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High-Voltage Graphene Nanowalls Supercapacitor

Graphene Task Force
Project Manager

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Mechanical and Mechatronics Systems Research Laboratories

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Outline

- Graphene
- Growing Graphene Nanowalls
- Chemical Analysis and Electric Measurement
- High Voltage Supercapacitor Application
- Conclusions
- Acknowledgements

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Global Offices

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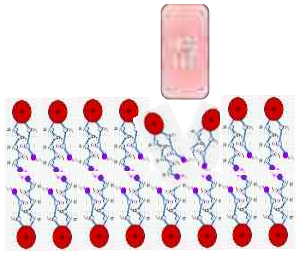
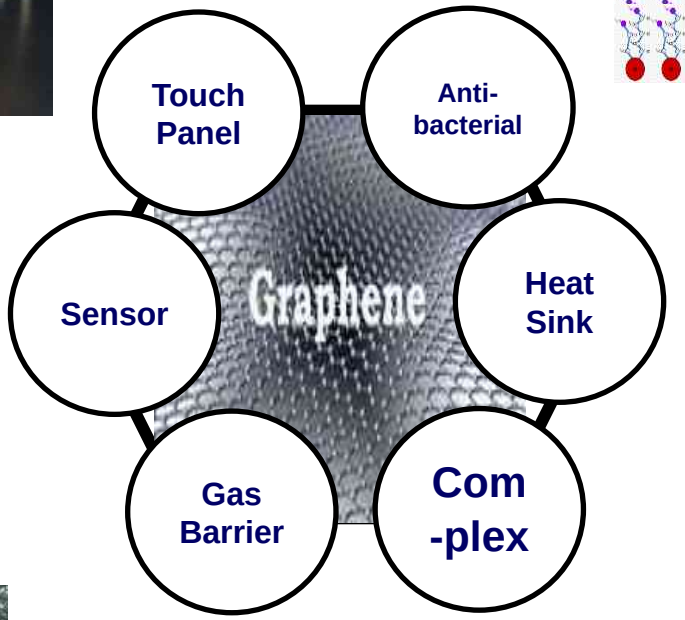
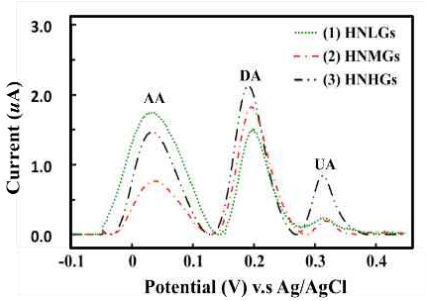
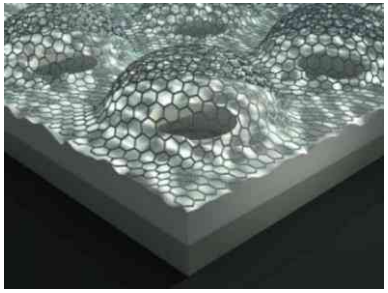
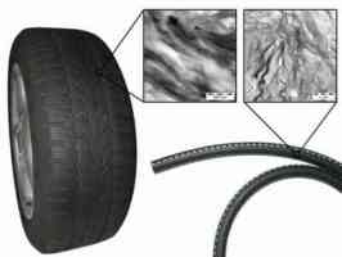
Pure Graphene Application











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Graphene in Taiwan
Maker (Graphene Powder)

Company 	Graphage 安炬科技	NITRONIX Nanotechnology Corporation 奈創科技	ANGSTRON MATERIALS 台灣安固強材料有限公司
Method	**Sheer Exfoliation**	**Electrolysis**	**Hummer Method**
Class	**Pure Graphene**	**rGOx**	**rGOx**
Product	**Anti-rust Coating Paint, Thermal Dissipation Paste, Composite**	**Shield Film, Thermal Dissipation Film, Conductive Additive**	**Gas Barrier, Paint, Thermal Dissipation Paste, Conductive Paste, Energy Storage Electrode**

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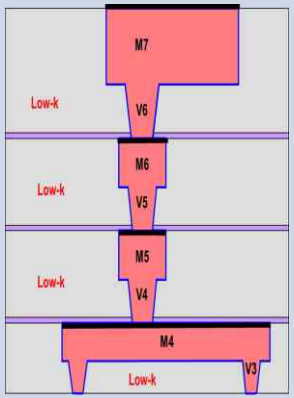
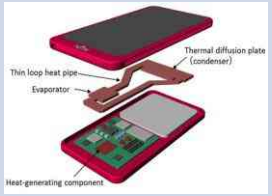
Graphene in Taiwan

User

Company	tsmc	TGC	FOXCONN	UPK
Application	**Device (BEOL)**	**Chemicals**	**Heat Sink**	**Energy Storage (Electrode)**





Supercapacitor

Power assisted Bike

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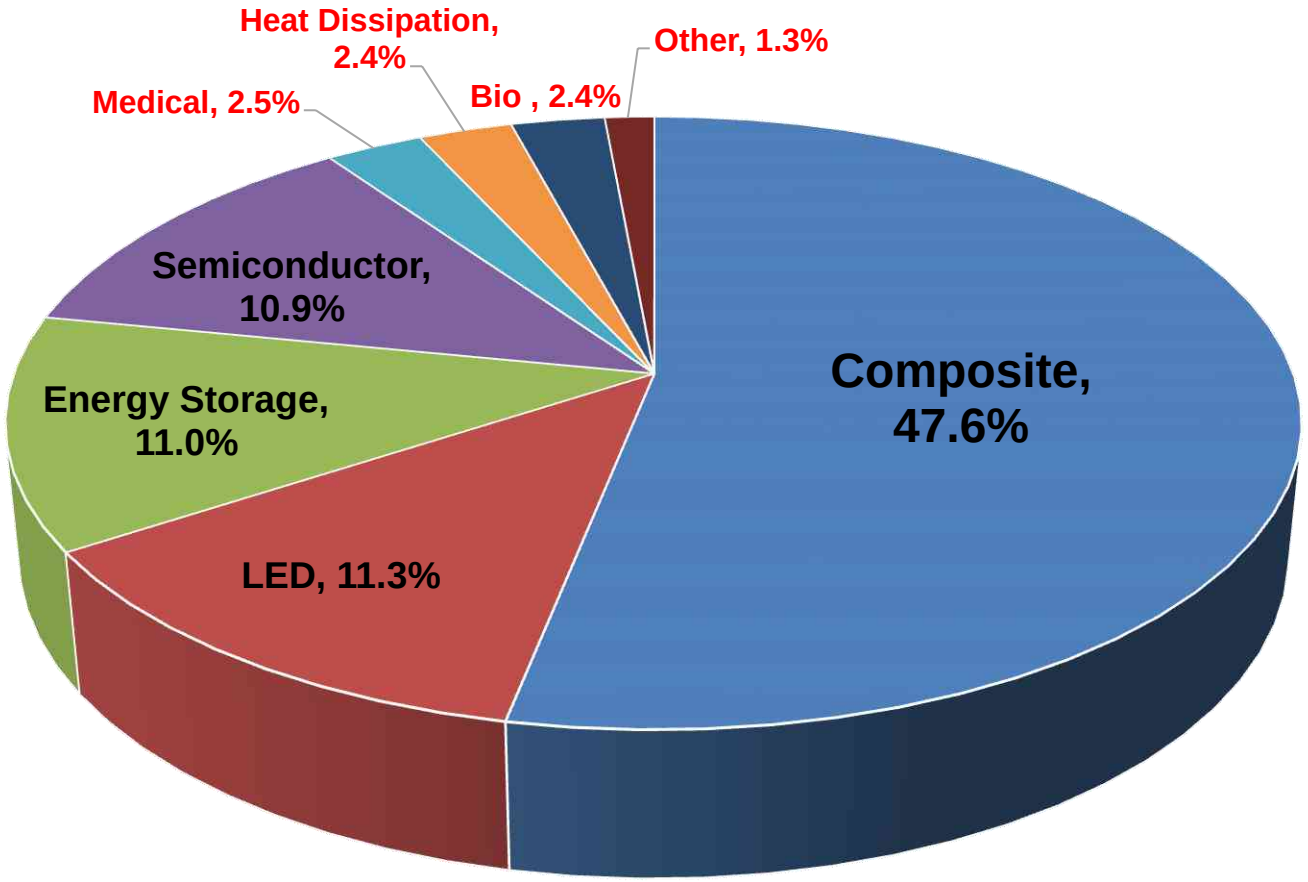
Patent Analysis



The top four fields almost occupy 80% graphene patent number.

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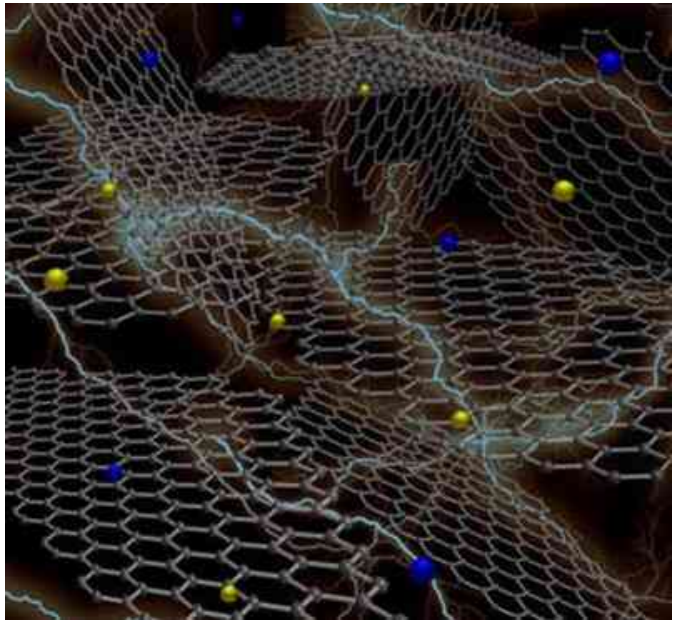
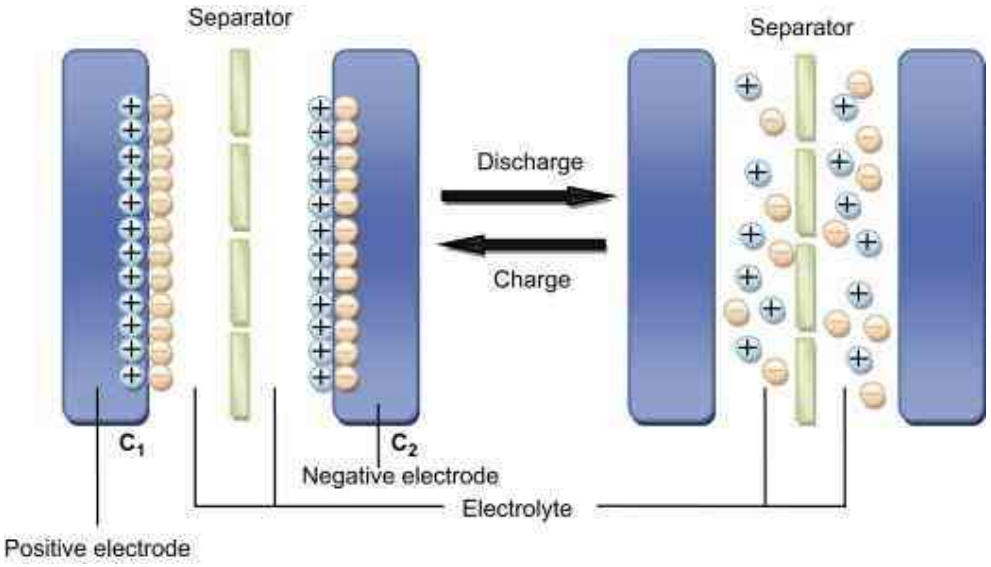
Graphene
Energy Storage

- High specific surface ratio (2630 m^2/g)
- High specific capacitor (530 F/g)
- High electron transport (200, 000 cm2·V−1·s−[1])





http://physicsworld.com/cws/article/news/2012/mar/20/laser-writer-makes-graphene-supercapacitors

http://energyeducation.ca/encyclopedia/Supercapacitor

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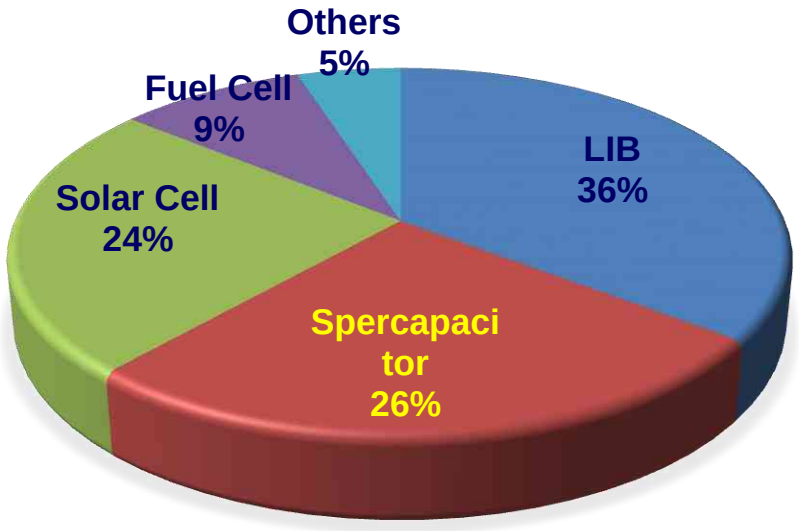
Graphene
Patent Analysis of Energy Storage

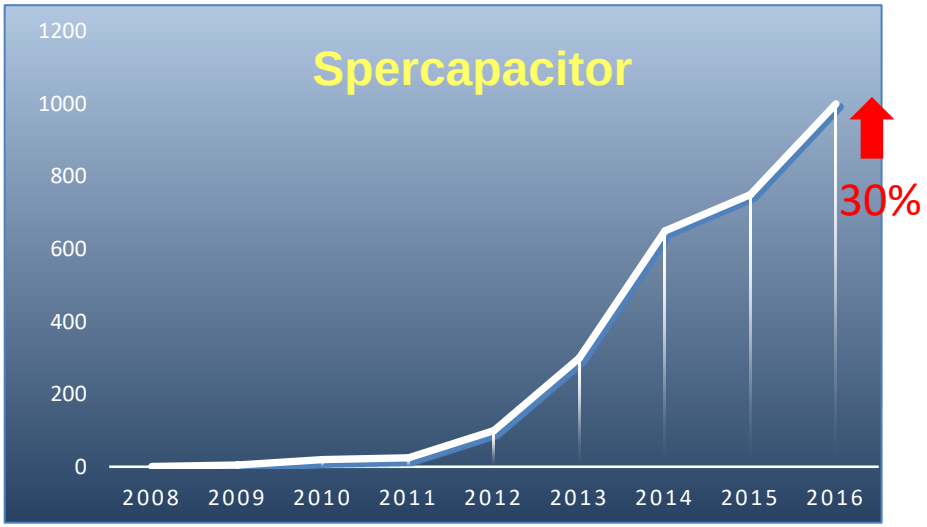
- Graphene supercapacitor can provide high power density (>2k W/h)
- Supercapacitor has longer cycle life (>10, 000 cycles)

Energy Storage Patent Analysis



~20,000 patents

Trend Chart of Supercapacitor Patent



30% annual growth

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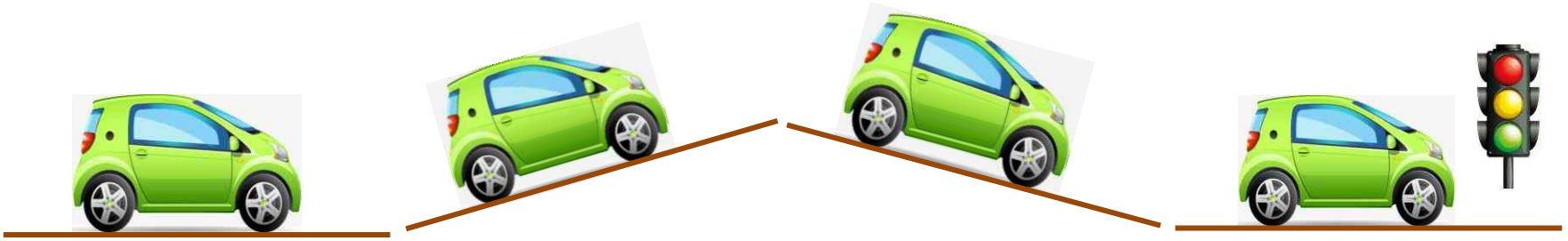
Graphene
LIB and Spercapacitor

Electric Vehicle (high power output/input)



Start / Accelerate | **Uphill** | **Downhill (Charge)** | **Start/Stop**

LIB. 3.7V

Supercap. 2.8V

Volume ?

//www.ecmag.com/section/your-business/tesla-gives-ev-battery-industry-jolt

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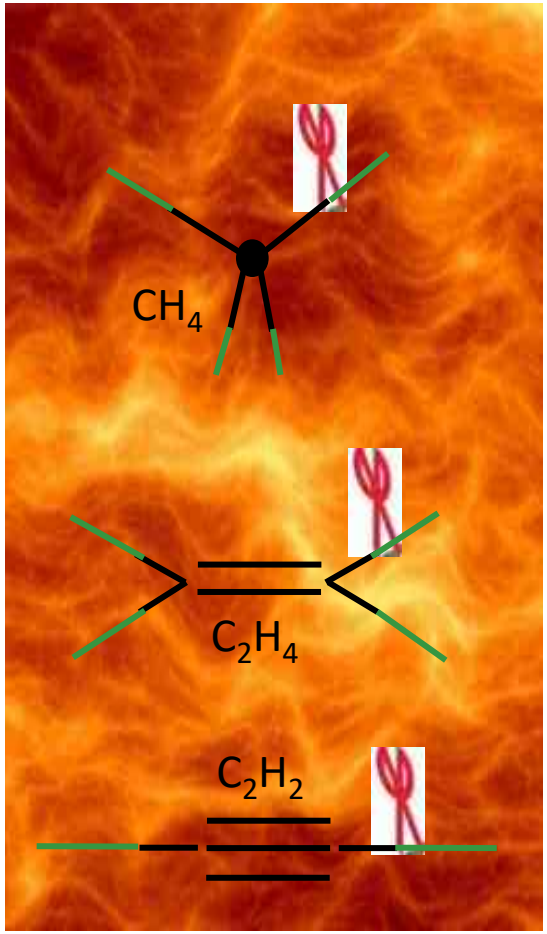
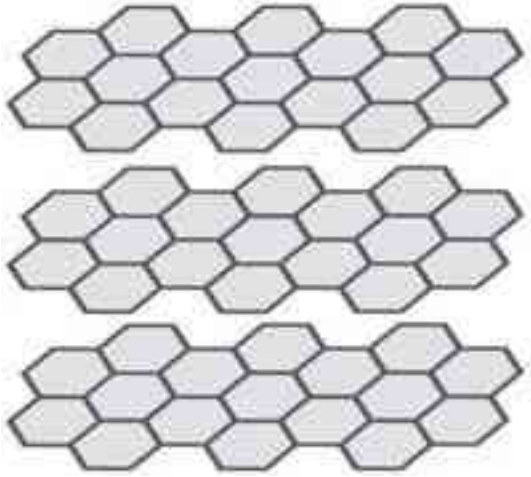
Bottom-Up Synthesis

Graphene





J. Mater. Chem., 2011, 21, 10685–10689

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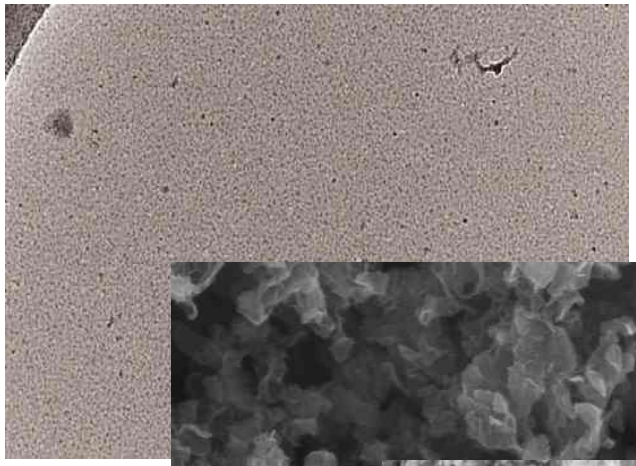
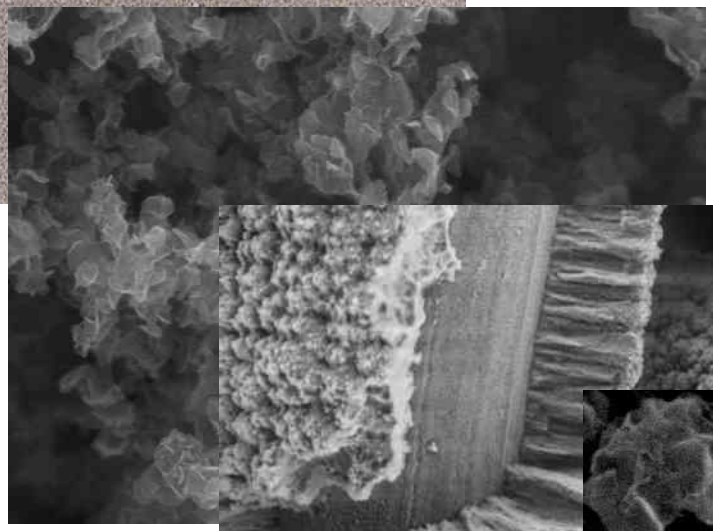
Bottom-Up Synthesis

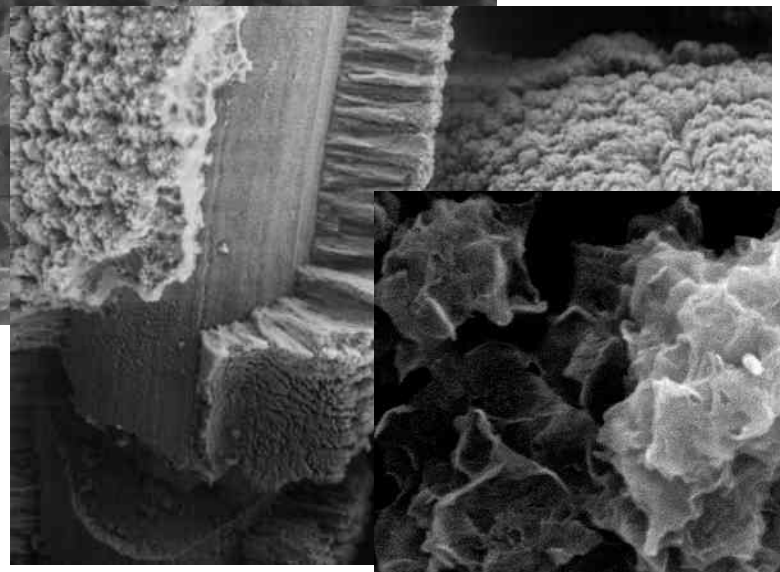
Graphene Allotrope



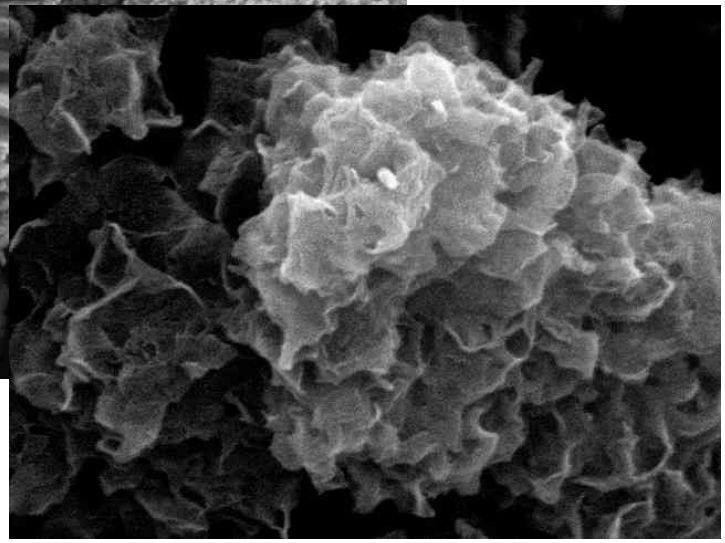
Graphene Film
(w/i substrate Cu or Ni)
(ECR、 PECVD、 APCVD)



Graphene Power (Pallet)
(w/o substrate)
(MPT、 MPJ) < 1 atm



Graphene Nanowalls
(w/i substrate Ti、 C、 Fe、 Ni)
(MPT、 ECR) < 1 atm



Graphene Flower
(w/o substrate)
(TCP、 RPS) < 1 atm

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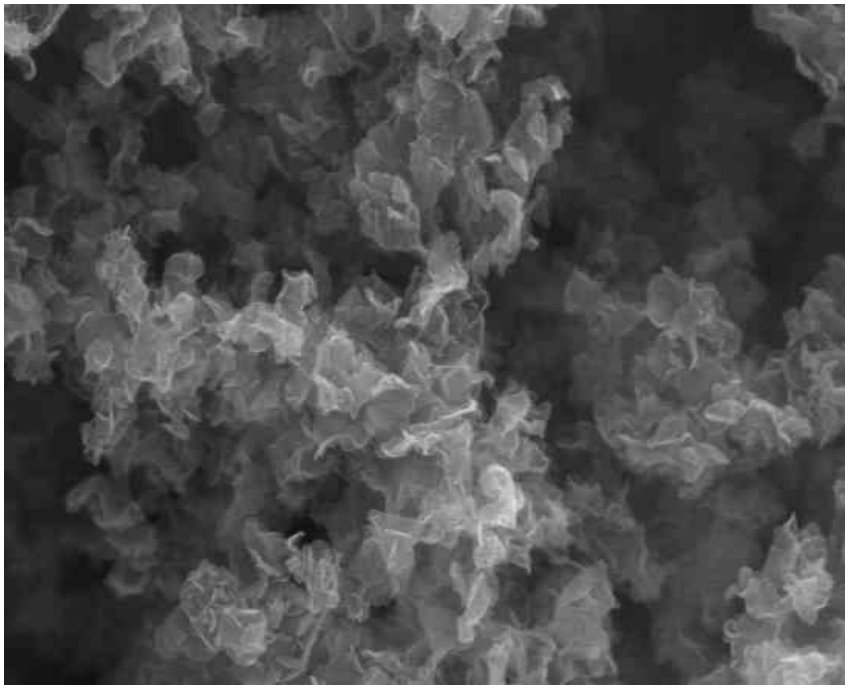
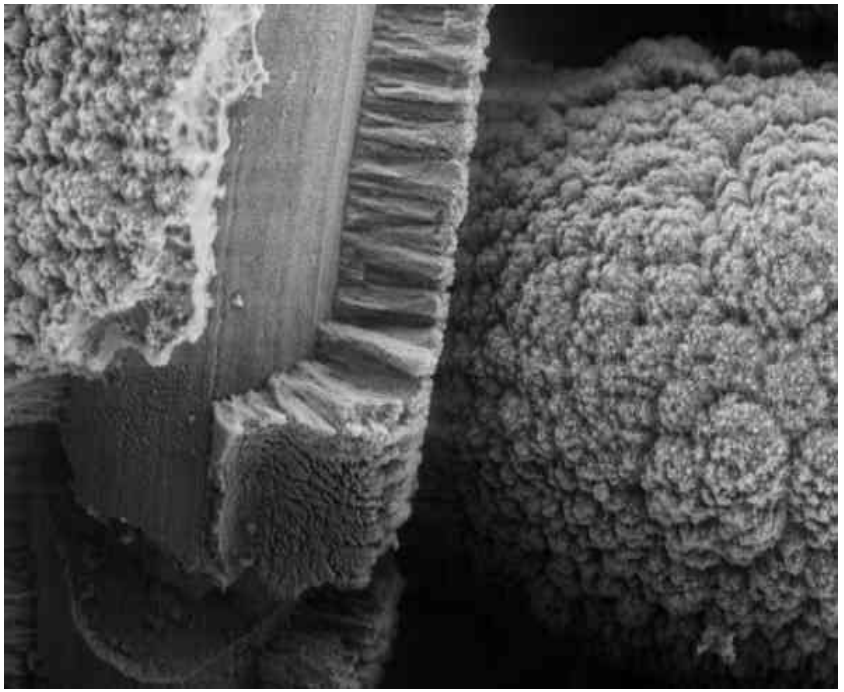
Supercapacitor
Electrode Materials

> 100 torr



Graphene Powder

< 100 torr



Graphene Nanowall

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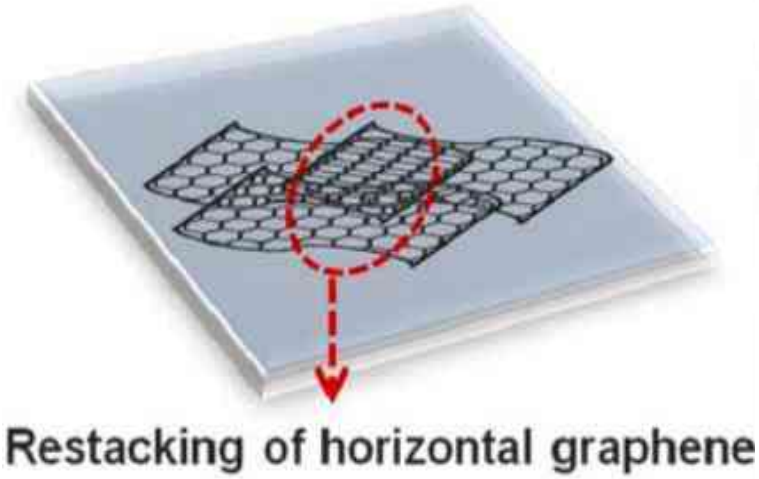
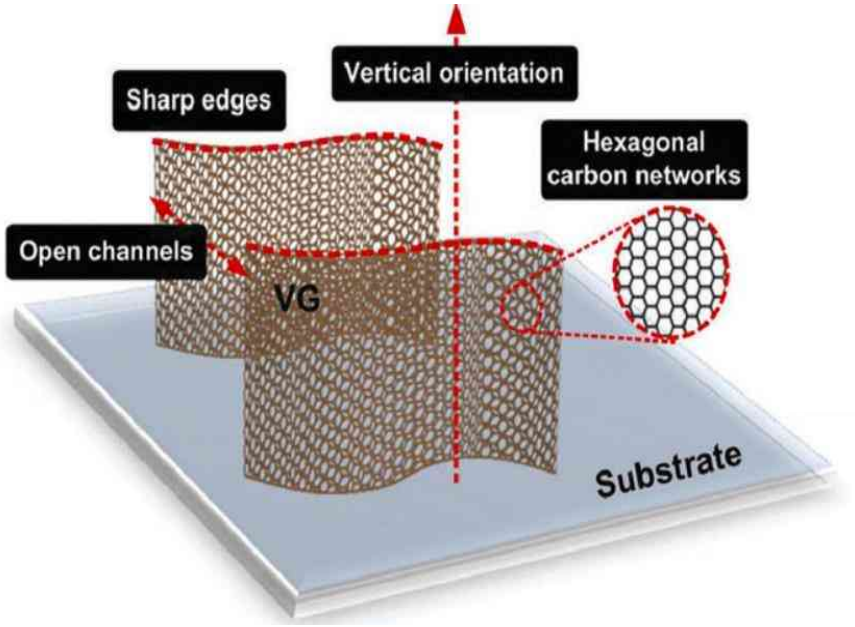
Supercapacitor
Powder vs GNW





Chen, J., Bo, Z., & Lu, G. (2015). Vertically-Oriented Graphene. Springer International Publishing Switzerland, DOI, 10, 978-3.

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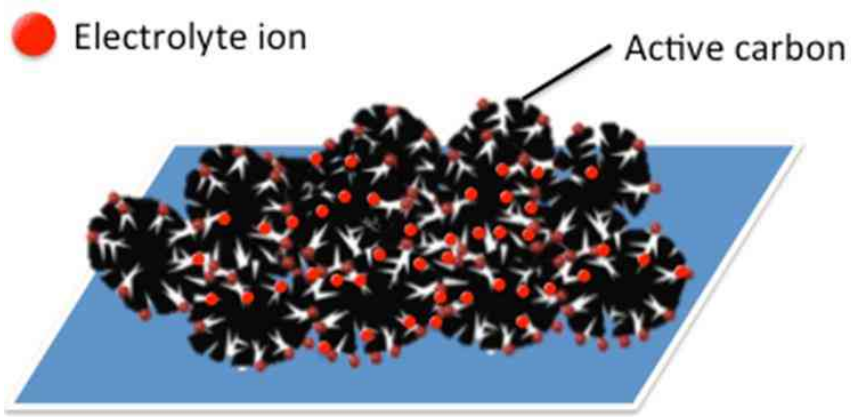
Supercapacitor
Powder vs GNW



Graphene powder with a lot reactive edges and random distribution. The is easy to happen reaction between the electrolyte and active material. (oxidation or HER)
➔ Cell voltage can't higher than 2.8V.

GNW with few edge and regular distribution and it provide these inner face between active material and electrolyte.
➔ without oxidation reaction or HER.
➔ Cell voltage raise to 4V.

Naoi, K. (2010). 'Nanohybrid capacitor': the next generation electrochemical capacitors. Fuel cells, 10(5), 825-833.

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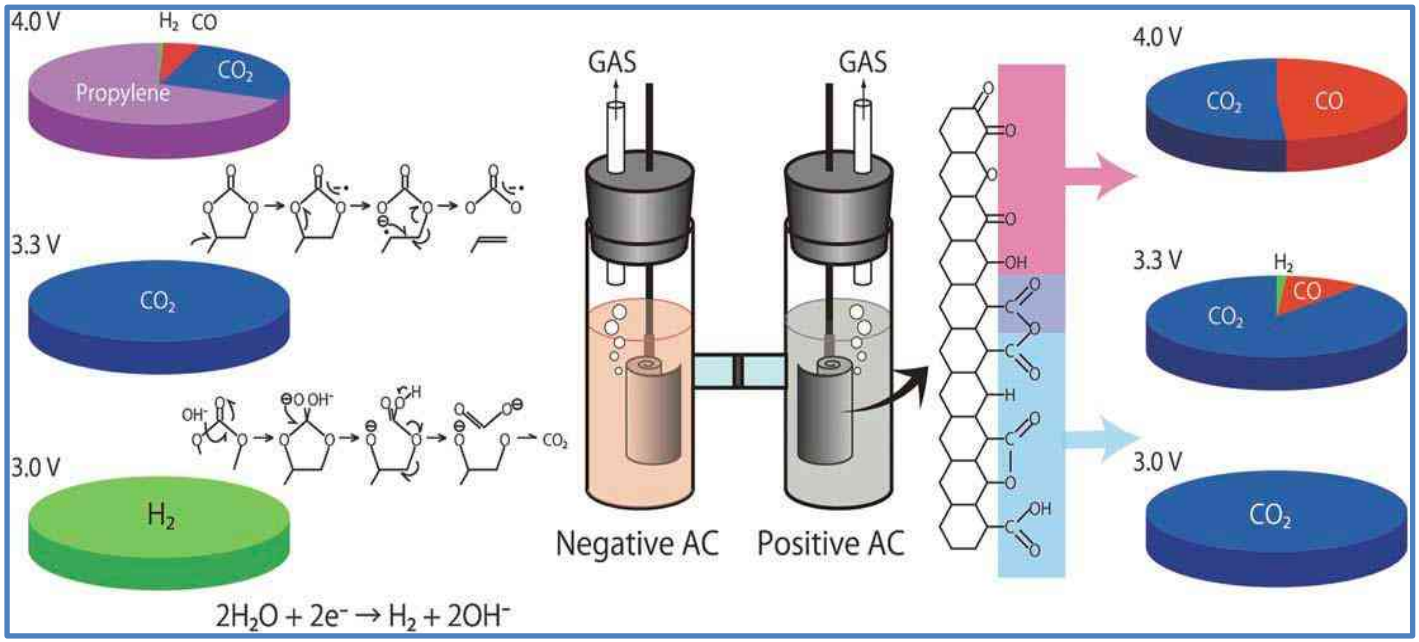
Supercapacitor
Edge Reaction

Reduce the electrode activity to electrolyte/the interface reactions

HER

Oxidation



Gas evolution from an EDLC cell upon over-voltage application.

Naoi, K. (2010). 'Nanohybrid capacitor': the next generation electrochemical capacitors. Fuel cells, 10(5), 825-833.

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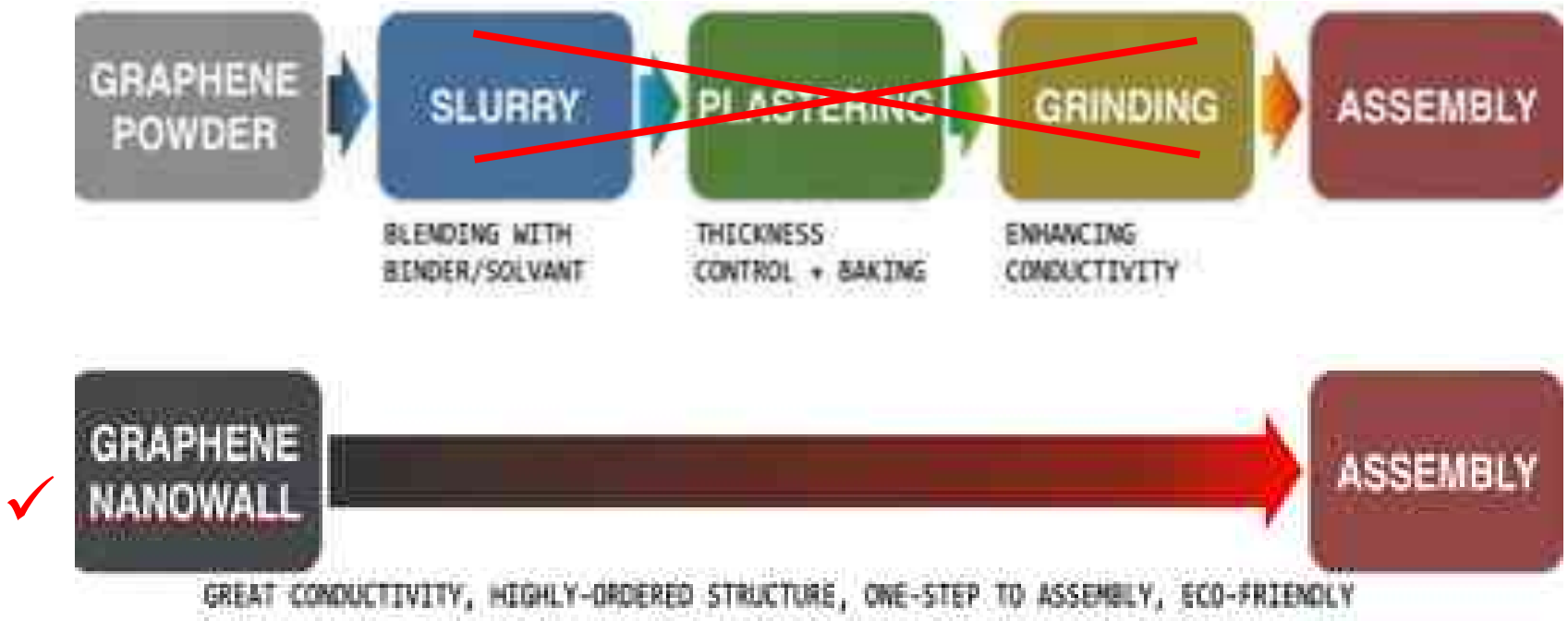
Supercapacitor
Powder vs GNW



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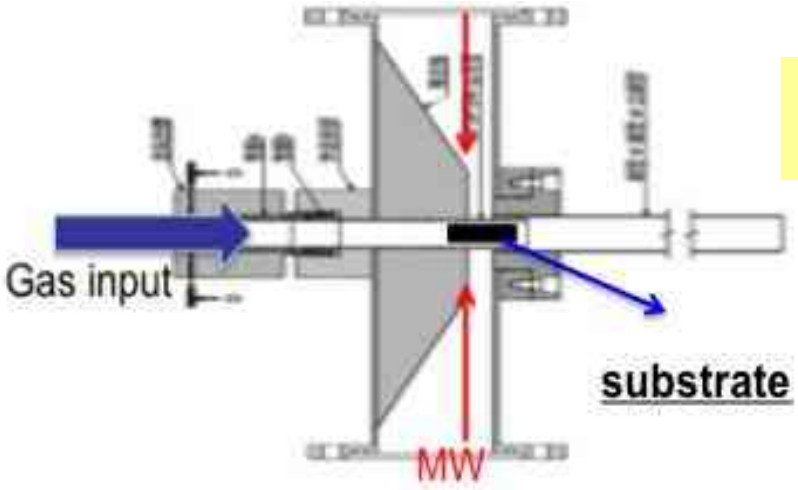
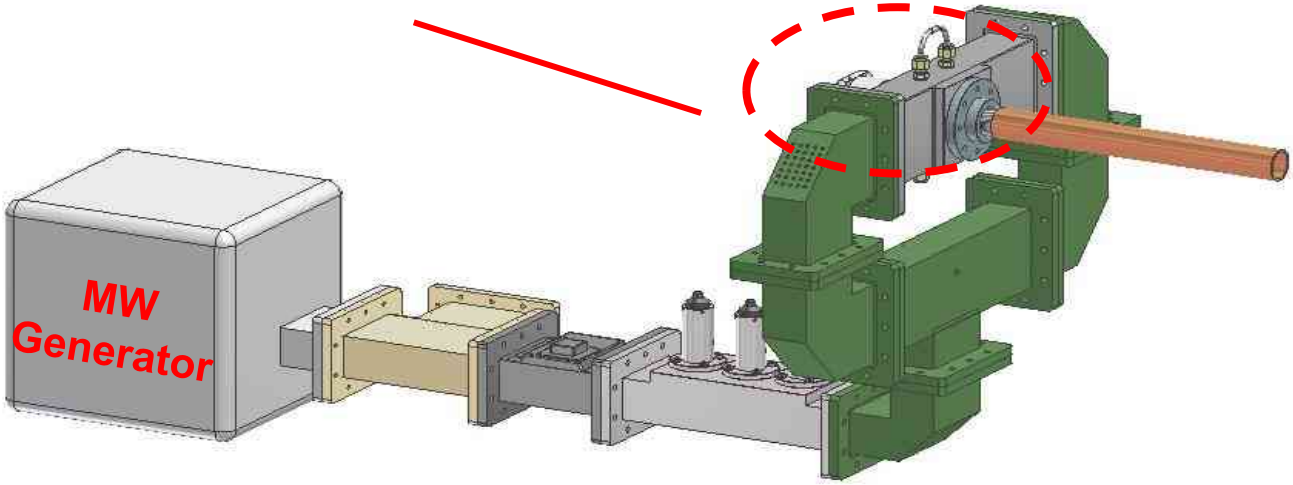
MPT CVD
Bottom-Up Synthesis

Ar
CH_4
N_2



Ionization > 40%
Plasma Density > 1E14 ion/cm^3

Reaction Area



Microwave Plasma enhanced Chemical Vapor Deposition

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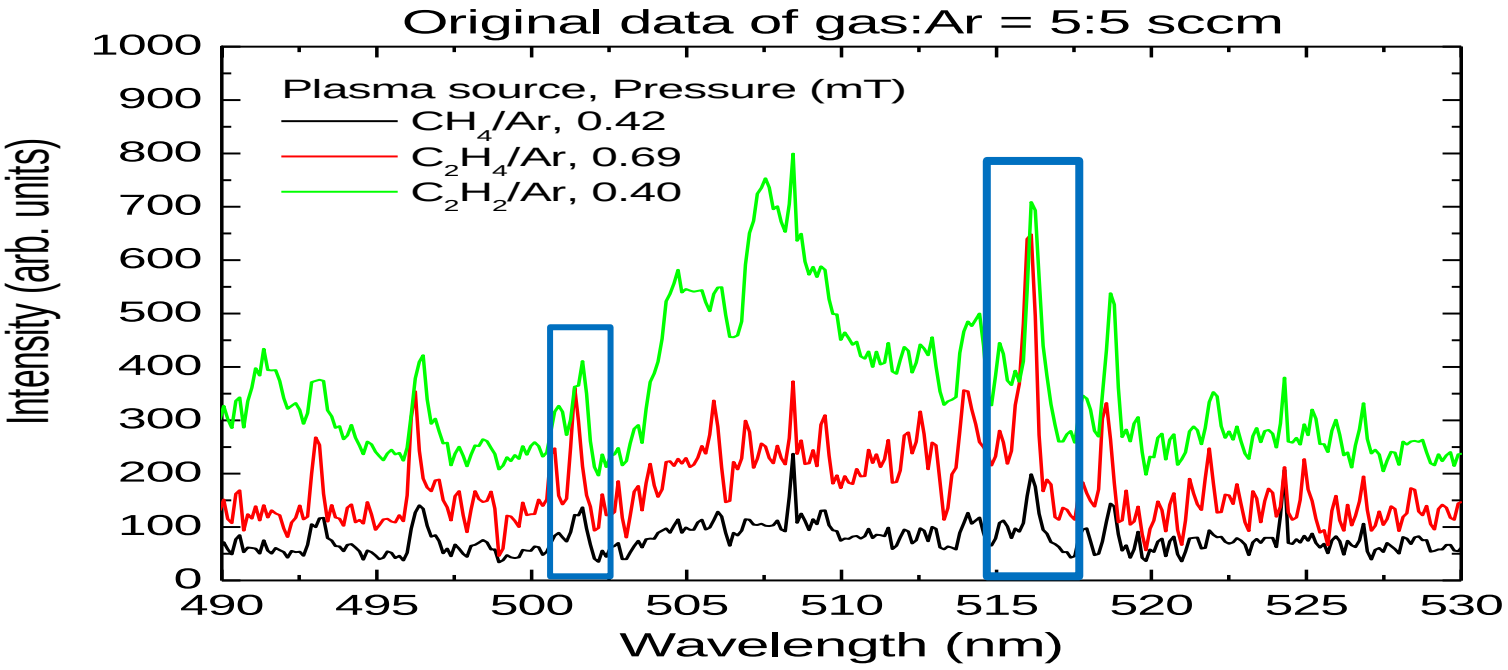
Doped Graphene Application
Plasma Analysis

Optical Emission Spectra



C_2H_2 can provide abundant C2 radicals.

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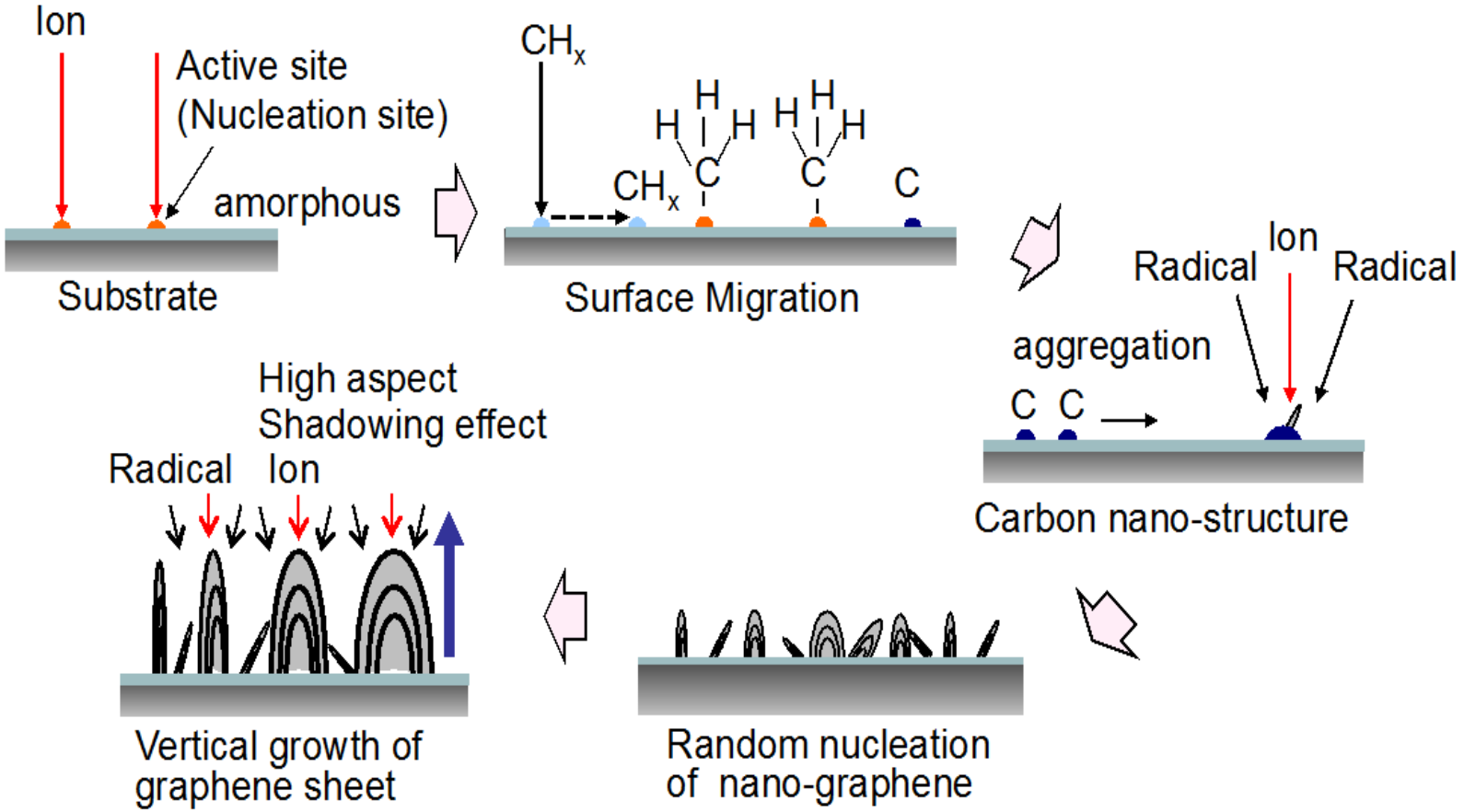
Growing Graphene Nanowalls
MPT CVD



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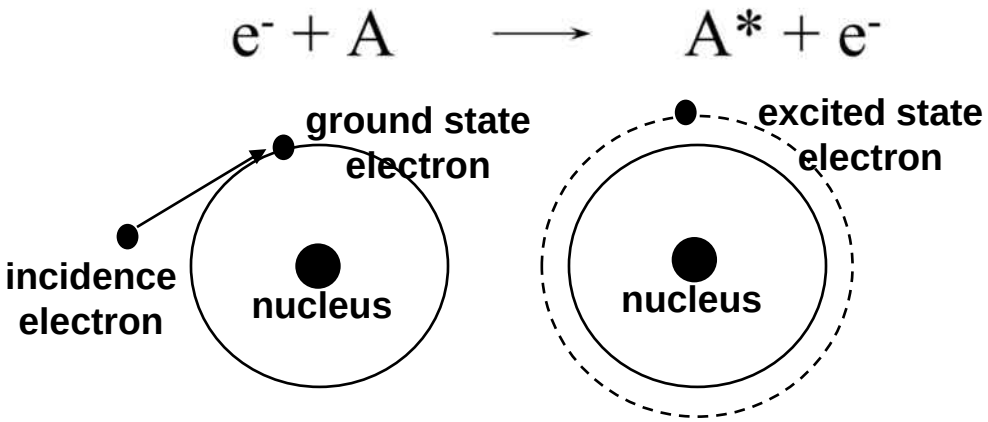
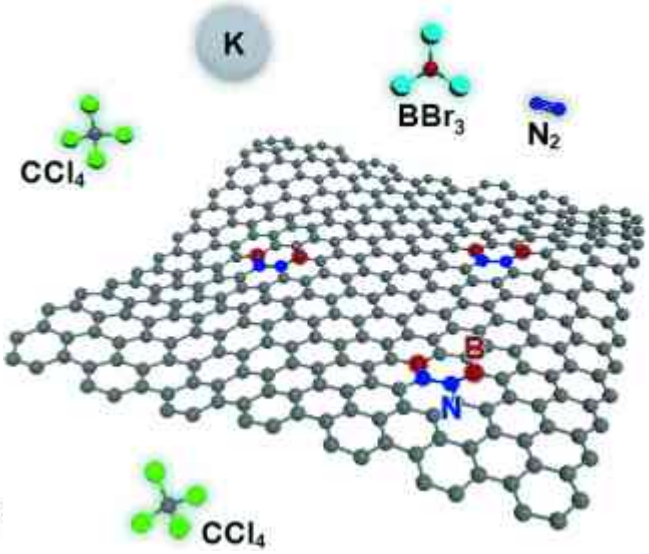
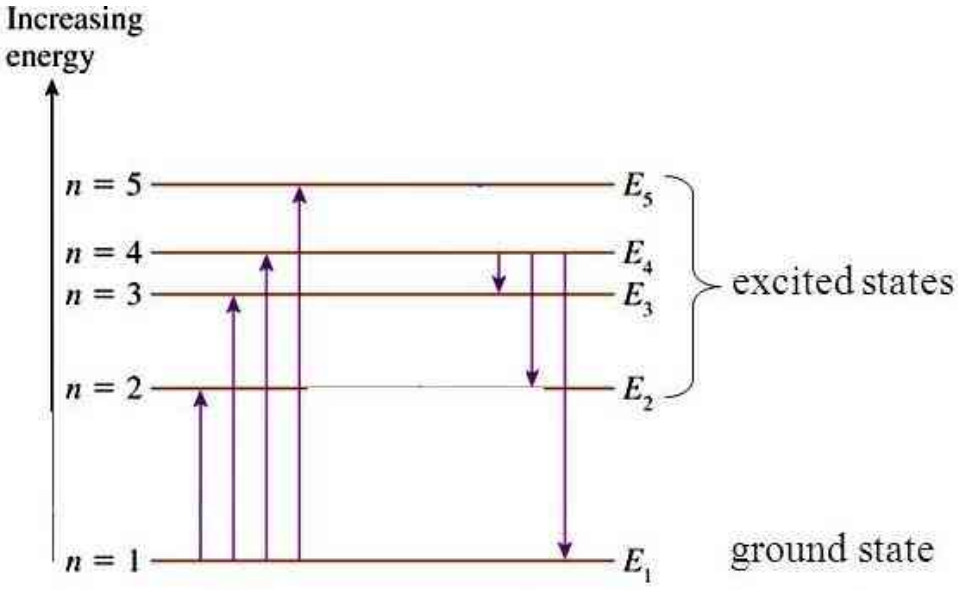
Doped Graphene Application
Radical Energy Level







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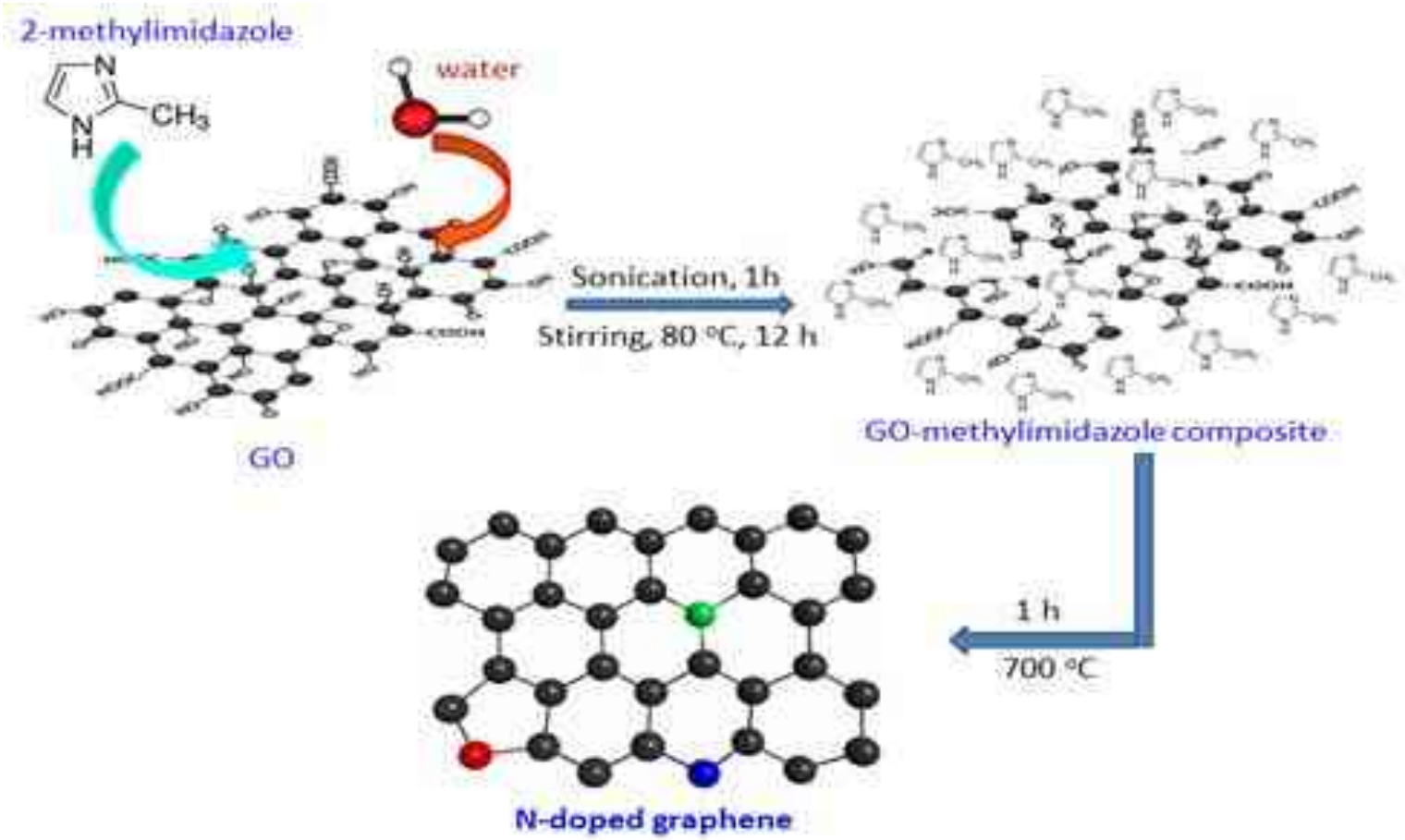
Graphene
N-doping



Journal of Nanotechnology and Materials Science
10.15436/2377-1372.15.006DOI

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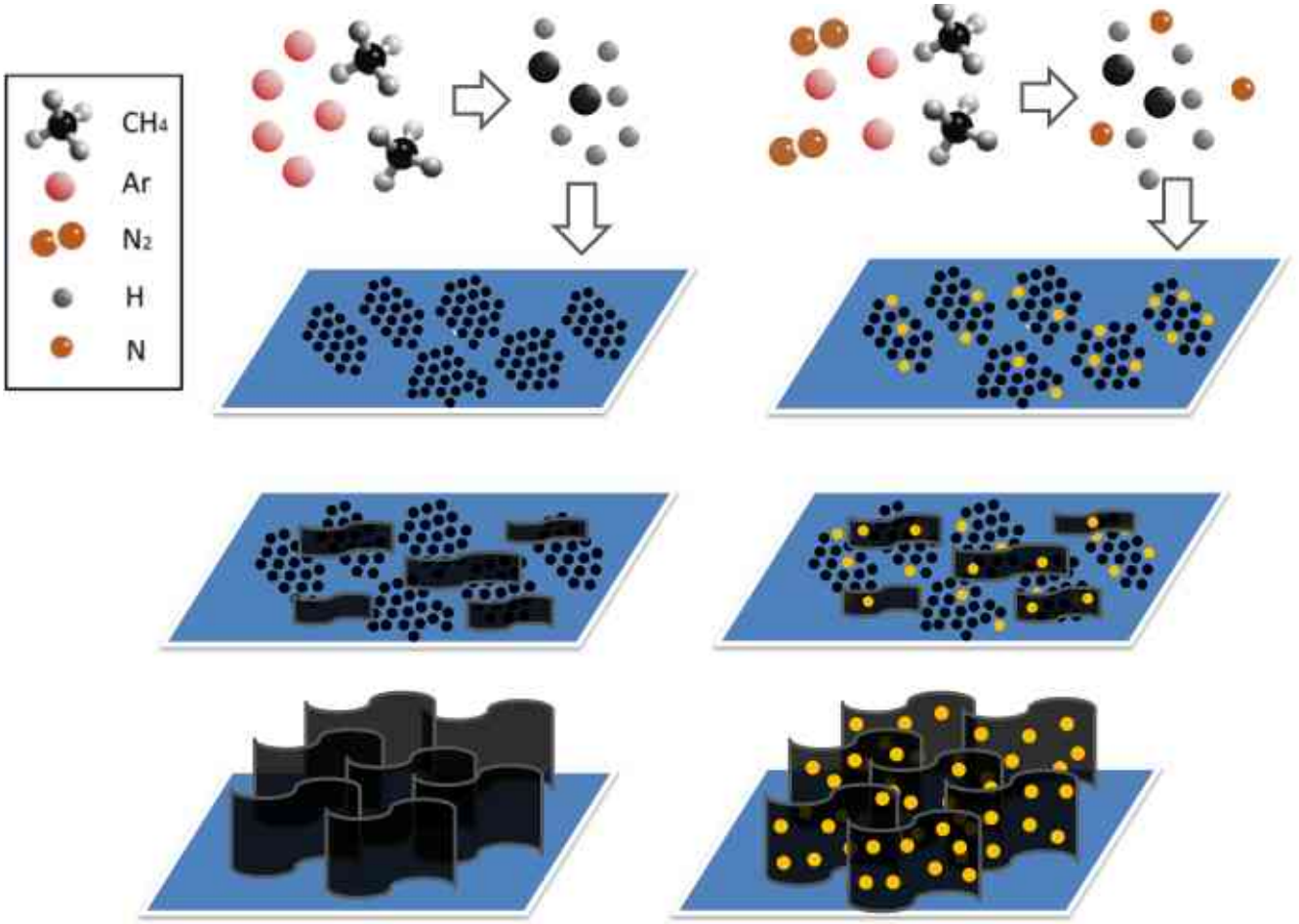
Graphene Nanowalls
Growth and Doping

NGNW growth through Plasma



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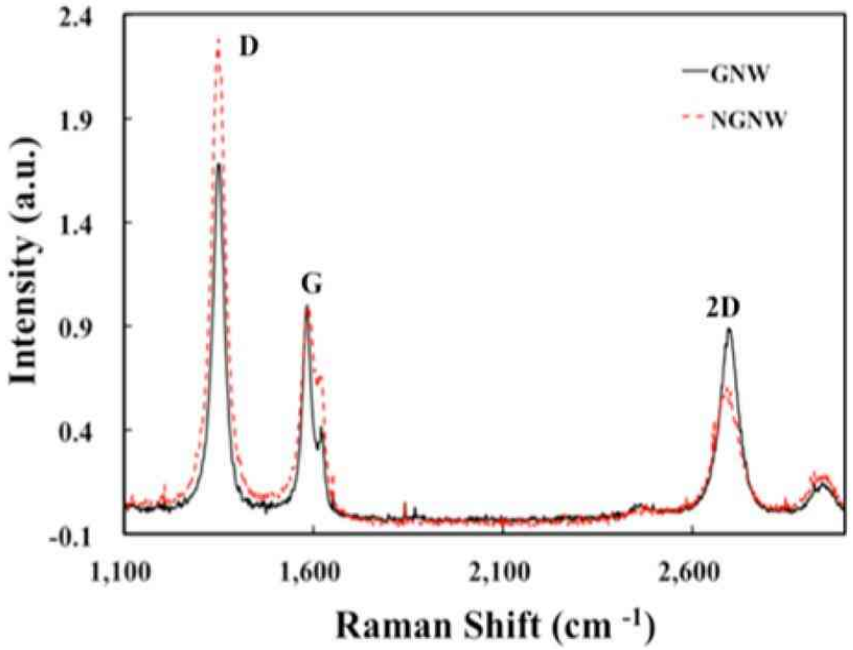
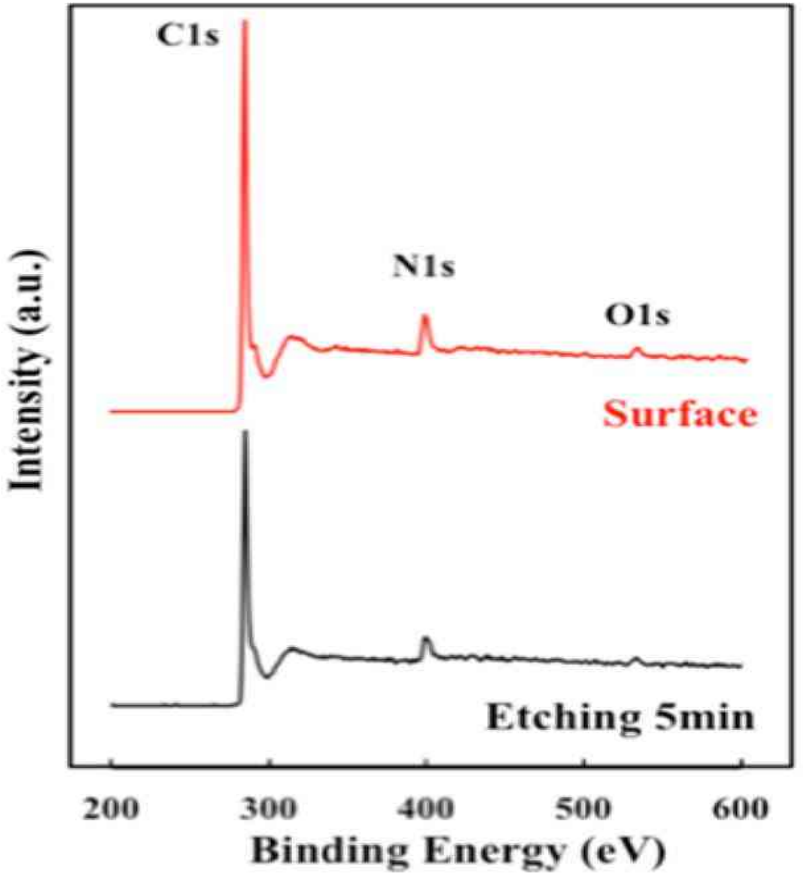
Graphene Nanowalls
Chemical Analysis

Raman



Nano Lett. 2016, 16, 5719−5727

XPS



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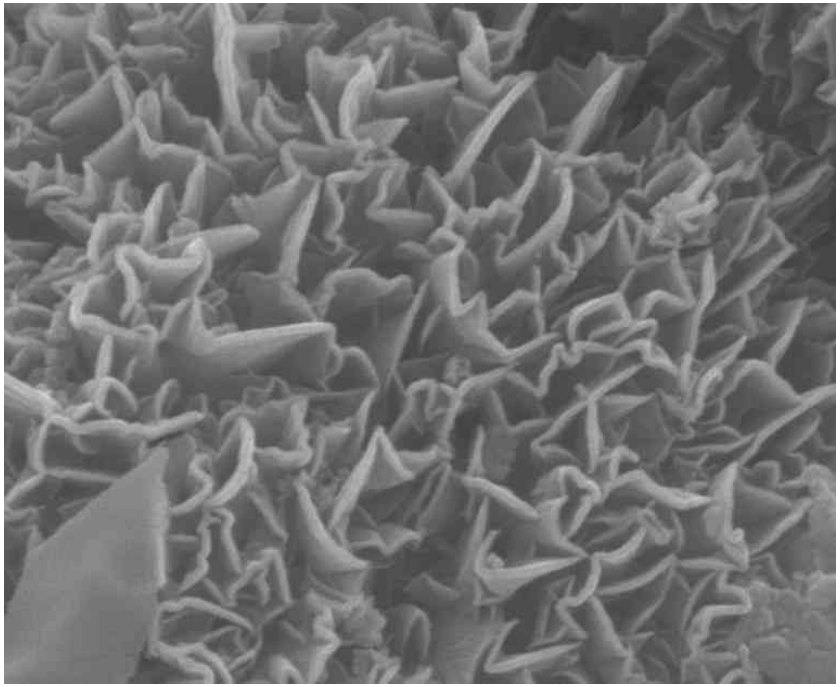
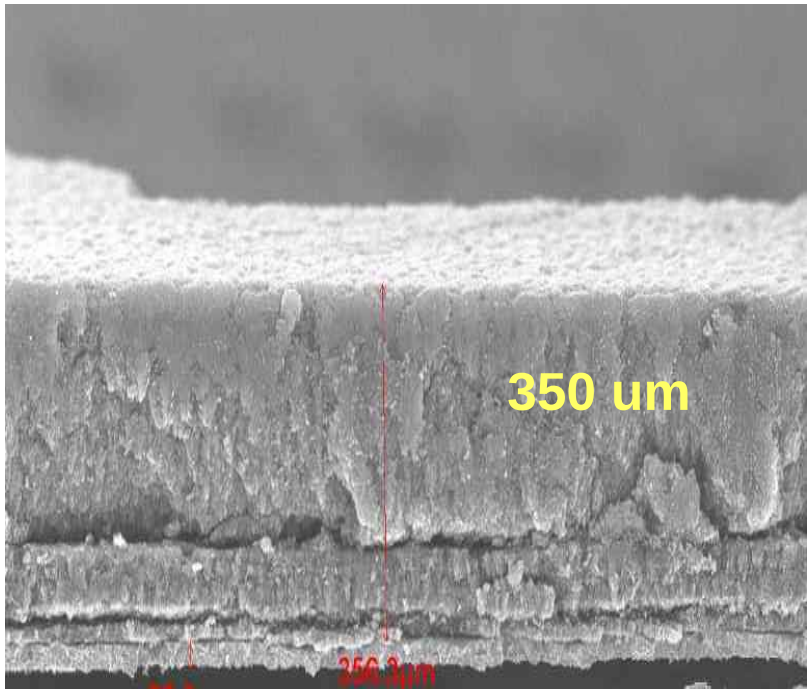
Graphene Nanowalls
SEM





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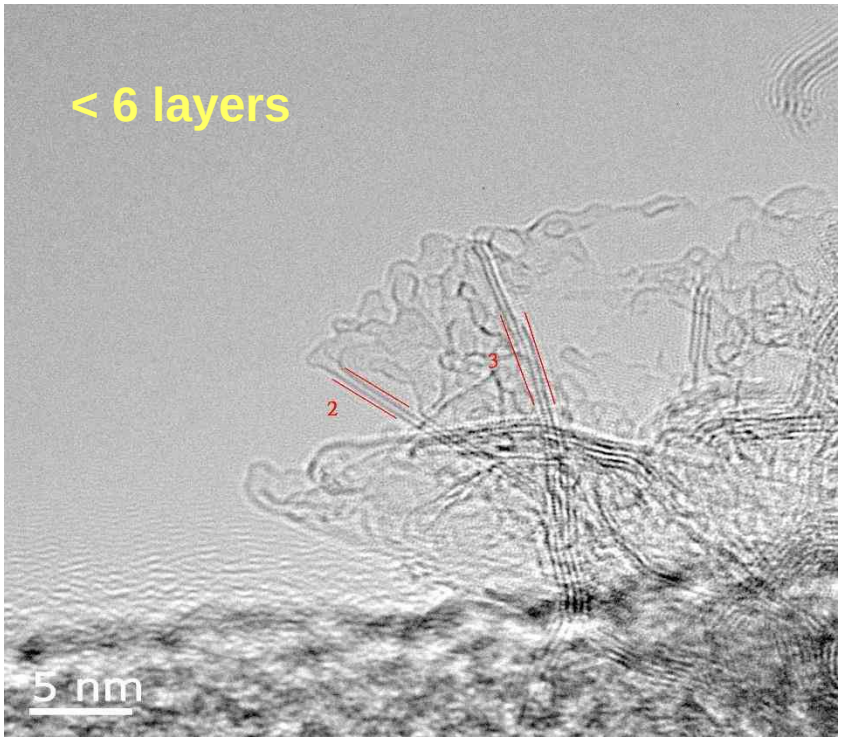
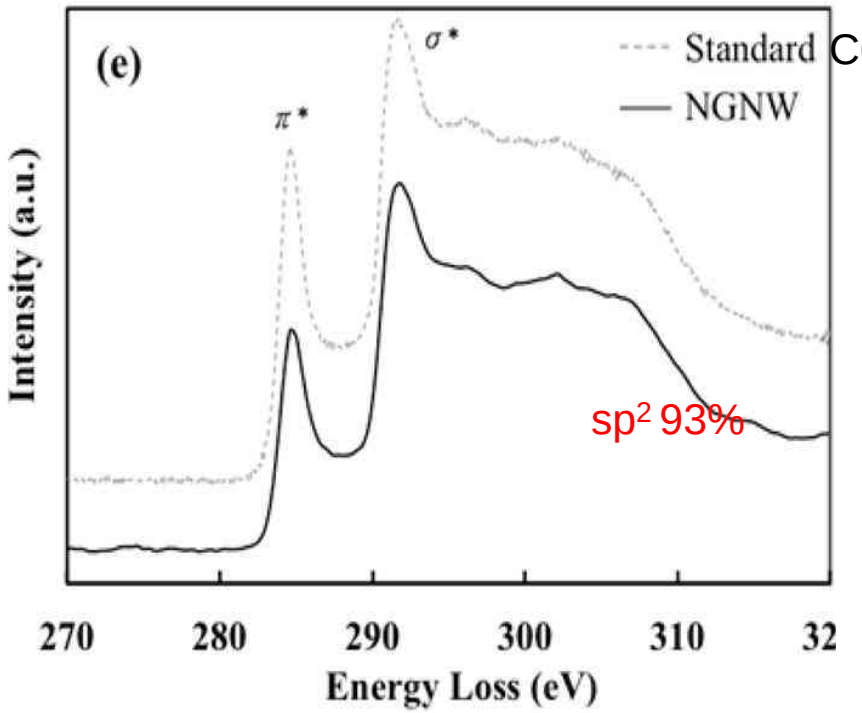
Graphene Nanowalls
LP HRTEM

TEM



EELS



Nano Lett. 2016, 16, 5719−5727

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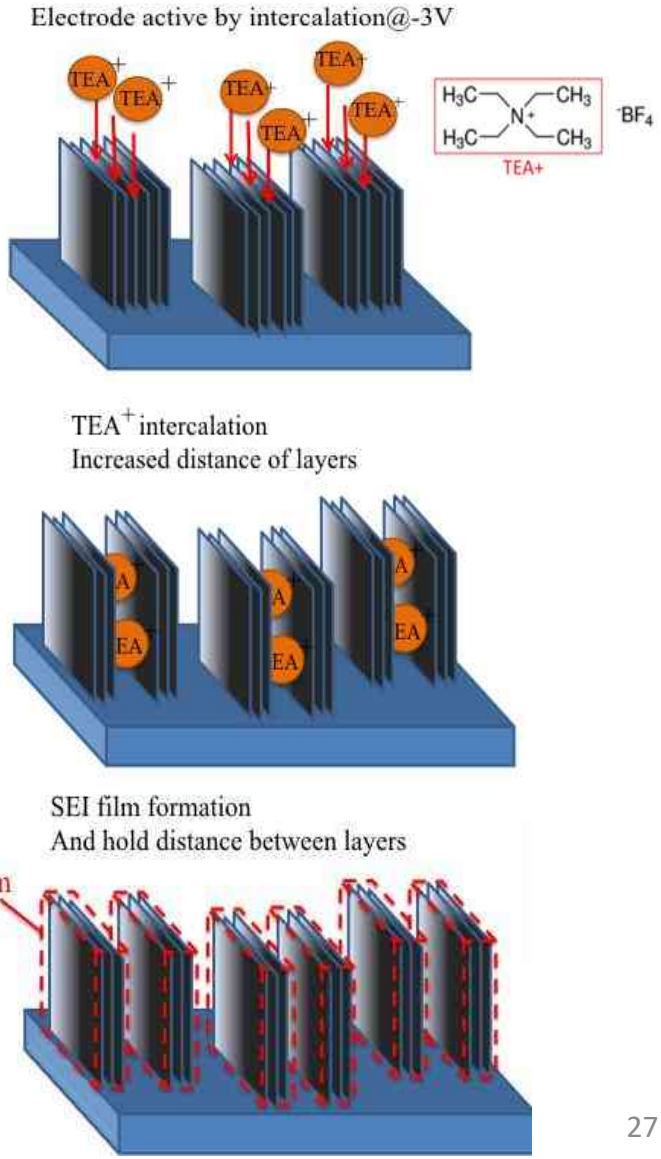
Supercapacitor
Electrode Electrochemical Activation

■ Purpose
GNW or NGNW proceed electrochemical activation by cyclic voltammetry (CV) in organic electrolyte (TEABF4/PC) to enhance the specific capacitances in order to be applied in asymmetric supercapacitors.

■ Activation method
GNW or NGNW proceed CV from 0V to -3V
➔ Increase capacitance (double, **48** F/g➔ **66** F/g)

■ Mechanism
When cell voltage reach -3V
➔ TEA+ intercalation ➔ increase distance between GNW layer
➔ Surface area raise ➔ Cs improve.



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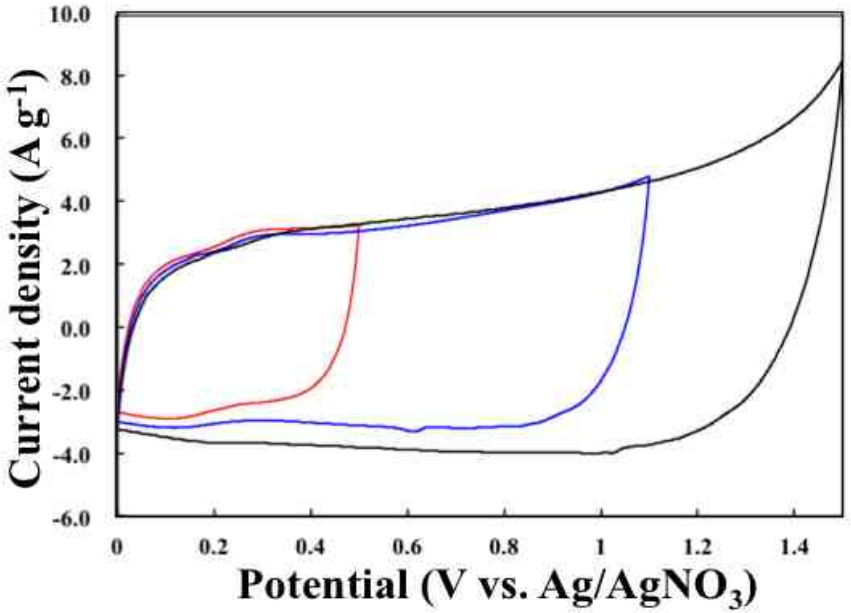
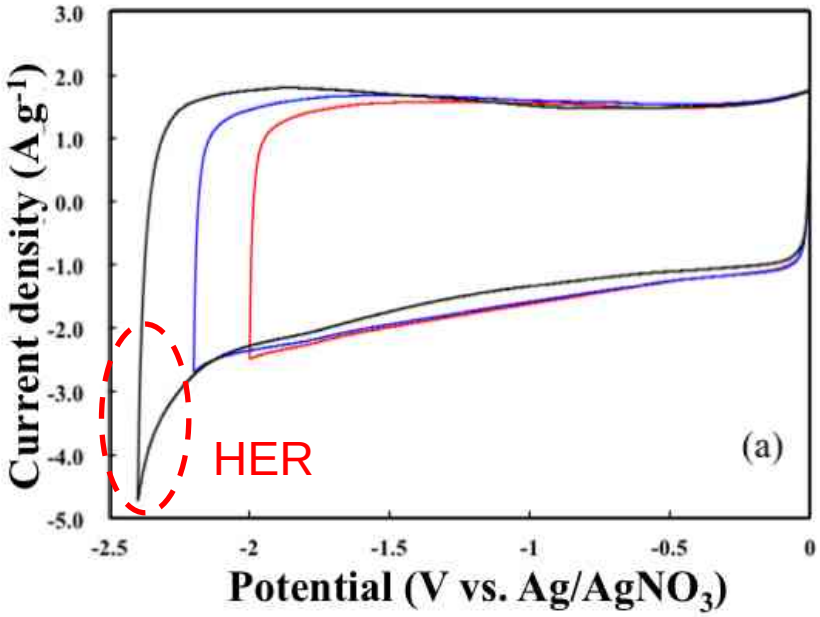
Supercapacitor
GNW

Positive



Negative



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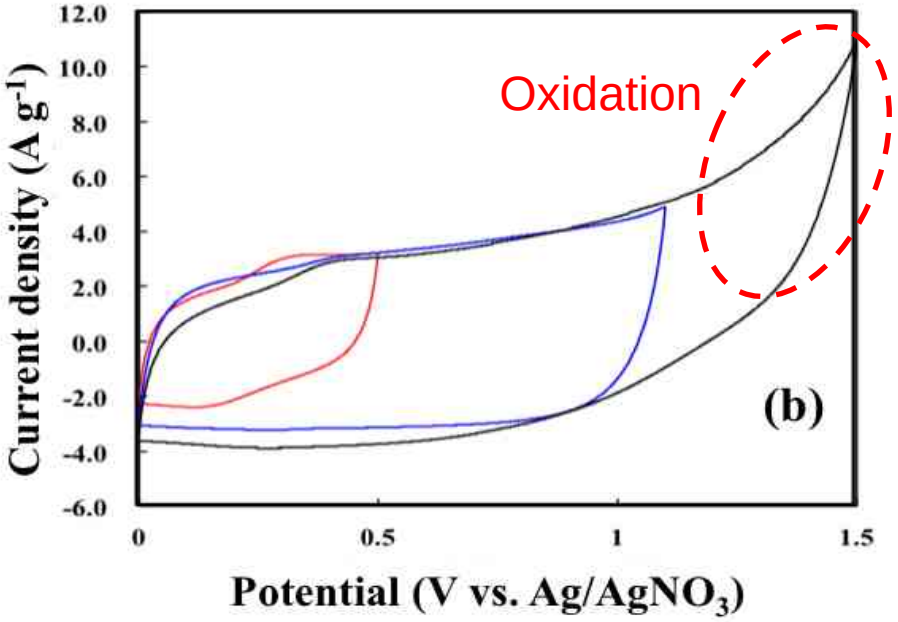
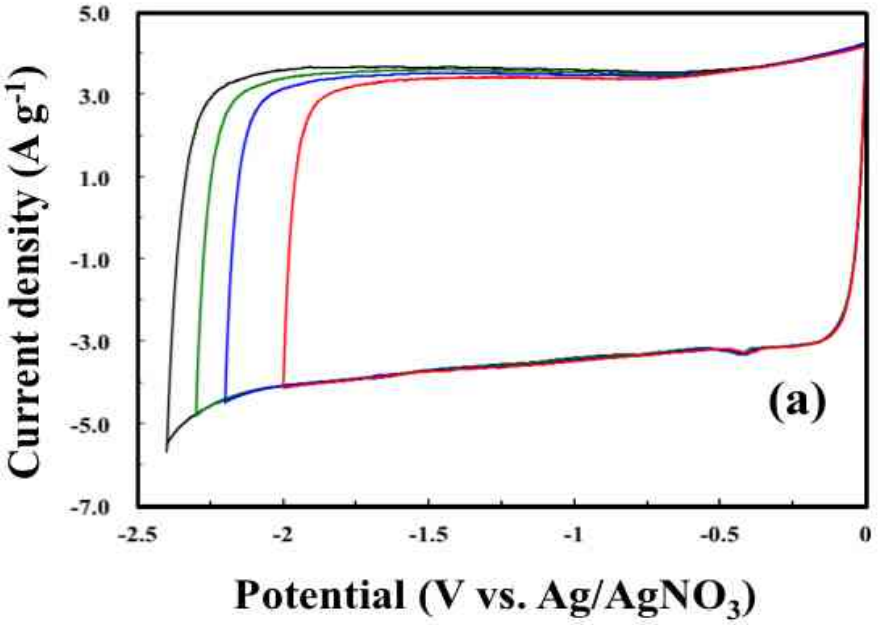
Supercapacitor
N-GNW

Positive



Negative



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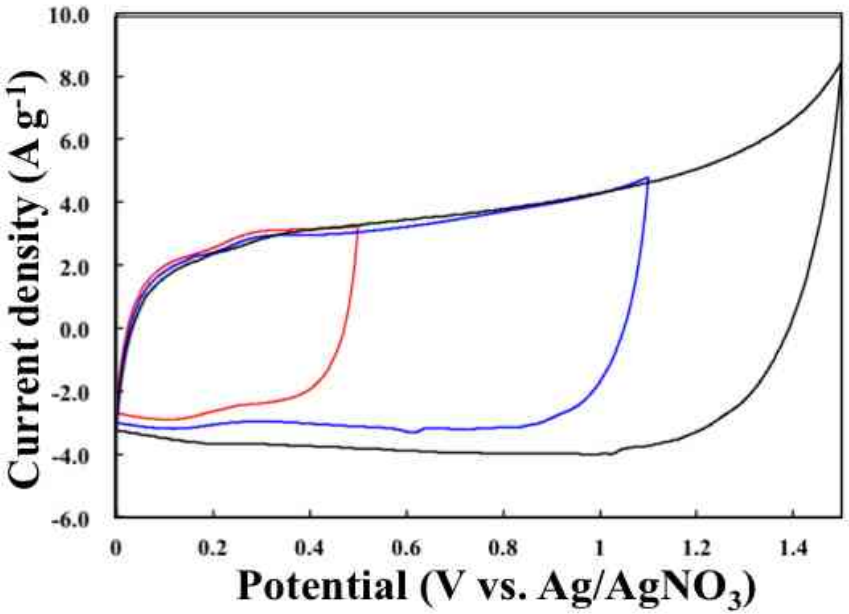
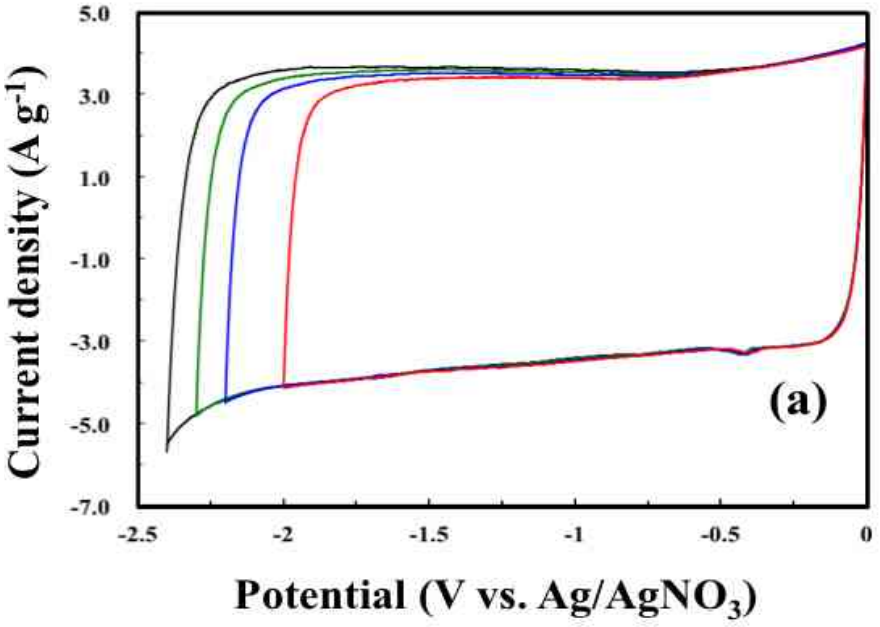
Supercapacitor
Asymmetric Electrodes

Positive: GNW Electrode



Negative: N-GNW



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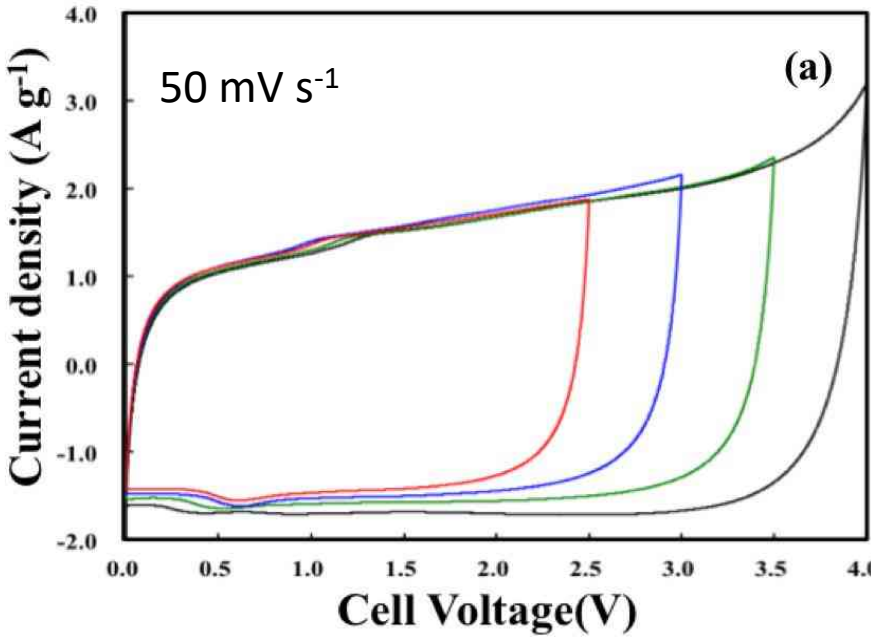
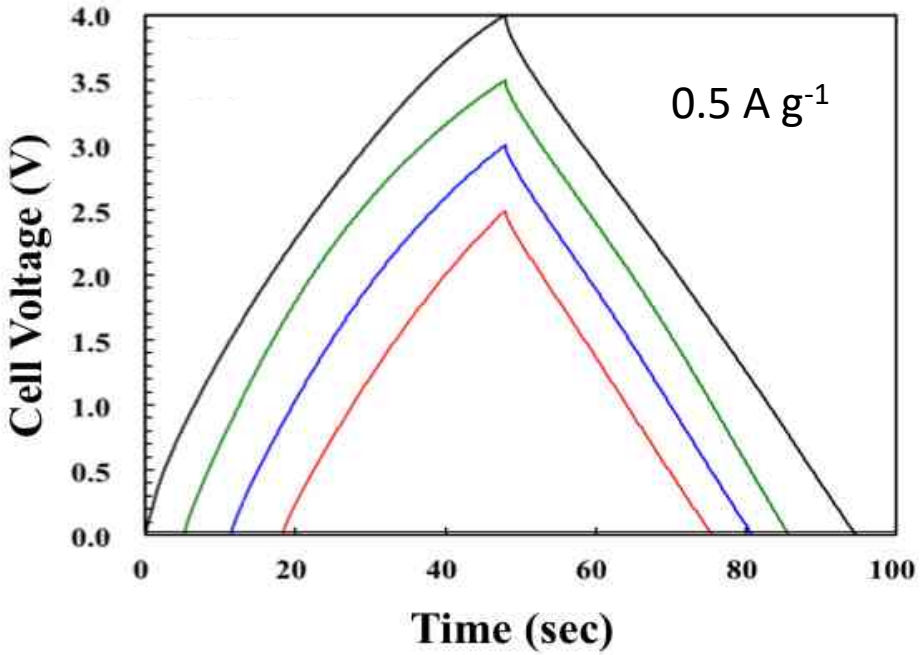
Supercapacitor
GNW \ N-GNW





(a) CV curves and (b) constant-*i* charge-discharge curves of an N-graphene //LQ graphene ASC in 1 M $TEABF_4$/PC with a cell voltage of 2.5, 3.0, 3.5, 4.0 V at 50 mV/s or 2 A/g.

N-graphene (-)//GNW (+) is a 4V EDLC

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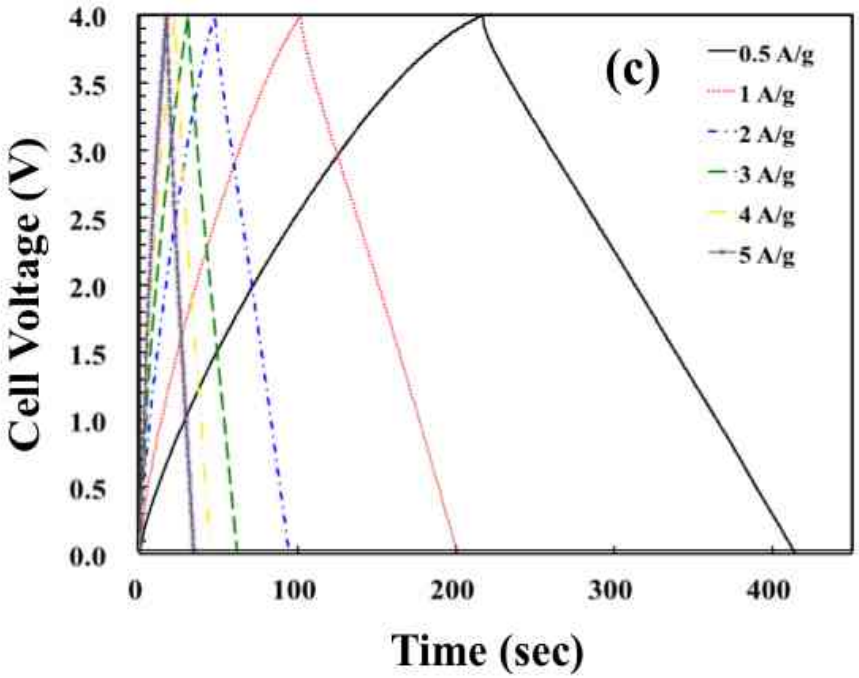
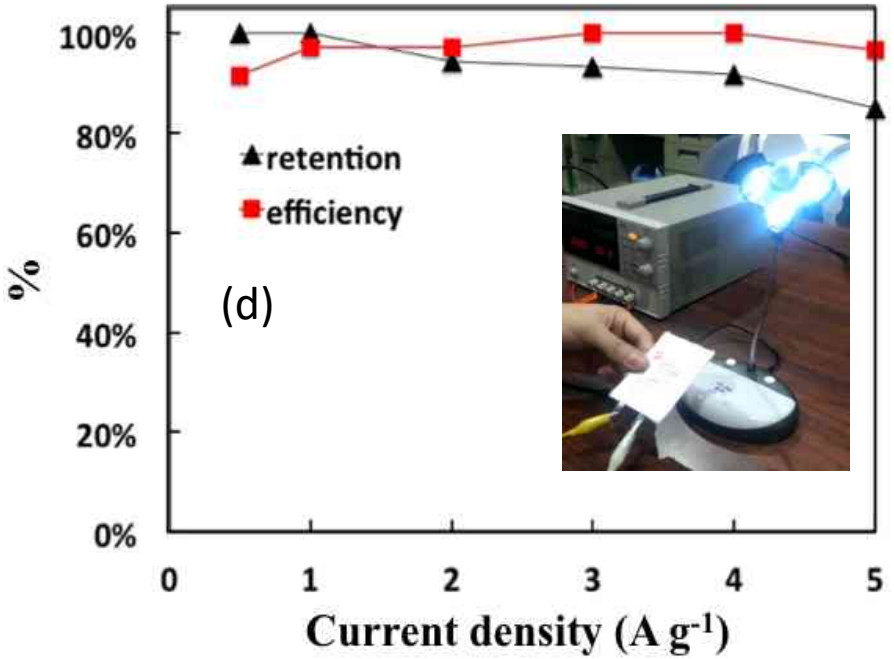
Supercapacitor

GNW \ N-GNW





(c) The charge-discharge curves of an N-GNW (-)//GNW (+) ASC in 1 M $TEABF_4$/PC with a cell voltage of 4.0 V at 0.3, 0.5, 1, 2, 3, and 5 A/g. (d) The C.E. and cell capacitance retention vs. charge-discharge current density for symmetric and asymmetric designs.

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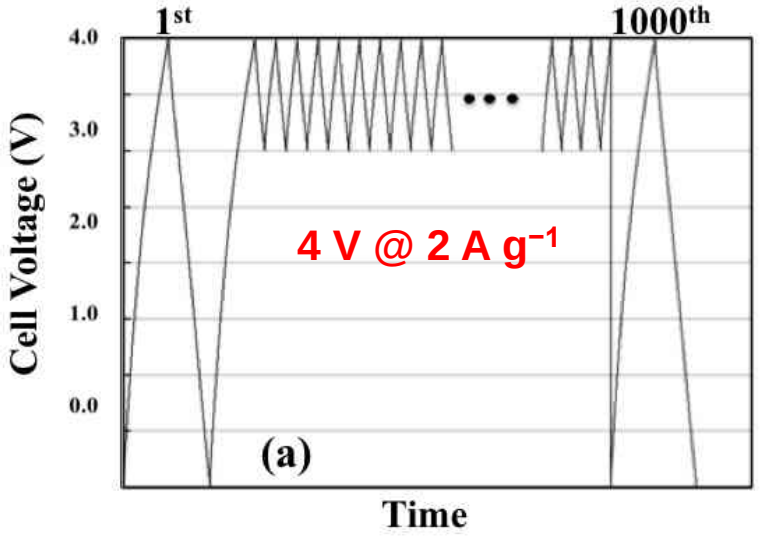
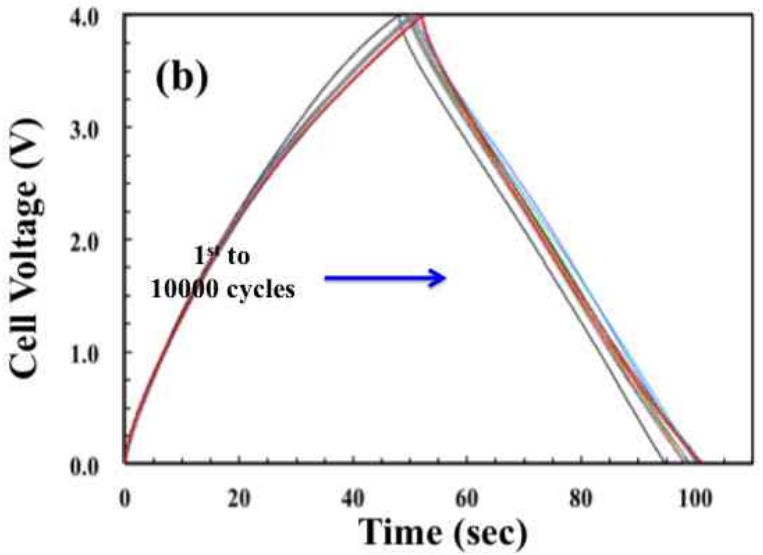
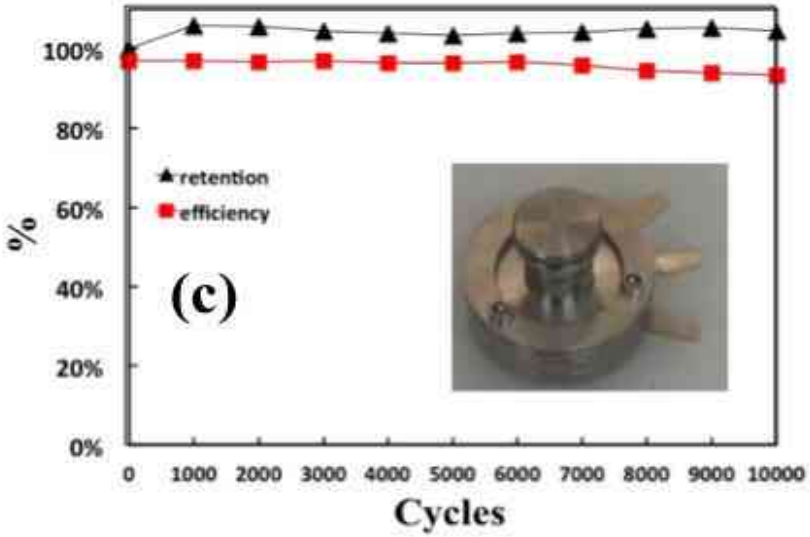
Supercapacitor
Cycle Life Test







After 10000 cycles, efficiency and retention are still maintain 93% and 100% respectively.

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Comparison

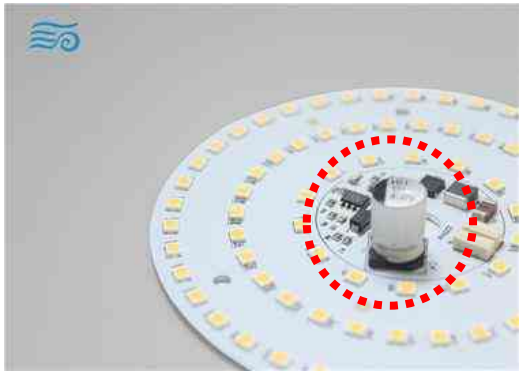
supercapacitors	Murata DMHA[1] supercapacitros	ITRI GNW supercapacitors
Cell voltage (V)	4.5 *a* (single=2.75V)	4.2 (single cell)
capacitance (mF)	35	35
ESR	300 mohm@1kHz	150 mohm@1kHz
Size / Dimension	20mm x 20mm	20mm x 10mm
Height - Seated (Max)	0.4mm	0.35mm
Price (USD)	3.7 *b*	2.0 *c*

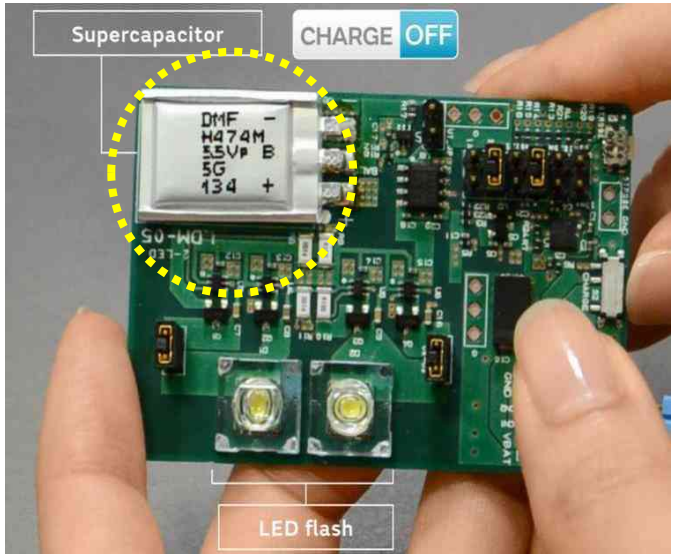
[1] https://www.digikey.com/product-detail/en/murata-electronics-north-america/DMHA14R5V353M4ATA0/490-17331-ND/7674906

a. Two cell in-series and single cell voltage is 2.75V.
b. 2500 cells price
c. Base on GNW growth area >400 cm2.

Application

- **Flatten out Electrolytic Capacitor**





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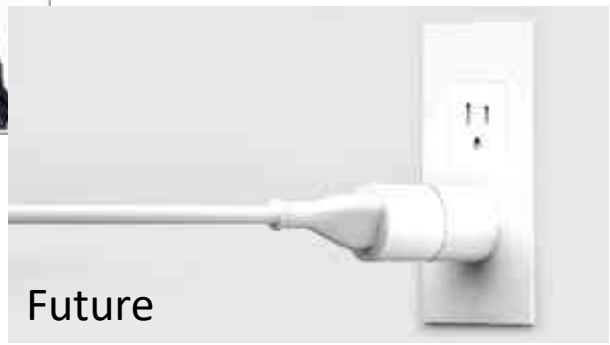
Application

- **Lighter and Thinner Converter Adaptor**

Past

Now



Future

GNW Supercapacitor

- **Flatten out LED Module**

https://www.youtube.com/watch?v=cY8Vma6mNP4

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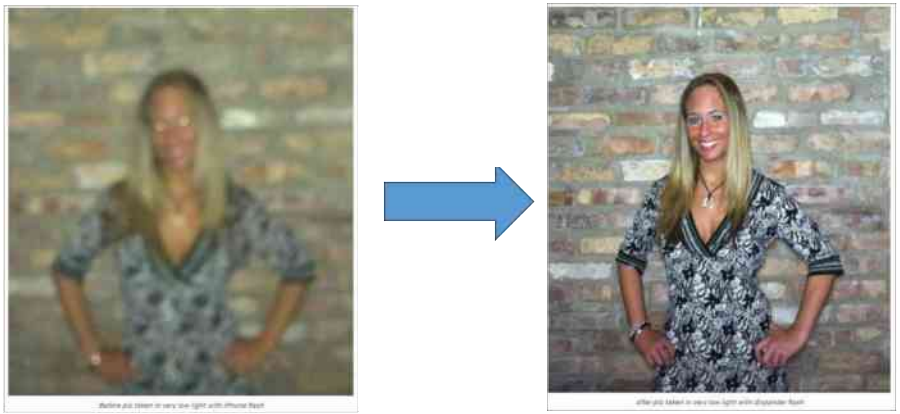
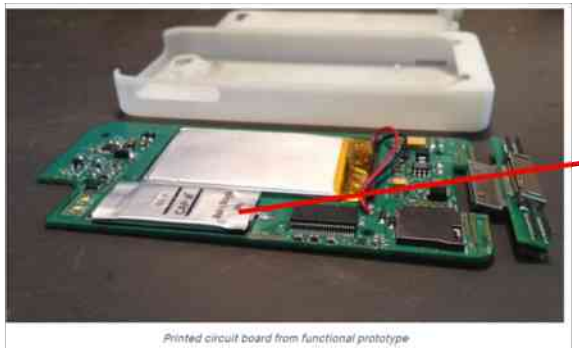
Application

- **Flash Lamp of Smart Phone**
  - ✓ **Rapid Charge and Discharge**

https://www.kickstarter.com/projects/108290897/iexpander-an-expansion-device-for-your-iphone-4-an





Printed circuit board from functional prototype

ITRI GNW UCs
Can provide more power
And more thinner

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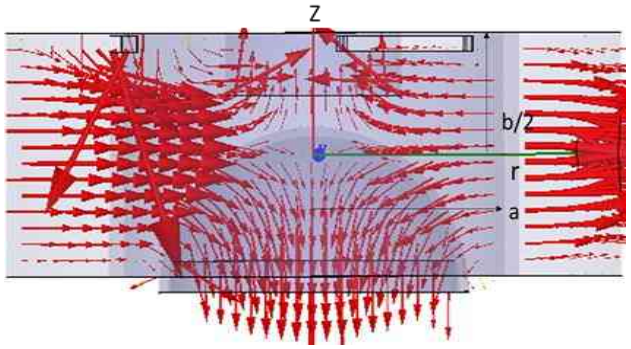
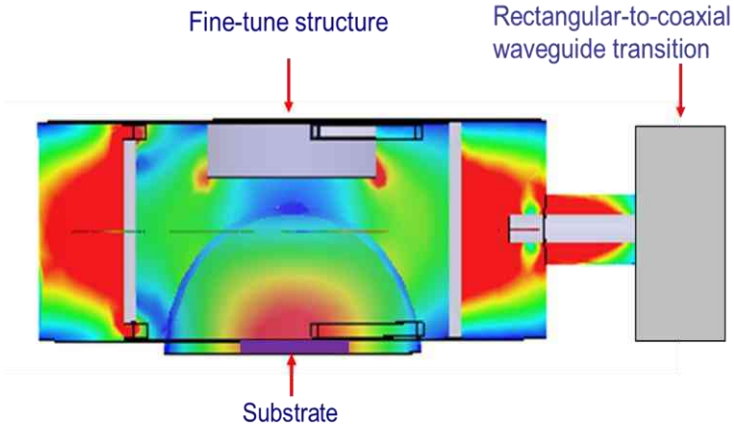
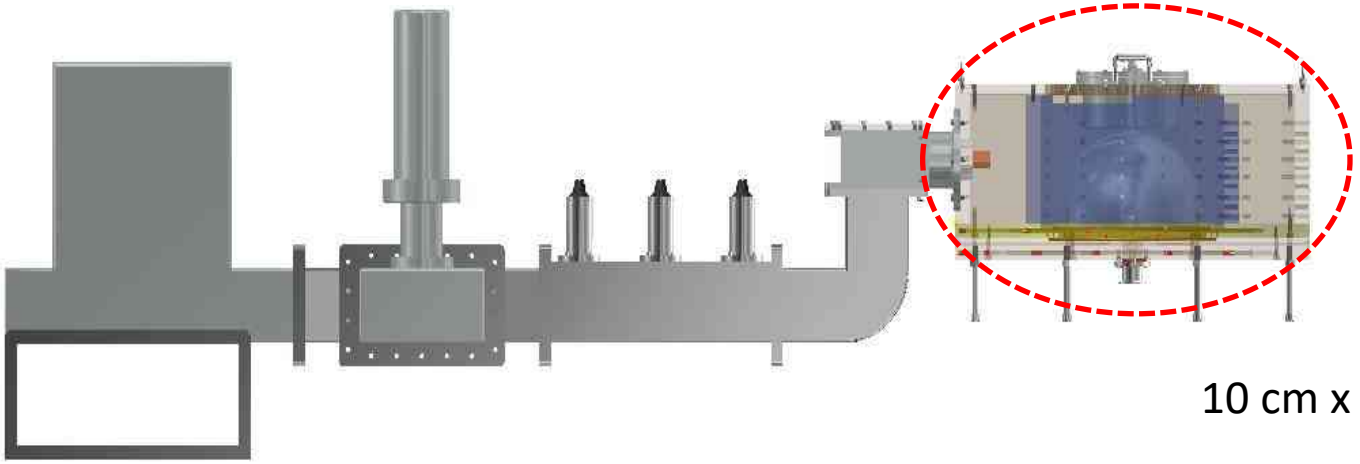
Large-area GNW

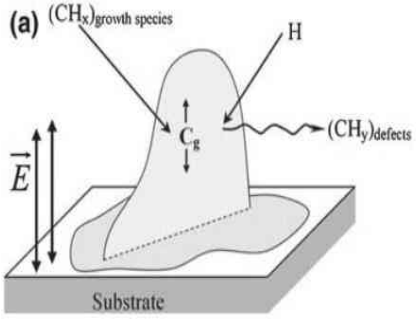
FMP CVD

Focus Microwave Plasma enhanced Chemical Vapor Deposition









10 cm x 10 cm

Patent Filing

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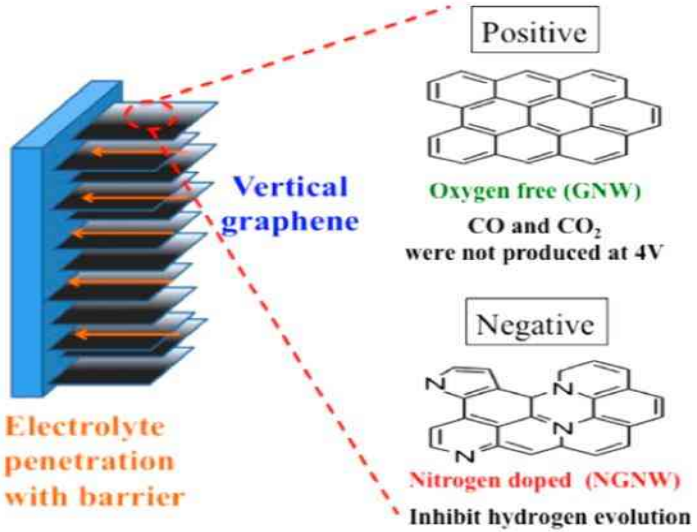
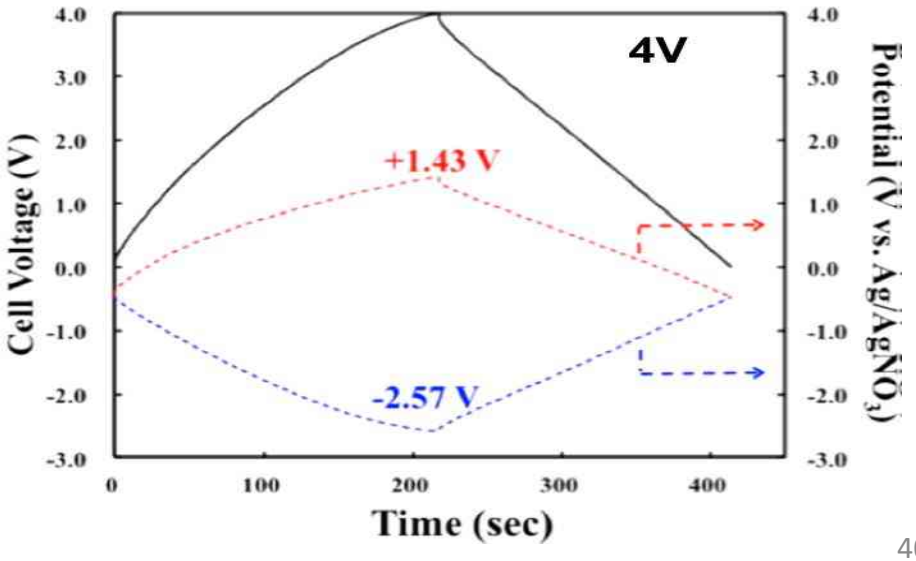
Conclusions

- GNW ➔ Oxygen free ➔ inhibit oxidation reaction ➔ Be positive electrode 1.43V
- NGNW ➔nitrogen inhibit HER reaction ➔ Be negative electrode -2.57V
- Asymmetric electrodes can accomplish 4V electrical double-layer capacitors. (Energy Density is 53 Wh/kg; Power Density is 8k W/kg)
- ITRI MMSL will develop FMP CVD for large-area graphene nanowalls.





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Collaboration

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Thanks for your attention!