Grapene and Graphene-based materials

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(Cited materials available in an internet space)

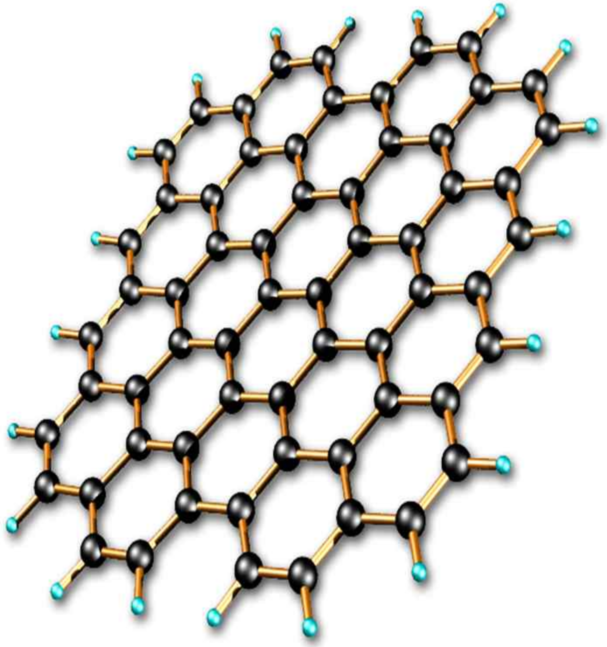
Contents

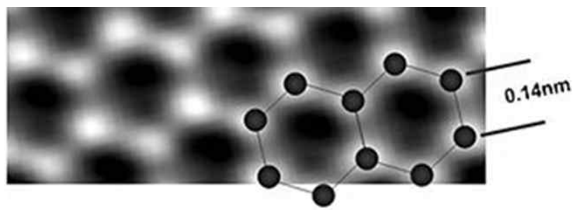
- Graphene
- Solar cell & LED applications (Examples)
- Graphene oxide
- Graphene quantum dot
- Biomedical applications (Examples)

The name 'graphene' comes from graphite + -ene = graphene

What is graphene?

In late 2004, graphene was discovered by Andre Geim and Kostya Novoselov (Univ. of Manchester).
- 2010 Nobel Prize in Physics





Q1. How thick is it?
→ a million times thinner than paper
(The interlayer spacing : 0.33~0.36 nm)

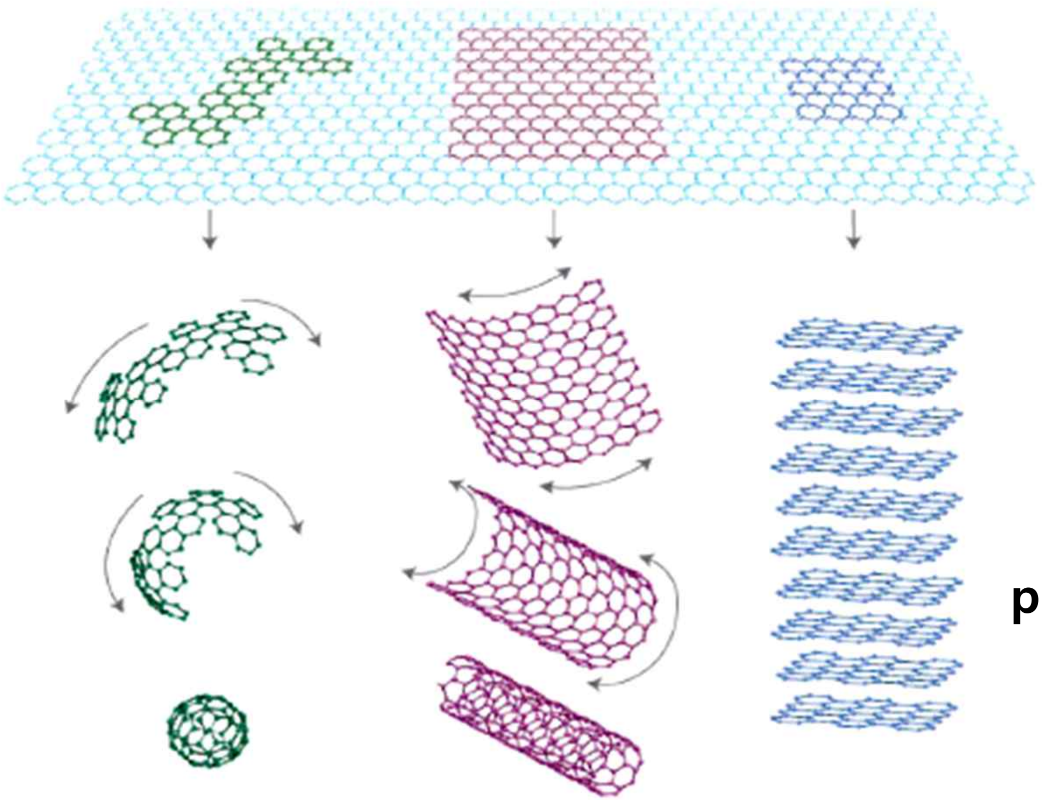
Q2. How strong is it?
→ stronger than diamond
(Maximum Young's modulus : ~1.3 TPa)

Q3. How conductive is it?
→ better than copper
(The resistivity : 10^{-6} Ω·cm)
(Mobility: 200,000 $cm^2 V^{-1} s^{-1}$)

But, weak bonding between layers
Seperated by mechanical exfoliation of 3D graphite crystals.

Molecular structure of graphene

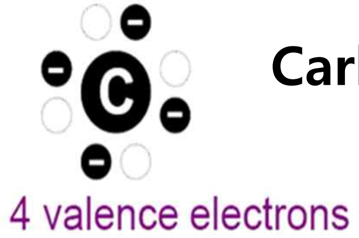
2D graphene sheet

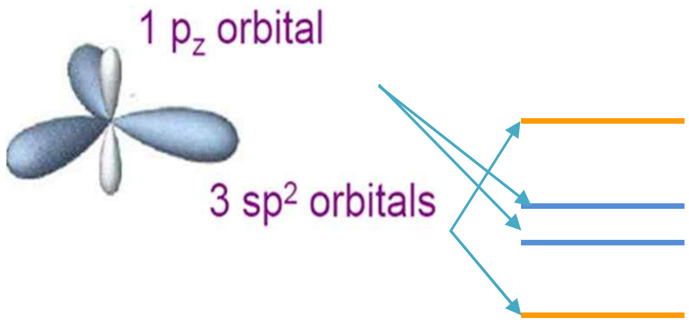


bucky ball **CNT** **3D graphite**

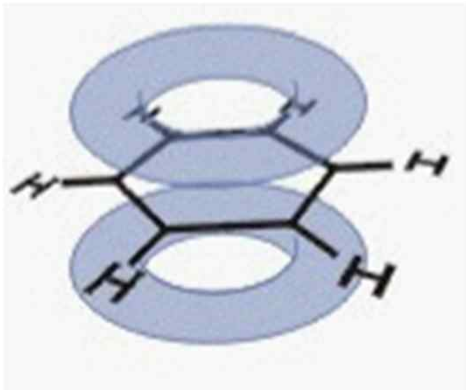
A. K. Geim, K. S. Novoelov, nature materials 6, 183-191 (2007)

Carbon



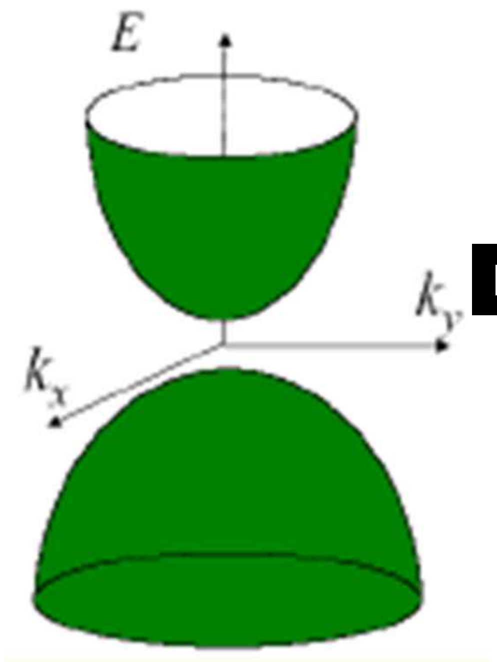


Electrons move freely across the plane through delocalized pi-orbitals

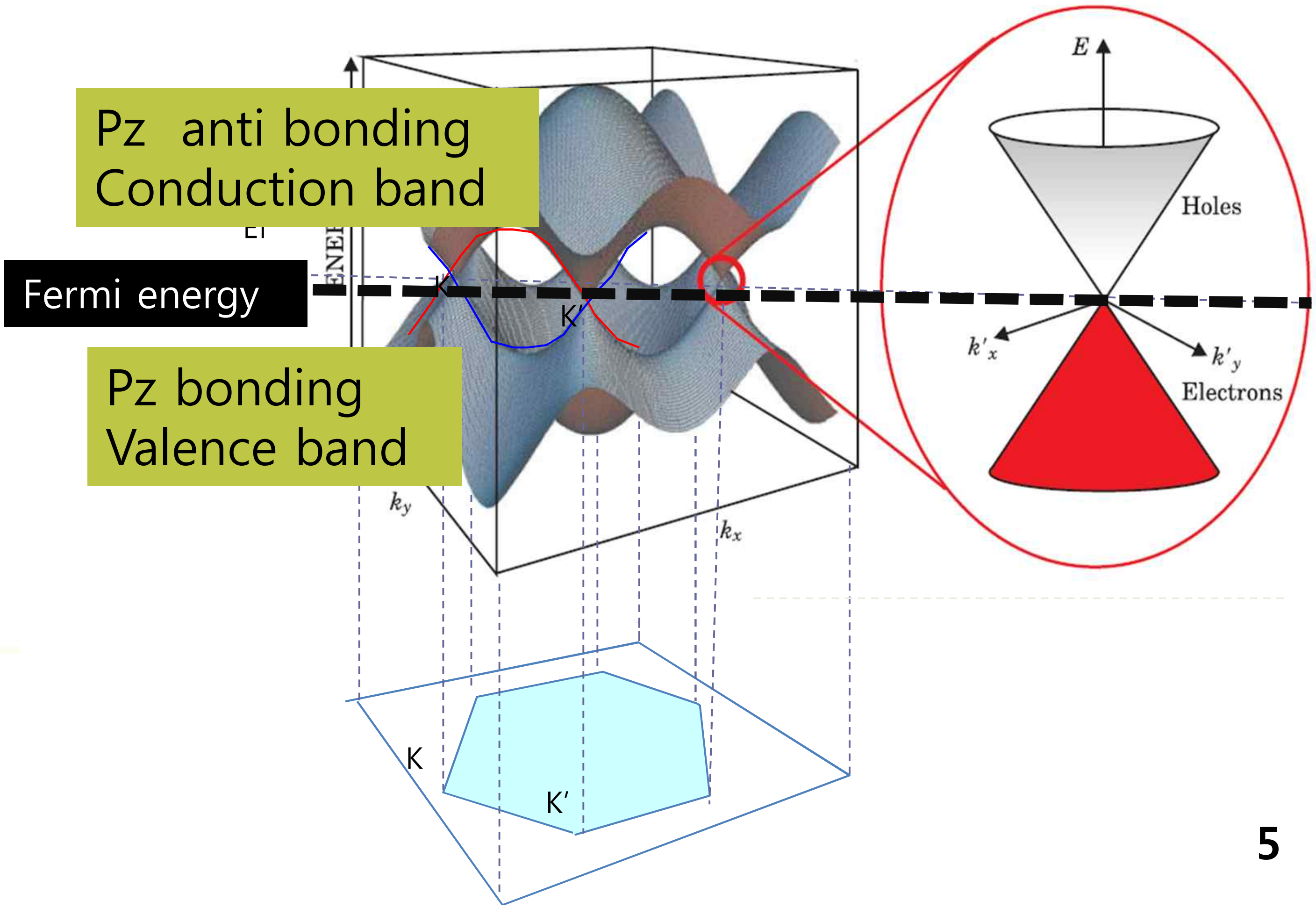


Electronic structure of graphene

Effective mass (related with 2^{nd} derivative of E(k)) ➔ Massless
Graphene charged particle is massless Dirac fermion.
→ **Zero gap semiconductor** **or** **Semi-metal**



2DEG

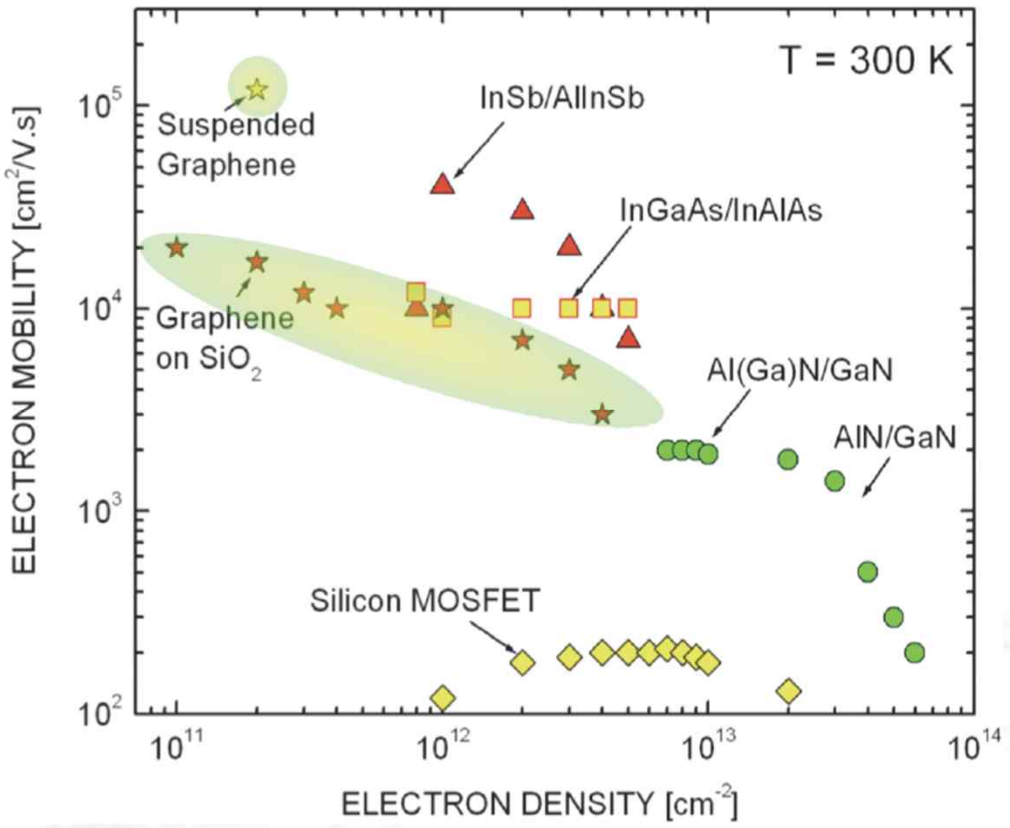


Electrical properties of graphene

High electron mobility at room temperature: Electronic device.
Si Transistor, HEMT devices are using 2D electron or hole.

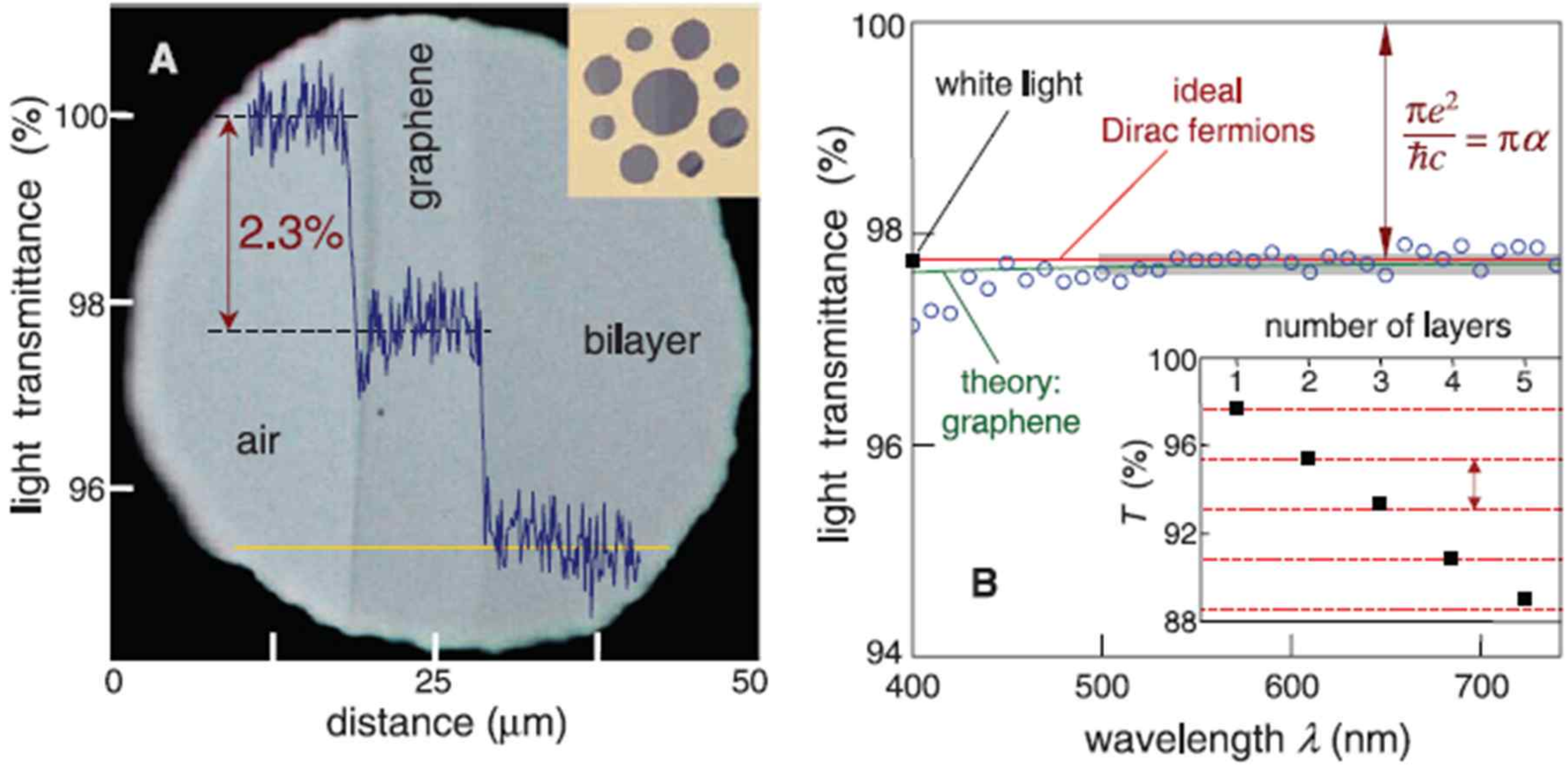
μ (mobility) = v_{avg} / E
(velocity/electric field)

$J_{drift} \sim \rho \times v_{avg}$



Optical properties of graphene

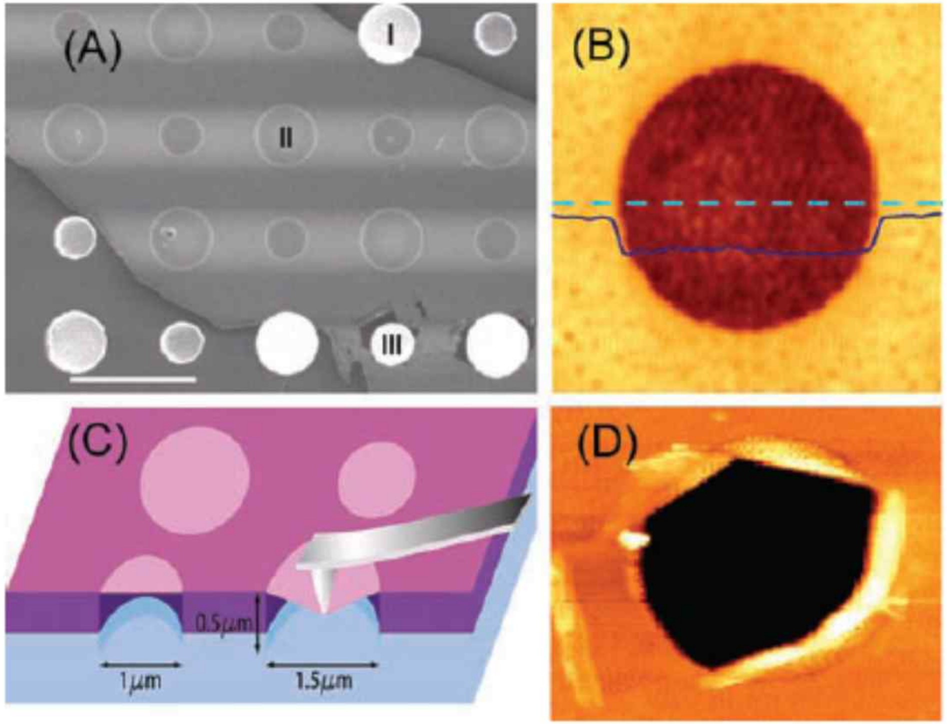
Optical transmittance control: **transparent electrode**
Reduction of single layer: 2.3%



F. Bonaccorso et al. *Nat. Photon.* **4**, 611 (2010)

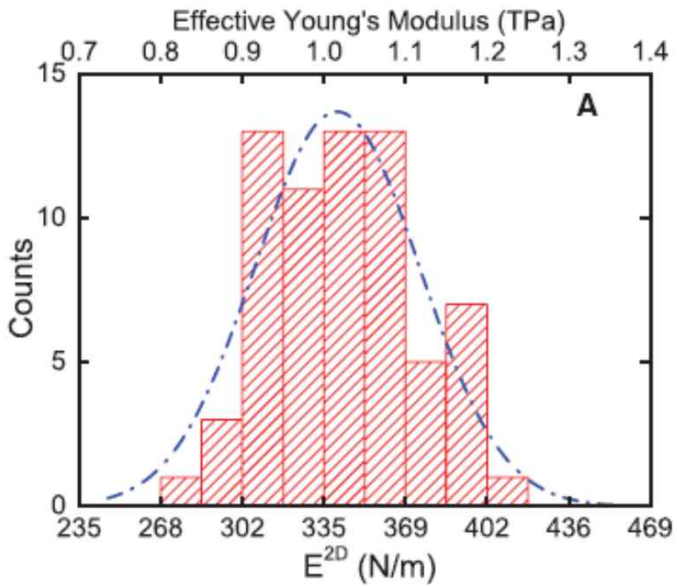
Mechanical properties of graphene

Mechanical strength for **flexible and stretchable devices**



Force-displacement measurement

Young's modulus
=tensile stress/tensile strain
Diamond ~ 1200 GPa



C. Lee et al. *Science* **321**, 385 (2008)

Syntheses of Graphene

- **Synthesis**

Preparation methods

Top-down approach (From graphite)

- Micromechanical exfoliation of graphite (Scotch tape or peel-off method)
- Creation of colloidal suspensions from graphite oxide or graphite intercalation compounds (GICs)

Bottom up approach (from carbon precursors)

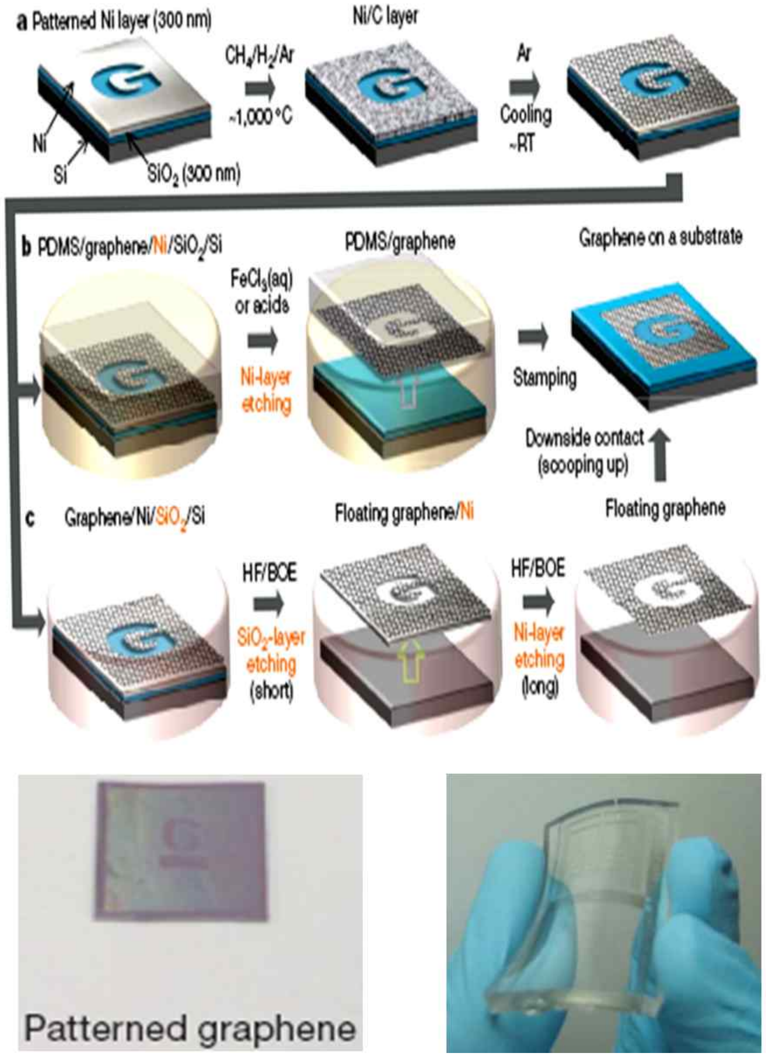
- By chemical vapour deposition (CVD) of hydrocarbon
- By epitaxial growth on electrically insulating surfaces such as SiC
- Total Organic Synthesis

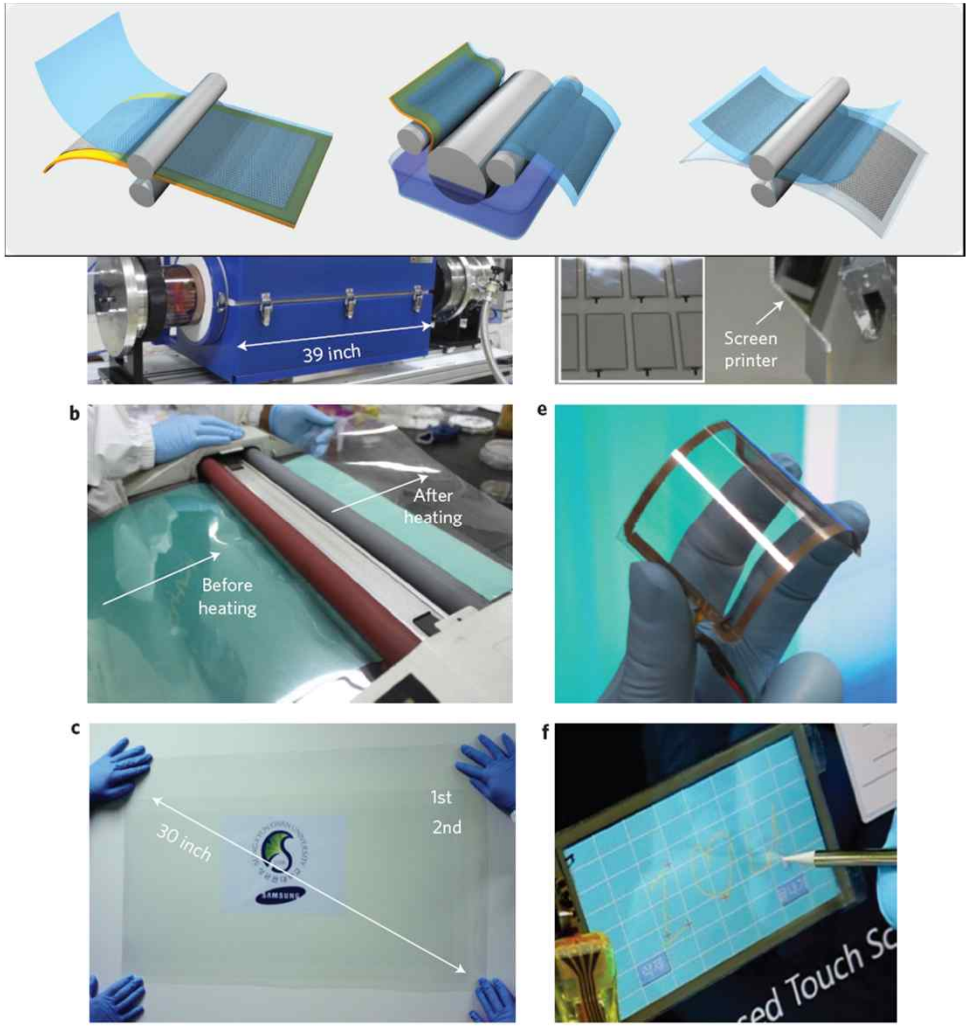
Table 1 – Advantages and disadvantages for techniques currently used to produce graphene.

	Advantages	Disadvantages
Mechanical exfoliation	Low-cost and easy No special equipment needed, SiO_2 thickness is tuned for better contrast	Serendipitous Uneven films Labor intensive (not suitable for large-scale production)
Epitaxial growth	Most even films (of any method) Large scale area	Difficult control of morphology and adsorption energy High-temperature process
Graphene oxide	Straightforward up-scaling Versatile handling of the suspension Rapid process	Fragile stability of the colloidal dispersion Reduction to graphene is only partial

S. Caterina, M. Ather and D. Erik, Carbon 48, 2127 –2150 (2010)

Large area graphene



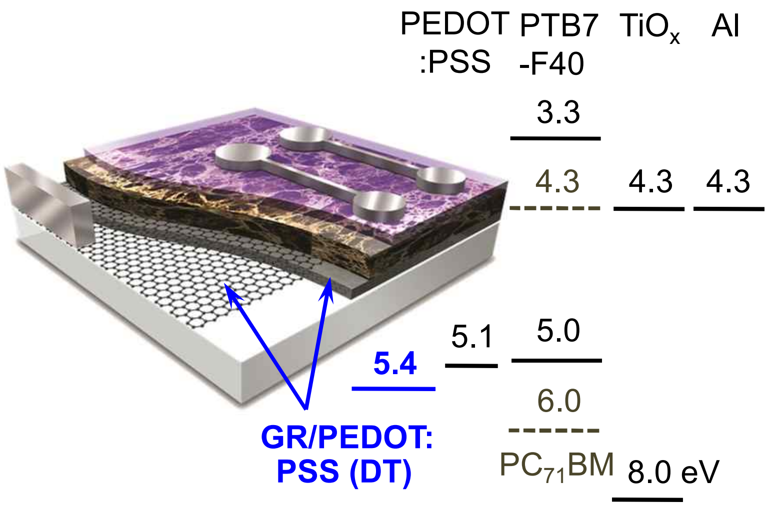


K. S. Kim et al. *Nature* **457**, 706 (2009)

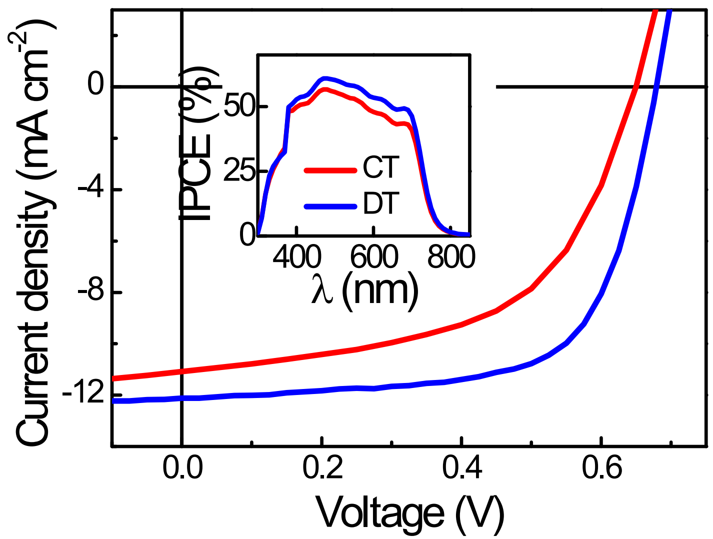
S. Bae et al. *Nat. Nano.* **5**, 574 (2010)

PSCs with graphene anodes

a

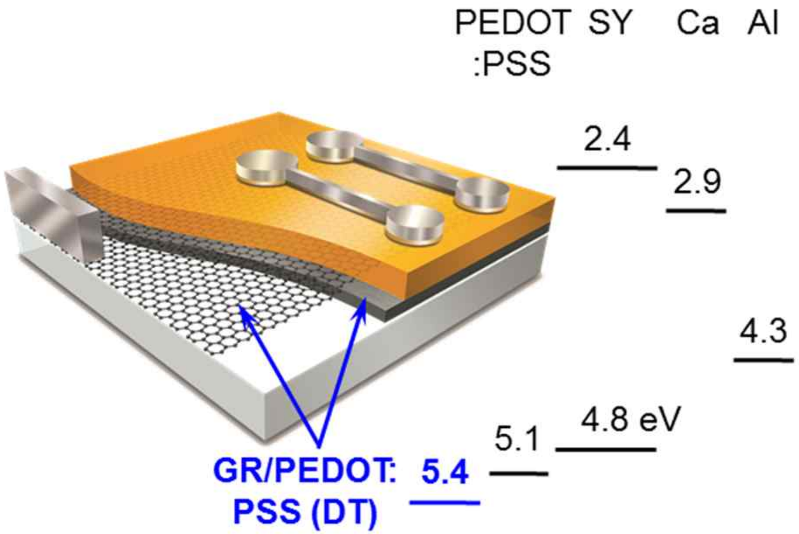


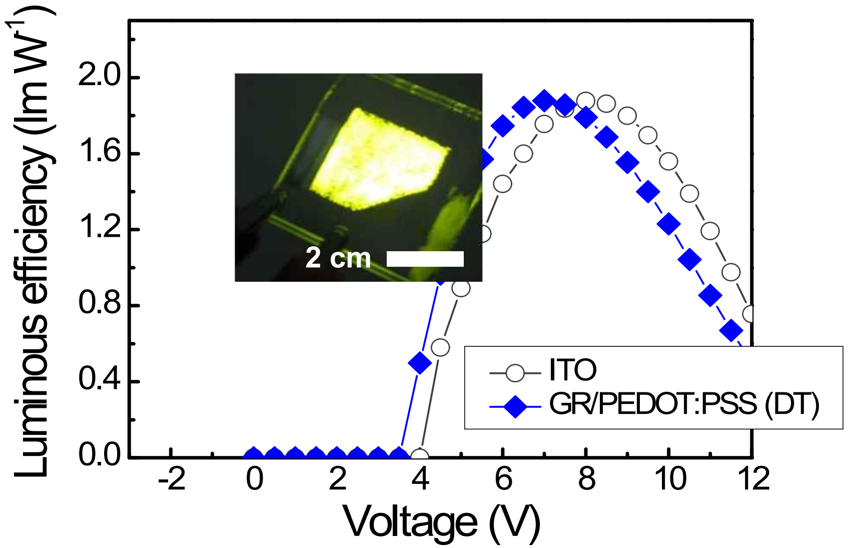
b



Device	Substrate	Electrode	Method	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%) Average	PCE (%) Best
PSC	Glass	ITO	RF sputtering	0.68	14.1	0.61	5.80 ± 0.06	5.86
		GR	CT	0.65	11.1	0.55	2.69 ± 1.80	3.92
			DT	0.68	12.1	0.67	4.85 ± 0.24	5.49
	PET	ITO	RF sputtering	0.64	14.3	0.52	4.52 ± 0.18	4.74
		GR	DT	0.64	12.5	0.60	4.57 ± 0.21	4.81

PLEDs with graphene or ITO anodes

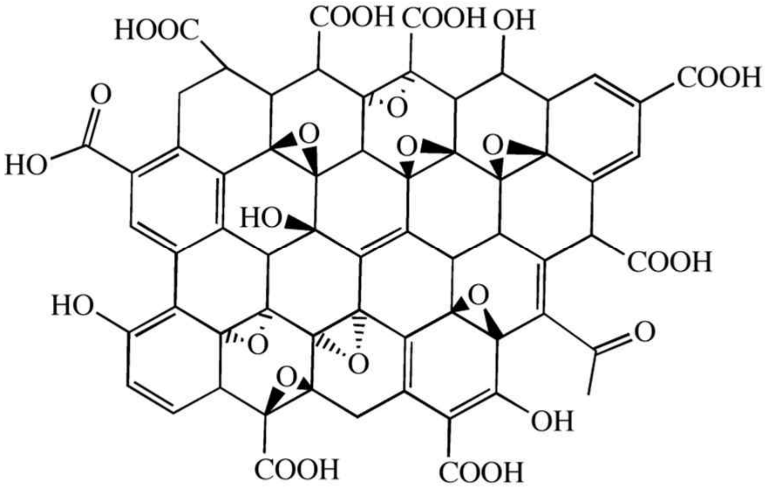




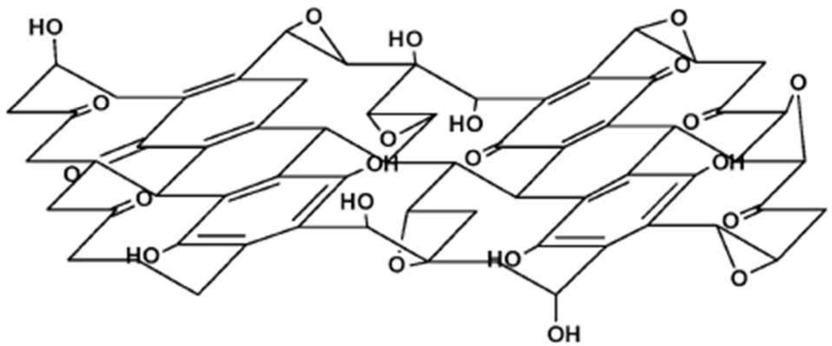
Device	Substrate	Electrode	Method	LE_{max} (lm W^{-1})	CE_{max} (cd A^{-1})	V_T (V)	L_{max} (cd m^{-2})
PLED	Glass	ITO	RF sputtering	1.87	5.15	4.5	4750
		GR	CT	1.37	3.69	4.5	3150
			DT	1.87	4.14	4.0	4000

Graphene Oxide (GO)

- Covalently decorated with oxygen containing functional groups – either on the basal plane or at the edges
- Precursor for graphene
- Considered as a promising materials for biological applications owing to its excellent aqueous processability, amphiphilicity, surface functionalizability, surface enhanced Raman scattering(SERS) property, and fluorescence quenching ability



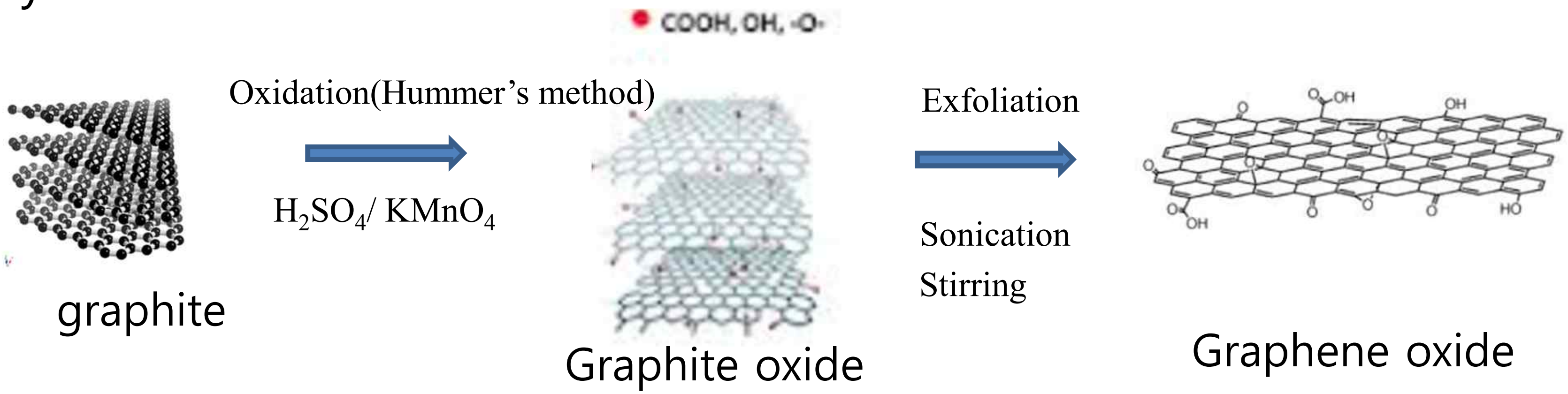
Lerf-Klinowski model



Dekany model

Graphene Oxide (GO)

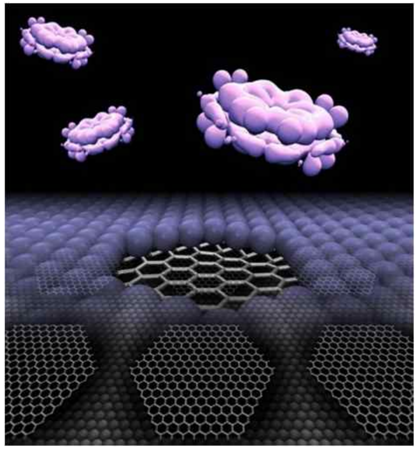
- Synthesis



- Property
- In contrast to pure graphene, GO is fluorescent over a broad range of wavelengths
- Manipulation of the size, shape and relative fraction of the sp2 hybridized domains of GO provides opportunities for tailoring its optoelectronic properties
- Chemical modification of functional groups in GO gives possibilities of potential use in polymer composites, sensors, photovoltaic application, and drug-delivery systems.

Graphene Quantum Dot (GQD)

- Small graphene fragments (size range below 20nm diameter, 2nm height), where electronic transport is confined in all three spatial dimensions



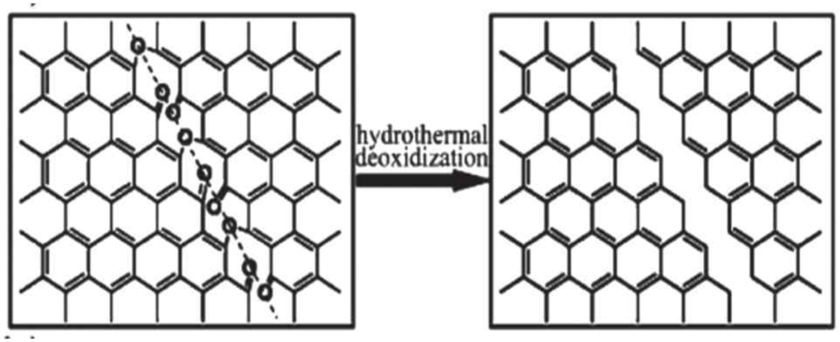
- **Property**

- Easier to handle compared to colloidal QDs and show the desirable electro-optic properties of quantum dots
- Non-toxic, highly soluble in various solvents, can be equipped with functional groups at their edges
- The PL bandwidth is much wider than semiconductor QDs and decreases with increasing excitation wavelength.
- Emits NIR fluorescence which is useful for cellular imaging due to the minimal cellular auto-fluorescence in this region
- Spectroscopic properties vary depending on the method of preparation, functional groups at the edges of the particles
- Upconversion luminescence

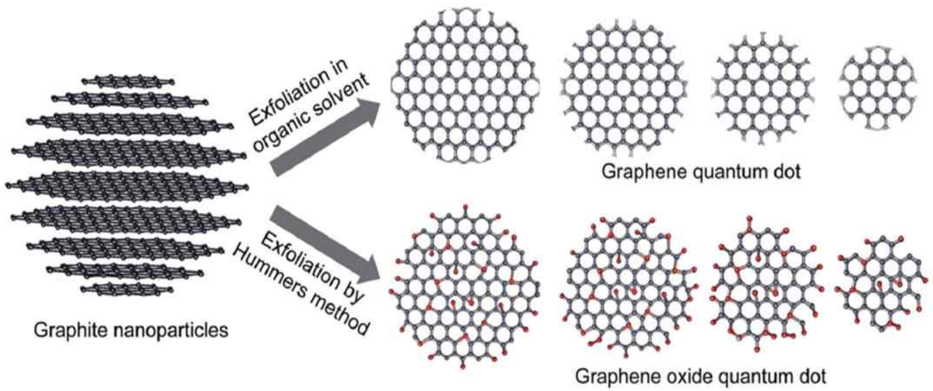
Graphene Quantum Dot (GQD)

- **Synthesis**

- top-down method: hydrothermal cutting, solvothermal cutting, electrochemical cutting, nanolithography, microwave-assisted cutting, nanotomy-assisted exfoliation, ultrasonic shearing

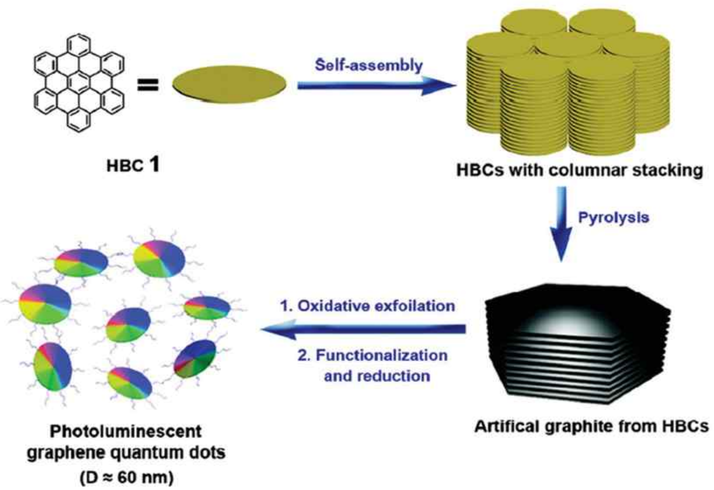


D. Pan , J. Zhang , Z. Li , M. Wu , *Adv. Mater. 22* , 734 , 2010



- bottom-up method: stepwise organic synthesis, cage opening of fullerenes

F. Liu , M.-H. Jang , H. D. Ha , J.-H. Kim , Y.-H. Cho , T. S. Seo , *Ad Mater.* **2013** , *25* , 3657 .

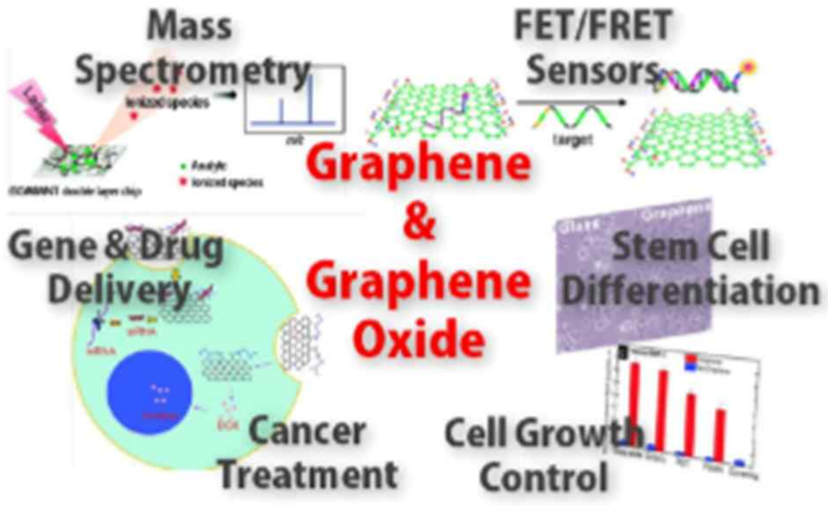


hexa-peri-hexabenzocoronene(HBC)
—a polycyclic aromatic hydrocarbon

R. Liu , D. Wu , X. Feng , K. Müllen , *J. Am. Chem. Soc.* **2011** , *133* , 15221 .

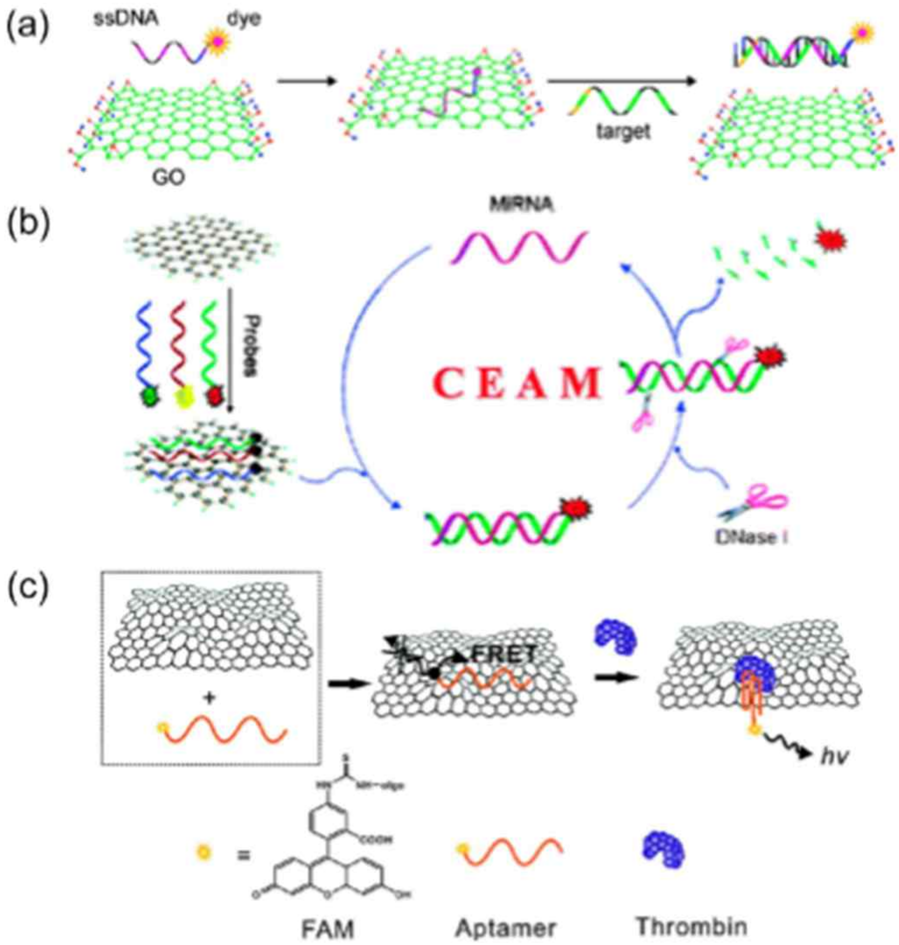
Biomedical applications of graphene-based materials

- Mass spectrometry
- FET/FRET sensors (Enzyme biosensors, DNA-based biosensors, immunosensors)
- Gene & Drug delivery
- Cancer treatment
- Cell growth control
- Stem cell differentiation
- Bio-imaging



B. H. Hong, D. H. Min, Accounts of chemical research 46, 2211, 2013

FRET sensors



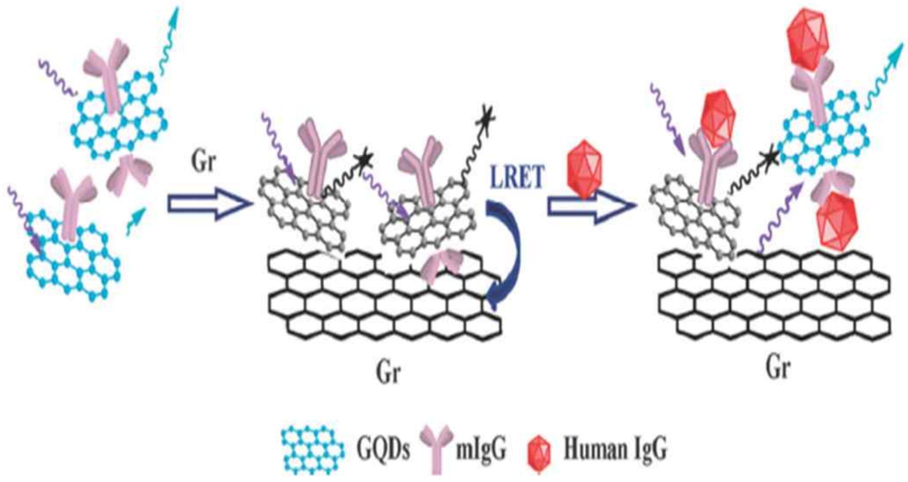
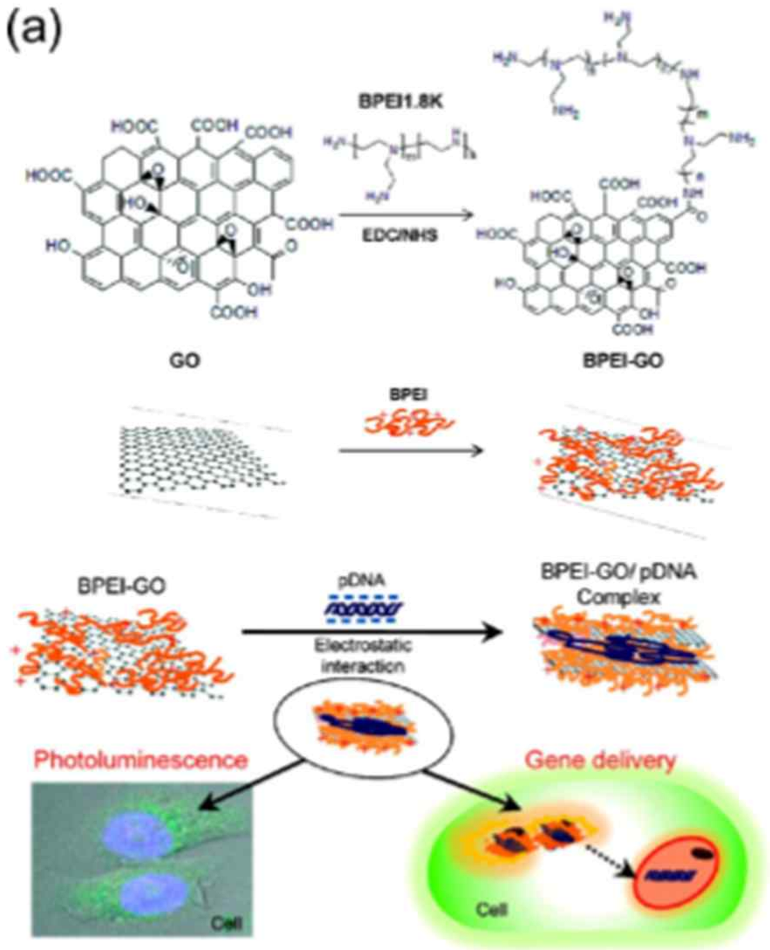


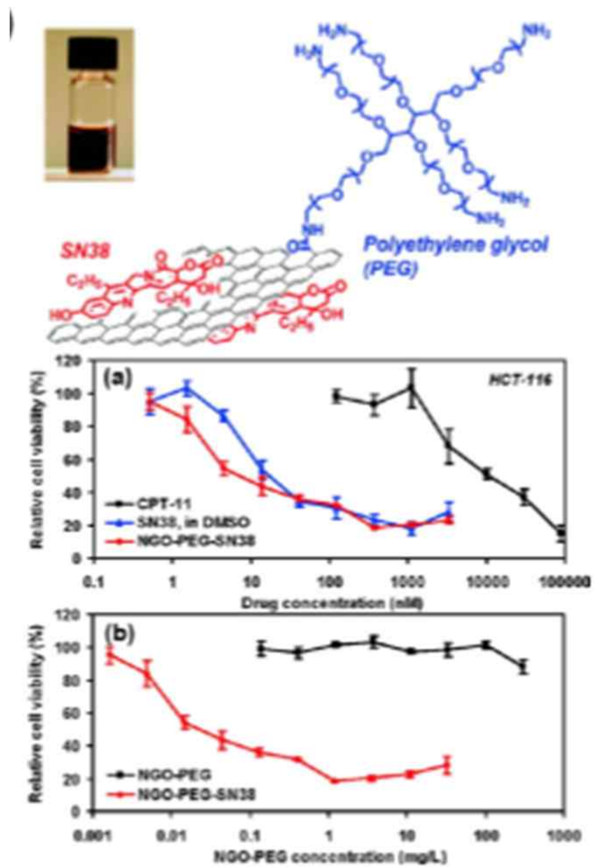
Figure 13. Schematic illustration of a universal immunosensing strategy based on regulation of the interaction between Gr and GQDs. Reproduced with permission.[71] Copyright 2013, Royal Society of Chemistry.

H. Zhao , X. Quan , *Chem. Commun.* **2013** , *49* , 234 .

(a) Lu, C. H, Chen, G. N. A , Angew. Chem., Int. Ed. 2009, 48, 4785–4787
(b) Cui, L, Yang, C. J., Chem. Commun. 2012, 48, 194–196..
(c) Chang, H, Jiang, J.; Li, J., Anal. Chem. 2010, 82, 2341–2346.

Gene & Drug delivery





Kim, H.; Namgung, R.; Singha, K.; Oh, I. K.; Kim, W. J. Bioconjugate Chem. 2011, 22, 2558–2567.

Liu, Z.; Robinson, J. T.; Sun, X.; Dai, H., J. Am. Chem. Soc. 2008, 130, 10876–10877.

Bio-imaging

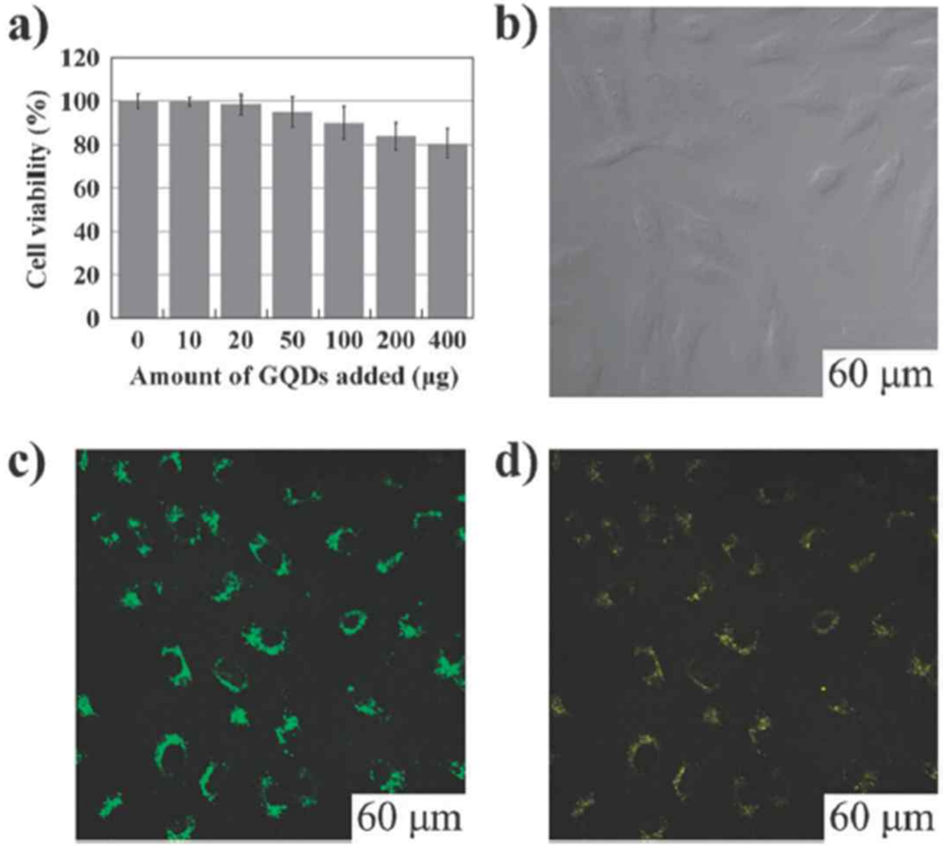


Figure 12. Cellular toxicity and cellular imaging of GQDs. a) Effect of GQDs on MG-63 cells viability. b–d) are washed cells imaged under bright field, 405 nm, 488 nm excitations, respectively. Reproduced with permission.[33] Copyright 2011, Royal Society of Chemistry.

S. Zhu , J. Zhang , C. Qiao , S. Tang , Y. Li , W. Yuan , B. Li , L. Tian , F. Liu , R. Hu , H. Gao , H. Wei , H. Zhang , H. Sun , B. Yang , *Chem. Commun.* **2011** , *47* , 6858 .