Supporting Information

Improving the Oxygen Evolution Activity by Constructing Perylene Imide Based Z-Scheme Heterojunction

Jie Zhang,[a,b] Deshuai Yang,[a] Jinyan Shi,[a,b] Zejin Wang,[a,b] Wenbo Zhu,[a,b] Ying Wang*[a,b] and Zhaoxu Chen*[a]

E-mail: wangy@nju.edu.cn

[a]School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210023, P. R. China.

[b]Eco-materials and Renewable Energy Research Center (ERERC), National Laboratory of Solid State Microstructures, Kunshan Innovation Institute of Nanjing University, Jiangsu Key Laboratory for Nanotechnology, Nanjing University, Nanjing, 210093, P. R. China.

1□ Computational details for free energy change and formation energy of PDI and CdS/PDI Z-scheme heterostructure

Then the Gibbs energy change (ΔG1 for *OH formation, ΔG2 for *O formation, ΔG3 for *OOH formation, ΔG4 for O_2 formation, ΔG5 for O_2 dissociation) of each reaction step was calculated at standard conditions (pH = 0, pressure (p) = 1bar, and temperature(T) = 298.15 K) by following equations:

$G1 = (E^*OH + 0.5\times EH_2 - EH_2O - E^*) + (ZPE^*OH + 0.5\times ZPEH_2 - ZPEH_2O - ZPE^*) - T\times(S^*OH + 0.5\times SH_2 - SH_2O - S^*)$ (7)

$G2 = (E^*O + 0.5 \times EH_2 - E^*OH) + (ZPE^*O + 0.5 \times ZPEH_2 - ZPE^*OH) - T \times (S^*O + 0.5 \times SH_2 - S^*OH)$ (8)

$G3 = (E^*OOH + 0.5\times EH_2 - EH_2O - E^*O) + (ZPE^*OOH + 0.5 \times ZPEH_2 - ZPEH_2O - ZPE^*O) - T \times (S^*OOH + 0.5 \times SH_2 - SH_2O - S^*O)$ or $G3 = (E^*O^*OH + 0.5 \times EH_2 - EH_2O - E^*O) + (ZPE^*O^*OH + 0.5 \times ZPEH_2 - ZPEH_2O - ZPE^*O) - T \times (S^*O^*OH + 0.5 \times SH_2 - SH_2O - S^*O)$ (9)

$G4 = E^* + 0.5 \times EH_2 + EO_2 - E^*OOH + (ZPE^* + 0.5 \times ZPEH_2 + ZPEO_2 - ZPE^*OOH)$

– T × (S* + 0.5 × SH_2 + SO_2 −S*OOH) or G4 = E* + 0.5 × EH_2 +E*OO – E*O*OH + (ZPE* + 0.5 × $ZPEH_2$ + ZPE*OO−ZPE*O*OH)–T×(S*+0.5×SH2+S*OO−S*O*OH) (10)

G5=E*+EOO–E*OO +(ZPE* + ZPEOO − ZPE*OO) – T × (S* + SOO − SOO*) (11)

where E is the electronic energy, ΔZEP, ΔS, and T refer to the zero-point energy (ZPE), entropy, and temperature, respectively. ΔS is calculated based on vibrational frequencies through the vaspkit.

3. Figures and tables

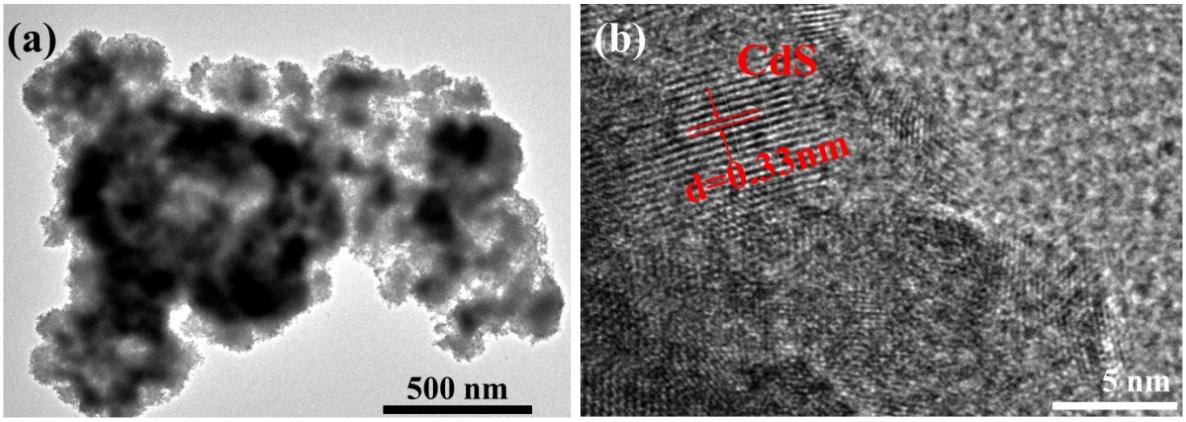

Figure S1. (a) TEM and (b) HRTEM of CdS

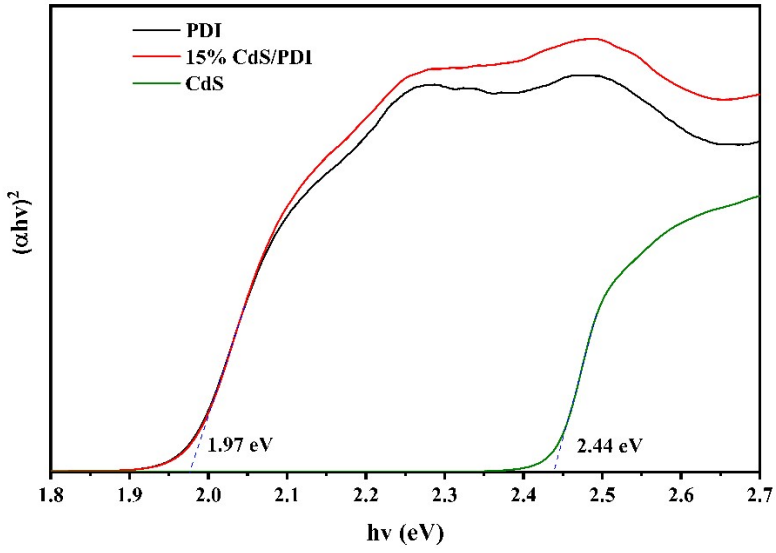

Figure S2. The corresponding plots of $(\alpha h\nu)^2$ versus hv of PDI, CdS and 15%CdS/PDI.

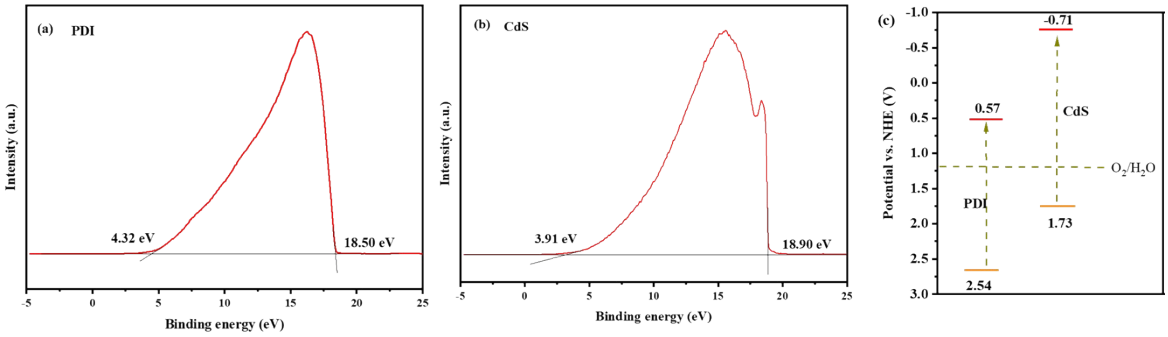

Figure S3. UPS of (a) PDI and (b) CdS. (c) Band structure of PDI and CdS according to the UPS

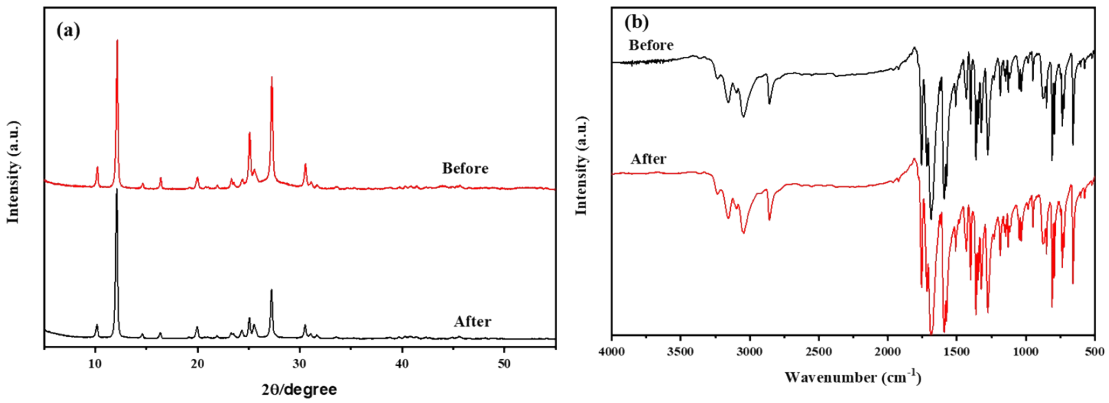

Figure S4 (a) XRD and (b) FT-IR spectra of before and after used 15%CdS/PDI Z-Scheme heterostructure sample after 16 h photocatalytic reaction.

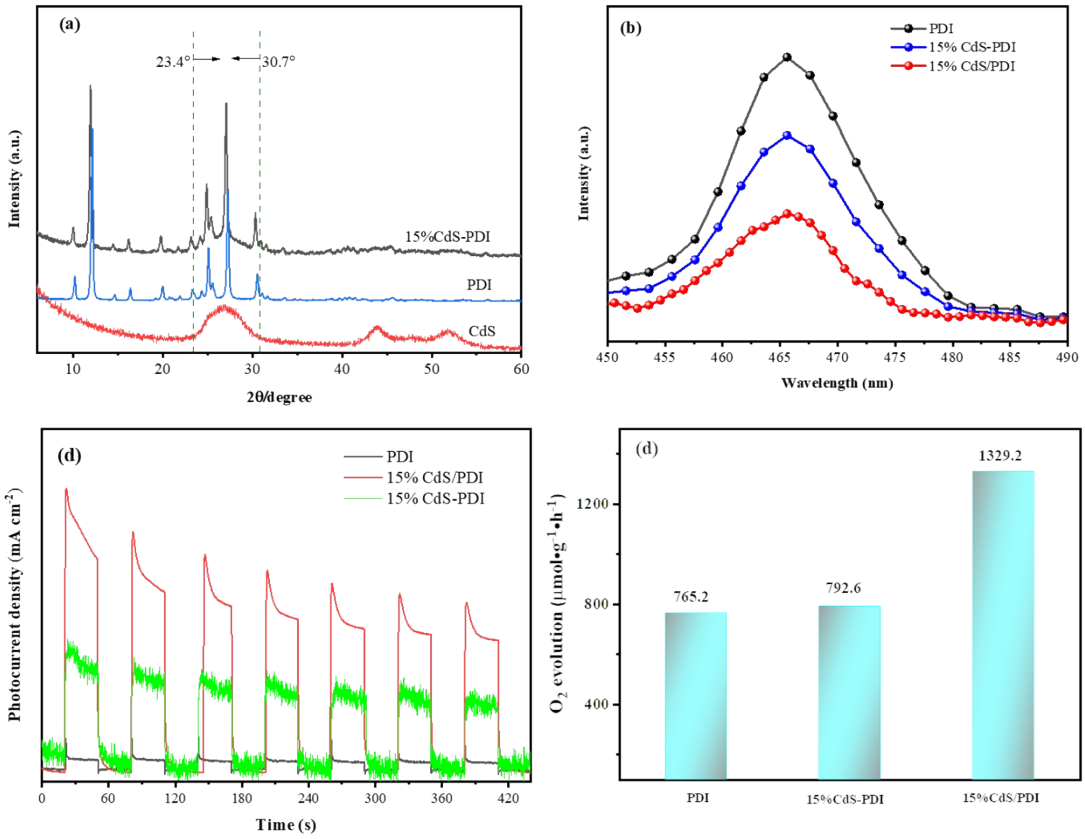

Figure S5. (a) XRD spectra of CdS, PDI and 15%CdS-PDI. (b) PL spectra of PDI, 15%CdS-PDI and 15%CdS/PDI. (c) Transient photocurrent response for PDI, 15%CdS-PDI and 15%CdS/PDI (d) Photocatalytic O_2 evolution tests of PDI, 15% CdS-PDI and 15% CdS/PDI.

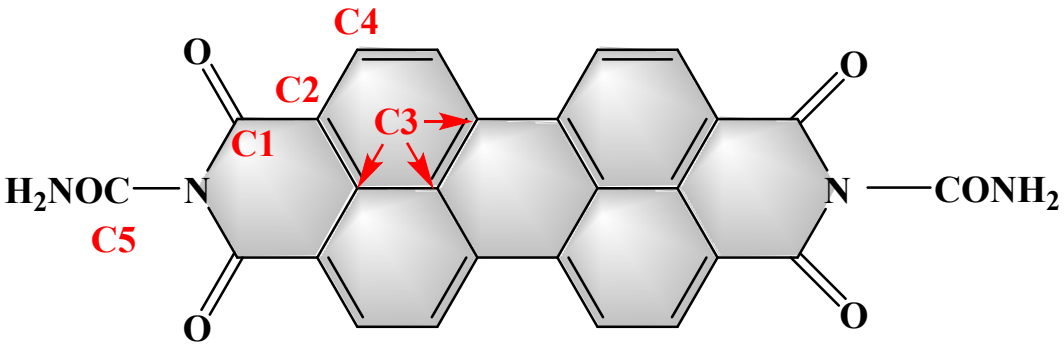

Figure S6. Five types of carbon in PDI

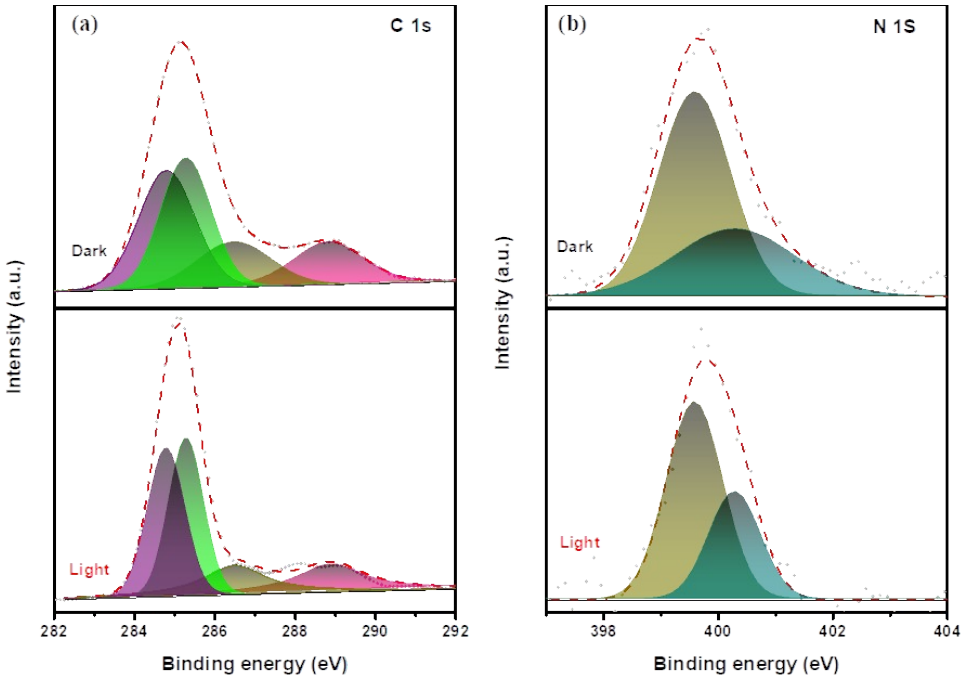

Figure S7. High-resolution C 1s and N 1s XPS spectra of PDI in the dark and light illumination situation.

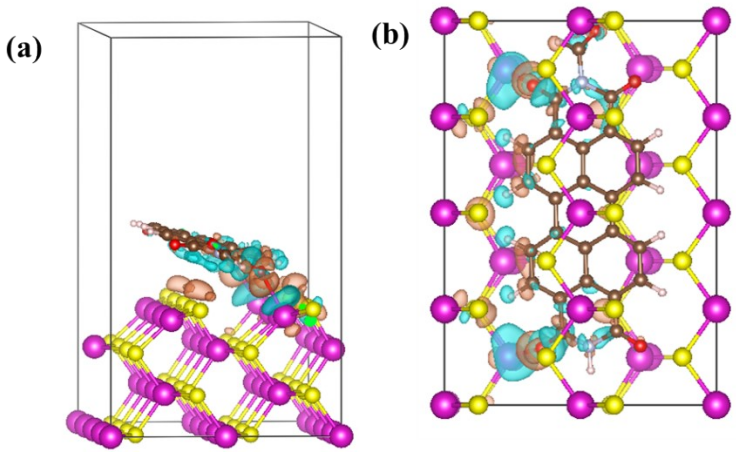

Figure S8. (a) The side view and (b) top view of the charge density different for CdS/PDI Z-scheme heterostructure. The cyan areas indicated electron depletion and the brown areas indicate electron accumulation.

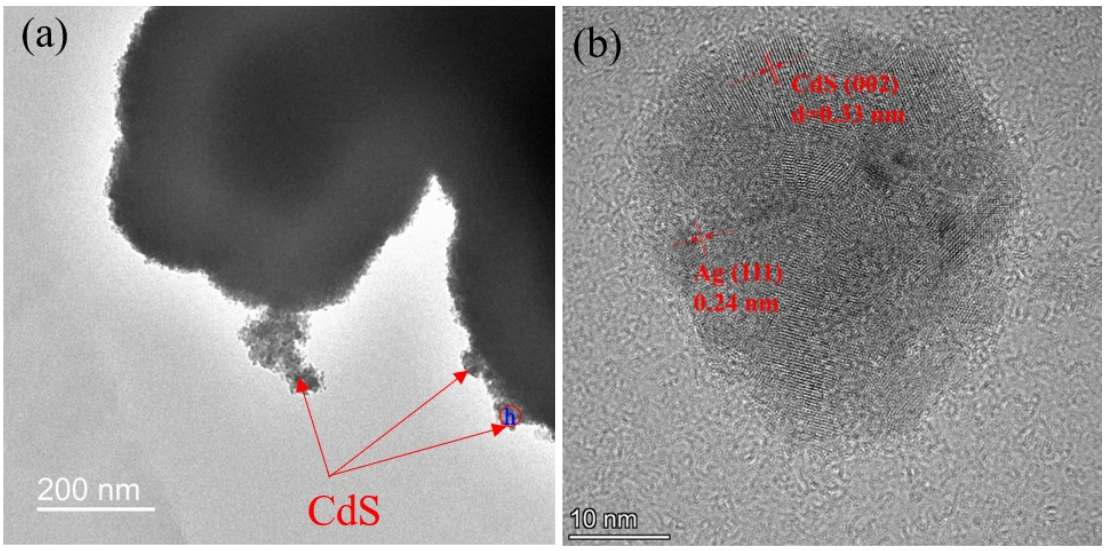

Figure S9. TEM images of 15% CdS/PDI after O_2 evolution reaction.

Table S1. The experiment results of three times repeated trials

Sample	PDI(T)	5%CdS/PDI	10%CdS/PDI	15%CdS/PDI	20%CdS/PDI
1	765.2	837.7	1066	1329	282.0
T_1	0.9816	0.6896	1.081	0.9271	0.9895
2	617.7	848.1	1181	1383	310.2
T_2	1.017	0.4576	0.8916	0.1324	0.0382
3	695.4	920.2	1140	1464	341.2
T_3	0.03591	1.147	0.1898	1.060	1.010
Mean value	692.8	868.7	1129	1392	311.3
sd	73.80	44.93	58.21	68.05	29.61