Supplementary Information

Promoted photocarriers separation by dipole engineering in two-dimensional perovskite/C$_2$N van der Waals heterostructures

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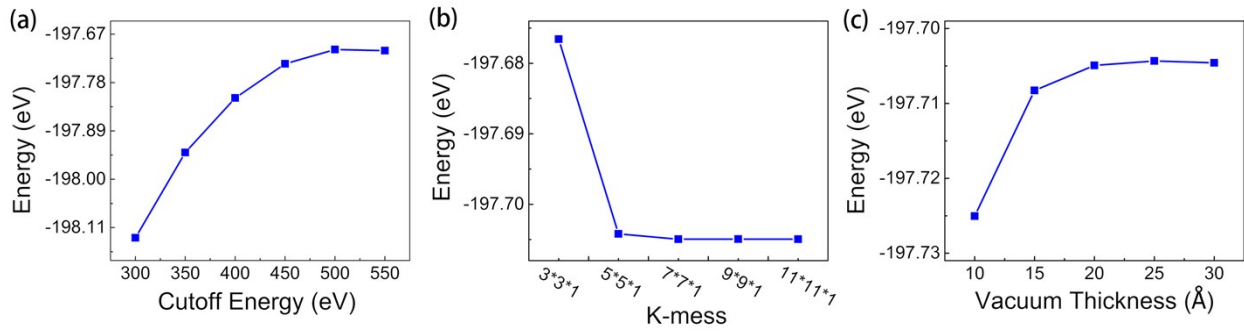
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Fig. S1. The convergence tests on the (a) cutoff energy, (b) *k*-points, and (c) thickness of vacuum layer.
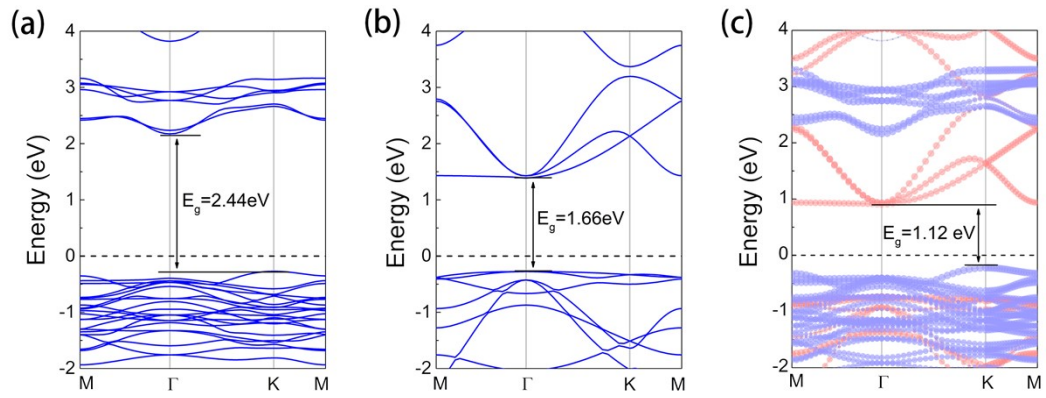
Fig. S2. Calculated band structures of (a) $Cs_3Bi_2I_9$ monolayer, (b) C_2N monolayer, and (c) $Cs_3Bi_2I_9/C_2N$ heterostructure calculated by PBE functional. The Fermi level is set to zero.
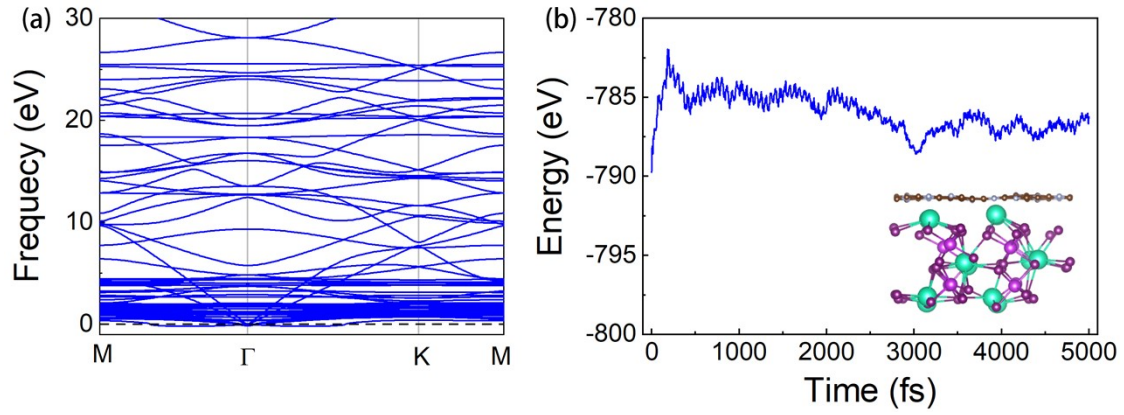
Fig. S3. (a) The phonon band dispersions and (b) potential energy fluctuations of $Cs_3Bi_2I_9/C_2N$ heterostructure. The inset shows the corresponding structure at 300 K after the simulation for 5 ps.
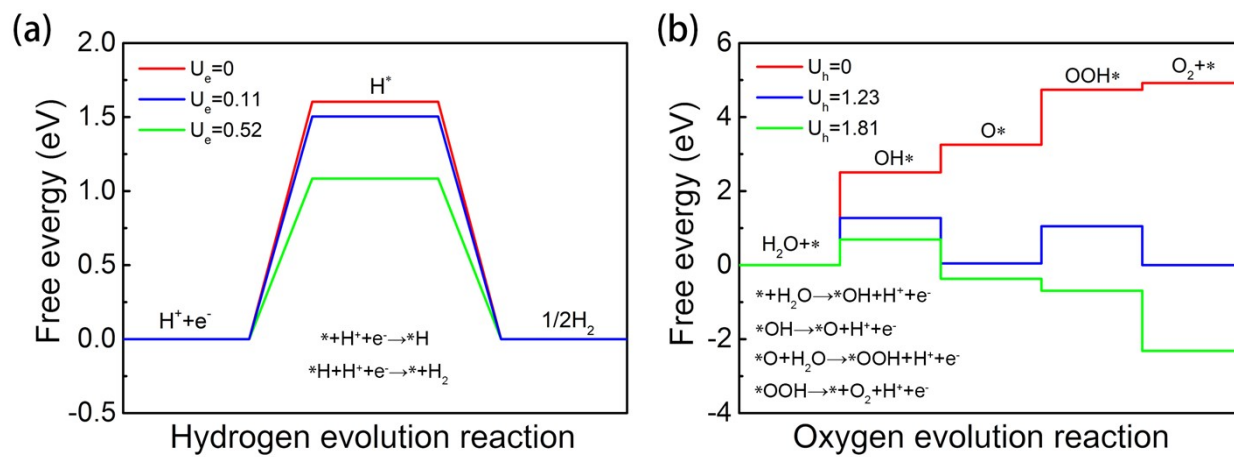
Fig. S4. ΔG of the (a) HER and (b) OER pathway. The insets show the reaction steps.

Figure (a) — Hydrogen evolution reaction:
- $U_e=0$
- $U_e=0.11$
- $U_e=0.52$

Labels: $H^+ + e^-$, H^*, $1/2H_2$
Reaction steps: $*+H^+ + e^- \rightarrow *H$; $*H + H^+ + e^- \rightarrow * + H_2$

Figure (b) — Oxygen evolution reaction:
- $U_h=0$
- $U_h=1.23$
- $U_h=1.81$

Labels: $H_2O + *$, $OH*$, $O*$, $OOH*$, $O_2 + *$
Reaction steps:
$*+H_2O \rightarrow *OH + H^+ + e^-$
$*OH \rightarrow *O + H^+ + e^-$
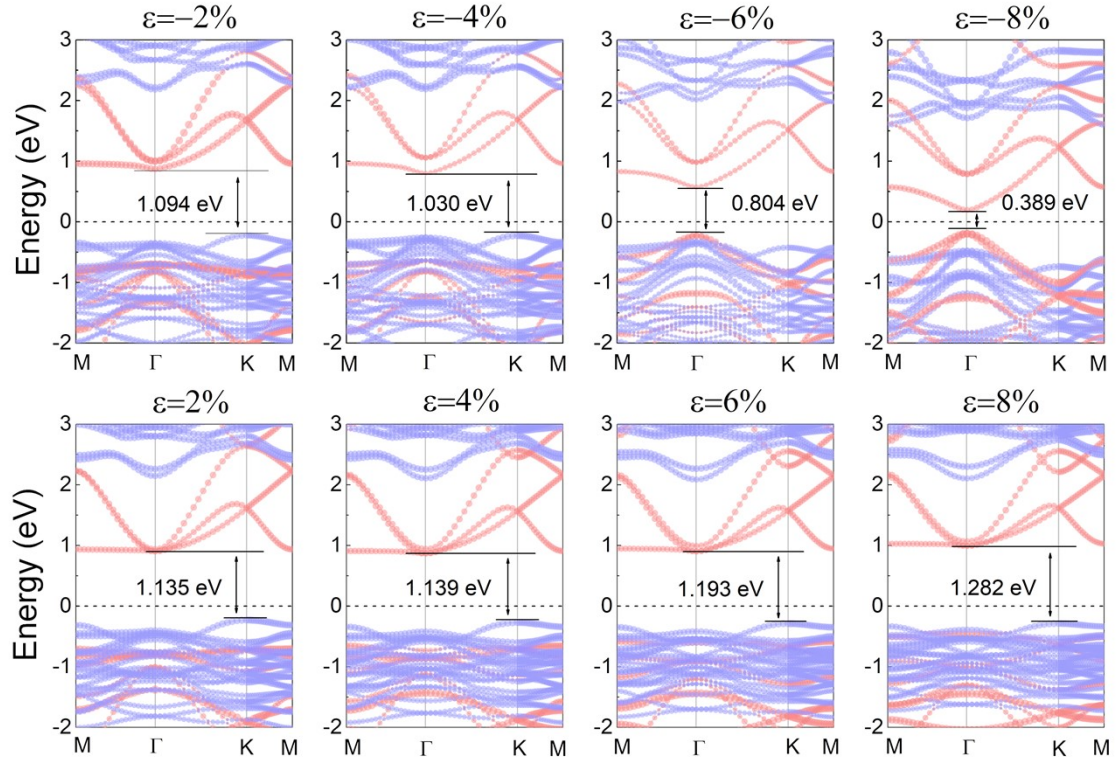$*O + H_2O \rightarrow *OOH + H^+ + e^-$
$*OOH \rightarrow * + O_2 + H^+ + e^-$

Fig. S5. The band structures of the $Cs_3Bi_2I_9/C_2N$ heterostructure under different in-plane biaxial strains based on PBE method. The Fermi level is set to zero.

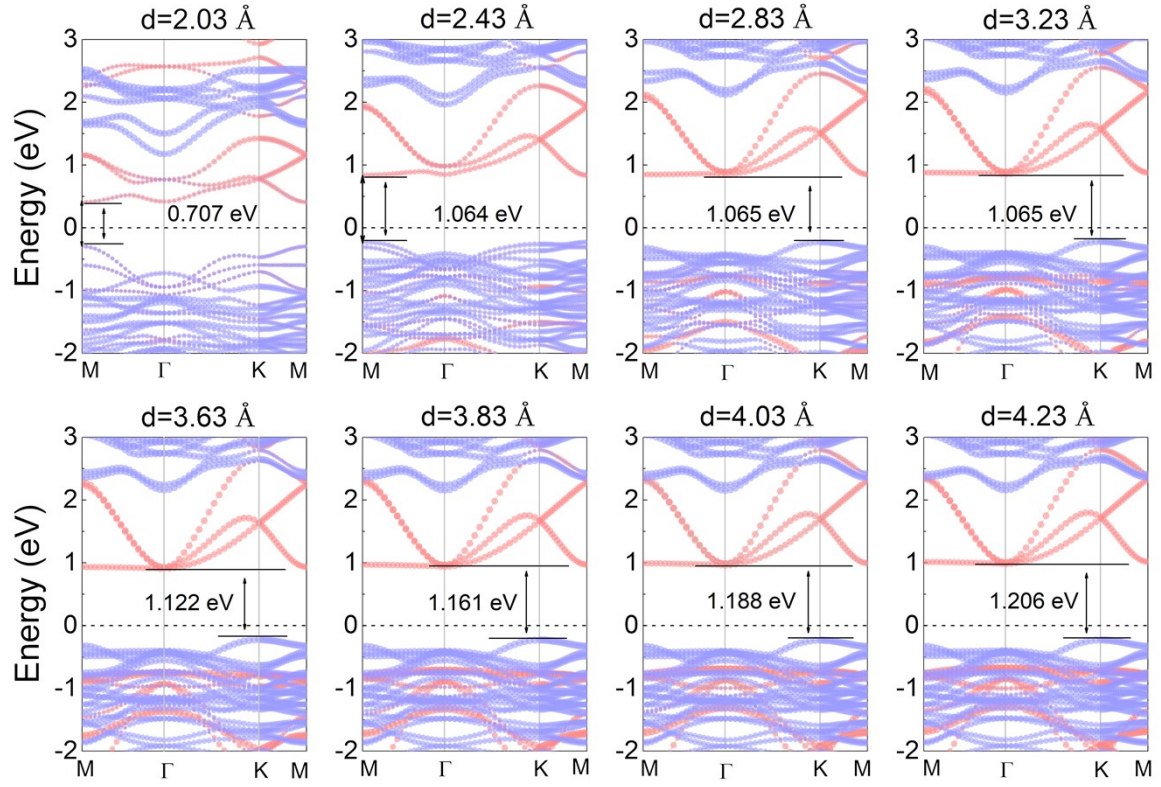**Fig. S6.** The band structures of the $Cs_3Bi_2I_9/C_2N$ heterostructure with different interlayer distances based on PBE method. The Fermi level is set to zero.
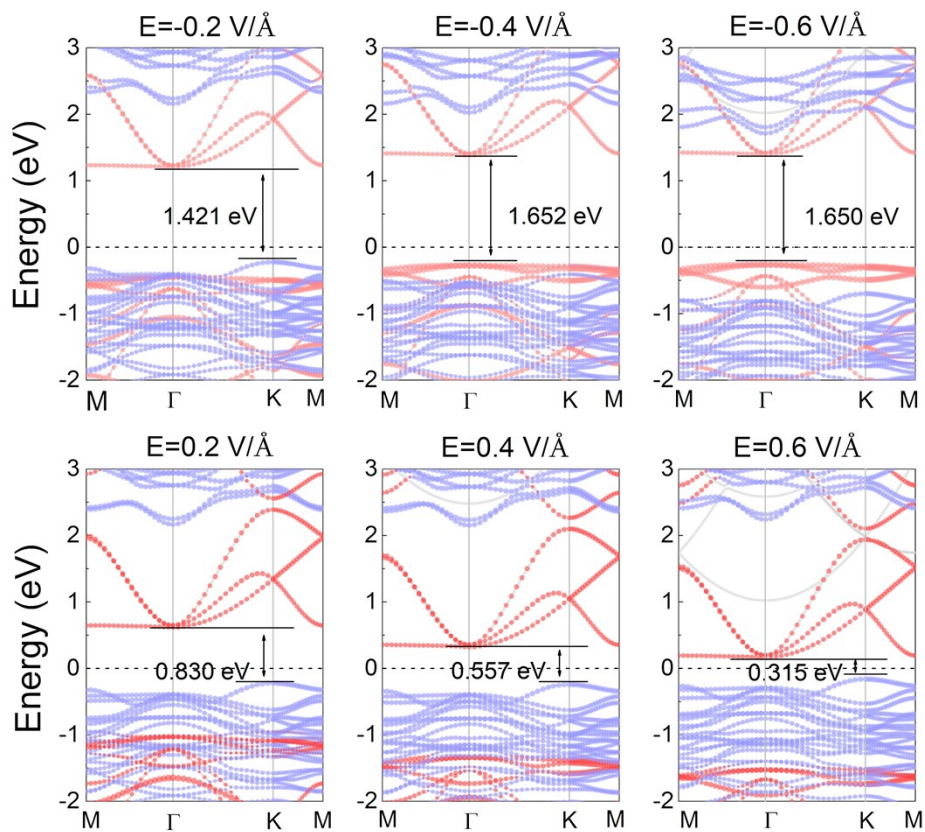
Fig. S7. The band structures of the $Cs_3Bi_2I_9/C_2N$ heterostructure with different electric fields based on PBE method. The Fermi level is set to zero.

Table S1. The lattice vectors and fractional coordinates of each atom in $Cs_3Bi_2I_9$ monolayer.

a[Å]	8.5967998505000001	0.0000000000000	0.0000000000000
b[Å]	-4.2983999252000000	7.4450470618000004	0.0000000000000
c[Å]	0.0000000000000	0.0000000000000	32.4808006287000026
Cs	0.6666666630000009	0.3333333260000018	0.6014199999999974
Cs	0.6666666630000009	0.3333333260000018	0.3985800290000014
Cs	0.0000000000000	0.0000000000000	0.5000000000000000
Bi	0.3333333260000018	0.6666666520000035	0.4337500130000009
Bi	0.3333333260000018	0.6666666520000035	0.5662499569999966
I	0.6748099949999968	0.8373999840000010	0.3864999919999974
I	0.1625999760000028	0.8374099749999999	0.3864999919999974
I	0.1625900209999998	0.3251899979999990	0.3864999919999974
I	0.6748099949999968	0.8373999840000010	0.6135000080000026
I	0.1625999760000028	0.8374099749999999	0.6135000080000026
I	0.1625900209999998	0.3251899979999990	0.6135000080000026
I	0.9976900449999988	0.4988499829999995	0.5000000000000000
I	0.5011499940000022	0.4988400240000033	0.5000000000000000
I	0.5011599810000007	0.0023099779999995	0.5000000000000000

Table S2. The lattice vectors and fractional coordinates of each atom in C_2N monolayer.

a[Å]	8.3287319581807910	-0.0000086375643439	0.0000000000000000
b[Å]	-4.1643734594268507	7.2128776652686950	0.0000000000000000
c[Å]	0.0000000000000000	0.0000000000000000	28.6035003661999987
C	0.6649572866375831	0.1584761652715319	0.5955600433095020
C	0.3349885443879356	0.8415201333268880	0.5956595566038005
C	0.8414926157747485	0.5064955199102057	0.5955571754278379
C	0.1584452948996779	0.4934817062717273	0.5956610035639622
C	0.4934733252926527	0.3350109869042917	0.5955641888062967
C	0.5064836582225742	0.6649773415631767	0.5956531663188126
C	0.1584470410483025	0.6649779869047788	0.5956589147980300
C	0.8414891099342869	0.3350094274929322	0.5955609477713283
C	0.5064848012035074	0.8415210432113602	0.5956545249771583
C	0.4934729002164080	0.1584767113576188	0.5955655530966505
C	0.3349890260971121	0.4934829240720786	0.5956606190163212
C	0.6649577975526456	0.5064937770785224	0.5955574130945321
N	0.0000345343050144	0.6688782423430601	0.5955862260575377
N	0.0000303720937557	0.3311047793888947	0.5955904449498829
N	0.3310876579249200	0.3311005900158068	0.5955960398514453
N	0.6688635075330792	0.6688793235882384	0.5955784847071436
N	0.6688656689146286	0.0000004111987619	0.5955828544814462
N	0.3310887337587158	-0.0000013558998655	0.5955944541683168

Table S3. The lattice vectors and fractional coordinates of each atom in $Cs_3Bi_2I_9/C_2N$ heterostructure.

a[Å]	8.3502998351999995	0.0000000084114841	0.0000000000000000
b[Å]	-4.1751499175999998	7.2315717865000000	0.0000000000000000
c[Å]	0.0000000000000000	0.0000000000000000	36.4038009643999985
C	0.6649399969999976	0.1584500000000020	0.6159800470000008
C	0.8415500139999992	0.5064899970000027	0.6159800470000008
C	0.4935099810000025	0.3350599870000011	0.6159800470000008
C	0.8415500059999985	0.3350599870000011	0.6159800470000008
C	0.4935100029999973	0.1584500000000020	0.6159800470000008
C	0.6649399840000001	0.5064899970000027	0.6159800470000008
C	0.3350599930000016	0.8414199540000027	0.6159700400000006
C	0.1585799899999998	0.4936399850000015	0.6159700400000006
C	0.5063599850000031	0.6649399969999976	0.6159700400000006
C	0.1585800129999981	0.6649399969999976	0.6159700400000006
C	0.5063599610000011	0.8414199540000027	0.6159700400000006
C	0.3350599939999981	0.4936399850000015	0.6159700400000006
N	0.0001900079999970	0.6684200199999992	0.6159800470000008
N	0.3315799900000016	0.3317699979999986	0.6159800470000008
N	0.6682299860000001	0.9998099499999995	0.6159800470000008
N	0.3315799929999983	0.9998099499999995	0.6159800470000008
N	0.6682299830000034	0.6684200199999992	0.6159800470000008
N	0.0001899940000030	0.3317699979999986	0.6159800470000008
Cs	0.6666666639999974	0.3333333280000019	0.5070600159999969
Cs	0.6666666639999974	0.3333333280000019	0.3198899819999994
Cs	0.0000000000000000	0.0000000000000000	0.4147700130000018
Bi	0.3333333280000019	0.6666666559999967	0.3559800089999996
Bi	0.3333333280000019	0.6666666559999967	0.4727999620000034
I	0.6796399699999967	0.8398200279999983	0.3128400249999999
I	0.1601799399999990	0.8398199620000000	0.3128400249999999
I	0.1601800480000009	0.3203600109999982	0.3128400249999999
I	0.6784899219999971	0.8392399700000013	0.5162000300000003
I	0.1607599649999969	0.8392499260000008	0.5162000300000003
I	0.1607500209999984	0.3215100070000005	0.5162000300000003
I	0.9910599990000009	0.4955300060000027	0.4142700149999996
I	0.5044700059999982	0.4955300060000027	0.4142700149999996
I	0.5044699910000006	0.0089399820000011	0.4142700149999996