Ultrathin carbon nanotube with single, double, and triple bonds

Eduardo Menéndez-Proupin
Departamento de Química Física Aplicada, Universidad Autónoma de Madrid
Departamento de Física, Grupo de Nanomateriales, Universidad de Chile

A metastable carbon nanotube with single, double, and triple bonds has been predicted by ab initio simulation. Ten-membered carbon rings are formed by breaking carbon bonds between adjacent hexagons in the starting folded-graphene structure. This structure is stable in molecular dynamics simulations at temperatures up to 1000 K. Raman and optical absorption spectra are simulated to allow its identification in the laboratory.
Santiago de Chile

Dept. of Physics, Fac. of Science, University of Chile

Group of nanomaterials (GNM)

Temporary Address:

Departamento de Química Física Aplicada, Universidad Autónoma de Madrid, Spain

www.gnm.cl
Collaborators

Ana Lilian Montero Alejo,
Faculty of Chemistry, University of Havana

José M. García de la Vega,
Dept. of Applied Physical Chemistry, Universidad Autónoma de Madrid
Outline

• About carbon nanotubes
• DFT calculations
• Structure and stability
• Electronic properties
• Spectra
• Conclusions
Single walled carbon nanotubes

The rolling vector is called chiral vector. In the figure above it is \( n=4, m=1 \), i.e., a \((4,1)\) carbon nanotube.
Armchair
Carbon nanotubes

The rolling vector is called chiral vector In the figure above it is n=4, m=1, i.e., a (4,1) nanotube.
Chiral vector $\approx$ Periodic Boundary condition

If nanotube is a folded graphene, *neglecting curvature*

$$\Psi(\vec{r} + n\vec{a} + m\vec{b}) = \Psi(\vec{r})$$

Hence

$$\vec{t}_1 = n\vec{a} + m\vec{b}, \quad \vec{t}_2 \text{ perpendicular to } \vec{t}_1$$

let $\vec{g}_1$ and $\vec{g}_2$ be the reciprocal lattice vectors
the allowed $\vec{k}$ points are

$$\vec{k} = \frac{n_1}{N_1} \vec{g}_1 + \frac{n_2}{N_2} \vec{g}_2, \quad n_1 = 0, 1, ..., N_i - 1$$

but in this case $N_1 = 1$, and $N_2 \to \infty$
Graphene bands folding
Thin nanotubes (d<1 nm)

The graphene folded-band models breaks up.

Some CNTs theoretically metallic have a gap, e.g., (9,0)

Some CNTs theoretically semiconductors are metallic, e.g., (5.0)

Full ab initio calculations enter in action.
Ultrathin carbon nanotubes

The thinnest freestanding CNT have $d>4$ Å
Smaller ones (~3 Å) inside a thicker CNT.

Planck et al, ACS Nano 4, 4515 (2010)
Ultrathin CNT (2,1)

It’s too strained to be stable. It could be metastable.

Bond angles as small as $97^\circ$ vs $120^\circ$ in $sp^2$ carbon.
Torsion angles as large as $67^\circ$ vs $0^\circ$ in $sp^2$ carbon.

Let us see what happen in a DFT relaxation.
Computational methods:

Density Functional Theory with the Quantum ESPRESSO Software. URL: www.quantum-espresso.org

Density Functional Perturbation Theory for IR and Raman spectra, Time-dependent DFT for optical spectra.

Functionals: PBE with Grimme's correction for vdW interaction. LDA for DFPT vibrational properties.

Molecular Dynamics with Brenner's classical bond order potentials, GULP code.

Mulliken population analysis with GAUSSIAN.
From idealized to possible structure

See animation
Stability issues

1) It may be unstable with a larger supercell.
2) It may be unstable at room temperature.
3) It may be extremely reactive with residual oxygen or other species.

Let us test 1) and 2). Valid in high vacuum.
Summary of the stable structure

Diameter 3.2 Å
Periodicity 11.15 Å
Chirality (2,1)

The theoretical bond length of graphene is 1.42 Å
The dashed lines are broken bonds.
Looking for symmetries

Chain of tri-coordinated carbons ($^3C$) fixed by dimers

Two inter-twinned chains linked by single bonds

**Open question:** Is this topology relevant for any physical property? In the case of Raman-active vibrational modes, YES.
**Charge density isosurfaces**

a) \( \rho = 0.2 \) au; b) \( \rho = 0.25 \) au; c) \( \rho = 0.3 \) au

**Electron Localization Function (ELF) isosurfaces**

<table>
<thead>
<tr>
<th>Bond</th>
<th>( ^2 \text{C} = ^2 \text{C} )</th>
<th>( ^2 \text{C} = ^{3} \text{C} )</th>
<th>( ^3 \text{C} = ^3 \text{C} )</th>
<th>( ^3 \text{C} = ^3 \text{C} )</th>
<th>Graphene</th>
</tr>
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<tbody>
<tr>
<td><strong>BL(Å)</strong></td>
<td>1.23</td>
<td>1.41</td>
<td>1.43</td>
<td>1.49</td>
<td>1.42</td>
</tr>
<tr>
<td><strong>BO</strong></td>
<td>2.46</td>
<td>1.21</td>
<td>1.45</td>
<td>1.00</td>
<td>1.24</td>
</tr>
</tbody>
</table>
Electronic structure

\( E_g = 1.23 \text{ eV (indirect, } \Gamma \rightarrow X) \)
\( E_g = 1.35 \text{ eV (direct, } \Gamma) \)
TDDFT absorption spectra
Infrared spectrum

- Anomalous big intensity, as for CNT (8,0).
- Lines at 279, 488, 711 are different to graphene, nanoribbons and conventional nanotubes.
Raman features

- No radial breathing mode, no G band.
- Line at 1297 cm\(^{-1}\) matches the D line.
- Line at 2036 cm\(^{-1}\) typical of triple bonds, in agreement with the bond order and ELF.
Raman-active phonons

<table>
<thead>
<tr>
<th>Mode</th>
<th>Frequency (cm(^{-1}))</th>
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<tbody>
<tr>
<td>22</td>
<td>411</td>
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<tr>
<td>32</td>
<td>537</td>
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<tr>
<td>47</td>
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<tr>
<td>63</td>
<td>1201</td>
</tr>
<tr>
<td>71</td>
<td>1297</td>
</tr>
<tr>
<td>78</td>
<td>2036</td>
</tr>
</tbody>
</table>

Only trifold-coordinated carbons move

Only twofold-coordinated carbons move
Related structures

Obtained by molecular dynamics over 1000 K.
Conclusions

- Chiral (2,1) carbon nanotube with broken bonds is stable for $T < 1000$ K.
- Ten- and eight-membered rings.
- Single, double and triple bonds.
- Raman and IR spectra with different patterns than conventional carbon nanotubes.
[6]Cycloparaphenylene
(the shortest nanotube)

(6,6) Armchair CNT

1

[6]CPP
97 kcal mol⁻¹ of strain energy!

A precursor for a crystal of nanotubes?

Resolved crystallographic structure. Contains some amount of solvent inside the tubes. The crystal have an orange color that is absent in solution.
Can the solvent be extracted?

Representation of n-hexane molecules inside the tubes.
There may be also CCl$_2$H$_2$

Relaxed structure with solvent
Preliminary results

- From DFT relaxation, the empty [6]CPP crystal is stable.
- Relaxation of the crystal filled with n-hexane is also stable.
- Optical and vibrational spectra are predicted.
Electronic structure

Is this peak responsible of the orange color of the crystal? Or it is due to the solvent?
Infrared spectrum
To be continued.

at the next school?
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