

Electronic Supplementary Information (ESI)

## Algorithm screening to accelerate discovery of 2D metal-free electrocatalysts for hydrogen evolution reaction

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Table S1. Metal-free materials with bandgap of 0 eV in different dimensions screened from the MP Database.

| Dimension   | The species of materials in the MP Database                  |                                                            |                                                             |                               |
|-------------|--------------------------------------------------------------|------------------------------------------------------------|-------------------------------------------------------------|-------------------------------|
| 0D<br>(113) | AsH <sub>3</sub> _27721.cif                                  | ClO <sub>3</sub> _1181699.cif                              | SBr <sub>3</sub> _974330.cif                                | Br <sub>3</sub> N_36891.cif   |
|             | As(IF <sub>3</sub> ) <sub>2</sub> _1205437.cif               | CN <sub>6</sub> Cl_1105904.cif                             | B <sub>13</sub> N <sub>2</sub> _534.cif                     | BrN_1058019.cif               |
|             | AsNF <sub>6</sub> _1078960.cif                               | CNCl_1071791.cif                                           | SeBr <sub>3</sub> _972874.cif                               | BrN_1059160.cif               |
|             | AsS_1103186.cif                                              | CO <sub>3</sub> _995196.cif                                | B <sub>4</sub> C_530074.cif                                 | BrN_1182030.cif               |
|             | As(S <sub>2</sub> F <sub>3</sub> ) <sub>2</sub> _27578.cif   | CSN <sub>3</sub> _1214236.cif                              | B <sub>4</sub> C_571655.cif                                 | BrO_1181998.cif               |
|             | AsSeBr_631257.cif                                            | H <sub>12</sub> C <sub>5</sub> N <sub>2</sub> _1225107.cif | B <sub>4</sub> C_8035.cif                                   | BrO_1207019.cif               |
|             | B <sub>12</sub> S_555170.cif                                 | H <sub>4</sub> N <sub>2</sub> O <sub>3</sub> _625635.cif   | ClO_1059242.cif                                             | BrO <sub>2</sub> _1182474.cif |
|             | Se <sub>2</sub> N <sub>3</sub> O <sub>8</sub> _1219375.cif   | H <sub>4</sub> N <sub>2</sub> O <sub>3</sub> _626155.cif   | SeO <sub>4</sub> _1179144.cif                               | BS <sub>2</sub> _1200183.cif  |
|             | B <sub>13</sub> P_1228630.cif                                | H <sub>5</sub> N <sub>2</sub> Cl_1181786.cif               | SeS_2559.cif                                                | H <sub>2</sub> S_24201.cif    |
|             | B <sub>13</sub> P <sub>2</sub> _13862.cif                    | HBr_23903.cif                                              | Si <sub>2</sub> B <sub>2</sub> O <sub>5</sub> _972793.cif   | H <sub>2</sub> Se_24420.cif   |
|             | Se(Br <sub>3</sub> N) <sub>2</sub> _1079177.cif              | HCl_23722.cif                                              | Si <sub>2</sub> O <sub>3</sub> _1179195.cif                 | H <sub>3</sub> S_1063581.cif  |
|             | Se(Br <sub>3</sub> O) <sub>2</sub> _1079970.cif              | IBr <sub>2</sub> _1184879.cif                              | Si <sub>3</sub> As_972752.cif                               | H <sub>3</sub> S_1063678.cif  |
|             | Se(NCl <sub>3</sub> ) <sub>2</sub> _1080652.cif              | ICl <sub>2</sub> _864616.cif                               | Si <sub>3</sub> As_978510.cif                               | H <sub>3</sub> S_1097767.cif  |
|             | Te(Br <sub>3</sub> N) <sub>2</sub> _1079732.cif              | I(ClO) <sub>4</sub> _1181085.cif                           | Si <sub>3</sub> Se_978501.cif                               | IN_1056900.cif                |
|             | Te(Br <sub>3</sub> O) <sub>2</sub> _1208558.cif              | I(NO <sub>3</sub> ) <sub>2</sub> _1080477.cif              | SiAs <sub>3</sub> _978567.cif                               | IN_1057979.cif                |
|             | BO <sub>3</sub> _1192099.cif                                 | NCl_1057084.cif                                            | SiB <sub>4</sub> _978496.cif                                | IN <sub>2</sub> _1097011.cif  |
|             | BO <sub>3</sub> _1214764.cif                                 | NCl_1058151.cif                                            | SiBO <sub>3</sub> _972822.cif                               | SO <sub>4</sub> _1070625.cif  |
|             | Br <sub>2</sub> Cl <sub>3</sub> _1183535.cif                 | NCIO <sub>3</sub> _1180304.cif                             | SiH <sub>2</sub> O_675098.cif                               | SO <sub>5</sub> _1209240.cif  |
|             | BSe <sub>2</sub> Cl_631529.cif                               | NCIO <sub>4</sub> _1077821.cif                             | SiN <sub>3</sub> F <sub>7</sub> _1191312.cif                | SO <sub>6</sub> _1196265.cif  |
|             | BT <sub>2</sub> As_631524.cif                                | P <sub>2</sub> O <sub>5</sub> _1182643.cif                 | Si(NF <sub>3</sub> ) <sub>2</sub> _1078546.cif              | NF_1067139.cif                |
|             | BT <sub>2</sub> O <sub>3</sub> _1183194.cif                  | P <sub>2</sub> O <sub>9</sub> _1201299.cif                 | Si(NF <sub>3</sub> ) <sub>2</sub> _1079023.cif              | NO_1180220.cif                |
|             | Te <sub>3</sub> (OF <sub>6</sub> ) <sub>2</sub> _1209223.cif | PBr_1064459.cif                                            | SNO <sub>4</sub> _1190641.cif                               | NO_1180282.cif                |
|             | C <sub>3</sub> N <sub>4</sub> _1078219.cif                   | PNF <sub>6</sub> _1209862.cif                              | C <sub>2</sub> NCl_1182108.cif                              | NO_1180334.cif                |
|             | C <sub>3</sub> N_1014286.cif                                 | PO <sub>4</sub> _1210362.cif                               | Te <sub>3</sub> Se_1187404.cif                              | NO_31000.cif                  |
|             | C <sub>3</sub> N_1014311.cif                                 | S <sub>2</sub> N <sub>3</sub> O <sub>8</sub> _1209119.cif  | Te <sub>4</sub> N <sub>5</sub> F <sub>21</sub> _1195987.cif | TeI <sub>4</sub> _1101136.cif |
|             | C <sub>3</sub> N_1014316.cif                                 | Te(I <sub>3</sub> N) <sub>2</sub> _1178999.cif             | Te <sub>7</sub> As <sub>5</sub> I_1101132.cif               | TeO <sub>6</sub> _1178936.cif |
|             | C <sub>3</sub> N_1014332.cif                                 | B <sub>9</sub> C_633538.cif                                | Te <sub>8</sub> I <sub>3</sub> _685011.cif                  | SN_1078816.cif                |
|             | C <sub>3</sub> N <sub>4</sub> O <sub>3</sub> _1198447.cif    | BN_601223.cif                                              | TeAs_10051.cif                                              | SN_1173453.cif                |
|             | C <sub>6</sub> I <sub>3</sub> N <sub>4</sub> _1203084.cif    |                                                            |                                                             |                               |

|               |                                                            |                                                            |                                                 |                                                             |
|---------------|------------------------------------------------------------|------------------------------------------------------------|-------------------------------------------------|-------------------------------------------------------------|
| 1D<br>(23)    | AsS_684081.cif                                             | HC <sub>6</sub> _995202.cif                                | Si <sub>3</sub> F_972767.cif                    | SN_1173466.cif                                              |
|               | C <sub>3</sub> N <sub>4</sub> _1182172.cif                 | HC_995195.cif                                              | Si <sub>3</sub> H_978497.cif                    | SN_235.cif                                                  |
|               | C(N <sub>2</sub> O) <sub>2</sub> _1182835.cif              | IClO <sub>3</sub> _1021667.cif                             | Si <sub>3</sub> P_972741.cif                    | SN_684642.cif                                               |
|               | CO_995183.cif                                              | IN <sub>3</sub> _684692.cif                                | SiBO <sub>3</sub> _972839.cif                   | TeI <sub>7</sub> _1105984.cif                               |
|               | HC <sub>2</sub> _995184.cif                                | IN <sub>4</sub> _1212209.cif                               | Si(CO) <sub>2</sub> _1001082.cif                | TeS <sub>3</sub> _1187407.cif                               |
|               | HC <sub>3</sub> _995200.cif                                | P <sub>3</sub> H_1186360.cif                               | SiH <sub>2</sub> O_1219307.cif                  |                                                             |
| 2D<br>(18)    | AsS_1182330.cif                                            | C <sub>3</sub> N_1014324.cif                               | SiTe <sub>2</sub> _2755.cif                     | C <sub>3</sub> N_1014296.cif                                |
|               | B <sub>2</sub> CN_1079333.cif                              | C <sub>3</sub> N_1096864.cif                               | SN_1066821.cif                                  | C <sub>3</sub> N_1014298.cif                                |
|               | B <sub>2</sub> O_614006.cif                                | CS_1147643.cif                                             | Te <sub>2</sub> PO <sub>7</sub> _1198178.cif    | Si <sub>4</sub> O <sub>9</sub> _1179275.cif                 |
|               | BC_1228623.cif                                             | Se <sub>2</sub> Cl <sub>2</sub> O <sub>5</sub> _-15968.cif | Te(AsO <sub>2</sub> ) <sub>2</sub> _1217487.cif | SiAs <sub>3</sub> _978499.cif                               |
|               | TeO <sub>3</sub> _1179069.cif                              | TeO <sub>4</sub> _1178951.cif                              |                                                 |                                                             |
| 3D<br>(54)    | As <sub>2</sub> S_1228819.cif                              | BC <sub>7</sub> _1095030.cif                               | Si <sub>2</sub> N <sub>3</sub> _1080623.cif     | SiO <sub>2</sub> _638038.cif                                |
|               | As <sub>2</sub> Se_1228838.cif                             | BC_984728.cif                                              | Si <sub>2</sub> O_1063118.cif                   | SiO <sub>2</sub> _638049.cif                                |
|               | As <sub>4</sub> C <sub>3</sub> _568505.cif                 | C <sub>11</sub> N <sub>4</sub> _1104513.cif                | Si <sub>2</sub> O_1208867.cif                   | SiO_32761.cif                                               |
|               | B <sub>2</sub> CN_1008525.cif                              | C <sub>2</sub> N <sub>3</sub> _1078791.cif                 | Si <sub>8</sub> C <sub>3</sub> _1179504.cif     | SiP <sub>2</sub> _21065.cif                                 |
|               | B <sub>2</sub> CN_1008526.cif                              | C <sub>3</sub> N_1014214.cif                               | Si <sub>8</sub> C <sub>3</sub> _1202928.cif     | SiP_8097.cif                                                |
|               | B <sub>2</sub> CN_1008527.cif                              | C <sub>3</sub> N_1014297.cif                               | SiAs <sub>2</sub> _21268.cif                    | Te <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> _766504.cif |
|               | BC <sub>5</sub> _1018649.cif                               | C <sub>3</sub> N_1014333.cif                               | SiB_978495.cif                                  | TeAs <sub>2</sub> _1217320.cif                              |
|               | BC <sub>5</sub> _1077125.cif                               | IO <sub>3</sub> _1181185.cif                               | SiC_1002206.cif                                 | TeN <sub>2</sub> _1061865.cif                               |
|               | BC <sub>5</sub> _1077743.cif                               | P <sub>2</sub> O <sub>5</sub> _990076.cif                  | SiC <sub>2</sub> _1019097.cif                   | TeN <sub>2</sub> _-13772.cif                                |
|               | BC <sub>5</sub> _1095514.cif                               | P <sub>2</sub> S_1220021.cif                               | SiC <sub>2</sub> _1102811.cif                   | TeO <sub>2</sub> _2237.cif                                  |
|               | BC <sub>7</sub> _1078935.cif                               | P <sub>2</sub> Se_1220020.cif                              | SiCN_8003.cif                                   | TeO <sub>6</sub> _1201116.cif                               |
|               | BC <sub>7</sub> _1079046.cif                               | P <sub>4</sub> N <sub>7</sub> _1190322.cif                 | SiO <sub>2</sub> _557194.cif                    | TePO <sub>5</sub> _776406.cif                               |
|               | BC <sub>7</sub> _1079661.cif                               | P <sub>4</sub> N <sub>7</sub> _1200550.cif                 | SiO <sub>2</sub> _558598.cif                    |                                                             |
|               | BC <sub>7</sub> _1080030.cif                               | PN <sub>2</sub> _1102941.cif                               | SiO <sub>2</sub> _638035.cif                    |                                                             |
| Mixed<br>(28) | B <sub>9</sub> C_1182537.cif                               | H <sub>7</sub> O <sub>4</sub> _696717.cif                  | Si <sub>3</sub> N <sub>4</sub> _603694.cif      | C <sub>3</sub> N_1014281.cif                                |
|               | B <sub>9</sub> N_1079812.cif                               | HIN <sub>2</sub> _1212460.cif                              | SiC <sub>3</sub> _972848.cif                    | C <sub>3</sub> N_1014287.cif                                |
|               | BrO <sub>3</sub> _1182115.cif                              | HIN <sub>2</sub> _1224351.cif                              | SiO <sub>2</sub> _556044.cif                    | C <sub>3</sub> N_1096892.cif                                |
|               | BrO <sub>3</sub> _1182120.cif                              | I <sub>2</sub> N <sub>3</sub> _1212113.cif                 | SiO <sub>2</sub> _685184.cif                    | Si <sub>3</sub> B_972733.cif                                |
|               | C <sub>10</sub> I <sub>3</sub> N <sub>4</sub> _1202855.cif | IN <sub>4</sub> _1188721.cif                               | Te <sub>2</sub> NO <sub>6</sub> _1196142.cif    | S <sub>3</sub> Br_974332.cif                                |
|               | TeNO <sub>4</sub> _1102544.cif                             | INO <sub>3</sub> _1181075.cif                              | Te <sub>2</sub> NO <sub>7</sub> _1203388.cif    | S <sub>3</sub> Cl_1186934.cif                               |
|               | H <sub>5</sub> N <sub>2</sub> Cl_644118.cif                | Se <sub>3</sub> Br_1187019.cif                             | Te(AsO <sub>2</sub> ) <sub>2</sub> _1173176.cif | H <sub>2</sub> O_990441.cif                                 |

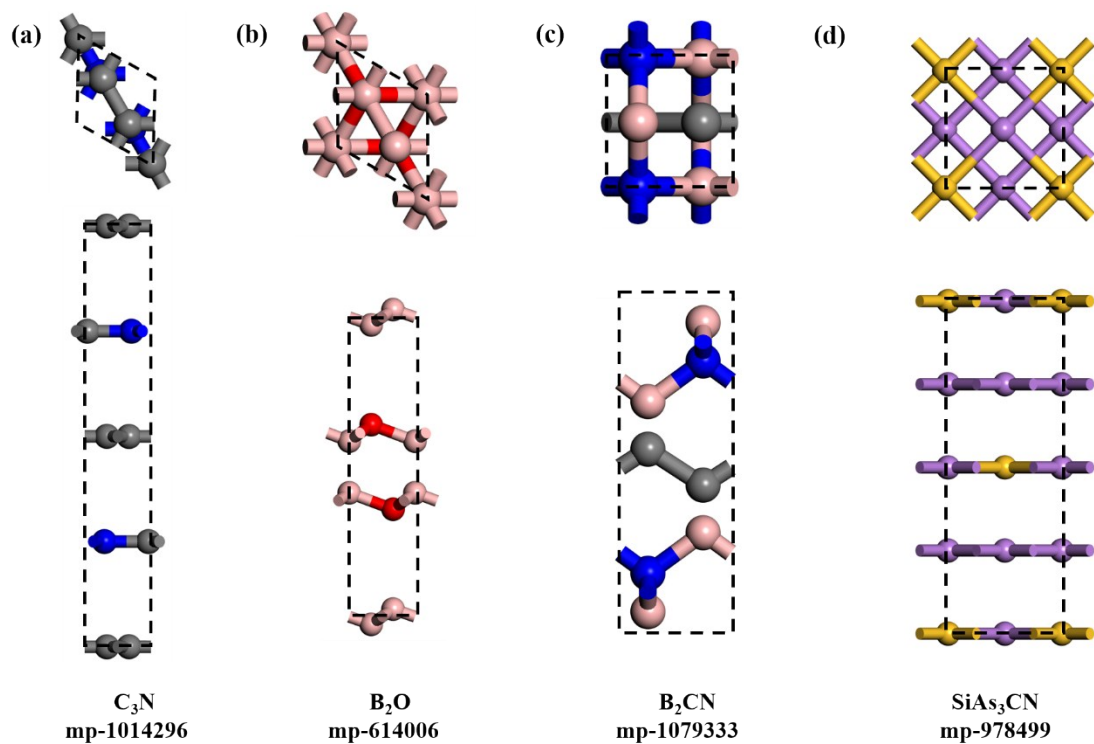
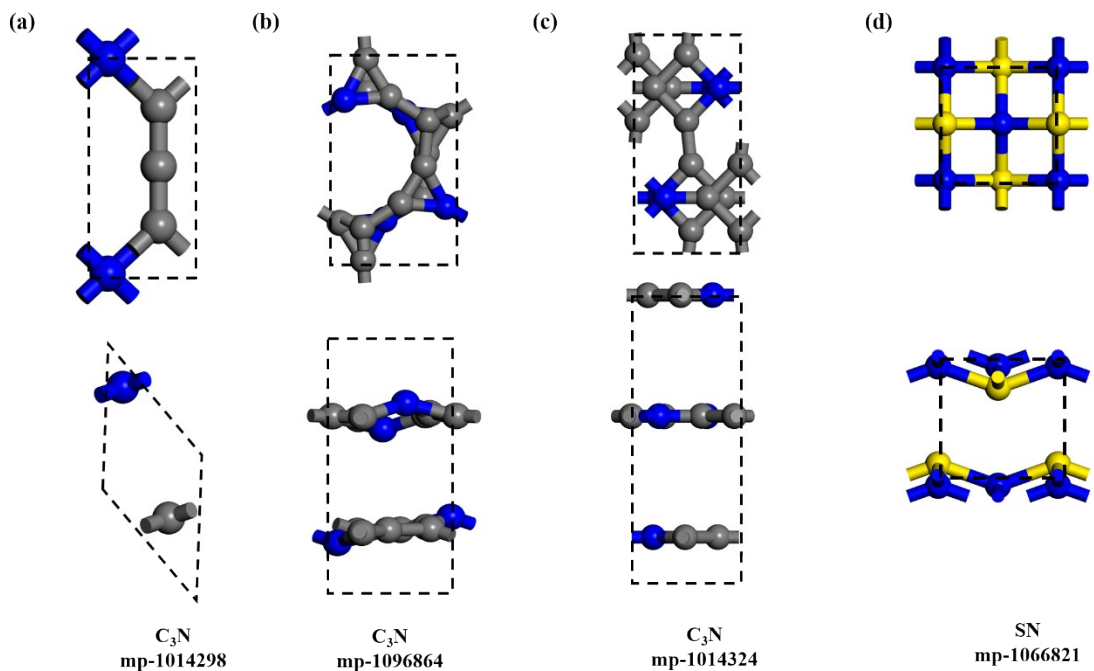
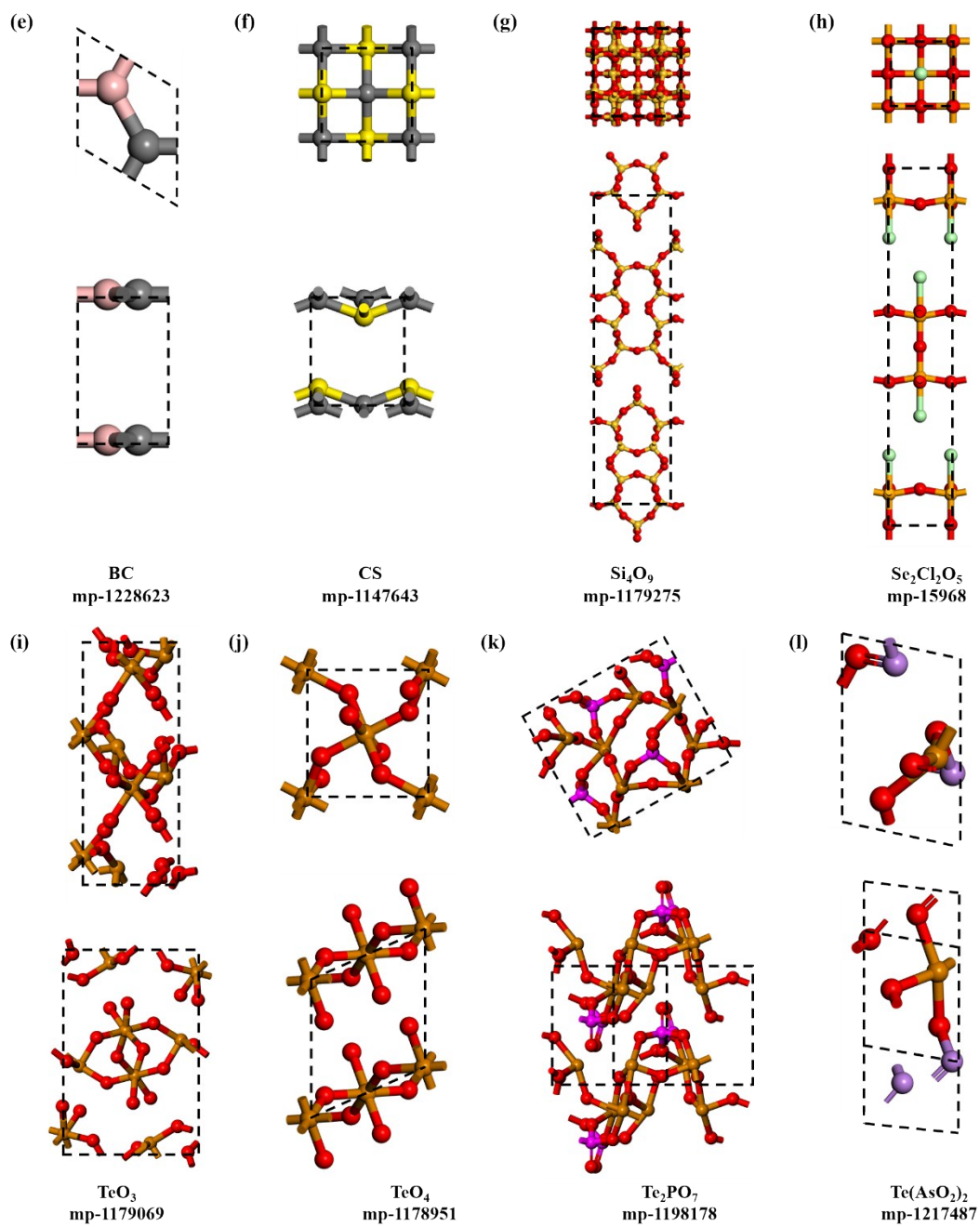


Fig. S1. Structures of screened layered heterojunction materials.





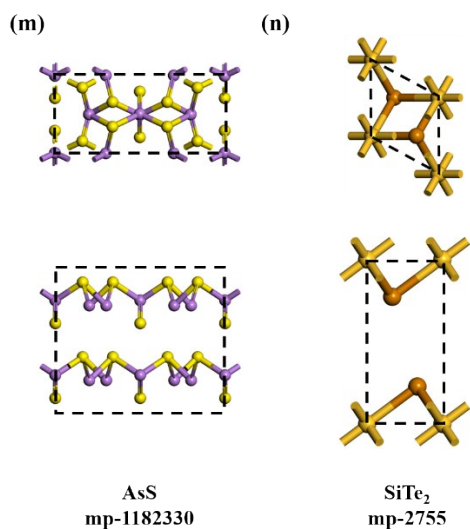
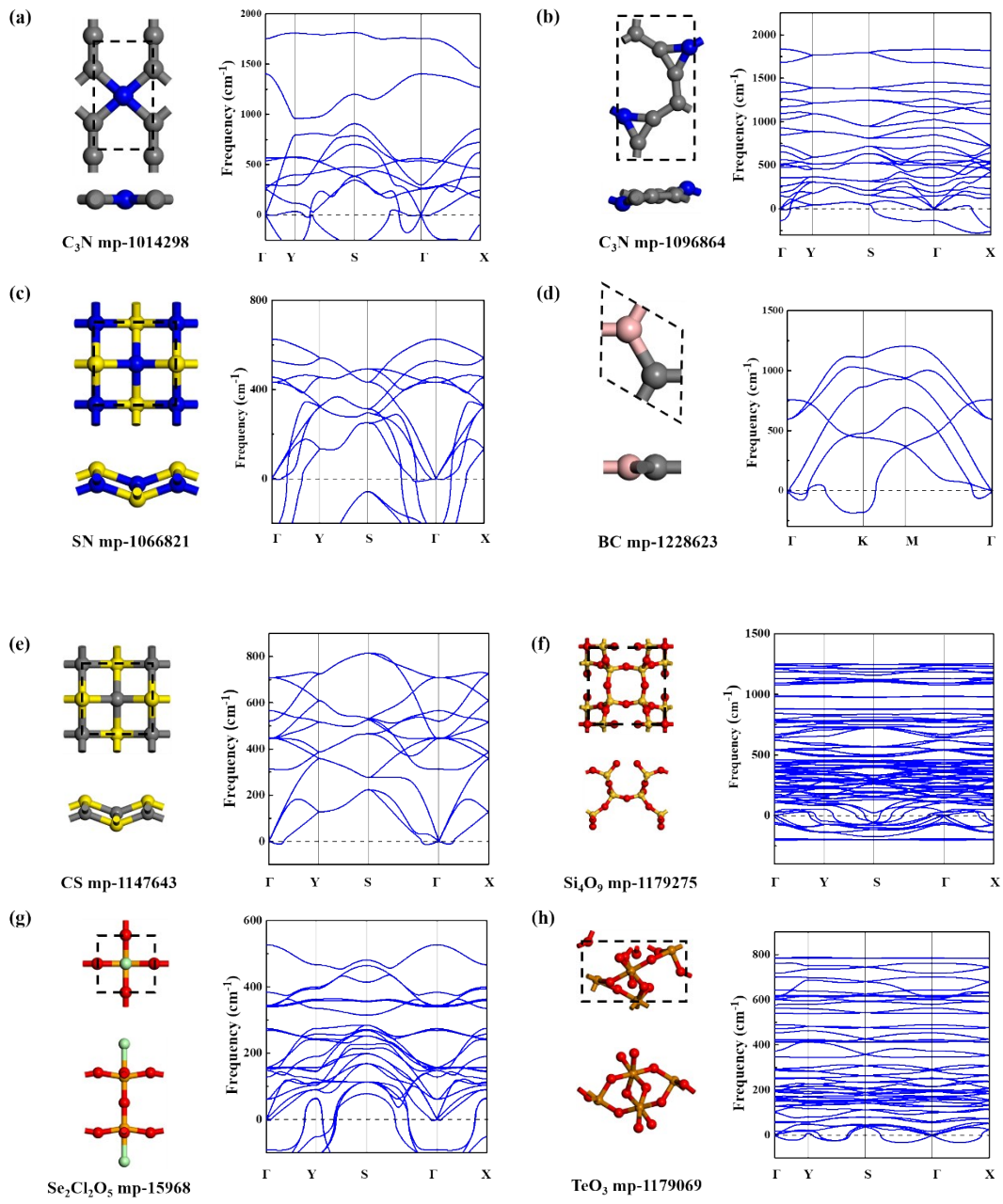


Fig. S2. Structures of screened pure layered materials.

Table S2. Lattice constants of exfoliated monolayers.

| monolayers                                  | a (Å) | b (Å) | monolayers                                                | a (Å) | b (Å) |
|---------------------------------------------|-------|-------|-----------------------------------------------------------|-------|-------|
| C <sub>3</sub> N (mp-1014298)               | 2.35  | 4.75  | Se <sub>2</sub> Cl <sub>2</sub> O <sub>5</sub> (mp-15968) | 3.70  | 3.70  |
| C <sub>3</sub> N (mp-1096864)               | 3.74  | 6.53  | TeO <sub>3</sub> (mp-1179069)                             | 8.32  | 4.81  |
| C <sub>3</sub> N (mp-1014324)               | 3.36  | 6.81  | TeO <sub>4</sub> (mp-1178951)                             | 5.13  | 4.61  |
| SN (mp-1066821)                             | 3.63  | 3.63  | Te <sub>2</sub> PO <sub>7</sub> (mp-1198178)              | 9.75  | 8.37  |
| BC (mp-1228623)                             | 2.68  | 2.68  | Te(AsO <sub>2</sub> ) <sub>2</sub> (mp-1217487)           | 6.32  | 5.40  |
| CS (mp-1147643)                             | 3.56  | 3.56  | AsS (mp-1182330)                                          | 11.33 | 5.15  |
| Si <sub>4</sub> O <sub>9</sub> (mp-1179275) | 7.03  | 7.03  | SiTe <sub>2</sub> (mp-2755)                               | 3.74  | 3.25  |



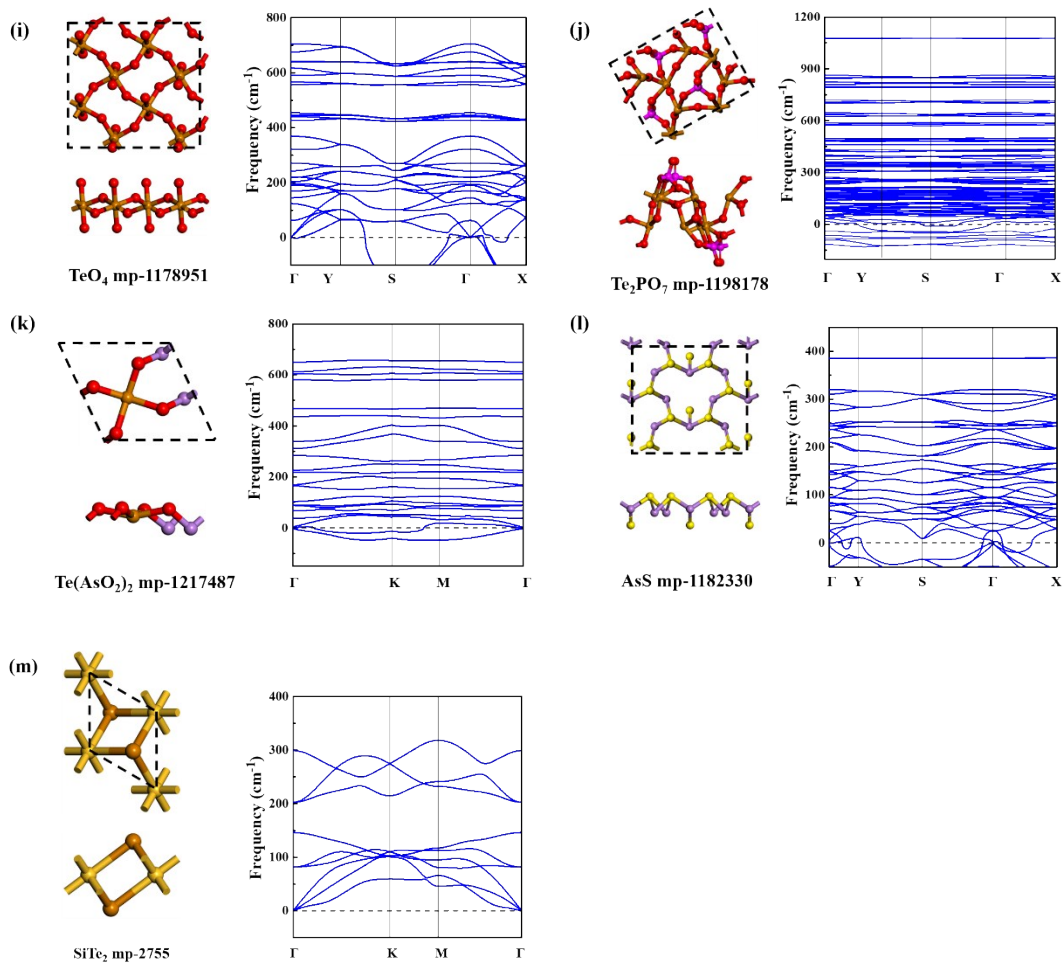


Fig. S3. Top-side views and phonon dispersion spectra of exfoliated monolayers.

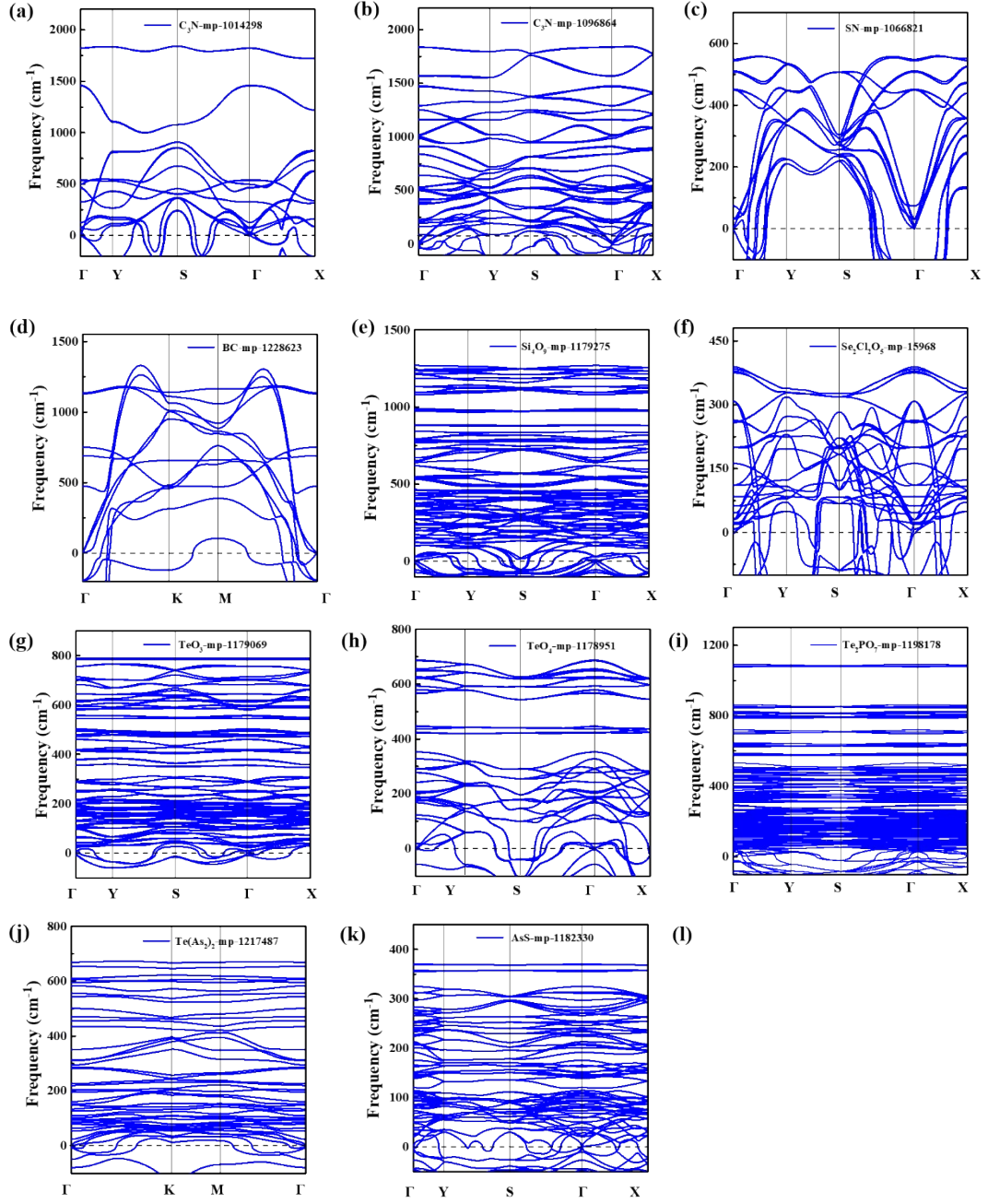


Fig. S4. Phonon dispersion spectra of bilayers for unstable 2D monolayers.

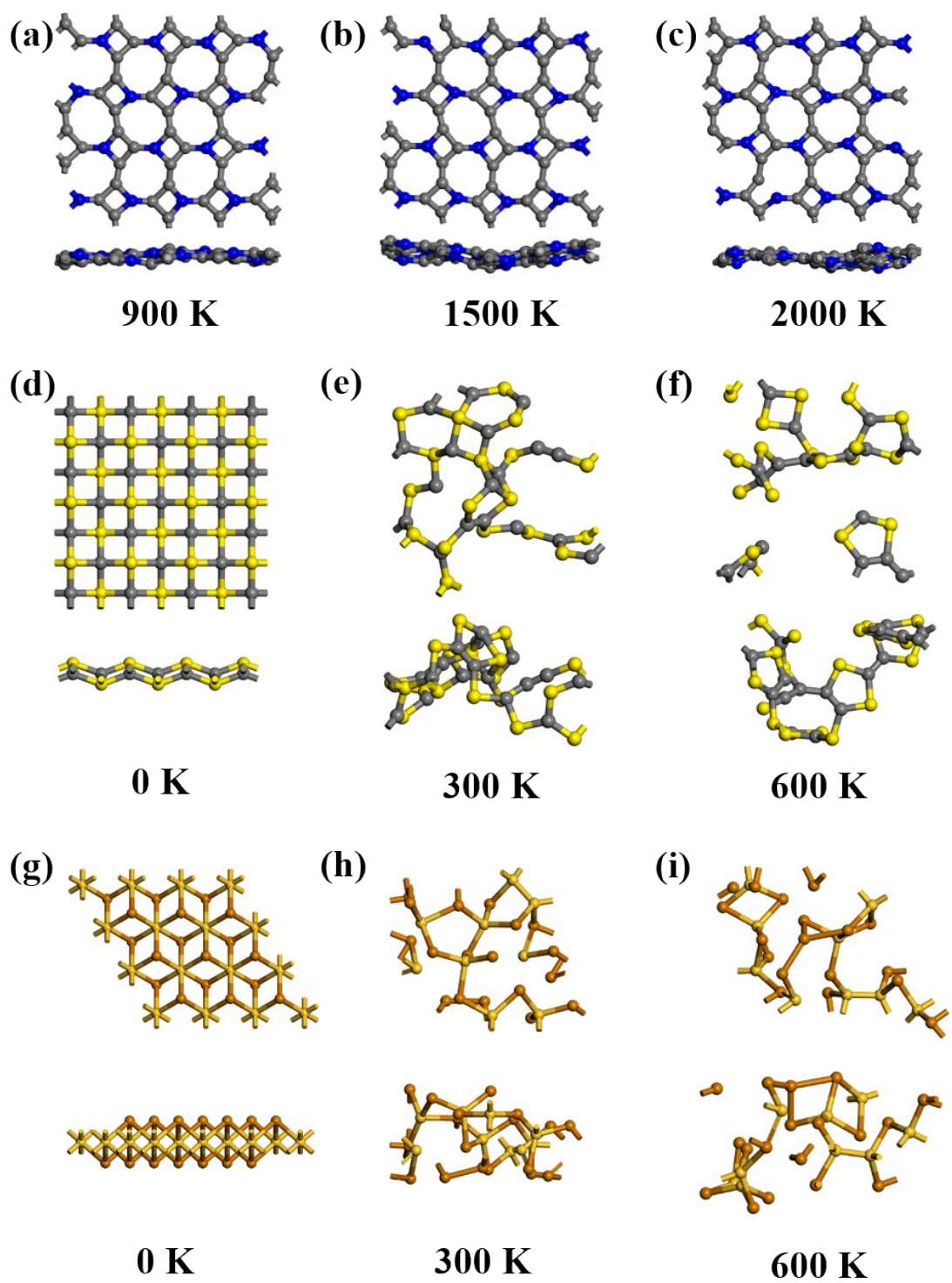
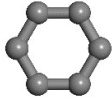
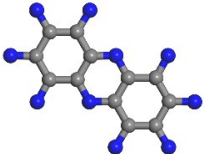
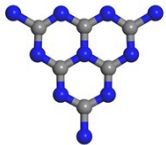
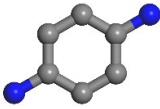


Fig. S5. Snapshots for the equilibrium structures of  $\text{C}_3\text{N}$  monolayer at temperatures of (a) 900 K, (b) 1500 K, (c) 2000 K; and CS,  $\text{SiTe}_2$  monolayers at temperatures of (d/g) 0 K, (e/h) 300 K and (f/i) 600 K after 10 ps AIMD simulations.

Table S3. Cohesive energies of some representative 2D materials

| 2D Materials                               | Cohesive energies (eV/atom) | Structures                                                                           |
|--------------------------------------------|-----------------------------|--------------------------------------------------------------------------------------|
| graphene                                   | 8.06                        |   |
| C <sub>2</sub> N                           | 6.88                        |   |
| g-C <sub>3</sub> N <sub>4</sub>            | 6.11                        |   |
| C <sub>3</sub> N (reported in experiments) | 7.14                        |   |
| C <sub>3</sub> N (this work)               | 6.75                        |  |

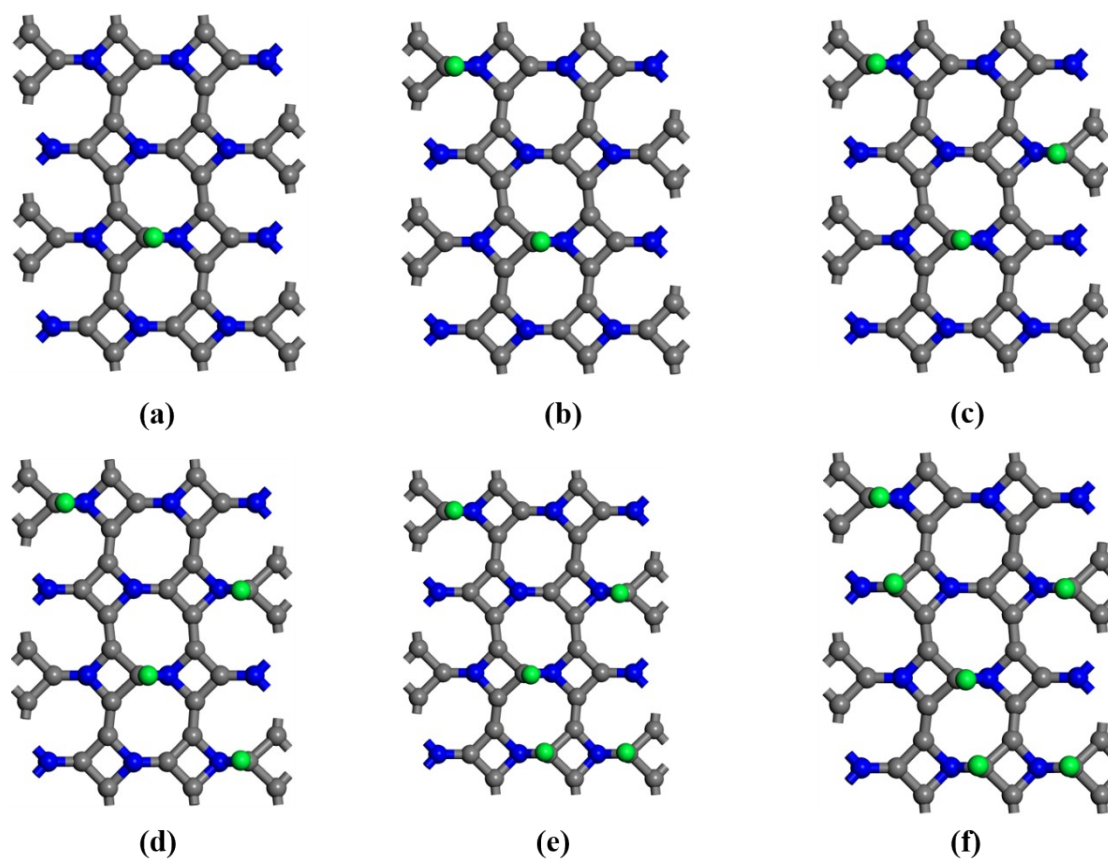


Fig. S6. (a-f) The optimized structures of  $C_3N$  monolayer with hydrogen coverage from 1/12 to 6/12.

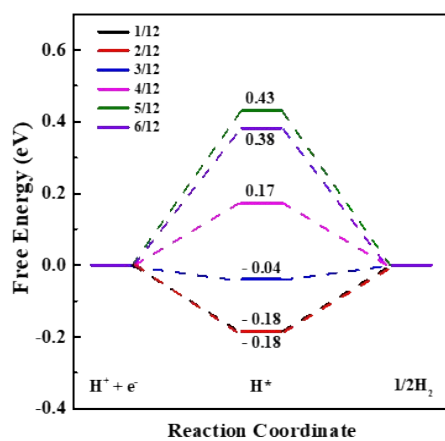


Fig. S7. Calculated free energies for hydrogen adsorption  $\Delta G_{H^*}$  on  $C_3N$  monolayer at different coverages in solvents.