# Is the Future Black ?

Klaus Müllen
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Mainz

## Screen-printable thin film supercapacitor …

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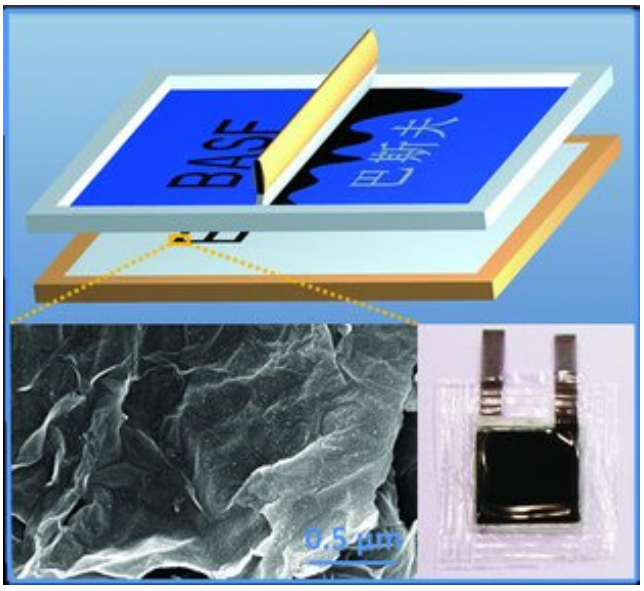
…from graphene/polyaniline inks




BASF
The Chemical Company

**Carbon Materials**
**Innovation Center CMIC**

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Adv. Energy Mater. 2013, 3, 1035

# Graphene, the "wonder substance"



**Remarkably high:**

- electron mobility at room temperature (reported values > 15,000 $cm^2 \cdot V^{-1} \cdot s^{-1}$)
- optical transparency (absorbs 2.3% of white light)
- thermal conductivity (higher than carbon nanotubes or diamond)

**Very:**

- thin (one-atom thickness)
- light (weighing only about 0.77 $mg/m^2$)
- strong (mechanical strength 100 times greater than steel)
- flexible (can be wrapped up into 0D fullerenes, rolled into 1D nanotubes)

# How to fabricate graphene ?

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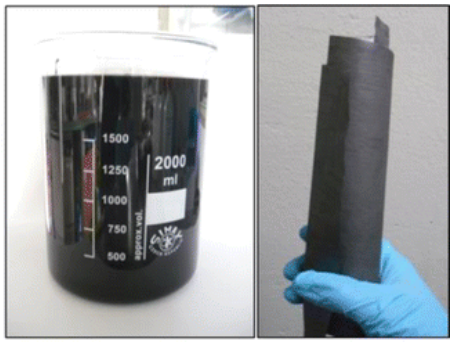
## Exfoliation of graphite

↓

Graphene solutions for composites and printable inks




J. Am. Chem. Soc. 2014, 136, 6083

Adv. Energy Mater. 2013, 3, 1035

## Chemical Vapor Deposition

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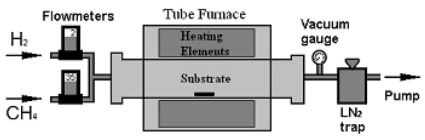
Large scale electronic devices



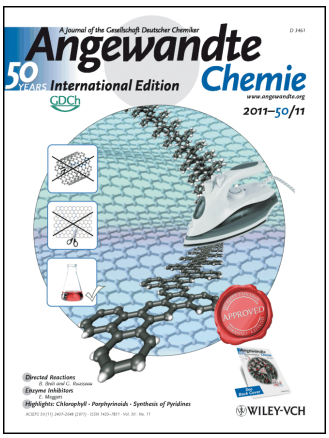


ACS Nano 2014, 8, 3337

## Precise bottom - up synthesis

↓

New graphene-based structures and materials

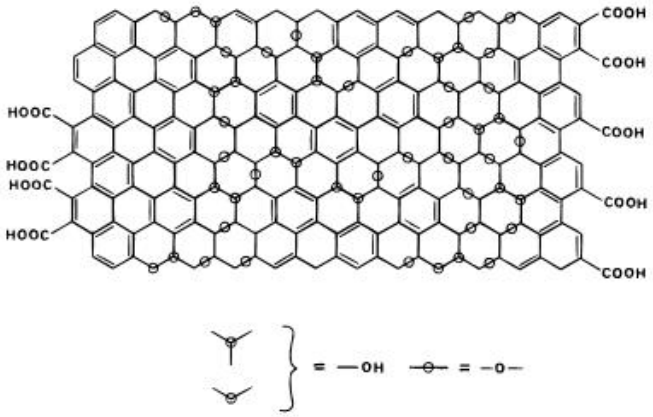


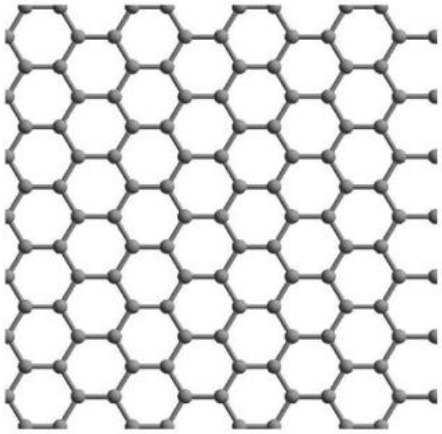

Angew. Chem. Int. Ed. 2011, 50, 2540

Nature 2010, 466, 470

# Graphene from graphene oxide

Dispersable in water



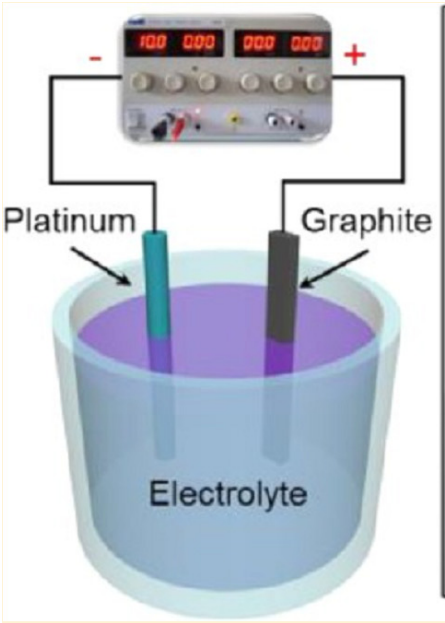

1. Chemical reduction using reducing agent
2. Thermal reduction at high temperature

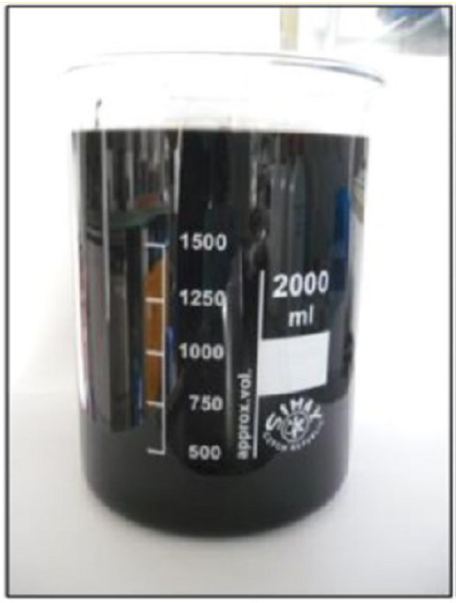
Easy synthesis and processing, high yield, large scale, cheap....



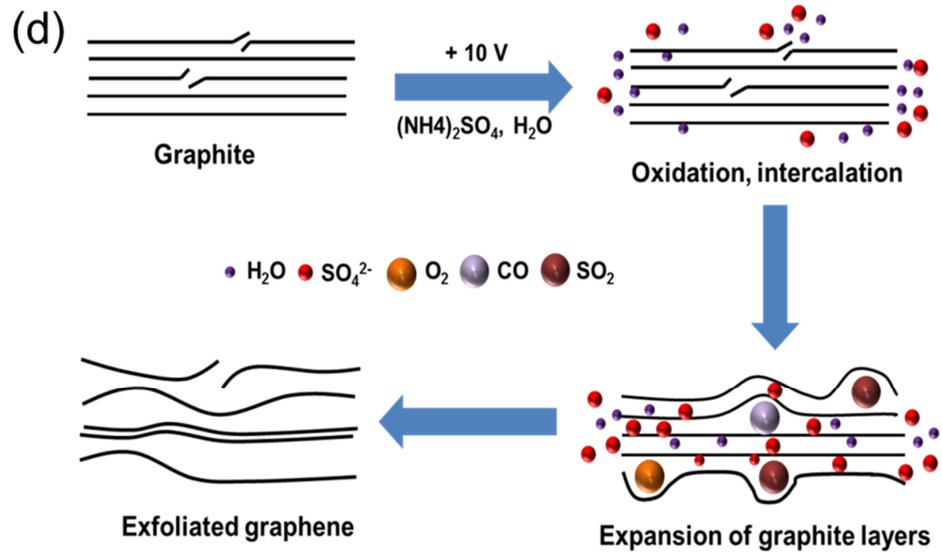
# Solution-processability of high-quality exfoliated graphene (EG)

- direct use in transparent films and conductive inks
- low-cost and environmentally friendly production




J. Am. Chem. Soc. 2014, 136, 6083


ACS Nano 2013, 7, 3598; J. Am. Chem. Soc. 2014, 136, 6083

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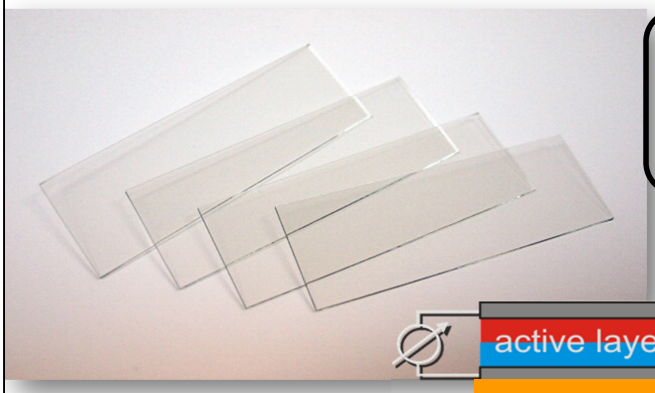
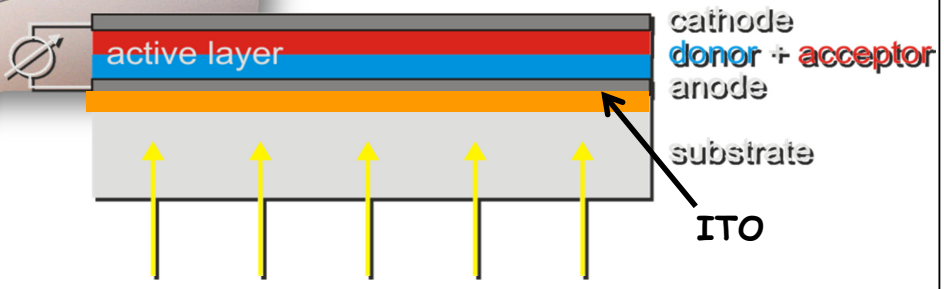
# Graphene for ITO replacement



- typically 90% $In_2O_3$, 10% $SnO_2$ by weight
- high electrical conductivity (~$10^4$S/cm) and high optical transparency

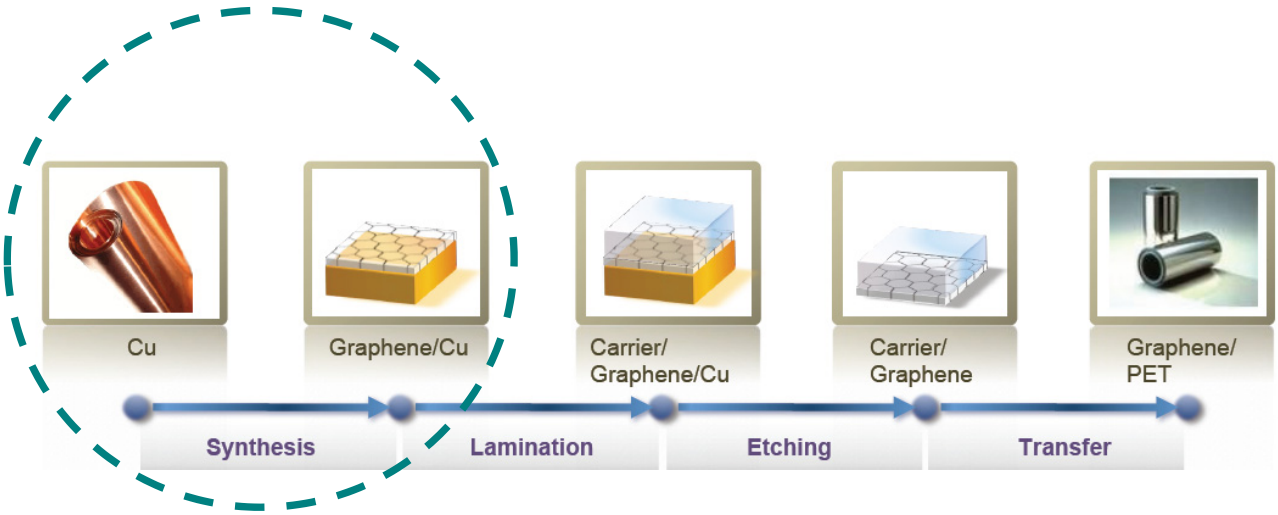



## Uses

- transparent conductive coatings for LC or plasma displays, flat or touch panels,
- solar cells, etc.
- as anode (hole injection layer) in organic light-emitting diodes

Angew. Chem. Int. Ed. 2008, 47, 2990; Nano Lett. 2008, 8, 323

# Graphene by CVD




**Substrate chemistry & growth process: Scientific focus at CMIC**

# Benefits of CMIC process

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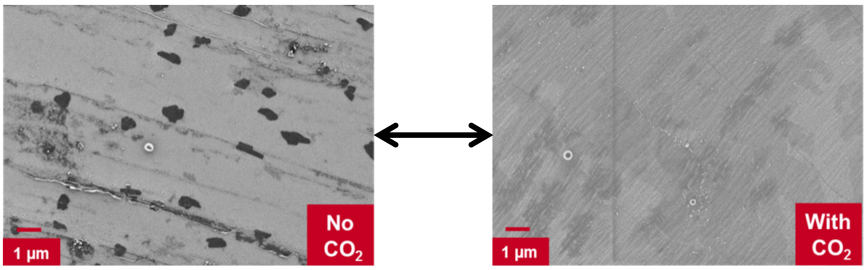
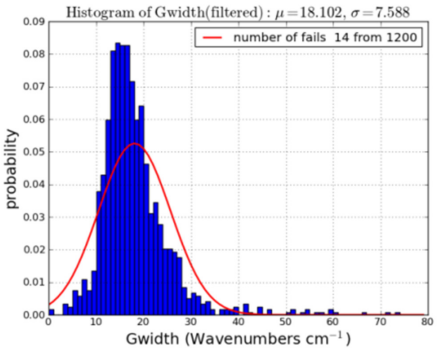
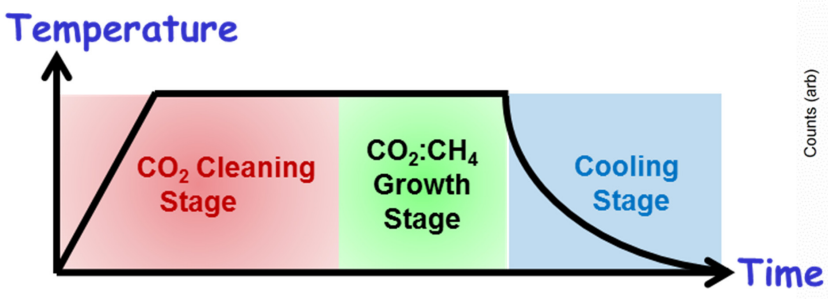
- $CO_2$ cleaning gives high
- reproducibility on Cu substrates



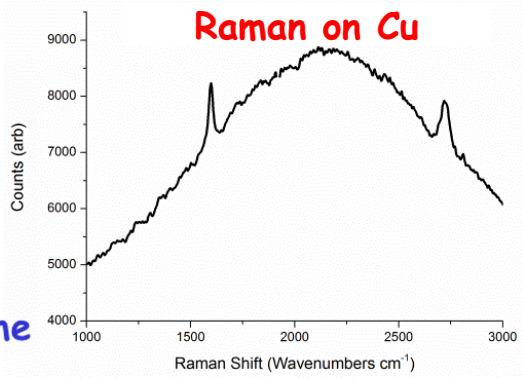

**Fitted FWHM of G Band**



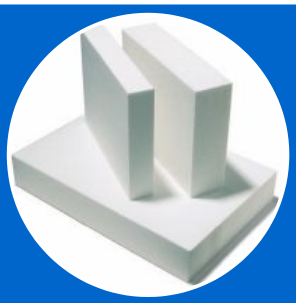

- High-quality graphene via new $H_2$-free growth recipe



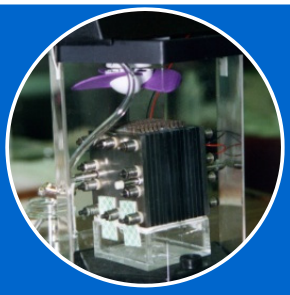

**Raman on Cu**



# Innovative energy concepts need…



1) Energy saving

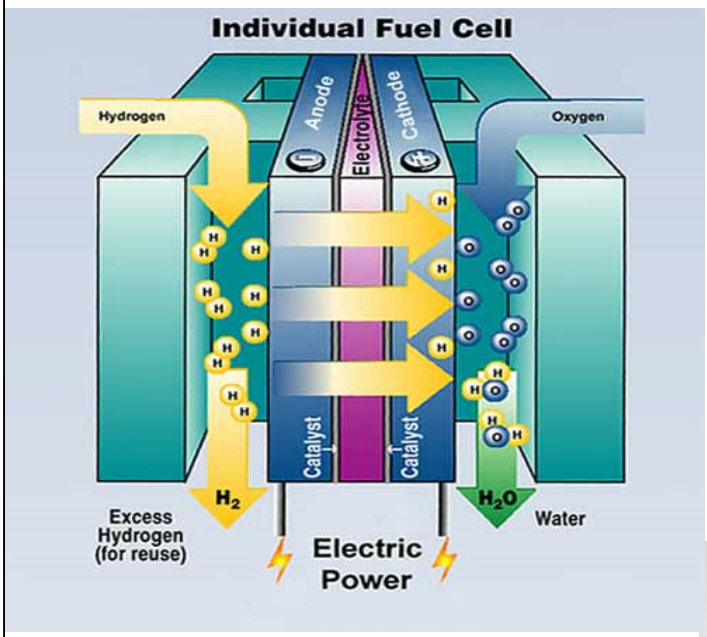


2) Energy transformation

3) Energy storage



# Fuel cell




**Platinum :**
- 58,000-80,000 $/kg

**Iron :**
- 0.2-0.5 $/kg
- 5.6 % of mass of the earth

**Cobalt :**
- 30-50 $/kg
- 25 ppb of mass of the earth

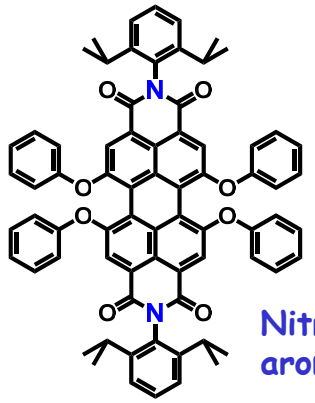
**Fe**

**Co**

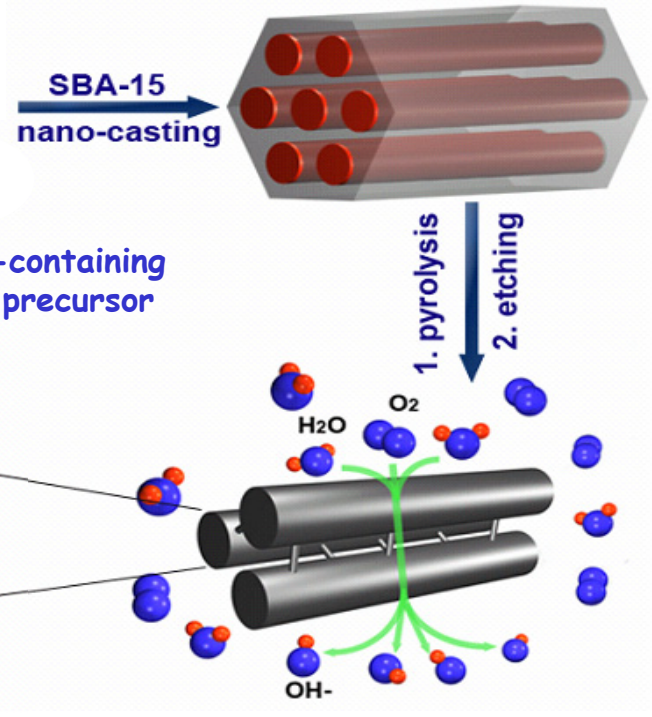
http://www.metalprices.com/

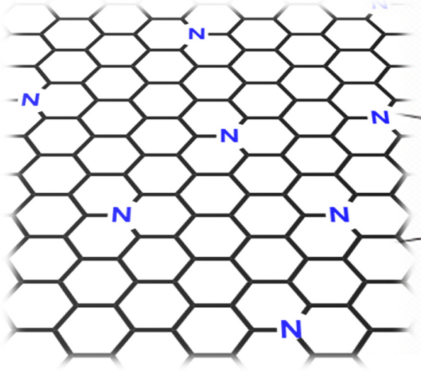
# Metal-free catalyst for oxygen reduction





Nitrogen-containing aromatic precursor



N-doped graphene

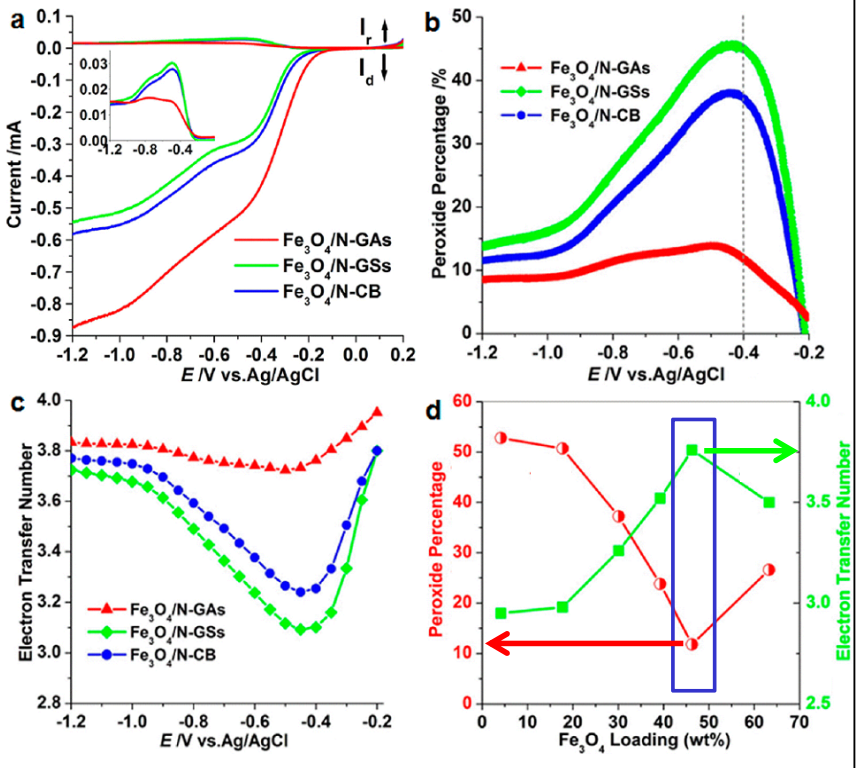
Angew. Chem. Int. Ed. 2010, 49, 2565

# Excellent electrocatalytic activity of $Fe_3O_4$/N-GAs



- lower $H_2O_2$ yield
- higher electron transfer number (~4)
- more positive onset potential
- higher current density

… and better durability than Pt/C



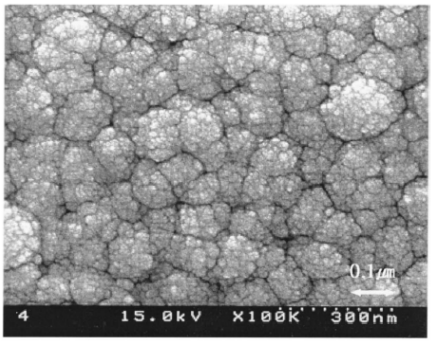

J. Am. Chem. Soc. 2012, 134, 9082

# Lithium-Ion-batteries

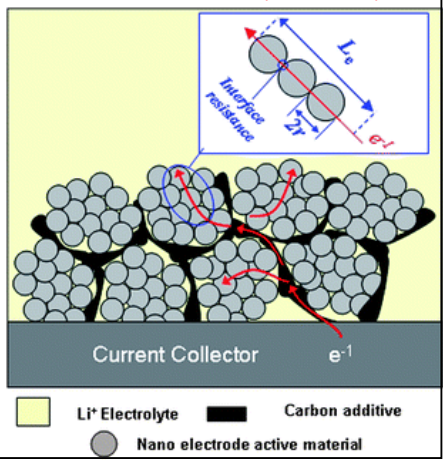
## Current anode and cathode materials

| Anode Materials | Theoretical Capacity (mAh/g) | Cathode Materials | Theoretical Capacity (mAh/g) |
|---|---|---|---|
| Li | 3860 | $LiCoO_2$ | 275 |
| $Li_xC_6$ | 372 | $LiNiO_2$ | 274 |
| Sn | 994 | $LiMn_2O_4$ | 148 |
| $SnO_2$ | 781 | $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ | 274 |
| Si | 4200 | $LiFePO_4$ | 170 |
| $Co_3O_4$ | 1100 | S | 1672 |

Poor cycle performance




Low rate capability




# Nanoparticles into Li-batteries



Cobalt oxide


**Pro:** high capacity

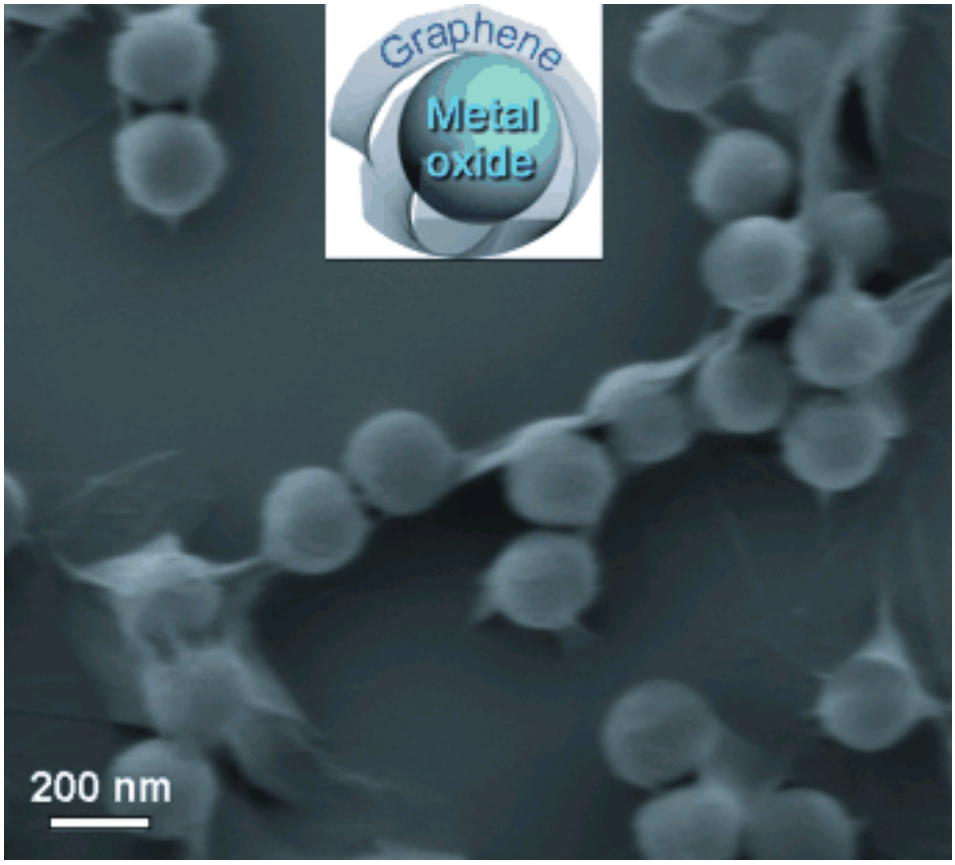
**Contra:** poor cycle performance

## The best of two worlds


Graphene sheet

High capacity and chemical stability

Angew. Chem. Int. Ed. 2010, 49, 8408;
Nature Communications 2013, DOI: 10.1038/ncomms3487




# In-plane micro-supercapacitors from graphene

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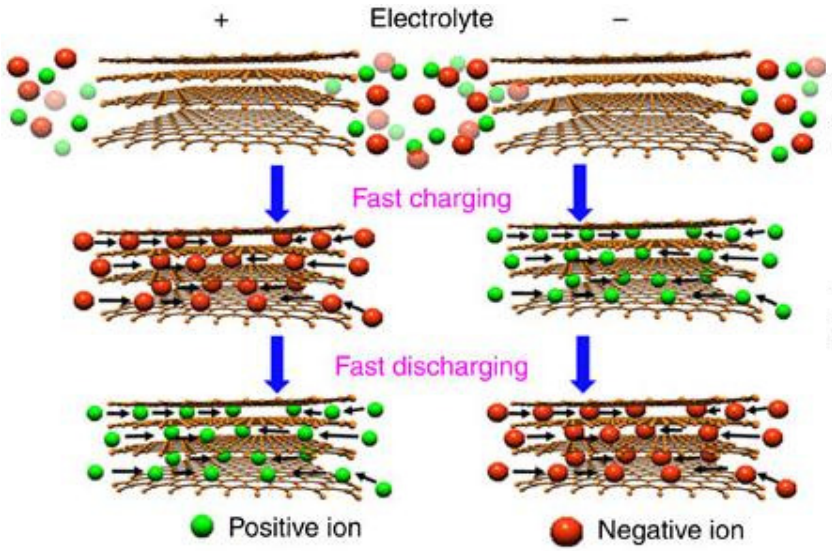
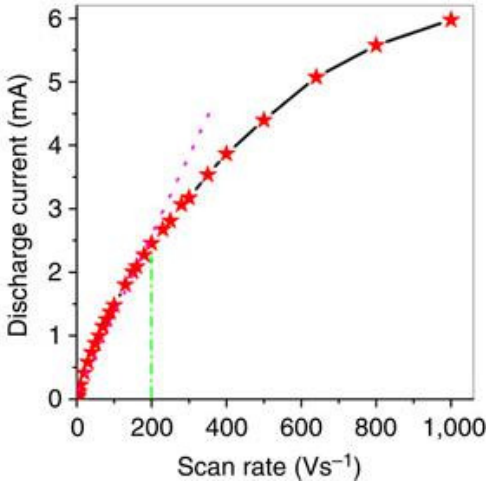



## Electrochemical characterization




## Supercapacitor performance

**High cycling stability**
(98.3% capacitance retention / 100,000 cycles)

Nature Communications 2013, DOI: 10.1038/ncomms3487

# Graphene Research & Development

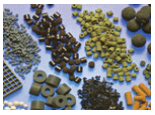
## BASF roadmap towards graphene applications

BASF
The Chemical Company

Short term

Mid term

Long term



- **Conductive Formulations and Inks**
  - Printable electronics, e-textiles, coatings
- **Composite Materials**
  - Antistatics, barrier, mechanical reinforcement
- **Energy Storage Materials**
  - Batteries, supercapacitors
- **Catalysis**
  - Fuel cells, catalyst supports
- **Transparent Conductive Layers**
  - OPV, OLED, display
- **Carbon Semi-Conductors**
  - FET, spintronics

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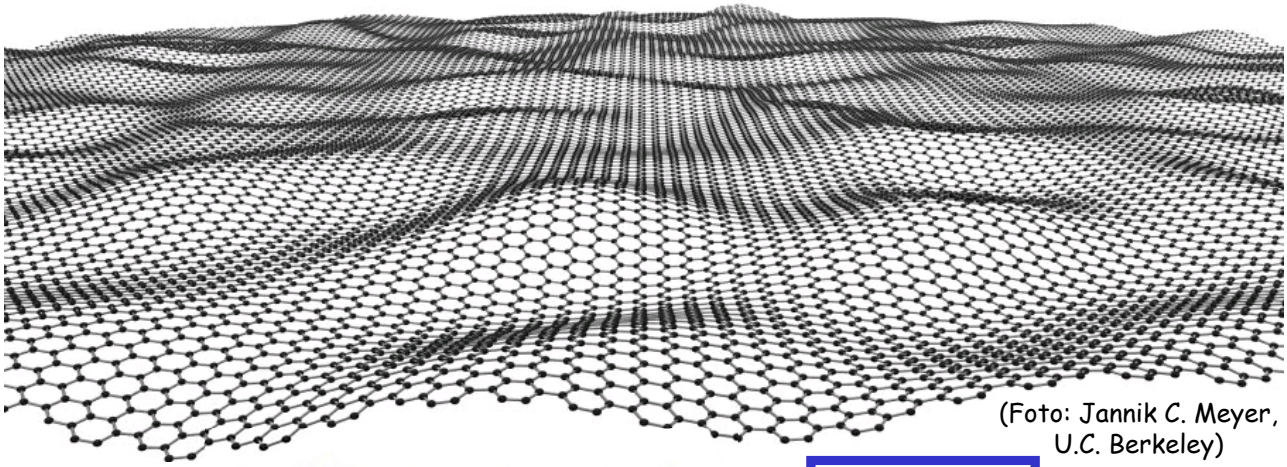
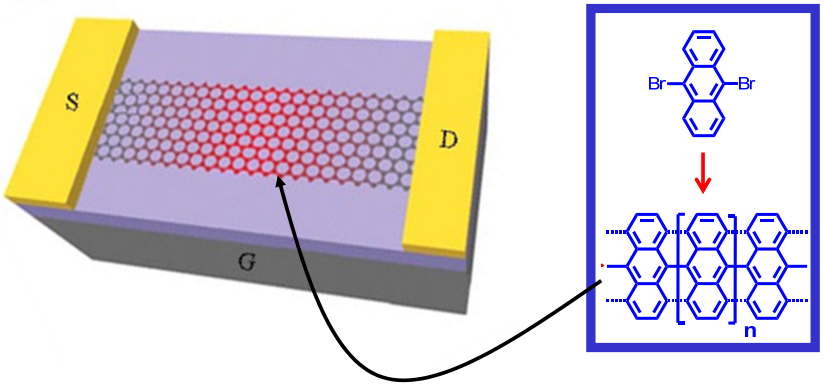
## Graphene nanoribbons: opening the band gap



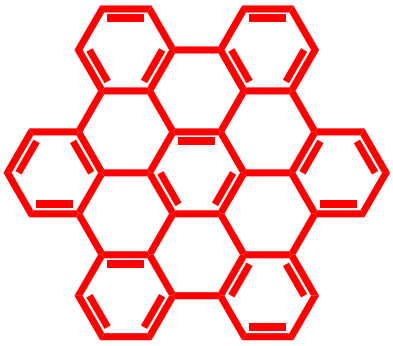
(Foto: Jannik C. Meyer, U.C. Berkeley)



# Polycyclic aromatic hydrocarbons (PAHs)



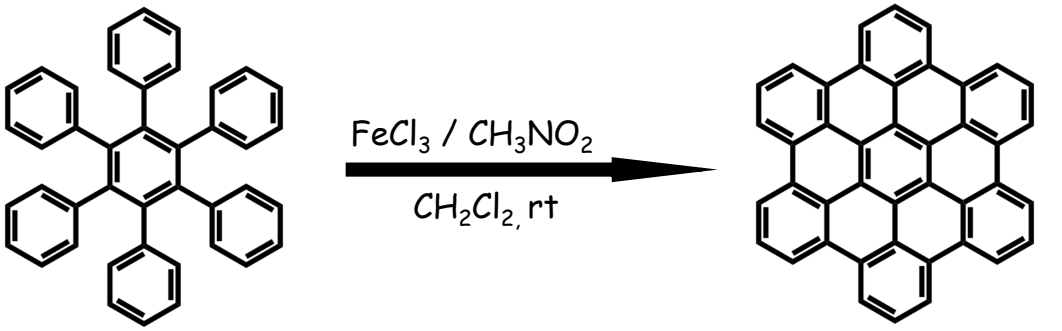
- found in interstellar space, in comets, and in meteorites

Source:www.wikipedia.org

# Flattening a propeller …






… by cyclodehydrogenation from 3D to 2D

Chem. Rev. 2007, 107, 718; Chem. Mater. 2011, 23, 554

# Perfect 3D-carbon polymer

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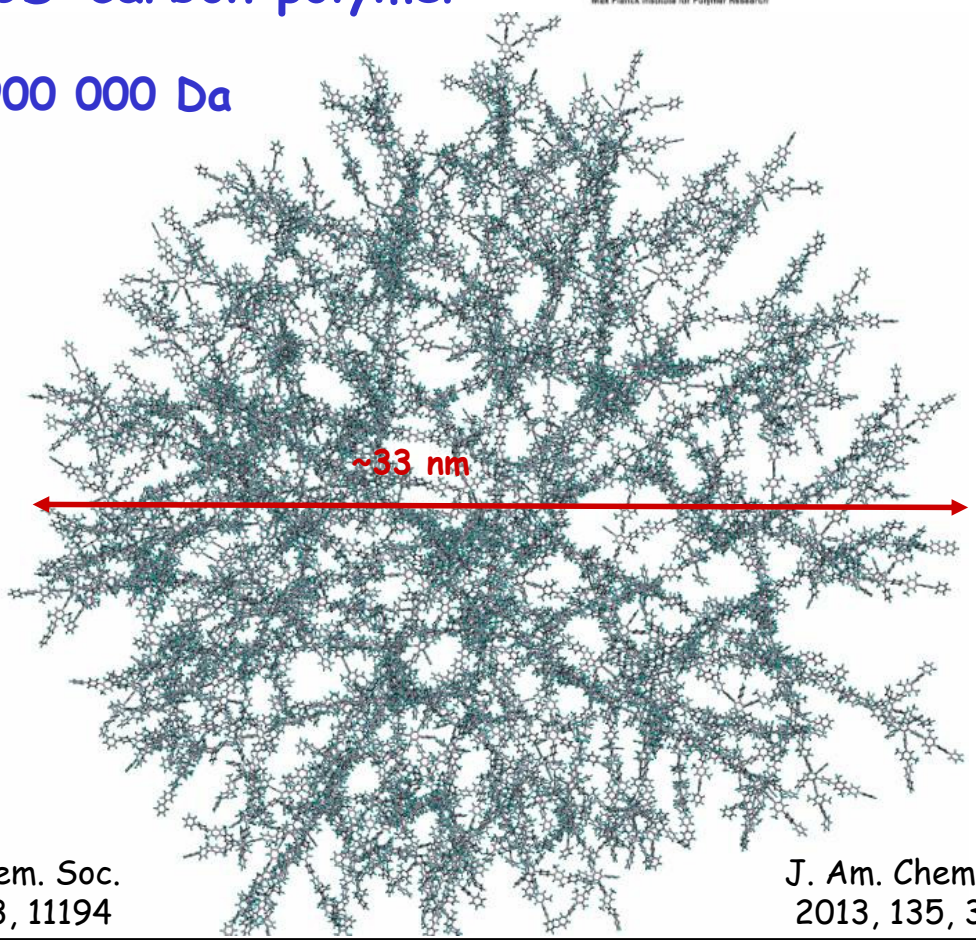
## MW = 1 900 000 Da

~3 nm




J. Am. Chem. Soc. 2011, 133, 11194

J. Am. Chem. Soc. 2013, 135, 34183

# Atomically precise edge chlorination of graphenes

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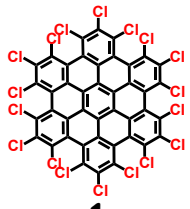
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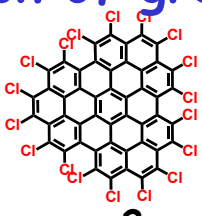
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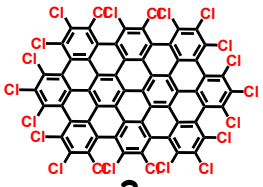
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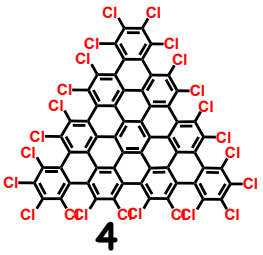
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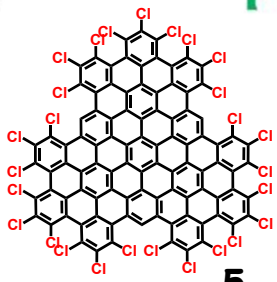
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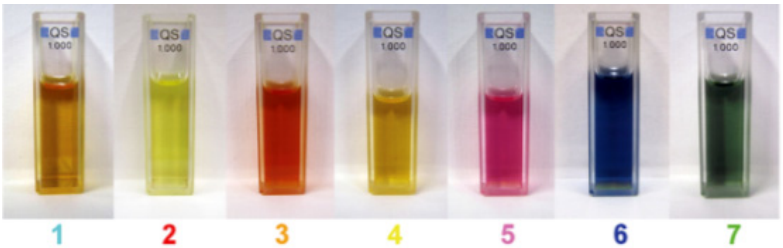


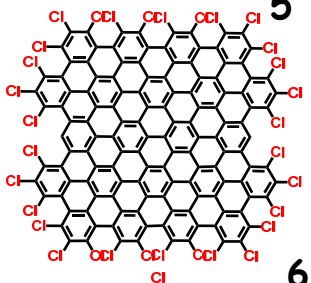
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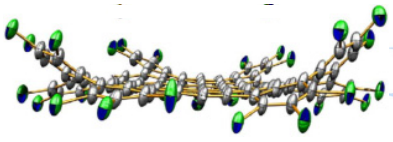
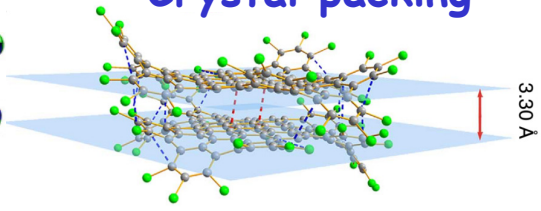
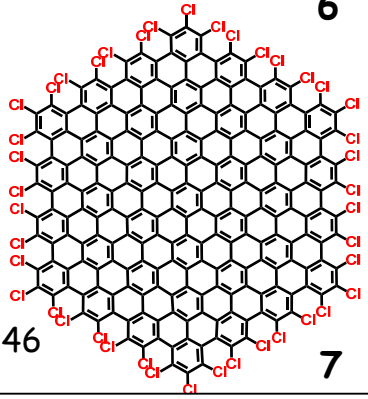
## Crystal packing







7

Nature Communications 2013, doi:10.1038/ncomms3646

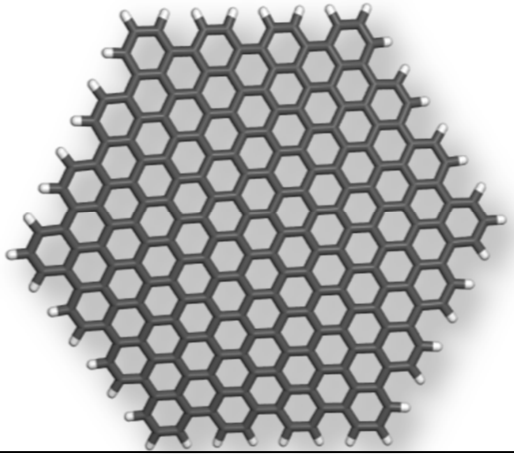
WIKIPEDIA
The Free Encyclopedia

Article Talk

## Graphene

From Wikipedia, the free encyclopedia

"graphene has been referred to as an infinite alternant polycyclic aromatic hydrocarbon (PAH). The largest known isolated flat molecule of this type consists of 222 atoms and is 10 benzene rings across*"



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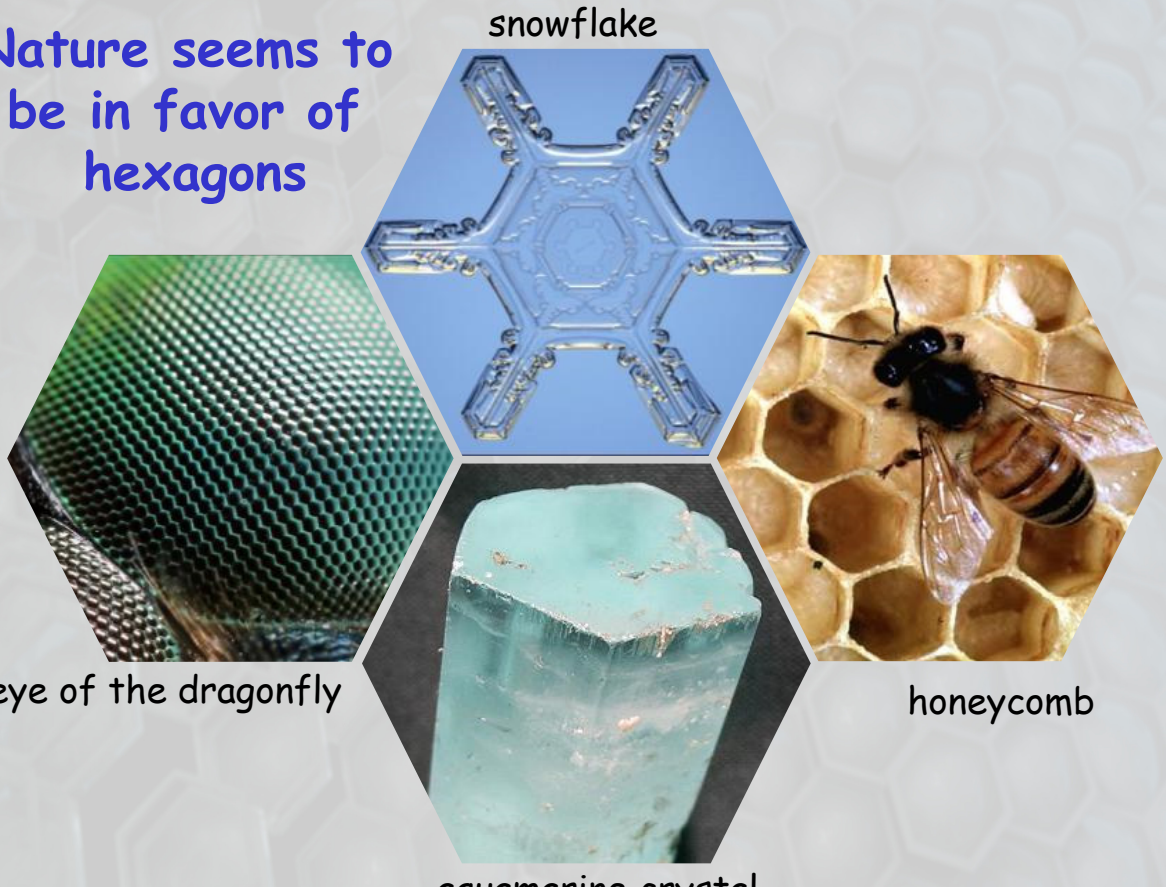
## Nature seems to be in favor of hexagons



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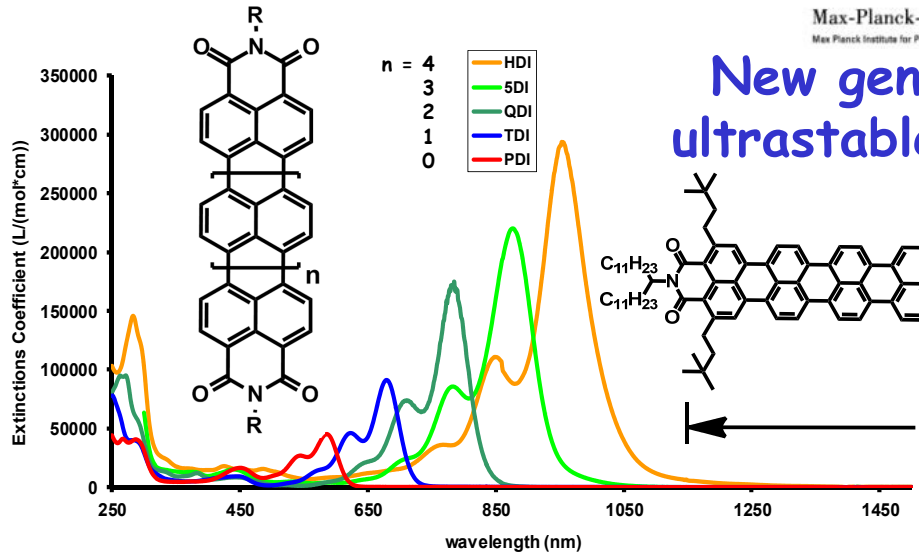
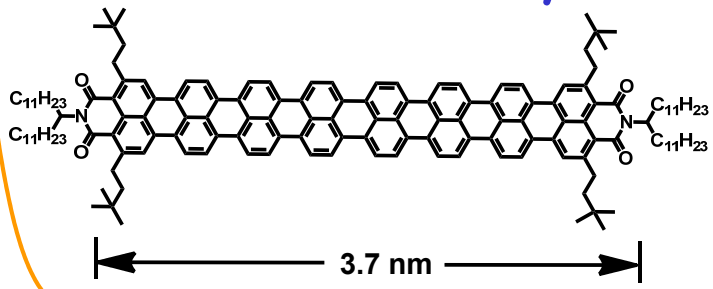
# New generation of ultrastable NIR-dyes





Nature 2010, 446, 905; Nature Photonics 2009, 3, 654

Nature Nanotechnology 2014, 9, 131; Nature Nanotechnology 2014, 9, 182

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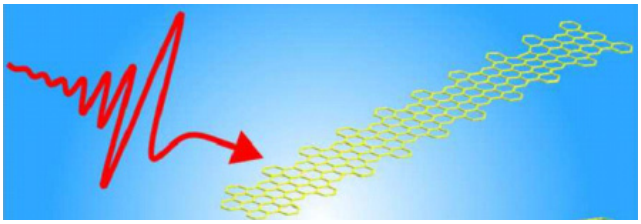
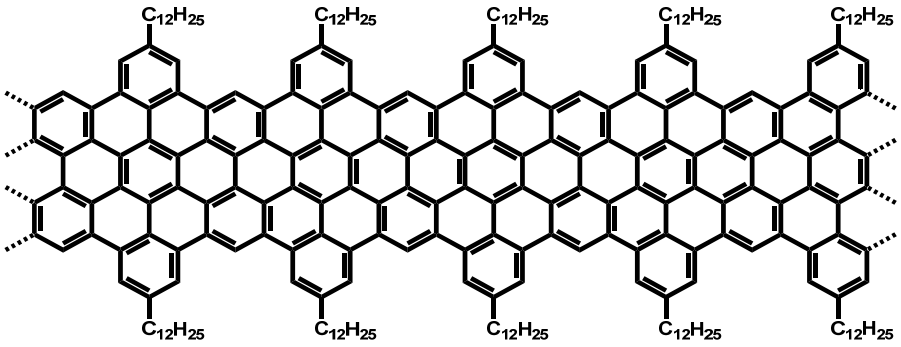
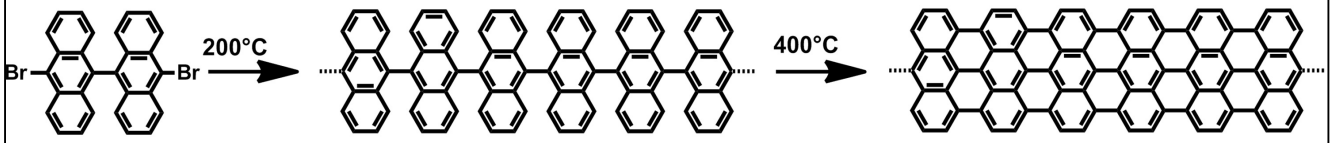


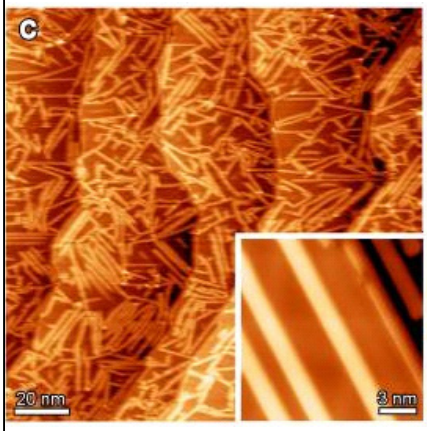


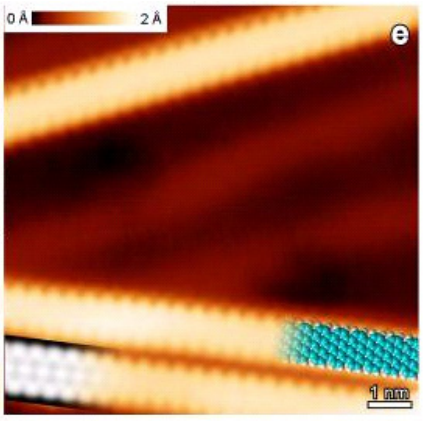

## Comparing the photoconductivity of GNRs with that of conjugated polymers

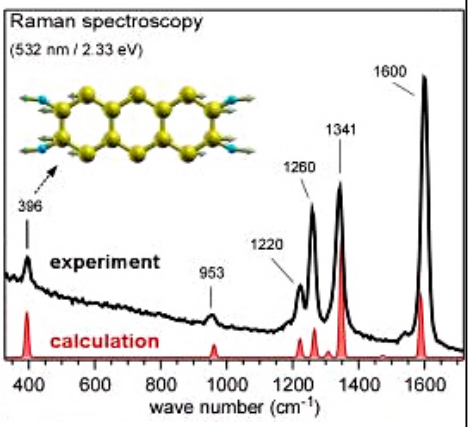
Nano Lett. 2013, 13, 5925; Nature Chemistry 2014, 6, 126

# The new paradigm of polymer synthesis: graphene nanoribbons with atomic precision




Nature 2010, 466, 470; Nature Chemistry 2014, 16, 126

# Graphene nanoribbons

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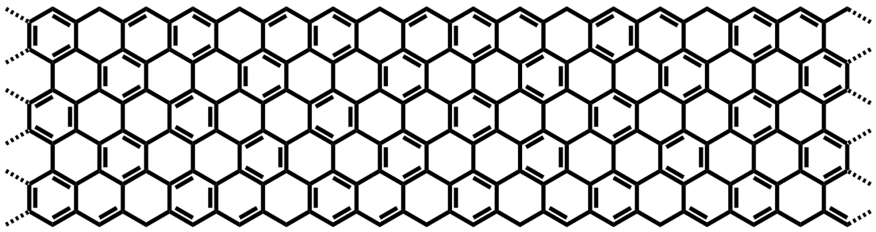
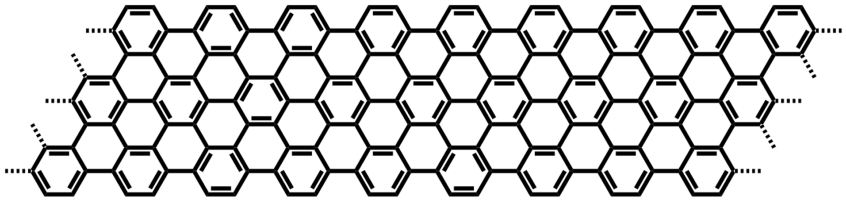
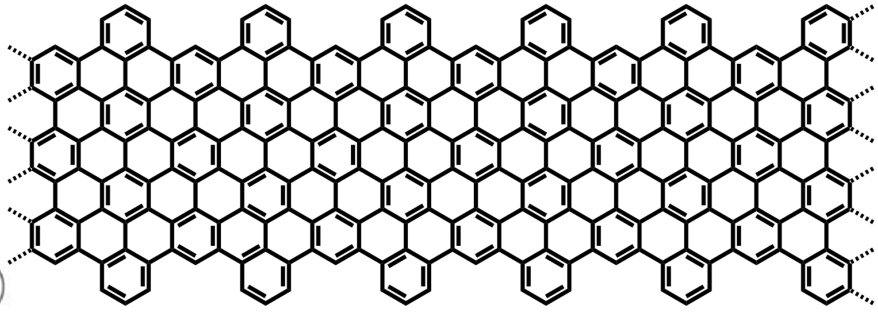


Zigzag edge
metallic



Armchair edge
semiconducting



Cove-shaped
semiconducting