Prospects for Hydrogen Storage in Graphene

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Outline

• The NEST lab in Pisa
• Introduction to Hydrogen Storage
• Epitaxial Graphene
• Hydrogen Storage by Corrugation (Chemisorption)
• Hydrogen Storage by Functionalization (Physisorption)
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NEST Pisa

National Enterprise for nanoScience and nanoTechnology

NEST is an interdisciplinary research and training centre where physicists, chemists and biologists investigate scientific issues at the nanoscale.
Research themes @ NEST Pisa

NanoPhysics
1. Quantum transport and phase coherent effects in superconductors
2. Physics of low-dimensional semiconductor systems
3. Graphene (Flagship)

Advanced Photonics
4. Intersubband polaritonics
5. Silicon-Germanium optoelectronics
6. THz photonics
7. OptoElectronics Materials: from nanoscale to bulk single crystals

NanoBioScience
8. Visualizing brain function and structure in the living mouse
9. Lab-on-a-chip technologies
10. Nanoscale and single-molecule spectroscopy and imaging of soft matter
NEST Pisa
NEST Pisa
NEST facilities

• UHV STM
  – 1 VT and 1 LT

S. Goler et al., arXiv:1111.4918v1
NEST facilities

- UHV STM
- Graphene Growth
NEST facilities

- UHV STM
- Graphene Growth
- Micro-Raman
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- SEM
- Theory
Research Activities

The physics of low-dimensional systems. This includes three aspects: (i) the synthesis of nanostructures, (ii) the manipulation of samples on the nanometer-scale, and (iii) their characterization with spatially resolved spectroscopic techniques.
Surface Science & Magneto-Transport

UHV-VT-STM

Scanning Gate Microscopy
300 mK, 9 T

UHV-LT-STM
Projects

GRAPHENE FLAGSHIP
Graphene for Hydrogen Storage

erc
Phosphorene

G. Gervais, Mc Gill University, Montreal, Canada
2D Materials

S. Suzuki, NTT
High-mobility Graphene
Recent Activities

• SGM on QPCs in III-V 2DEGS
• Magneto-transport in Graphene
• Hydrogenated Graphene
• Hydrogen Storage in Graphene
• Phosphorene
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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-fuelled vehicles
Hydrogen-fuelled vehicles

Fuel Cell Vehicle

A vehicle running on hydrogen

National Enterprise for nanoScience and nanoTechnology
Hydrogen & energy

As a **fuel**, hydrogen has advantages:

- Highest energy-to-mass ratio
- \( \text{H}_2 + 1/2 \text{O}_2 \rightarrow \text{H}_2\text{O} \quad \Delta H = -2.96 \text{eV} \)
- Non-toxic and “clean” (product = water)
- Renewable, unlimited resource
- Reduction in \( \text{CO}_2 \) 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 Storage

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

**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
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
H storage in graphene

- Atomic hydrogen chemisorption has a small or negligible chemisorption barrier ⇒ feasible but H\textsubscript{2} must be cracked.

- Physisorption weakly bounds hydrogen ⇒ acceptable storage densities only at low temperatures and/or high pressure.

- Molecular hydrogen chemi(de)sorption has high barrier (theoretical estimate ~eV) ⇒ chemisorbed H is stable for transportation etc, but catalytic mechanisms are necessary in the loading-release phases.
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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 sp$^3$ C-Si bonds.

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

Buffer Layer

Bias: +1.7V
Current: 0.3nA

$6\sqrt{3} \times 6\sqrt{3}$ quasi-(6x6)

FIG. 2. (Color online) Total charge density of the buffer layer on SiC(001). (a) total charge density in the 6R3-SiC unit cell. (b) cross section of the total charge density along the line defined in (a). The black dots that appear when the cross section goes through the middle of an atom are due to the use of pseudopotentials (no core electrons).


6$\sqrt{3}$x6$\sqrt{3}$-Superstructure

30 nm, 1V, 100 pA

E = 75 eV
Monolayer Graphene

STM

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Graphene Curvature

- Exploit graphene curvature for hydrogen storage at room temperature and pressure

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- Exploit graphene curvature for hydrogen storage at room temperature and pressure
- The hydrogen binding energy on graphene is strongly dependent on local curvature and it is larger on convex parts
- Atomic hydrogen spontaneously sticks on convex parts; inverting curvature H is expelled

H-dimers and tetramers

Para-dimer
Ortho-dimer
Tetramer

STS after hydrogenation

H adsorption and desorption

RMS roughness

DFT calculations

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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

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 should reduce the mobility of Ti-atoms and lead to more and smaller islands.

Raman

Distribution of defects

Average number of induced defects per 100nm²

Average Number of Islands per 100 nm²

Average diameter of individual Ti-Islands

“Active” 3D-surface per 100nm²

Increase by factor \(\sim 4\)

Increase in active surface

• The fraction \( r \) of surface Ti atoms to Ti atoms in the bulk increases.

• The ratio \( r_{Ti-G} \) of Ti surface to graphene surface increases.

• Larger islands are 2 – 3 layers high: \( r \sim 0.3 – 0.5 \).

• Small islands are of monolayer height: \( r = 1 \).

“Active” 3D-surface per 100nm²

![Graph showing the relationship between total island surface (nm²) and sputter energy (eV). The graph includes data points and error bars, with annotations indicating the range $r_{Ti-G} \sim 0.15 - 0.2$ and $r_{Ti-G} \sim 0.55$.](image)

Hydrogen Uptake

- We assume $n_{H2} = 1$ H$_2$ molecule per Ti surface atom.
- Agrees within factor 2.5 with estimate from TDS experiment ($n_{H2} = 0.4$).

Gravimetric Density

- GD = $M_H / (M_{Ti} + M_G + M_H)$
- Small islands ($r = 1$ and $r_{Ti-G} = 0.55$): GD ~ 1.8%.
- With $r_{Ti-G} = 1$: GD ~ 2.4%.
- Larger islands ($r = 0.15 – 0.2$ and $r_{Ti-G} = 0.3 – 0.5$): GD ~ 0.5 – 0.75%.
- Reducing island size further ($n_{H2} = 4$), GD = 7% seems feasible.
Conclusions

• Graphene is a promising material for hydrogen storage

• Curvature-dependent adsorption and desorption of hydrogen
  – reusable hydrogen storage devices that do not depend on
    temperature or pressure changes.

• Graphene functionalized by Ti:
  – Stability of hydrogen binding at room temperature
  – Hydrogen desorbes at moderate temperatures
  – Modifying the size and distribution of Islands by sputtering and
    increasing the active surface
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