

## Supporting information

# Surface Engineering of Two-dimensional Hexagonal Boron-Nitride For Optoelectronic Devices

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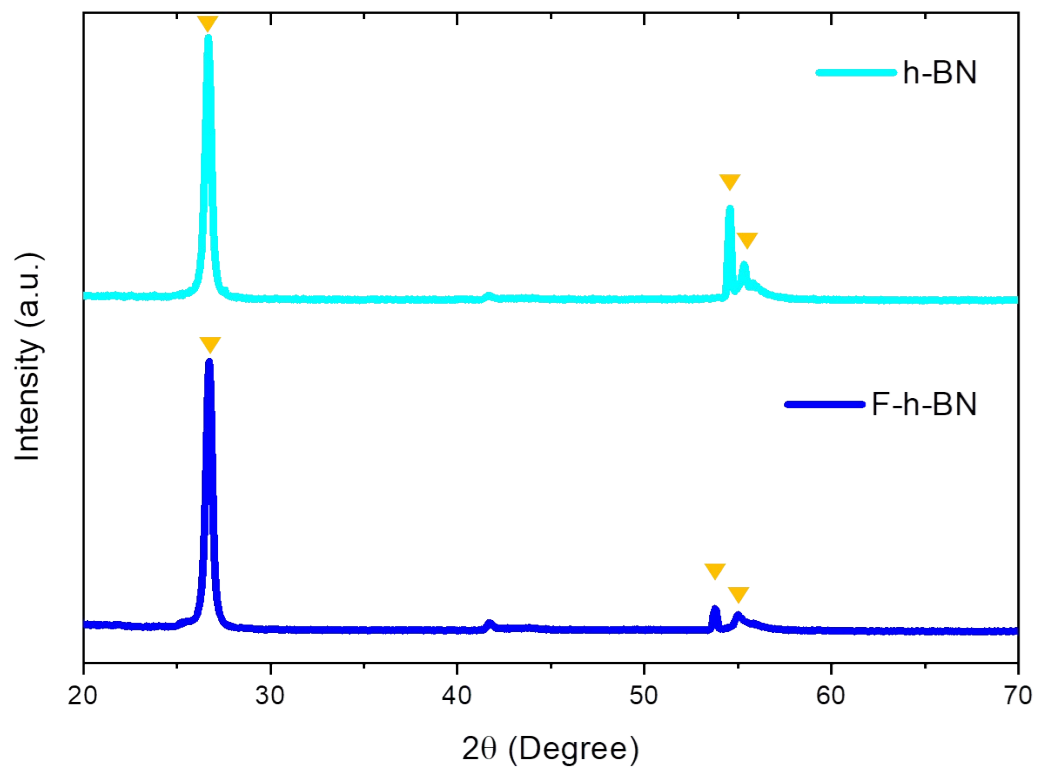
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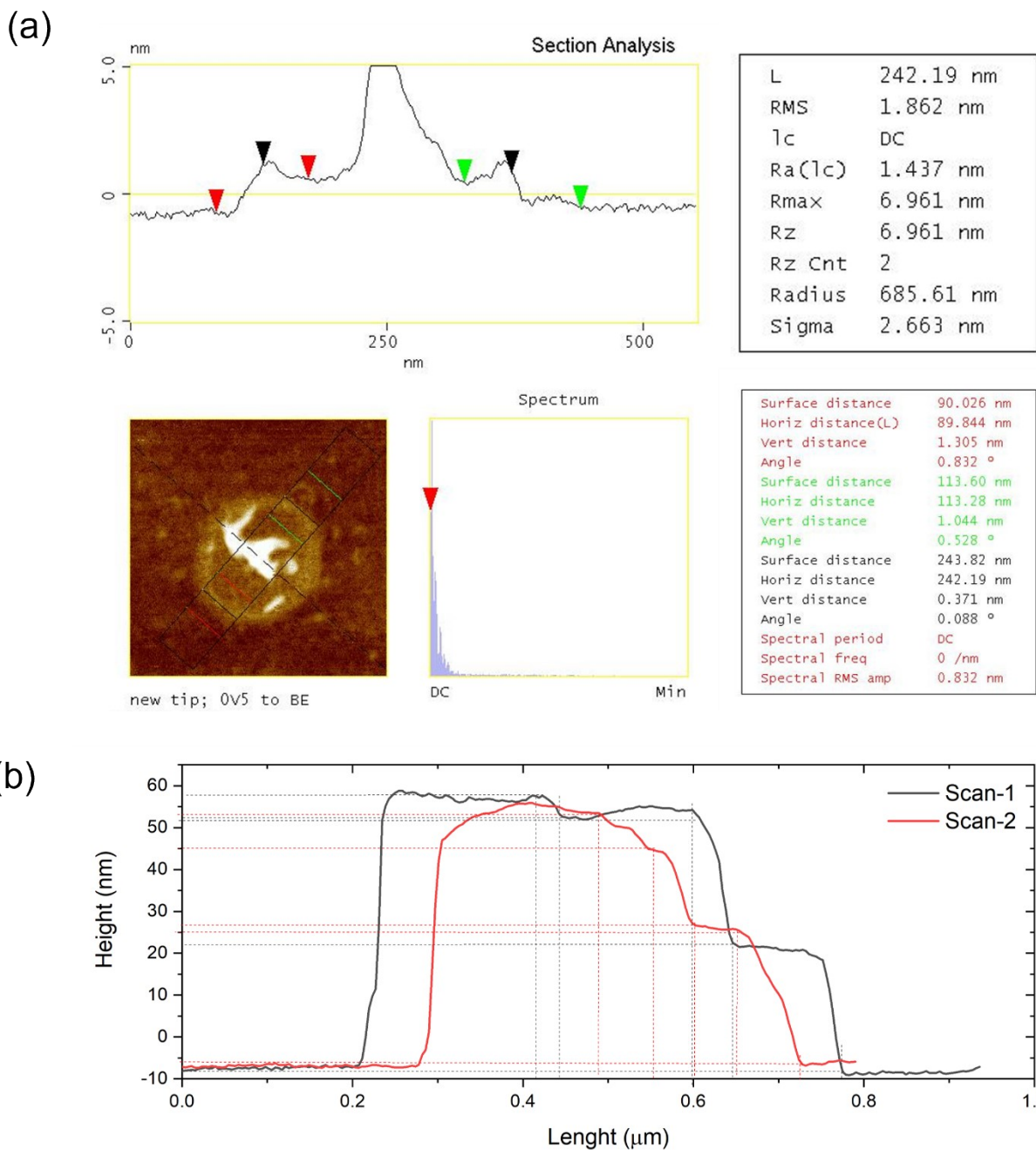
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**Figure S1.** XRD spectra of as synthesized h-BN and F-h-BN nanoflakes spin coated on glass substrate.

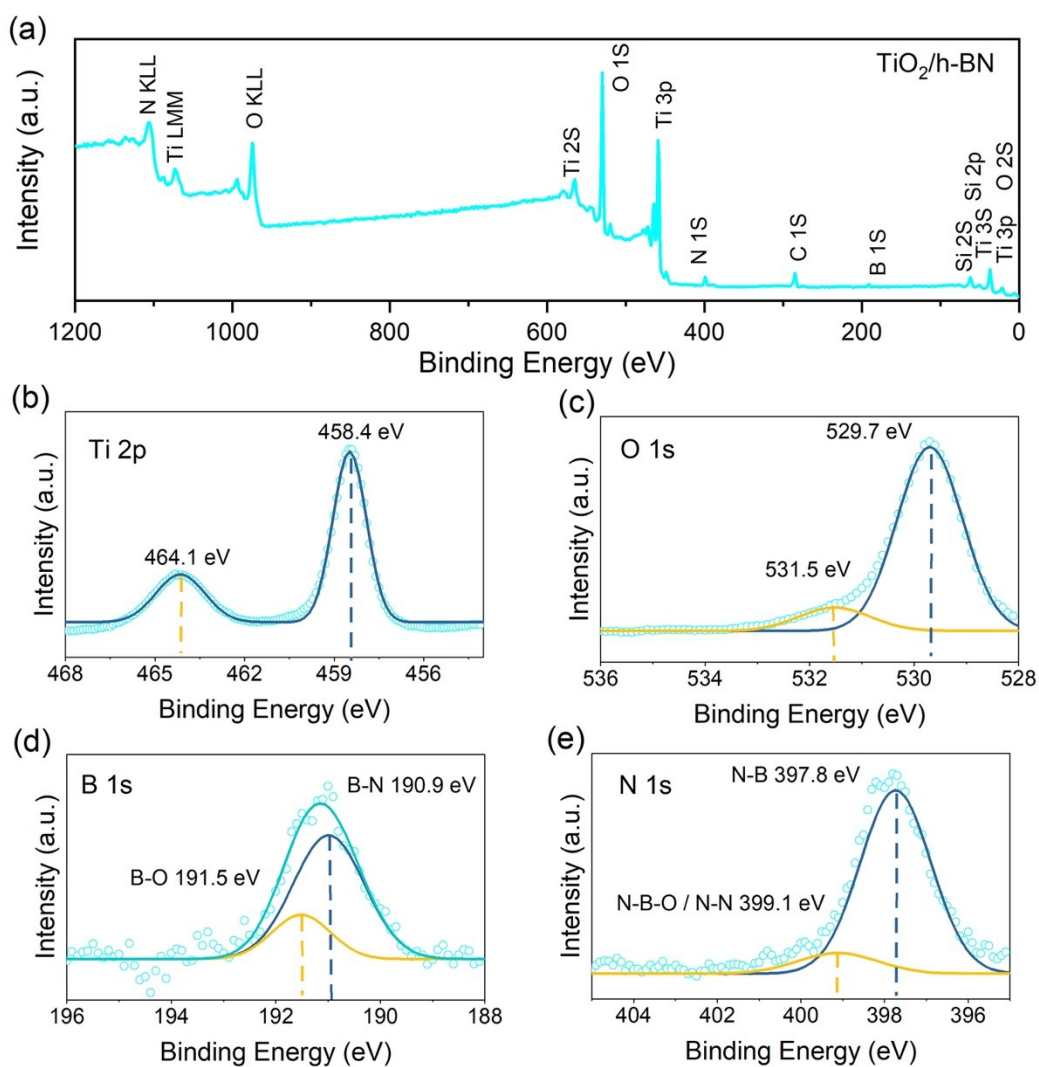


**Figure S2.** (a) AFM tip scan and calculated average thickness of each layer in the 3D image of F-h-BN nanoflake. (b) AFM thickness analysis of scan 1 and scan 2 of F-h-BN nanoflakes

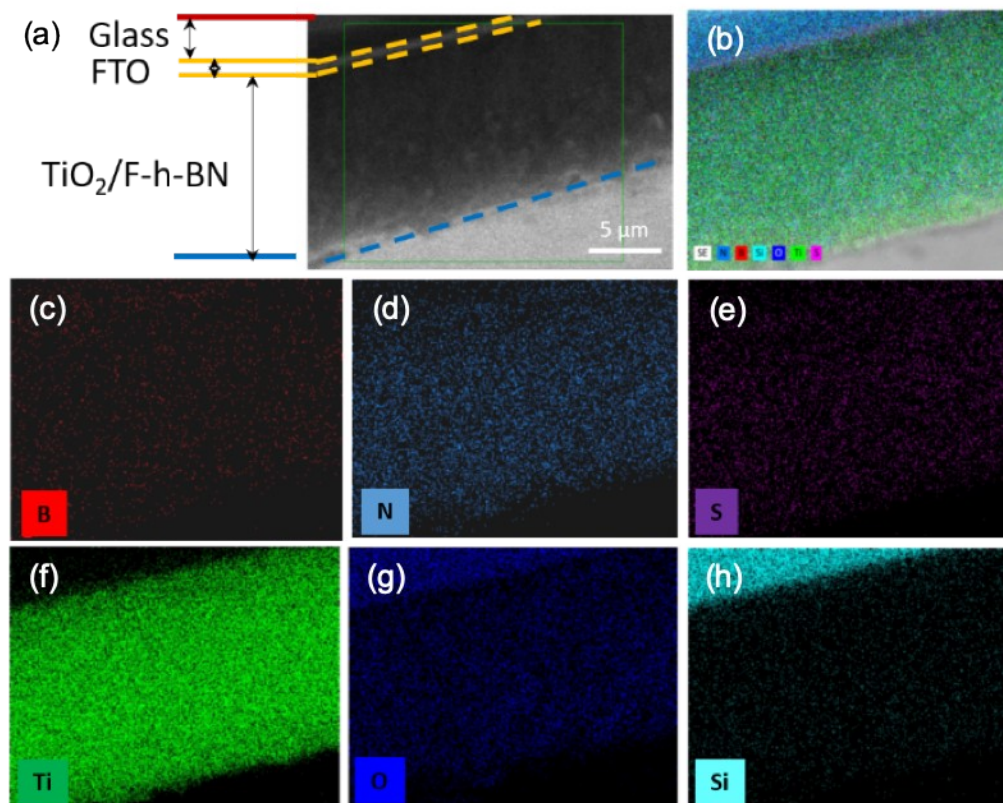
**Table S1.** Calculated thickness of F-h-BN nanoflakes from the AFM scan

Profile	Point $X_i$ (nm) ( $i = 0 - 4$ )	$Y_j$ (nm) ( $j = 0 - 4$ )	Length (nm)	Thickness (nm)	Angle (deg)
Scan-2	0.48	53			
	0.51	50	29	3	-6.36

	0.55	44	41	5.0	-7.86
	0.61	27	52	17 (2-3 layers)	-19.16
	0.73	-6.0	133	33 (3-4 layers)	-13.94
Scan-1	0.42	57			
	0.44	52	45	5	-6.14
	0.59	54	130	2	0.80
	0.66	21	63	33 (3-4 layers)	-27.53
	0.79	-8	130	29 (3-4 layers)	-13.03

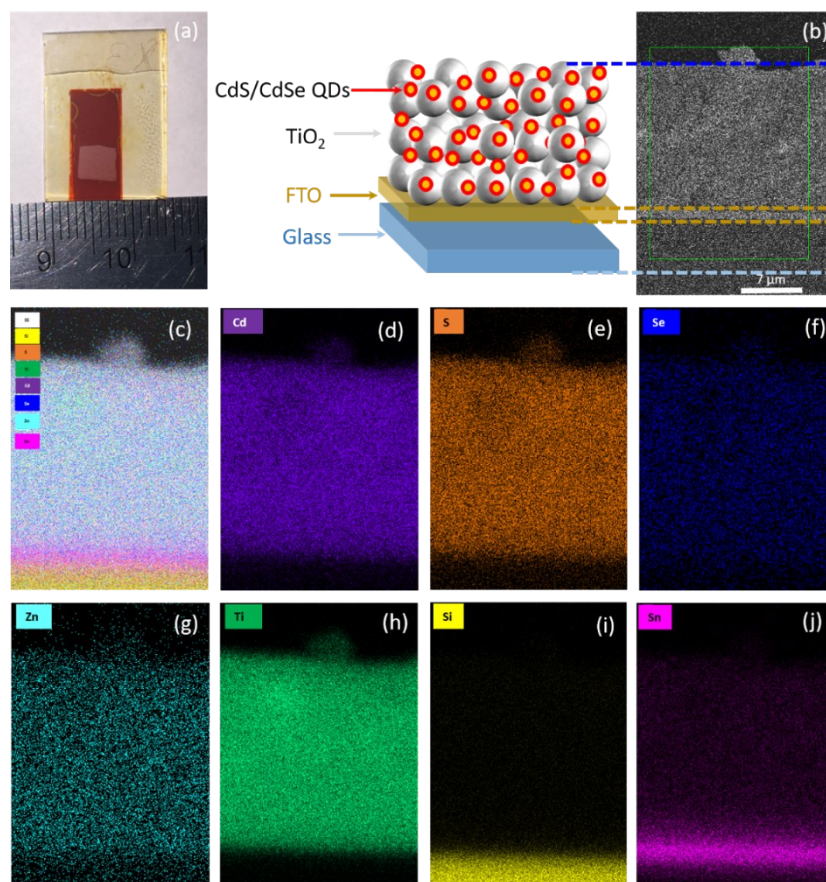


**Figure S3.** XPS analysis of TiO<sub>2</sub>/h-BN photoanode: (a) a survey spectrum; (b) Ti 2p<sub>3/2</sub>; (c) O 1S; (d) Boron (1S); (e) Nitrogen 1S.

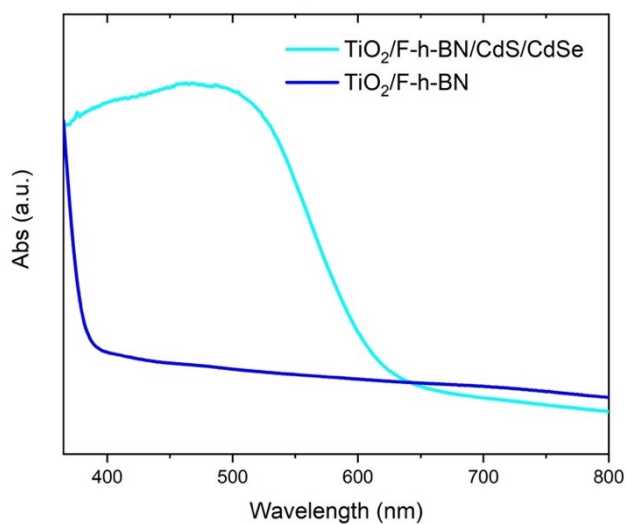


**Figure S4.** Elemental mapping of  $\text{TiO}_2/\text{F-h-BN}$  hybrid photoanodes by EDS spectroscopy: (a) Cross-sectional SEM with selected area for EDS mapping in green color rectangle; (b) all elements; (c) B; (d) N; (e) S; (f) Ti; (g) O and (h) S.

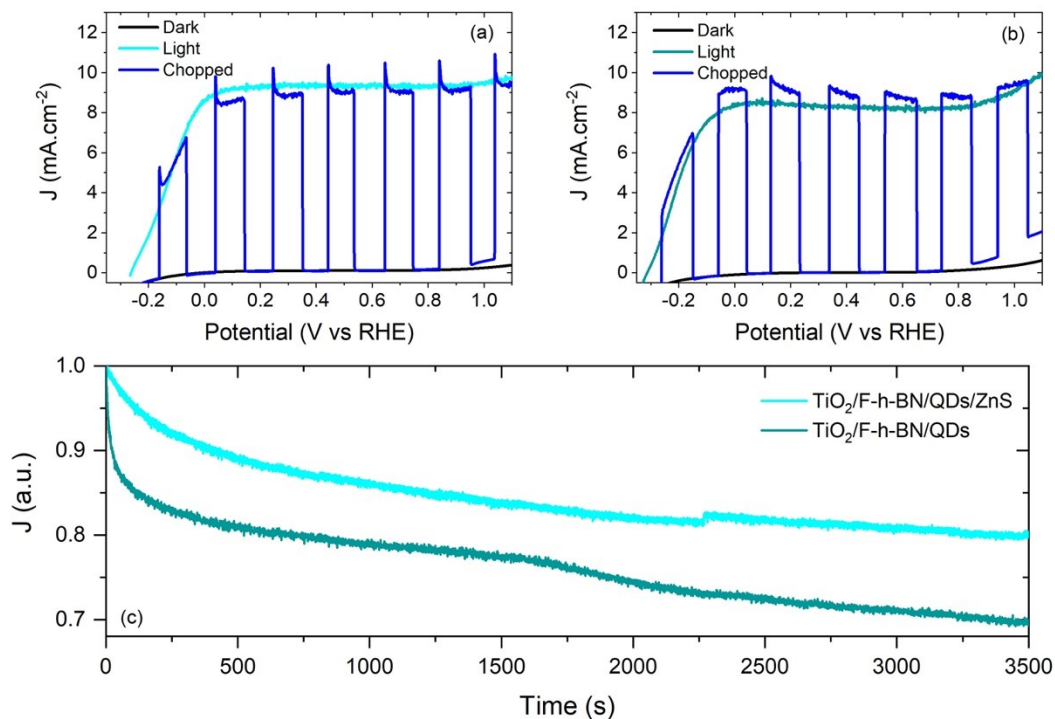




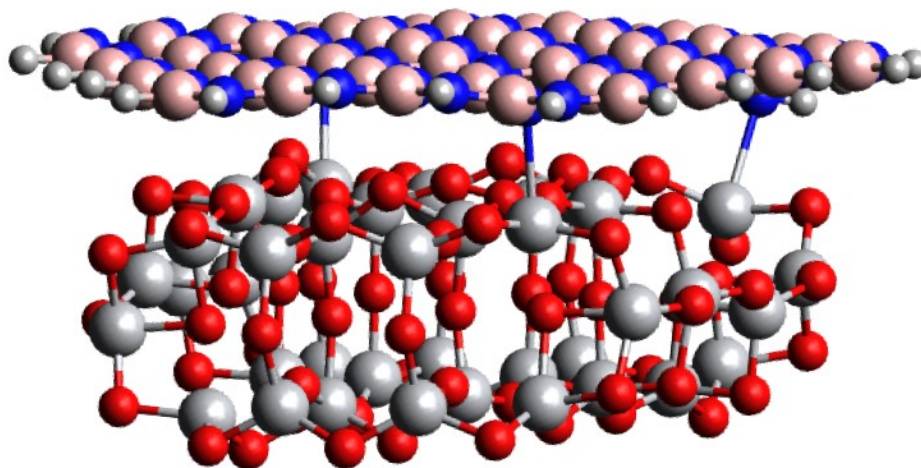
**Figure S5.** (a) Camera pictures of  $\text{TiO}_2$  mesoporous film sensitized with CdS/CdSe cascade QDs. EDS elemental mapping of  $\text{TiO}_2/\text{CdS}/\text{CdSe}$  QDs photoanodes: (b) Cross-sectional SEM with schematic diagram to clarify the photoanode structure (left side) and selected area for EDS mapping in green color rectangle; (c) all elements; (d) Cd; (e) S; (f) Se; (g) Zn; (h) Ti; (i) Si and (j) Sn.



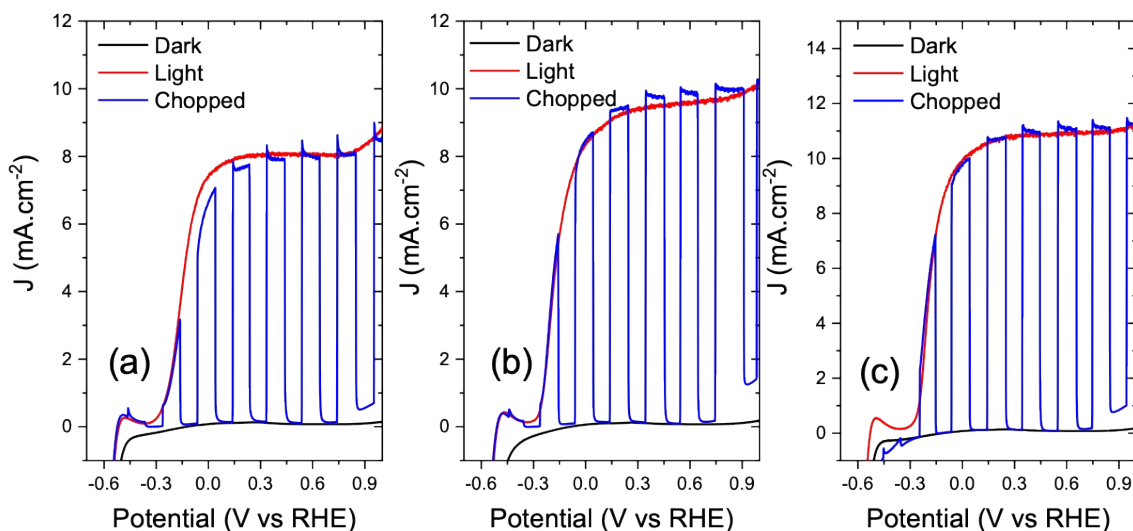
**Figure S6.** UV-visible absorption spectra of  $\text{TiO}_2/\text{F-h-BN}$  photoanode and  $\text{TiO}_2/\text{F-h-BN}/\text{CdS}/\text{CdSe}$  photoanodes.



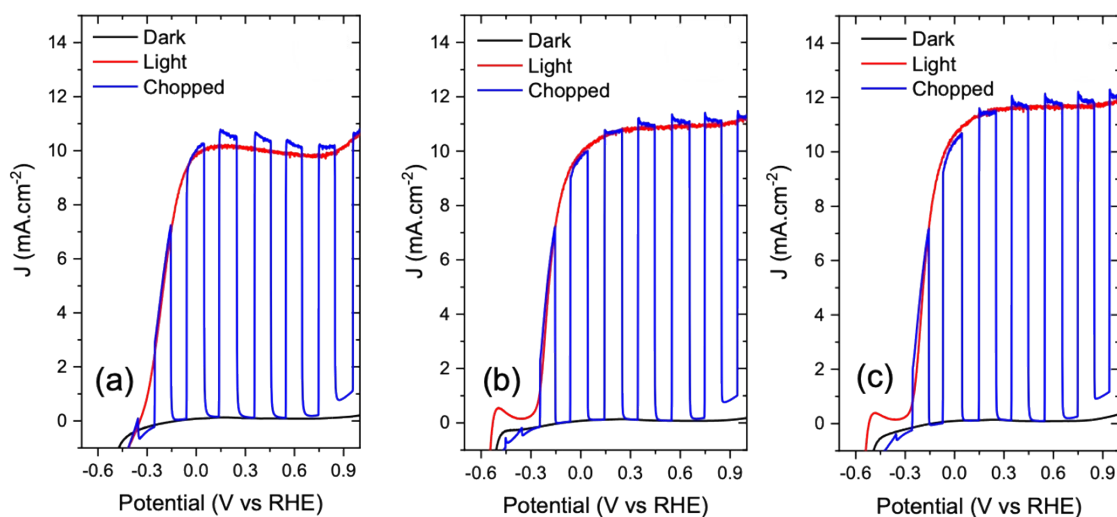
**Figure S7.** Photocurrent density vs potential (vs RHE) of PEC devices under dark, chopped and continuous one sunlight illumination (AM 1.5G, 100 mWcm<sup>-2</sup>): (a) TiO<sub>2</sub>/F-h-BN/QDs/ZnS; (b) TiO<sub>2</sub>/F-h-BN/QDs. (c) Comparison of normalized photocurrent density (a.u.) versus time curves of PEC devices based on TiO<sub>2</sub>/F-h-BN/QDs/ZnS and TiO<sub>2</sub>/F-h-BN/QDs under continuous one sun illumination (AM 1.5G, 100 mW·cm<sup>-2</sup>) at 0.6 V (versus RHE).



**Figure S8.** Schematic of the optimized structure of the nano-flake covered titania nanoparticle applied in DFT calculation.

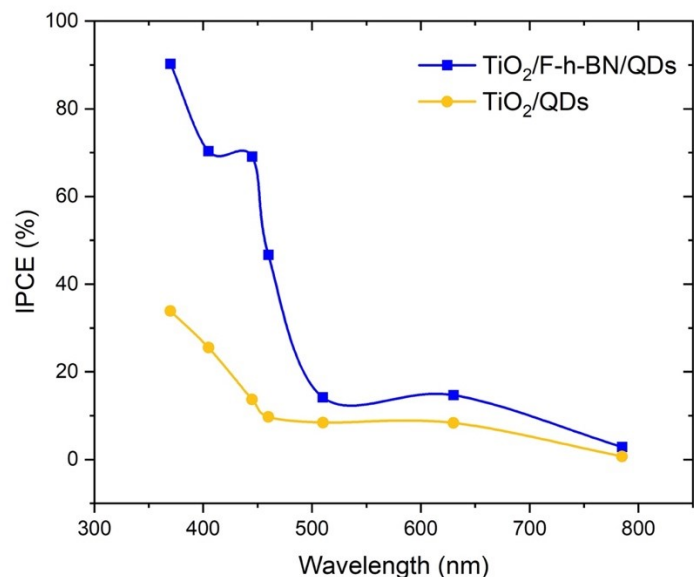


**Figure S9.** Photocurrent density vs potential (vs RHE) of PEC devices under dark, chopped and continuous one sun light illumination (AM 1.5G,  $100 \text{ mWcm}^{-2}$ ): (a)  $\text{TiO}_2/\text{QDs}$ ; (b)  $\text{TiO}_2/\text{QDs}$  with scattering layer of 150-400 nm  $\text{TiO}_2$  nanoparticles; (c)  $\text{TiO}_2\text{-CNTs}/\text{QDs}$  with scattering layer of 150-400 nm  $\text{TiO}_2$  nanoparticles.

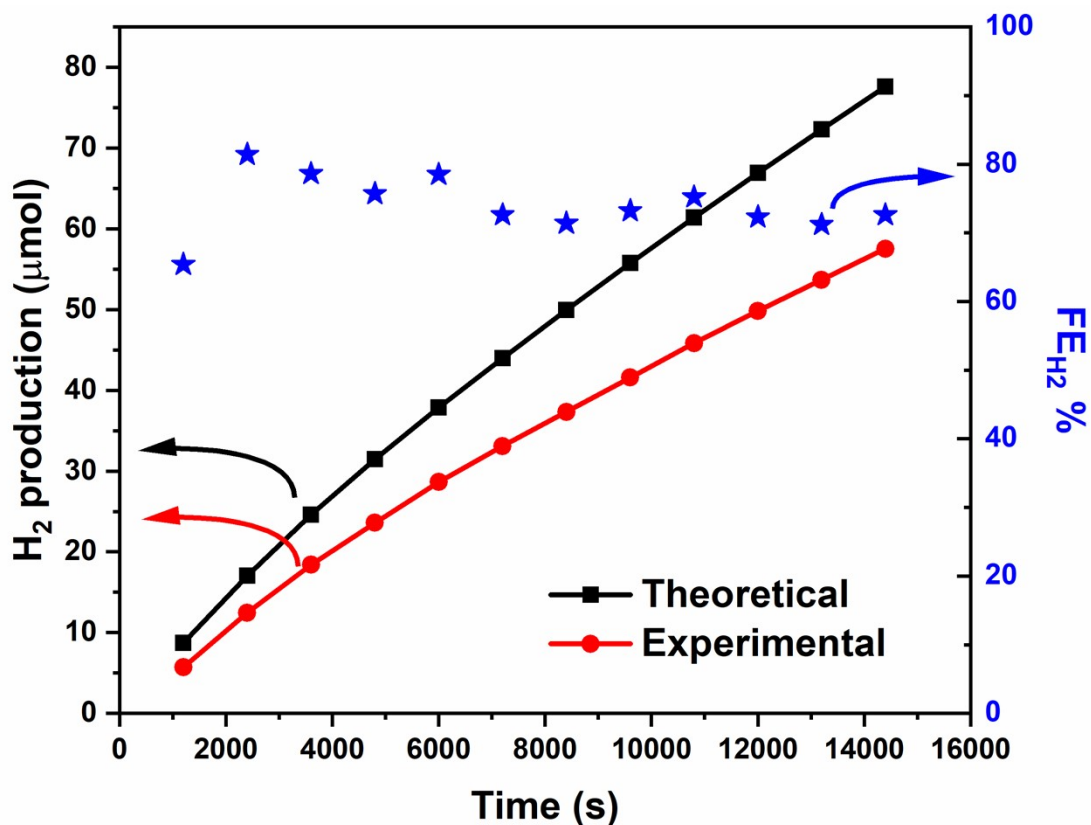


**Figure S10.** Photocurrent density vs potential (vs RHE) of PEC devices under dark, chopped and continuous one sun light illumination (AM 1.5G,  $100 \text{ mWcm}^{-2}$ ): (a)  $\text{TiO}_2/\text{QDs}$ ; (b)  $\text{TiO}_2/\text{F-h-BN}/\text{QDs}$  with scattering layer of 150-400 nm  $\text{TiO}_2$  nanoparticles; (c)  $\text{TiO}_2\text{-CNTs}/\text{F-h-BN}/\text{QDs}$  with scattering layer of 150-400 nm  $\text{TiO}_2$  nanoparticles.





**Figure S11.** The IPCE measurements for PEC devices based on TiO<sub>2</sub>-CNTs/F-h-BN/QDs and TiO<sub>2</sub>-CNTs/QDs photoanodes were carried out under one sun illumination (AM 1.5 G, 100mWcm<sup>-2</sup>) at 0.8V vs RHE.



**Figure S12.** H<sub>2</sub> evolution of PEC cells based on TiO<sub>2</sub>-CNTs/F-h-BN/QDs photoanode as a function of time. The measurement was conducted at 0.6 V vs. RHE under continuous one sun illumination (100 mW/cm<sup>2</sup>, AM 1.5 G). The theoretical (calculated from the measured

photocurrent) and experimental (measured from GC) evolution of H<sub>2</sub> are shown as black square and red circle, respectively. The FE<sub>H<sub>2</sub></sub> value (blue star) of the corresponding PEC device is shown in the right vertical axis.

The ionization potential (IP), which is the difference between the vacuum level and valence band maximum (VBM), can be calculated by subtracting the widths of UPS spectra from the excitation energy value (21.22 eV “Helium source energy”)

- For TiO<sub>2</sub>, the IP = 21.22 – 13.87 = 7.35 eV, therefore the VBM of TiO<sub>2</sub> is -7.35 eV vs. vacuum.
- For TiO<sub>2</sub>/F-h-BN, the IP = 21.22 – 13.36 = 7.86 eV, therefore VBM of TiO<sub>2</sub>/F-h-BN is -7.86.54 eV vs. vacuum.

To calculate the conduction band minimum level, we subtracted the optical band gap obtained from UV-Vis measurements from the IP values, in Figure 6 (f) to the VBM.

- For TiO<sub>2</sub>, the CBM = 7.35 - 3.19 = 4.16 eV therefore CBM of TiO<sub>2</sub> is -4.34eV vs. vacuum.
- For TiO<sub>2</sub>/F-h-BN, the CBM = 7.86 - 3.21 = -4.65 eV therefore CBM of TiO<sub>2</sub>/F-h-BN vs Vacuum

To change the values from Vacuum to SHE, we use the following equation:

$$\text{SHE} = -(\text{Vacuum} + 4.5)$$

- For TiO<sub>2</sub> {VBM = -(-7.35 + 4.5) = 2.85 eV | CMB = -(-4.16 + 4.5) = -0.34 eV Vs SHE}
- For TiO<sub>2</sub>/F-h-BN {VBM = -(-7.86 + 4.5) = 3.36 eV | CBM = -(-4.65 + 4.5) = 0.15 eV Vs SHE}

To change the values from SHE to RHE, we use the following equation:

$$\text{RHE} = \text{SHE} - (0.059 \cdot \text{pH})$$

- For TiO<sub>2</sub> {VBM = 2.85 – (0.059\*13) = 2.08 eV | CMB = -0.34 – (0.059\*13) = -1.11 eV vs RHE}
- For TiO<sub>2</sub>/F-h-BN {VBM = 3.36 – (0.059\*13) = 2.59 eV | CBM = 0.15 – (0.059\*13) = -0.62 eV Vs RHE}

**Table S2.** Calculated PV parameters from the J-V measurements of QDSCs based on TiO<sub>2</sub>-CNTs/QDs and TiO<sub>2</sub>-CNTs/F-h-BN/QDs under one sun illumination (AM 1.5G, 100 mWcm<sup>-2</sup>)

Photoanode structure	$J_{sc}$ (mA.cm <sup>-2</sup> )	$V_{oc}$ (V)	$FF$ (%)	$PCE$ (%)
TiO <sub>2</sub> -CNTs/QDs	10.73	0.555	48	2.87
TiO <sub>2</sub> -CNTs/F-h-BN/QDs	11.86	0.568	50	3.40