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

John A. Rogers Group
University of Illinois at Urbana-Champaign

Rogers et al, Science, 2015, 347, 6218
Our Approach to Flexible Electronics

1. New structure: microstructured PDMS (polydimethylsiloxane)

2. New material: organic materials (polyisodigobithiophene-siloxane, PII2T-Si) (poly(3-hexylthiophene-2,5-diy1), P3HT)

- Silicon mould
- ITO/PET
- PET
- Microstructured PDMS
- Laminate
- Pil2TSi semiconducting polymer
- Thin PDMS
- BCB
- Polyimide
- Au source / drain
- SWNT-coated PDMS
- Electrochromic polymer (act as pigment cells)
- SWNT-coated PDMS
- SWNT-coated pyramid layer (act as tactile sensing)

In our transistor, we have used 7,9,10,9,860 oligothiophene units, 8010, 9, 860 as a flexible and wearable sensor. A wearable and flexible sensor can be used in a pulse monitor.

Ho-Hsiu, Chou, Z Bao, Nature Comm 2015, 6:8011
Carbon-Based Materials: CNTs

NOR logic gate

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NAND Gate

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Highly Robust All-CNT Stretchable Transistors

Elastic Dielectric
Elastic Substrate

0->100% strain

Carbon-Based Materials: 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$^{-6}$Ωm lower than silver


2. It is flexible, transparent and biocompatible
Better Interaction between Carbon-Based Materials

Graphene CNTs Graphene

SiO₂/Si

Vs.

SiO₂/Si

Contact resistance (Ω)

Mobility (cm²/Vs)

(Vg-Vth)

RT Graphene RT Au

G

Au

275K

100K

G

G

50K

G

Au

Unpublished work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

As the doping time increases, sheet resistance decreases and 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
Design New n-type Dopant

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

- \( o\text{-MeO-DMBI-I} \)

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

- \( o\text{-MeO-DMBI} \) is air-stable and can be stored and handled in air for extended periods without degradation
- Solution process or vacuum deposition
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

Peng Wei†; Nan Liu†; Z Bao, Nano Lett. 2013, 13, 1890
Ultraviolet photoelectron spectroscopy (UPS):

- 0.5 eV 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

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

Nan Liu, Z Bao, Nano Lett, 2014, 14, 3702
Photoresponse of p-n Junctions

Schematic of the p-n junction photodector

Setup of the phototest

Photocurrent density $(10^{-4} \text{A/cm}^2)$

$\frac{(5.50 \pm 0.47) \times 10^4}{(1.20 \pm 0.11) \times 10^4}$

- Positive IR photoresponse
- Fast response speed
- High responsivity

Nan Liu, Z Bao, Nano Lett, 2014, 14, 3702
Transparent and Flexible IR Photodetectors

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

Nan Liu, Z Bao, Nano Lett, 2014, 14, 3702
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
Outline

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.

H Dai, Science 2008, 319, 1229
Synthetic Approaches to GNRs — Bottom up

1. High Temperature Growth

Lack scalability and not small enough


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)
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

Nan Liu, Z Bao, ACS Nano, 2015, ASAP
Effect of Chemical Structure on the Graphitization Degree

Polymer with a random metal loading is expected to have less resistivity, indicating metal-binding functional groups is crucial.

Nan Liu, Z Bao, ACS Nano, 2015, ASAP
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, ACS Nano, 2015, ASAP
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: to GNRs

To flexible electronics
Acknowledgement

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