Controlling Defects: Doped Graphene, In-plane Heterojunctions and van der Waals Solids

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  Bunshi Fugetsu
  Bartolomeu Cruz Viana
  Francisco Wellery

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  J. Zhu (Physics)
  N. Alem (MatScE)
  T. Mayer (Engineering)
  Z.W. Liu (Engineering)
Perfect Layered Materials

- Graphite
- Chalcogenides
  - MoS$_2$
  - WS$_2$
  - NbS$_2$
  - TaS$_2$
  - VS$_2$
  - VS$_2$
  - ReS$_2$
  - WSe$_2$
  - MoSe$_2$
- OTHERS: VO$_5$, NiCl$_2$, MgB$_2$
- Carbon Nitride
- Boron Nitride
- Boron Carbo-Nitride
The Rise of Two-Dimensional Materials

Benoit Dubertret
CNRS, ESPCI
Thomas Heine
Jacobs University
Mauricio Terrones
The Pennsylvania State University
Defects in Graphene

1. Structural Defects, responsible of Curvature Changes (Pentagons, Heptagons, etc.)

2. Topological Defects (Bond Rotations, Stone-Thrower-Wales Type Transformations)

3. Substitutional Atoms (Impurities, Doping)

4. Vacancies, Interstitials and Edges

5. Folding, Surface Distortions?
Doped Graphene
Fermi Level Shift in Graphene Caused by Doping: No Band Gap
Applications of N-doped graphene (NG)

• High-frequency FET

• Bio-sensing

• Metal-free fuel cell catalyst

• Ultracapacitors

• Photovoltaic devices
  Cui TX, et al. *Carbon* 2011, 49: 5022-5028

• Photocatalytic splitting of water for hydrogen

How nitrogen atoms are embedded in the graphene lattice?
Raman mapping of NG sheet on SiO₂/Si substrate

Raman mapping settings:
514 nm, 4.8 mW, 2 s, 100x, Spot size = 1 μm, Area: 47 x 44.5 μm², Raster scan, Step: 0.4 μm, Total 13,216 points, Time = 18 hours

Calculated N1s binding energies for CNx structures

(XPS – X-ray Photoelectron Spectroscopy)

N. Hellgren, PhD. Thesis 1999 (Sweden)

STM images of NG sheets on SiO$_2$/Si substrate

(STM – Scanning Tunneling Microscopy)


In collaboration with M.G. Pan (ORNL)
A. Botello & J.C. Charlier (UCL)
Band Gap Opening: Unbalanced Doping within Sublattices


Lopez-Urias, et al., unpublished (2012)
Molecular sensing properties of N-doped graphene

Crystal Violet (CRV)

CRV on N-doped graphene sheet
CRV on Pristine graphene sheet

S. Feng unpublished (2013)
Surface Enhanced Raman Scattering (SERS)


Boron-doped Graphene

Boron-doped Graphene

Transfer and HTEM Studies

A. B-doped graphene

B. Monolayer and multilayer

C. Details of the graphene structure

D. Atomic resolution imaging

STM / STS of BG sheet on SiO$_2$/Si substrate

with M.G. Pan (ORNL), V. Meunier (RPI) & A. Botello & J.C. Charlier (UCL)

B-doped Graphene as Gas sensors: NO$_2$ and NH$_3$

In collaboration with G. Chen and A. Harutyunyan

## B-doped Graphene as Gas sensors: NO$_2$ and NH$_3$

<table>
<thead>
<tr>
<th>Target gas</th>
<th>Sensing material</th>
<th>Lowest concentration tested</th>
<th>Detection limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_2$</td>
<td>Mechanically exfoliated graphene(47)</td>
<td>100 ppm</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>CVD graphene-like films(48)</td>
<td>65 ppm</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>Ozone-treated graphene(49)</td>
<td>200 ppm</td>
<td>1.3 ppb</td>
</tr>
<tr>
<td></td>
<td>Ethylenediamine-modified rGO(50)</td>
<td>1 ppm</td>
<td>70 ppb</td>
</tr>
<tr>
<td></td>
<td>Sulfonated rGO(50)</td>
<td>5 ppm</td>
<td>3.6 ppm</td>
</tr>
<tr>
<td></td>
<td>Epitaxial graphene from SiC(51)</td>
<td>2.5 ppm</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>MPECVD graphene(52)</td>
<td>100 ppm</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>rGO(53)</td>
<td>5 ppm</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>rGO(54)</td>
<td>2 ppm</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>Carbon Nanotubes/rGO hybrid(55)</td>
<td>0.5 ppm</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>Mechanically exfoliated graphene(56)</td>
<td>1 ppm</td>
<td>The order of 1 ppb</td>
</tr>
<tr>
<td></td>
<td>CVD graphene(57)</td>
<td>100 ppb</td>
<td>100 ppb</td>
</tr>
</tbody>
</table>

| NH$_3$     | rGO(53) | 5 ppm | -- |
|           | Mechanically exfoliated graphene(56) | 1 ppm | -- |
|           | CVD graphene(58) | 65 ppm | -- |
|           | rGO/Polyaniline hybrid(59) | 5 ppm | -- |
|           | Mechanically exfoliated graphene(60) | 10 ppm | -- |
|           | rGO(61) | 20 ppm | -- |
|           | CVD graphene(57) | 500 ppb | 500 ppb |
|           | rGO(62) | 10000 ppm (1%) | -- |
|           | rGO(54) | 10000 ppm (1%) | -- |

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*R.T. Lu, et al., unpublished (2013).*
Si-doped Graphene: Synthesis

![Graphene Synthesis Diagram](image)

*R.T. Lu, et al., Advanced Materials (2014)*
Si-doped Graphene: Raman spectroscopy & XPS analysis

(c) C1s

(d) Si2p

Si-doped Graphene: Raman spectroscopy & XPS analysis
Defects in Other 2D systems

1. Structural Defects, responsible of Curvature Changes (Square, Octagons, Heptagons, etc.)

2. Topological Defects (Bond Rotations, Stone-Thrower-Wales Type Transformations)

3. Substitutional Atoms (Impurities, Doping)

4. Vacancies, Interstitials and Edges

5. Folding, Surface Distortions?
Chemical exfoliation

- Lithium intercalation assisted exfoliation of TMDs: violent reaction between Li and water.

Intercalation and Exfoliation of h-BN and Graphite

Mallouk, Crespi, Terrones
N. Kovtyukhova JACS 135, 8372 (2013)
New Result: Intercalation and Exfoliation of Graphite using Brønsted Acids

Mallouk, Crespi, Terrones
N. Kovtyukhova Nature Chemistry (2014)
New Result: Intercalation and Exfoliation of Graphite using Brønsted Acids

Mallouk, Crespi, Terrones
Chemical Synthesis of MoSe₂ Nanoflowers

Na₂MoO₄, 8 mL of oleic acid, and 2 mL of 1-octylamine were mixed together and degassed under vacuum at 120 °C for ~10 min. The reaction vessel was then purged with Ar(g) and slowly heated to ~240 °C at ~5 °C/min; a clear, dark, red-brown solution was formed. Next, 2 mL of the ODE-Se was added.
Chemical Synthesis of MoSe$_2$ Nanoflowers

Schaak & Terrones
Beyond Graphene

Doping Layers And Hetero-layers

$V_2O_5$, $NiCl_2$, $MgB_2$
WS$_2$: Clusters & Monolayers

Extraordinary room-temperature photoluminescence in WS$_2$ monolayers

Extraordinary PL
Synthesis of WS$_2$ monolayers with CVD

---- from islands to films

WO$_3$ + S $\rightarrow$ WS$_2$

2D WS$_2$ islands and edge-enhanced photoluminescence

2D WS₂ islands and edge-enhanced photoluminescence


Nano Lett. (2013) DOI: 10.1021/nl3026357
Different WS$_2$ island morphologies within a two-zone furnace

*Terrones-Crespi Collaboration*

A. Berkdemir, et al. (Unpublished)
Hexagonal Islands of WS$_2$

Terrones & Crespi

Y. Wang, A. Berkdemir, unpublished (2013)

A. Berkdemir, et al. (Unpublished)
SEM and PL of Hexagonal Islands of WS₂

Terrones & Crespi

A. Berkdemir, et al. (Unpublished)
Raman modes in layered MoS$_2$

<table>
<thead>
<tr>
<th>No. of layer</th>
<th>Point group</th>
<th>Center of inversion</th>
<th>In plane mode</th>
<th>Out of plane mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Odd</td>
<td>D$_{3h}$</td>
<td>No</td>
<td>E'</td>
<td>A'$_1$</td>
</tr>
<tr>
<td>Even</td>
<td>D$_{3d}$</td>
<td>Yes</td>
<td>E$_{12g}$</td>
<td>A$_{1g}$</td>
</tr>
<tr>
<td>Bulk</td>
<td>D$_{6h}$</td>
<td>Yes</td>
<td>E$_{12g}$</td>
<td>A$_{1g}$</td>
</tr>
</tbody>
</table>

Resonant Raman on WS$_2$ Monolayers

Resonant Raman on WS$_2$ Monolayers

Resonant Raman on WS$_2$ Monolayers

Resonant Raman on WS$_2$ Triangular Monolayers

E. Del Corro, et al in preparation
Resonant Raman on MoS$_2$ and WSe$_2$ Monolayers


New First Order Raman-active Modes in WSe$_2$

Terrones, Balicas & Mallouk

New First Order Raman-active Modes in WSe$_2$

New First Order Raman-active Modes in Few Layers
Terrones, Balicas & Mallouk

Raman Active Modes for WSe$_2$ L=5 layers

This intermediate electronic state is only present in the **monolayer**. Calculation of the double resonance (for constant matrix elements) confirms the effect.

Phonon dispersion and electronic band structures

A. Berkdemir, H. R. Gutiérrez, et al. (Nature Scientific Reports 3, 1755 (2013)}
Grain Boundaries in WS$_2$ monolayers

In Collaboration with N. Alem, P. Ercuis (NCEM), A. Azizi, B. Yakobson

Low Angle GB

High Angle GB

Dislocation Cores

Using geometric phase analysis (GPA); see Ultramicroscopy 74, 131–146 (1998)
Synthesis of MoS$_{2(1-x)}$Se$_x$ atomic layers

PL of MoS$_{2(1-x)}$Se$_x$ atomic layers

Terrones & Ajayan


Nano Letters (2014)
New Direct Bandgap Semiconductors: Heterostructures of TMD

Large Scale Synthesis of MoS$_2$/WS$_2$ Vertical Heterostructures

Gong, et al. under review.
Large Scale Synthesis of MoS$_2$/WS$_2$ Vertical Heterostructures

Gong, et al. under review.
Bottom up synthesis of TMD heterostructures

<table>
<thead>
<tr>
<th>Lateral heterostructure</th>
<th>Central region</th>
<th>Peripheral region</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS$_2$-WS$_2$</td>
<td>MoS$_2$</td>
<td>WS$_2$</td>
</tr>
<tr>
<td>MoSe$_2$-WSe$_2$</td>
<td>MoSe$_2$</td>
<td>WSe$_2$</td>
</tr>
<tr>
<td>MoS$_2$-MoSe$_2$</td>
<td>MoS$_2$</td>
<td>MoSe$_2$</td>
</tr>
<tr>
<td>WS$_2$-WSe$_2$</td>
<td>WS$_2$</td>
<td>WSe$_2$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Vertical heterostructure</th>
<th>Bottom layer</th>
<th>Top layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS$_2$-WS$_2$</td>
<td>MoS$_2$</td>
<td>WS$_2$</td>
</tr>
</tbody>
</table>

Huang, et al. Nat. Mater. doi: 10.1038/nmat4064
Large Scale Synthesis of MoS$_2$/WS$_2$ In-plane Heterostructures

Large Scale Synthesis of MoS$_2$/WS$_2$ In-plane Heterostructures

Collaboration with P.M. Ajayan, J. Lou

HRTEM studies of Mo$_x$W$_{1-x}$S$_2$ triangular monolayers

N. Alem, A. Azizi, et al. under review
Optical characterization of MoS$_2$ monolayers

(a) Raman spectrum

(b) PL spectrum

(c) Raman mapping

(d) PL mapping

(e-h) Fluorescence images

Mike contributed to fluorescence imaging.
Unprecedented 2D material: Mo$_x$W$_{1-x}$S$_2$ monolayers with tunable stoichiometry and band gap

<table>
<thead>
<tr>
<th></th>
<th>$A'<em>1$ ratio $I</em>{WS2}/I_{MoS2}$</th>
<th>$E'$ position of MoS$_2$</th>
<th>$E'$ - $A'_1$ separation of MoS$_2$</th>
<th>PL peak energy</th>
<th>PL peak width</th>
</tr>
</thead>
<tbody>
<tr>
<td>Center</td>
<td>0.6</td>
<td>383 cm$^{-1}$</td>
<td>24 cm$^{-1}$</td>
<td>1.85 eV</td>
<td>~80 meV</td>
</tr>
<tr>
<td>Edge</td>
<td>7.8</td>
<td>373 cm$^{-1}$</td>
<td>33 cm$^{-1}$</td>
<td>1.93 eV</td>
<td>~80 meV</td>
</tr>
</tbody>
</table>

Ana helped with analyzing Raman and PL spectra.
Vertical structures: MoS$_2$-WSe$_2$

Annealed at 300 °C

Collaboration with Lance Li
Vertical structures: MoS$_2$-WSe$_2$

(a) WSe$_2$ $E_{2g}^1$, $A_{1g}$
- MoS$_2$
- 2LA(M)
- 248, 260
- uM/W
- cM/W
- 251
- Annealed
- 249, 260

(b) MoS$_2$ $E_{1g}$, WSe$_2$ $B_{1g}^1$
- MoS$_2$
- 387, 402
- uM/W
- cM/W
- 384, 309
- cM/W

(c) MoS$_2$ $E_{2g}^1$, $A_{1g}$
- MoS$_2$
- 384, 404
- uM/W
- cM/W
- 384
- Annealed
- cM/W

(d) MoS$_2$
- WSe$_2$
- 5 µm

(e) MoS$_2$ $E_{1g}$
- WSe$_2$ $B_{1g}^1$
- Intensity (a.u.)
- 1
- 0
- 5 µm

Collaboration with Lance Li
Vertical structures: MoS$_2$-WSe$_2$

(a) PL Intensity (a.u.)

MoS$_2$

uM/W

cM/W

WSe$_2$

1.65

1.85

1.59

Annealed

(b) Absorption

MoS$_2$

uM/W

cM/W

WSe$_2$

Energy (eV)

Collaboration with Lance Li
WE THANK

ARO MURI W911NF-11-1-0362: Atomic Layers of Nitrides, Oxides, and Sulfides (ALNOS)
AFOSR MURI FA9550-12-1-0035: Synthesis and Characterization of 3D Carbon Nanotube Solid Networks

Penn State Center for Nanoscale Science