Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

A significant enhancement of bulk charge separation in photoelectrocatalysis by ferroelectric polarization induced in CdS/$BaTiO_3$ nanowires

Zhiqi Jiang[a,b], Zhaohui Xiao[a,b], Zui Tao[a,b], Xu Zhang[a,b] and Shiwei Lin [a,b*]

[a] State Key Laboratory of Marine Resource Utilization in South China Sea, Hainan University, Haikou 570228, Hainan, China

[b] School of Materials Science and Engineering, Hainan University, Haikou 570228, Hainan, China

(**Summary of Content:** 9 pages, 15 Figures)

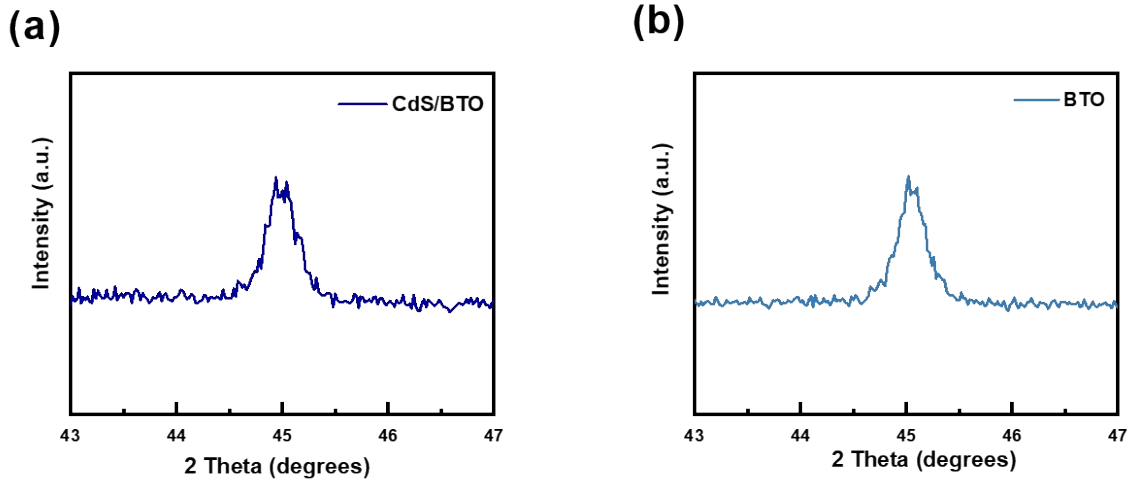

Figure S1. XRD patterns of (a) the CdS/BTO, (b) BTO NWs samples around 45°.

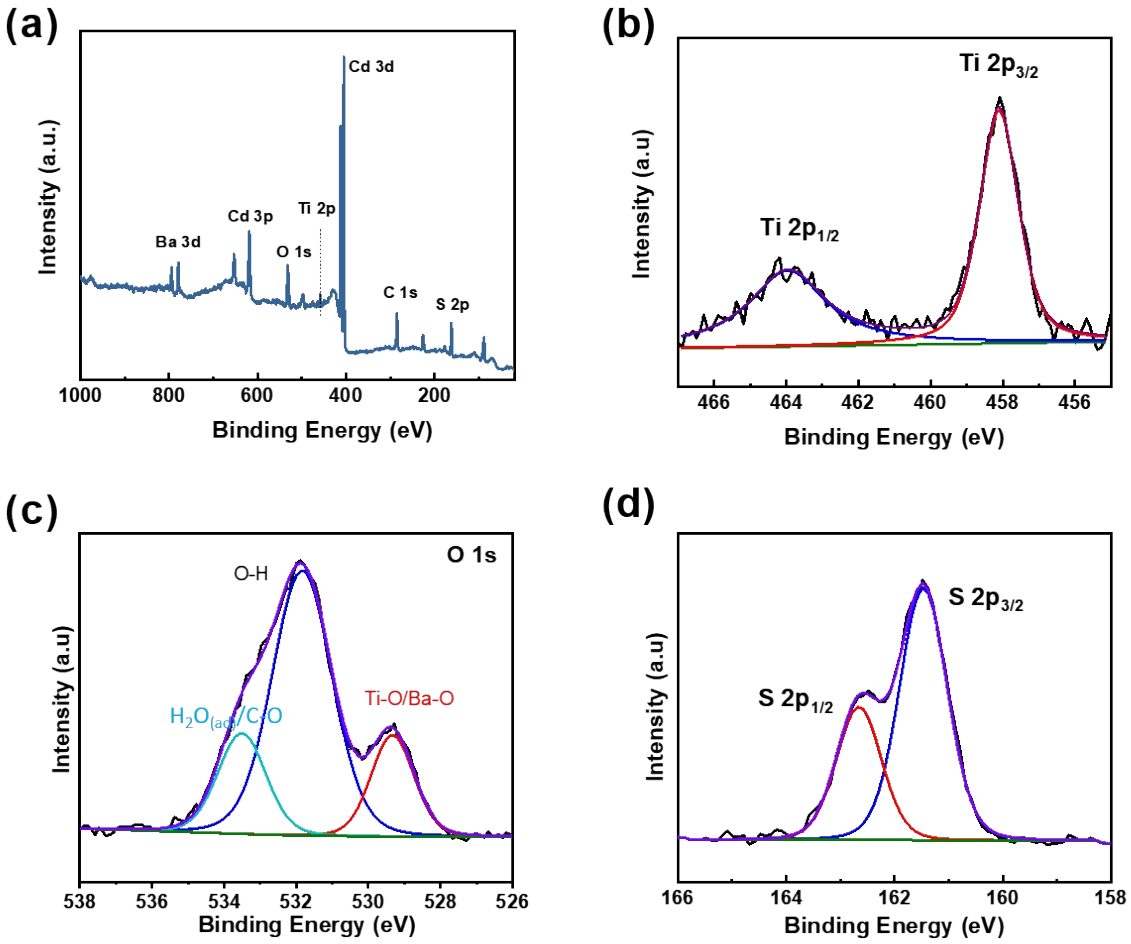

Fig. S2 XPS spectra of the CdS/BTO NWs samples: (a) Survey scan, (b) Ti 2p, (c) O 1s, and (d) S 2p.

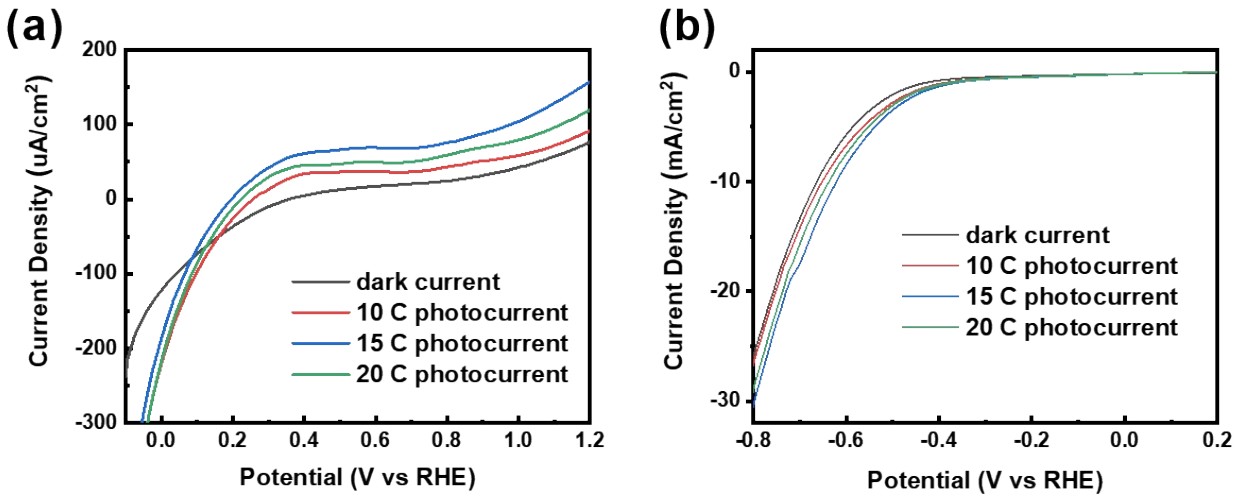

Fig. S3 LSV curves of the 10 C, 15 C, 20 C CdS/BTO NWs samples in (a) positive voltage section (-0.1 V to +1.2 V), and (b) negative voltage section (0.2 V to -0.8 V).

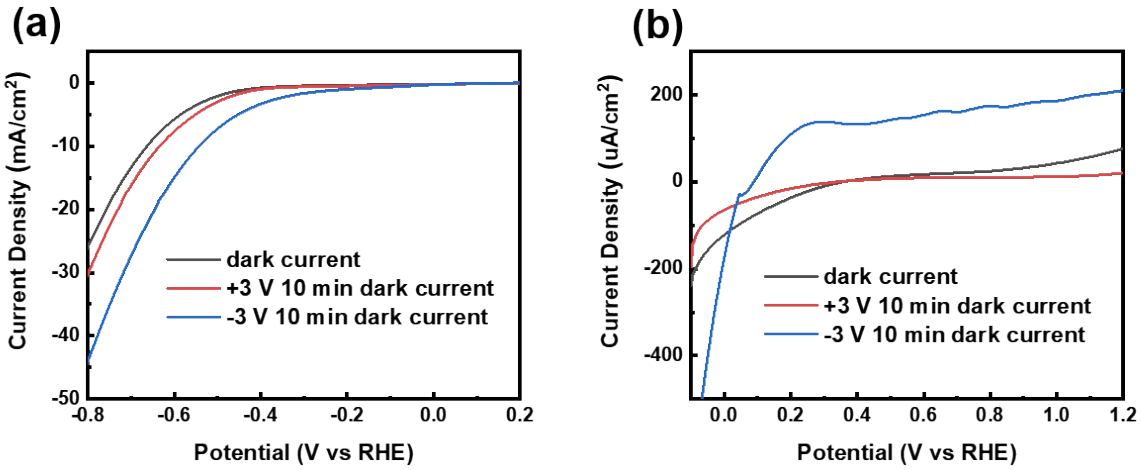

Fig. S4 Dark current of the CdS/BTO NWs samples after different polarizations in (a) negative voltage section (0.2 V to -0.8 V) and (b) positive voltage section (-0.1 V to +1.2 V).

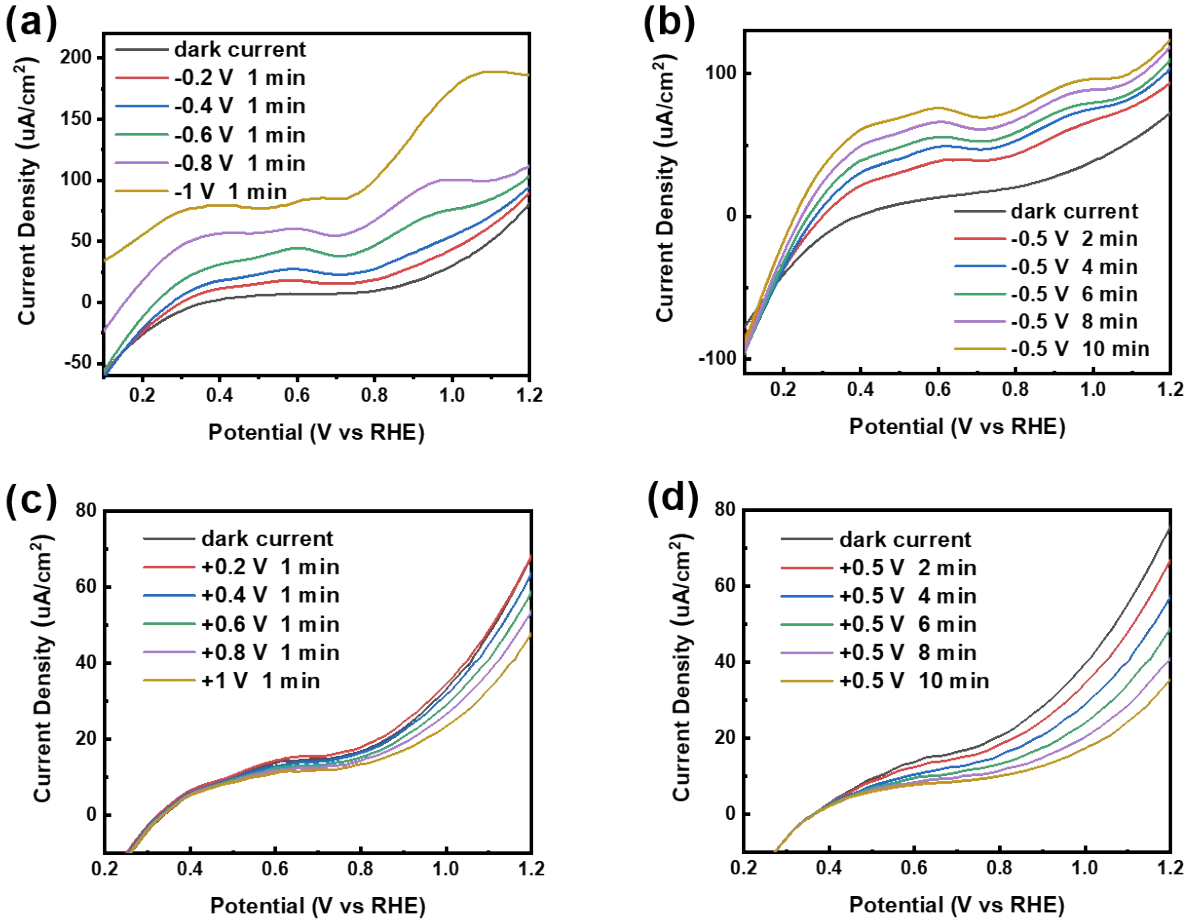

Fig. S5 LSV curves in the dark with (a) -0.2, -0.4, -0.6, -0.8, -1 V polarization for 1 min, (b) -0.5 V polarization for 2, 4, 6, 8, 10 min, (c) +0.2, +0.4, +0.6, +0.8, +1 V polarization for 1 min, and (d) +0.5 V polarization for 2, 4, 6, 8, 10 min, respectively.

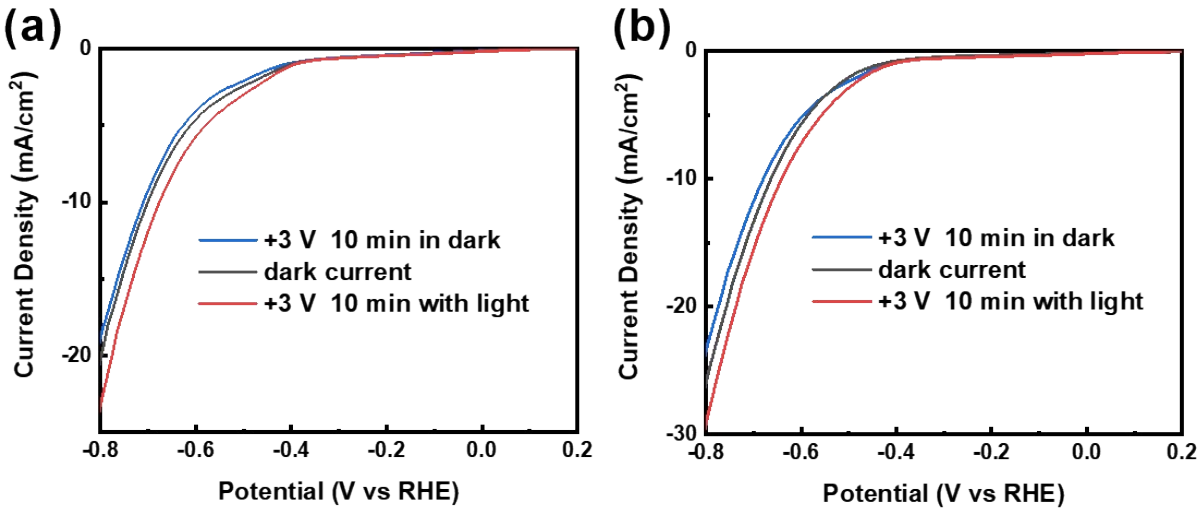

Fig. S6 LSV curves with +3 V polarization of (a) the BTO NWs and (b) CdS/BTO NWs samples.

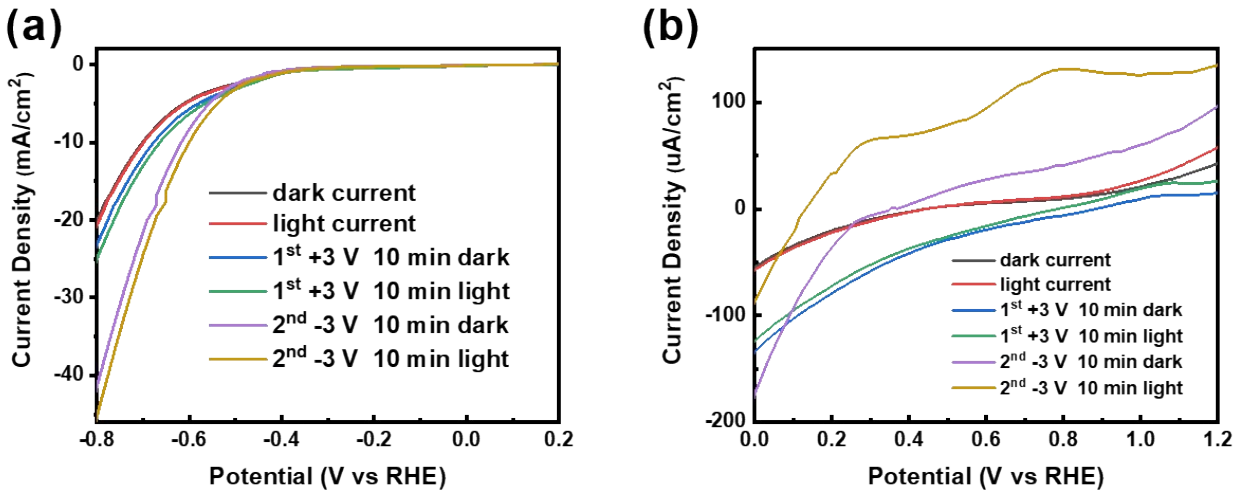

Fig. S7 LSV curves of the pure BTO NWs samples after different polarizations in (a) negative voltage section (0.2 V to -0.8 V) and (b) positive voltage section (-0.1 V to +1.2 V).

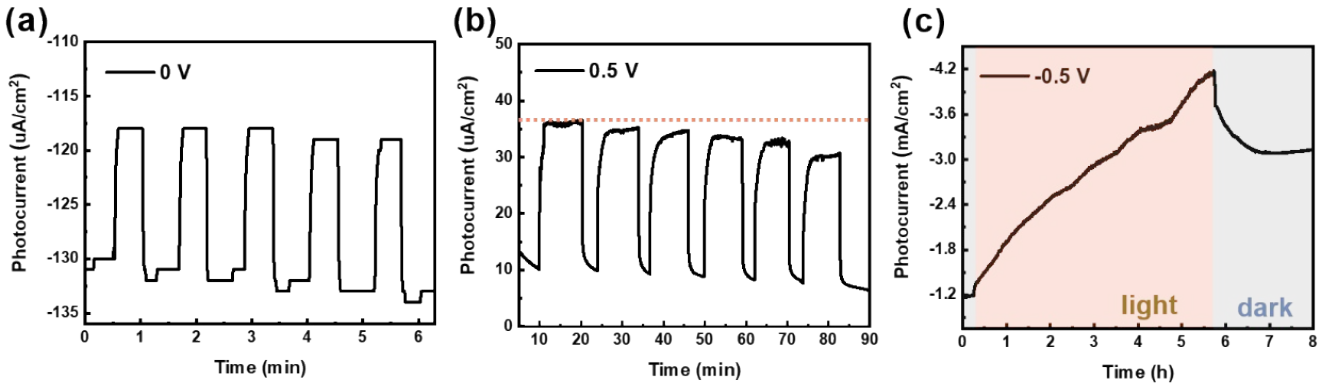

Fig. S8 Photocurrent densities of the CdS/BTO NWs samples at (a) 0 V, (b) +0.5 V, and (c) -0.5 V bias.

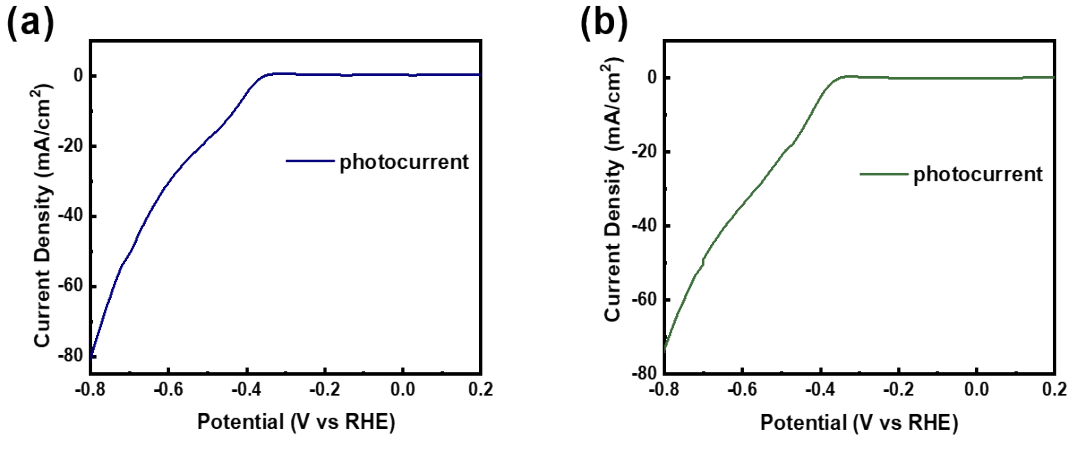

Fig. S9 The photocurrent densities of CdS/BTO NWs samples with (a) -3 V/-3 V/+3 V and (b) +3 V/+3 V/-3 V polarizations after two months.

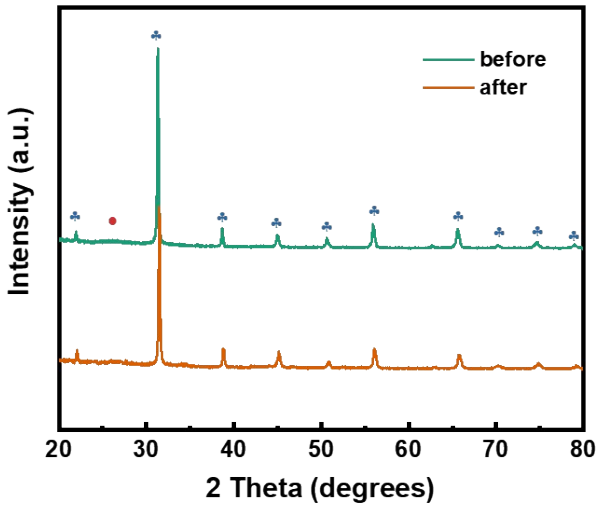

Fig. S10 XRD patterns of the CdS/BTO NWs sample before and after polarization.

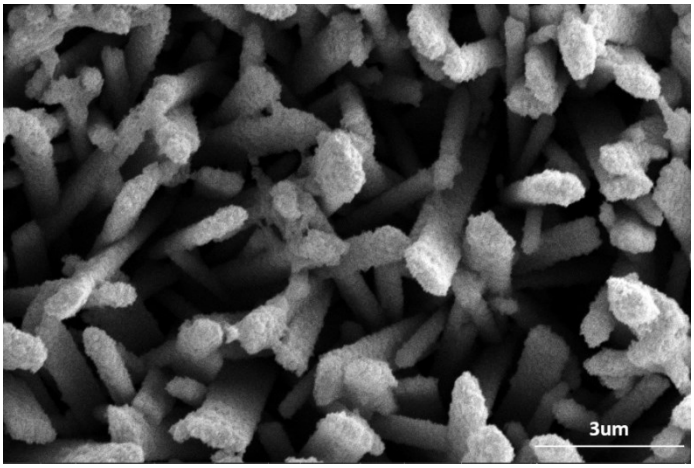

Fig. S11 SEM image of the CdS/BTO NWs sample after polarization.

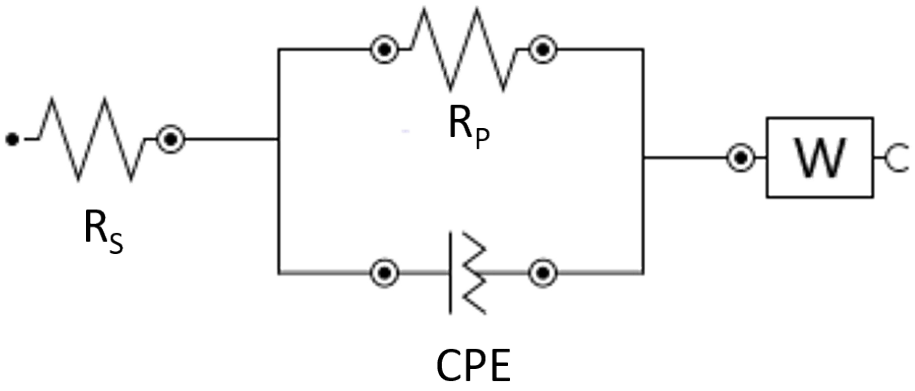

Fig. S12 The equivalent circuit used for modeling the measured electrochemical response. R_p is related with the kinetics of the interfacial charge transfer reaction, R_s represents solution resistance. CPE and W represent the pseudocapacitance and Warburg impedance, respectively.

Table. S1 Summary of the impedance fitting data for the CdS/BTO NWs samples.

Sample	R_p (Ω)	R_s (Ω)	CPE_p (mF)
dark current	1333.00	1.78520	0.06534
photocurrent	730.870	2.99120	0.11769
1st +3V 10min	1520.30	1.53840	0.05509
+1V 3min	1229.10	2.78370	0.01561
+0.5V 3min	900.730	1.46280	0.39652
-0.5V 3min	490.030	1.98660	0.02070
-1V 3min	402.040	1.53260	0.02089
1st -3V 10min	30.8510	3.05340	0.14456

2nd -3V 10min	27.3430	2.74870	0.09363
2nd +3V 10min	2019.70	3.68880	0.06978

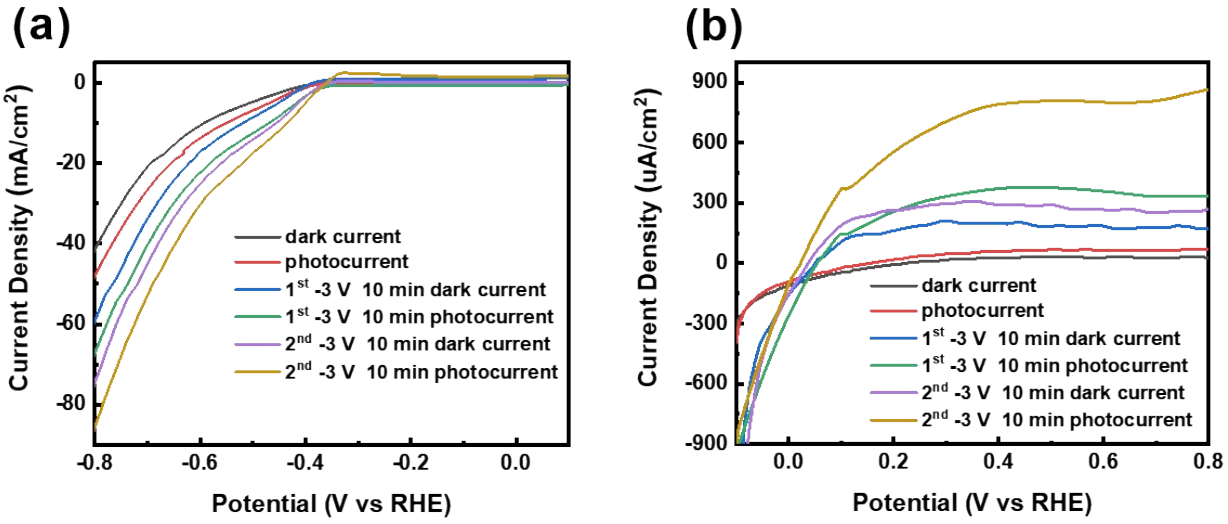

Fig. S13 LSV curves of the CdS/BTO NWs samples measured in 1 M Na_2SO_3 electrolyte in (a) negative voltage section (0.1 V to -0.8 V) and (b) positive voltage section (-0.1 V to +0.8 V).

As present in Fig. S13, under the unpolarized condition, the photocurrent at -0.8 $V_{(vs.RHE)}$ can reached 47.71 mA/cm^2, which is 6.55 mA more than that of the dark current (41.16 mA/cm^2) and the photocurrent at +0.8$V_{(vs.RHE)}$ is 71.51 uA/cm^2, 43.01 uA higher than the dark current (28.49 uA/cm^2). When we look at the case of the first polarization at -3 V for 10 min polarization, the photocurrent at -0.8 $V_{(vs.RHE)}$ increases

to 66.75 mA/cm^2, which is 7.9 mA/cm^2 higher than that of the dark current (58.84 mA/cm^2). The photocurrent at +0.8 $V_{(vs.RHE)}$ is 170.97 uA/cm^2, 162.36 uA/cm^2 larger than the dark current. The experiment adopts the method of applying polarization twice. Then the photocurrent at -0.8 $V_{(vs.RHE)}$ increases by 11.07 mA/cm^2 compared with the dark current, which are 74.3 and 85.37 mA/cm^2, respectively. Meanwhile, the difference of the photocurrent and dark current at +0.8 V is 597.85 uA/cm^2, which are 267.74 and 865.59 uA/cm^2, respectively.

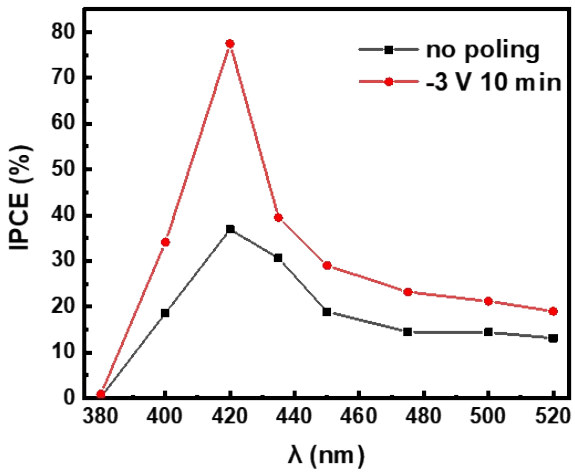

Fig. S14 IPCE spectra measured at 0 $V_{(vs.RHE)}$ for CdS/BTO NWs with no poling and after negative polarization with -3 V for 10 min.

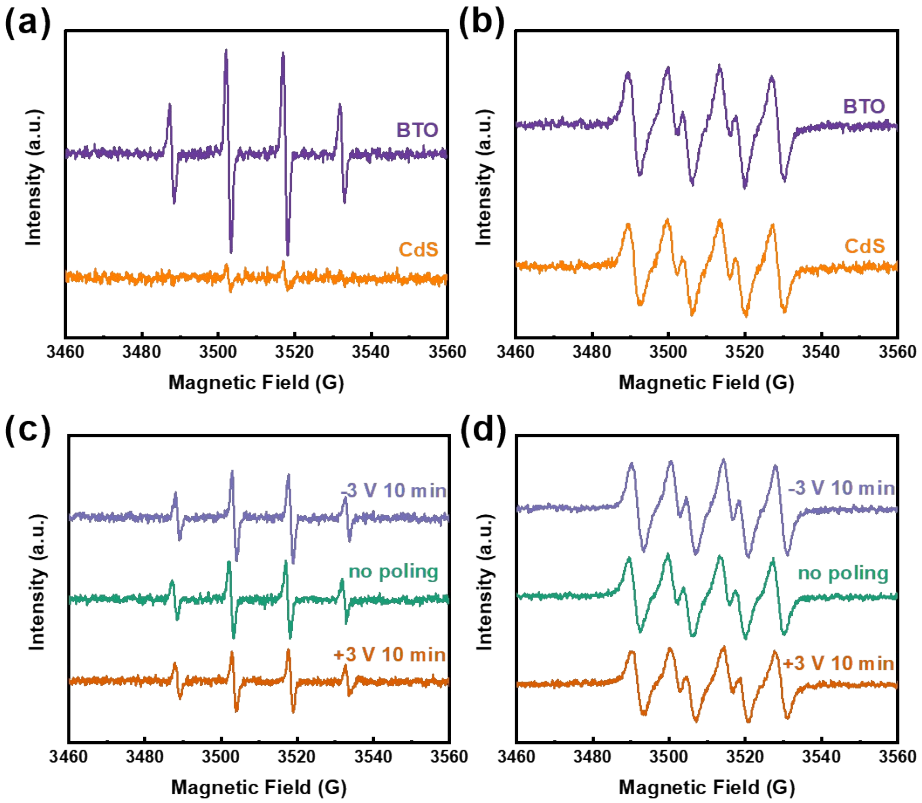

Fig. S15 ESR spectra of the pure BTO and CdS samples under light irradiation for detection of (a)•OH, (b) •-O_2. ESR spectra of the CdS/BTO NWs samples with no poling and polarization at +3 V/-3 V for 10 min under light irradiation for detection of (c) •OH and (d)•-O_2.