FET Flagship Graphene

WP Energy (ramp-up phase)

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Scientific work packages

- WP1 Materials
- WP2 Health & Environment
- WP3 Fundamental science of graphene and 2D materials beyond graphene
- WP4 High Frequency Electronics
- WP5 Optoelectronics
- WP6 Spintronics
- WP7 Sensors
- WP8 Flexible Electronics
- WP9 Energy Applications
- WP10 Nanocomposites
- WP11 Production
In the 10-year perspective, this WP will develop and demonstrate the industrial potentials of key enabling graphene-based technologies for:

- Energy production systems: photovoltaics, fuel cells
- Energy storage systems: batteries, supercapacitors and hydrogen storage
Photovoltaics

Partners: CEA-Liten (CEA), Uni. Oxford (UOXF), Italian Institute of technology (IIT), Technological Education Institute of Crete (TEIC).

Criteria: conversion efficiency, €/Wp

- 3 technological routes privileged:
  - Inorganic thin film PV: chalcogenide, wet process (CEA).
  - Organic PV (TEIC)
  - QD cells (IIT)

- Integration of Graphene:
  - Electrodes (e- and hole extraction layers),
  - Absorber layer.

- Support optronic modelling (UOXF)
Photovoltaics

- Chalcogenide (CIGS, CZTS) wet processed solar cells

**Conventional process**
- TCO by sputtering
- CdS: chemical bath
- co-evaporation or sputtering
- Sputtering

**Innovative wet process**
- G-based electrode
- Cd-free buffer layer
- CIGS or CZTS* by wet process
- Sputtering

World record cell: PCE = **20.3%** in co-evaporation

* Cu$_2$ZnSn(S$_{1-x}$Se$_x$)$_4$ based solar cell produced by selenization of vacuum deposited precursors
Photovoltaics

- Organic solar cells: world record cell: $\eta \approx 9\%$ in single junction (visible)

Present issues

**ITO**: scarcity, lack of flexibility, poor transparency in Near Infrared.

**PEDOT:PSS**: acidic solution, unstable.

Novel GO reduction approach: TCO electrodes

Flexible OPV Cells with In Situ Non thermal Photoreduction of Spin-Coated Graphene Oxide Electrodes
Photovoltaics

- QD solar cells: tunable bandgaps for less thermalization losses

World record: PCE = 4.4% with ZnO / PbS QD heterojunctions.


Present issues

Extraction of photo-carriers difficult!

High rate of recombinations

Operating solar cells with QD-functionalized graphene as PV absorber:

QD = Cu_{2-x}S or Cu_{2-x}Se
Partners: Sabancy University (SU)

**Criteria:** catalyst utilization efficiency W/g.Pt, lifetime.

- 2 technological routes privileged:
  - Pre-functionalization of G-sheets: control the Pt/Pt alloy catalyst grafting
  - Graphene-based nanocomposites (WP10)

- Integration of Graphene
  - Single fuel cells for electrical characterization.
Proton Exchange Membrane Fuel Cells

- Use of functionalized G-sheets: better control of electrode surface area, conductivity, catalyst localization and water draining.

\[ \text{H}_2 \rightarrow 2\text{H}^+ + 2e^- \quad \frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O} \]

Present issues

- High Pt content (ink): \(-0.4\text{mg/cm}^2\)
- Only a few % Pt is effective


5kW/g.Pt (SoA~1kW/gPt)
Batteries

**Partners:** CEA-Liten (CEA), NOKIA.UKL, REPSOL (REP), Uni. Cambridge (UCAM), CIC Energygune (CIC).

**Criteria:** power density (kW/kg), energy density (Wh/kg), charging time, lifetime

- **3 technological routes:**
  - GO-based route for the coating of electrodes (CEA).
  - Graphene/nanocrystals electrodes (UCAM).
  - Flexible electrodes: CVD graphene-Cu foil and graphene ink processing (NOKIA).

- **Support characterisation activities**
  - NMR characterisation during battery operation (UCAM).
  - Conventional battery testing (REP, CIC, CEA).
  - Dynamic modelling for lifetime prediction (REP).
Li⁺ Batteries

- GO-based route for the coating of electrodes: charging time

**Statement:**

- Most electrode active materials suffer from a poor conductivity (LiFePO₄, LiMnPO₄, Si, Li₁₊ₓMₓO₂, where M=Mn, Ni, Co, ...)

- Carbon coating by high T°C pyrolysis of C-precursors under controlled atmosphere: energy demanding.

Optimize GO process implementation

Better control of G thickness and structure
Graphene/nanocrystals electrodes: lifetime.

**Statement:**
- Active materials suffer from huge volume changes during charging/discharging.
- Affect the cycle lifetime.

Use of nanocrystal-based hosting materials: Si for inst.

=> Requires nano-engineering

**Flagship approach**
- *Ex-situ* or *In-situ* growth of Si nCs between graphene layers.

- Porous FeOx ribbons grown on graphene (WP10)

Battery with much higher cycle lifetime: >1000

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**C-coated Si nCs**

**Granule made of Carbon interconnected Si nCs**

Work done at Georgia Tech. (2010)

~10µm
Supercapacitors

Partners: CIC Energygune (CIC), Thales (TRT), Uni. Cambridge (UCAM).

Criteria: power density (kW/kg) and energy density (Wh/kg)

- 2 technological routes for electrochemical double layer capacitors:
  - GO-based route for the development of cost effective synthesis of electrodes (CIC).
  - Mesoporous electrodes combining CNT and graphene (TRT).

- Support characterisation activities
  - NMR characterisation: charging mechanisms versus electrode microstructure (UCAM)
**Supercapacitors**

- GO-based route: Microwave process for cost effective synthesis of electrodes.

  **Objective:** maximize the surface area of carbon electrodes

  ![GO to a-MEGO process diagram]

  Conductivity = 270 S/m  
  Surface area ~500 m²/g

  (*) C ~190 F/g in KOH

  Target: >20 Wh/Kg

Mesoporous electrodes combining CNT and graphene

Conventional process:
✓ Electrode = activated carbon (high surface area).
✓ Very small pores (1 nm) not easily accessible to ions of electrolyte.

Innovative approach:
✓ Use of a composite electrode: graphene + CNT.
✓ Recently demonstrated*:
  • C = 290F/g in aqueous electrolyte.
  • Energy density = 62Wh/Kg
  • Power density = 58.5kW/Kg.

Hydrogen storage

Partners: CNR Pisa, Uni. Umea, Technical Uni. Dresden (TUDr), Bruno Kessler Foundation (FBK)

Criteria: storage capacity (Kg/m$^3$) and density (Wt%), ease of uptake/release of H$_2$

- 3 technological routes for the hosting material:
  - Decorated graphene with metal ad-atoms or molecular groups (FBK, UMEA, TUDr).
  - Intercalated multilayered graphene (UMEA).
  - Curved graphene sheets (CNR, UMEA).

- Support activities
  - Modelling studies: interaction G-H2 with/without interlayer metal spacers, H2 storage capacity vs G-functionalization, etc… (CNR, TUDr)
  - Preliminary integration studies: testing tank (FBK).
Hydrogen storage

- Decorated graphene with metal ad-atoms or molecular groups
  - Tuning of surface kinetics of ad- and de-sorption reactions (H2-H spill-over process)

Modify graphene with various chemical species, such as Calcium or transition metals (Titanium) or Nitrogen

Capacity up to 5-9 wt%

Target: 3% wt% at RT
Hydrogen storage

- Curved graphene sheets
- Control H2 uptake/release via graphene curvature

* Change with curvature of H binding E on graphene (modelling)

Thank you for your attention