NEO-Energy
Novel Energy-Oriented Materials

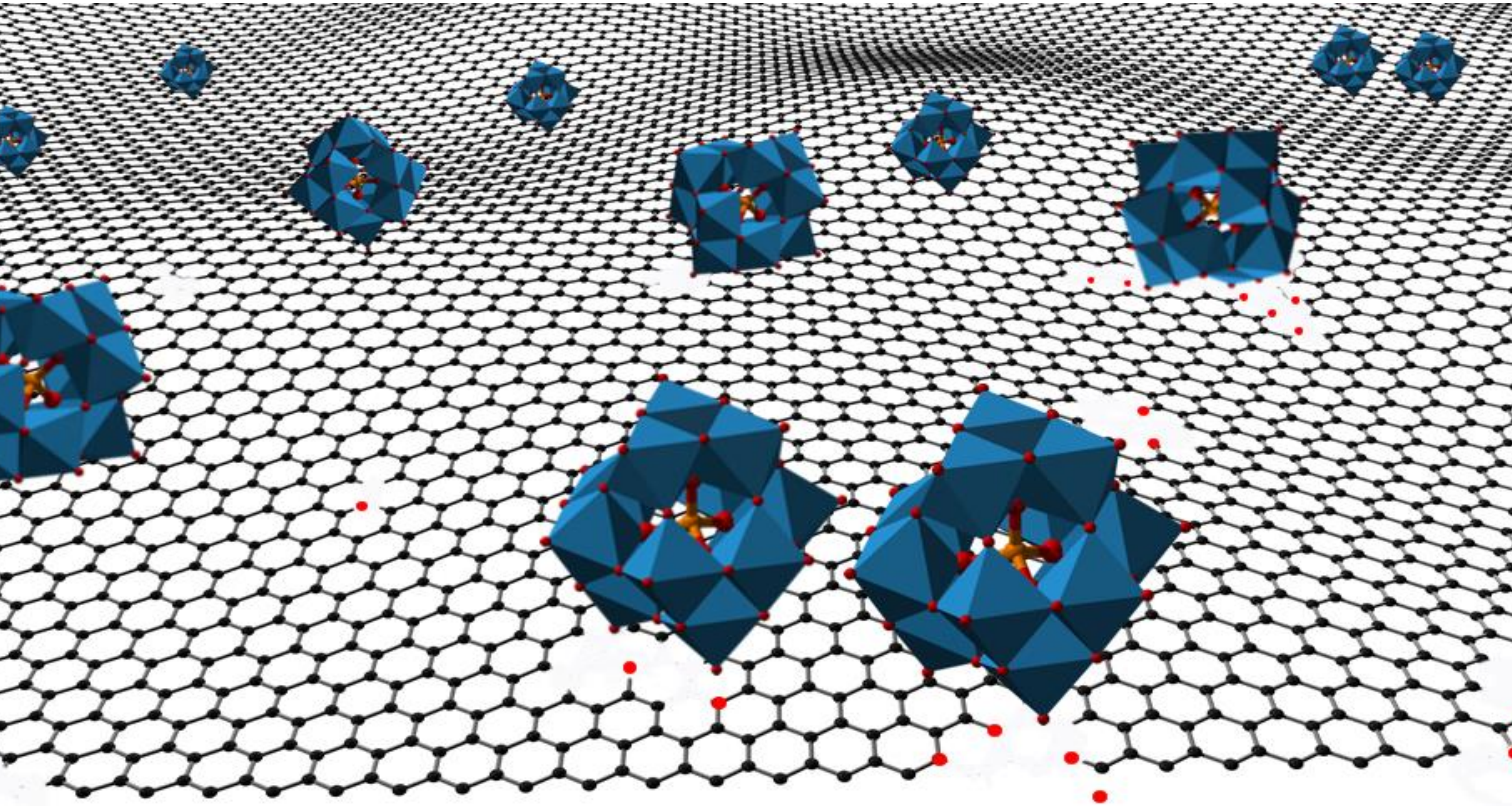
Prof. Pedro Gómez-Romero

Institut Català de Nanociència i Nanotecnologia

EXCELENCIA SEVERO OCHOA

CSIC

# What could be better than graphene for energy storage



# The new Energy Landscape

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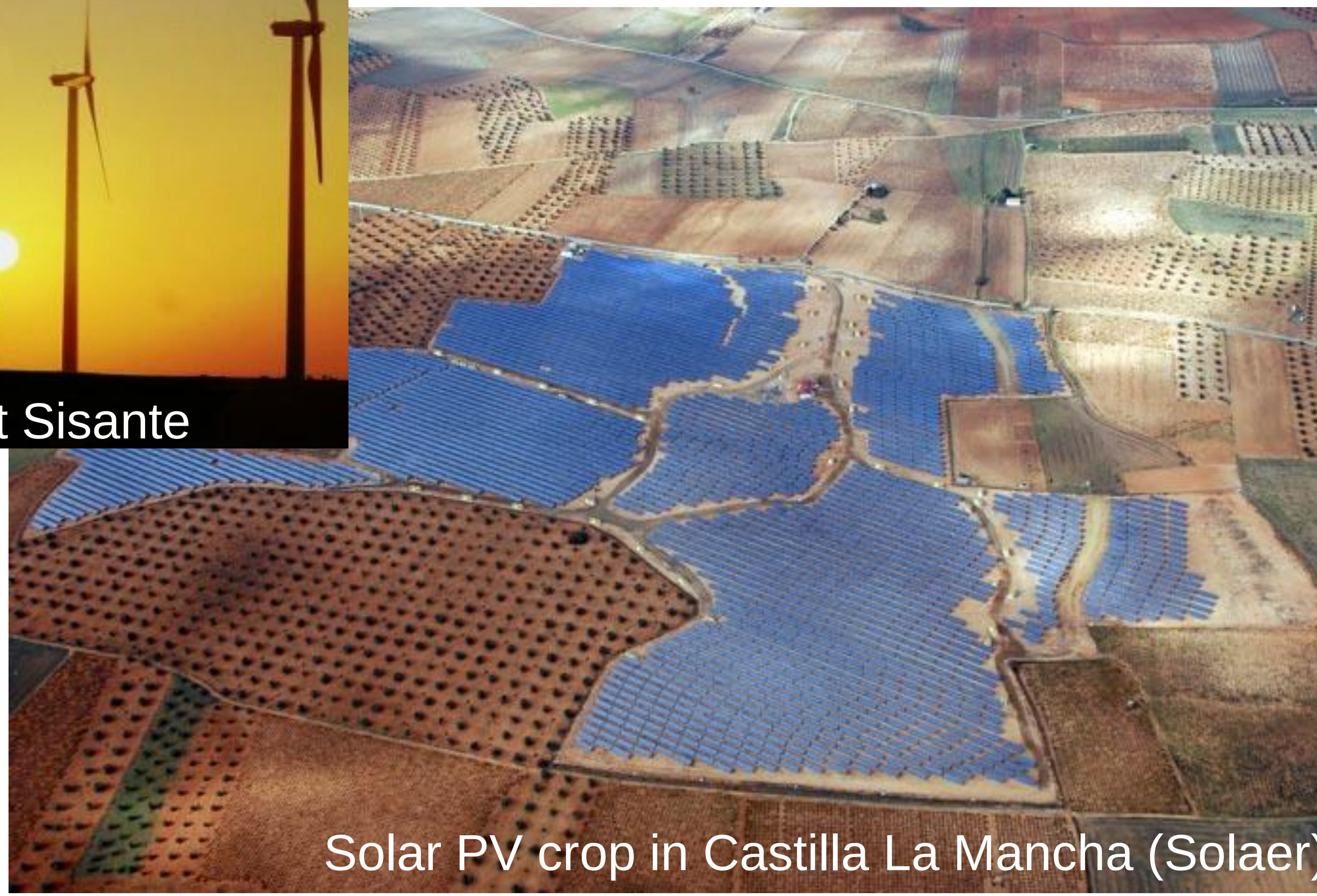
Wind power at Sisante
La Mancha
Spain

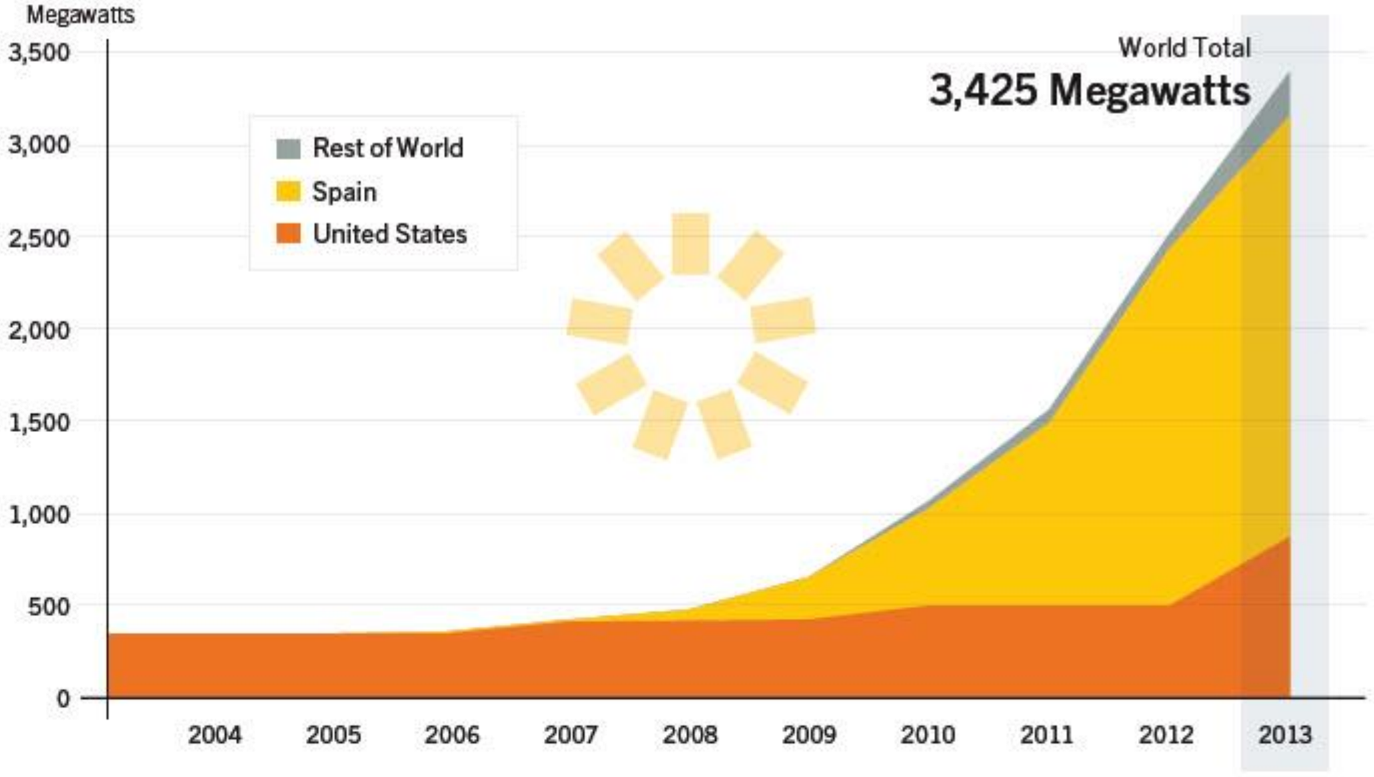


Solar PV crop in Castilla La Mancha (Solaer)

# The new Energy Landscape

Pioneer thermosolar power plant. Sanlucar (Sevilla) Spain (Abengoa)

# Spain, the largest thermosolar power.




http://cleanleap.com/02-market-and-industry-trends/concentrating-solar-thermal-power-csp

# The new Energy Landscape

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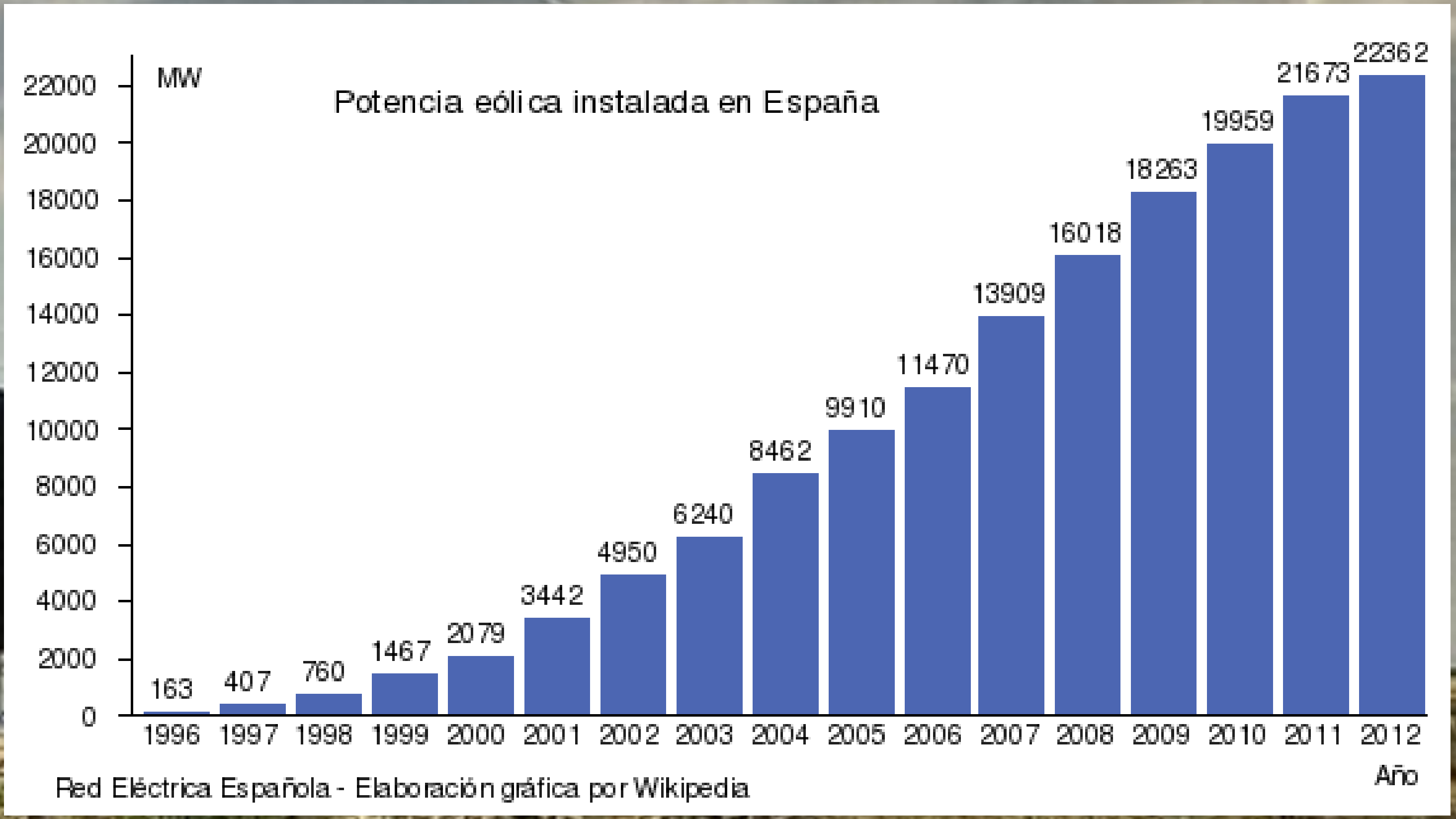

# Renewable electricity in Spain (%)

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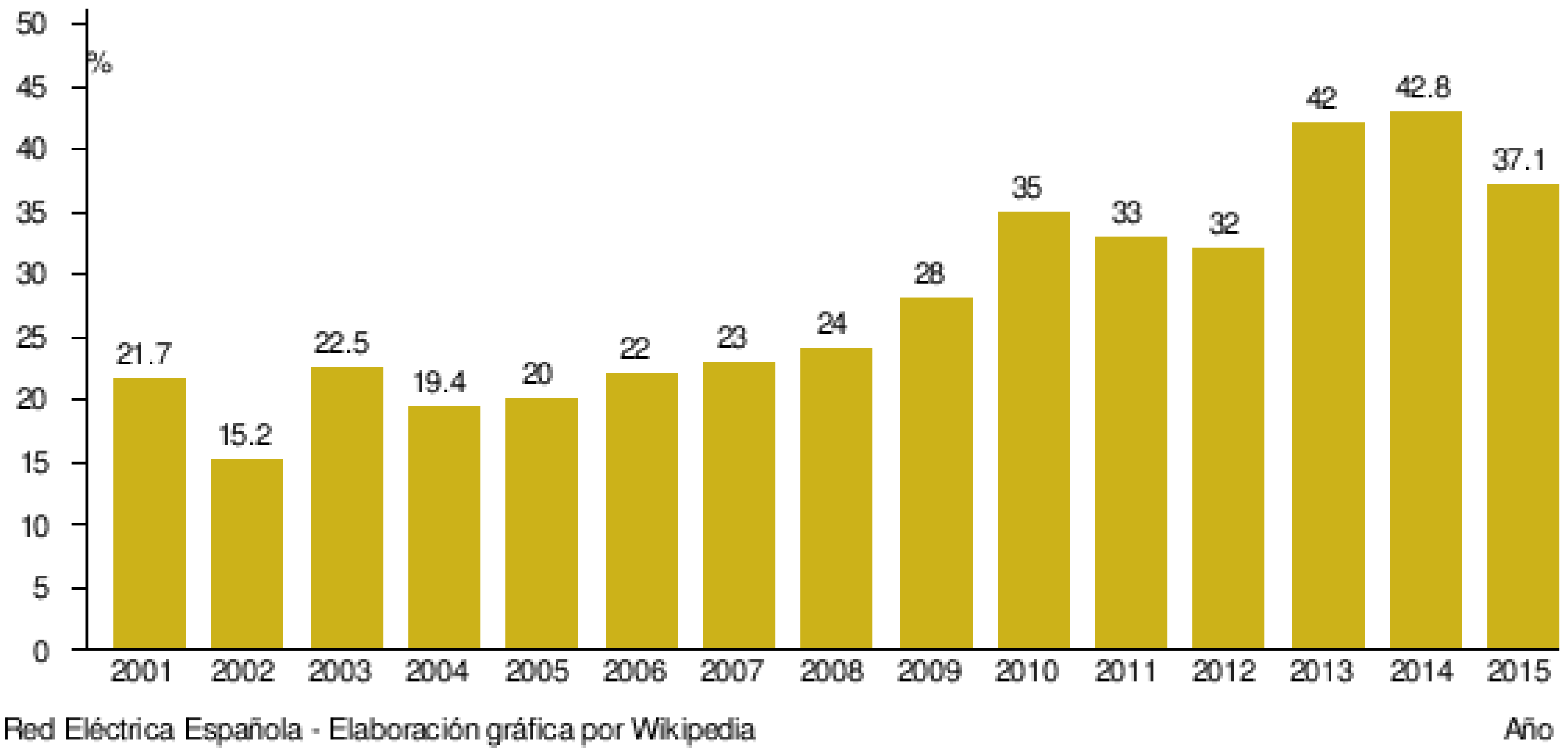
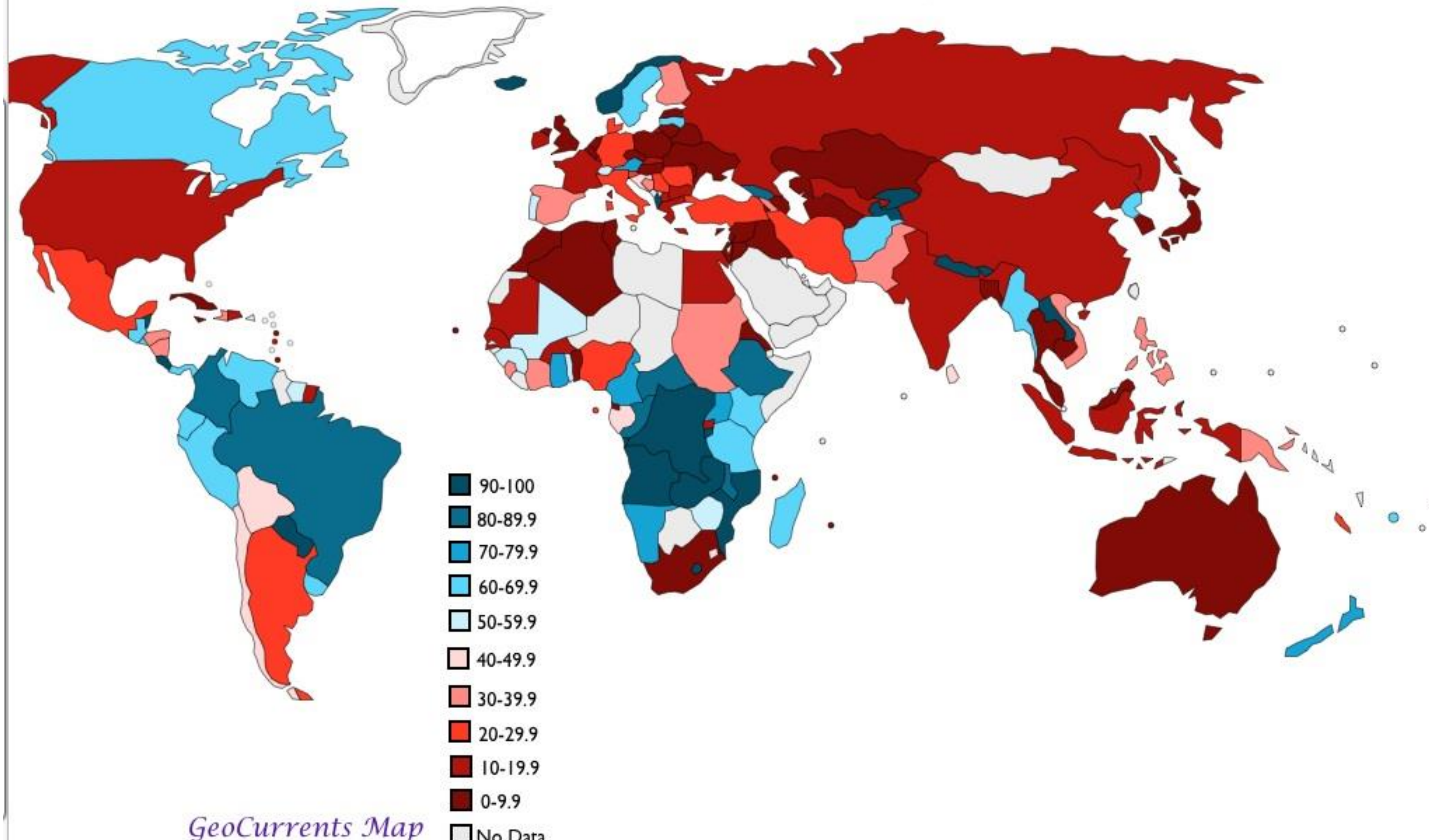


# Percentage of Electricity Generation from Renewable Sources

(Hydro, Geothermal, Solar, Biomass, Wind)




Data Source: http://en.wikipedia.org/wiki/List_of_countries_by_electricity_production_from_renewable_sources

# *pros* and cons of renewable energies

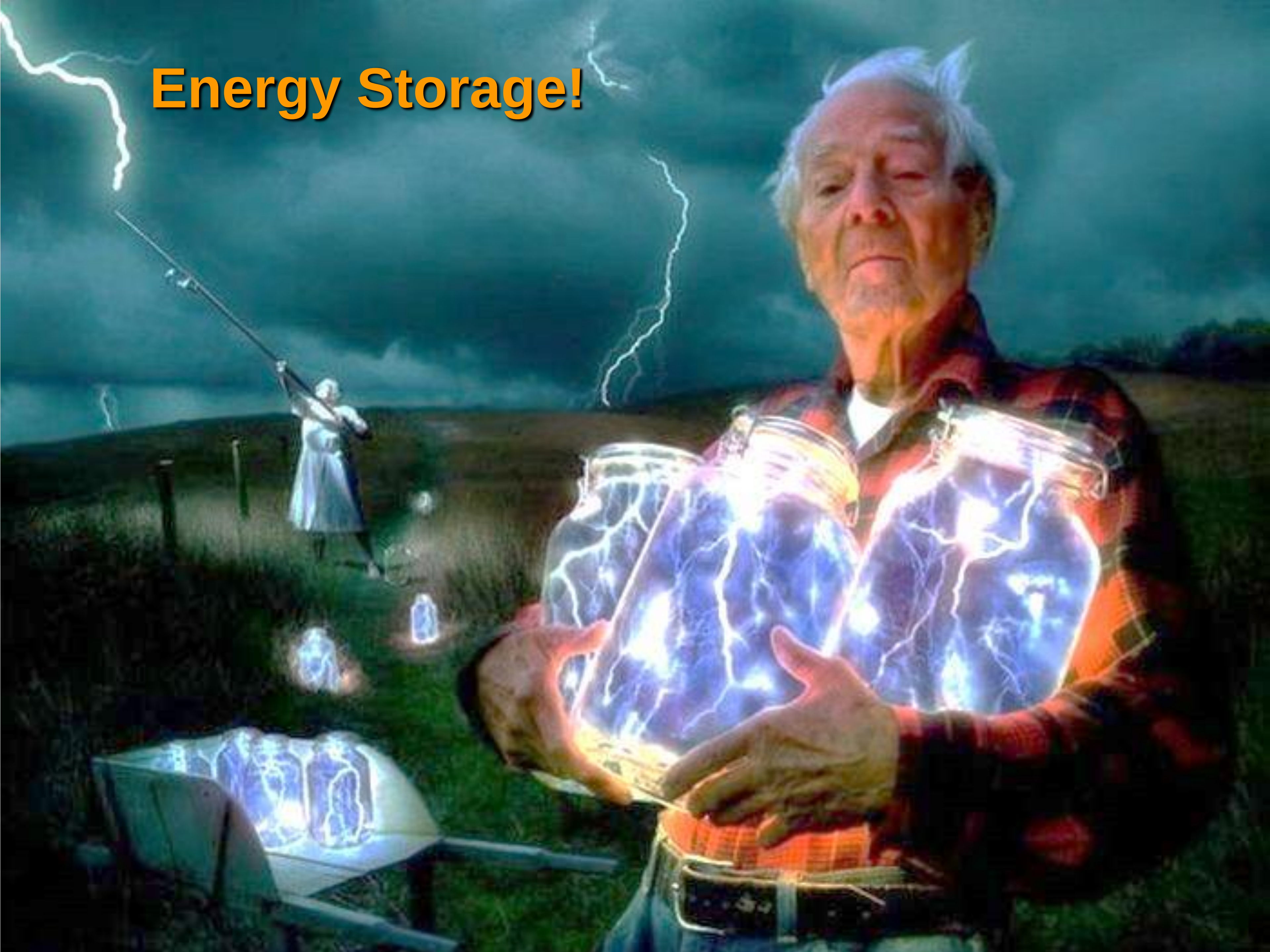
## cons

| | |
|---|---|
| Solar | Does NOT work at night |
| Wind | Does NOT work in the absence of wind |

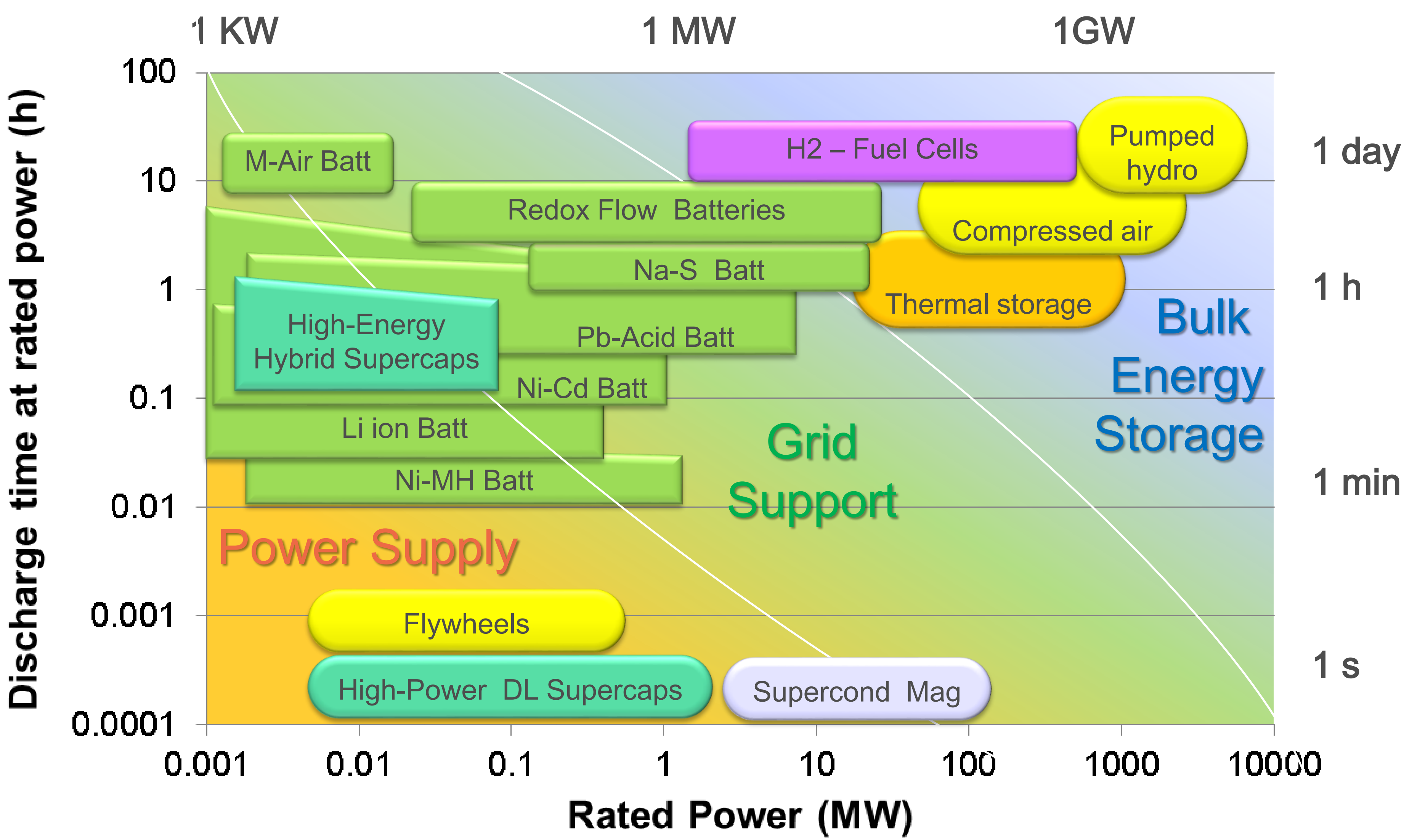
## pros

| | |
|---|---|
| Solar | It DOES work in the absence of wind |
| Wind | It DOES work at night |

# Energy Storage!



# Energy storage systems



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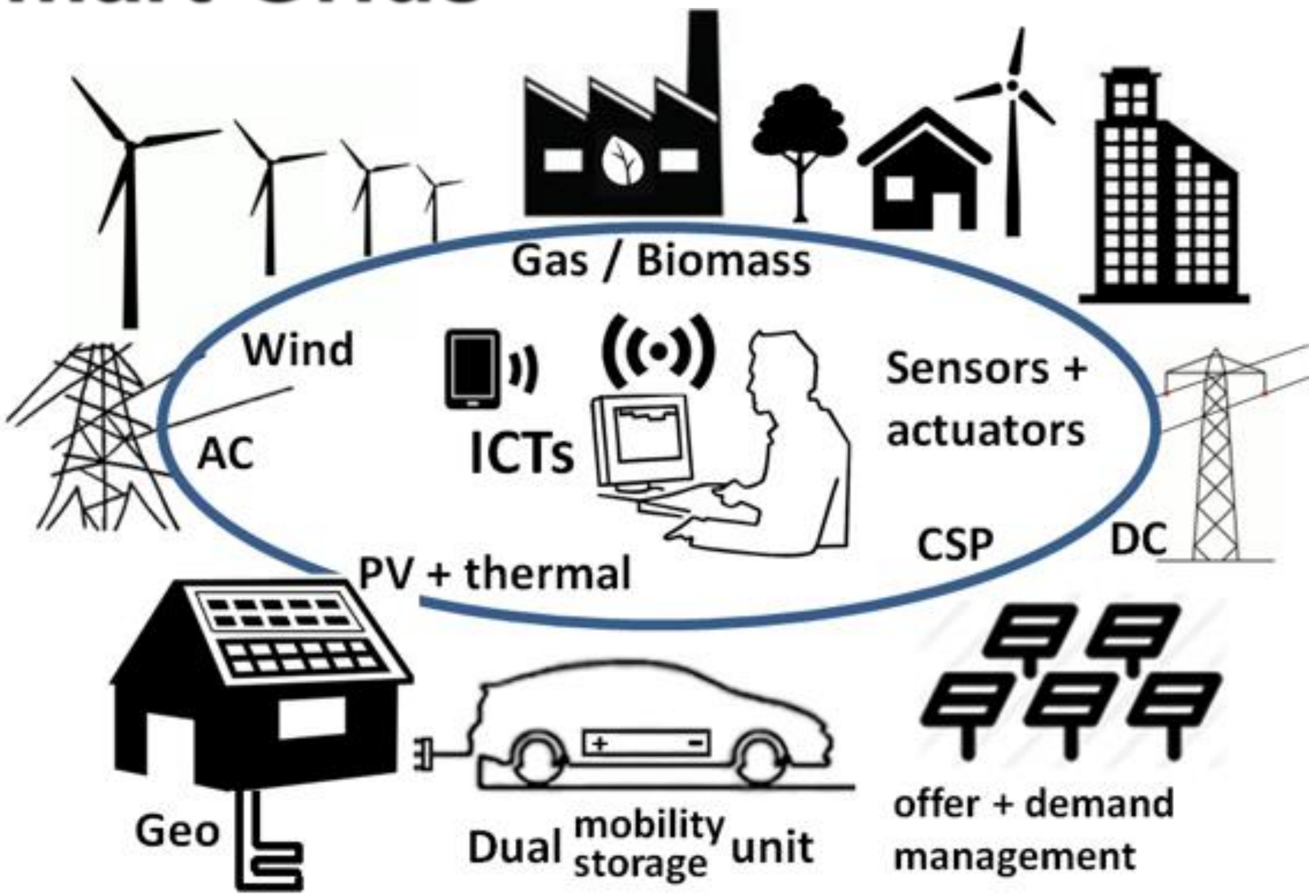
# Energy storage in transition

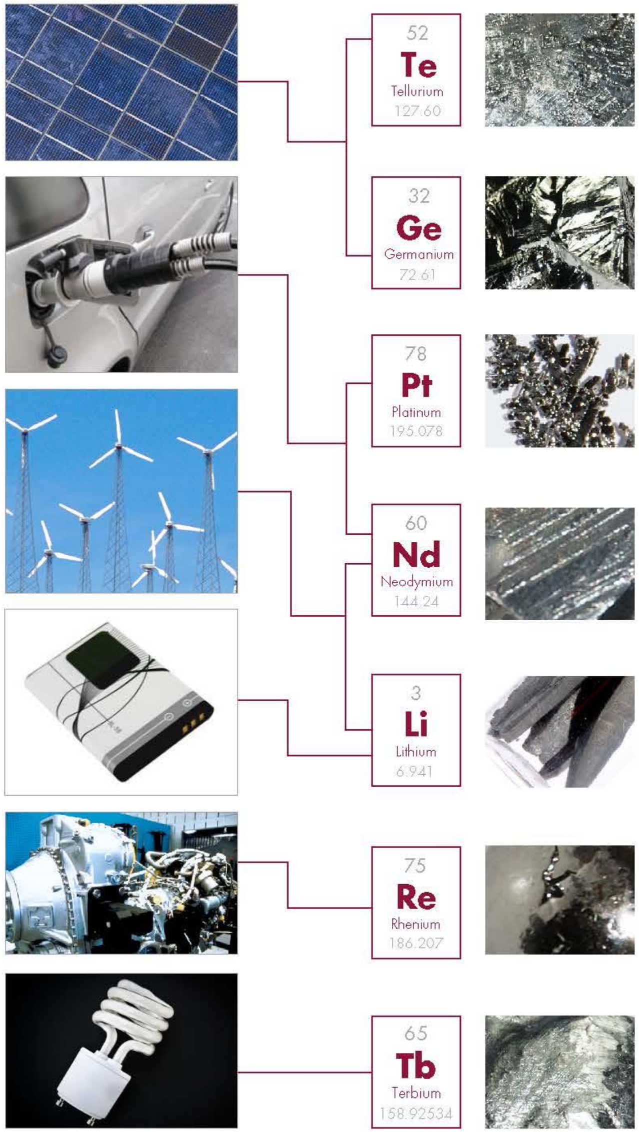

PLUG-IN
HYBRID

# Centralized AND Distributed Energy

## Smart Grids



# Energy Critical Elements




**TELLURIUM**—brittle, silvery-white metallic element used in solar panels

**GERMANIUM**— hard, grayish-white element with metallic luster; used in solar panels

**PLATINUM**—silvery-white, lustrous, ductile and malleable; used in pollution control devices for cars, and in fuel cells

**NEODYMIUM**—bright, silvery rare-earth metal element; used in wind turbines and hybrid cars

**LITHIUM**—a soft, silver-white metallic element; used in wind turbines and lithium-ion batteries in hybrid cars

**RHENIUM**—silvery-white metal with one of the highest melting points of all elements; used to make advanced turbines and jet engine parts

**TERBIUM**—a soft, silvery-white rare earth metal; used along with its fellow rare earth europium in compact fluorescent light bulbs to provide an acceptable color balance

# ALIEN, our future material(s)

**A**bundant

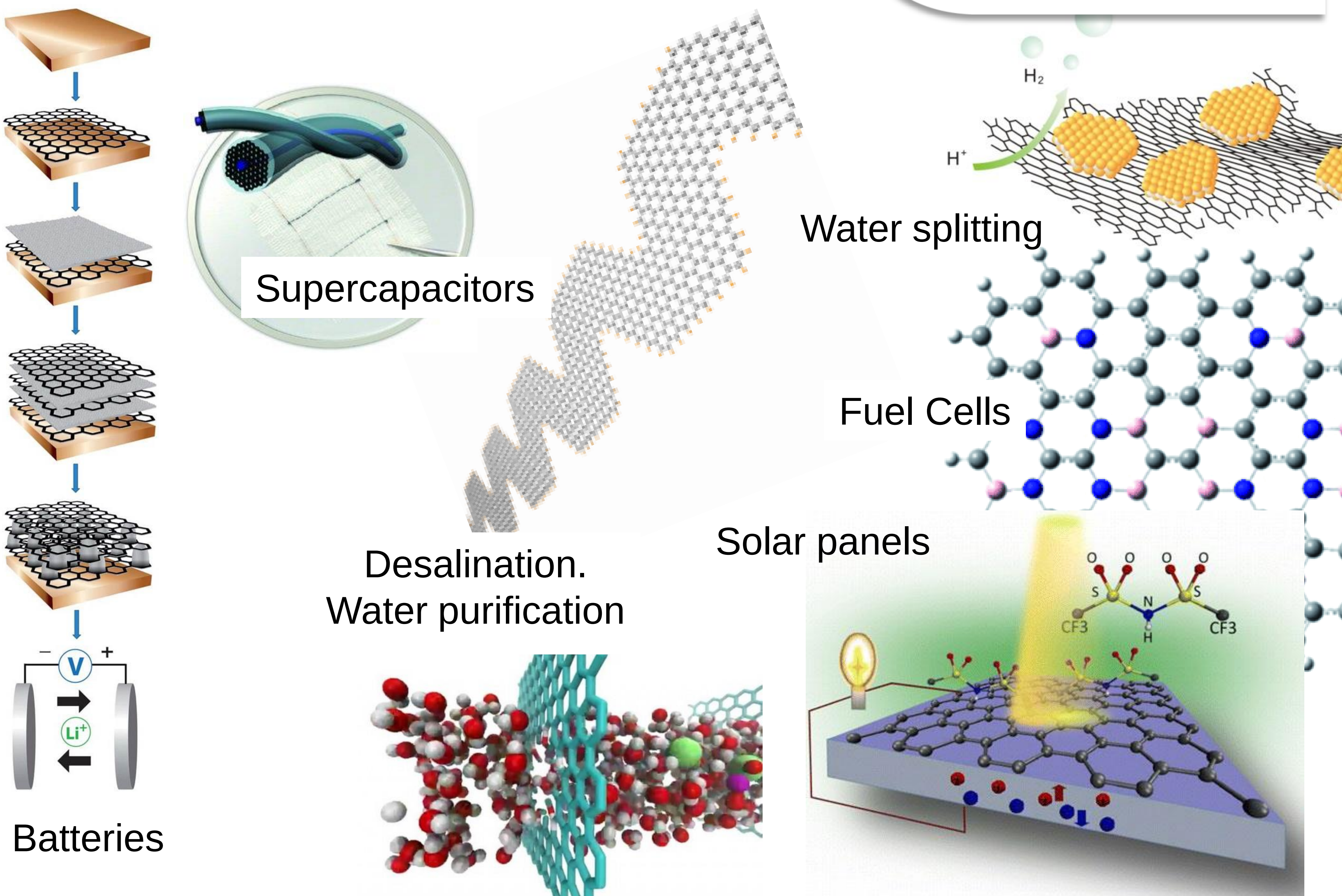
**L**ower costs

**I** mproved performance

**E**nvironmentally friendly

**N**ew props tricks and apps

# Graphene for a sustainable society

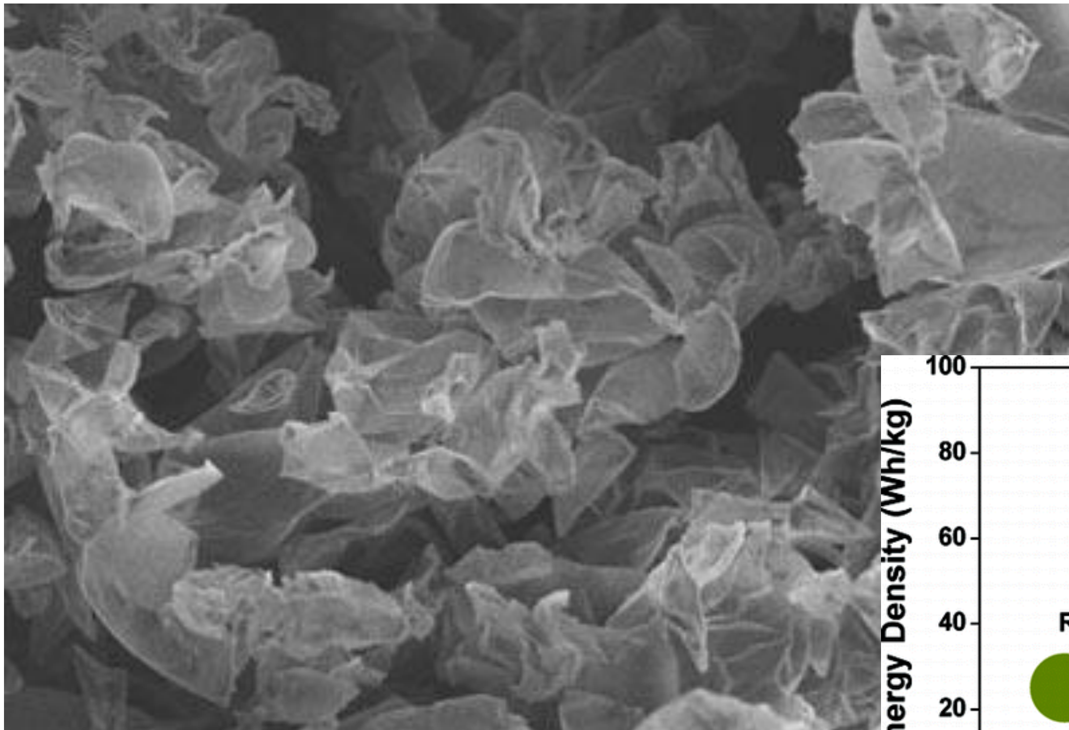


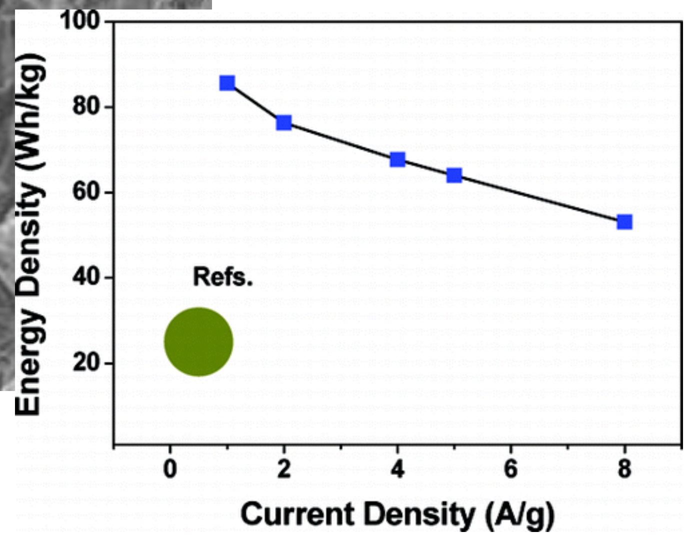
# What could be better than

# Graphene

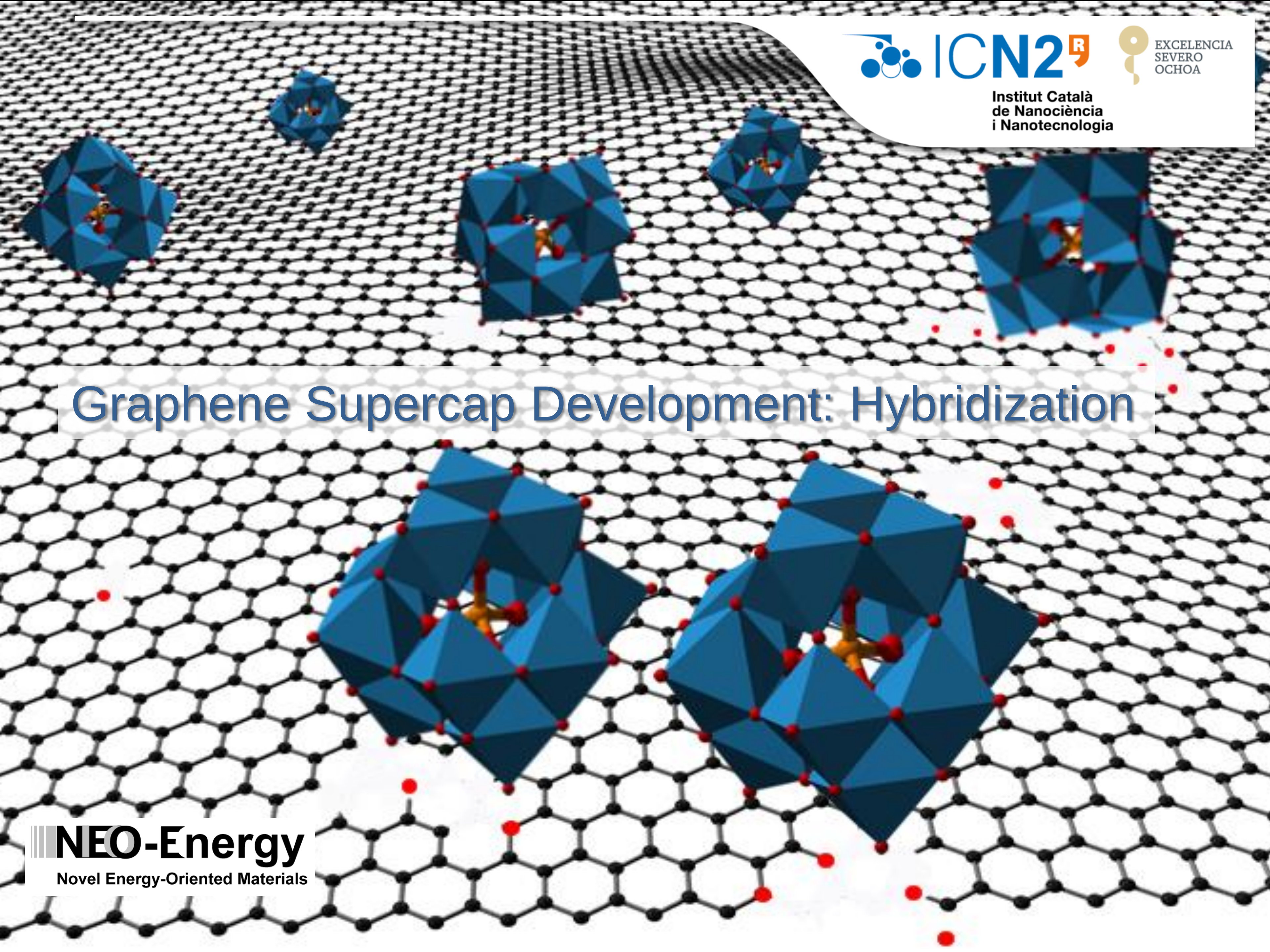
- Light as plastic
- Harder than diamond
- Stronger than steel
- Conducting like metals
- Transparent like glass
- As simple as carbon

# Graphene Supercap Development: Microstructure






*Chenguang Liu, Zhenning Yu, David Neff, Aruna Zhamu, and Bor Z. Jang**
*Nano Lett.*, 2010, 10 (12), pp 4863–4868



# Graphene Supercap Development: Hybridization

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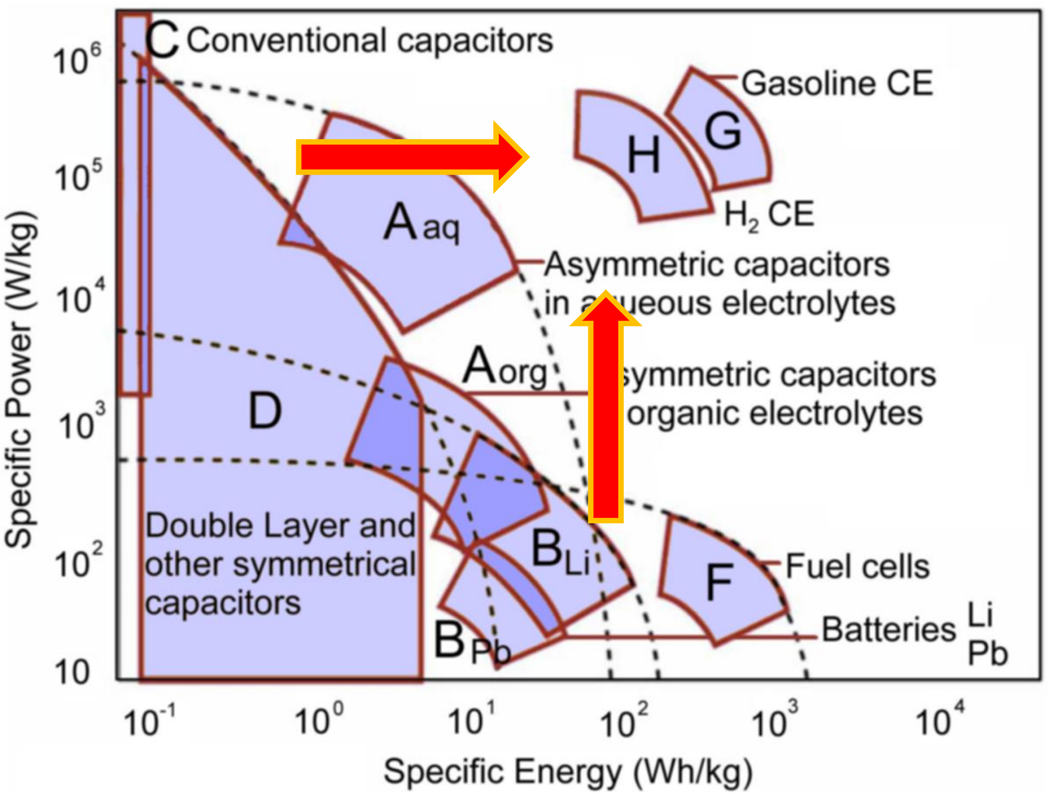
# Energy storage: Power vs. Energy densities




Hybrid Energy Storage. The merging of battery and supercapacitor chemistries.
D. P. Dubal, O. Ayyad, V. Ruiz, and P. Gomez-Romero* Chem.Soc.Rev. 44(7):1777-90 **2015**

# Supercapacitors applications

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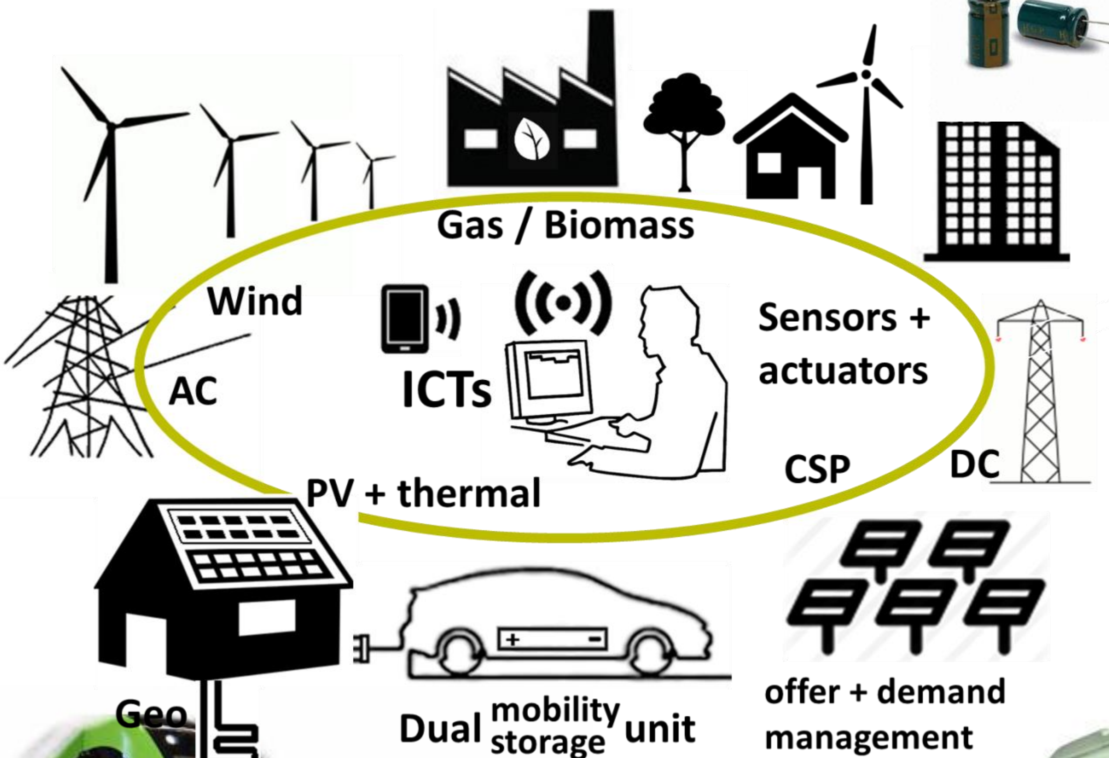
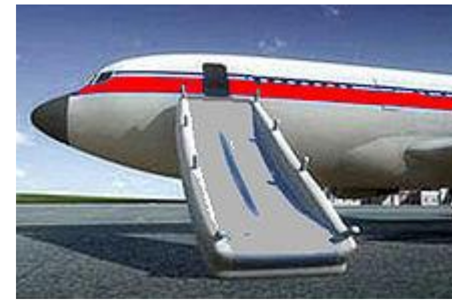


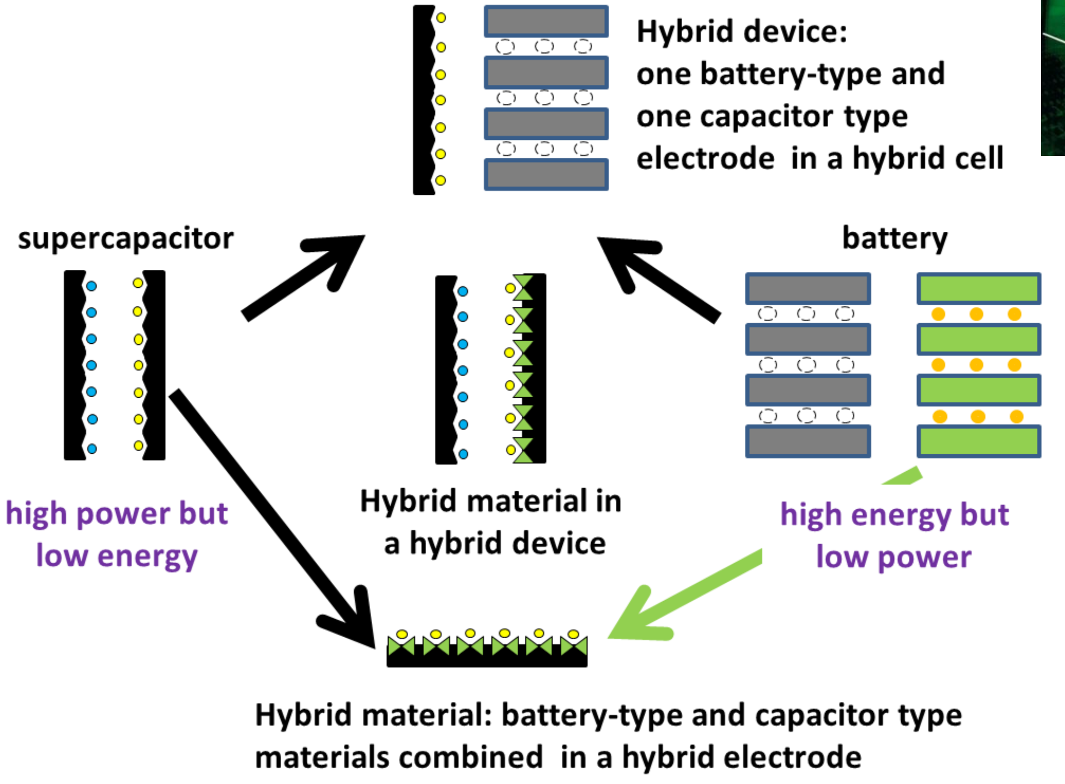

# Hybrid approaches

Hybrid devices

Hybrid electrodes

Hybrid materials

# possible hybridization approaches between supercapacitor and battery electrodes and materials.




Hybrid Energy Storage. The merging of battery and supercapacitor chemistries.
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# Hybrid materials

organic inorganic

dissimilar components
Integrated at the molecular level

opportunity for synergy

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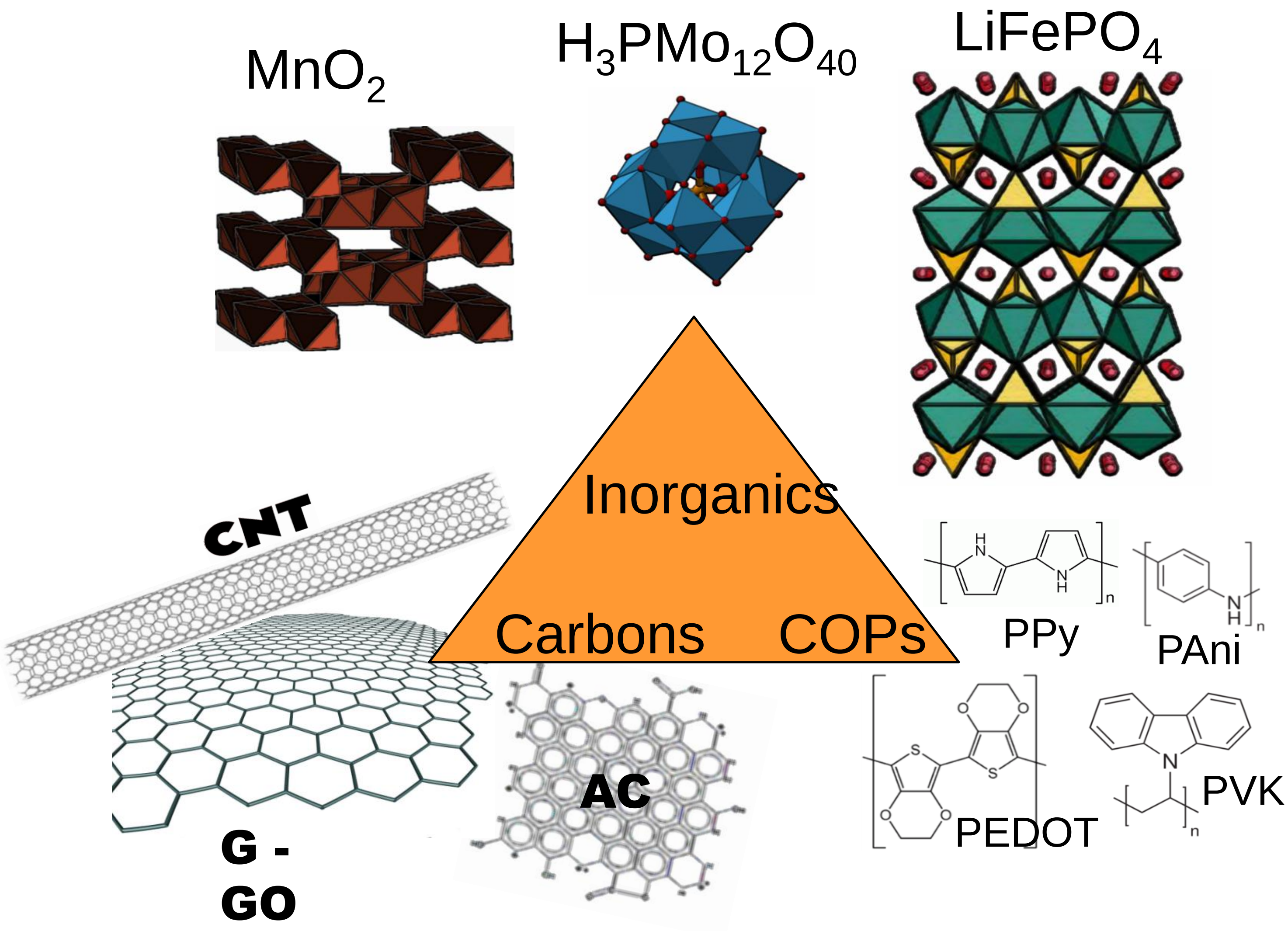
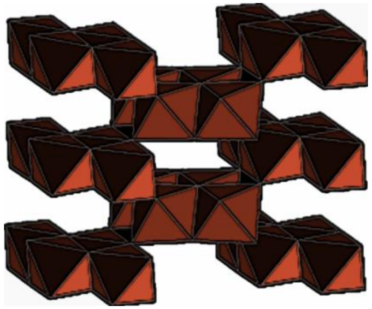
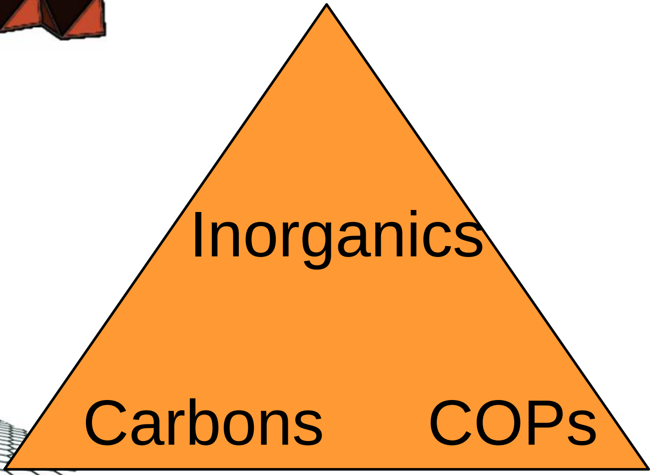
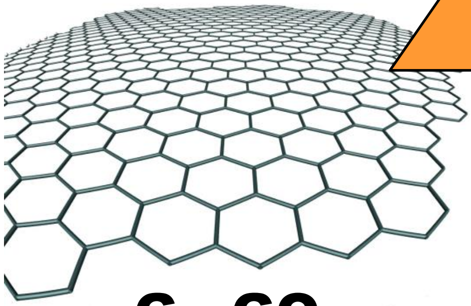
# Our window to the hybrid material landscape



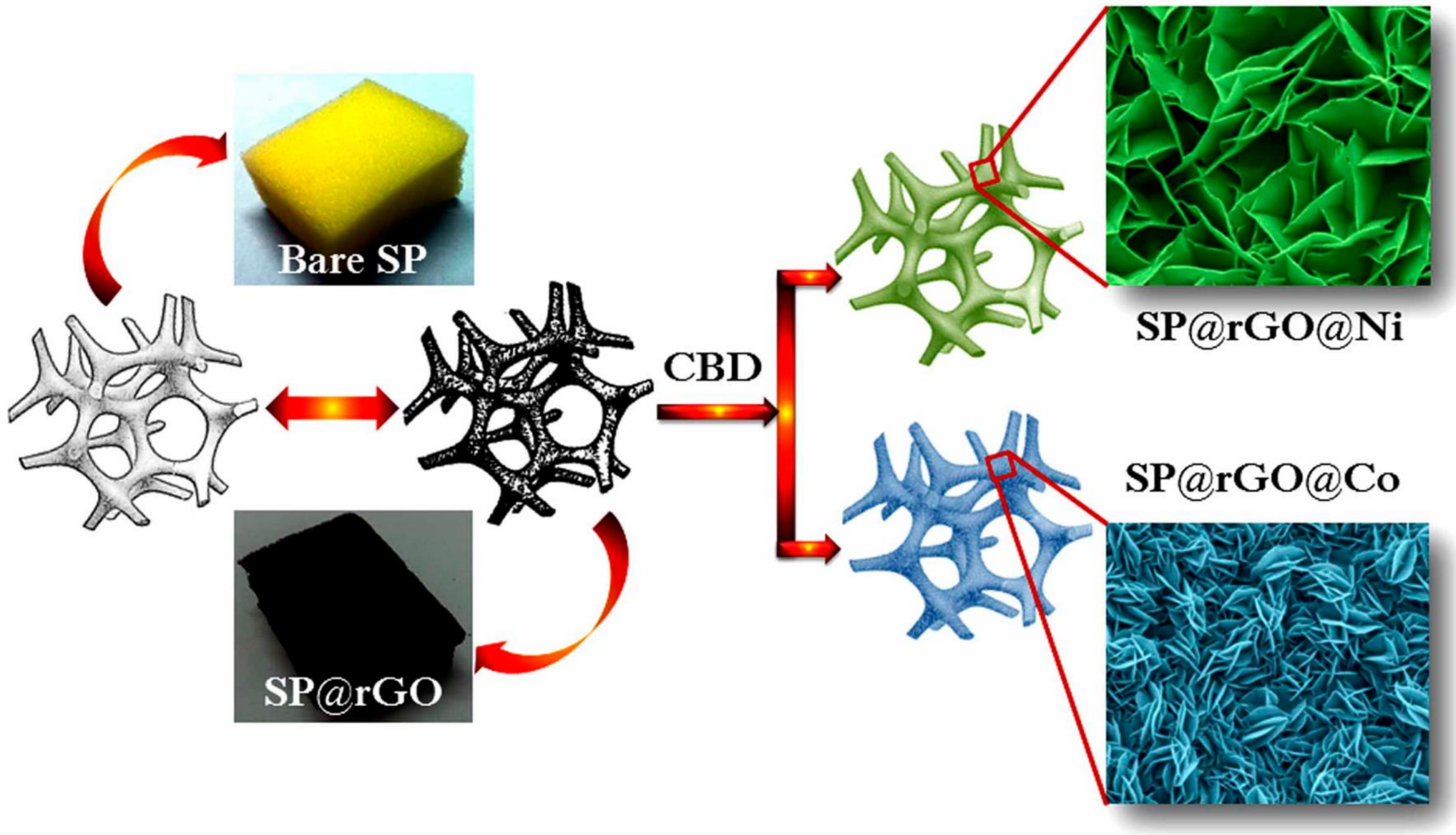
# hybrid materials with extended phases



# Hybrid reduced graphene oxide and transition metal hydroxides on sponge support for hybrid energy storage devices

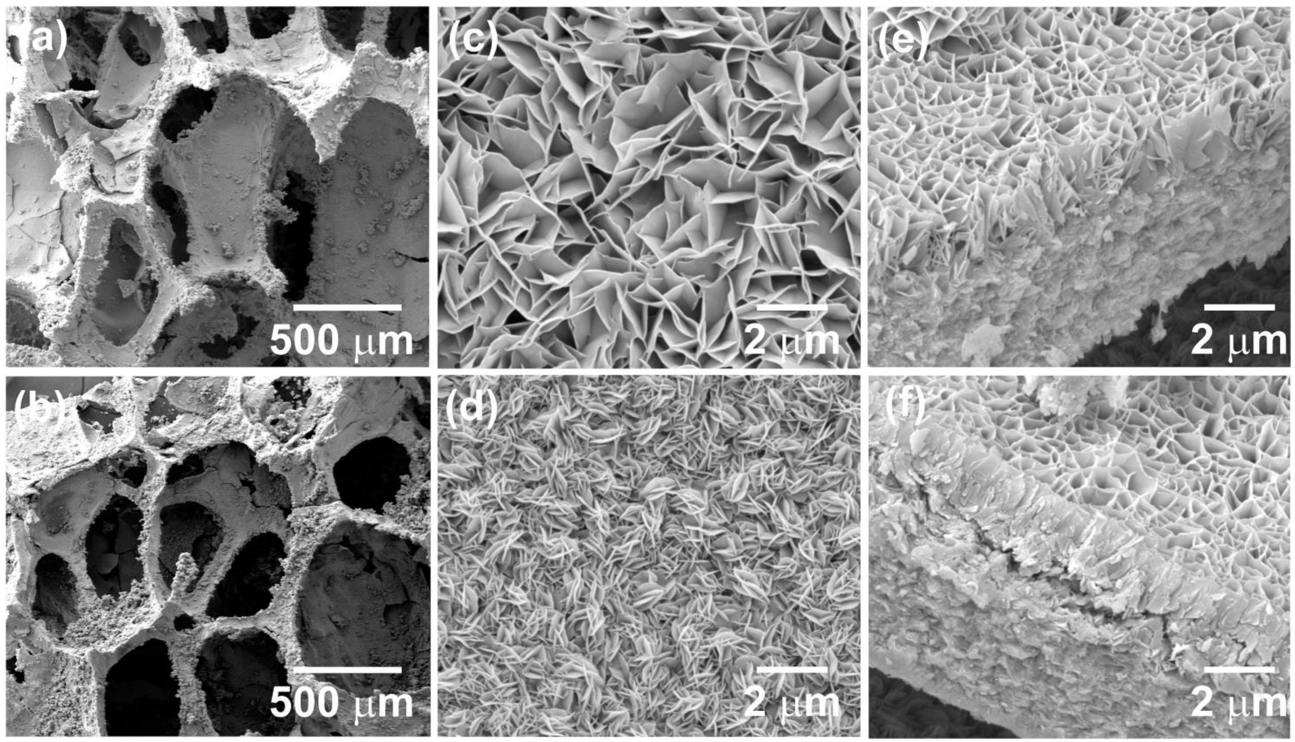



D.P. Dubal*, R. Holze, P. Gomez-Romero*. Scientific Reports **2014**, 4 : 7349

# Hybrid reduced graphene oxide and transition metal hydroxides on sponge support for hybrid energy storage devices

SP@rGO@Ni

SP@rGO@Co




D.P. Dubal*, R. Holze, P. Gomez-Romero*. Scientific Reports **2014**, 4 : 7349

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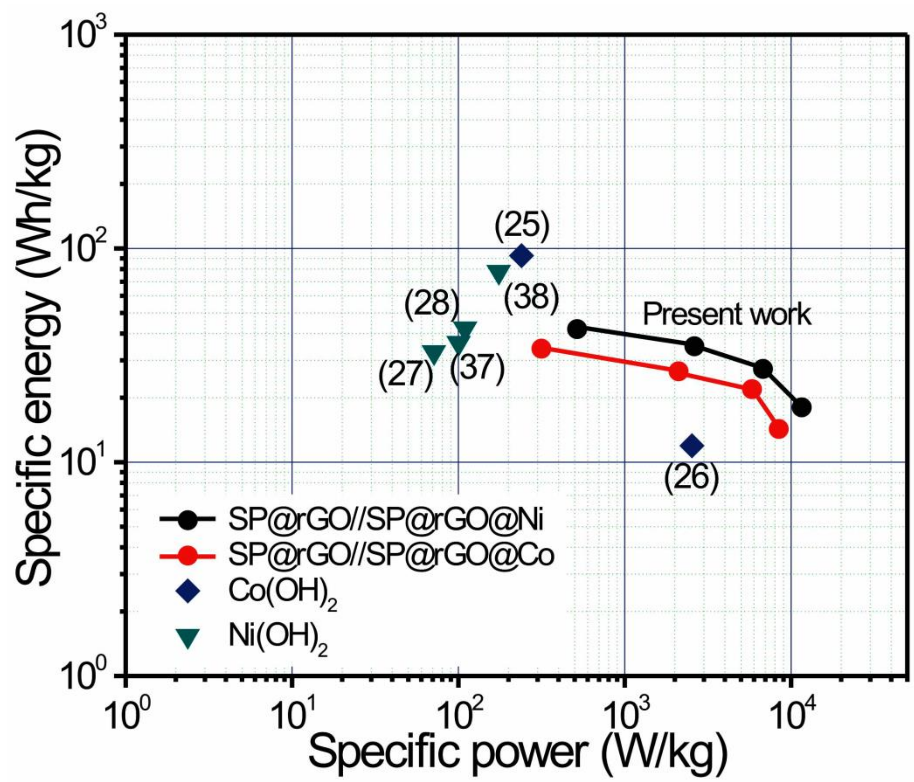
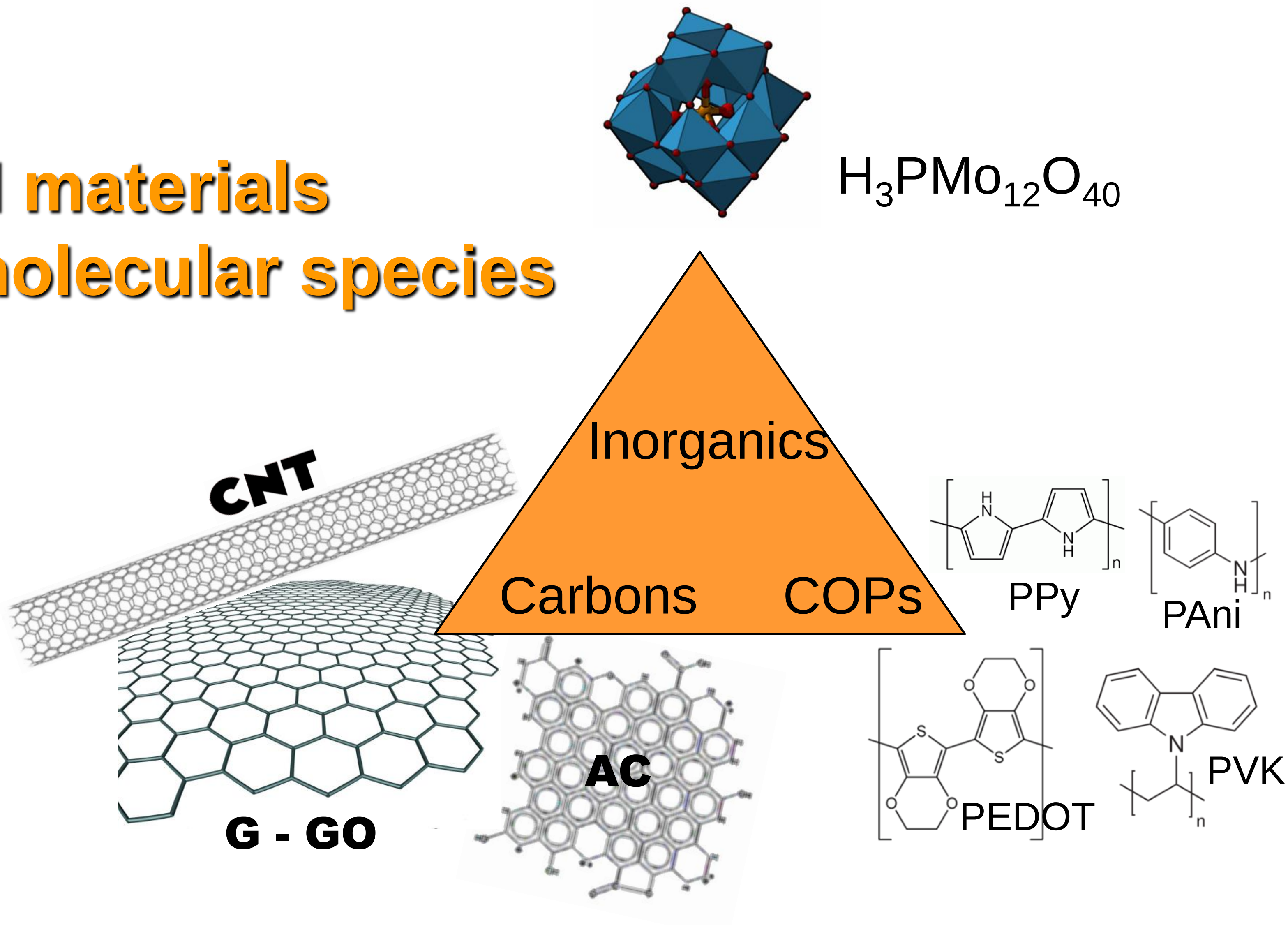



D.P. Dubal*, R. Holze, P. Gomez-Romero*. Scientific Reports **2014**, 4 : 7349

# hybrid materials with molecular species



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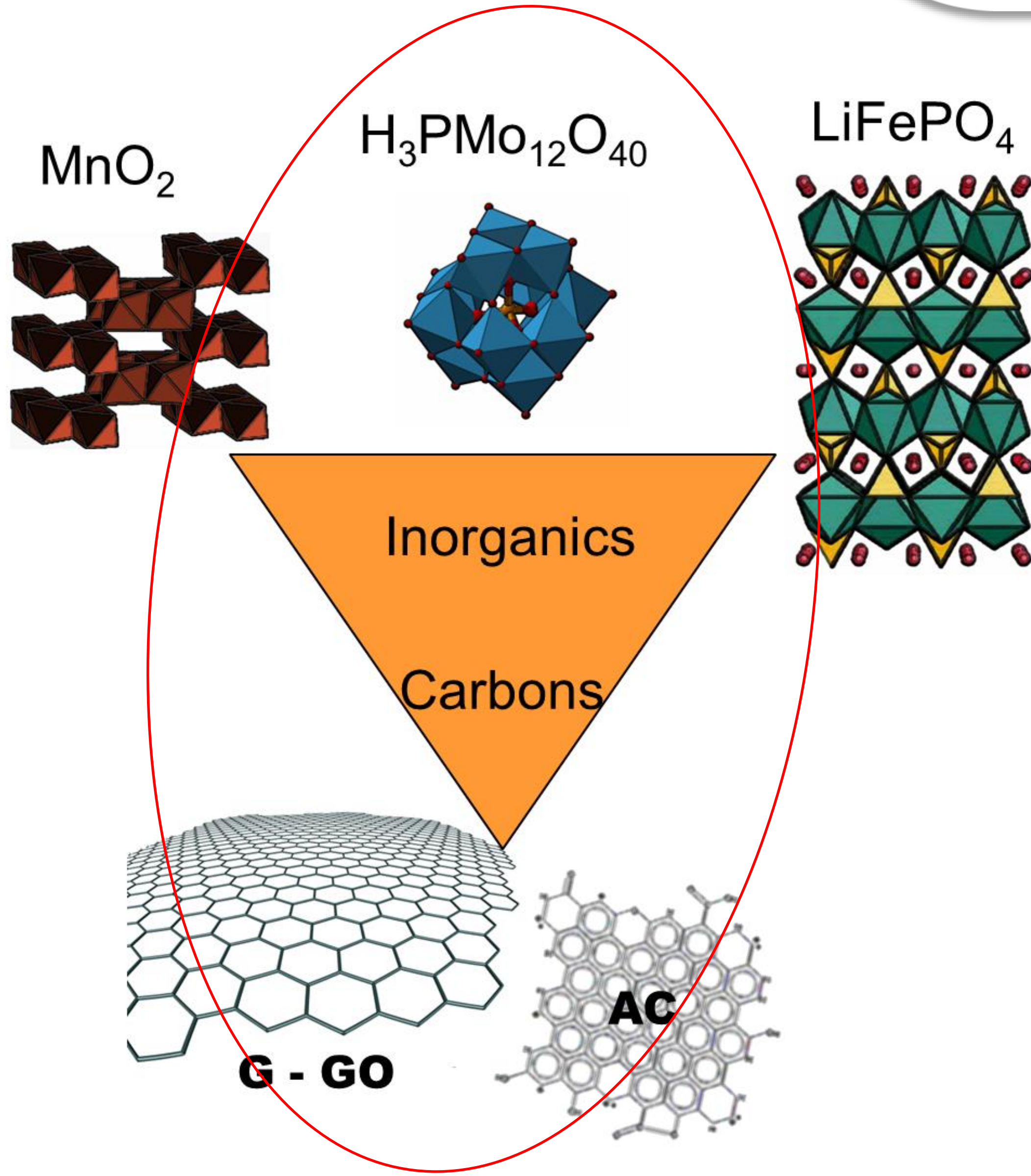
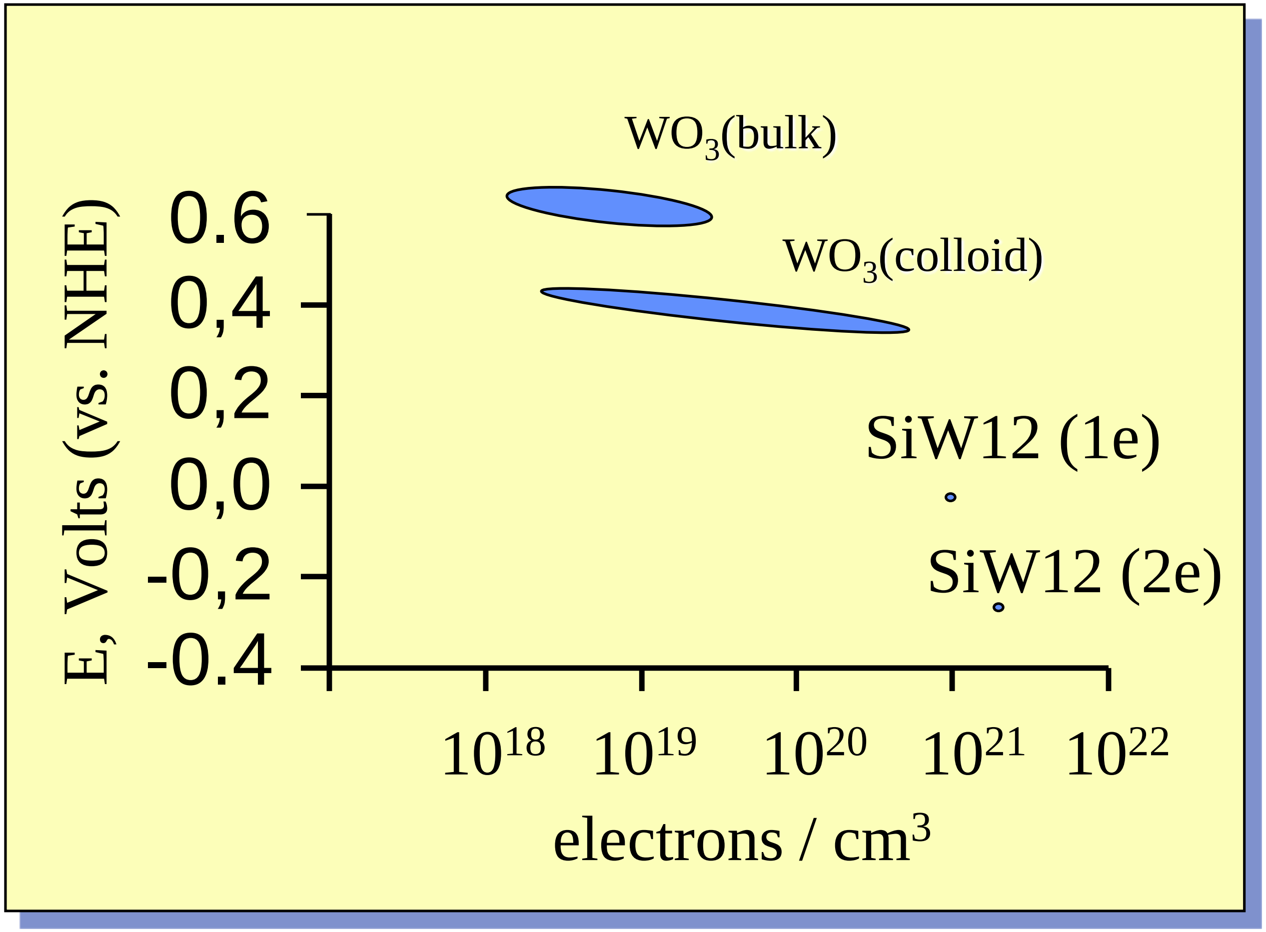
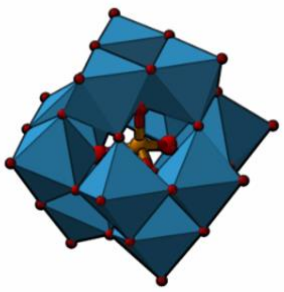


# Polyoxometalates (POMs) as models for quantum-sized oxides



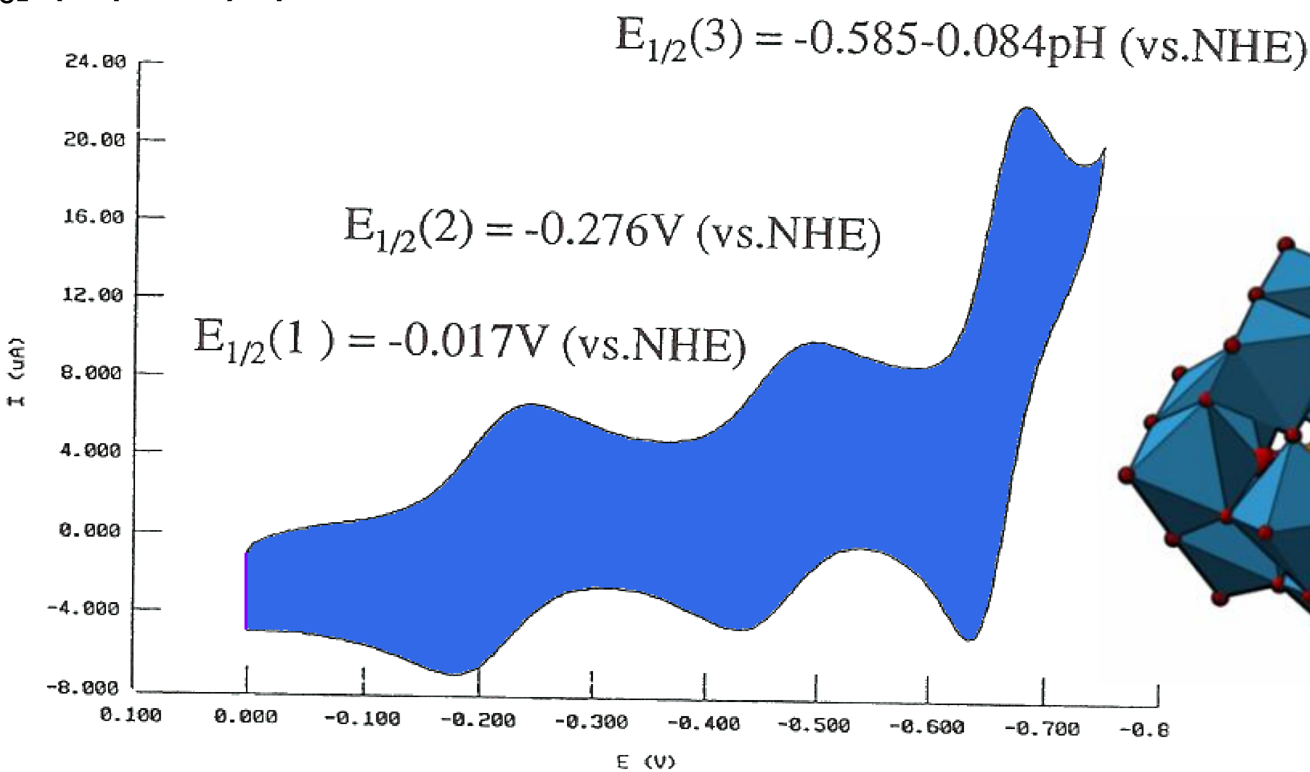
Effect of particle size on flat-band potential

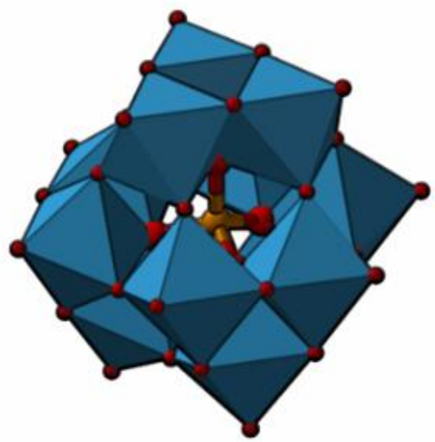
P. Gomez-Romero Solid State Ionics 1997, 101-103, 243-248

# RedOx Chemistry of Polyoxometalates (POMs)

## Cyclic Voltammogram (CV) of $H_4\,[SiW_{12}O_{40}]$ (SiW12)

$H_4\,[SiW_{12}O_{40}]$ (aq.HCl), pH=0.8



Photoredox Chemistry in Oxide Clusters. Photochromic and Redox Properties of Polyoxometalates in Connection with Analog Solid State Colloidal Systems.
Pedro Gómez-Romero* et al J.Phys.Chem. **1996**, 100(30), 12448-54.

# Hybrid Energy Storage

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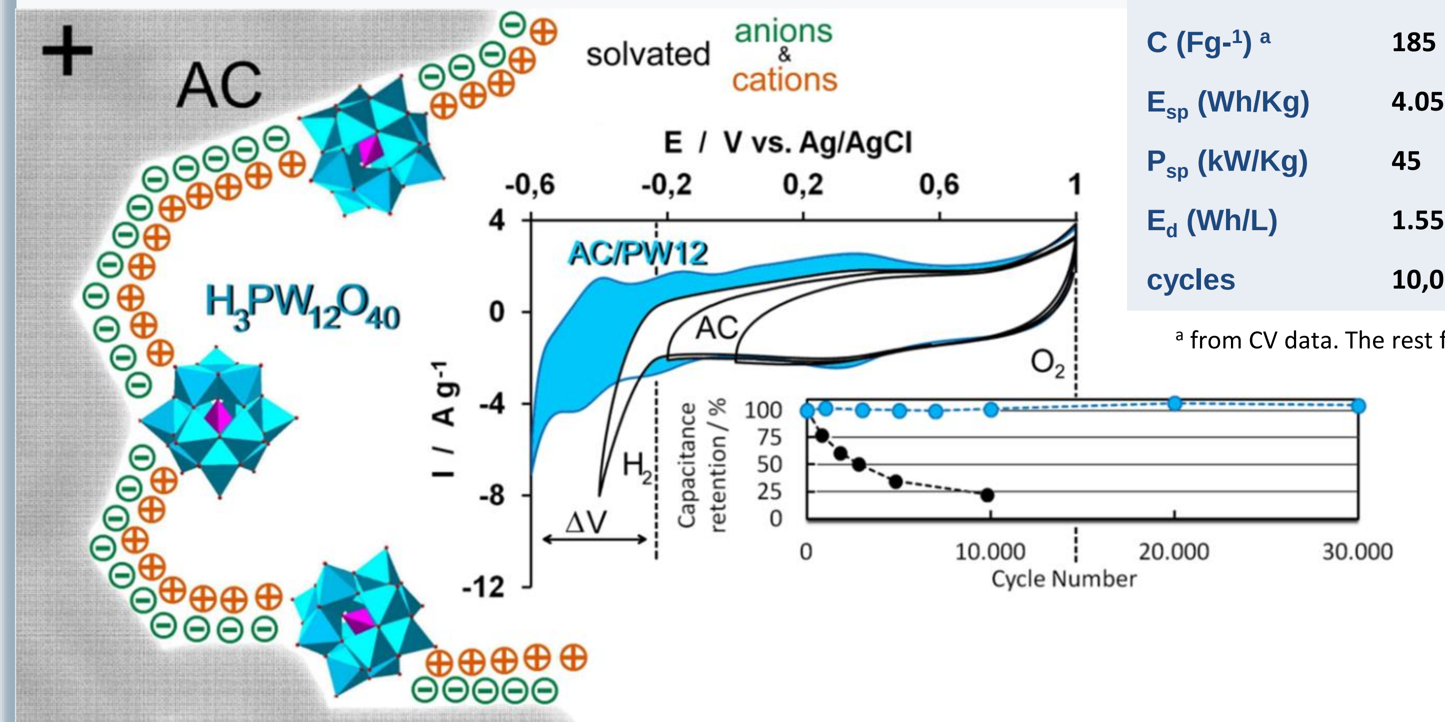
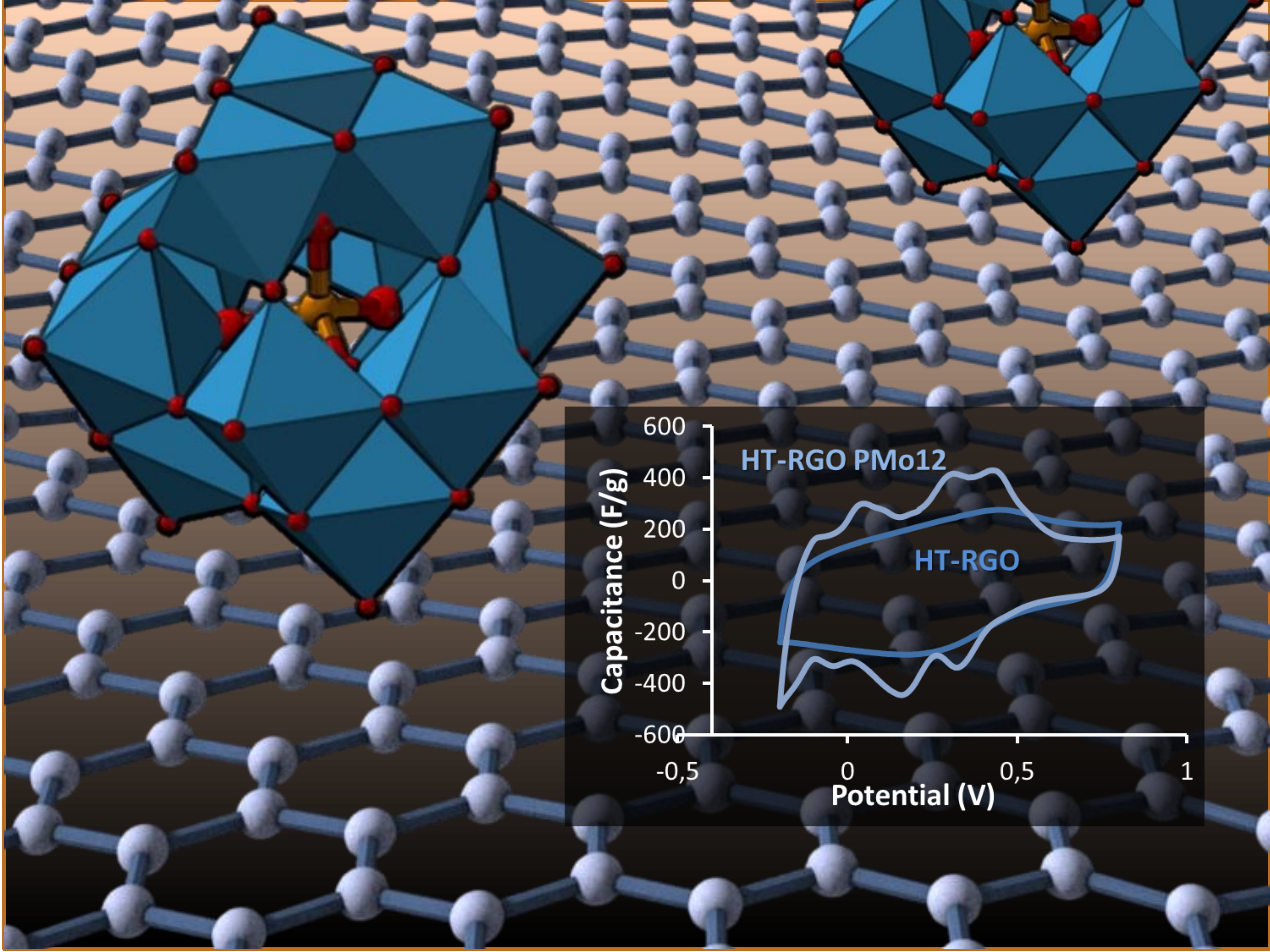



| | AC | AC-PW12 |
|---|---|---|
| C (Fg-1) [a] | 185 | 254 |
| $E_{sp}$ (Wh/Kg) | 4.05 | 4.96 (1.6 A/g) |
| $P_{sp}$ (kW/Kg) | 45 | 115 |
| $E_d$ (Wh/L) | 1.55 | 2.32 |
| cycles | 10,000 | > 30,000 (6 A/g) |

[a] from CV data. The rest from charge-discharge data

Hybrid Electrodes Based on Polyoxometalate-Carbon Materials for Electrochemical Supercapacitors
V. Ruiz, J. Suárez-Guevara, P. Gomez-Romero. Electrochemistry Communications **2012**, 24, 35-8

Hybrid Energy Storage: High Voltage Aqueous Supercapacitors based on Activated C-Phosphotungstate Hybrid Materials.
J. Suárez-Guevara, V. Ruiz, P. Gomez-Romero J. Mater. Chem. A, **2014**, 2 (4), 1014-1021



HT-RGO PMo12
HT-RGO
Capacitance (F/g)
600
400
200
0
-200
-400
-600
-0,5
0
0,5
1
Potential (V)

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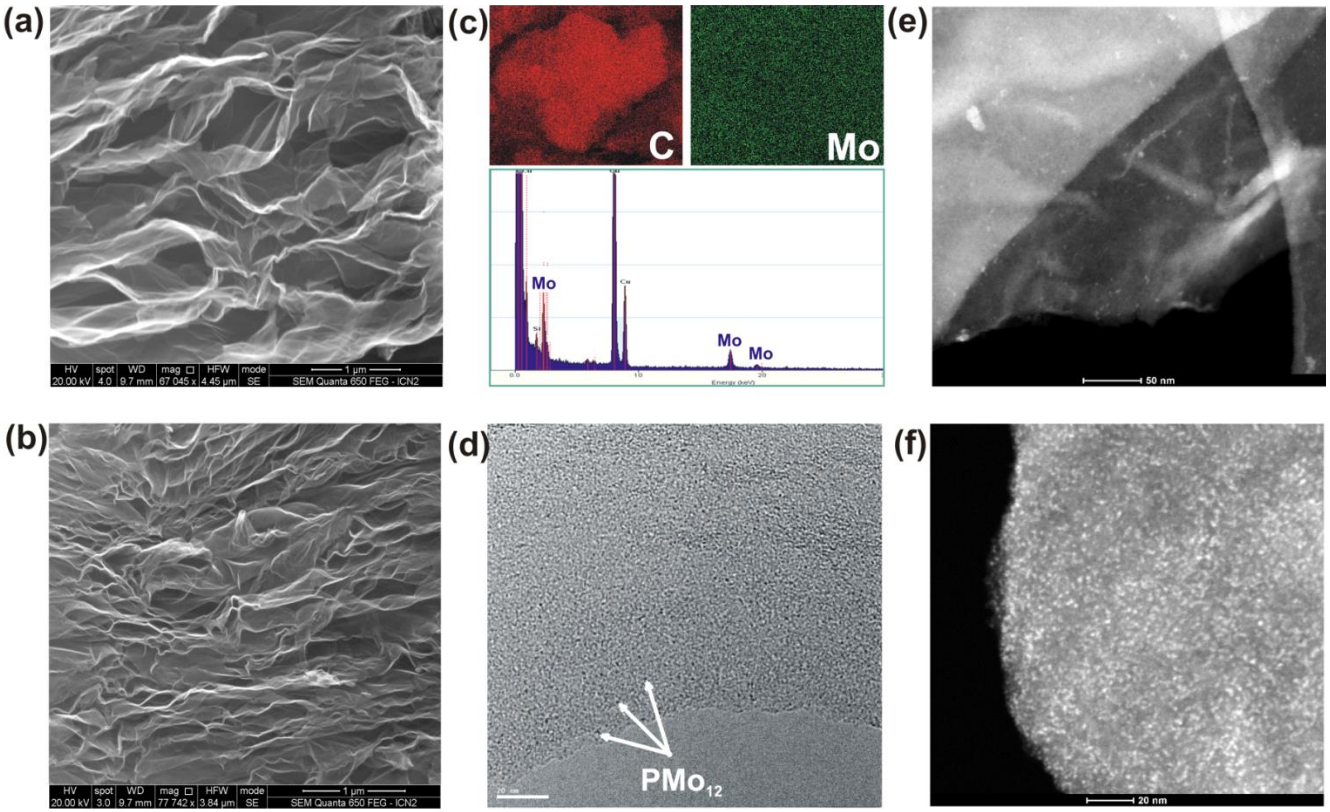
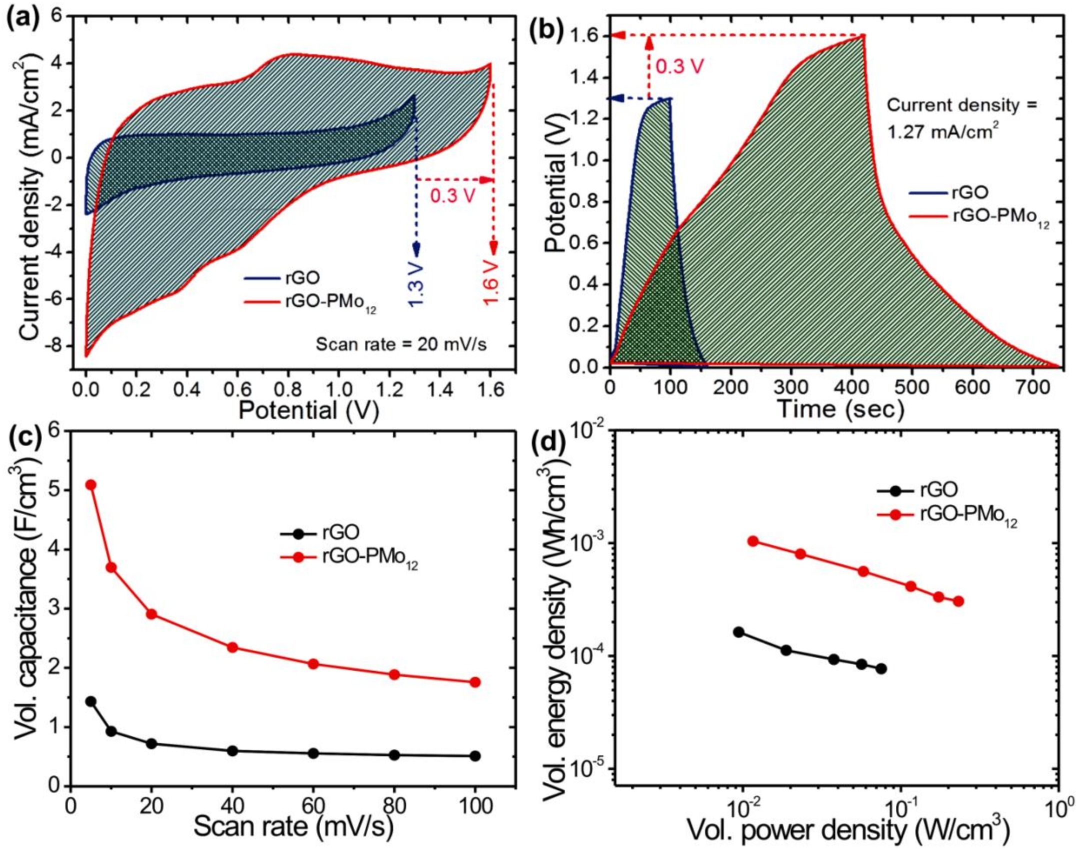
# Hybrid rGO-$H_3PMo_{12}O_{40}$




SEM images of (a) rGO and (b) rGO-$PMo_{12}$ hybrid materials, respectively, (c) EDS mapping of rGO-$PMo_{12}$ hybrid sample, (d) HR-TEM image of rGO-$PMo_{12}$ sample, (e, f) STEM images of rGO and rGO-$PMo_{12}$ hybrid samples, respectively.

D.P. Dubal J. Suarez-Guevara, D. Tonti, E. Enciso, P. Gomez-Romero Journal of Materials Chemistry A, 2015, 3(46), 23483

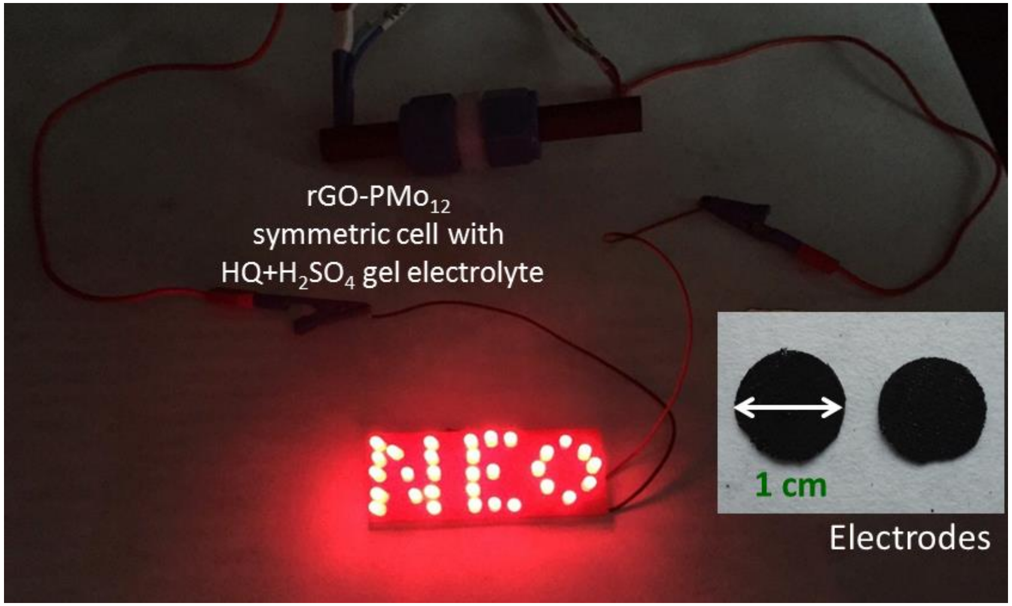
# Hybrid rGO-$H_3PMo_{12}O_{40}$




(a) CV and (b) Carge-discharge curves of rGO and rGO-$PMo_{12}$ symmetric cells
(c) Variation of volumetric capacitance of rGO and rGO-$PMo_{12}$ based symmetric cells as a function of scan rates,
(d) volumetric power and energy density values of rGO and rGO-$PMo_{12}$ symmetric cells.

D.P. Dubal J. Suarez-Guevara, D. Tonti, E. Enciso, P. Gomez-Romero Journal of Materials Chemistry A, 2015, 3(46), 23483

# Hybrid rGO-$H_3PMo_{12}O_{40}$




31 LED indicators with word “NEO” powered rGO-$PMo_{12}$ symmetric cell with 0.2 M HQ doped polymer gel electrolyte.
30 s charge 2 min lit

D.P. Dubal J. Suarez-Guevara, D. Tonti, E. Enciso, P. Gomez-Romero Journal of Materials Chemistry A, 2015, 3(46), 23483

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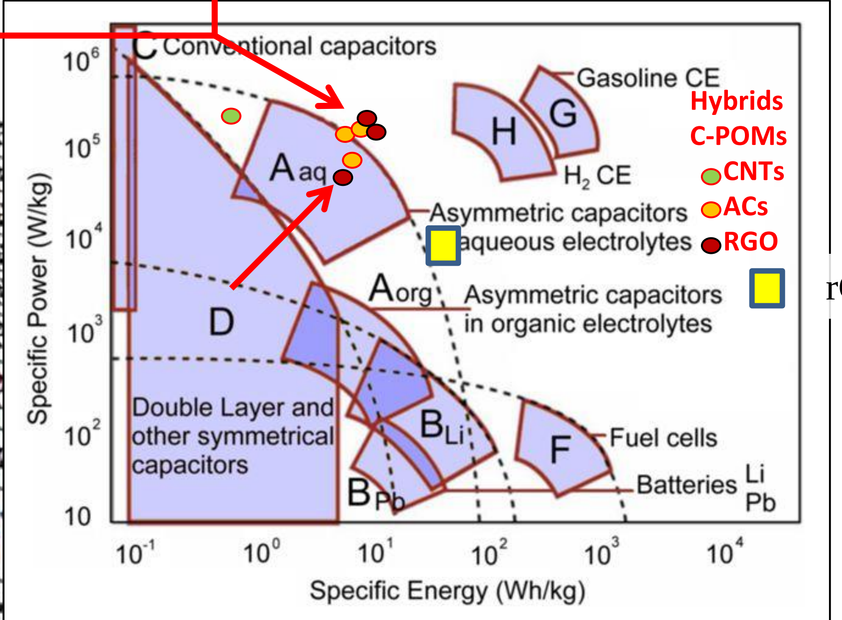
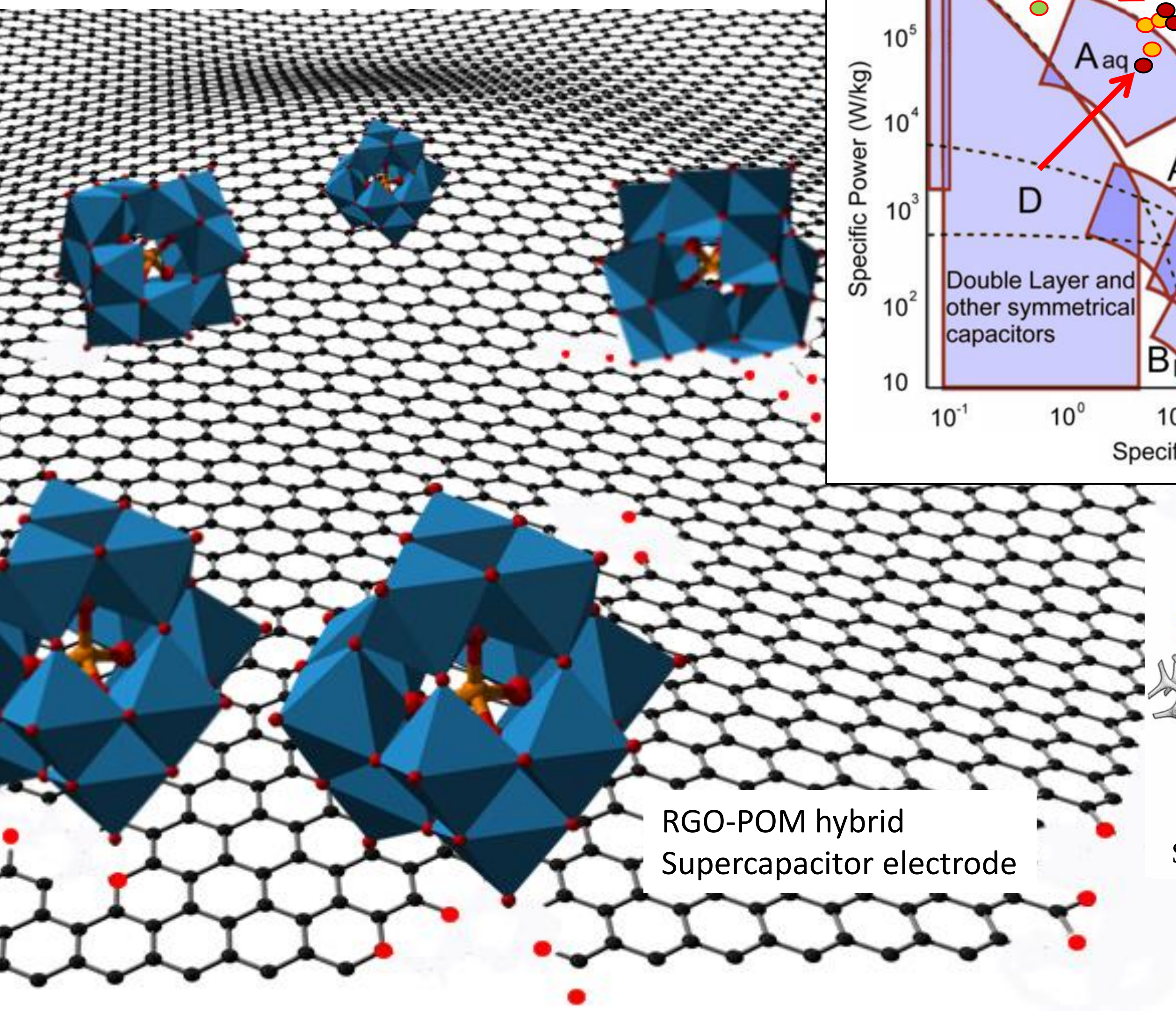
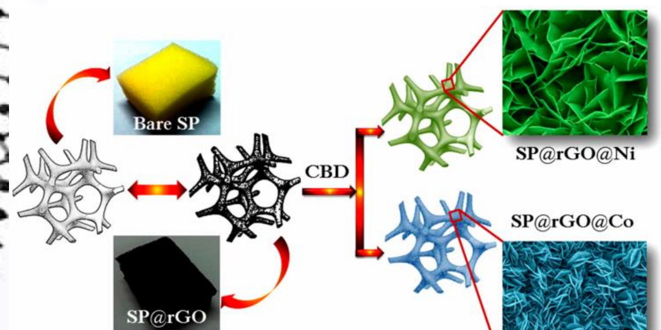
NB: our devices are SYMMETRICAL Supercapacitors and thus benchmark comparison should be with area "D"




rGO $Ni(OH)_2$



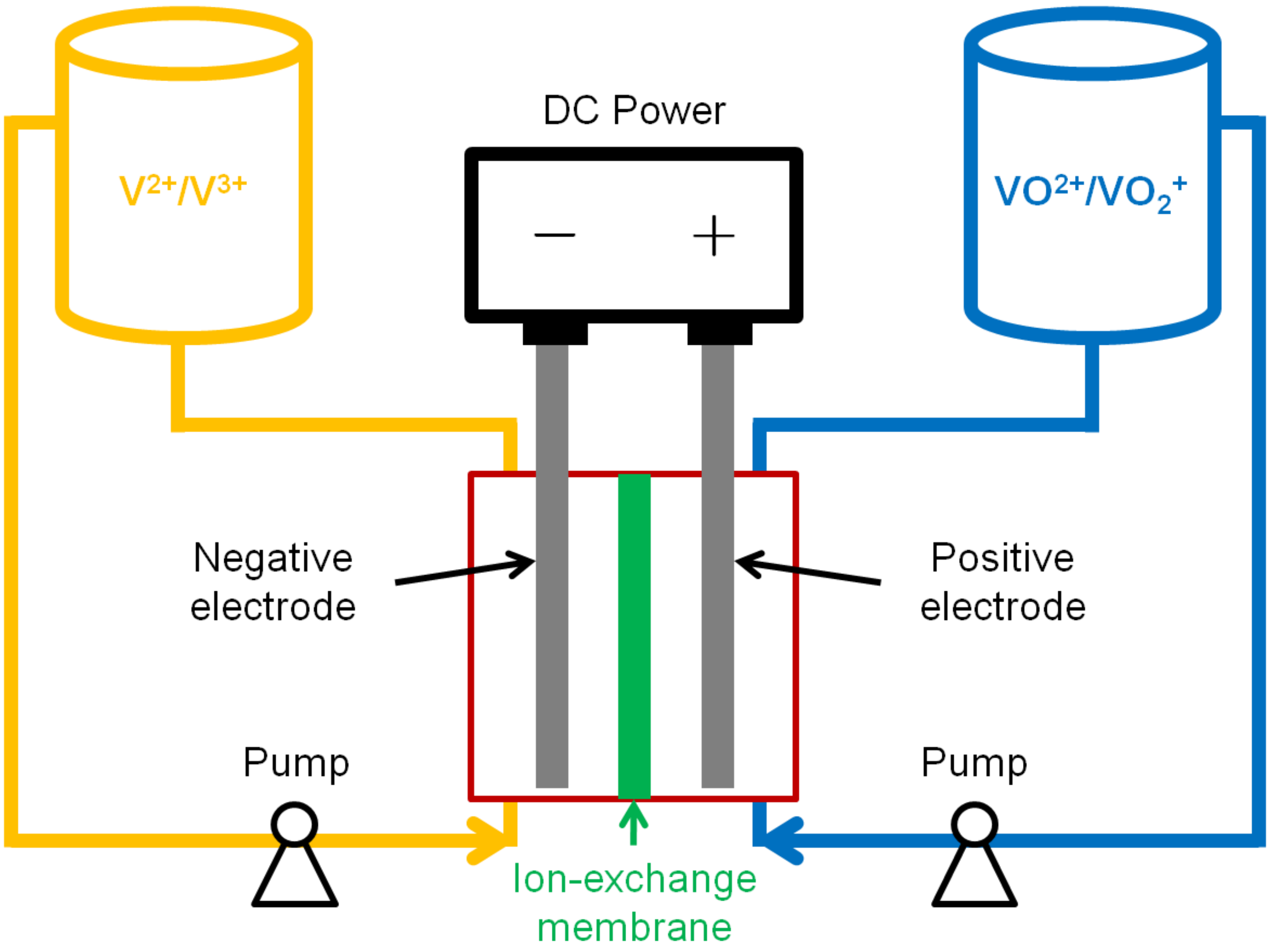
RGO-POM hybrid Supercapacitor electrode



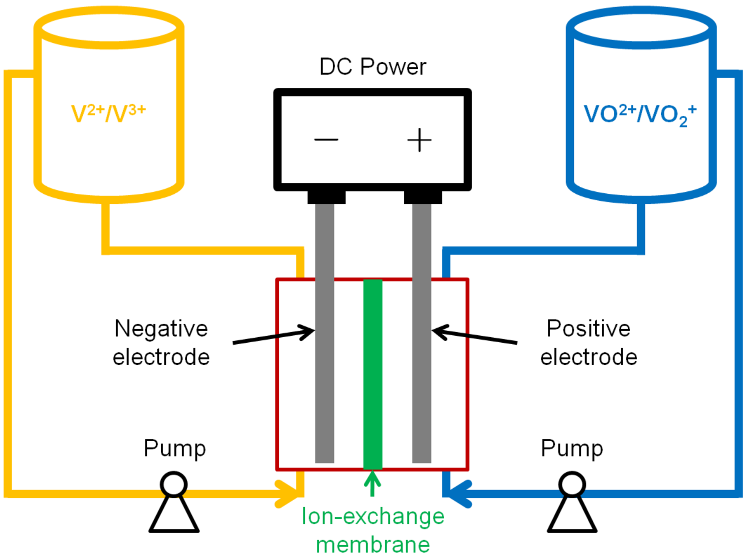

Scientific Reports **2014**, 4 : 7349

# Electroactive Graphene Nanofluids
# A new way of deliver graphene electrodes

# Redox Flow Batteries



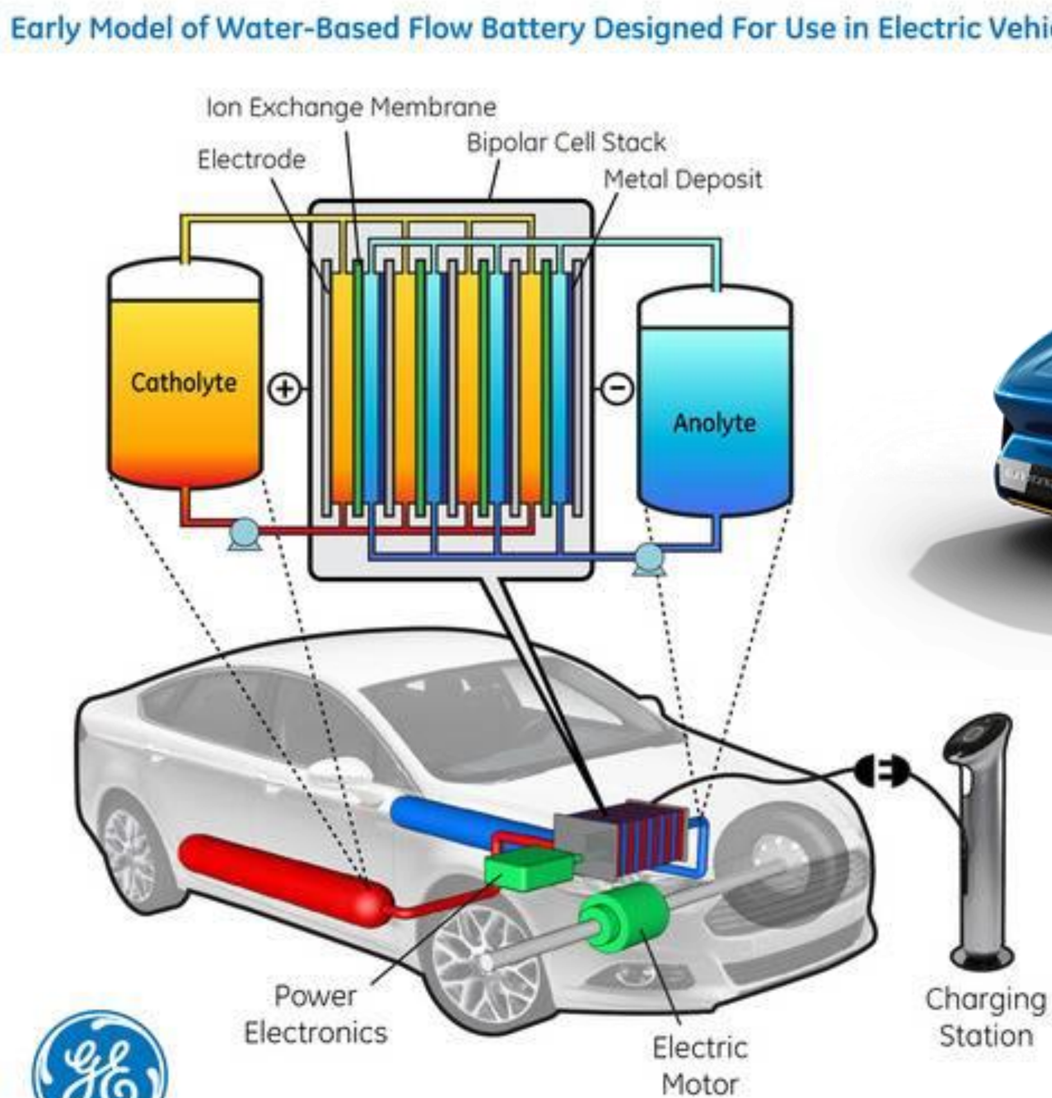
# Redox Flow Batteries




Decouples Energy and Power
Scalability
Long cycle Life
Ideally suited for Stationary applications. Load leveling Renewables

Limited solubility of salts (V ca. 1-2 M solutiond)
Low Energy density

# Prototype Electric vehicles with Flow technology




Quantino

250-liter tanks to hold liquids that flow past an electrochemical cell

**Flowing liquid is undisclosed**

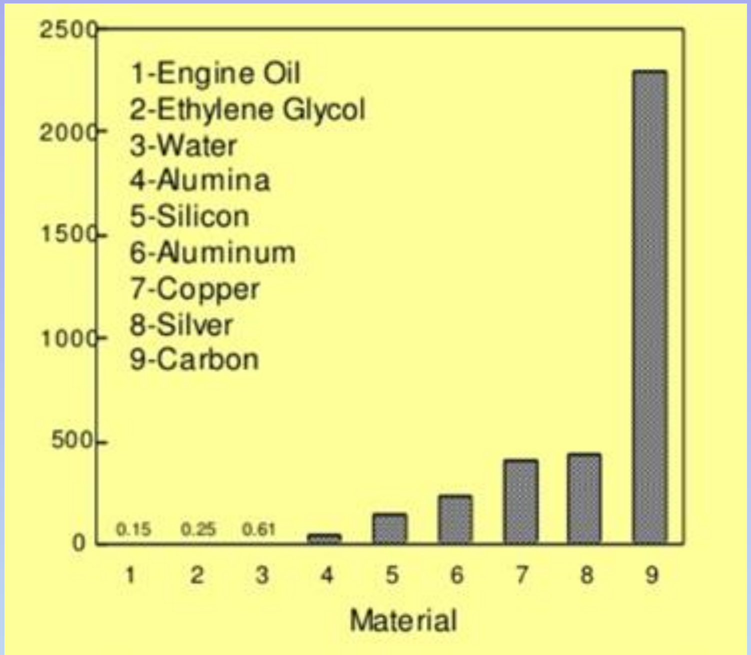
http://arpa-e.energy.gov/?q=slick-sheet-project/nanoelectrofuel-flow-battery-electric-vehicles

# Nanofluids: size matters

dispersions of nanoparticles in base fluids

# Thermal Nanofluids concept

- Conventional Heat transfer Fluids (HTFs) have poor thermal conductivity compared to solids
- Fluids containing microparticles lead to engineering problems (precipitation, clogging…)
- Nanofluids provide enhanced performance from dispersed solid nanoparticles without those problems




Termal conductivity of solids:
Orders of magnitud larger than
Those of conventional HTFs

# Electroactive Nanofluids

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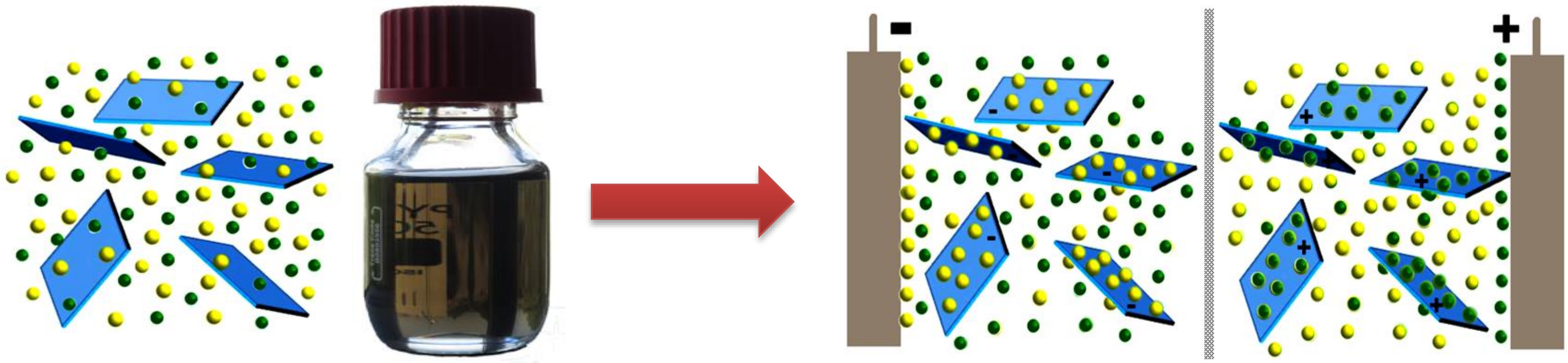
## Electroactive Nanofluids: An Emerging Field

Electroactive nanofluids. NEO-Energy: international pioneering role

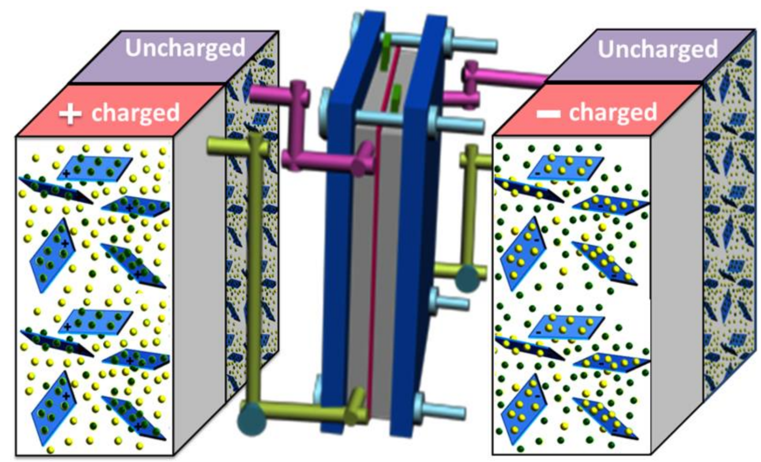


**Energy Storage. New Flow Cell Concepts.**

Electroactive nanofluids (eg rGO) in water to store energy in Flowing Capacitive Cell

Target applications:

- storage of renewable energies.
- fuelling electric vehicles.




*D. P. Dubal, D. Gomez, P. Gómez-Romero, Patent Pending. "Electroactive nanofluids on graphene-based materials for energy storage in flow cells." 20-05-2015*

# Electroactive Graphene Nanofluids for New Flow Cell Concepts.

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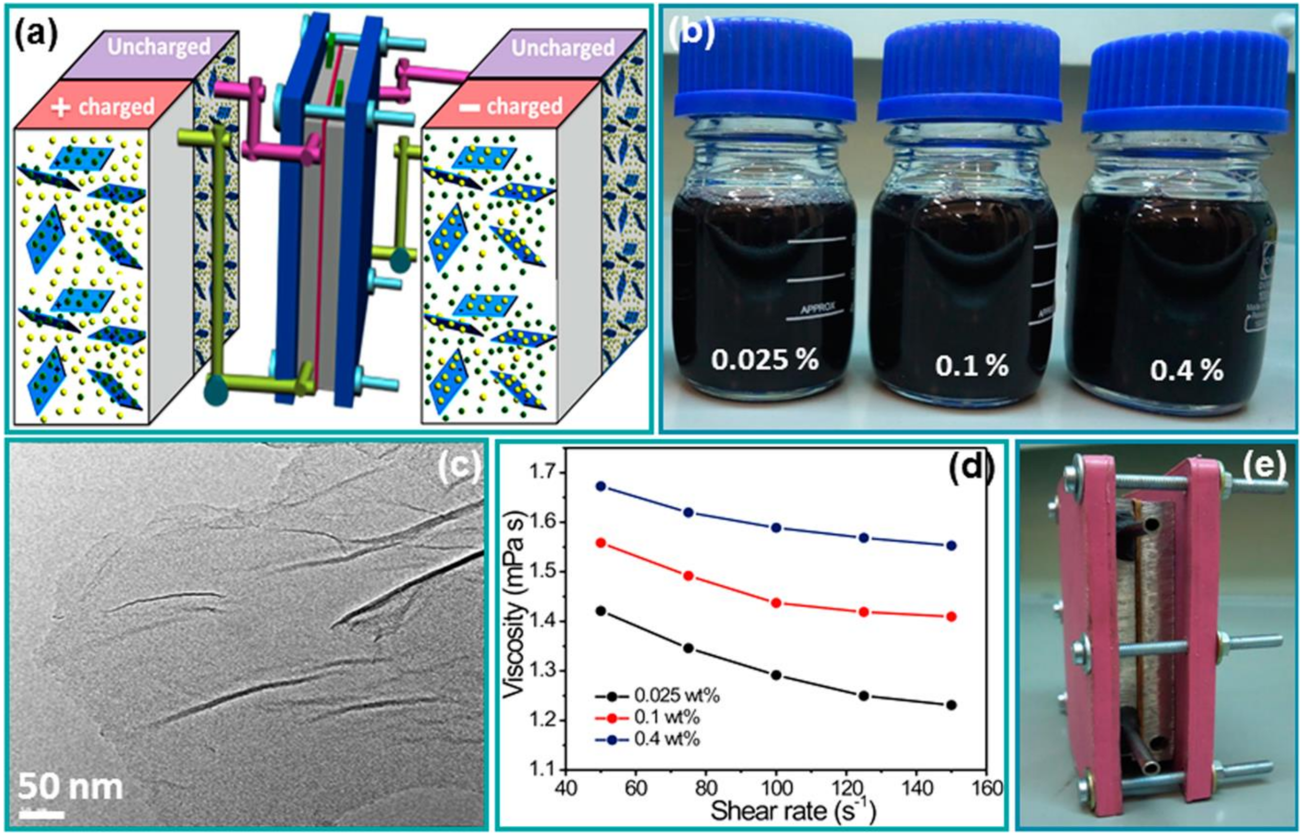
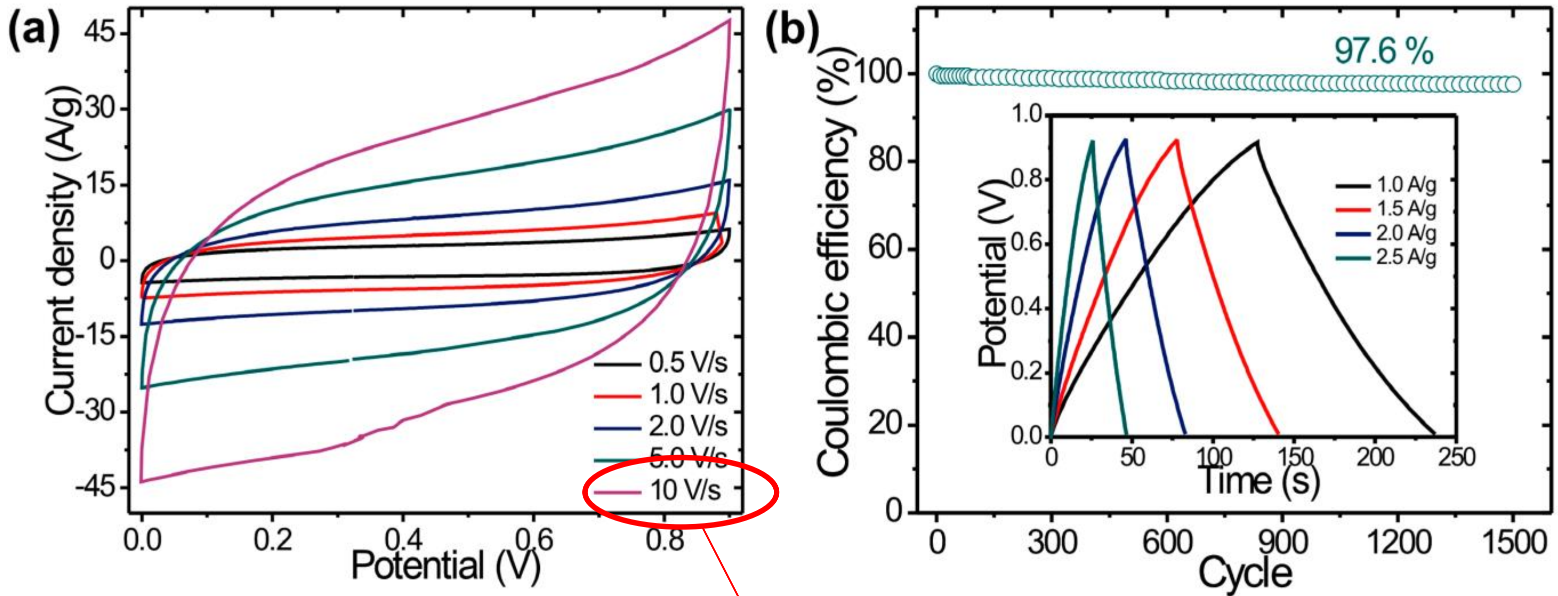



*D. P. Dubal, D. Gomez, P. Gómez-Romero, Patent ES1641.1064. “Electroactive nanofluids on graphene-based materials for energy storage in flow cells.” 20-05-2015*

Electroactive Graphene Nanofluids for Fast Energy Storage.

D.P. Dubal and P. Gomez-Romero 2D-Materials **2016**, 3, 031004

# Electroactive Graphene Nanofluids for New Flow Cell Concepts.

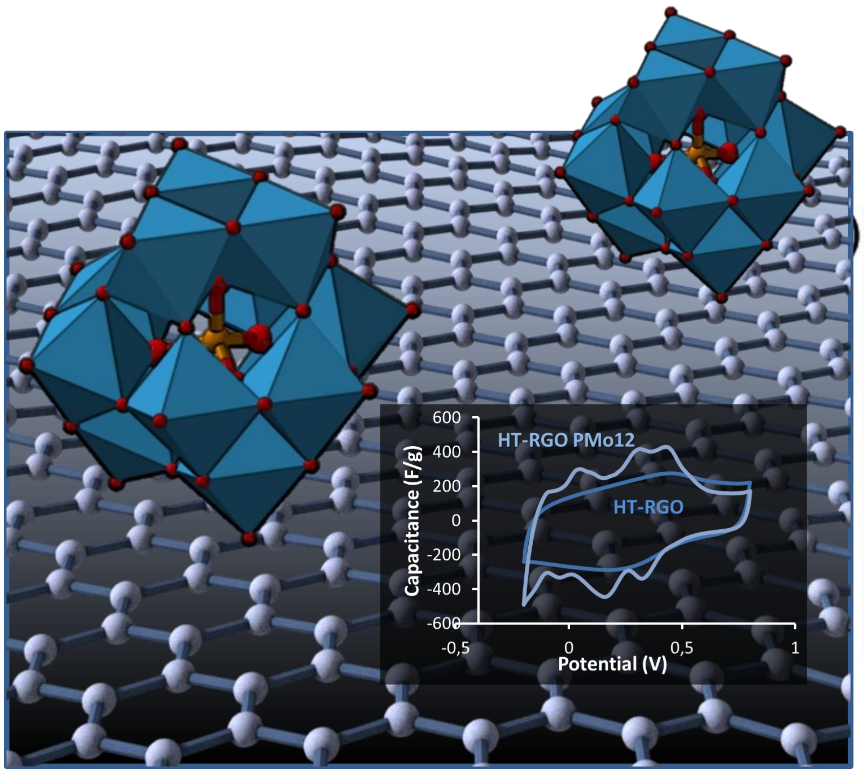



ultrafast electrochemical response

Electroactive Graphene Nanofluids for Fast Energy Storage.

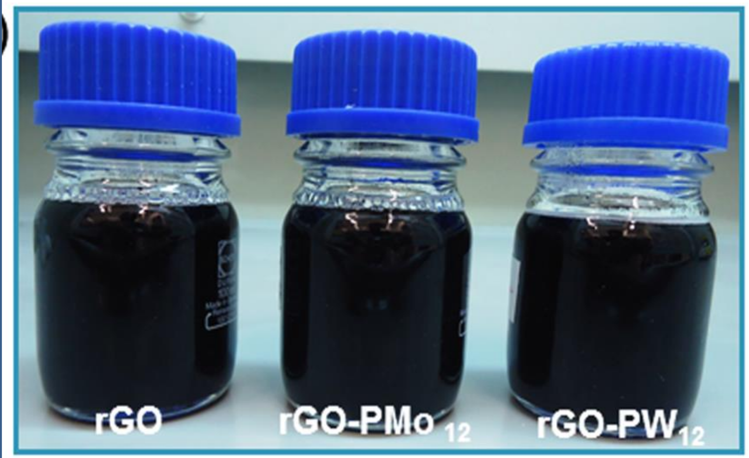
D.P. Dubal and P. Gomez-Romero 2D-Materials **2016**, 3, 031004

# Hybrid Electroactive Graphene Nanofluids for New Flow Cell Concepts.




$H_3PMo_{12}O_{40}$

$H_3PW_{12}O_{40}$



# Conclusions

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## Graphene Hybrids and Nanofluids for Energy Storage

- Graphene itself has been proposed and tested for a wide variety of energy and environmental applications, particularly in supercapacitors
- For supercap apps, microstructure and hybrid developments can be key
- Despite its high degree of oxidation and precisely due to that, Graphene oxide (GO) and also reduced GO (rGO) feature a functionalized active surface useful for hybridization.
- The hybrid approach widens enormously the potential of G, GO and rGO by combining them with a plethora of inorganic phases polymers or molecules which add functionality and allow for synergy and enhanced energy density.
- Dispersion of graphene in nanofluids provides a new format for G, GO or rGO electrodes suitable for novel Flow Cells


Acknowledgments

# NEO-Energy Lab

Prof. Pedro Gómez-Romero

MINISTERIO DE CIENCIA E INNOVACIÓN

ICN2 EXCELENCIA SEVERO OCHOA
Institut Català de Nanociència i Nanotecnologia

CSIC

SEVENTH FRAMEWORK PROGRAMME

# NEO-Energy Group: The people (Feb 2016)

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Institut Català de Nanociència i Nanotecnologia

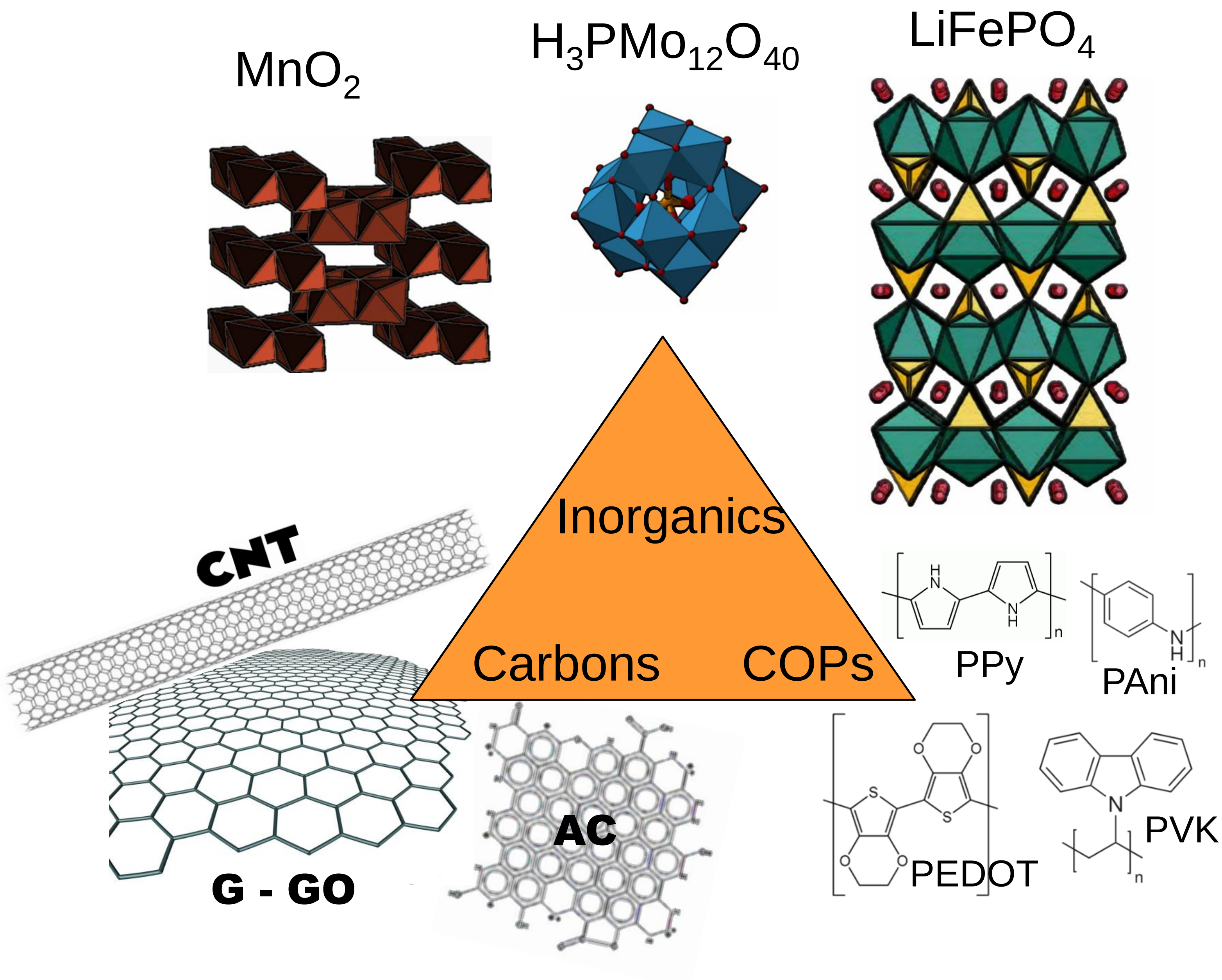
EXCELENCIA SEVERO OCHOA

Vanesa Ruiz

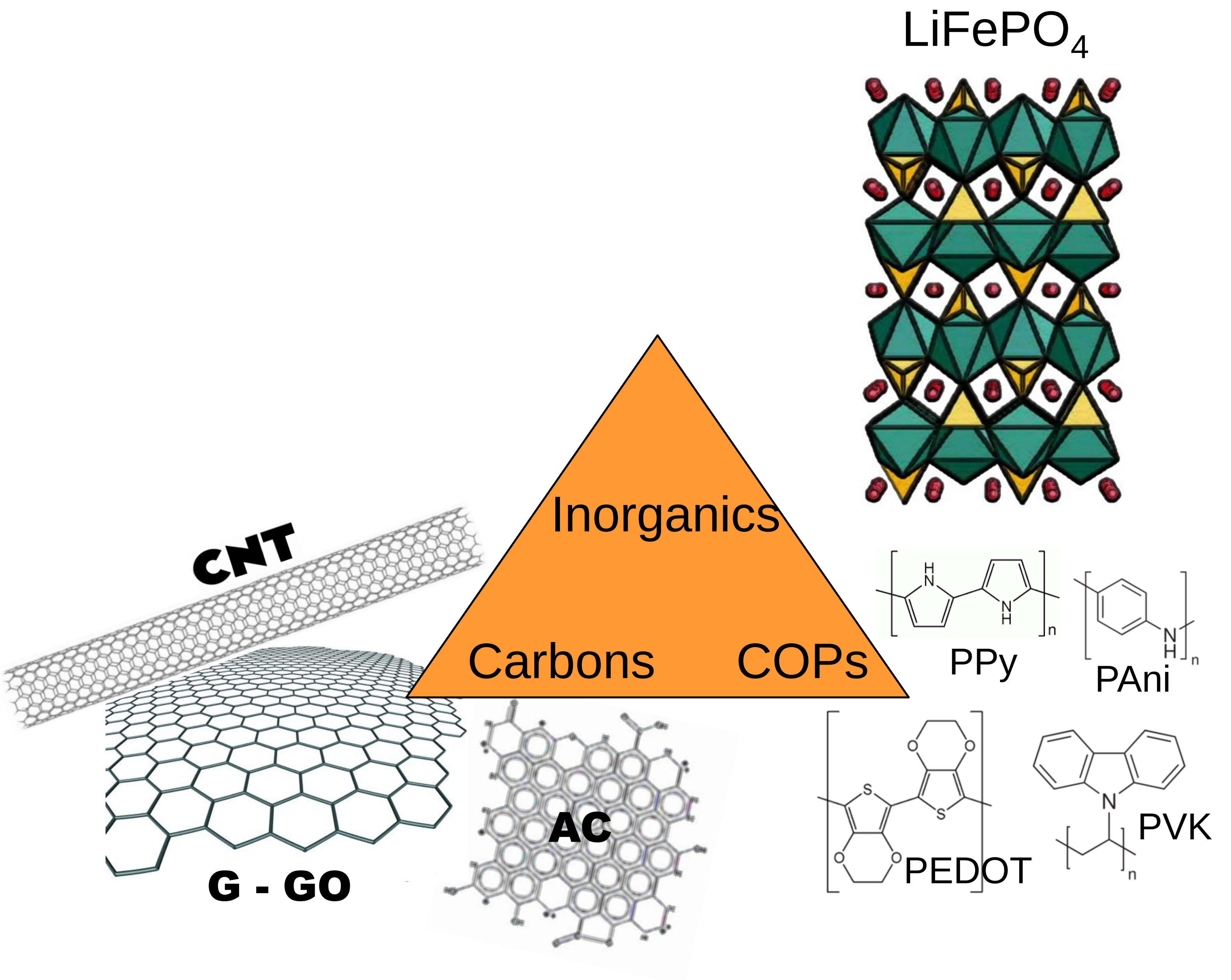
Jullieth Suárez


neoenergy.cat
Gracias
… for your attention!

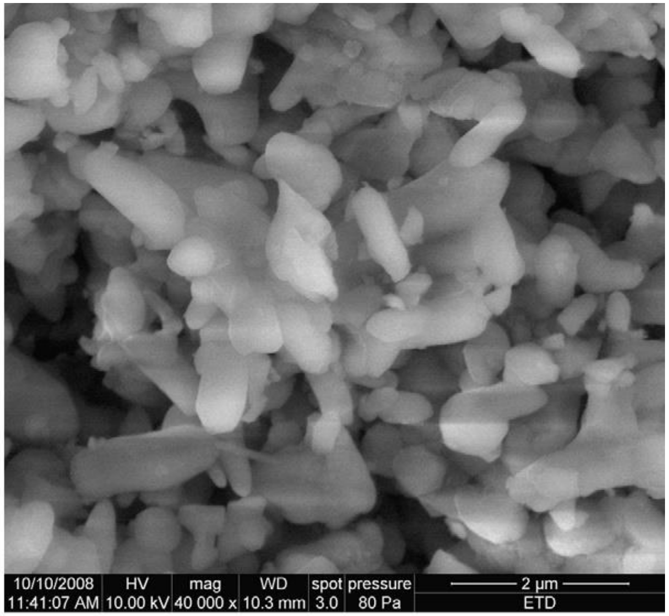
# Our window to the Hybrid Materials landscape



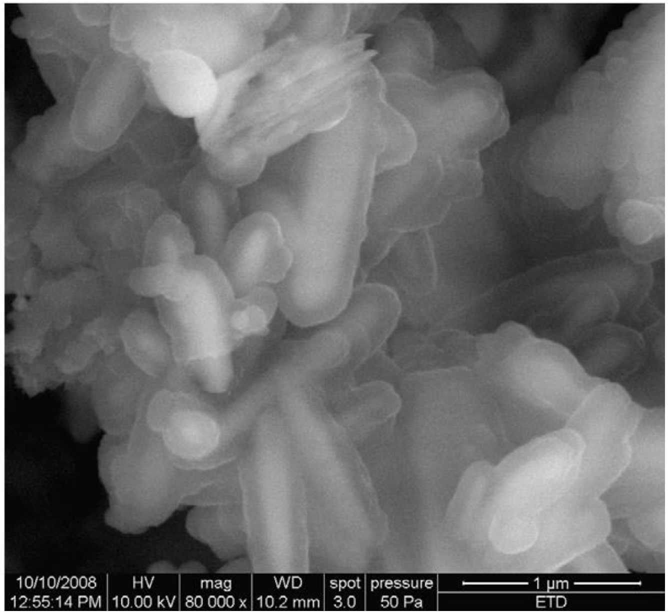
# Our window to the Hybrid Materials landscape



# LiFePO4 – PPy/PEG hybrids



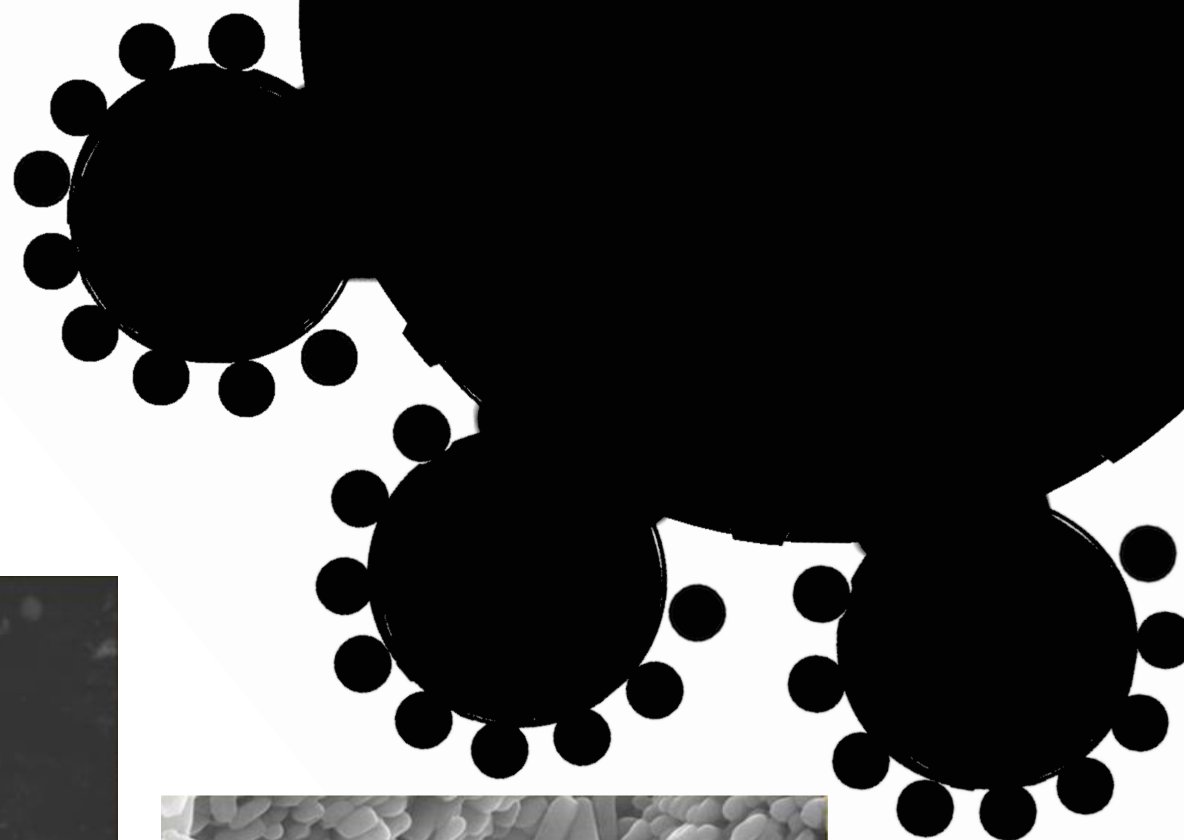

LiFePO4

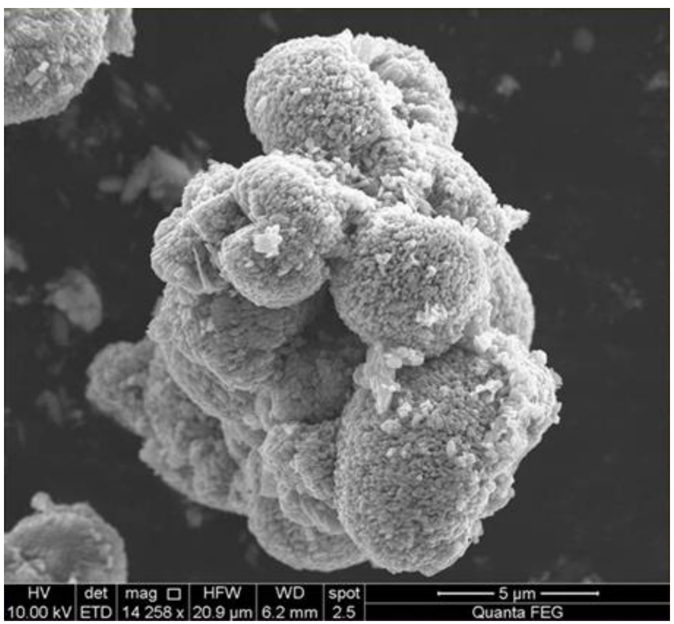


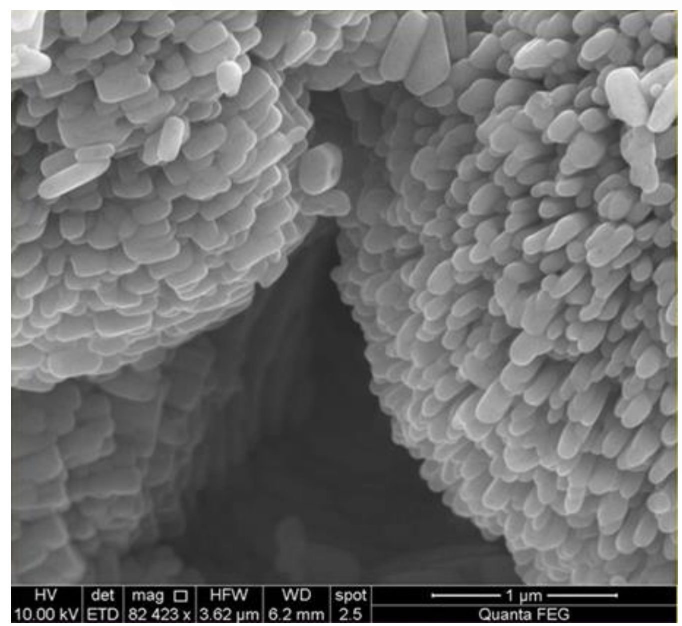

LiFePO4 – PPy

A. Fedorkova, A. Nacher-Alejos, P. Gomez-Romero, R. Orinakova, D. Kaniansky
Electrochimica Acta 55 (2010) 943–947

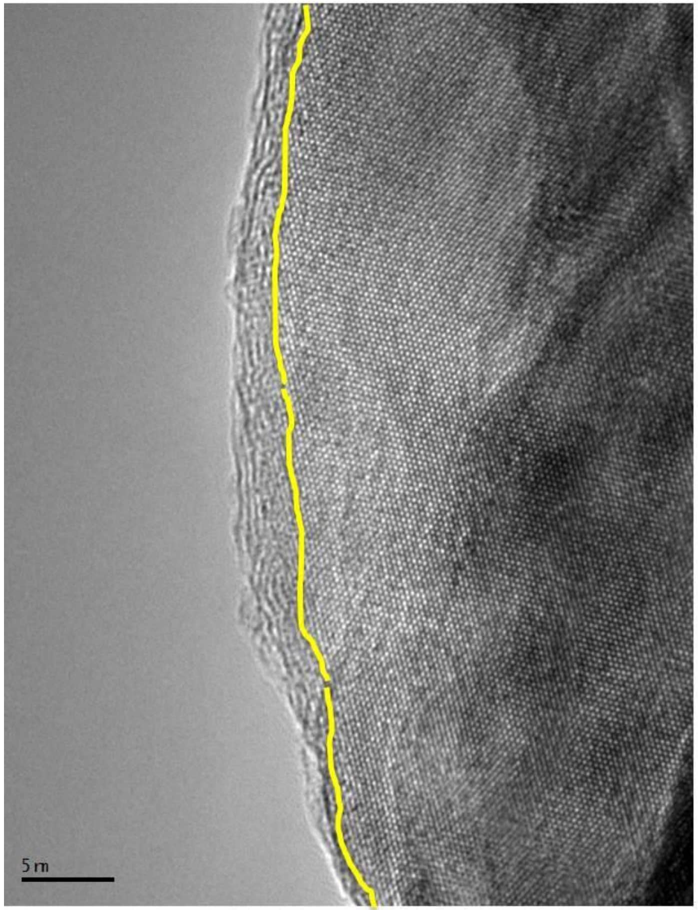
# Fractal granularity in $LiFePO_4$

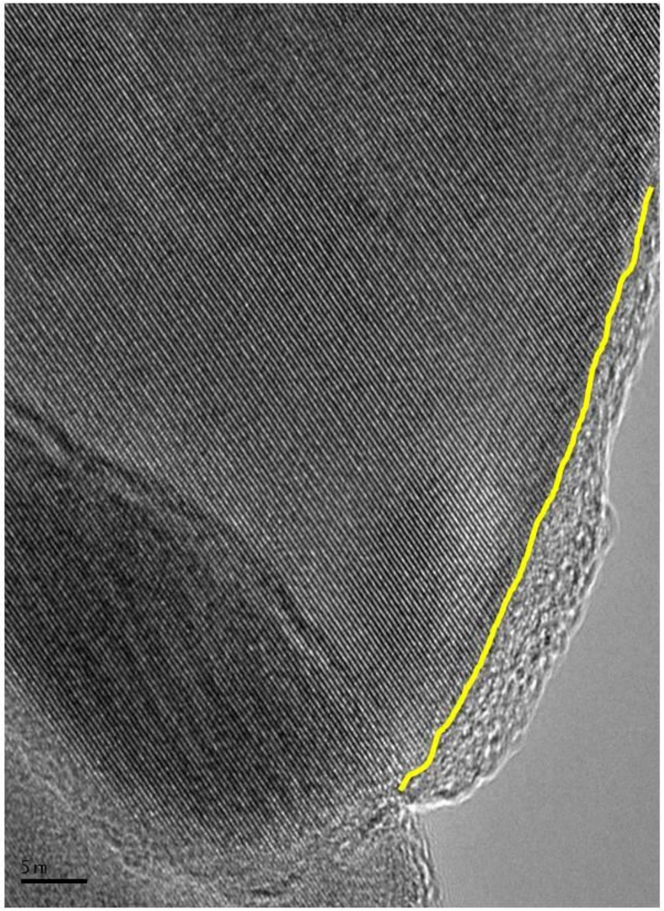




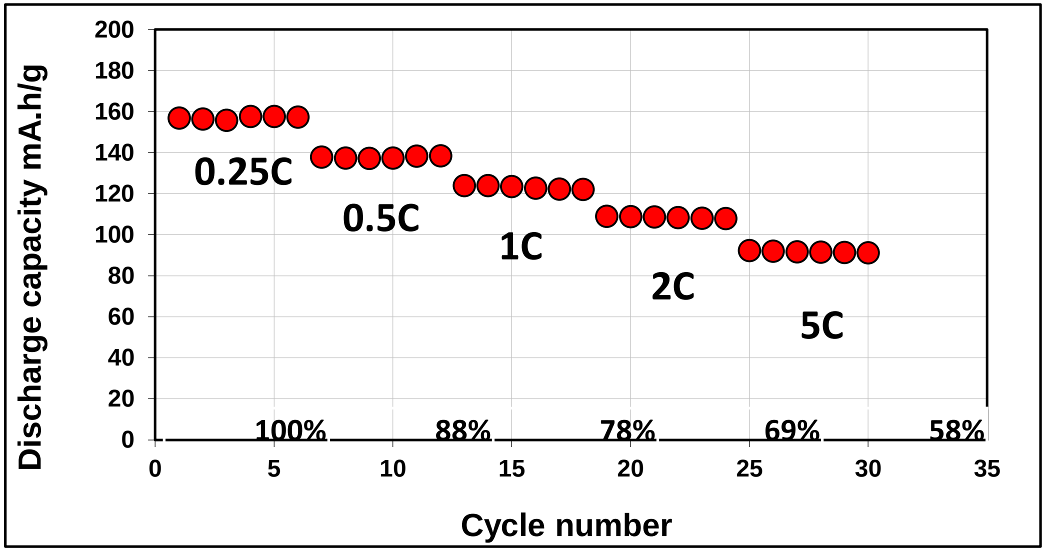
# C coated $LiFePO_4$

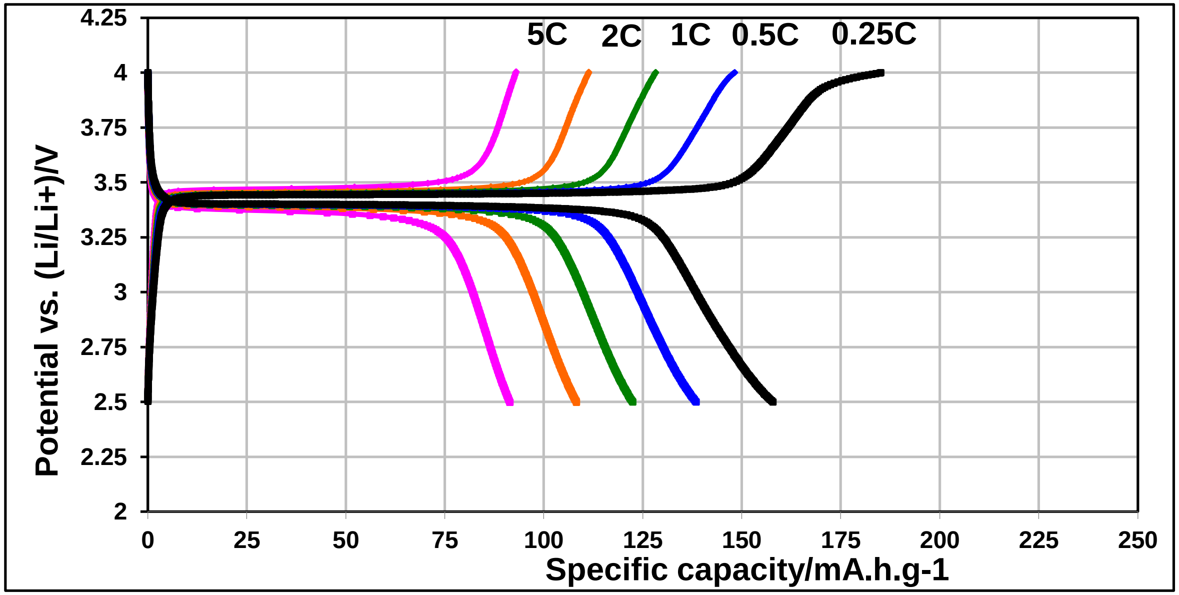




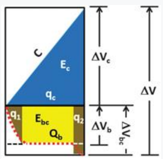
presently working on Graphene-$LiFePO_4$

# Rate Performance of C-coated LFP microspheres vs. Li

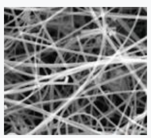


# NEO-Energy Active Research Lines

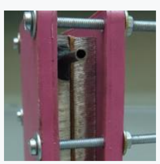


**Hybrid materials for Hybrid Energy Storage.** We work on batteries (high energy, poor power), we work on supercapacitors (high power, poor energy). Now we also work on hybrids for extra energy density whith high power

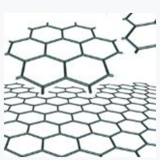


**Micro-Supercapacitors with Silicon Nanowires** A collaborative European project (NEST; Nanowire Energy Storage, Coord. CEA). MnO2 coated SiNWs

**Nanofluids.** Heat Transfer Fluids (HTFs) have shown they are great at transferring heat al low temperatures. We want them working at high temperatures for boosting thermal solar energy. We also optimize them for ink-jet printing.



**Energy Storage with New Flow Cell Concepts.** Electroactive nanofluids to store energy in large tanks externally to the electrochemical reactor that we call battery. Targets: storage of renewable energies. Fuelling electric vehicles.



**New industrial Methods for the Preparation of High-quality Graphene.** Ease of preparation, eco-friendly methods beyond Hummer's. Larger amounts than CVD.

# The NEO-Energy TEAM

www.neoenergy.cat
www.icn.cat/index.php/en/research/core-research/novel-energy-oriented-materials-group/overview

**NEO – ENERGY 2015**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Rocío Rodriguez
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**Master** Daniel Rueda

**Undergrad** Hong Chen

**Engineer** Carlos Marchante

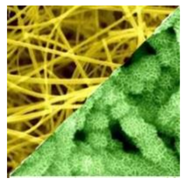
chemists engineer physicists

# Main Colaborations

ICN2
Institut Català de Nanociència i Nanotecnologia
EXCELENCIA SEVERO OCHOA

## External | Colaborations | Internal ICN2

NEST
G. Bidan, CEA, FR
Fraunhofer, DE
PTU, PL
Iolitec, DE



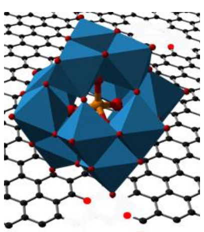
**μ-Supercaps**

NEO-Energy
Novel Energy-Oriented Materials

**Nanofluids.**

P2N
PHONONIC & PHOTONIC NANOSTRUCTURES
Clivia Sotomayor
Thermal Nanofluids (HTFs)

EXCELENCIA SEVERO OCHOA



**Hybrid nanocomposites**
**Electroactive nanofluids**

NACARFLOW
E. Enciso UCM, Madrid, ES
Dino Tonti, ICMAB, BCN, ES

NANO
Bioelectronics & Biosensors Group
Arben Merkoçi
Ink-Jet Printing of Graphene for Energy and Biosensors