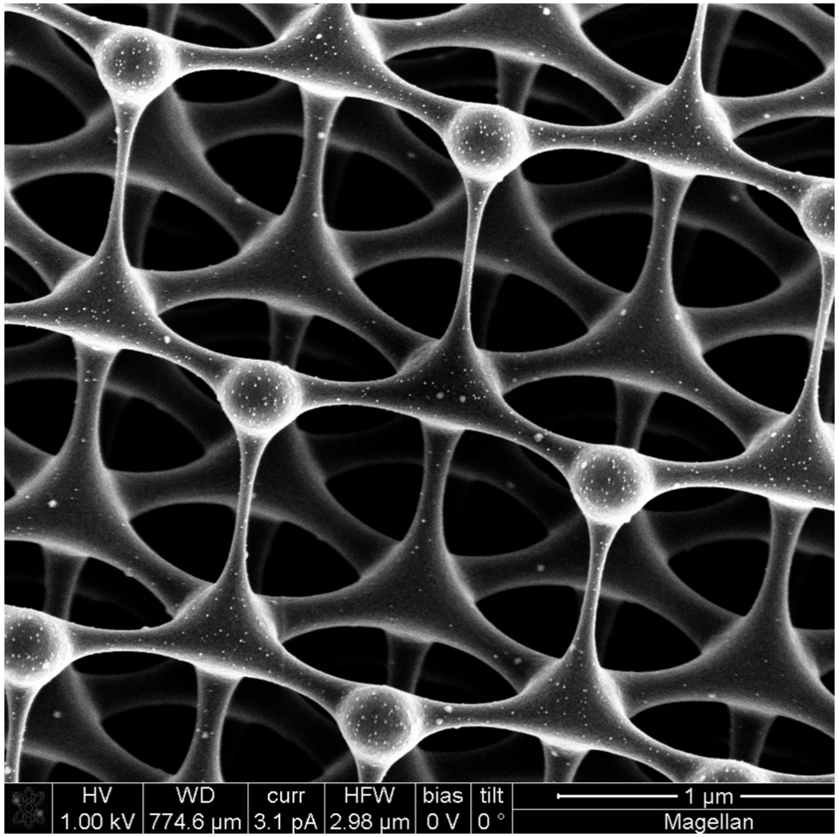
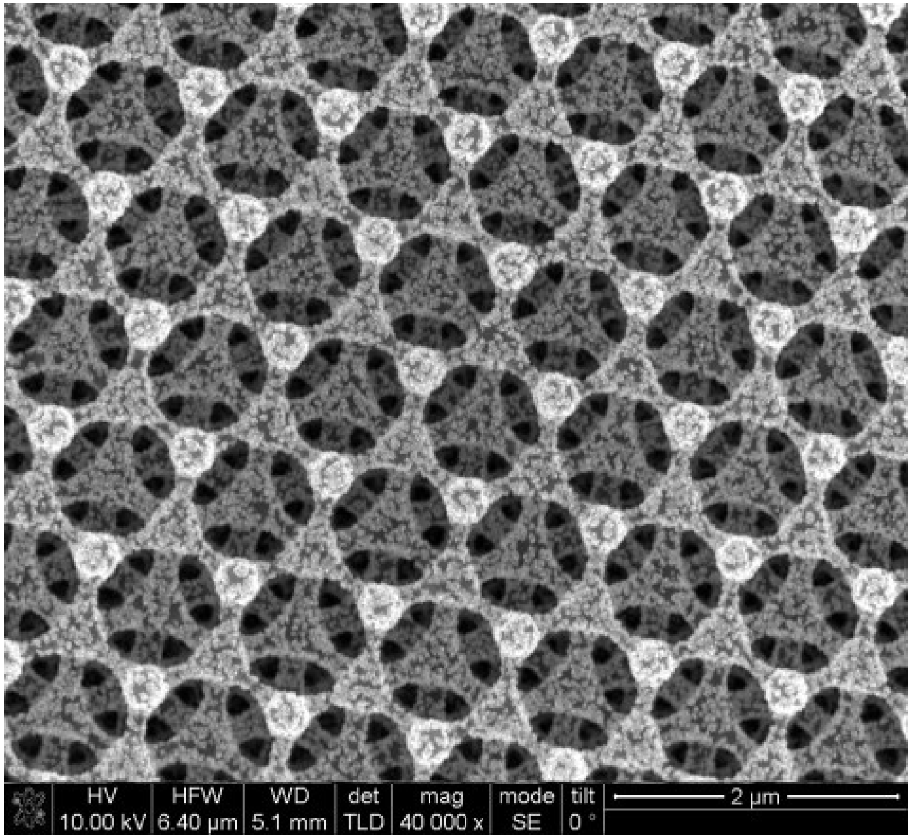
3D Pyrolyzed Carbon

SAND2015-7790C





D. Bruce Burckel, Sandia National Laboratories

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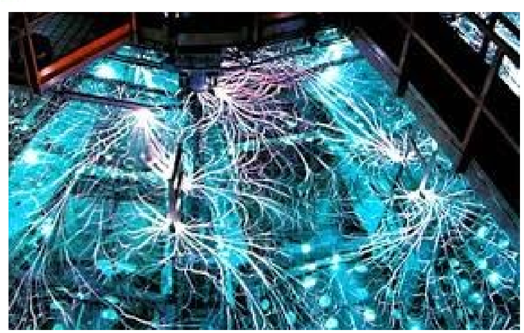

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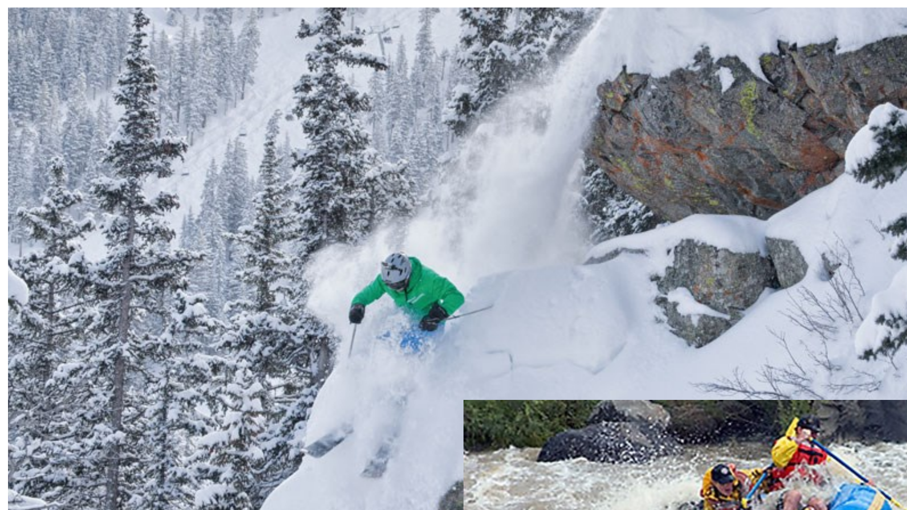
Postcards from Albuquerque



Outline

1. Formation of 3D Carbon Scaffolds

2. Physical Properties of 3D Carbon Scaffolds

3. Conversion to few-layer 3D Graphene

4. Application: Non Enzymatic Glucose Sensor

5. Application: SERS Substrate

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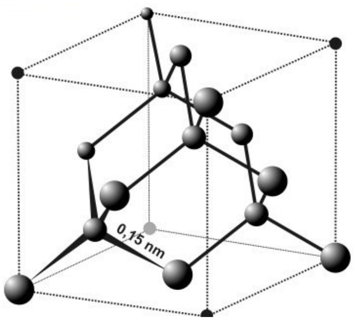
Faces of Carbon

C
6

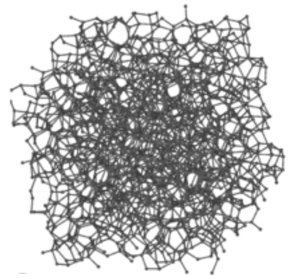
- Highest elemental melting point (sublimes at ~3900K)
- Forms ~ 10 million different compounds
- Resistant to acids, bases and all but the strongest oxidizers
- Biologically compatible

sp^3 bonds
Diamond



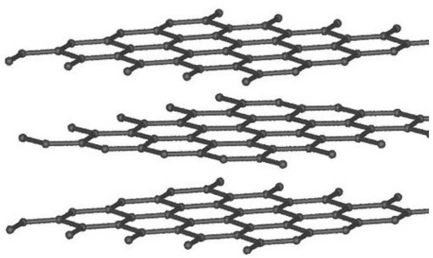
Hardest material
Good abrasive
Electrical insulator
Good thermal conductor
Optically transparent

Amorphous Carbon



High Modulus
Tunable DC Conductor
Optically Opaque

sp^2 bonds
Graphite



One of the softest materials
Good lubricant
Electrical Conductor
Can act as thermal insulation
Optically opaque

Images from Wikipedia

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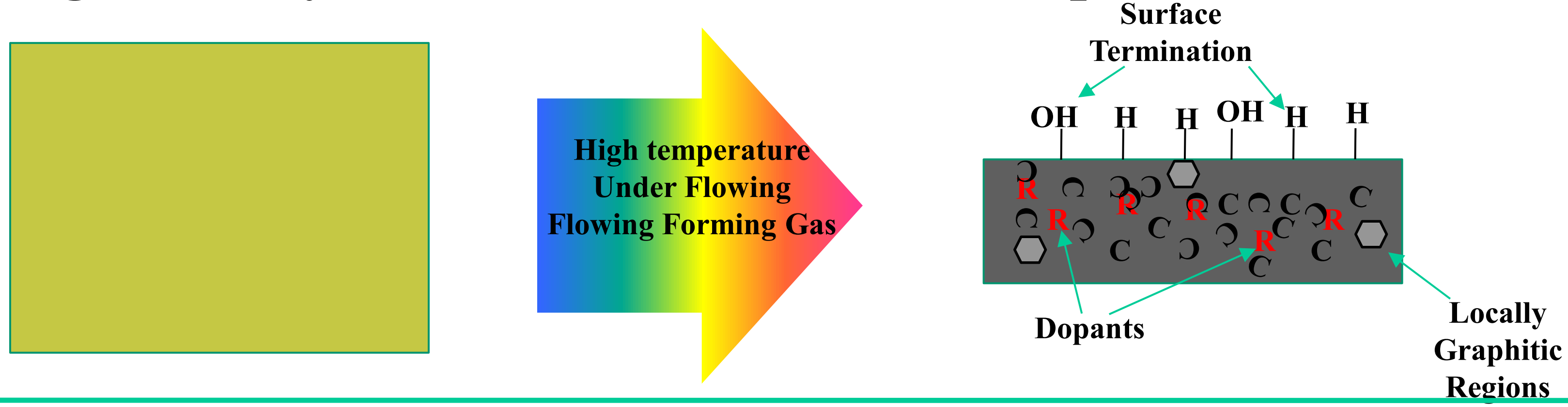
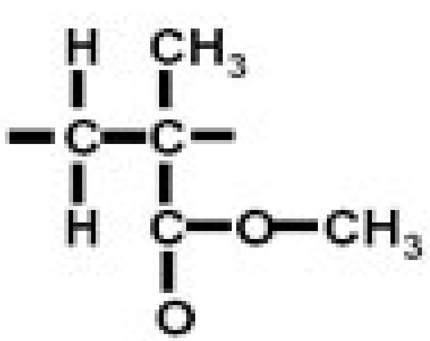
Synthesis Route to Amorphous Carbon: Pyrolysis of Organic Polymers

Organic Polymer → Pyrolysis → Amorphous Carbon

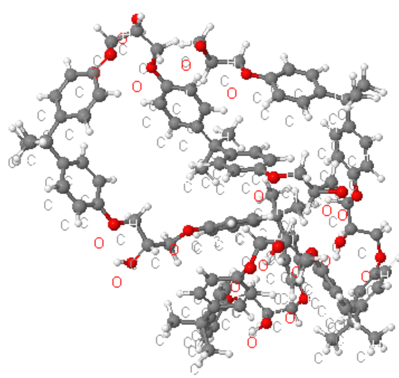


Typical Photopatternable Organic Polymers

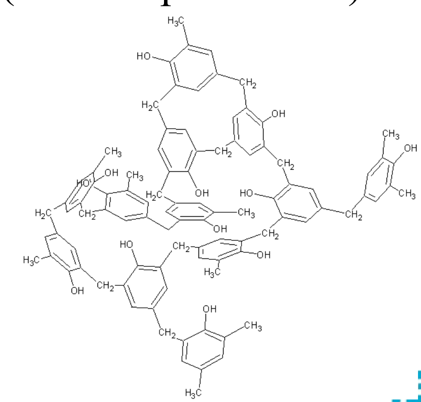
Polymethyl Methacrylate (PMMA)



Epoxide Resist (SU 8)



Phenol formaldehyde resin (novolac photoresist)

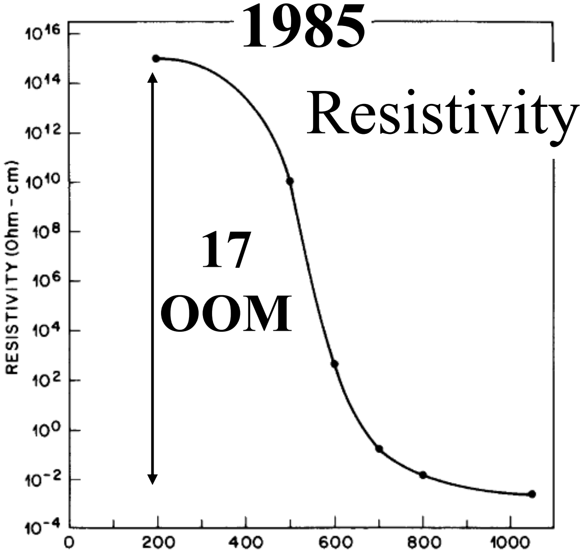


http://www.3dchem.com/moremolecules.asp?ID=326&othername=Epon

Wikipedia – Phenol fomaldehyde resin

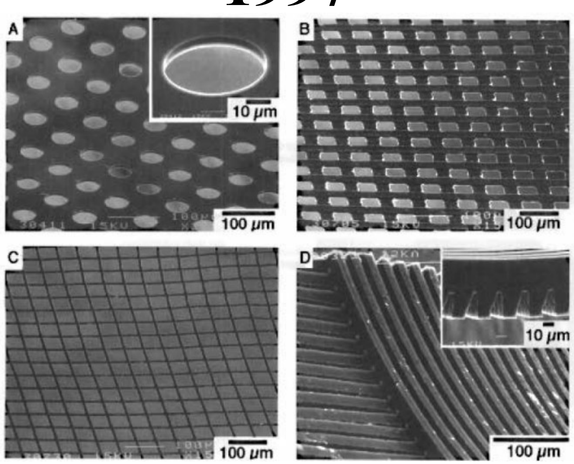
Visual History and Properties of Pyrolyzed Resist

1985



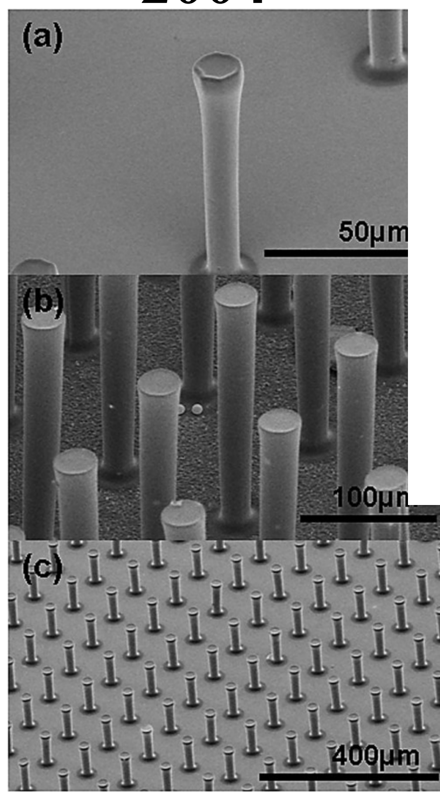
J. NonCryst Sol. **70**, 99-109 (1985)

1997

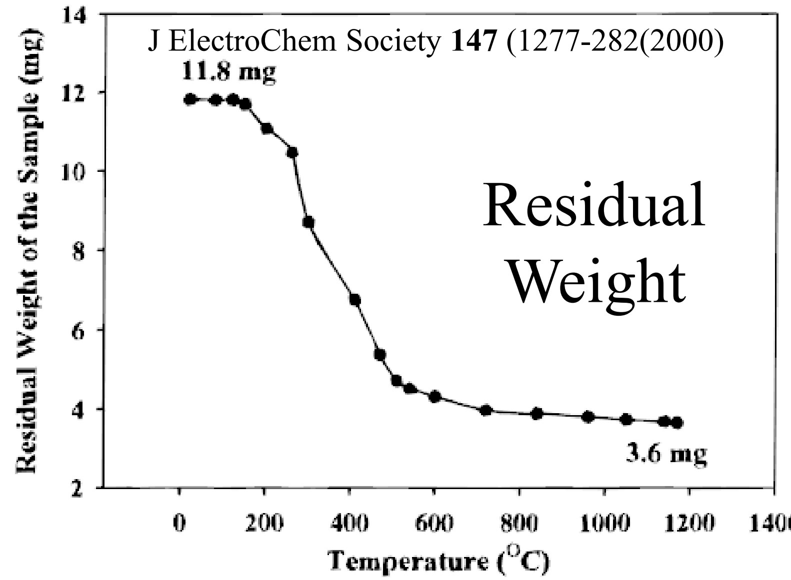


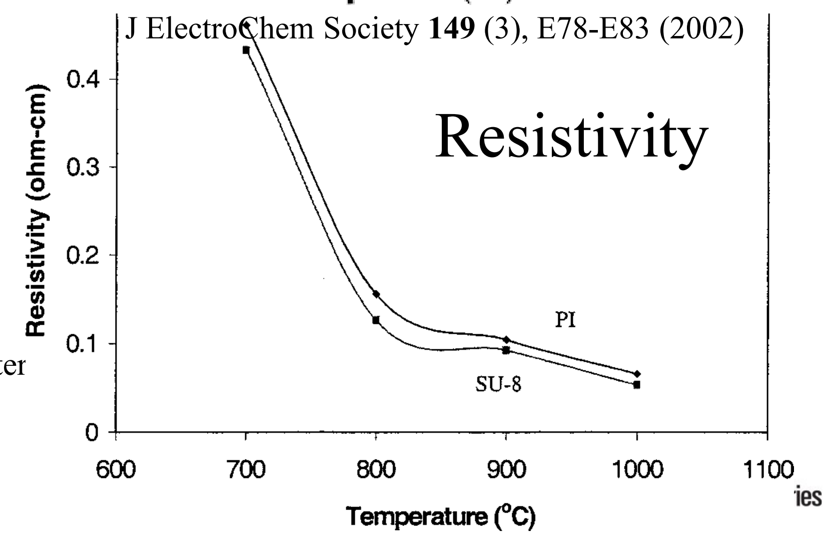
Adv. Mater. **9**, (6) 477-480 (1997)

2004



Electrochemical and Solid State Letter **7**, (11) A435-A438 (2004)





ies

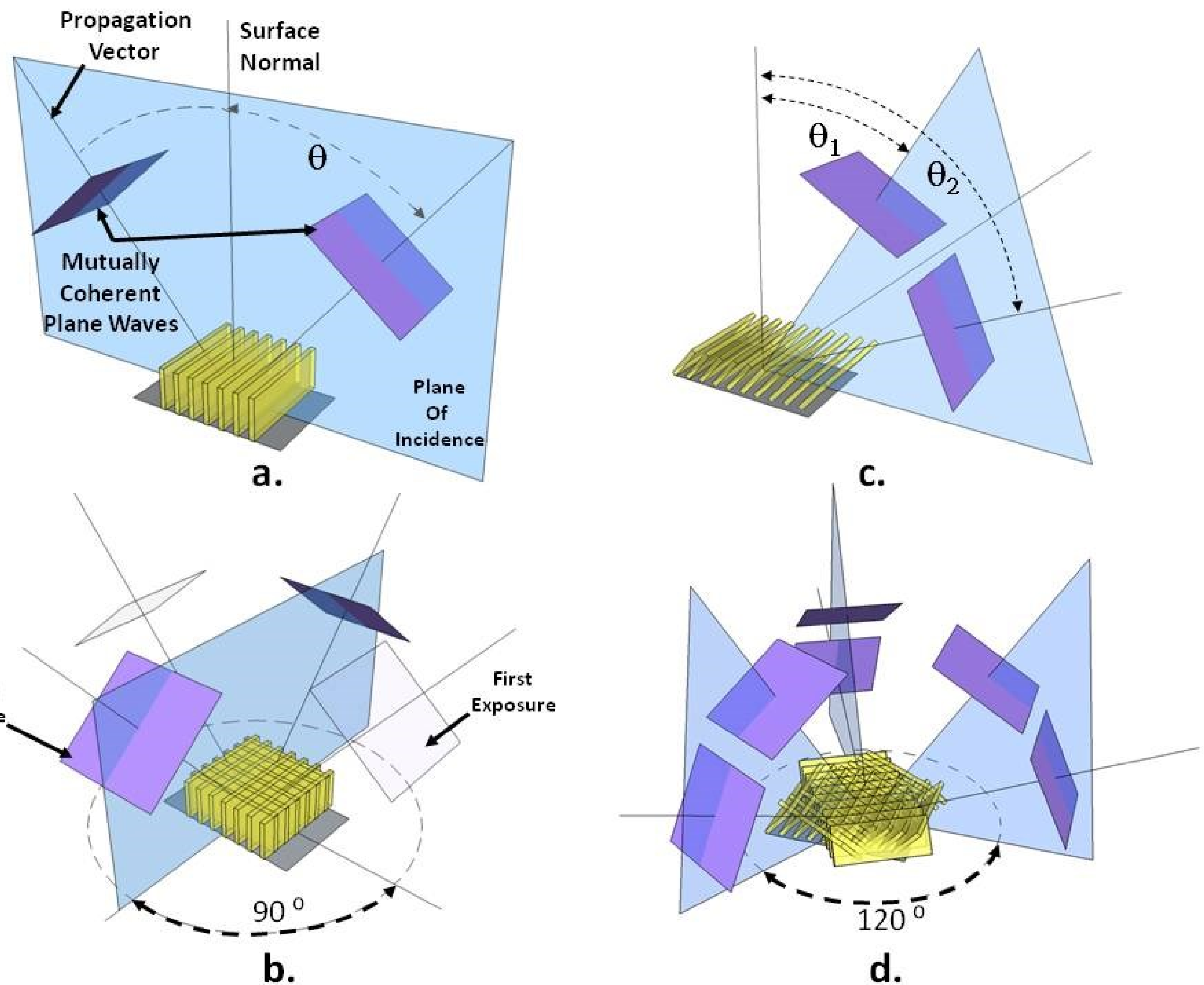
Interferometric Lithography

1-D Lines

Tilted 1-D Lines

2-D Crystal

3-D Crystal



Burckel et al, *JVST B*, **28**, C6P14 (2010).

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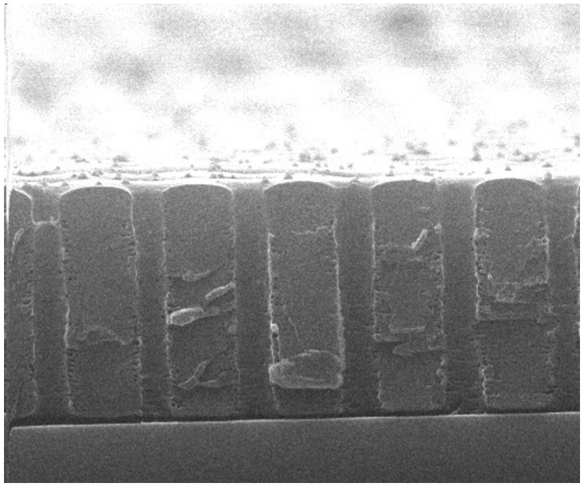
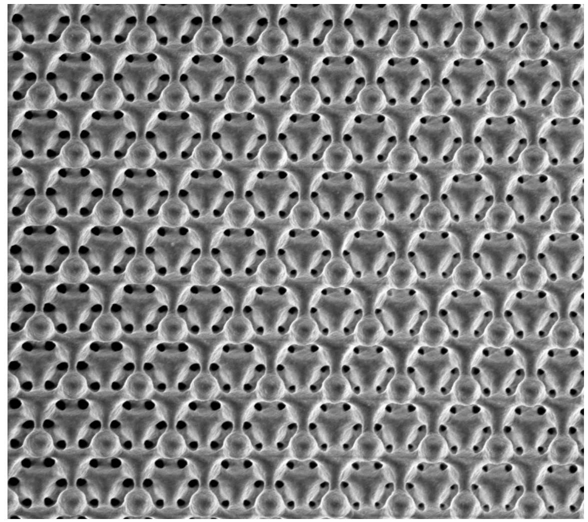
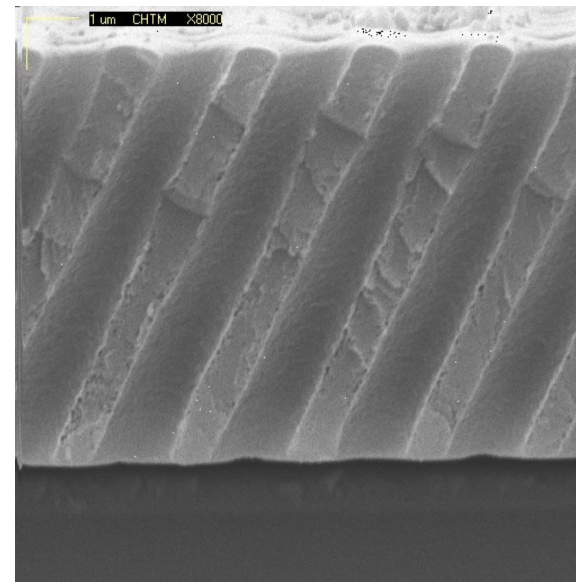
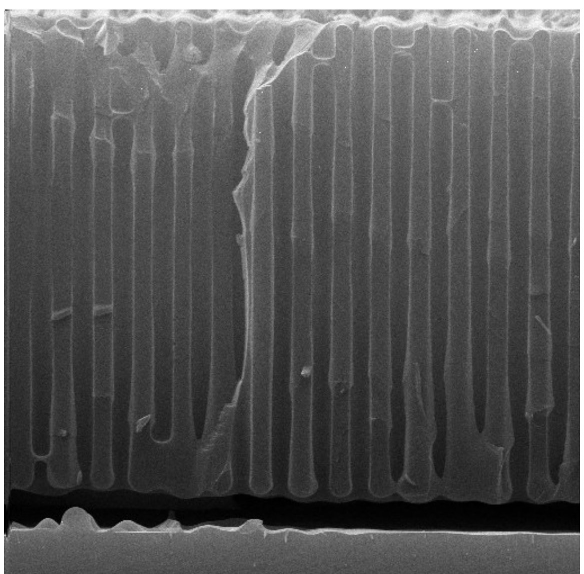
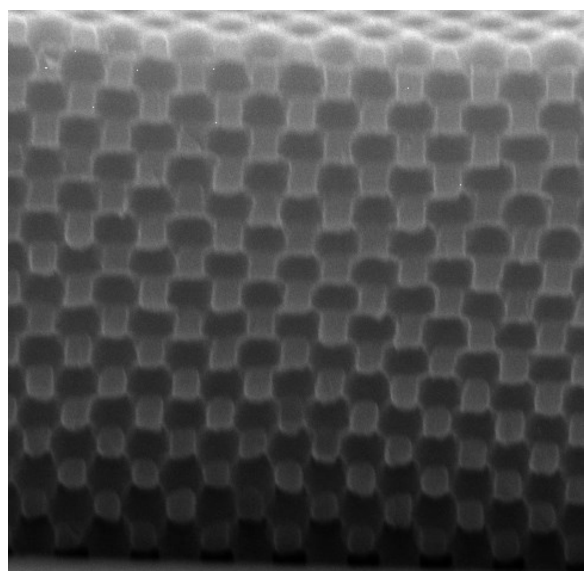
Sub-Micron 3D Resist Patterns Via Interferometric Lithography











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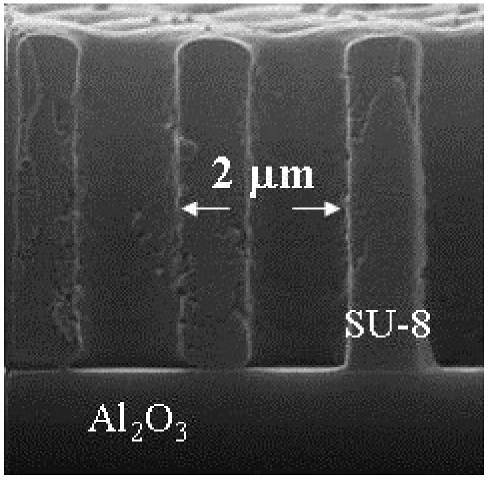
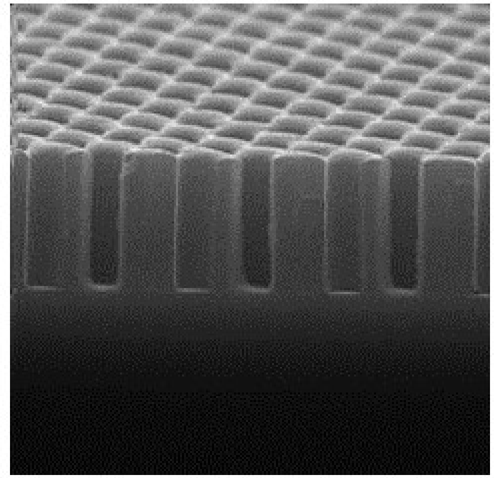
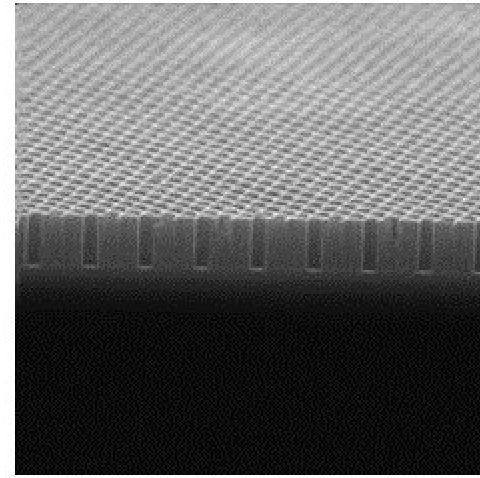
Conversion of 2-D Resist Structure to 2-D Carbon Structure

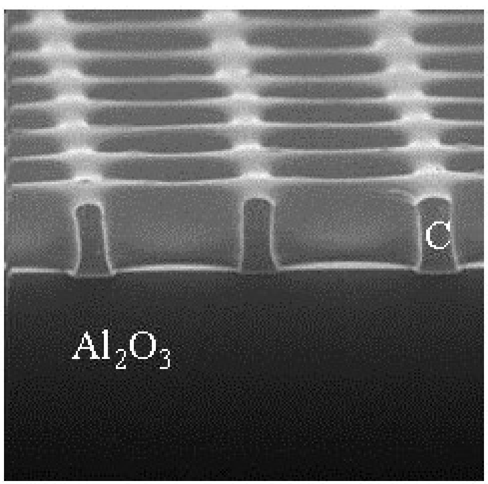
Resist

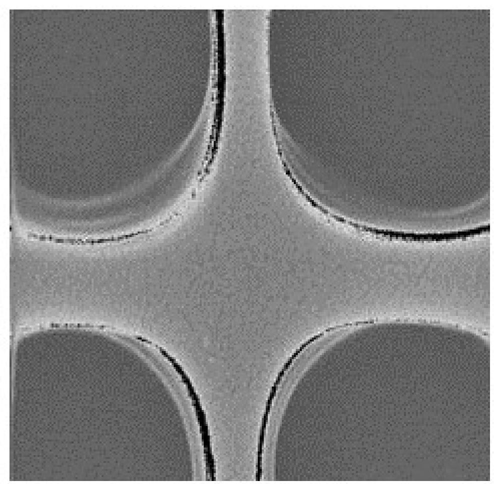


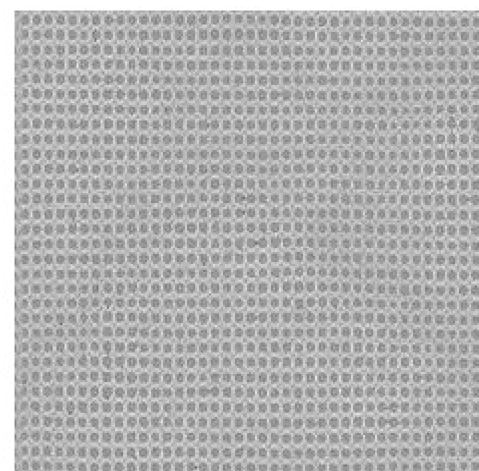




Carbon

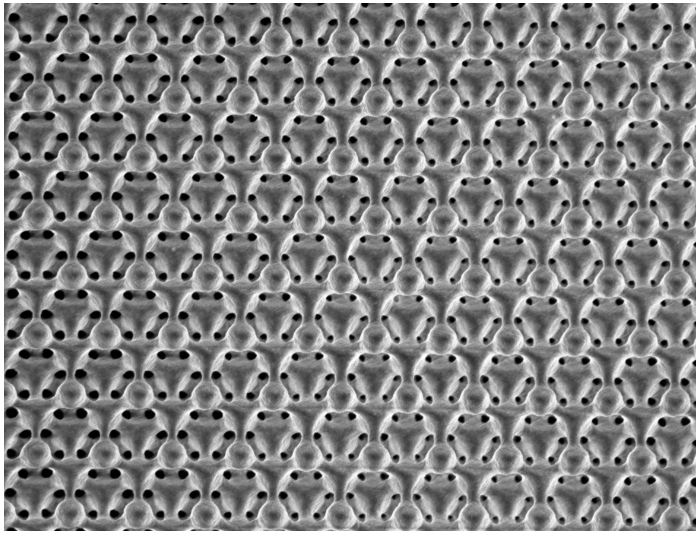


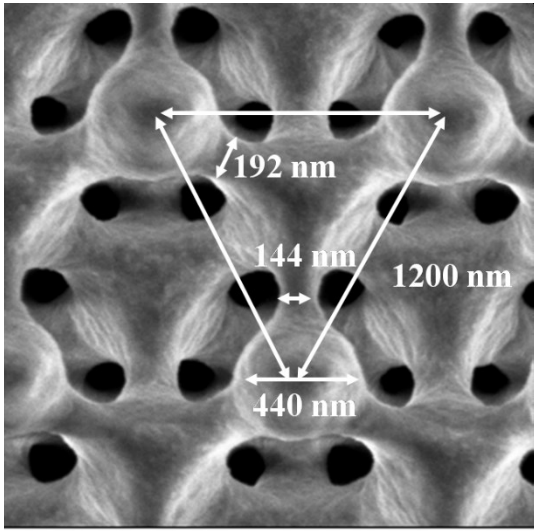




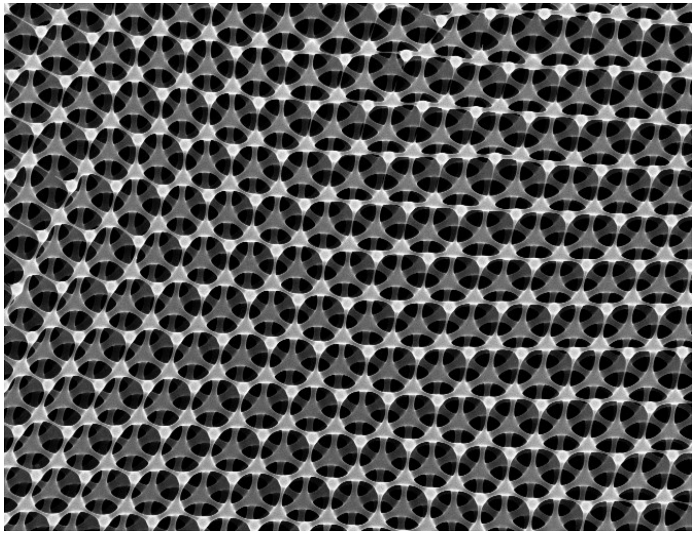
Conversion of 3-D Resist Structure to 3-D Carbon Structure

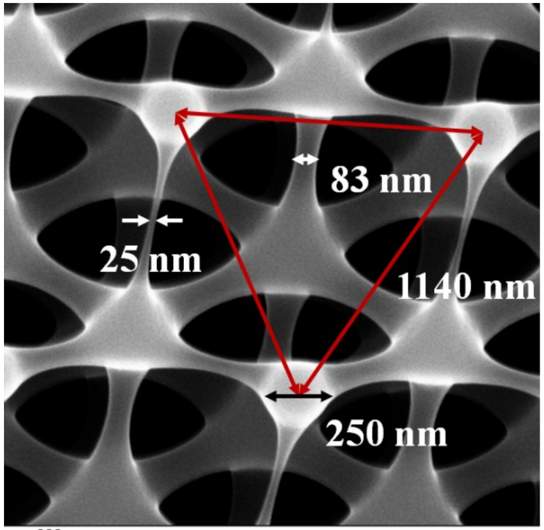
Resist





Carbon





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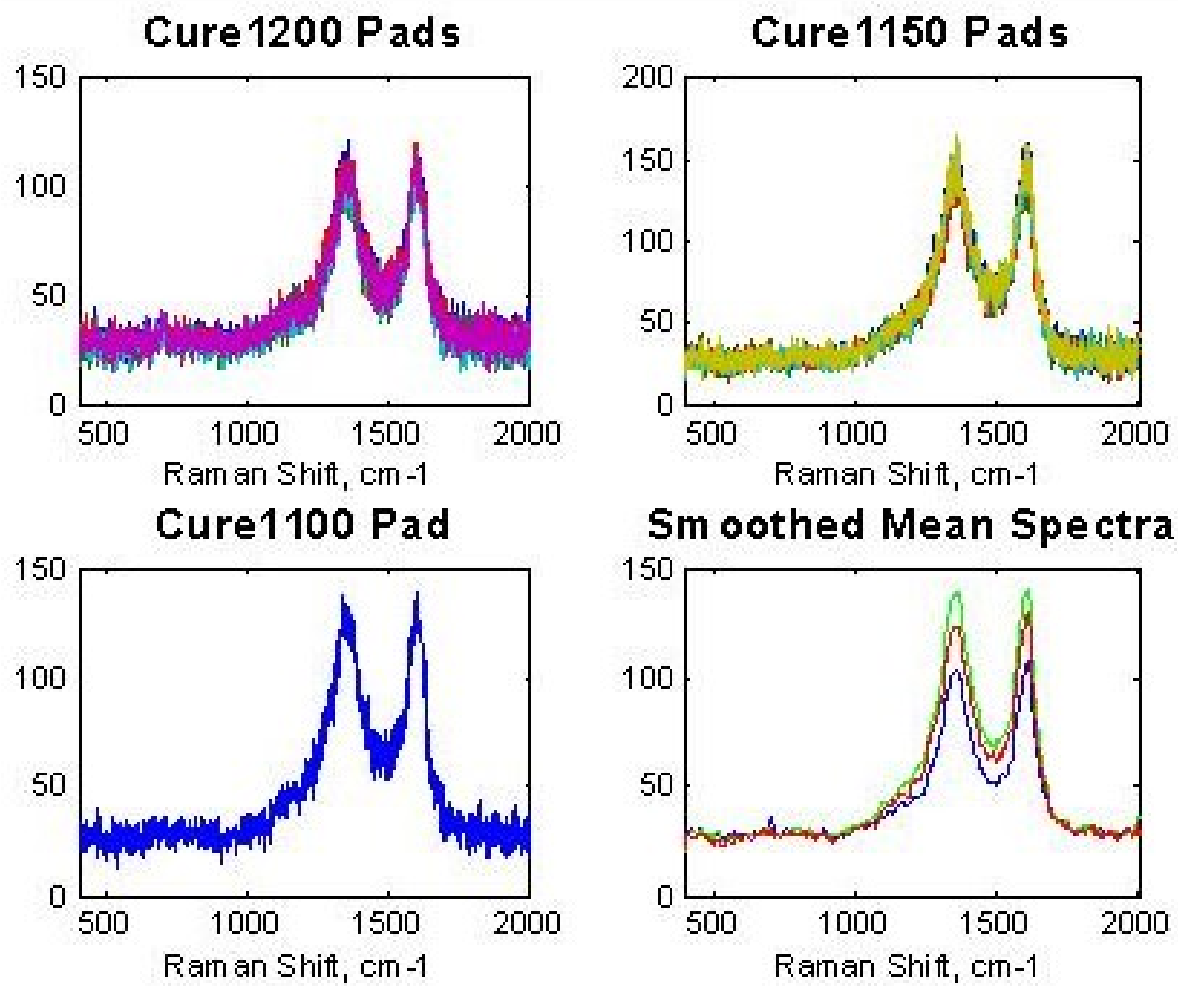
Properties of 3-D Carbon Scaffolds

Raman Spectroscopy of Pyrolyzed Resist

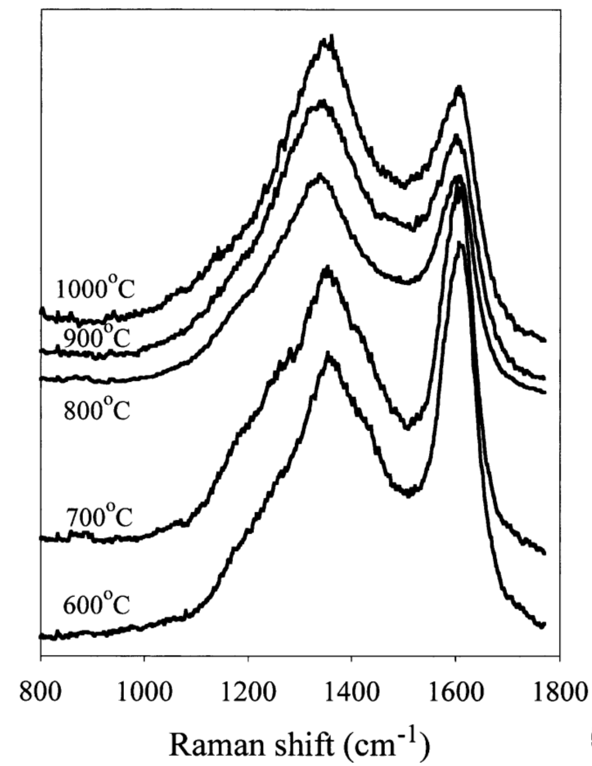


Comparison To Literature Values

J. Non Cryst Solids 396 (2001) 36-43

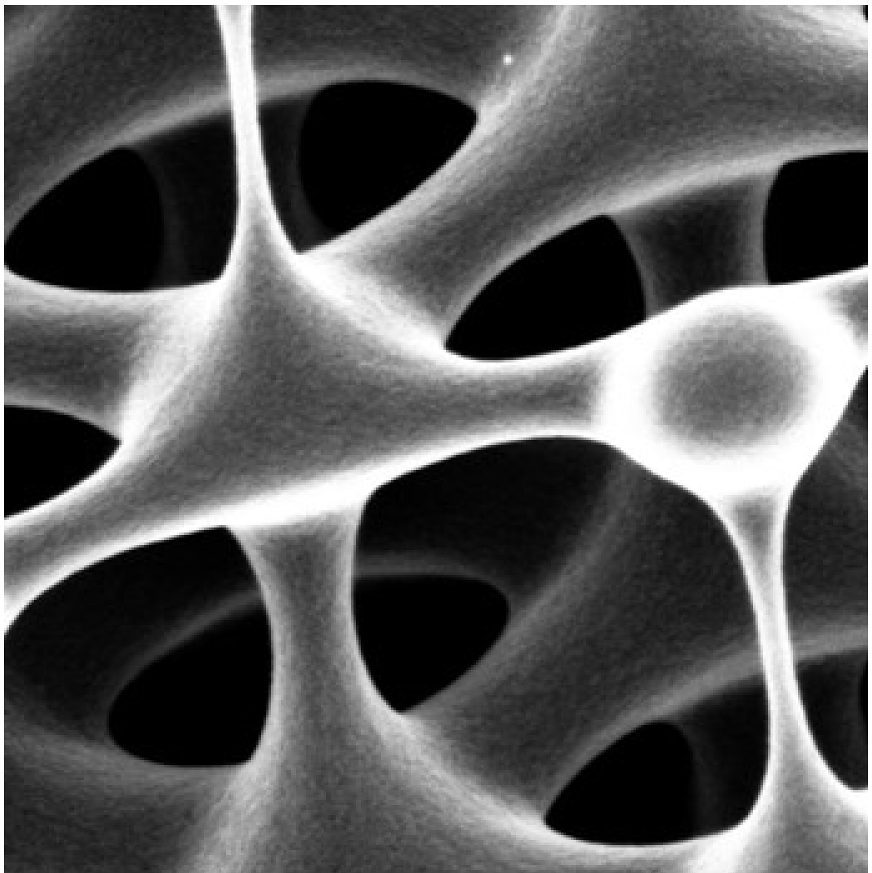
1344 cm^{-1} 1591 cm^{-1} ← **HOPG**

1367 cm^{-1} 1622 cm^{-1} ←**Disordered C**

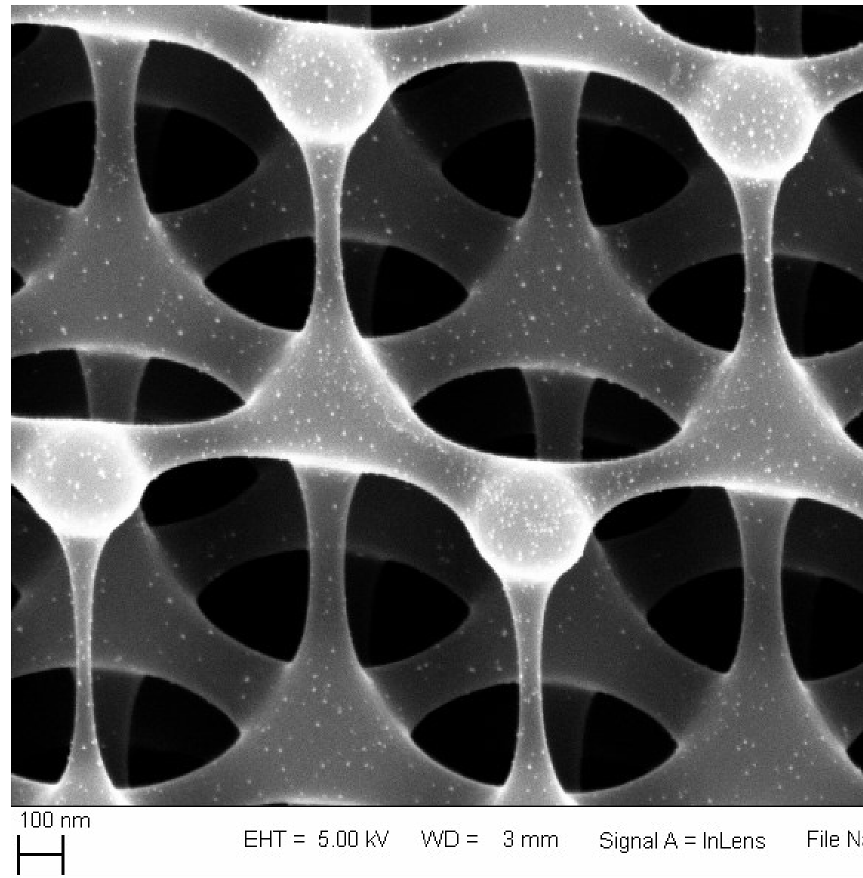


Nearly Atomically Smooth Surface

Smoothness of bare carbon –
no preferential nucleation sites



Ultra small, uniform NP formation



Burckel et al, *Small*, **5**, pp2792-2796 (2009).

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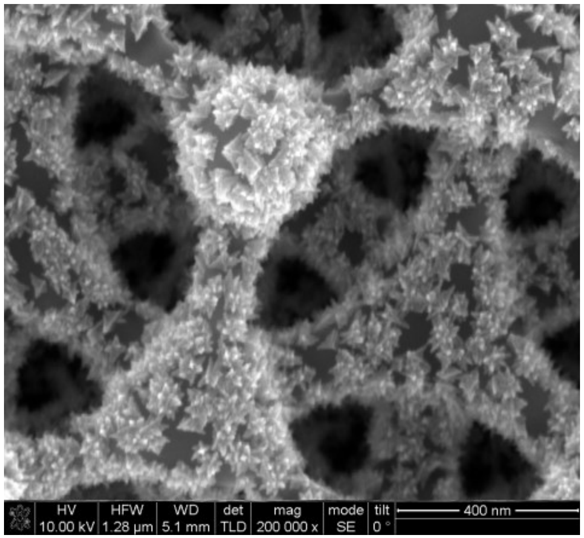
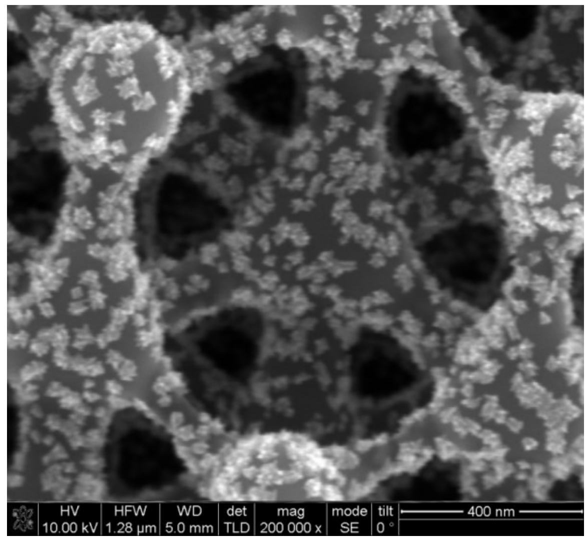
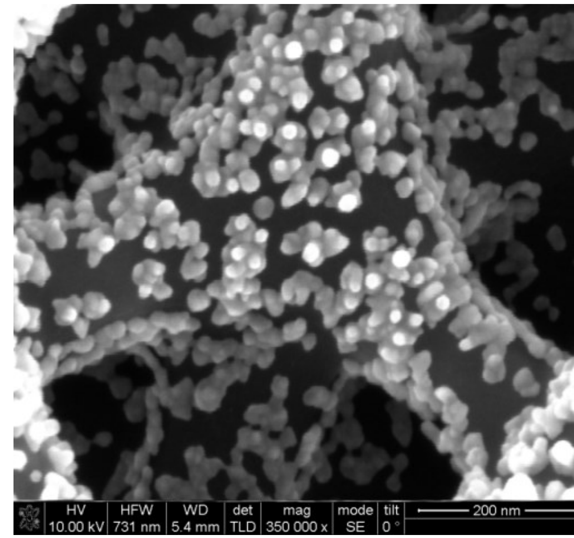
Electrodeposition Conditions Impact Nanoparticle Morphology







100 s Deposition | 50 s Deposition | 100 s Deposition

-0.65 V | -0.45 V

Pd Nanocrystals

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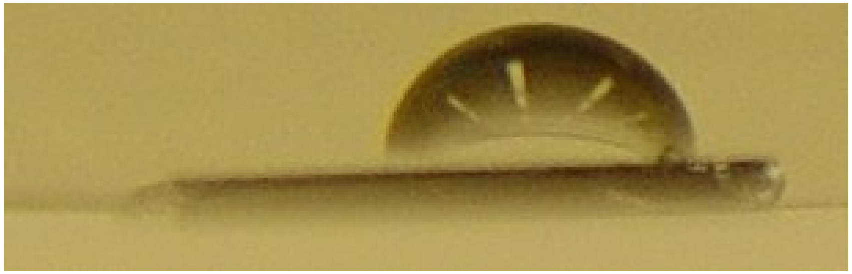
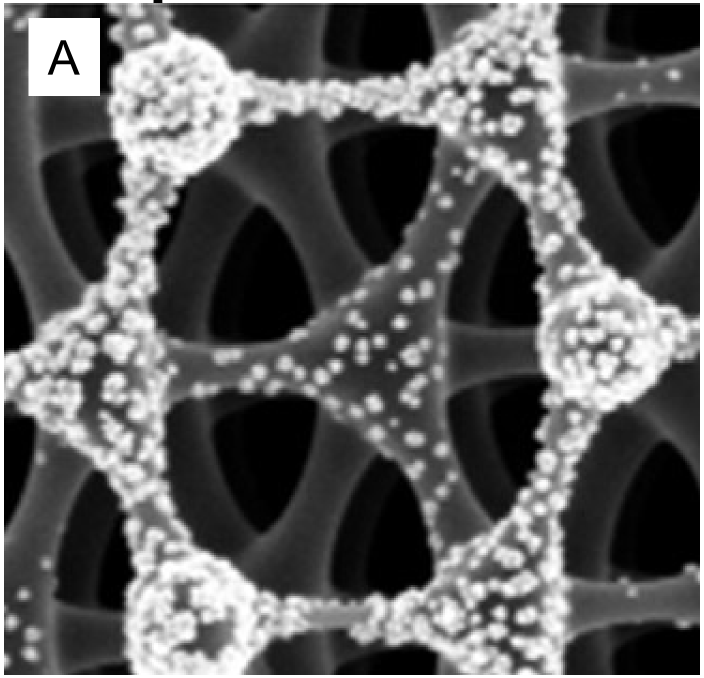
Impact of Carbon Hydrophobicity

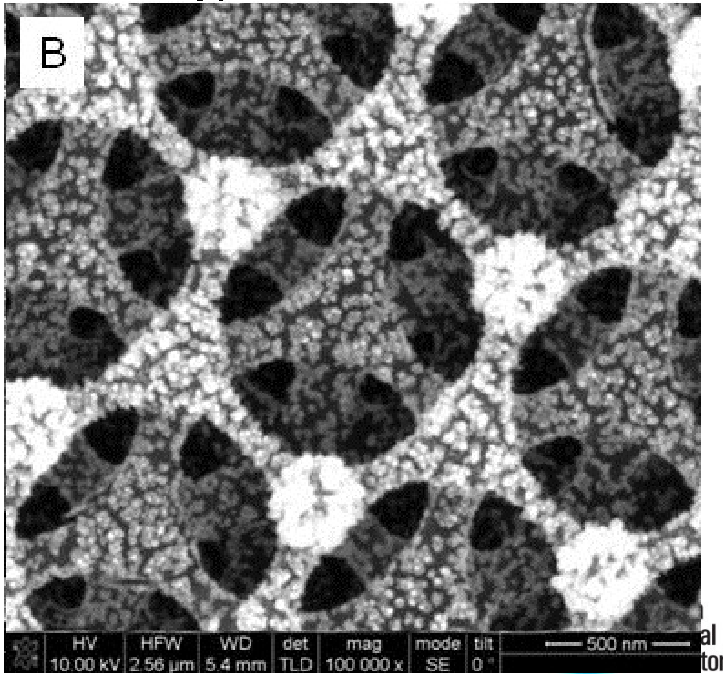
3D carbon
is hydrophobic



Deposition from Aqueous Solution



Deposition from Organic Solvent



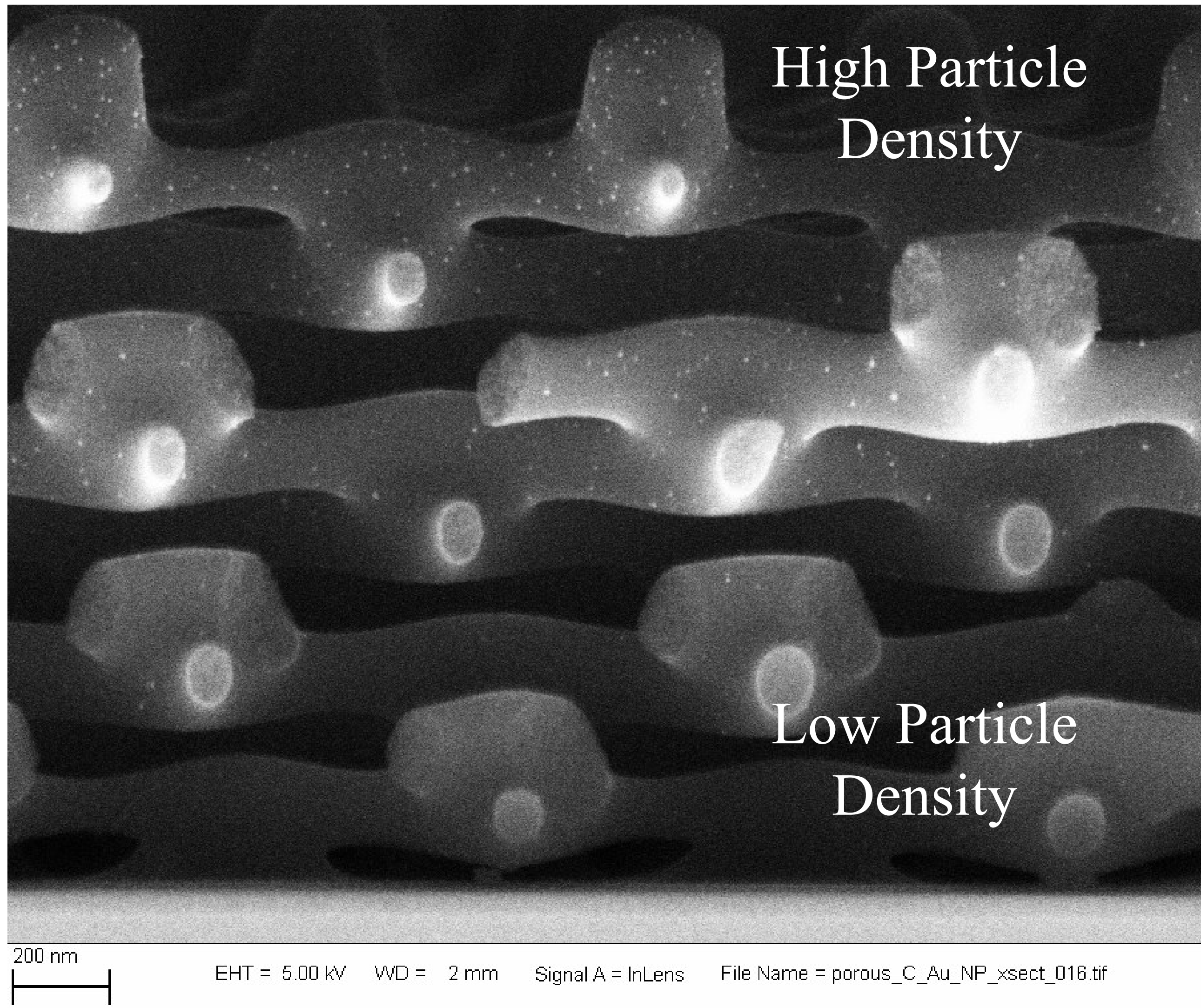
al
tories

Vertical vs. Horizontal Shrinkage

Significant vertical shrinkage

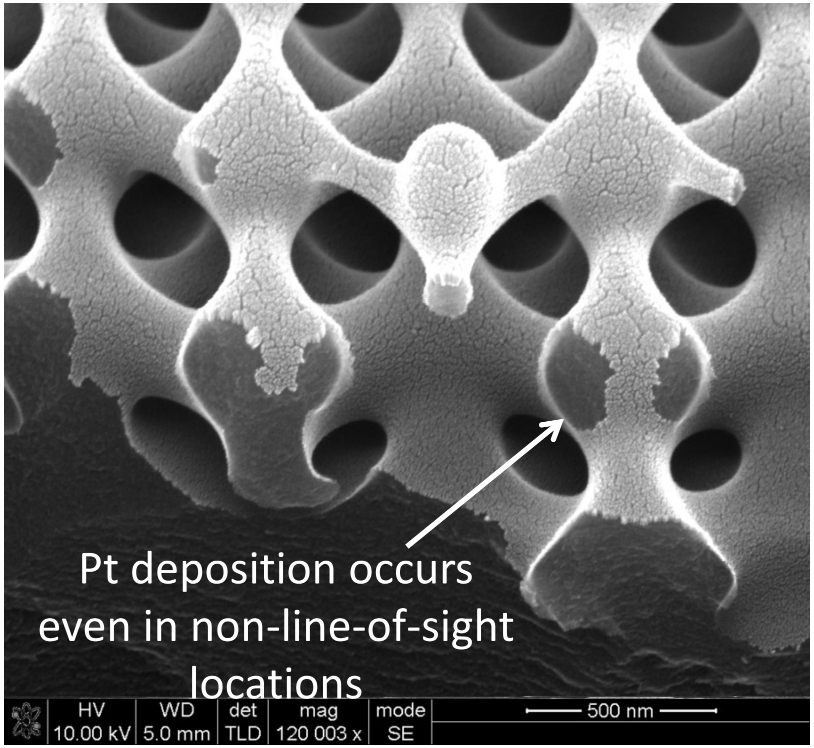
Extremely small, highly uniform NPs

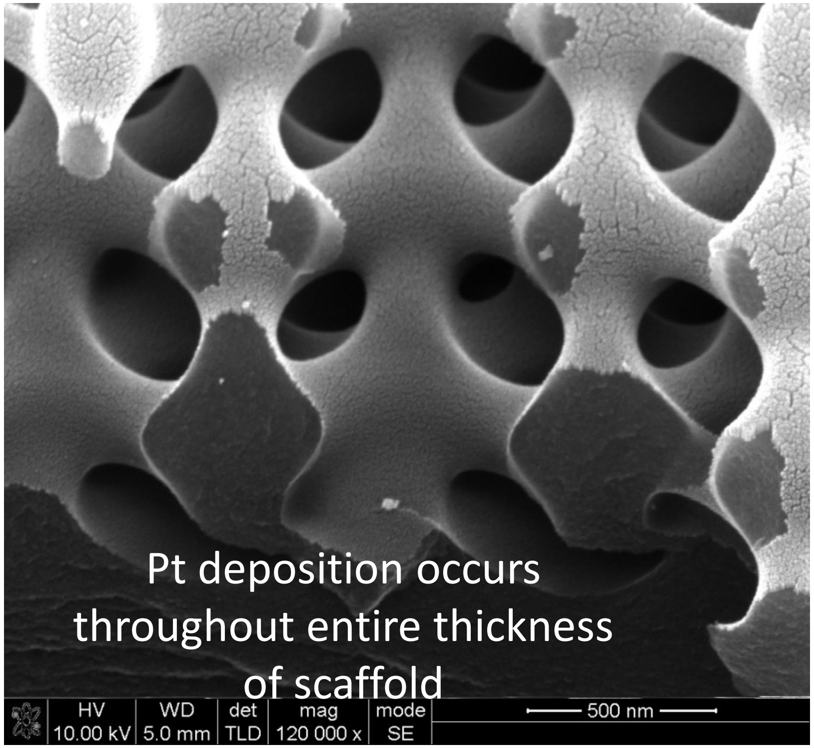
Inhomogeneous wetting



Burckel et al, *Small*, **5**, pp2792-2796 (2009).

Modification of Carbon Scaffold: PVD





Pt sputtered @ 1A/s

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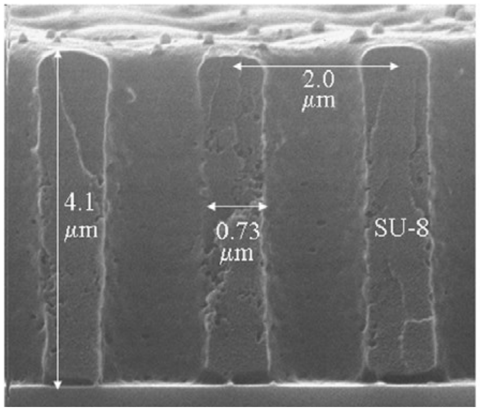
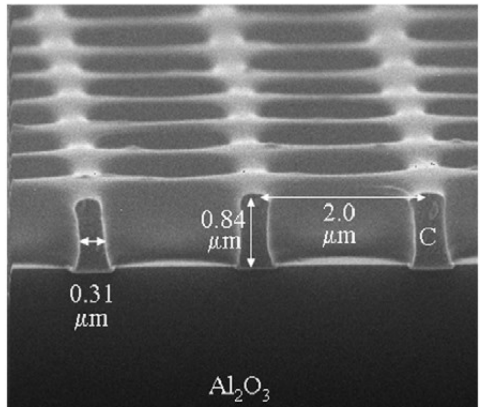
Pyrolyzed Carbon GaN Growth Masks
(High Temperature Stability)

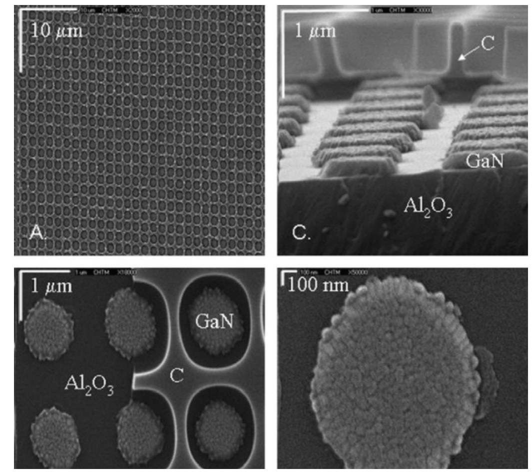
Resist



Carbon



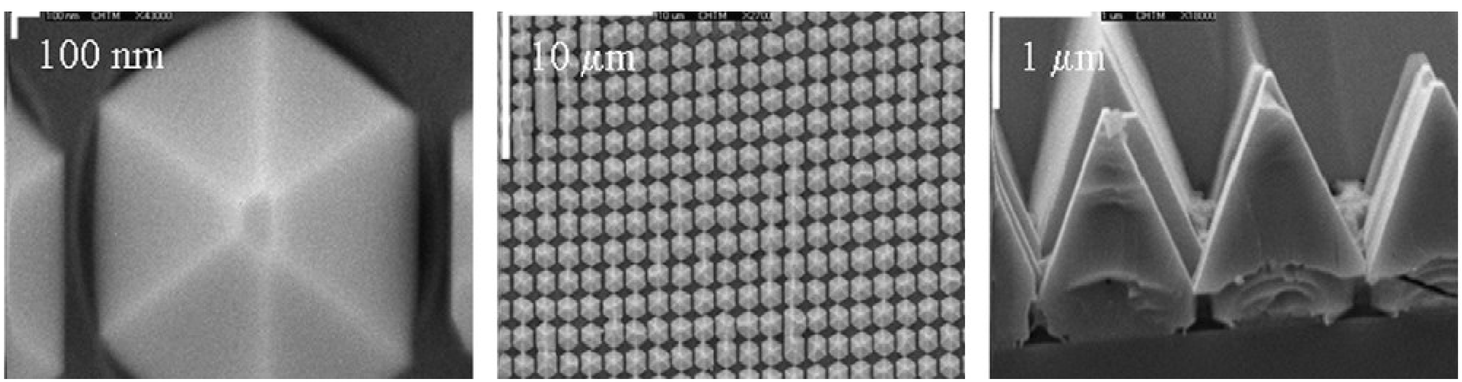
Nucleation Layer



530 °C

Crystalline GaN

(1050 °C, TMGa, NH_3)



Aligned Facets = Registration To Substrate

Burckel, et. al. "Lithographically defined carbon growth templates for ELOG of GaN," Journal of Crystal Growth, 310, 3113-3116 (2008).

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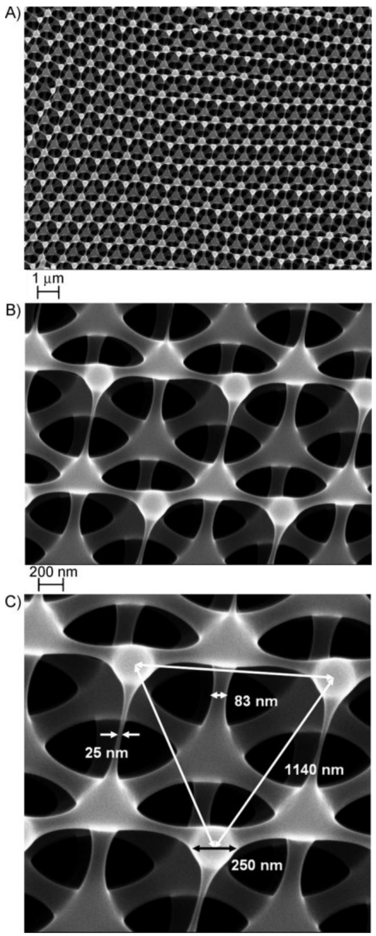
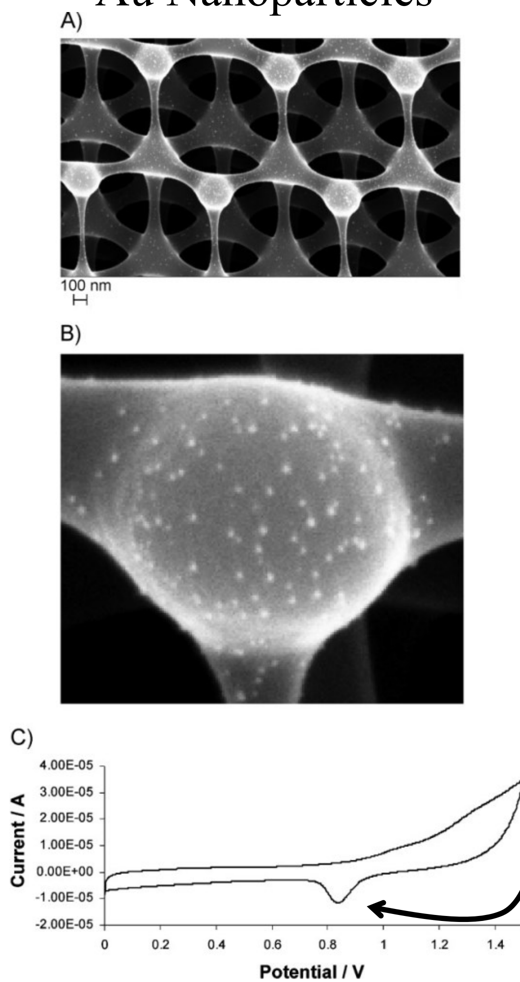
3D Carbon Electrodes

Bare Carbon Scaffold

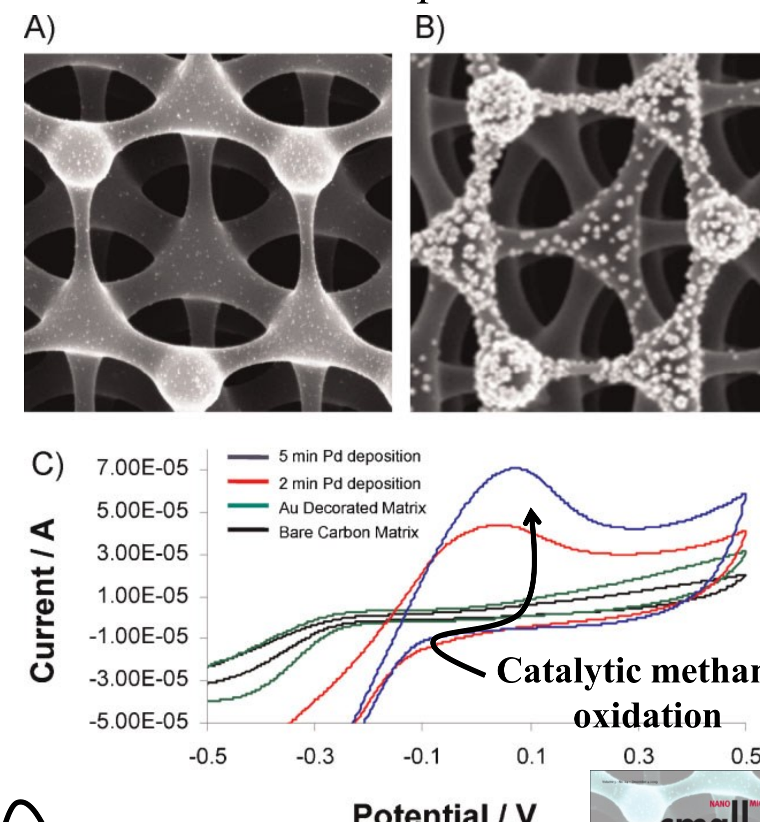


Electrodeposited Au Nanoparticles



Surface oxide reduction

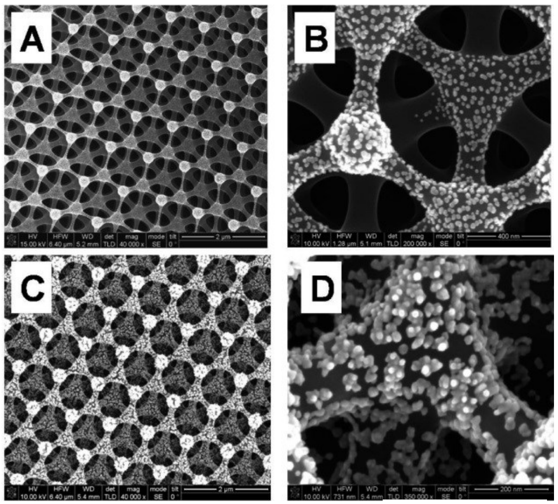
Electrolessly-Deposited Pd nanoparticles

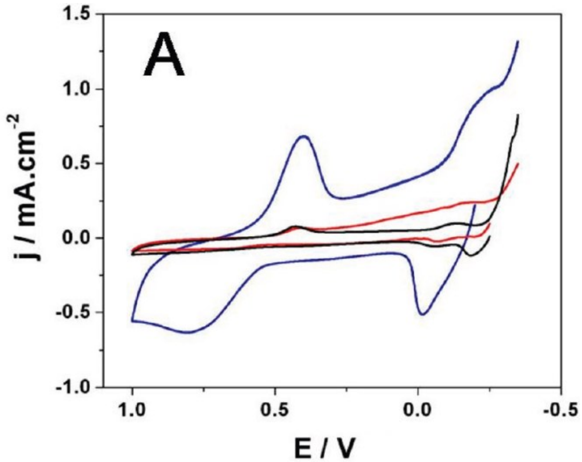


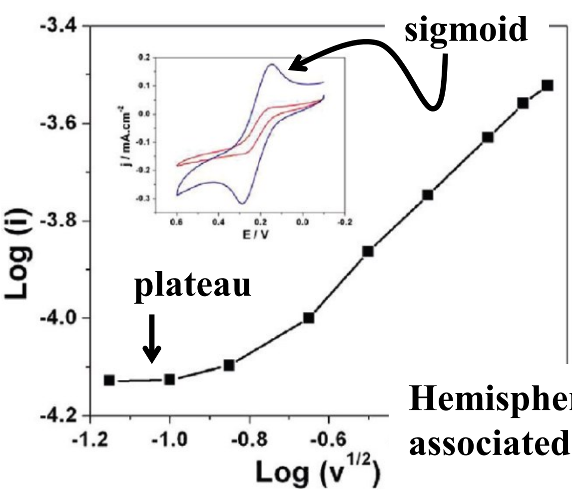
Catalytic methanol oxidation

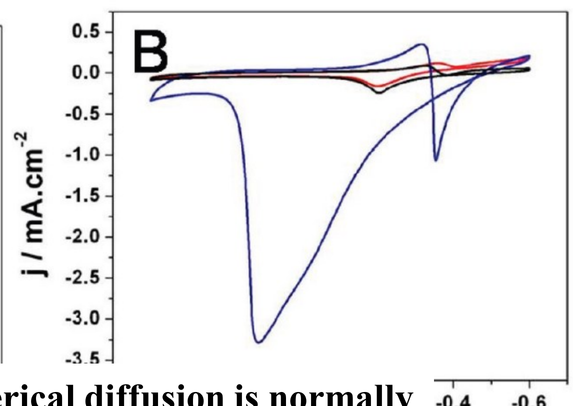
Burckel, et. al. "Lithographically defined porous carbon electrodes," Small, 5, 2792-2796 (2009).

Enhanced Mass Transport
(Fluidic Impact of μm Pores)



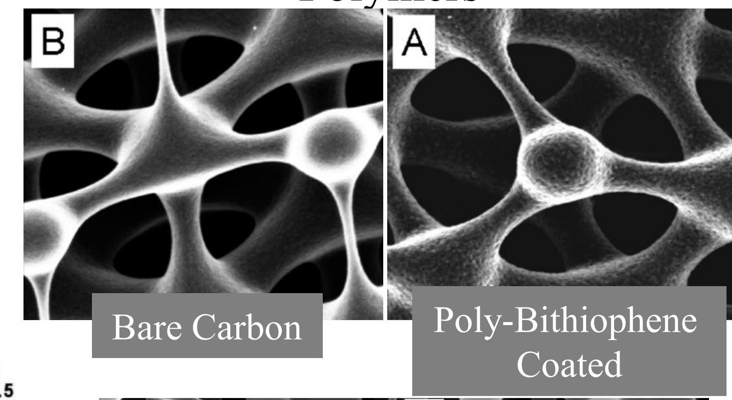


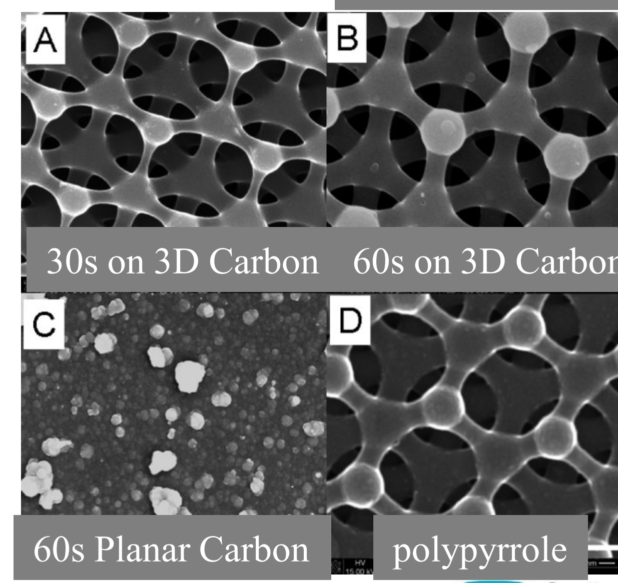




Hemispherical diffusion is normally associated with microelectrodes.

Electrodeposited Conducting Polymers





Xiao, et. al. "Increased mass transport at lithographically defined 3D porous carbon electrodes," ACS Applied Materials and Interfaces, **2**, 3179-3184 (2010).

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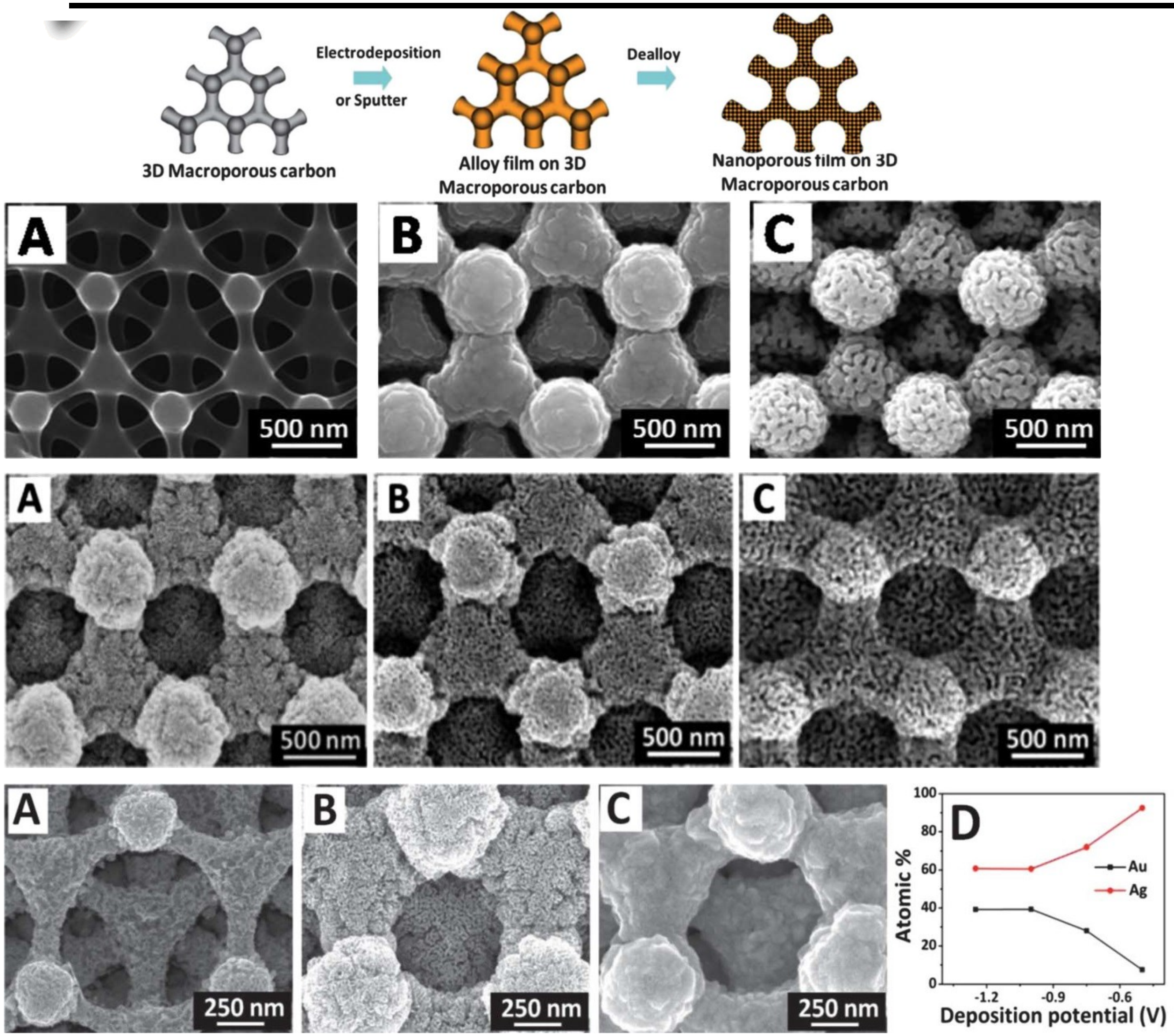
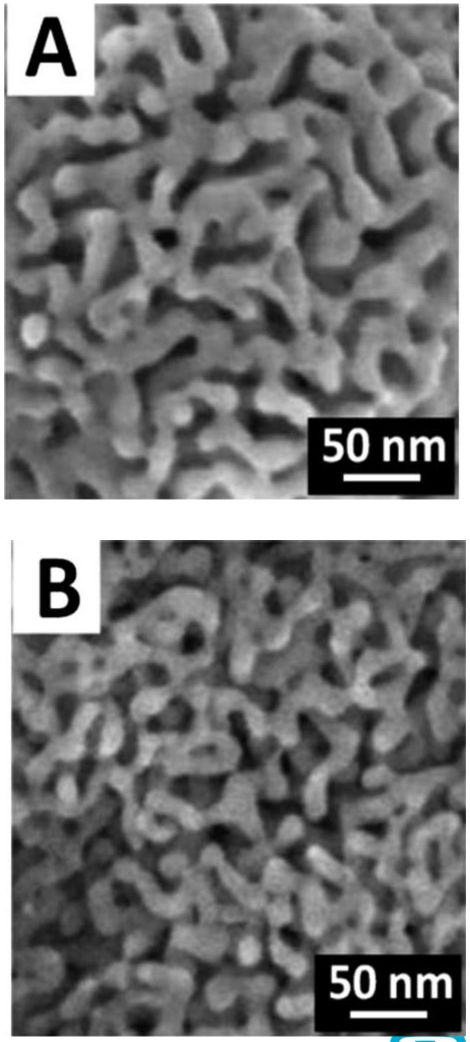
Hierarchical Nano-Microporous Au-C





Sattayasamitsathit, et. al. “Highly ordered tailored 3D hierarchical nano-microporous Au-C architectures,” J. of Mat Chem, **22**, 11950 (2012).

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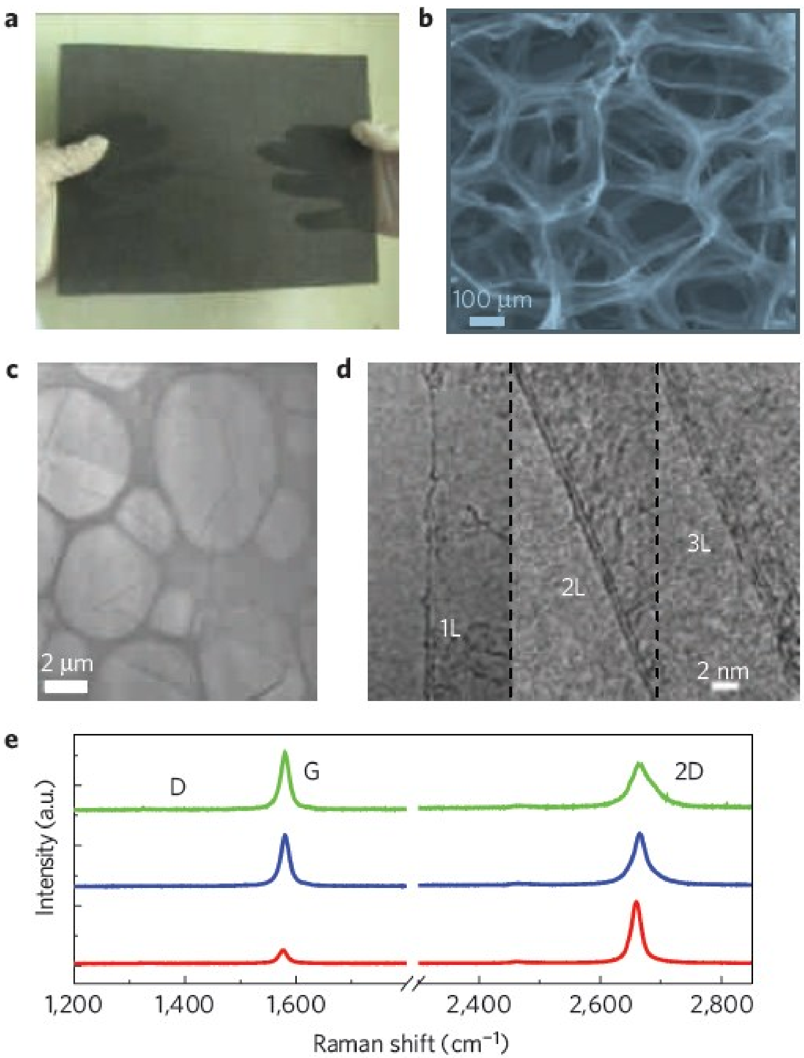
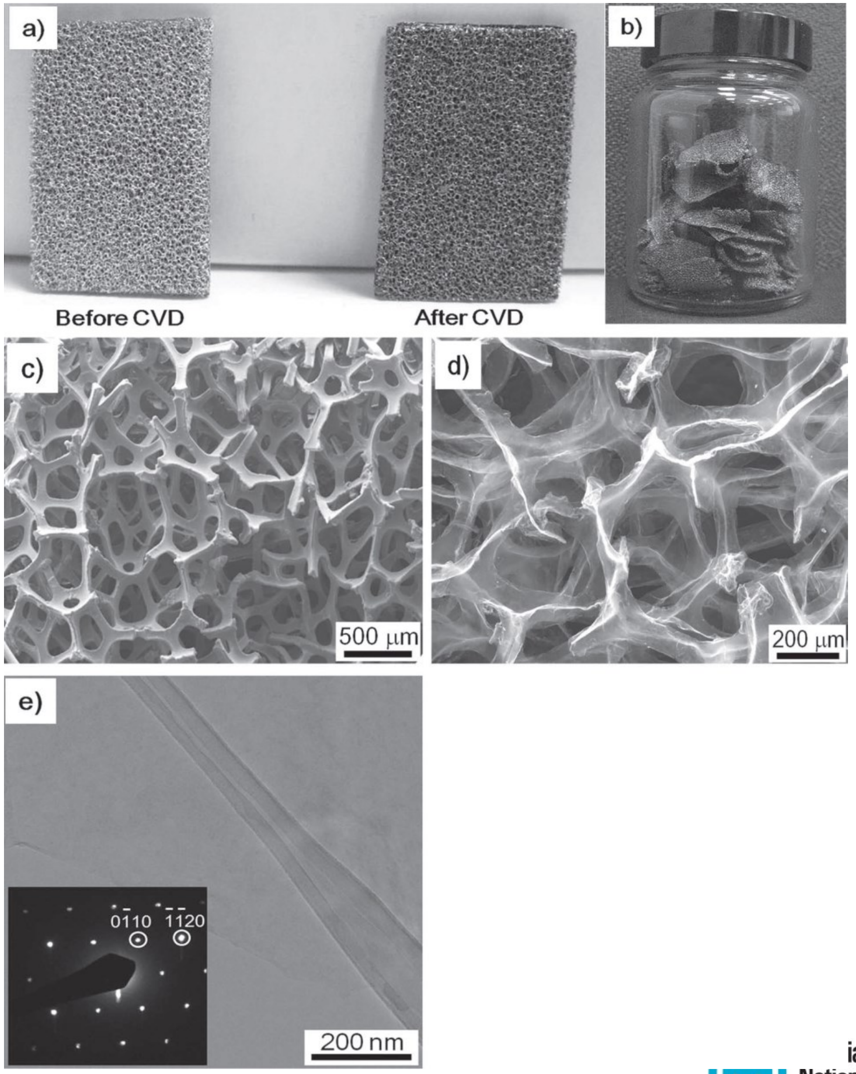
3-D Few-Layer Graphene

Xiao et al, ACS Nano, **6**, pp. 3573-3579 (2012).

3D Graphene From Nickel Foam



Chen et al. Nature Materials, **10**, pp 424-428 (2011)



Cao et al. Small, **7**, pp 3163-3168 (2011)

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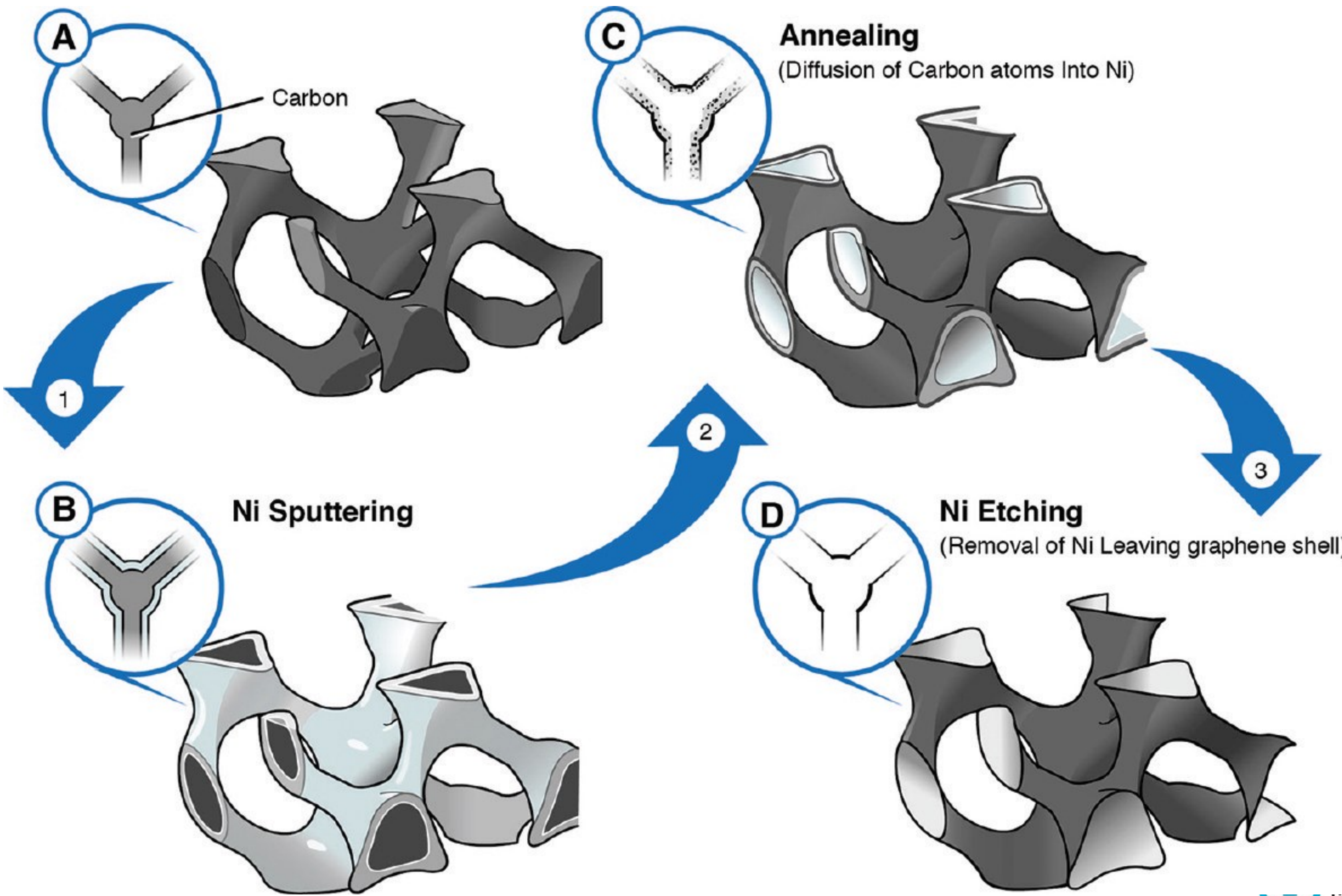
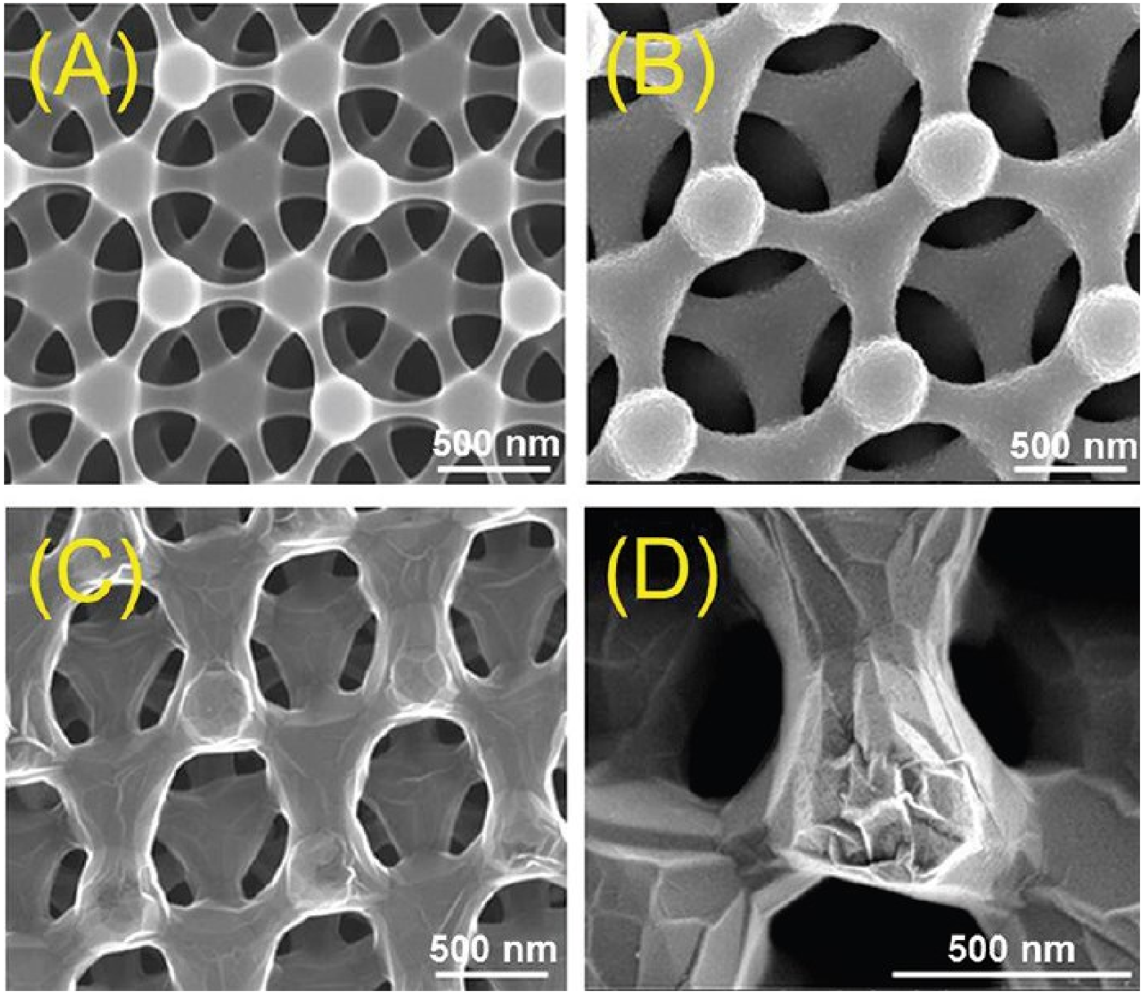
Chemical Conversion to Graphene



SEM Images of Conversion Steps

Amorphous Carbon

Conformal Sputtered Nickel



Acidic Washing Of Nickel

High Mag Image 3D Graphene

Xiao et al, ACS Nano, **6**, pp. 3573-3579 (2012).

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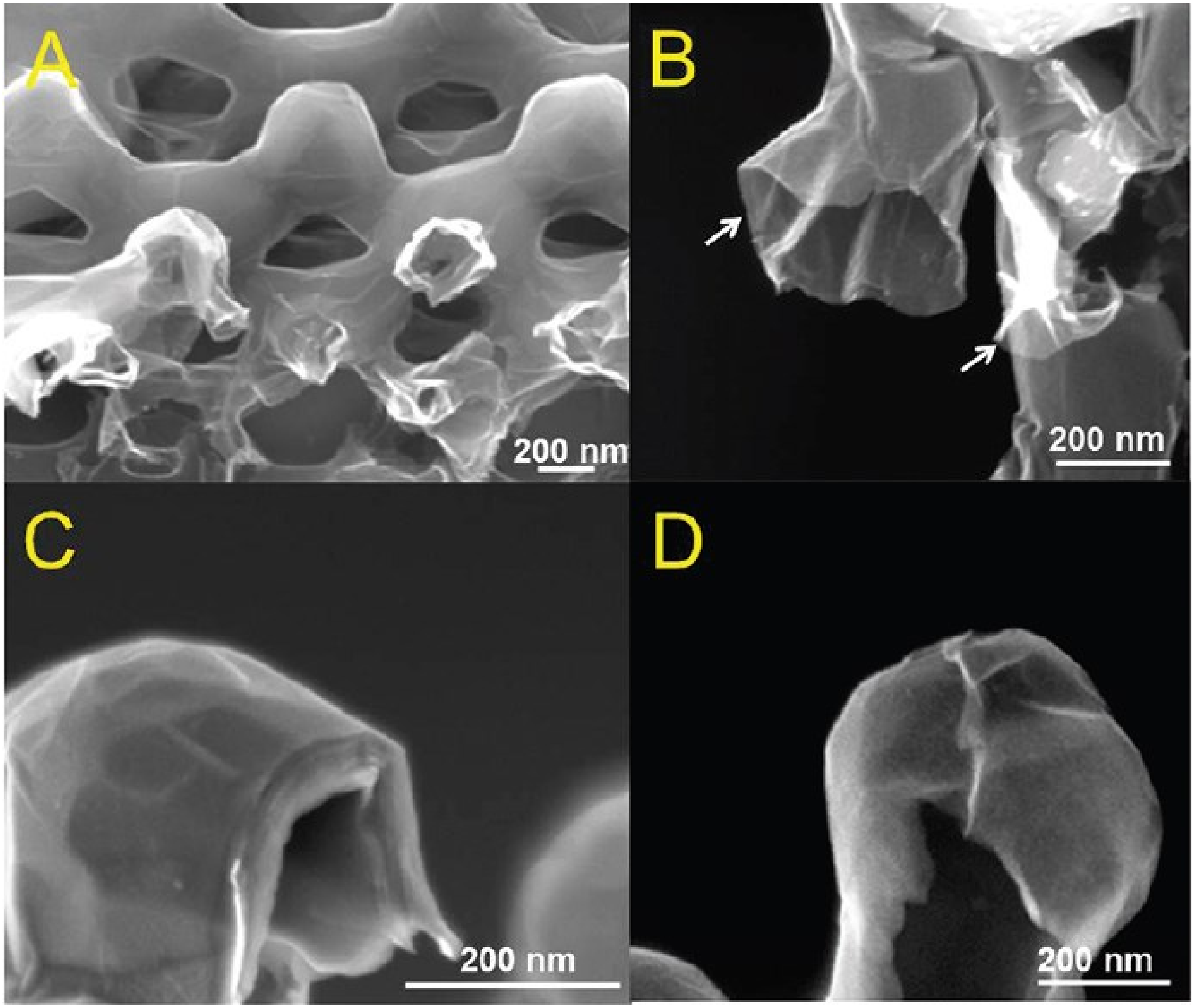
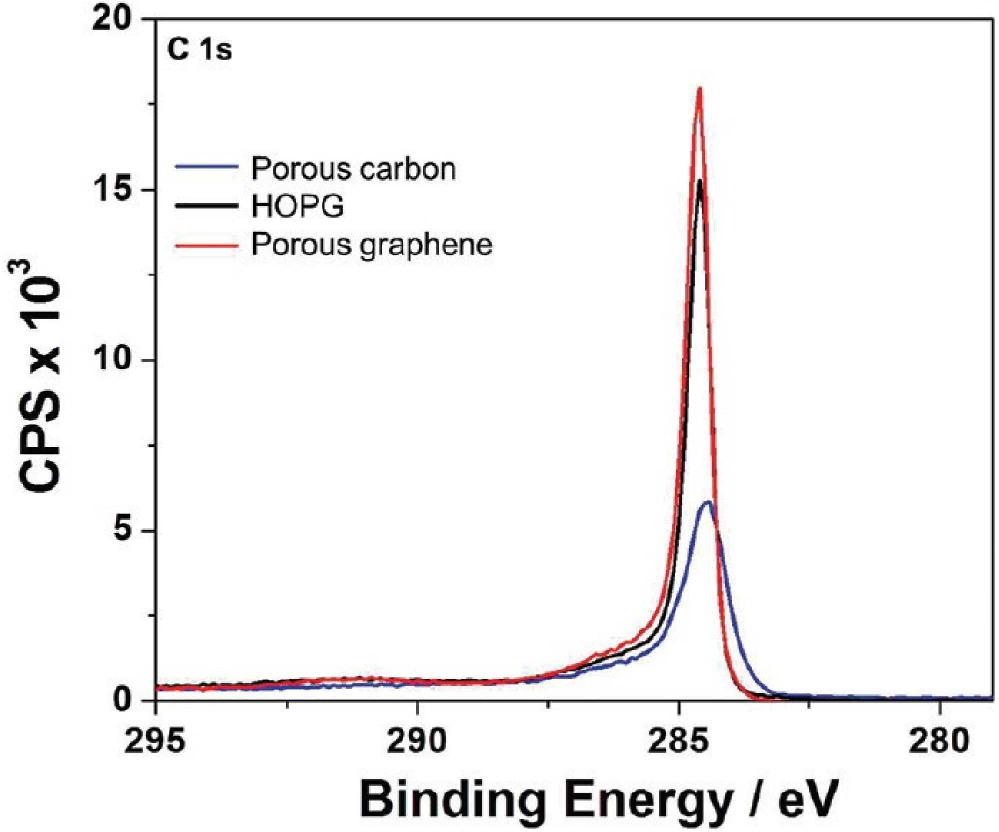
SEM Images of 3D Graphene



Confirmation 3D Graphene: XPS



X-ray photoelectron spectroscopy – surface measurement technique

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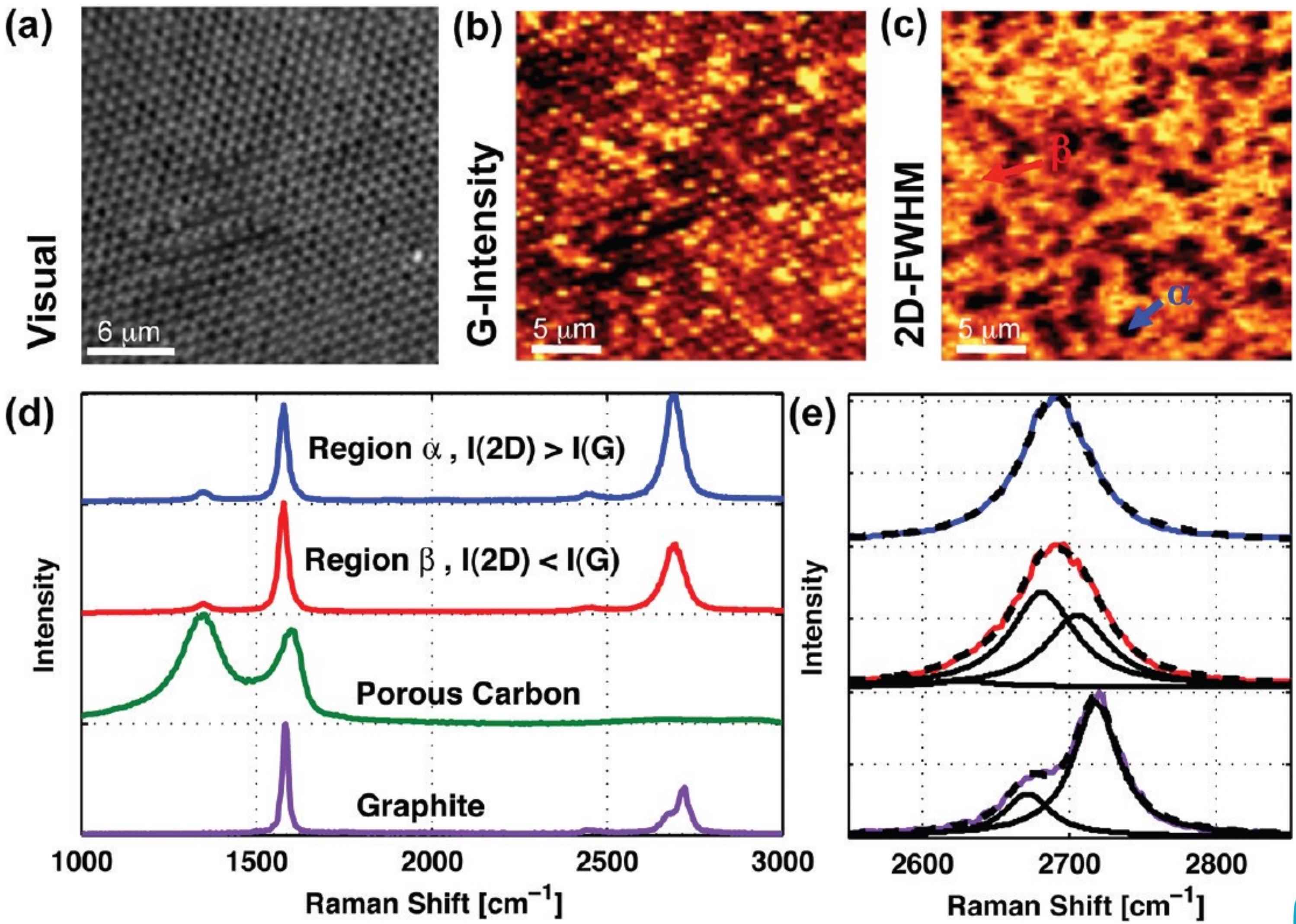
3D Graphene: Micro-Raman



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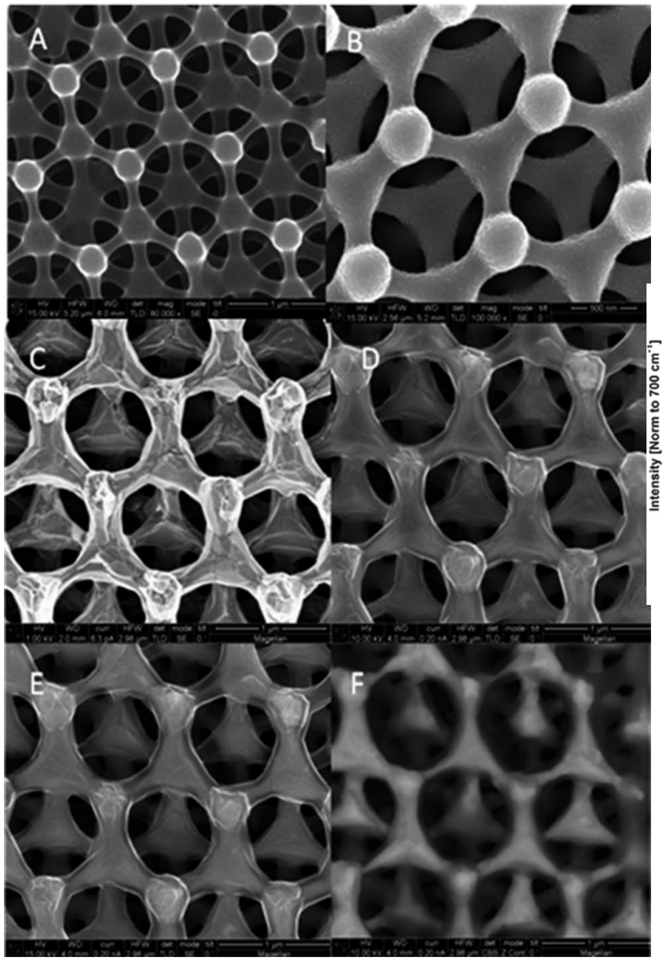
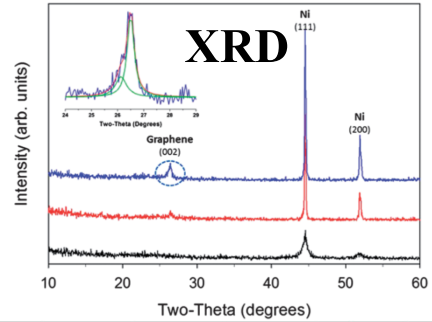
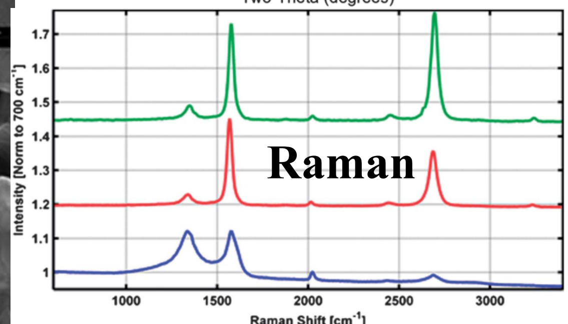
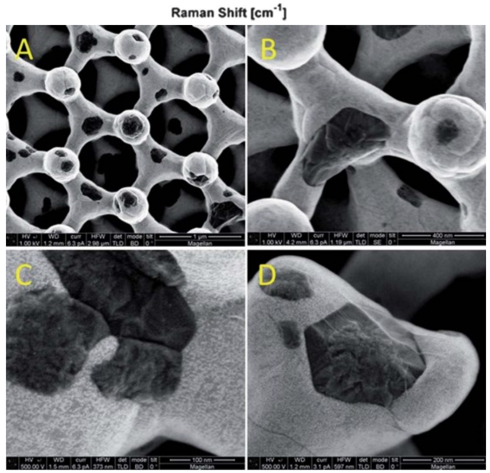
Nickel-Graphene Composite Scaffolds
(Morphology vs Electrochemical Performance)

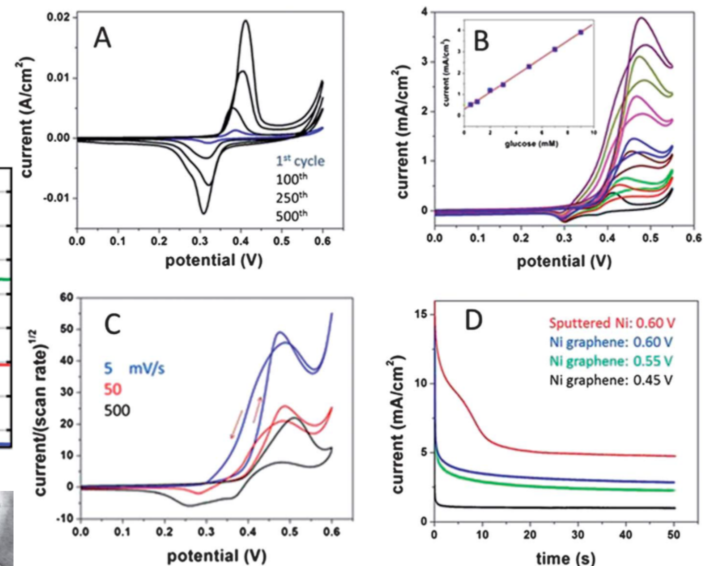


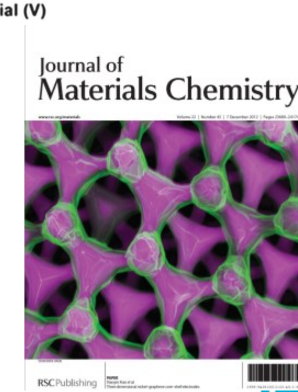






Electrochemical detection of glucose.





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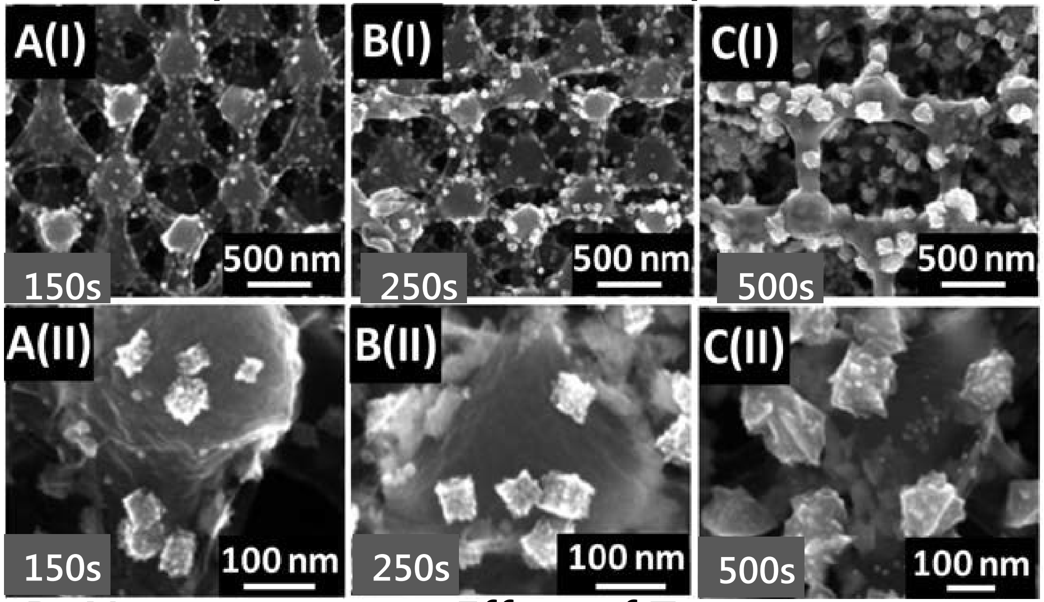
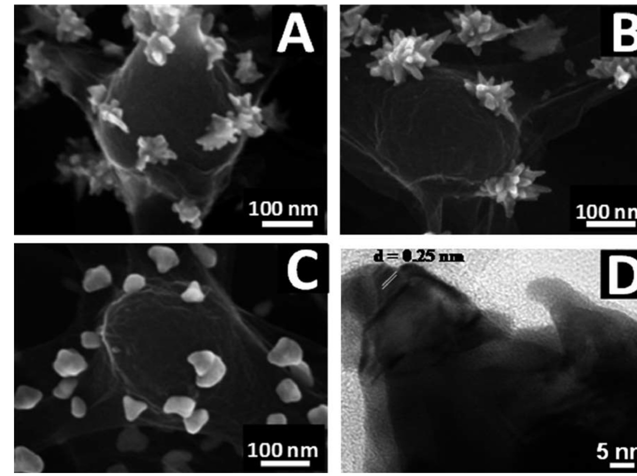
Xiao, et. al. "Three dimensional nickel-graphene core-shell electrodes," J. of Mat Chem, **22**, 23749-23754 (2012).

Deposition Condition Control Over Nanostructure Morphology

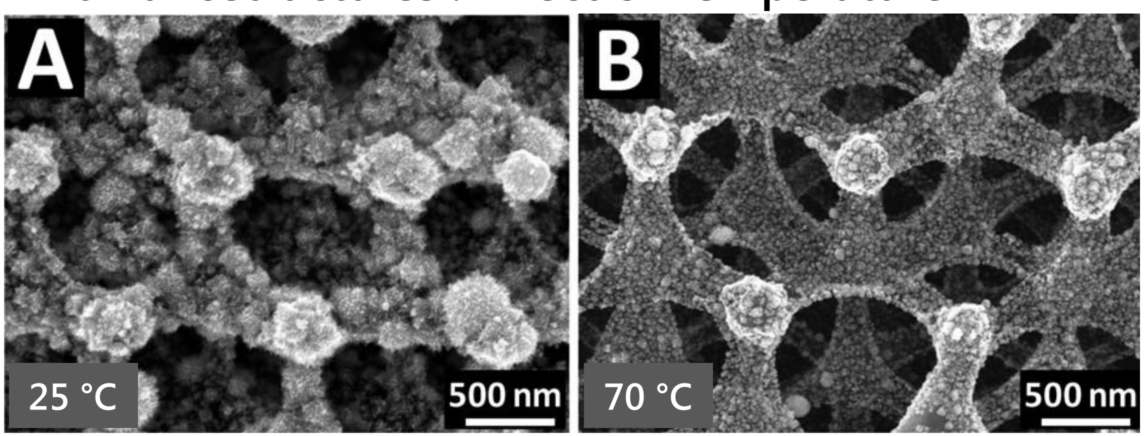
Pd Nanoparticles : Effect of Dep Time



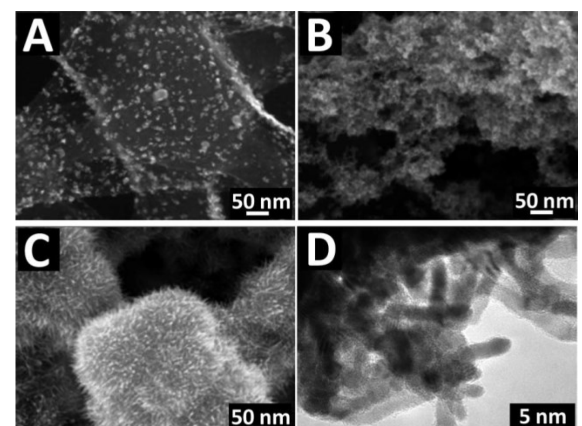
Au Nanoparticles : Effect of Au Conc.



Pt Nanostructures : Effect of Temperature

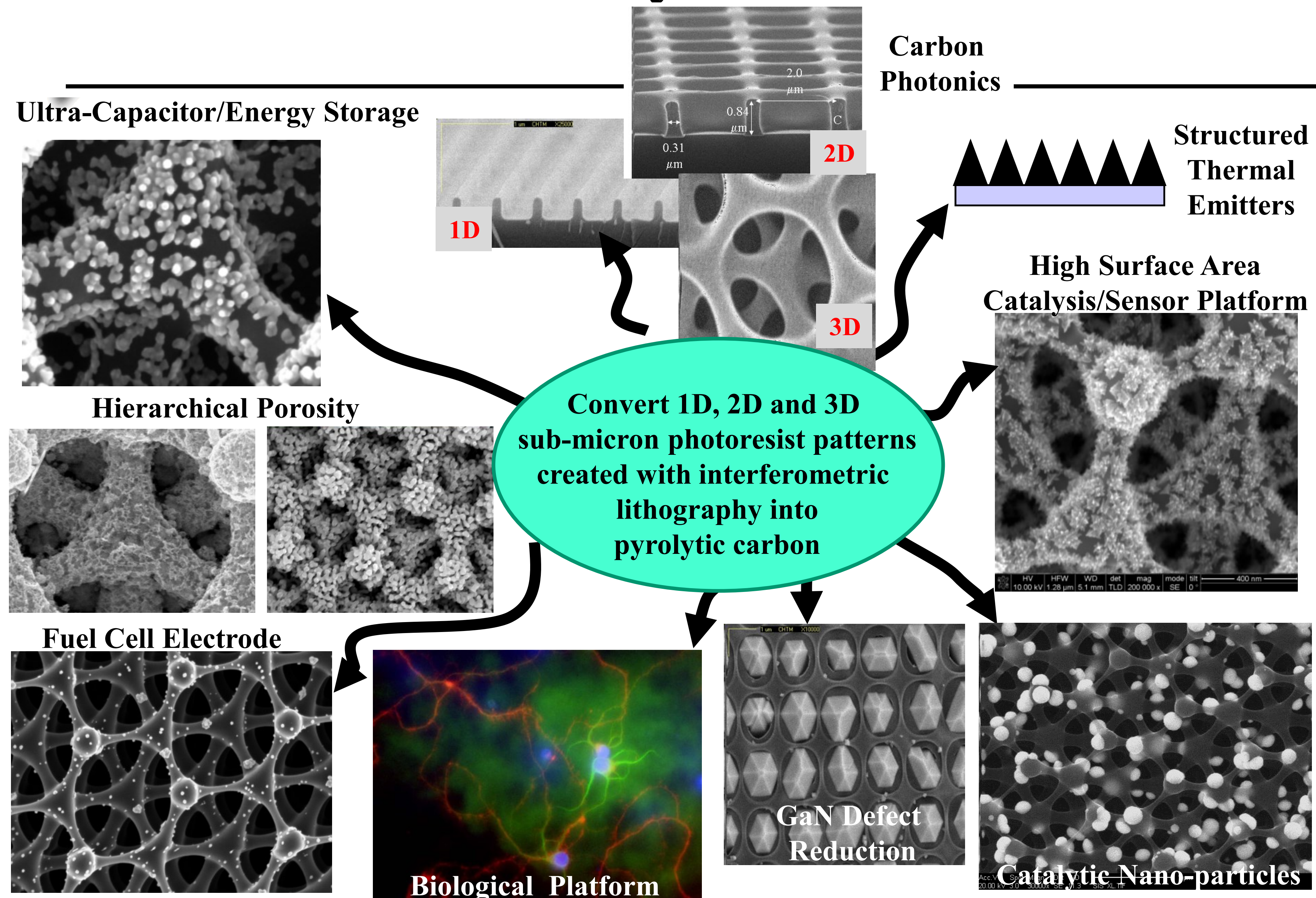


Pt Nanoparticles : Effect of Pt Conc.



Sattayasamitsathit, et. al. “Highly ordered multilayered 3D graphene decorated with metal NPs,” J. of Mat Chem A, **1**, 1639 (2013).

Interferometrically Patterned Carbon



Conclusions

• Lithographically structured pyrolyzed carbon provides a path toward leveraging inherent physical properties of elemental carbon in technologically relevant applications.

• Lithographically patterned carbon structures can be modified either electrochemically or through PVD to create a variety of sensor platforms.

• 3D amorphous carbon can be converted to 3D few layer graphene chemically

• Demonstrated 10 mm detection limit for glucose with fast response times (~5s 95% response).

• Demonstrated SERS platform with spatially homogeneous enhancement factor of $\sim 5 \times 10^9$.

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Acknowledgements

• Ronen Polsky, Xiaoyin Xiao, Cody Washburn, Thomas Beechem and Dave Wheeler (SNL)

Questions?

dbburck@sandia.gov

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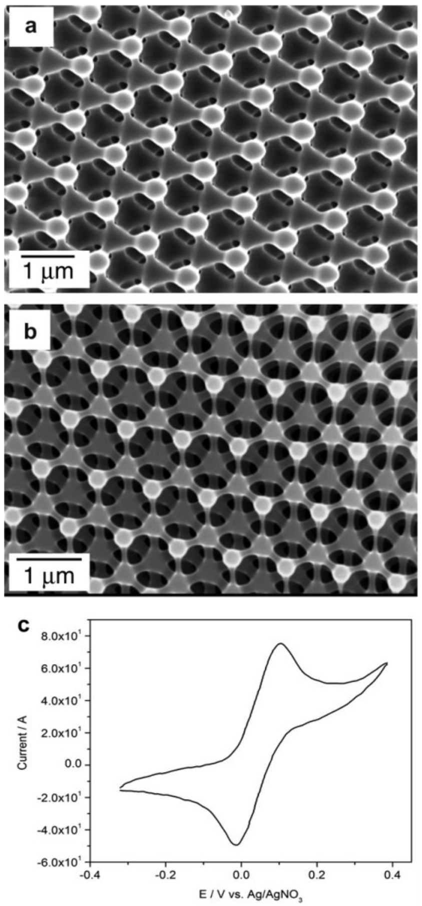
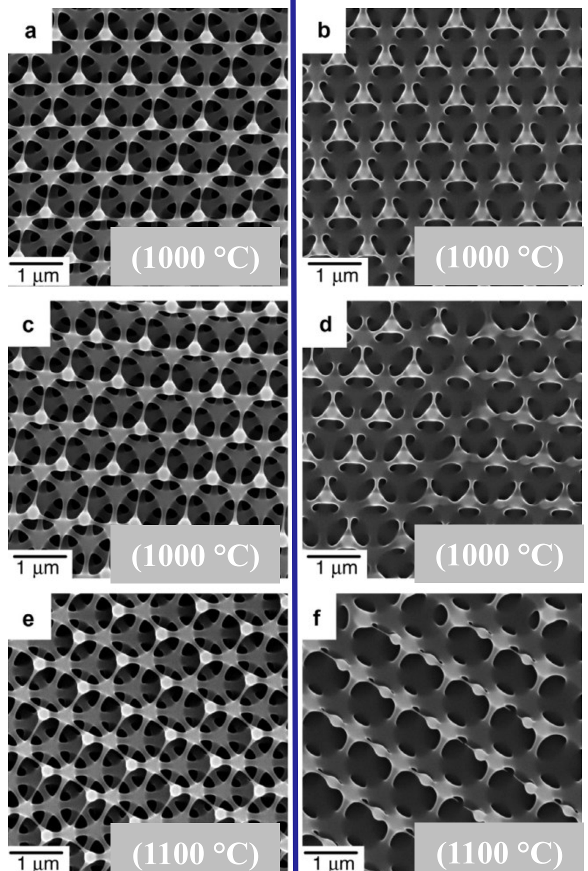
Backup Slides

How Fast Can We Pyrolyze?
(Morphology vs Electrochemical Performance)

Oven-Pyrolyzed
(3 °C/min; 60 min dwell)



(10 °C/s) **(100 °C/s)**



30s dwell

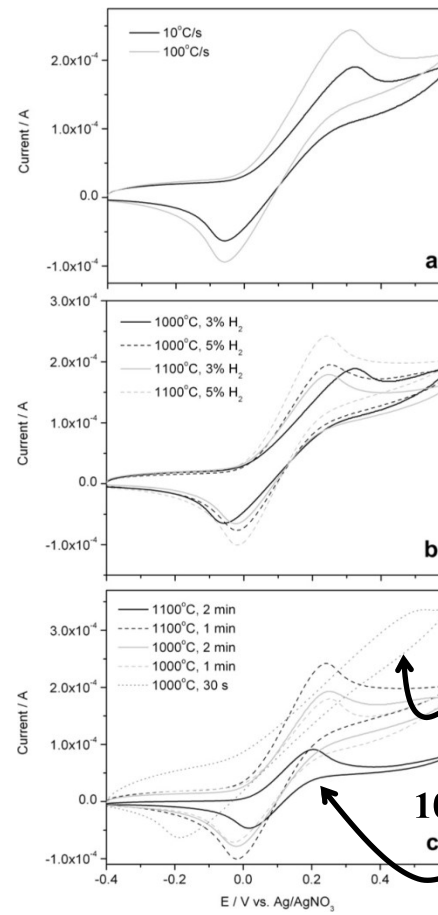
120s dwell

60s dwell

Similar Morphology

Reflow Evident

Electrochemical Performance



1000 °C;30s

1100 °C;120s

Spoerke, et. al. "Rapid thermal pyrolysis of interferometrically patterned resist," Carbon, **50**, 2894-2898 (2012).

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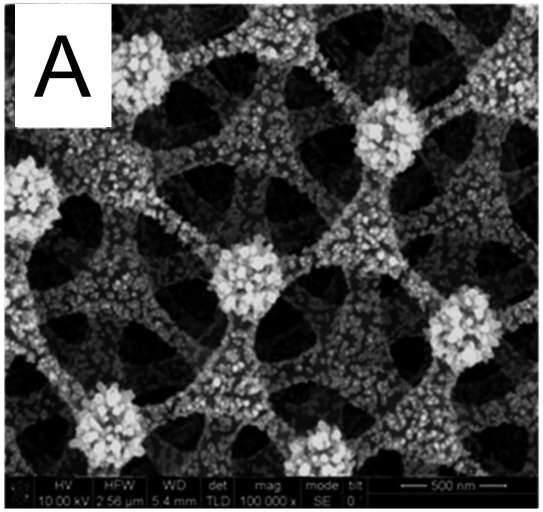
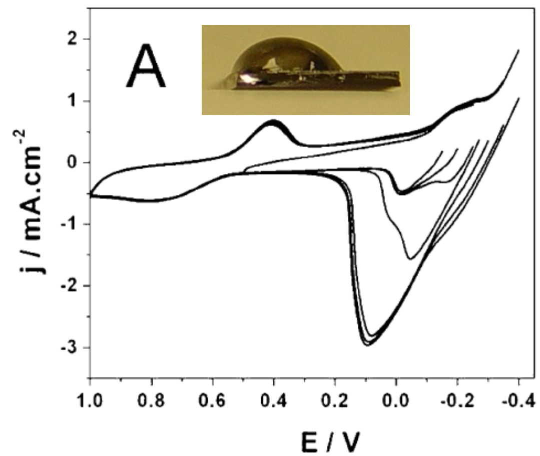
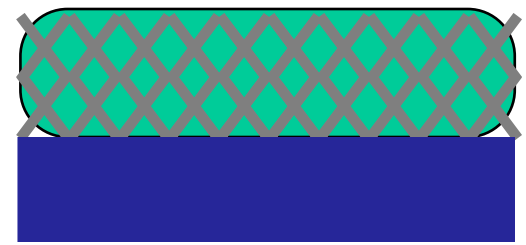
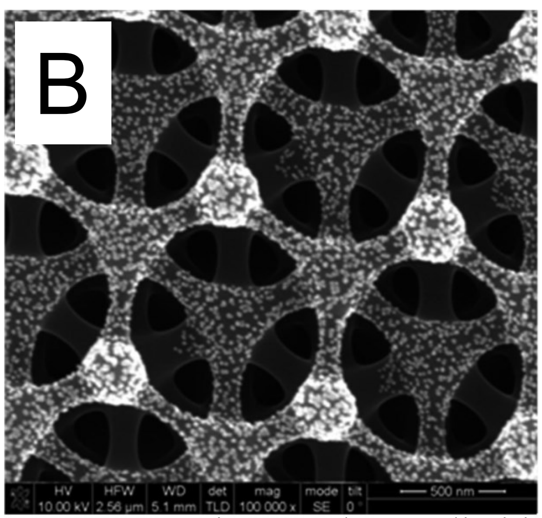
Non-Limiting Hydrogen Electrosorption
(Gas/Fluid Phase Impact of Hydrophobicity)

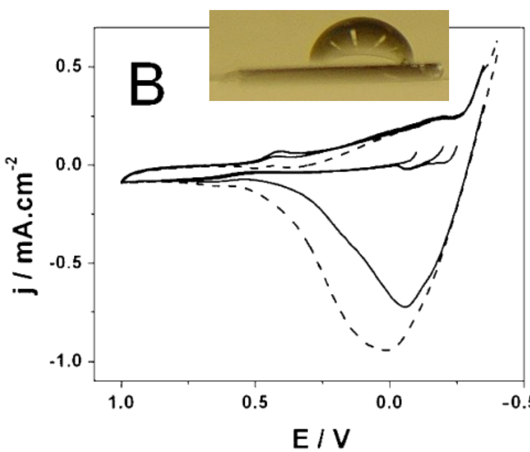


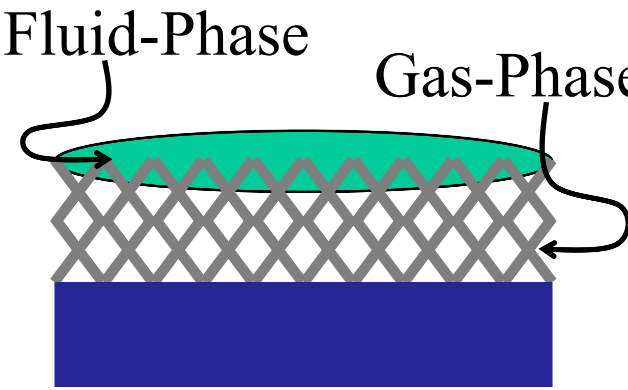


All Fluid Phase









Xiao, et. al. "Nonlimiting hydrogen electrosorption properties of asymmetric palladium nanoparticle-modified porous carbon electrodes," Electroanalysis, **24**, 153-157 (2012).

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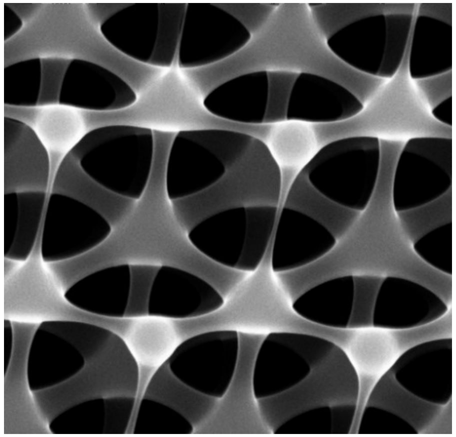
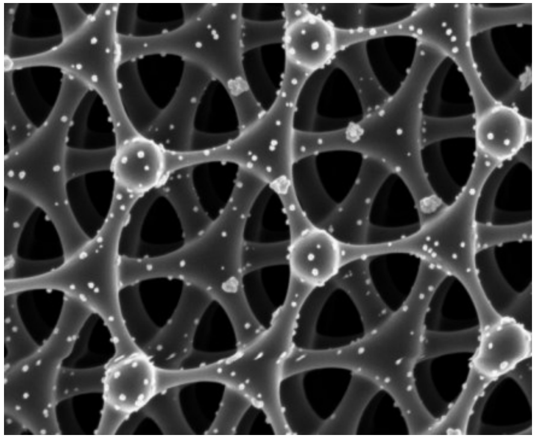
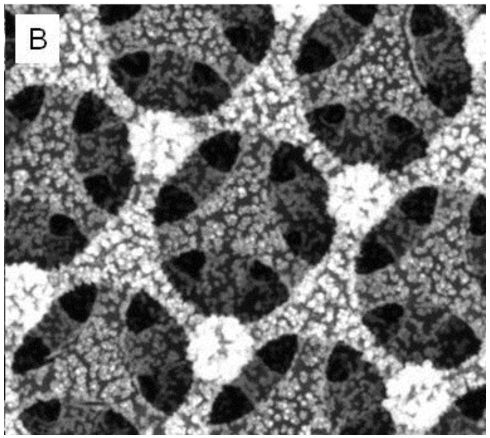
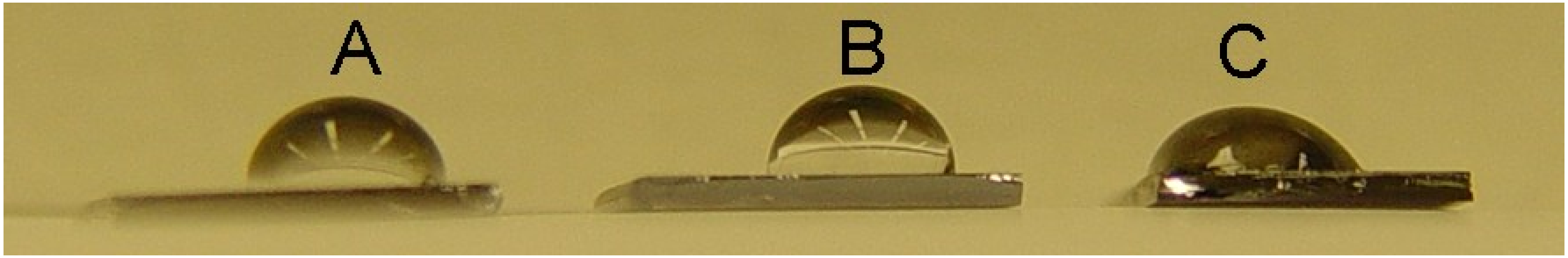
Lithographically Patterned Carbon



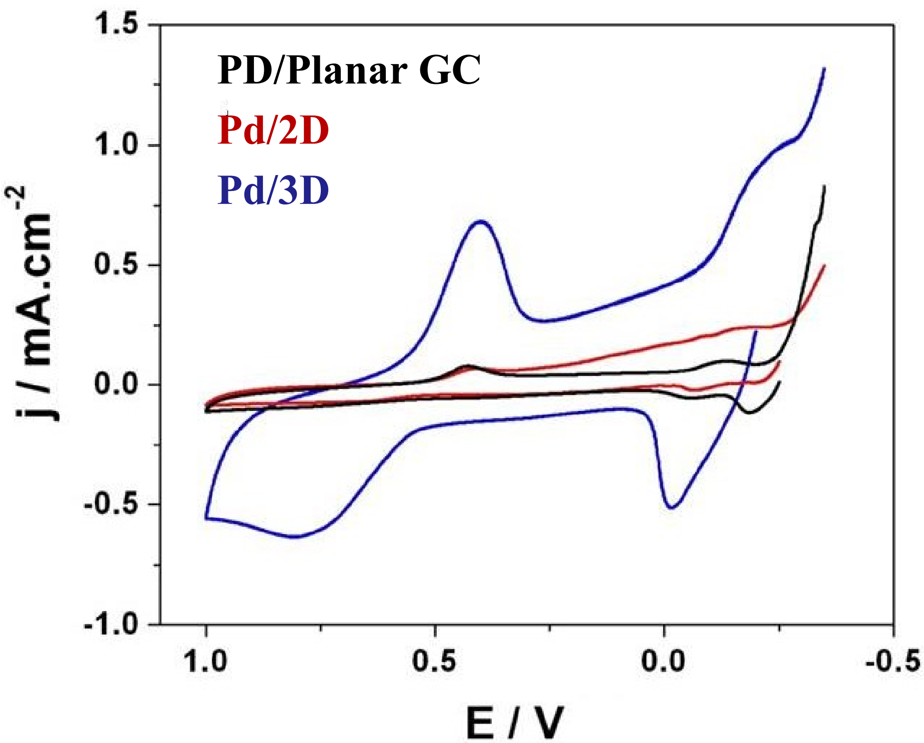






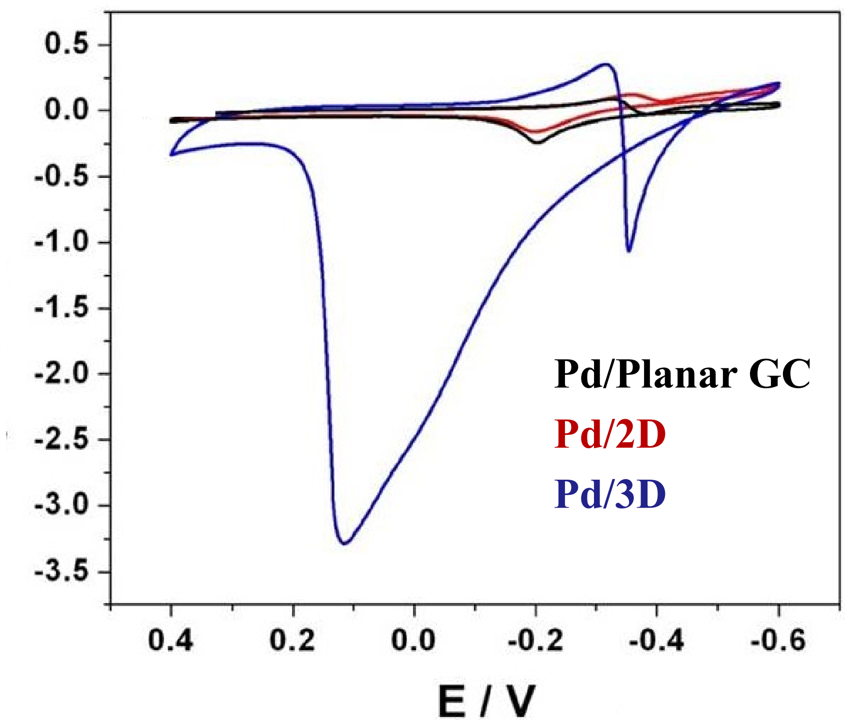
Electrode Characterization – Pd Catalytic MeOH Oxidation

Cycling in $HClO_4$



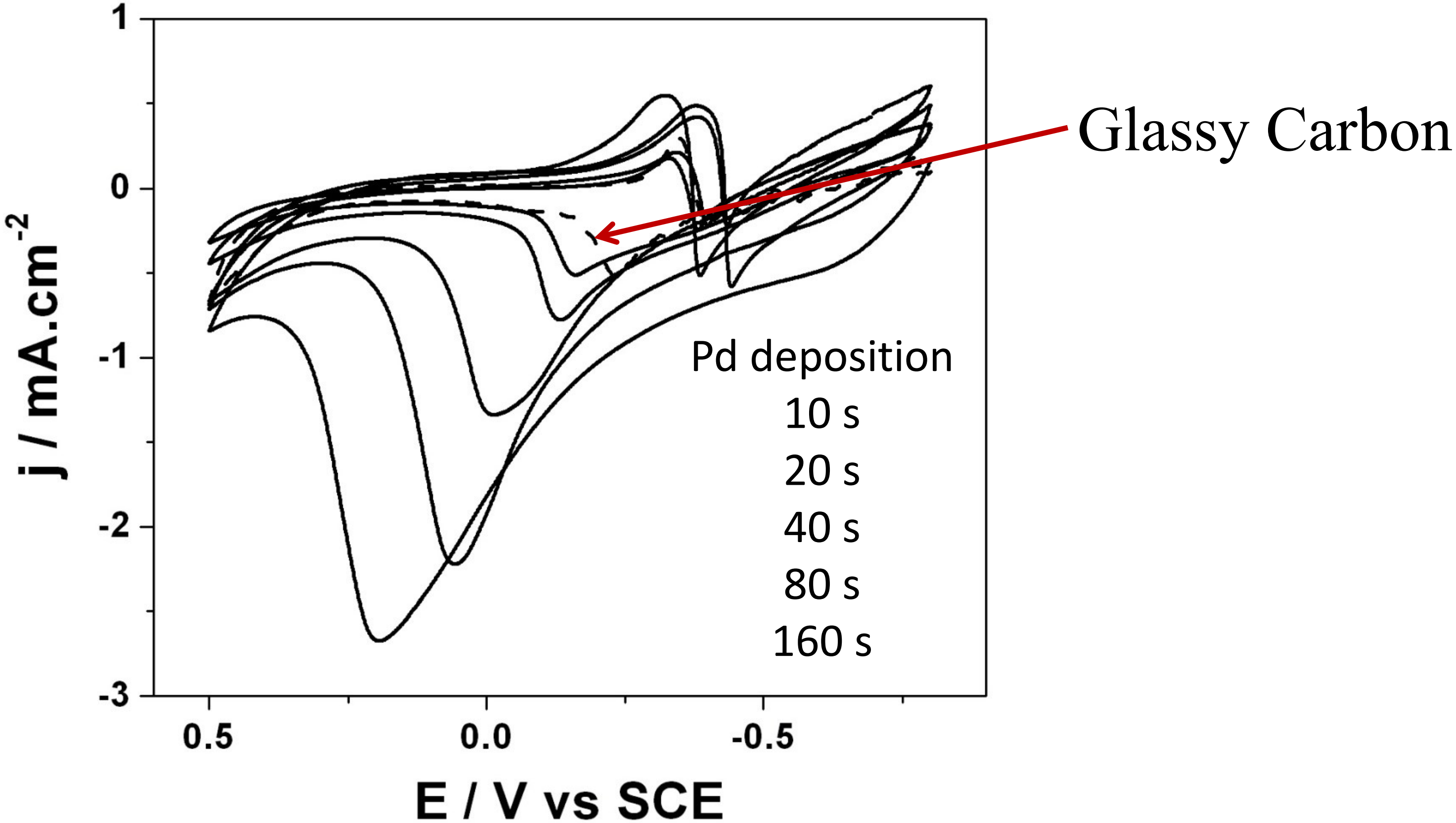
Accessible Pd surface area ~ 20x higher

Methanol Oxidation



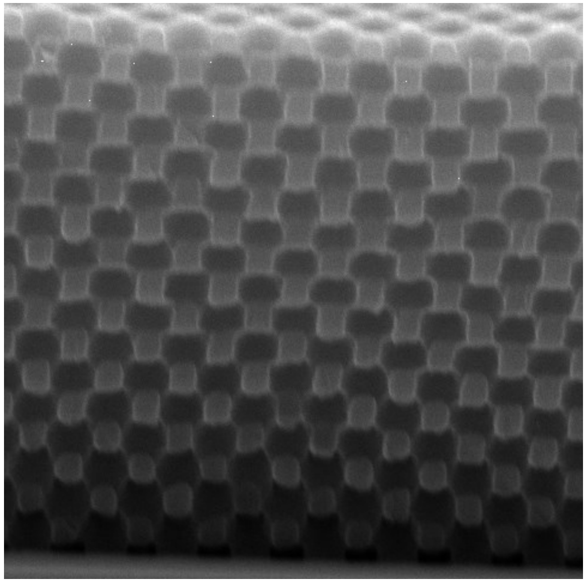
~ 200x increase in Methanol oxidation

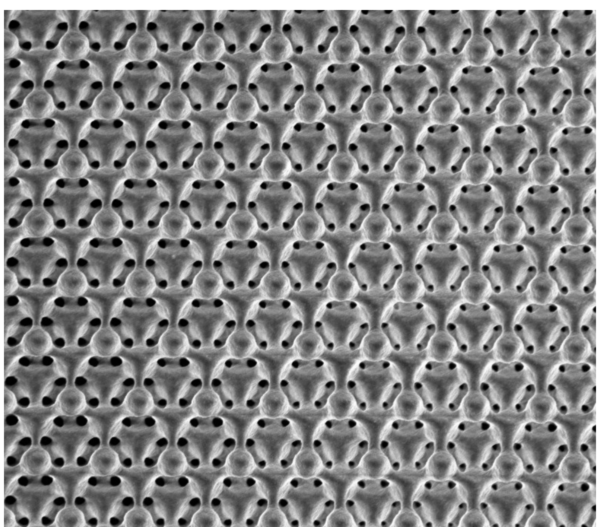
Electrode Response *vs* Pd Particle Size

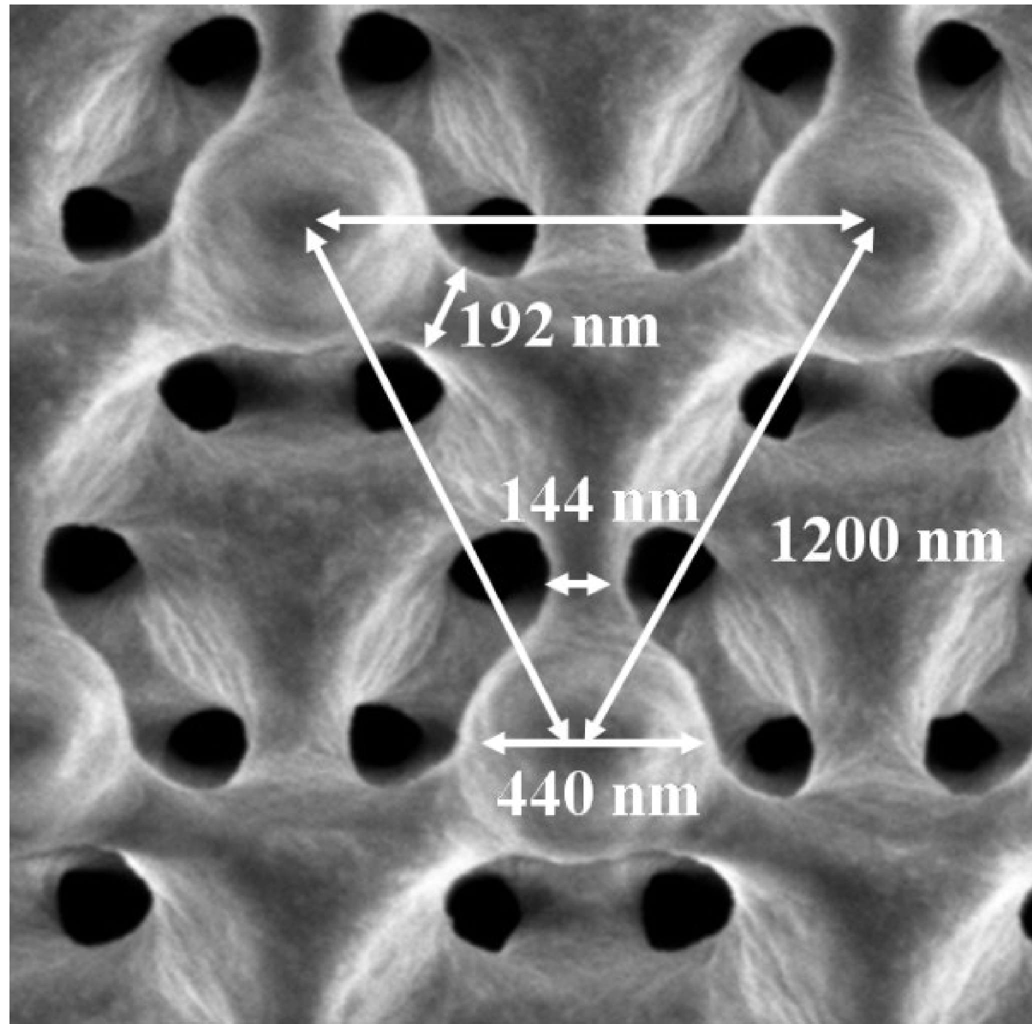


Cyclic voltammograms of Pd/Porous at variable Pd loading in 0.1 M NaOH + 5 mM glucose. The dashed line is from Pd/GC for comparison. Scan rate: 20 mV/s.

3-D Resist Structure







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3-D Carbon Electrode Application: Surface Enhanced Raman Scattering (SERS) Sensor Platform

Xiao et al, Chem. Commun., **47**, pp. 9858-9860 (2011).

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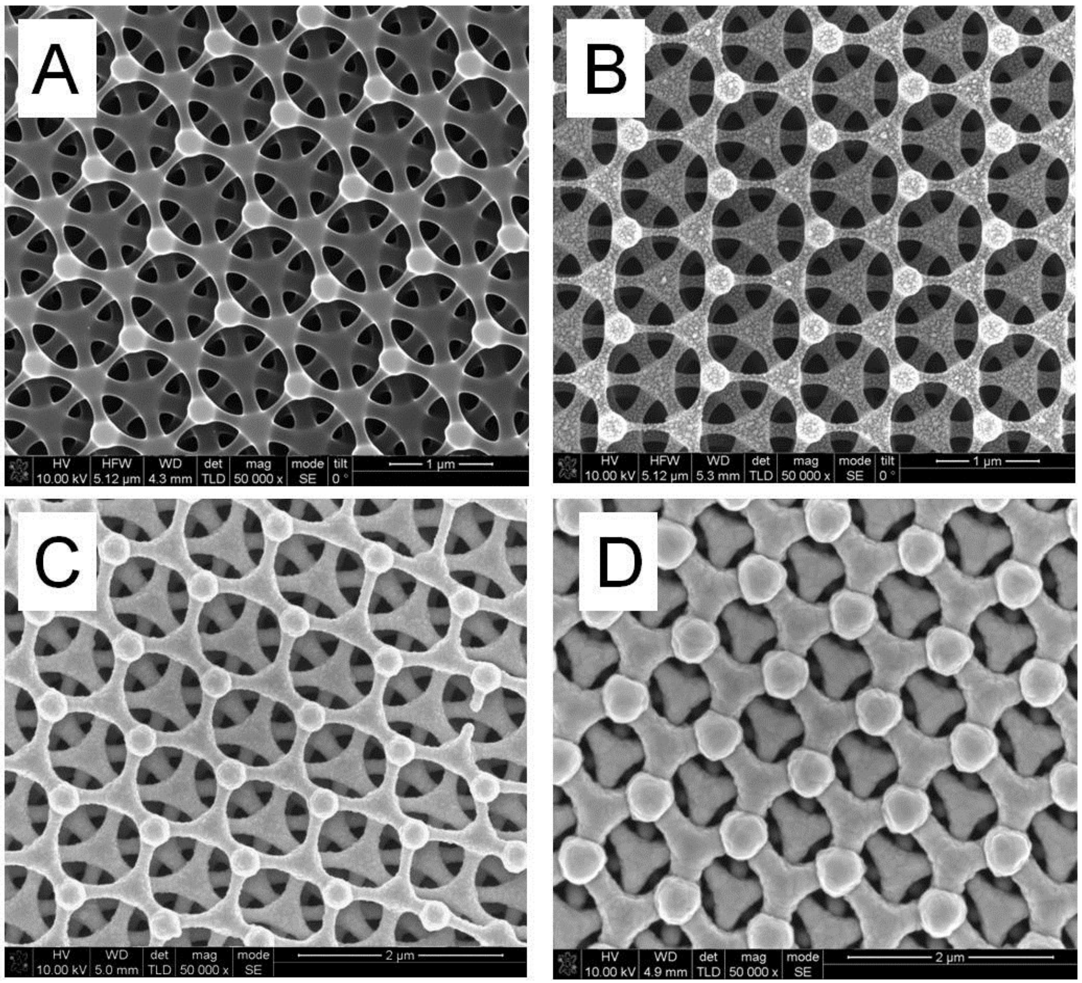
PVD Ag Scaffold Modification

Sputtered Ag (1 Å/s)

islands



Thin film

Sputtering Time

A – 0 (bare carbon)

B – 150 s

C – 1100 s

D – 3300 s

Xiao et al, Chem. Commun., **47**, pp. 9858-9860 (2011).

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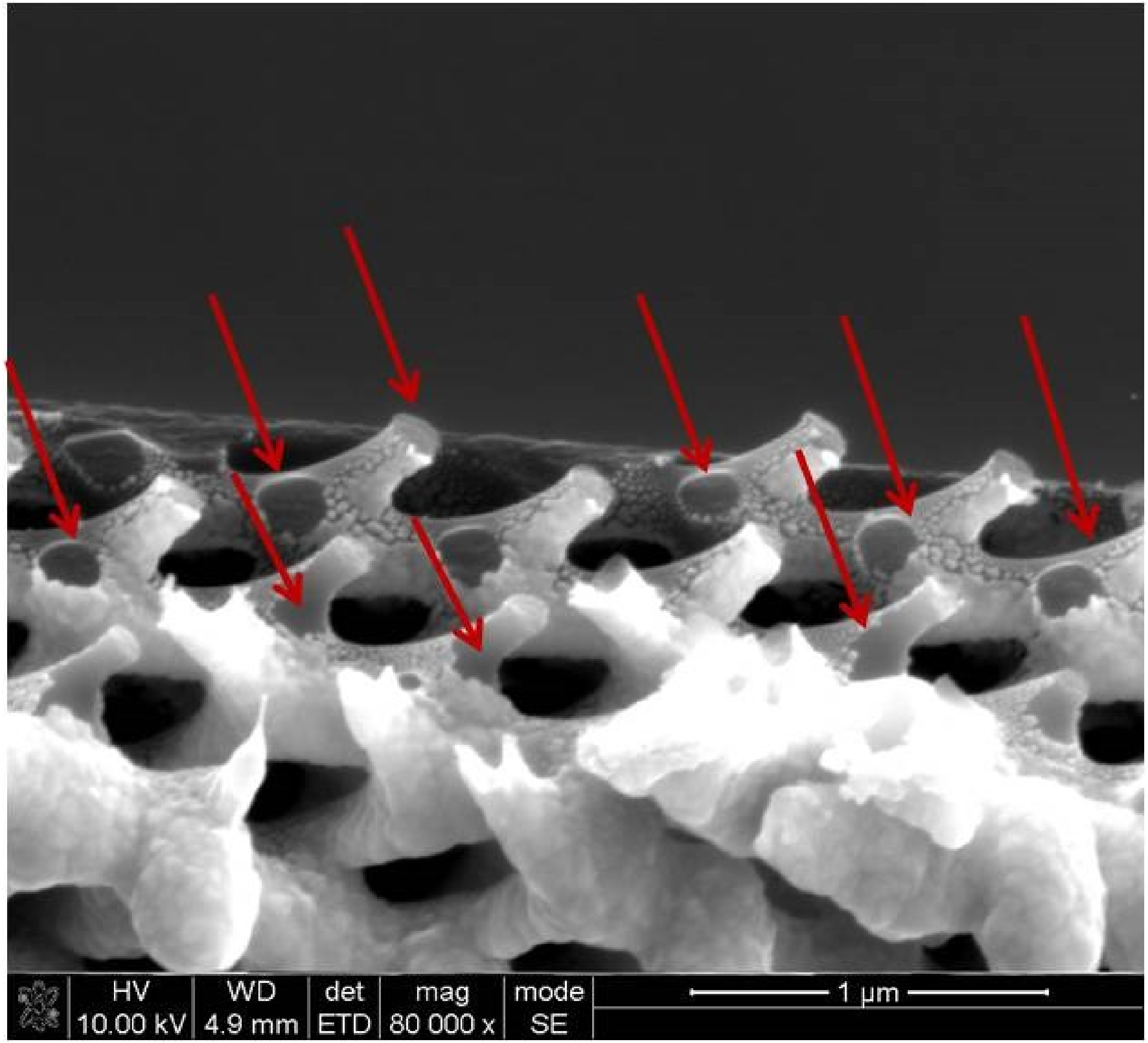
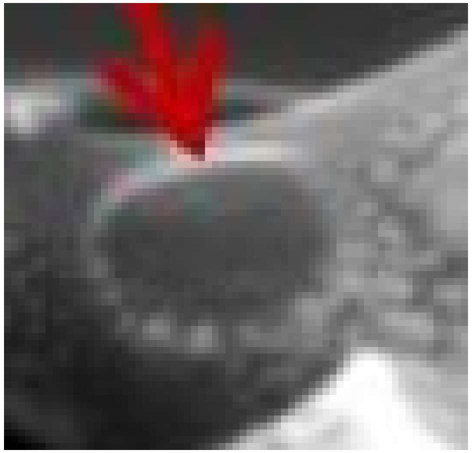
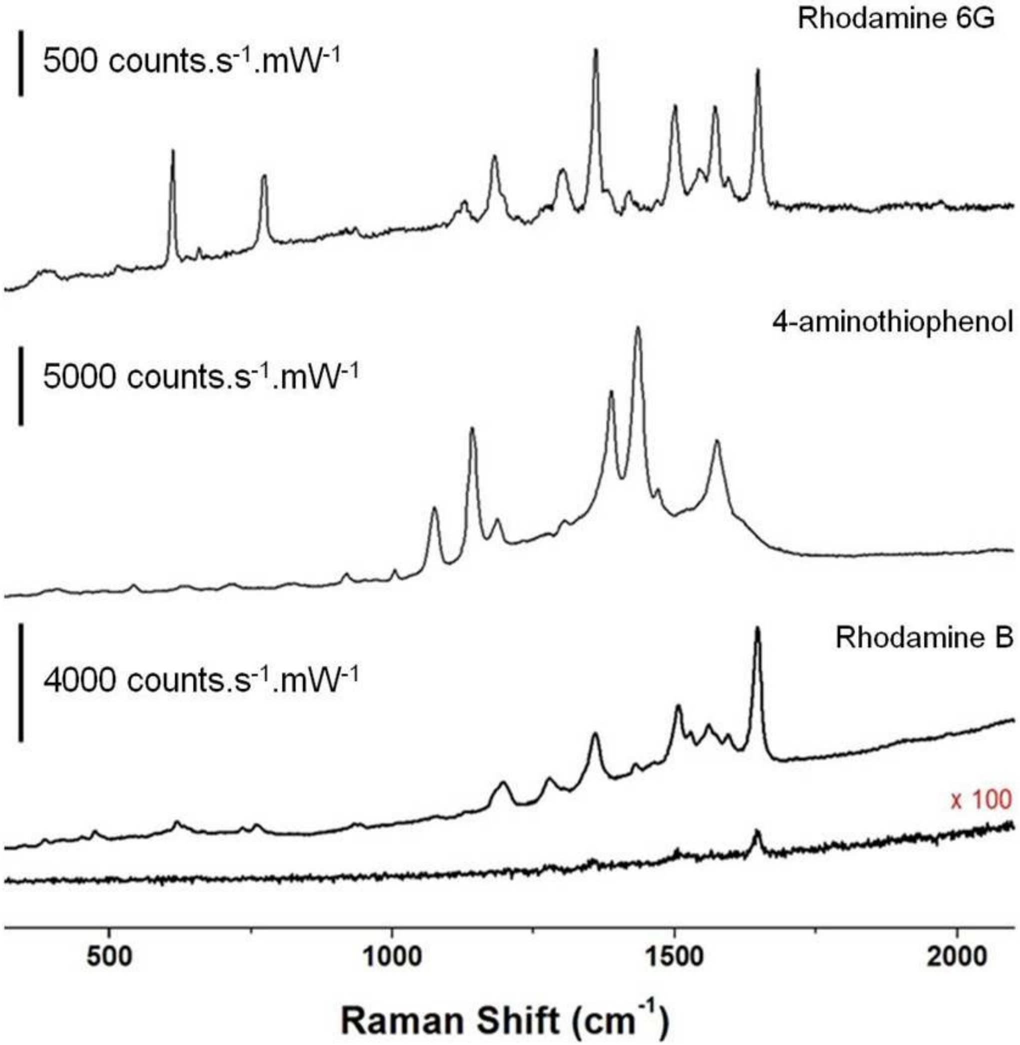
Sputtering coats bottom side too!





Xiao et al, Chem. Commun., **47**, pp. 9858-9860 (2011).

SERs Signals for 3 Organic Molecules



Increase in signal not due to surface area.

Only a 4x increase in surface area between planar carbon and 3D carbon with identical sputtering times.

planar carbon with sputtered Ag islands **x 100**

Xiao et al, Chem. Commun., **47**, pp. 9858-9860 (2011).

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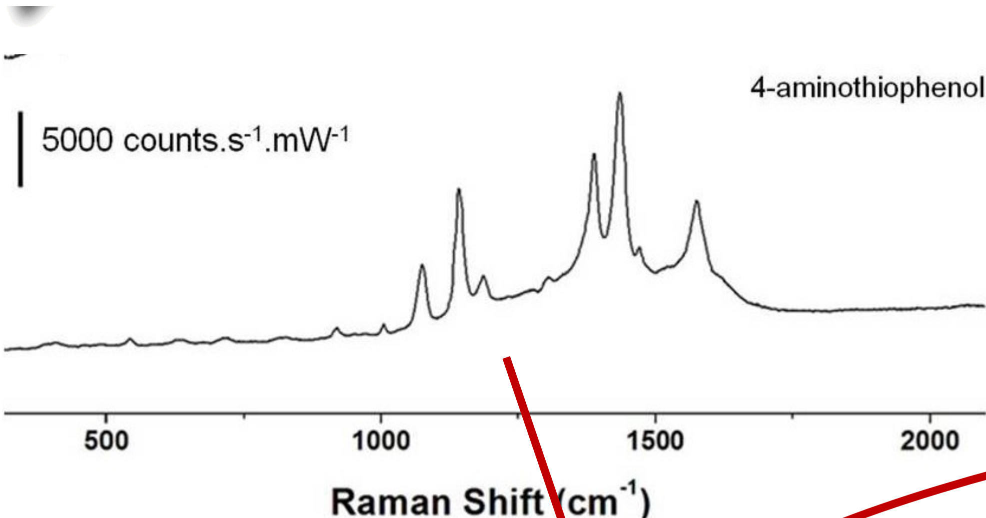
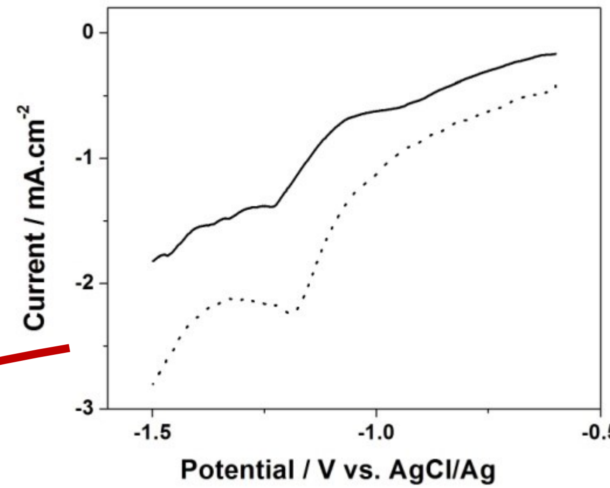
Enhancement Factor: 4-aminothiophenol



Measure # of molecules



Electrochemical Stripping

$$EF = \frac{I_{3D\ Carbon}}{\#\ molecules} \Big/ \frac{I_{solution}}{\#\ molecules}$$

$$EF \sim 5 \times 10^{9}$$

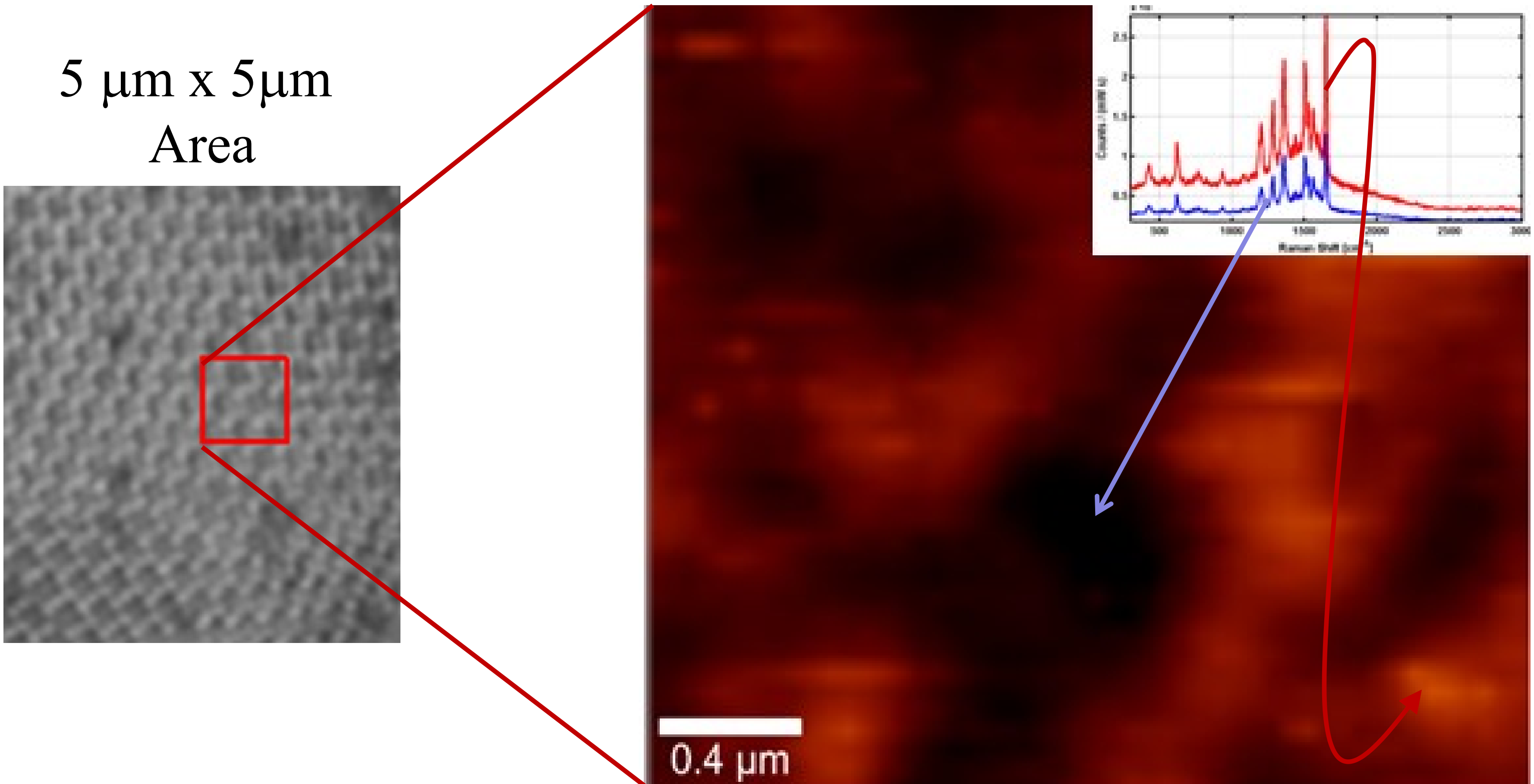
Compared to response of neat control solution

No Spatial Hotspots

Spatially resolved Raman Mapping

5 µm x 5µm
Area

$\frac{\text{Max Signal}}{\text{Min Signal}}$ only ~ factor of 2.5



3-D Carbon Electrode Application: Non-Enzymatic Detection of Glucose

Xiao et al., Biosensors and Bioelectronics, **26**, pp 3641-3646 (2011)

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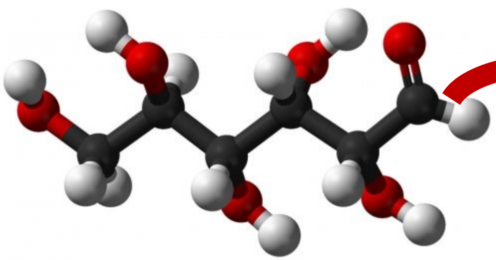
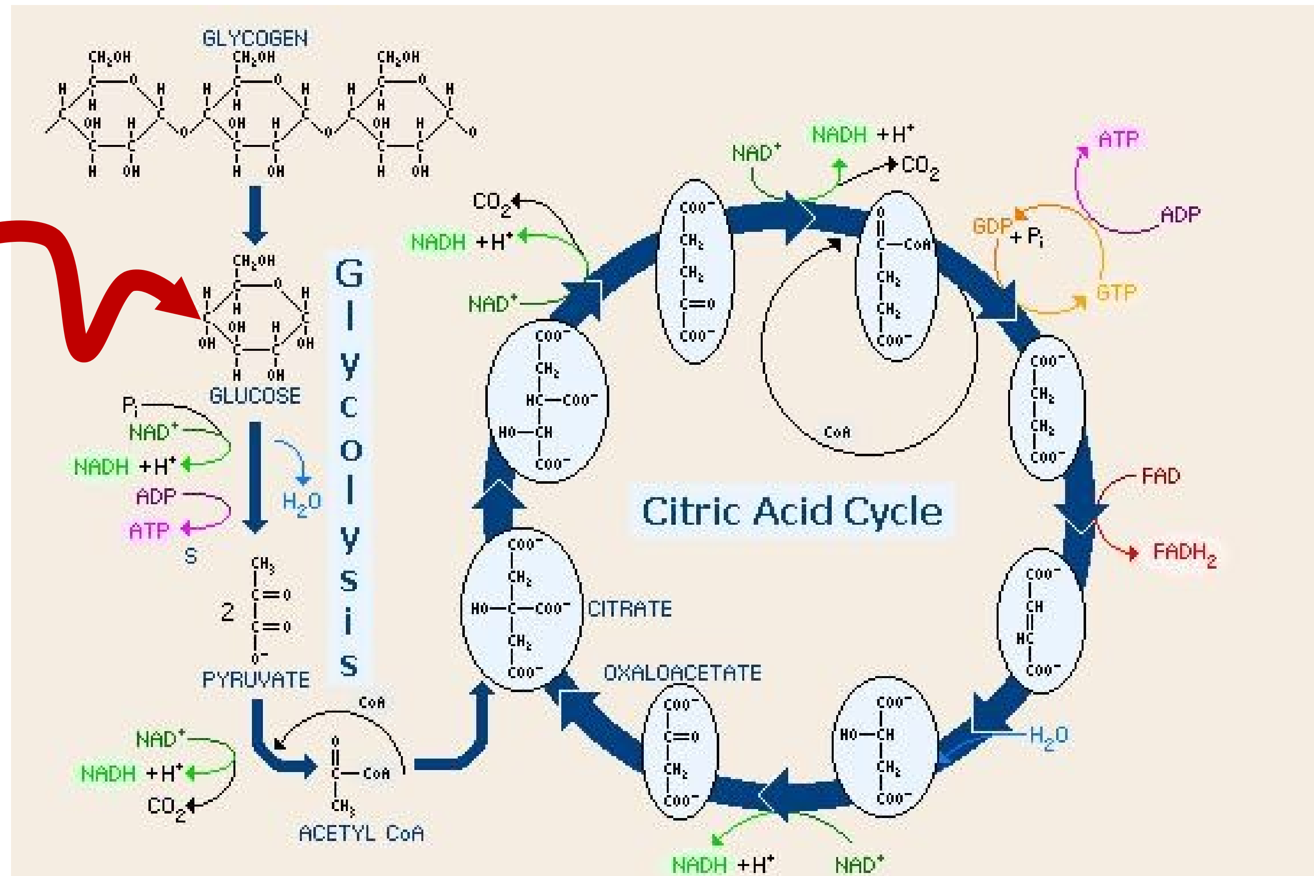
Why is Glucose Oxidation Important?

Glucose Molecule





glucose oxidase (GOx)

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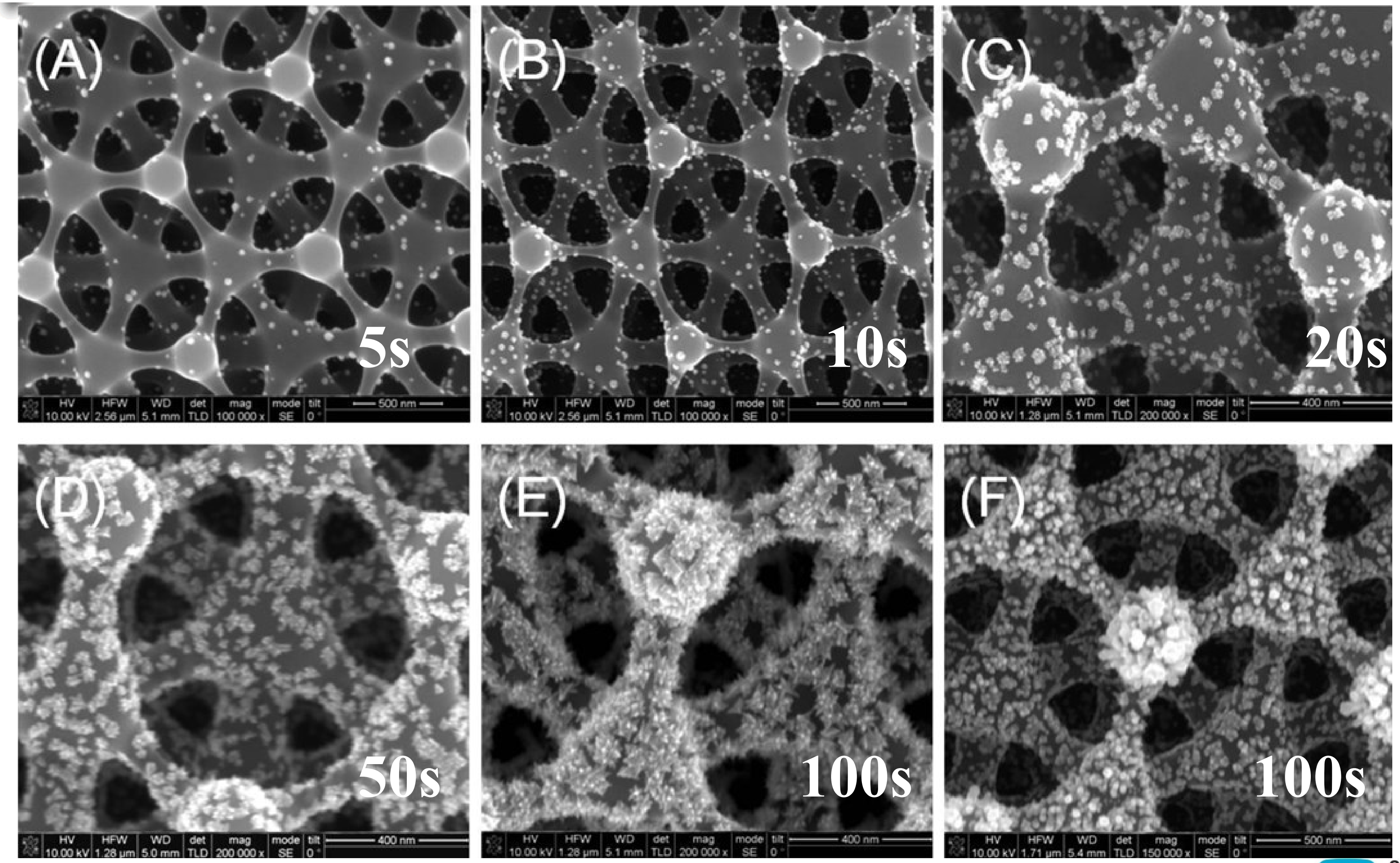
Electrodeposition of Pd Nanoparticles



Xiao et al., Biosensors and Bioelectronics, **26**, pp 3641-3646 (2011)

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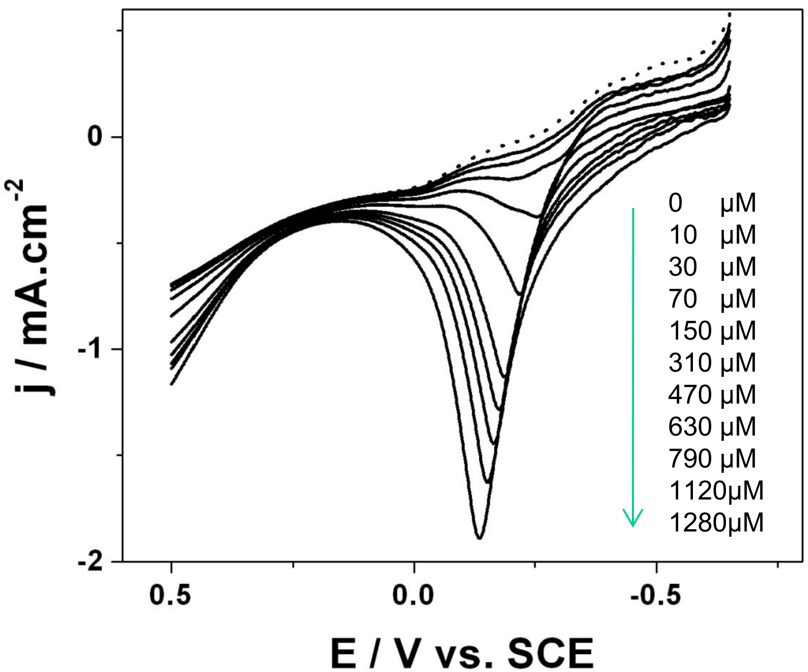
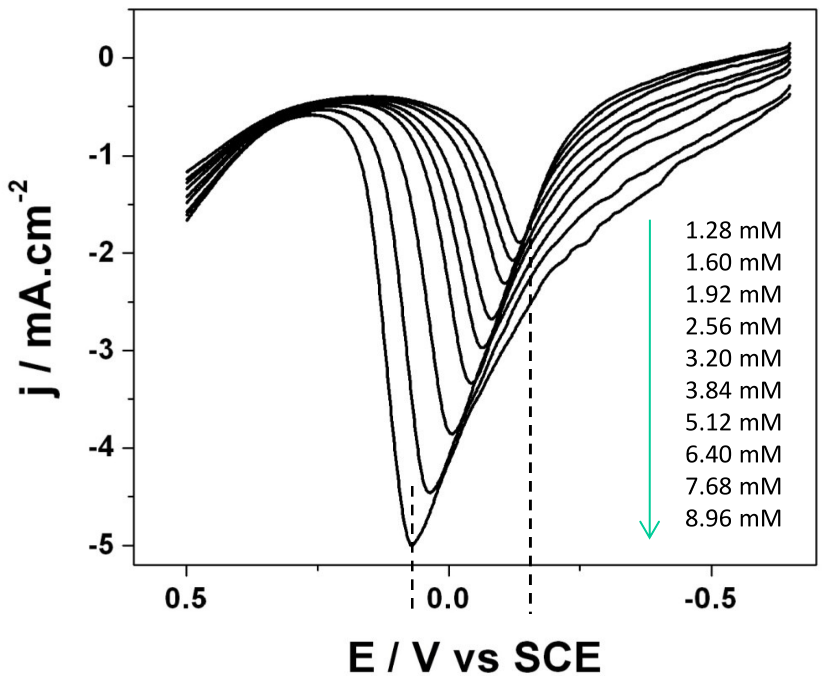
Electrode Response to Glucose Additions

µm concentrations



mm concentrations



Linear scan voltammograms of Pd/Porous in 0.1 M NaOH + x M glucose. Pd deposition: 100s, Scan rate: 20 mV/s.

Potential was cycled hundreds of times without noticeable current decay – SEM images indicate no change in Pd particles.

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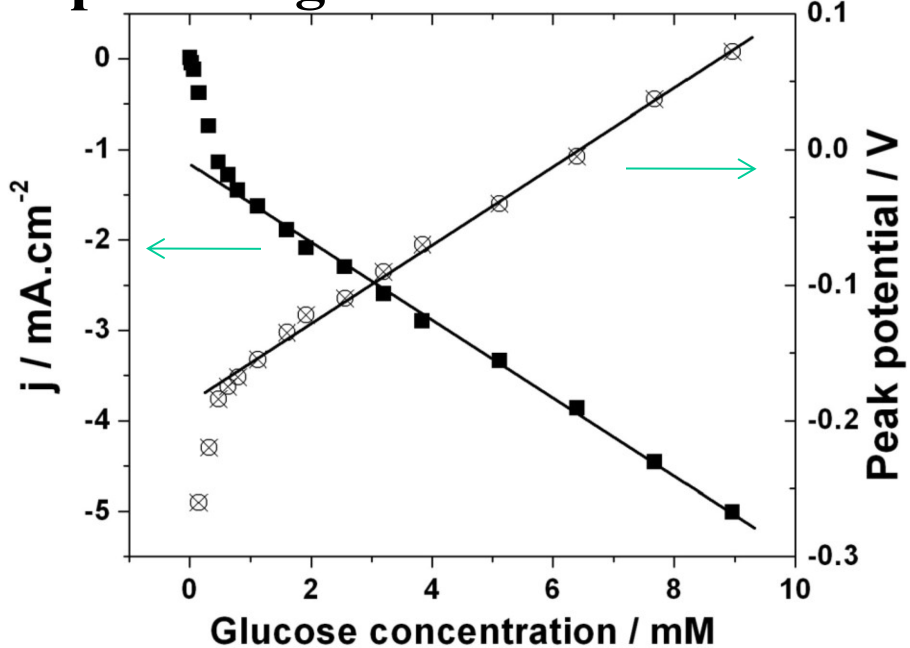
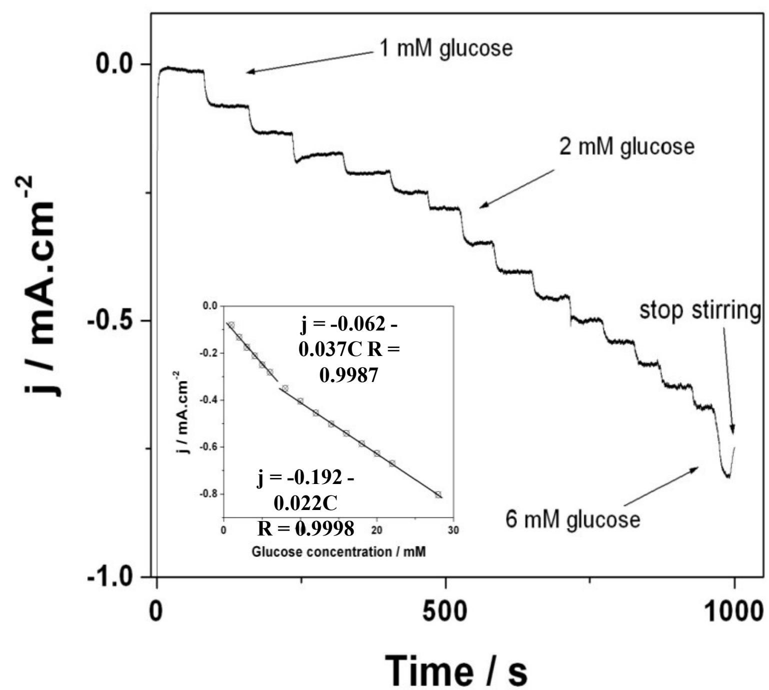
Current and Potential Response to Glucose Concentration

Both current and peak potential respond to glucose concentration





Plots of corresponding current and peak potential vs. glucose concentration. Pd deposition: 100s, Scan rate: 20 mV/s (A) and typical amperometric response of a Pd/Porous towards successive additions of glucose in 0.1 M NaOH with continuous stirring. The inset figure shows the current-concentration relationship (B).

Xiao et al., Biosensors and Bioelectronics, **26**, pp 3641-3646 (2011)

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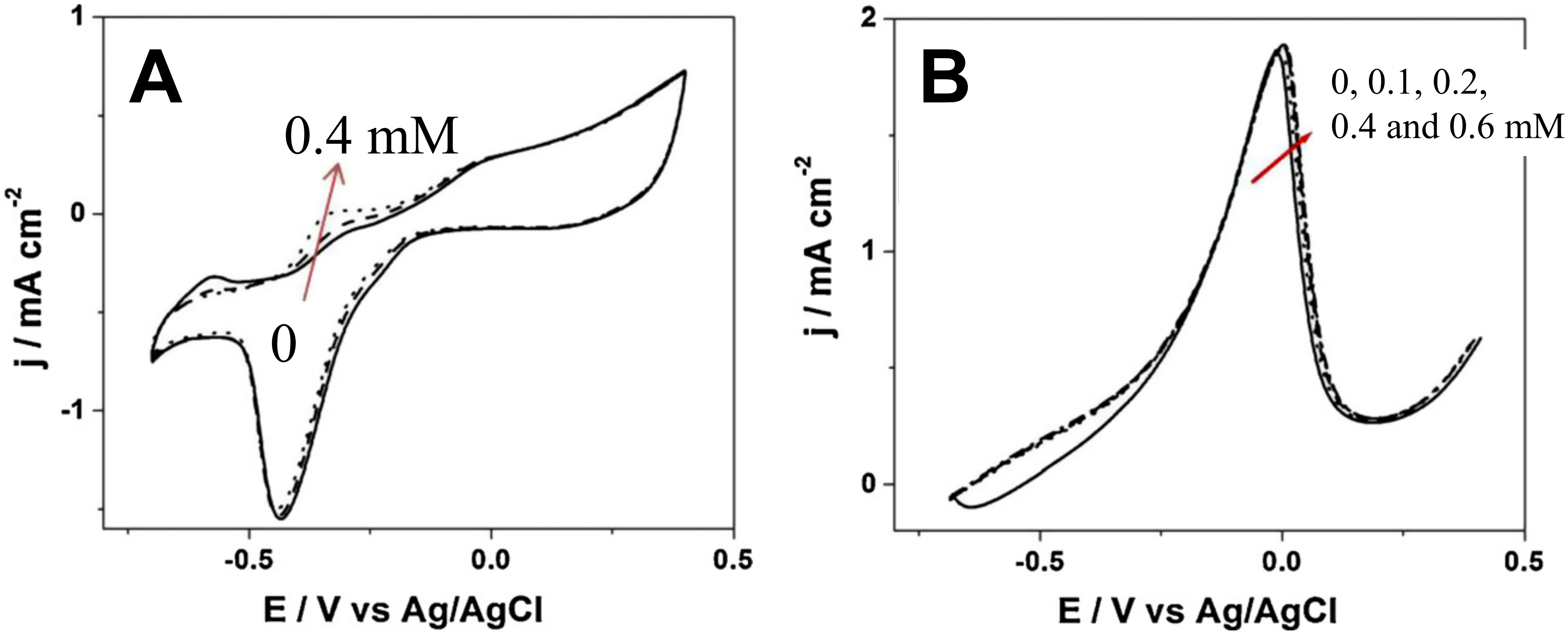
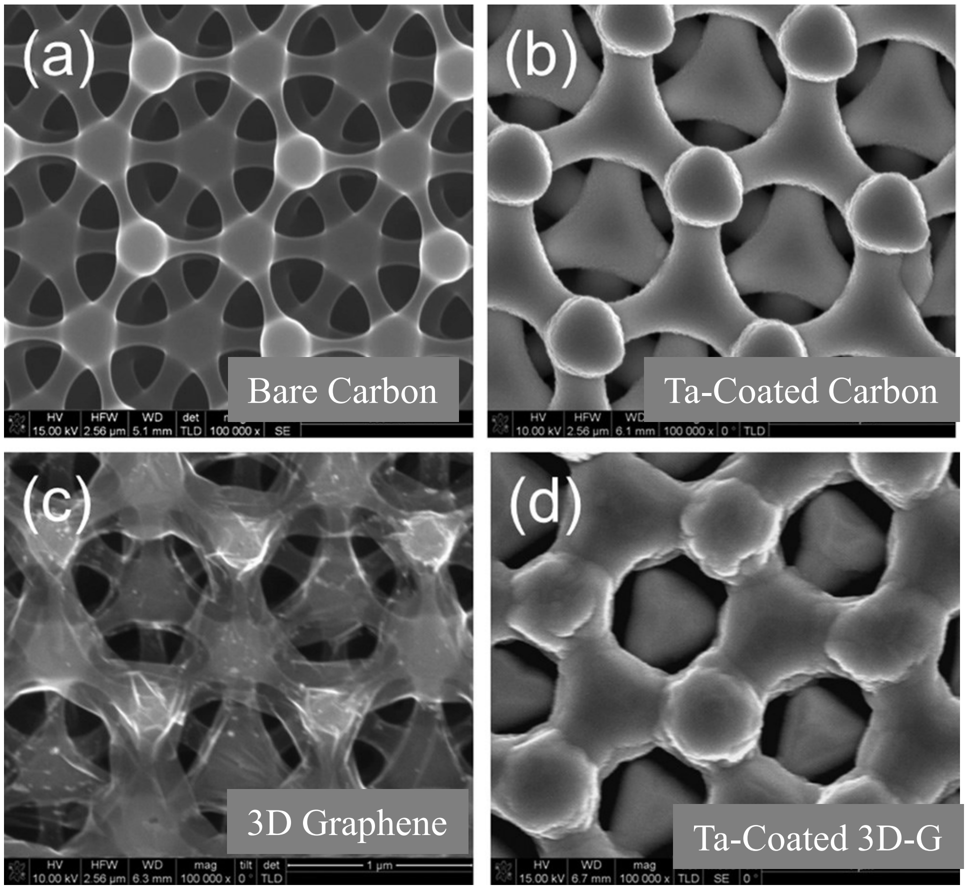
Electrode Response *vs* Ascorbic Acid

Typical ascorbic acid concentration in blood - ~0.1mM

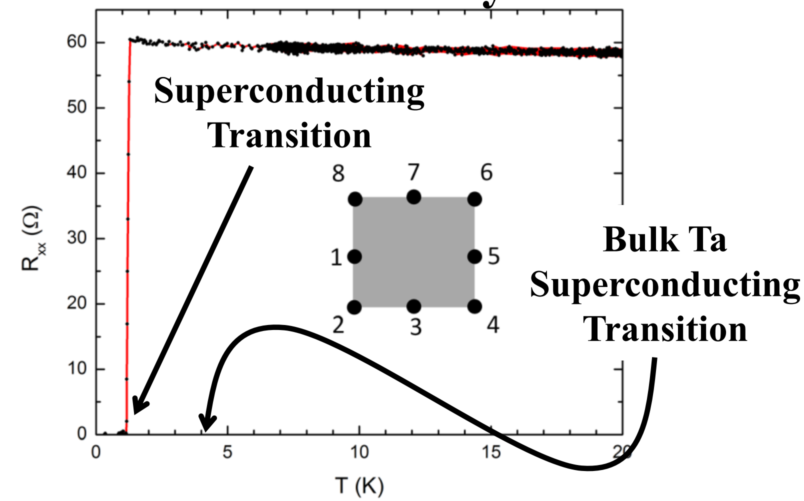


Response of 3mM glucose in the presence of 0, 0.1, 0.2, 0.4 and 0.6 mM ascorbic acid

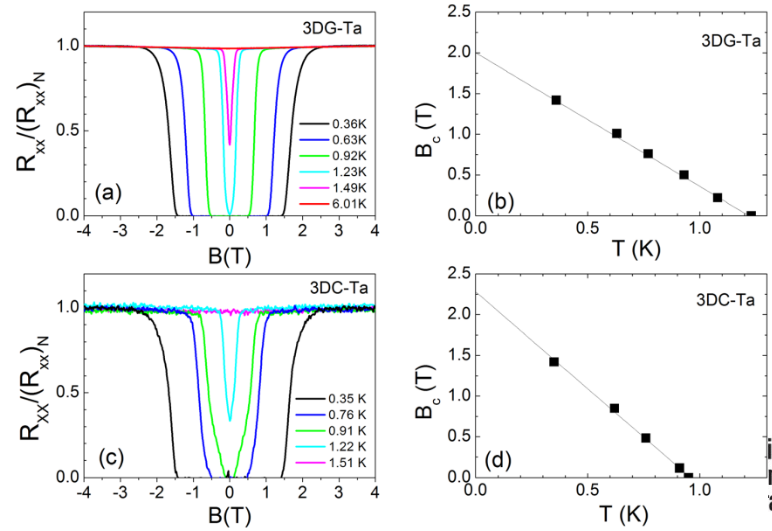
Superconducting Film Properties



Resistivity



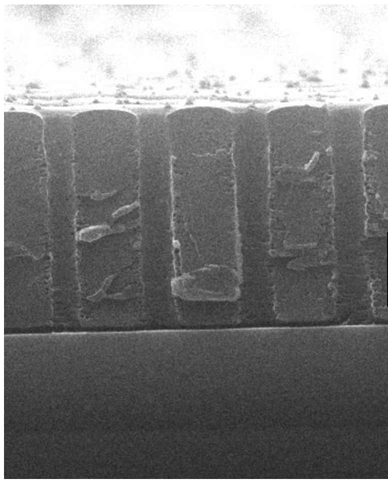
Critical Field



Cobaleda, et. al. "Superconducting properties in Ta decorated 3D graphene and carbon structures," APL, **105**, 053508 (2014).

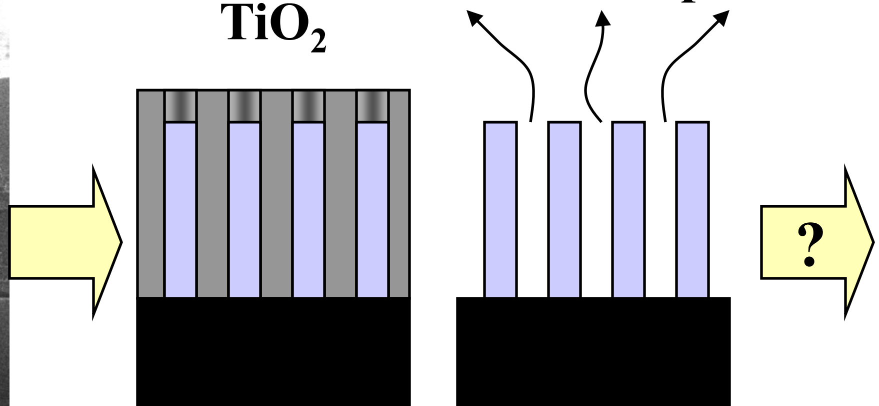
An Unexpected Result

Before "Calcination"

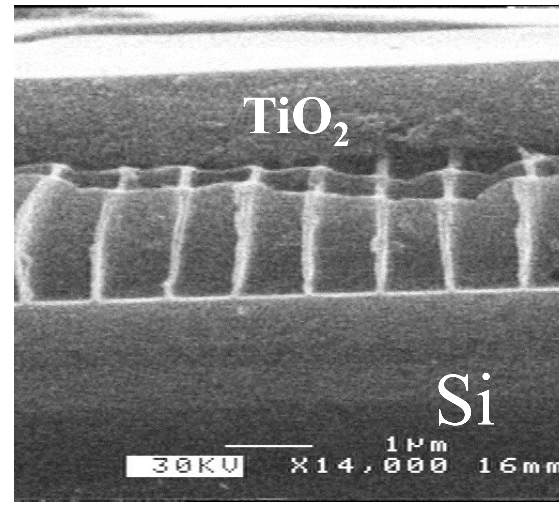


Infiltrate TiO_2

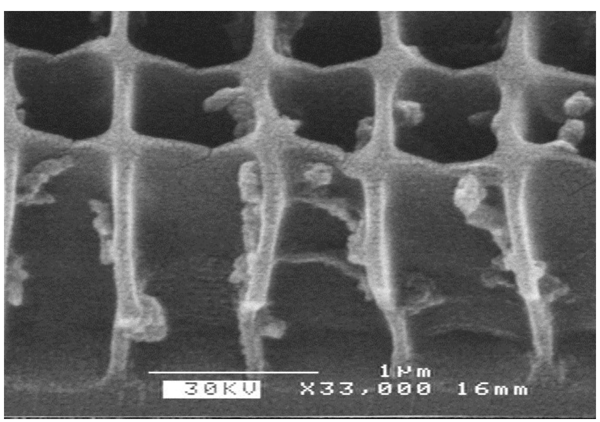
Burn out resist template

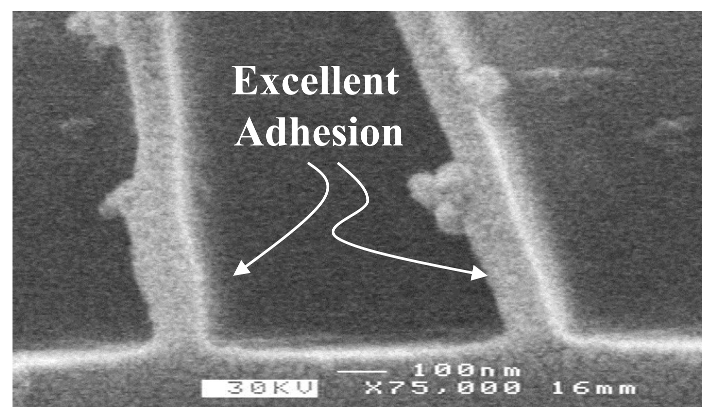


What The Hell?



Pyrolyzed Carbon Resist Structure





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