Functionalization of 3D Graphene with Metal Nanoparticles: Perspectives for Hydrogen Storage

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Sustainable Renewable Energy

- Solar energy
- Wind energy
- Hydraulic energy

Hydrogen Economy

- Decarbonization → Renewable Energy Sources
- Renewable sources are intermittent → Energy storage
- Chemical energy storage under form of Hydrogen → Hydrogen storage
Graphene

• First 2D material discovered
• Carbon allotrope

• Astonishing properties
  ▪ High specific surface area (2630 m²/g)
  ▪ High strength (~ $10^3$ times more than Steel or Kevlar)
  ▪ High charge carriers mobility
    (~200000 cm²/Vs)
  ▪ High conductivity both electric and thermal
    (up to $\sigma \sim \frac{\text{MS}}{\text{m}}$ and $\kappa \sim 4000 \frac{\text{W}}{\text{mK}}$)
  ▪ Linear band dispersion at K and K’ points
Why 3D?

• The adsorption of 1 mg of $H_2$ on monolayer graphene would need ~260 m$^2$ of graphene

• For fit large area into a small volume the 3$^\text{rd}$ dimension is needed

→ 3D Graphene
Porous Silicon Carbide

- New 3D Carbon-based material
- Electrochemically porousified Silicon Carbide (SiC) wafer

- Metal Assisted Photochemical Etching (MAPCE)
- PhotoElectroChemical Etching (PECE)

Graphenization of the SiC porous structure via thermal decomposition at 1650 K under Ultra High Vacuum condition

- 200 times more available surface

- Raman spectroscopy
  - High quality graphene

3D Graphene – New Generation

- New etching procedure: MAPCE → PECE → MAPCE
- Same graphene growth condition
- High quality Graphene
New vs. 1\textsuperscript{st} Gen.

Large improvement in the graphene \textit{homogeneity}, \textit{quality} and \textit{quantity} along the porous layer.
**New Gen. – Hydrogen Storage**

**TDS measurements**

- **\( \alpha \) and **\( \beta \)** peaks
  - 216°C and 314°C (1.2 and 1.5 eV)
  - Only upon D exposure

- **\( \gamma \) and **\( \delta \)** peaks
  - 535°C and 641°C (2.0 and 2.3 eV)
  - Catalytic splitting of D\(_2\)

- **P peak**
  - Physisorption
  - “Fast” delayed emission: from \( \tau \sim 15 \) min to \( \tau \sim 70 \) s

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New Gen. – Hydrogen Storage

Uptake Comparison

<table>
<thead>
<tr>
<th>Sample</th>
<th>Uptake - D$_2$</th>
<th>Uptake - D</th>
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<tbody>
<tr>
<td>1$^{st}$ gen.</td>
<td>$2 \cdot 10^{-12}$ mol</td>
<td>$7 \cdot 10^{-12}$ mol</td>
</tr>
<tr>
<td>New gen.</td>
<td>$3 \cdot 10^{-11}$ mol</td>
<td>$9 \cdot 10^{-11}$ mol</td>
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<td>$2 \cdot 10^{-10}$ mol</td>
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- Higher Temperature Degassing
  - Appearance of the X peak at 778°C (2.7eV)
  - Observed also after D$_2$ exposure
  - About 100 times higher uptake
3D Graphene – Metal Functionalization

- Gold NPs
  Water $\rightarrow$ Ethanol

- Gold 1.1
  - 1 drop of solution

- Gold 1.2
  - 3 drops of solution

- Gold 1.3
  - 45 min immersion under sonication

- Gold 1.4
  - 24h immersion
  - Surface NPs density, $\sigma \sim 4 \text{ NPs/}\mu\text{m}^2$
  - Pores NPs density, $\rho \sim 1.5 \text{ NPs/}\mu\text{m}^2$
AuNPs Functionalization

- AuNPs on New gen.
  - 24h immersion
  - $\sigma = 220 \pm 25 \text{ NPs/}\mu\text{m}^2$
  - $\rho = 15 \pm 1 \text{ NPs/}\mu\text{m}^2$
  - NPs high diffusion length

- Further experiments:
  - Longer immersion
  - Higher concentration
Palladium NPs 1\textsuperscript{st} Synthesis

- Palladium Acetate, Pd(OAc)$_2$, in Sodium Dodecyl Sulphate, SDS, refluxed at 100°C under magnetic stirring → SDS-PdNPs
- NPs collection by ultra-high speed centrifugation
- NPs dispersion in ethanol
- AFM measurements
  - Monodispersed NPs
  - Tendency to cluster
SDS-PdNPs Functionalization

- Immersion in the SDS-PdNPs colloidal solution for 24h
- Successful functionalization
- NPs clustering
• Annealing from 350°C to 800°C
• 800°C needed to restore the chemisorption
• Lower temperature is needed for Physisorption
• 30 min $D_2$ exposure doesn’t lead to an uptake increase
  • “Fast” delayed emission
SDS-PdNP-Functionalized 3D Graphene – SEM/EDX

- SEM-EDX analysis
  - Clustering
- Amorphous carbon residuals
- Sulfur poisoning

Palladium NPs 2\textsuperscript{nd} Synthesis

- Palladium Acetate, Pd(OAc)$_2$, and Poly(NVinyl-2-Pyrrolidone), PVP, in Ethylene Glycol, EG, heated under magnetic stirring $\rightarrow$ PVP-PdNPs
- Smaller cap layer molecules $\rightarrow$ less amorphous carbon
- AFM measurements
  - Less monodispersed
  - Clustering is absent
PVP-PdNPs Functionalization

- Immersion in the PVP-PdNPs colloidal solution for 24h
- Successful functionalization
- No clusters
- Diffusion inside the pores
- Large amount of deposited Pd is confirmed by XPS
PVP-PdNP-Functionalized 3D Graphene – Hydrogen Storage

• Annealing from 600°C to 800°C

• Much larger chemisorption signal compared to SDS-NPs

• Physisorption less affected (uptake similar to pristine)
Pristine vs. Functionalized

- Compatible uptakes
- Spectral shape change
- Small reduction from $3 \times 10^{-11}$ mol to $2 \times 10^{-11}$ mol
- Appearance of a new peak at $118 \degree$ C (1 eV)

All Hydrogenation experiments were performed in a UHV chamber (Hydrogenation pressure $10^{-7}$ mbar)

- Palladium Hydride need $P > 10$ mbar (at RT)
- Spillover need high pressure to be effective (even tens of bar)

- High pressure experiments have to be performed

Main Results

- Large improvement in the 3D graphene homogeneity, quality and quantity along the porous layer

- 100 times larger uptake of molecular deuterium on 3D graphene

- Found an effective metal NP functionalization procedure (demonstrated both with Au and Pd, and which should apply for every metal)

- Found optimal condition for PdNP functionalization

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Outlook

• Ongoing studies
  • Higher pressure Hydrogenation experiments
  • Computational simulations
  • TEM measurements

• Possible applications
  • Supercapacitors
  • Surface Enhanced Raman Spectroscopy
  • Sensors (Hydrogen, Food, etc.)
Thank you for your attention!

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