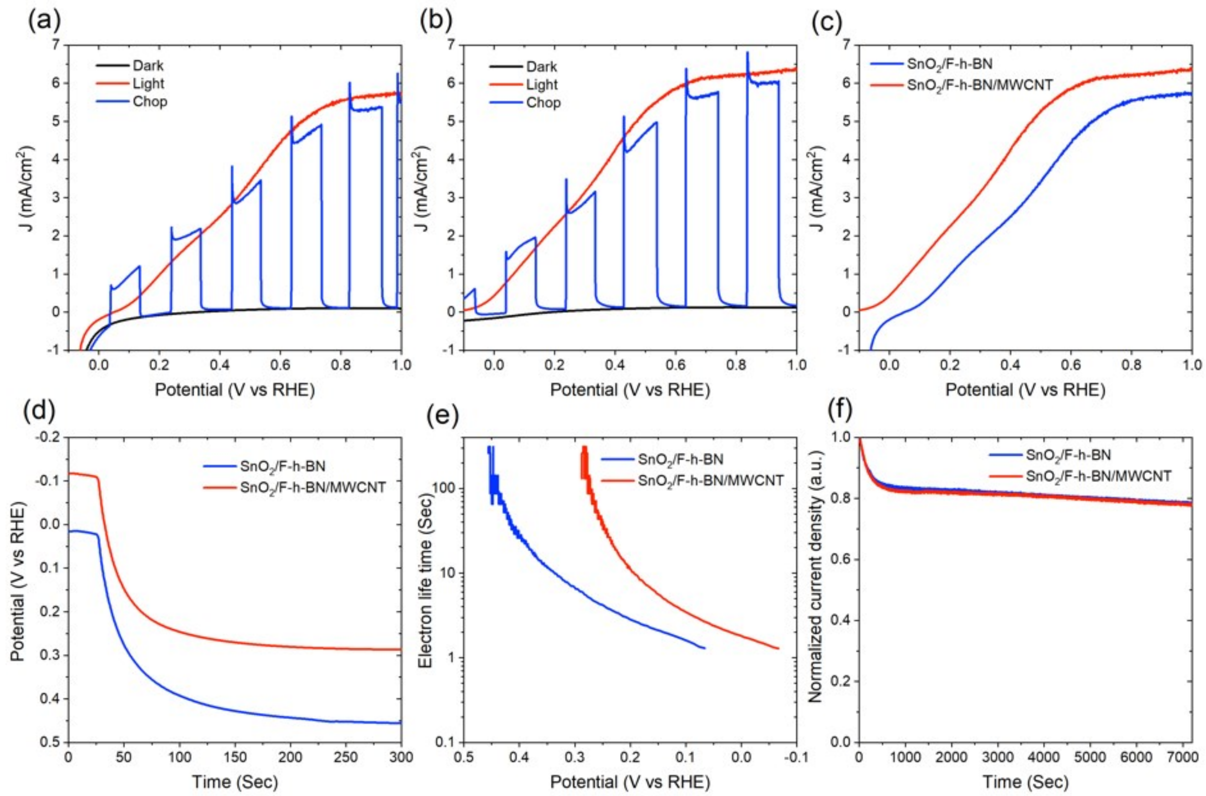

Figure S8 PEC performance under dark, light and chop for three layers SnO_2/CdS/CdSe/ZnS photoanode: (a) with F-h-BN; (b) with F-h-BN and MWCNTs; (c) Comparison of photocurrent density vs potential (V vs RHE) for PEC devices based on F-h-BN and F-h-BN/MWCNT under continuous illumination. (d) Open circuit voltage. (e) Electron lifetime. and (f) Stability performance: Normalized current density vs time (sec).

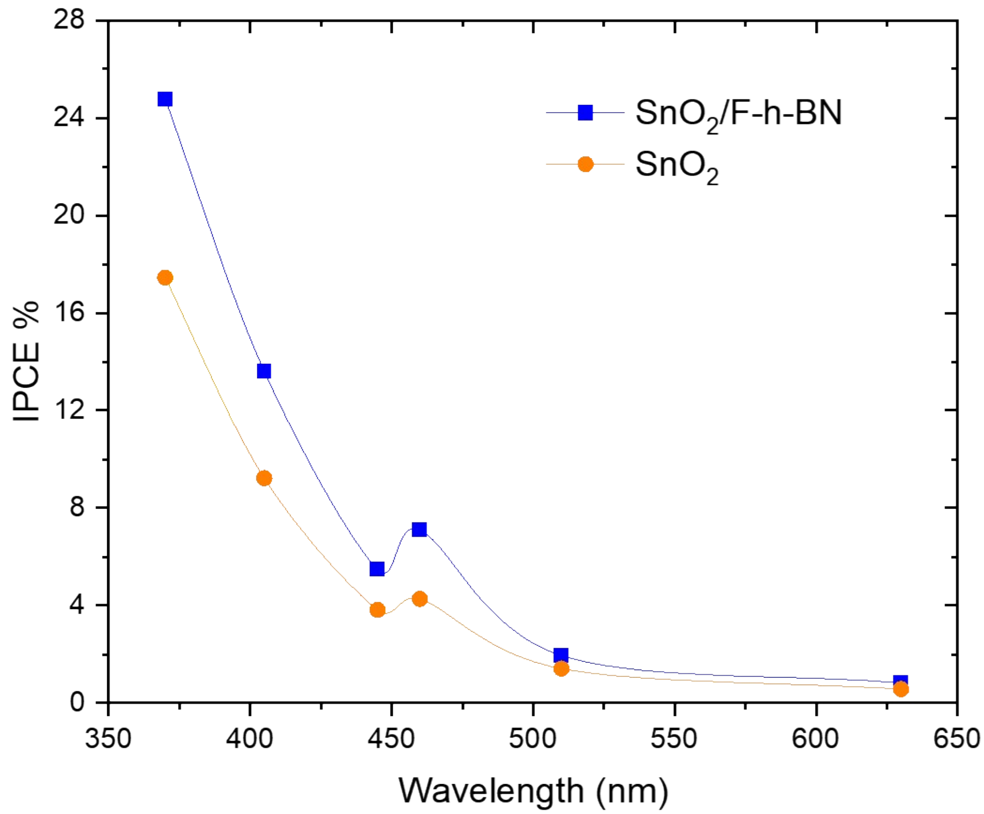

Figure S9 IPCE measurement for PEC device based on SnO_2 mesoporous film, with and without F-h-BN, sensitized with CdS/CdSe QDs.

We observe significant differences between the photocurrent density values measured from the J-V curves and the those calculated from the IPCE data. The photocurrent density values from J-V measurements are 6.05 $mA.cm^{-2}$ and 5.4 $mA.cm^{-2}$, whereas the values obtained from the IPCE measurements are 1.53 $mA.cm^{-2}$ and 1.04 $mA.cm^{-2}$ for SnO_2/F-h-BN and SnO_2, respectively. The significant differences between photocurrent density values obtained from J-V measurements as opposed to values calculated from IPCE data, is due to the experimental procedures we adopted for the IPCE measurements. For instance, in this specific case, we used a manual system for the IPCE measurement by placing optical filters of different wavelengths in front of the solar simulator to obtain monochromatic light. The overall light intensity obtained through these optical filters may be lower compared to the intensity of the monochromatic light source (built in the IPCE system). In addition, the light intensity is different between the monochromatic optical filter measured using a reference cell and the PEC measurement cell. The number of photons is also not equivalent due to the difference in the refractive index of the materials and electrolyte used in the PEC device. Further, the illumination area is smaller in the IPCE measurement than that in the J-V measurement. When the illuminated area is limited, a larger number of micro shunt resistances are present (acting as recombination centers) that reduce the photogenerated current density values obtained from the IPCE measurements.

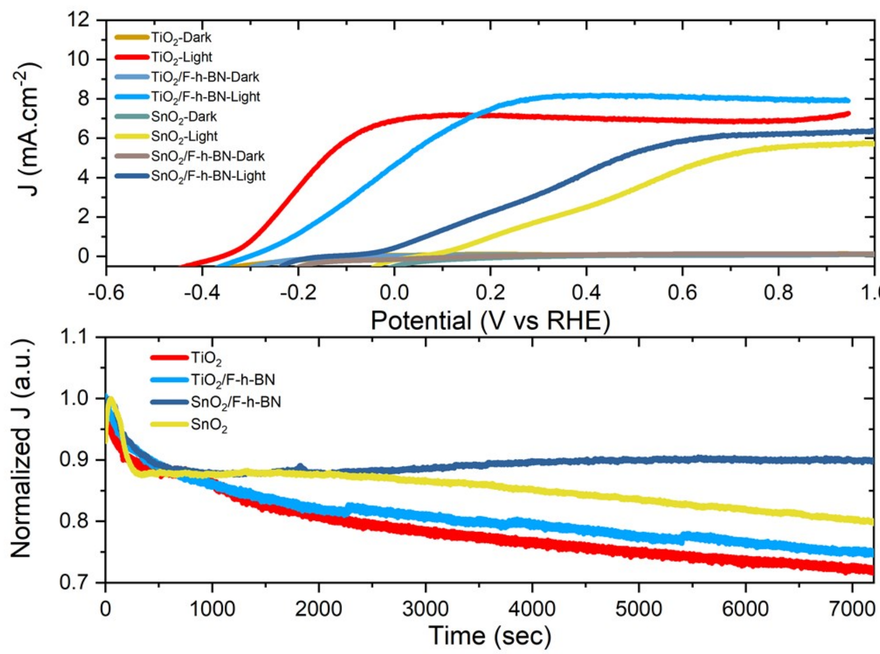

Figure S10. PEC performance comparison between SnO_2/CdS/CdSe/ZnS and TiO_2/CdS/CdSe/ZnS with and without F-h-BN photoanode: (a) dark and light performance of the photoanodes. (b) Stability performance of the corresponding PEC devices: Normalized saturated photocurrent density vs time (sec).

The calculation process for the band structure in Figure S11:

From the UPS measurement in Figure S11 (d), we can obtain the valence band offset and work function, from Figure S11 (c) and (e), respectively.

The ionization potential (IP), which is the difference between the vacuum level and valence band maximum (VBM), can be calculated by adding the (valence band offset) to the (21.22 eV "Helium source energy" work function)

- In the case of SnO_2, the IP = 4.04 + (21.22 – 17.12) = 8.14 eV, therefore the VBM of SnO_2 is -8.14 eV vs. vacuum.
- In the case of SnO_2/F-h-BN, the IP = 4.06 + (21.22 – 16.74) = 8.54 eV, therefore VBM of SnO_2/F-h-BN is -8.54 eV vs. vacuum.

To calculate the conduction band minimum (CBM) we added the optical band gap obtained from UV-Vis measurements, in Figure S11 (a) to the VBM.

- In case of SnO_2, The CBM = -8.14 + 3.80 = - 4.34 eV vs Vacuum
- In case of SnO_2/F-h-BN, The CBM = -8.54 + 3.89 = - 4.65 eV vs Vacuum

To change the values from Vacuum to SHE, we use this equation: SHE = - (Vacuum + 4.5)

- For SnO_2 {VBM = - (-8.14 + 4.5) = 3.64 eV | CMB = - (-4.34 + 4.5) = -0.16 eV Vs SHE}
- For SnO_2/F-h-BN {VBM = - (-8.54 + 4.5) = 4.04 eV | CBM = - (-4.65 + 4.5) = 0.15 eV Vs SHE}

To change the values from SHE to RHE, we use the following equation: RHE = SHE – (0.059*pH)

- For SnO_2 {VBM = 3.64 – (0.059*13) = 2.87 eV | CMB = -0.16 – (0.059*13) = -0.92 eV vs RHE}
- For SnO_2/F-h-BN {VBM = 4.04 – (0.059*13) = 3.27 eV | CBM = 0.15 – (0.059*13) = -0.61 eV Vs RHE}

The HER and OER calculations

- HER = 0 – (0.059*13) = -0.767 eV
- OER = 1.23 – (0.059*13) = 0.463 eV

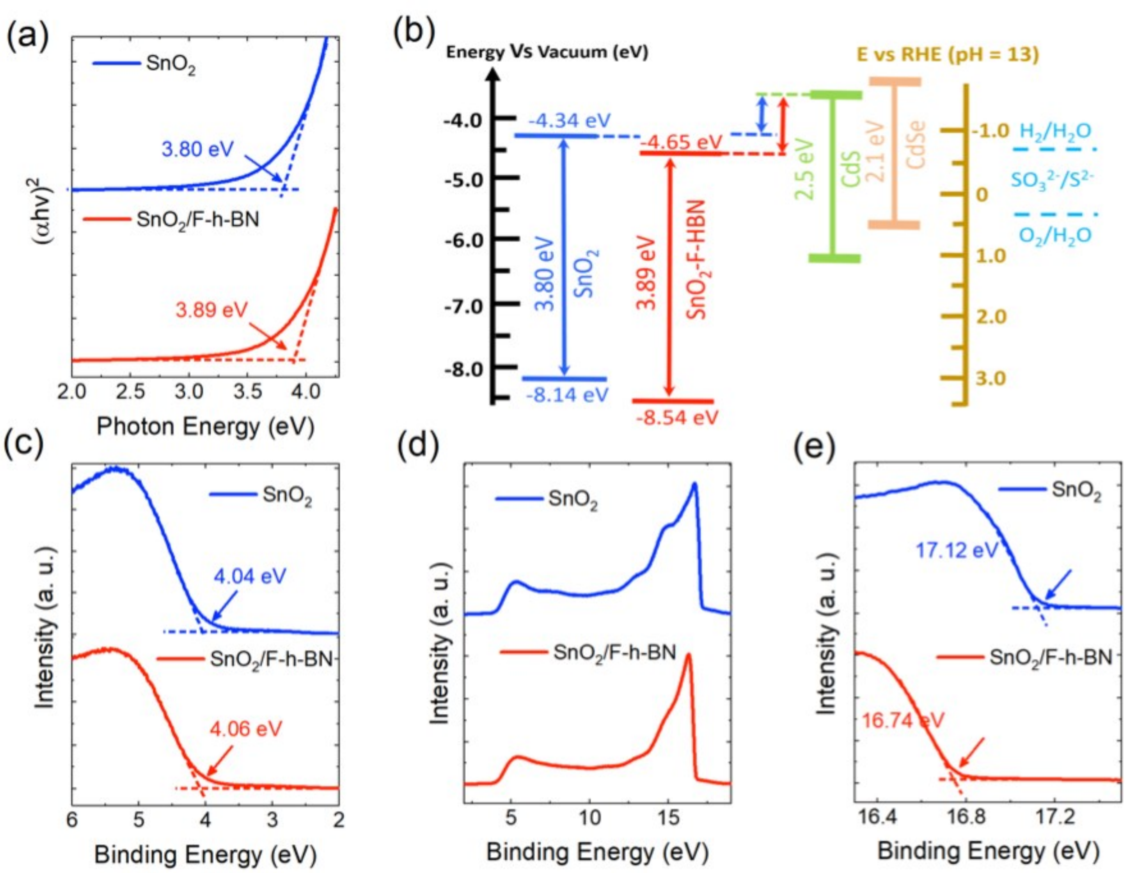

Figure S11 Band alignment of SnO_2 and SnO_2/F-h-BN: (a) measured band gaps of SnO_2 and SnO_2/F-h-BN (b) schematic of the overall band structure of SnO_2 and SnO_2/F-h-BN with respect to CdS-CdSe QDs; UPS measurement of SnO_2 and SnO_2/F-h-BN: (c) Fermi level estimation; (d) Full spectra; (e) VBM estimation.

Table S2 EIS measurement under the dark condition for SnO_2 and SnO_2/F-h-BN

Data	SnO_2	SnO_2/F-H-BN	Unit
R1	15.2	12.5	Ohm
R2	5.23×10^{5}	3.00×10^{5}	Ohm
R3	25203	5.40×10^{5}	Ohm
C2	4.53×10^{-5}	8.19×10^{-6}	F
C3	3.64×10^{-6}	1.75×10^{-5}	F
Ws1-R	63142	1.42×10^{5}	Ohm
Ws1-T	1.649	5.5	Sec
The constant phase elements used to calculate the capacitance			
CPE1-T	3.33×10^{-5}	7.04×10^{-6}	Q
CPE1-P	0.90293	0.832	n
CPE2-T	4.03×10^{-6}	1.50×10^{-5}	Q
CPE2-P	0.958	0.932	n

Table S3 Onset potential values for different PEC devices

PEC Device	Potential (V vs Ag/AgCl)
SnO_2/CdS	0.36
SnO_2/F-h-BN/CdS	0.33
SnO_2/CdS/CdSe	0.29
SnO_2/F-h-BN/CdS/CdSe	0.12