Rational Control of the Electronic Properties via Graphene-Organic Interface

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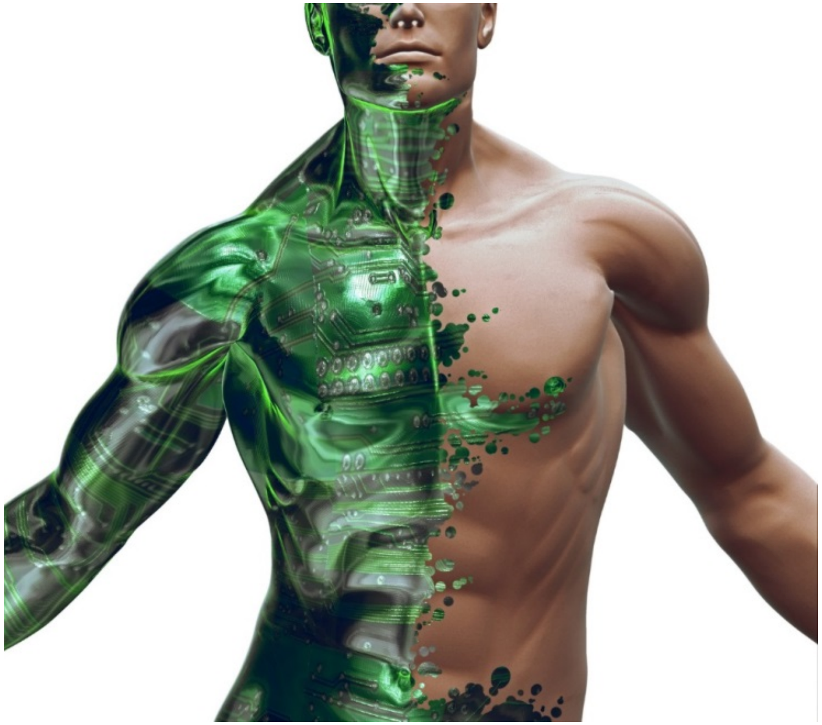
Electronic skin

Electronic skin: electronic devices that mimic skin function



- ❖ Touch (pressure) sensors
- ❖ Temperature sensors
- ❖ Chemical sensors
- ❖ Flexible, stretchable materials
- ❖ Self-powered – stretchable solar cells
- ❖ Self healing

- To build electronic skin devices, new materials need to be developed to enable versatile skin functions

A Sokolov, Z Bao, Acc. Chem. Research, 2012, 45, 361
M Hammock, Z Bao, Adv. Mater., 2013, 25, 5997

Various materials for electronic skin in our group

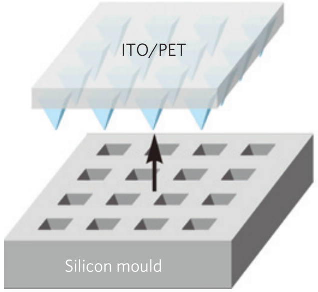
1 Microstructured PDMS (polydimethylsiloxane)

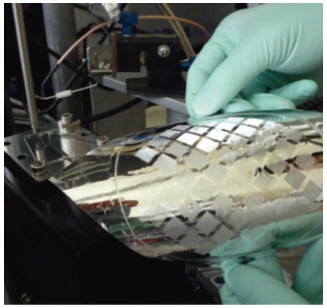
2. Conducting spray-deposited CNT arrays

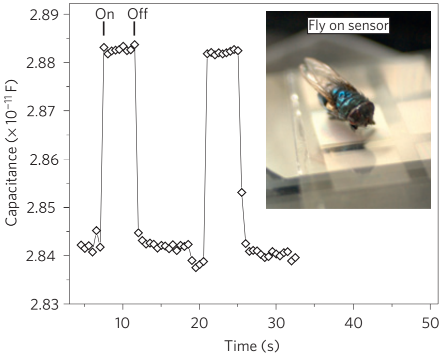
3. New conjugated polymer (polyisoindigobithiophene-siloxane (PiI2T-Si))

4. Self-healing polymer

Integrate microstructured PDMS as dielectric layer to form a capacitive pressure sensor







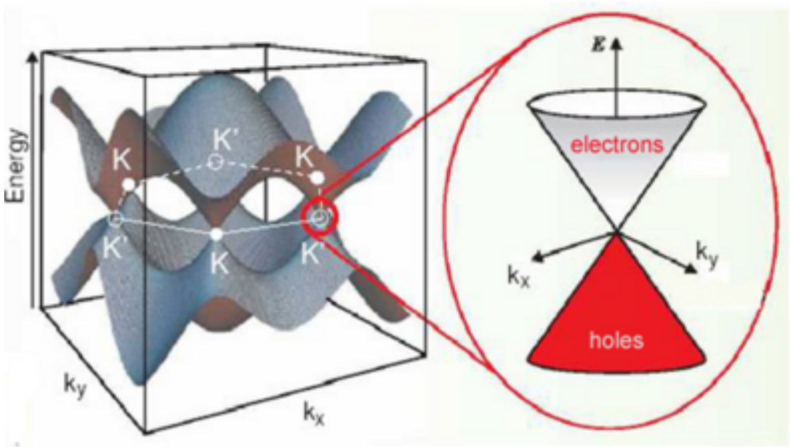
5. Graphene?

S Mannsfeld, Z Bao, Nature Materials, 2010, 9, 860

Advantages of Graphene

1. The electrons in graphene behave as massless Dirac Fermions

- High electron mobility ($15{,}000\ cm^2/Vs$ in Experiment; $200{,}000\ cm^2/Vs$ in Theory);
- Resistivity $10^{-6}\Omega m$ lower than silver



S Sarma, Review of Modern Physics, 2011, 83, 407

2. It is flexible, transparent and biocompatible

Outline

1) Bao Group research on solution processed graphene

2) To control graphene electronic properties via graphene-organic interface

a) To control Fermi level

b) To open up band gap

Work in Bao group using RGO

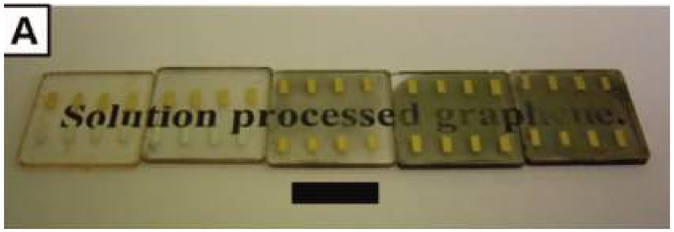
Advantages of GO:

- Solution processible
- Flexible
- Transparent
- Large scale and low cost

Main challenge: low conductivity

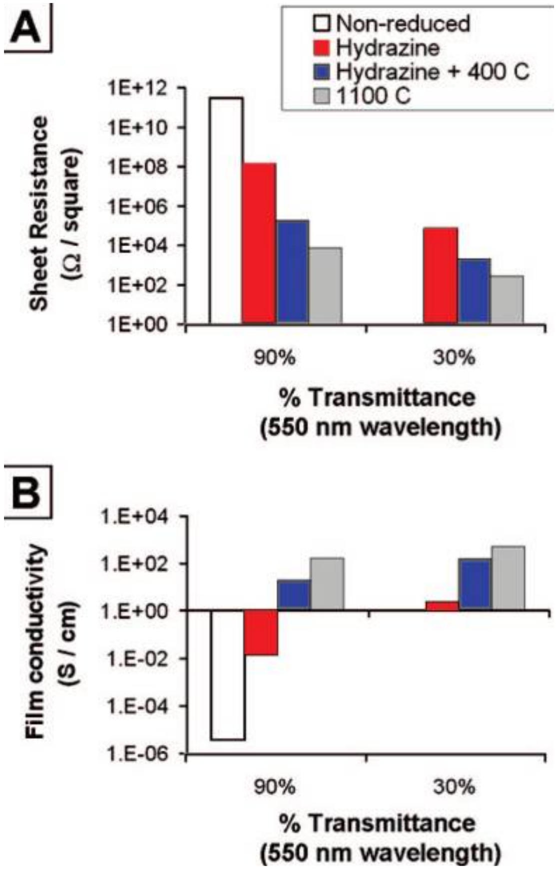
Thermal graphitization from Graphene oxide (GO) to reduced graphene oxide (RGO)

~ 100 Ω/sq @ 80% transmittance for 550nm light



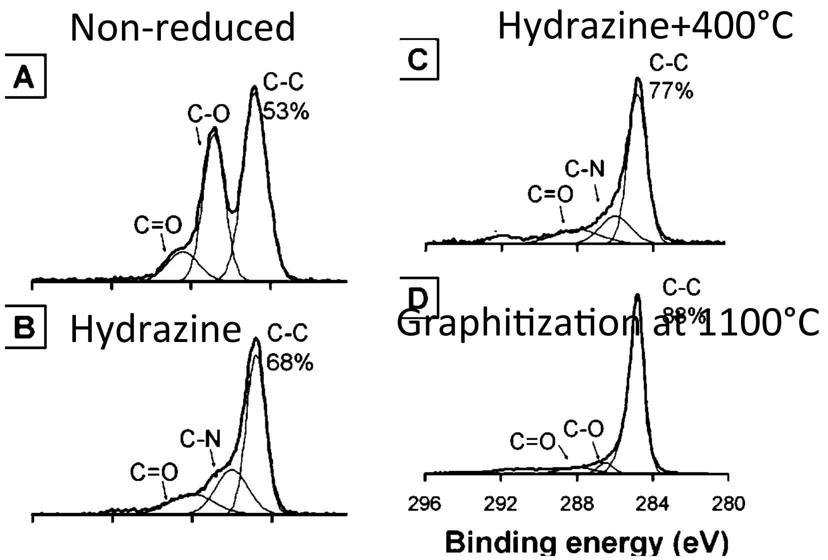
H Becerril, Z Bao, ACS Nano 2008, 2, 463

Reduction of graphene oxide



Sheet resistance decreases (Film conductivity increases): non-reduced, hydrazine, hydrazine +400°C, graphitization at 1100°C

X-ray photoelectron spectroscopy (XPS)



B and C: significant C-N signals, forming hydrazone groups, partially reduced byproducts
D: indicates higher conductivity is due to higher percentage of C-C bond

H Becerril, Z Bao, ACS Nano 2008, 2, 463

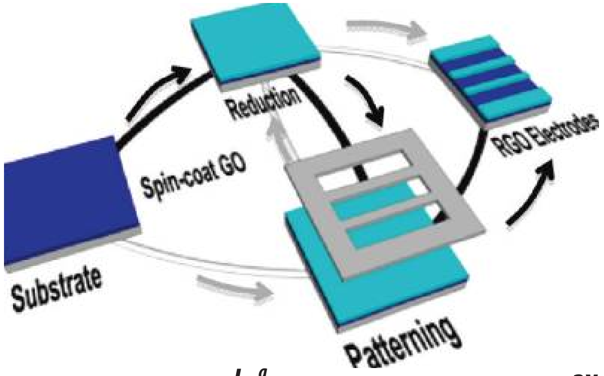
Work in Bao group using RGO

Applications in:

1. Organic thin film transistors (OTFTs)
2. Organic light emitting diodes (OLEDs)
3. Solar cells

OTFT using RGO as electrodes

Fabrication process of RGO electrodes



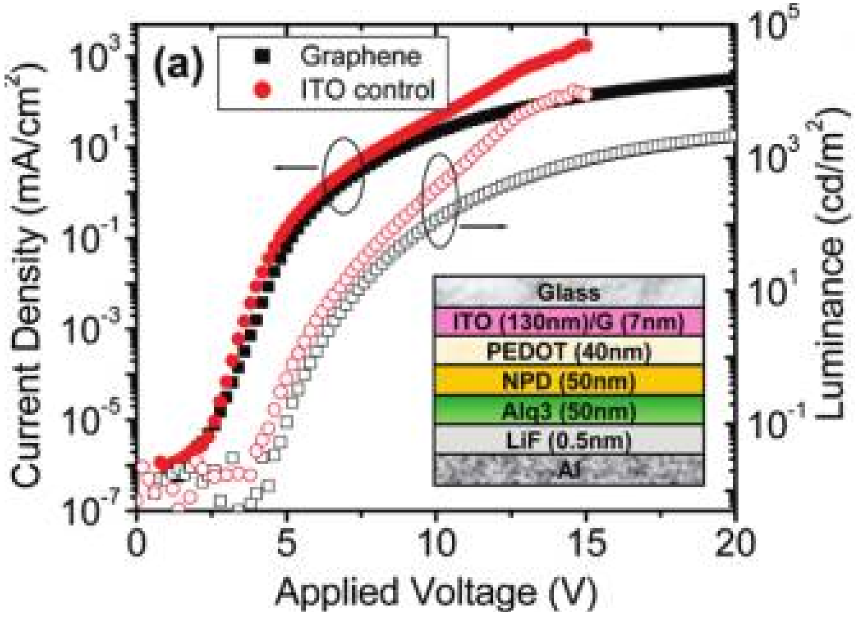
material	contact	I_{DS}[a]	av FET-μ[b]	I_{ON}/I_{OFF}[e]
pentacene	RGO	$1.19 \times 10^{-4} \pm 9\%$	$1.80 \times 10^{-1} \pm 14\%$	5.23×10^{6}
	gold	$9.95 \times 10^{-6} \pm 9\%$	$1.05 \times 10^{-2} \pm 0.2\%$	5.75×10^{5}
$F_{16}CuPc$	RGO	$1.60 \times 10^{-5} \pm 26\%$	$2.76 \times 10^{-2} \pm 23\%$	1.00×10^{7}
	gold	$4.41 \times 10^{-7} \pm 17\%$	$1.10 \times 10^{-3} \pm 25\%$	6.23×10^{5}
PQTBTz-C_{12}	RGO	$6.34 \times 10^{-6} \pm 75\%$	$8.96 \times 10^{-3} \pm 77\%$	1.04×10^{6}
	gold	$4.65 \times 10^{-7} \pm 13\%$	$1.07 \times 10^{-3} \pm 15\%$	3.54×10^{4}

Key figures of merits (on-current, mobility, on/off) of RGO-contacted TFT shows an enhancement of ~10x compared to those with gold contacts.

H Becerril, Z Bao, ACS Nano 2010, 4, 6343

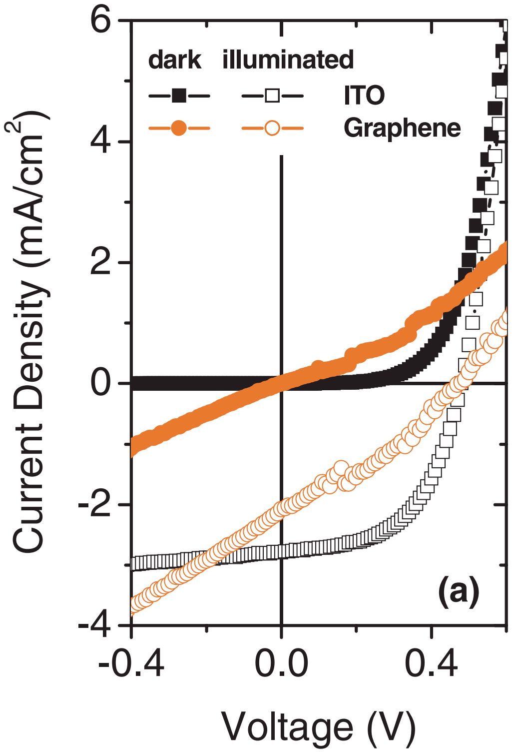
RGO electrodes in OLEDs and SCs

Graphene/glass vs. ITO/glass as anode



J Wu, Z Bao, ACS Nano 2010, 4, 43

Solar cell using RGO as electrodes



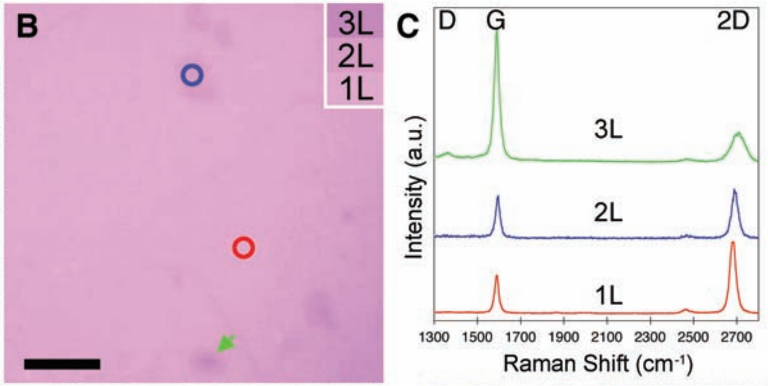
J Wu, Z Bao, Applied Physics Lett, 2008, 92, 263302

Device characteristics is comparable to control devices on ITO transparent anodes, while using earth-abundant materials and solution process

Chemical vapor deposition (CVD) grow graphene

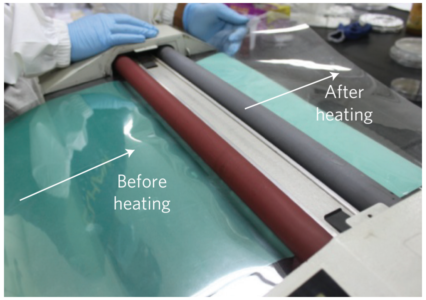
- High conductivity and electron mobility

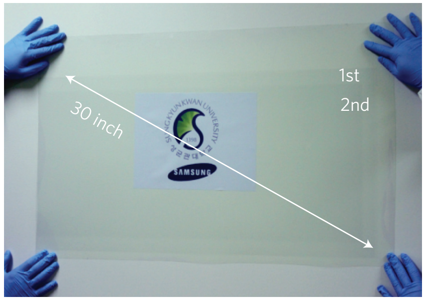
- Uniform and highly crystalline single layer



R Ruoff, Science, 2009, 324, 5932

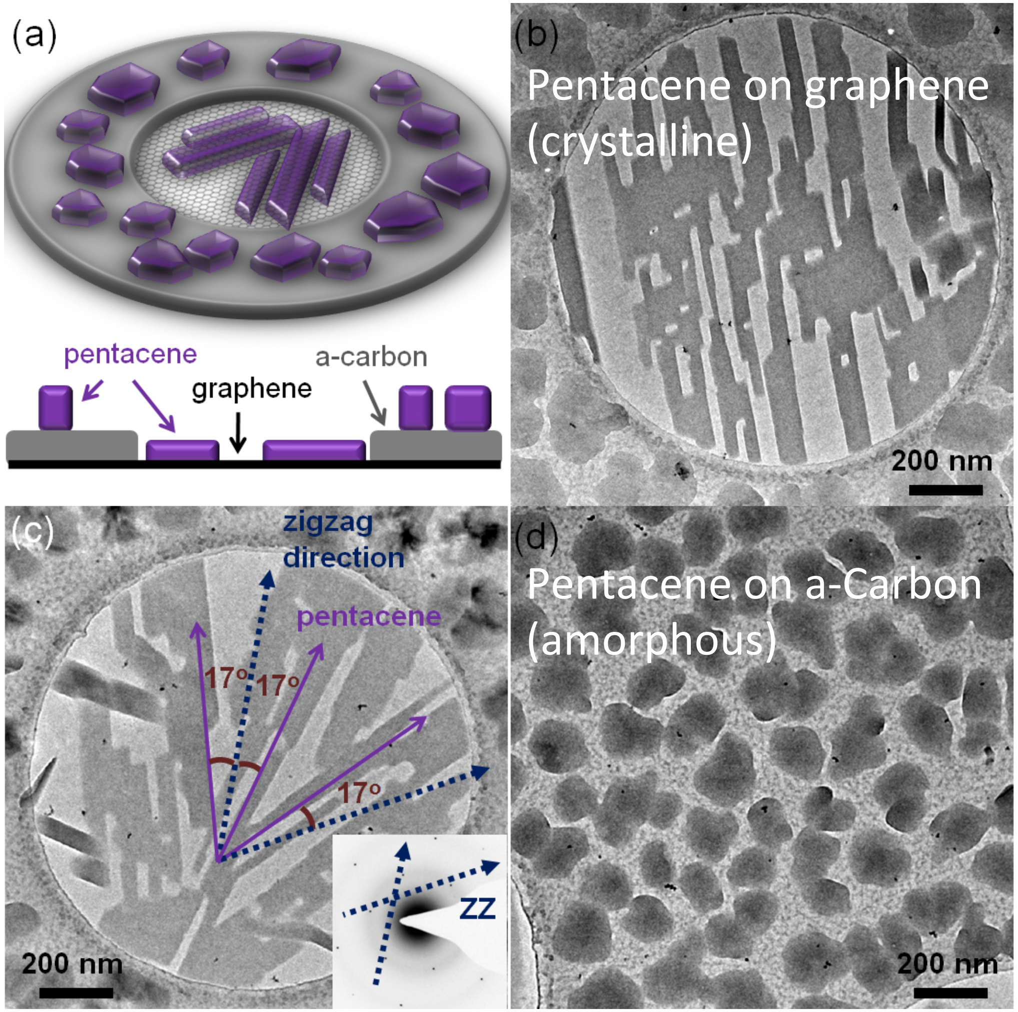
- Over a large area





B H Hong, Nature Nanotechnology, 2010, 5, 574

Graphene-organic interaction



High resolution TEM to show the morphology of pentacene deposited on graphene vs. a-carbon:

- On graphene pentacene is highly crystallized with a preferential lattice orientation
- On a-carbon it shows island growth without particular orientation

Can we harness this strong interaction to enable a tuning in graphene's properties?

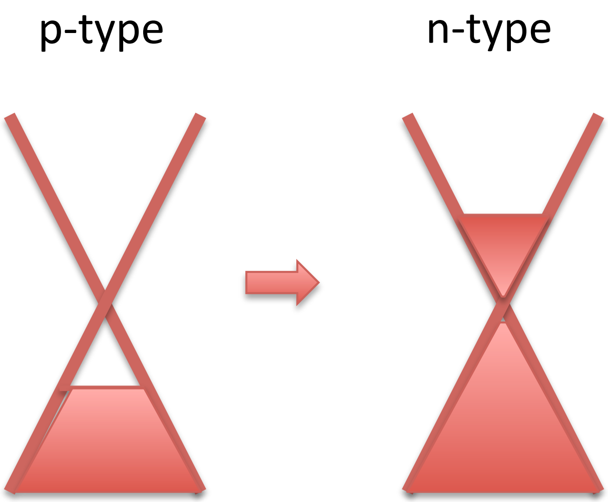
K Kim, Z Bao,2014, to be submitted

Outline

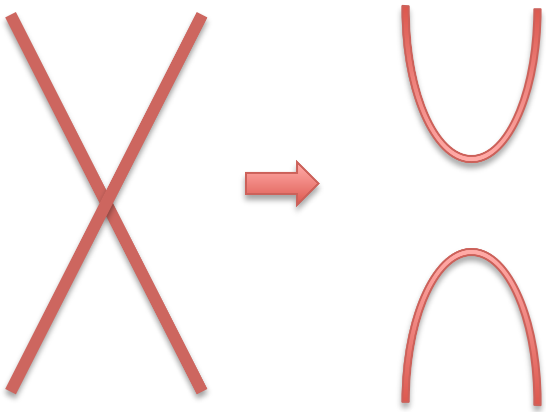
1) Bao Group research on solution processed graphene

2) To control graphene electronic properties via graphene-organic interface

a) To control Fermi level



b) To open up band gap

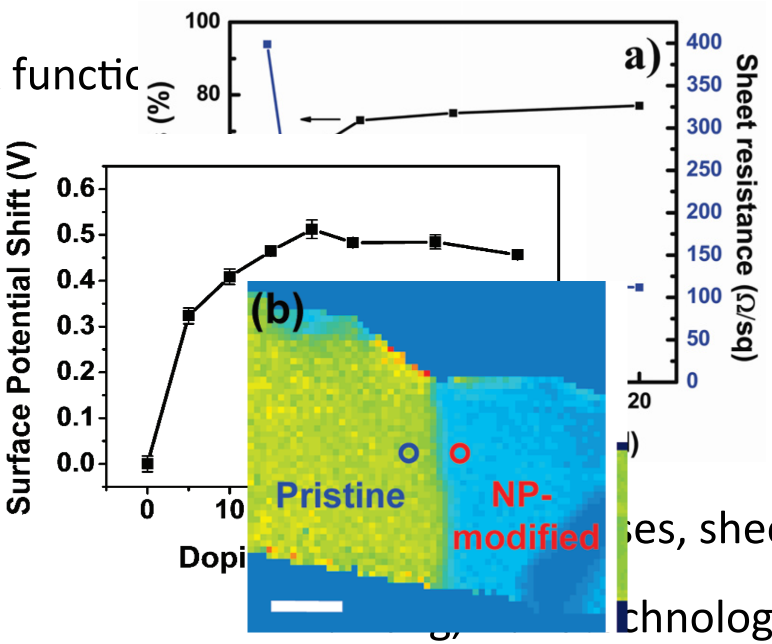


Importance of controlled Fermi level

1) Tuning conductivity

2) Modulating work functic

3) Creating heteros



As t … ses, sheet resistance decreases

chnology, 2010, 21, 285205

By changing the doping time, the surface potential of graphene is modulated to make efficient contact to different materials

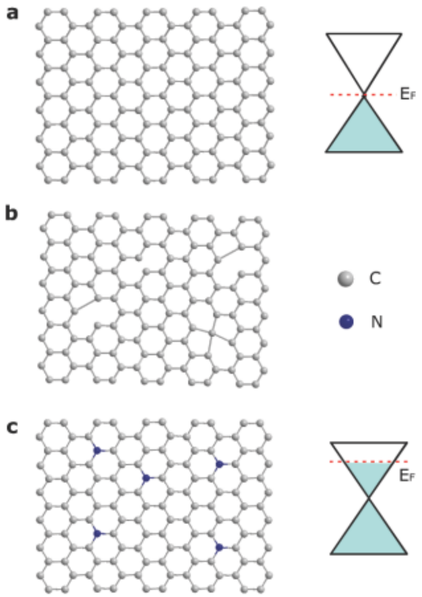
By having complementary doping, p-n junctions can be created.

Y Chen, ACS Nano, 2011, 3, 26051

J Kong, ACS Nano, 2010, 5, 2689

Doping to control graphene Fermi level

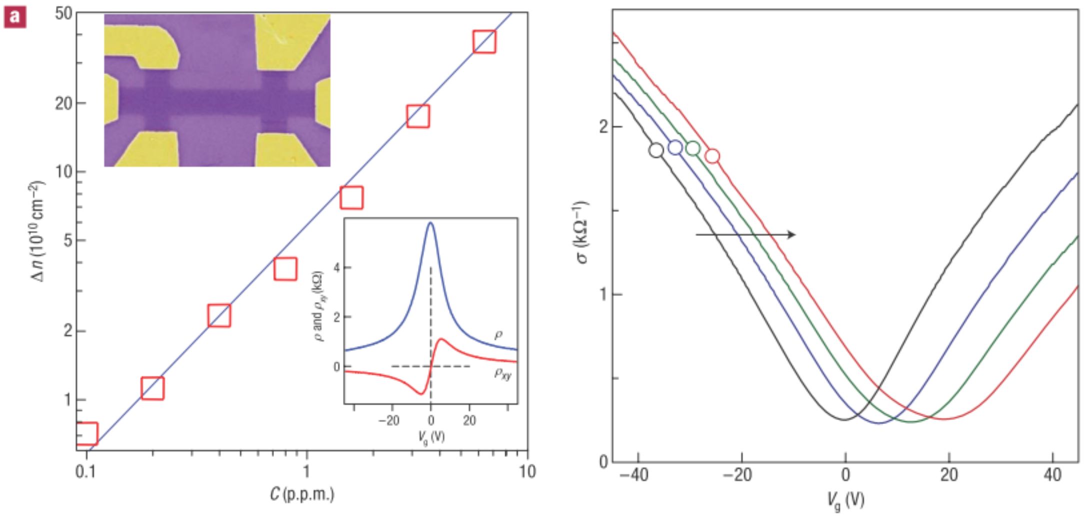
1) Substitute C in the lattice



Limitation: disrupts the honey comb lattice of graphene

J Gong, Nano Lett. 2010, 10, 4975

2) Physically adsorbed gaseous molecules



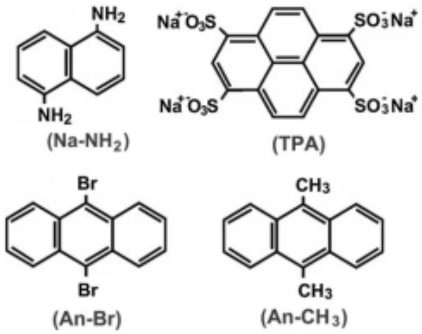
Limitation: not a stable doping way, tend to dissociate from the surface

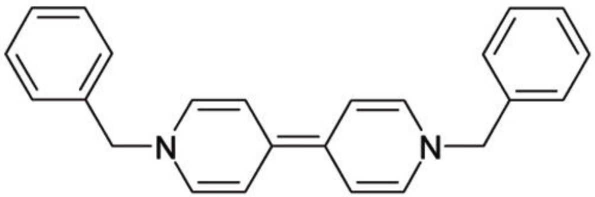
K.S. Noveselov. Nature Materials 2007, 6, 652

Doping to control graphene Fermi level

3) Noncovalent binding of nongaseous organic molecules

- Stable;
- Preserving the honeycomb structure.





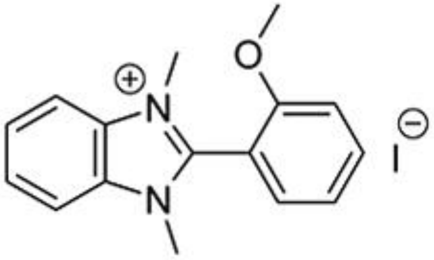
Reduced 1,1' Dibenzyl-4,4'-bipyridinium

Pyrene derivatives bearing withdrawing or donating functional groups

L Li, Small 2009, 5,1422

Design new n-type dopant

2-(2-Methoxyphenyl)-1,3-dimethyl-1H-benzoimidazol-3-ium Iodide



o-MeO-DMBI-I

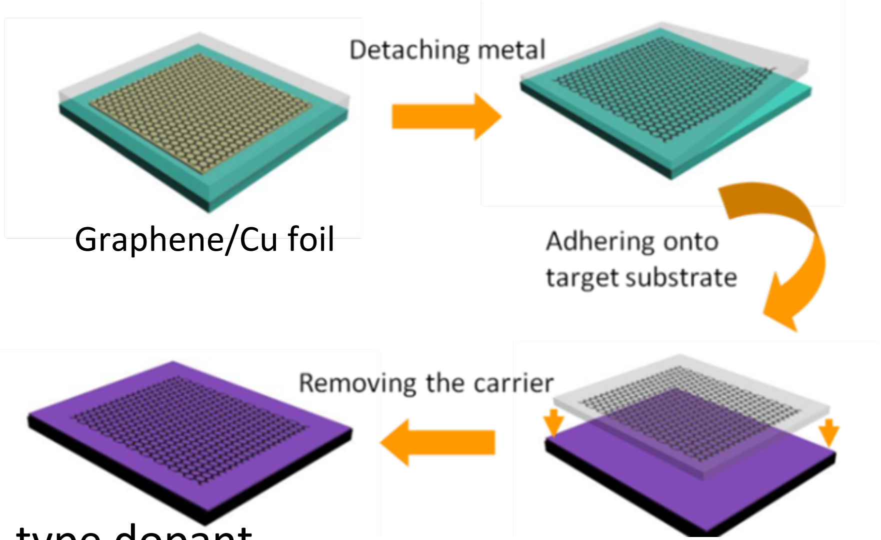
P Wei, Z Bao, J. Am. Chem. Soc. 2012, 134, 3999
P Wei, Z Bao, J. Am. Chem. Soc. 2010, 132, 8852

- *o*-MeO-DMBI is air-stable and can be stored and handled in air for extended periods without degradation
- Solution process or vacuum deposition

Can we tune the Fermi level of graphene using this molecule?

Process of doping graphene

1. Transfer graphene and fabricate graphene devices



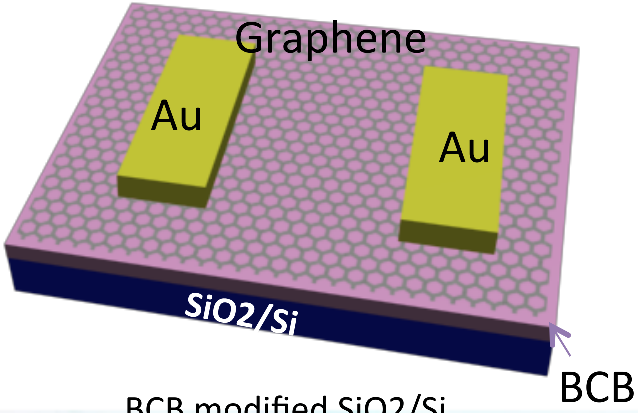
Detaching metal

Graphene/Cu foil

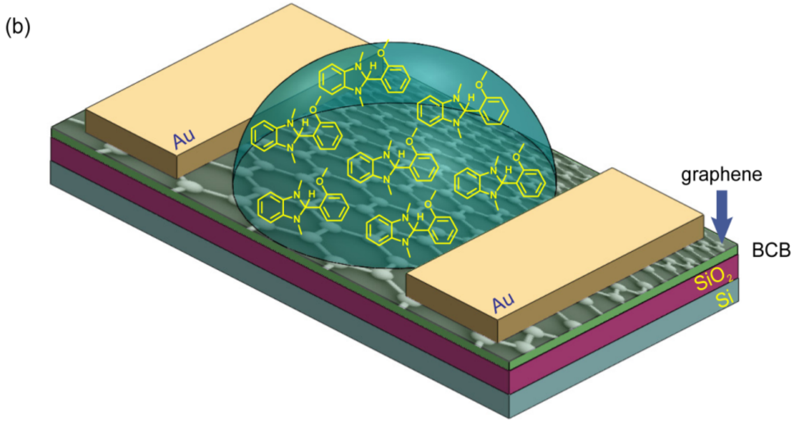
Adhering onto target substrate

Removing the carrier

2. Spin-coating of n-type dopant

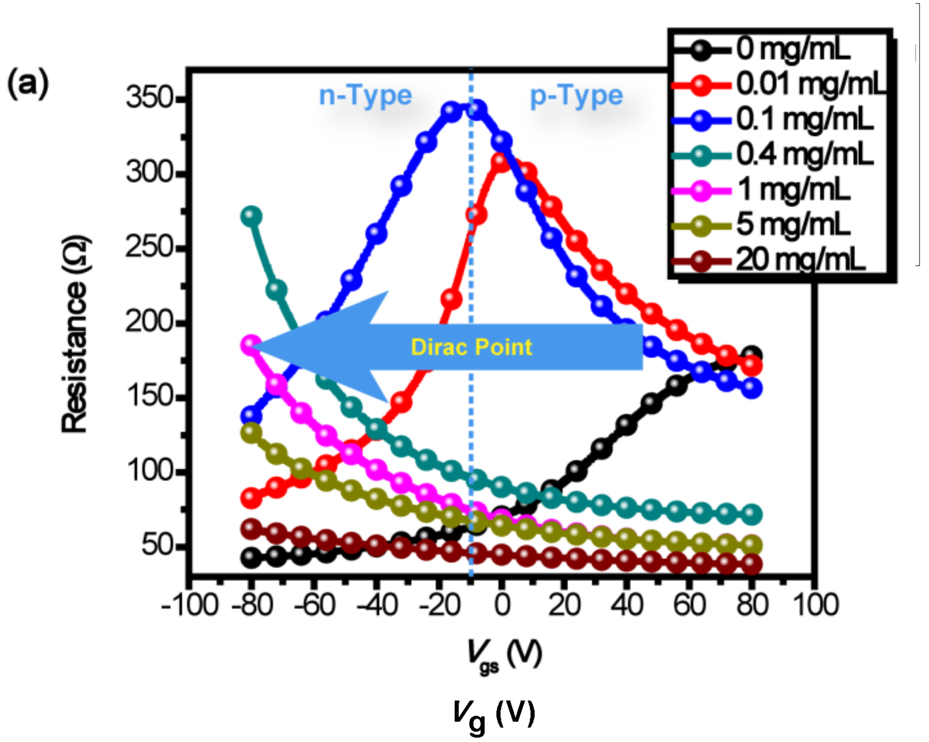


BCB modified SiO2/Si

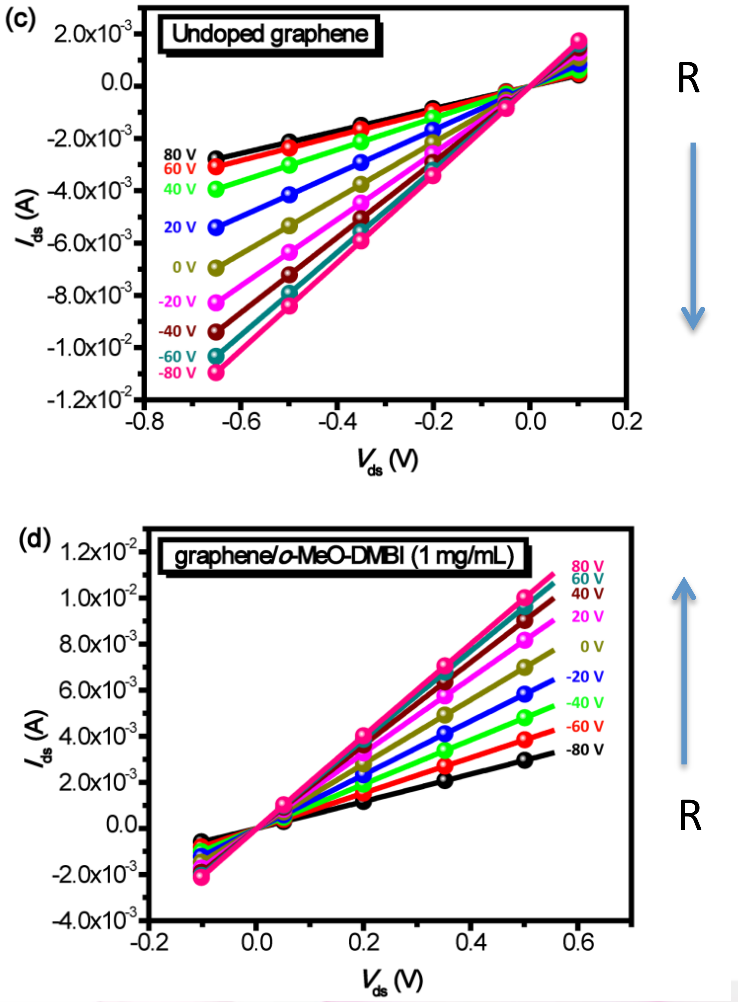


Peng Wei†; Nan Liu†; Z Bao*, Nano Lett. 2013, 13, 1890

Transport behavior before and after n-doping



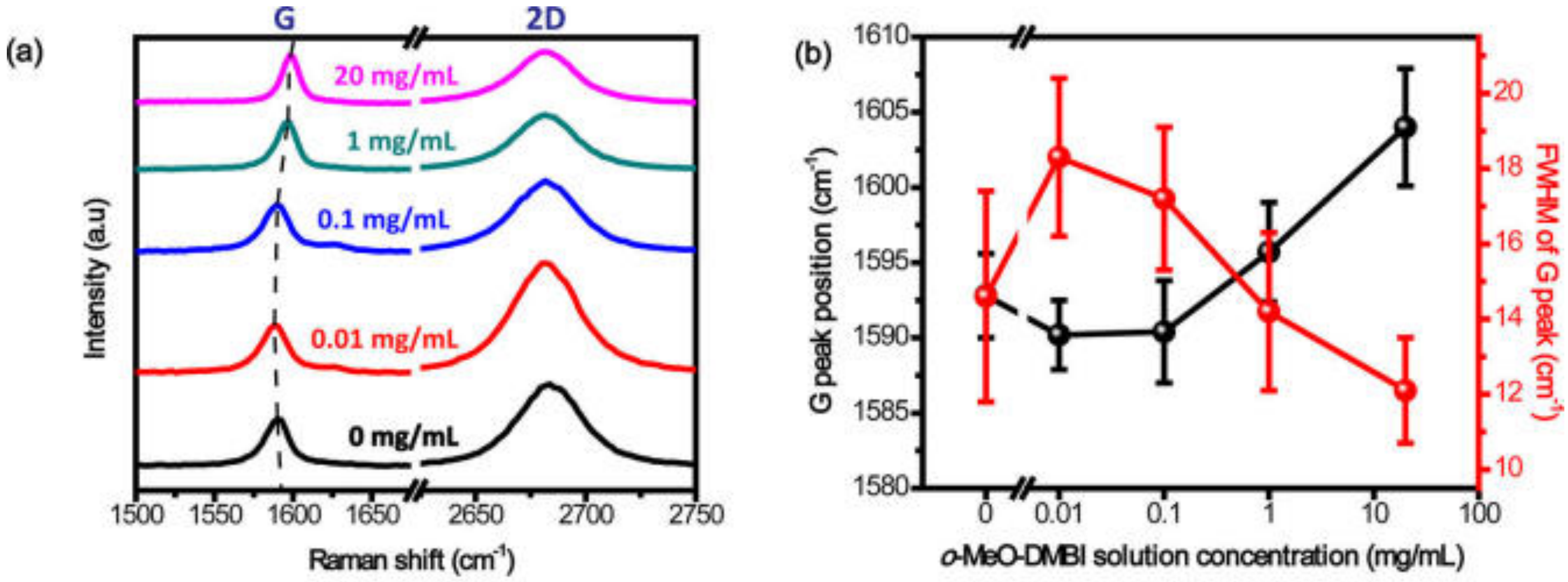
Transfer curves: charge neutrality points (CNPs) shift downwards.
Indicating: p-type to ambipolar to n-type



Before doping: p-type; after doping: n-type

Peng Wei†; Nan Liu†; Z Bao*, Nano Lett. 2013, 13, 1890

Raman studies before and after n-doping

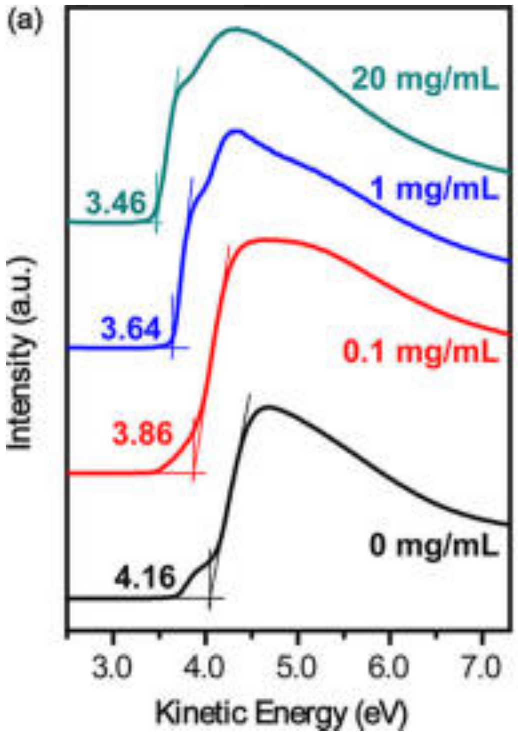


- Doping of graphene up-shifts the G peak position and decreases peak width
- The G peak position (width) is at minimum (maximum) at the 0.01 and 0.1 mg/ml, suggesting it is tuned to be intrinsic
- Further increase dopant concentration upshifts the G peak position and decreases peak width, suggesting it is tuned to be heavily n-doped

Peng Wei†; Nan Liu†; Z Bao*, Nano Lett. 2013, 13, 1890

UPS study before and after n-doping

Ultraviolet photoelectron spectroscopy (UPS):

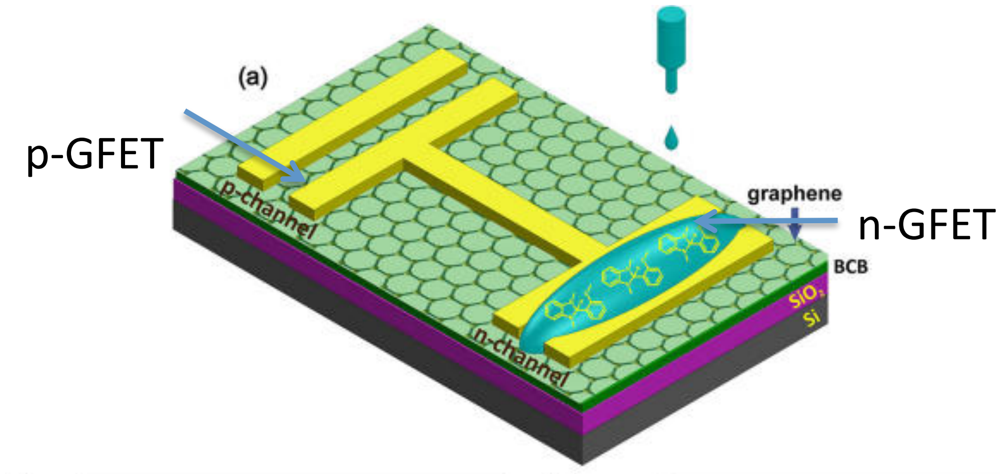


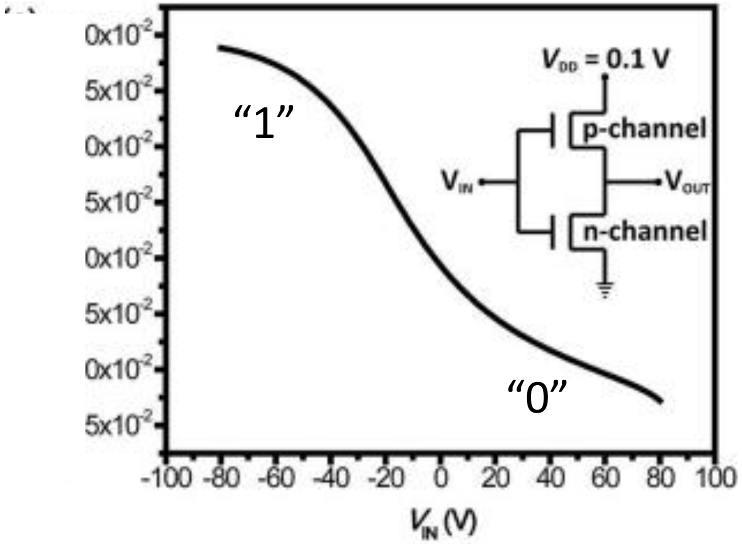
- 0.5eV shift of work function by n-type doping
- This indicates an interfacial charge transfer from the n-type dopant to the underlying graphene

Peng Wei†; Nan Liu†; Z Bao*, Nano Lett. 2013, 13, 1890

Application 1: inverter

A complementary inverter, that integrates both p- and n- type graphene transistors



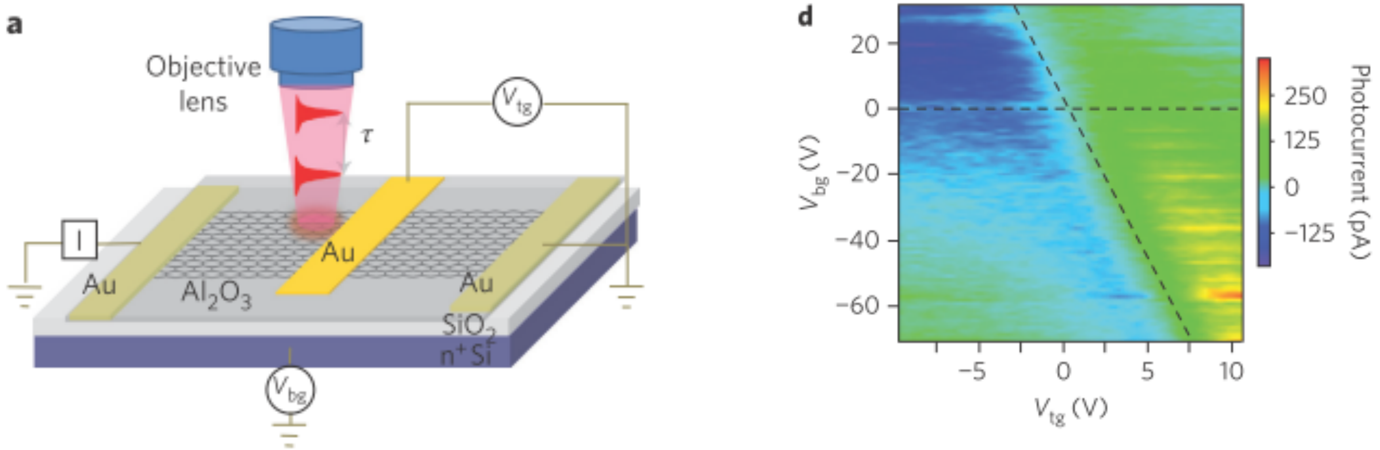


An inverter behavior: output level at low; input level at high

Peng Wei†; Nan Liu†; Z Bao*, Nano Lett. 2013, 13, 1890

Application 2: p-n junction

Using dual gates to fabricate graphene p-n junction as a photosensing device



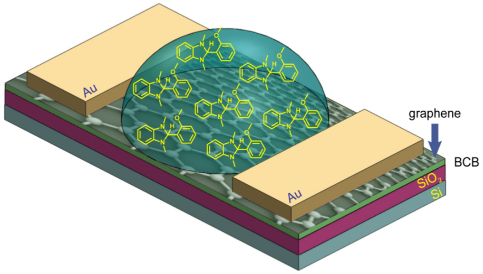
- It requires 4 terminals to operate the device, which complicates both fabrication and the operation of the photodetector.
- Metal top gates prevent creation of flexible, all-transparent photodetectors

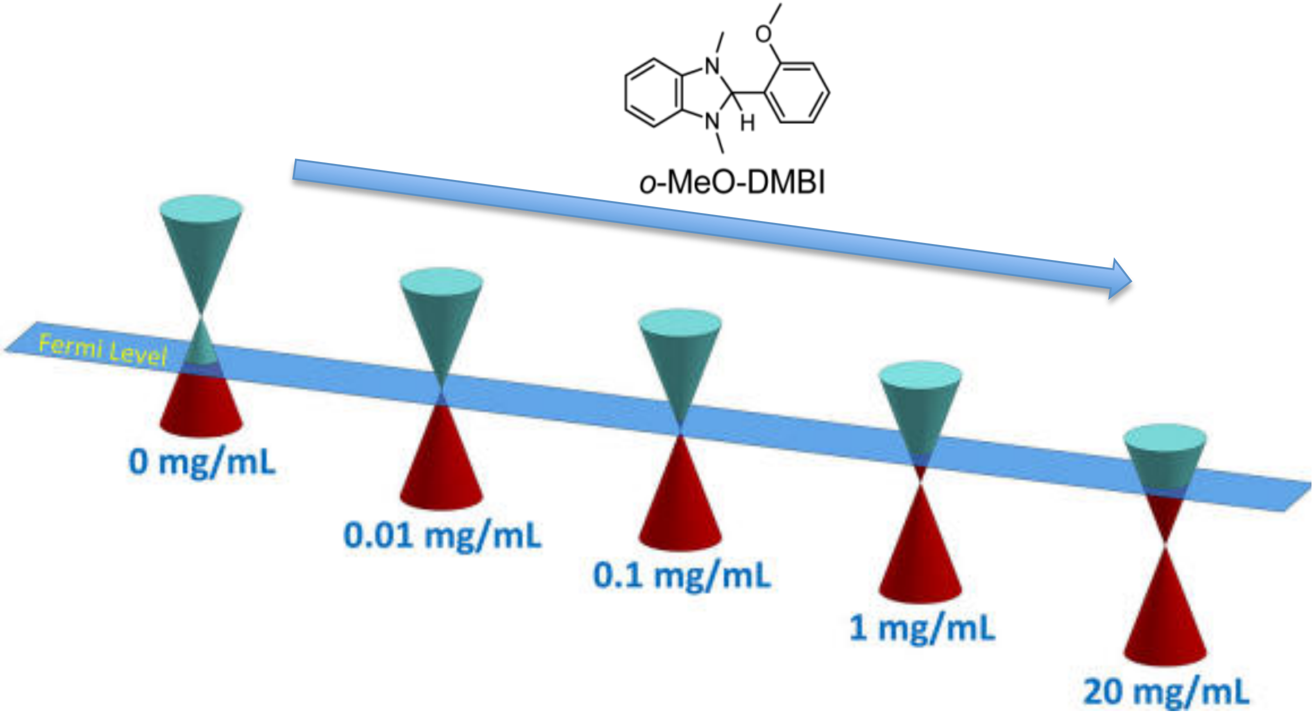
Can we use chemical doping to create p-n junctions to address these challenges?

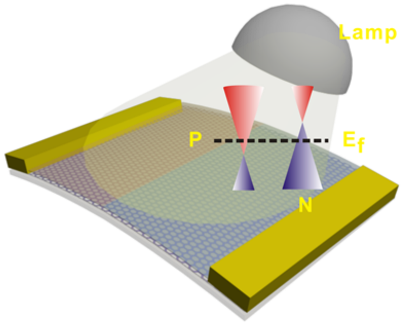
X Xu, Nature Nanotechnology 2012, 7, 114

Summary I

- O-MeO-DMBI is an efficient n-dopant for graphene
- New device structures (flexible and all transparent graphene photodetectors)are enabled by chemical n-doping







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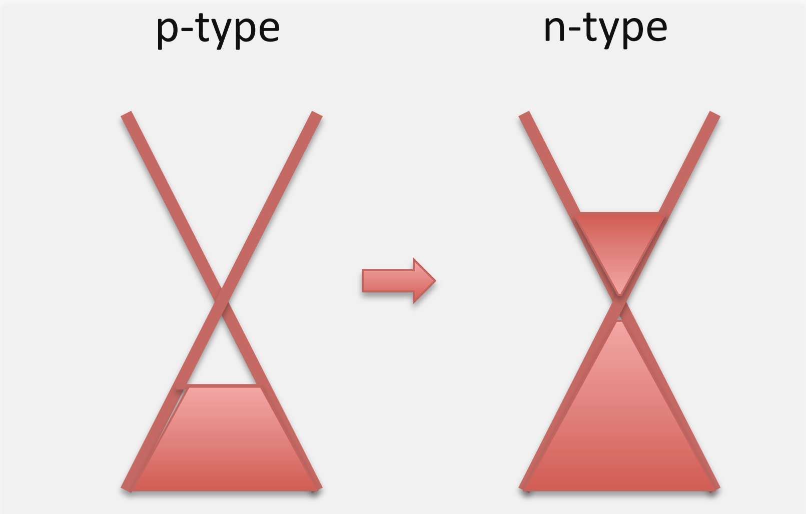
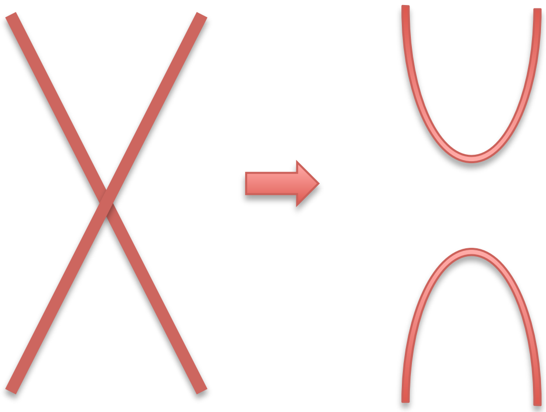
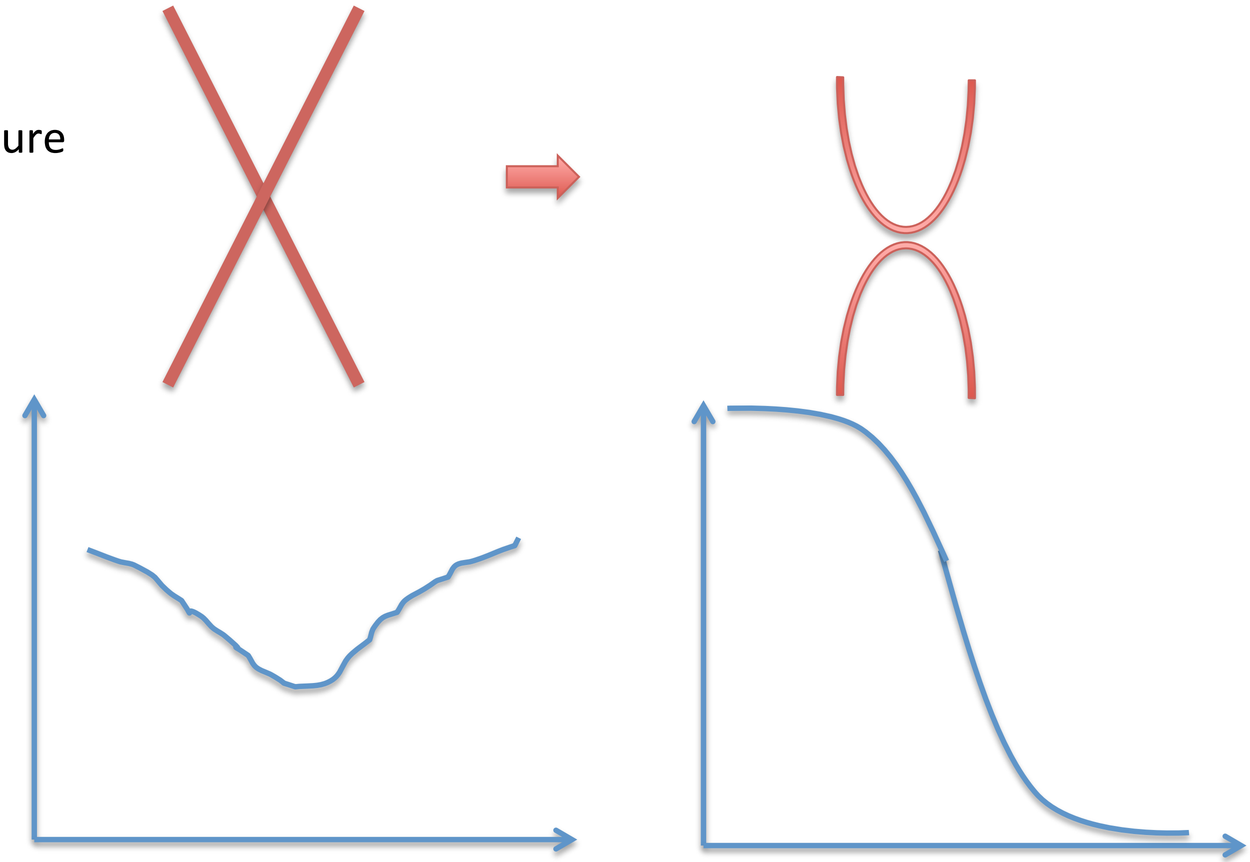


b) To open up band gap



Why bandgap?

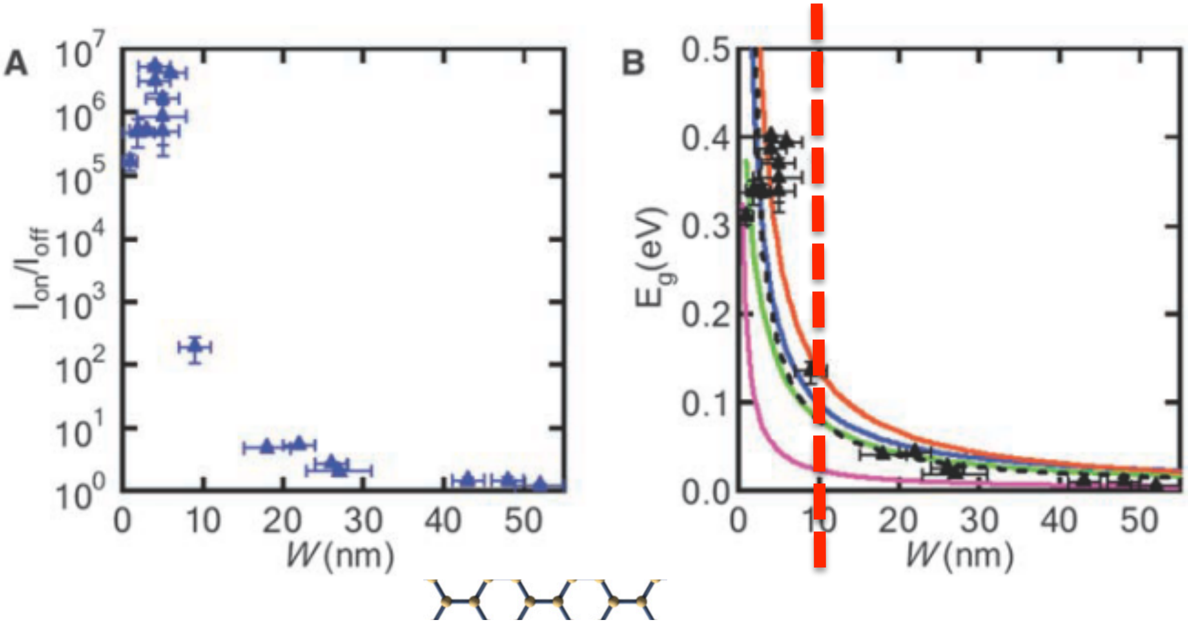


Band structure

Transport curves

- The application of graphene in digital electronics is limited by its lack of a band gap.
- No full turn-off; poor on/off ratio; large static power consumption

Bandgap in GNR



$$E_g(eV) = \frac{0.8}{w(nm)}$$

GNR below 10 nn will result in a sufficient band gap and large on/off ratio for room temperature operation.

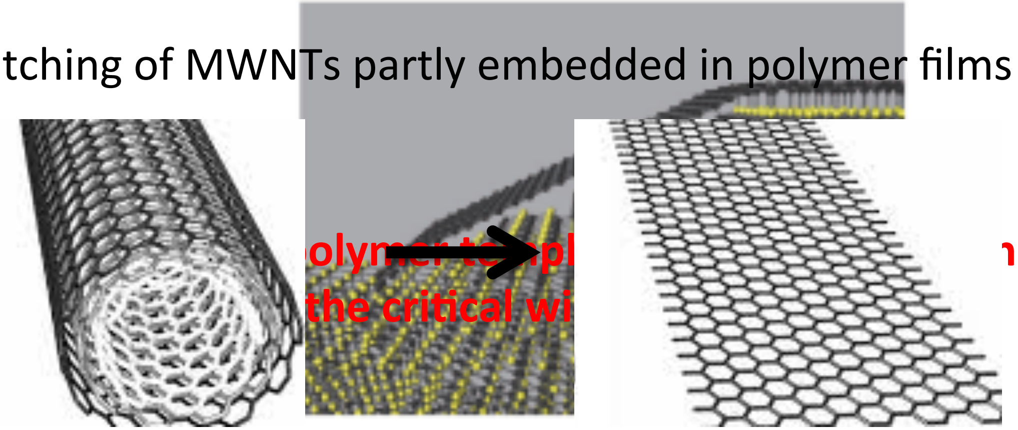
H Dai, Science 2008, 319, 1229

Methods of GNR Synthesis

1. Unzipping CNTs

2. Epitaxial growth on templated SiC

Etching of MWNTs partly embedded in polymer films



Limitation: width about 40 nm

Limitation: scalable fabrication

The problem is that direct growth of sub-10 nm ribbons has not been possible.

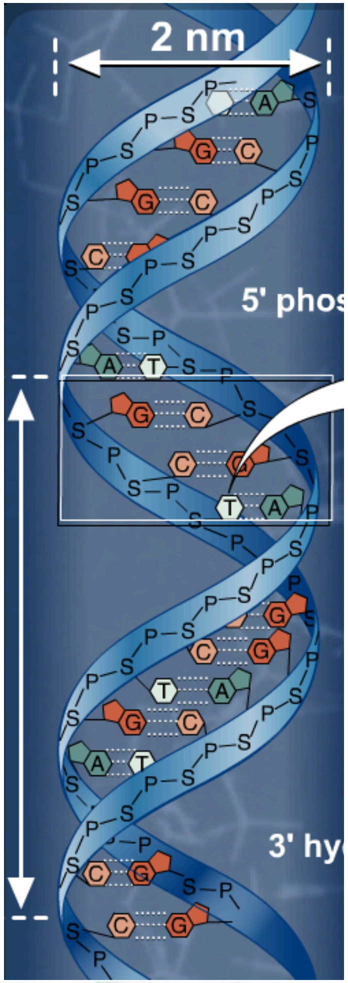
H Dai, Nature 2009, 458, 877

W de Heer, Nature Nanotechnology, 2010, 5, 729

W de Heer, Nature, 2014, 506, 349

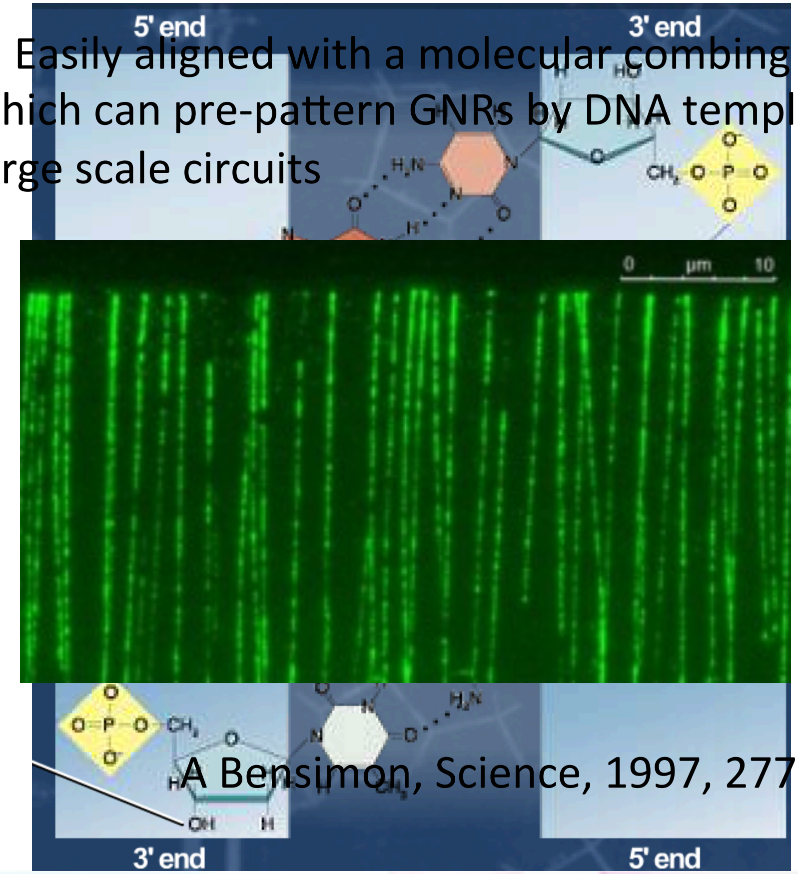
DNA Bio-template to GNRs

1. DNA width ~2 nm



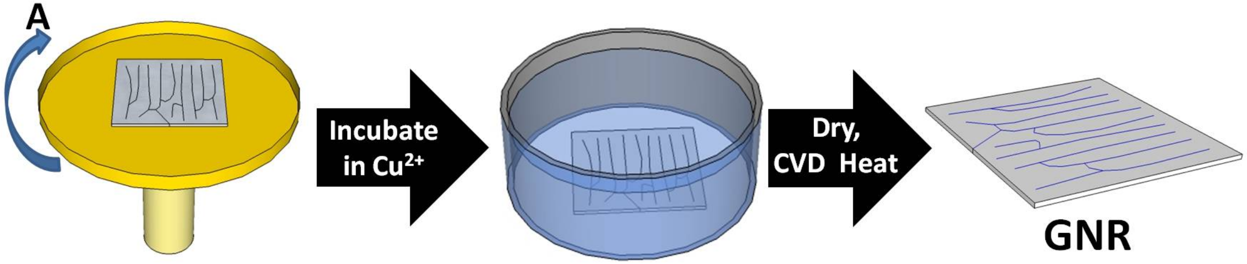
2. Phosphate backbones act as metal binding sites to catalyze the growth of graphitic structures

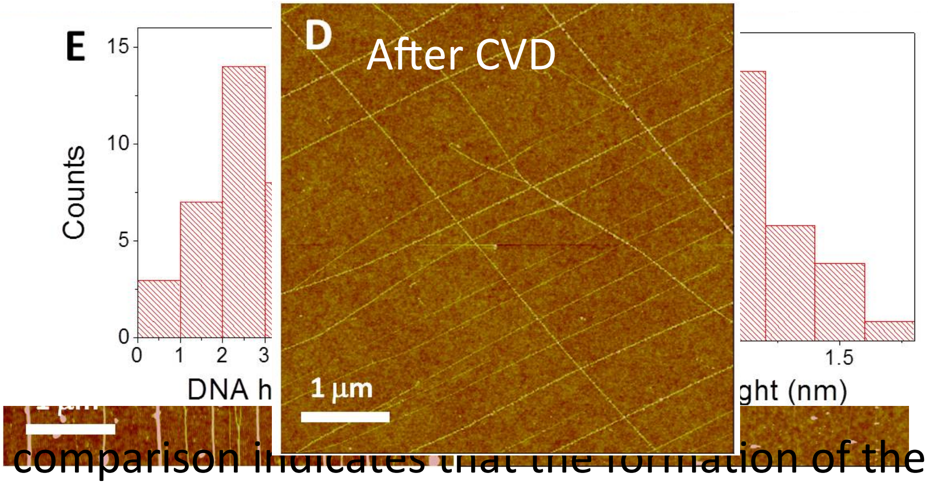
3. Easily aligned with a molecular combing method, which can pre-pattern GNRs by DNA template for large scale circuits



A Bensimon, Science, 1997, 277, 1518

Templated growth of GNRs





Height comparison indicates that the formation of these 1D features are templated by DNA

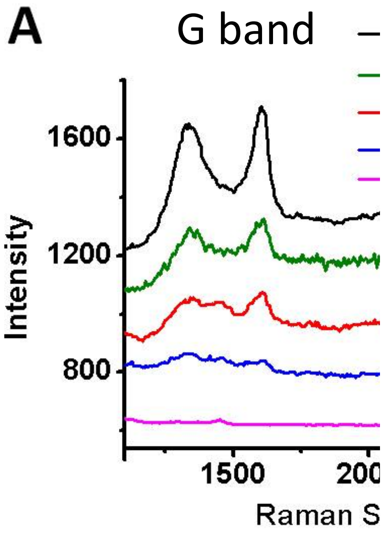
Morphology of the post-growth surface duplicate that of the DNA template (crossbar)

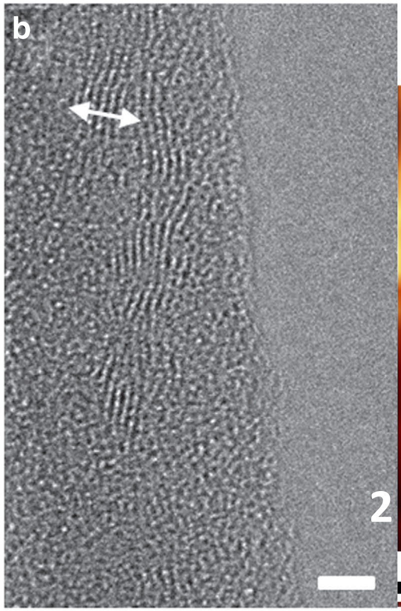
Morphology of the post-growth surface duplicate that of the DNA template (1D parallel lines)

BAO RESEARCH

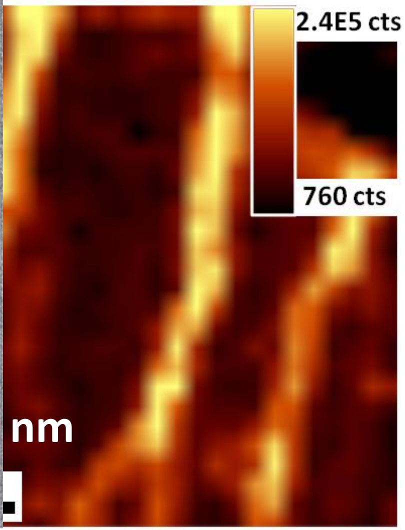
A Sokolov†, F. Yap†, N Liu, Z Bao, Nature Comm 2013,4:2402

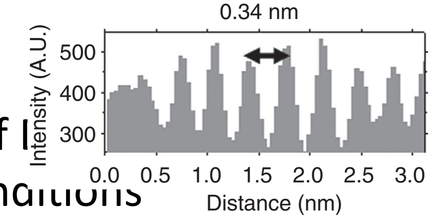
Structure of GNRs





nsity map of G peak





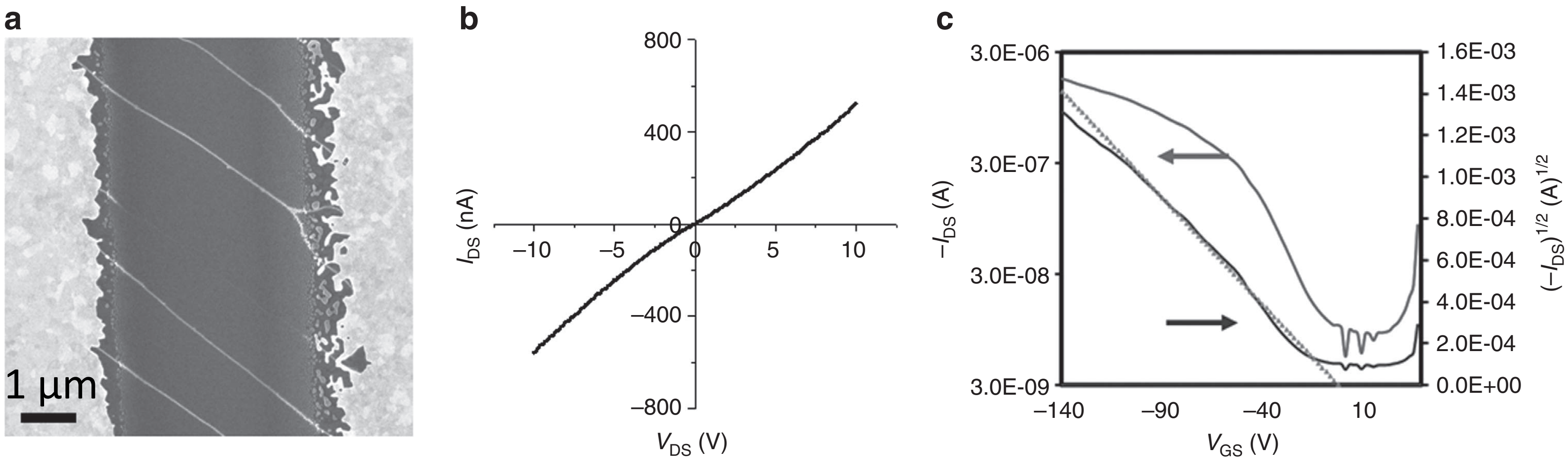
- Raman spectra of I e the post growth materials at different CVD conditions
- Strongest G peak when using H_2/CH_4 with Cu
- TEM further confirms the formation of GNR from DNA templates
- Maps of G peak localized the 1D structure: G band signals are localized on these 1D structures

BAO RESEARCH

A Sokolov†, F. Yap†, N Liu, Z Bao, Nature Comm 2013,4:2402

Electrical properties of GNRs

A sufficiently narrow GNR to function as FETs at RT

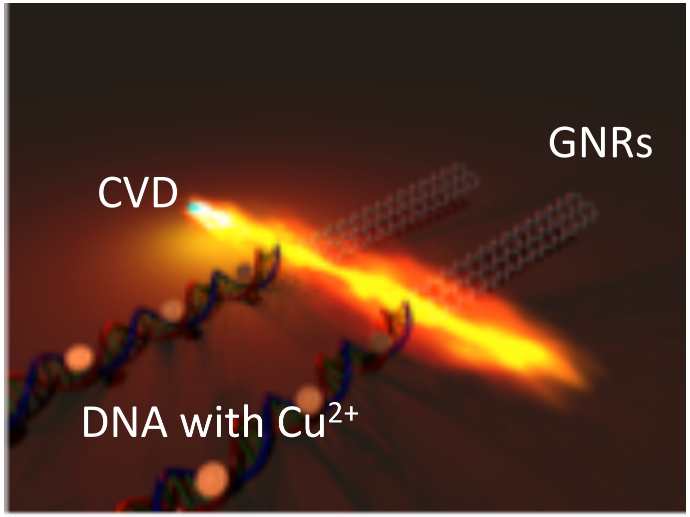


- Channel length about 5 um with ~10 GNRs between S and D electrodes
- Linear I-V curve
- p-type transistor with an on/off ratio ~200
- First time proof of concept that sub-10 nm ultra-thin GNRs can be synthesized by polymer templates over a large scale

A Sokolov†, F. Yap†, N Liu, Z Bao, Nature Comm 2013,4:2402

Summary II

- First demonstration of large scale, DNA templated sub-10-nm GNR growth
- Dimensionality-enhanced on/off ratio of GNR-FET device



Current effort:

- Understanding the effect of polymer templates
- Design, synthesis and application of novel polymer templates for GNR growth
- Integration of polymer-derived GNR with electronic skin devices

Conclusion

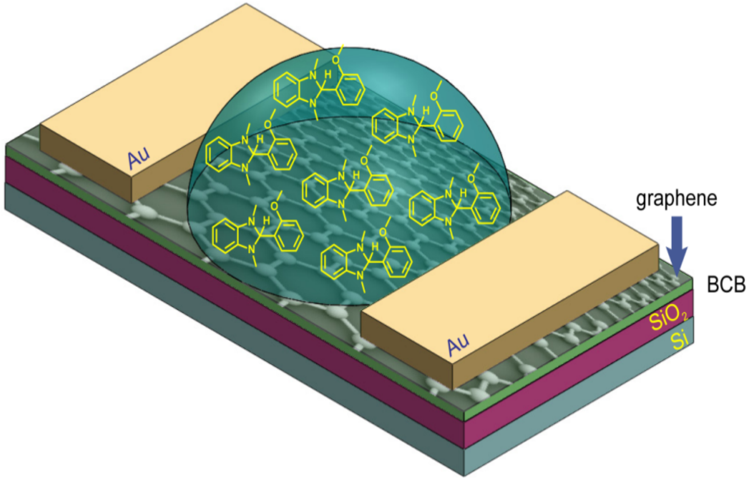
To control graphene electronic properties via graphene-organic interface

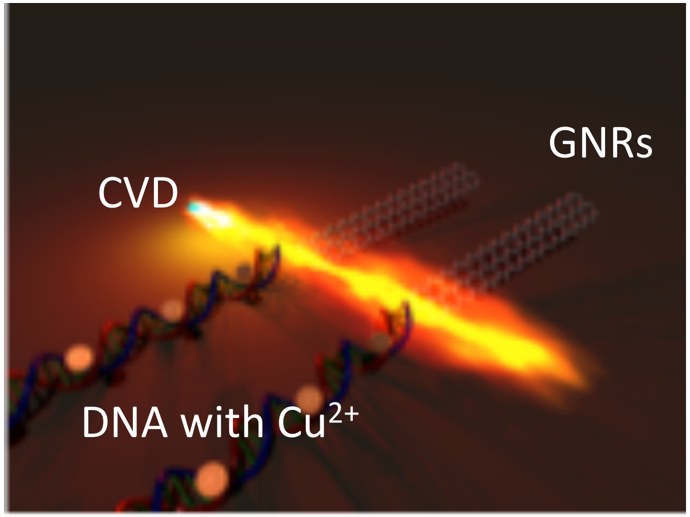
Graphene-organic molecules

Graphene-polymer

a) To control Fermi level: n-type doping

b) To open up band gap: DNA to GNRs





Thanks for your attention!