Elena Sheka
Peoples’ Friendship University of Russia
Moscow, Russia

Graphene:
Nanochemistry, Nanomagnetism,
Nanophotonics, Nanomechanics

Nano and Giga Challenges
in Electronics, Photonics and Renewable Energy
Moscow - Zelenograd, Russia, September 12-16, 2011
Graphene is an allotrope of carbon, whose structure is one-atom-thick planar sheets of sp²-bonded carbon atoms that are densely packed in a honeycomb crystal lattice.
Graphene possesses both 2D crystalline and peculiar molecular properties

Two theoretical approaches should be applied:
• 2D Solid state theory
• Molecular theory
Main concepts of the molecular theory of graphene:

1. odd electrons;
2. molecular magnetism;
3. donor-acceptor contribution into intermolecular interaction;
4. deformation as a mechanochemical reaction;
5. vibration-induced mechanical transformation
Odd electrons and nanochemistry of graphene

\[ \text{Molecular chemical susceptibility} \]

\[ N_D = \sum_{i,j=1}^{\text{NORBS}} D_{ij}, \]

Interatomic distance, \( \text{Å} \)
Odd electrons and nanochemistry of graphene

Atomic chemical susceptibility

\[ N_{DA} = \sum_{i \in A} \sum_{B=1}^{NAT} \sum_{j \in B} D_{ij}. \]
Odd electrons and nanochemistry of graphene

Chemical functionalization of graphene
Odd electrons and nanochemistry of graphene

Graphene-fullerene hybrid structures
Odd electrons and nanomagnetism of graphene

Spin density on edge atoms

\[ J = \frac{E_B(0) - E(S_{\text{max}})}{S_{\text{max}}^2} \]

Table. NGrs electronic characteristics in kcal/mol

<table>
<thead>
<tr>
<th>Nanographenes (^{1})</th>
<th>The number of “magnetic” (odd) electrons</th>
<th>( E_{S=0}^{\text{UBSHF}} )</th>
<th>( J )</th>
<th>( E_{S=0}^{PS} )</th>
<th>Singlet-triplet gap (^{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(15, 12)</td>
<td>400</td>
<td>1426.14</td>
<td>-0.42</td>
<td>1342.14</td>
<td>0.84</td>
</tr>
<tr>
<td>(7, 7)</td>
<td>120</td>
<td>508.69</td>
<td>-1.35</td>
<td>427.69</td>
<td>2.70</td>
</tr>
<tr>
<td>(5, 6)</td>
<td>78</td>
<td>341.01</td>
<td>-2.01</td>
<td>262.72</td>
<td>4.02</td>
</tr>
</tbody>
</table>

\(^{1}\)Nomenclature of nanographenes is given in Footnote 2 to Table 1. 
\(^{2}\)For pure-spin states the singlet-triplet gap \( E_{S=1}^{PS} - E_{S=0}^{PS} = -2J \).
Odd electrons and nanomagnetism of graphene

Magnetism of graphene is size-dependent and can be observed when linear dimensions of the sheet are \( \sim 3-5 \) nm. Magnetization is provided by mixing the ground singlet state with higher spin (triplet) ones and becomes recordable when \( J \) approaches value of \( 10^{-2} - 10^{-3} \) kcal/mol. Critical size is about 3-5 nm.

\[
J_{n_a n_z} \sim J_{hgn} / n,
\]
Donor-acceptor intermolecular interaction and nanophotonics of graphene

$R^{00}$ minimum corresponds to charge transfer complex $A+B$

$R^{+-}$ minimum corresponds to a chemically bonded composite $AB$
Donor-acceptor intermolecular interaction and nanophotonics of graphene

Raman scattering spectra

Colloidal solution of shungit nanoglobules in toluene

Intensity, arb. units

exc=405 nm
exc=476.5 nm
exc=496.5 nm
exc=514.5 nm

Wave numbers, cm⁻¹

6*(5,5)nanographene

<d>~3nm
Donor–acceptor intermolecular interaction and nanophotonics of graphene

Enhanced photoluminescence of C$_{60}$-based fullerene in toluene solution in the presence of graphene nanoglobules
Deformation of graphene as a mechanochemical reaction

Uniaxial tension
Coordinate-of-reaction approach
Mechanochemical internal coordinates
Deformation of graphene as a mechanochemical reaction

Deformation mode ‘armchair’

Structures of (5,5) nanographene non-terminated (left) and hydrogen-terminated (right) under successive steps of the ach regime of deformation. Numbers above the structures numerate steps.
Deformation mode ‘zigzag’: Tricotage-like failure of the graphene body

Structures of (5,5) nanographene non-terminated (left) and hydrogen-terminated (right) under successive steps of the zg regime of deformation. Numbers numerate steps.

E. Sheka et al. JETP, 112, 602-611, 2011
Deformation of graphene as a mechanochemical reaction

Graphene failure as seen experimentally

Deriving Carbon Atomic Chains from Graphene,
PHYS. REV. LETT. 102, 205501 (2009)
Microscopic characteristics of the graphene failure (bare edges)

$zg$ mode  $ach$ mode
Deformation of graphane as a mechanochemical reaction

Mechanochemical internal coordinates

armchair (ach) mode

zigzag (zg) mode

Atoms marked in blue are excluded from the optimization procedure
Deformation of graphane as a mechanochemical reaction

$zg$ mode

23

24

0

31

$ach$ mode

30

71
Deformation of graphene and graphane as a mechanochemical reaction

Comparative analysis

First stages of deformation
Benzenoid units are responsible for stiffness and mechanical anisotropy of the graphene body.

How situation must change when graphene is chemically modified and the benzenoid units are substituted by other ones?
## Deformation of graphene and graphane as a mechanochemical reaction

### Mechanical parameters of graphane and graphene

<table>
<thead>
<tr>
<th>Species</th>
<th>Mode</th>
<th>$\varepsilon$ (for $\sigma_{cr}$)</th>
<th>$F_{cr}$, N·$10^{-9}$</th>
<th>$\sigma_{cr}$, N/m$^2$·$10^9$</th>
<th>$E$, TPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzene</td>
<td>ach</td>
<td>0.29</td>
<td>19.62</td>
<td>120.47</td>
<td>0.76</td>
</tr>
<tr>
<td></td>
<td>zg</td>
<td>0.22</td>
<td>19.18</td>
<td>97.13</td>
<td>0.99</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>ach</td>
<td>0.44</td>
<td>15.69</td>
<td>93.76</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>zg</td>
<td>0.36</td>
<td>14.99</td>
<td>74.57</td>
<td>0.74</td>
</tr>
<tr>
<td>(5,5) nanographene</td>
<td>ach</td>
<td>0.18</td>
<td>54.56</td>
<td>119.85</td>
<td>1.09</td>
</tr>
<tr>
<td></td>
<td>zg</td>
<td>0.14</td>
<td>47.99</td>
<td>106.66</td>
<td>1.15</td>
</tr>
<tr>
<td>(5,5) nanographane</td>
<td>ach</td>
<td>0.3</td>
<td>43.41</td>
<td>74.37</td>
<td>0.61$_\sigma$(0.54$_e$)</td>
</tr>
<tr>
<td></td>
<td>zg</td>
<td>0.23</td>
<td>36.09</td>
<td>63.24</td>
<td>0.57$_\sigma$(0.52$_e$)</td>
</tr>
</tbody>
</table>
Vibration-induced mechanical transformation

\[ \nu^{\text{CHXN}}_{c-c} = \eta \nu^{\text{BZN}}_{c-c} \]
\[ \eta = \sqrt{\frac{E^{\text{CHXN}}_{\sigma}}{E^{\text{BZN}}_{\sigma}}} \]

Table. Young’s moduli and stretching C-C vibrations

<table>
<thead>
<tr>
<th>Species</th>
<th>Def. mode</th>
<th>( E_{\sigma} )</th>
<th>( \eta )</th>
<th>( \nu^{\text{CHXN}}_{c-c} ), cm(^{-1} )</th>
<th>( \nu_{c-c} ), cm(^{-1} )</th>
<th>( \eta_{\text{exd}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>BZN</td>
<td>ach</td>
<td>0.76</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>zg</td>
<td>0.99</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CHXN</td>
<td>ach</td>
<td>0.40</td>
<td>1.38</td>
<td>1159</td>
<td>1070</td>
<td>1.49</td>
</tr>
<tr>
<td></td>
<td>zg</td>
<td>0.74</td>
<td>1.16</td>
<td>1378</td>
<td>1388 [26]</td>
<td>1.15</td>
</tr>
<tr>
<td>graphene</td>
<td>ach</td>
<td>1.09</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>zg</td>
<td>1.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>graphane</td>
<td>ach</td>
<td>0.61</td>
<td>1.34</td>
<td>1167</td>
<td>1330-1000 [27]</td>
<td>1.18-1.60</td>
</tr>
<tr>
<td></td>
<td>zg</td>
<td>0.57</td>
<td>1.46</td>
<td>1071</td>
<td>1000 [27]</td>
<td></td>
</tr>
</tbody>
</table>
Molecular theory of graphene is not over

On a schedule there are:
  • Chemical modification of graphene under stress;
  • Enhancement of polymer rigidity by nanographenes;
  • Nanographenes as catalysis amplifiers;
  • Hybrid structures;
  • Hydrogen fuel cells;
  • and so forth...
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