Lightweight Supercapacitors with Porous Nanocarbon Platforms

PI: Yi Lin (National Institute of Aerospace)

Co-I: **Jae-Woo Kim** (National Institute of Aerospace)

Collaborator: **Liangbing Hu** (U. Maryland – College Park)

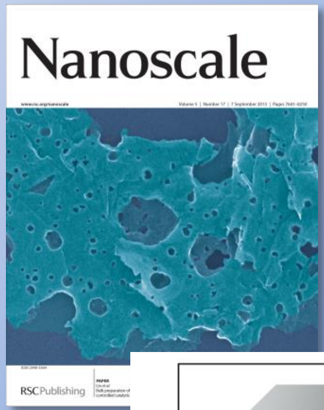
NASA Aeronautics Research Mission Directorate (ARMD)

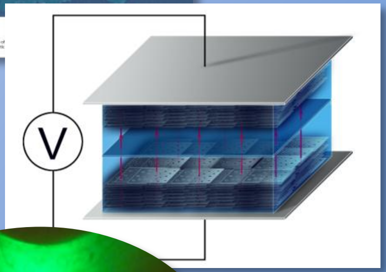
FY12 LEARN Phase I Technical Seminar

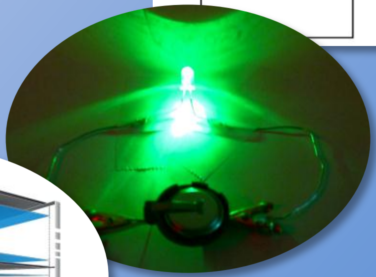
November 13, 2013

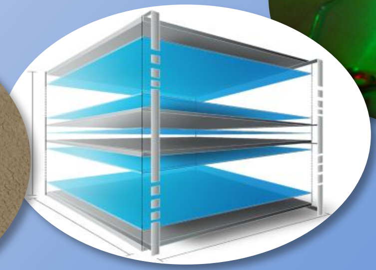
Outline

- Project Overview
- Background: Innovation/Goal/Impact
- Phase I Efforts
  - Technical approach
  - Results to date
  - Publications, Patents, Presentations
- Next steps (Phase-II)
- Summary









Project Overview I

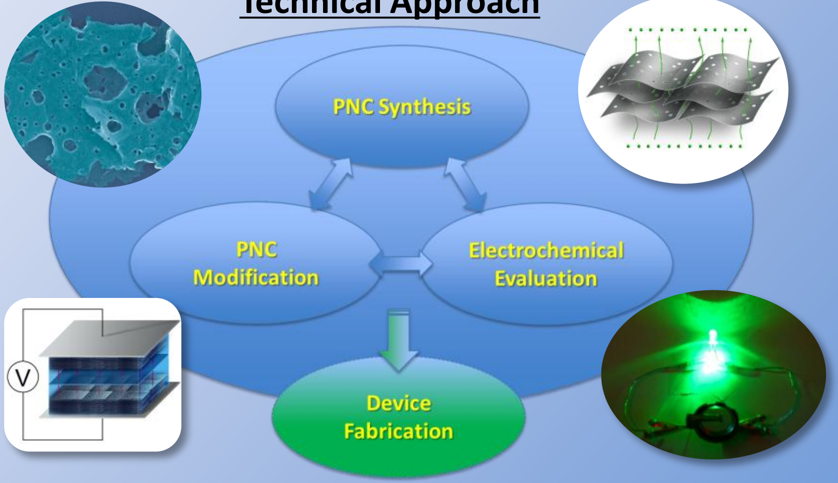
<u>Innovation</u>: Porous nanocarbon (PNC) materials

- ❑PNCs: Holey graphenes (hGs) and holey carbon nanotubes (hCNTs)
- ❑Porosity introduced directly onto sp^2 graphitic surfaces of nanocarbons - retained crystallinity/conductivity
- ❑Unique approach(es) for scalable production

<u>Objective</u>: Lightweight , Low-Volume Supercapacitors for Aeronautics

- ❑ <u>Phase-I Objective</u>: To obtain electrochemical performance – structural relationships of synthesized and modified PNC materials for supercapacitor applications

<u>Technical Approach</u>



<u>Team</u>:

- ❑Dr. Yi Lin (PI)
- ❑Dr. Jae-Woo Kim (Co-I); Dr. Kent Watson (Co-I)
- ❑Prof. Liangbing Hu (U. of Maryland – College Park)
- ❑Dr. John Connell (NASA LaRC)
- ❑Students/Postdocs: Caroline Campbell (NIA); Michael Funk (W&M-LaRC); Xiaogang Han (UMD); Jiaqi Dai (UMD)

<u>Budget</u>: $200k total;

- ❑~$34k Electrochemical station (modular/expandable)
- ❑~$20k Essential electrochem supplies and equipment

<u>Achievements</u>: TRL: 1-2 (starting) to 3-4 (current)

❑ <u>Milestones:</u>

- Controlled synthesis of PNCs by varying experimental parameters.
- Modification of PNCs to improve capacitive performance.
- Electrochemical evaluation of all synthesized and modified PNCs.

❑ <u>Distribution/dissemination:</u>

- 1 published journal article, 1 patent application, 1 provisional patent application, 1 invited talk

<u>Next Step</u>:

Phase-II: PNC Optimization & Supercap Prototype Demo

Publications, Patents, Presentations

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- **Peer-Reviewed Journal Article**:
  - Lin, Y.; Waston, K. A.; Kim, J.-W.; Baggett, D. W.; Working, D. C.; Connell, J. W. *Bulk Preparation of Holey Graphene via Controlled Catalytic Oxidation. Nanoscale* **2013**, *5*, 7814-7824 (Cover Article).
- **Non-Provisional Patent Application**:
  - Watson, K. A.; Lin, Y.; Ghose, S.; Connell, J. W. "Bulk Preparation of Holey Carbon Allotropes via Controlled Catalytic Oxidation." U.S. patent application filed on 04/01/2013.
- **Provisional Patent Application** :
  - Lin, Y.; Kim, J.-W.; Connell, J. W; Funk, M. R.; Campbell, C. J. "Single-Step, Solvent-Free, Catalyst-Free Preparation of Holey Carbon Allotropes." Invention disclosure filed on 04/04/2013; provisional patent filed on 10/14/2013.
- **Invited Talk**:
  - Lin, Y.; Kim, J.-W.; Funk, M. R.; Connell, J. W. Lightweight Platforms toward Composite and Energy Storage Applications. 2nd International Symposium on Graphene for Energy. 246th American Chemical Society (ACS) National Meeting, Indianapolis, IN (September 2013).
- **Symposium Organization**:
  - "Two Dimensional Materials for Energy and Fuel" for 247th ACS National Meeting, Dallas, TX (March 2014).

What is a Supercapacitor?

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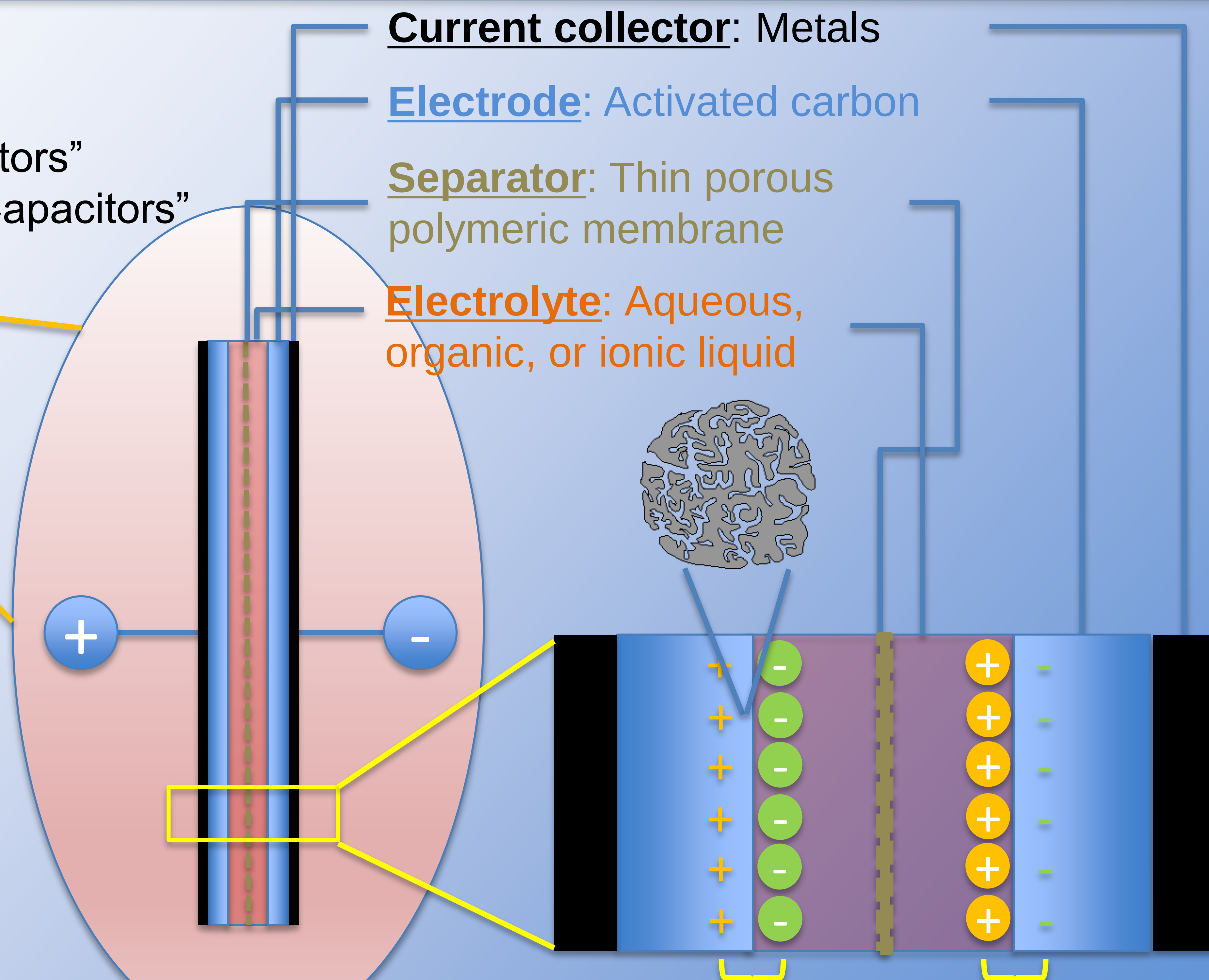
"Supercapacitors"
= "Ultracapacitors"
= "Electrochemical Capacitors"
= "Electric Double-Layer Capacitors"



Energy Storage: Electrostatic Double-Layer

When compared to a battery:

- ❑ *Long lifetime*
- ❑ *Low cost per cycle*
- ❑ *High power density*
- ❑ *High peak currents*
- ❑ *No overcharge*
- ❑ *Environment friendly*
- ❑ *Safe*

Where are (will) they being used?

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Examples of Applications

- ❑ Consumer (**portable**) electronics
- ❑ Wireless transmission
- ❑ Medical device
- ❑ Vehicle control system
- ❑ Uninterrupted power supply
- ❑ Backup power and pulse

Aeronautics

- ❑Backup power systems
- ❑Avionics
- ❑Communication systems
- ❑UAVs

What's Out There?

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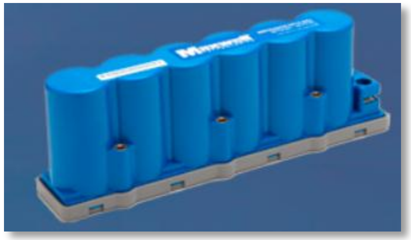
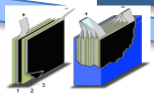
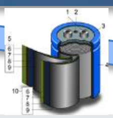
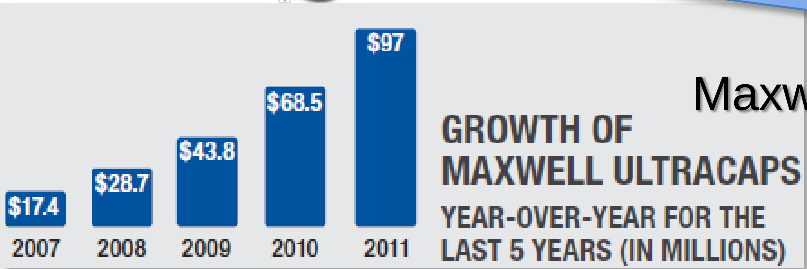




Maxwell Ultracapacitors

Electrode material: Activated carbon

Tecate Group
The power of the future. Today.

Cap-XX

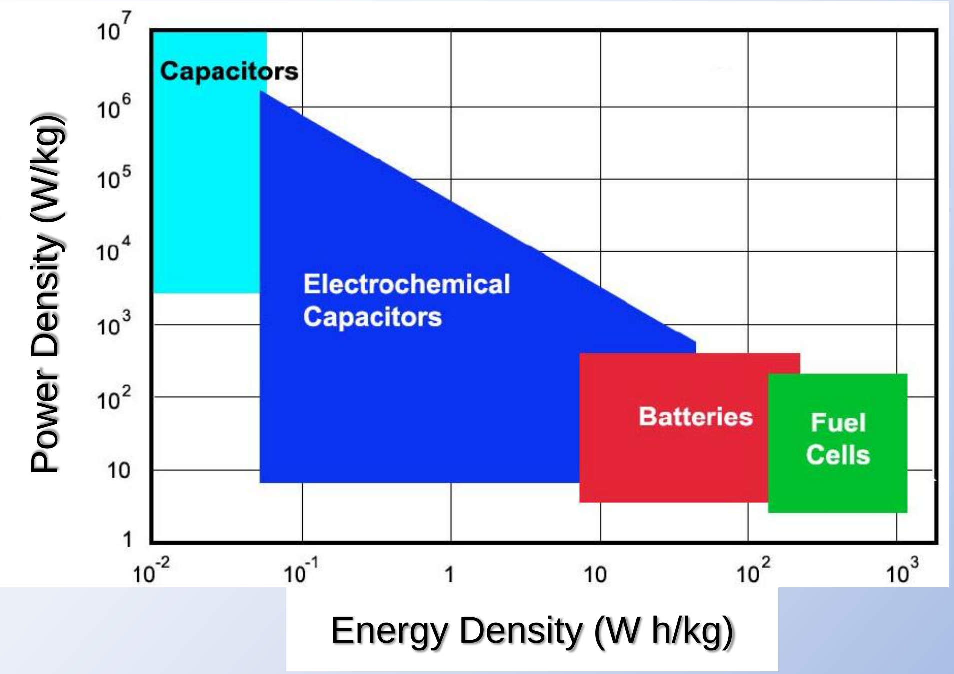
Cap-XX

Murata

http://www.cap-xx.com

- From 10 mF – 2.8 F
- Small footprint:
  - 28.5mm x 17 mm (one cell);
  - 39mm x 17 mm (dual cell)
- Thickness: 0.7 – 3.9 mm
- Lightweight packaging
- Wide operation temperature range (-40 – ~80 ºC)

Evaluation Criteria of Supercapacitor Electrodes



The Ragone Plot

Power Density

"How fast can you go"

$$P = \frac{V^2}{4Rs}$$

Energy Density

"How far can you go"

$$E = \frac{1}{2} C\, V^2$$

C: Specific Capacitance (F/g; F/cm^3)

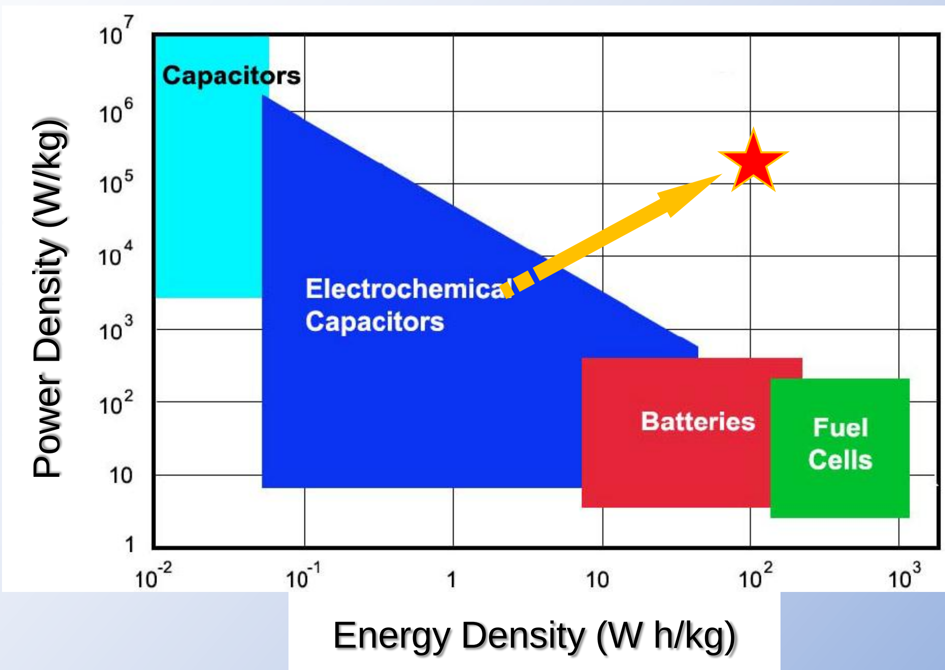
R_S: Internal resistance (Ω): determined by bulk conductivity

V: Operating voltage (V) determined by *electrolyte*

Goal & Impact

Goal: Lightweight and Low-Volume Supercaps

Improve both power density and energy density – by weight *and* volume



$$P = \frac{V^2}{4Rs}$$

$$E = \frac{1}{2} C V^2$$

Applications

- Backup power systems
- Avionics
- Communication systems
- UAVs

Impacts

- Improve aircraft reliability and operation time
- Improve energy efficiency
- Reduce emissions
- Improve aircraft safety

Nanocarbon (NC) Electrodes

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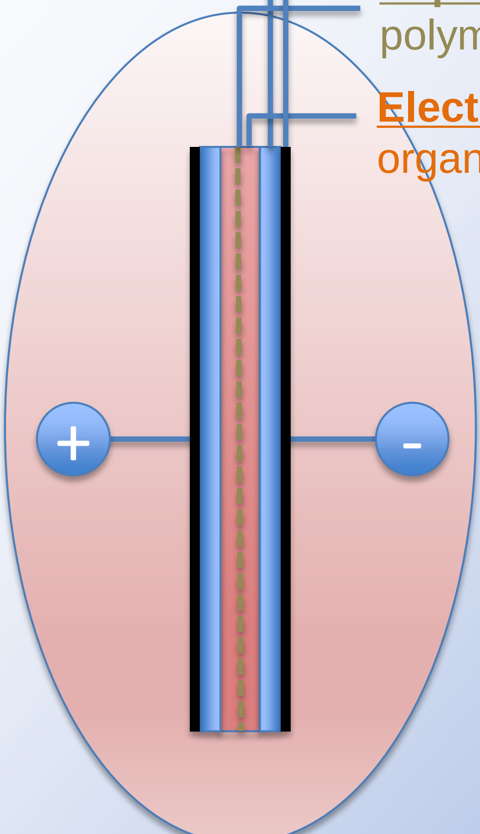
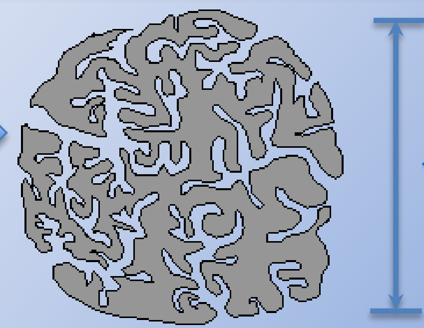


Current collector: Metals

Electrode: Activated carbon

Separator: Thin porous polymeric membrane

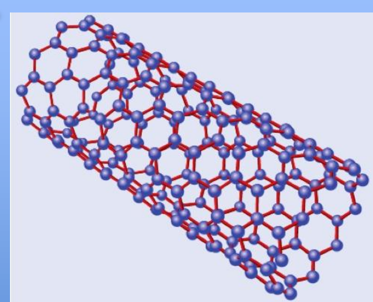
Electrolyte: Aqueous, organic, or ionic liquid



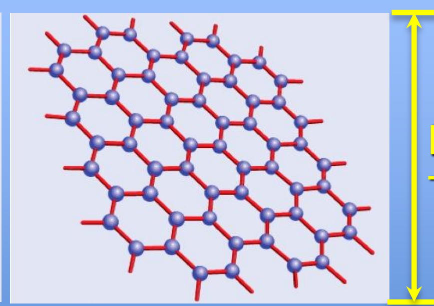
~0.02 – 0.8 mm

Nanocarbons

L < 5 µm
D < 100 nm



Carbon Nanotubes



Graphene

L < 10 µm
T < 5 nm

- ✓ High theoretical surface area
- ✓ High electrical conductivity

Improve Accessible Surface Area of NCs

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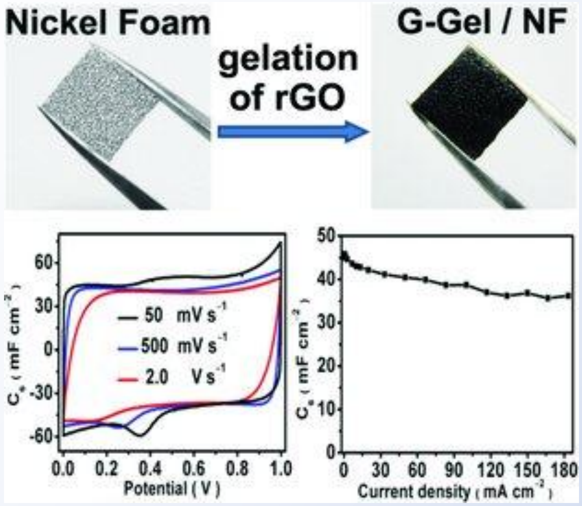
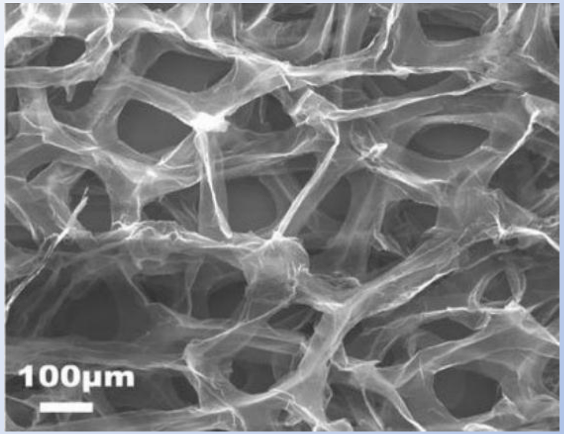
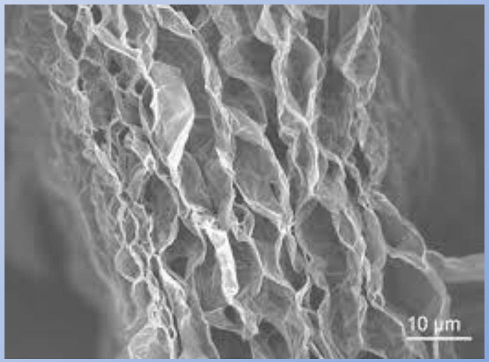
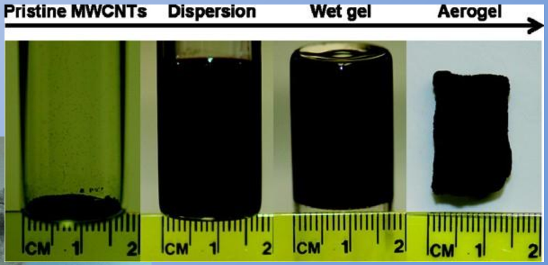




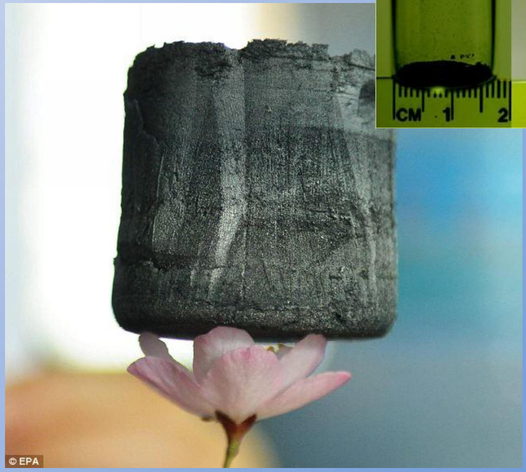




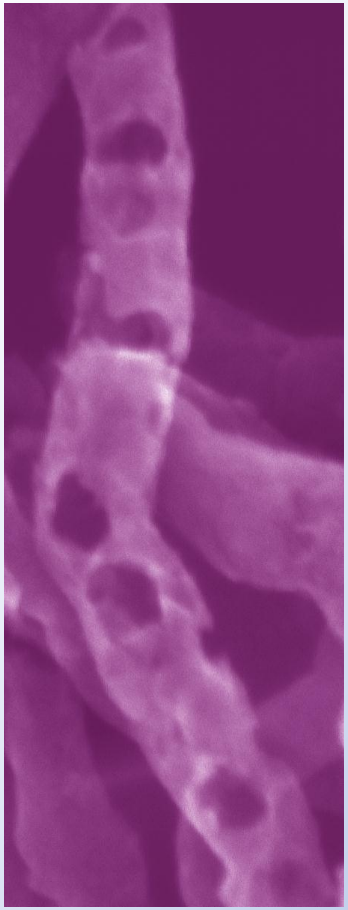
Graphene/CNT Foams/Aerogels:

✓Lightweight
✓Porous

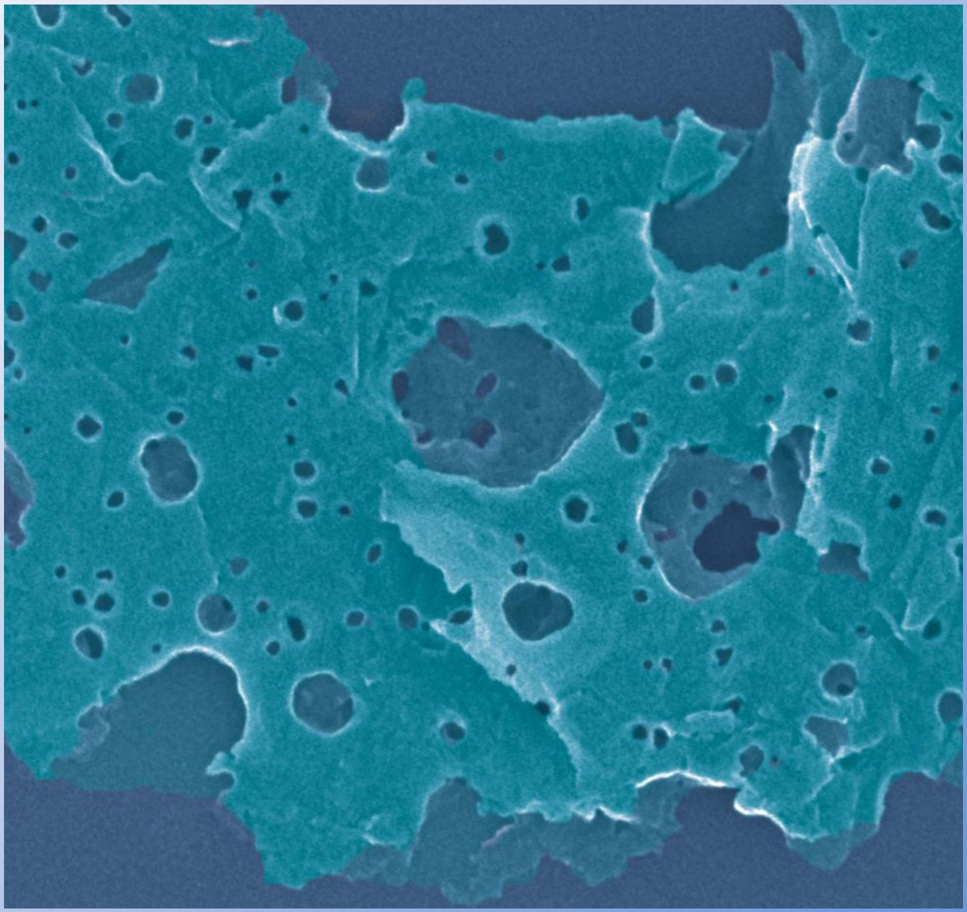
Large volume



Our Innovation:
Porous Nanocarbons (PNCs)



Holey Carbon Nanotube (**hCNT**)



Holey Graphene (**hG**)

Graphene vs. Holey Graphene

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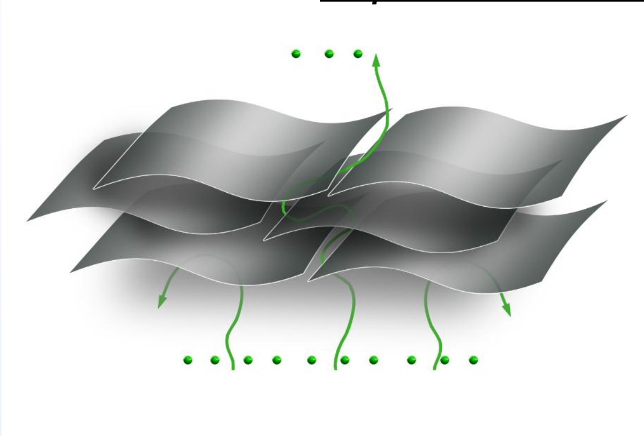
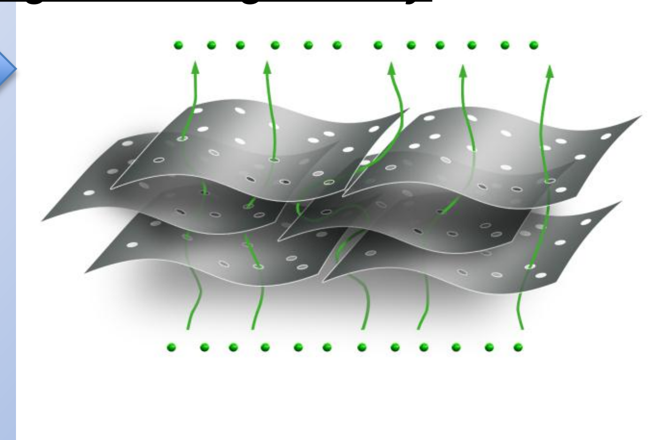
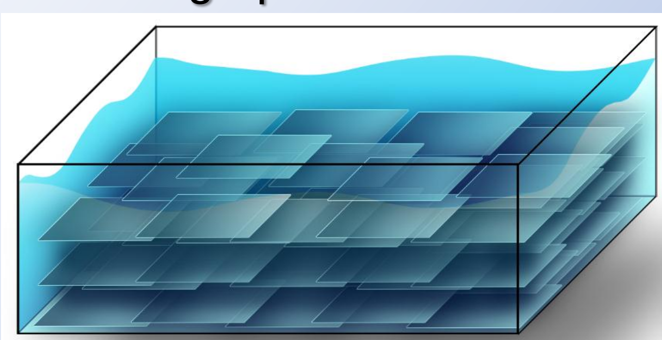
Improved ion transport path at high stacking density



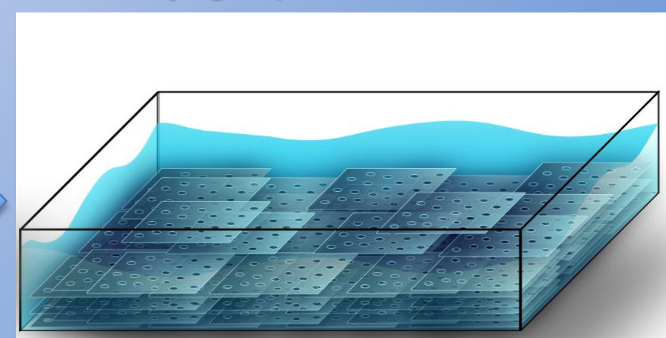


Raw graphene electrode

Holey graphene electrode



Equivalent Capacitance

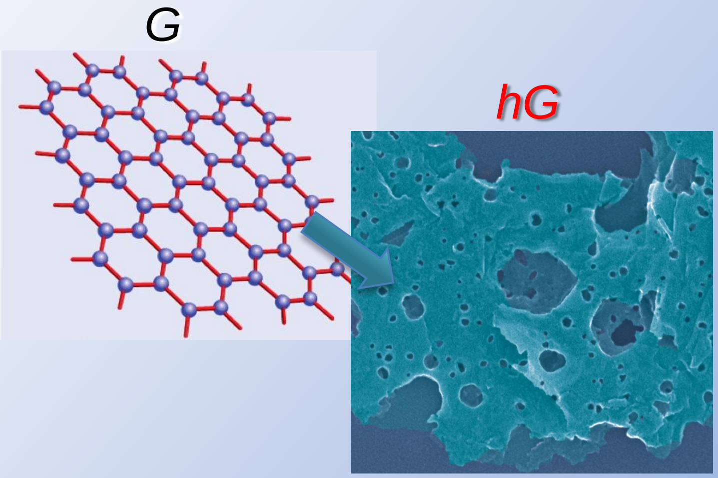


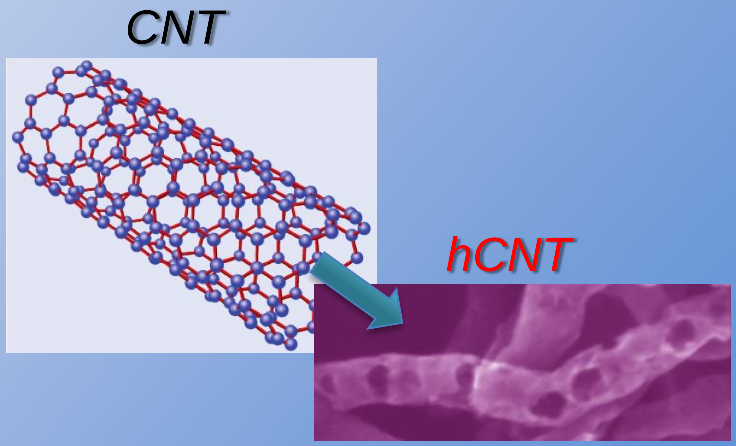
High volume

Low volume

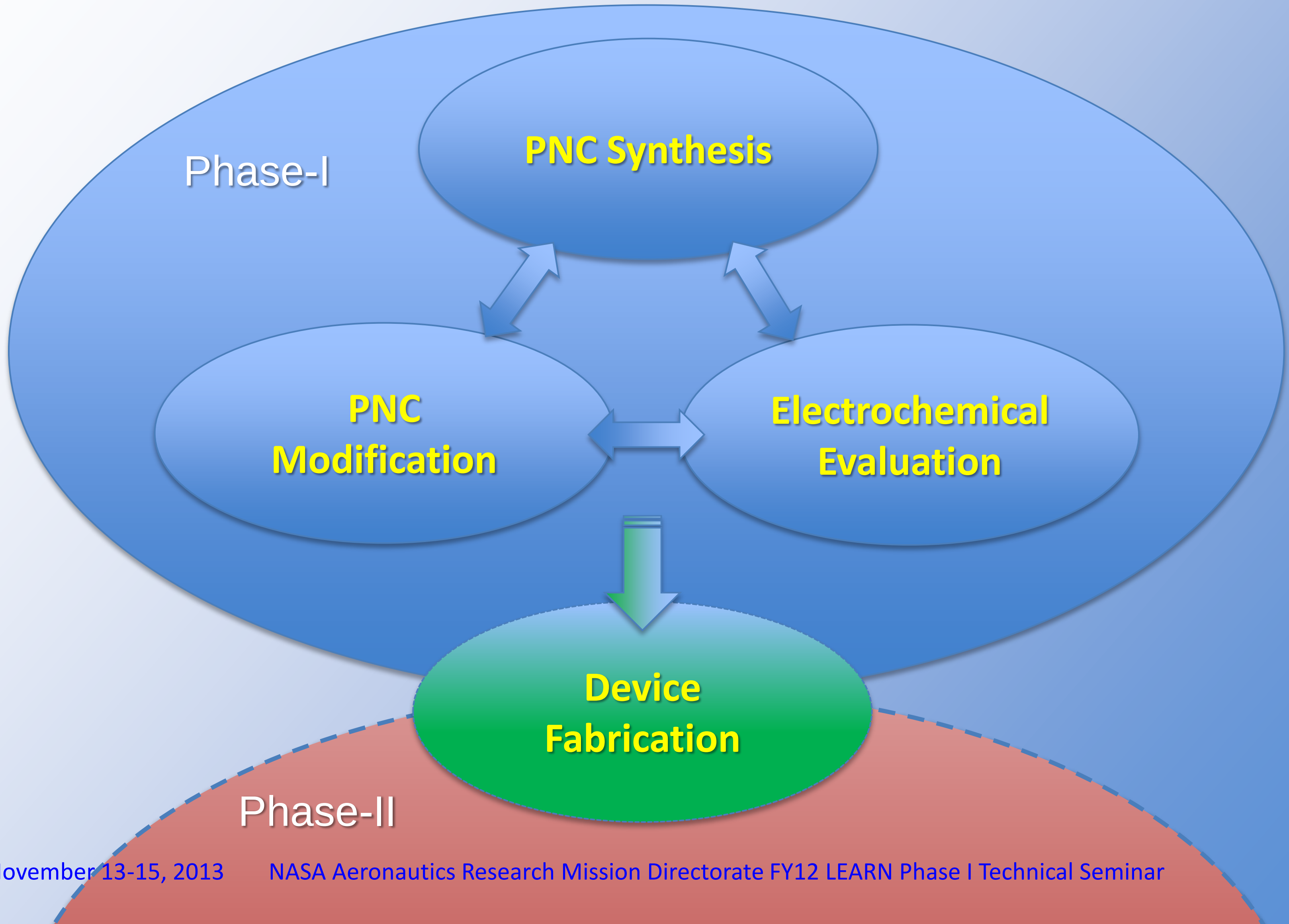
PNCs vs. NCs for Supercapacitors

- In-plane porosity: Improve ion transport path
- Accessible surface area: Improve gravimetric capacitance
- Volume reduction: Mitigate need to create large pores/spacing
- Electrical Conductivity: Retain graphitic crystallinity

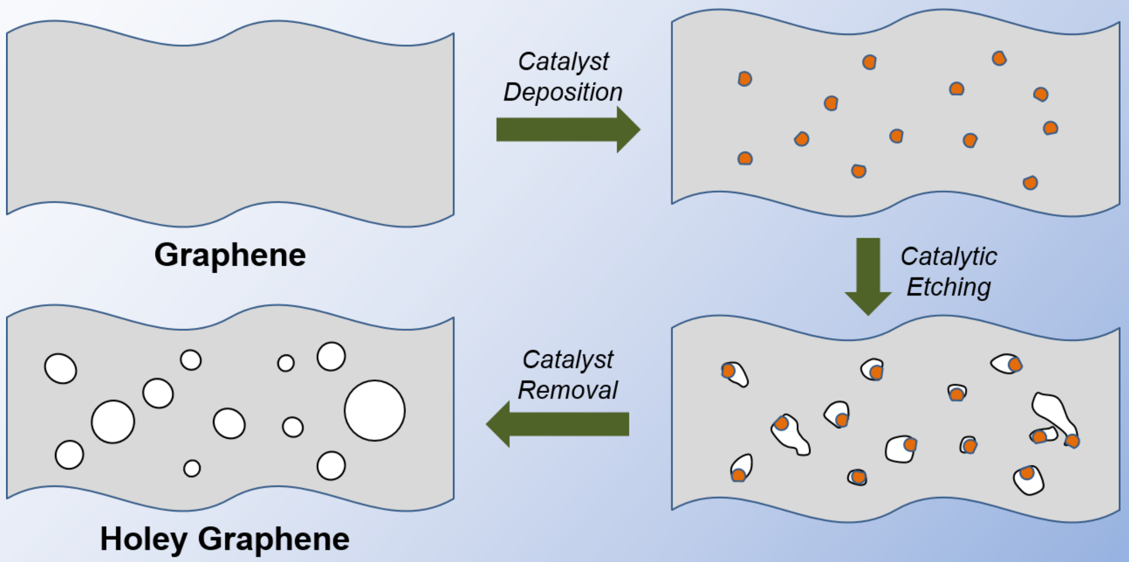




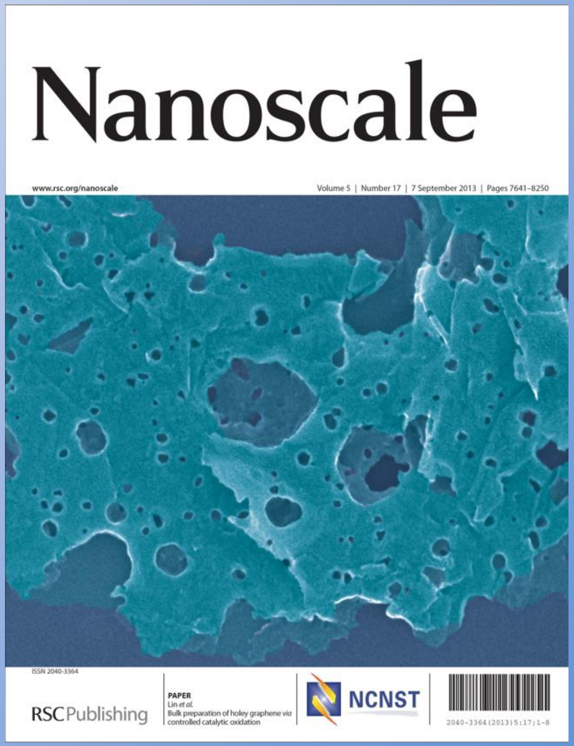
Phase-I: Technical Approach



Scalable Synthesis of PNCs



Controlled Catalytic Oxidation



Nanoscale **2013**, *5*, 7814.

U.S. patent application filed on 04/01/2013

Catalyst Deposition: A Scalable Approach

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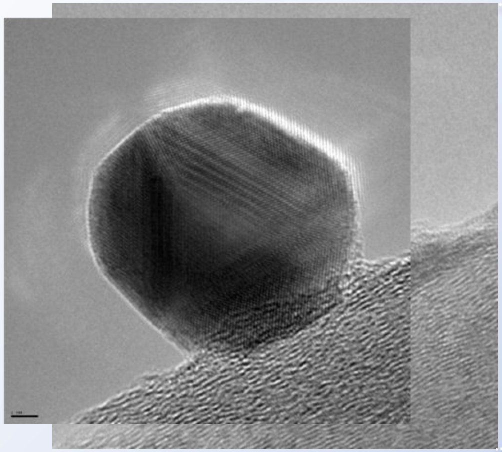
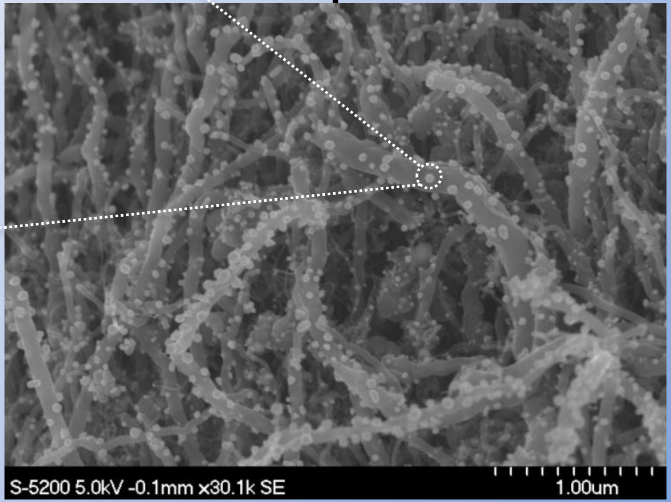
Silver (Ag) Acetate

Graphene or Carbon Nanotubes (CNTs)

Mix and Heat
in N_2 @ 350 ^{o}C



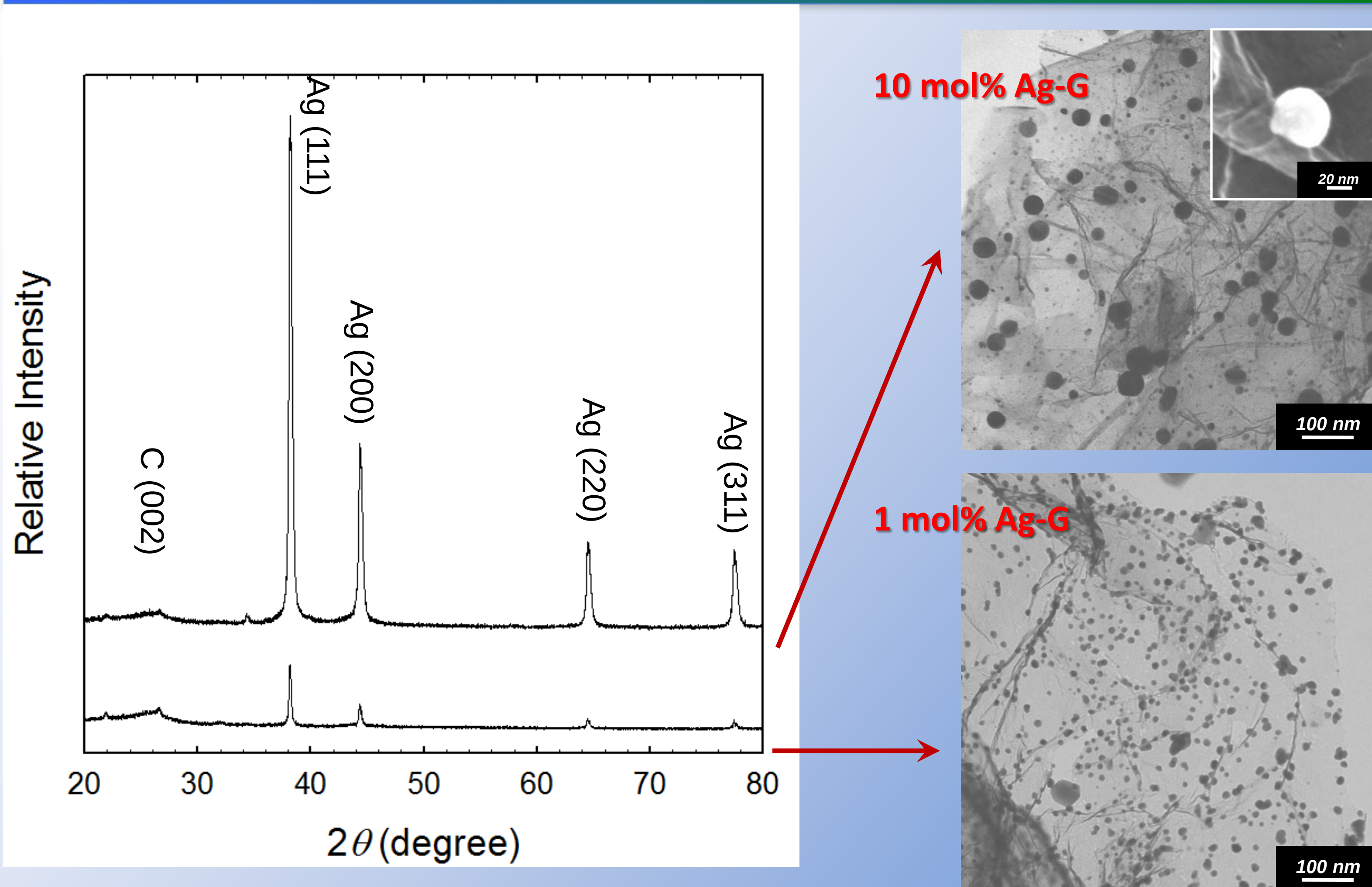


Ag Nanoparticle-Decorated CNTs

Lin, et al., *ACS Nano* 2009, *3*, 871.

- ✓**Solid-state**
- ✓No reducing agent
- ✓No electrochemistry
- ✓Rapid
- ✓**Scalable**
- ✓Versatile

Step I: Catalyst (Ag) Deposition



- ❑ Ag nanocatalyst sizes increase with precursor loading.

Step II: Catalytic Oxidation ("Etching")

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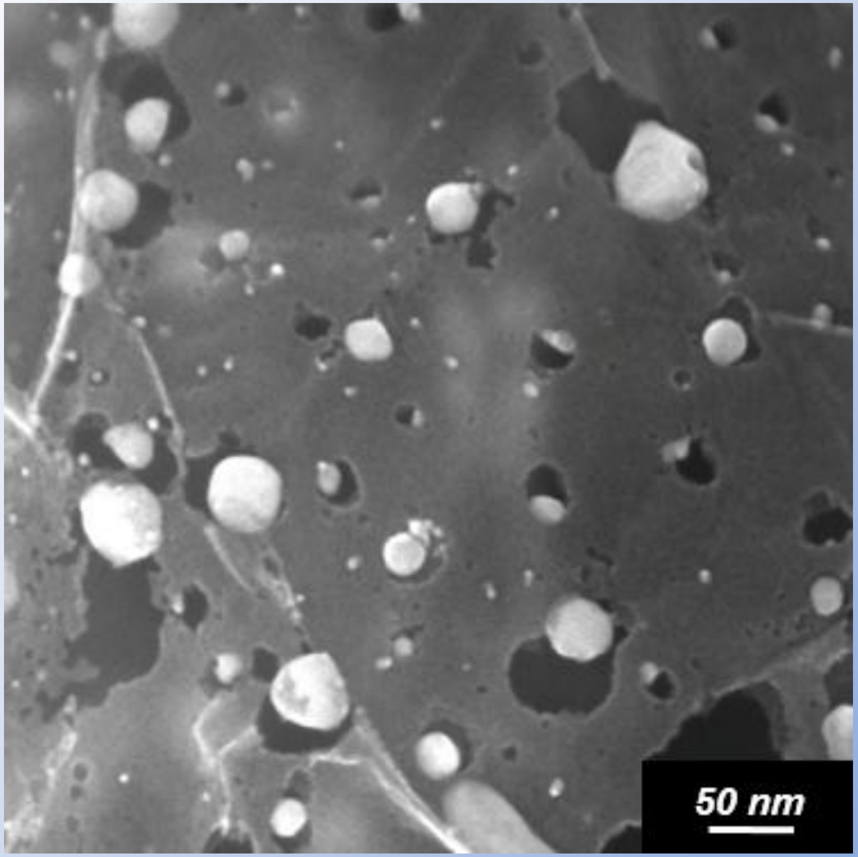
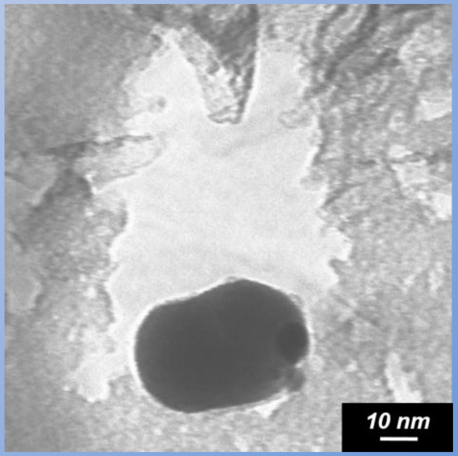


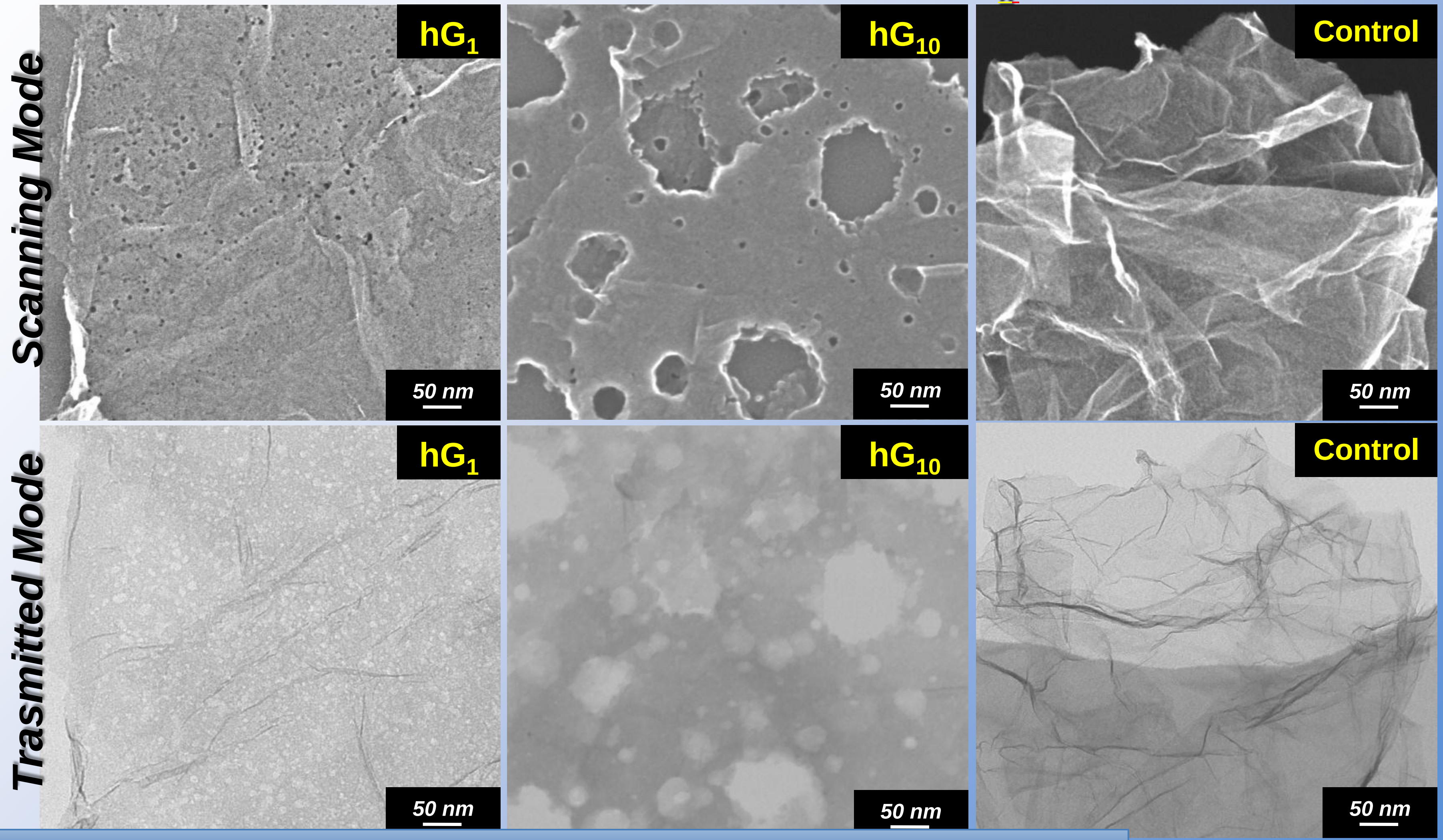


- ❑ Heat Ag nanocatalyst-loaded graphene in air to ~250 – 400 ^{o}C for 3 h.

Step III: Catalyst Removal

- ❑ Catalyst Removal: HNO3 (2.6 M), 2h reflux

hG$_x$ (X: Starting Ag Loading)



- ❑ Hole size is dependent on the starting Ag nanocatalyst loading.

Dependence on Etching Temperature

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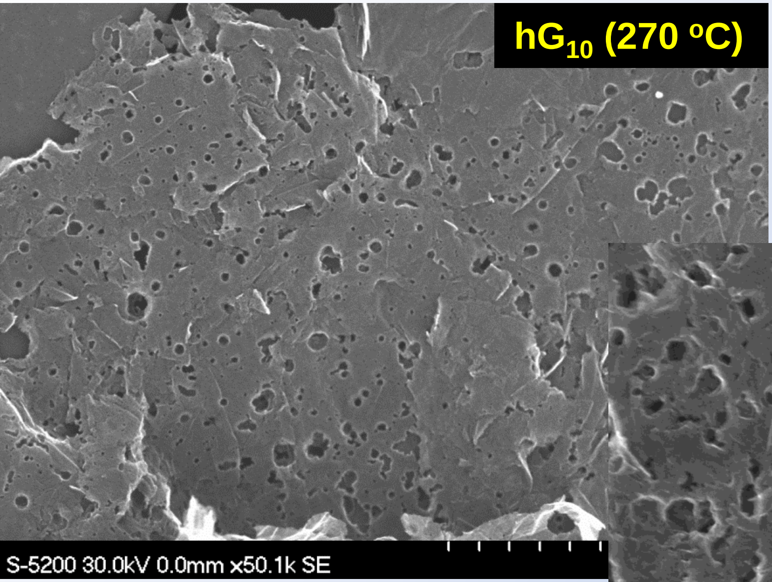
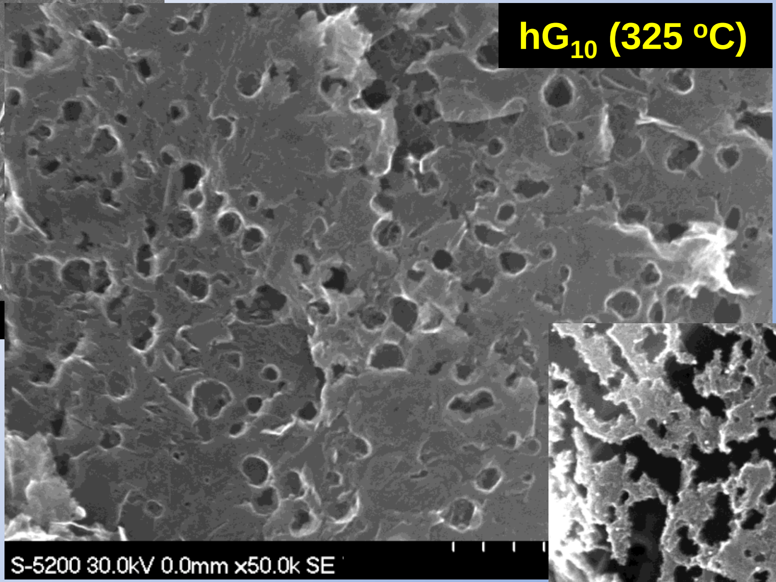
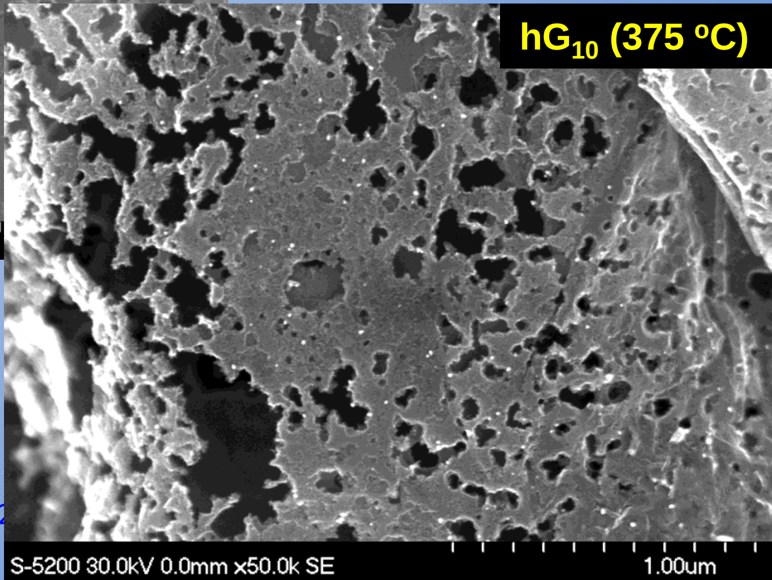
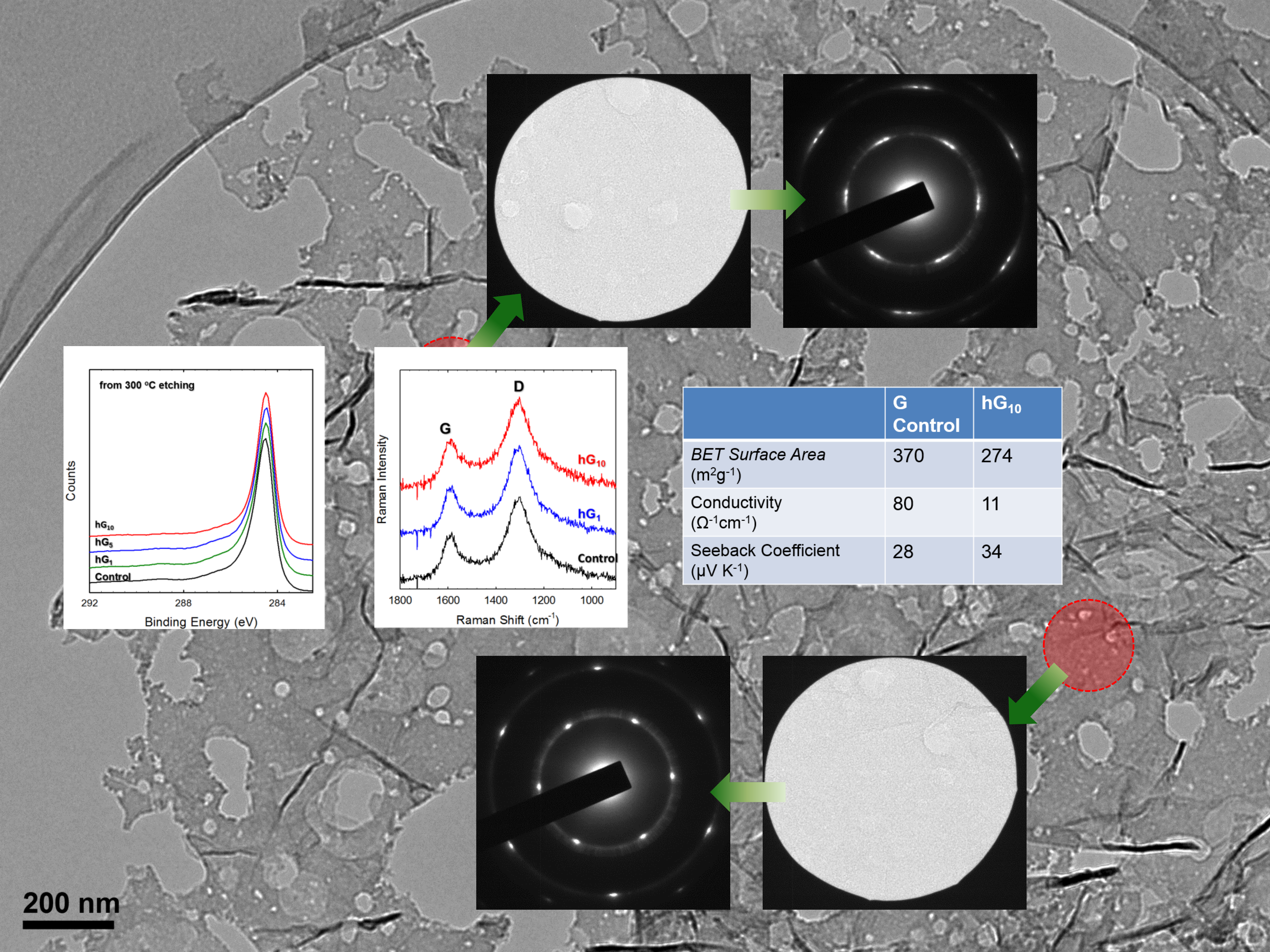
- ❑ Hole size/morphology can be tuned by etching temperature.





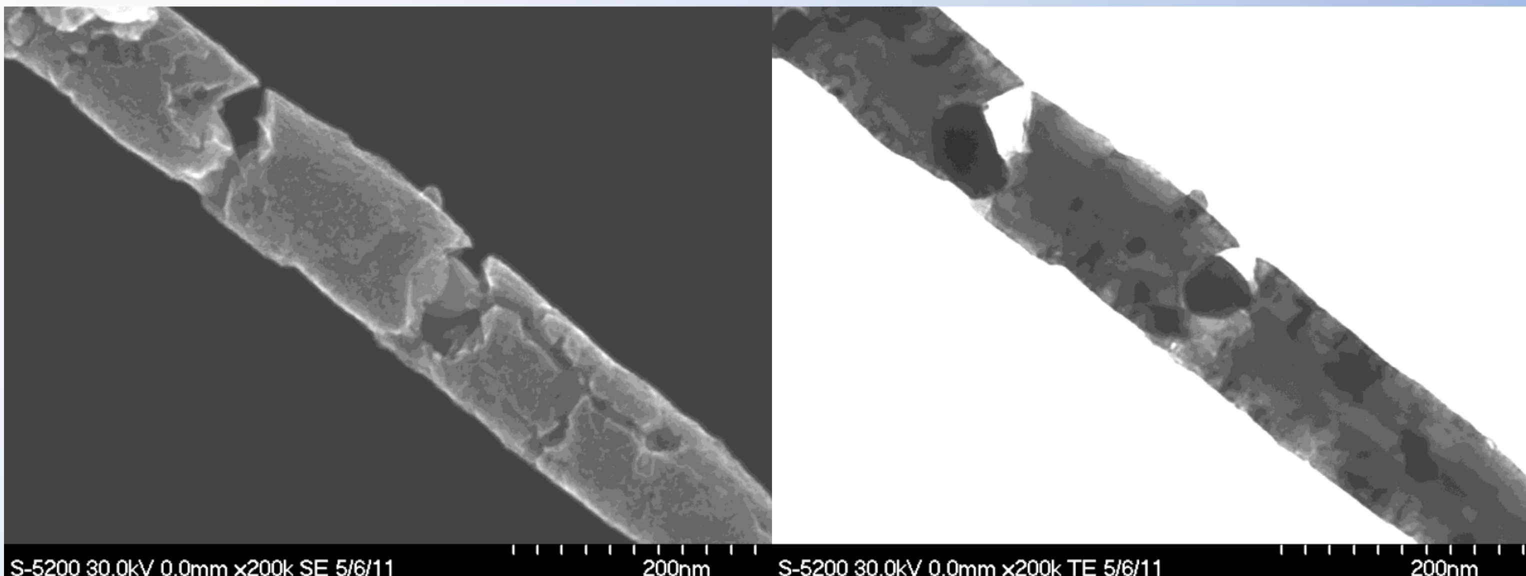


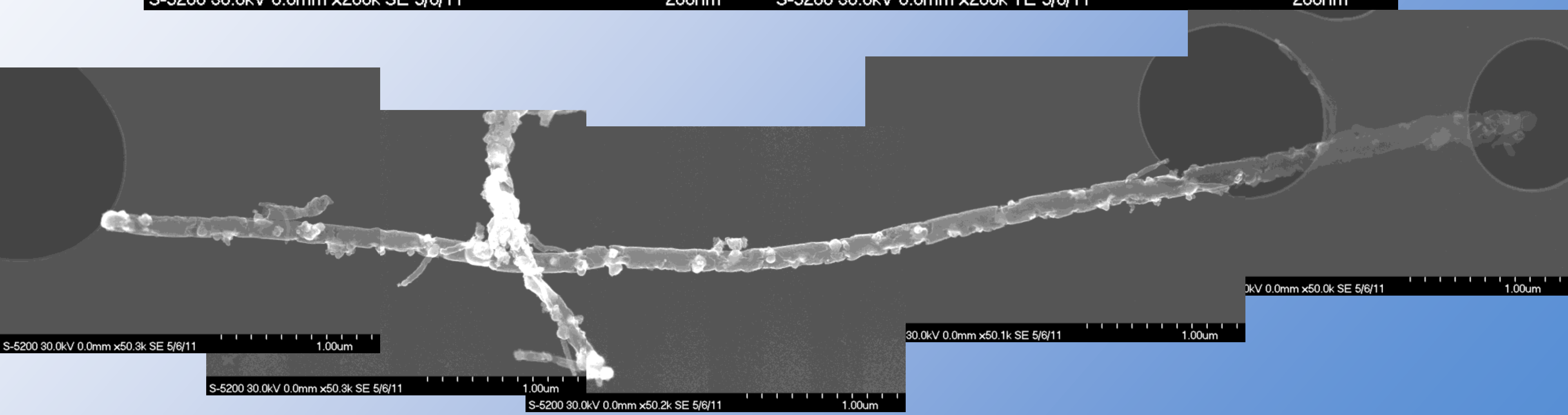
- ❑ <u>Catalytic Oxidation (“Etching”)</u>: 10 mol% Ag, <400 ºC, Air
- ❑ <u>Catalyst Removal</u>: HNO_3 (2.6 M), 2h reflux



	G Control	hG_{10}
BET Surface Area (m^2g^{-1})	370	274
Conductivity ($\Omega^{-1}cm^{-1}$)	80	11
Seeback Coefficient ($\mu V\ K^{-1}$)	28	34

hCNTs


S-5200 30.0kV 0.0mm x200k SE 5/6/11
200nm
S-5200 30.0kV 0.0mm x200k TE 5/6/11
200nm


S-5200 30.0kV 0.0mm x50.3k SE 5/6/11
1.00um
S-5200 30.0kV 0.0mm x50.3k SE 5/6/11
1.00um
S-5200 30.0kV 0.0mm x50.2k SE 5/6/11
1.00um
30.0kV 0.0mm x50.1k SE 5/6/11
1.00um
0kV 0.0mm x50.0k SE 5/6/11
1.00um

hCNTs

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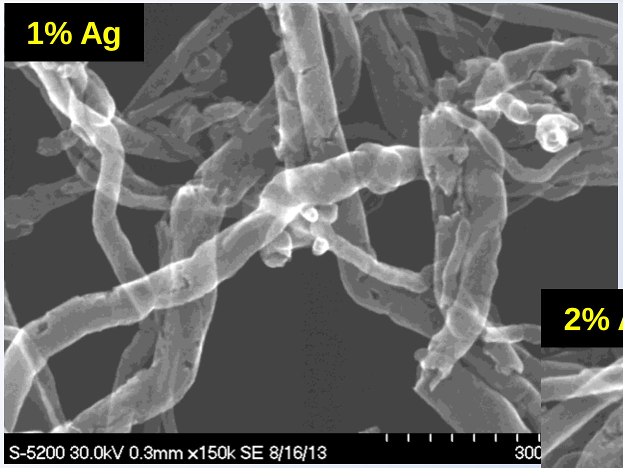
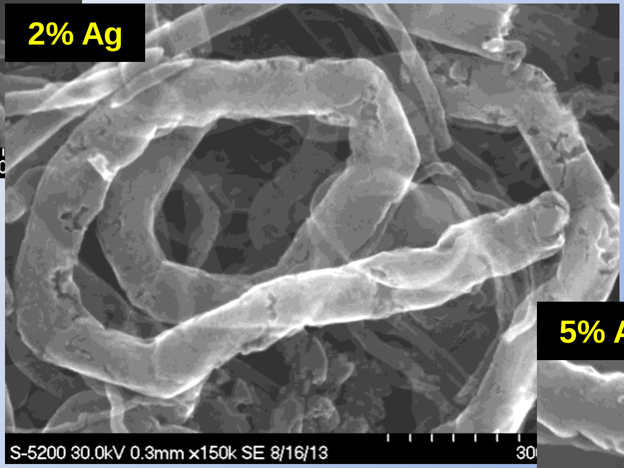
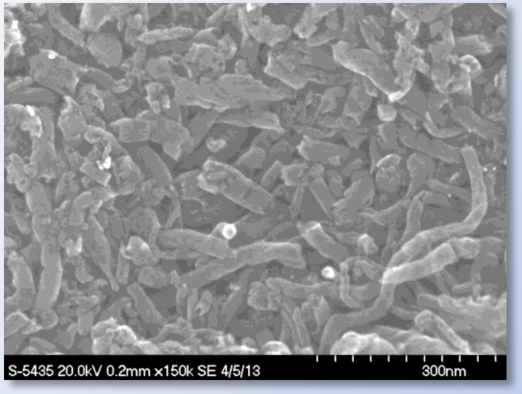
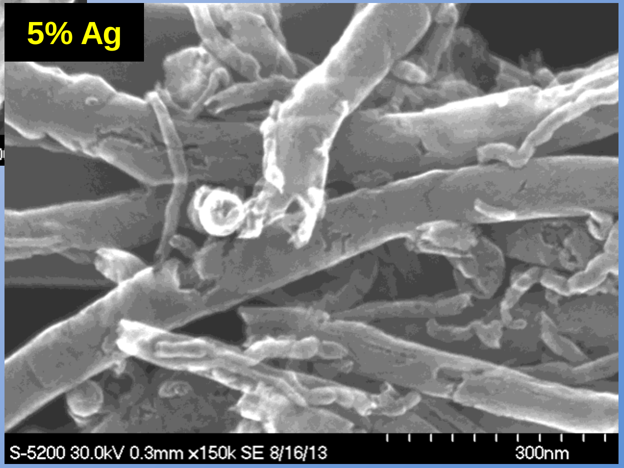


CNT of various average diameters were used

- **SWNT** ("Single-walled"): ~1.4 nm
- **FWNT** ("Few-walled"): 3 – 8 nm
- **MWNT** ("Multi-walled"): 10-30 nm, 40-60 nm, 60-100 nm







<u>CNT shortening should be avoided</u>

- Loss of long-range conjugation
- Loss of conductivity

Basic Electrochemical Evaluation

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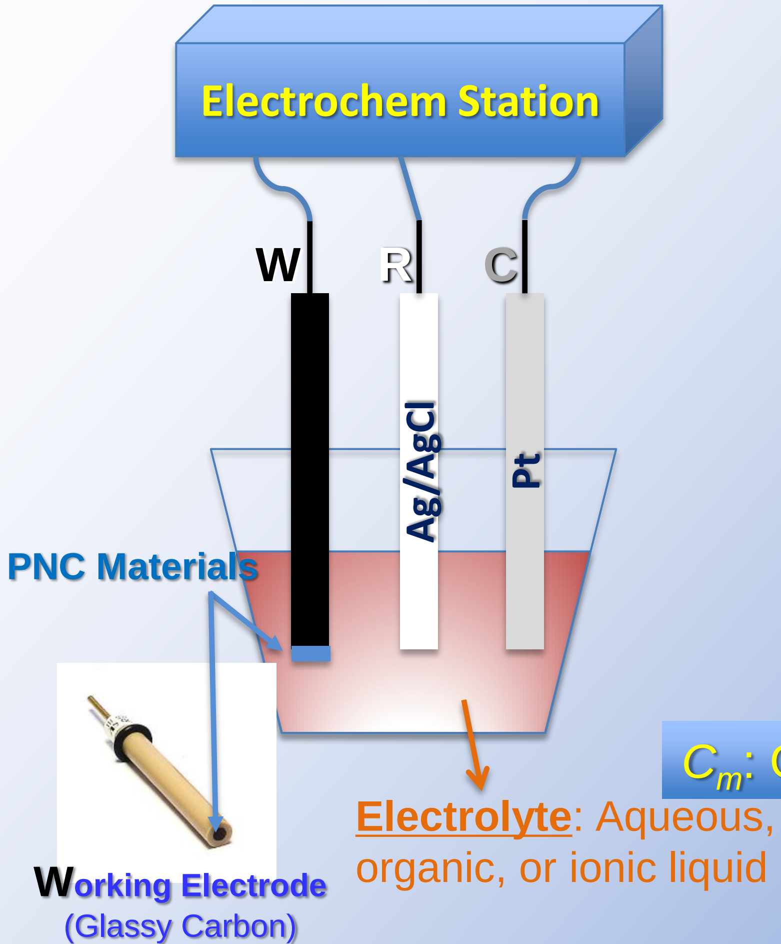
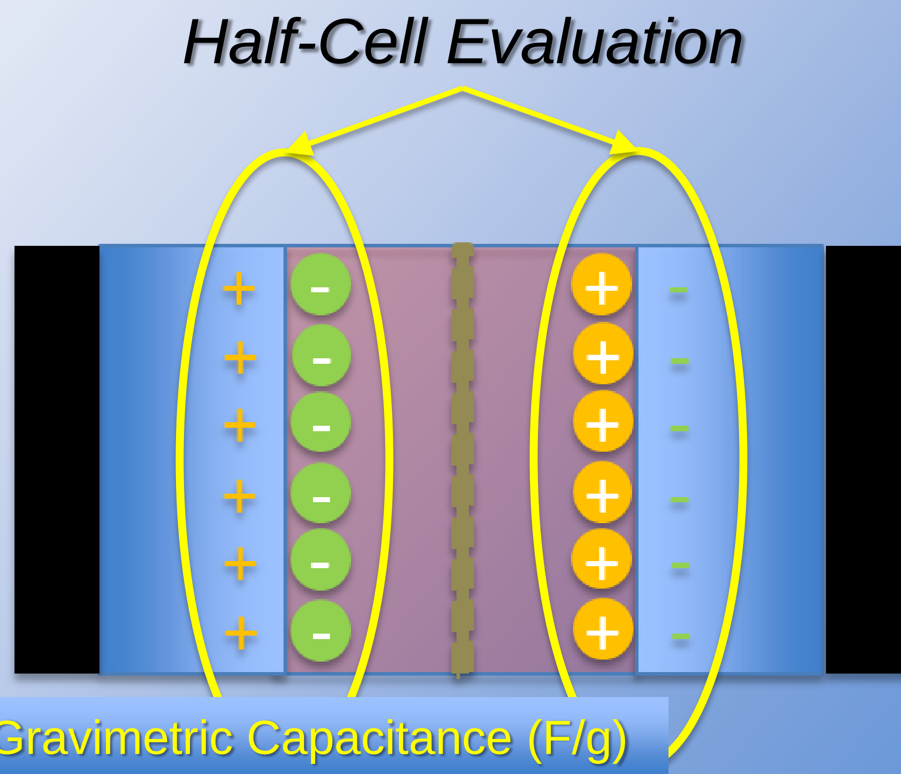




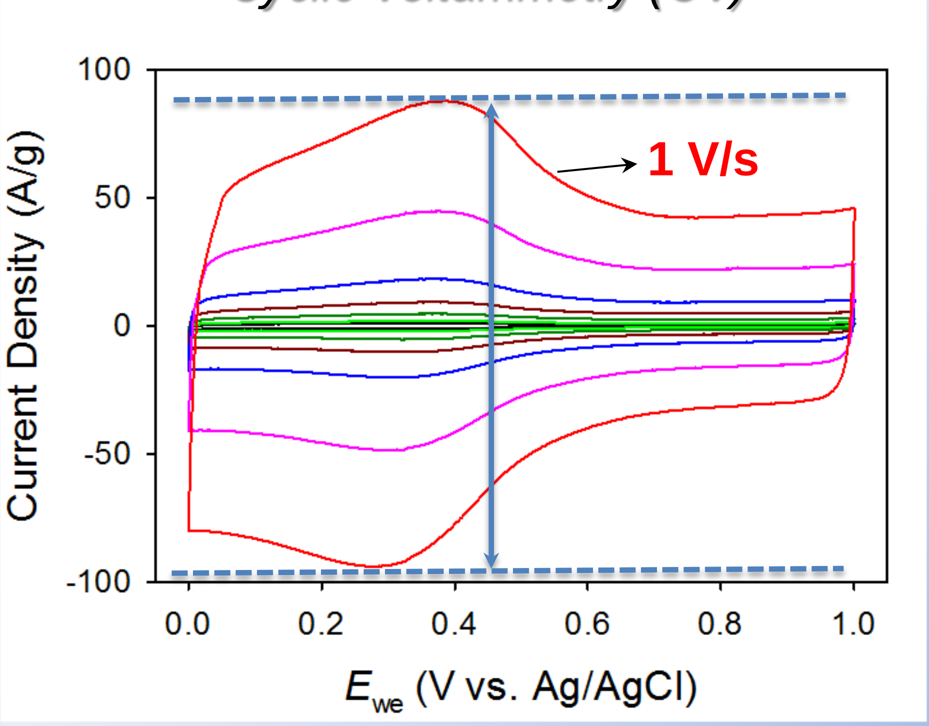
$$P = \frac{V^2}{4Rs}$$

$$E = \frac{1}{2} C V^2$$

Only a small amount of the test material is needed.

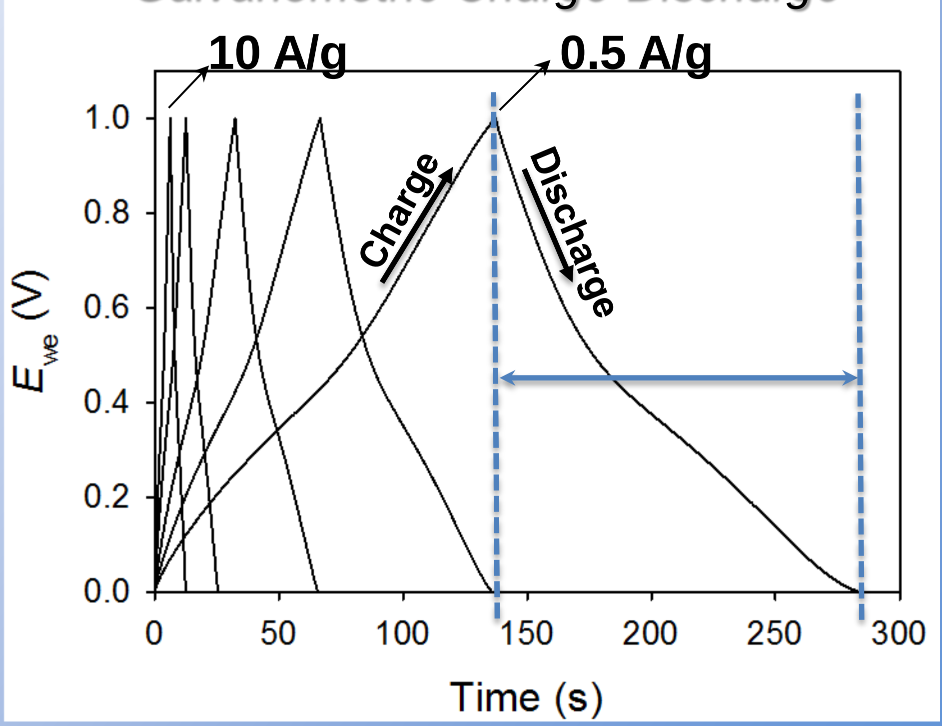
hG for Supercapacitors

Cyclic Voltammetry (CV)



Scan rate: 10, 20, 50, 100, 200, 500, 1000 mV/s

Galvanometric Charge-Discharge



Current Density: 10, 5, 2, 1, 0.5 A/g

$$C_m = \int I \, dV / 2mv$$

$$C_m = I / m \left(\frac{dV}{dt} \right)$$

- ❑ 0.5 M H_2SO_4
- ❑ 3-electrode configuration ("half cell")

Effect of Holes?

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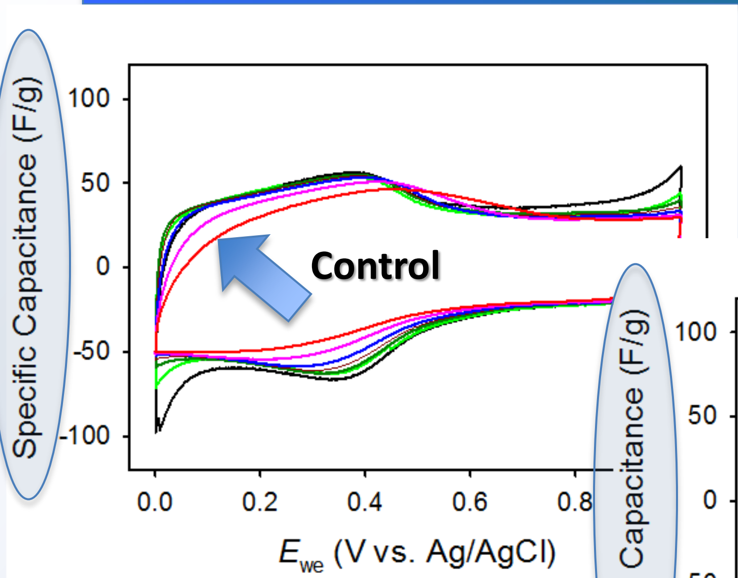
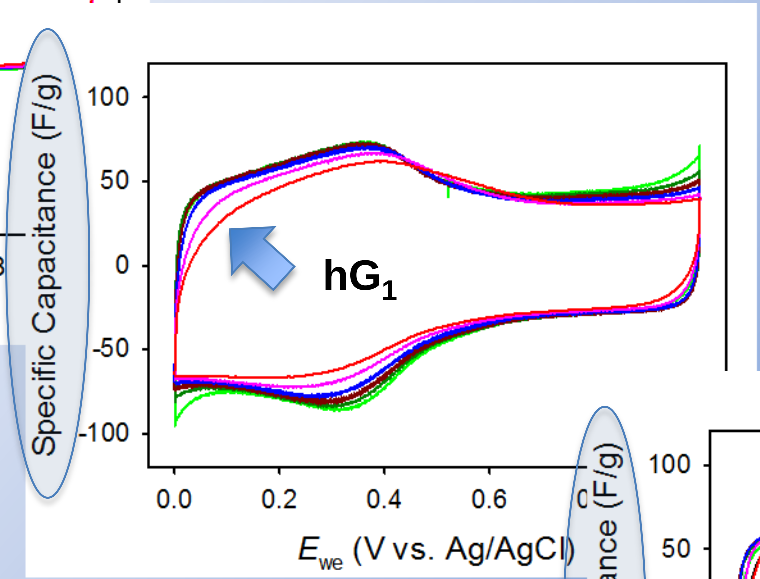
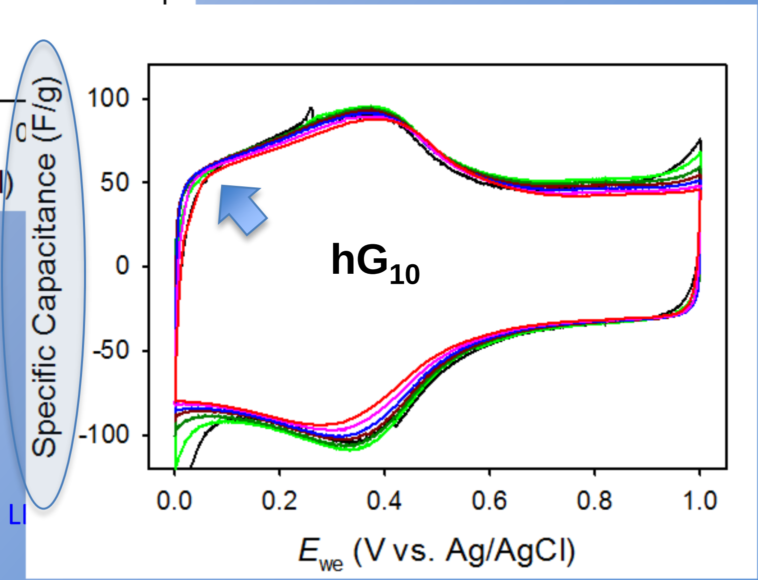
Scan rate: 10, 20, 50, 100, 200, 500, 1000 mV/s

- ❑ 0.5 M H_2SO_4
- ❑ Half-cell







*CV curves of hGs are less distorted at higher scanning rate: **improvement of ion transport**.*

Catalyst Loading ⟷ Hole Size

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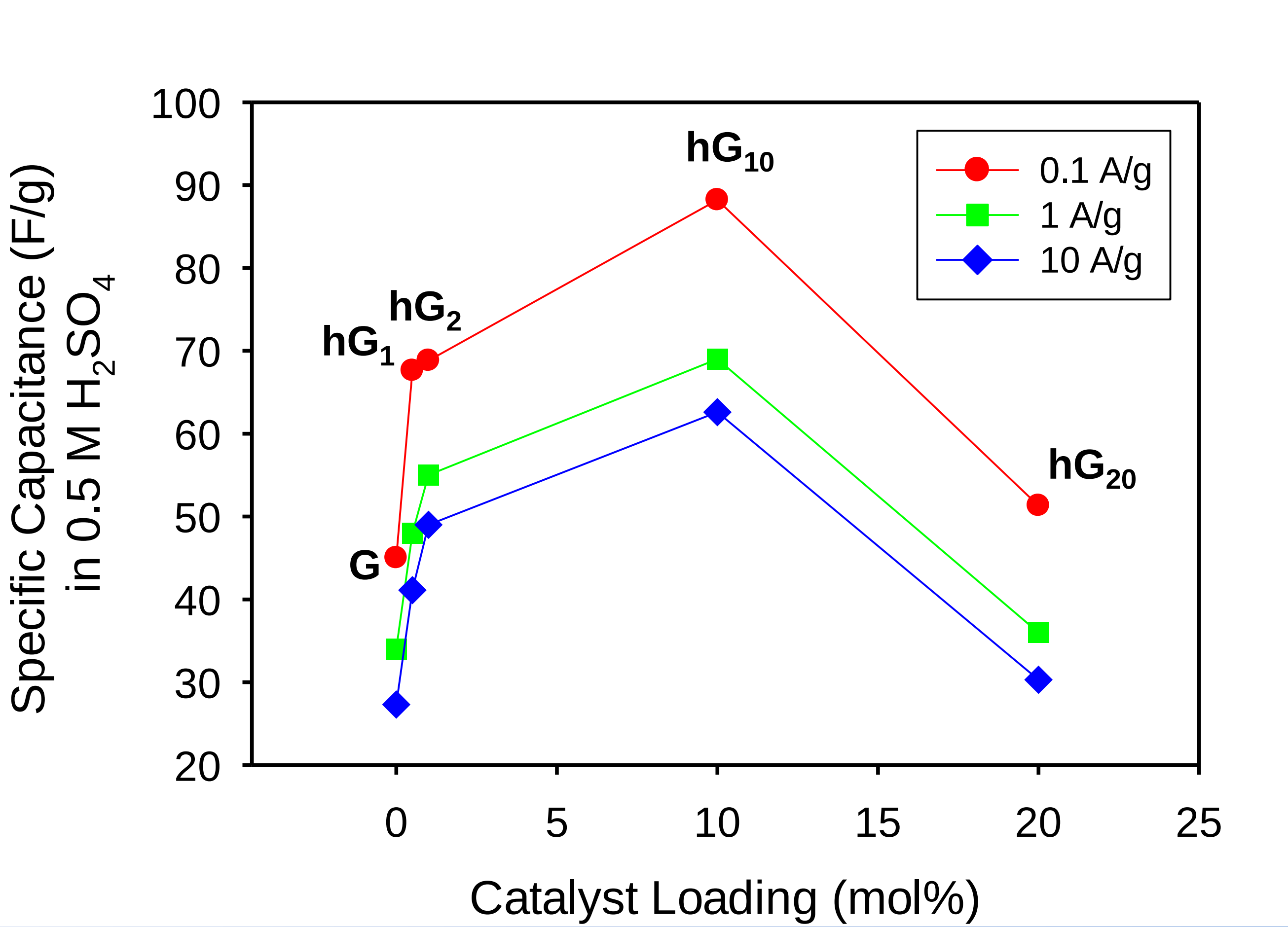
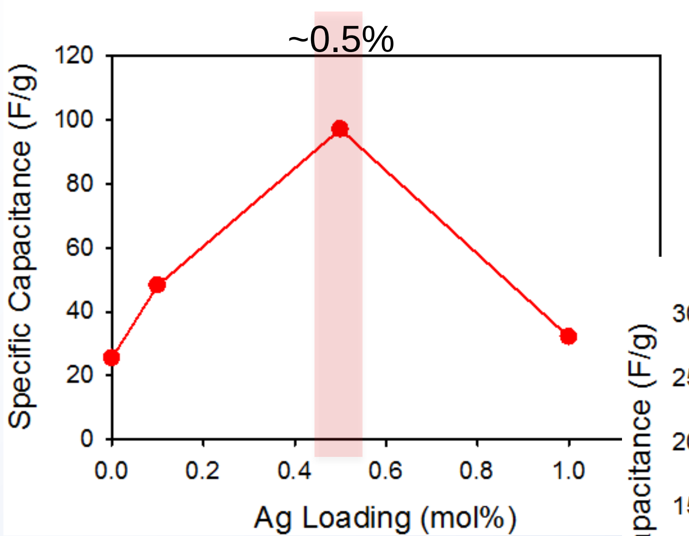


- More catalyst, larger holes.
- Optimal capacitance at ~10 mol% Ag

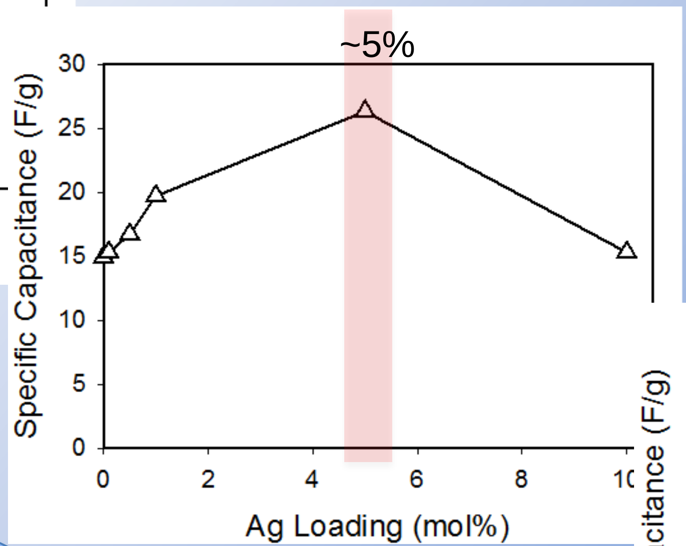
Improvement of capacitance (ion transport) *was achieved at an optimum catalyst loading (≈ hole size).*

hCNTs for Supercapacitors

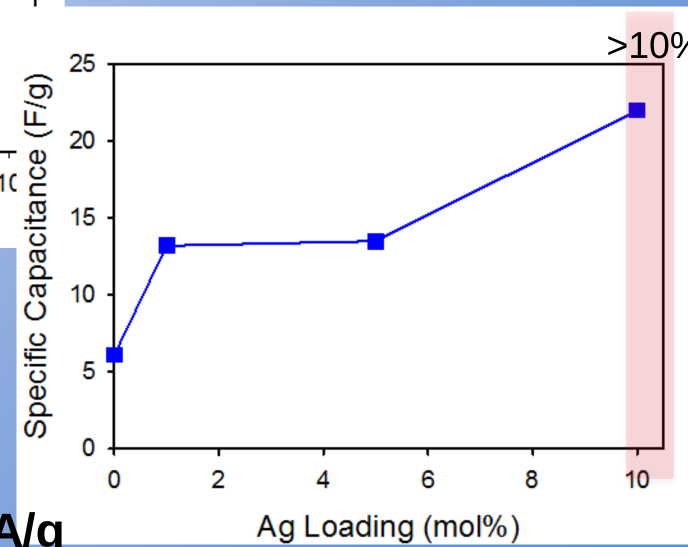
***Improvement of capacitance (ion transport)** for hCNTs was achieved at an optimum catalyst loading, which increases with increasing CNT diameter.*



FWNT (< 5 nm)



MWNT (10-30 nm)



MWNT (60-100 nm)

CNT Diameter Increase

- ❑ 6 M KOH; 3-electrode tests
- ❑ Calculated from galvanometric charge-discharge @ **1 A/g**

hG Modification: Oxygen Functional Groups

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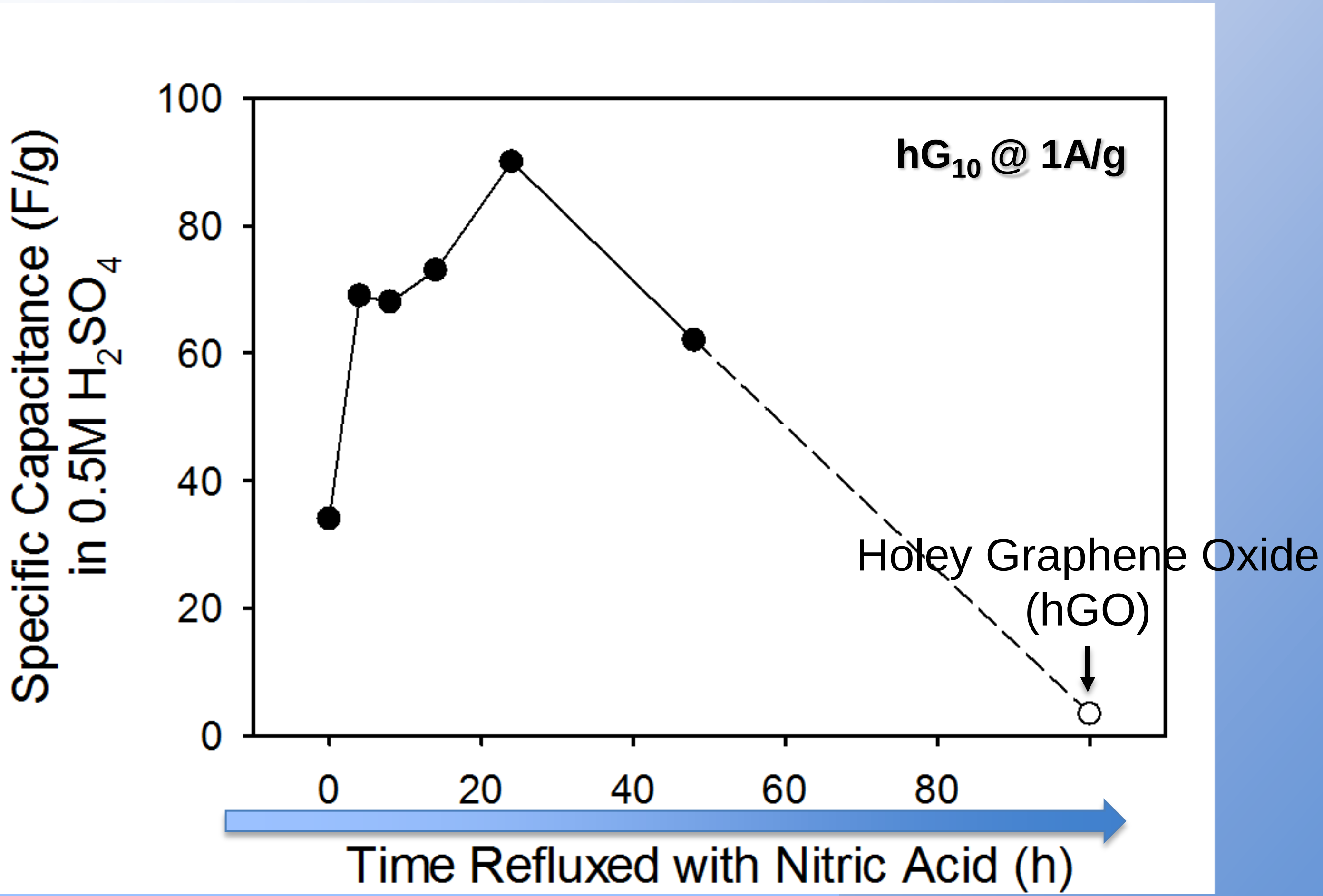

***Further improvement of hG capacitance** was achieved by introducing more oxygen functional groups.*

hG Modification: Conductive Polymers/Metal Oxides

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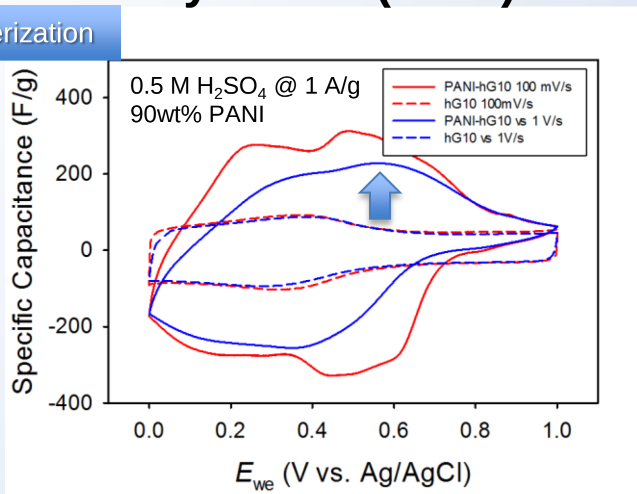
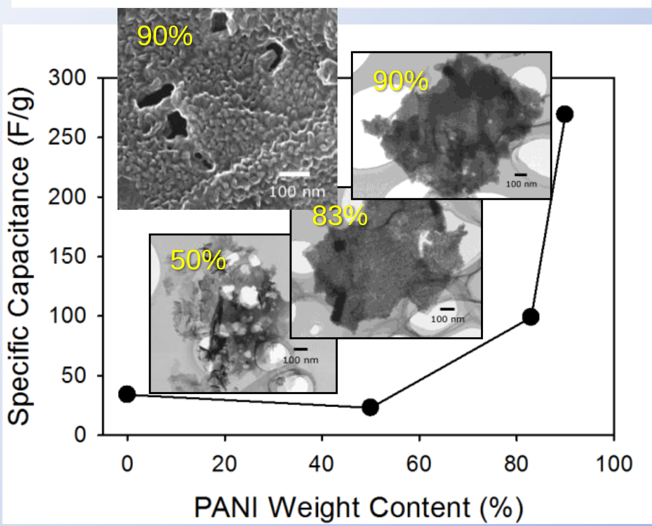
Polyaniline (PANI)

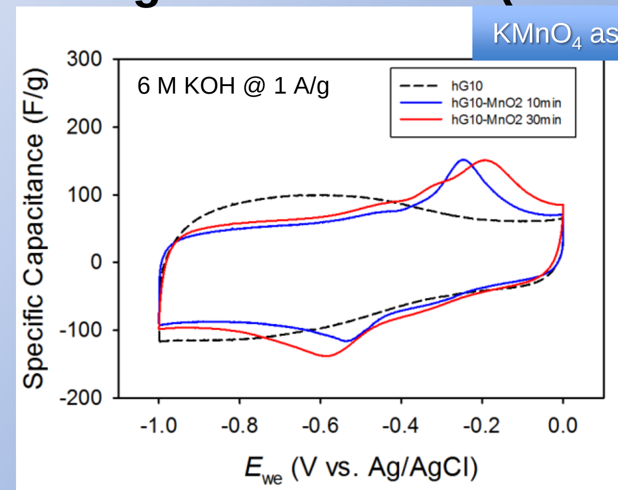
In situ polymerization

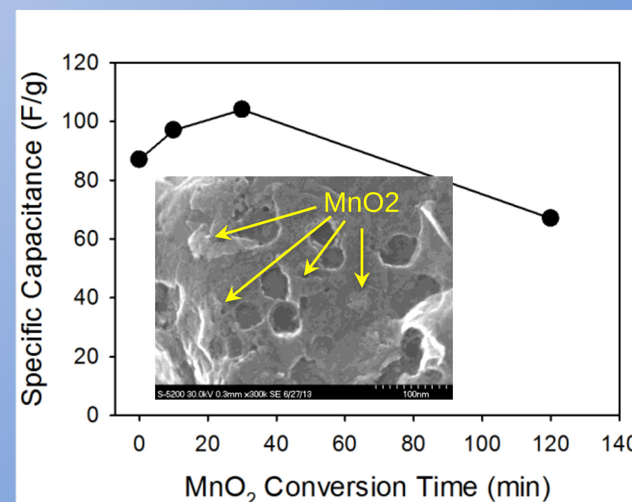




Manganese Dioxide (MnO_2)

$KMnO_4$ as precursor





Further improvement of hG capacitance *can also be achieved by introducing conductive polymer/metal oxides.*

Catalyst-Free Synthesis of PNCs

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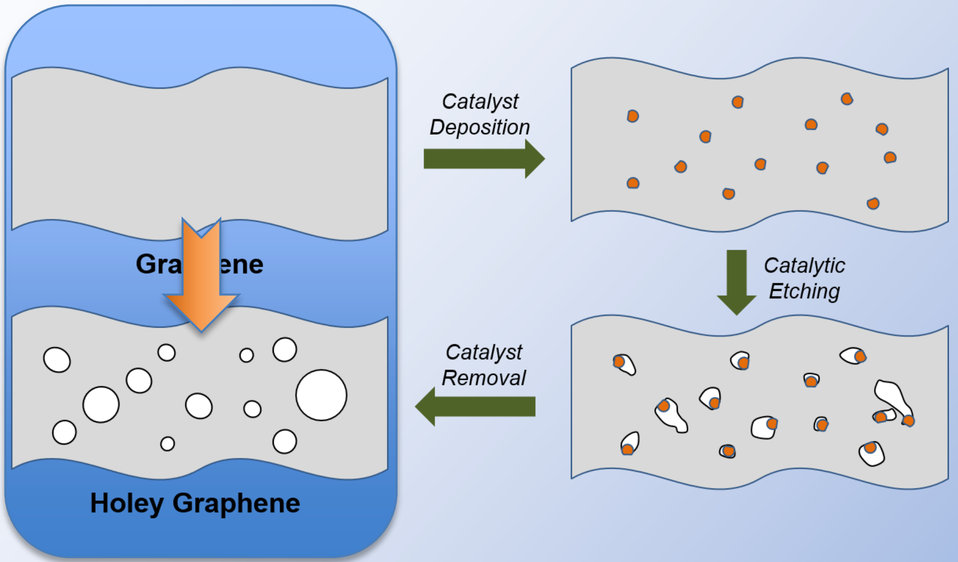
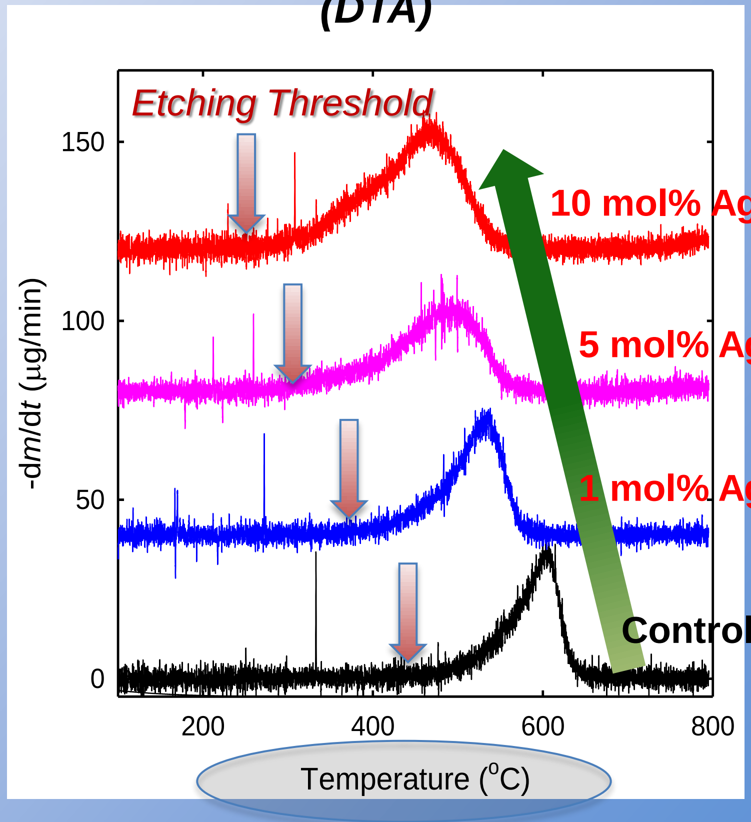


Differential Thermogravimetric Analysis (DTA)



Invention disclosure submitted 04/02/2013; provisional patent filed 10/14/2013.

Catalyst-Free Synthesis of hGs

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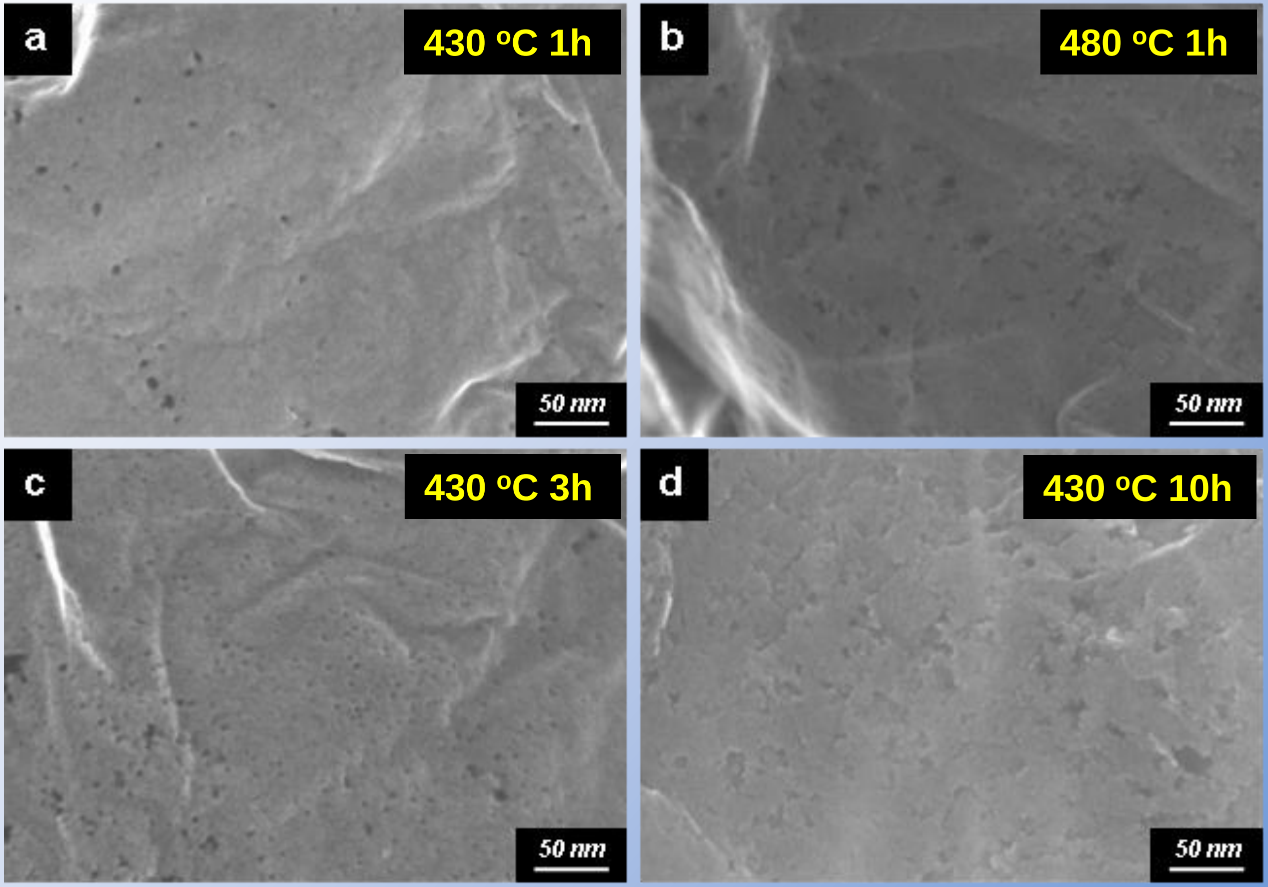
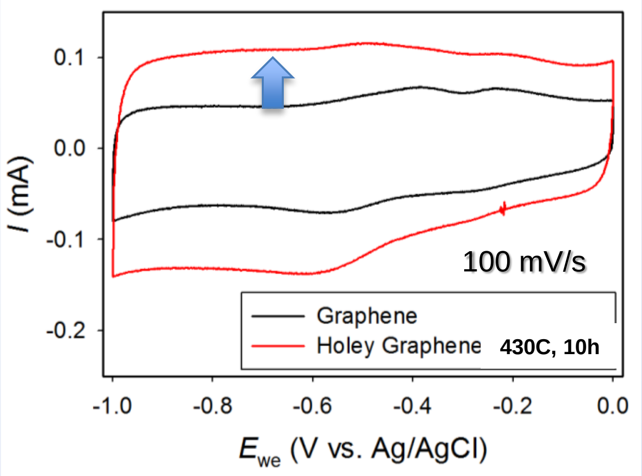
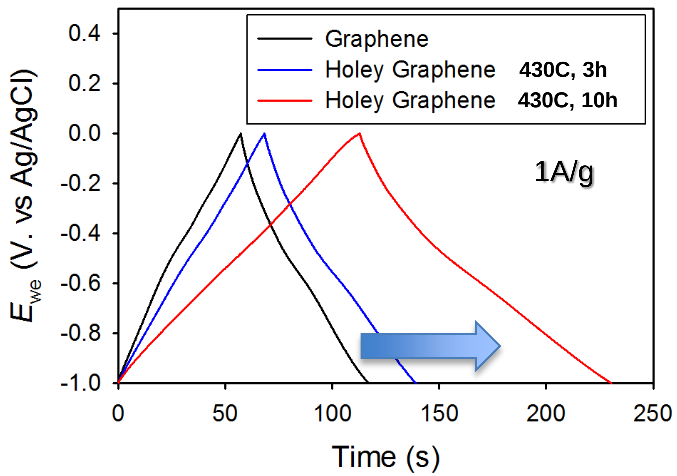
hG_0

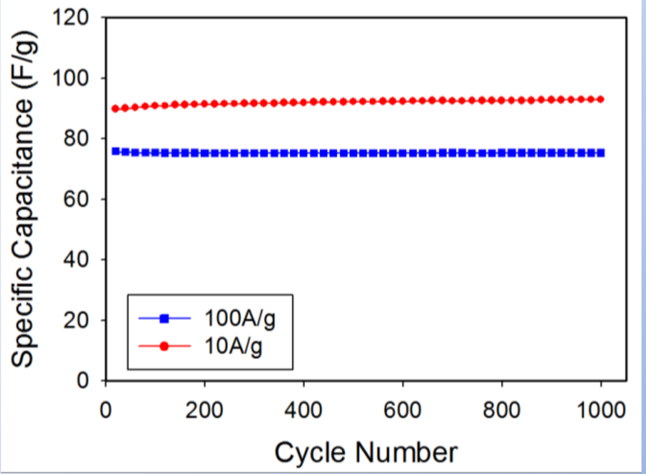


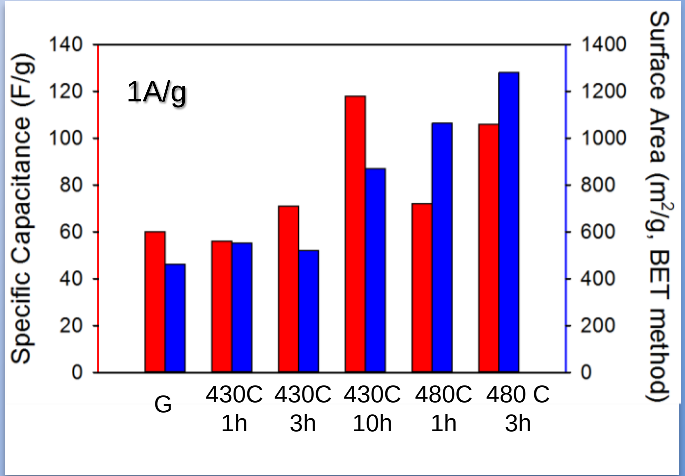
- Catalyst-free partial oxidation of graphene (or CNTs) at higher temperature than catalytic method
- Minimal processing, single-step
- Typical hole sizes < 10 nm for hG_0

hG_0 Supercapacitors









- *High capacitance performance*
- *Reduced processing steps; low-cost*
- *Limit on the hole size variations?*

"Cat-Free" hCNTs – Powder & Sheets

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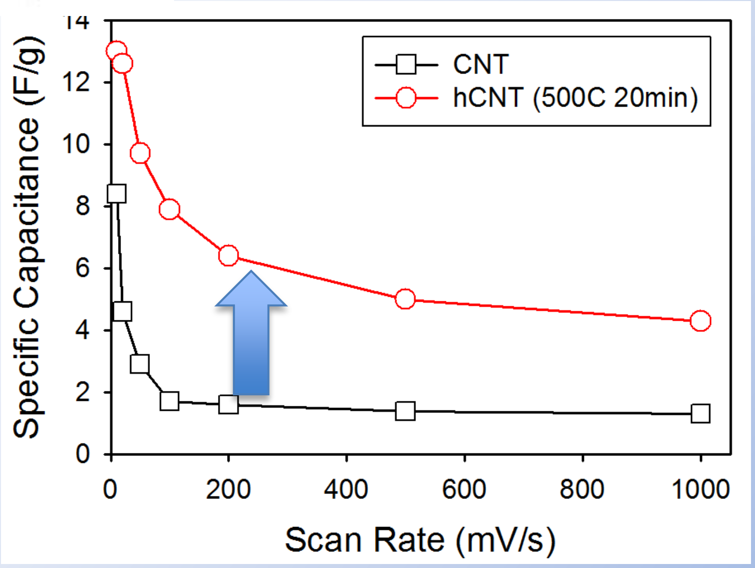
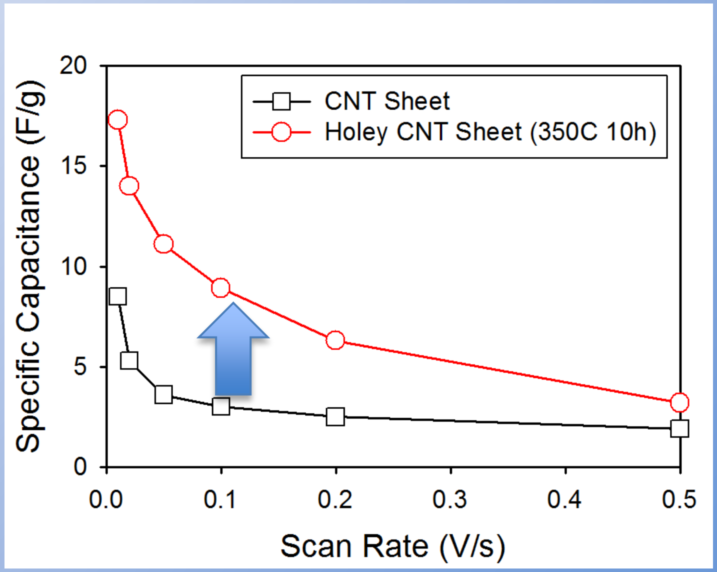
CNT Powder

CNT Sheets





- ❑ The single-step procedure is applicable to any assembled structures of CNT and graphene materials

<u>Carbon Nanotube Sheets</u>
❑Thickness: ~ 30 µm
❑Density: ~ 0.7 g/cm^3

Cat-Free process *is more versatile in regard to the starting material morphology.*

Device Fab: Full Cell Assembly

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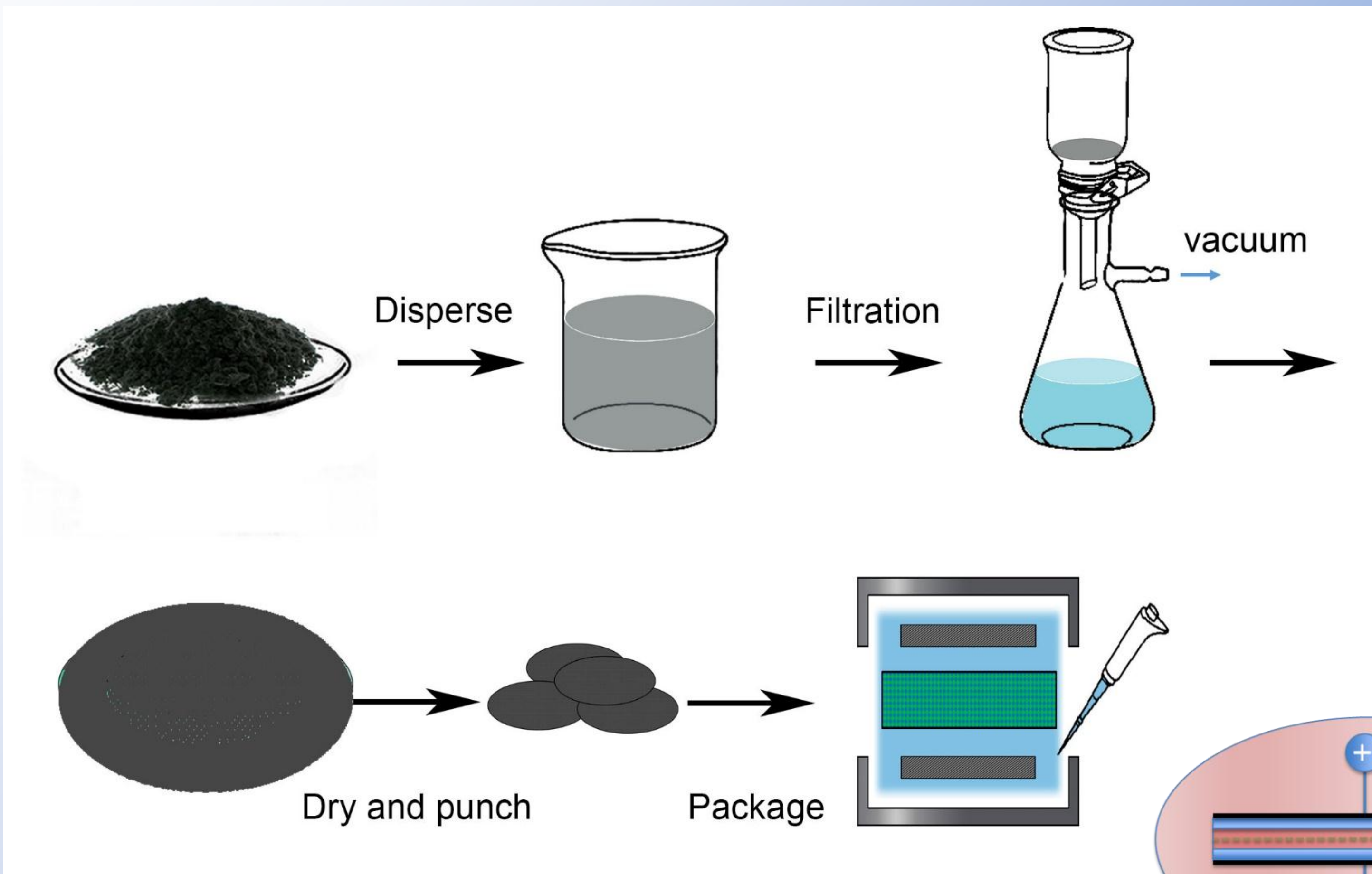

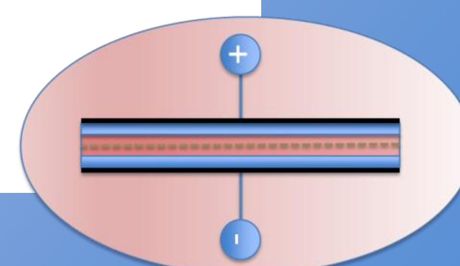

Holey Graphene Supercapacitors

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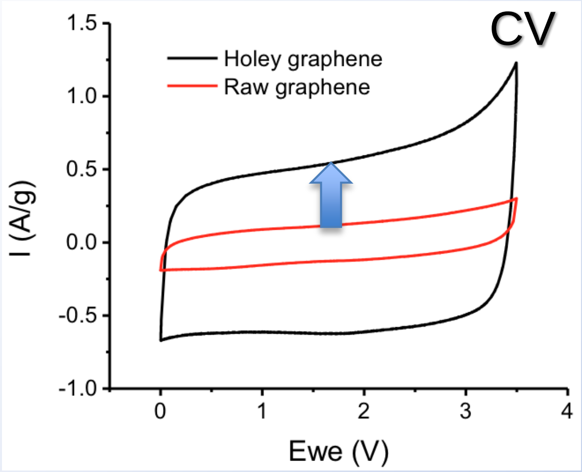

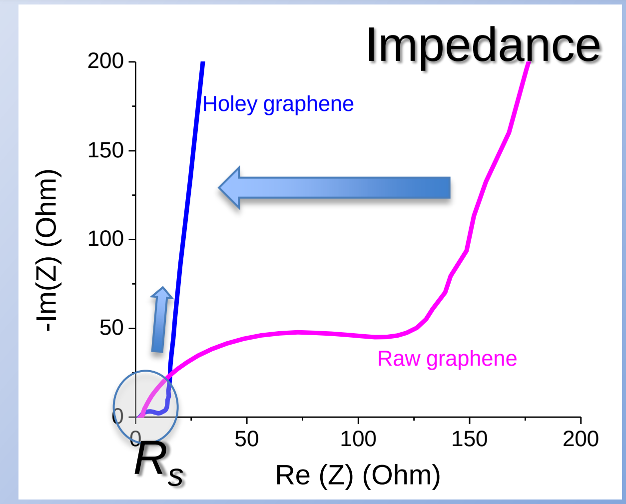

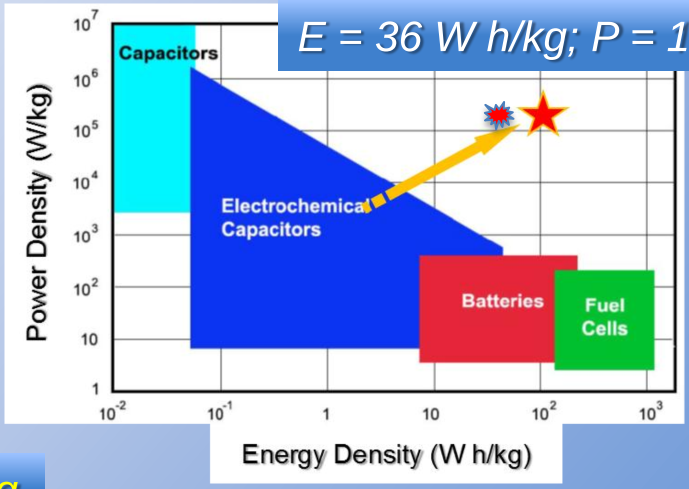

E = 36 W h/kg; P = 170 kW/kg

$$P = \frac{V^2}{4Rs}$$

$$E = \frac{1}{2} C V^2$$

Total hG_0 electrode weight: ~0.4 mg

Graphene vs. Holey Graphene

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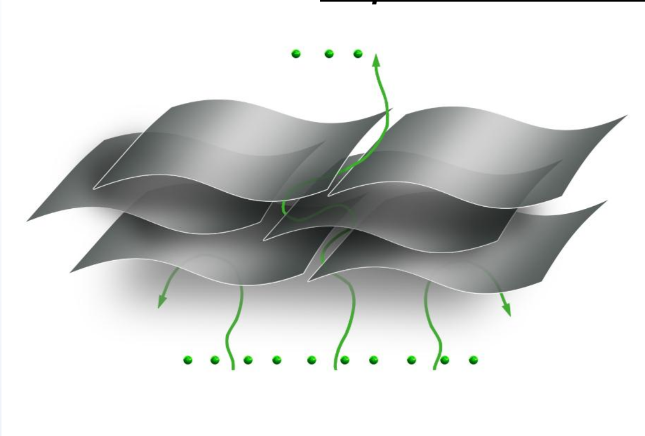
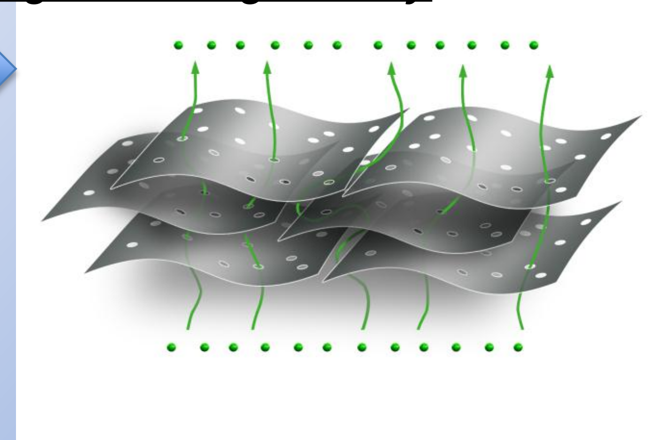
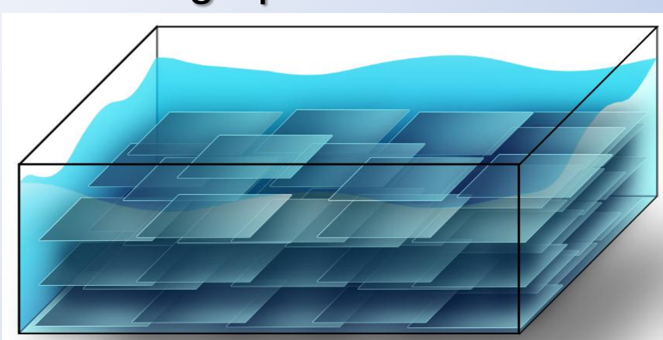
Improved ion transport path at high stacking density



Raw graphene electrode

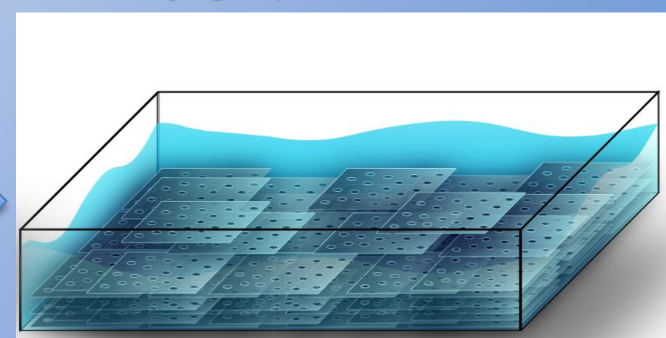


Holey graphene electrode



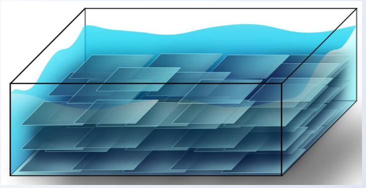
High volume

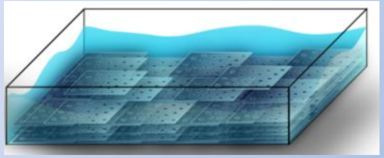
Equivalent Capacitance

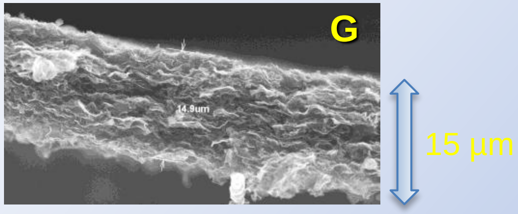


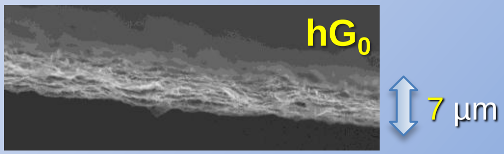
Low volume

Volumetric Performance in Full-Cell



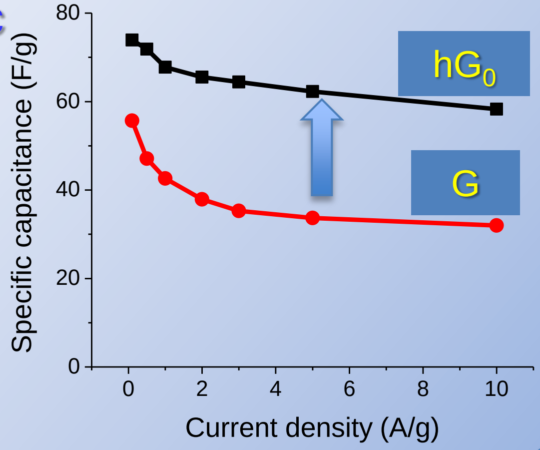






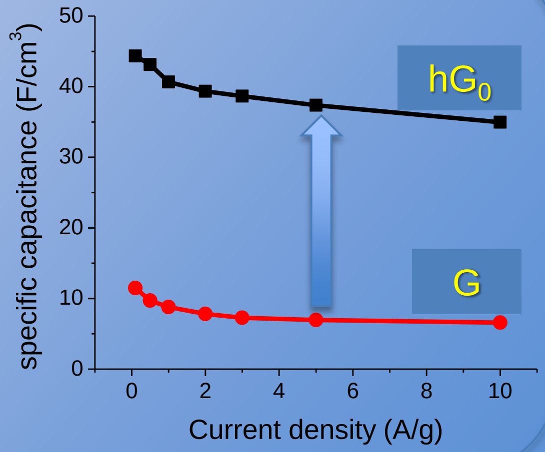
Gravimetric

Lightweight

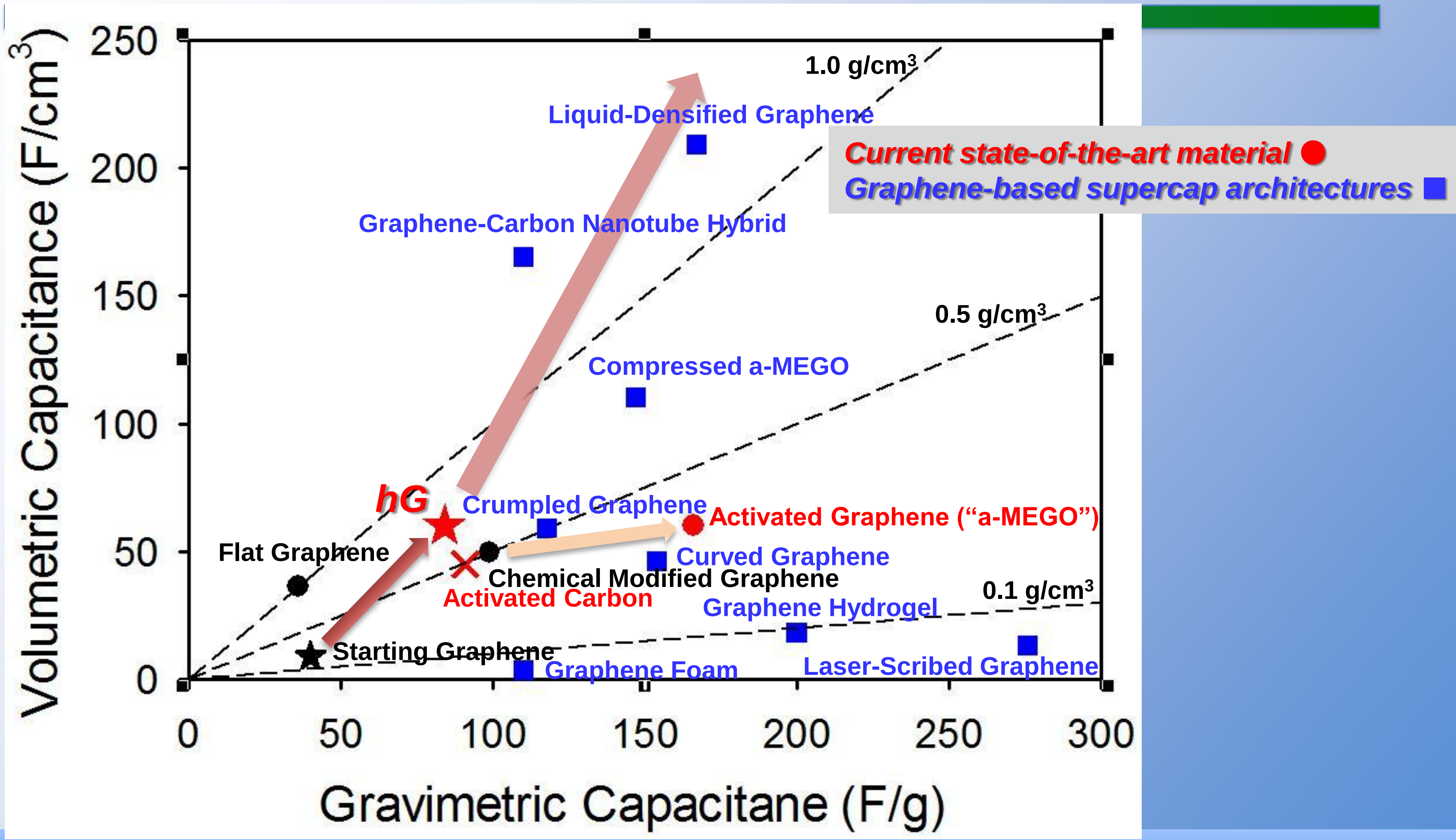


Volumetric

Low-Volume



Volumetric Capacitance: Current Status



- *Volumetric performance of a non-optimal hG material is already on-par with the state-of-the-art graphene materials and commercial activated carbon.*
- *Architecture optimization (Phase-II) would lead to much better performance.*

A Clear Path into Phase-II

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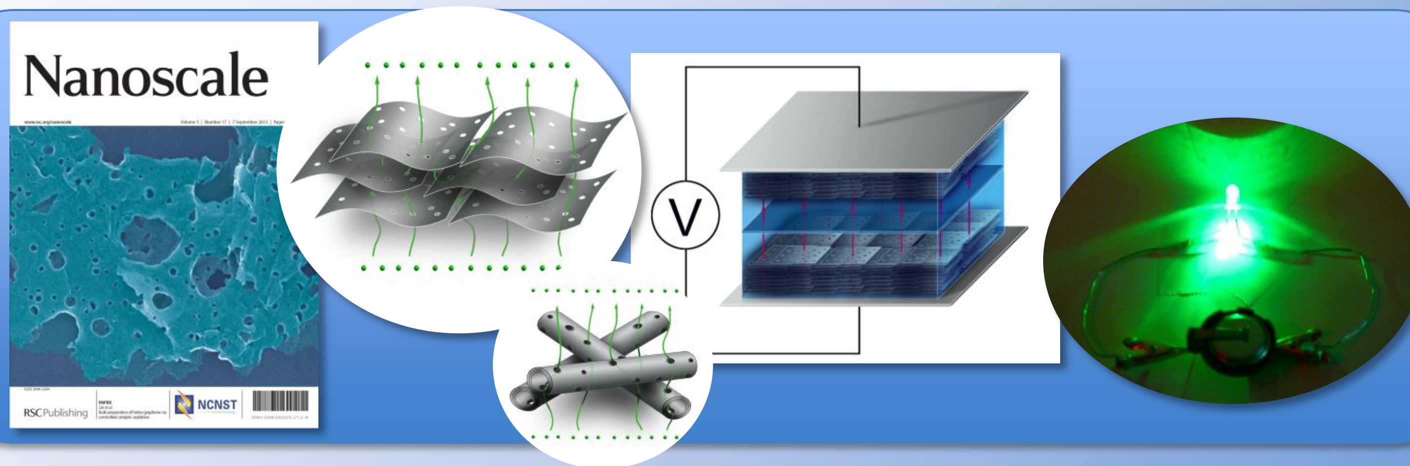
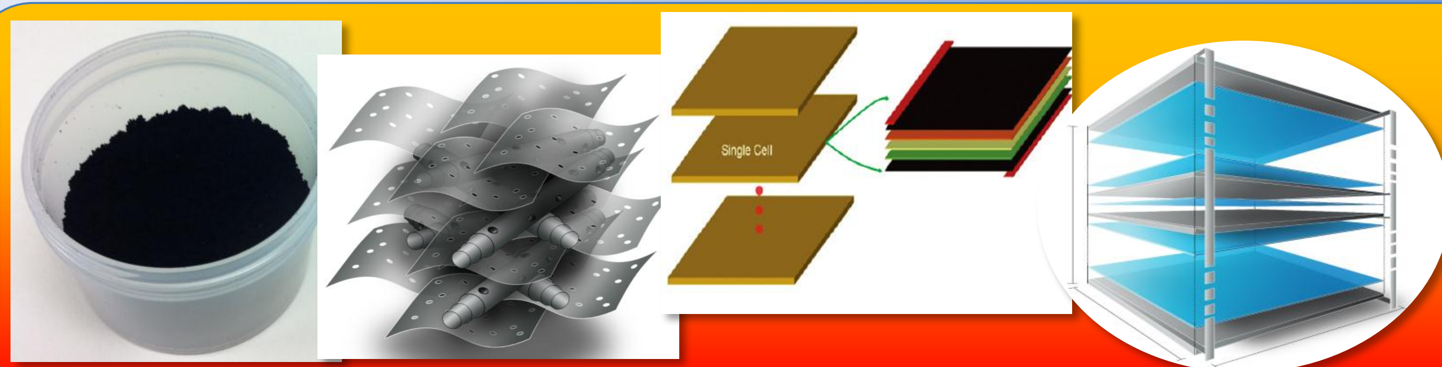
PHASE I

PNC Synthesis and Modification with EC Evaluation



PHASE II

PNC Supercap Optimization and Prototype Demo



Next Steps: Phase II Tasks

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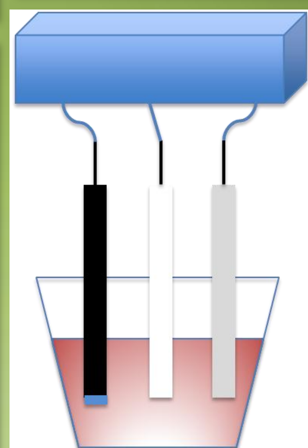
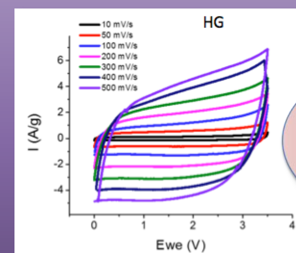
Task 1: **Electrode Optimization**

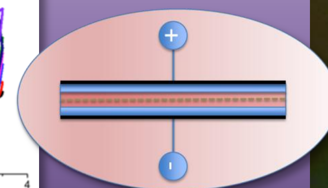


Materials & Architecture

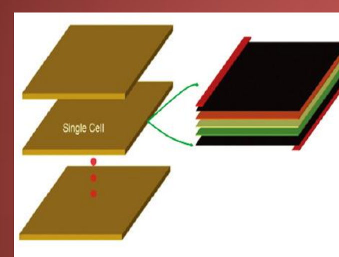
Task 2: **Full-Cell Evaluation**

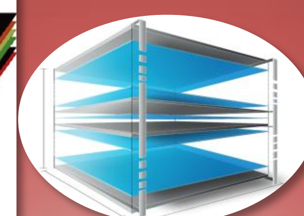





Power/Energy Density by *volume*

Task 3: **Prototype Demo**






Stacking Single Cells

- ❑ **Team**: NIA (Lin/Kim) + UMD (Hu) + NASA LaRC (Connell)
- ❑ **TRL** ~ 5-6

Summary

- Synthesized, modified, and characterized PNCs (i.e., hGs & hCNTs) of various hole sizes and chemistry for a better understanding of structure-performance relationship.
- Demonstrated the potential of PNCs as advanced supercapacitor electrode materials toward aeronautics applications.
- Assembled a multi-institutional team ready for challenge in LEARN**2** for further optimization in a clear path toward a prototype demo.