Metal-functionalized Graphene for Hydrogen Storage

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Research themes @ NEST Pisa

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2. Physics of low-dimensional systems
3. Graphene

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2. THz photonics
3. OptoMechanics

**NanoBioScience**
1. Visualizing brain function in the living mouse
2. Lab-on-a-chip technologies
3. Nanoscale single-molecule spectroscopy of soft matter
Outline

• Introduction to Hydrogen Storage
• Epitaxial Graphene
• Hydrogen Storage by Functionalization
  – Ti-functionalization
  – Li-functionalization
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Hydrogen Life Cycle

Complete energy loop relying on renewable sources

Hydrogen Storage in a safe and cheap way is a critical issue
Hydrogen & energy

As a fuel, hydrogen has advantages:

- Highest energy-to-mass ratio
- \( H_2 + 1/2 O_2 \rightarrow H_2O \quad \Delta H = -2.96eV \)
- Non-toxic and “clean” (product = water)
- Renewable, unlimited resource
- Reduction in CO\(_2\) emission
- Reduction of oil dependency

However, hydrogen is NOT an energy source: it must be produced e.g. by electrolysis, needing +2.96 eV, with zero balance with respect to energy production.
Hydrogen-fuelled Vehicles

Hyundai and Toyota are at the forefront of developing environmentally friendly vehicles. Hyundai promotes the market and guides it with innovative technologies. They initiate research and development of clean energy sources. At the end of the road, they have developed fuel cells that produce water vapor as a byproduct, instead of greenhouse gas emissions.
Hydrogen-fuelled Train

Coradia iLint regional train
Hydrogen-fuelled Airplane

Zero-emission air transport – first flight of four-seat passenger aircraft HY4

29 September 2016
Hydrogen-Storage

- Storing enough hydrogen on-board a vehicle to achieve a driving range of 400 km is a significant challenge.
- Needed: 4 kg of hydrogen for 400 km.
- At room temperature and atmospheric pressure, 4 kg of hydrogen occupies 45 m³, which corresponds to a balloon of 5 m diameter.
4 kg of H₂ gas
Hydrogen Storage

Targets for transport applications not reached yet:
- $\rho_m > 5.5$ wt%
- $\rho_v > 50$ kg H$_2$/m$^3$
- $P_{eq} \approx$1bar at $T< 100$°C

**Compressed H$_2$:**
High pressure and heavy container to support such pressure

**Liquid H$_2$:**
Liquefaction needs energy and consumes more than 20% of the recoverable energy

**Solid State:**
Physisorption
Chemisorption

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**Operating temperature**

<table>
<thead>
<tr>
<th>Heat Storage Method</th>
<th>LH$_2$</th>
<th>Activated carbon</th>
<th>Laves Phase Comp. / FeTiH$_3$</th>
<th>CGH$_2$</th>
<th>NaAlH$_4$</th>
<th>MgH$_2$</th>
<th>H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mat.wt.%</td>
<td>100</td>
<td>6.5</td>
<td>2</td>
<td>100</td>
<td>5.5</td>
<td>7.5</td>
<td>11</td>
</tr>
</tbody>
</table>

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Corresponding energy to release hydrogen in MJ per kg H$_2$

<table>
<thead>
<tr>
<th>Heat Storage Method</th>
<th>Liquid</th>
<th>Cryo-adsorption</th>
<th>Interstitial metal hydride</th>
<th>Compressed hydrogen</th>
<th>Alanate</th>
<th>Salt-like metal hydride</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mat.wt.%</td>
<td>0.45</td>
<td>3.5</td>
<td>15</td>
<td>n/a</td>
<td>23</td>
<td>37</td>
<td>142</td>
</tr>
</tbody>
</table>
... but it better be safe
Graphene for hydrogen storage

- Graphene is lightweight, inexpensive, robust, chemically stable
- Large surface area (~ 2600 m$^2$/g)
- Functionalized graphene has been predicted to adsorb up to 9 wt% of hydrogen

Yang et al., PRB 79 (2009) 075431
Graphene for hydrogen storage (2)

- To store 4 kg of H\textsubscript{2}, assuming $\rho_m = 10$ wt\%, we need 40 kg of graphene.
- Graphene surface area: $\sim 2600$ m\textsuperscript{2}/g.
- 40 kg of graphene cover $\sim 10^8$ m\textsuperscript{2} or 10 km x 10 km.
- Assuming a layer distance of 1 nm, we can put $10^9$ graphene layers in a stack of 1 m height.
- Then in 1 m\textsuperscript{3} we have $10^9$ m\textsuperscript{2} graphene.
- Thus, 40 kg of graphene would fit into a 100 liter tank.
H storage in graphene

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Graphene growth on SiC(0001)

Buffer Layer
Topologically identical atomic carbon structure as graphene. Does not have the electronic band structure of graphene due to periodic sp³ C-Si bonds.

Superstructure of both the buffer layer and monolayer graphene on the Si face from the periodic interaction with the substrate.


$6\sqrt{3} \times 6\sqrt{3}$-Superstructure

Graphene

SiC

30 nm, 1V, 100 pA

$E = 75\text{ eV}$
Hydrogen Intercalation

Buffer Layer (BL)

SiC

Buffer Layer

SiC

Quasi-free standing monolayer graphene (QFMLG)

Si C H

Quartz tube
P ~ atmospheric pressure
T ~ 800° C

H₂

purifier

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Functionalized Graphene

- Functionalized graphene has been predicted to adsorb up to 9 wt% of hydrogen.
- Modify graphene with various chemical species, such as calcium or transition metals (Titanium).

Lee et al., Nano Lett. 10 (2010) 793  
Durgen et al., PRB 77 (2007) 085405
Titanium on graphene

ML graphene on SiC(0001) with reconstruction

After deposition of Ti at RT

Titanium on graphene

Titanium Islands on Graphene on SiC0001 (100x100nm²)

Titanium island growth

Thermal desorption spectroscopy

- Deposition of different amounts of Titanium
- Offering Hydrogen (D$_2$)
  - (1x10$^{-7}$ mbar for 5 min)
- Heating sample with constant rate (10K/s) up to 550°C
- Measuring mass-sensitive desorption with a mass spectrometer

Spectra for different Ti-coverages

Different bonding types

Thermal desorption spectroscopy

Forming of Islands

Hydrogen adsorption capacity of adatoms on double carbon vacancies of graphene: A trend study from first principles

K. M. Fair,¹,² X. Y. Cui,³,⁴,* L. Li,¹ C. C. Shieh,¹ R. K. Zheng,¹,³ Z. W. Liu,³,⁵ B. Delley,⁶ M. J. Ford,² S. P. Ringer,³,⁴ and C. Stampfli¹,⁷

FIG. 1. (Color online) The binding energy of adatoms to graphene DCVs (blue), and pristine graphene (red), as well as the cohesive energy of the respective metal (green). Also included are the binding energies per adatom of two Ca and Sr (“2Ca” and “2Sr”) adatoms with one on either side of the DCV.

DCV = Double Carbon Vacancy
Defects in the graphene film are expected to reduce the mobility of Ti-atoms and to lead to a larger number of smaller islands.

Raman

Average Number of Islands per 100 nm²

Sputtered 150 s and Deposition of 0.5 ML Titanium

Higher number of defects leads to smaller Ti islands

Estimated gravimetric density:
- 0.5% - 0.75%
- 1.8% - 2.4%

Amorphous Graphene

Ti deposition 0.55ML

51nm x 64nm total area 3259 nm²

Ti grains
area; 2375 nm² (73.8%)
volume; 693 nm³
average height: 0.29 nm
number of grains:
6.6 per 100nm²
avg. diameter: 3.8 nm

Collaboration with Prof. Dongmok Whang
SKKU Advanced Institute of Nanotechnology
Calorimetry of Ti-functionalized SLG

- **Our system:** Single Layer Graphene (SLG) functionalized with Ti
- **Measurement idea:** detect the heat release during deuterium loading with a gold film thermometer
- **Methodology:** tailored Wheatstone bridge with lock-in signal acquisition
- **Sensitivity:** $\Delta T \approx 0.01 \text{ K}$

| $G3_{(1)}$ | $12.4$ | $1.32 \pm 0.07$ | $23.4 \pm 4.7$ | $21.8 \pm 1.3$ |
| $G3_{(2)}$ | $16.6$ | $1.24 \pm 0.09$ | $58 \pm 12$ | $53.8 \pm 4.3$ |

STM image of SLG on gold

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Li on Graphene: Motivation

Hydrogen Storage

$\begin{align*}
d_1 &= 1.82 \, \text{Å} \\
d_2 &= 2.11 \, \text{Å} \\
E_4 &= 0.19 \, \text{eV} \\
E_4 &= 0.21 \, \text{eV}
\end{align*}$

g_d = 12.8 \, \text{wt} \%$


Battery Technology

New Graphene Lithium-Air Batteries

Superconductivity

Li-intercalation

F. Bisti et al.,
PRB 91 (2015) 245411.

K. Sugawara et al.,

C. Virojanadara et al.,

I. Deretzis et al.,
PRB 84 (2011) 235426.
0.031 ML Li on EMLG

• Right: $6\sqrt{3}$, left: not.
• Step height: 1.44 Å
• Corrugation:
  – Right: 0.45 Å (EMLG)
  – Left: 0.22 Å

0.031 ML Li on EMLG

0.031 ML Li

0.047 ML Li

- Features related to Li deposition
- No bilayer inclusions:
  - No bilayer before Li deposition
  - Height difference between monolayer and bilayer: 0.8 Å (while here 1.5 Å)
  - Bilayer shows $6\sqrt{3}$

0.031 ML Li on EMLG

0.031 ML Li

0.047 ML Li

- Features related to Li deposition
- From atomically resolved STM: graphene in surface (no Li cluster at the surface)
- Li intercalation (QFBLG)
- Starts from step edges

0.28 ML Li on EMLG


QFBLG

Si atom(s) not saturated by Li.

30% of C-atoms of the buffer layer form covalent bonds to Si atoms of the SiC substrate.

Excellent quantitative agreement!
The $\sqrt{3}$ has been associated in literature to intercalation between the two graphene layers.

The $\sqrt{3}$ has been associated in literature to intercalation between the two graphene layers.

Li on Buffer Layer

Li on Buffer Layer

- No $6\sqrt{3}$ on top of islands
- Islands are QFMLG
- Have same nature as stripes for EMLG

Li on Buffer Layer

Model

(a)

\begin{align*}
4.92 \pm 0.28 \text{ Å} \\
2.6 \pm 0.2 \text{ Å} \\
2.32 \pm 0.08 \text{ Å}
\end{align*}

\begin{itemize}
  \item [\square] Measured data
  \item [\square] Literature data
  \item [\square] Obtained data
\end{itemize}

Model

(a) Li

4.92±0.28 Å

2.6±0.2 Å

2.32±0.08 Å

SiC

QFMLG

BL

buffer layer

(b) Li

4.1±0.5 Å

3.35±0.15 Å

1.6±0.2 Å

3.59±0.14 Å

2.23±0.16 Å

SiC

QFBLG

EMLG

first layer graphene

buffer layer

Conclusions

- Graphene is a promising material for hydrogen storage.
- Graphene functionalized by Ti:
  - Stability of hydrogen binding at room temperature.
  - Hydrogen desorbs at moderate temperatures.
  - Modifying the size and distribution of Islands by sputtering and increasing the active surface.
- Li-intercalated Graphene offers new and exciting possibilities for hydrogen storage.
Funding
Thank you for your attention!