Supplementary Information

Tribology-Driven Modulation of Piezoelectricity in 2D CdS Bilayers: A First-Principles Investigation

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Initial structure of the bilayer CdS with AB Stacking Pattern

(scf.in file for Quantum Espresso)

```
&CONTROL
   calculation   = "scf",
   pseudo_dir    = "I:/dft/BURAI1.3_Windows/BURAI1.3_Windows/pseudopot",
   outdir       =  "temp"
   prefix       = 'CdS'
   tprnfor      = .TRUE.
   tstress      = .TRUE.
   tefield      = .TRUE.
   dipfield     = .TRUE.
/

&SYSTEM
   a                  =  4.250756
   b                  =  4.250756
   c                  =  20
   cosab                 = -0.500000
   ecutrho               =  350
   ecutwfc               =  45
   ibrav                 =  4
   nat                   =  4
   ntyp                  =  2
   input_dft             =  "vdw-df-ob86"
/

&ELECTRONS
   conv_thr       =  1.00000e-06
   electron_maxstep = 100
   mixing_beta     =  4.00000e-01
   startingpot     = "atomic"
   startingwfc     = "atomic+random"
/

K_POINTS (automatic)
 15 15 1 0 0 0

ATOMIC_SPECIES
Cd    112.41100  Cd.pbe-n-kjpaw_psl.1.0.0.UPF
S     32.07000  S.pbe-n-kjpaw_psl.1.0.0.UPF

ATOMIC_POSITIONS {angstrom}
Cd      0.000433518   2.451704995   2.000000000
S      -2.125241961   3.678908793   2.000000000
S      -0.000661139   2.452589238   5.140000000
Cd      2.124939694   1.225561474   5.140000000
```

Initial structure of the bilayer CdS with AC Stacking Pattern

(scf.in file for Quantum Espresso)

```
&CONTROL
   calculation   = "scf",
   pseudo_dir    = "I:/dft/BURAI1.3_Windows/BURAI1.3_Windows/pseudopot",
   outdir       =  "temp"
   prefix       = 'CdS'
   tprnfor      = .TRUE.
   tstress      = .TRUE.
   tefield      = .TRUE.
   dipfield     = .TRUE.
/

&SYSTEM
   a                  =  4.250756
   b                  =  4.250756
   c                  =  20
   cosab                 = -0.500000
   ecutrho               =  350
   ecutwfc               =  45
   ibrav                 =  4
   nat                   =  4
   ntyp                  =  2
   input_dft             =  "vdw-df-ob86"
/

&ELECTRONS
   conv_thr       =  1.00000e-06
   electron_maxstep = 100
   mixing_beta     =  4.00000e-01
   startingpot     = "atomic"
   startingwfc     = "atomic+random"
/

K_POINTS (automatic)
 15 15 1 0 0 0
ATOMIC_SPECIES
Cd    112.41100  Cd.pbe-n-kjpaw_psl.1.0.0.UPF
S     32.07000  S.pbe-n-kjpaw_psl.1.0.0.UPF

ATOMIC_POSITIONS {angstrom}
Cd      0.000433518   2.451704995   5.140000000
S      -2.125241961   3.678908793   5.140000000
S      -0.000661139   2.452589238   2.000000000
Cd      2.124939694   1.225561474   2.000000000
```

Initial structure of the bilayer CdS with AA Stacking Pattern

(scf.in file for Quantum Espresso)

```
&CONTROL
   calculation   = "scf",
   pseudo_dir    = "I:/dft/BURAI1.3_Windows/BURAI1.3_Windows/pseudopot",
   outdir       =  "temp"
   prefix       = 'CdS'
   tprnfor      = .TRUE.
   tstress      = .TRUE.
   tefield      = .TRUE.
   dipfield     = .TRUE.
/

&SYSTEM
   a                  =  4.250756
   b                  =  4.250756
   c                  =  20
   cosab                 = -0.500000
   ecutrho               =  350
   ecutwfc               =  45
   ibrav                 =  4
   nat                   =  4
   ntyp                  =  2
   input_dft             =  "vdw-df-ob86"
/

&ELECTRONS
   conv_thr       =  1.00000e-06
   electron_maxstep = 100
   mixing_beta     =  4.00000e-01
   startingpot     = "atomic"
   startingwfc     = "atomic+random"
/

K_POINTS (automatic)
 15 15 1 0 0 0

ATOMIC_SPECIES
Cd    112.41100  Cd.pbe-n-kjpaw_psl.1.0.0.UPF
S     32.07000  S.pbe-n-kjpaw_psl.1.0.0.UPF

ATOMIC_POSITIONS {angstrom}
Cd      0.001323952   2.430616951   2.000000000
S      -2.105168060   3.647067138   2.000000000
S      -2.105381731   3.647402503   5.140000000
Cd      0.001132939   2.430922773   5.140000000
```

Table S1. Interlayer spacing and binding energies for AB and AC stacked bilayer CdS using different vdW correction schemes.

vdW correction schemes	Interlayer distance	Binding energy
Grimme D2	3.08 Å (AB) 3.09 Å (AC)	–2.981 eV (AB) –2.952 eV (AC)
DFT-D3	3.16 Å (AB) 3.15 Å (AC)	–2.633 eV (AB) –2.667 eV (AC)
optB86b-vdW	3.14 Å (AB and AC)	–2.713 eV (AB) –2.702 eV (AC)

Figure S1

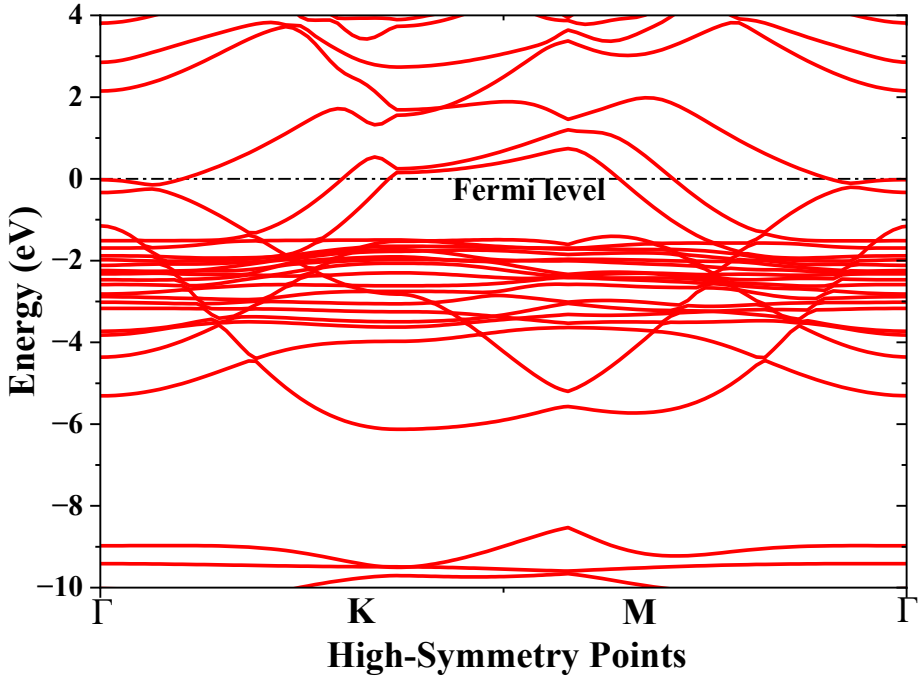

Figure S1. Calculated band structure of the Au/CdS heterostructure, showing the relative alignment of the Fermi level with the conduction and valence bands of CdS in the presence of the Au contact.

Lattice mismatch between CdS and Au, and the supercell matching strategy:

The lattice constants of 2D CdS and Au are 4.25 Å and 4.17 Å, respectively, resulting in a lattice mismatch of:

Lattice mismatch (%) = $\frac{a_{CdS} - a_{Au}}{a_{CdS}} \times 100 \approx 1.88\%$

To minimize strain and construct a commensurate interface, we employed a supercell matching strategy. Specifically, we used a 1 × 1 CdS unit cell aligned with a 1 × 1 Au (111) surface cell along the in-plane directions. The small lattice mismatch (~1.9%) was accommodated by applying a slight tensile strain to Au, which is within the range commonly accepted in heterostructure modeling (<2%) and is not expected to significantly alter the electronic or structural properties.