Hundreds of New 2D and 1D Weakly Bonded Solids Revealed by Data Mining and their Electromechanical Properties

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Beyond Graphene: We have identified over 1000 layered materials with a full spectrum of properties


Some single layer materials (e.g. MoS$_2$) are piezoelectric with useful magnitudes

Some single layer materials (e.g. MoTe$_2$) have the potential to exhibit structural phase changes under electrostatic gating and other conditions

- Prospects for phase change applications
We discover new 2D and 1D materials

- We discover 1173 2D layered materials, 487 1D materials, 98 lattice-commensurate heterostructures and 325 materials with piezoelectric monolayers
  - ~10x greater than known layered materials

- We develop an algorithm that screens crystal structures found in Materials Project database

G. Cheon et al., Nano Letters, 2017
Data Mining for New Two- and One-Dimensional Weakly Bonded Solids and Lattice-Commensurate Heterostructures
Layered materials have a vast potential in applications

Graphene

h-BN

Transition metal dichalcogenides (TMDs)

Energy storage

Transistors

Resonators


We screen for van der Waals-bonded 2D or 1D crystals

Look for these structures:

Strong covalent bonds

Weak van der Waals bonds

2D materials

1D materials

G. Cheon et al., Nano Letters, 2017
We develop an algorithm for identifying 2D or 1D crystals from database of bulk materials.

0D structure (molecule)

1D structure

2D structure

Unit cell

2X2X2 supercell

Shaded area stays constant

Shaded area increases X 2

Shaded area increases X 4

G. Cheon et al., Nano Letters, 2017
We compile a genome of 1173 2D materials

- 1173 weakly bonded layered materials identified, lots of new candidates!
- 23 families of similar chemical compositions (>5 materials), but >80% don’t belong to a family

![Families of 2D Materials](image)

TS\textsubscript{2}: TMDs, MoS\textsubscript{2}, WSe\textsubscript{2},

Ac: actinides
As: large pnictogens (As, Sb, Bi)
F: halogens
S: chalcogens excluding O
La: lanthanides
T: transition metals

G. Cheon et al., Nano Letters, 2017
We compile a genome of 1173 2D materials

- Diverse spectrum of layered materials
- Materials Project IDs of all layered materials available in Supporting Information

G. Cheon et al., Nano Letters, 2017
Data Mining for New Two- and One-Dimensional Weakly Bonded Solids and Lattice-Commensurate Heterostructures
HOW TO USE THE DATABASE

- Think of the database as statistical in nature, providing candidates for further study
  - Screen candidates for your application using chemical composition, bandgap, and symmetry
- The database is not complete
- Materials in the database have not been studied for cohesive energy, mechanical stability as free-standing 2D layers, or air stability
- ~90% of the (bulk) structures in the MP database have been experimentally characterized
- MP database entries are time-dependent
  - Bandgaps and other properties can change with time
  - Symmetries are sensitive to atomic relaxation

There is a growing selection problem/opportunity for 2D materials.
We find a wide spectrum of 2D material band gaps

Band Gap Distribution (2D Materials)

(Semi-local DFT band gaps for bulk materials from the Materials Project database)

G. Cheon et al., Nano Letters, 2017
We discover 487 1D materials

- Our algorithm can find 1D dimensions of subunits

BPS$_4$, a material found in this work

Chain-like structure of t-Se that grow into nanowires.
Xia et al., Adv. Mat., 15, 5, 353-389; 2003

Quasi-1D TaSe$_3$ low-noise nanowire devices

- Some inorganic ‘molecular wires’ have been predicted to possess structural stability and versatile material properties, but only ~20 known

G.Cheon et al., Nano Letters, 2017
We compile a genome of 487 1D materials

- 487 1D materials identified, 8 families of similar chemical compositions (>5 materials)

**Families of 1D Materials**

<table>
<thead>
<tr>
<th>Ac</th>
<th>As</th>
<th>F</th>
<th>S</th>
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</tr>
</thead>
<tbody>
<tr>
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N, P, Al and O are NOT grouped together

G.Cheon et al., Nano Letters, 2017
We compile a genome of 487 1D materials

- **487 1D materials** identified, **8 families** of similar chemical compositions (>5 materials)

G. Cheon et al., Nano Letters, 2017
We find a wide spectrum of 1D material band gaps

Band Gap Distribution (1D Materials)

(Semi-local DFT band gaps for bulk materials from the Materials Project database)

G.Cheon et al., Nano Letters, 2017
We discover lattice-commensurate vertical heterostructures

- We discover **intrinsic, lattice-commensurate heterostructures** that preclude the need for artificial stacking:

![Diagram showing different heterostructures](image)

- **Not a heterostructure**
  - MoS$_2$

- **Heterostructures**:
  - Different chemical compositions
  - Or
  - Number of atoms in each layer

- **Identical clusters**
- **Different clusters**

G. Cheon et al., Nano Letters, 2017

Data Mining for New Two- and One-Dimensional Weakly Bonded Solids and Lattice-Commensurate Heterostructures
We discover lattice-commensurate heterostructures

- We identify 98 lattice-commensurate heterostructures:
- Experimentally reported in bulk crystals

HgSb₄S₈ (Livingstonite)  Cd₄Te₆Cl₆O₁₃  Te₃W₂Se₄(Cl₄O)₂

2D  2D+1D  1D

G. Cheon et al., Nano Letters, 2017
Data Mining for New Two- and One-Dimensional Weakly Bonded Solids and Lattice-Commensurate Heterostructures
van der Waals interactions in layered materials are longer range than between atoms

We study the importance of role of three body effects (beyond DFT-D)

Hamaker form (simplified)

monolayers $\sim 1/l^4$  

atoms $\sim 1/l^6$

Three body effects

two particles

three particles
van der Waals interactions in layered materials are longer range than between atoms.

- Lifshitz model gives vdW energies within 10-20% of ACFDT values.
- Orders of magnitude faster than ACFDT.
- There is potential for repulsive three-body vdW interactions in layered materials.

Zhou, Pellouchoud, Reed, 2D Materials 4, 025005, 2017
Crystal symmetry determines important physical properties, e.g. piezoelectricity:

Piezoelectric materials must exhibit:

1. An electronic bandgap
2. A lack of centrosymmetry

- 2H Mo- and W- TMDs:
  1. Semiconducting
  2. NOT centrosymmetric in MONOLAYER

G. Cheon et al., Nano Letters, 2017  Data Mining for New Two- and One-Dimensional Weakly Bonded Solids and Lattice-Commensurate Heterostructures
Transition Metal Dichalcogenides: MoS$_2$, MoSe$_2$, MoTe$_2$, WS$_2$, WSe$_2$

Trigonal prismatic structure:

✓ Semiconducting ($E_{\text{gap}} \sim 1-2$ eV)
✓ Not centrosymmetric
  ✓ 3m point group leads to non-zero $d_{11}$ and $e_{11}$ coefficients
Our HPC-enabled approach enables identification of promising materials.

We discover that a variety of TMDS have significant piezoelectric effects.

Piezo-coefficients of trigonal prismatic TMD structures are comparable to bulk wurtzite structures.


Piezoelectricity in C$_3$N$_4$ few layers:
We discover 325 2D piezoelectric candidates

353 non-centrosymmetric monolayer materials, 325 with nonzero band gap (piezoelectric candidates)

Layered Material Point Group Distribution

- Non-centrosymmetric (Piezoelectric candidates)
- Centrosymmetric

Point Groups

G. Cheon et al., Nano Letters, 2017
TMD MONOLAYERS (MoS$_2$, WS$_2$ etc.) CAN EXIST IN MULTIPLE CRYSTAL STRUCTURES

- **2H**
  - Semiconducting (1-2 eV)
- **1T**
  - Metallic
- **1T’**
  - Semi-metallic
Our semi-local DFT calculations indicate MoTe₂ and WTe₂ exhibit the smallest 2H-1T' energy difference.
1. **Conservation of stress**
   - Perhaps most appropriate for freely-suspended monolayers
     - Hydrostatic case: \( G_{\text{hydro}}(\sigma, T) = A - ab\sigma \)
     - Uniaxial case: \( G_y(F_y, T) = A - F_yb \)

2. **Conservation of area**
   - Perhaps most appropriate for freely-suspended monolayers
   - Potential for mixed-phase regimes

3. **Conservation of lattice** supposes that \( a \) and \( b \) lattice constants are fixed through transition.
   - Perhaps most appropriate for a monolayer on a substrate with friction

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**Monolayers on substrates could obey combinations of these constraints.**
Discontinuities occur across the phase transition. These suggest a mixed-phase regime for constant area constraint.

Phase boundary predicted to be in the range of 1% to 6% tensile strain in MoTe$_2$ depending on the nature of mechanical constraint.

**Hydrostatic case:**

\[ G_{\text{hydro}}(\sigma, T) = A - ab\sigma \]

**Uniaxial stress case (assuming no crystal re-orientation):**

\[ G_y(F_y, T) = A - F_y b \]

- Discontinuities occur across the phase transition
- These suggest a mixed-phase regime for constant area constraint.
LITTLE IS UNDERSTOOD REGARDING KINETICS OF 2D STRUCTURAL CHANGES

- Anecdotal evidence in the literature suggests T’ to H transformation times ranging from minutes to days or longer.
- The potential for useful fragile kinetic behavior is unclear in this crystal to crystal transition.

Preliminary calculations suggest that nucleation processes may exhibit high barriers suggesting slow kinetics, particularly near the phase boundaries.

CAN ELECTRICAL GATING DRIVE A STRUCTURAL PHASE TRANSITION IN A 2D MATERIAL?

Li, Duerloo, Reed, Nature Communications 7, 10671 (2016).
CAN ELECTRICAL GATING DRIVE A STRUCTURAL PHASE TRANSITION IN A 2D MATERIAL?

Fixed Charge $Q$

$$E(Q) = E^I(Q, s^I) + E^{II}(-Q, s^{II}) + E_c$$
$$= E^I(Q, s^I) + E^{II}(-Q, s^{II}) + \frac{Q^2}{2C}$$

Fixed Voltage $V$

$$\Phi_g(Q, V) = E(Q) - QV$$
$$\Phi_g^{eq}(V) = \Phi_g(Q^{eq}(V), V) = E\left(Q^{eq}(V)\right) - Q^{eq}(V)V$$

Li, Duerloo, Reed, Nature Communications 7, 10671 (2016).
Charge densities between $10^{13}$ and $10^{14}$ cm$^{-2}$ can transform MoTe$_2$.

Li, Duerloo, Wauson, Reed, Nature Communications 7, 10671 (2016).
A bandgap in the H phase makes the negatively charged material higher energy than the gapless T’ phase.

Li, Duerloo, Reed, Nature Communications 7, 10671 (2016).
Transformation charges and voltages may be achievable in MoTe₂ using ionic liquids.

Li, Duerloo, Wauson, Reed, Nature Communications 7, 10671 (2016).
$\text{Mo}_{0.67} \text{W}_{0.33} \text{Te}_2$ PHASE BOUNDARIES AT FIXED VOLTAGE

$\text{Mo}_x \text{W}_{1-x} \text{Te}_2$ alloys have the potential to exhibit reduced transition voltages, below the HfO$_2$ breakdown.

Li, Duerloo, Wauson, Reed, Nature Communications 7, 10671 (2016).
(A) STM image of a single crystal of 2H-TaSe$_2$.
(B) Image of the (T-phase?) surface region in (A) after a voltage modification pulse of -1.3V had been applied to the tip.

TaSe$_2$ PHASE BOUNDARIES AT FIXED VOLTAGE

Computed transformation voltages are roughly comparable to reported STM bias, but transformation predicted to occur only under positive voltage.

Li, Duerloo, Wauson, Reed, Nature Communications 7, 10671 (2016).
TaSe$_2$ EXHIBITS ONLY ONE PHASE BOUNDARY BECAUSE WHILE MoTe$_2$ EXHIBITS TWO

The gapless nature of the H and T phases of TaSe$_2$ lead to a single phase boundary while the semiconducting H phase of MoTe$_2$ provides two.

Li, Duerloo, Wauson, Reed, Nature Communications 7, 10671 (2016).
Acknowledgements

This work is supported by:

• Army High Performance Computing Research Center (AHPCRC)
• NSF EECS-1436626 and DMR-1455050
• Office of Naval Research N00014-15-1-2697
• Army Research Office W911NF-15-1-0570

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Also:
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