

Carbon-Based Materials for Flexible Electronics

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Flexible Electronics in Life



Display



Skin-Attached Sensor



**MP3 Player
Embedded Jacket**



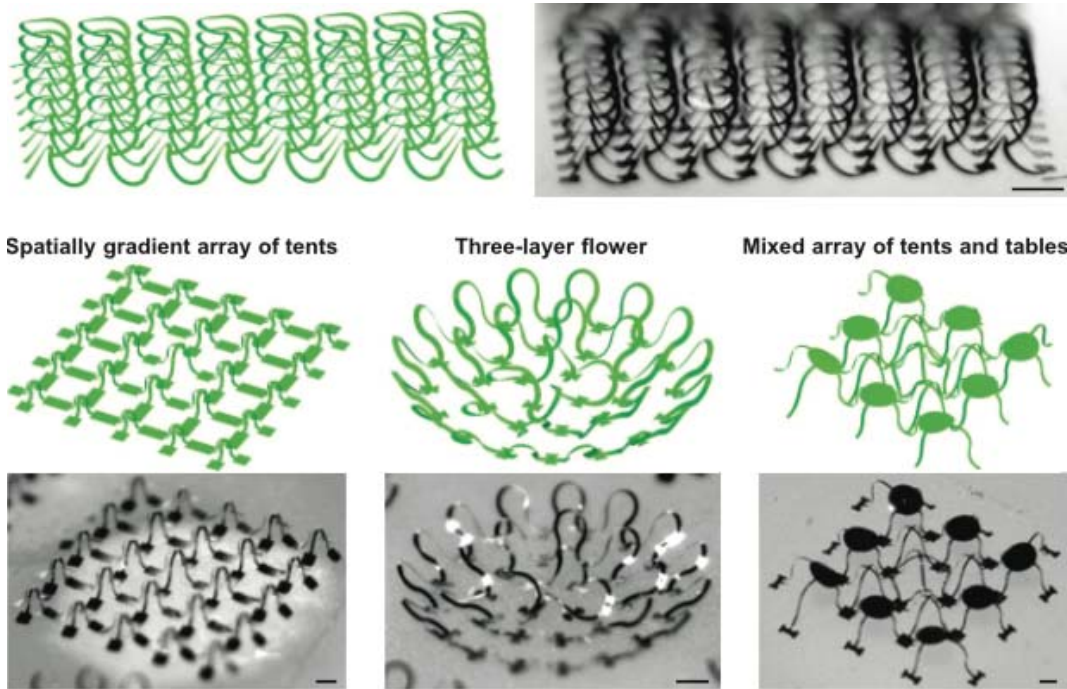
Solar Cell on Bags



Sensor for Meat Freshness

Approach to Flexible Electronics

With conventional materials/processes

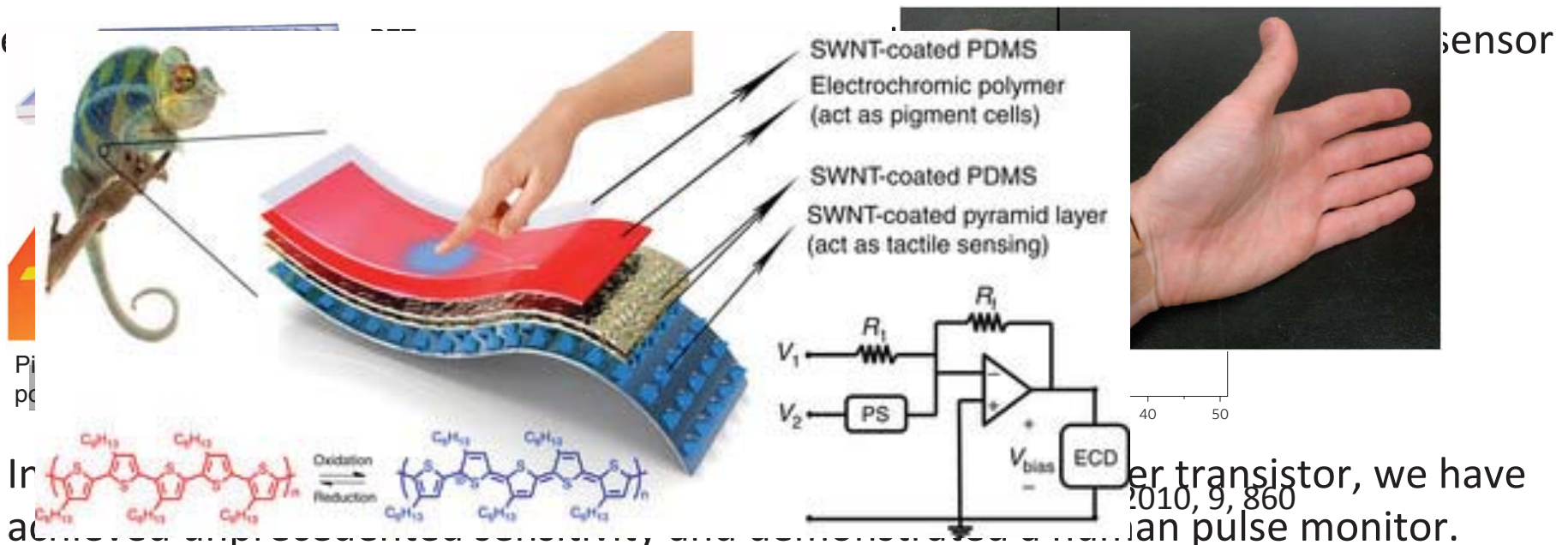


- Etched thin silicon with conventional device fabrication process
- **Expensive** for the process
- Limitations for wearables due to its **own stiffness**

Our Approach to Flexible Electronics

1. New structure: microstructured PDMS (polydimethylsiloxane)
2. New material: organic materials (polyisobindigobithiophene-siloxane, PiI2T-Si)
(poly(3-hexylthiophene-2,5-diyl), P3HT)

Inte

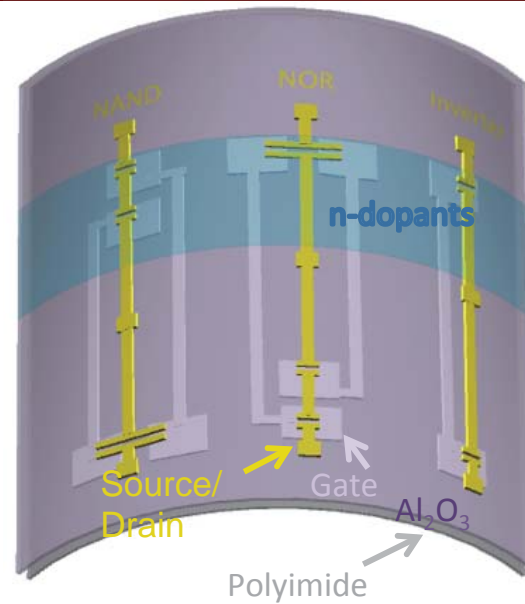
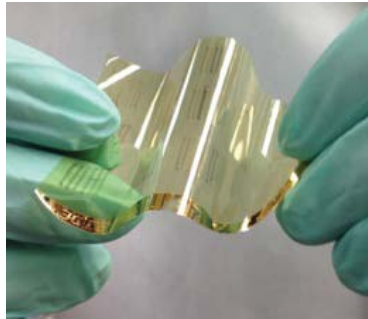


Ir
al

er transistor, we have
an pulse monitor.

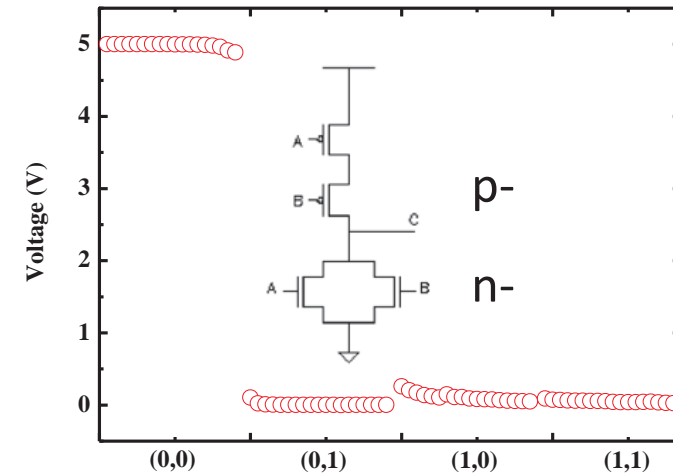
Ho-Hsiu, Chou, Z Bao, Nature Comm 2015,6:8011
G Schwartz, Z Bao, Nature Comm 2013,4:1859

Carbon-Based Materials: CNTs



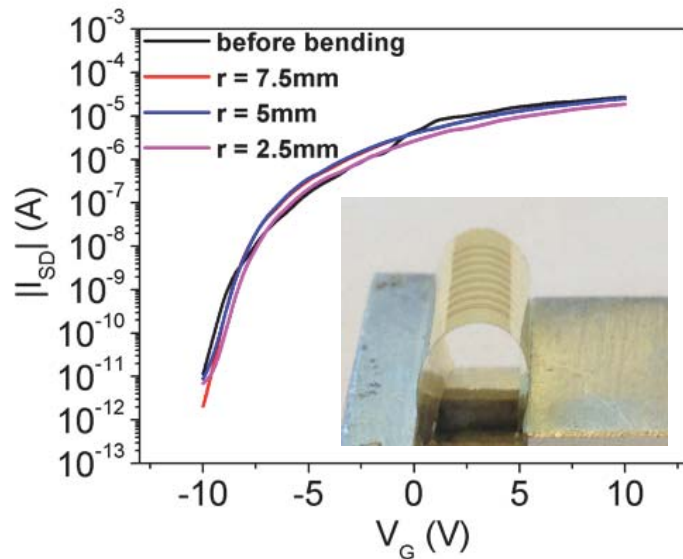
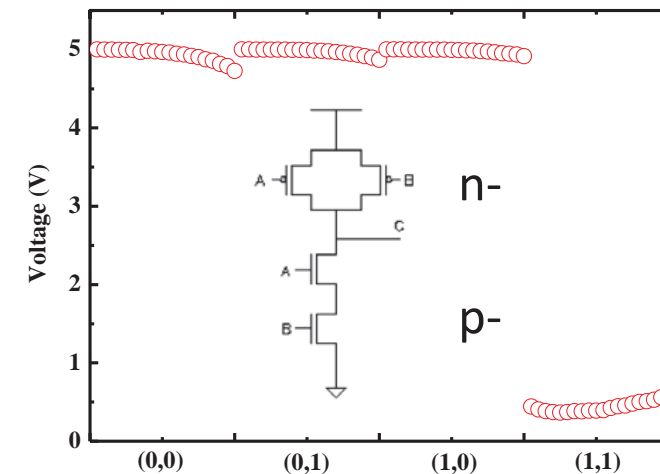
NOR logic gate

INPUT		OUTPUT
A	B	
0	0	1
0	1	0
1	0	0
1	1	0

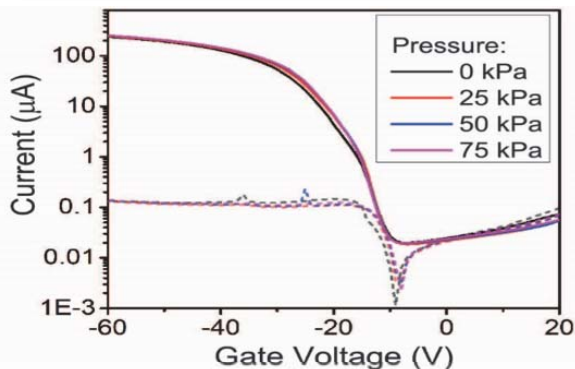
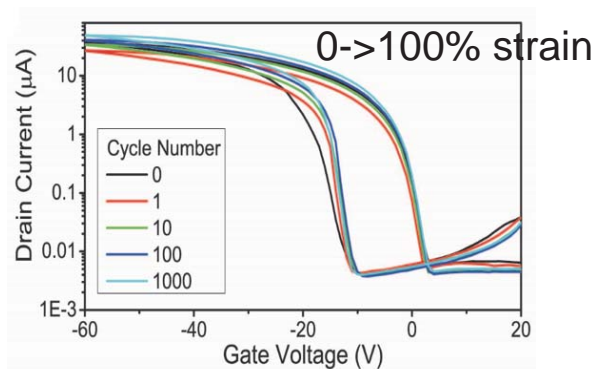


NAND Gate

INPUT		OUTPUT
A	B	
0	0	1
0	1	1
1	0	1
1	1	0

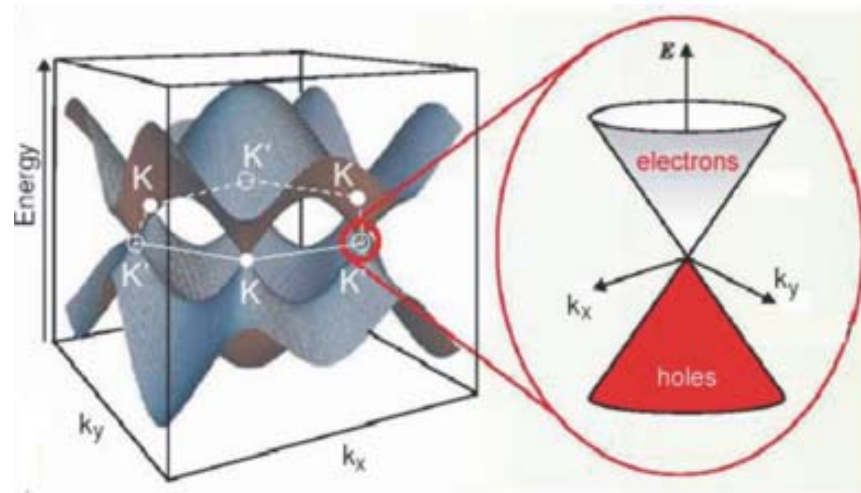


Highly Robust All-CNT Stretchable Transistors



1. The electrons in graphene behave as massless Dirac Fermions

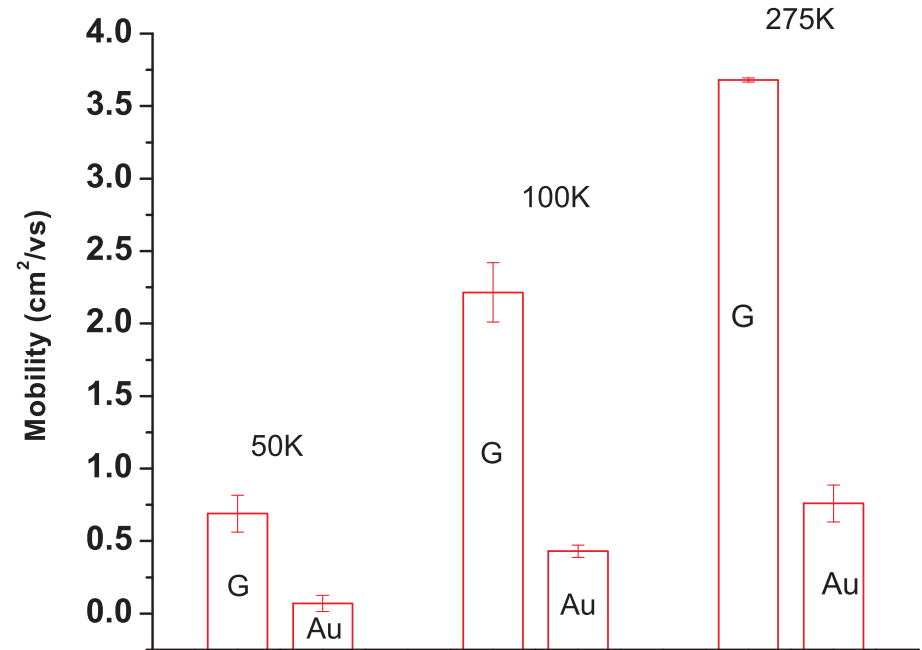
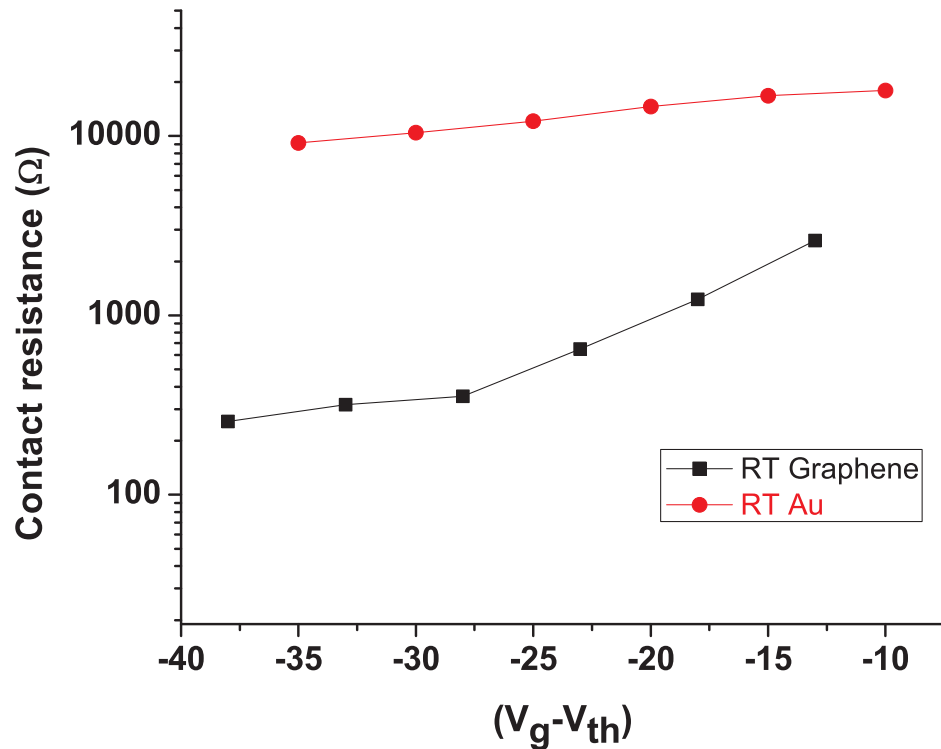
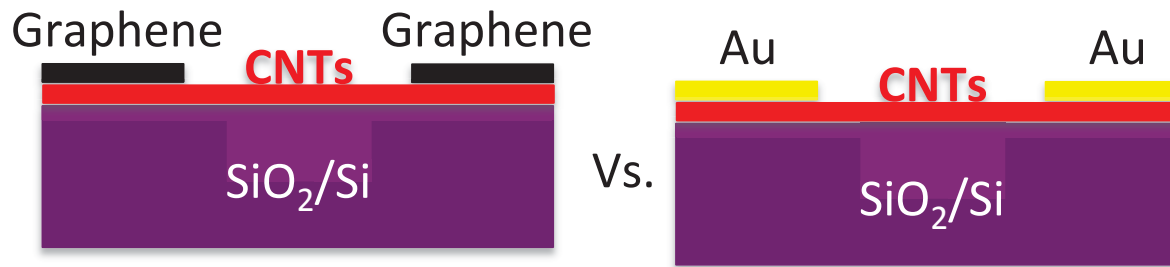
- High electron mobility (15,000 cm²/Vs in Experiment; 200,000 cm²/Vs in Theory);
- Resistivity 10⁻⁶Ωm lower than silver



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

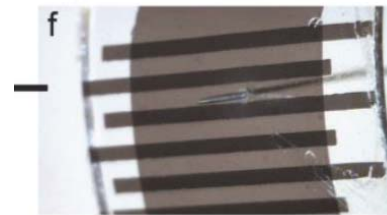
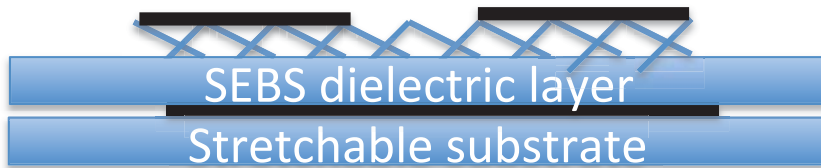
2. It is flexible, transparent and biocompatible

Better Interaction between Carbon-Based Materials

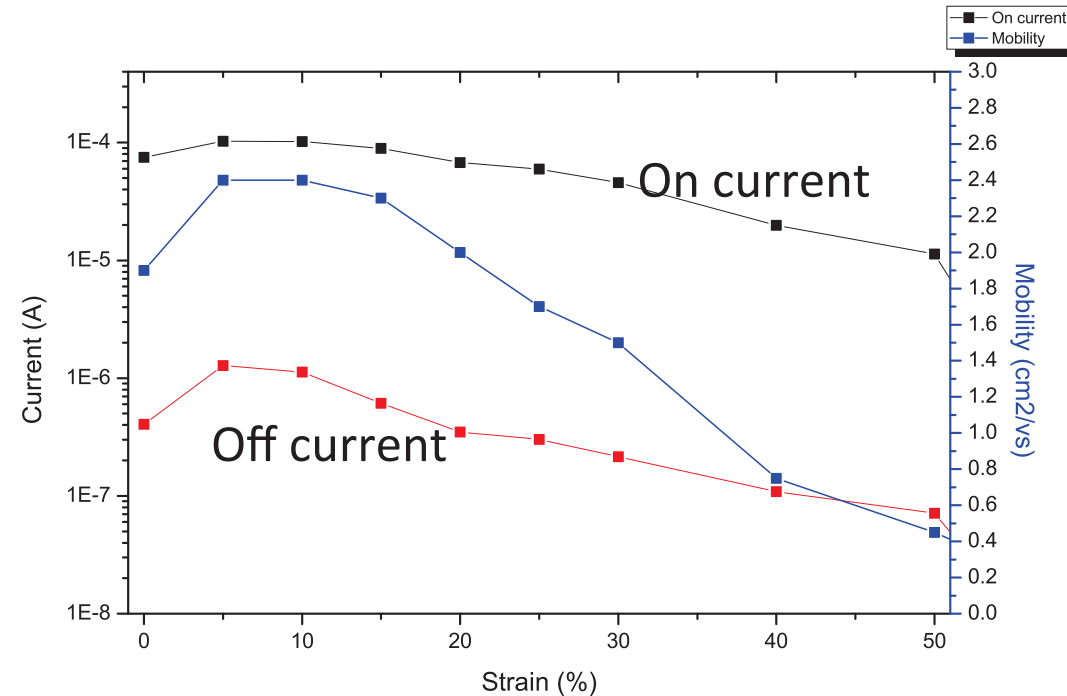
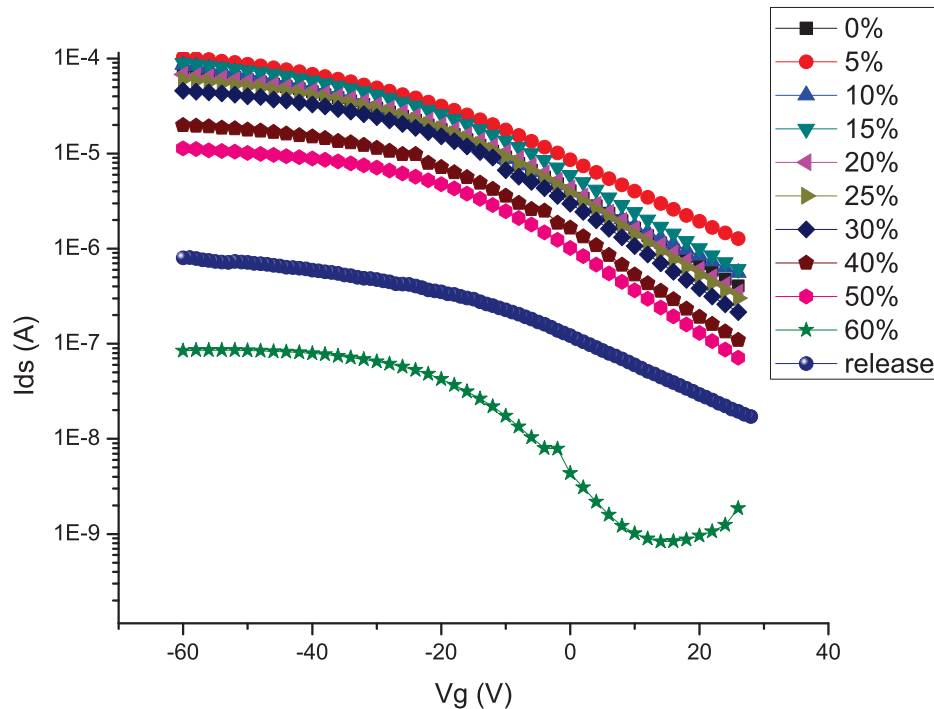


Graphene-CNT Stretchable Transistors

Our goal is to fabricate ultra-transparent and stretchable Graphene-based transistors.



VS



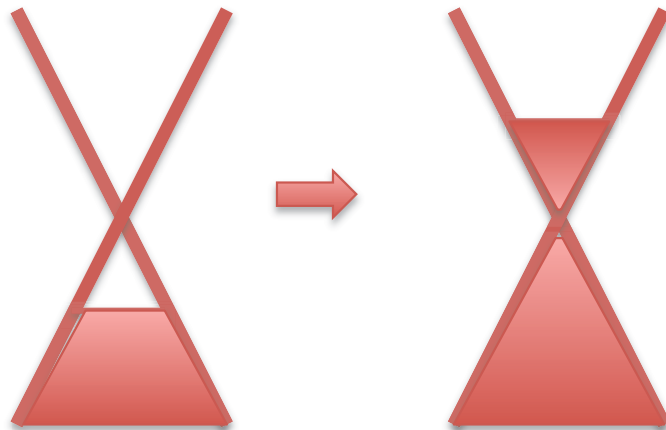
Graphene toward Ideal Electronic Materials

To control graphene electronic properties via graphene-organic interface

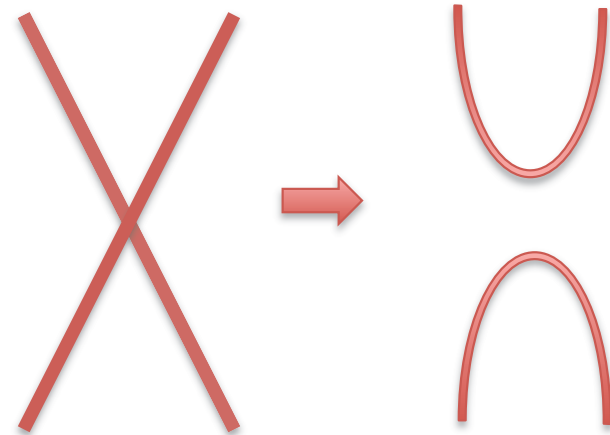
a) To control Fermi level

p-type

n-type



b) To open up band gap

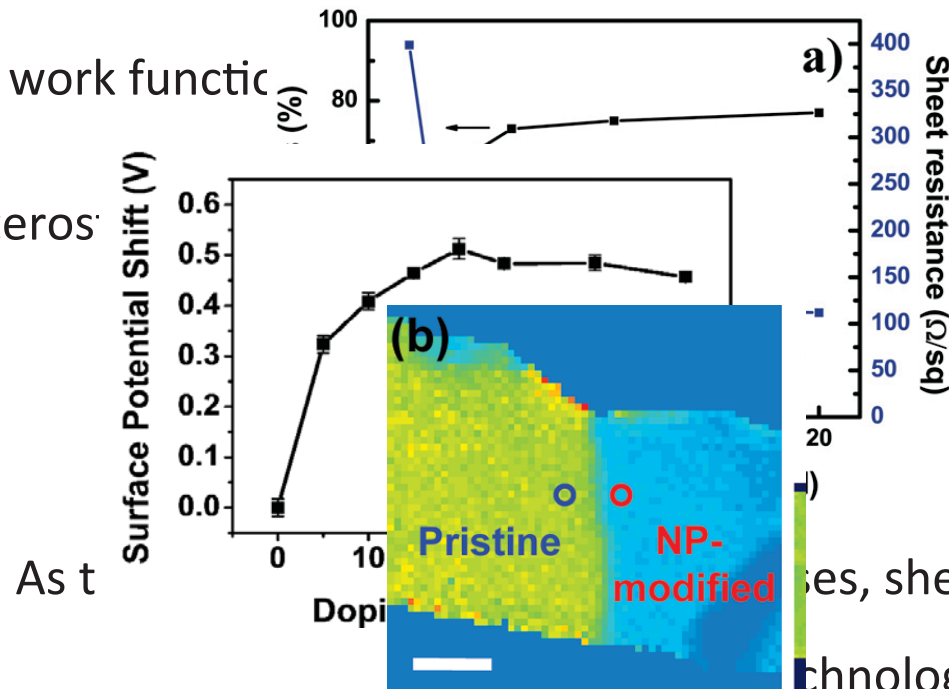


Importance of Controlled Fermi Level

1) Tuning conductivity

2) Modulating work function

3) Creating heteros



As t increases, sheet resistance decreases

Technology, 2010, 21, 285205

By changing the doping time, the surface potential of graphene is modulated
By having complementary doping, p-n junctions can be created.
to make efficient contact to different materials

Y Chen, ACS Nano, 2011, 3, 26051

J Kong, ACS Nano, 2010, 5, 2689

Design New n-type Dopant

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



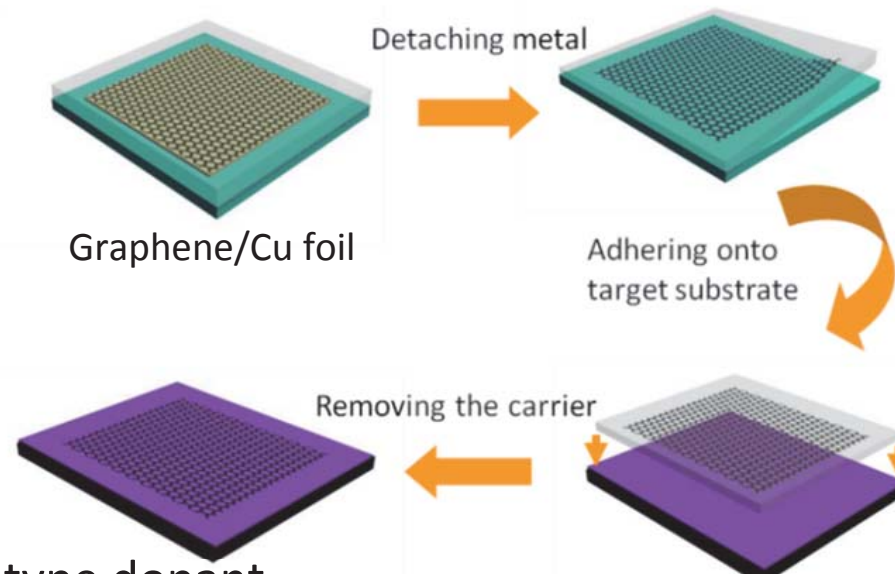
P Wei, Z Bao, J. Am. Chem. Soc. 2012, 134, 3999

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

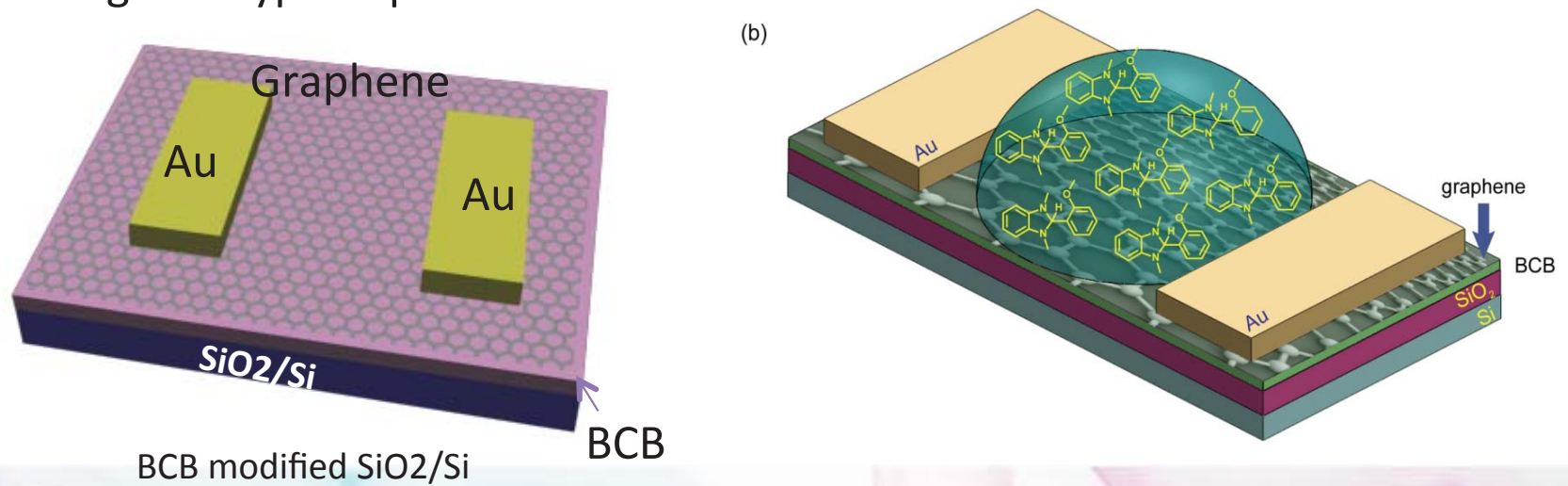
- o-MeO-DMBI is air-stable and can be stored and handled in air for extended periods without degradation
- Solution process or vacuum deposition

Process of Doping Graphene

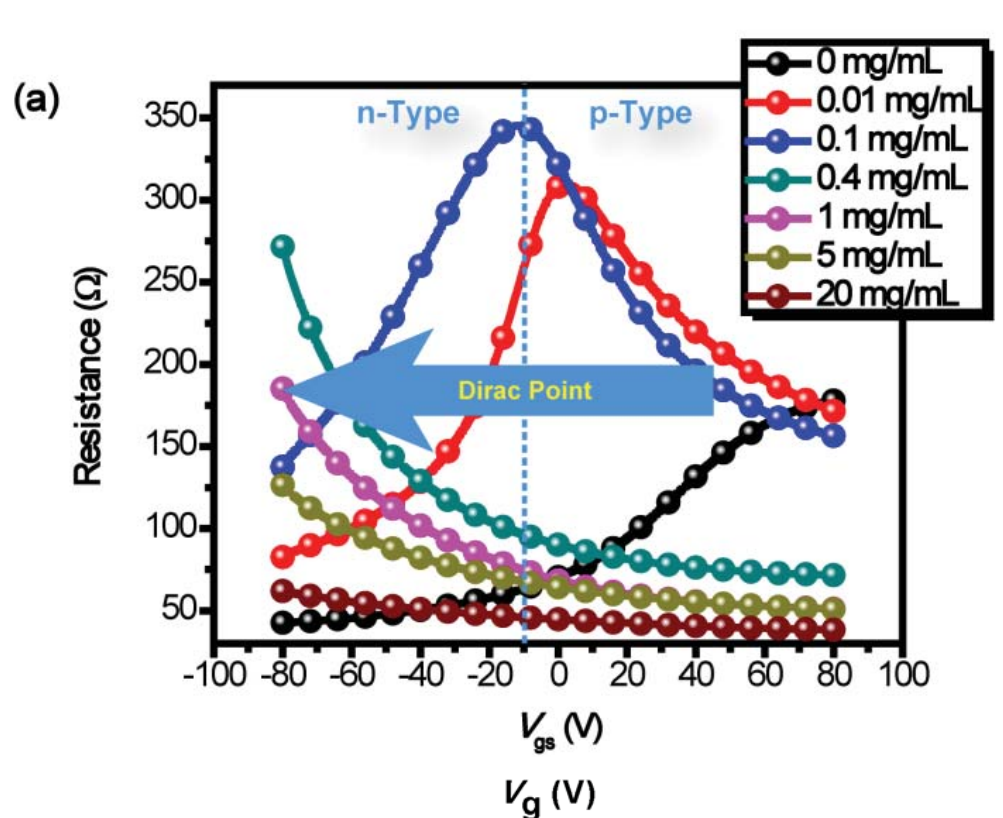
1. Transfer graphene and fabricate graphene devices



2. Spin-coating of n-type dopant



Transport Behavior Before and After n-doping

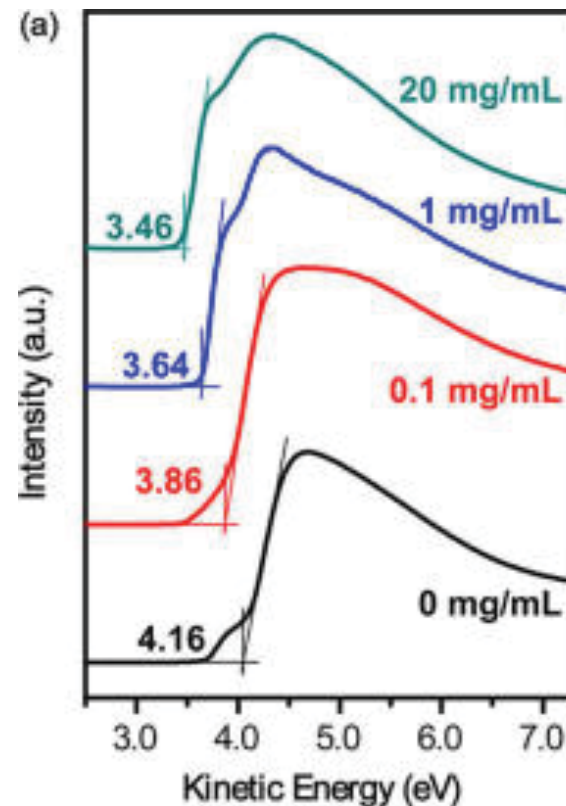


Transfer curves: charge neutrality points (CNPs) shift downwards.

Indicating: p-type to ambipolar to n-type

UPS Study Before and After n-doping

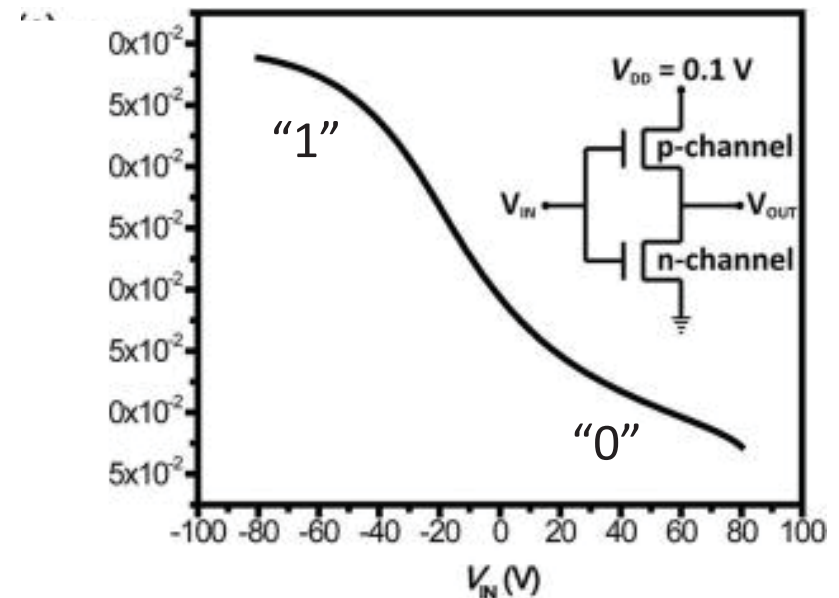
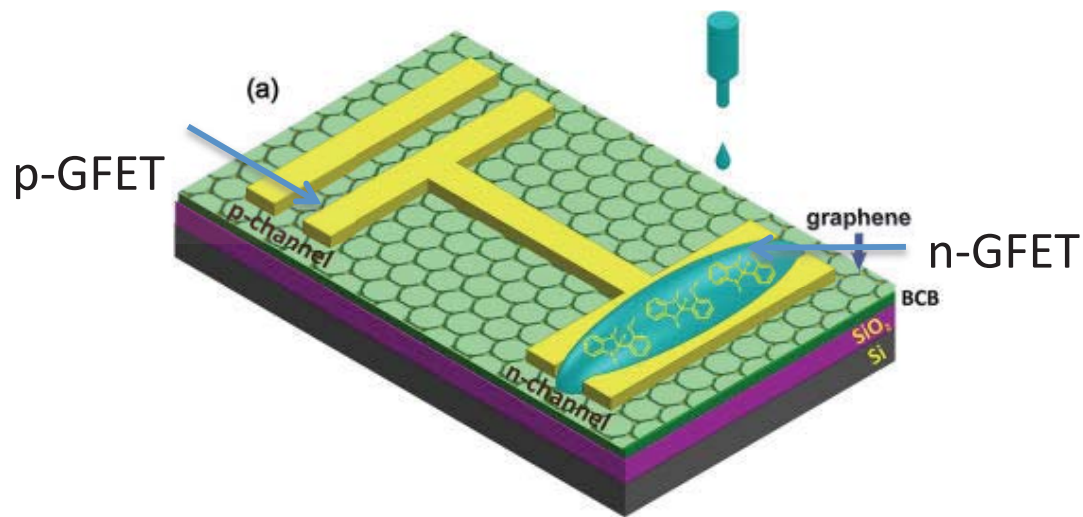
Ultraviolet photoelectron spectroscopy (UPS):



- 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

Application 1: Inverter

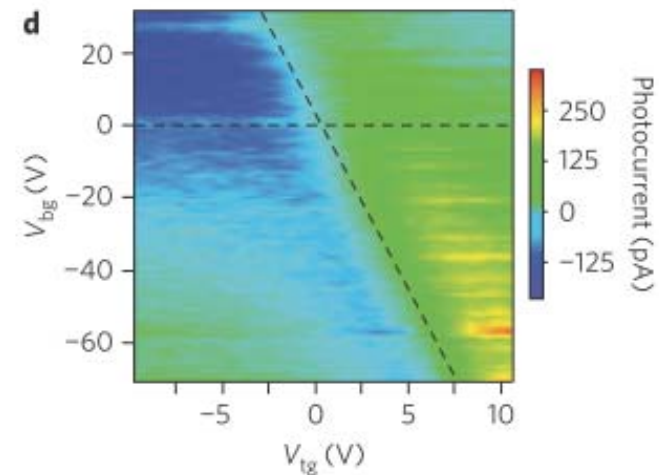
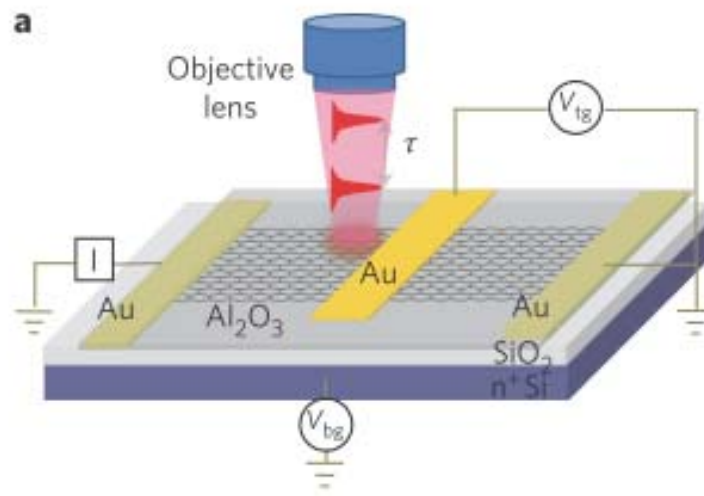
A complementary inverter, that integrates both p- and n- type graphene transistors



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

Application 2: p-n Junction

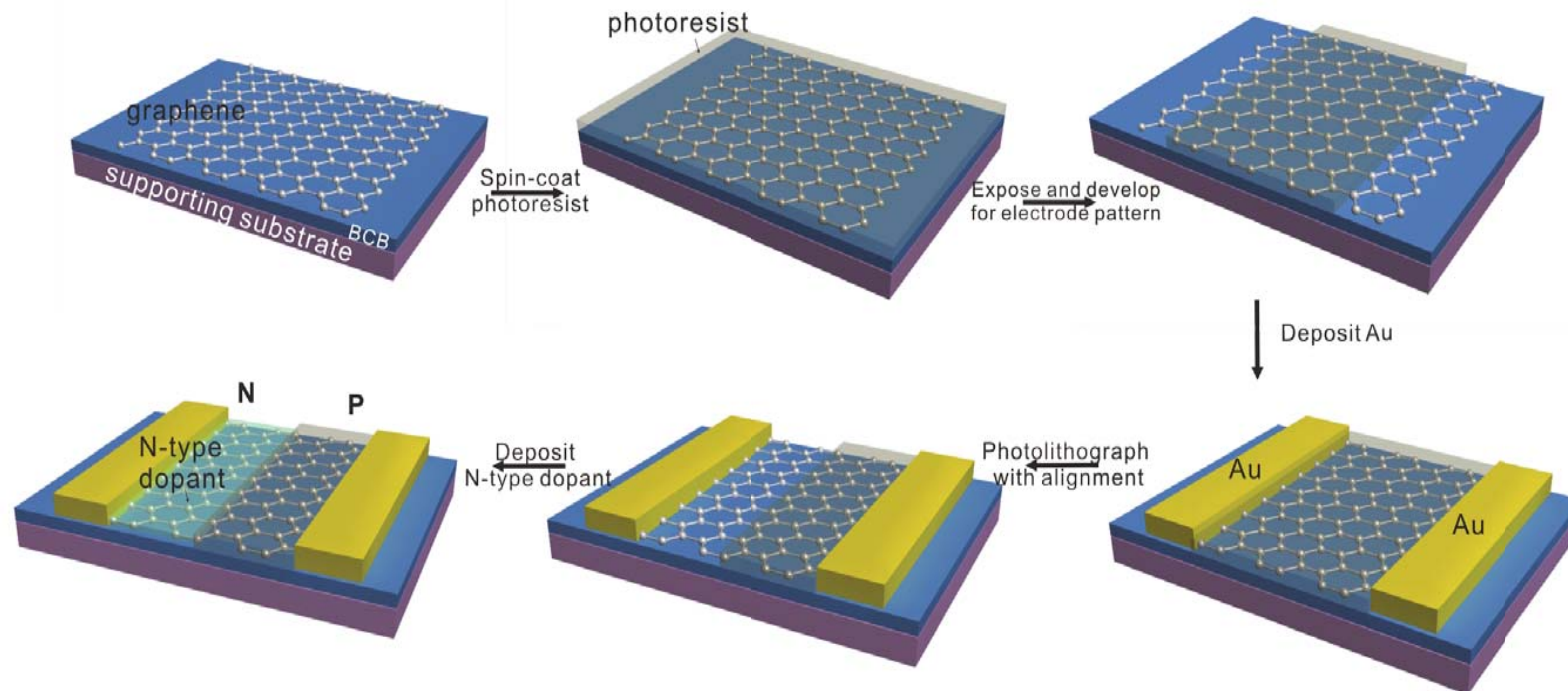
Using dual gates to fabricate graphene p-n junction as a photosensing device



- 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

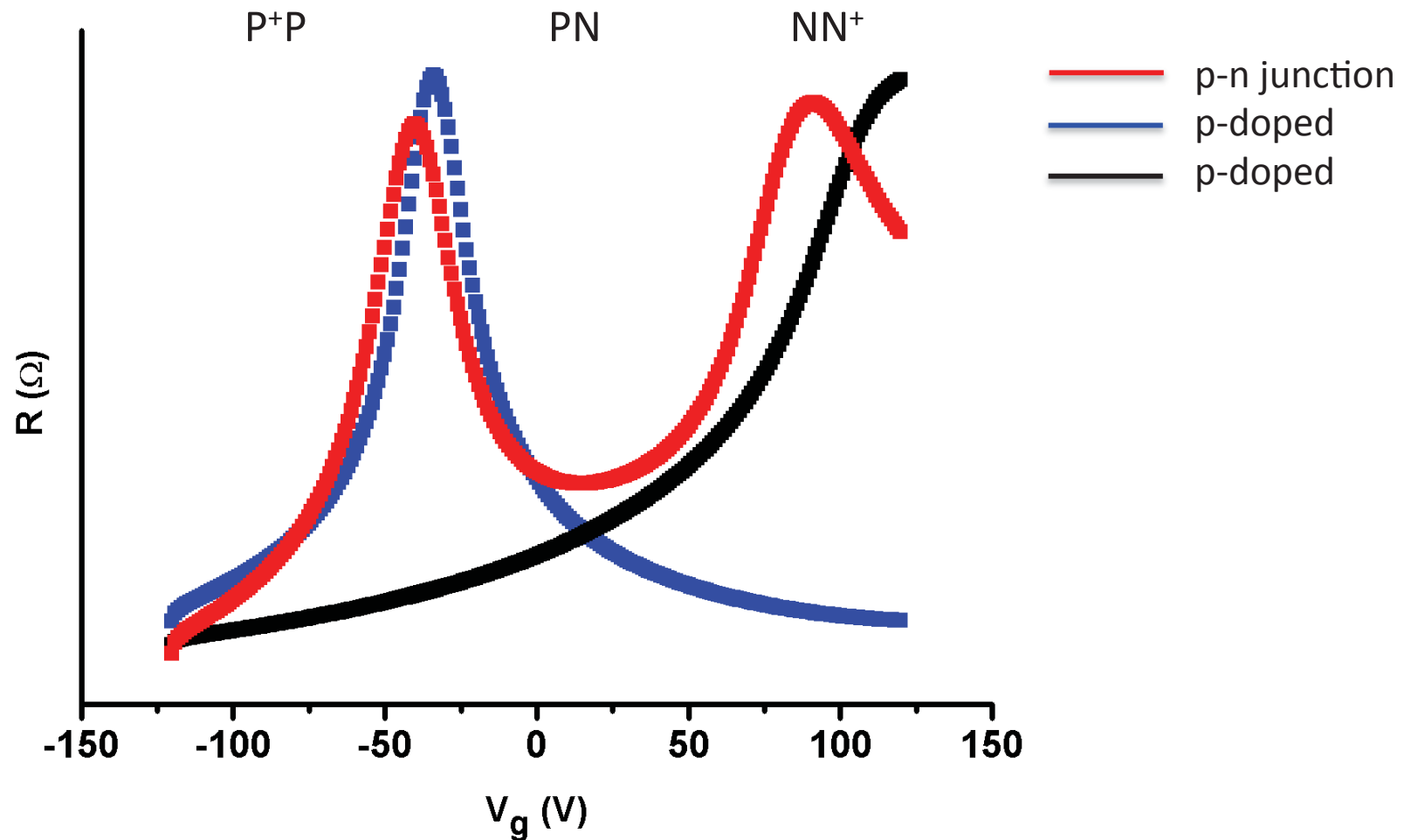
Can we use chemical doping to create p-n junctions to address these challenges?

Fabrication of Graphene p-n Junctions



- Selectively mask part of the channel and apply n-dopant to the exposed part
- P-region: as-transferred graphene; N-region: n-type doped graphene

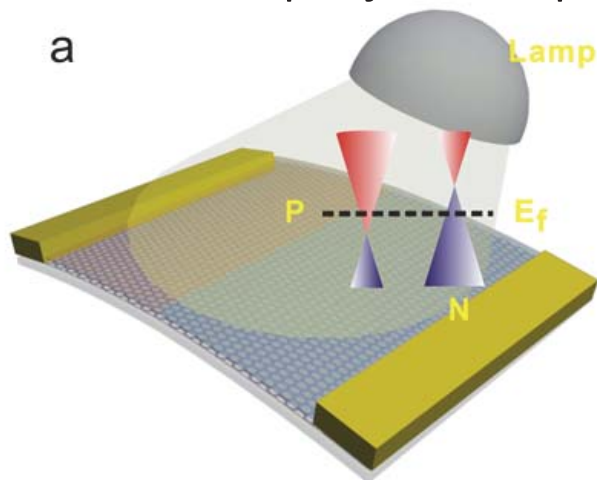
Formation of p-n Junctions



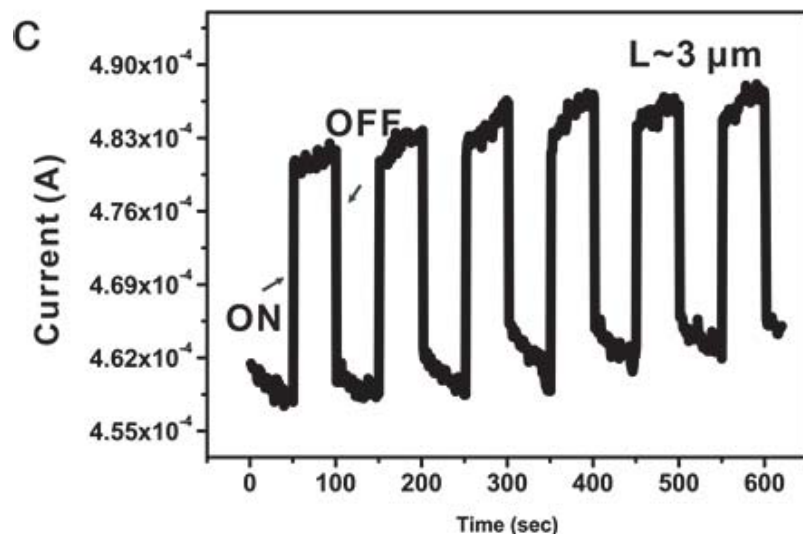
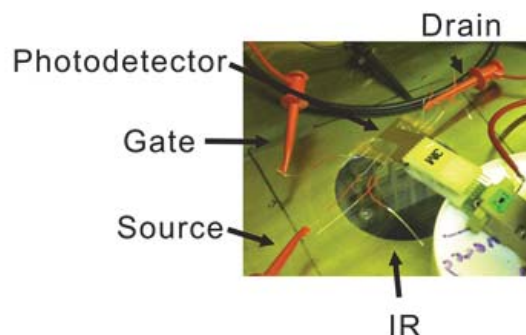
Double charge neutrality points (CNPs) confirms the formation of p-n junction.

Photoresponse of p-n Junctions

Schematic of the p-n junction photodetector



Setup of the phototest



Photocurrent density
(10^{-4} A/cm^2)[†]

$$(5.50 \pm 0.47) \times 10^4$$

Photoresponsivity
(mA/W)

$$(1.20 \pm 0.11) \times 10^4$$

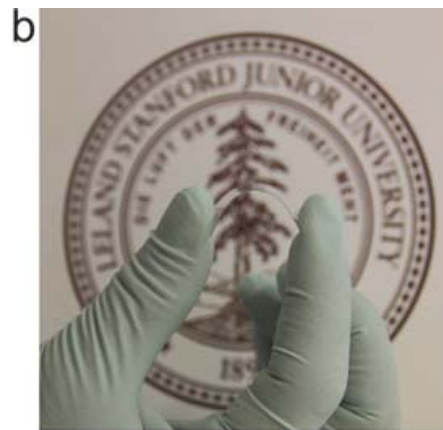
- Positive IR photoresponse
- Fast response speed
- High responsivity

Transparent and Flexible IR Photodetectors

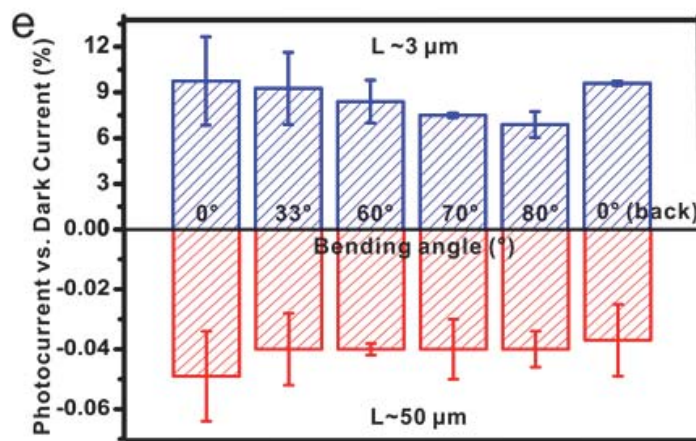
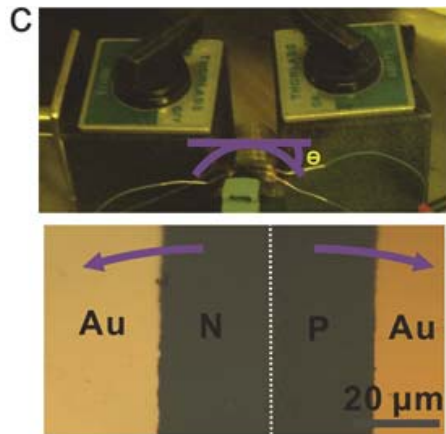
Transparency



Flexibility



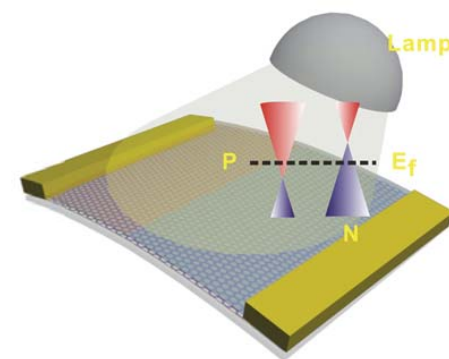
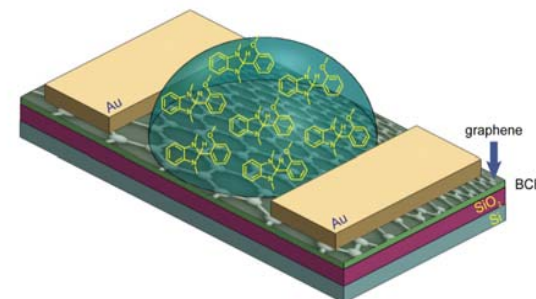
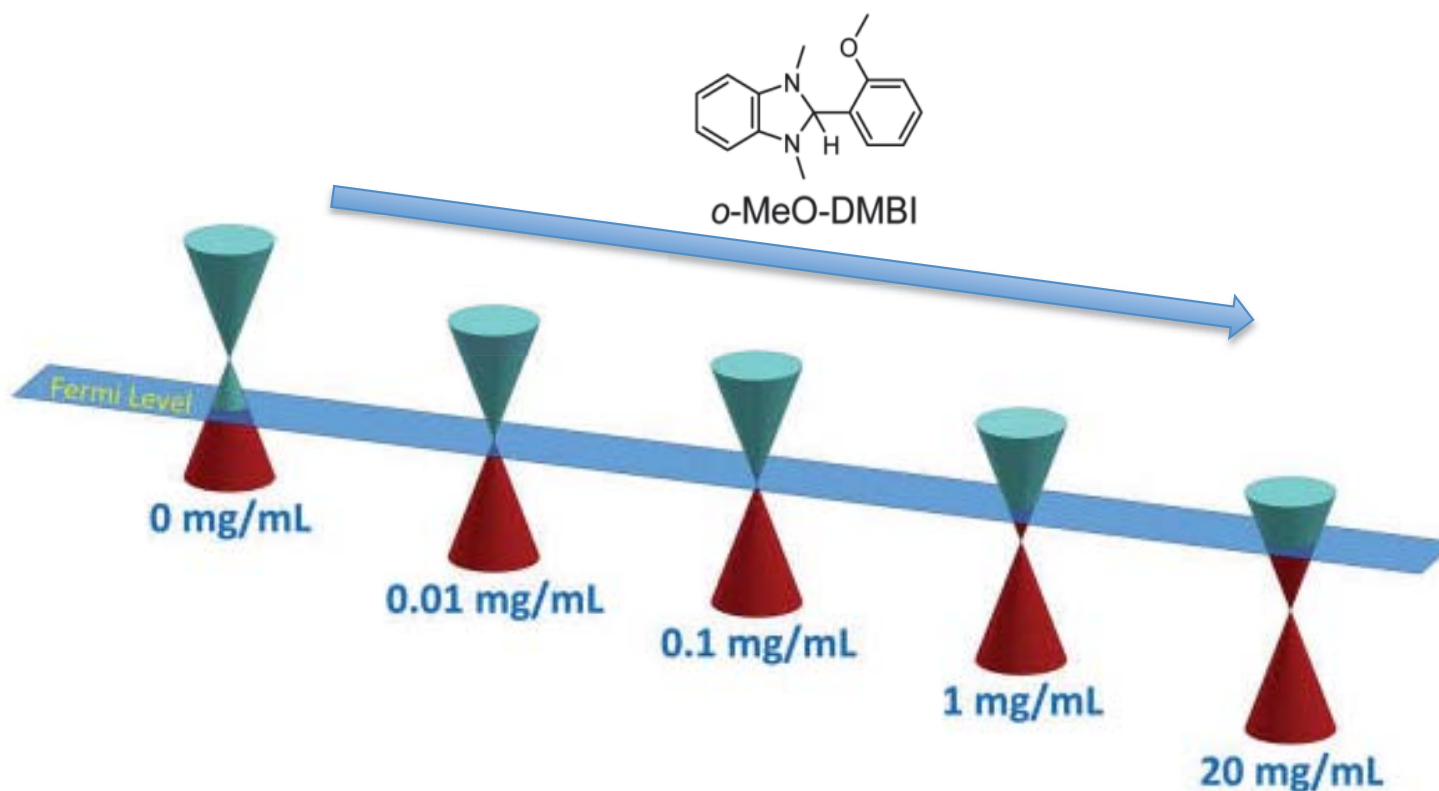
Bending test



- The photocurrent is almost same at different bending angles up to 80 degrees
- The bending/releasing processes can be repeated for many times

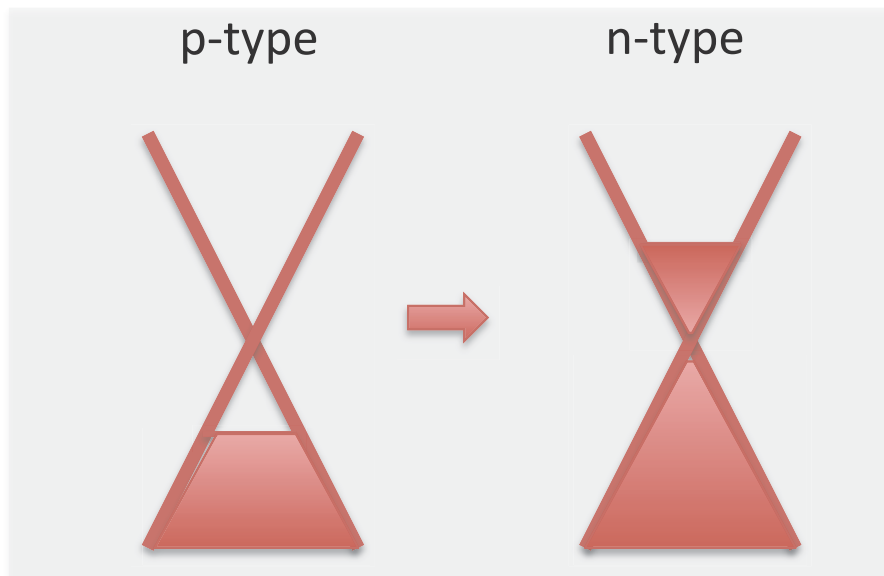
Summary I

- 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

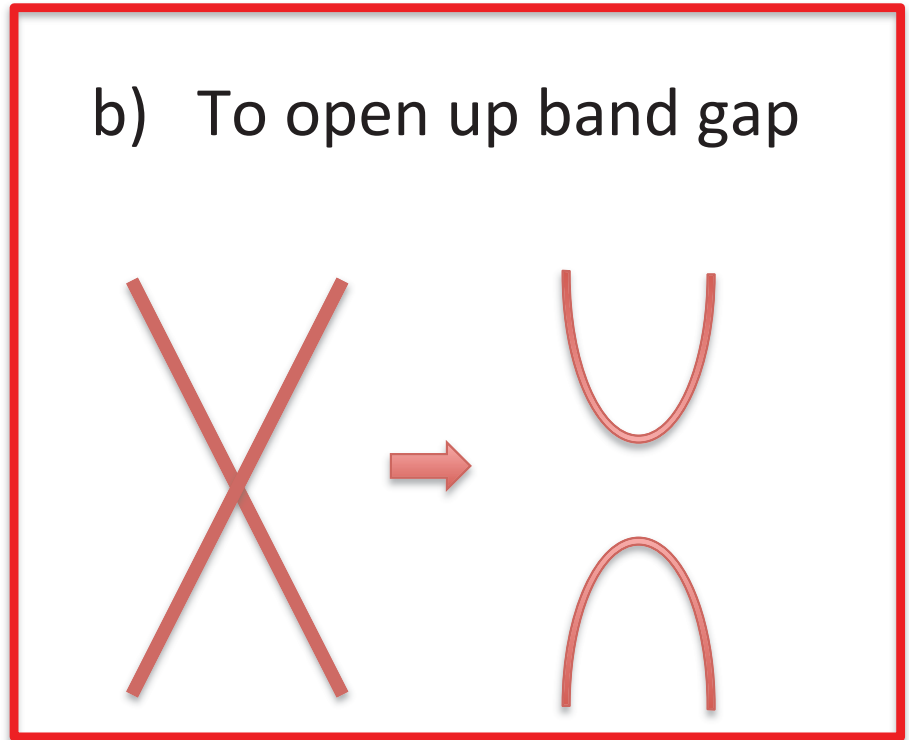


To control graphene electronic properties via graphene-organic interface

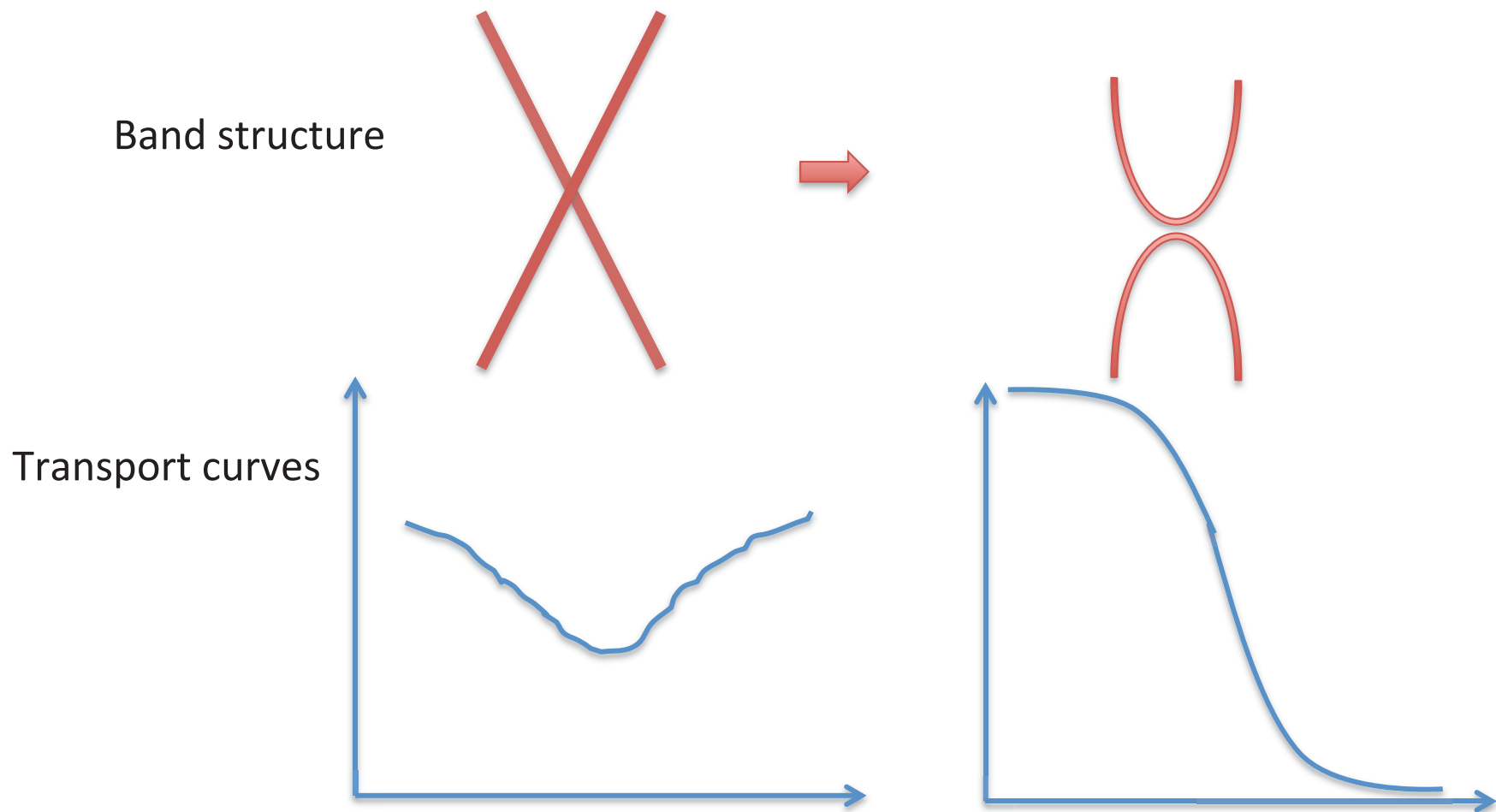
a) To control Fermi level



b) To open up band gap

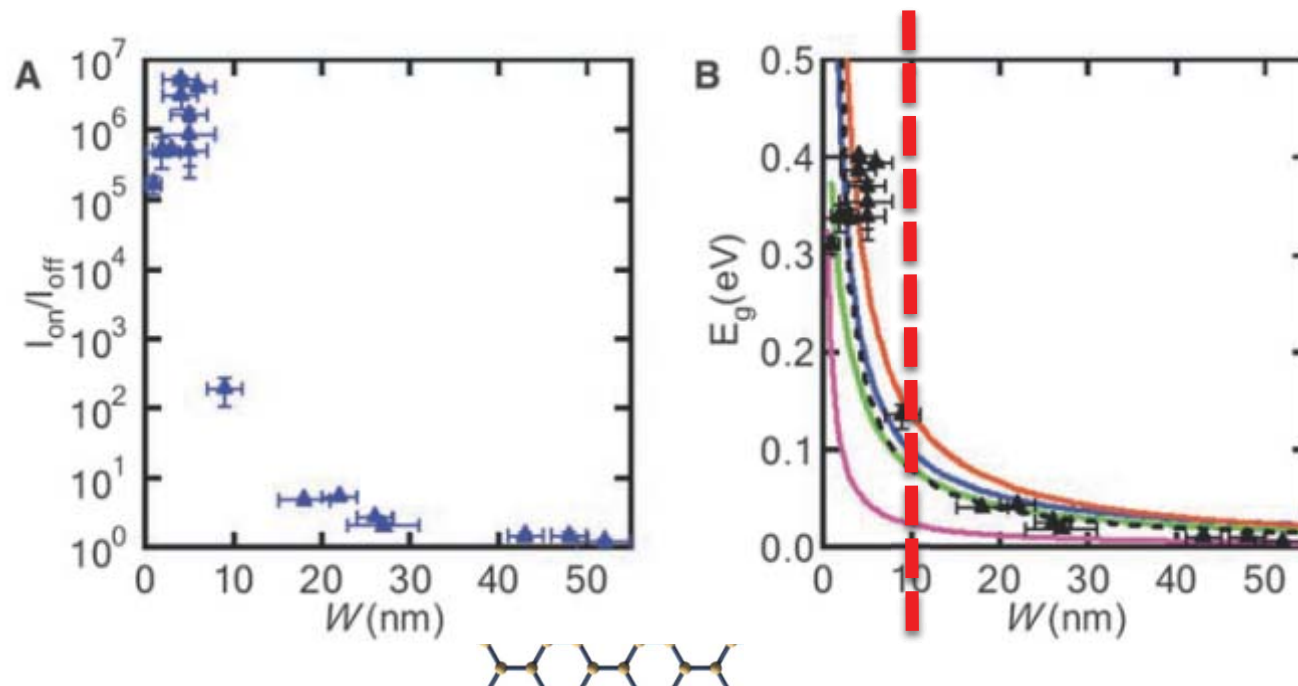


Why Bandgap?



- 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

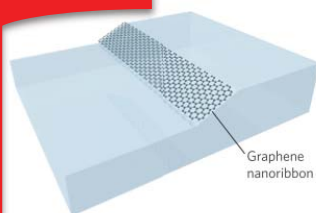


$$E_g (eV) = \frac{0.8}{w(nm)}$$

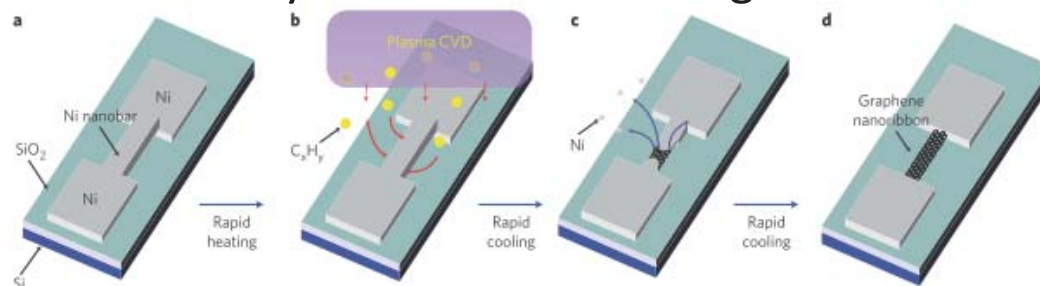
GNR below 10 nm will result in a sufficient band gap and large on/off ratio for room temperature operation.

Synthetic Approaches to GNRs — Bottom up

1. High Temperature Growth



Lack scalability and not small enough

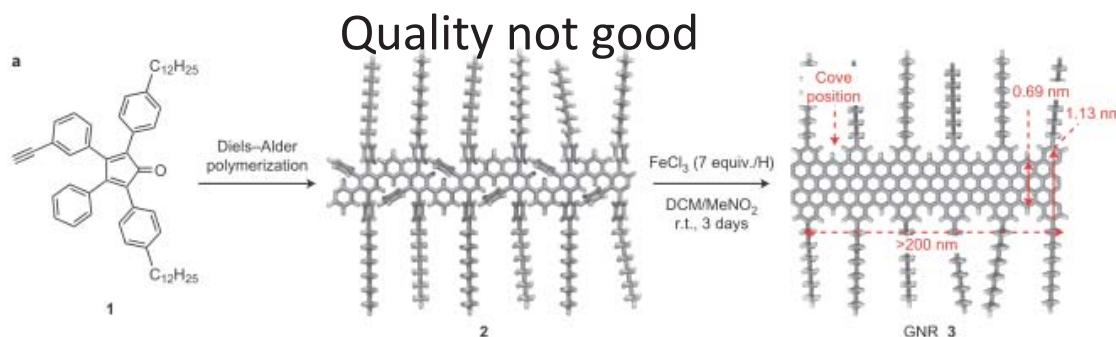


Walt A. de Heer*, et al. Nature Nanotechnology, 2010, 5, 729

Walt A. de Heer*, et al. Nature 2014, 506, 349

Toshiaki Kato* et al, Nature Nanotechnology, 2012, 7, 651

2. Organic Synthesis

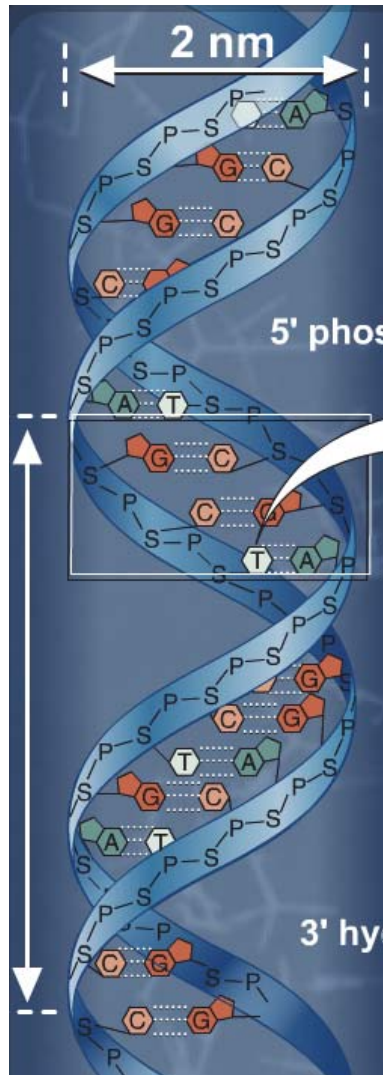


Quality not good

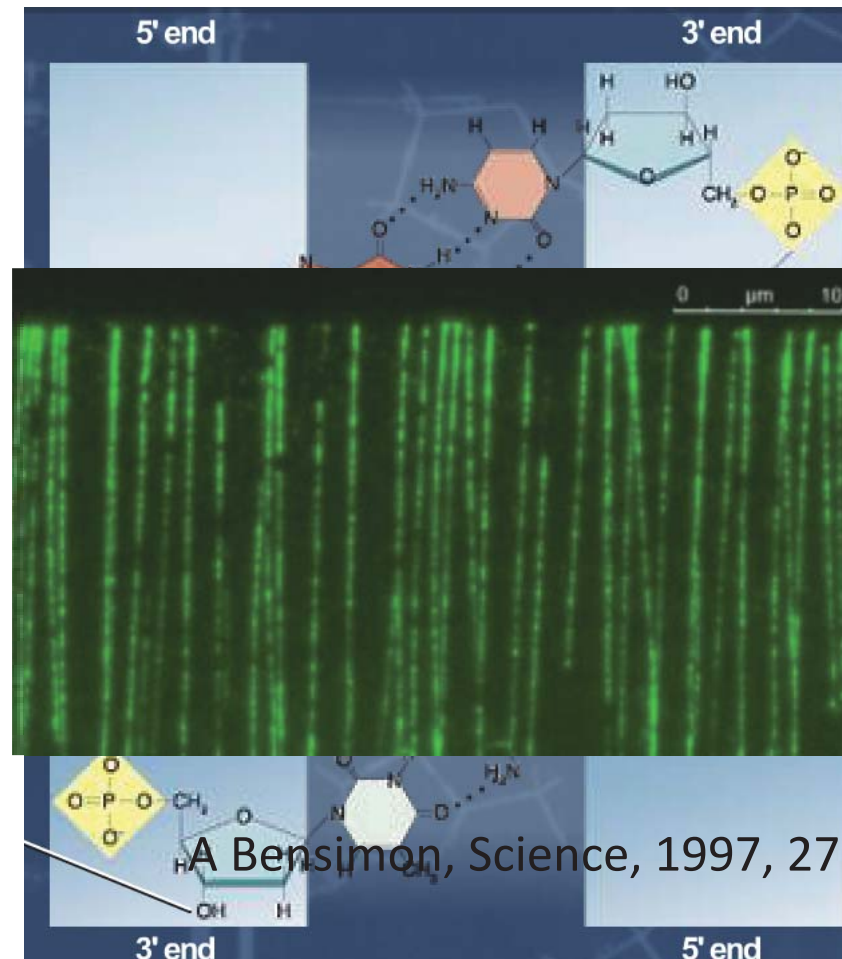
Klaus Mullen* et al, Nature Chemistry, 2014, 6, 126

DNA Bio-template to GNRs

1. DNA width ~ 2 nm

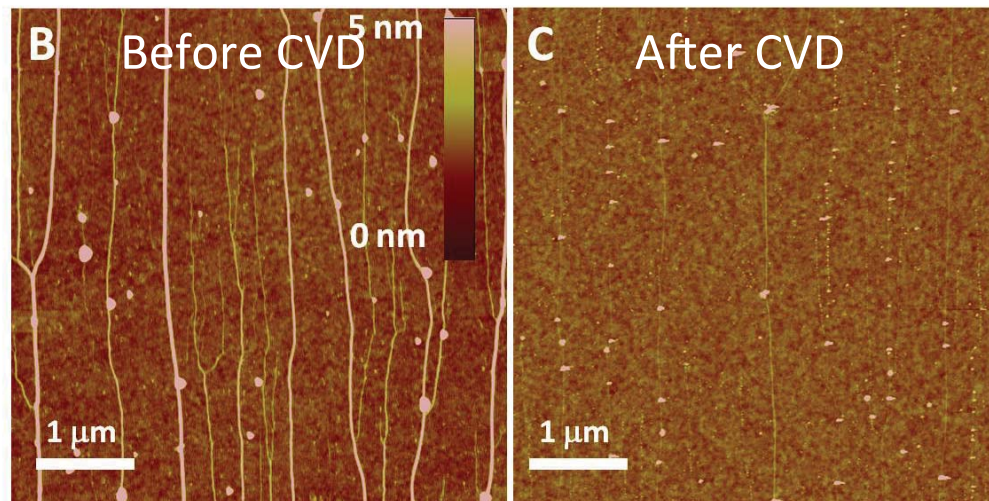
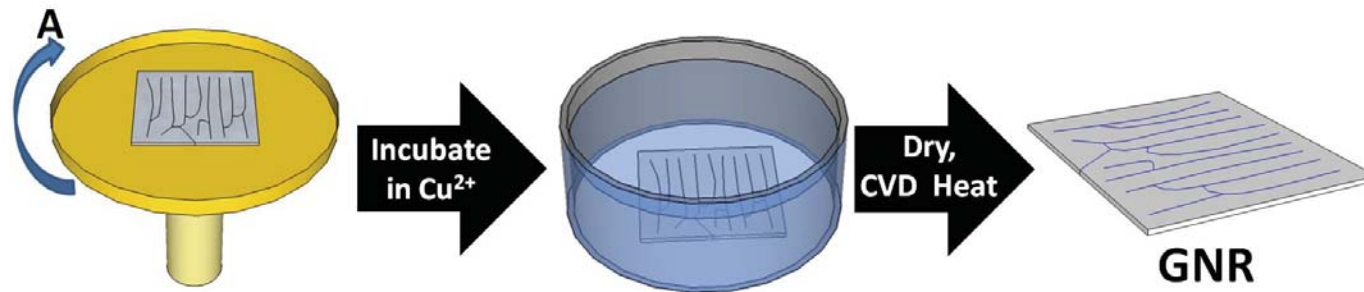


2. Easily aligned with a molecular combing method, which can pre-pattern GNRs by DNA template for large scale circuits



A Bensimon, Science, 1997, 277, 1518

GNRs from DNA



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

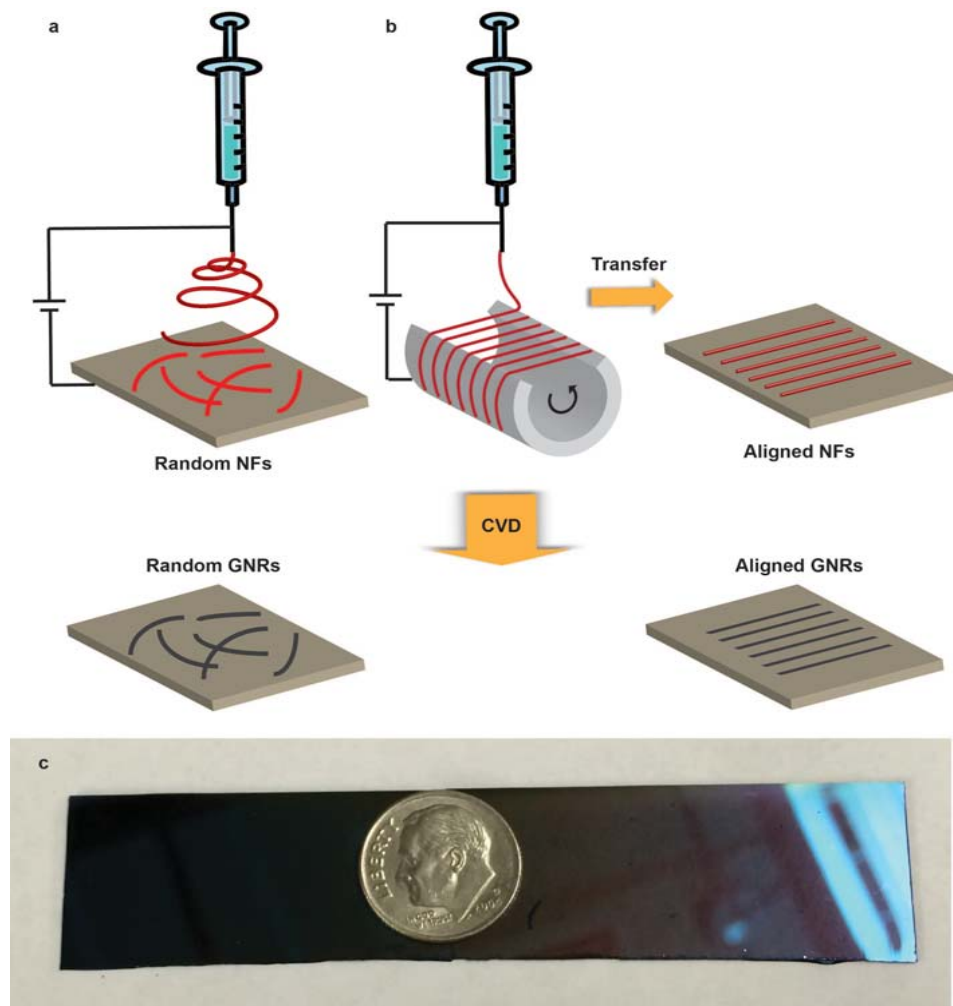
Electrospinning

❖ Particularly interested in electrospun polymer



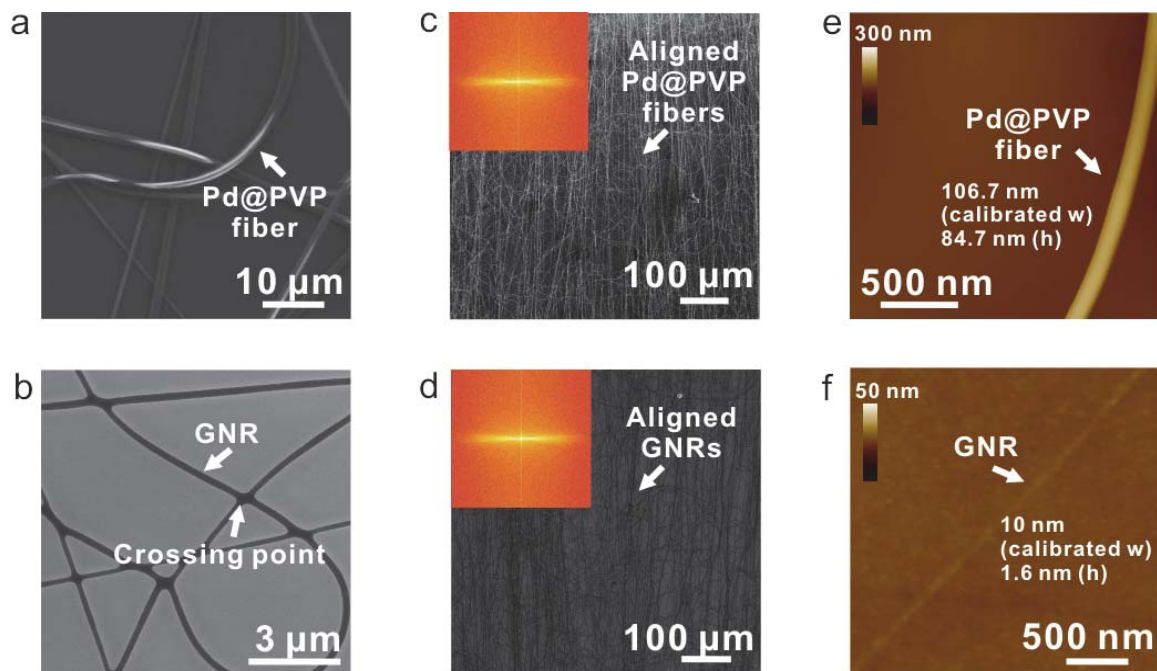
1. A larger variety of polymer can be electrospun, allowing us to explore the correlation between chemical structure and GNRs.
2. A powerful tool to create 1D polymer with higher scalability and lower cost.

Electrospun Polymer to GNRs



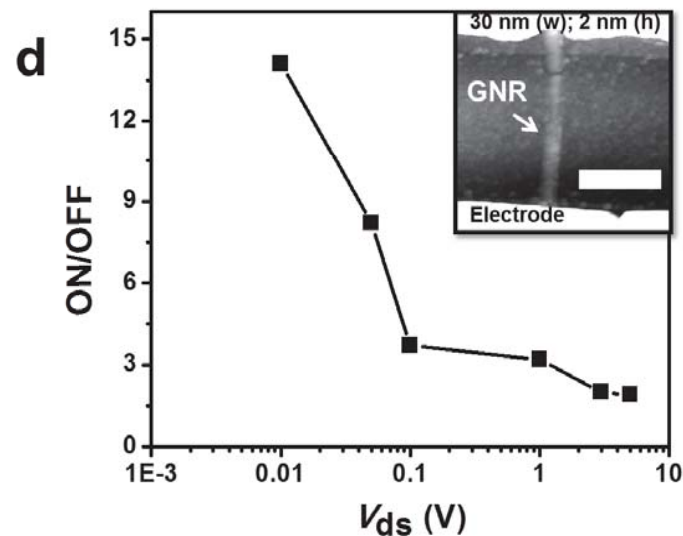
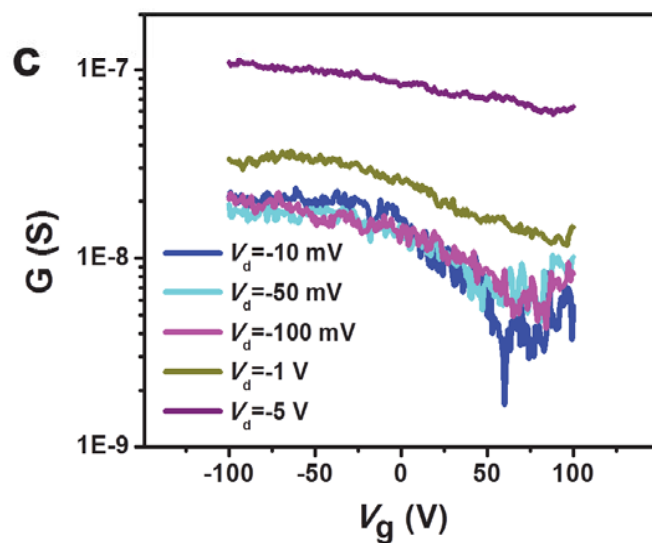
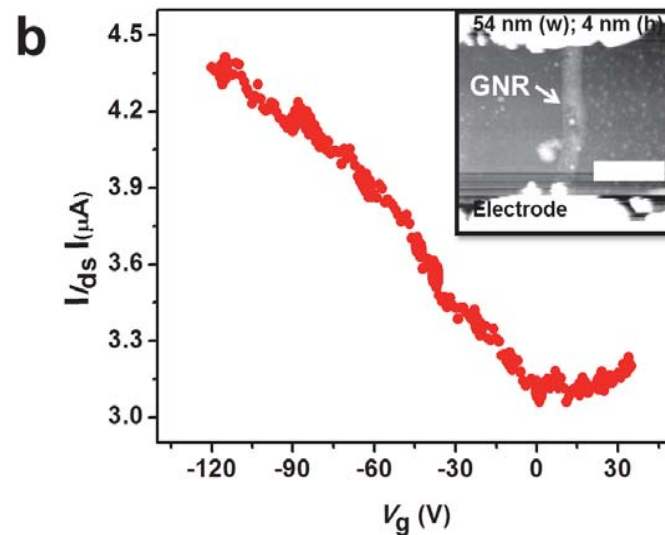
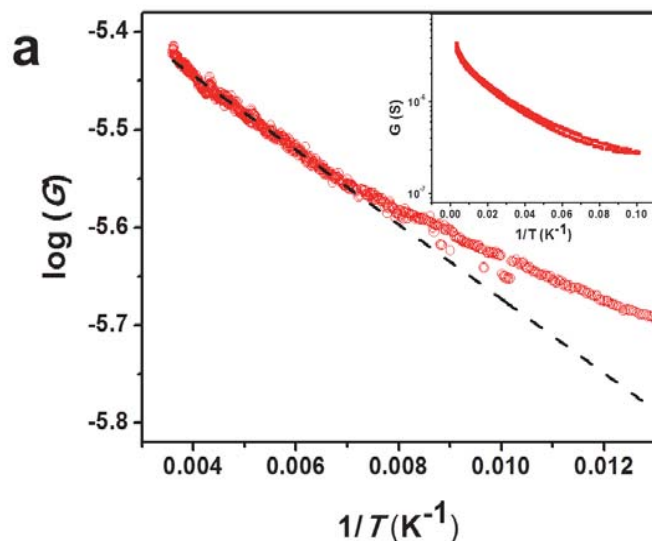
1. Methane CVD on these nanofiber templates yielded highly-graphitic GNRs with well-controlled widths.
2. These nanofibers can be aligned on a metallic rotor with a gap.
3. Scalable demonstration

Overview of the GNRs - Morphology

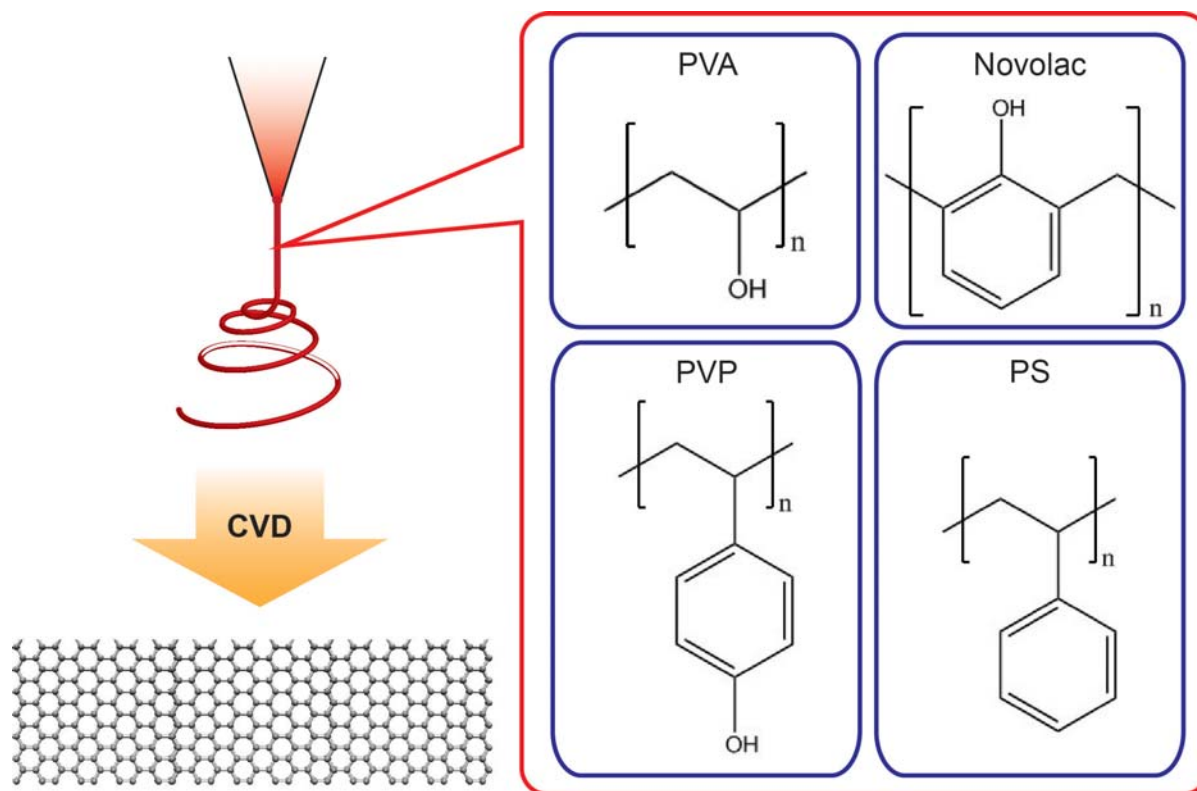


- ❖ The post-growth substrate shows a similar morphology of the polymer fibers before growth.
- ❖ The 1D structures on the post-growth substrates are extremely long.

Overview of the GNRs – Electronic Properties

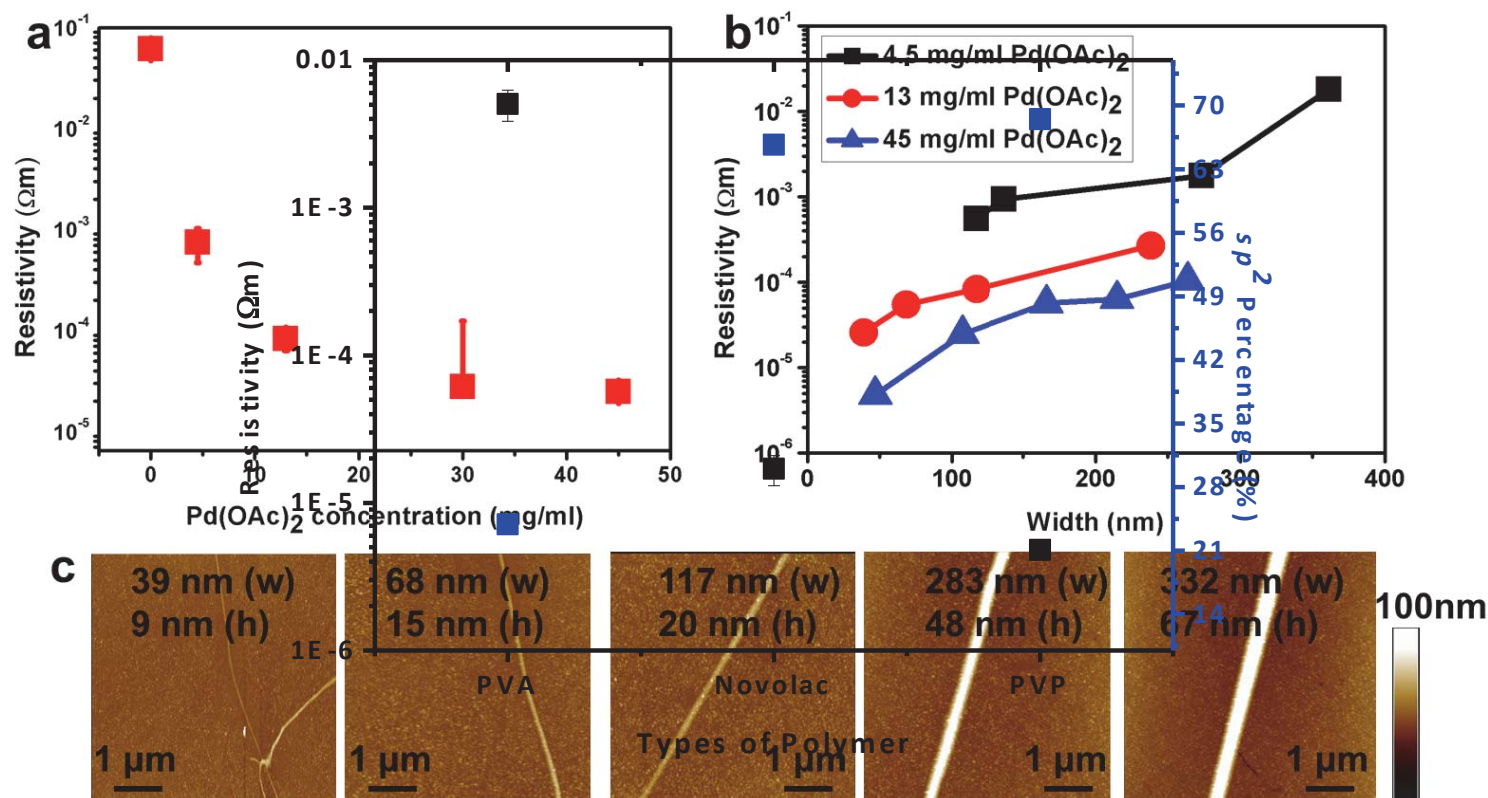


Effect of Chemical Structure on the Graphitization Degree



- ✓ Metal-binding functional groups
- ✓ Aromatic moieties

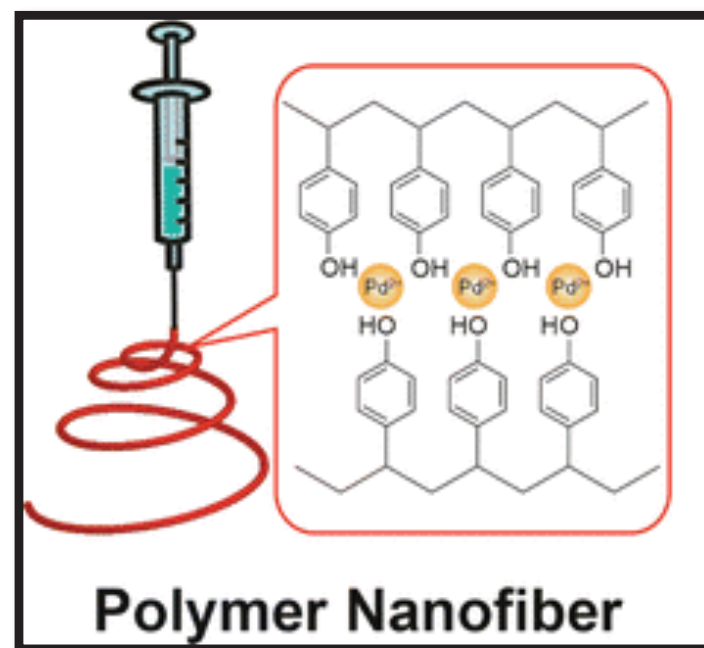
Effect of Chemical Structure on the Graphitization Degree



- ❖ Polymer with aromatic moieties leads to higher sp^2 with lower resistivity, indicating metal-binding functional groups is crucial.

Summary II

- First demonstration of large scale, polymer templated GNR growth
- Understand the effect of chemical structure on the quality of GNR



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

Nan Liu, Z Bao, J. Am. Chem. Soc., 2014, 136, 17284

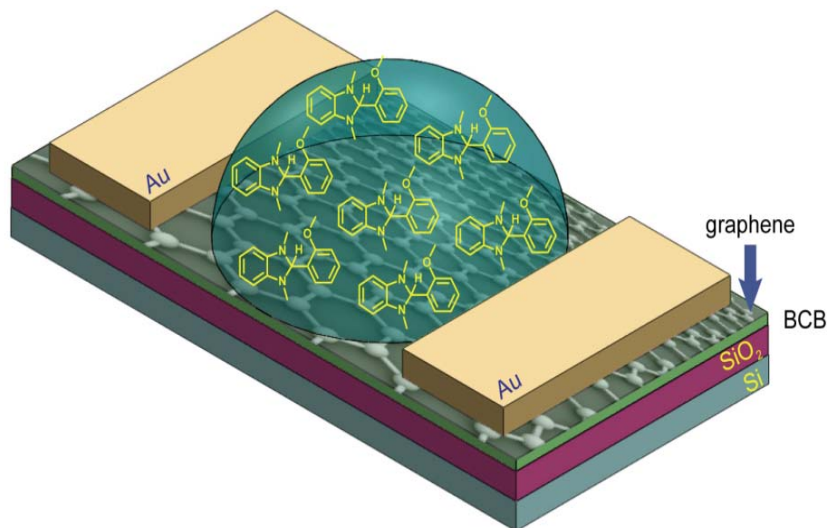
Nan Liu, Z Bao, ACS Nano, 2015, ASAP

Conclusion

To control graphene electronic properties via graphene-organic interface

Graphene-organic molecules

a) To control Fermi level: n-type doping



Graphene-polymer

b) To open up band gap: to GNRs



To flexible electronics

Acknowledgement

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Dr. Fung Ling Yap

Dr. Kwanpyo Kim

Dr. Hao Yan



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Collaborator:
Professor Yi Cui



Any questions?

Thank you all for coming and listening!

