# Synthesis and Modification of Holey Graphene for Energy Storage

*Emerging Holey 2D Nanomaterials*

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# Next-Gen Energy Storage Devices: Lightweight AND Low-Volume

**Power (Density)**

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

**Energy (Density)**

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

*V*: Cell voltage
$R_s$: Internal resistance
*C*: Capacitance

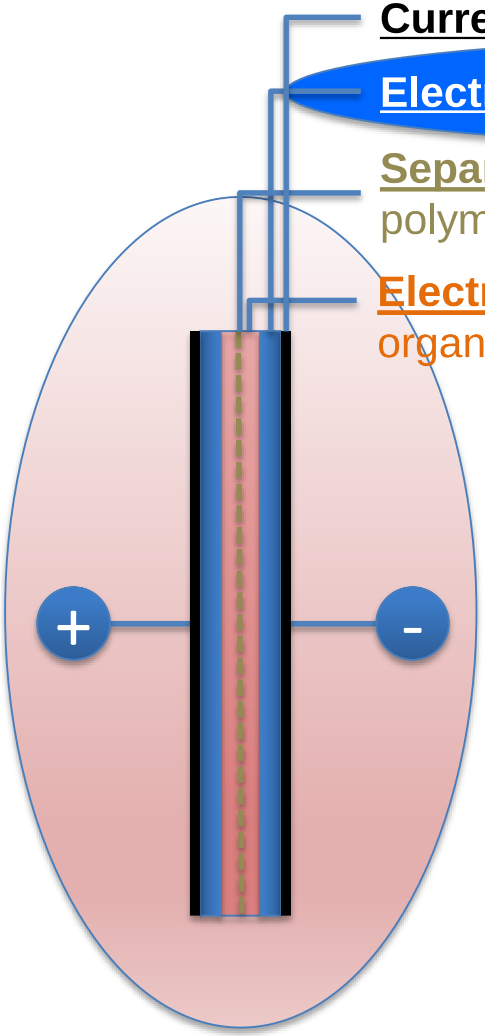
**Applications**

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

**Impacts**

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

# Nanocarbon Electrodes




**Current collector**: Metals

**Electrode**: Activated carbon (0.1 – 0.8 mm)

**Separator**: Thin porous polymeric membrane

**Electrolyte**: Aqueous, organic, or ionic liquid

## Nanocarbons

Carbon Nanotubes: L < 5 µm; D < 100 nm
Graphene : L < 10 µm; T < 5 nm

- ✓ High theoretical surface area
- ✓ High electrical conductivity

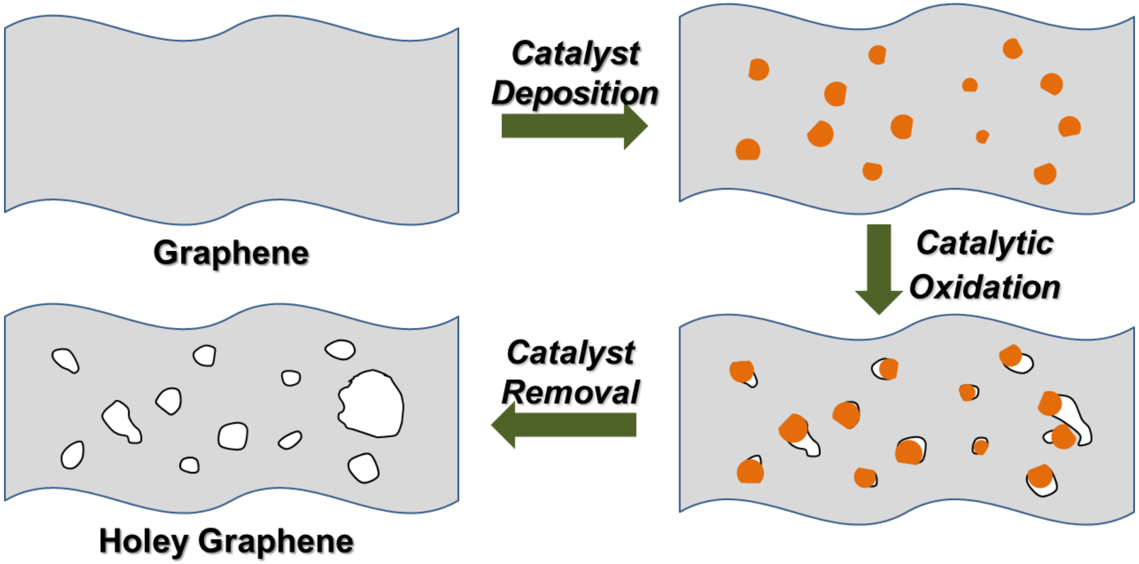
# Improving Accessible Surface Area

- Graphene foams & aerogels
  - Porous
  - High gravimetric capacitance
  - But LARGE volume (i.e., low volumetric performance)

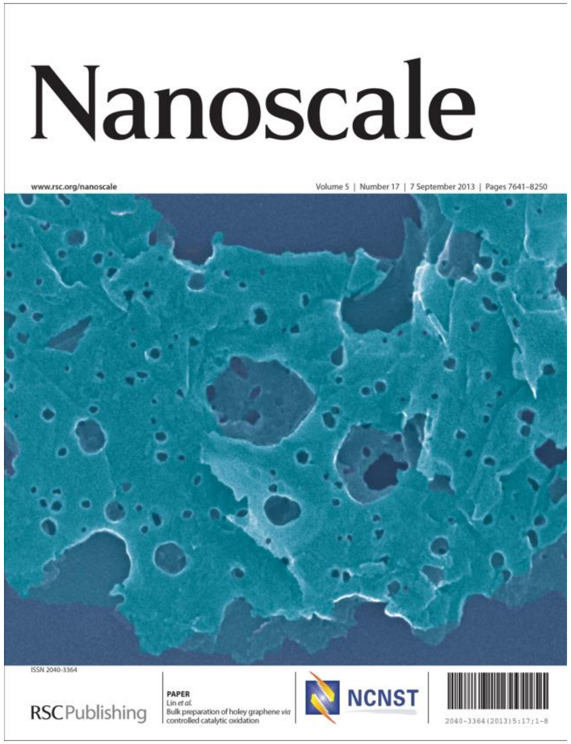

For example:

- Zou et al., *ACS Nano* **2010**, *4*, 7293.
- Ji et al., *Nano Lett.* **2012**, *12*, 2446.
- Chen et al., *Adv. Mater.* **2012**, *24*, 4569.
- Sun et al., *Adv. Mater.* **2013**, *25*, 2554.

# Our Solution: Holey Graphene (hG)



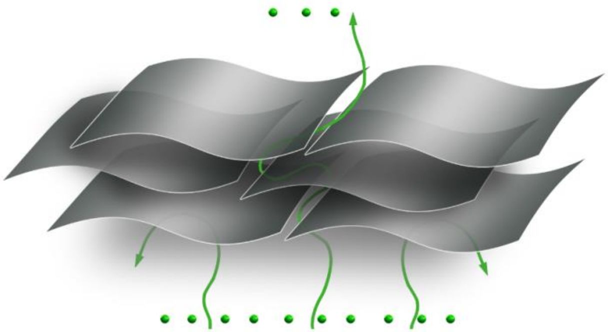

Controlled Catalytic Oxidation

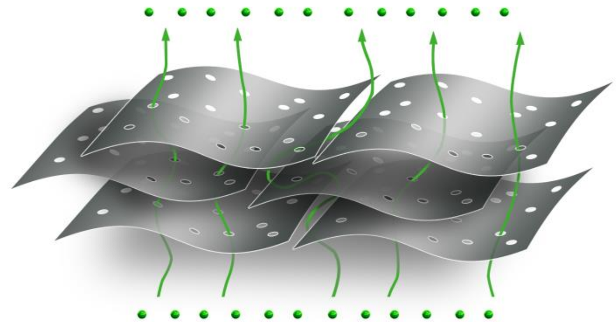



*Nanoscale* **2013**, *5*, 7814.

# Holey Graphene vs. Graphene

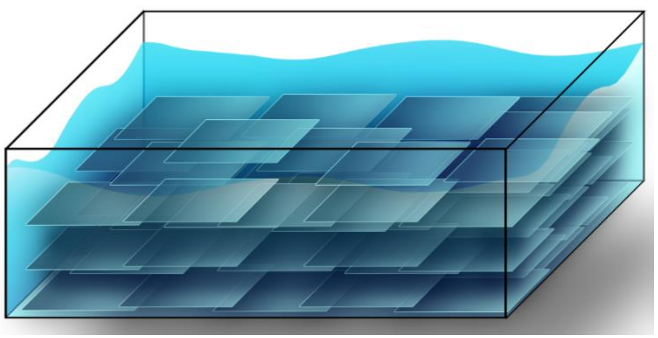
<u>*Improved ion transport path at high stacking density*</u>



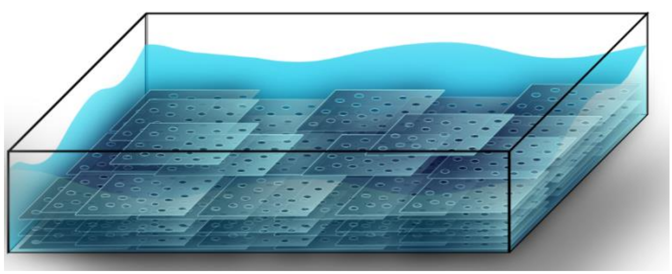


Raw graphene electrode

Holey graphene electrode



***Equivalent Capacitance***

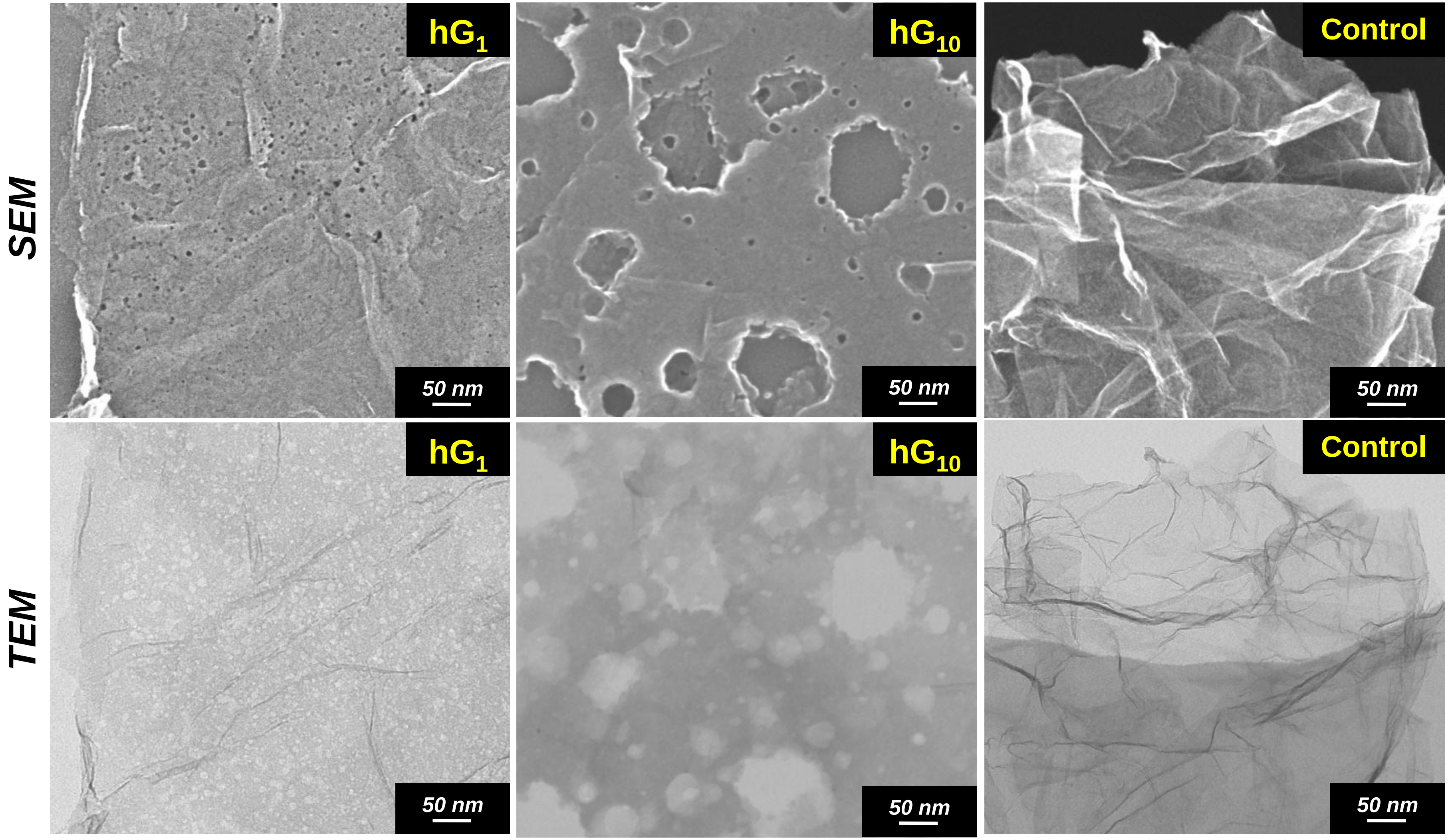


High volume

Low volume

Courtesy: Prof. Liangbing Hu (UMD)

# Hole Size Control

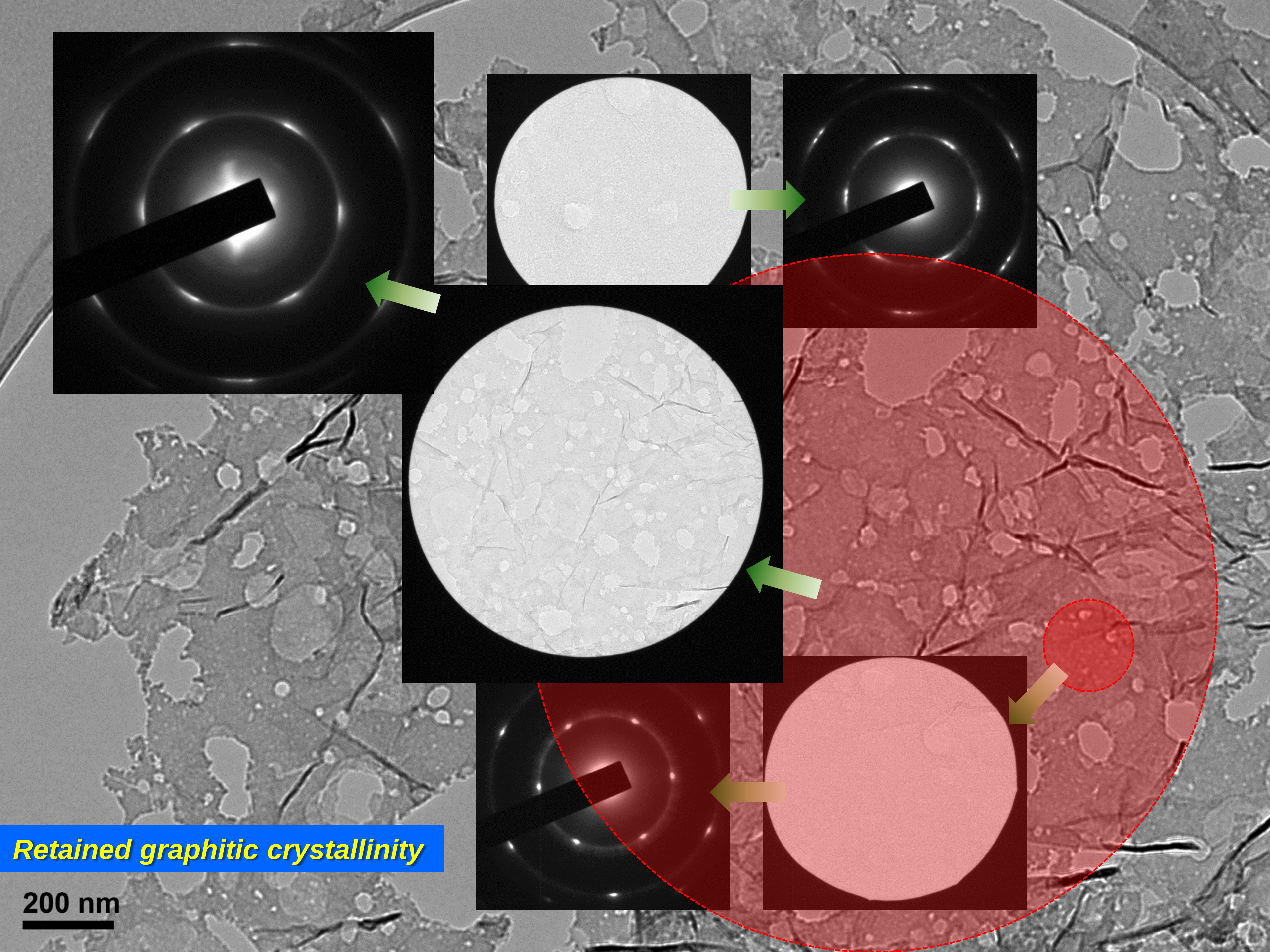



**Catalyst Removal:** $HNO_3$(2.6 M), 2h reflux

**hG$_x$**(**X**: Starting Ag Content)

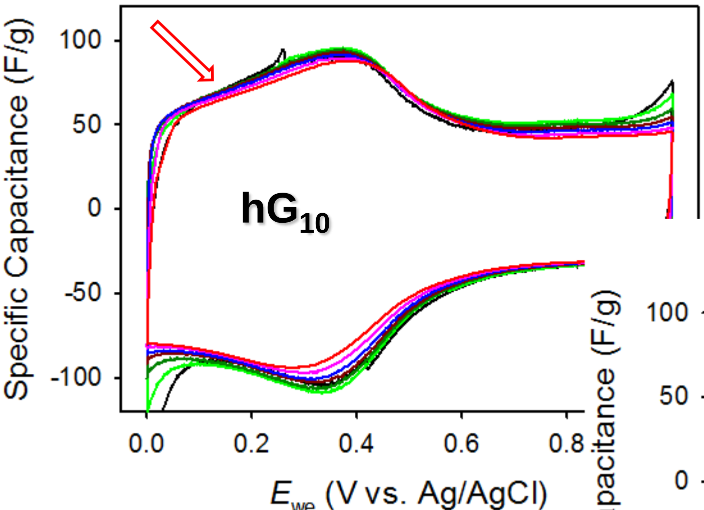
# Holey Graphene vs. Graphene for Supercapacitors

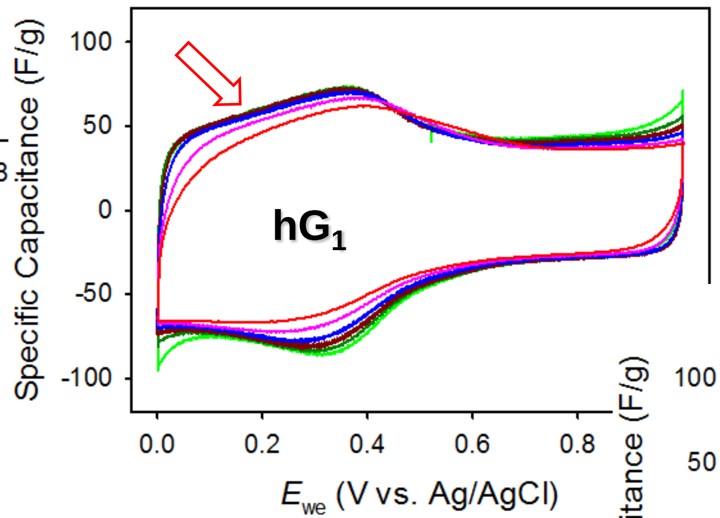
- ❑ In-plane porosity: Improve ion transport path
- ❑ Accessible surface area: Improve gravimetric capacitance
- ❑ Volume reduction: Mitigate need to create large pores/spacing
- ❑ Electrical Conductivity: Retain graphitic crystallinity

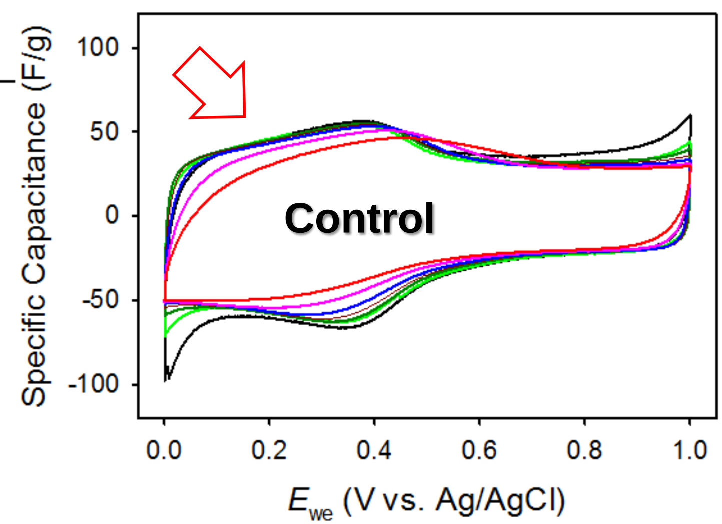

Retained graphitic crystallinity
200 nm

# Effect of Holes?

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

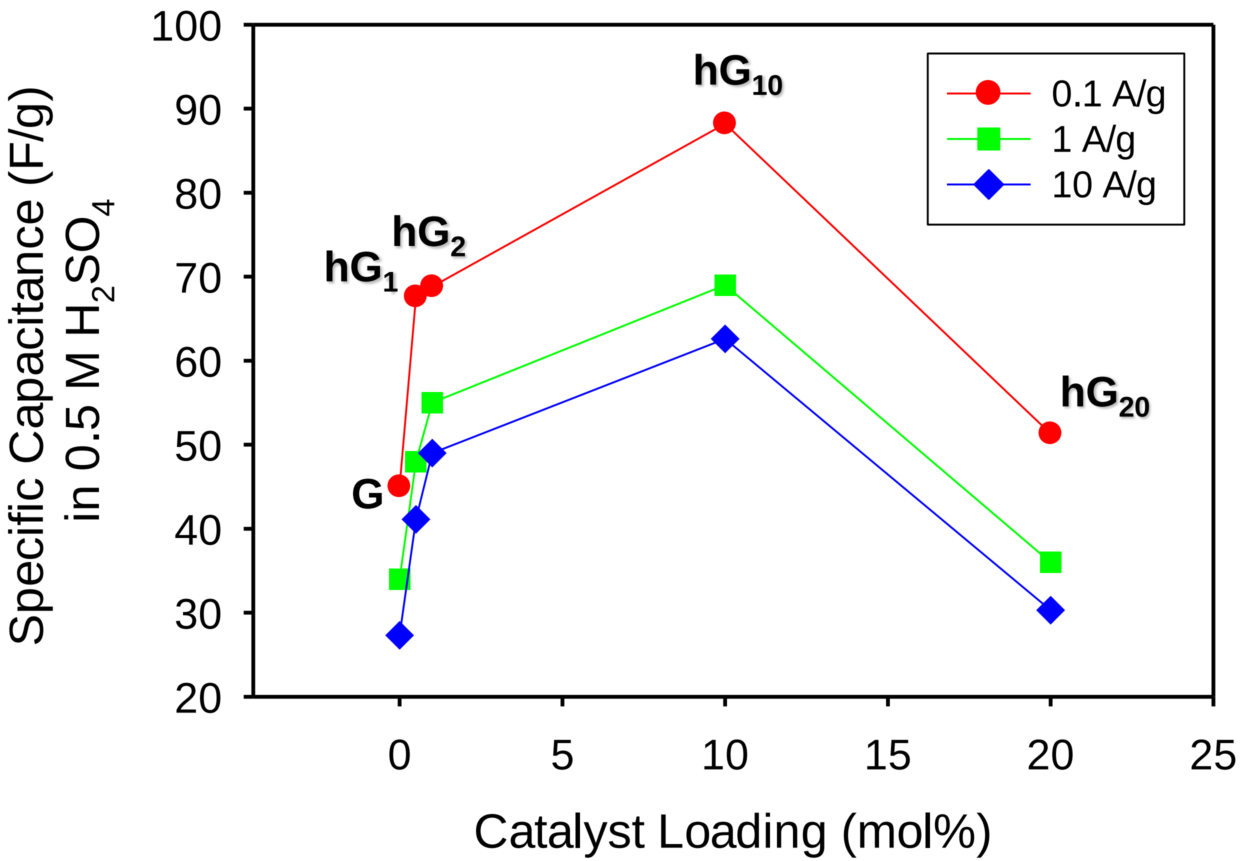



- ❑ 0.5 M $H_2SO_4$
- ❑ 3-electrode Configuration

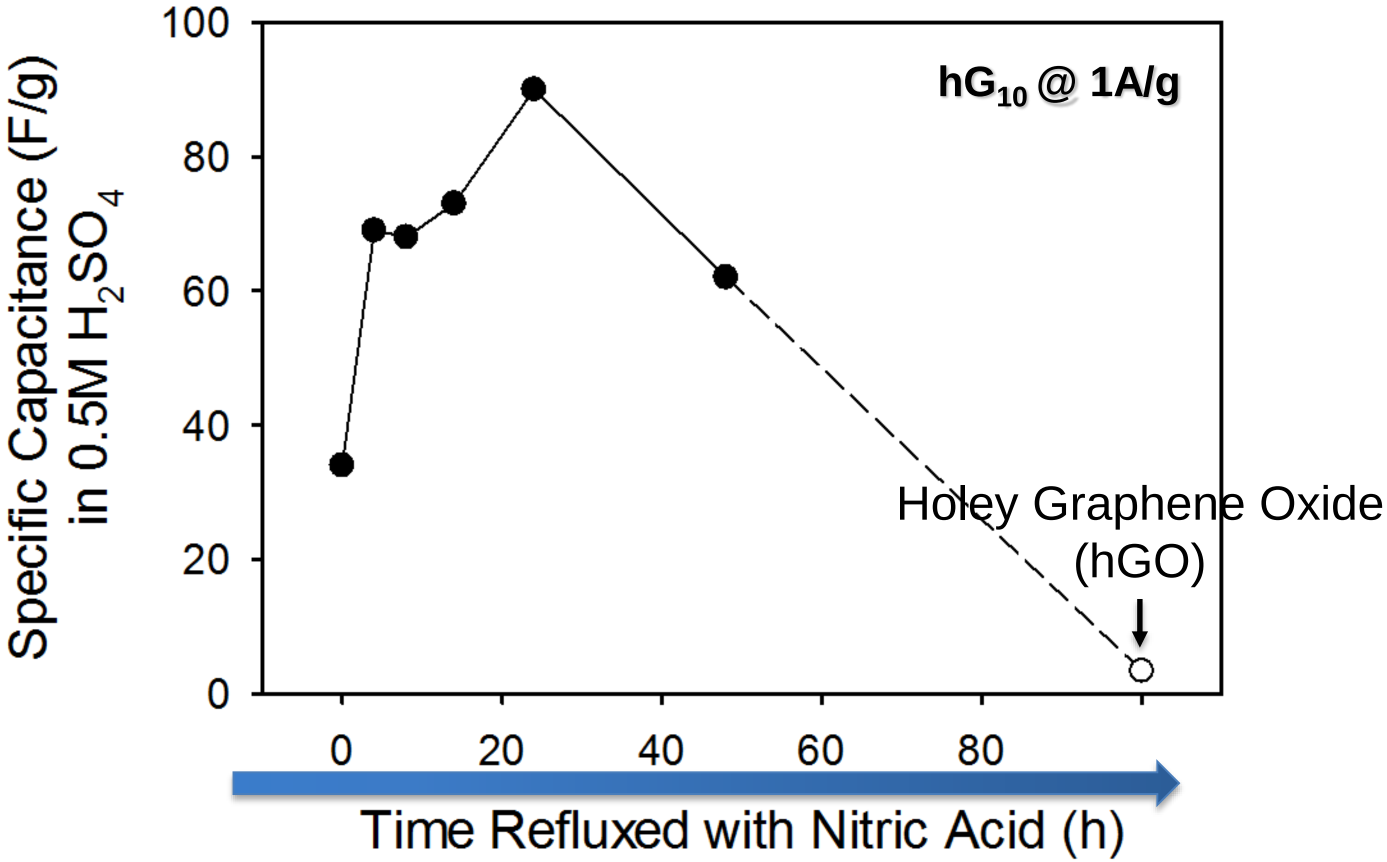
# Catalyst Loading ⟺ Hole Size




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

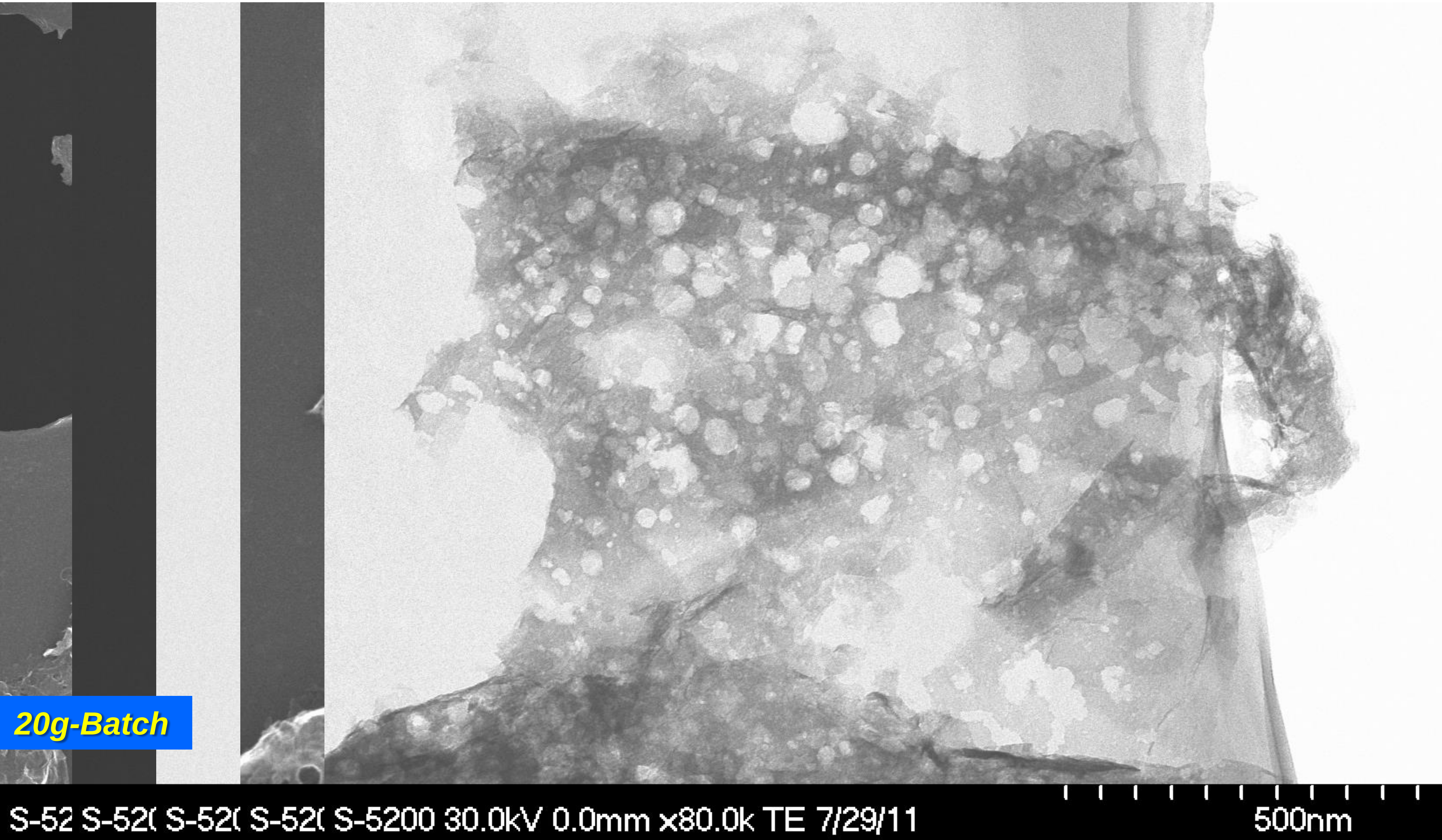
- ❑ More catalyst, larger holes.
- ❑ Optimal capacitance at ~10 mol% Ag

# hG: Effect of Acid Treatment

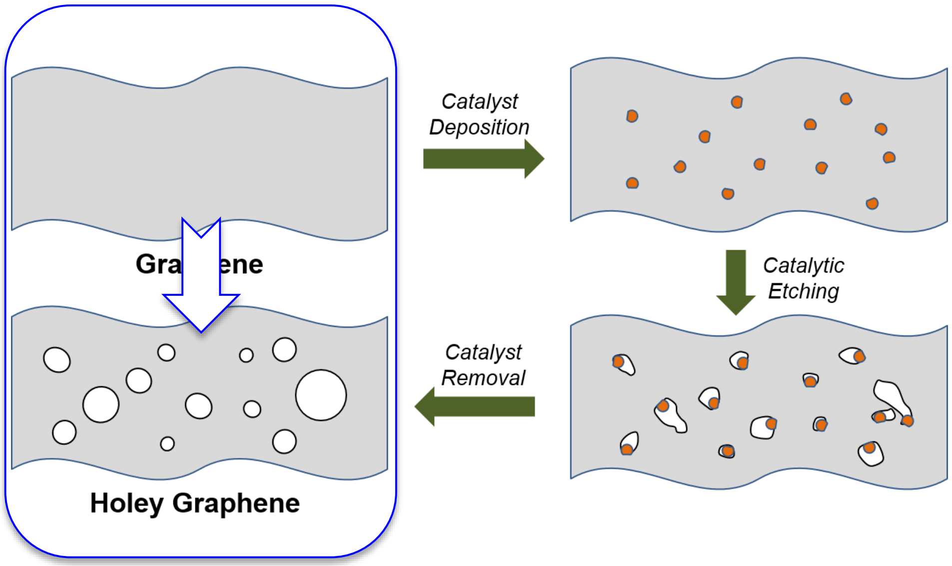



***Further capacitance improvement** was achieved by introducing more oxygen functional groups.*

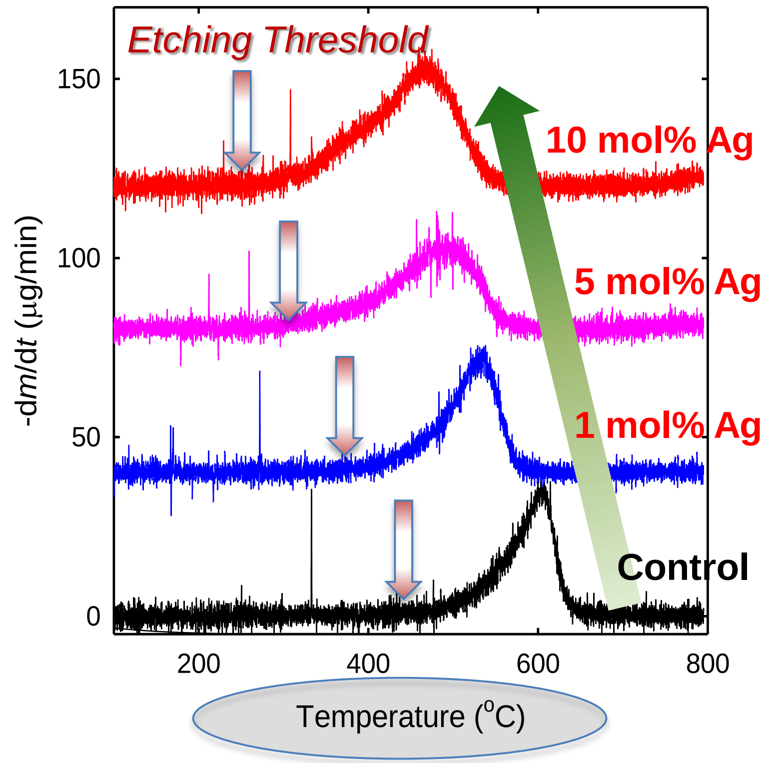
# Scalability



# Catalyst-Free Synthesis of hG: "Generation II" "$hG_0$"




***Differential Thermogravimetric Analysis (DTA)***

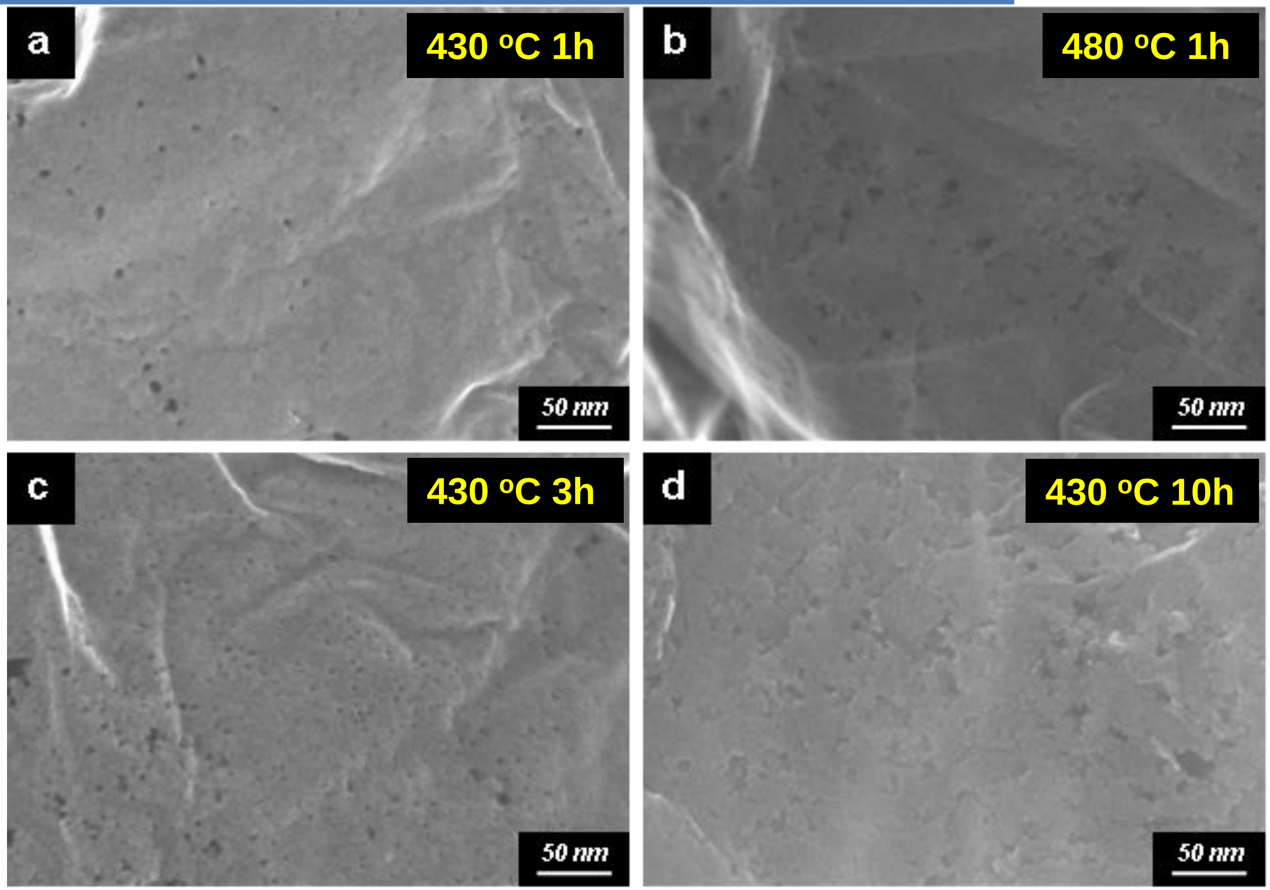



***Single Step + Catalyst-Free = Highly scalable!***

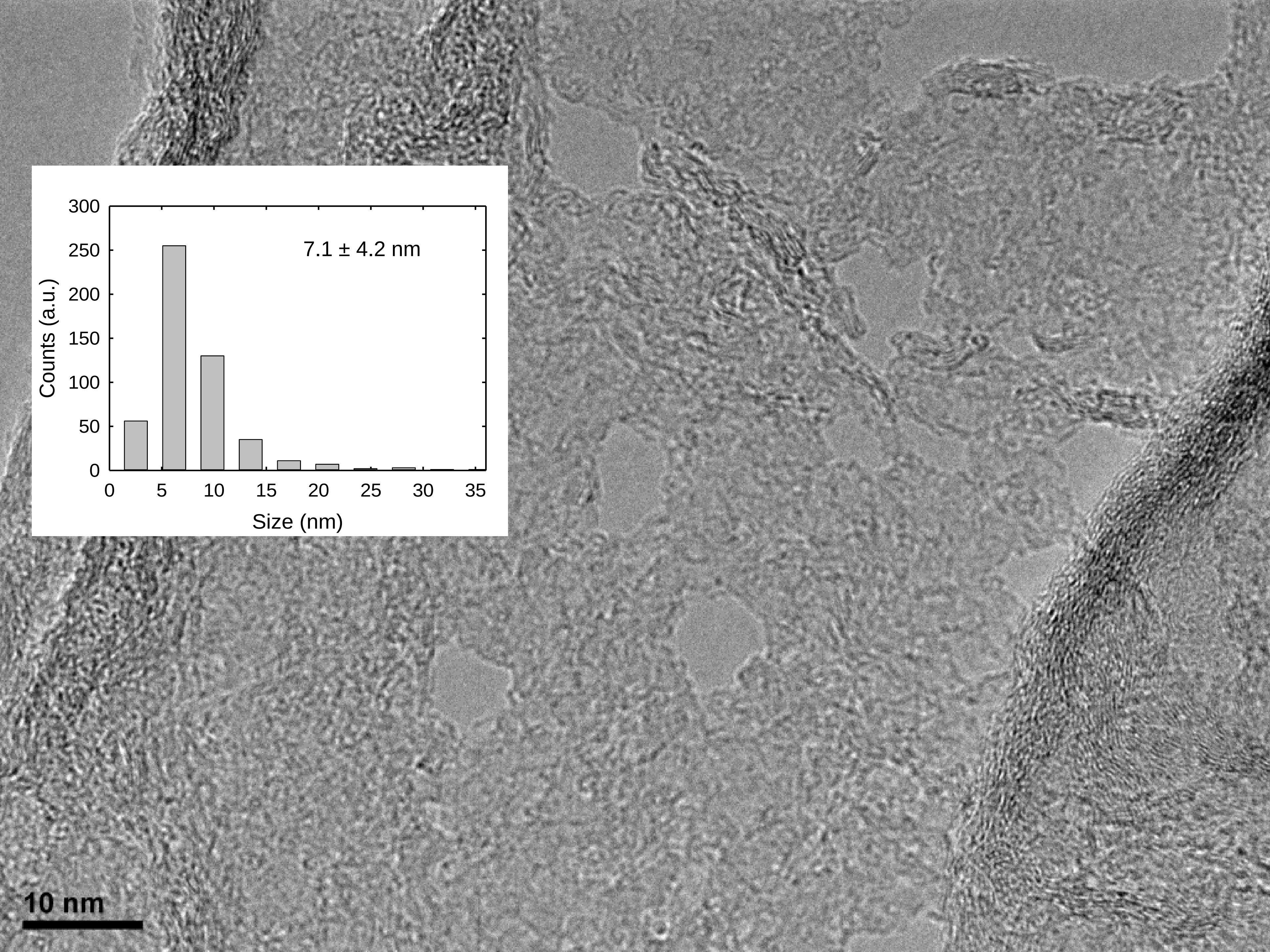
ACS Nano **2014**, *8*, 8255.

# Catalyst-Free Synthesis of $hG_0$

$hG_0$

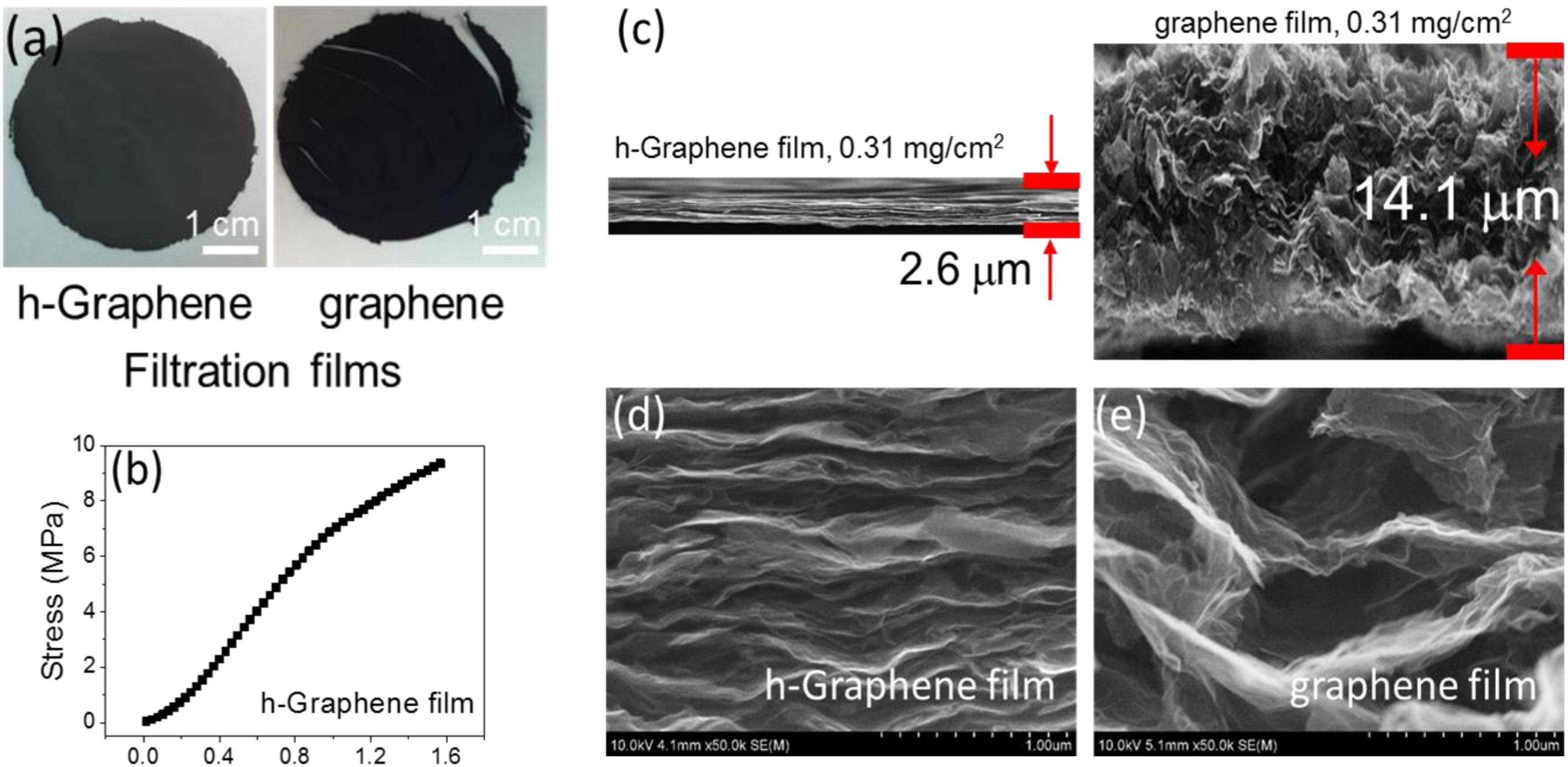



- ❑ Catalyst-free partial oxidation of graphene (or CNTs) at <u>higher temperature</u> than catalytic method
- ❑ Minimal processing, single-step
- ❑ Typical hole sizes < 10 nm for $hG_0$



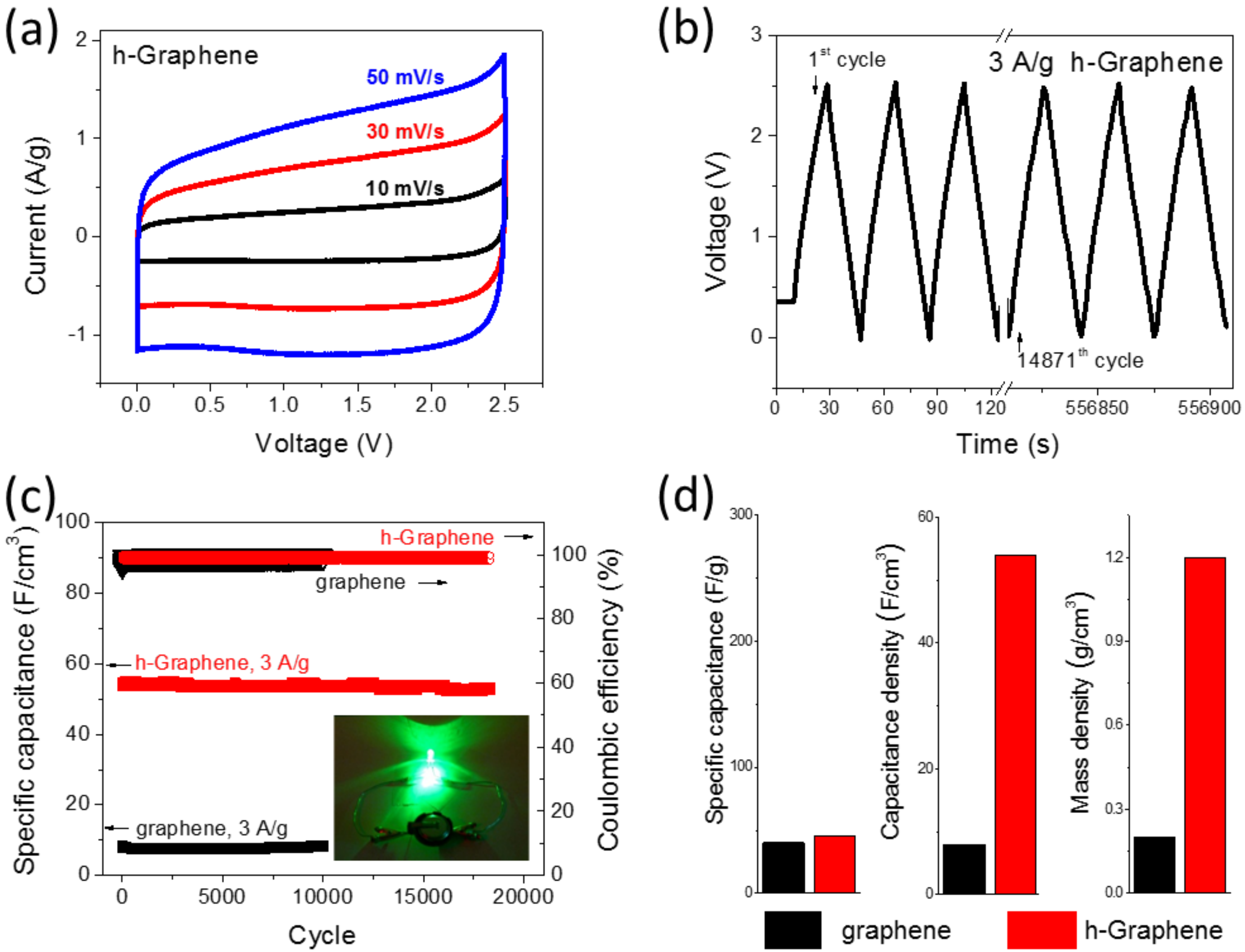
7.1 ± 4.2 nm
Counts (a.u.)
Size (nm)
0
50
100
150
200
250
300
0
5
10
15
20
25
30
35
10 nm

# $hG_0$: Facile Thin Film Fabrication




ACS Nano **2014**, *8*, 8255.

# Enhanced Volumetric Performance

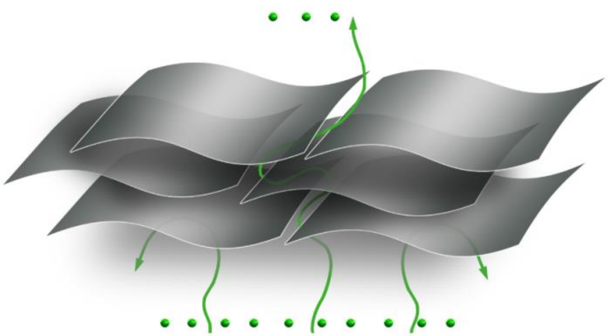


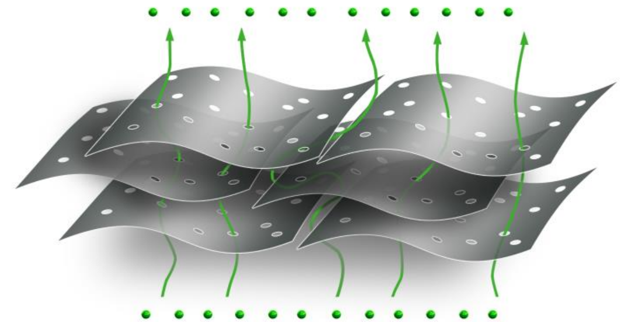

ACS Nano **2014**, *8*, 8255.

***Improved volumetric performance.***

# Graphene vs. Holey Graphene

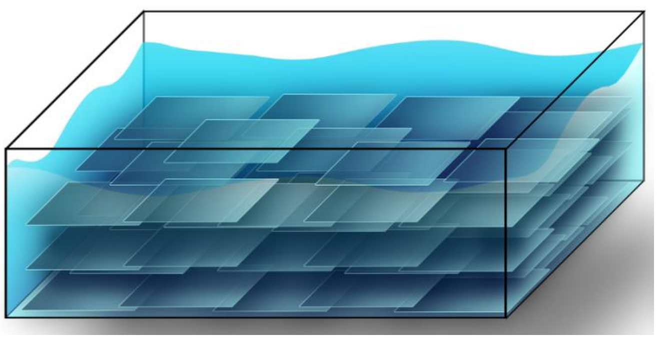
*Improved ion transport path at high stacking density*



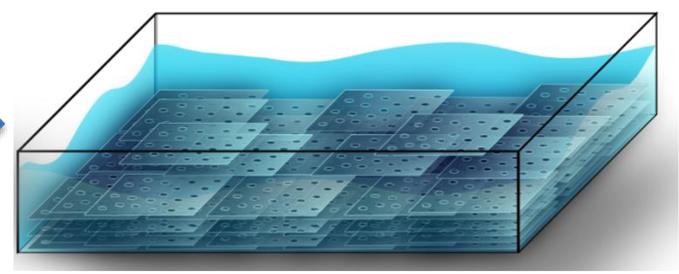


Raw graphene electrode

Holey graphene electrode



***Equivalent Capacitance***

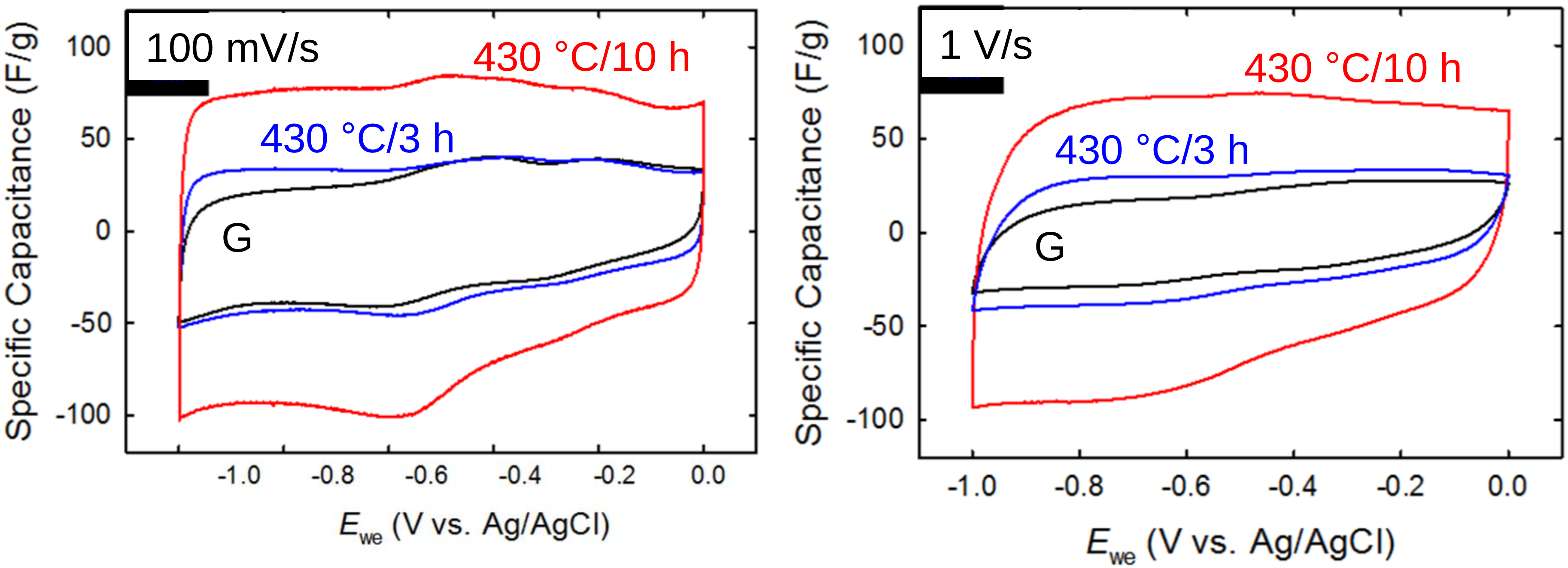


High volume

Low volume

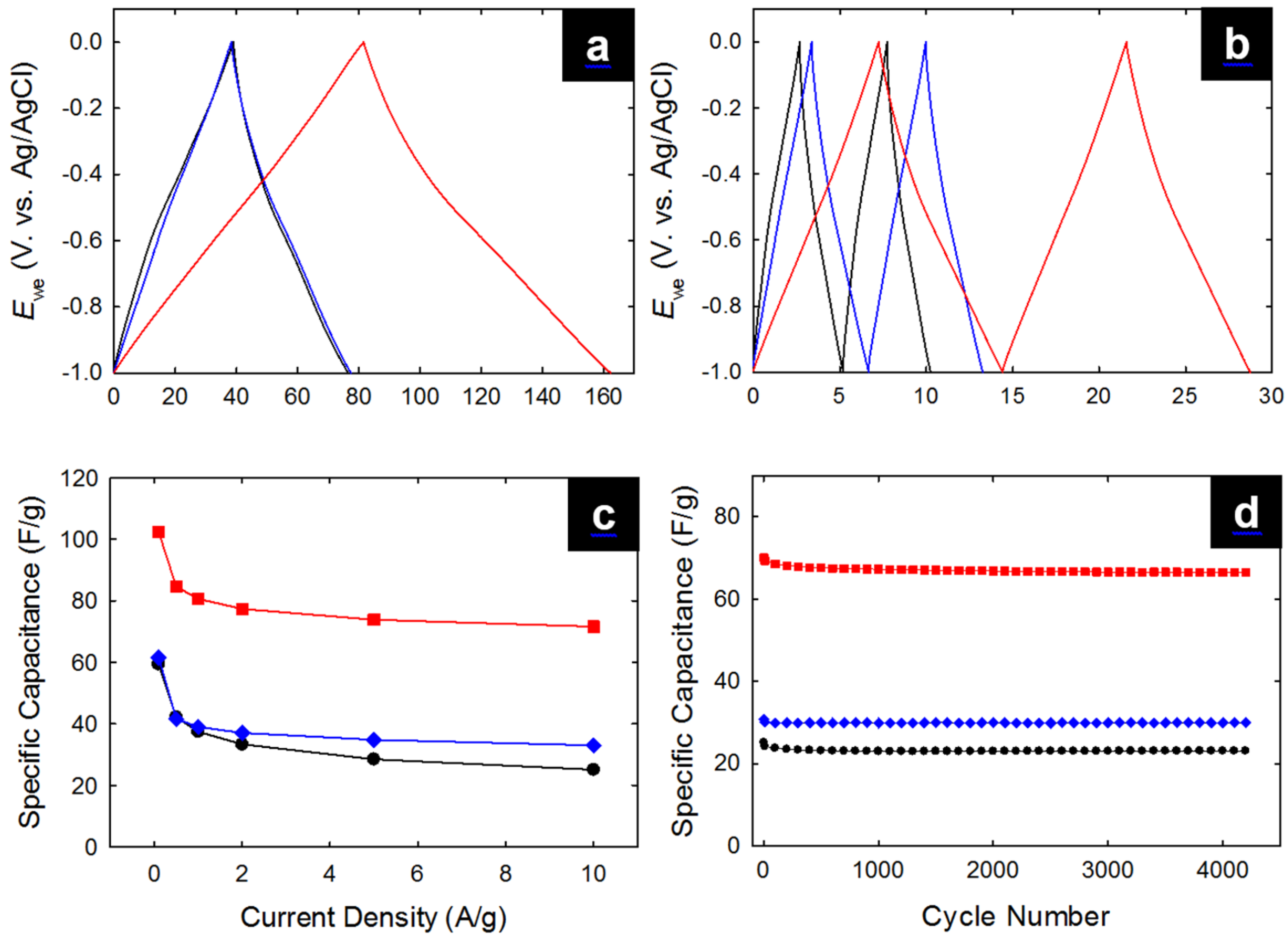
Courtesy: Prof. Liangbing Hu (UMD)

# Intrinsic Capacitive Properties of $hG_0$




***Presence of Holes ≠ Capacitance Improvement***

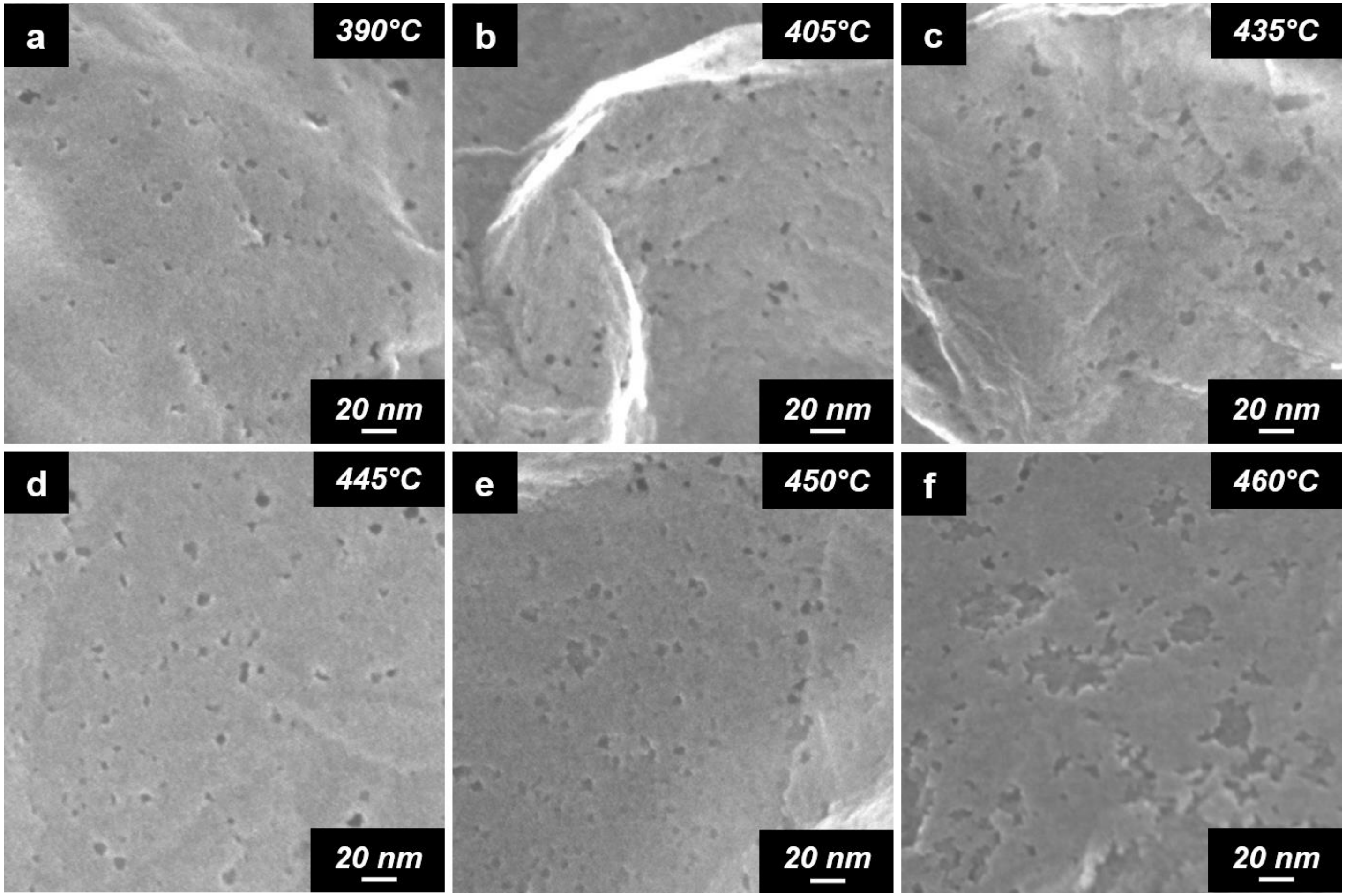
# Material Properties:
# Capacitive Performance of $hG_0$



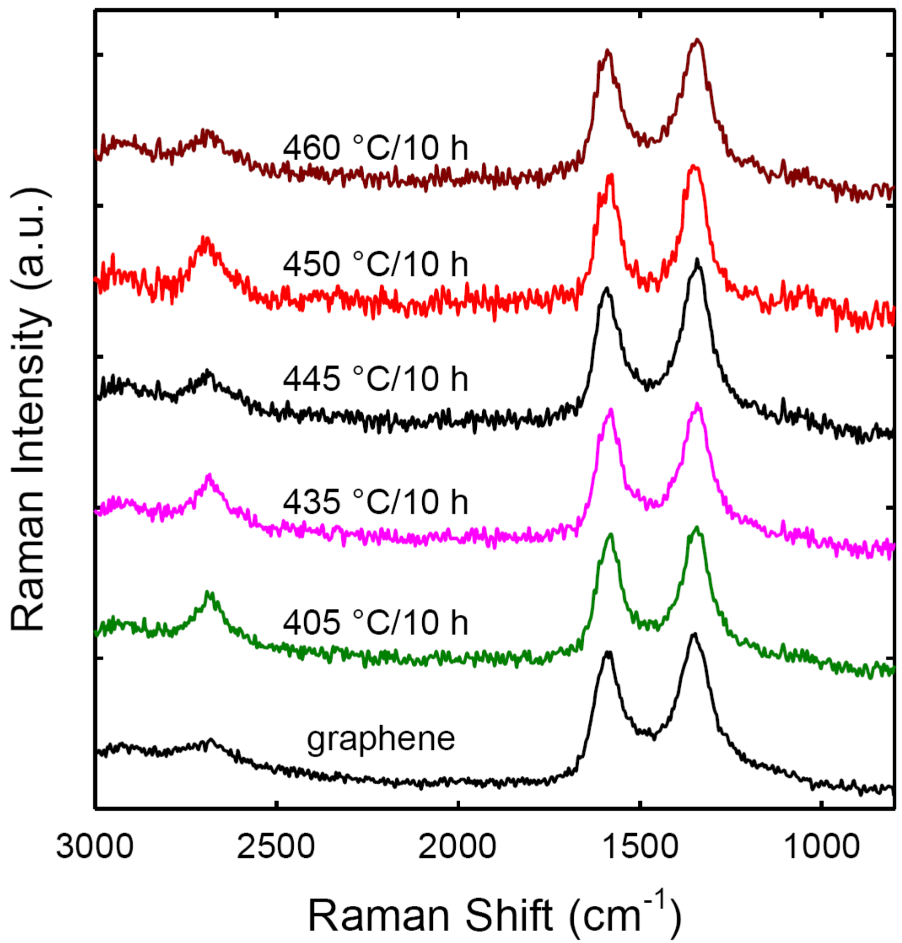

G 430 °C/3 h 430 °C/10 h

***Presence of Holes ≠ Capacitance Improvement***

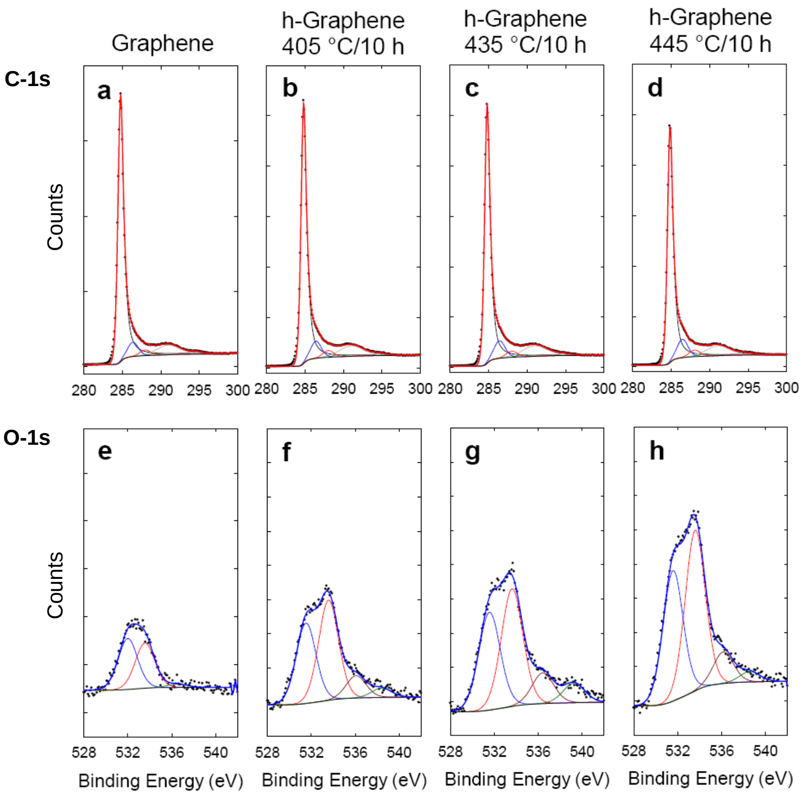
# $hG_0$: Synthesis Temperature



# $hG_0$: Raman Properties

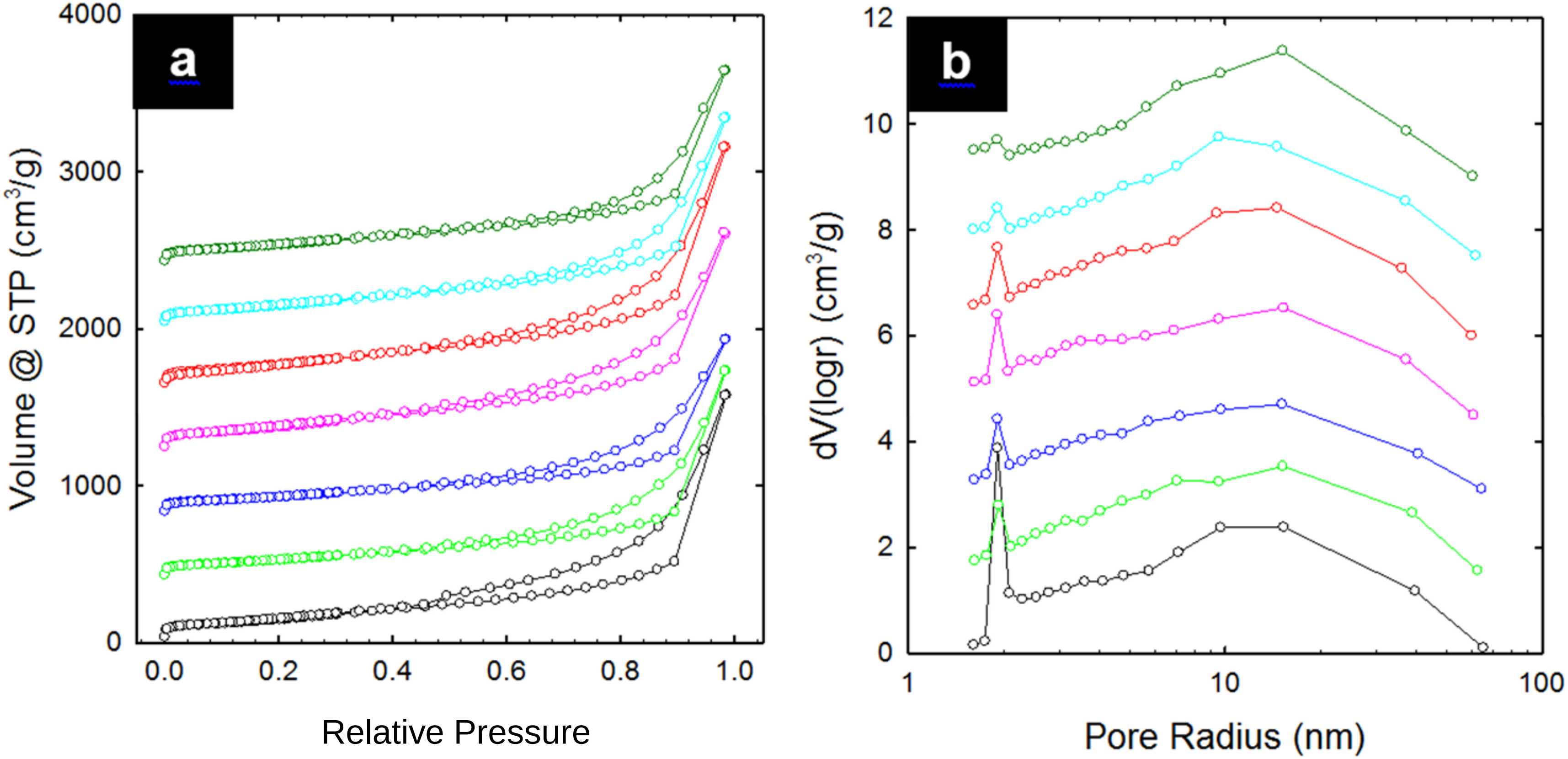


# $hG_0$: Chemical Composition (XPS)

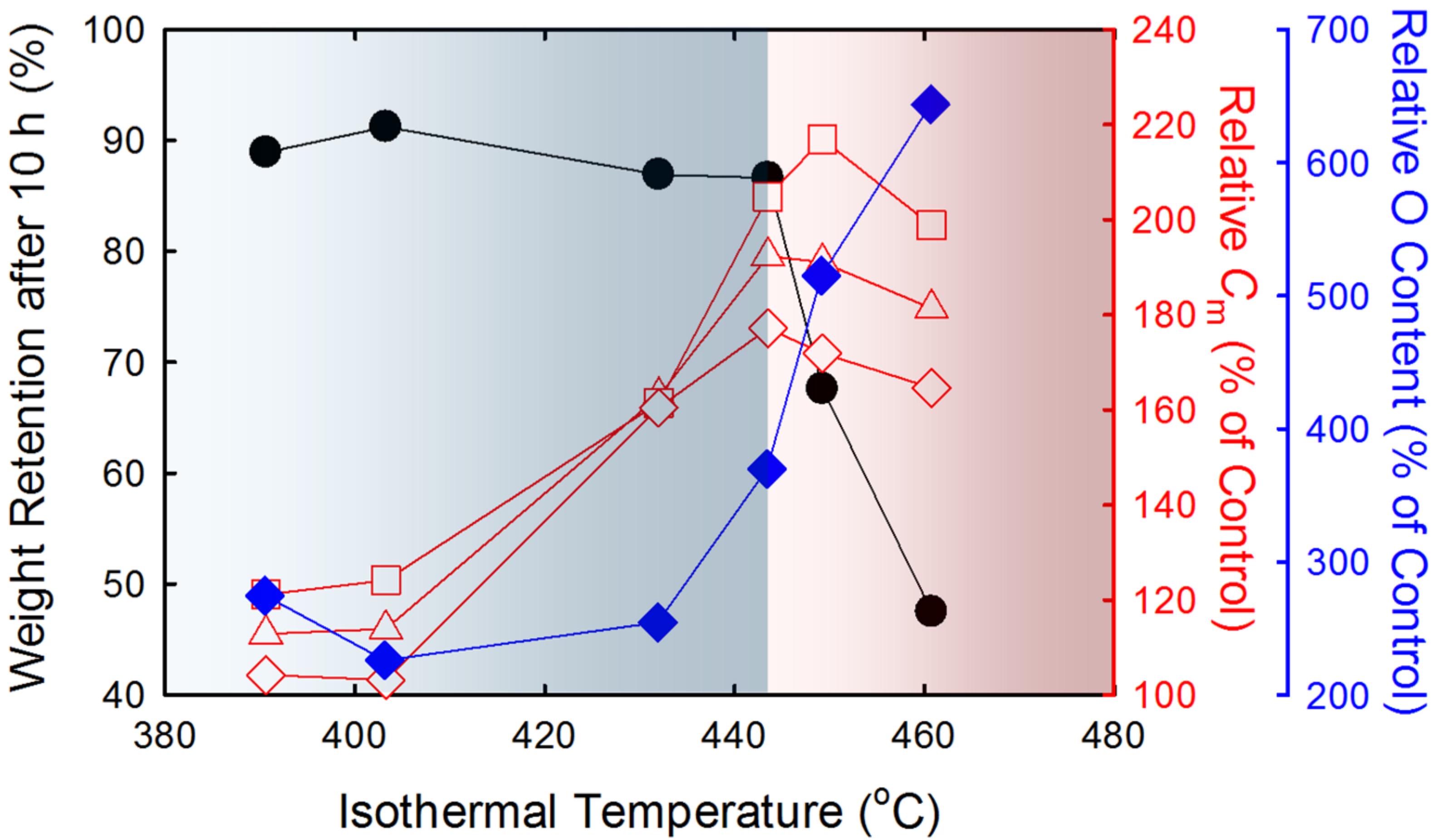



| Fitted Peaks | Binding Energy (eV) | Area (%) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | G | h-Graphene (10 h air oxidation) | | | | | |
| | | | 395 °C | 405 °C | 435 °C | 445 °C | 450 °C | 460 °C |
| **From C-1s** | | | | | | | | |
| $sp^2$ | 284.8 | 74.9 | 70 | 70.7 | 69.7 | 68.4 | 65.4 | 67 |
| C-OR | 286.4 | 8.2 | 10.3 | 9.8 | 10.5 | 11.5 | 13.2 | 12.6 |
| C=O | 288 | 3.2 | 3.8 | 3.9 | 3.7 | 4.2 | 6 | 4 |
| COOR | 289.3 | 1 | 1.3 | 1.2 | 1.2 | 1.6 | 1.7 | 1.8 |
| **From O-1s**[a] | | | | | | | | |
| O-C | 531.6 | 51.1 | 38.4 | 37.9 | 36.8 | 39.2 | 34.7 | 33. 9 |
| O=C | 533.6 | 45.4 | 46.8 | 47.2 | 44.2 | 48.2 | 44.6 | 44.3 |
| Doped O 1 | 536 – 536.5 | 3.5 | 9.4 | 10.5 | 11.6 | 9.5 | 15.5 | 13.8 |
| Doped O 2 | 538.2 – 539.2 | — | 5.4 | 4.4 | 7.4 | 3.1 | 5.2 | 8 |

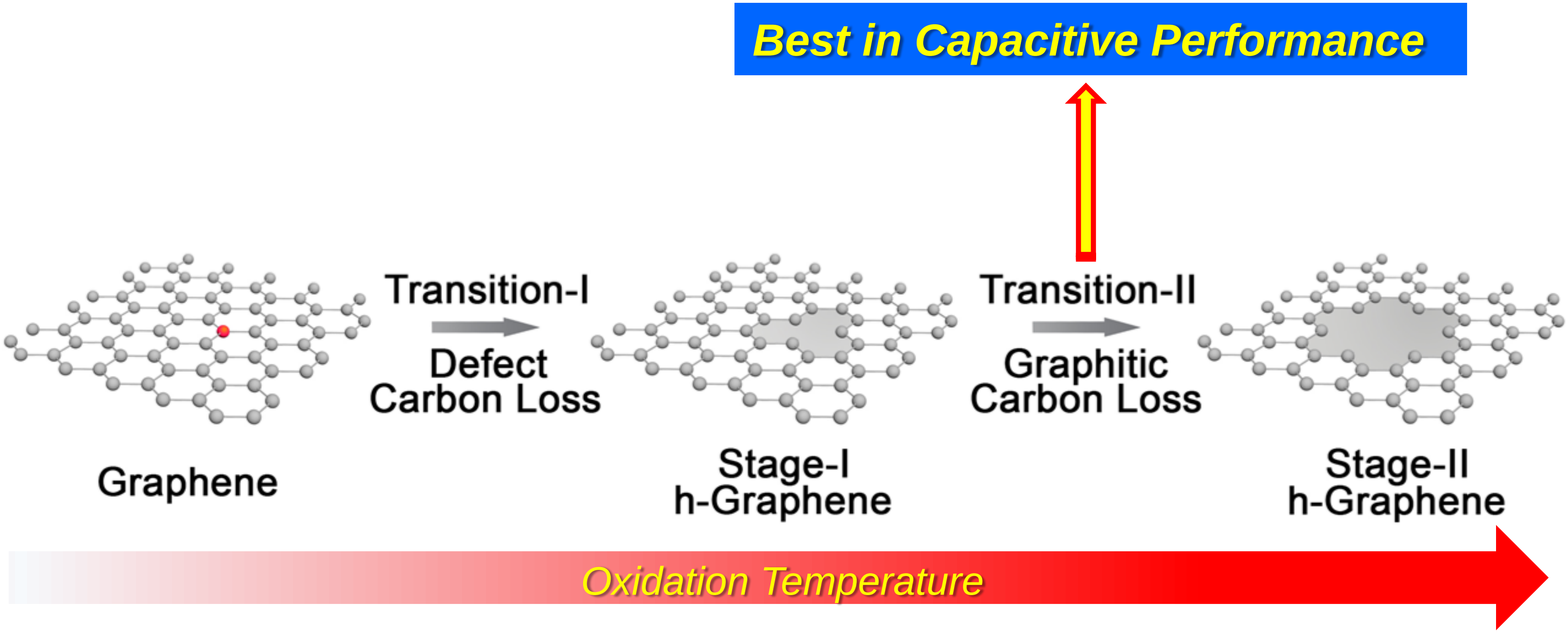
# $hG_0$: Surface Area and Pore Size



# Capacitance vs. O Content vs. Weight Retention

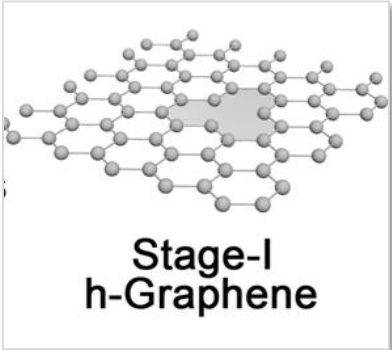


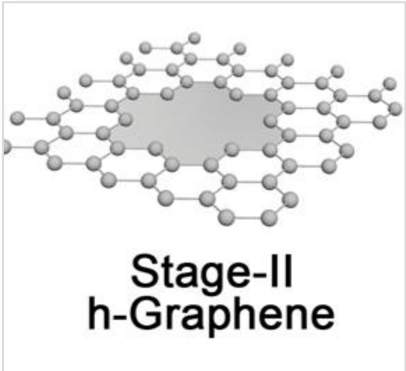
# $hG_0$ Formation Mechanism



# Application Challenges

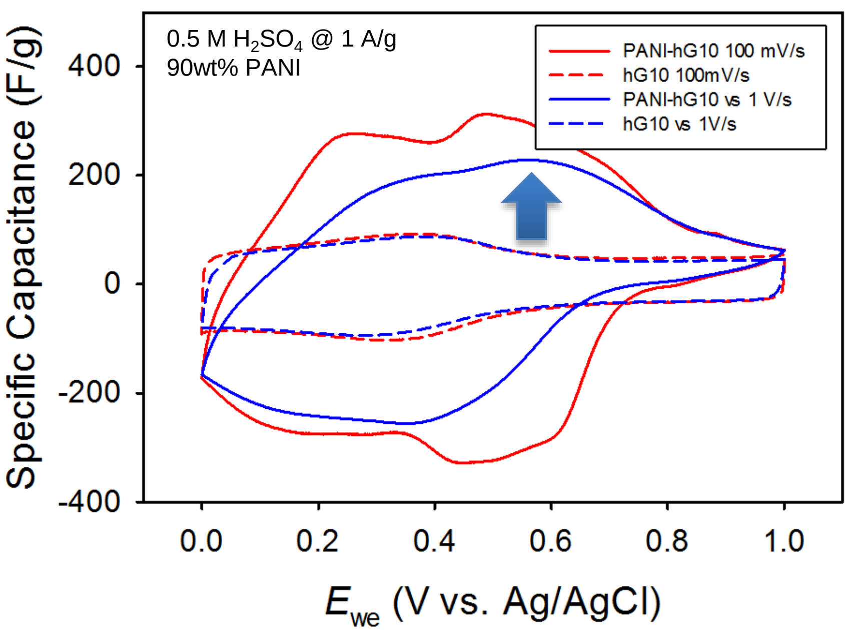
- Which structure-composition is the most appropriate for a specific application?
  - ❑ Sensors
  - ❑ Catalysis
  - ❑ Supercapacitor electrodes
  - ❑ Battery electrodes
  - ❑ Membranes
  - ❑ Electronic devices
  - ❑ Composites

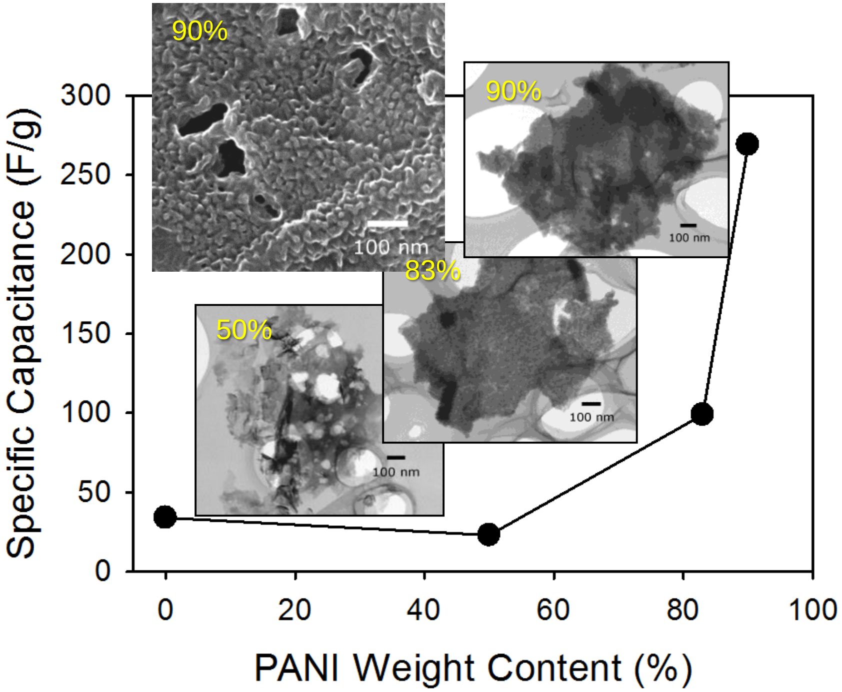


# hG Modification: Conductive Polymers

**Polyaniline (PANI)**



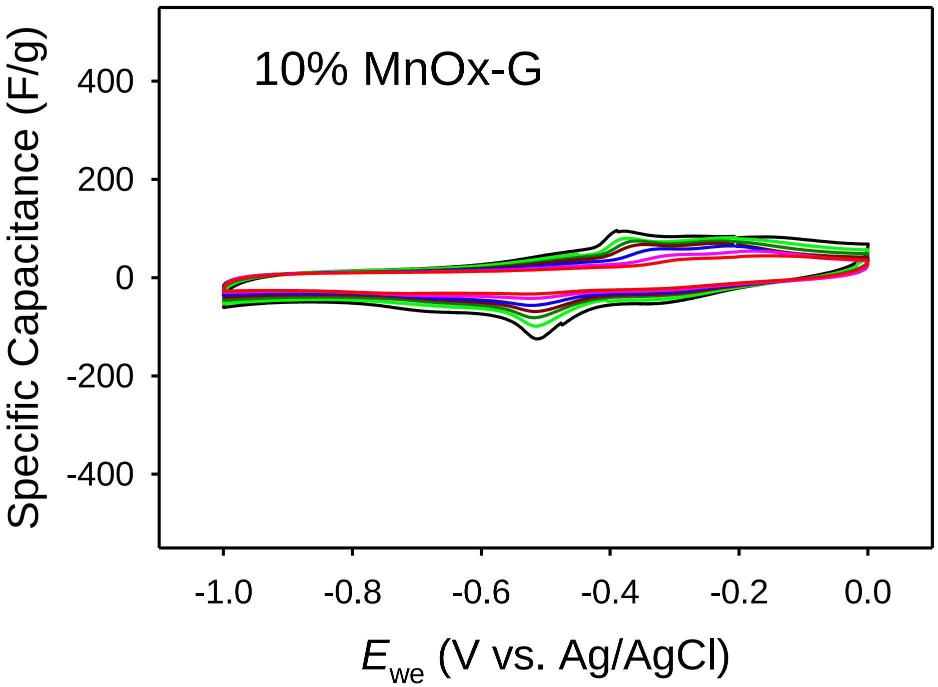



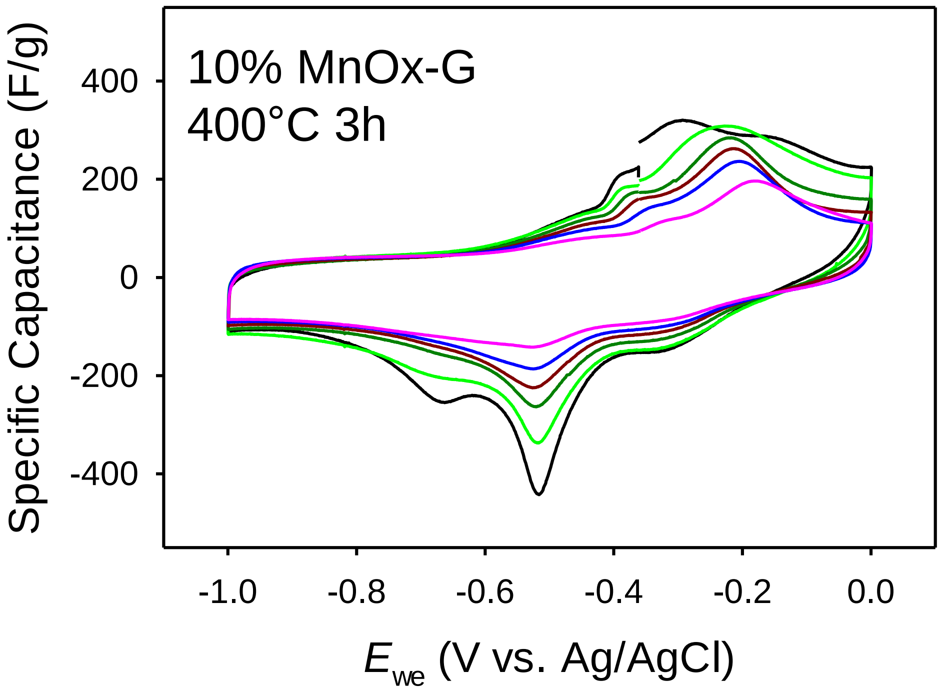

In situ polymerization

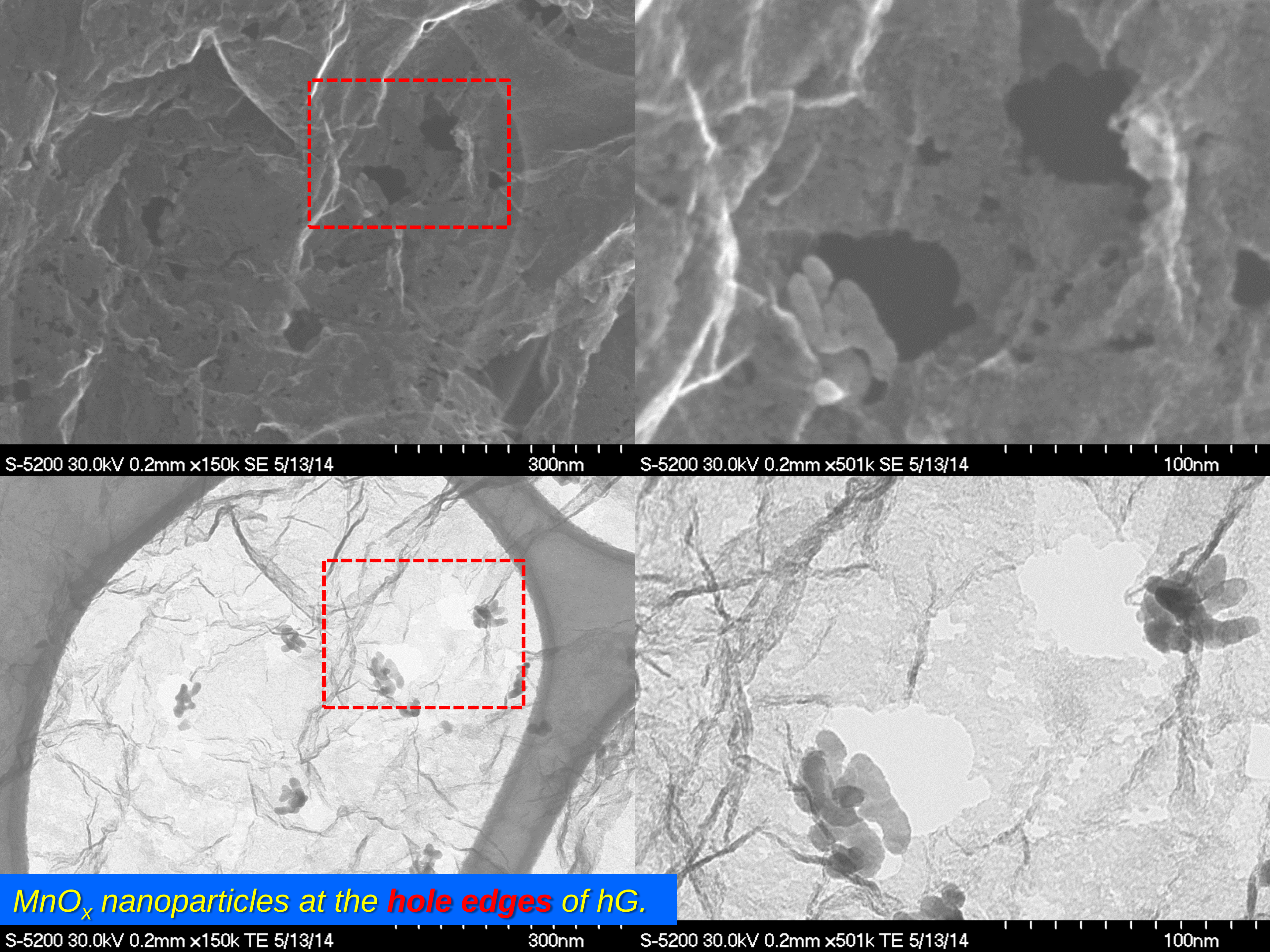
***Further capacitance improvement** can also be achieved by introducing pseudocapacitance.*

# hG Modification: Metal Oxides

**Manganese Oxide ($MnO_x$)**






*$MnO_x$ nanoparticles at the **hole edges** of hG.*

# 2D Nanomaterials Beyond Graphene

- Hexagonal boron nitride (h-BN)
- Metal dicharcogenides (e.g. $MoS_2$, $WS_2$, etc.)
- Others

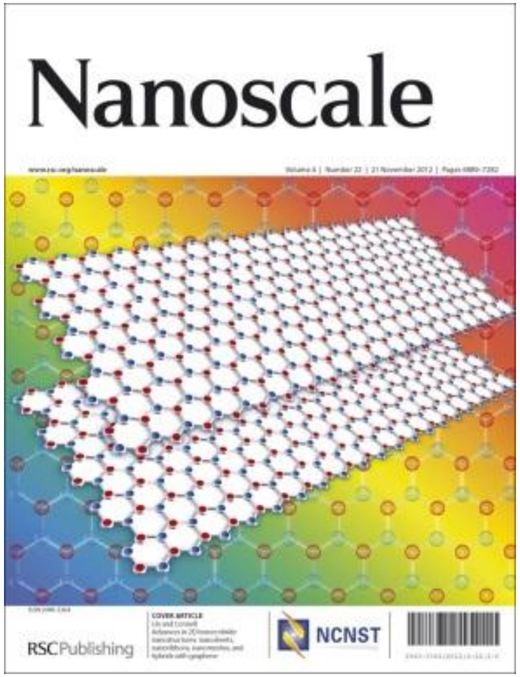
***Can they be also etched to form holes?***

# Our Experience in Boron Nitride Nanomaterials

- Nanosheets (BNNS) vs nanotubes (BNNT) ≈ Graphene vs CNT
  - “White” graphene (insulating; bandgap ~ 6eV)
  - Thermal stability (>800°C in air)
  - Chemical inertness
  - High thermal conductivity
  - High mechanical strength
  - Radiation resistant
  - Low toxicity
  - Potentially low cost

- Potential applications
  - Thermal conductive (but electrically insulating) fillers
  - Low optical absorption or transparency
  - Robust coatings
  - High quality dielectric substrate for graphene electronics:
    - require large area (preferably >10 μm) sheets

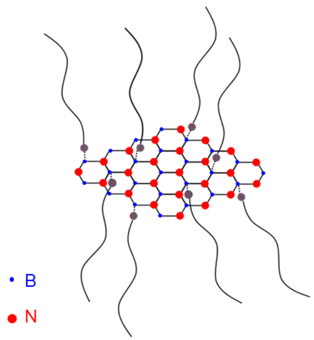
- Current Bottleneck:
  - High-yield production
  - Size control
  - Actual program needs



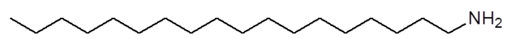

*Nanoscale* **2012**, *4*, 6908-6939.

# BNNS from Exfoliation of h-BN

***Chemical Functionalization***

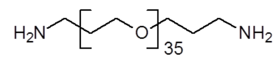



***lipophilic***

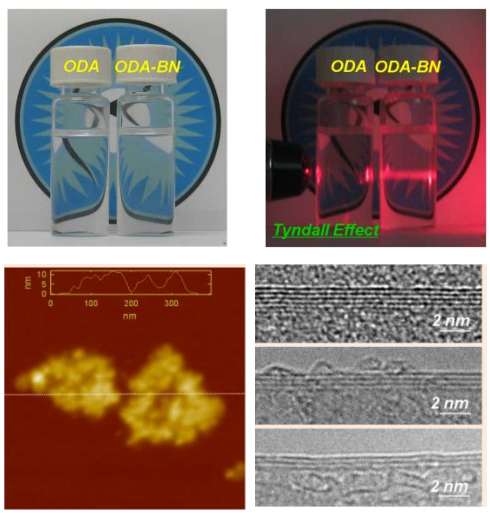



Octadecylamine (ODA)

***hydrophilic***



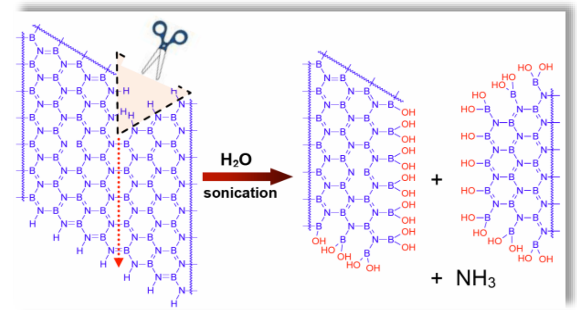

Polyethylene glycol (PEG), amine-terminated

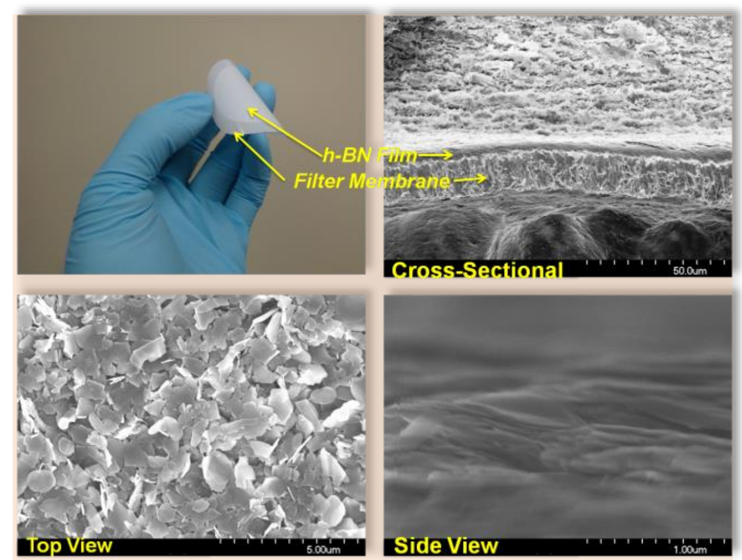



*J. Phys. Chem. Lett.* **2010**, *1*, 277.

*J. Phys. Chem. C* **2010**, *114*, 17434.

***Sonication-Assisted Direct Solvent Dispersion***

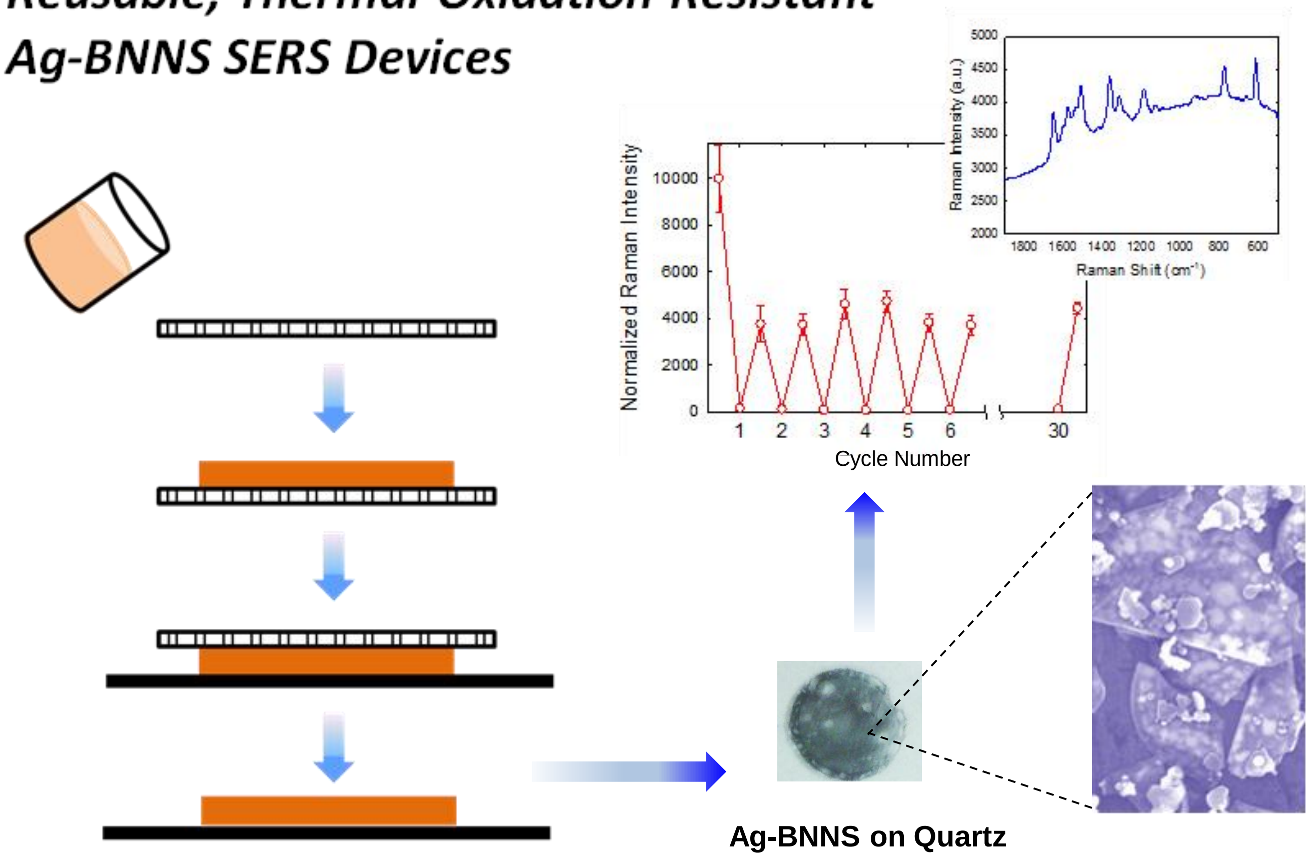



*J. Phys. Chem. C* **2011**, *115*, 2679.

# BNNS-Based SERS Sensors

***Reusable, Thermal Oxidation-Resistant Ag-BNNS SERS Devices***

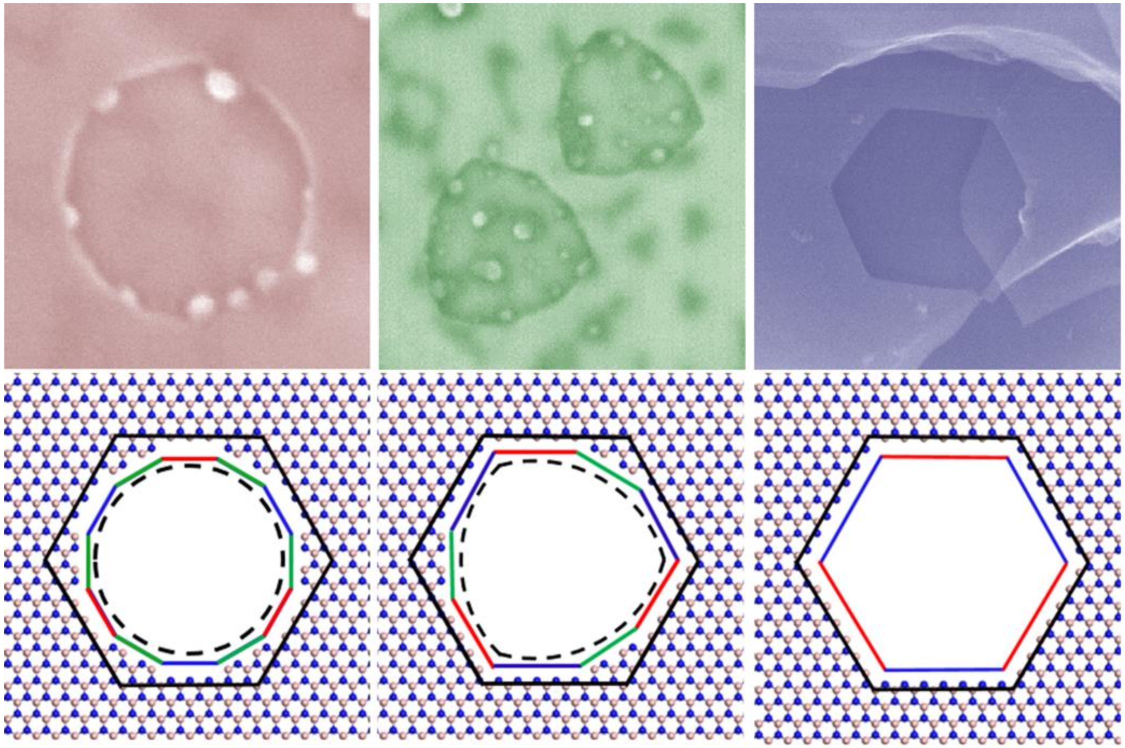



Thermal/oxidation resistance and low-color of BNNS is unique and should be further explored.

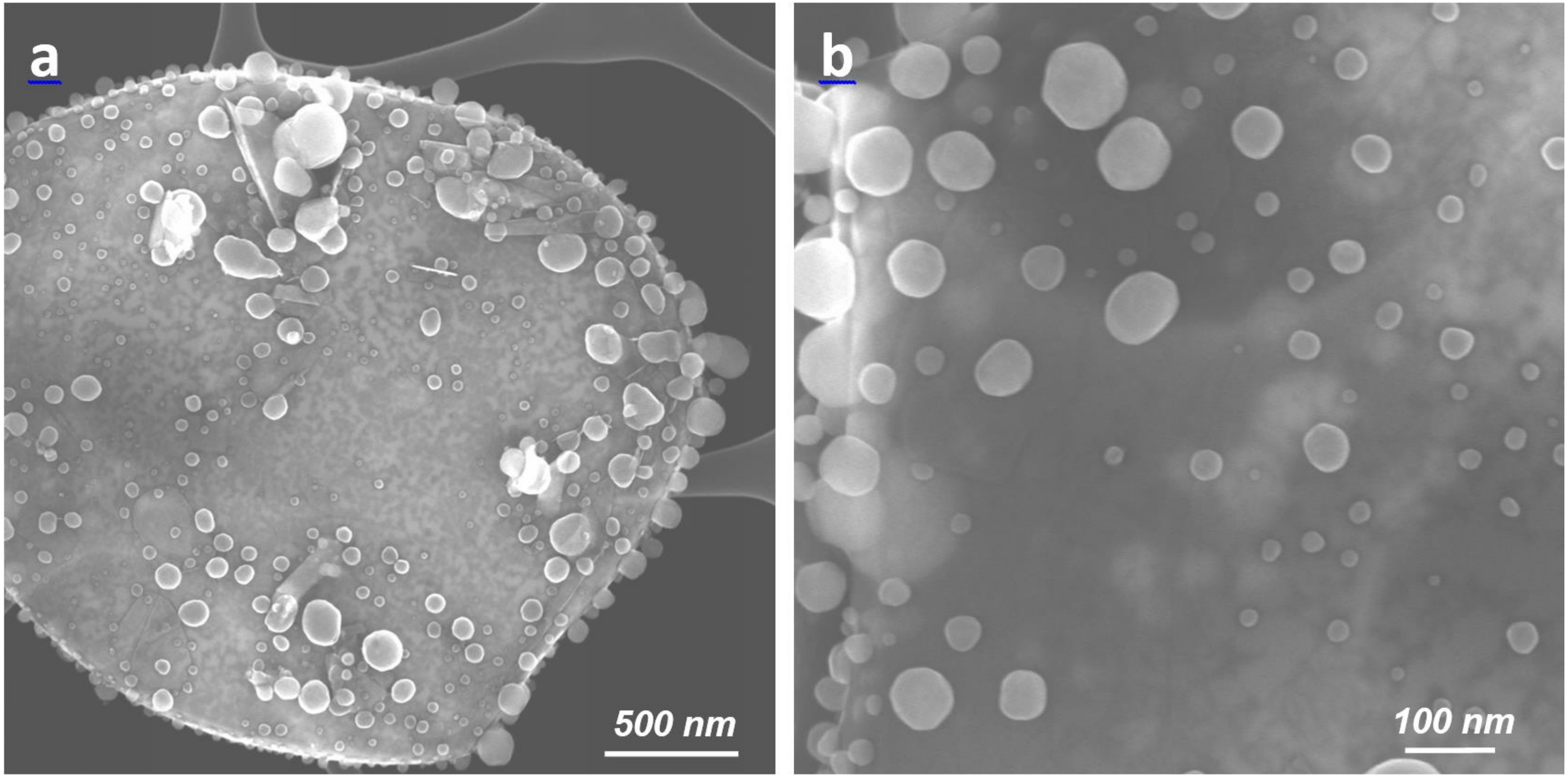
*ACS Appl. Mater. Interfaces* **2012**, *4*, 1110.

# Holey BN?

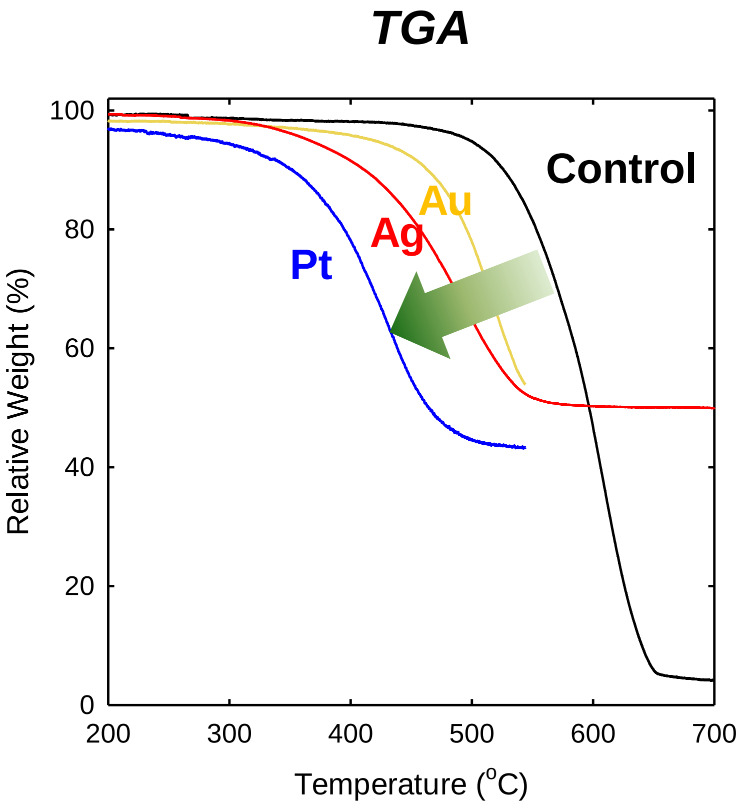
- How can we etch the inert 2D surface?

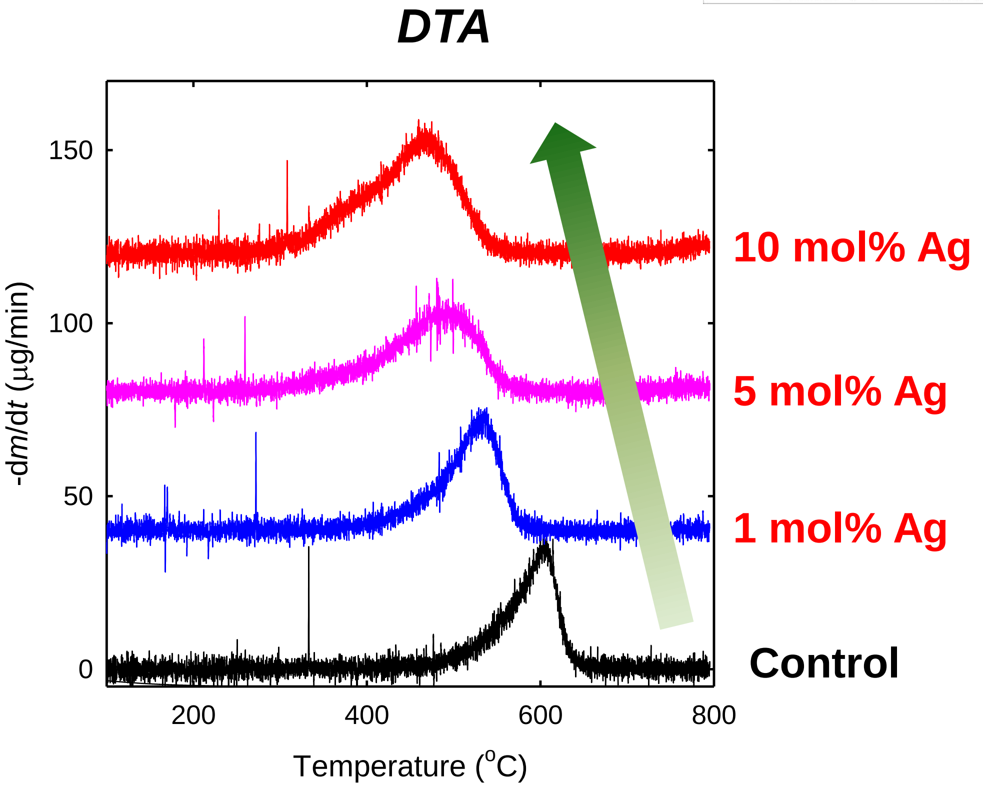


# Ag-Decorated h-BN (Ag-BN)



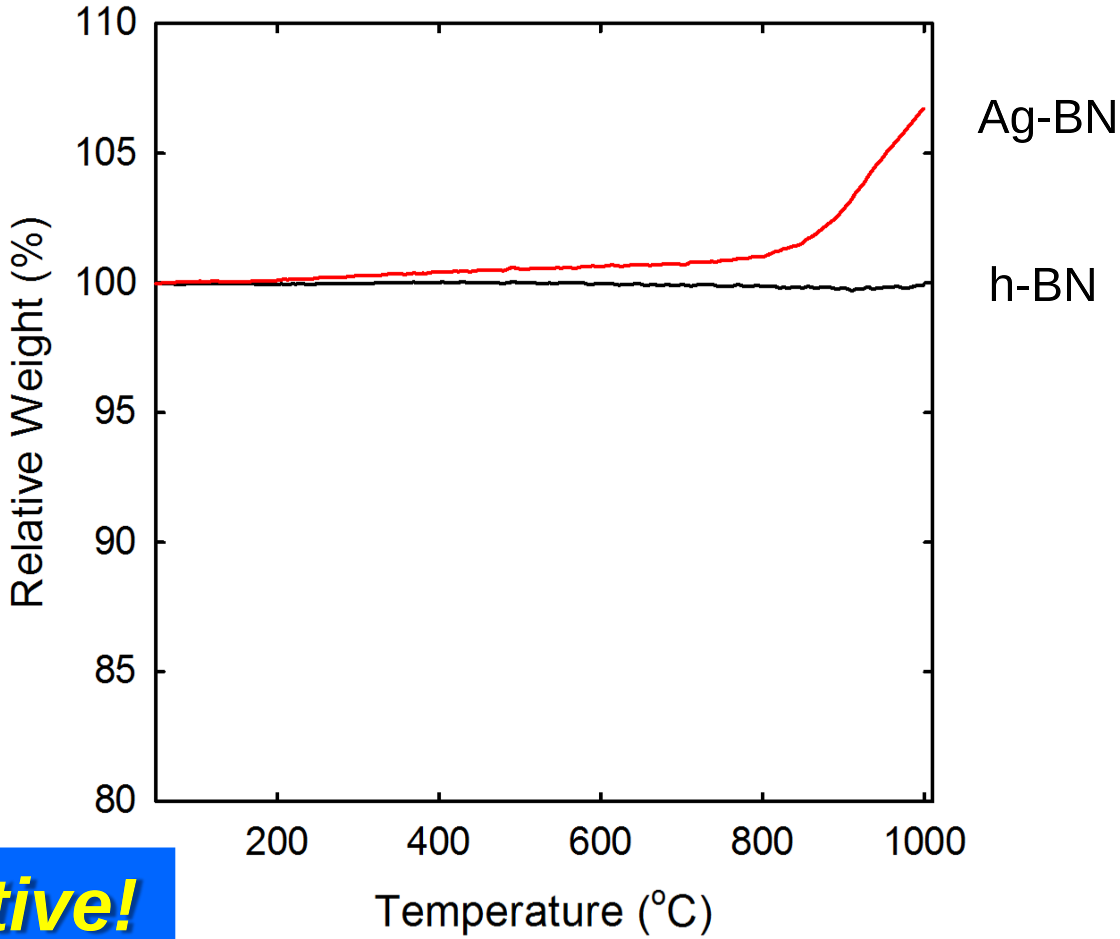
# Ag-Catalyzed Graphene Oxidation


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

# Ag-Catalyzed BN Oxidation

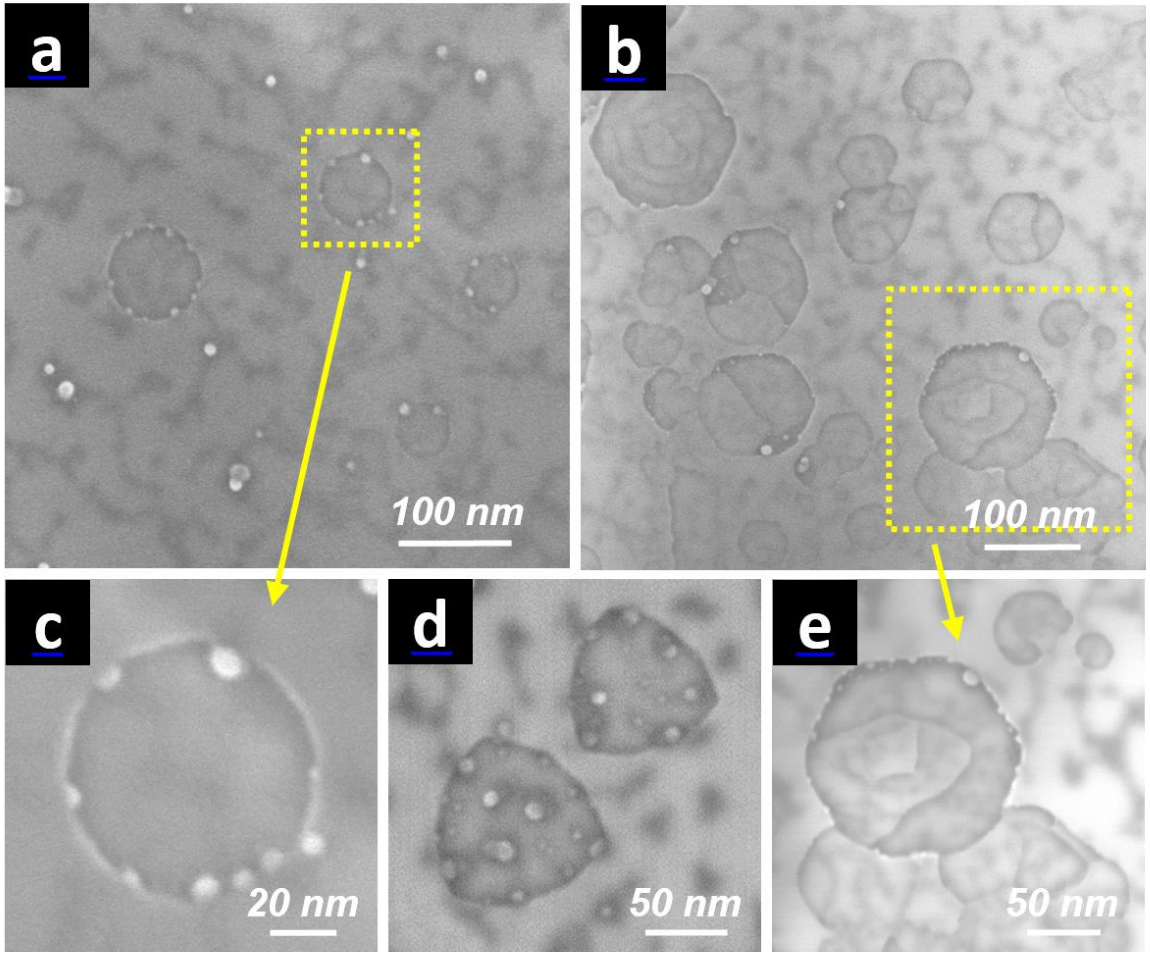



***Inert is relative!***

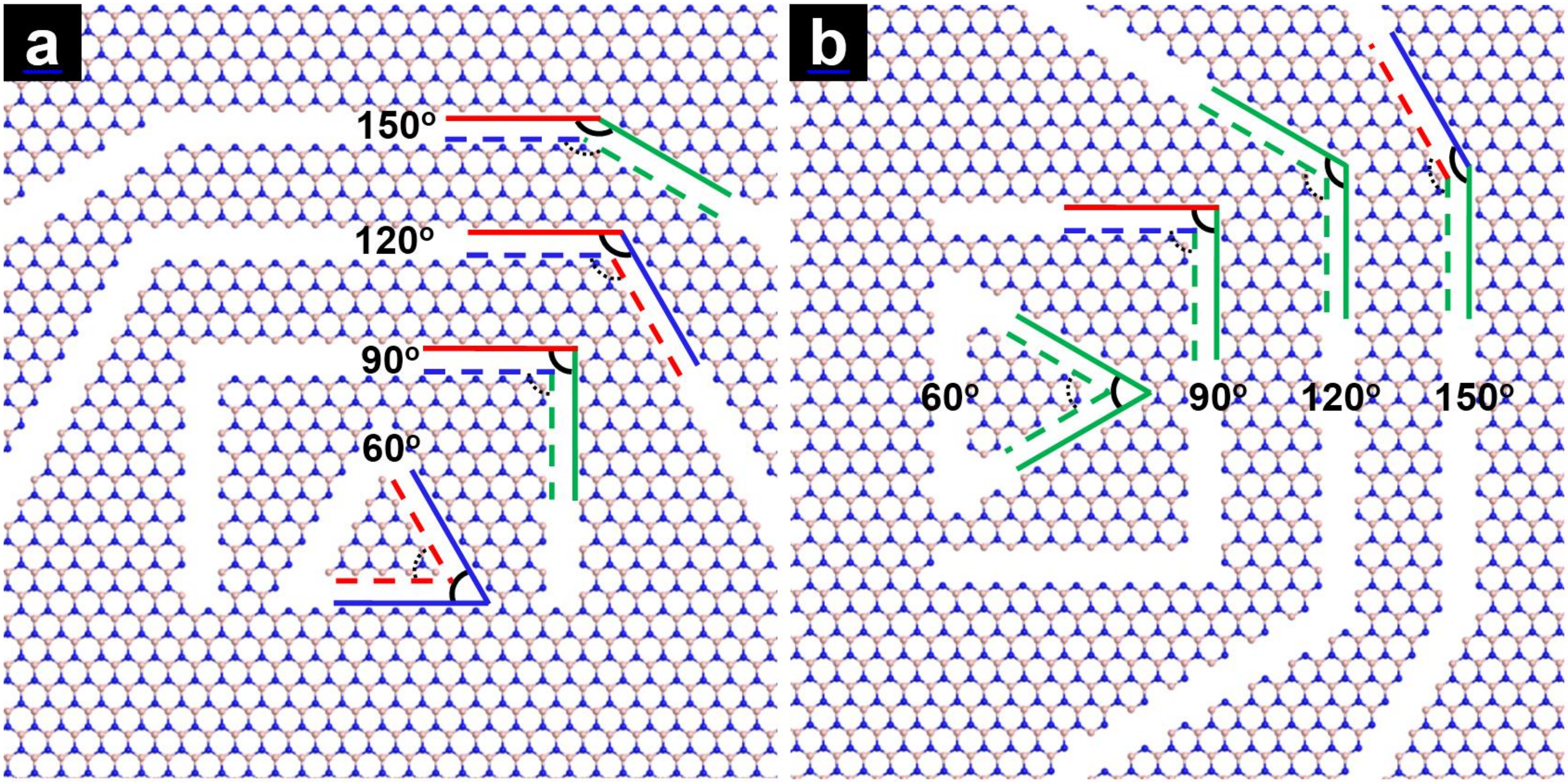
Thermal Gravimetric Analysis (TGA): 10 °C/min, air

# Ag-Catalyzed BN Oxidation

**800 °C, 3h**

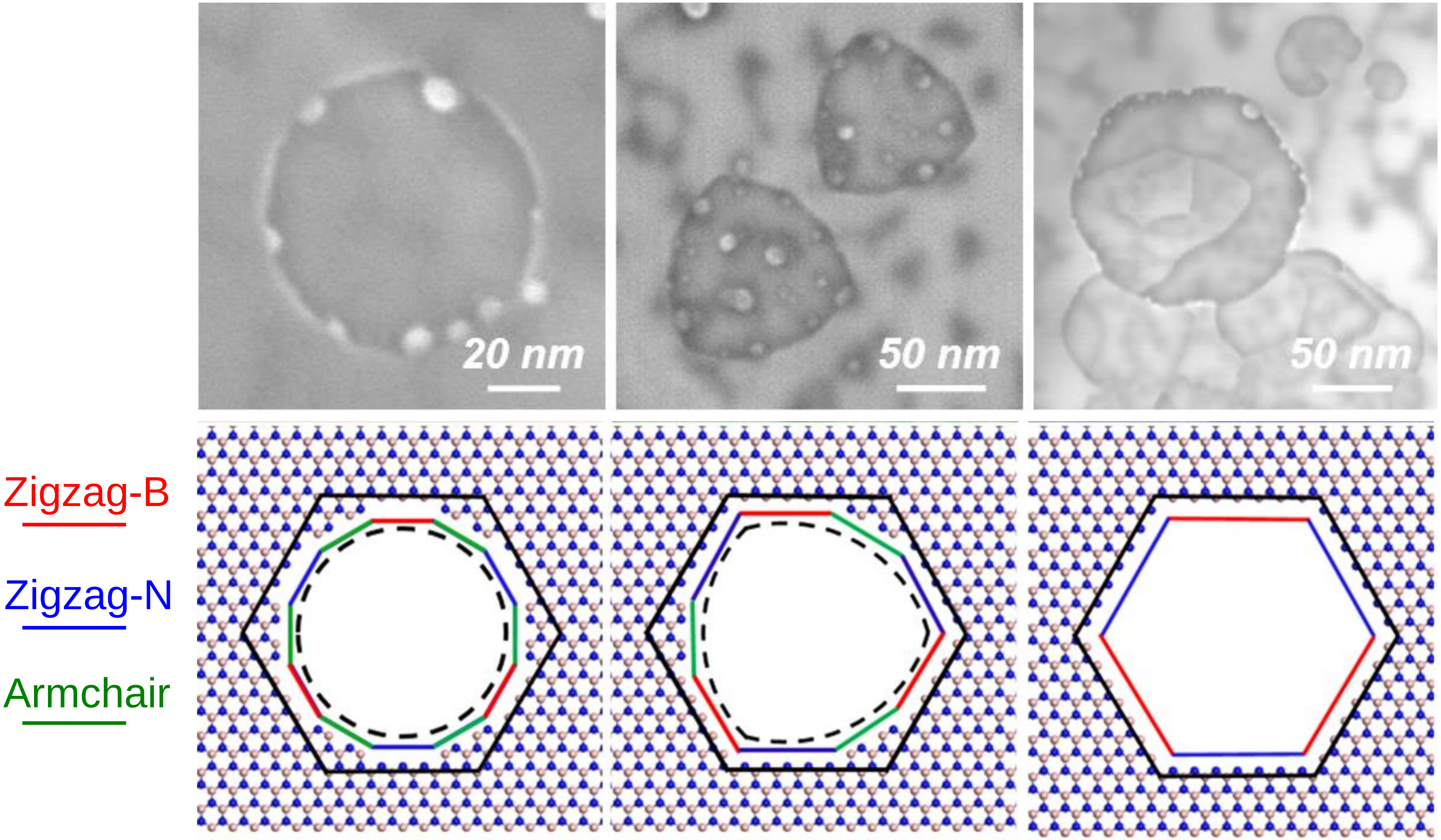


# Edge Structure of BNNS




Zigzag-B Zigzag-N Armchair

# Atomic Structure




Dodecagon
(≈ Circle)

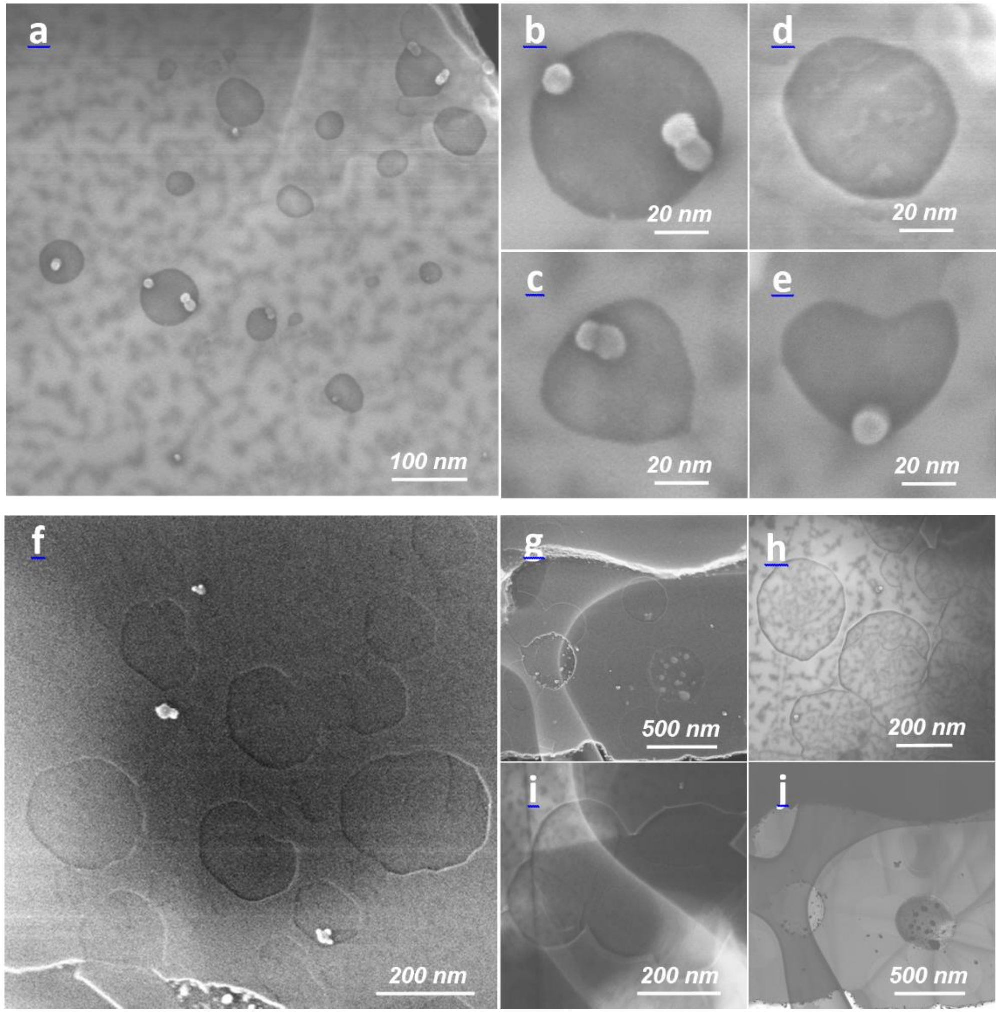
Nonagon
(≈ Reuleaux Triangle)

Hexagon

# Pit Growth

800 °C, 1h

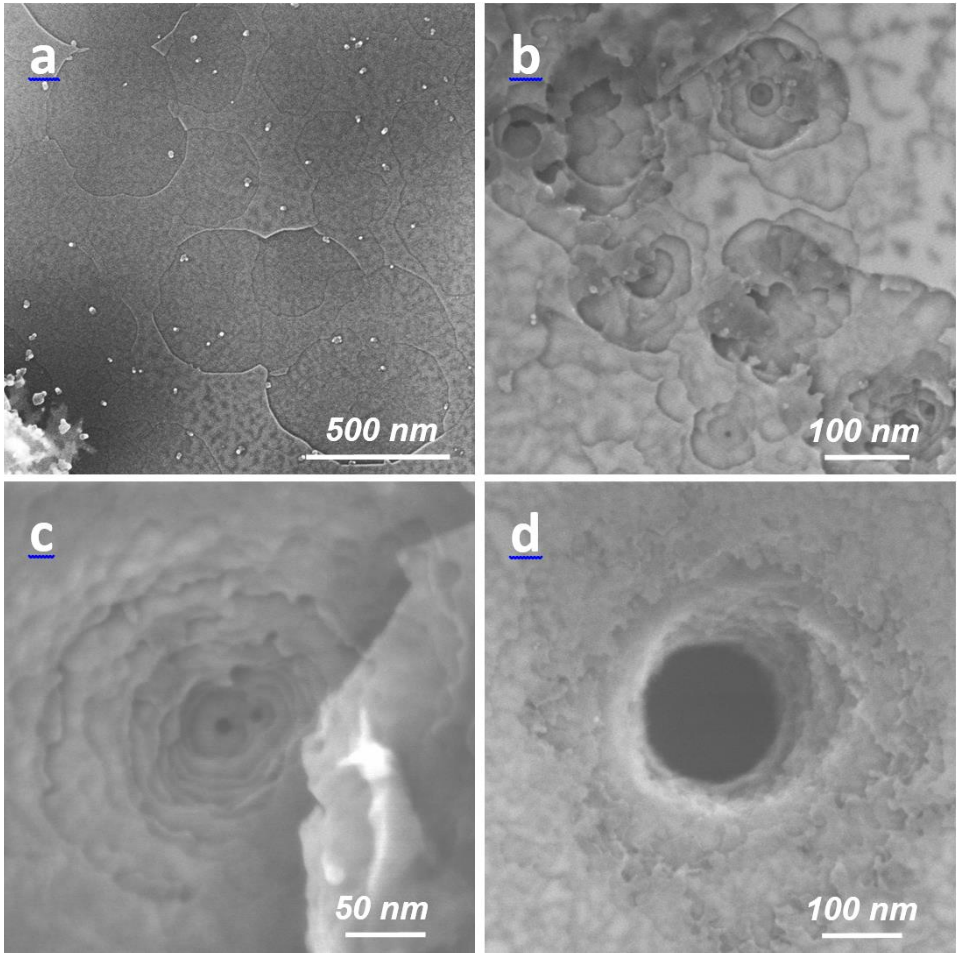
800 °C, 10h



# Temperature Effect

900 °C, 3h

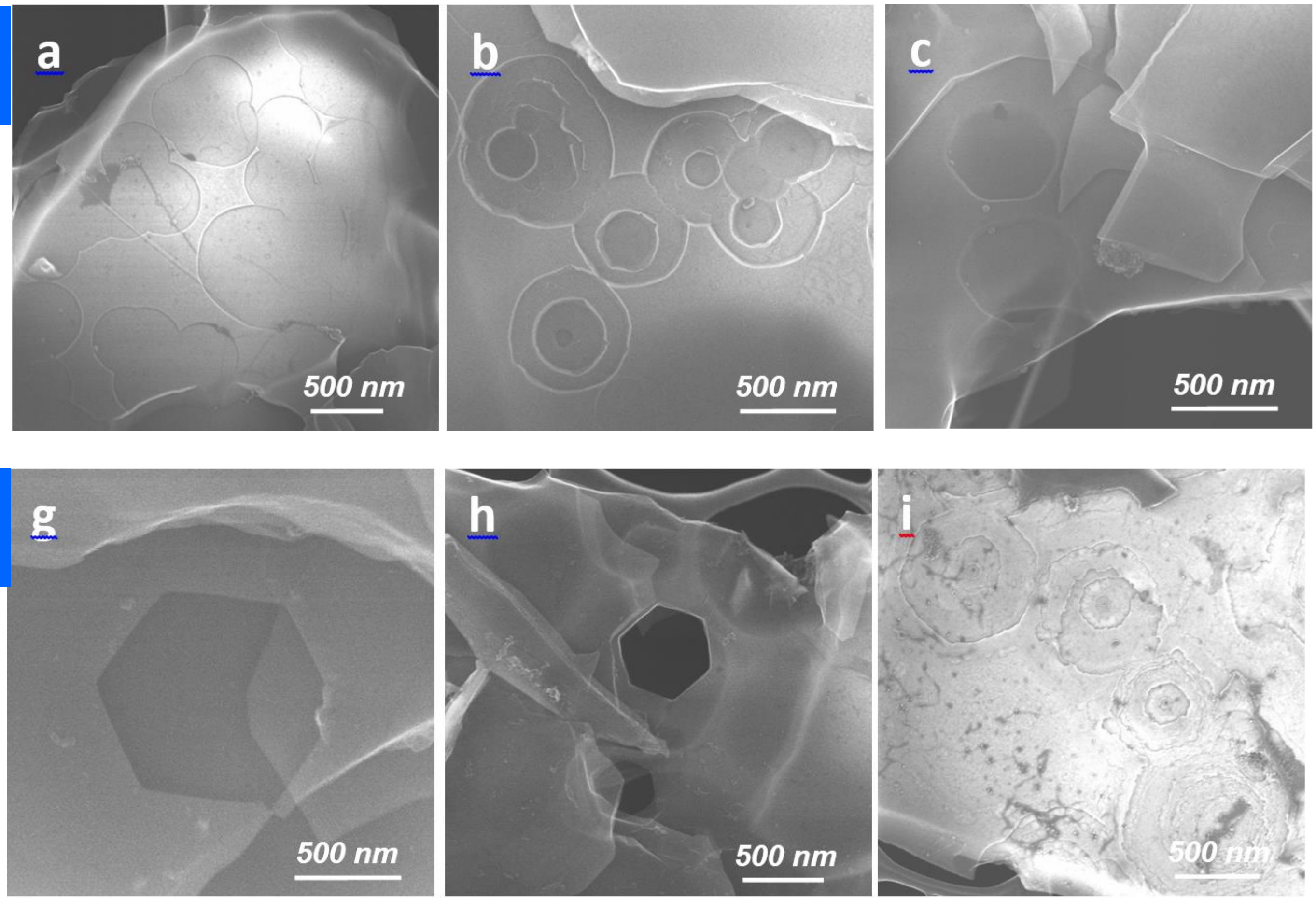
1000 °C, 3h



# Temperature Effect: Acid Purification

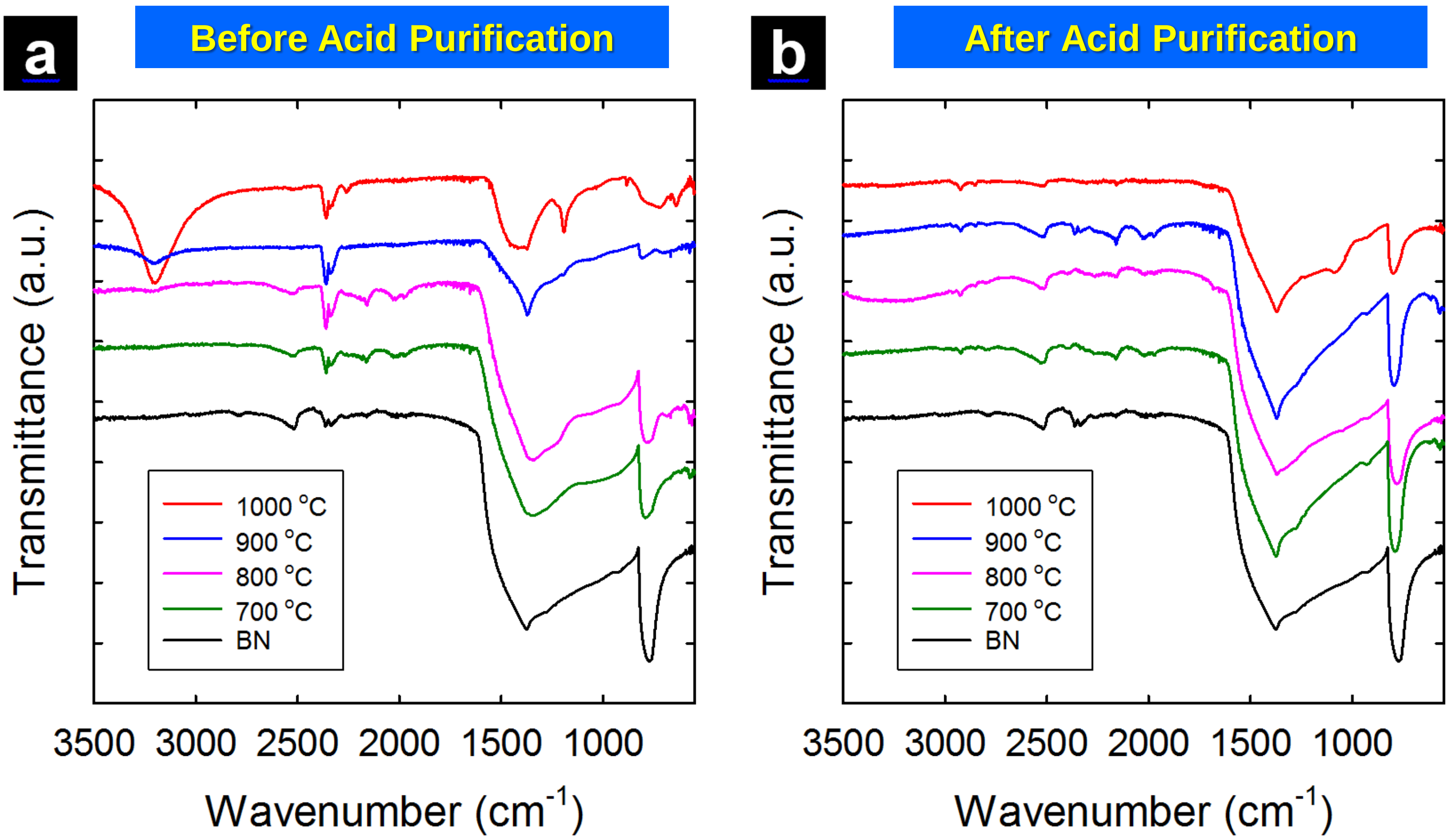
**900 °C, 3h**
**Acid-purified**

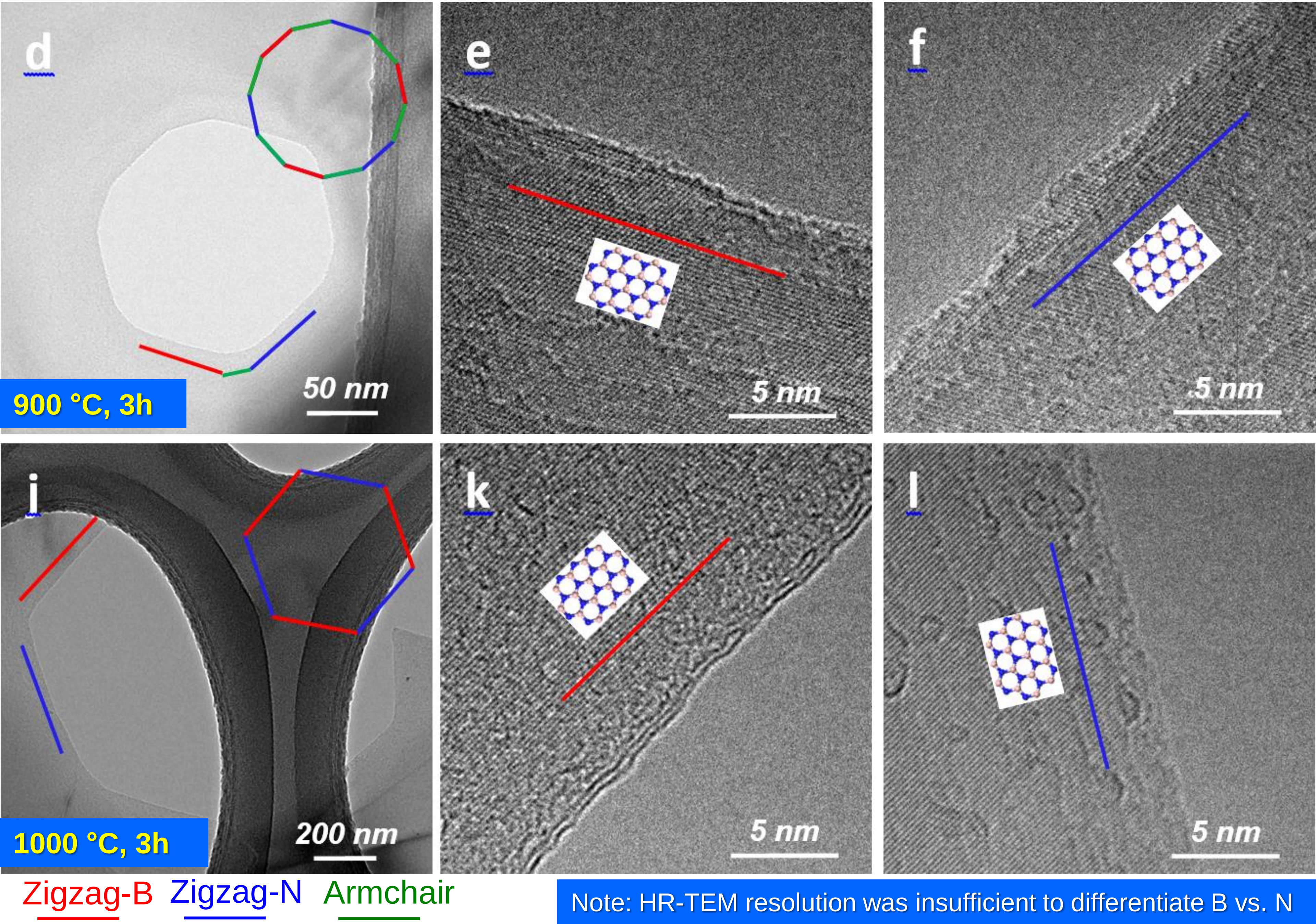
**1000 °C, 3h**
**Acid-purified**




After purification with nitric acid, intrinsic shapes of pits/holes were revealed.

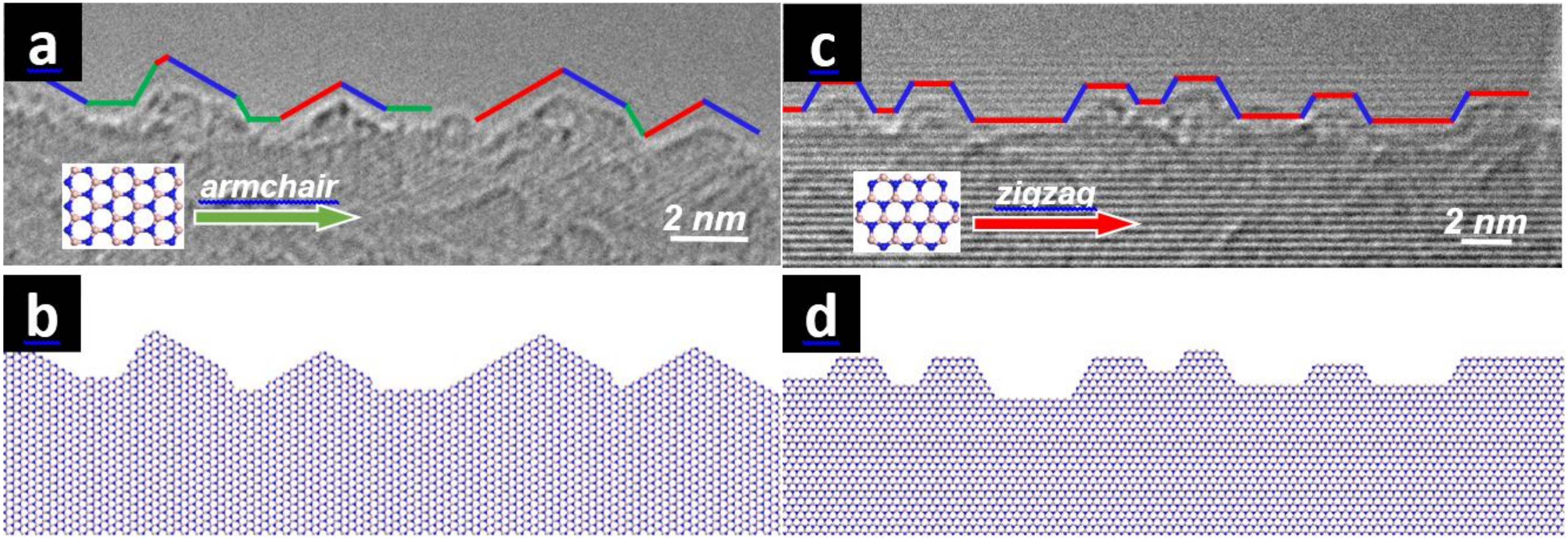
# FT-IR


a
Before Acid Purification
b
After Acid Purification
Transmittance (a.u.)
Wavenumber (cm-1)
3500 3000 2500 2000 1500 1000
1000 °C
900 °C
800 °C
700 °C
BN



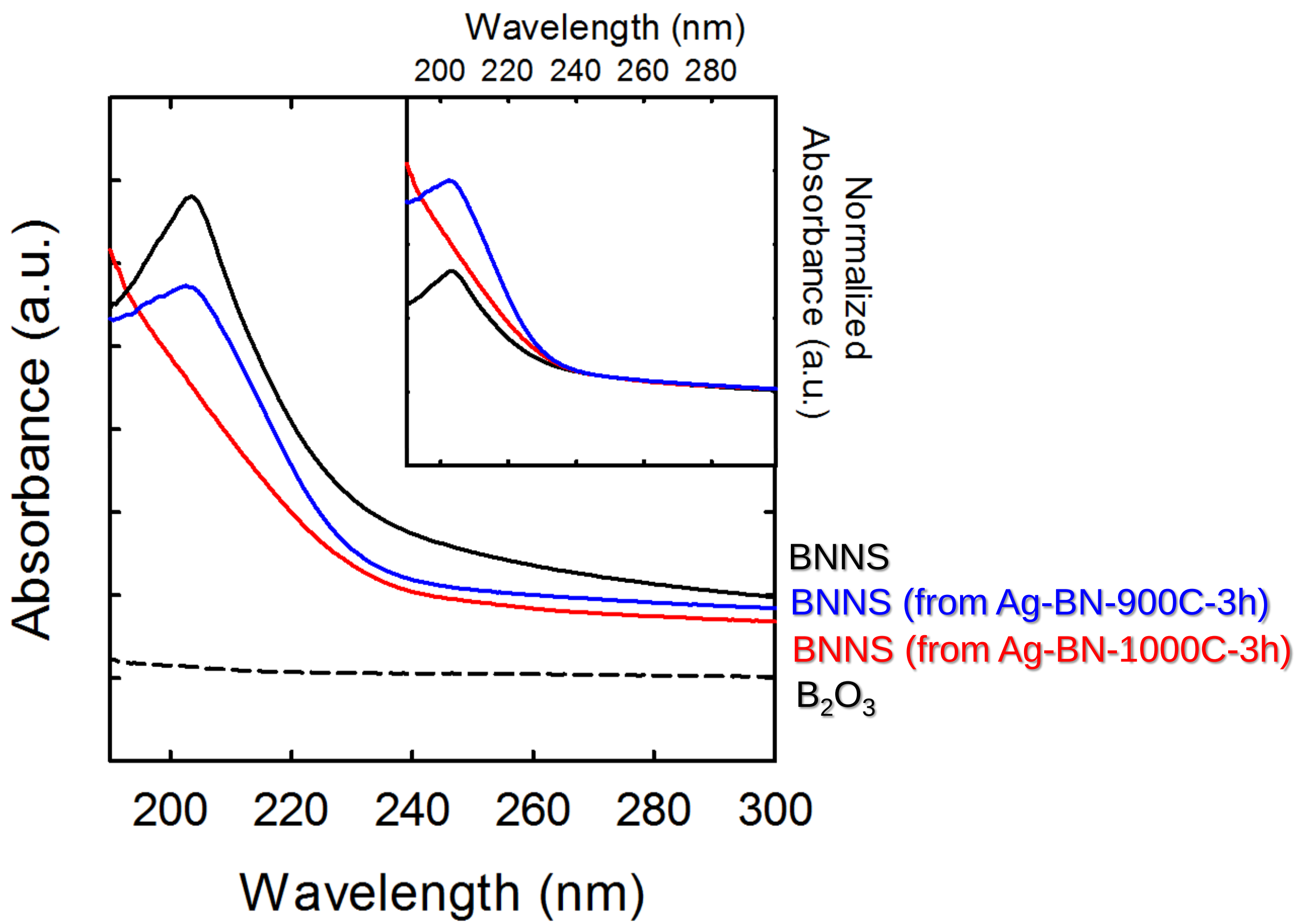
d
e
f
j
k
l
900 °C, 3h
1000 °C, 3h
50 nm
200 nm
5 nm
5 nm
5 nm
5 nm
5 nm
Zigzag-B
Zigzag-N
Armchair
Note: HR-TEM resolution was insufficient to differentiate B vs. N

# Zigzag-edge Enriched!



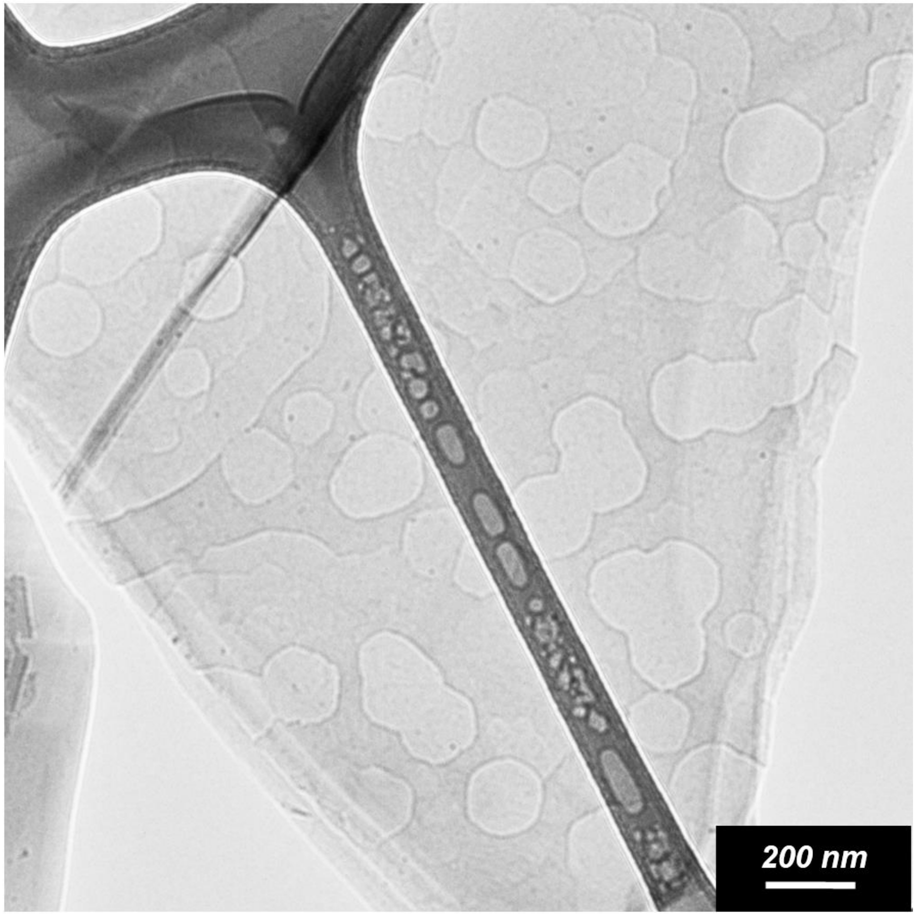

Zigzag-B Zigzag-N Armchair

# Modulation of Bandgap?



# Holey BNNS:
# Where to go from here?

- ❑ Scalability
- ❑ Hole density
- ❑ Properties:
  - ➢ Holey BNNS
  - ➢ Zigzag edge-enriched BNNS
- ❑ Applications
  - ➢ Membranes
  - ➢ Catalysis



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