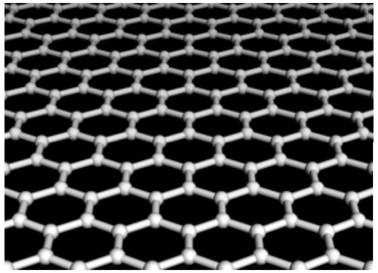
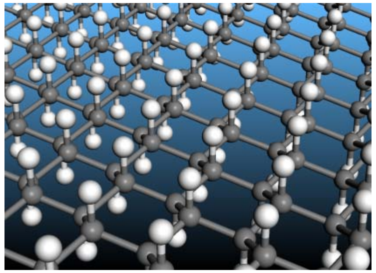
Part II-2

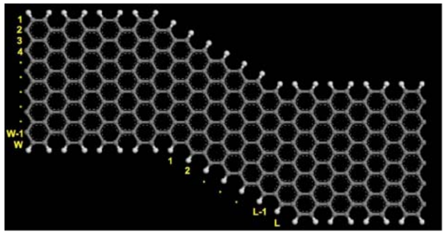
Bilayer graphene and Gap Opening

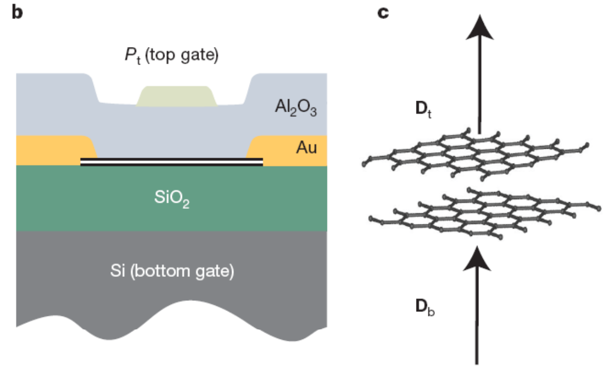
Gap opening

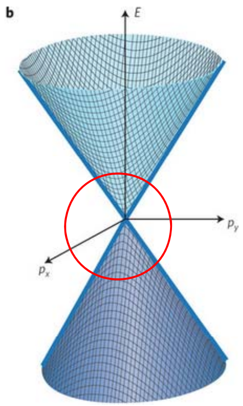
Graphene (sp^2) | Graphane(sp^3) | Graphene ribbon | Under applied E field

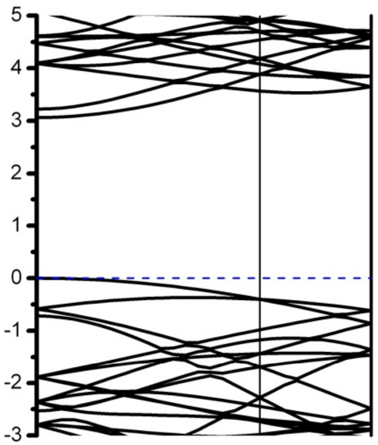


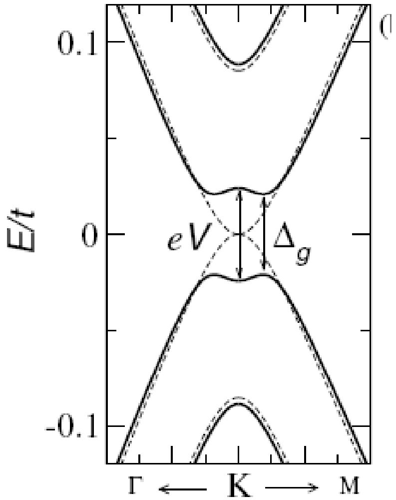


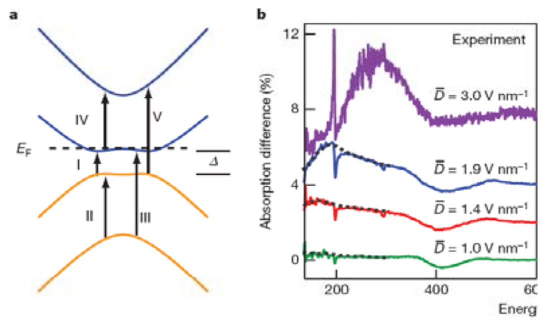












No band gap

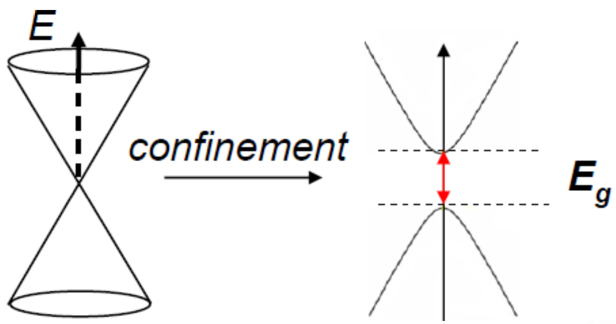
Wide band gap

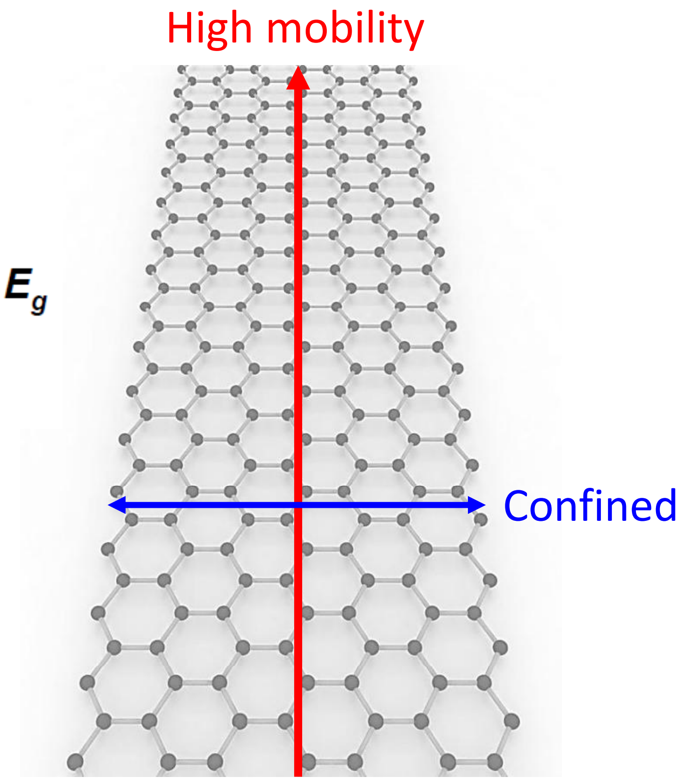
Elias et al,
Science, 323,5914,2009

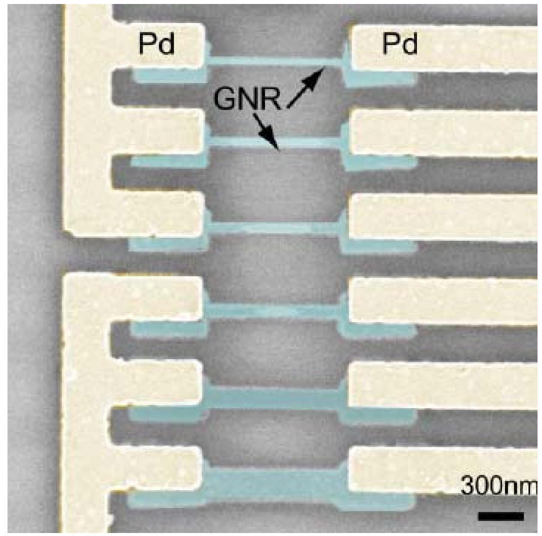
Nature, 2009,Vol.459,p820

Electronic Structures of GNRs

- **Open a gap in graphene-graphene nanoribbon (GNR)**
- **High mobility along the specific direction**
- **Quantum confinement effect**



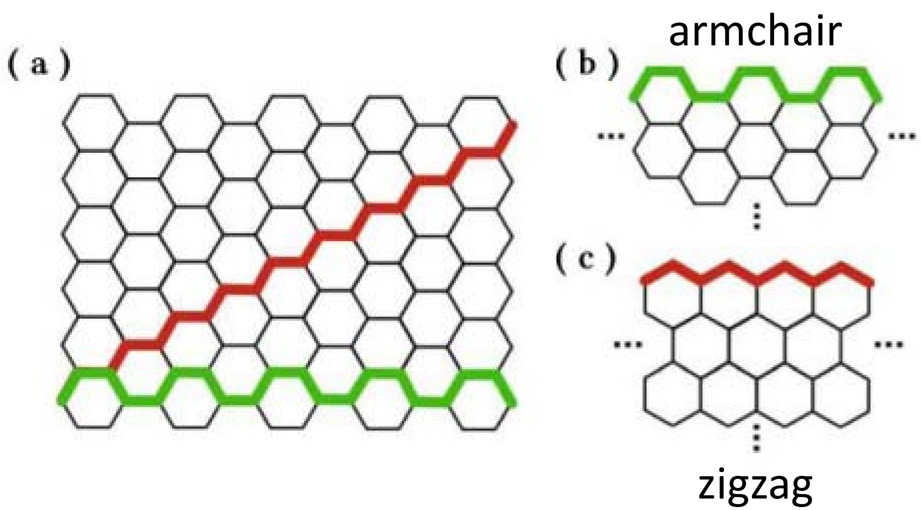


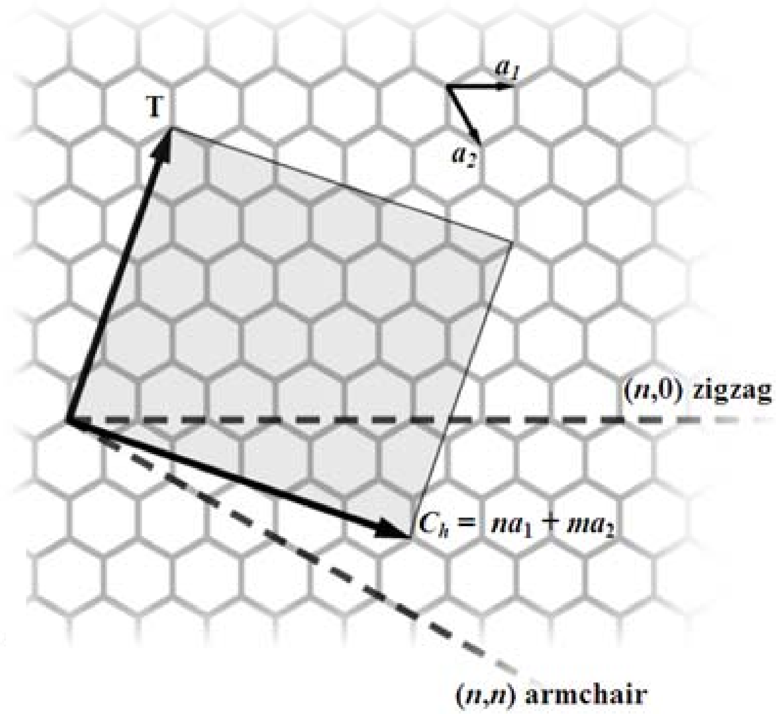


Physical E, 40, 228, (2007)

Graphene Nanoribbon (GNR)

- Structure
  - Graphene strips
  - Charity
    - Two types of edge

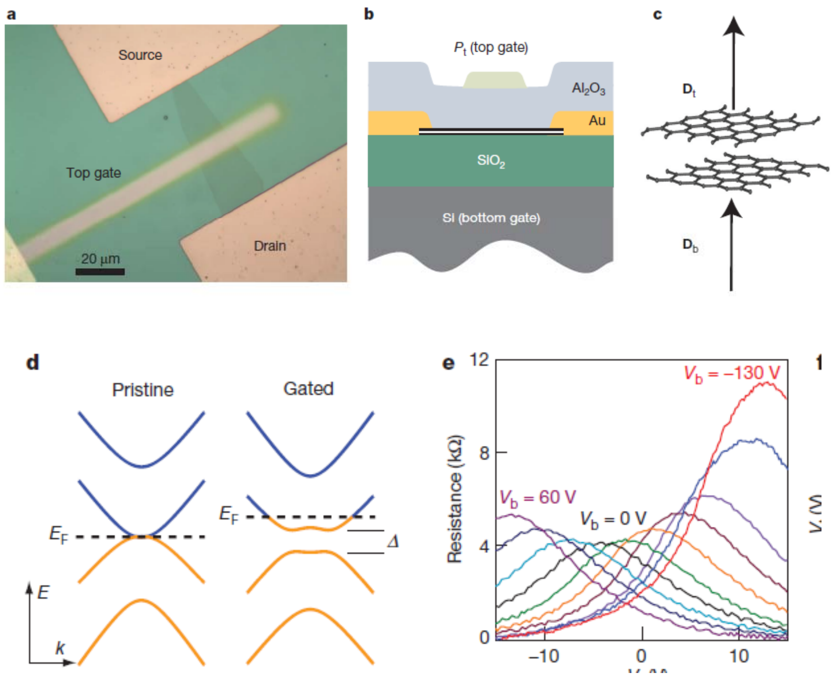




Some of armchair GNRs are semiconucting
metallic: n = 3m+2
semiconducting: n = 3m or 3m+1

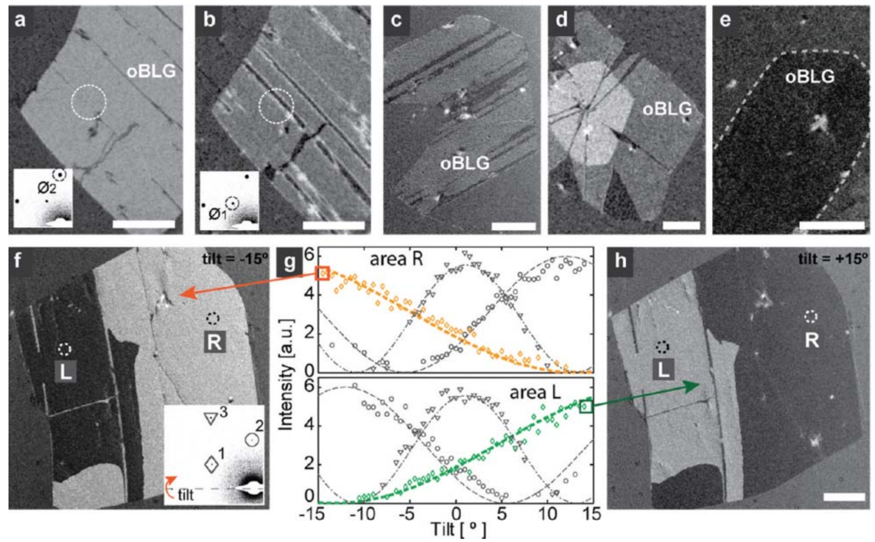
Gap-opening of Bilayered-graphene

Mechanically exfoliated garpehene



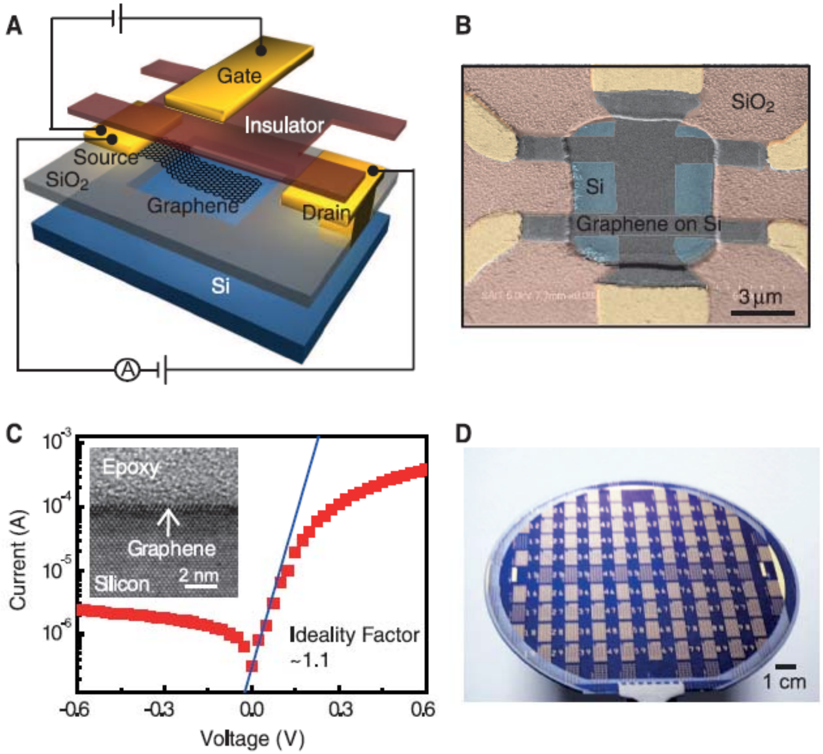
Nature, 2009,Vol.459,p820

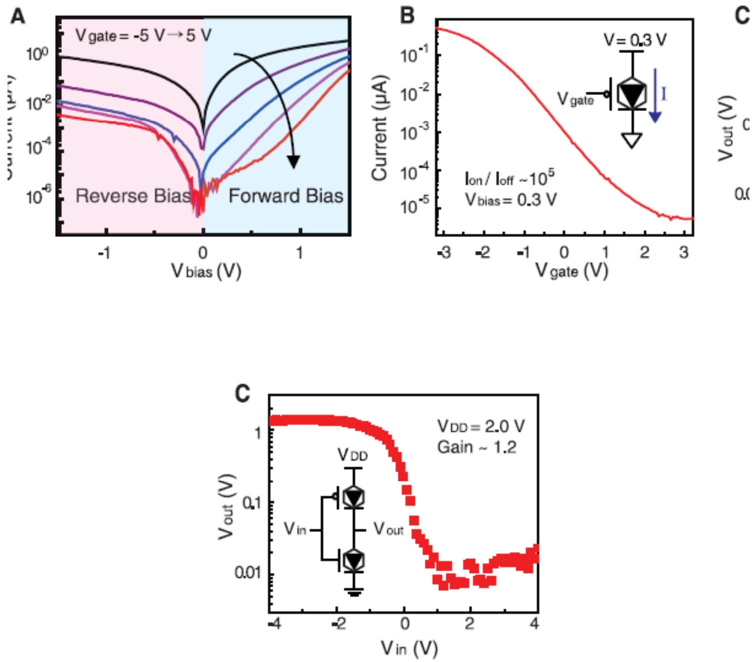
CVD-graphene



Nano Letters, 2012,12, 1609

Graphene Barristor- a gate controlled Schottky barriar



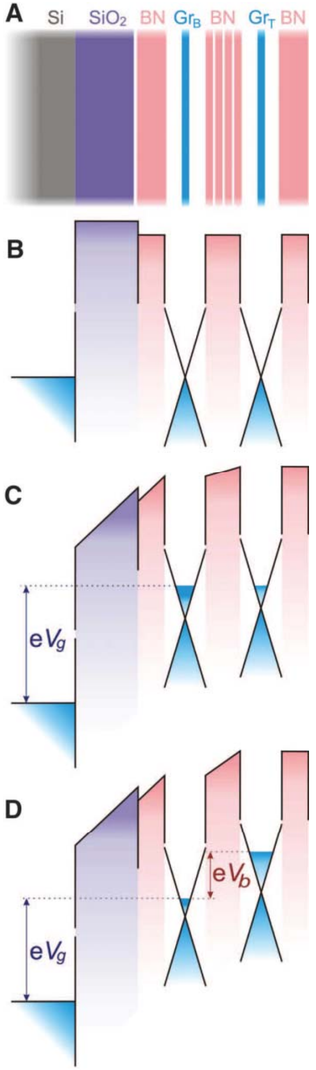


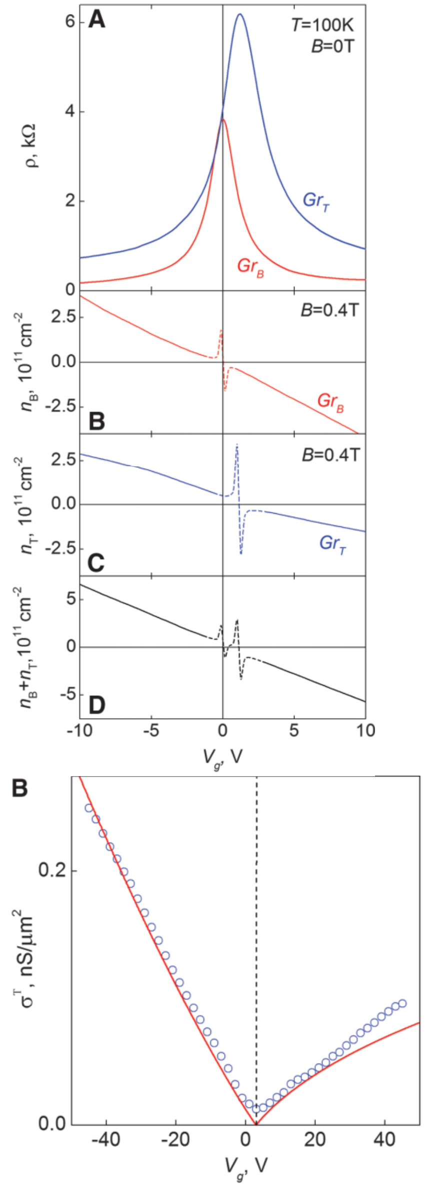
Adjusting graphene workfunction

High on/off ratio~ 10^5

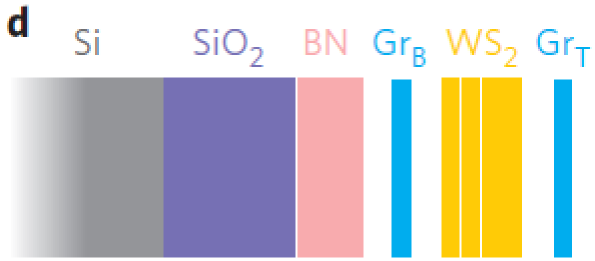
Yang et al, Science, Vol. 336, 1140, 2012

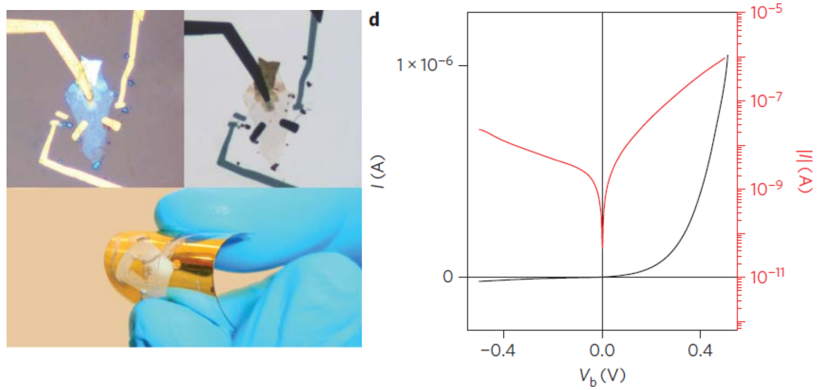
Vertical transnsitor





Science, 335 947-950 (2012)





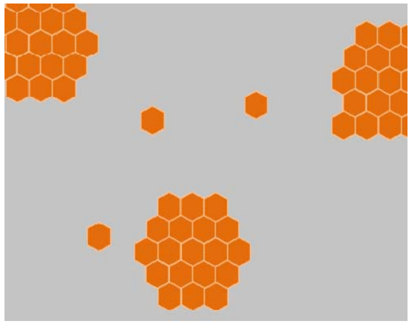
Nature Nanotechnol. 8, 100–103 (2013)

- Combine kinds of 2-D material
- Control tunneling barrier through ultra-thin barrier
- Very Difficult to fabricate

Tunable conduction in graphene based materials

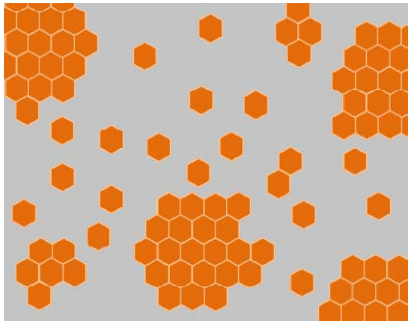
GO

Highly sp^3



Reduction

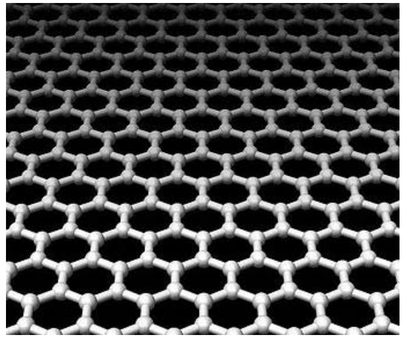
r-GO



$10^3 \sim 10^5\ \Omega$/sq

Graphene

Pure sp^2



$<100\ \Omega$/sq
at 90% T

Insulator

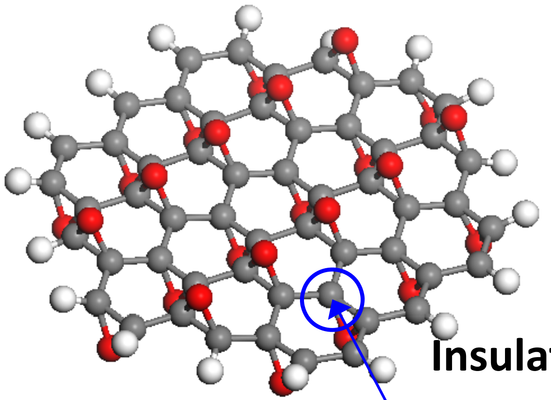
Conductor

Thin tunneling barrier

Transparent conducting electrode

Atomic and electronic structure of GO/Graphene

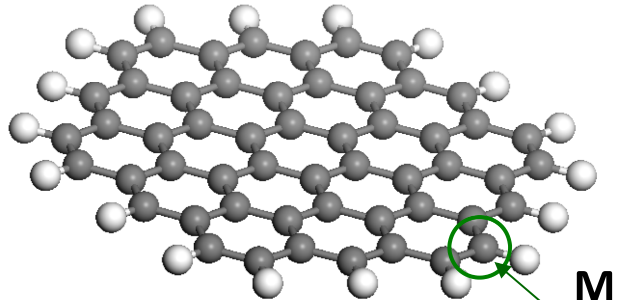
GO nanosheet



Ideal structure

Reduction

Graphene

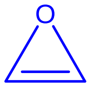


Insulator-like

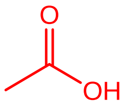
Metallic-like

Distorted sp^3

sp^2 (planar)

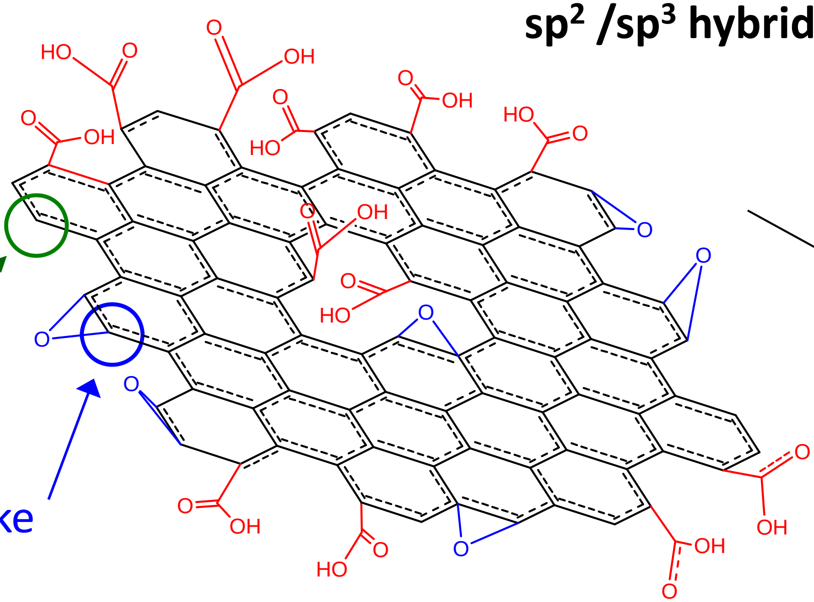


Epoxide group



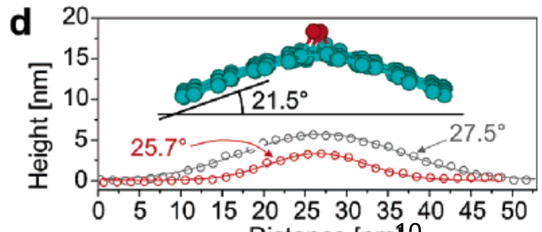
Carboxyl group

sp^2 /sp^3 hybrid (Real structure)



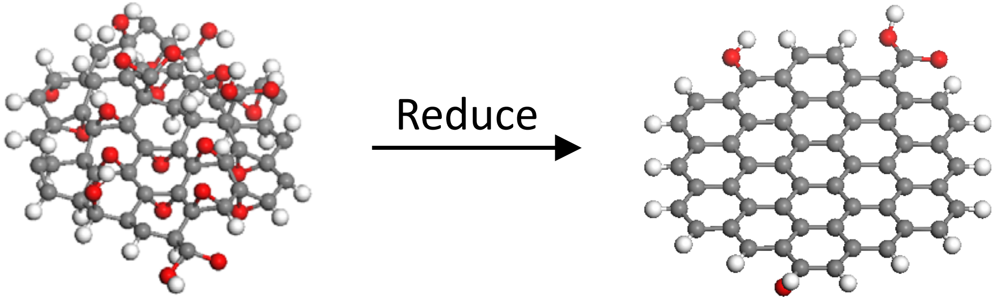
Sp^2-like

sp^3-like

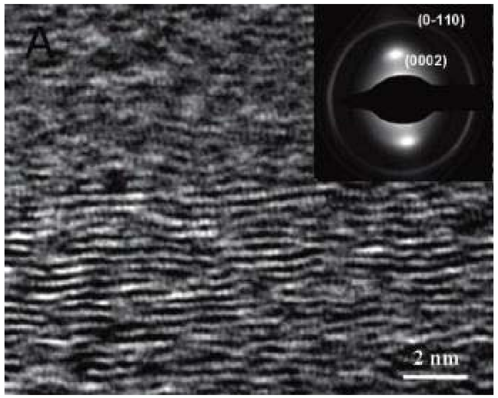


Akasay et al, J of Phys. Chem. B Lett., 110, 8535, 2006

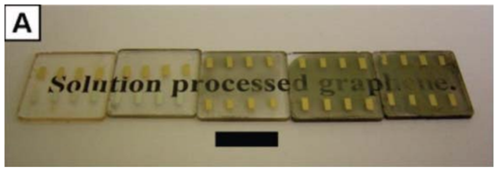
Preparation of reduced GO



UHV thermal anneal

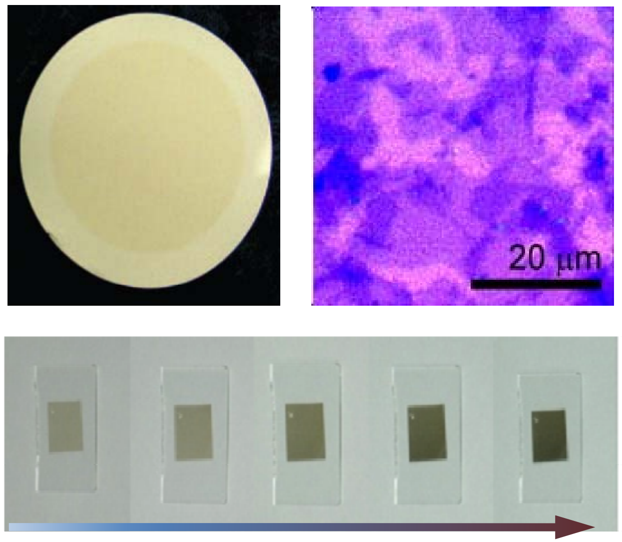


X. Wang *et al. Nano Lett*. 8 323-327 (2008)



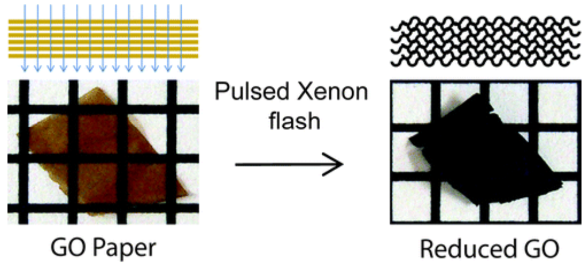
H. A. Becerril *et al. ACS Nano* 2 463-370 (2008)

N_2H_4 vapor



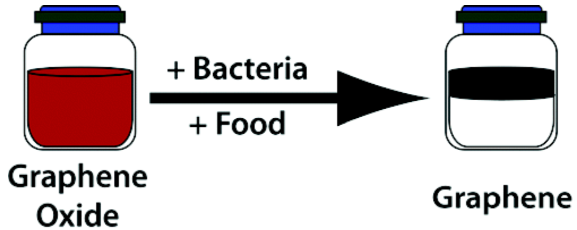
Eda *et al. Nature Nanotech.* 3 270-274 (2008)

Flash light reduction



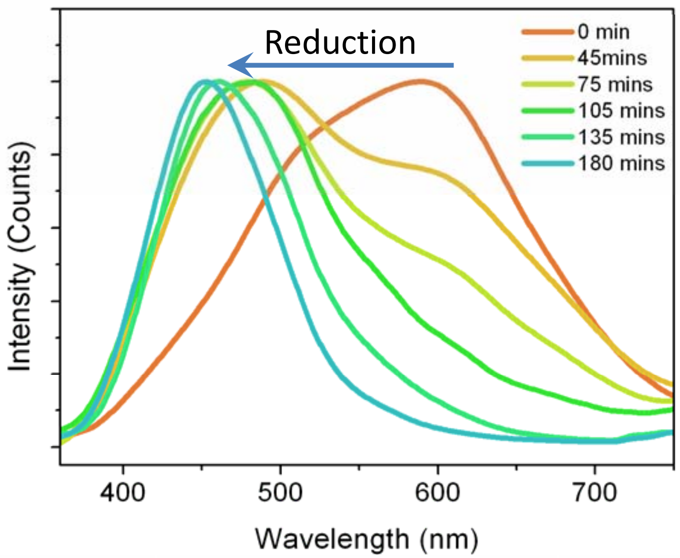
L. J. Cote *et al. JACS* 131 11027-11032 (2009)

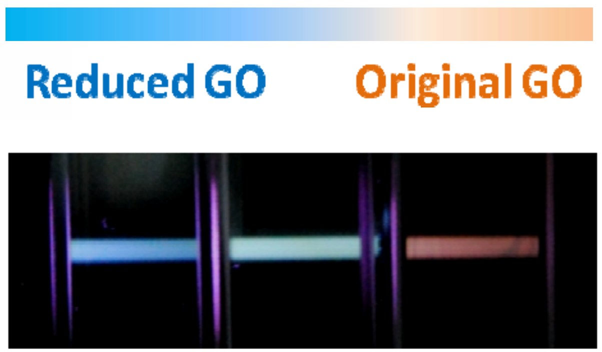
Biological reduction

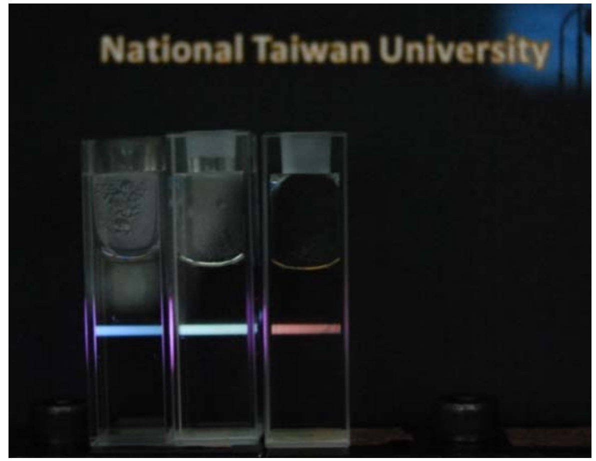


E. C. Salas *et al. ACS Nano* 4 4852-4856 (2010)

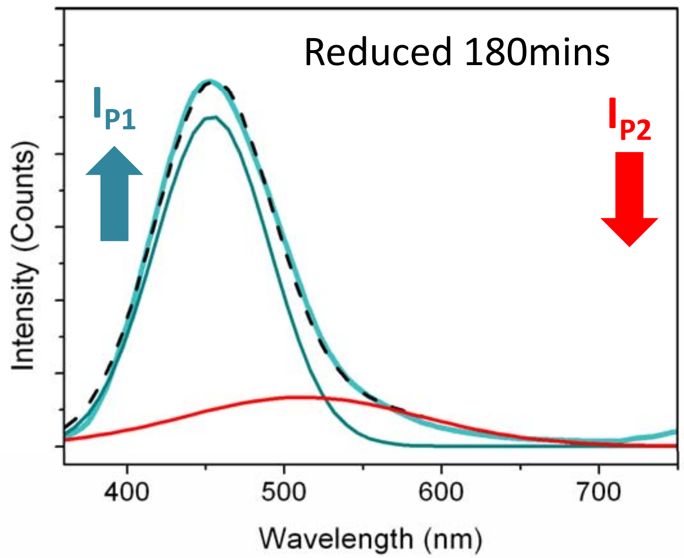
Evolution of photoluminescence of graphene oxide with reduction (I)

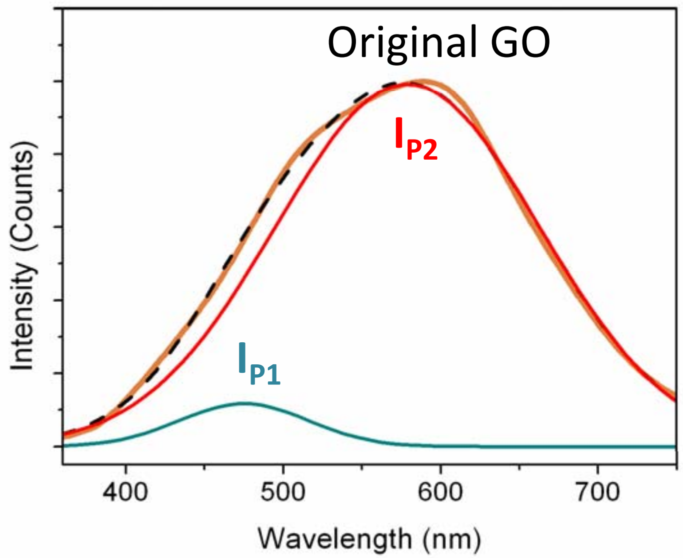






Angewandte Chemie Int. Ed., 51, 6662, (2012)

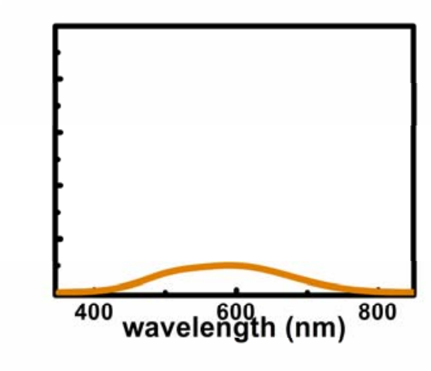


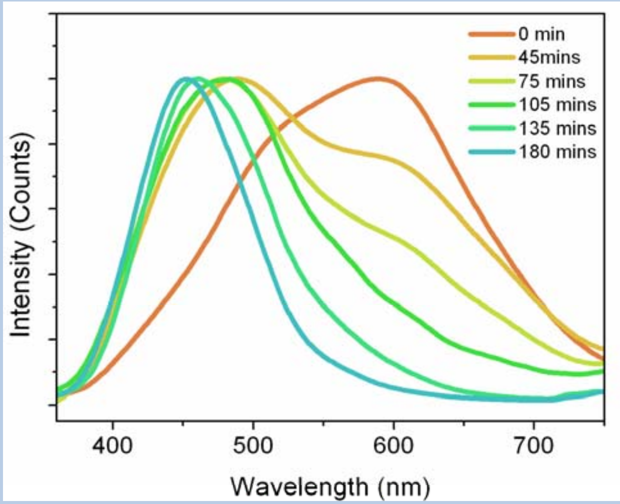


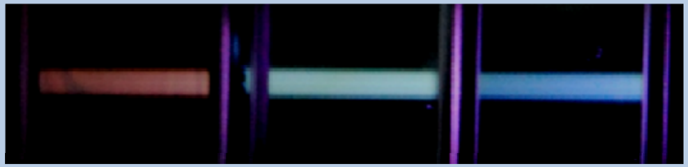
Evolution of photoluminescence of GO and r-GO

Angewandte Chemie Int. Ed., 51, 6662, (2012)

defect

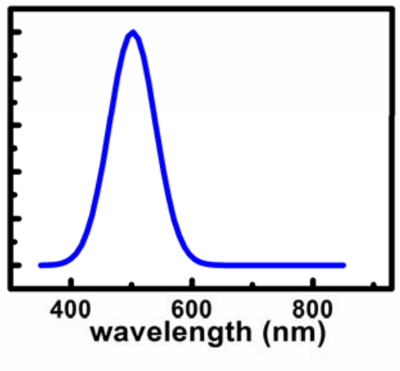


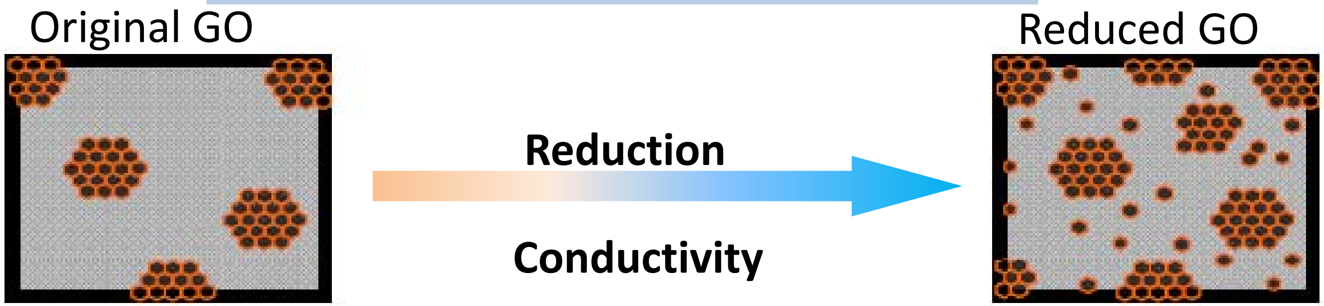




Tunable PL

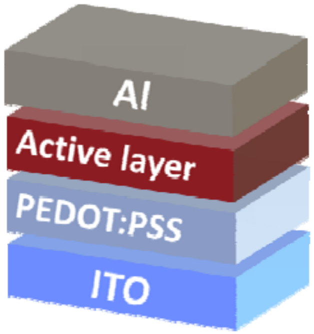
Cluster-like state
nall sp2 clusters or
atomic chains)

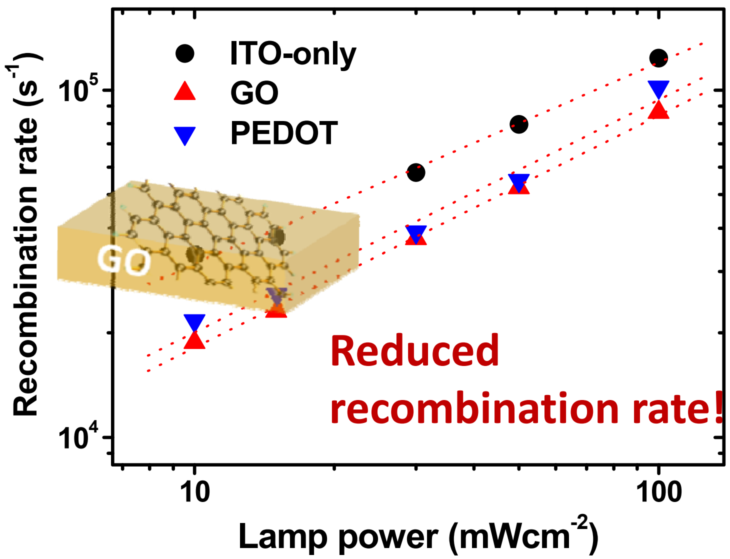


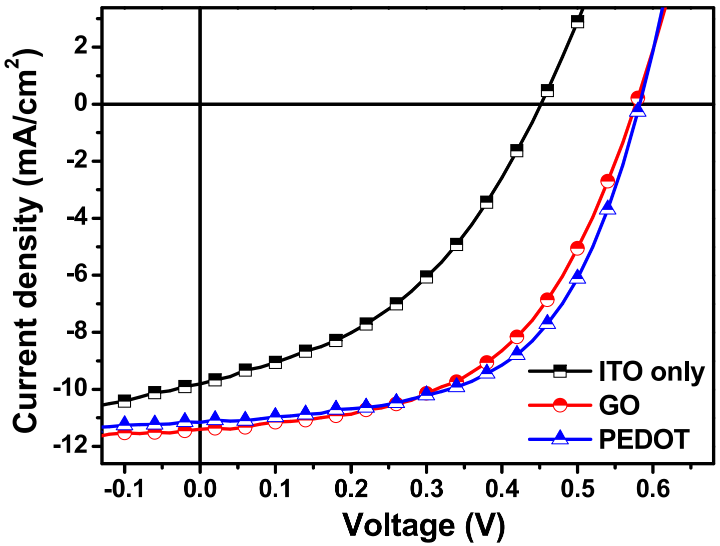


Dept. of Materials Science and Engineering, National Taiwan University

GO as a hole transport layer (replace PEDOT:PSS)



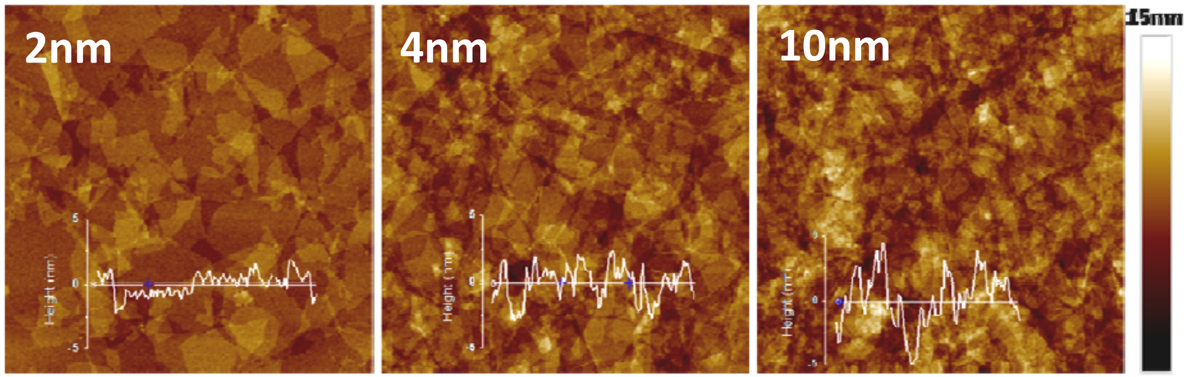




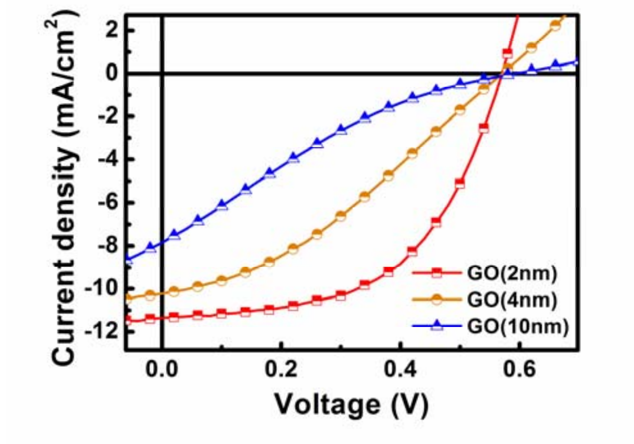
	Voc (V)	Jsc ($mAcm^{-2}$)	FF (%)	η (%)
ITO only	0.45	9.84	41.51	1.84
ITO/GO	0.58	11.40	54.34	3.53
ITO/PEDOT	0.58	11.15	56.86	3.69

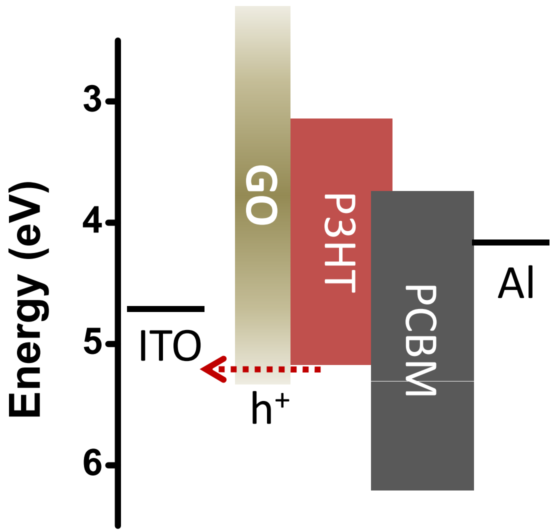
ACS Nano, Vol. 4 , 3169, (2010)

GO act as a thin tunneling barrier for hole transport

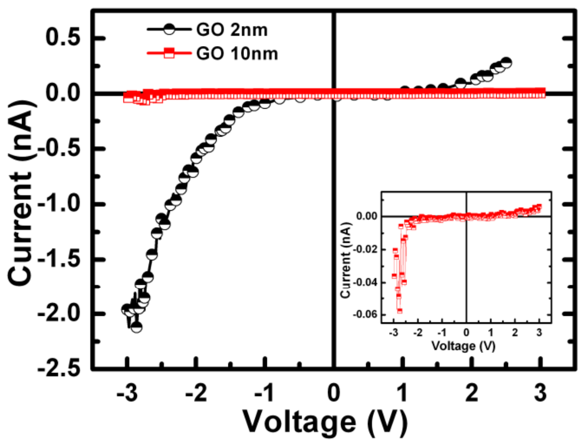


I-V





Conductive-AFM

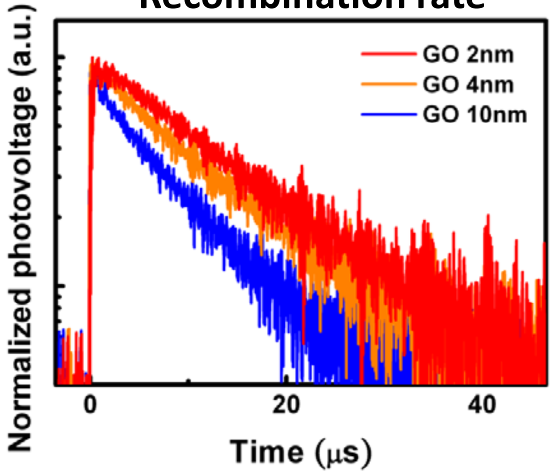


Tunneling current

I_{2nm}= 2 nA

I_{10nm} = 0.06nA

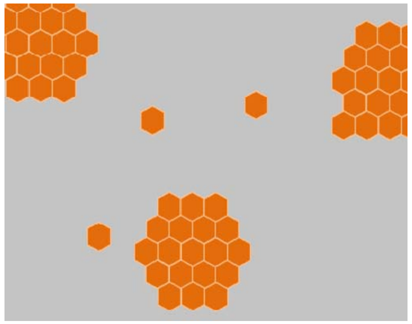
Recombination rate



Tunable conduction in graphene based materials

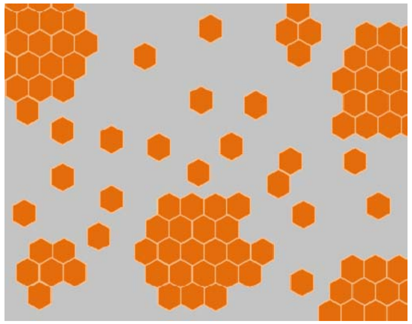
GO

Highly sp^3



Reduction

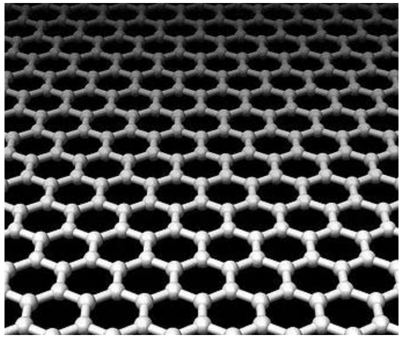
r-GO



10^3 ~ 10^5 Ω/sq

Graphene

Pure sp^2



<100 **Ω/sq**
at 90% T

Insulator

Conductor

Thin tunneling barrier

Transparent conducting electrode

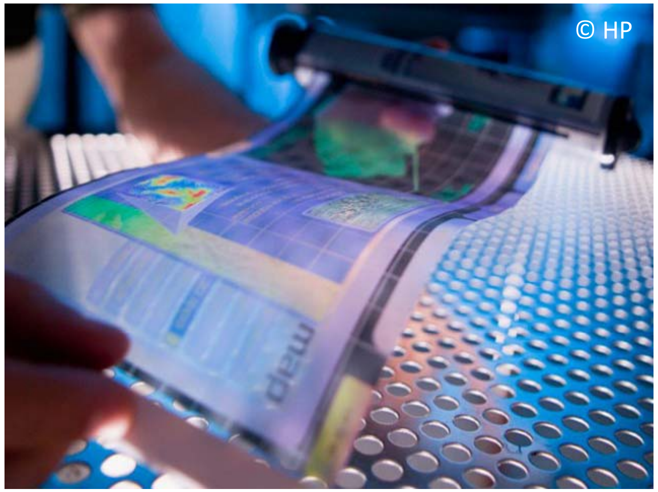
Graphene for transparent electrode

Next generation production ?

© NOKIA

Household appliances

- High conductivity
- High transparency
- Good mechanical property
- Flexible
- Good thermal conductivity
- etc.

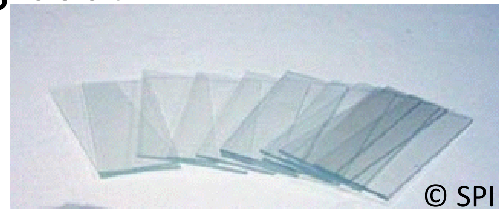


E-paper

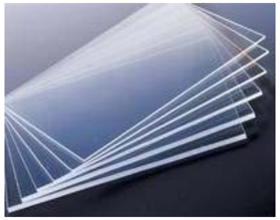
Communication production

Conventional Transparent Electrode

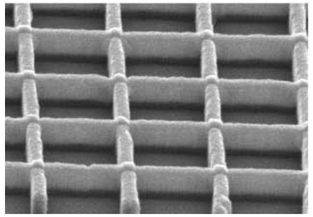
- **ITO (Indium Tin Oxide)**
  - Scarcity of indium and high manufacturing cost
  - Vacuum process
  - Relatively brittle



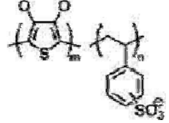
- **Alternative :**

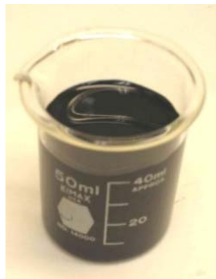


- Conducting oxides
  – Al doped ZnO



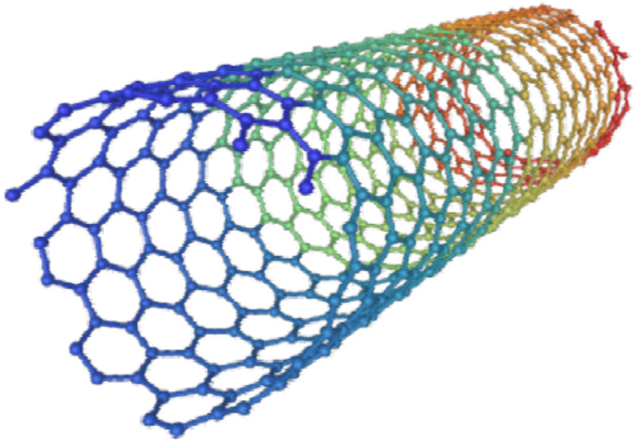
- Metal wire mesh
  – Ag nanowire, Cu grid
- Conductive polymer, PEDOT:PSS





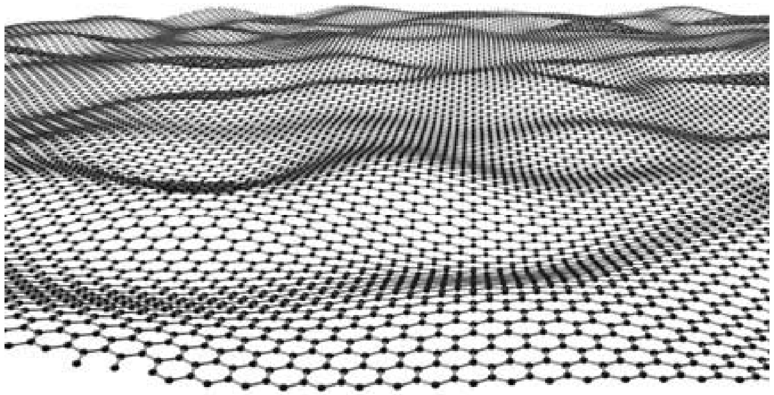
Low Dimensional Nanocarbon Materials

Single walled carbon nanotube (ID)



- 1-D material
- Metallic and semiconducting
- High carrier mobility (120,000 $cm^2V^{-1}s^{-1}$)
- High current carrying capacity
- Excellent mechanical strength

Graphene (2D)



- sp^2 bonded carbon
- 2-D honeycomb crystal lattice
- High carrier mobility (200,000 $cm^2V^{-1}s^{-1}$)
- Low electrical resistivity (10^{-6} Ω·cm) (< siliver)
- Good mechanical properties

List of various end applications, their key features, and the suitability of each material

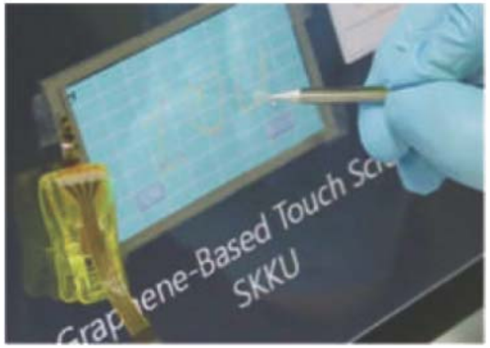
Application	Key Features	Nanotube	Graphene	Metal Nanowires
Touch Panels	Flexibility	o	o	x
	Patterning	o	o	o
	Sheet resistance	o	-	o
	Transparency	-	-	o
LCD	Surface roughness	-	o	x
	Ionic impurities	x	x	x
	Conformal Coating	o	o	x
	Color/Haze	o	o	x
OLED/Solar Cell	Work Function	o	o	x
	Sheet resistance	x	x	o
	Surface Roughness	-	o	x
	Stability	o	o	x

("o" = superior, "-" = good, "x" = poor).

Hecht, D. S. et. Al., *Adv. Mater.* **2011,** *23,* 1482–1513

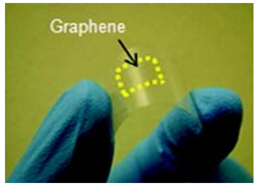
- **Transparent conducting electrode**

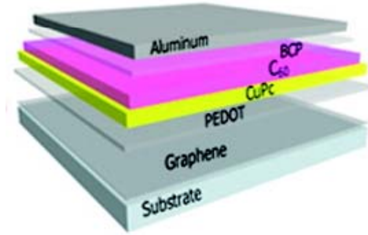
Touch Panel

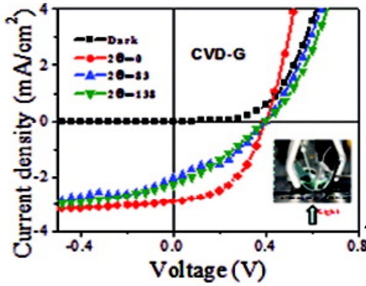


Bae, S. *et al.*
Nature Nanotech. ***4, 574–578 (2010).***

Solar Cell

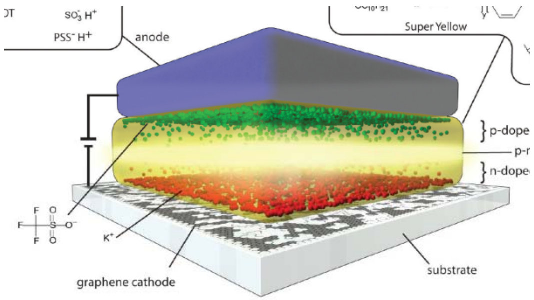


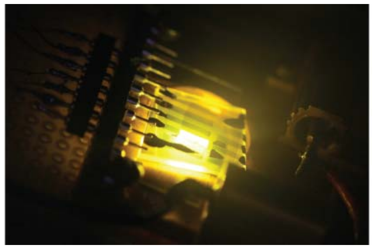




De Arco, L. G. *et al*
ACS Nano **4, 2865–2873 (2010)**

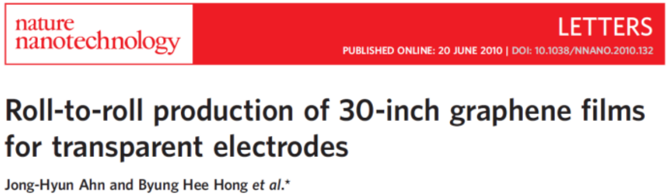
Light Emitting Diode





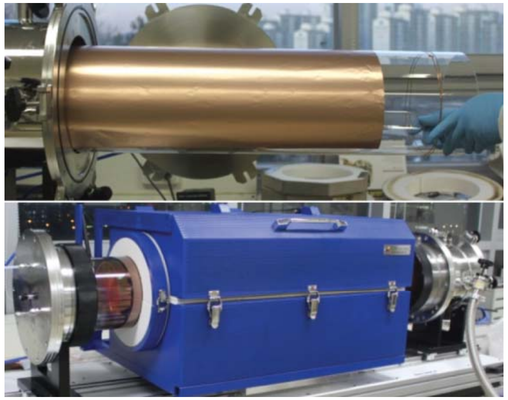
Matyba, P. *et al.*
ACS Nano ***4, 637–642 (2010).***

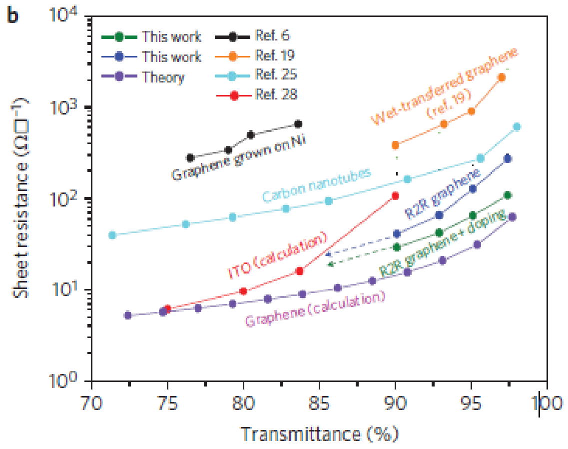
Large area CVD grown graphene for optoelectonic applications

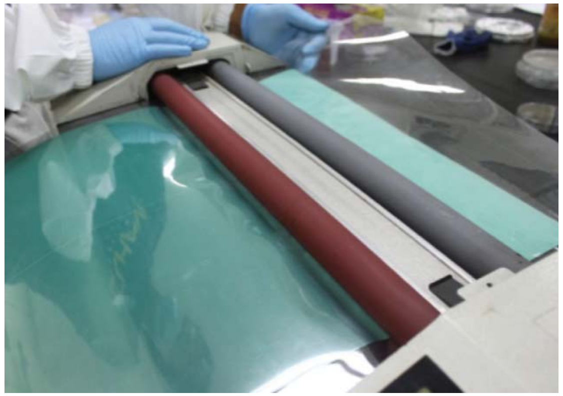

nature nanotechnology LETTERS
PUBLISHED ONLINE: 20 JUNE 2010 | DOI: 10.1038/NNANO.2010.132

Roll-to-roll production of 30-inch graphene films for transparent electrodes

Jong-Hyun Ahn and Byung Hee Hong *et al.**

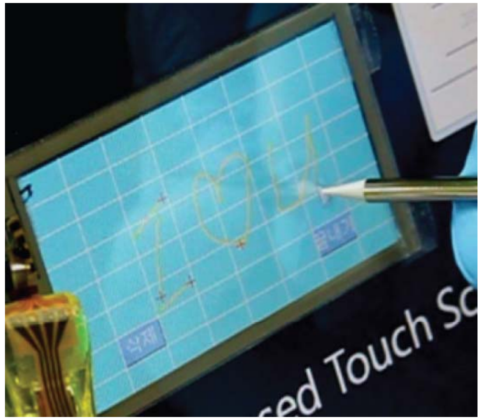






Roller printing

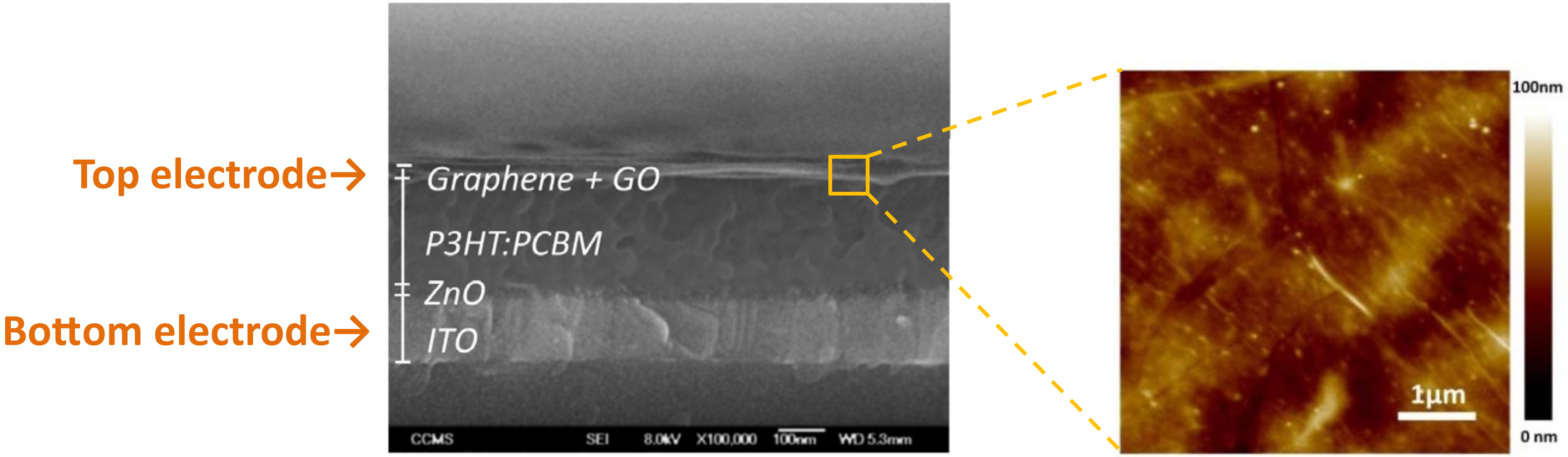
Scale up

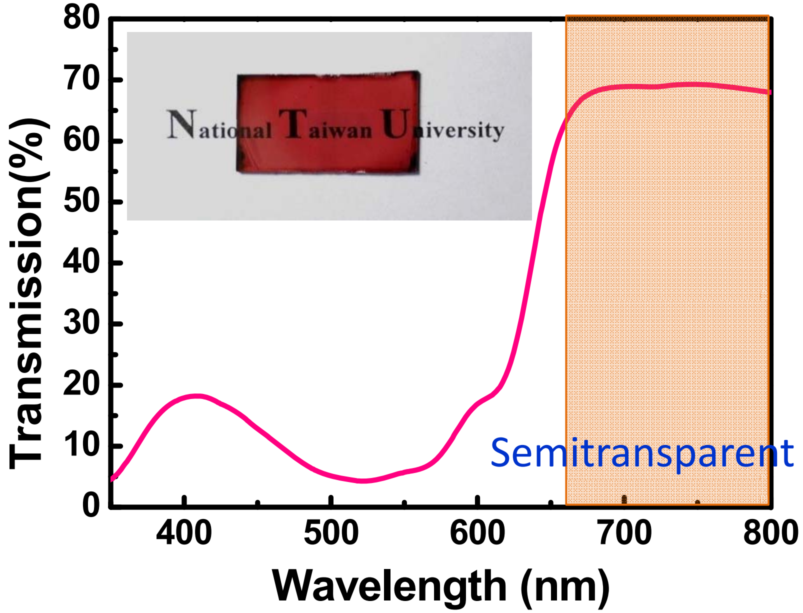


Touch panel

Bae et al. Nature Nanotechnology 5, 574–578 (2010)

Top laminated graphene electrode in a semitransparent polymer solar cell

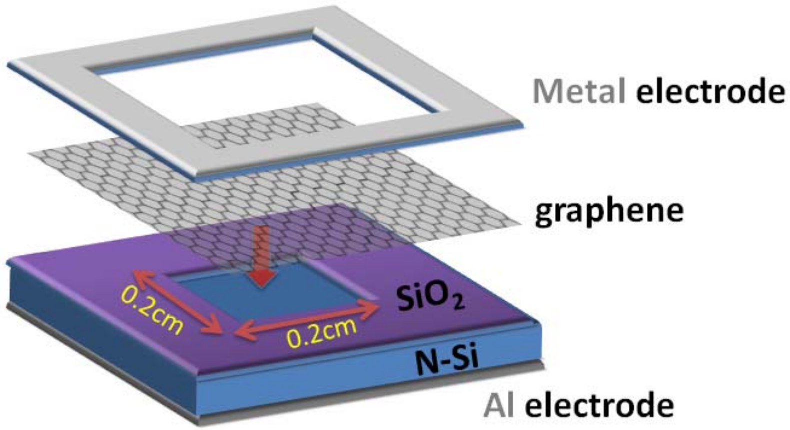


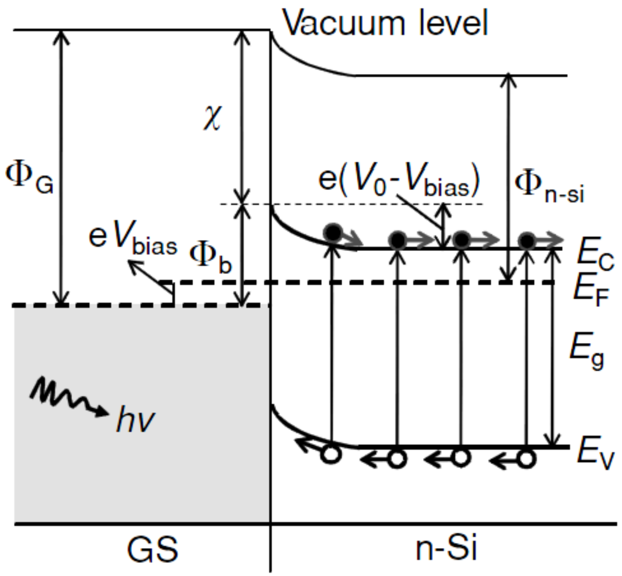


ACS Nano ,Vol.5, 6564, (2011)

Si/Graphene junction solar cell

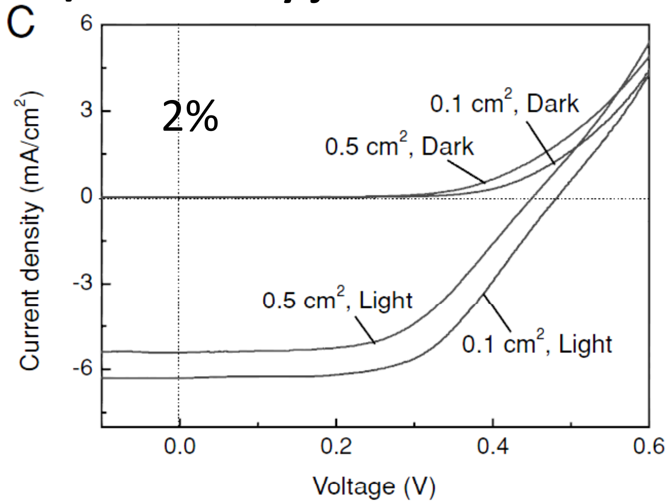
Device structure



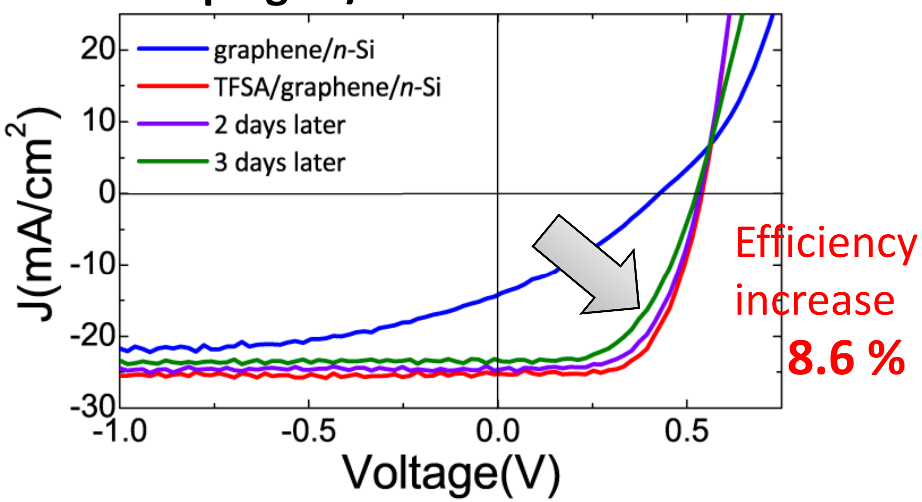


Energy diagram of the forward-biased GS/n-Si Schottky junction

Gr/Si schottky junction solar cell



P doping Gr/Si

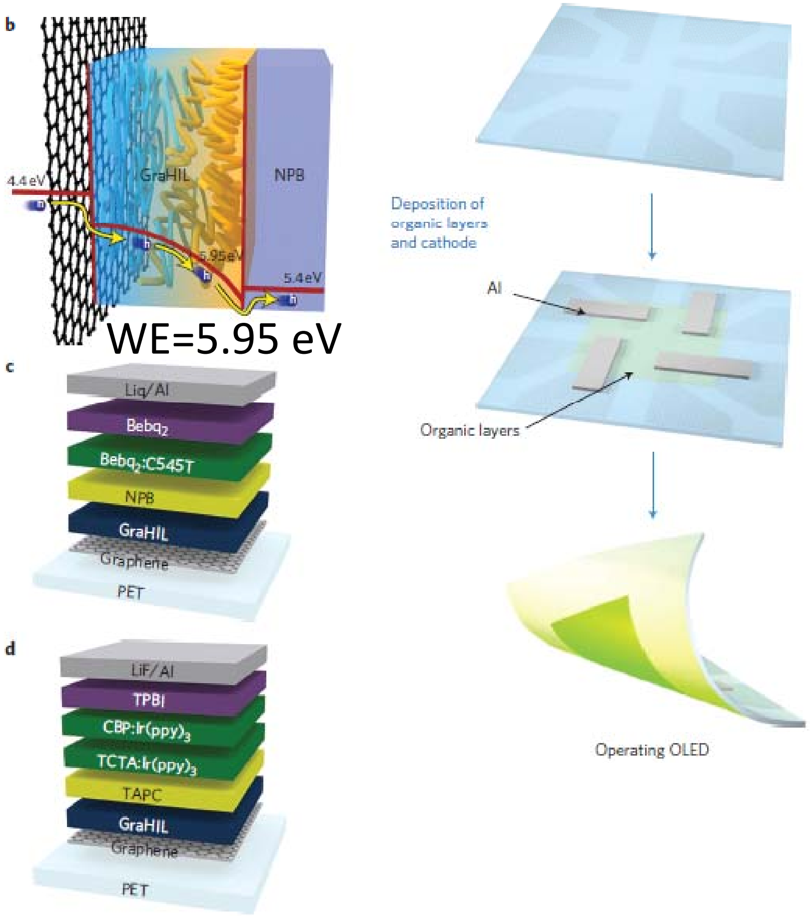


Li. X. et. al., Adv. Mater. **2010**, *22*, 2743–2748

Miao, X. Et. al., *Nano Lett*. **2012**, *12*, 2745−275(

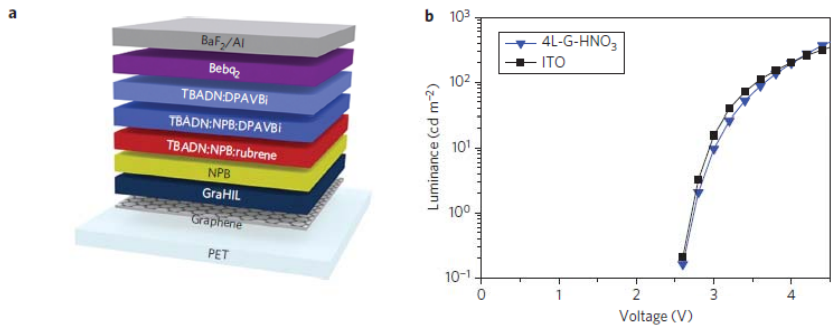
The Future development of large area CVD graphene in OLED applications

4-layered HNO_3 doped Gr~ 30 Ω/□

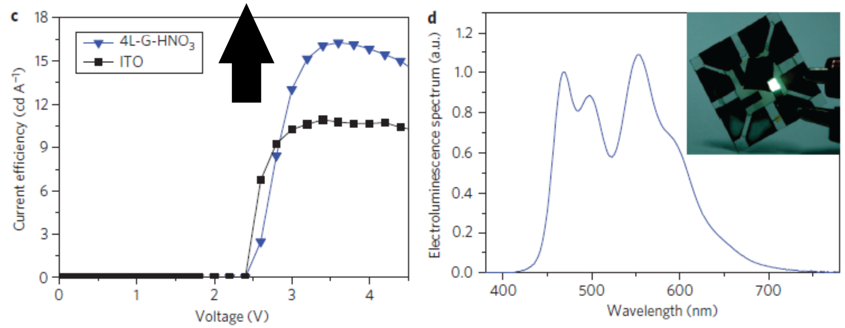


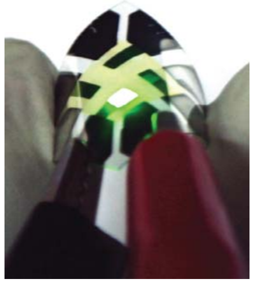
WE=5.95 eV

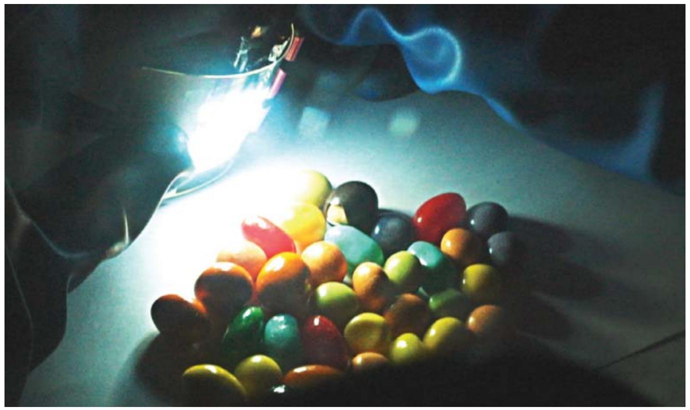
Gra HIL: Self-organized gradient hole injection layer



The white OLEDs with the graphene anode exhibited a much higher the ITO anode



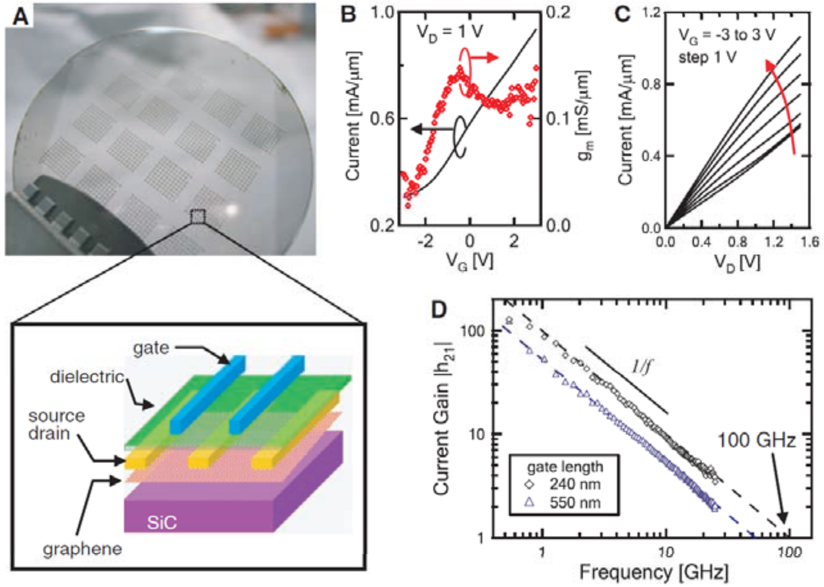




T.H. Han, et al., *Nature Photonics*, **6**, 105–110, (2012).

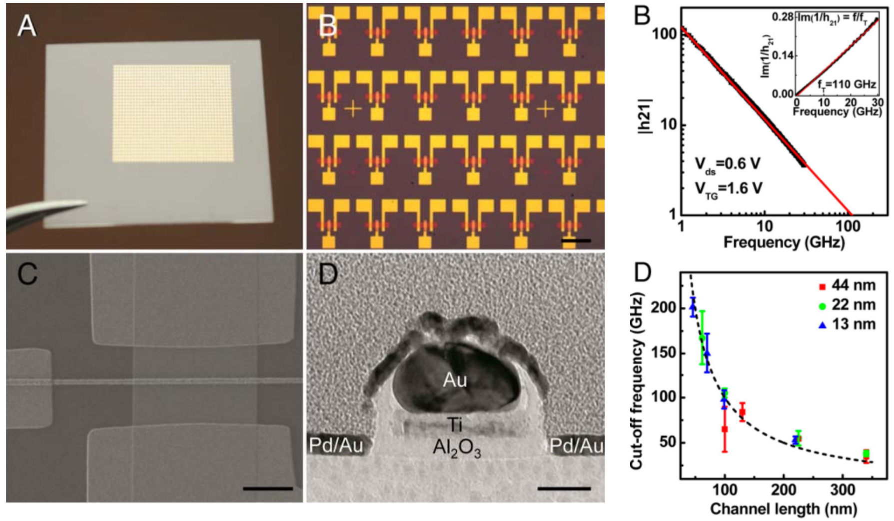
Graphene for other applications

Graphene for Radio Frequency (RF) Transistor



Science, 327 , 662 (2010)

up to 100 GHz (cut-off frequency)



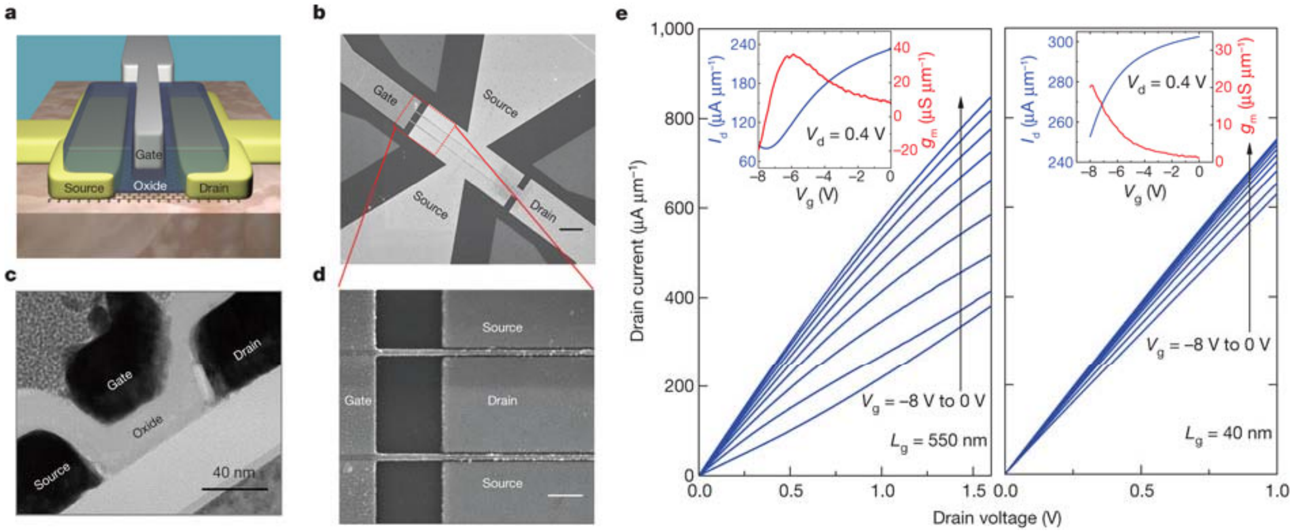
Proc. Natl. Acad. Sci. U.S.A. 109, 11588–11592 (2012)

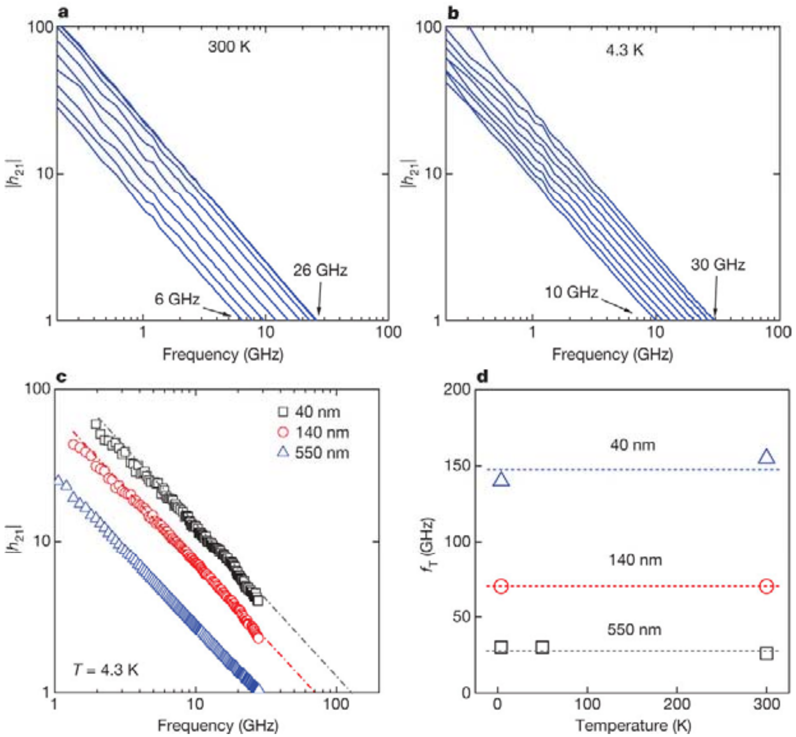
up to 427 GHz

Why use graphene in RF-tech

- Low on-off ratio => fail in CMOS tech
- High mobility, carrier saturation velocity, and large current density=> high cut-off frequency
- High quality graphene => Toward Terahertz regime in the future

High-frequency, scaled graphene transistors on diamond-like carbon



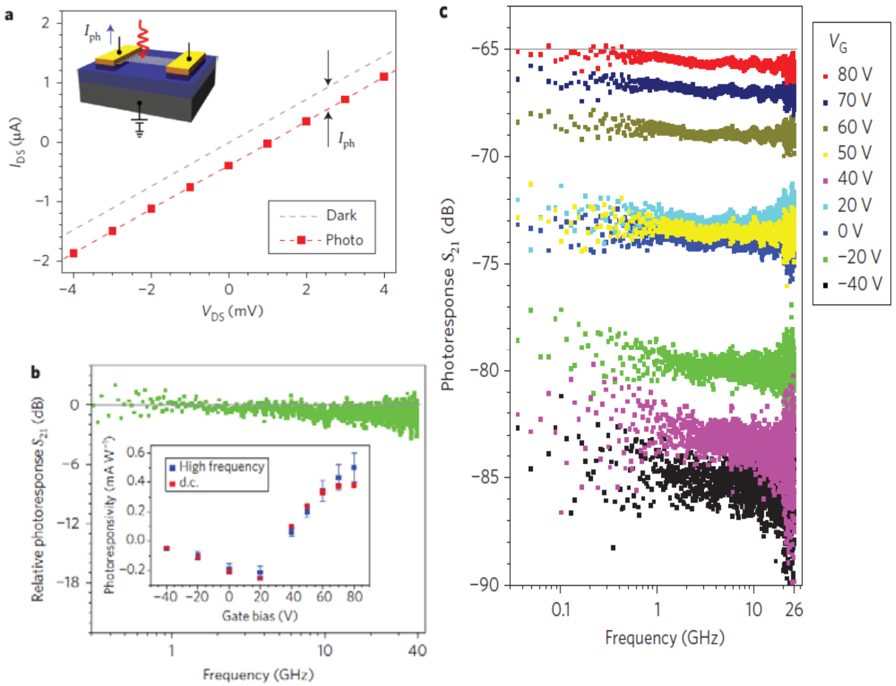


Cut-off frequencies as high as 155 GHz have been obtained for the 40-nm transistors, and the cut-off frequency was found to scale as 1/(gate length).

Wu, Y., et. al. *Nature*, 2011, 472, 74–78

Ultra fast and Ultra high gain Photodetector

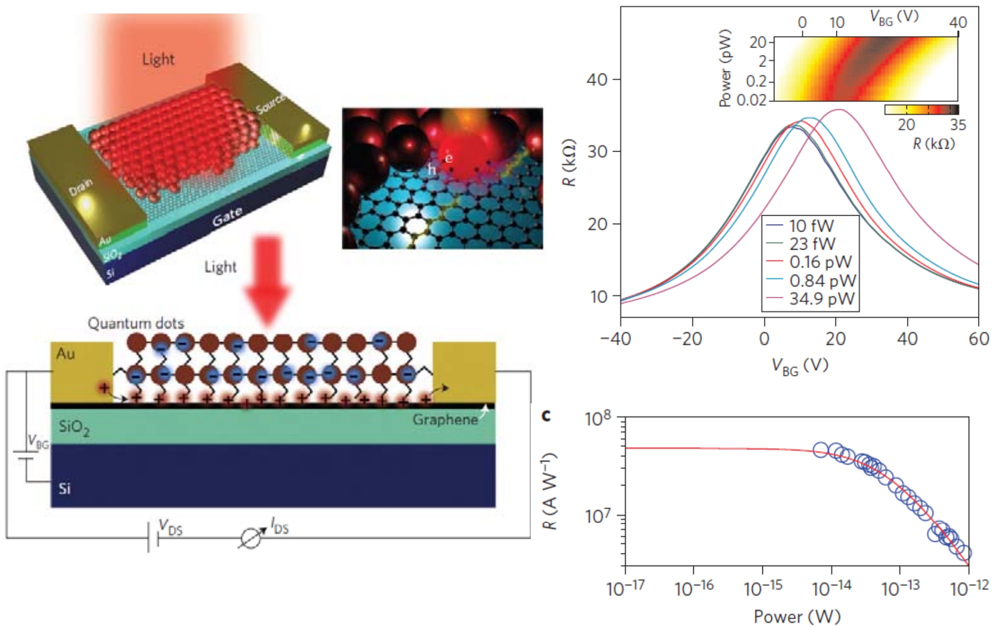
Ultra fast photodectector



Nature Nanotech. 4, 839–843 (2009)

- Light is absorbed by graphene
- P-n junction between channel and graphene covered with metal
- Gate dependent photoresponse
- Could be operated at frequency as high as 40GHz

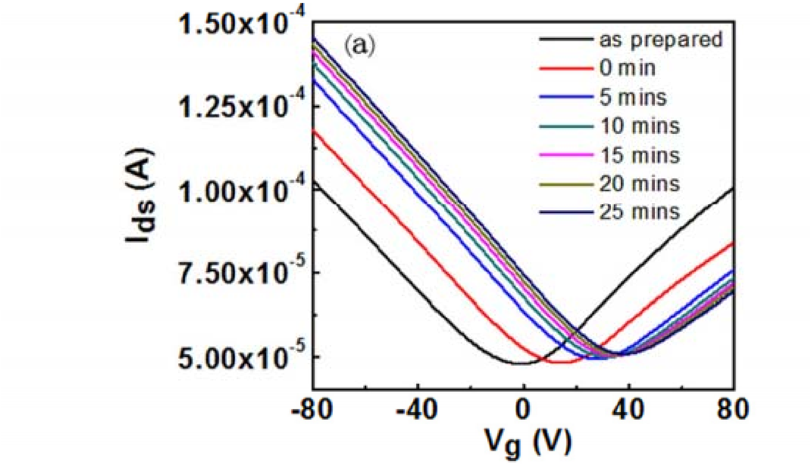
Ultra high gain photodectector

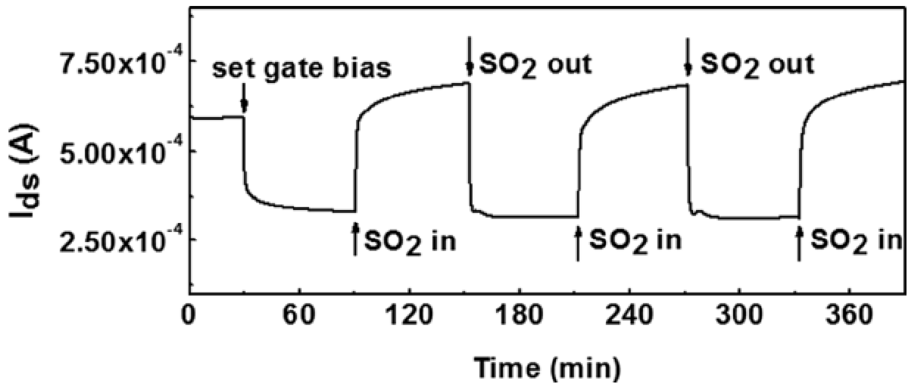


Nature Nanotech. 7, 363–368 (2012)

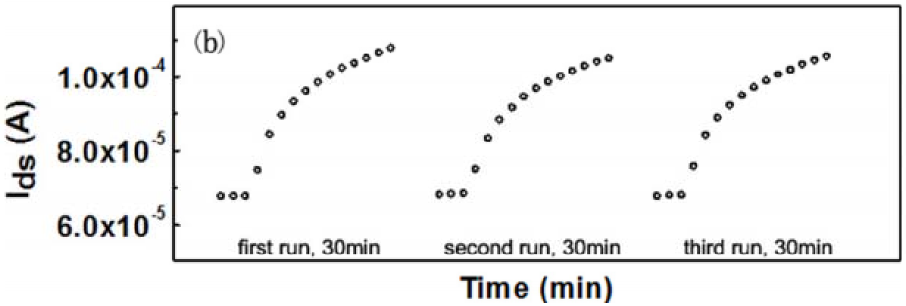
- Light is absorbed by photo-active material on graphene
- Charge transfer from photo-active material to graphene
- Gain could be very large due to inherent high mobility of graphene

Detection of sulfur dioxide (SO_2) gas with graphene field effect transistor





SO_2 strongly p-dopes the graphene

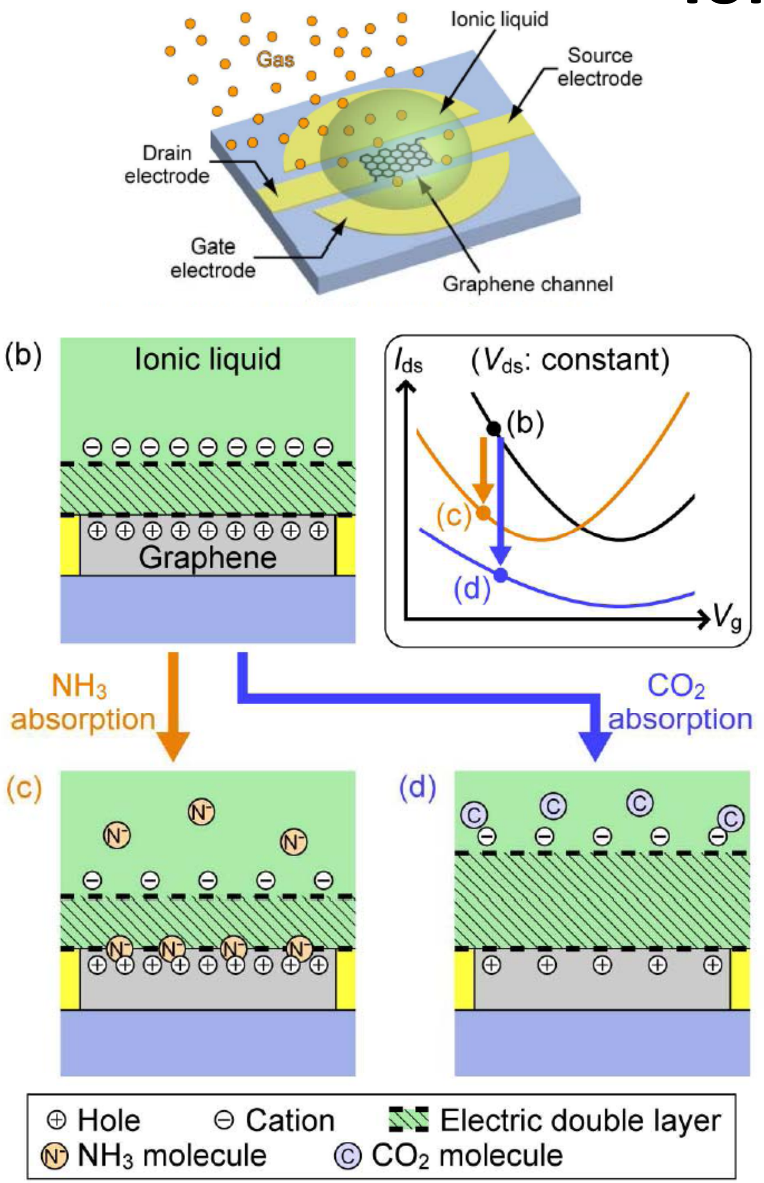


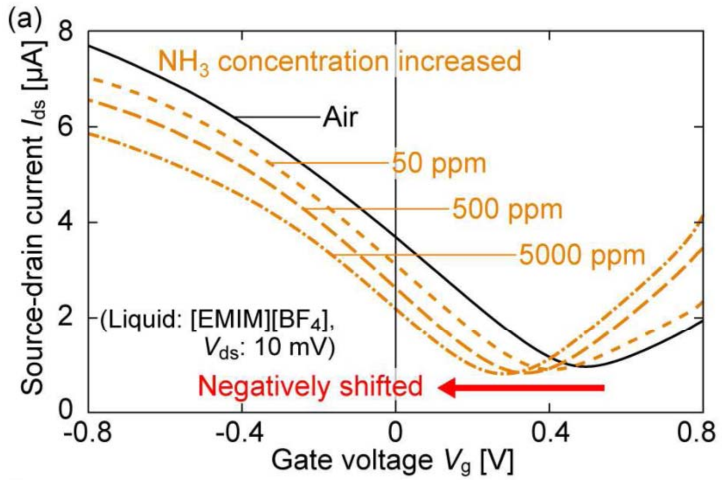
Reproducibility of the graphene FET as a SO_2 gas detector

1. the Dirac point shifted 0.678V/ppm to the positive side
2. the resistance decreased about 60% at a SO_2 concentration of 50 ppm.

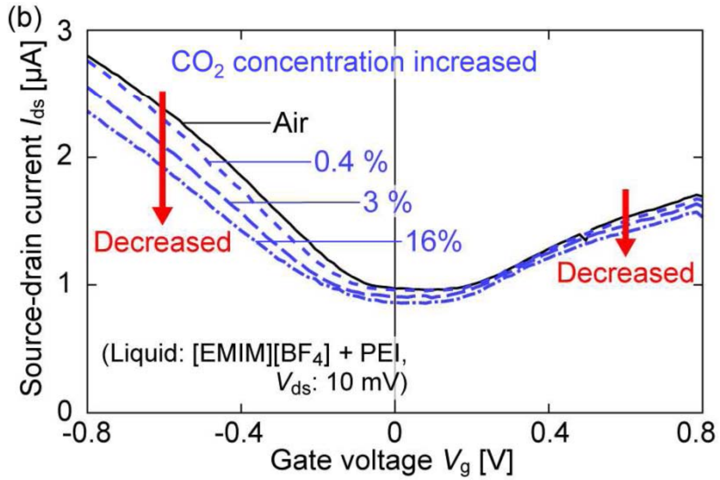
Ren, Y. et. al., Appl. Phys. Lett. 2012, 100, 163114

A Graphene FET Gas Sensor (CO_2, NH_3) Gated by Ionic Liquid





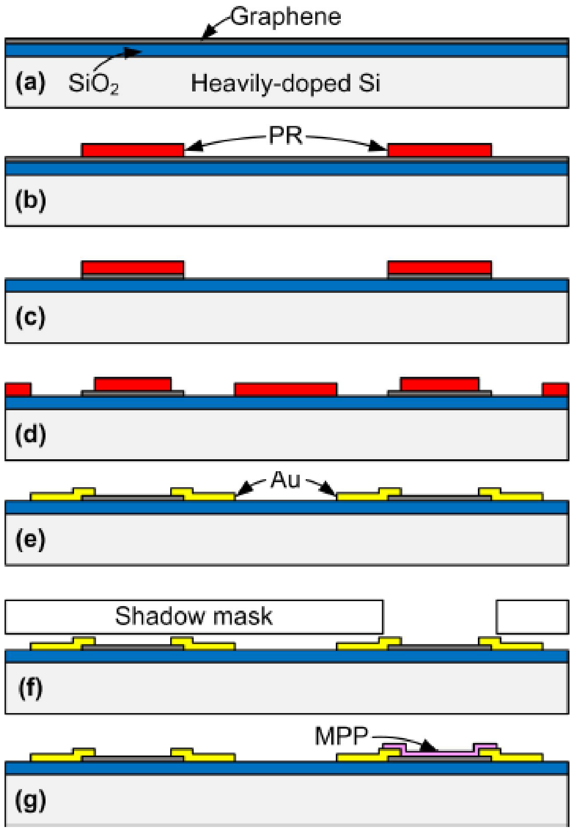
NH_3 molecules transferred negative charge to graphene channel



The decrease in I_{ds} over the entire voltage caused by CO_2 denotes that capacitance of the EDL was reduced.

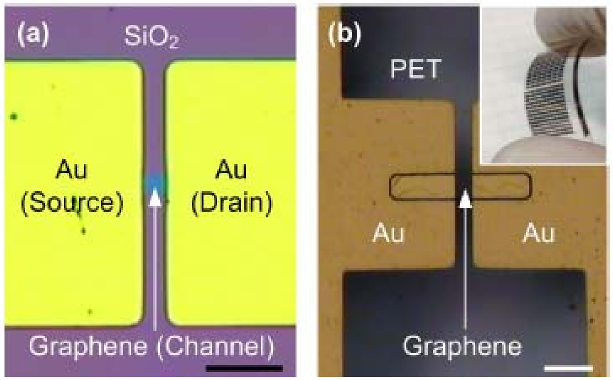
A. Inaba, et. al. IEEE, 2013, 969

Transparent and Flexible Toluene Graphene Sensor



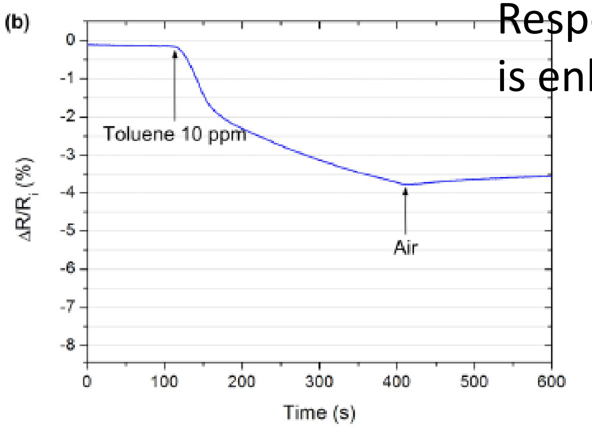
Cobalt-metalloporphyrin (Co-MPP)-functionalized graphene toluene sensor

1. highly sensitive
2. Transparent
3. flexible

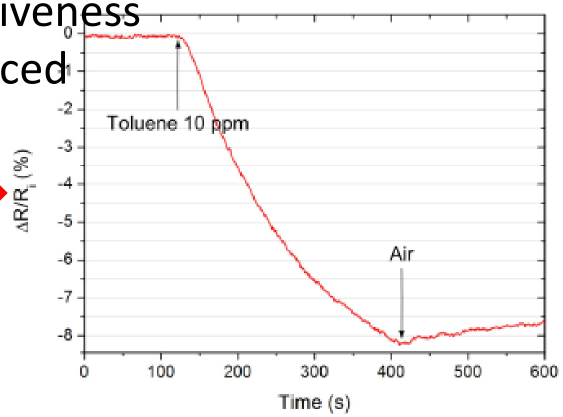


The functionalization of MPP enhanced responsiveness (ΔR/Ri) over 200% compared to pristine graphene

Responsiveness is enhanced

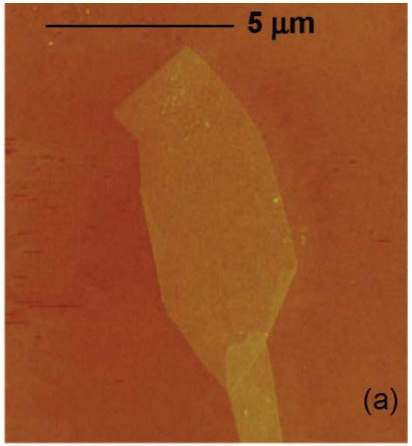


Pristine graphene

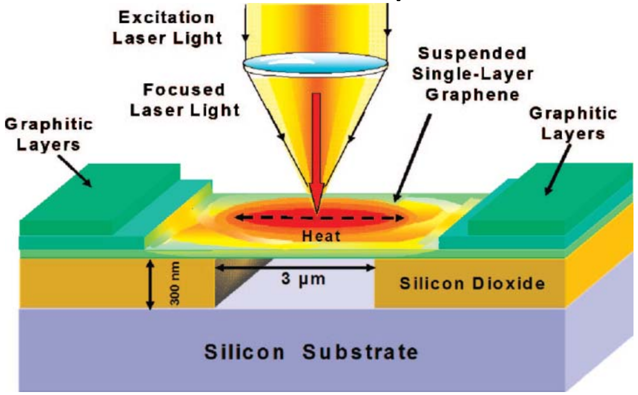


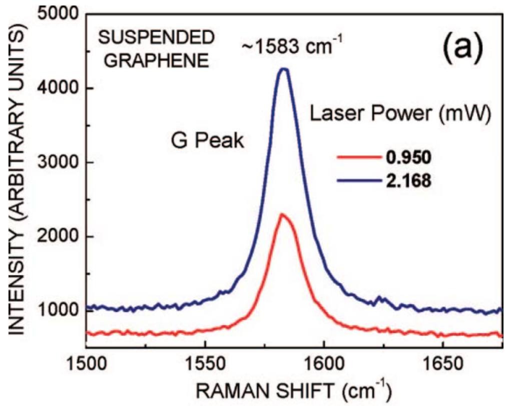
Co-MPP graphene

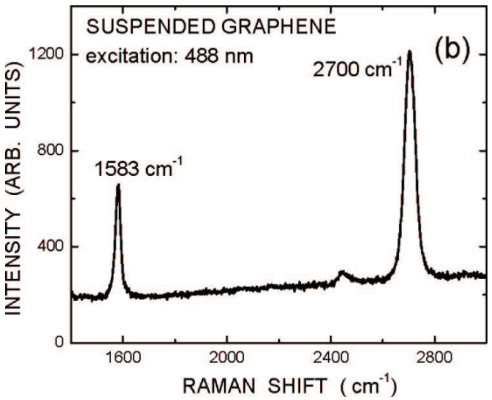
Superior Thermal Conductivity of Single-Layer Graphene

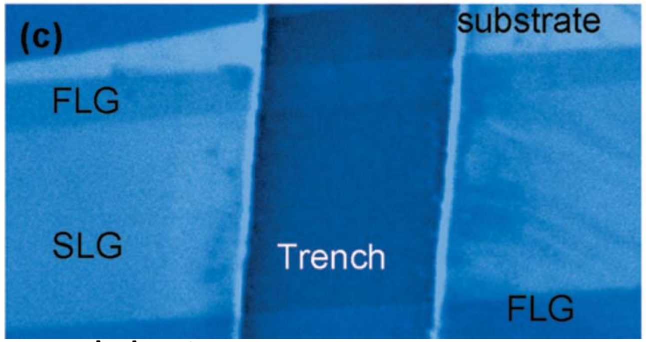


Measurement setup

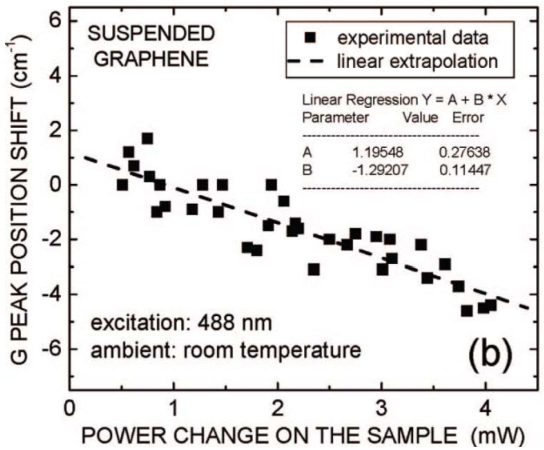








Real device



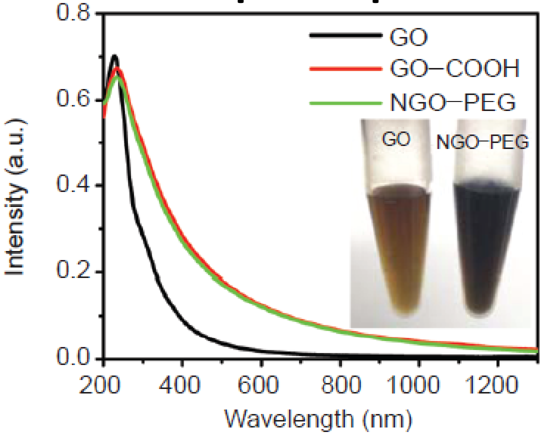
Thermal conductivity of Gold~ 318 W/mK

The room temperature values of the thermal conductivity in the range ~(4.84 × 10^3 to (5.30 × 10^3 W/mK were extracted from the dependence of the Raman *G* peak frequency on the excitation laser power and independently measured *G* peak temperature coefficient

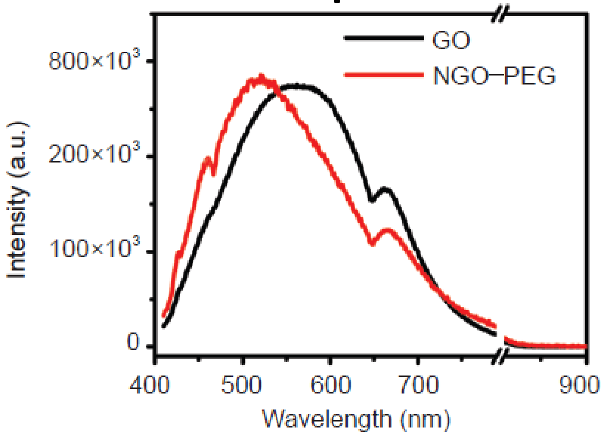
Balandin, A. A., et. al. *Nano Lett. 2008*, 8, 902.

Functionalized graphene oxide for Cellular Near IR Imaging

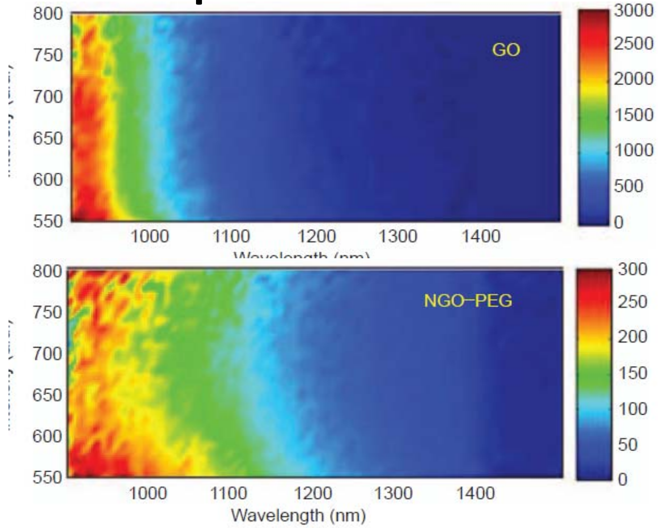
Absorption spectra



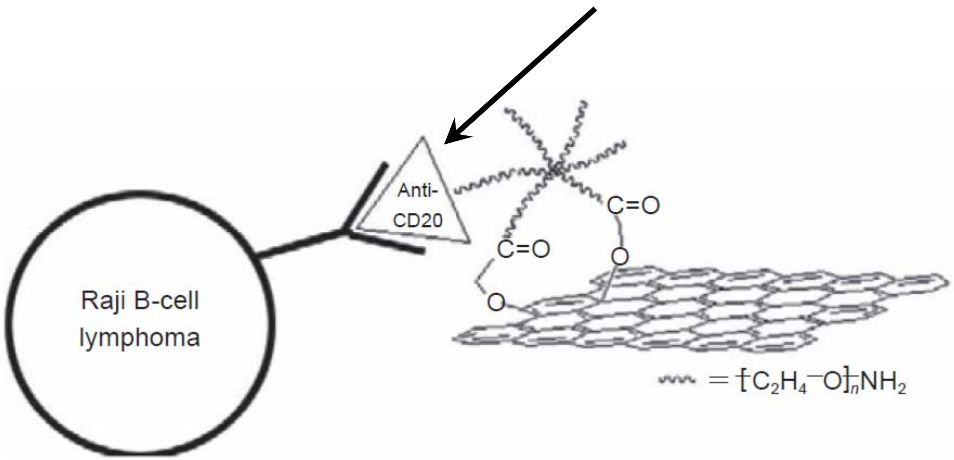
PL spectra



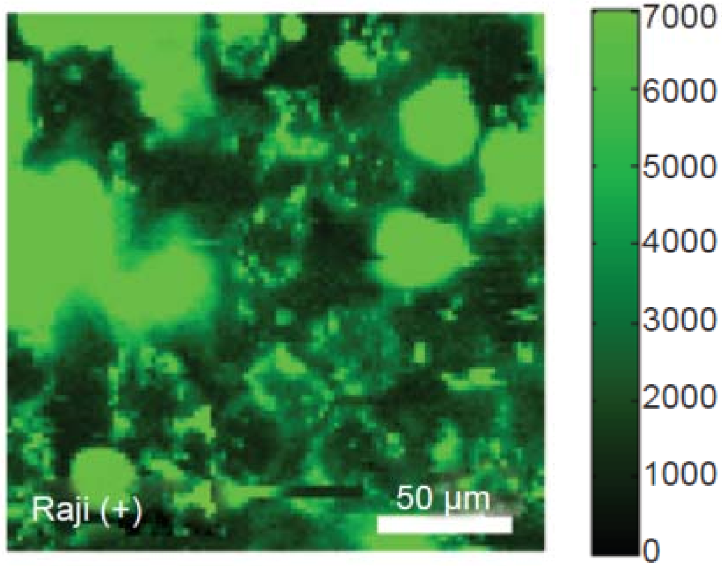
The PLE spectra of GO and NGO



Selective binding and cellular imaging of NGO-PEG conjugated with anti-CD20 antibody



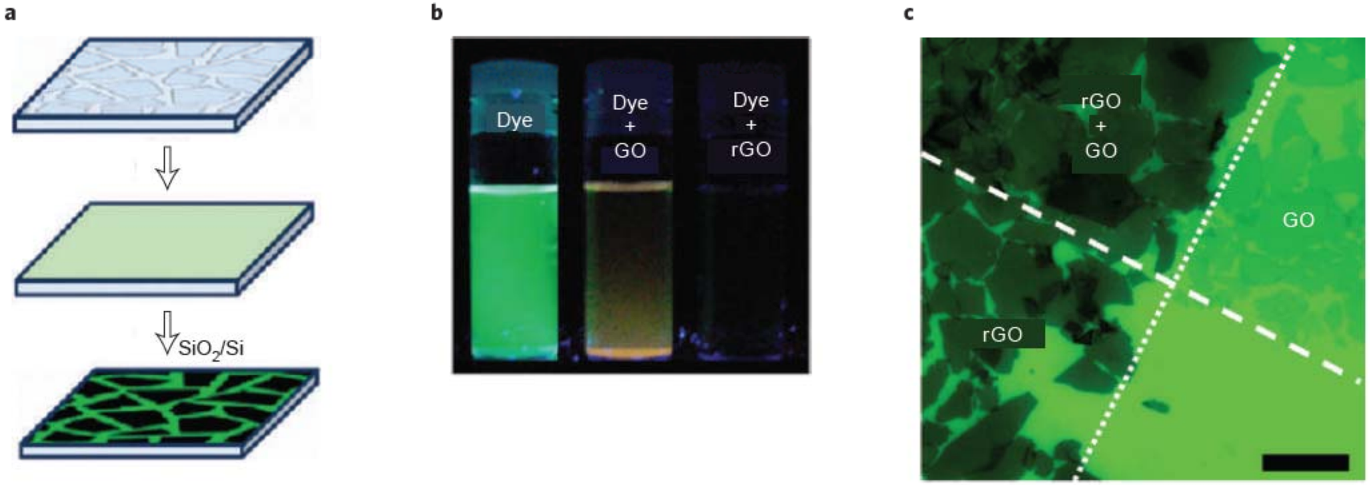
NIR fluorescence image (1100~2200 nm)



B-cells

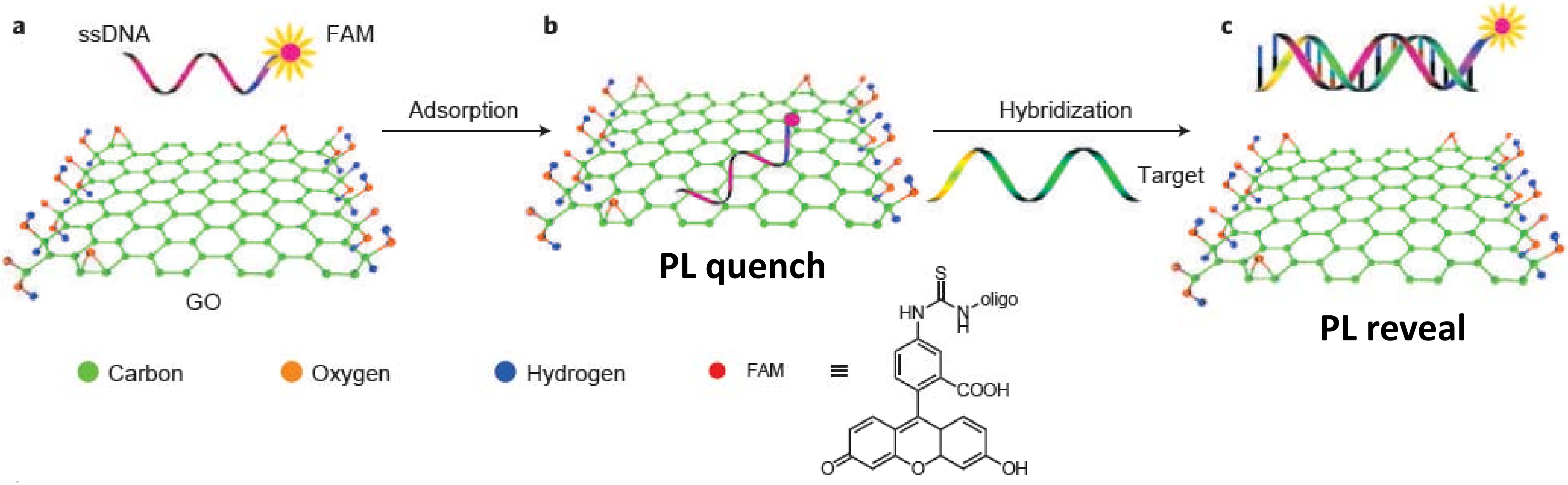
Sun, X. et. al., Nano Res (2008) 1: 203 212

Fluorescence-quenching of GO and rGO



Kim, J., et. Al., *J. Am. Chem. Soc.* ***132,*** *260–267 (2010).*

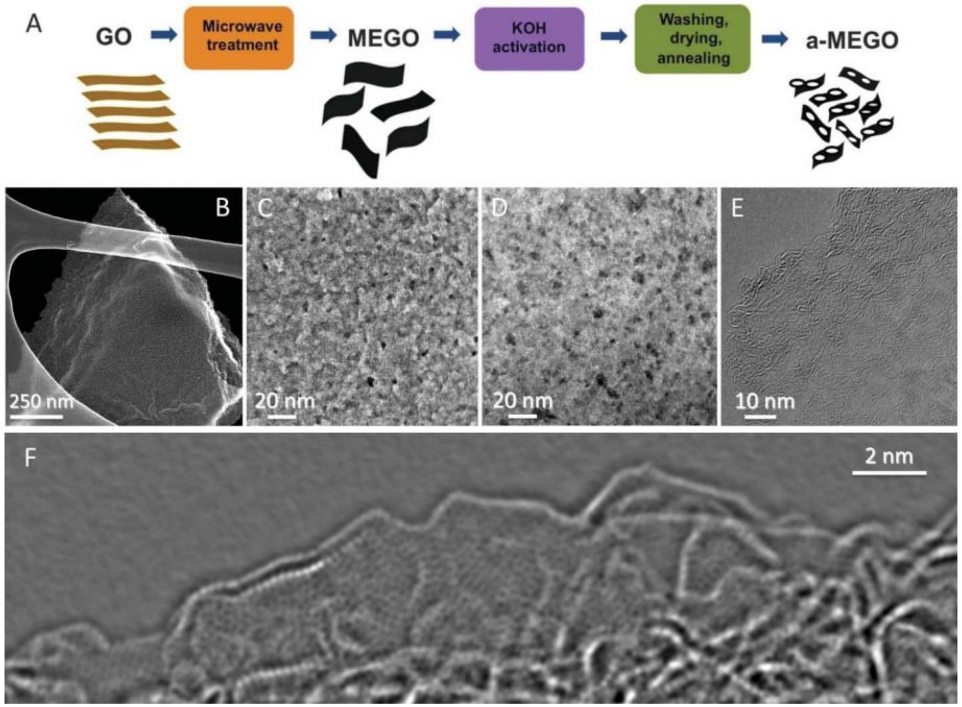
Biosensing by fluorescence quenching in GO

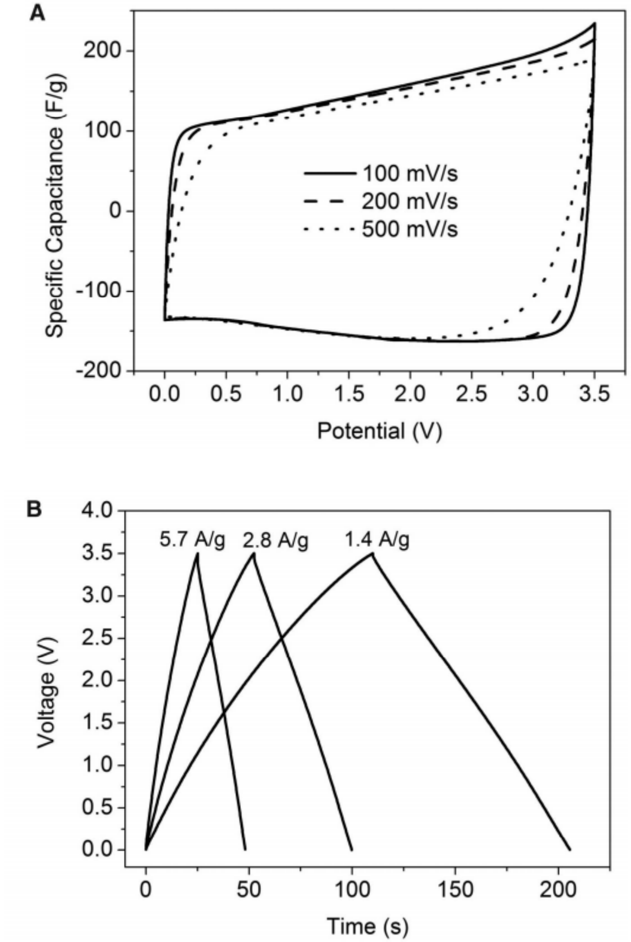


Lu, C.-H. et. Al., *Angew. Chem. Int. Ed.* ***48****, 4785–4787 (2009).*

3. Energy applications

Carbon-Based Supercapacitors Produced by Activation of Graphene





The advantages of MEGO:

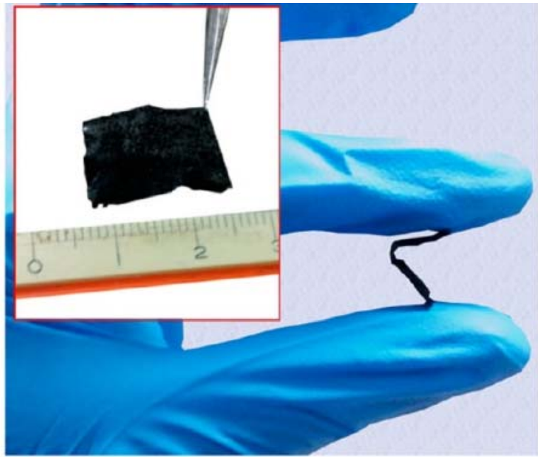
- High electrical conductivity
- Low oxygen and hydrogen content.
- sp^2 -bonded carbon with continuous 3D network

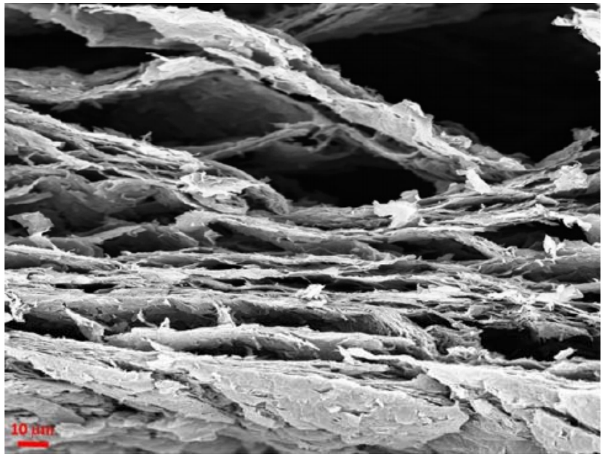
For a packaged cell, the power density of ~75 kW/kg is one order higher than the values from commercial carbon supercapacitors.

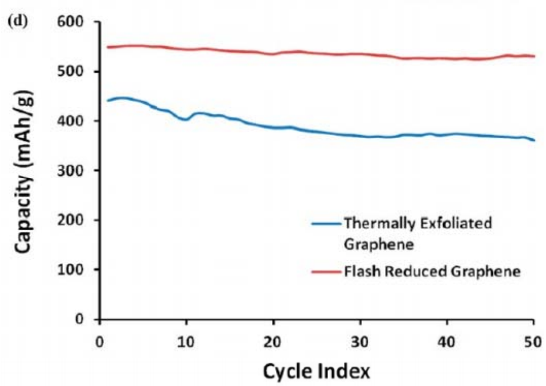
Zhu, Y., et. al., Science, 2011, 332, 24

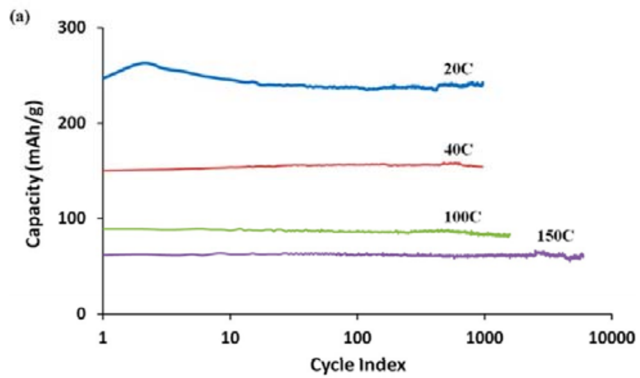
Photothermally Reduced Graphene as High-Power Anodes for Lithium-Ion Batteries

Graphene oxide → Flash light → Reduced graphene oxide









For reduced graphene anodes

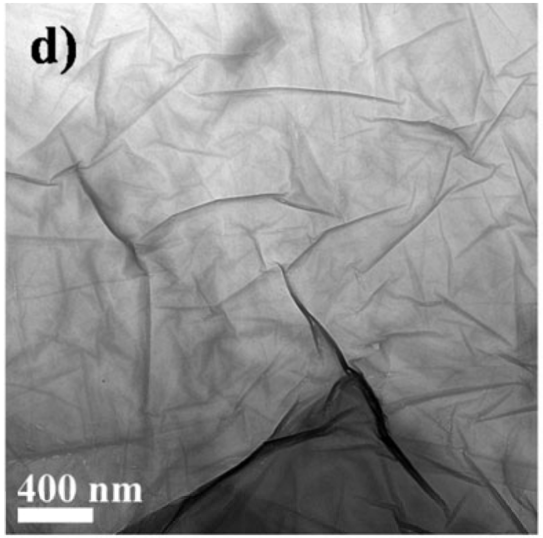
At high charge/discharge rates of ~40 C,

1. A steady capacity of ~156 mAh/g over 1000 cycles
2. a stable power density of~10 kW/kg

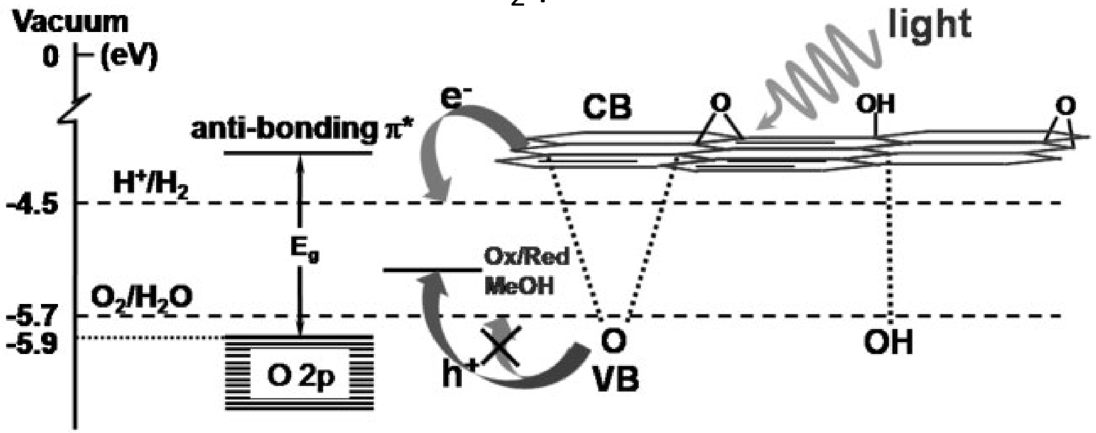
Mukherjee, R. ACS Nano, 2012, 6, 7867.

Graphite Oxide as a Photocatalyst for Hydrogen Production from Water

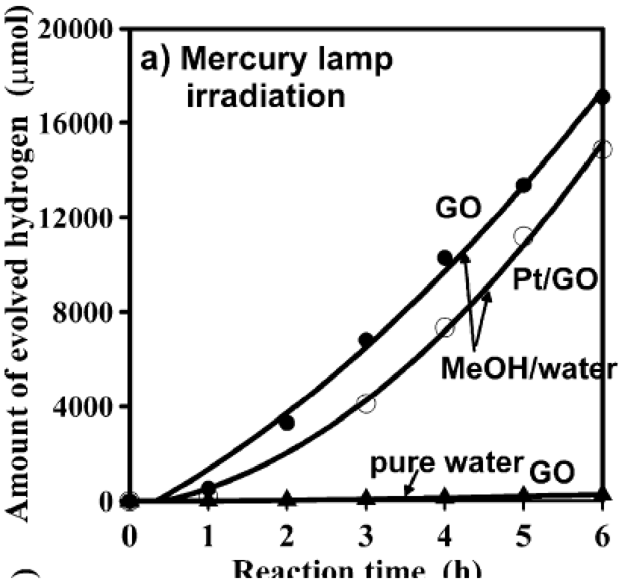
GO sheets

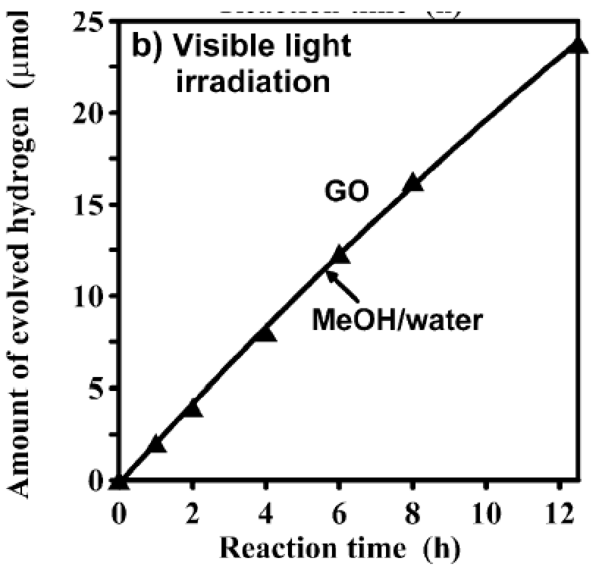


Mechanism of H_2 production from GO sheet

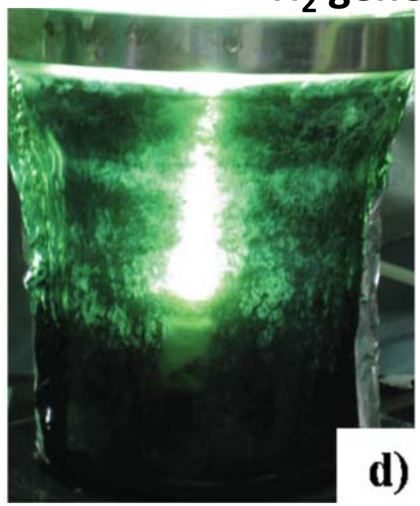


$$GO + h\nu \rightarrow GO(e^- + h^+)$$
$$6\,H^+ + 6\,e^- \rightarrow 3\,H_2$$
$$CH_3OH + 6\,OH^- + 6h^+ \rightarrow CO_2 + 5\,H_2O$$

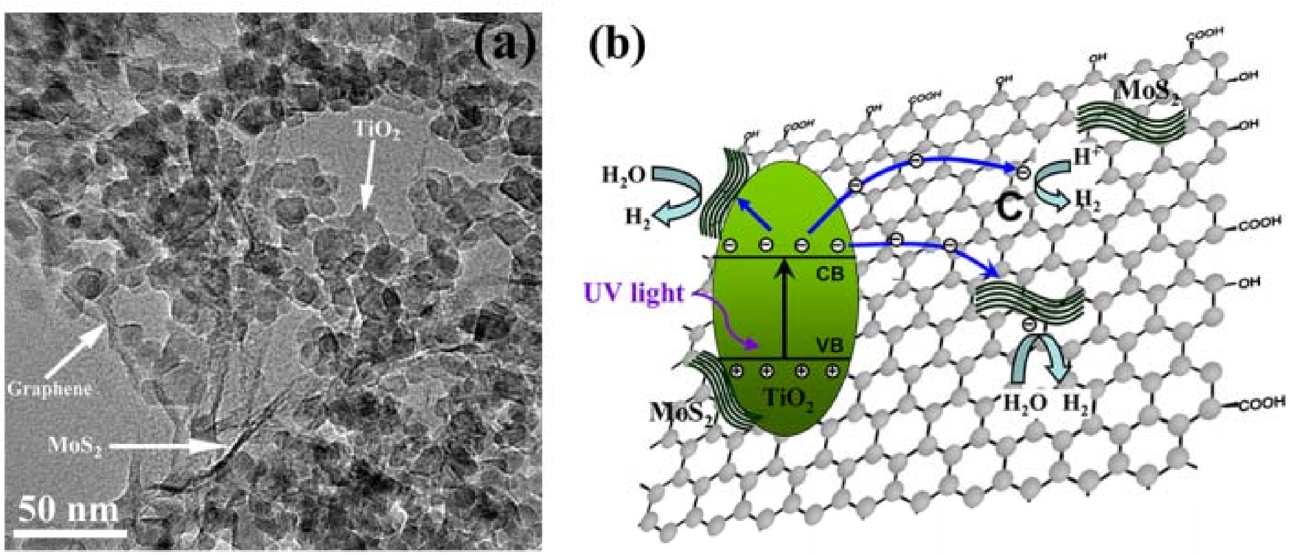


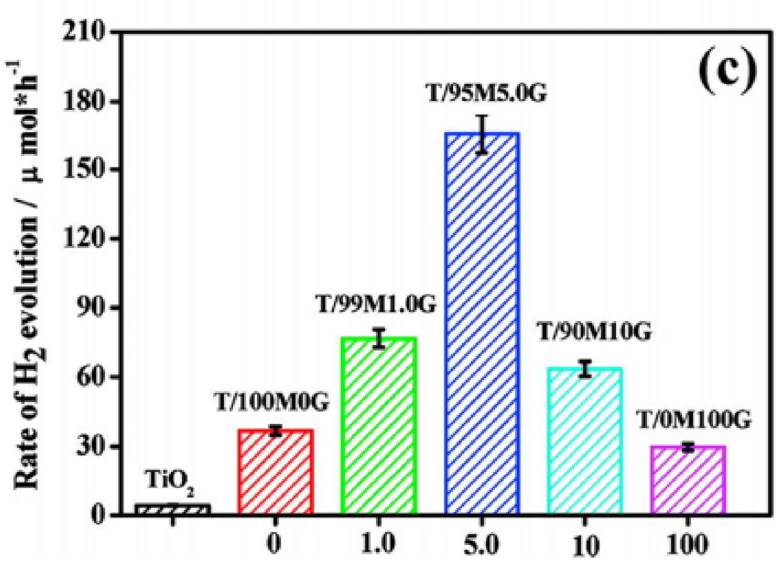


H_2 generation



MoS$_2$ and Graphene as Cocatalysts for Enhanced Photocatalytic H$_2$



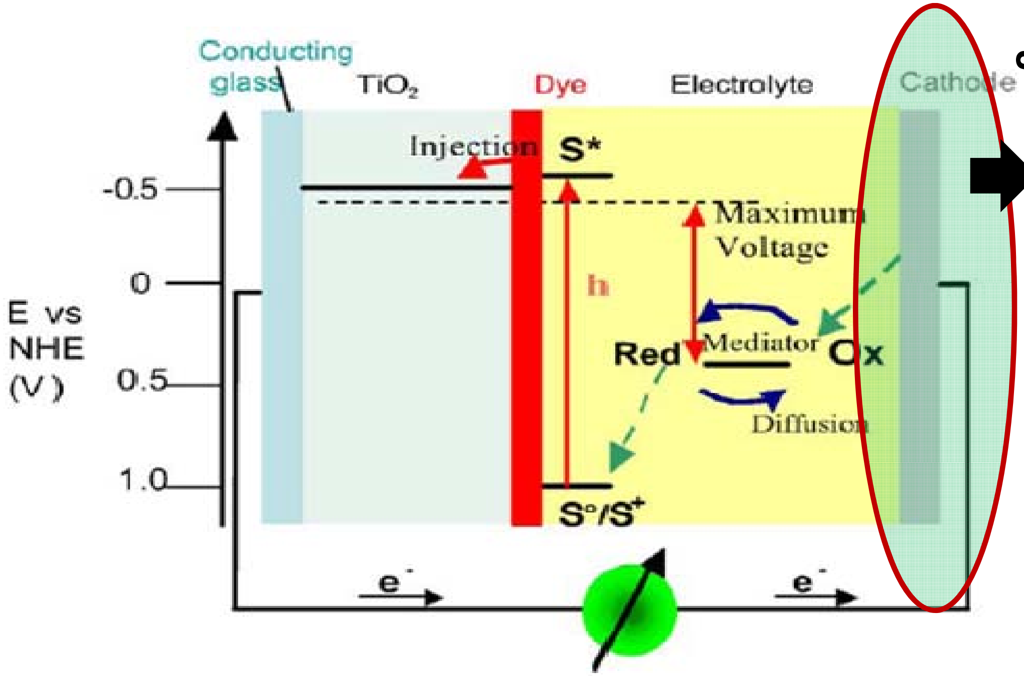


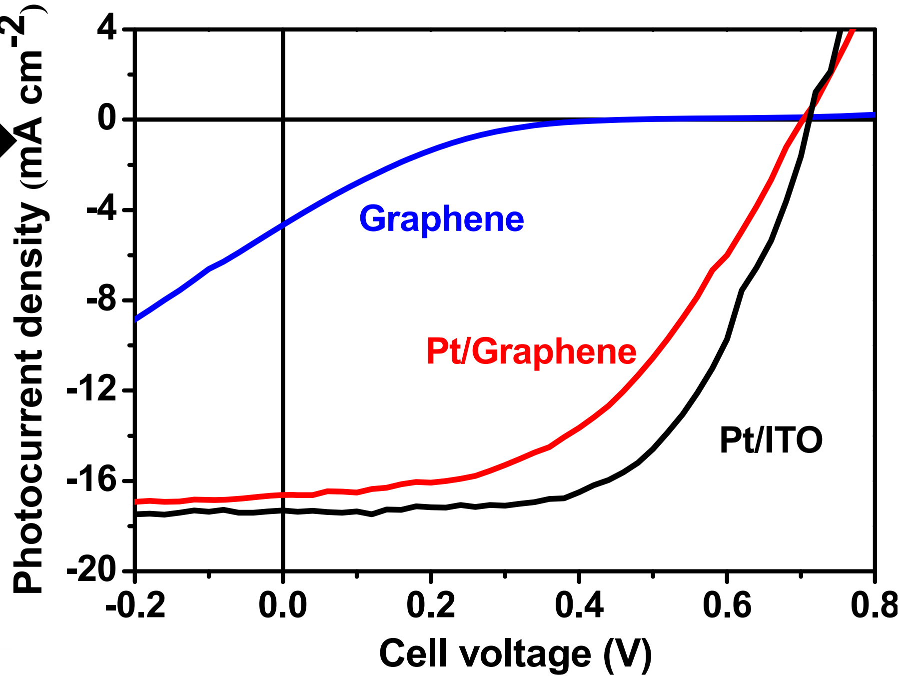
The photoexcited electrons are transferred from the CB of TiO$_2$ not only to the MoS$_2$ nanosheets but also to the C atoms in the graphene sheets, which can effectively reduce H$^+$ to produce H$_2$

The TiO$_2$/MoS$_2$/graphene composite reaches a high H$_2$ production rate of 165.3 μmol h^{-1}

Xiang, Q., et. al. J. Am. Chem. Soc. 2012, 134, 6575−6578

Graphene based counter electrode for DSSCs





Counter electrode	*Voc*(V)	*Jsc*(mA)	*FF*	Efficiency(%)
Graphene	0.46	4.83	0.16	0.35
Pt/Graphene	0.70	16.58	0.48	5.57
Pt/ITO	0.71	17.40	0.59	7.29

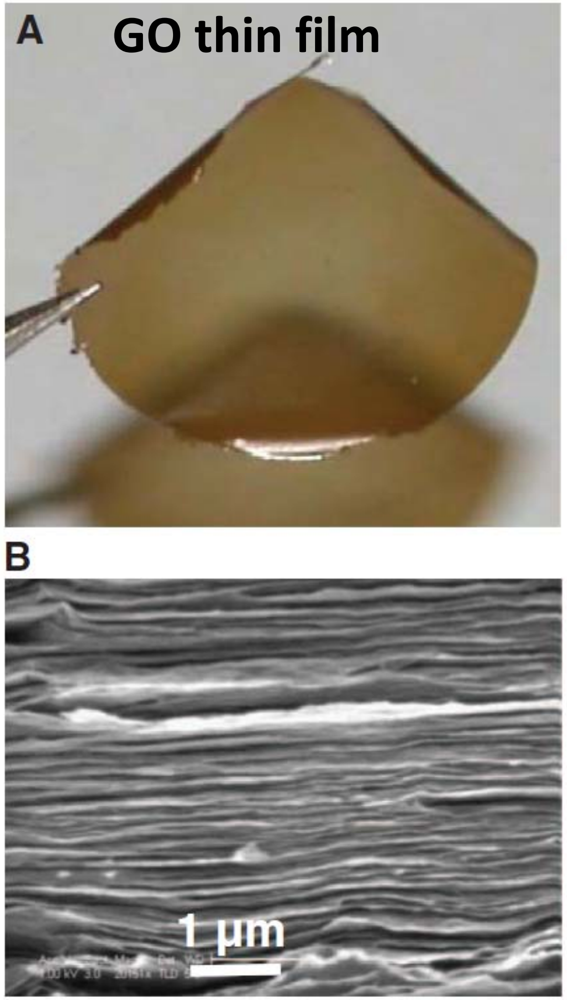
4. For environmental and other applications

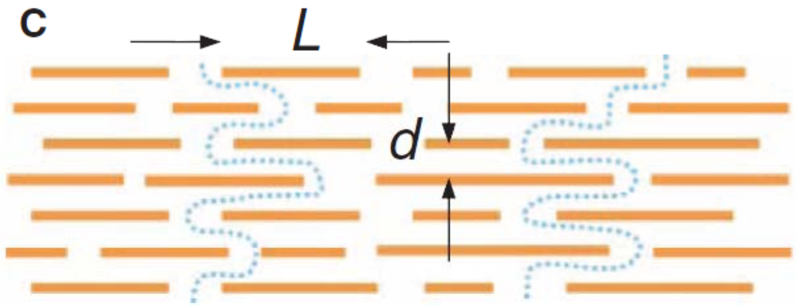
Permeation of Water
→ Desalination of sea water

Heavy metal remover

Superior thermal conductor

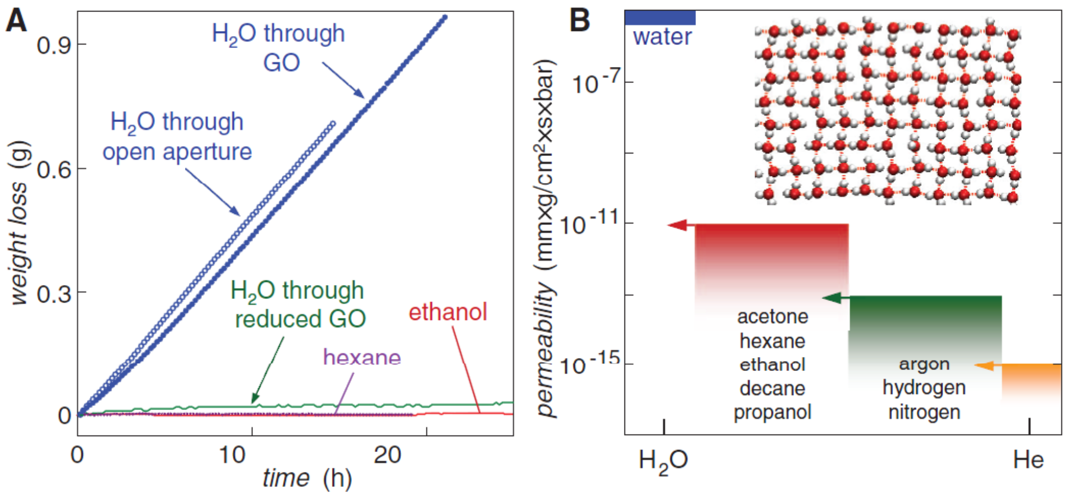
Unimpeded Permeation of Water Through Helium-Leak–Tight Graphene-Based Membranes





Completely impermeable: liquids, vapors, and gases

Unimpeded permeation: water H_2O

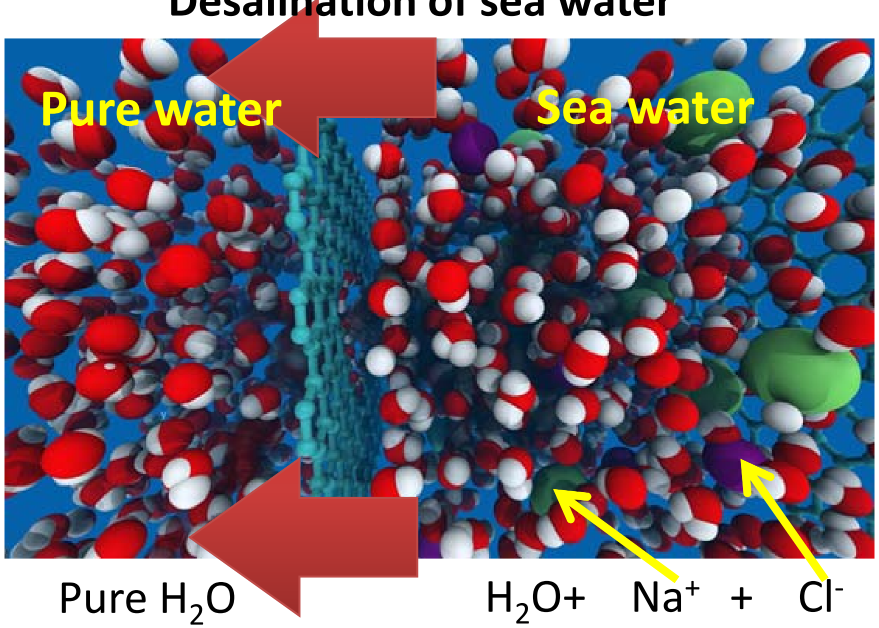


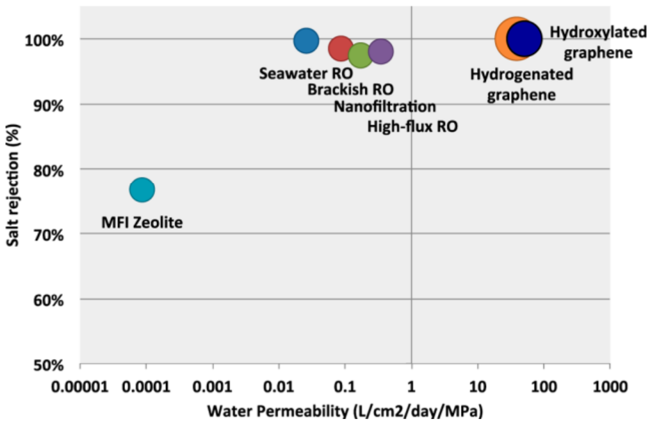
H_2O permeates through the GO at least 10^{10} times faster than He gas

R. R. Nair, et. al., Science, 2012, 335, 442

Graphene sheets for desalination of sea water and arsenic removal

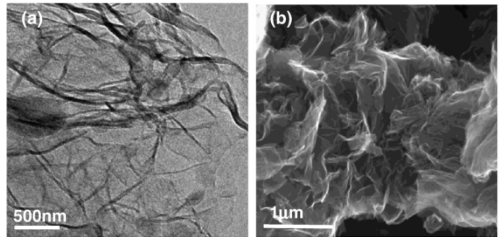
Desalination of sea water

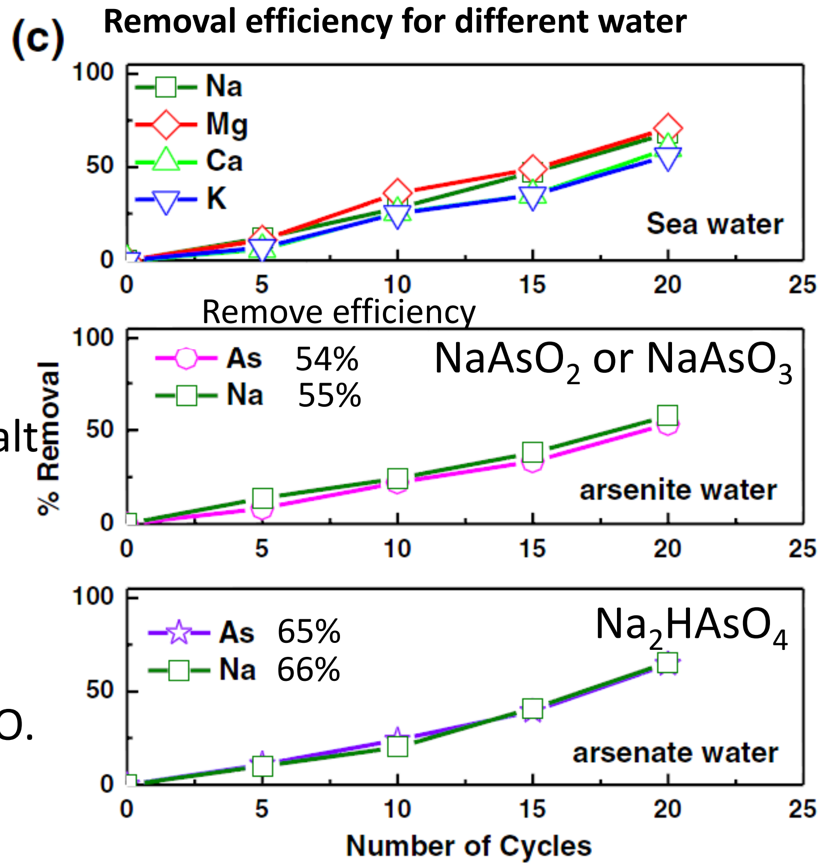




The graphene nanopores reject salt ions with a water permeability 2–3 orders of magnitude higher than commercial RO.

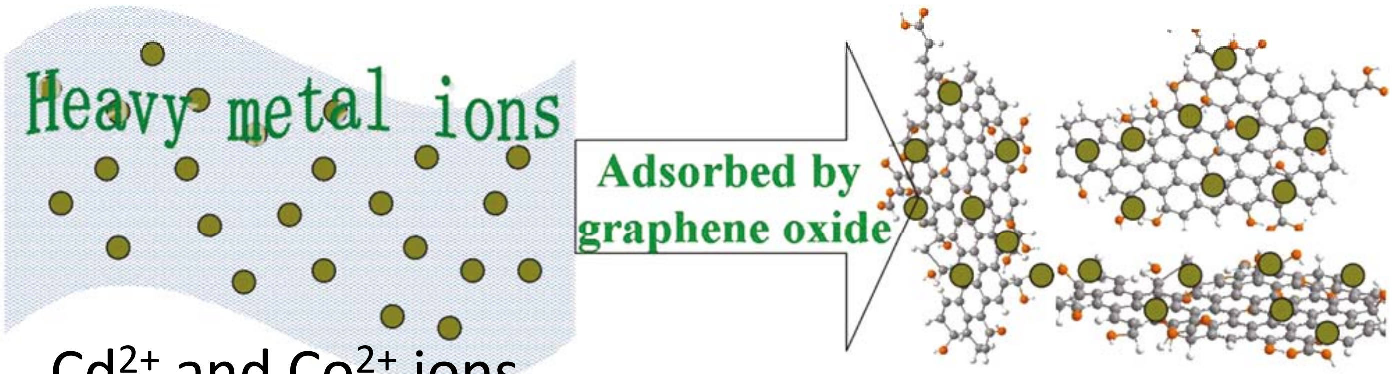
TEM SEM



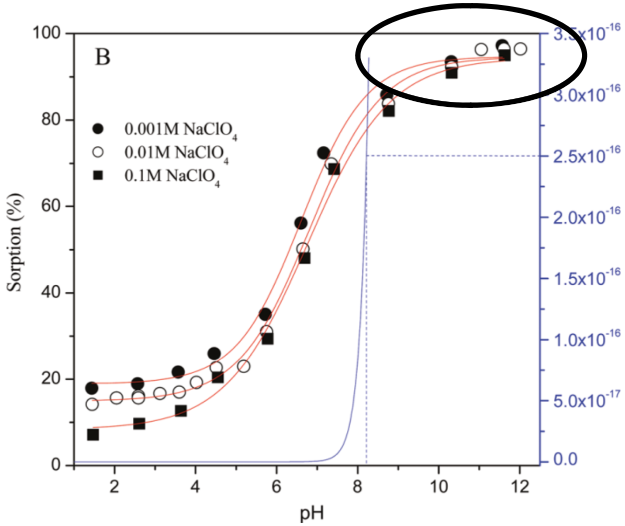


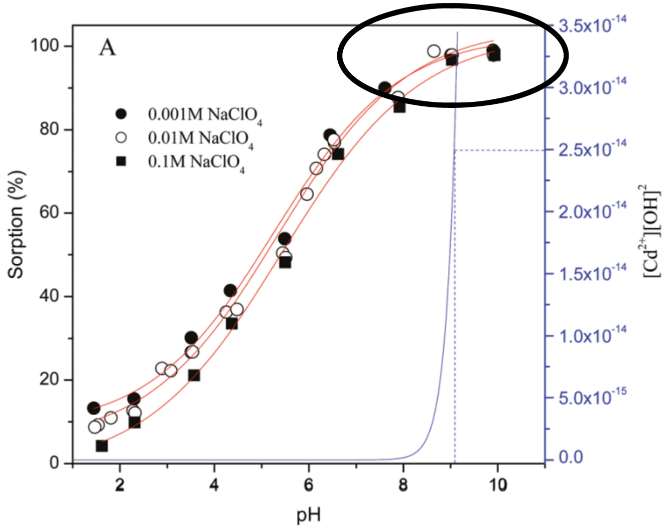
Cohen-Tanugi D. et. al., Nano Lett. 2012, 12, 3602−3608
Ashish Kumar Mishra,et. al., Desalination 282 (2011) 39–45

Few-Layered Graphene Oxide Nanosheets As Superior Sorbents for Heavy Metal Ion Pollution Management



Cd^{2+} and Co^{2+} ions





Most Cd^{2+} and Co^{2+} is adsorbed on GO nanosheets at pH > 9.

Zhao, G., et. al. Environ. Sci. Technol. 2011, 45, 10454–10462