

Doping and Characterization of Graphene & GNWs

Kuei-Hsien Chen

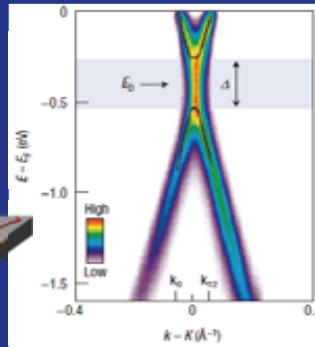
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chenkh@pub.iams.sinica.edu.tw*

Outline

- **Introduction**
- **N-doping of GNWs**
- **BN-codoping of graphene**
 - **In-situ doping**
 - **XPS, UV-Vis analysis**
 - **STEM analysis**
 - **XES & XANES analysis**
- **Summary**

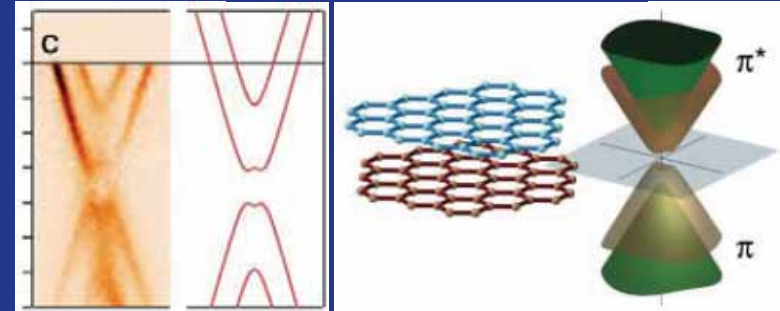
Gap-opening in Graphene

Substrate-induced bandgap opening



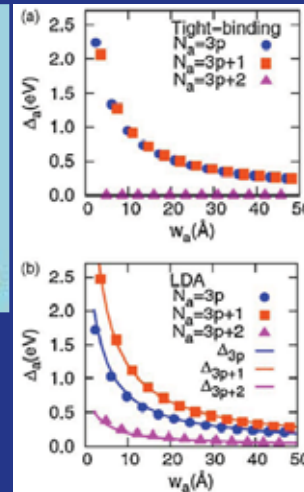
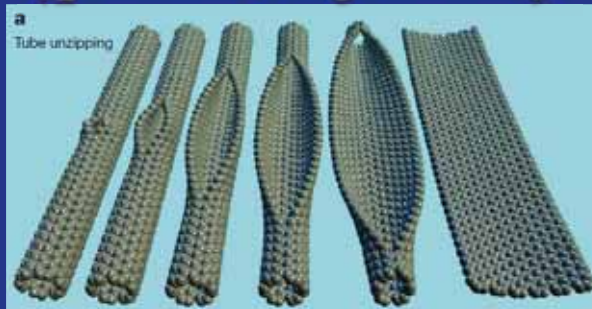
Nature Materials 2007, 6, 770

Bilayer graphene



Science 2011, 313, 951

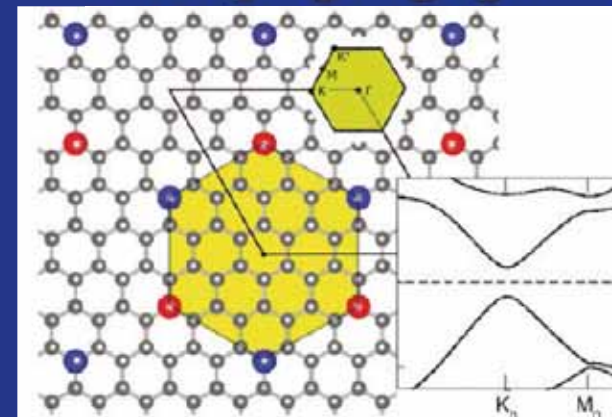
Graphene nanoribbons (quantum confinement)



Nature 2009, 458, 872

Phys. Rev. Lett. 2006, 97, 216803

BN doping in graphene



J. Phys. Chem. C 2011, 115, 3250

ACS Nano 2011, 5, 385

ACS Nano 2010, 4, 7619

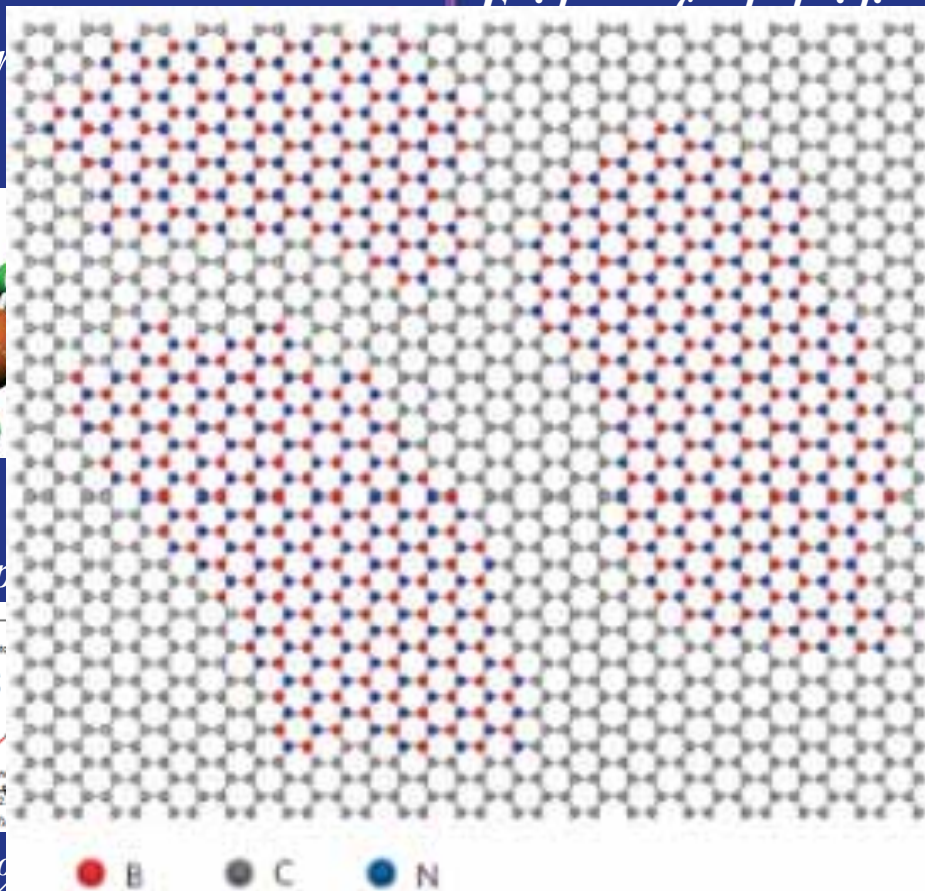
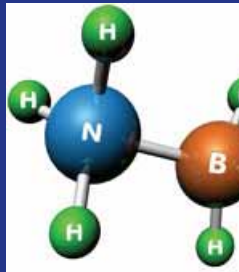
J. Appl. Phys. 2010, 108, 073711

B-N Co-doping

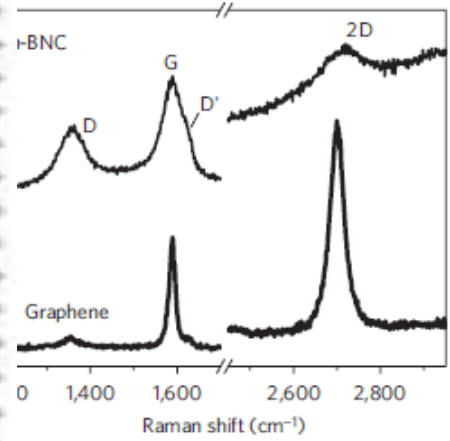
Atomic layers of hybridized boron nitride and graphene domains



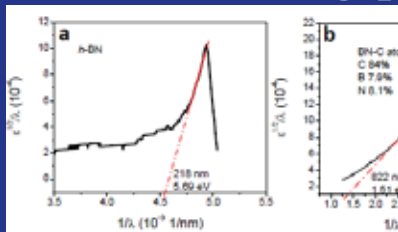
Ammonia Borane



Evidence for hybridized h-BN and graphene domains in h-BCN



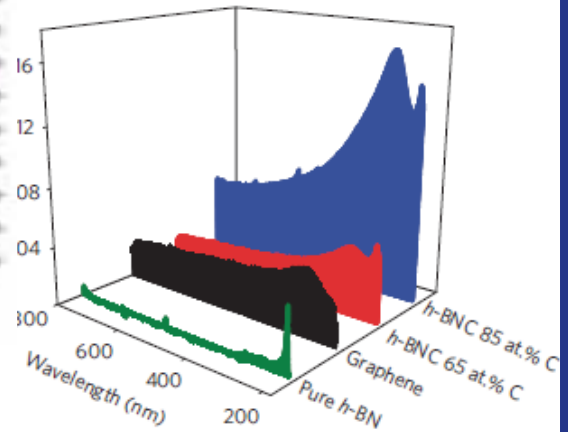
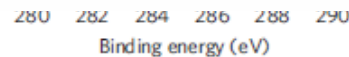
Band gap



Pure h-BN
5.69eV

16%
1.51eV
3.85eV

1.62eV
4.48eV



Pulickel M. Ajayan et al. Nature Materials, 9, 430 (2010)

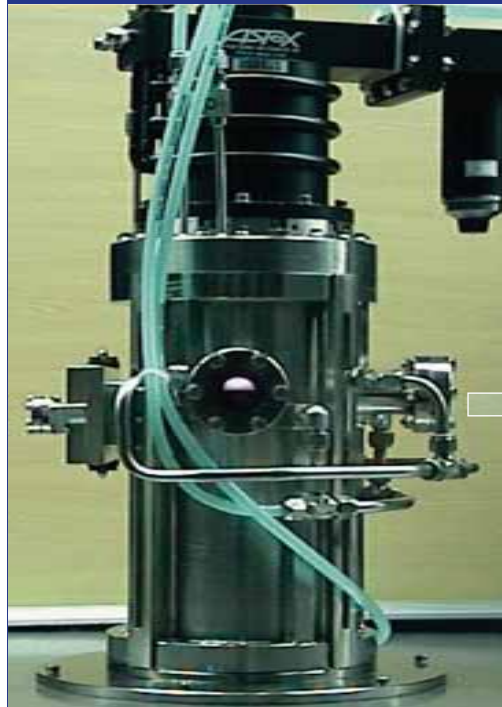
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Growth of Graphene Nanowalls

Microwave Plasma CVD reactor
(MWCVD)

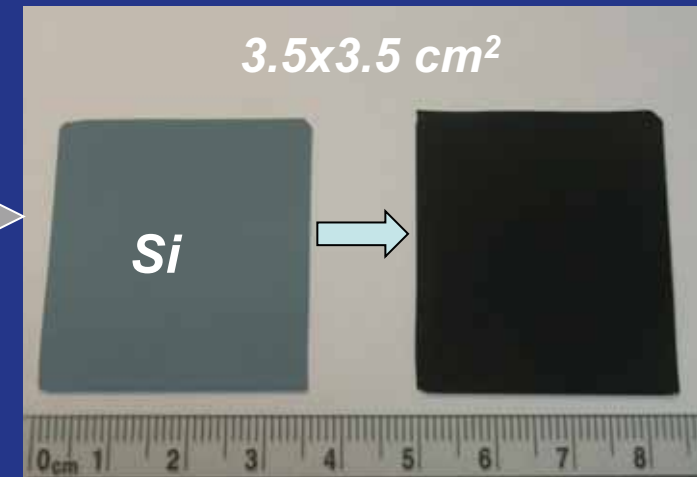
Source reactants: $\text{SiH}_4 / \text{CH}_4 / \text{H}_2$
Gas ambient : H_2
Microwave power : 1000-2000 W
Growth temperature : 900-1100 °C



$\text{SiH}_4 / \text{CH}_4 / \text{H}_2$ plasma



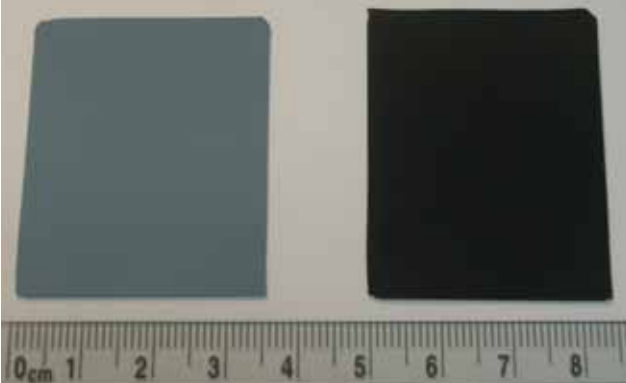
Si



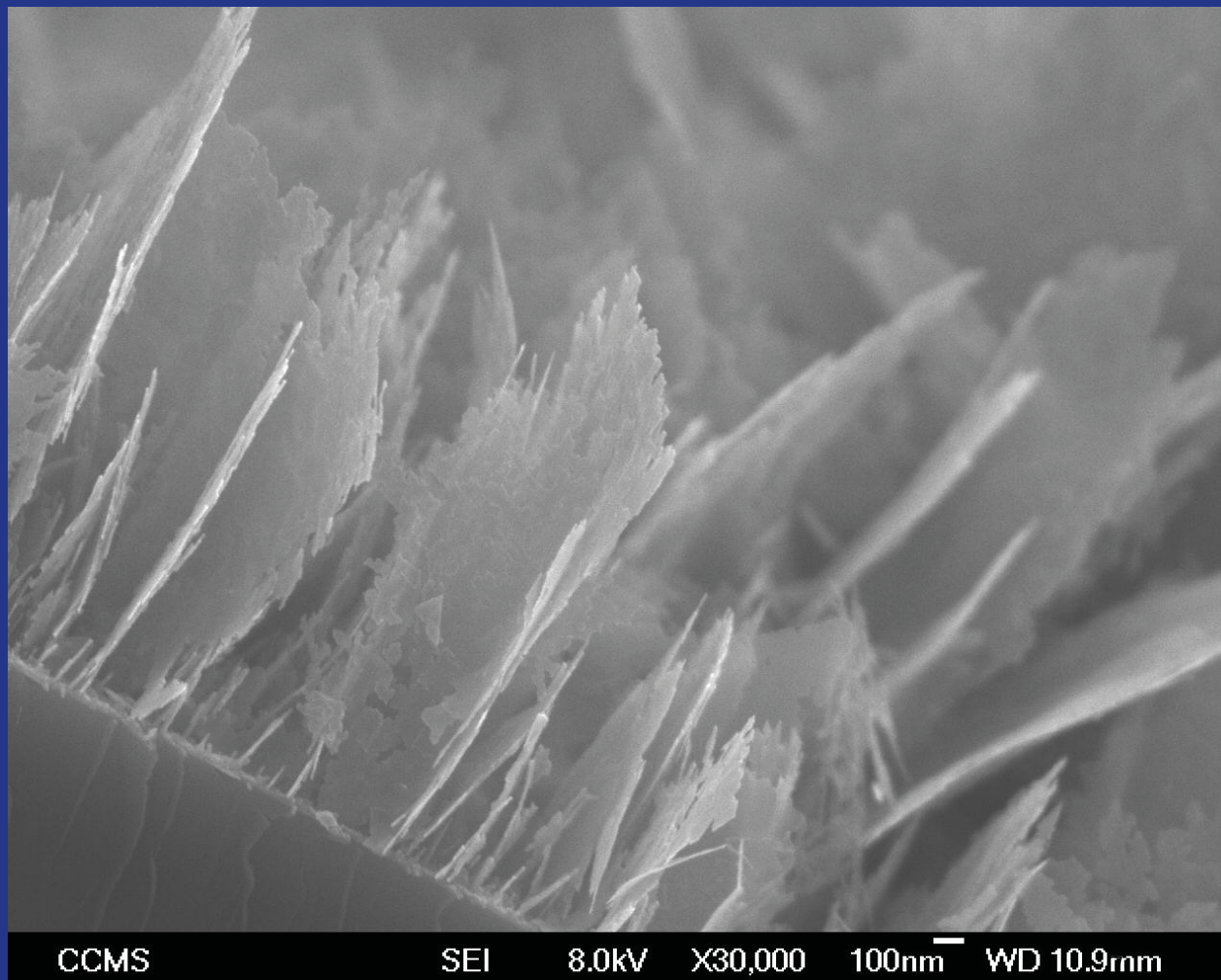
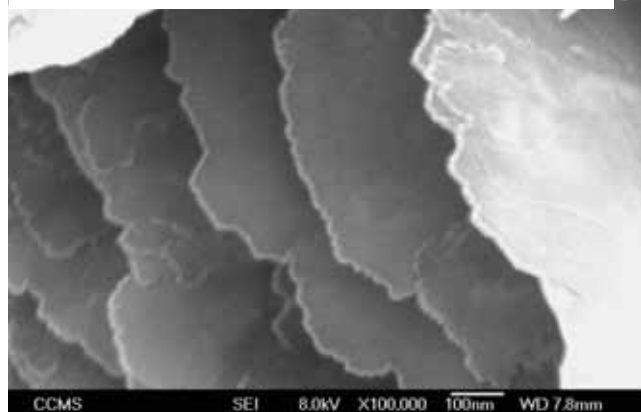
Carbon 49, 4911 (2011) ⁶

Large-Scale Production Ultrathin Sheet-like Morphology

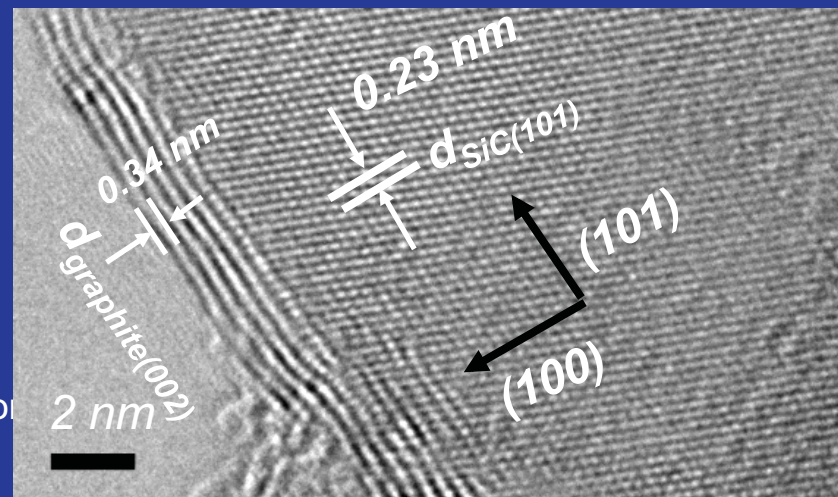
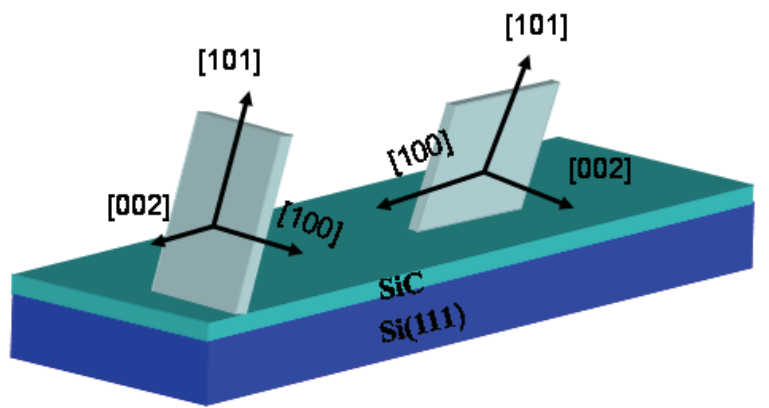
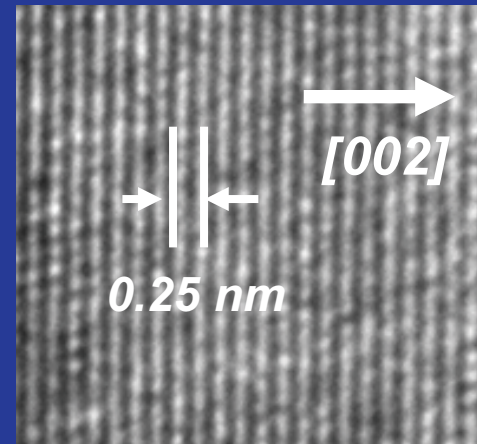
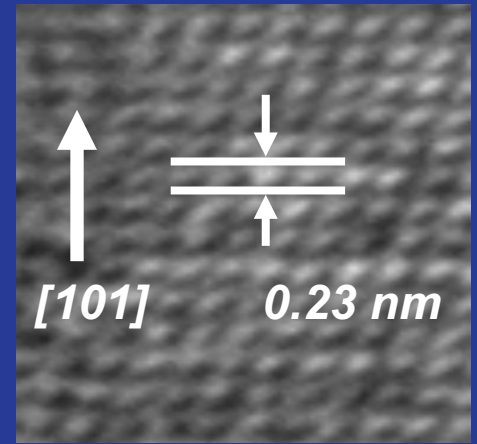
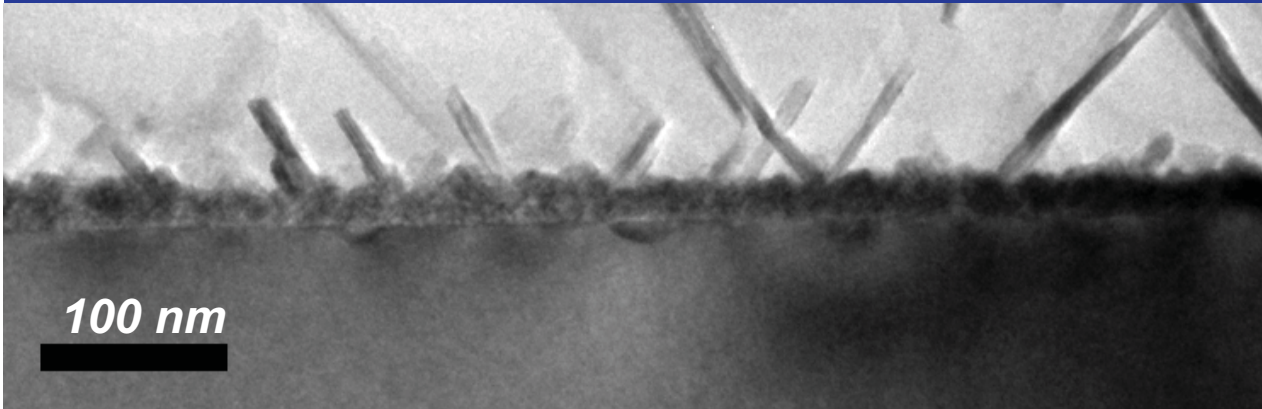
3.5x3.5 cm²



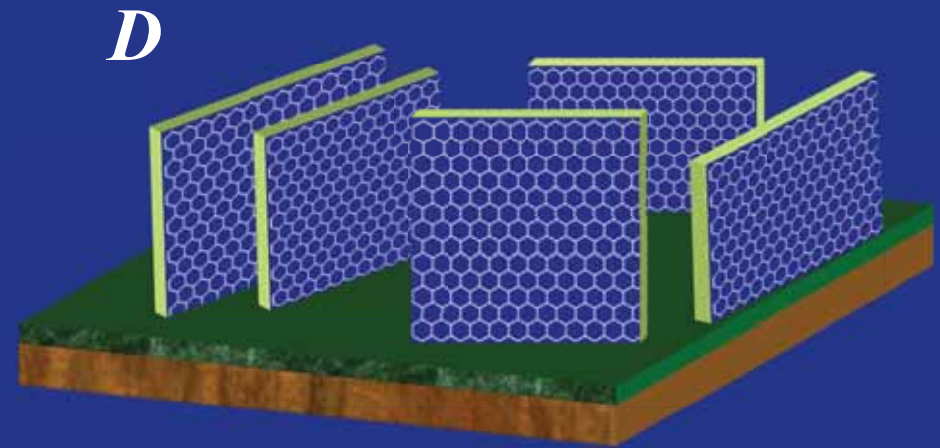
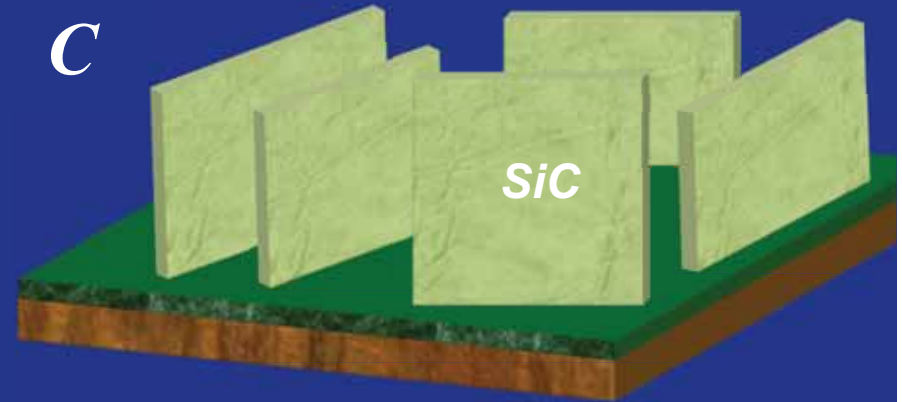
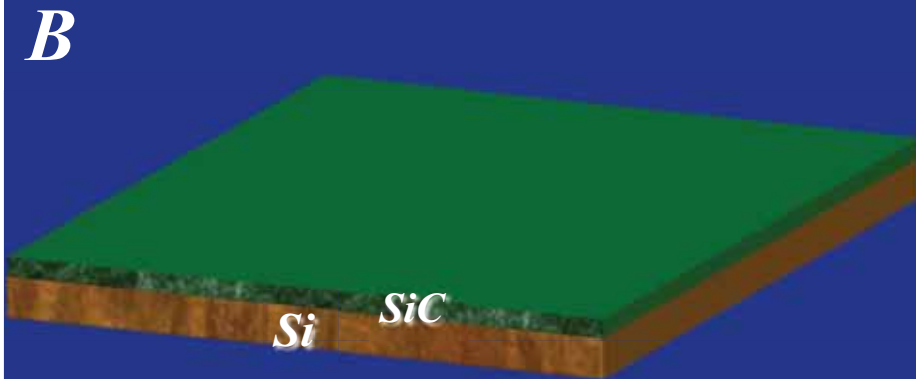
Thickness : 4 -7 nm



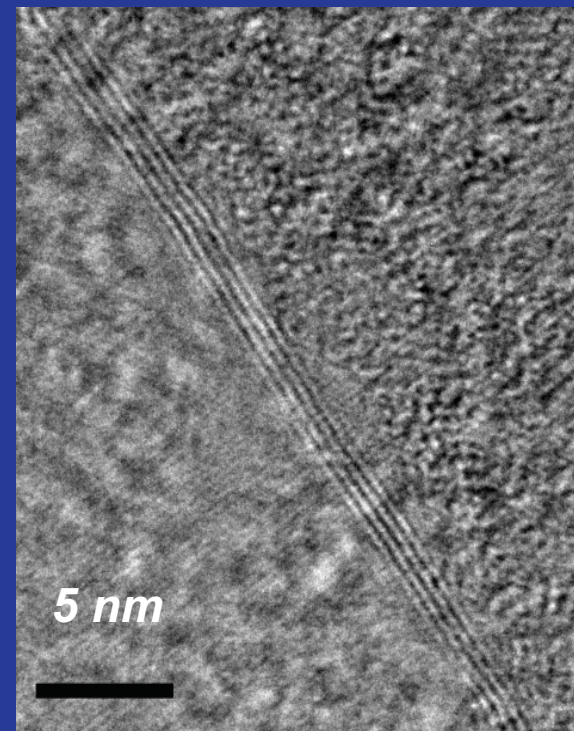
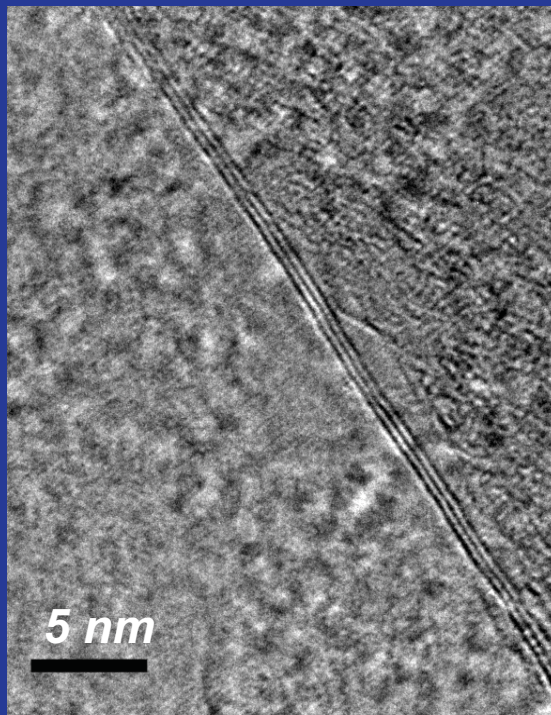
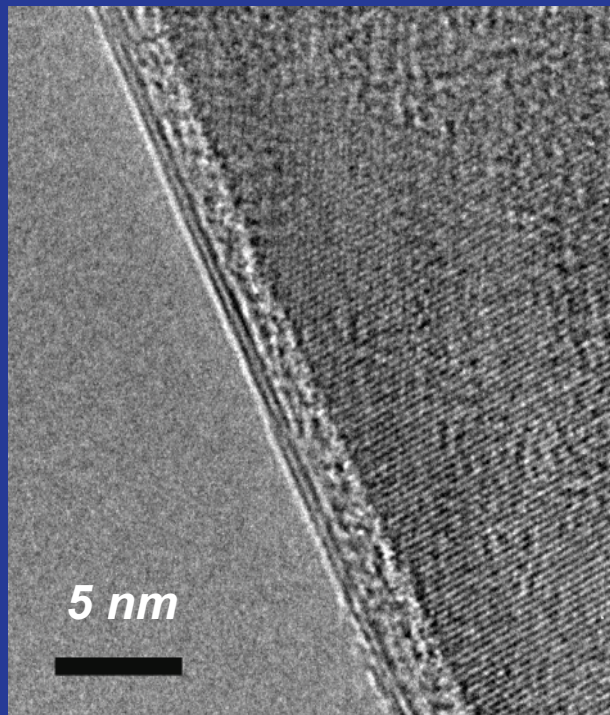
Microstructures



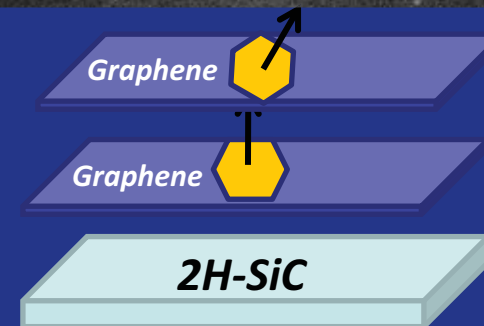
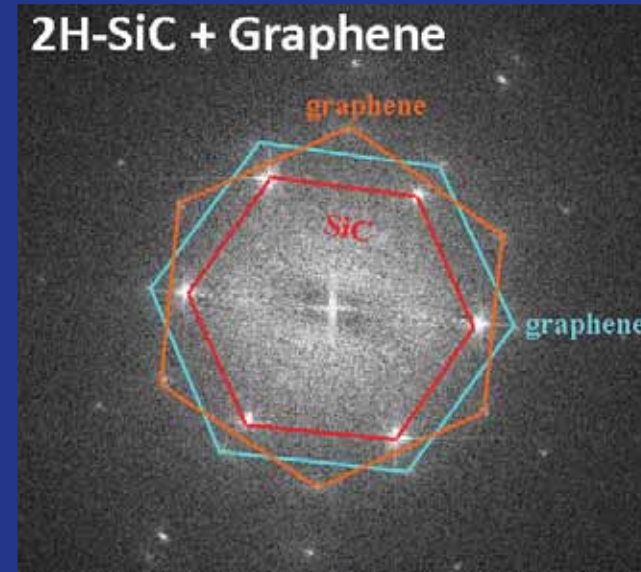
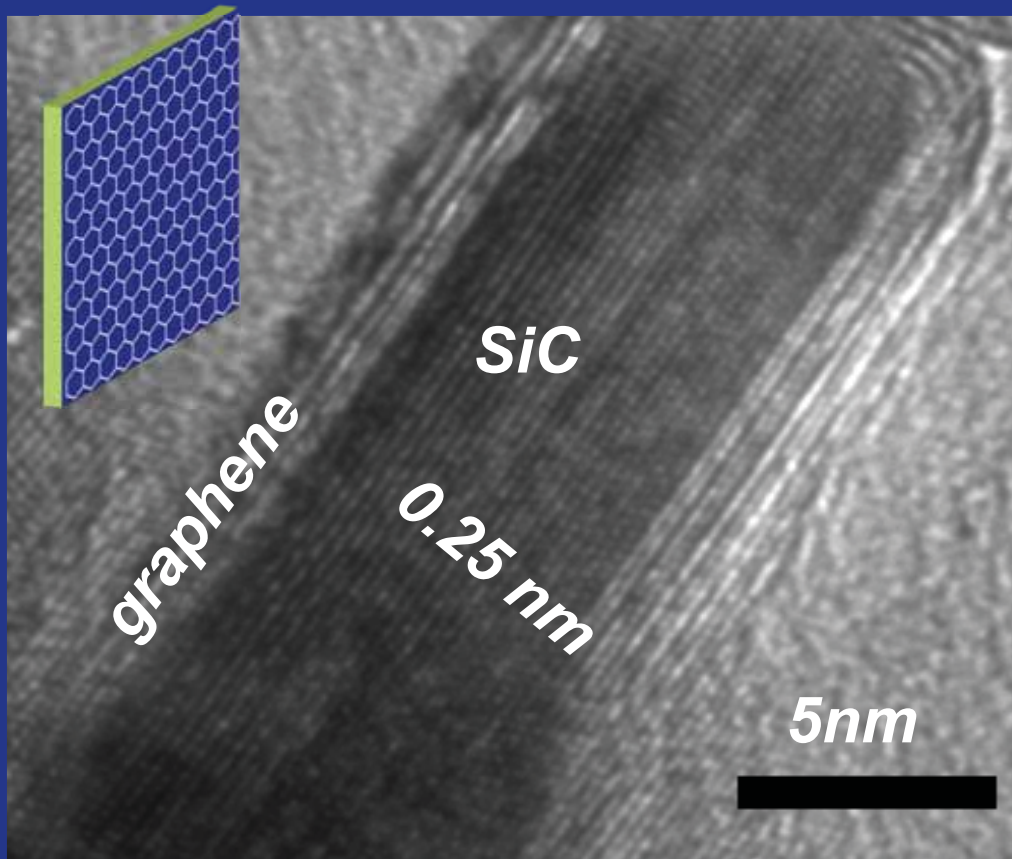
Schematic of Hybrid GNWs Growth



Layer Number Control

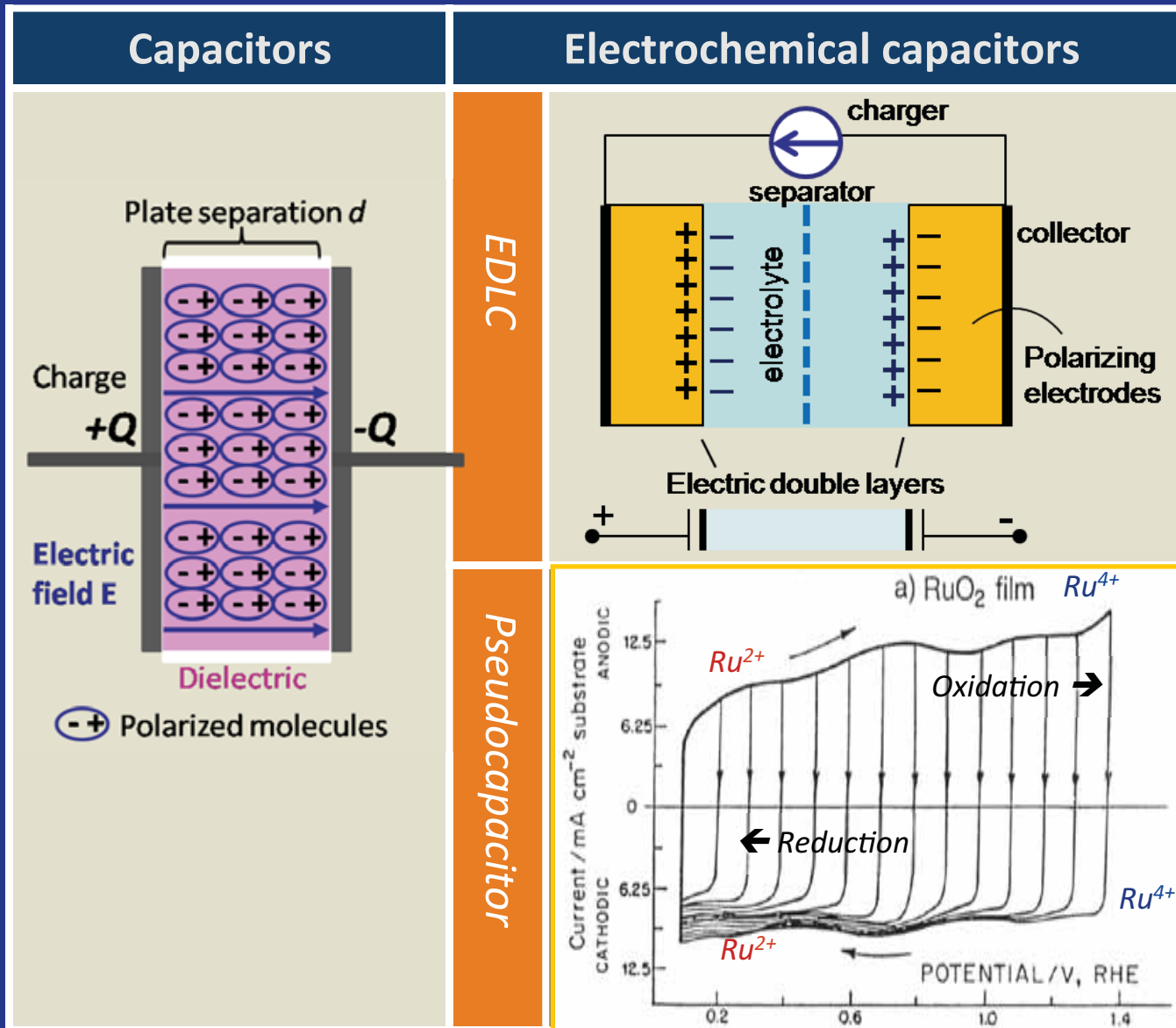


TEM Analysis

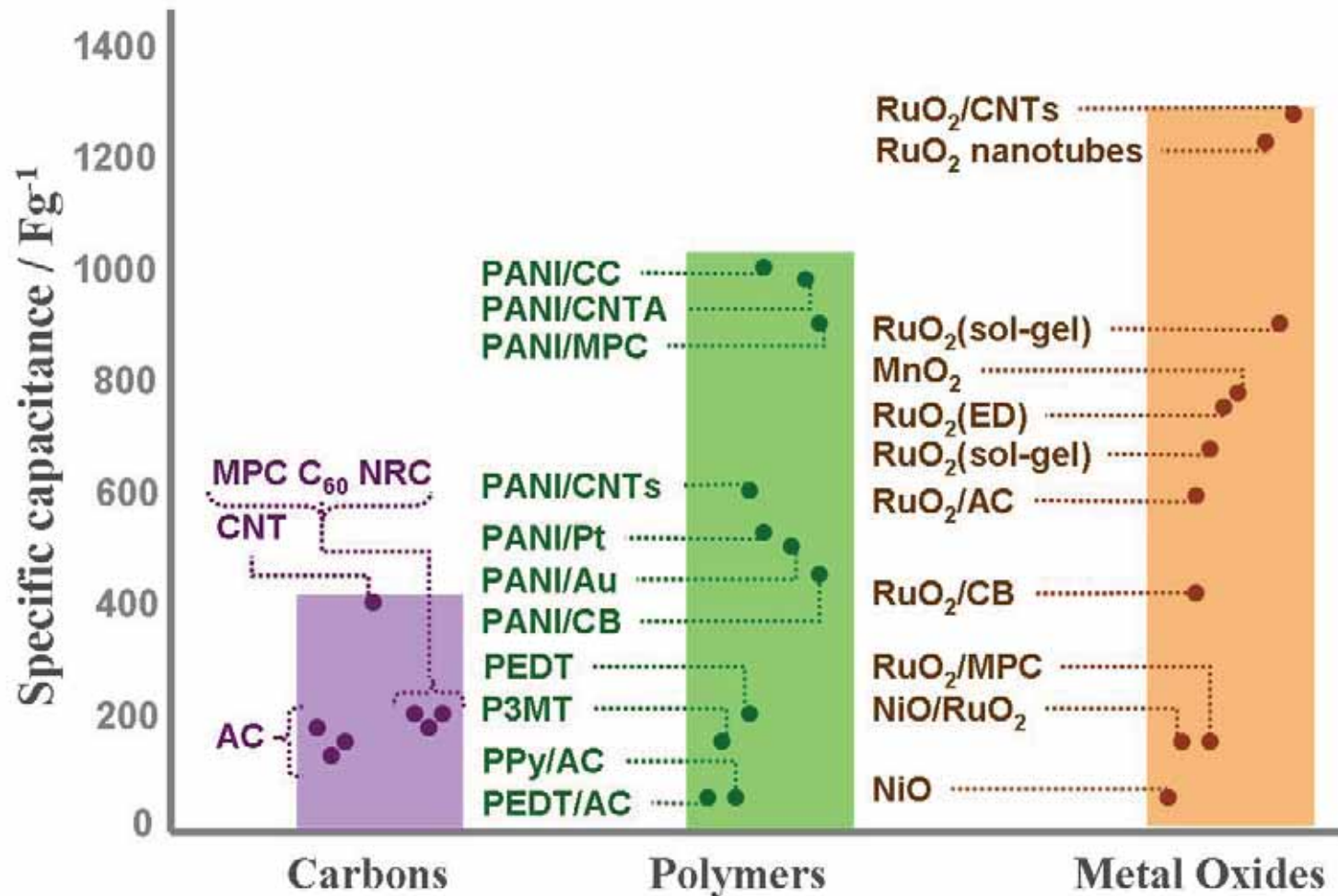


Graphene layer by CVD layer

GNWs for Supercapacitors



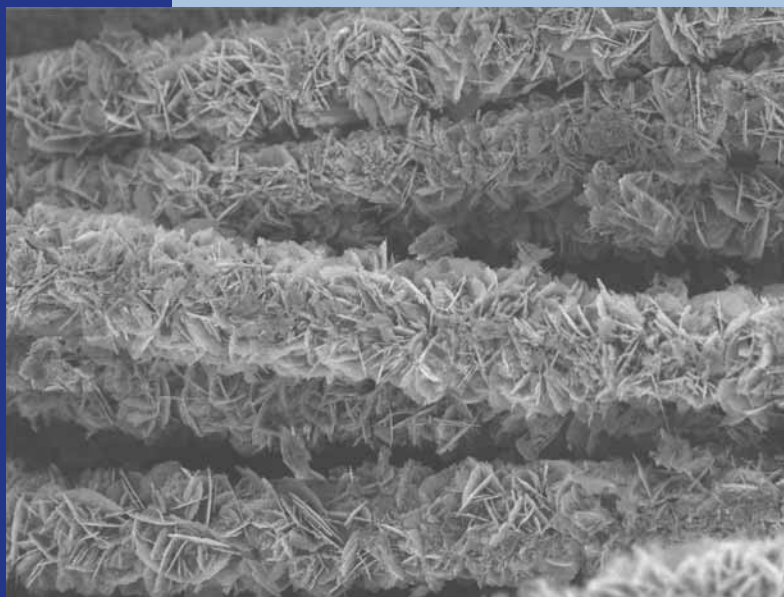
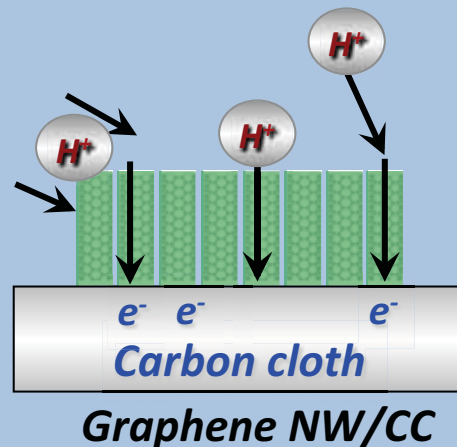
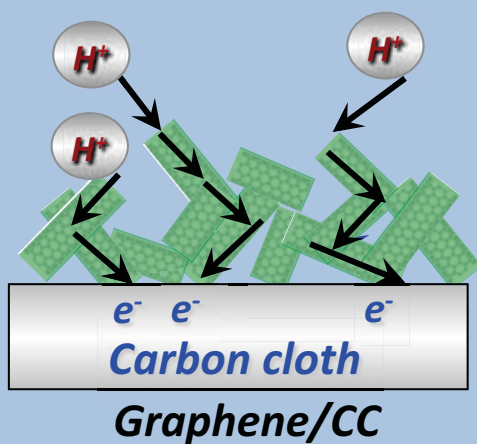
Supercapacitors



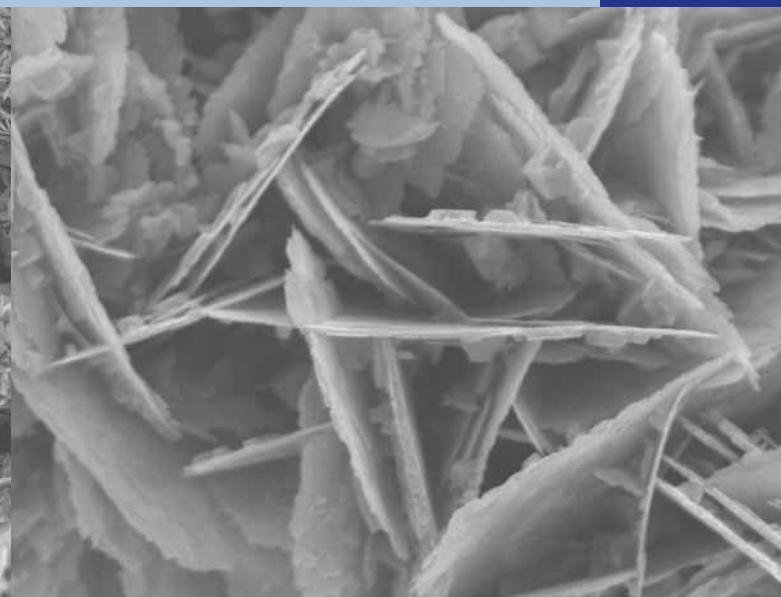
MPC: mesoporous carbon P3MT: poly(3-methylthiophene) CB: carbon black
 NRC: nitrogen-rich carbon PEDT: poly(3,4-ethylenedioxythiophene) ED: electrochemical deposition
 CNTA: carbon nanotube array CC: carbon cloth

GNWs on CC

Mixing Method vs. Direct Growth

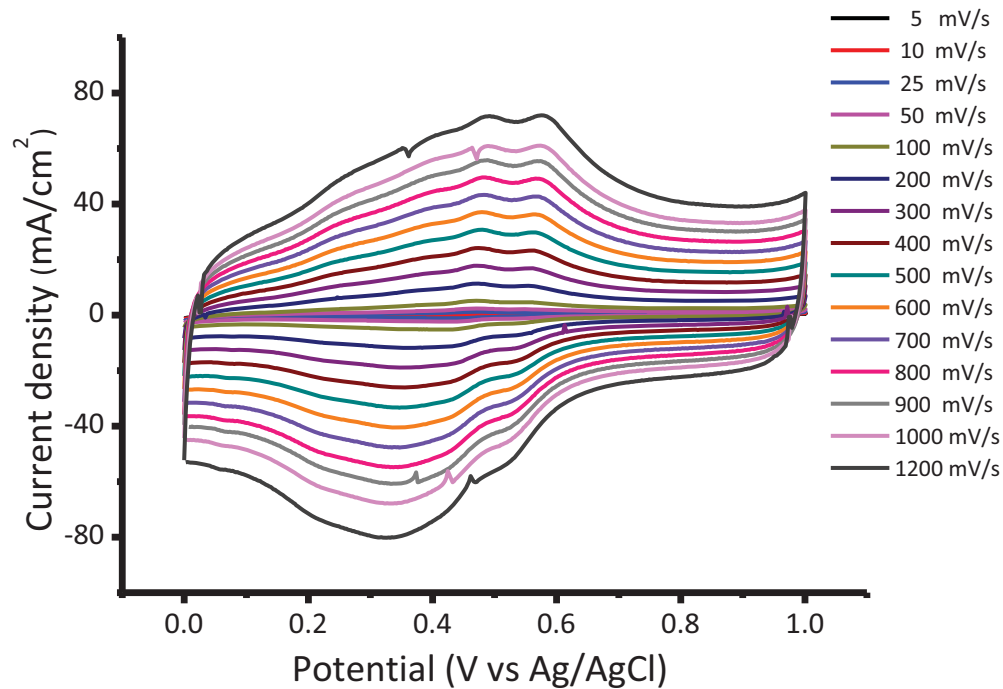


CCMS SEI 6.0kV X1,500 10 μ m WD 6.8mm

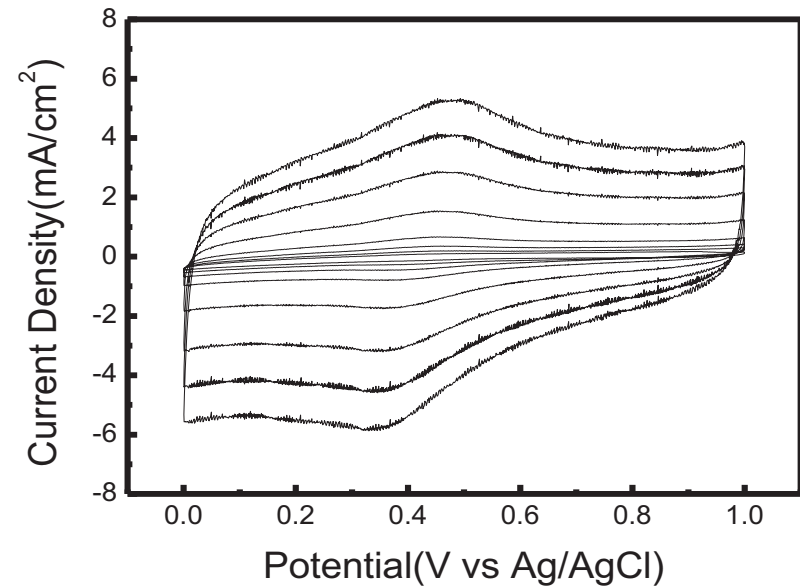


CCMS SEI 6.0kV X20,000 1 μ m WD 6.8mm

Capacitor Performance

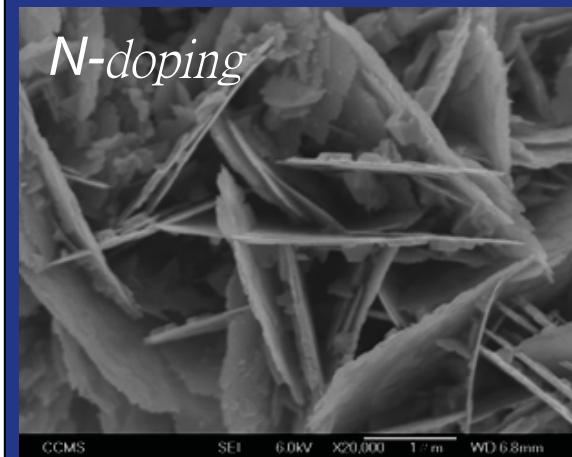
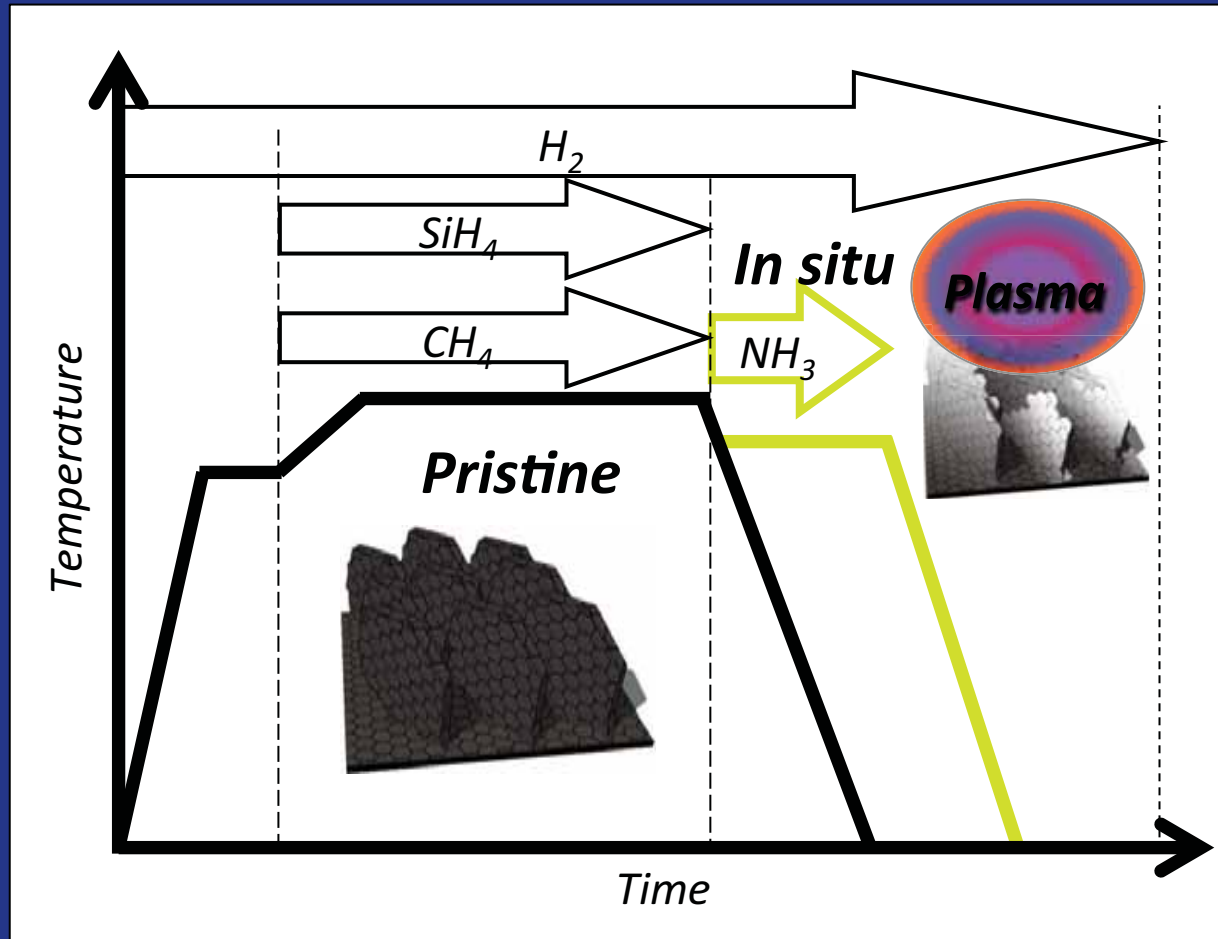


CNWs/CC

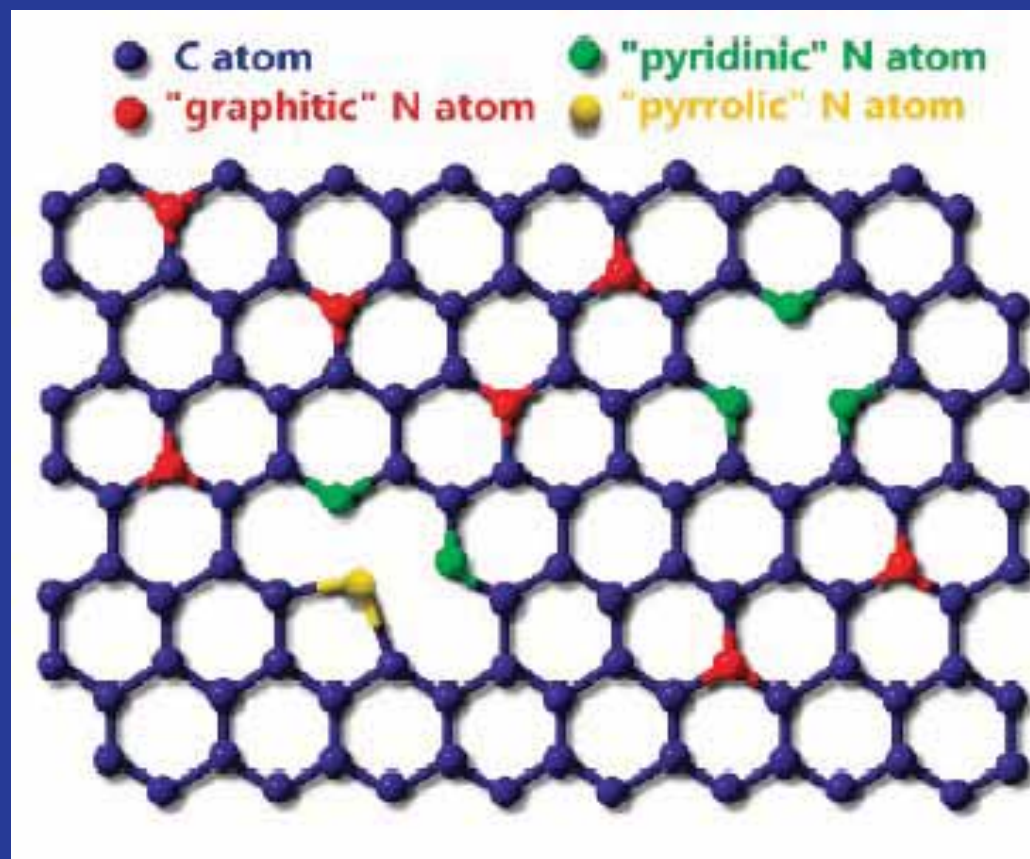


CC only

N-doped GNWs on Carbon Cloth



Where does N sit in graphene?



Pyridinic N (six-member ring) 398.2 eV

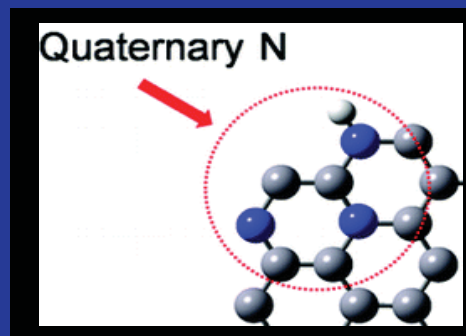
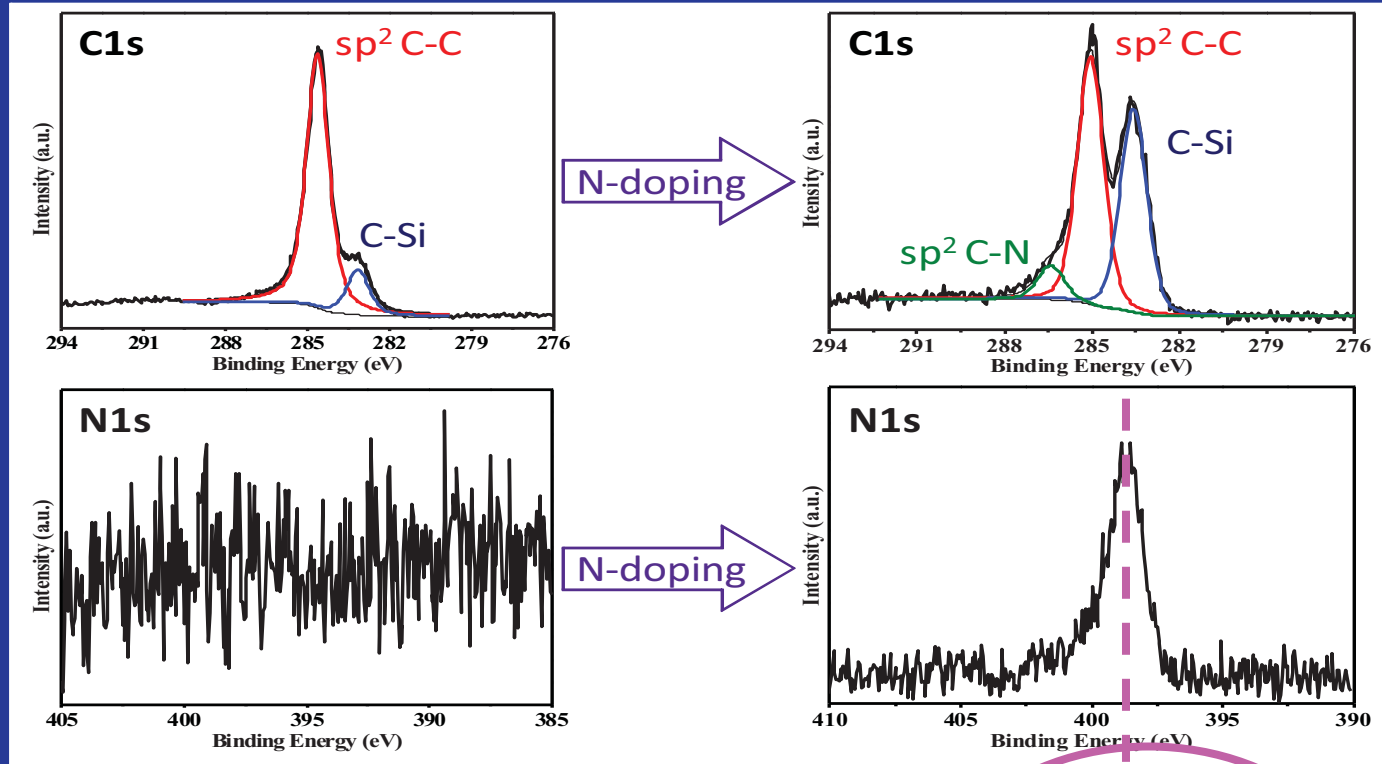
Pyrrolic N (five-member ring) 400.1 eV

Graphitic N 401.1 eV

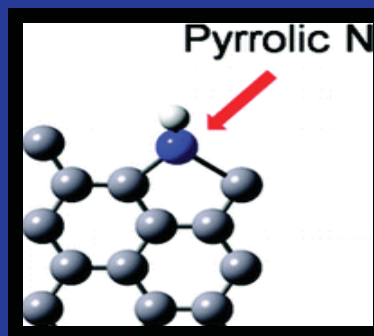
Li et al. JACS 131, 15939 (2009)

Wang et al. ACS Nano 4, 1790 (2010)

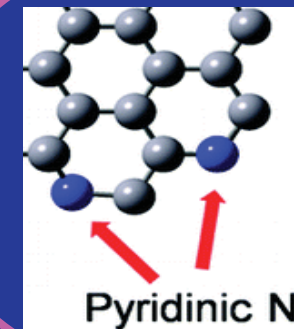
XPS: Pristine FLGs vs. N-doped FLGs



~401.1 eV



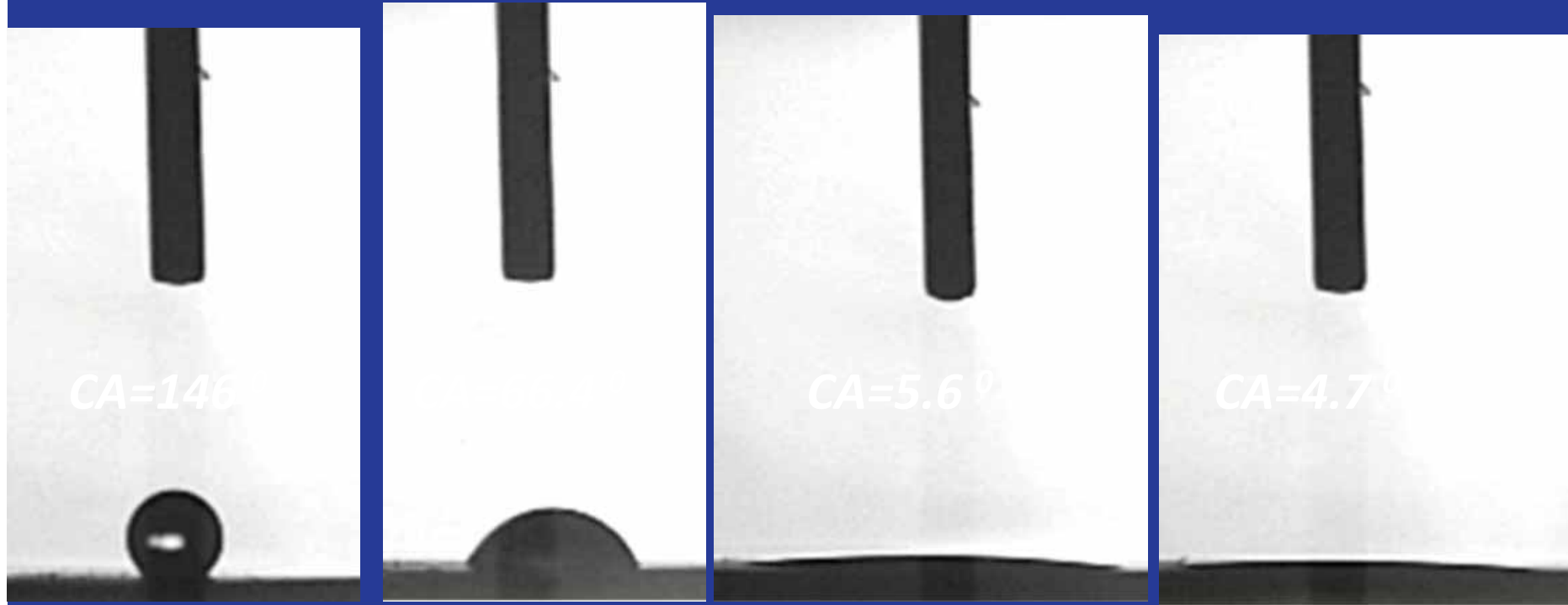
~400.1 eV



~398.2 eV

Tunable Wetting Property of Graphene:

Contact Angle vs. NH₃ Plasma Exposure Time



0 min

5 min

15 min

30 min

Hydrophobic



Hydrophilic

Ragone Plot

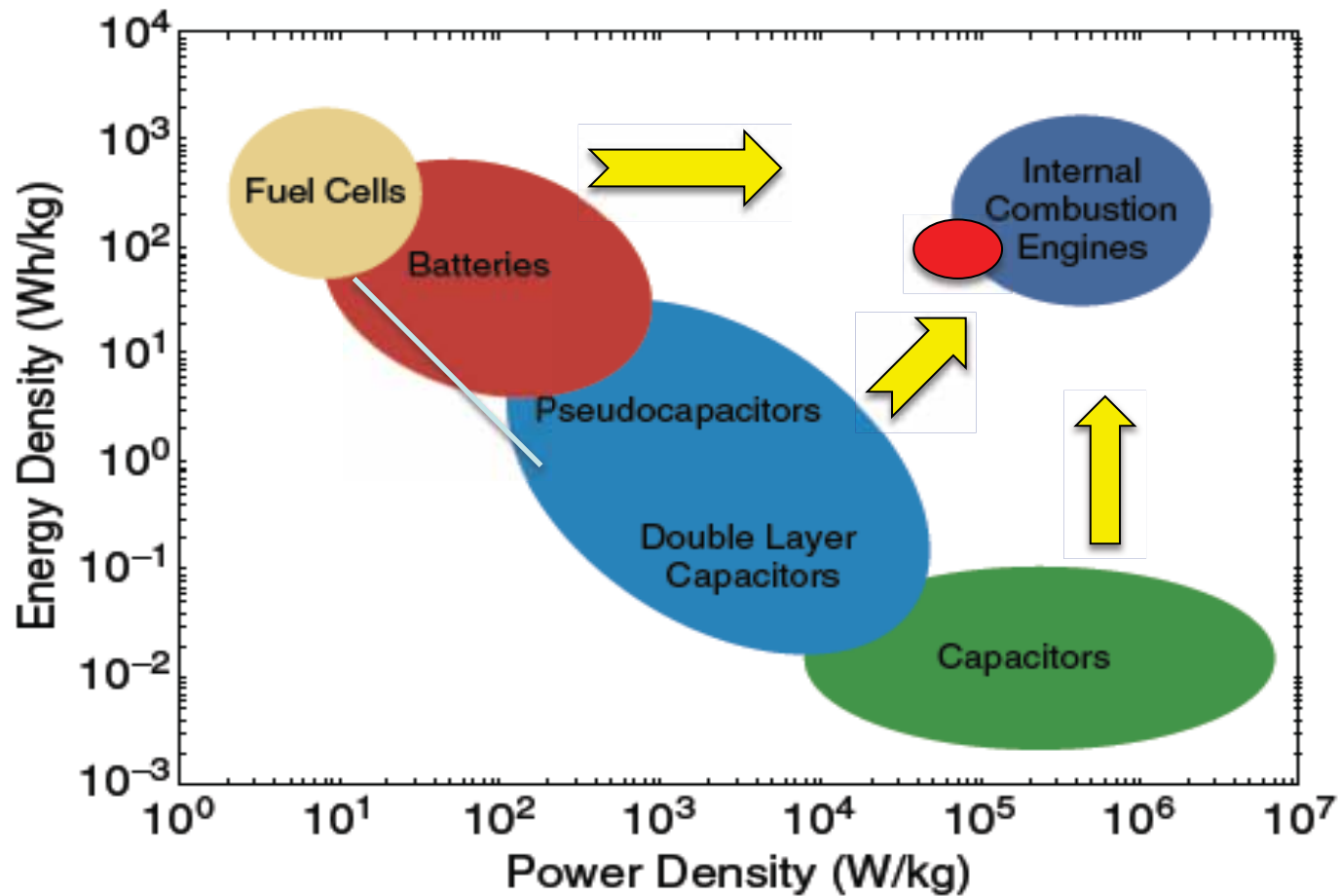
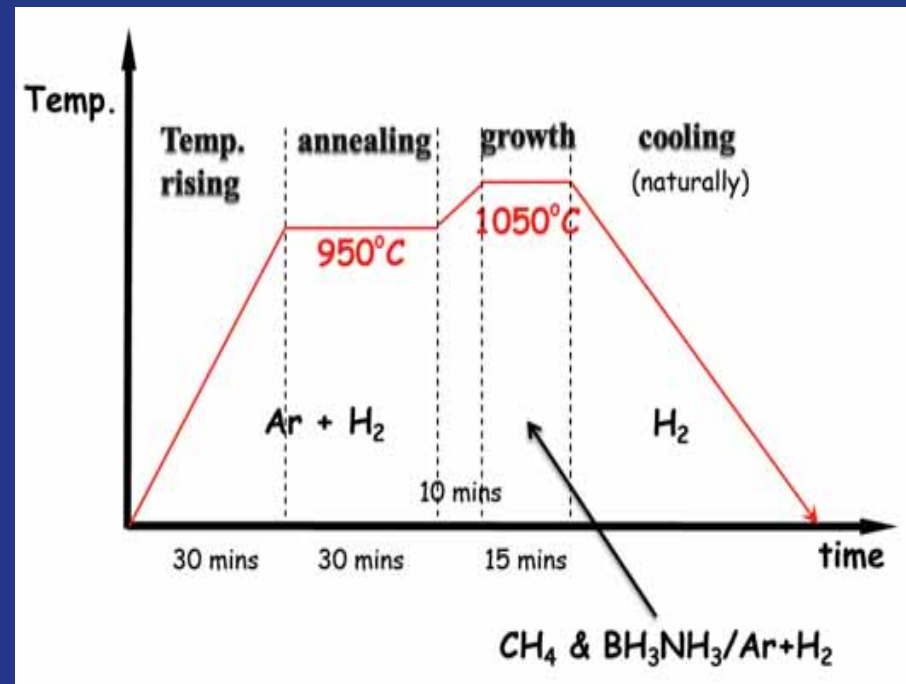
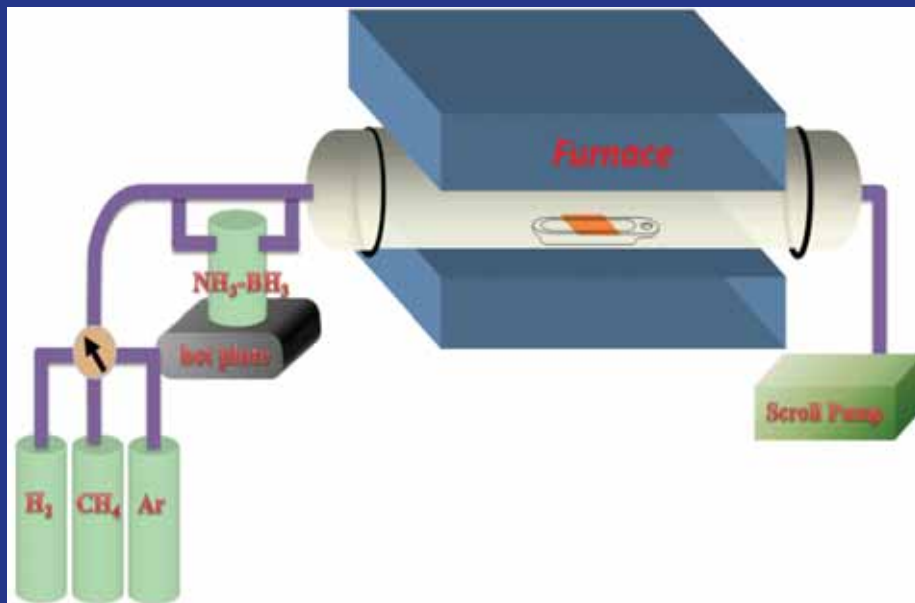


Figure 2. Comparison of the power density and energy density for batteries, capacitors, and fuel cells. (Energy is the capacity to do work; power is the rate at which work is done.)

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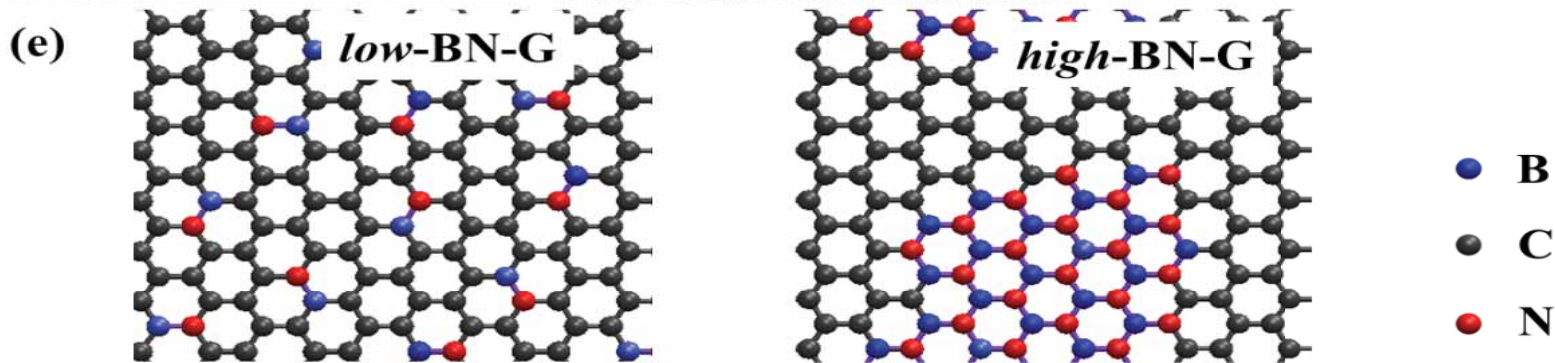
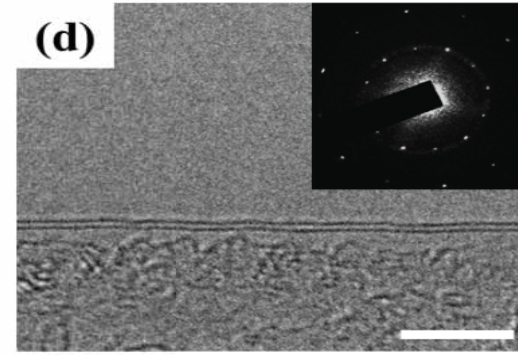
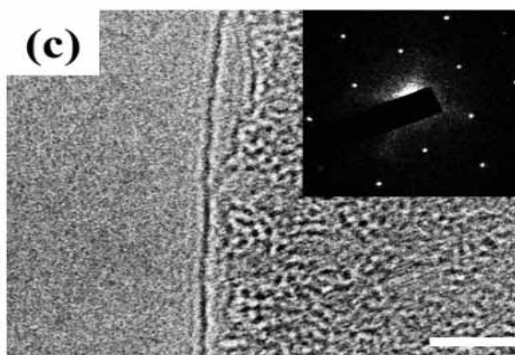
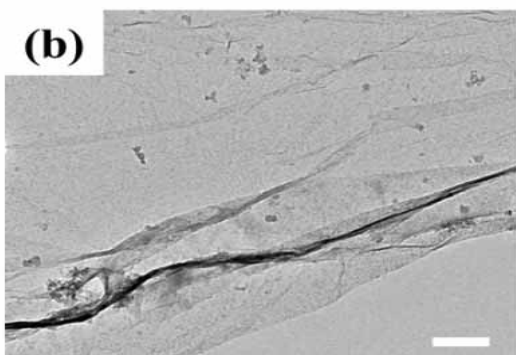
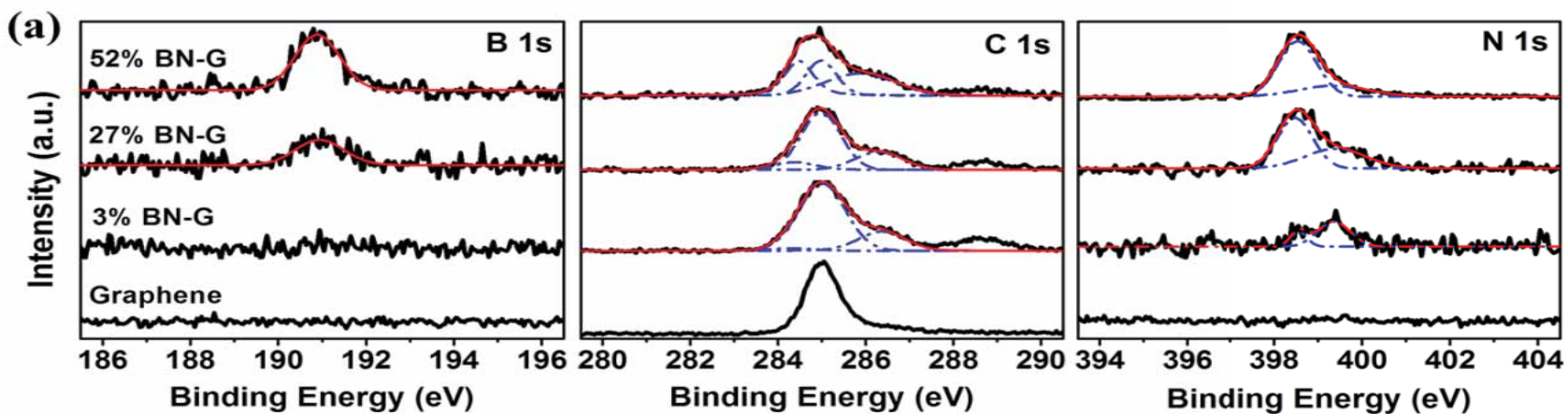
In-situ BN-doping



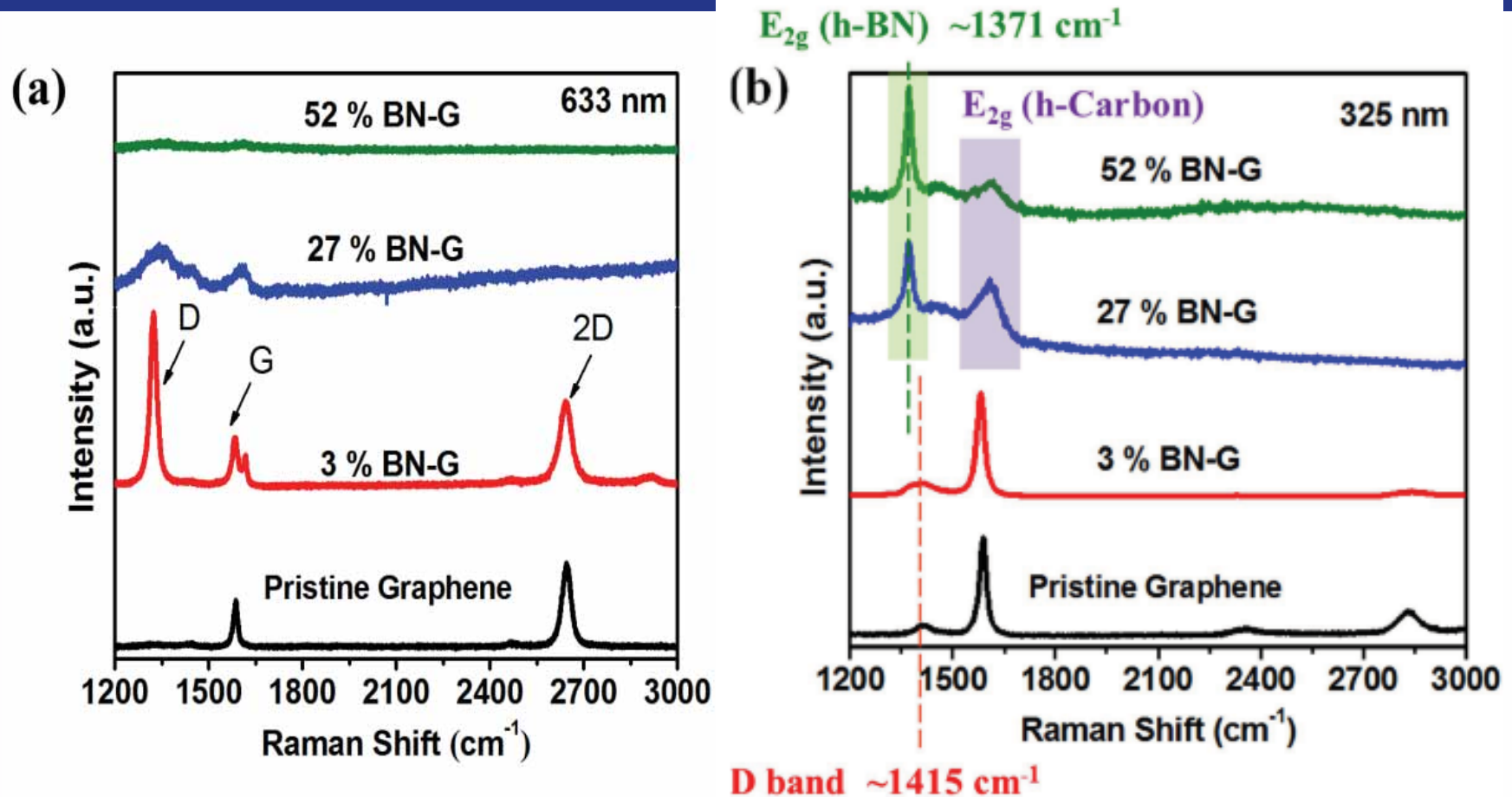
Advantages:

- *In situ BN doping*
- *Large-scaled growth*
- *Easy control of BN concentration in graphene*

XPS and TEM Analysis

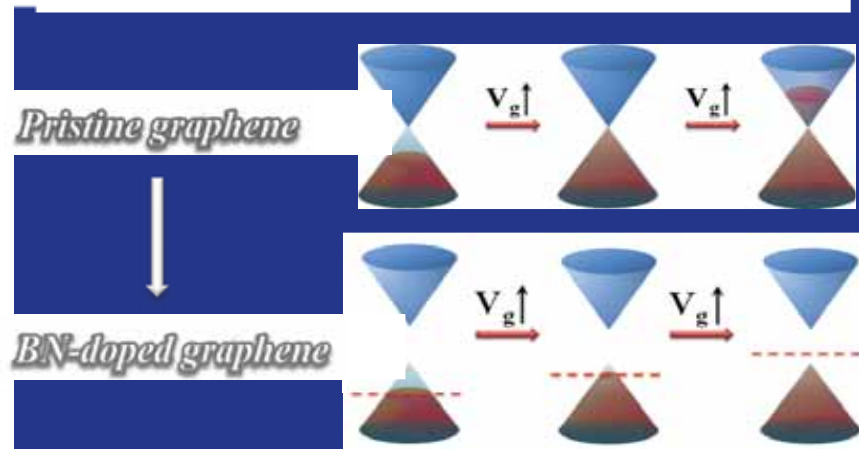
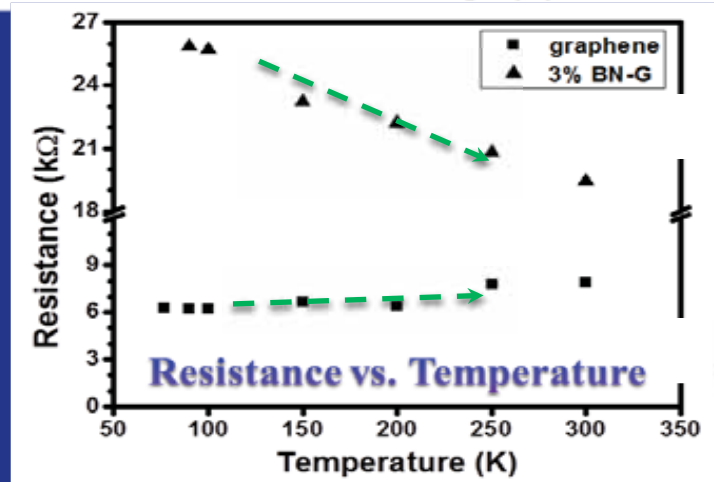
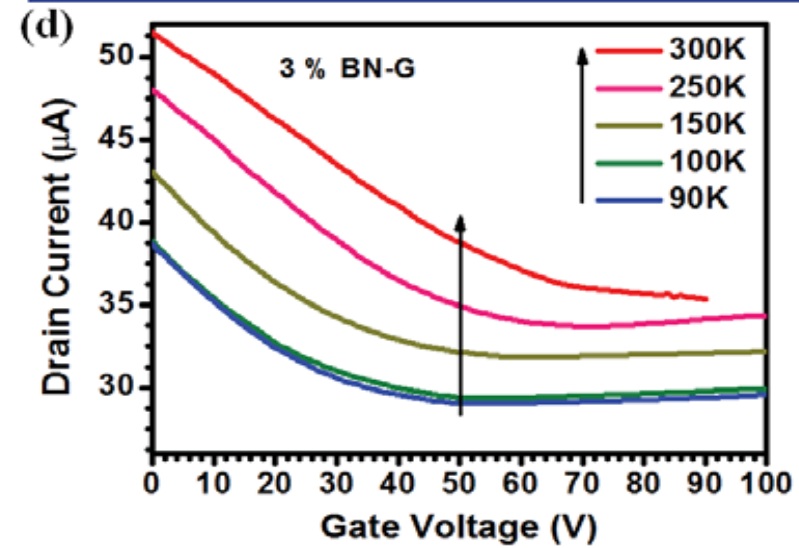
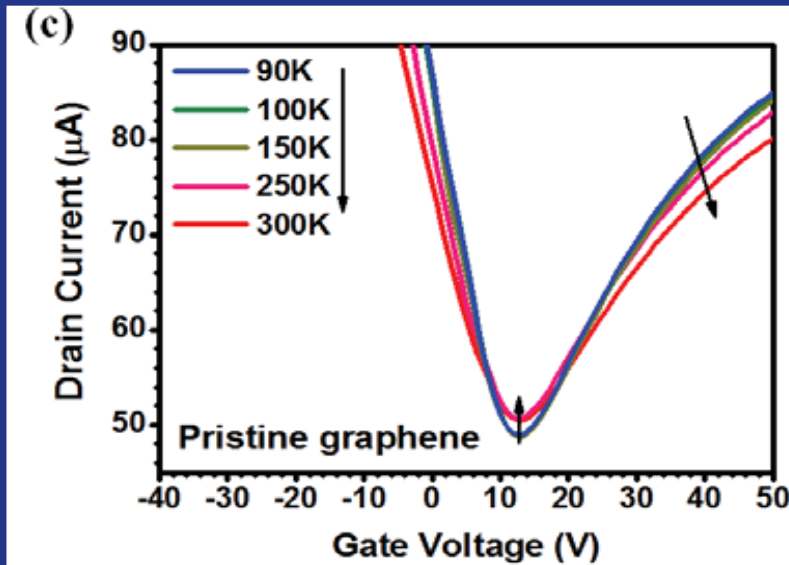


Raman Analysis



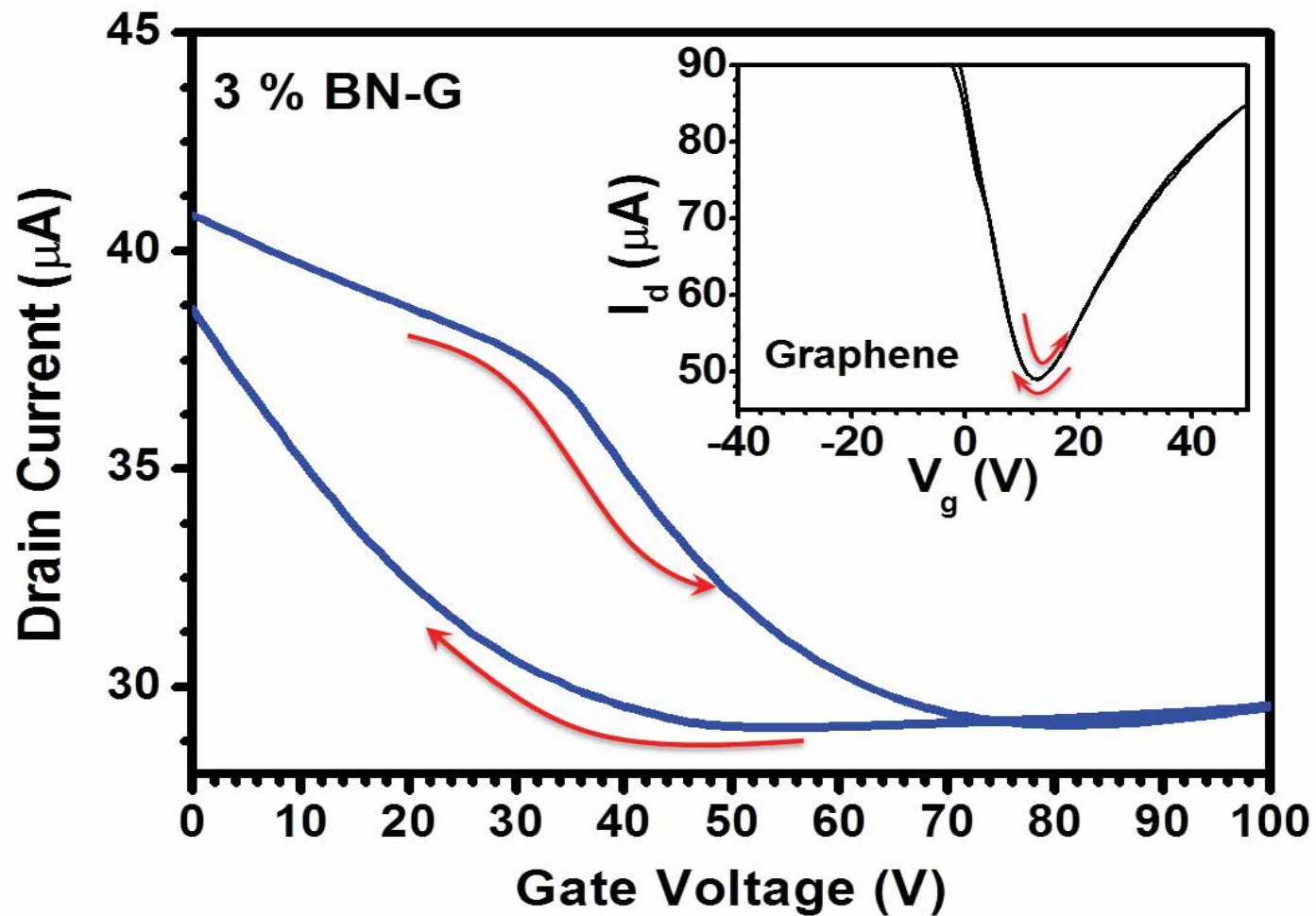
- *Clear evidence of BN domains in high BN-doped (>27%) graphene.*

FET Analysis

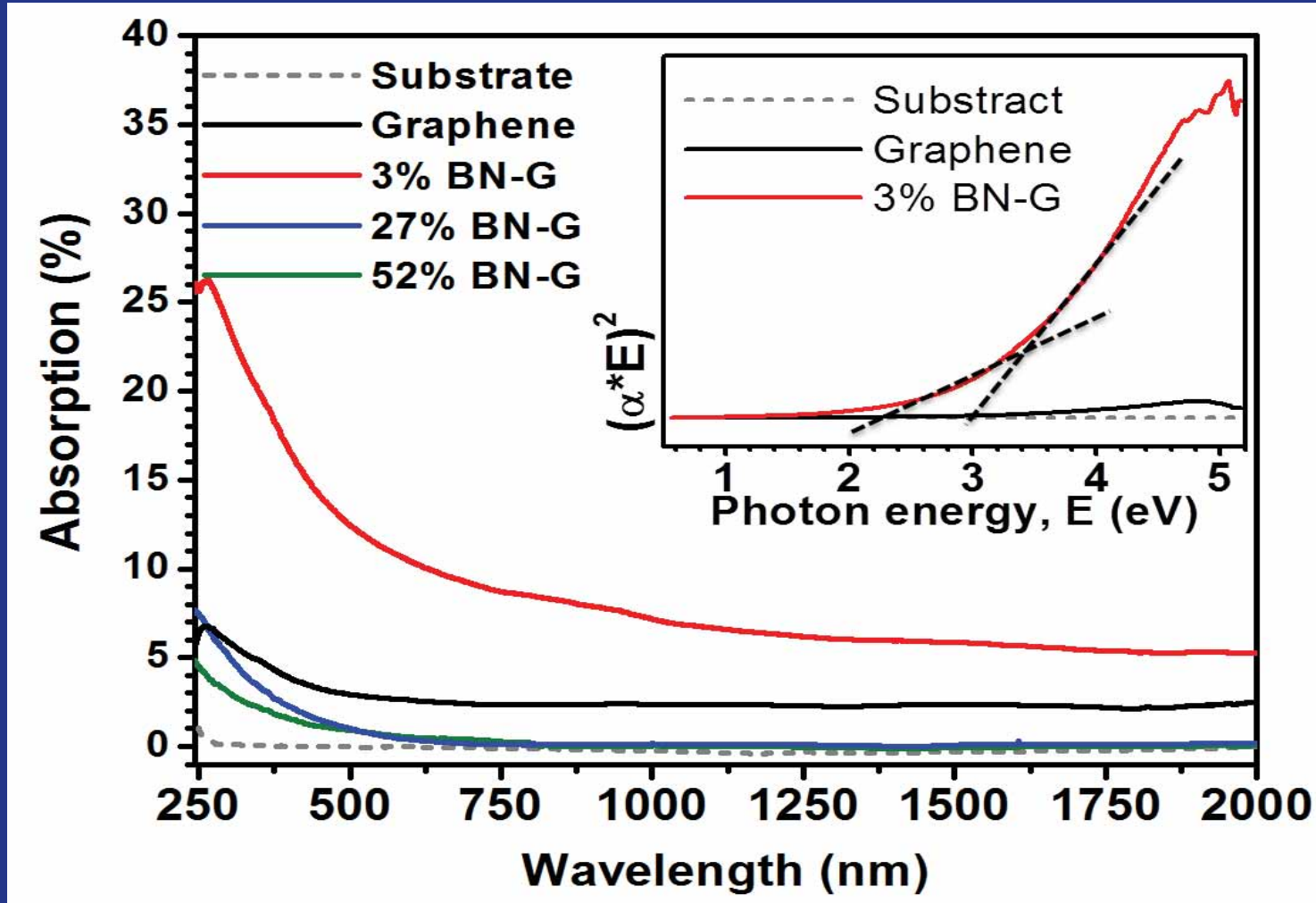


- **Semiconducting behavior is observed for 3% BN in graphene.**

FE Characteristic



Optical Absorption



Summary

- **N-doped GNWs/CC provides the material for EC applications such as supercapacitor.**
- **Evidence of gap-opening via BN-codoping of graphene is proposed.**

Acknowledgement

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Prof. S. Isota, Prof. W.F. Pong, Prof. Li-Chyong Chen

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AOARD, AFOSR