Light-Matter Interaction in Heterostructures made of 2D Crystals

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OVERVIEW

DIAMOND-LIKE CARBONS

- Protective Barrier
  - PET bottles

- Permeation barrier

- Nucleation
  - PRL 2004, Science 2005

GRAPHENE & 2D CRYSTALS

- Heterostructures

RAMAN SPECTROSCOPY

- Diamond-like carbons (3D)
  - PRB 2006, 339 citations

- Graphene (2D)
  - Identification, Strain, Defects
  - Doping, Superlattices, etc

Graphene Nanoribbons (1D)
- Nature Chemistry 2014, ACS Nano 2014, etc

Casiraghi, Goodacre, Manchester Prof Samori, CNRS Strasbourg  Prof Müllen, MPI Mainz
The Family of 2D-Crystals

- Graphene
- Graphane
- h-BN
- NbSe$_2$
- MoS$_2$
- etc.
There are several methods of mass-production of graphene, as shown in Table 1 below. These methods include chemical vapor deposition (CVD), SiC (electronics, RF transistors), molecular assembly (nanoelectronics), and liquid-phase exfoliation (coating, composites, inks, energy storage, bio, transparent conductive layers).

Table 1: Properties of graphene obtained by different methods

<table>
<thead>
<tr>
<th>Method</th>
<th>Sample size</th>
<th>Charge carrier mobility (at ambient temperature)</th>
<th>Price (for mass production)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical vapor deposition (CVD)</td>
<td>Infinite as a layer of overlapping flakes</td>
<td>Coatings, paint/ink, composites, transparent conductive layers</td>
<td>High</td>
</tr>
<tr>
<td>SiC (electronics, RF transistors)</td>
<td>1,000</td>
<td>Photonics, nanoelectronics</td>
<td>Medium</td>
</tr>
<tr>
<td>Molecular assembly (nanoelectronics)</td>
<td>Infinite as a layer of overlapping flakes</td>
<td>Conductive layers, energy storage, bioapplications</td>
<td>Low</td>
</tr>
<tr>
<td>Liquid-phase exfoliation</td>
<td>1,000</td>
<td>Conductive layers, sensors, bioapplications</td>
<td>Very high</td>
</tr>
</tbody>
</table>

Graphene electronics may well find applications within a shorter timescale than flexible electronics. However, considering that the quality of graphene improves every year, graphene electronic applications are being developed, using the other available candidate at the moment. Moreover, the fracture strain of graphene is much higher than that of any other available (probably not ideal in terms of quality) material. Figure 2 and Table 2 list some of the possible applications and the time that it may take for graphene-based prototypes to be demonstrated.
LIQUID-PHASE EXFOLIATION

- Exfoliation of their bulk counterparts via chemical wet dispersion followed by ultra-sonication.
- Low-cost and mass scalable
- Able to produce high QUALITY graphene (i.e. Oxygen free)

LATERAL SIZE and COMPOSITION strongly depends on the experimental conditions.

NEVER 100% single-layer

Works only with ORGANIC SOLVENTS  
**Exfoliation in Water**

**Exfoliation with Surfactants**

Surfactant is not easy to remove, yield of monolayer is < 10%
**OUR WATER-BASED INKS**

**EXFOLIATION with STABILIZERS**

- **XPS**
  - Binding energy (eV) vs. Intensity (arb. units)

- **Raman spectroscopy**
  - Raman Shift (cm⁻¹) vs. Intensity (arb. units)

- Up to 60-70% high-quality single-layers

- Reduced amount of stabilizer

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*Parviz et al., ACS Nano, 2012*

*Yang et al., Carbon, 2012*
OUR WATER-BASED INKS

Schlierf et al, Nanoscale 2013

In collaboration with Vincenzo Palermo, CNRS Bologna (Italy) and David Bejonne, University of Mons (Belgium)

Funded by the European Science Foundation
Figure S18 shows the coulombic and van der Waals contributions to the interaction energy of the pyrene-core for each of the pyrene derivatives at the global minima (fully adsorbed states). One can see that with increasing number of $\pm SO_3$ groups the pyrene-core interaction with the solvent increases, which is due to the induced charge on the pyrene-core making it less hydrophobic.

The trend, however, is different upon going from Py-$1SO_3$ to Py-$2SO_3$, which shows that the introduction of $-OH$ groups neutralizes the induction of charge from the $\pm SO_3$ groups. The same qualitative behavior has been observed in the exfoliation of graphite (see Fig. 9b in Ref. 3b). Extended to other 2D crystals, exfoliation dominated by interaction molecule-solvent.

UK Patent Application
No 1401721.4
Other 2D Crystals - TEM

1. Low mag. TEM
   a) MoS$_2$

2. HRTEM
   b) BN

3. Filtered HRTEM
   c) WS$_2$

4. Filtered HRTEM
FABRICATION

- Drop casting
- Vacuum filtration

Options:
- WS₂
- h-BN
- CVD Gr

Steps:
1. Add graphene
2. Add WS₂ or h-BN
3. Add CVD graphene
4. Final product
HETEROSTRUCTURES

Photoresponsivity \( \approx 0.1 \text{ mA/W} \)

\( P \approx 0.5 \text{ mW} \)

Withers et al, Nano Lett 2014
RAPID GROW: $5 billion in 2012 -> $35 billion in 2020 -> $300 billion by 2030

Printed Electronics

IDTechEx 2011-2021 Forecast

- smart packaging
- pharmacy
- active clothing
NMP-BASED INKS

Torrisi et al, ACS Nano, 6, 2992 (2012)

- Coffee ring effect
- Post-processing
- Residuals

Finn, D. J.; et al.
J. Mater. Chem. C, 2, 925 (2014)
**WATER-BASED INKS**

**ONE POT method:** Stable Graphene inks printed on paper, glass, plastic, silicon, etc

ON PEL™

UK Patent Application
No 1401721.4
Successful printing of BN, MoS$_2$, WS$_2$ inks on PET and on Silicon.
Raman Spectroscopy of Graphene

- **Identification**
  - Ferrari, Casiraghi et al. PRL 2006

- **Doping**
  - Pisana, Casiraghi et al. Nature Mat. 2006
  - Casiraghi et al. APL 2007

- **Disorder**
  - Casiraghi RRL-PSS 2009
  - Eckmann et al, NL 2012
  - Otto et al, Nanoresearch 2014
  - Kim et al, ACS Nano 2012

- **Chemical Derivatives**
  - Eckmann et al, NL 2012; PRB 2013
  - Felten et al, Nanotechnology 2013;
  - Small 2012

- **Heterostructures, Superlattices**
  - Eckmann et al, NL 2013
  - Zhou et al, ACS Nano 2014

- **Strain**
  - Zabel et al NL 2012

- **Edges**
  - Casiraghi et al., NL 2009

- **e-p, e-e interactions**
  - Piscancec et al PRL 2004
  - Basko, PRB 2008
  - Casiraghi, PRB 2009
  - Klar et al, PRB 2013

...AND MORE!
Synthesis of structurally well-defined and liquid-phase-processable graphene nanoribbons

Akimitsu Narita, Xinliang Feng, Yenny Hernandez, Søren A. Jensen, Mischa Bonn, Huafeng Yang, Ivan A. Verzhbitskiy, Cinzia Casiraghi, Michael Ryan Hansen, Amelie H. R. Koch, George Fytas, Oleksandr Ivasenko, Bing Li, Kunal S. Mali, Tatyana Balandina, Sankarapillai Mahesh, Steven De Feyter and Klaus Müllen

Bandgap = 1.88 eV
Mobility = 150 – 15,000 cm²V⁻¹s⁻²
Ribbon vs dimer and trimer

Supplementary Figure 16. Raman spectra of GNR, dimer, and trimer measured at 514.5 nm on powder samples with laser power below 0.1 mW.

Characterization of polyphenylene precursor S18 and GNR showed a regular pattern of signals reaching $m/z = \sim 25,000$ with an interval of $\sim 1,052$, which was in agreement with the molecular weight of one repeating unit, i.e. 1,054 (Supplementary Fig. 17).

Fragmentation of the alkyl chains was observed as small peaks in the spectrum. Reflectron-mode MALDI-TOF MS analysis of the same sample of S18 displayed peaks at $m/z = 5,294, 6,348, 7,402, 8,455, 9,510$, corresponding to the molecular weight of cyclic oligomers with sodium ion (Supplementary Fig. 18).

This MALDI-TOF MS result as well as the SEC profiles of precursor S18 (Supplementary Fig. 19) suggested formation of cyclic oligomers by intramolecular Diels–Alder cycloaddition in a similar manner to that of precursor 2 (Supplementary Fig. 4).
Aim: understanding origin of the RLBM and its dependence on structure in collaboration with Ferrari, Cambridge and Molinari, Modena

Narita, Casiraghi, Feng, Müllen, ACS Nano, 2014
Acknowledgements

MY GROUP

A. Eckmann*
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D. Prezzi

THANKS FOR YOUR ATTENTION!

THE ROYAL SOCIETY
Graphene Week 2015 will be held during 22 – 26 June 2015, in Manchester, UK. The conference is commissioned by the Graphene Flagship, with support from the University of Manchester, the National Graphene Institute (NGI), and the City of Manchester.