



# ITRI

Industrial Technology  
Research Institute

## High-Voltage Electrical Double-Layer Capacitors

Graphene Task Force  
Project Manager

**Dr. Kun-Ping Huang**



Mechanical and Mechatronics  
Systems Research  
Laboratories

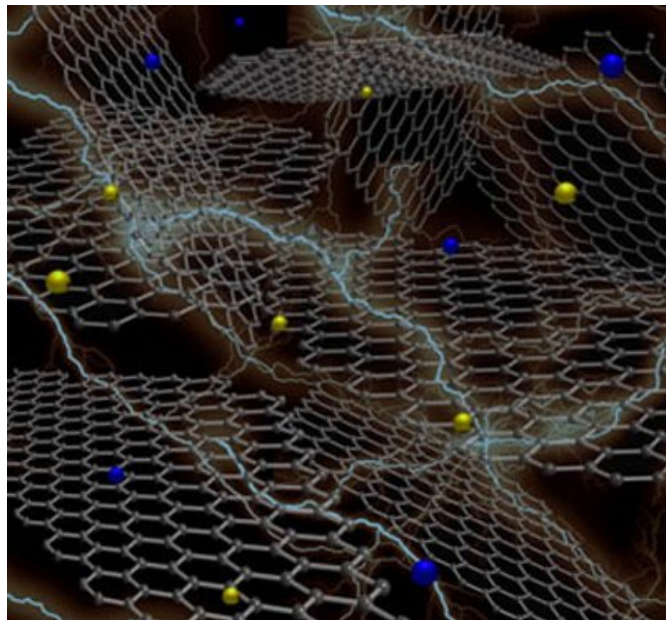
Industrial Technology  
Research Institute (ITRI)

Taiwan, ROC

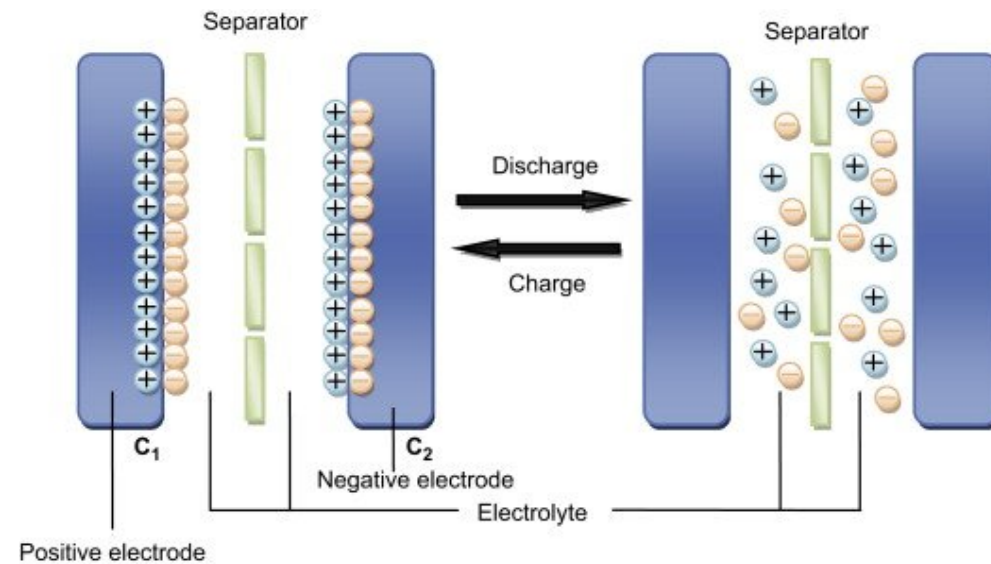


# Graphene Background

- High specific surface ratio (2630 m<sup>2</sup>/g)
- High specific capacitor (530 F/g)
- High electron transport (200, 000 cm<sup>2</sup>·V<sup>-1</sup>·s<sup>-1</sup>)



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



<http://energyeducation.ca/encyclopedia/Supercapacitor>

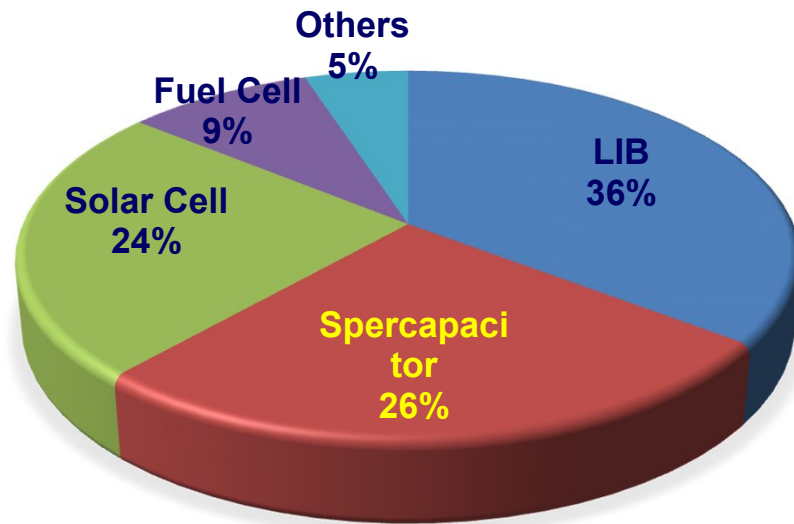


# Graphene

## Patent Analysis of Energy Storage

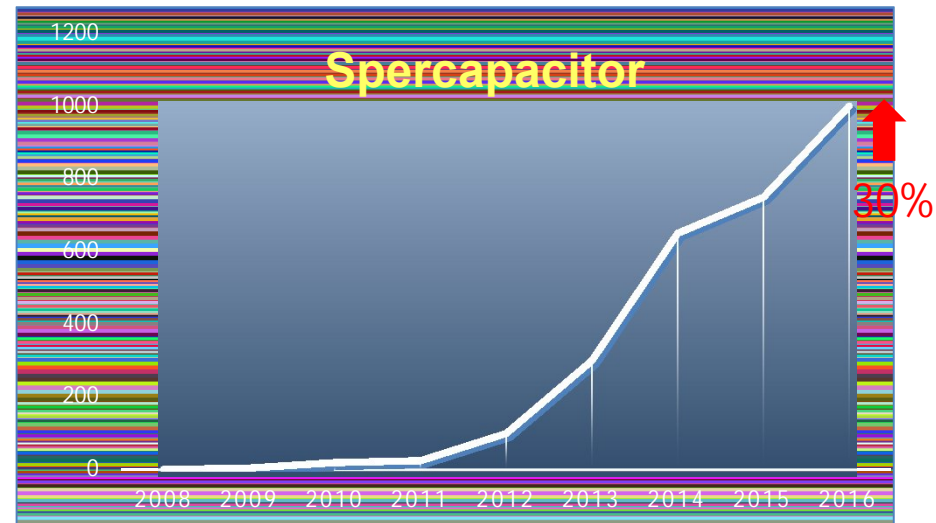
- Graphene supercapacitor can provide high power density (>2k W/h)
- Supercapacitor has longer cycle life (>10, 000 cycles)

Energy Storage Patent Analysis



11,852 patents

Trend Chart of Supercapacitor Patent

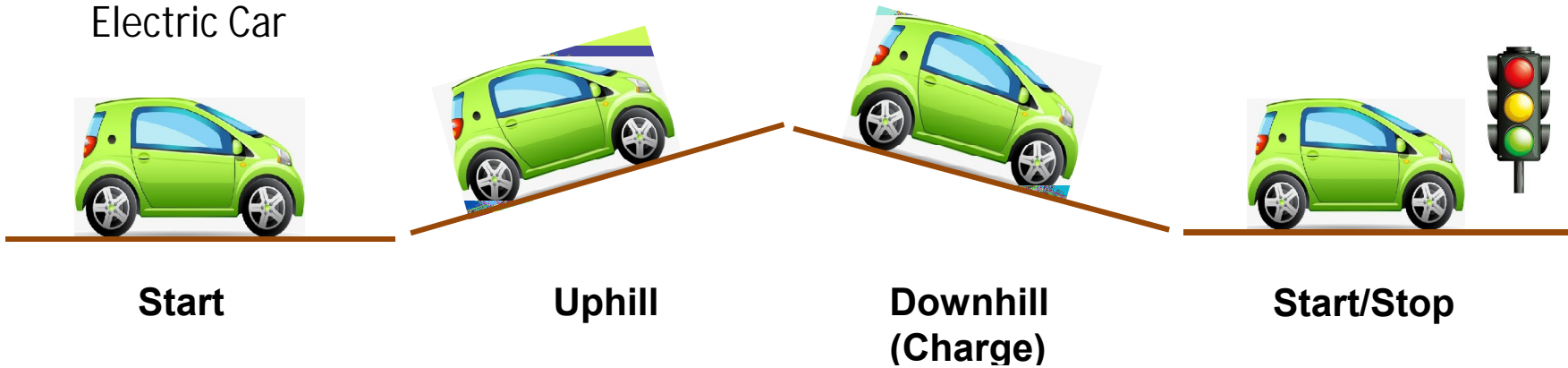


30% annual growth



# Graphene LIB and Spercapacitor

Electric Car



Working Voltage ~2.8V

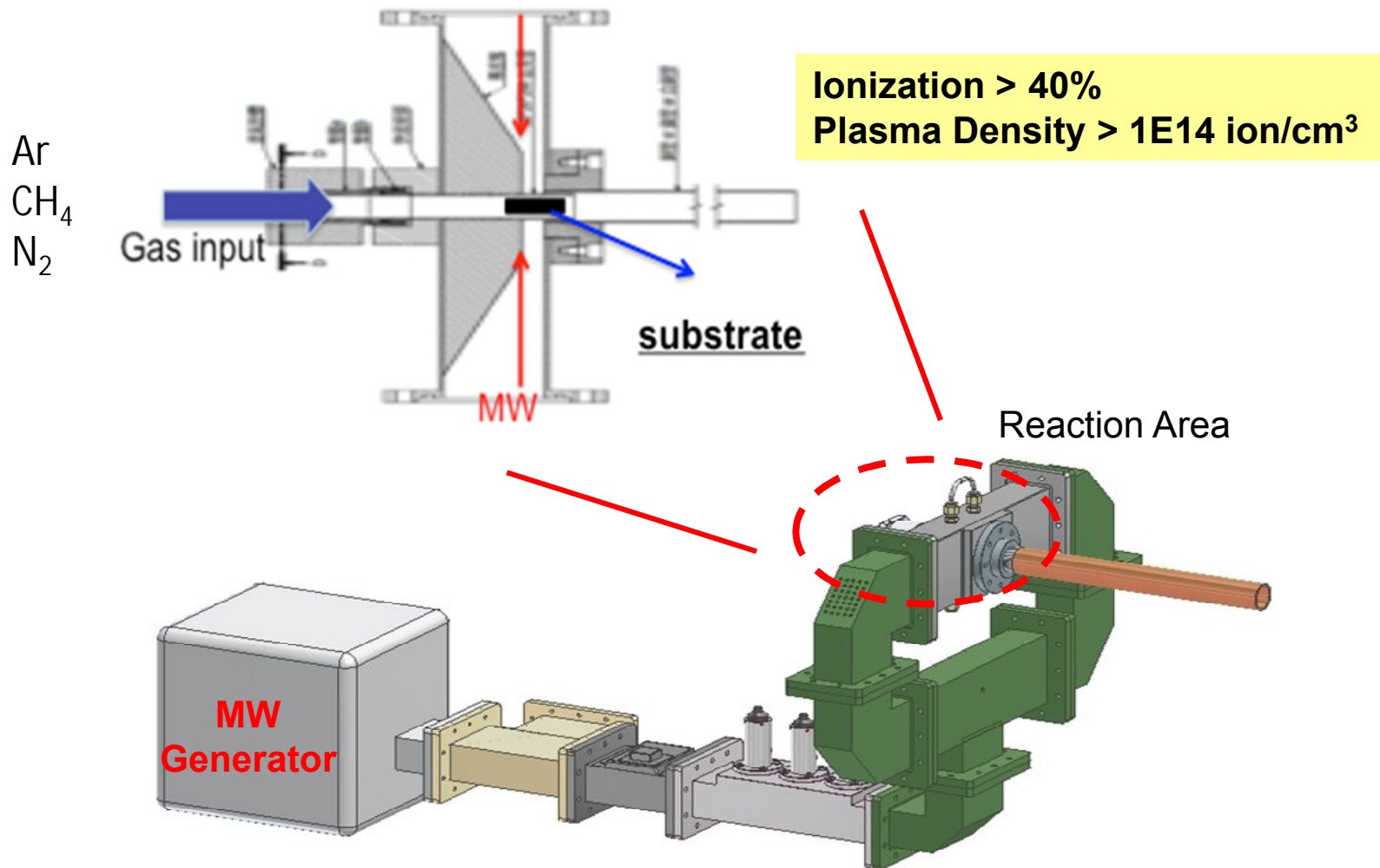


Volume ?



# MP CVD

## Bottom-Up Synthesis



Microwave Plasma enhanced Chemical Vapor Deposition

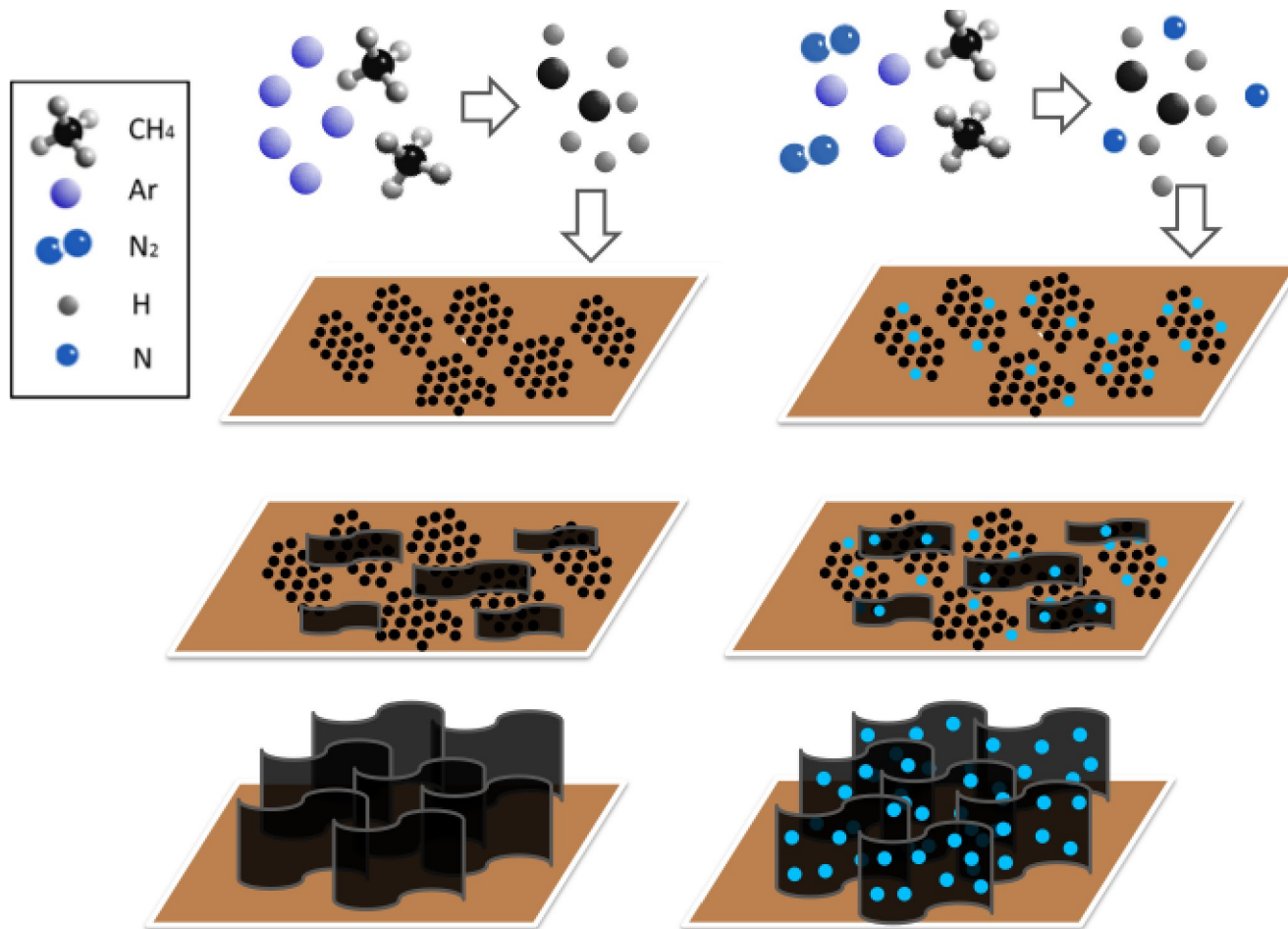




# Graphene Nanowalls

## Growth and Doping

### NGNW growth through Plasma



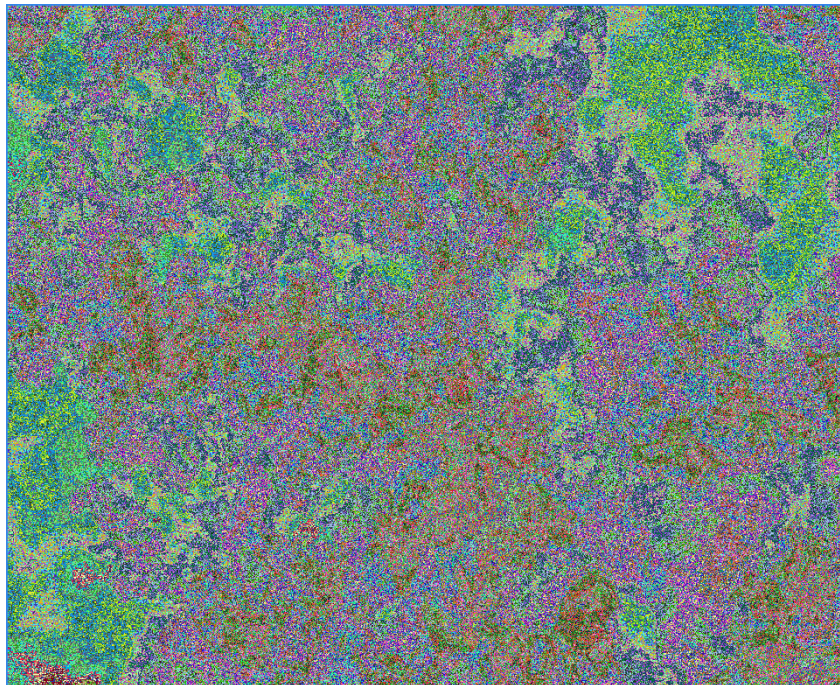
**Growth**

**N Doping**



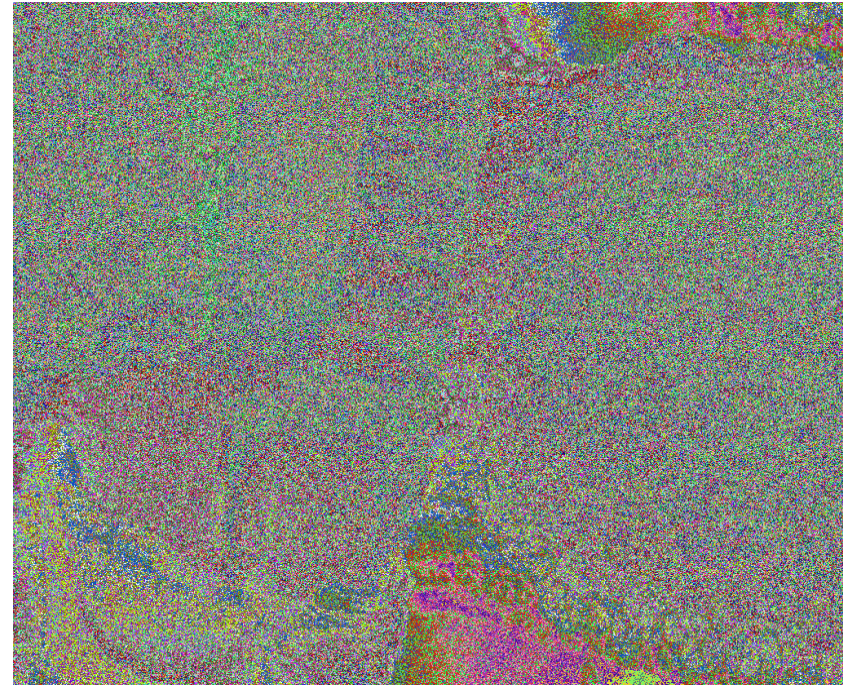
# Bottom-Up Synthesis Graphene Allotrope

> 100 torr



Graphene Powder

< 100 torr

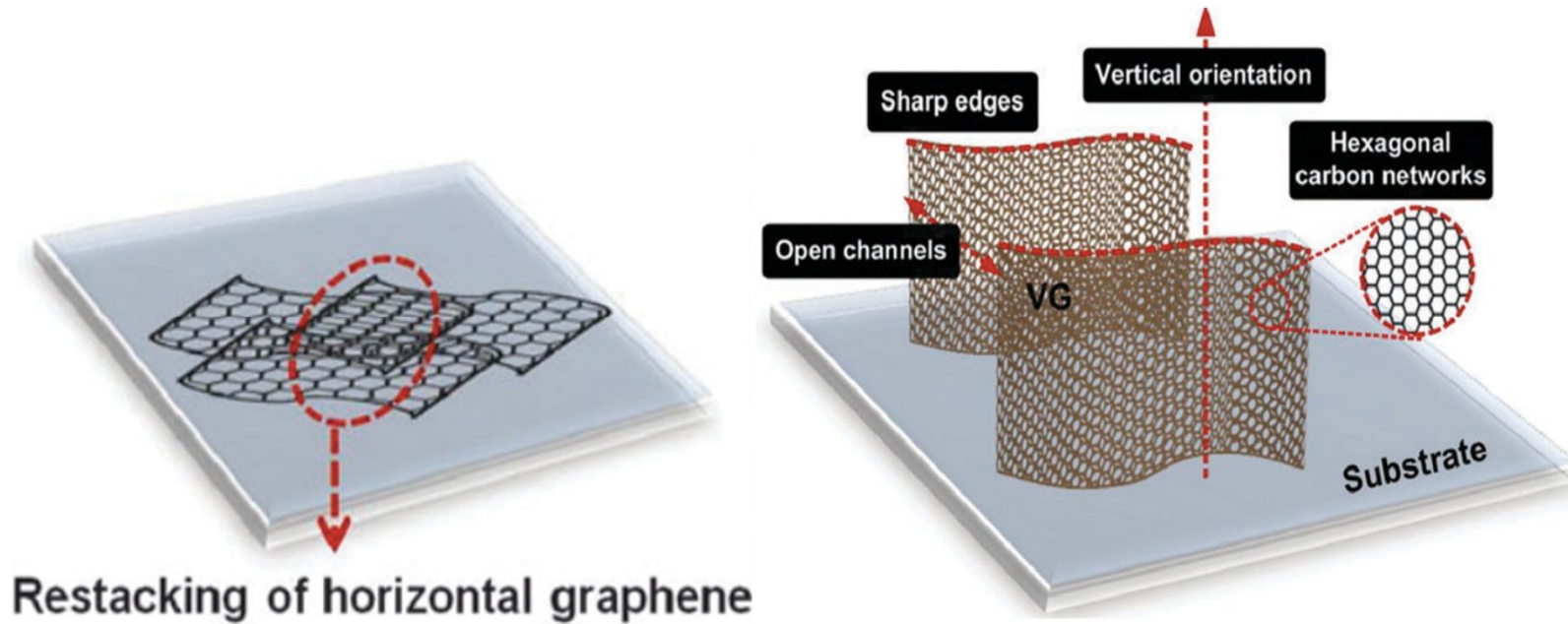


Graphene Nanowall





# Supercapacitor Powder vs GNW

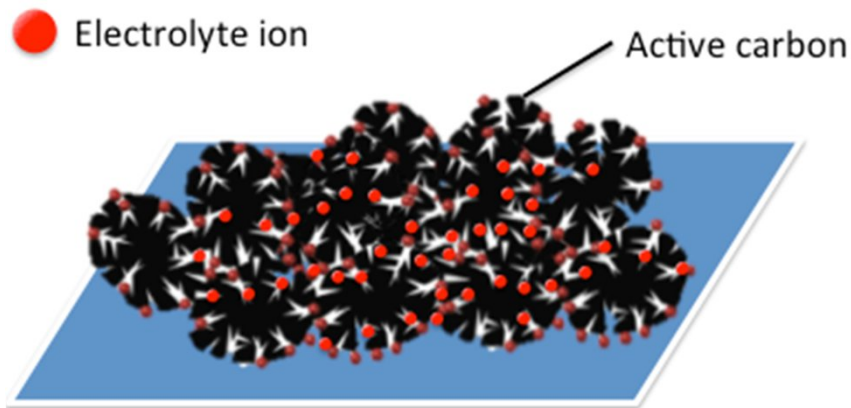


Chen, J., Bo, Z., & Lu, G. (2015). Vertically-Oriented Graphene. Springer International Publishing Switzerland, DOI, 10, 978-3.

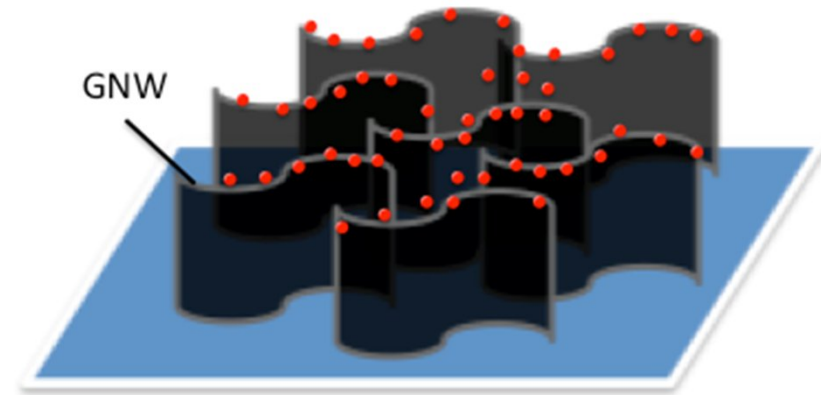




# Supercapacitor Powder vs GNW



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

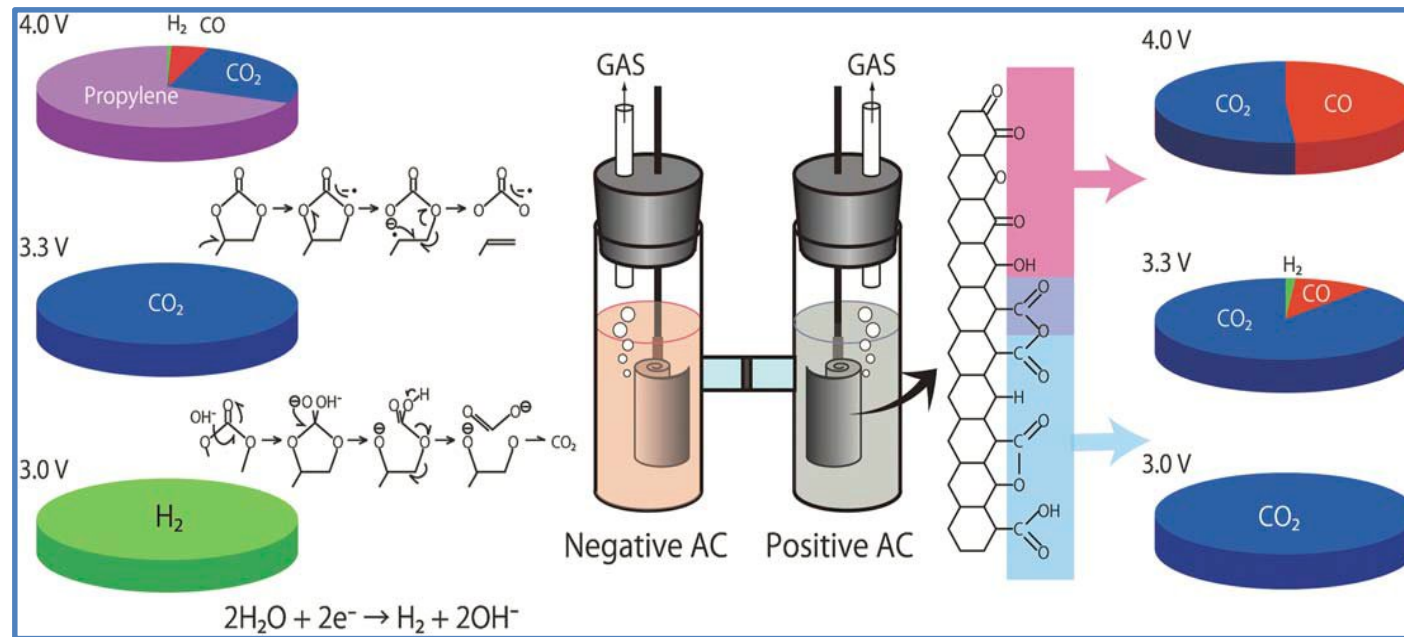


GNW with few edge and regular distribution and it provide these inner face between active material and electrolyte.  
→ without oxidation reaction or HER.  
→ Cell voltage raise to 4V.



# Supercapacitor Edge Reaction

Reduce the electrode activity to electrolyte/the interface reactions



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



# Supercapacitor Powder vs GNW



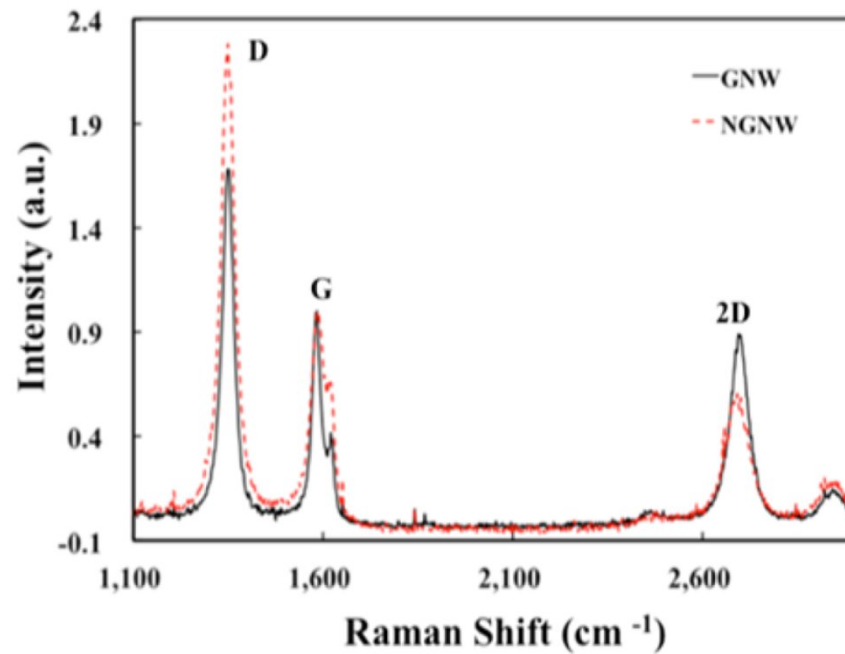




# Graphene Nanowalls

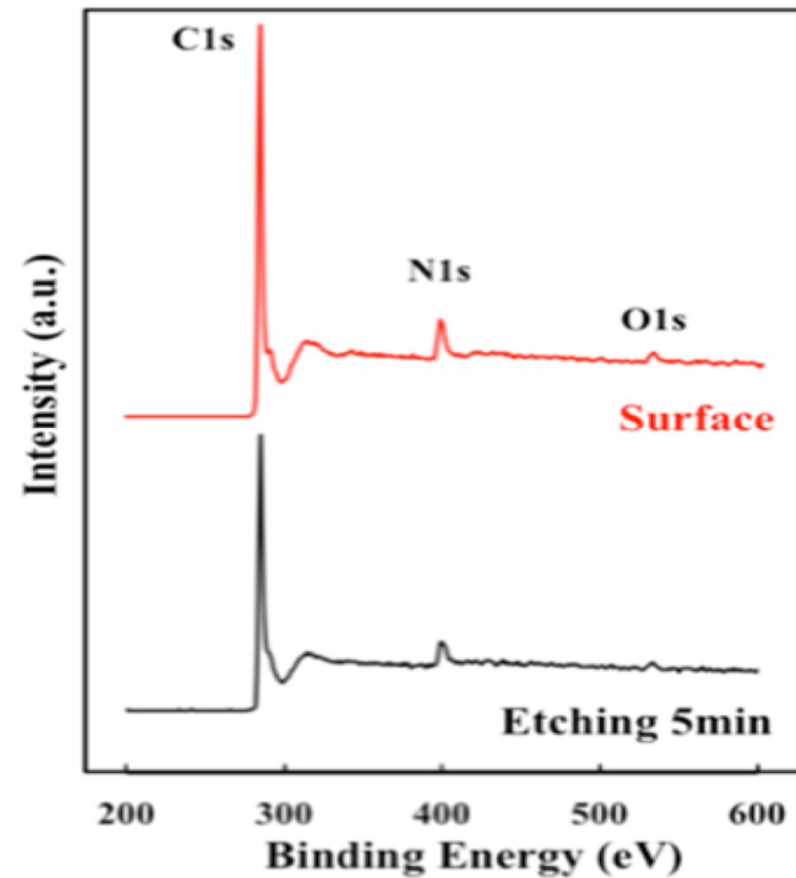
## Chemical Analysis

### Raman



Nano Lett. 2016, 16, 5719–5727

### XPS

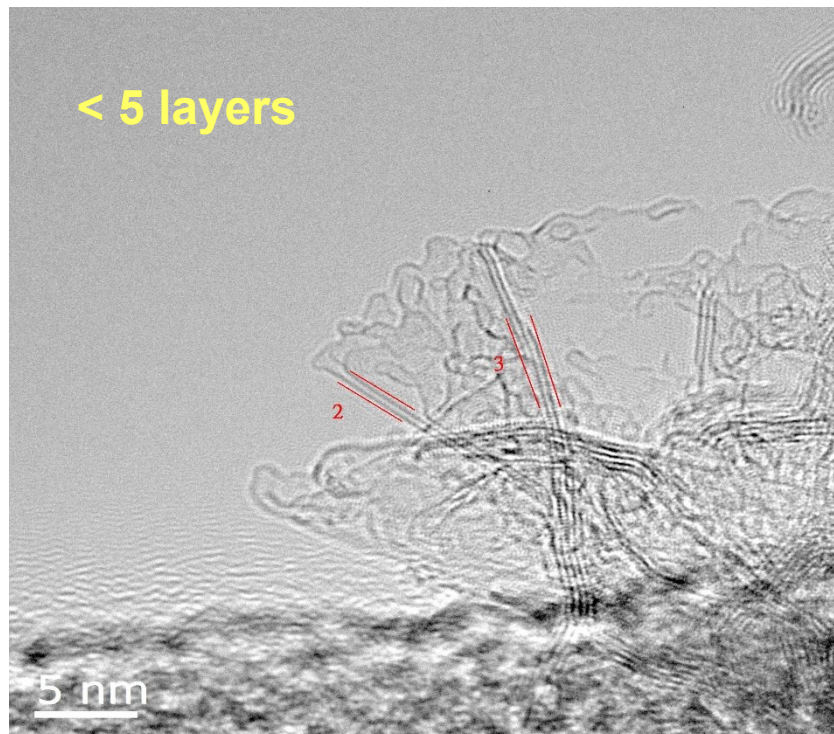




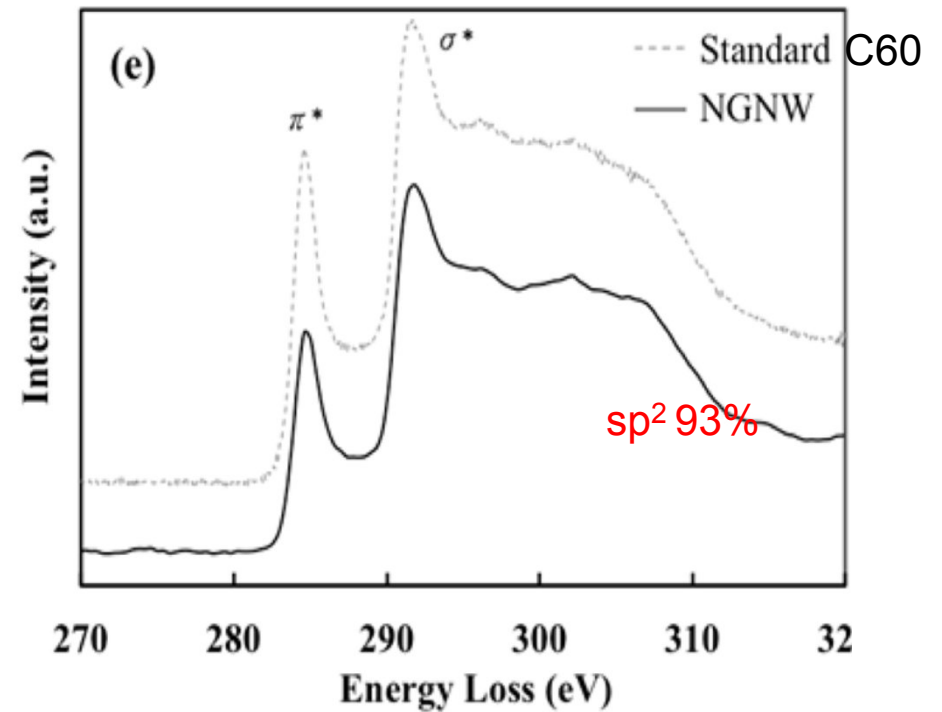
# Graphene Nanowalls

## LP HRTEM

### TEM



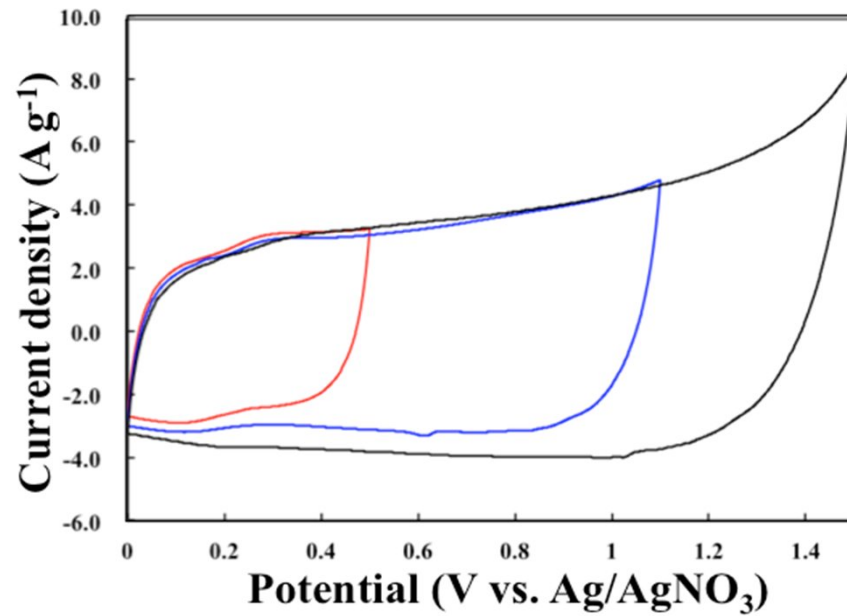
### EELS



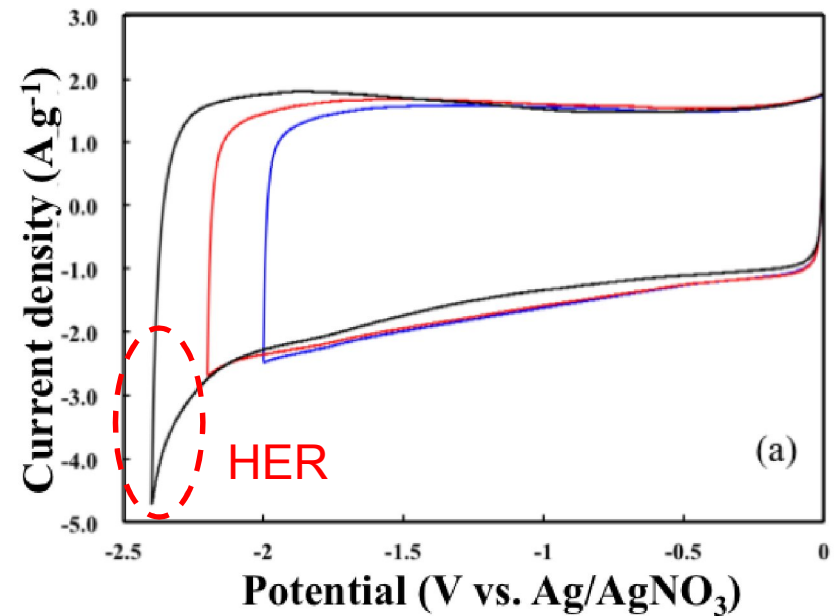


# Supercapacitor GNW

**Positive**



**Negative**

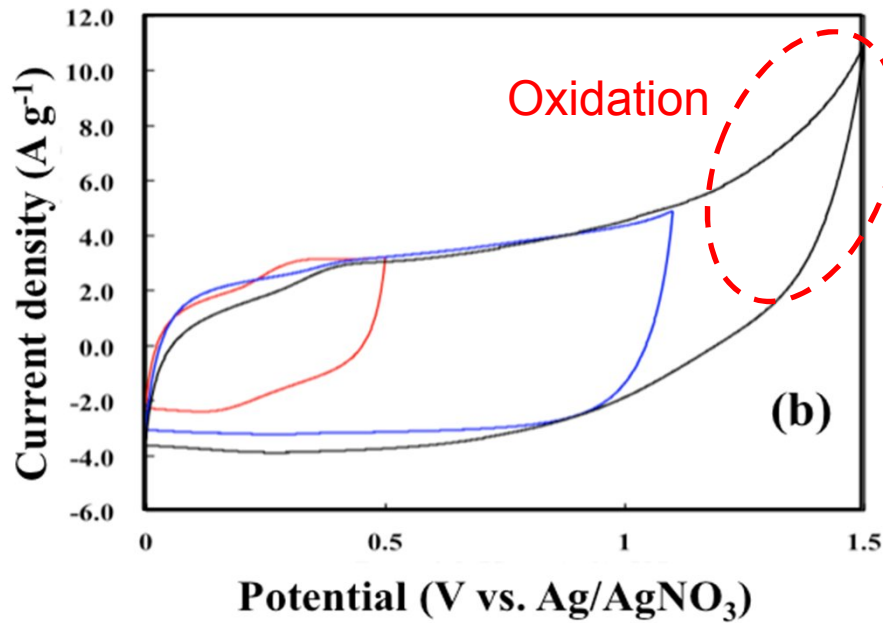




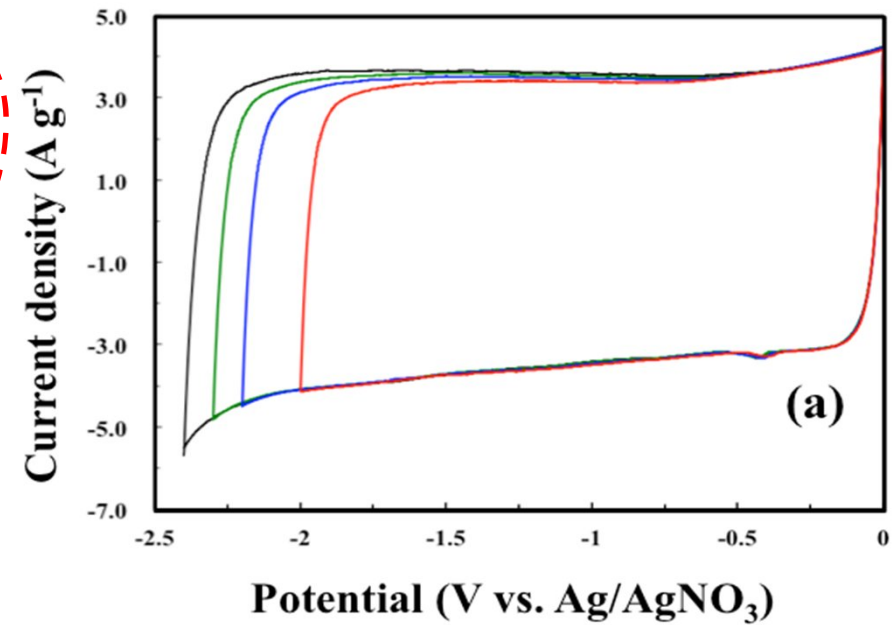


# Supercapacitor NGNW

**Positive**

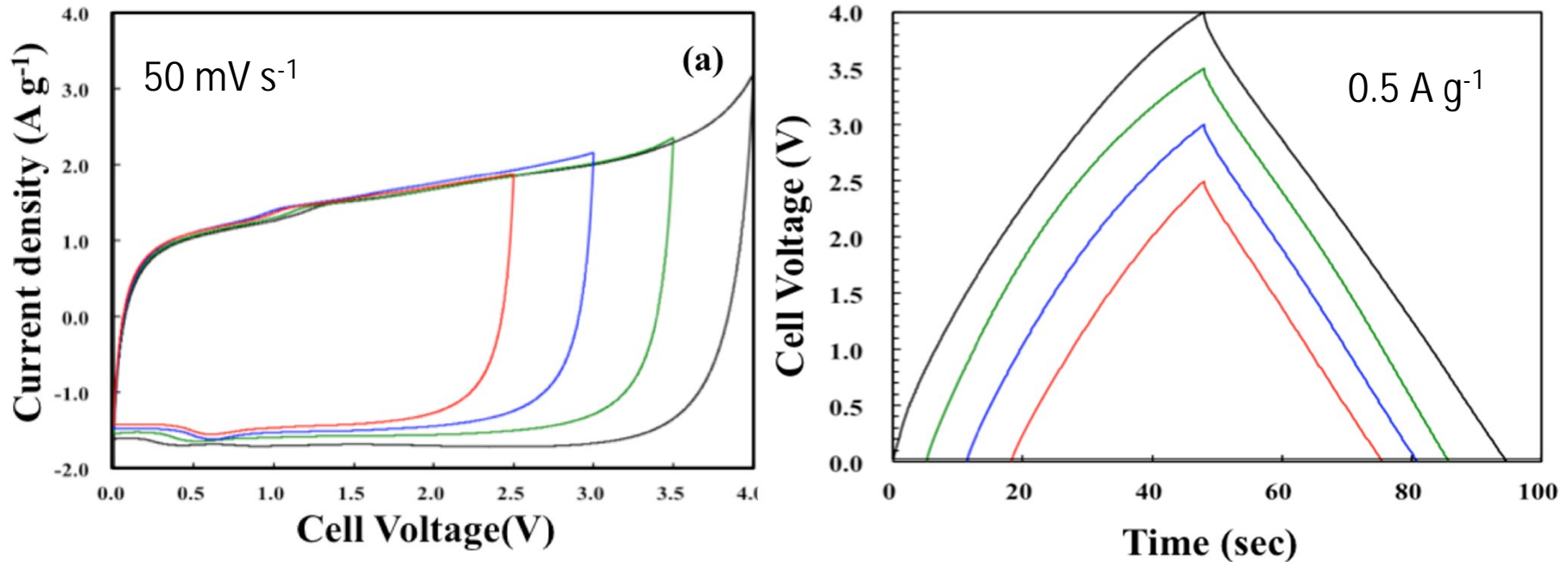


**Negative**





# Supercapacitor GNW-NGNW

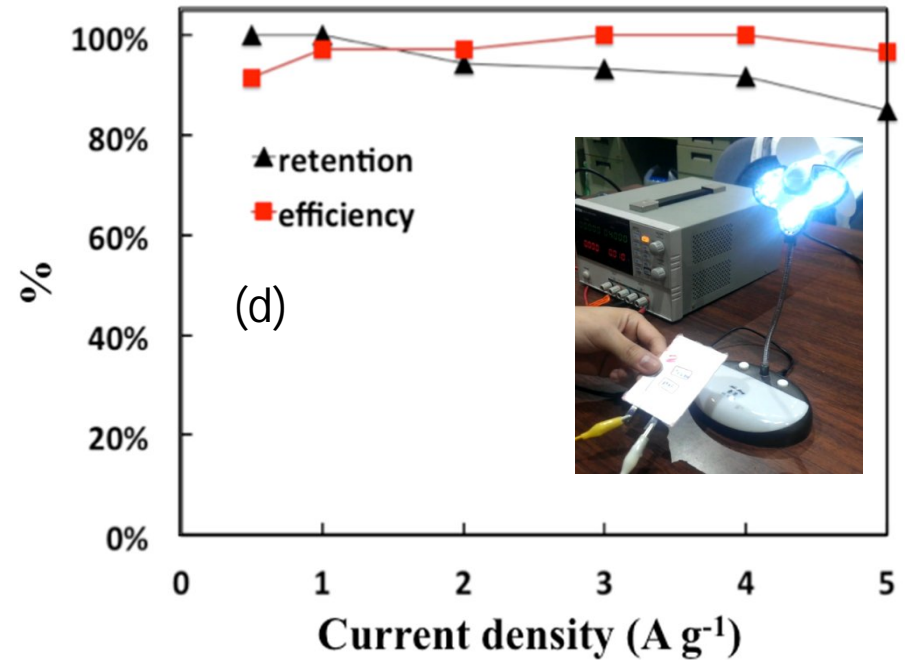
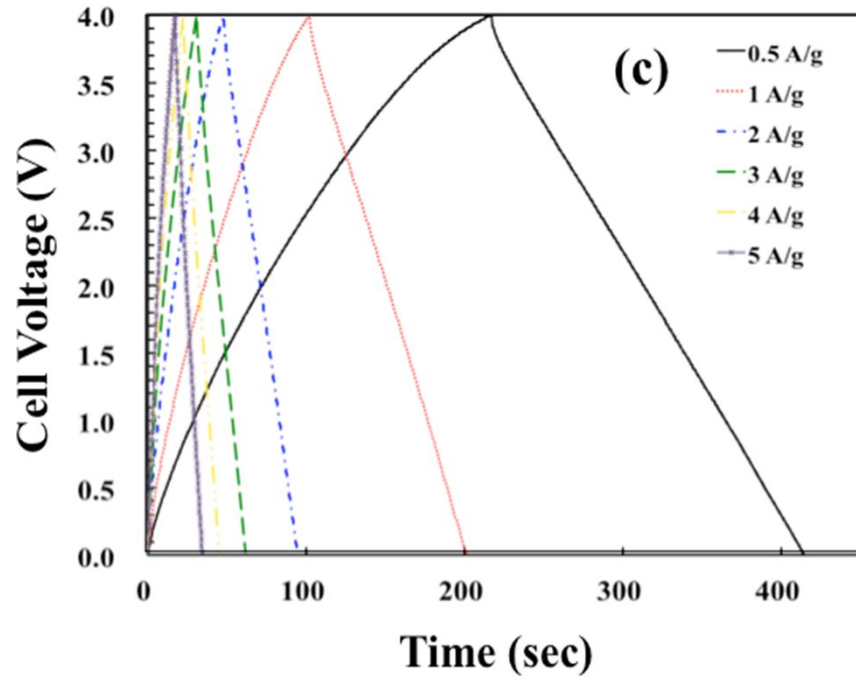


(a) CV curves and (b) constant- $i$  charge-discharge curves of an N-graphene //LQ graphene ASC in 1 M TEABF<sub>4</sub>/PC with a cell voltage of 2.5, 3.0, 3.5, 4.0 V at 50 mV/s or 2 A/g.

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



# Supercapacitor GNW-NGNW

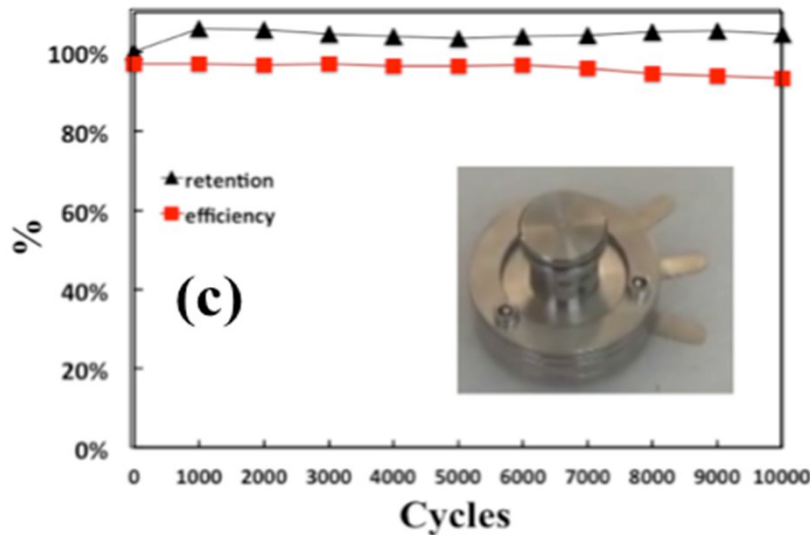
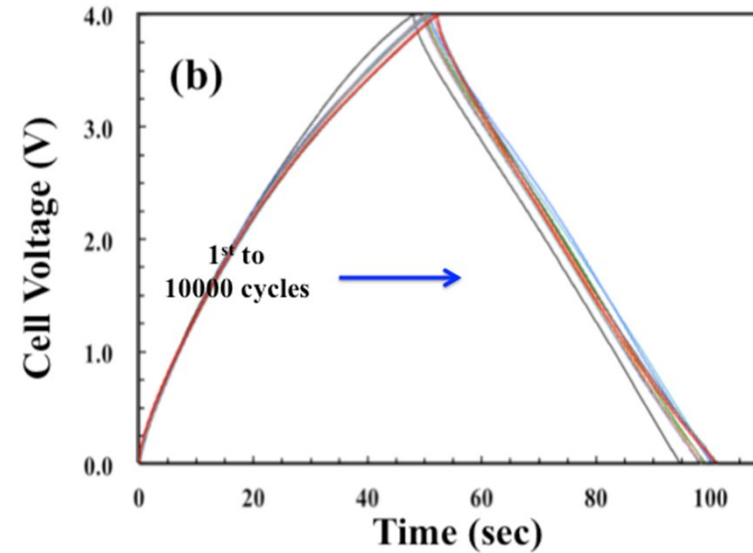
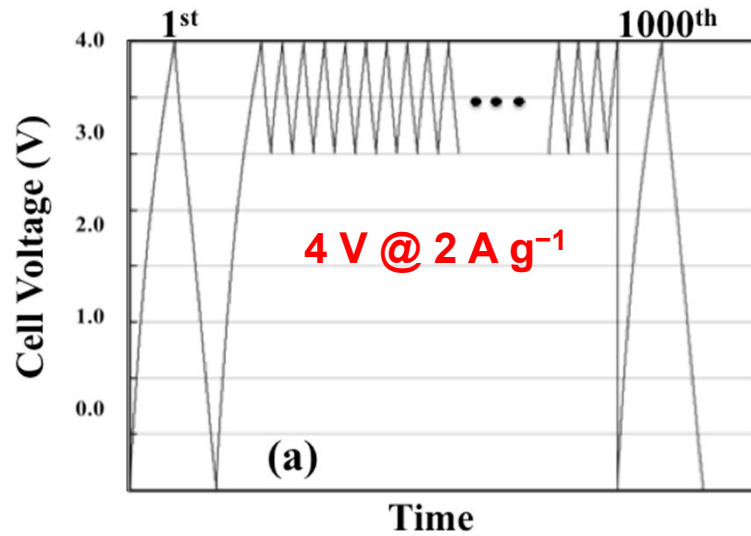


(c) The charge-discharge curves of an N-GNW (-)//GNW (+) ASC in 1 M TEABF<sub>4</sub>/PC with a cell voltage of 4.0 V at 0.3, 0.5, 1, 2, 3, and 5 A/g. (d) The C.E. and cell capacitance retention vs. charge-discharge current density for symmetric and asymmetric designs.





# Supercapacitor Cycle Life Test

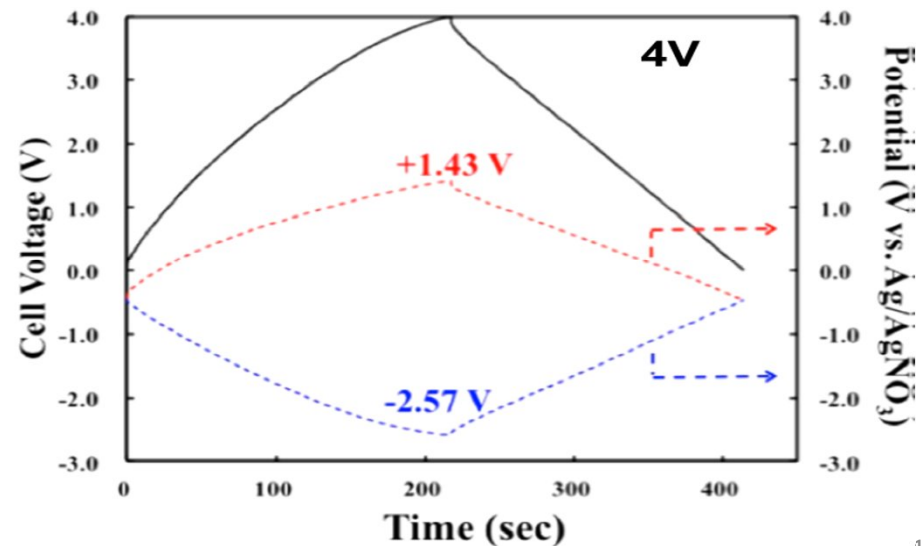
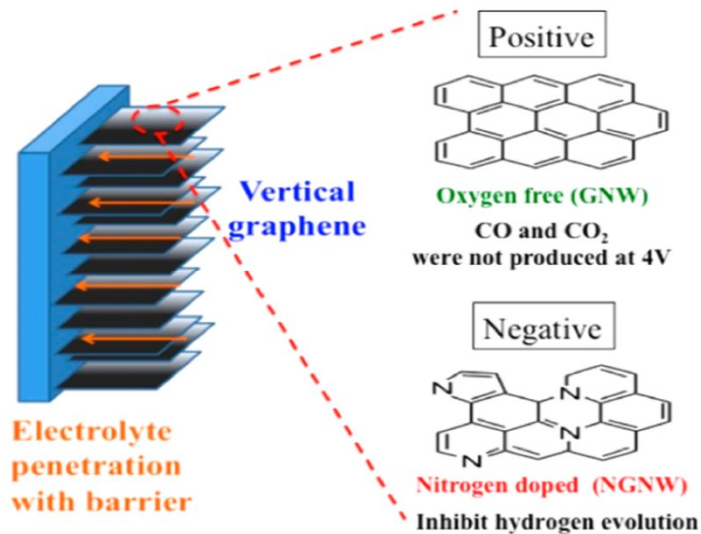


After 10000 cycles,  
efficiency and retention are  
still maintain 93% and 100%  
respectively.



# Conclusions

- MP CVD can grow and dope graphene at the same time.
- 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)





# Acknowledgements

## Funding

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## Collaboration



## Graphene Task Force

### Consultant



Prof. C. S. Kou



Prof. C. C. Hu

### Team Members



Dr. C. C. Chang



Miss Y. W. Chi



Mr. H. F. Wang



Mr. J. C. Ho



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**Thanks for your attention!**