Hydrogen Storage in Metal-functionalized Graphene

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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

\[ \text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} \quad \Delta H = -2.96\text{eV} \]

• 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 Train

Coradia iLint regional train

ALSTOM
Hydrogen-fuelled Airplane

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

29 September 2016
Hydrogen Storage

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

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

Solid State:
- Physisorption
- Chemisorption

Liquid H$_2$:
Liquefaction needs energy and consumes more than 20% of the recoverable energy
... but it better be safe
Graphene for hydrogen storage

• Graphene is lightweight, inexpensive, robust, chemically stable
• Large surface area (~ 2600 m²/g)
• Functionalized graphene has been predicted to adsorb up to 9 wt% of hydrogen

Yang et al., PRB 79 (2009) 075431
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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

30 \text{ nm}, 1 \text{V}, 100 \text{ pA}

E = 75 \text{ eV}
Hydrogen Intercalation

Buffer Layer (BL) → Quasi-free standing monolayer graphene (QFMLG)

Buffer Layer

SiC

ML

SiC

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 island growth

Thermal desorption spectroscopy

- Deposition of different amounts of Titanium
- Offering Hydrogen ($D_2$)
- ($1 \times 10^{-7}$ 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

\[ \text{Strong Ionic Character} \]

\[ \text{Weak Ionic Character} \]

\[ \text{Physisorption} \]

Forming of Islands

100 nm, 1 V, 82 pA

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. Stampfl¹,⁷

DCV = Double Carbon Vacancy

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

Distribution of defects

Average number of induced defects per 100nm$^2$

Average Number of Islands per 100 nm$^2$


Sputtered 150 s and Deposition of 0.5 ML Titanium
Estimated gravimetric density: 0.5% - 0.75%

Estimated gravimetric density: 1.8% - 2.4%

Higher number of defects leads to smaller Ti islands.

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**: $\Delta T \approx 0.01$ K

<table>
<thead>
<tr>
<th>Ti (ML)</th>
<th>$E_a$/molecule (eV)</th>
<th>$H_r$ (μJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>TDS</td>
</tr>
<tr>
<td>$G3(1)$</td>
<td>12.4</td>
<td>1.32 ± 0.07</td>
</tr>
<tr>
<td>$G3(2)$</td>
<td>16.6</td>
<td>1.24 ± 0.09</td>
</tr>
</tbody>
</table>

Calorimetric results summary

STM image of SLG on gold

Thermal signal during Hydrogen loading. Ti coverage 100%, $P(D_2) = 10^{-7}$ mbar

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Li on Graphene: Motivation

Hydrogen Storage


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.
LEED

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

Features related to Li deposition

- 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**

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

**0.047 ML Li**

- Features related to Li deposition
- From atomically resolved STM: graphene in surface (no Li cluster at the surface)
- Li intercalation (QFB LG)
- 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.
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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)

[Diagram showing Li, buffer layer, SiC, QFMLG, BL, with measured distances 4.92±0.28 Å, 2.6±0.2 Å, 2.32±0.08 Å.]

(b)

[Diagram showing Li, buffer layer, SiC, QFBLG, EMLG, with measured distances 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.]

Measured data □  Literature data □  Obtained data □

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