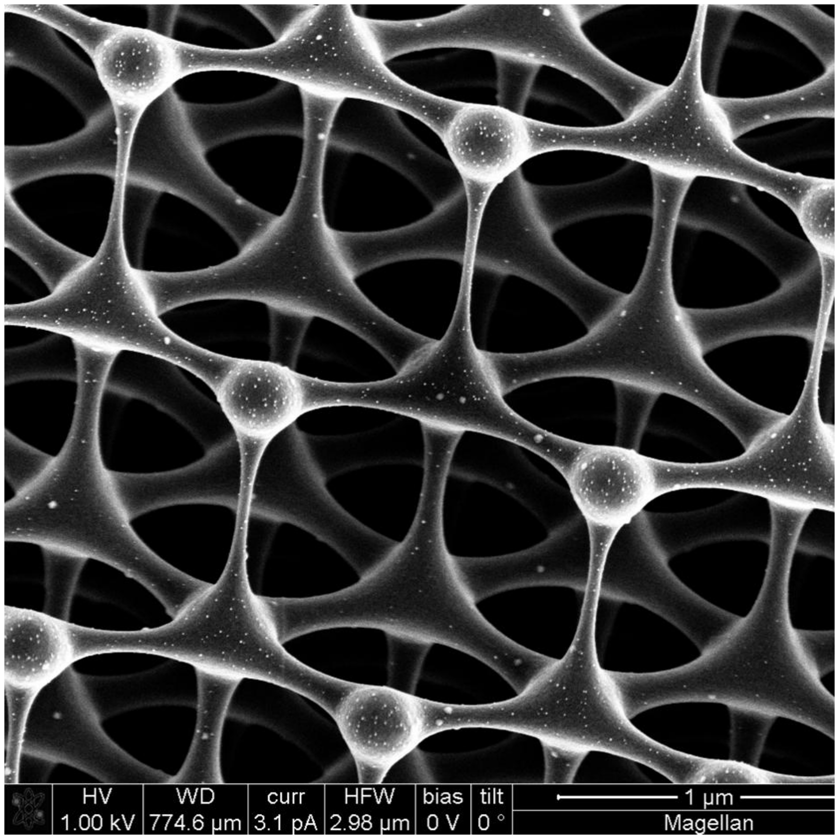
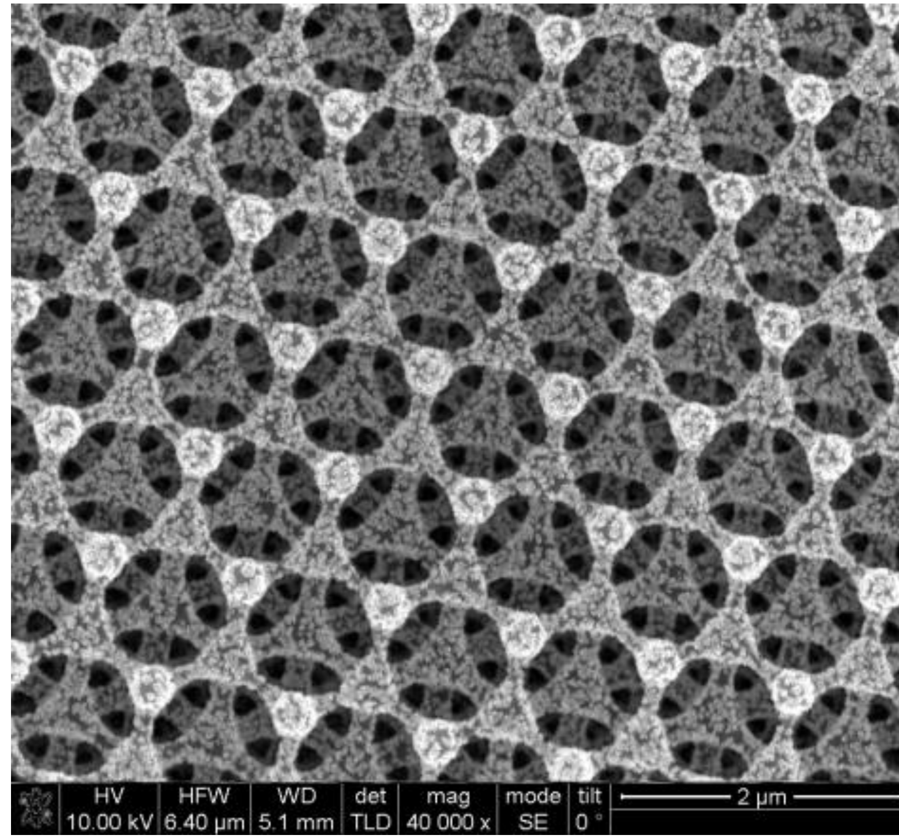
3D Pyrolyzed Carbon Electrodes For Sensing Applications

SAND2012-4547C





D. Bruce Burckel, Sandia National Laboratories
dbburck@sandia.gov

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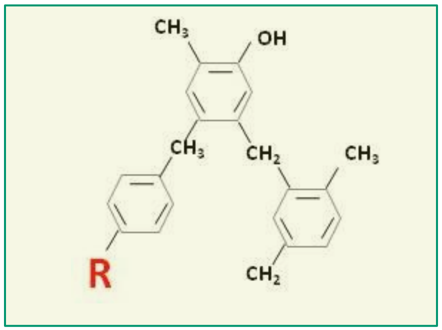
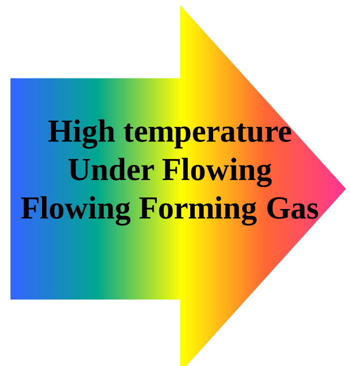
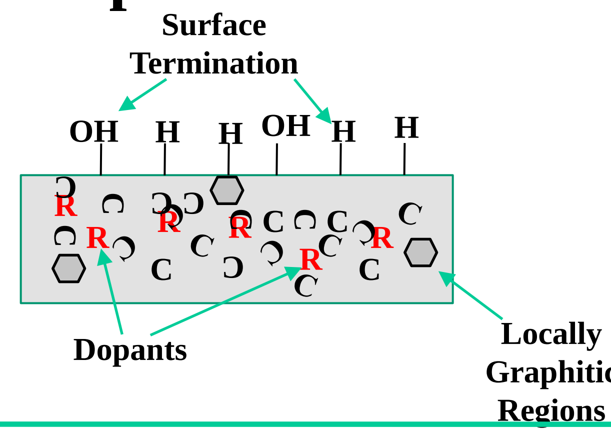
Synthesis Route to Amorphous Carbon: Pyrolysis of Organic Polymers

Organic Polymer → Pyrolysis → Amorphous Carbon

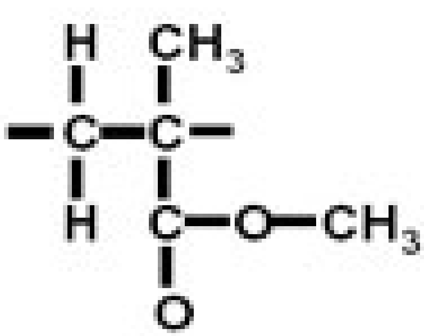




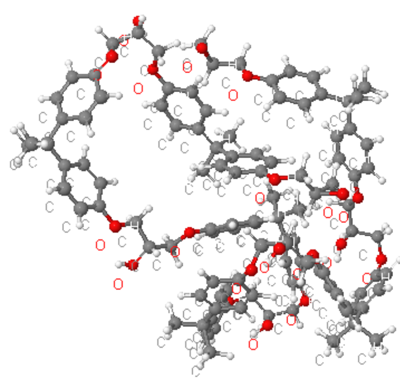


Typical Photopatternable Organic Polymers

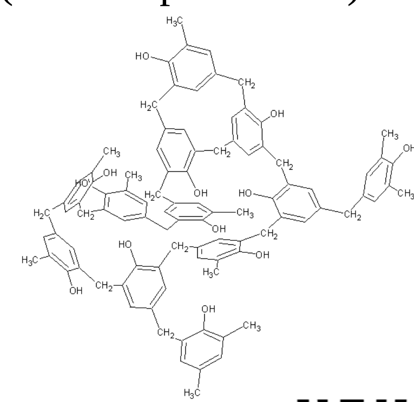
Polymethyl Methacrylate (PMMA)



Epoxide Resist (SU 8)



Phenol formaldehyde resin (novolac photoresist)



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

Wikipedia – Phenol fomaldehyde resin

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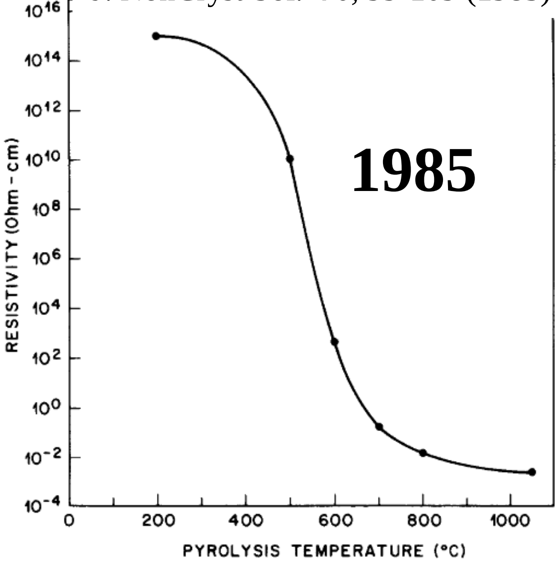
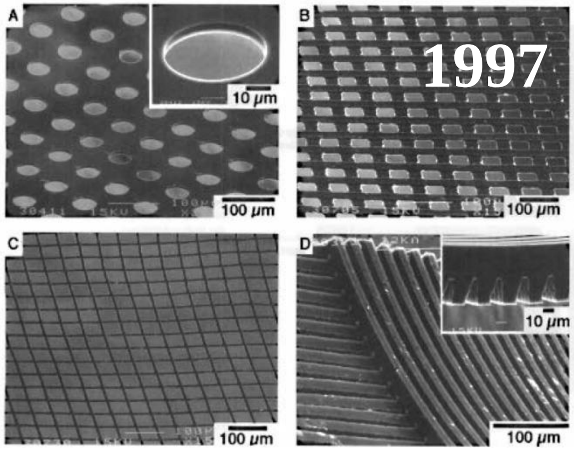
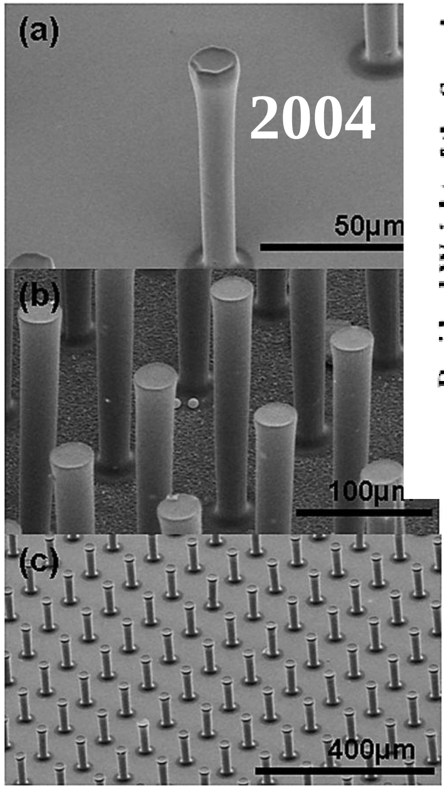
Visual History and Properties of Pyrolyzed Resist

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



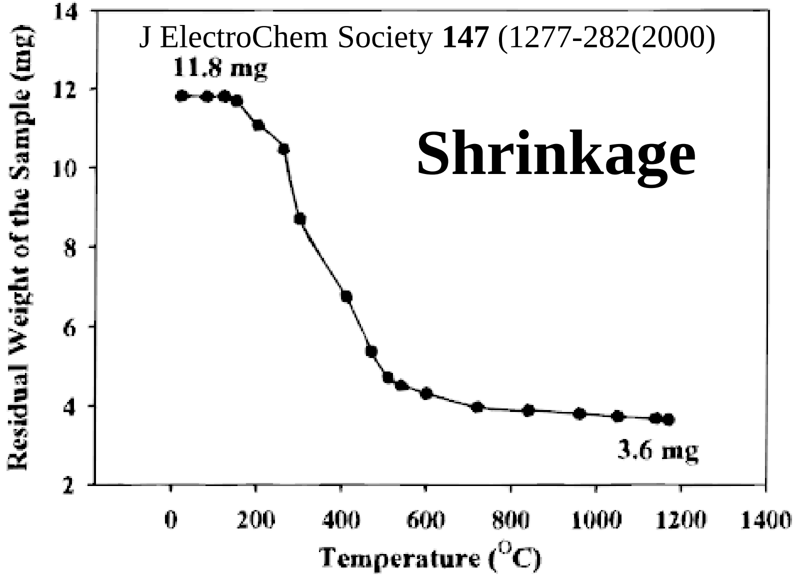


Adv. Mater. **9**, (6) 477-480 (1997)

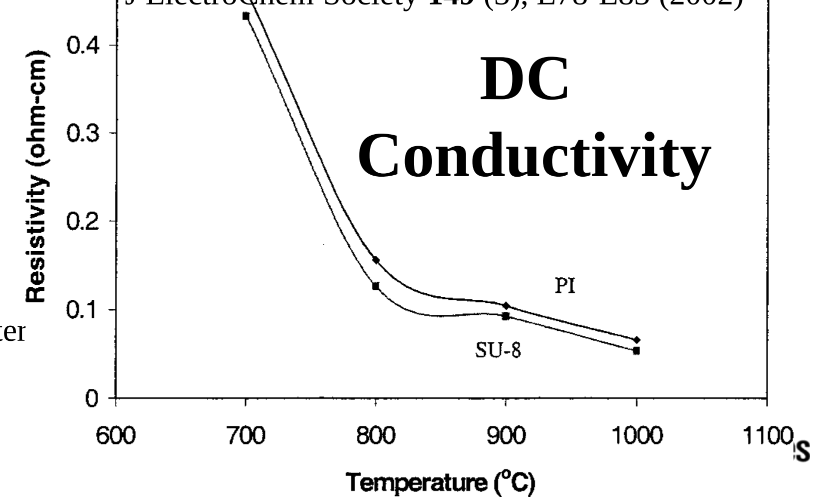


Electrochemical and Solid State Letter **7**, (11) A435-A438 (2004)

J ElectroChem Society **147** (1277-282(2000)



J ElectroChem Society **149** (3), E78-E83 (2002)



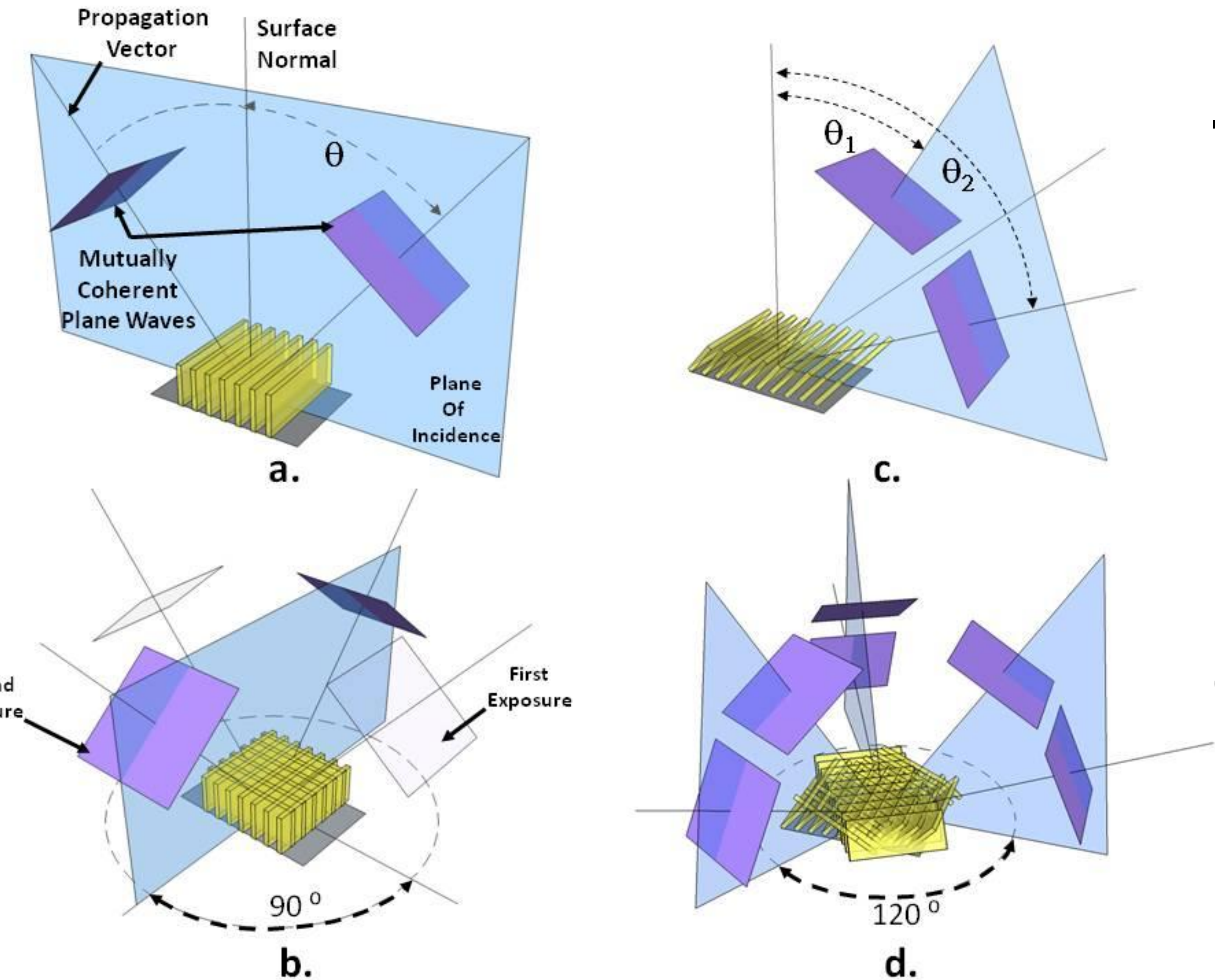
Sub-Micron 3D Resist Patterns Via Interferometric Lithography

1-D Lines

Tilted 1-D Lines

2-D Crystal

3-D Crystal



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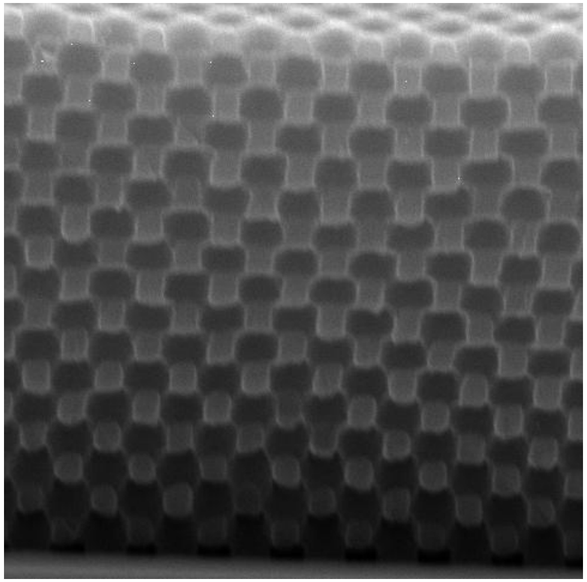
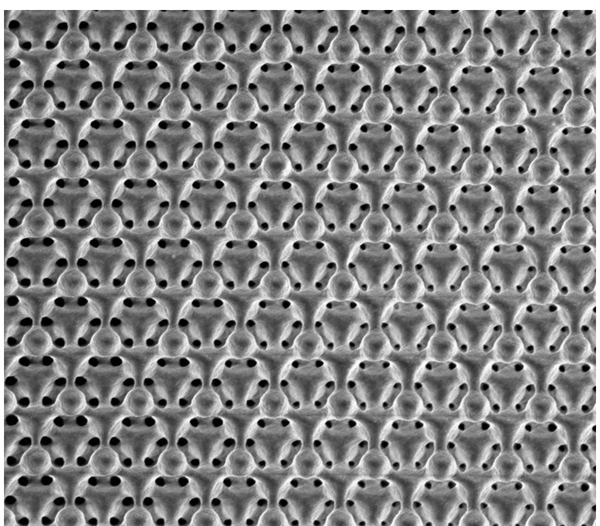
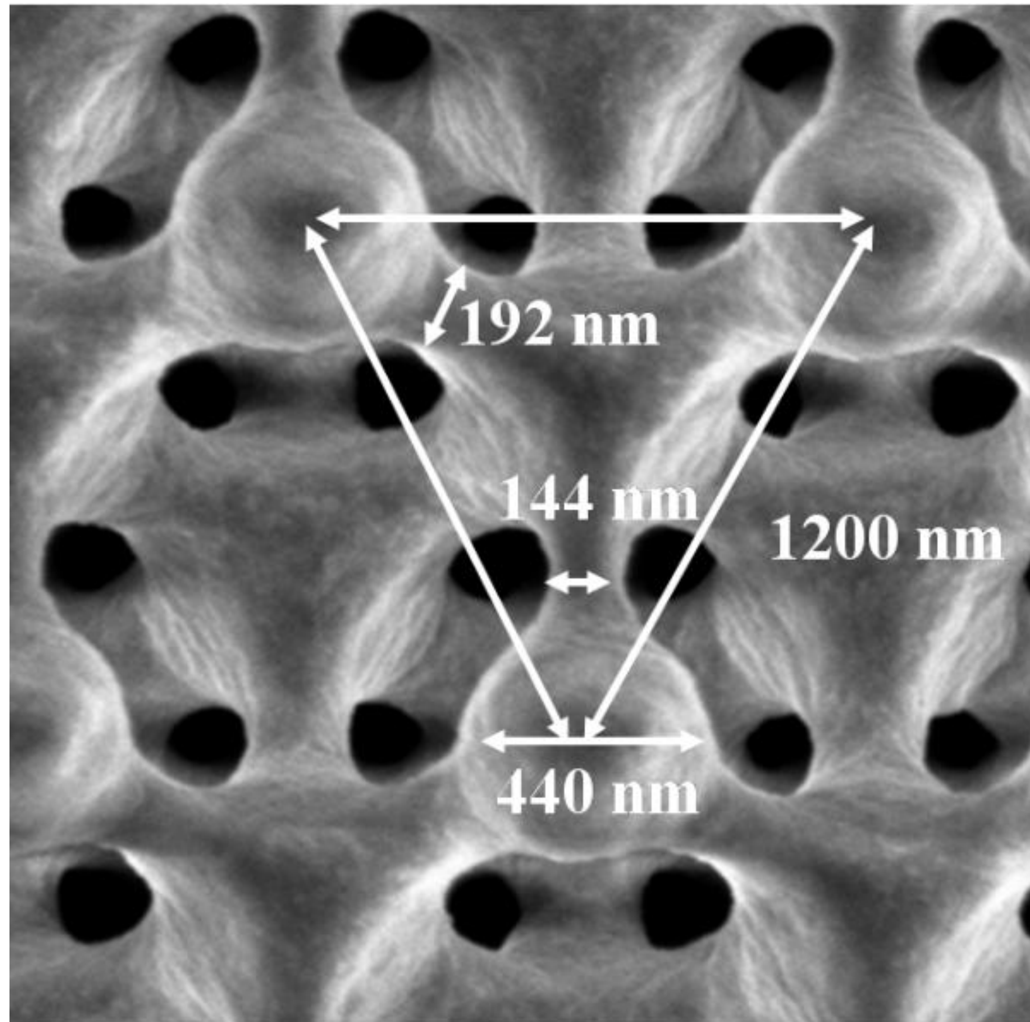
3-D Resist Structure

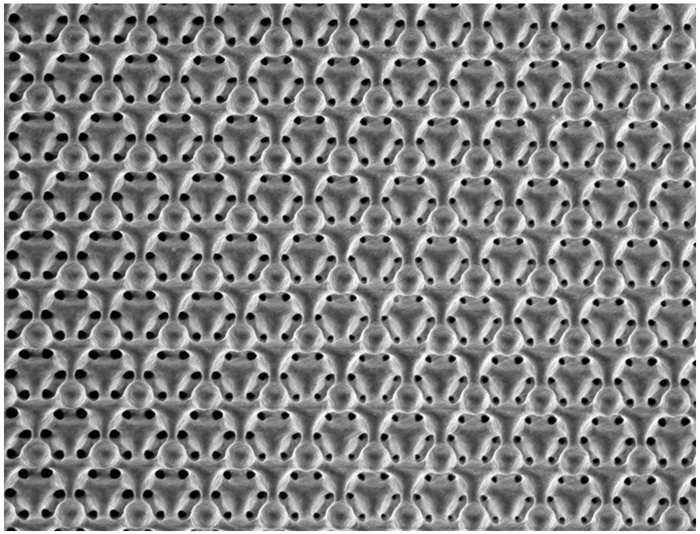


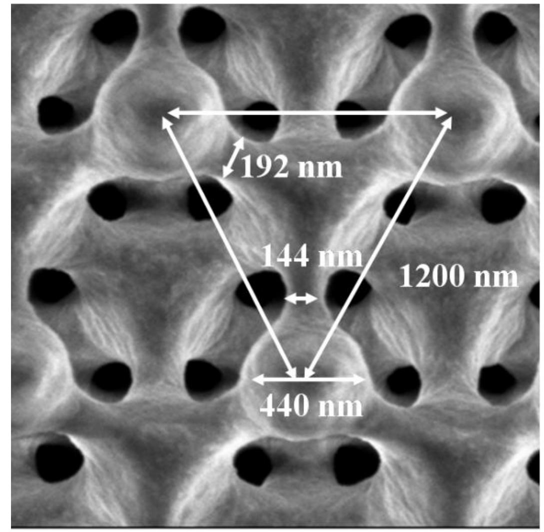




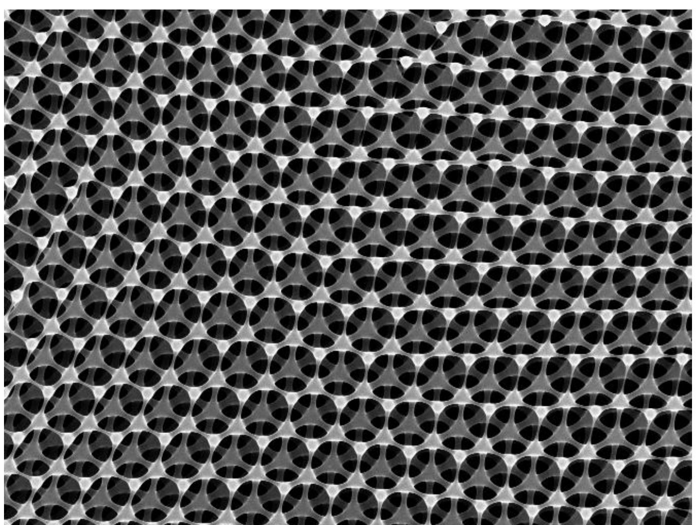
Conversion of 3-D Resist Structure to 3-D Carbon Structure

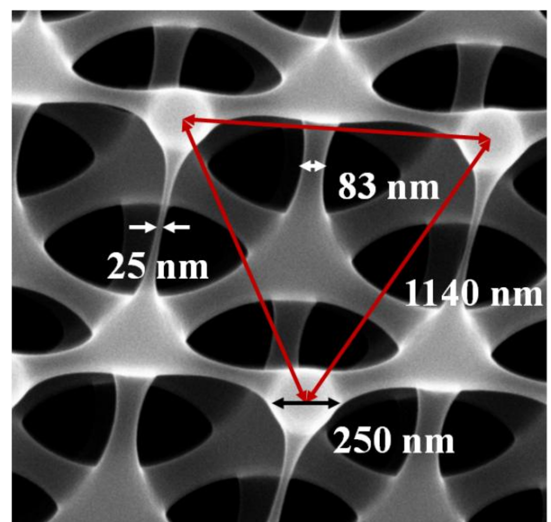
Resist





Carbon





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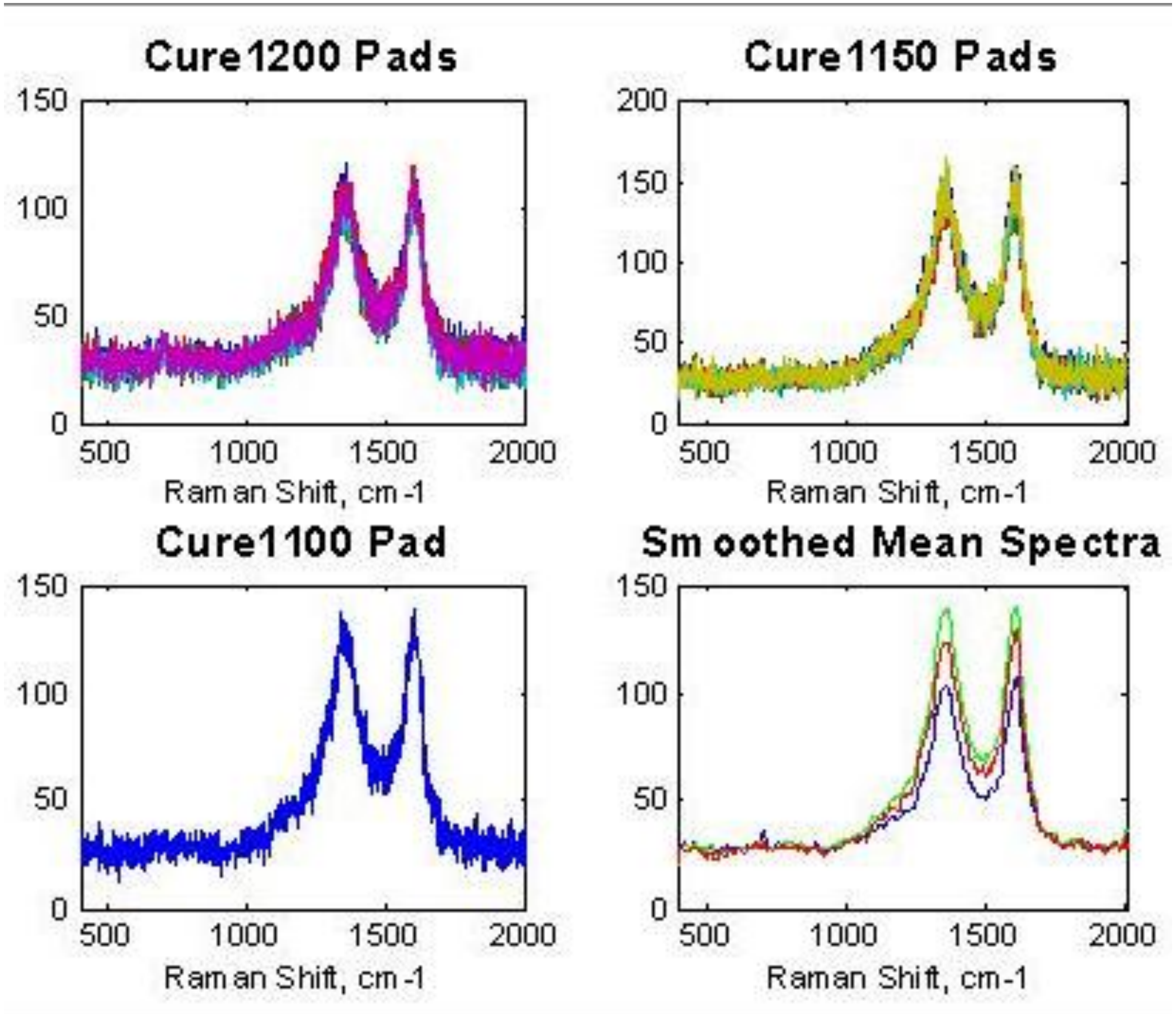
Properties of 3-D Carbon Scaffolds

Raman Spectroscopy of Pyrolyzed Resist

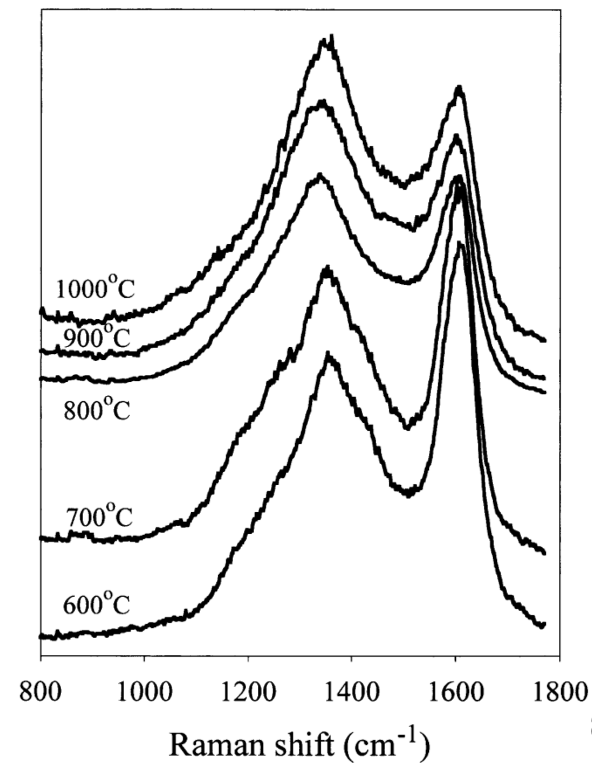


Comparison To Literature Values

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

1344 cm^{-1} 1591 cm^{-1} ← **HOPG**

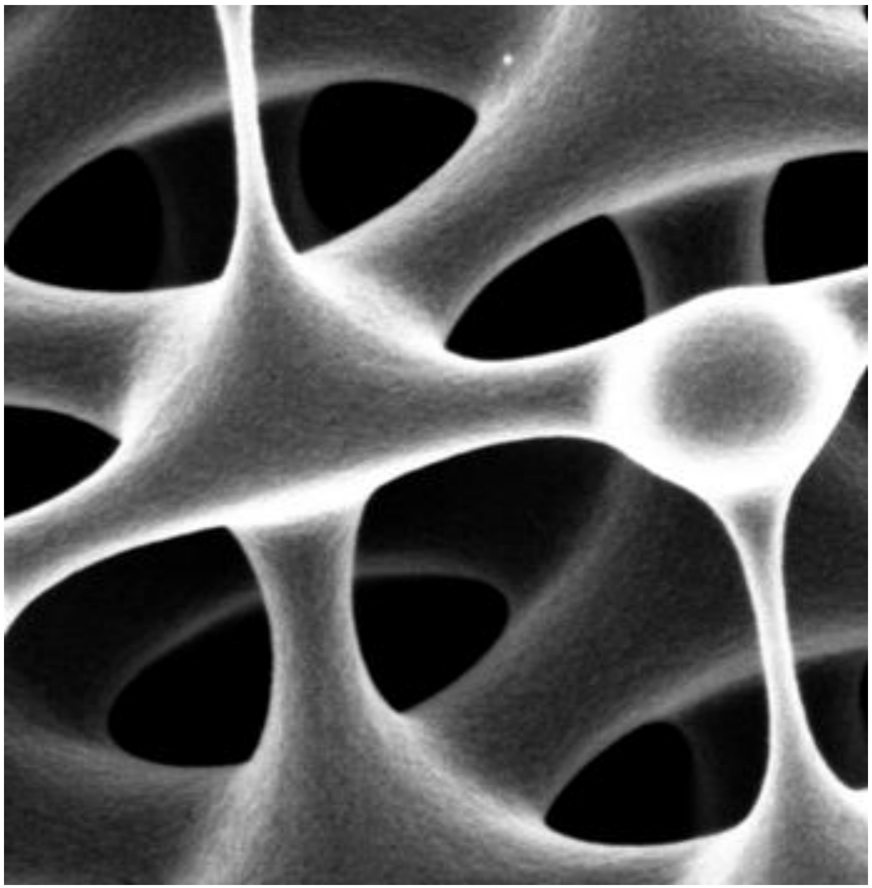
1367 cm^{-1} 1622 cm^{-1} ← **Disorderd C**

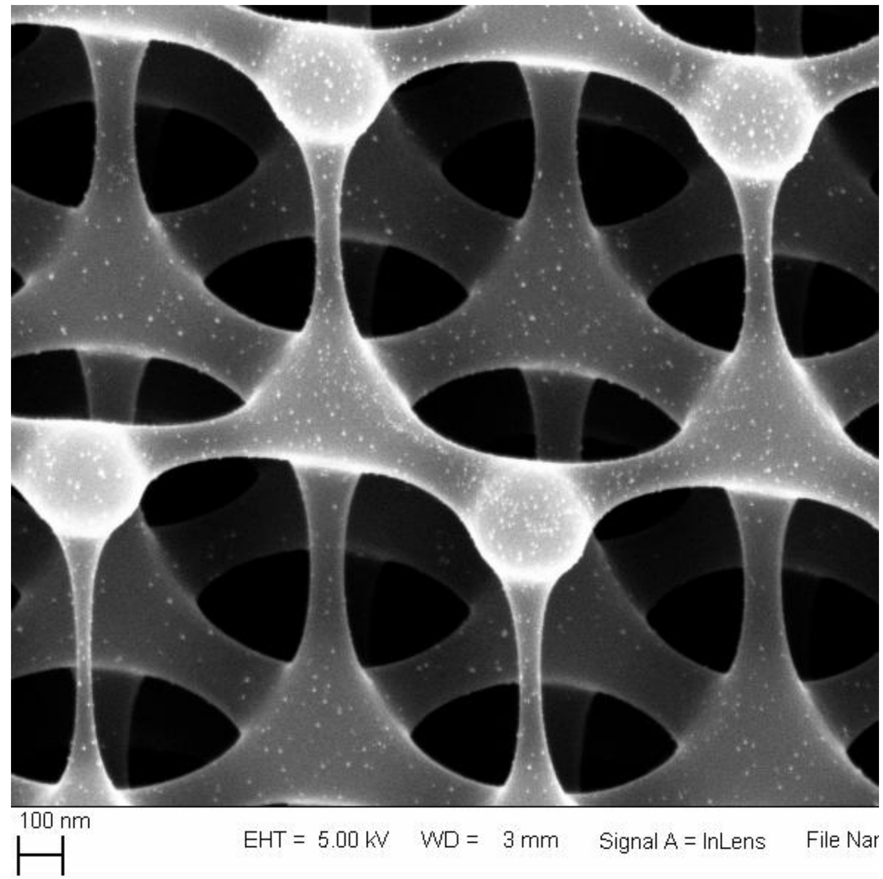


Nearly Atomically Smooth Surface

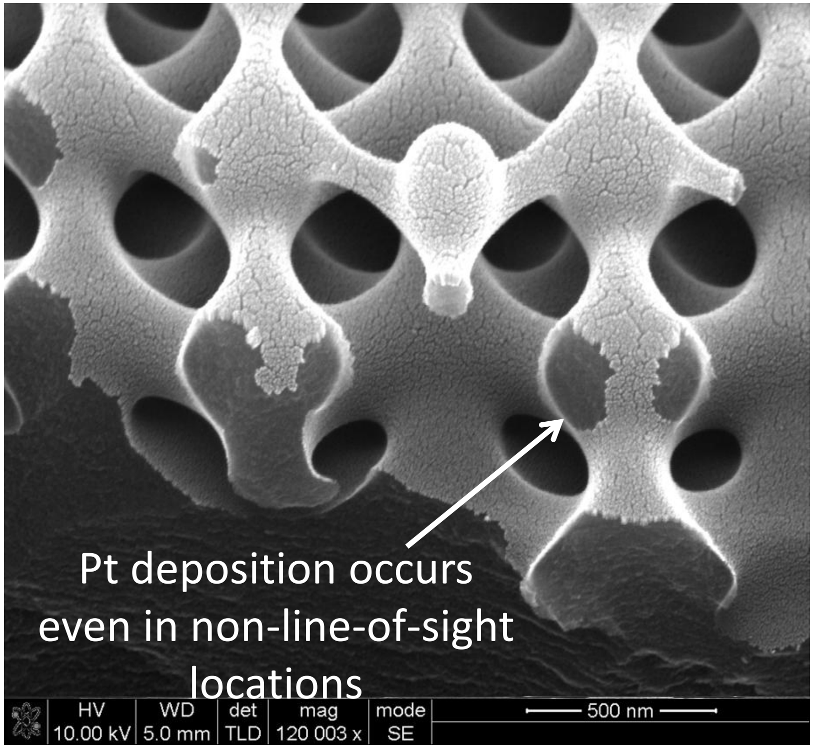
Smoothness of bare carbon – no preferential nucleation sites

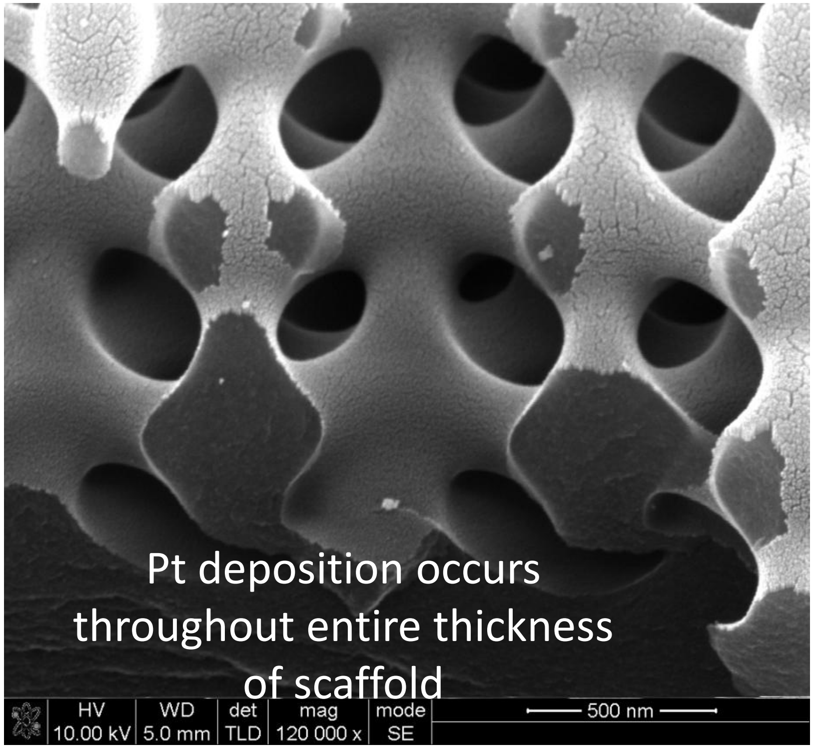
Ultra small, uniform NP formation





Conformal Coating During Sputtering





Pt sputtered @ 1A/s

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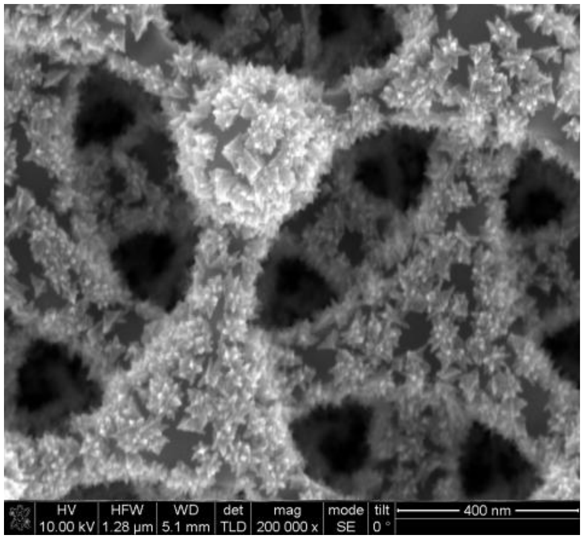
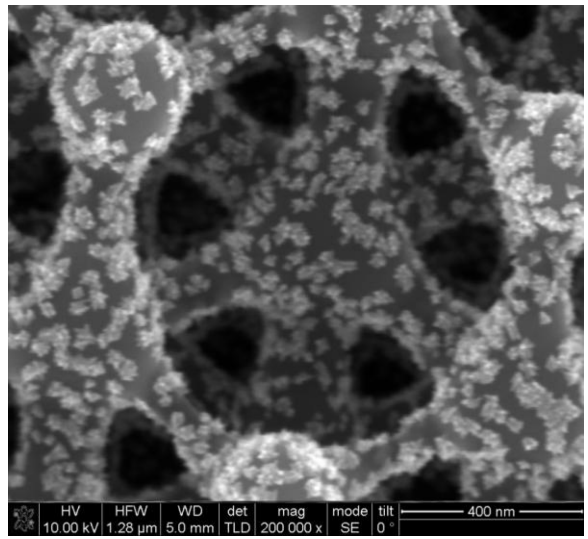
Electrodeposition Conditions Impact Nanoparticle Morphology

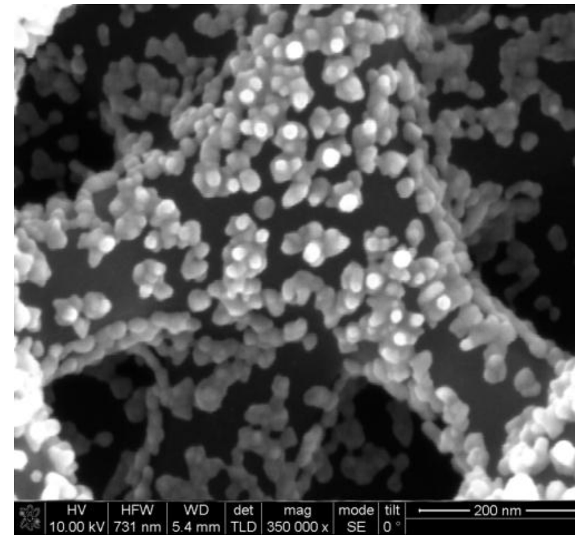


100 s Deposition



50 s Deposition

-0.65 V



100 s Deposition

-0.45 V

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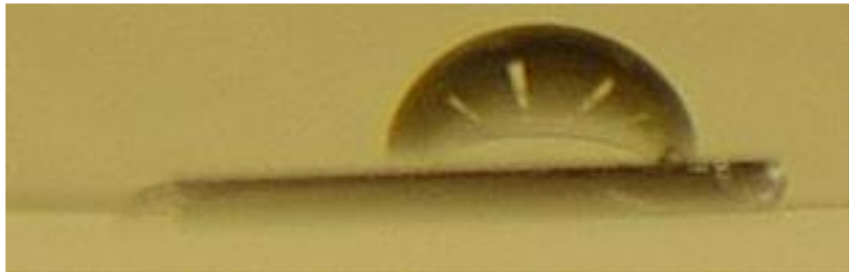
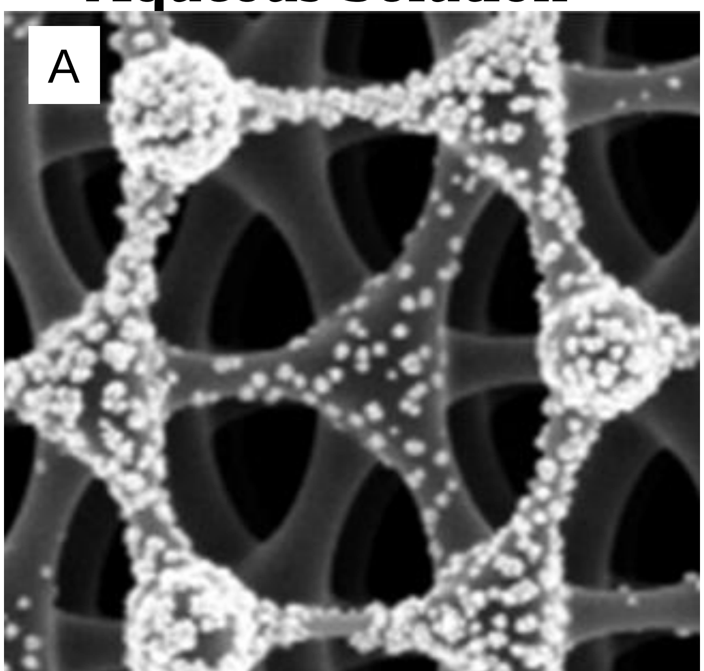
Impact of Carbon Hydrophobicity

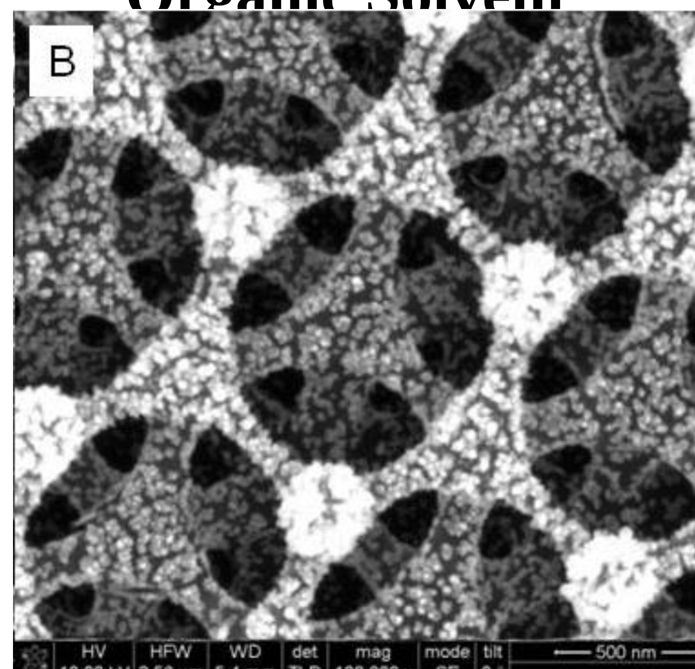
3D carbon
is hydrophobic



Deposition from Aqueous Solution



Deposition from Organic Solvent

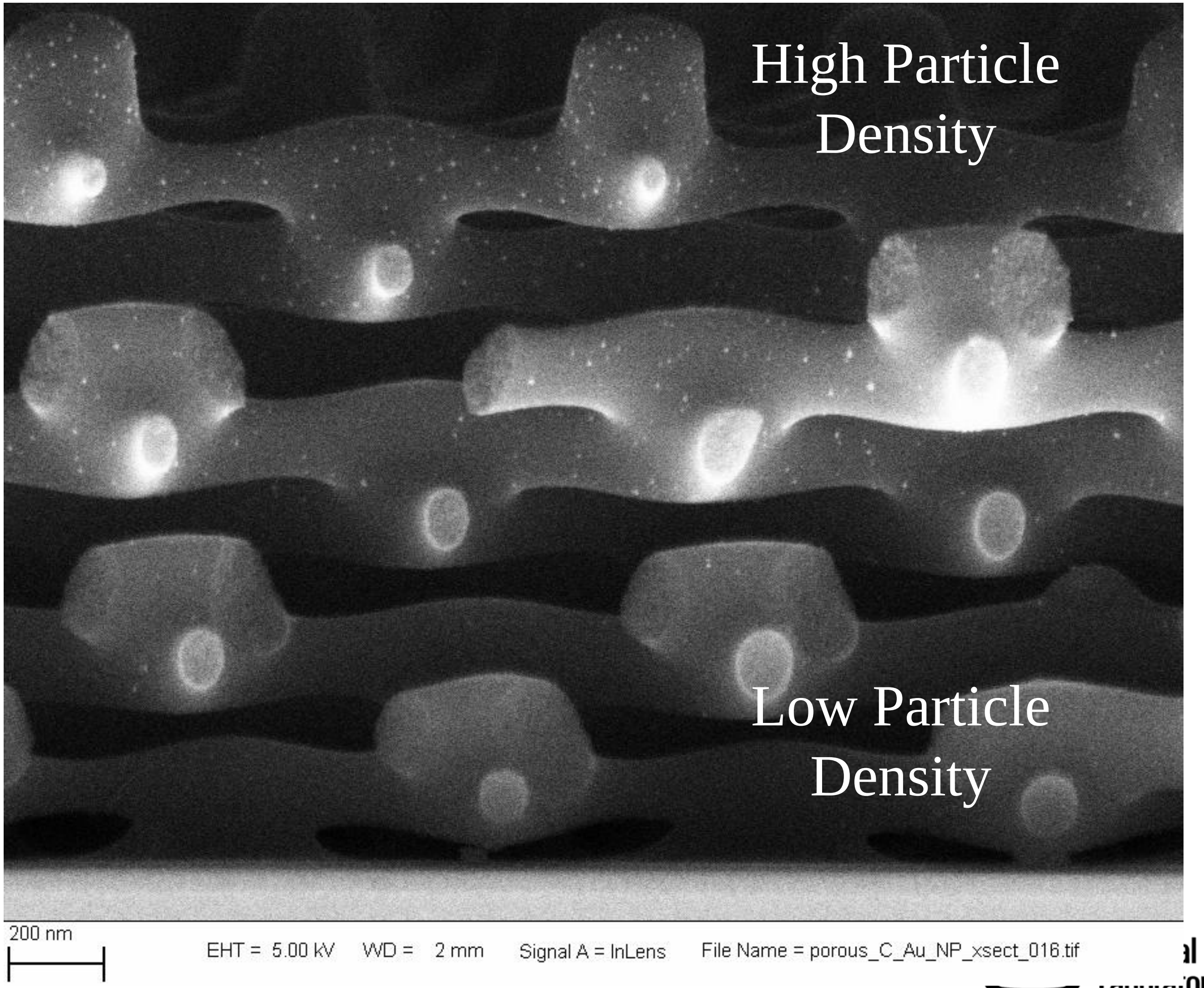


Vertical vs. Horizontal Shrinkage

Significant vertical shrinkage

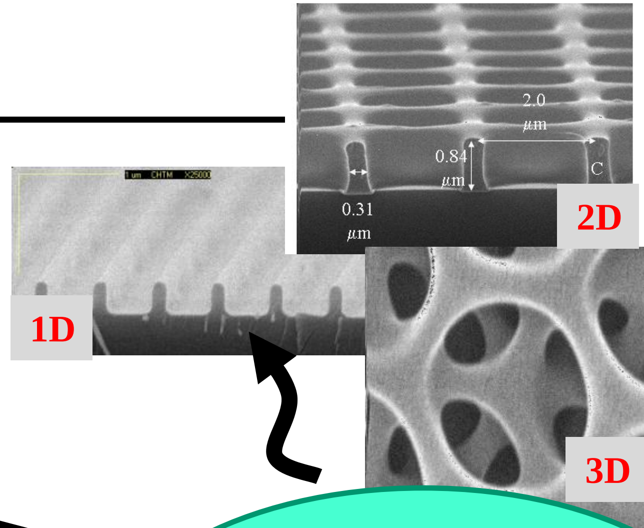
Extremely small, highly uniform NPs

Inhomogeneous wetting

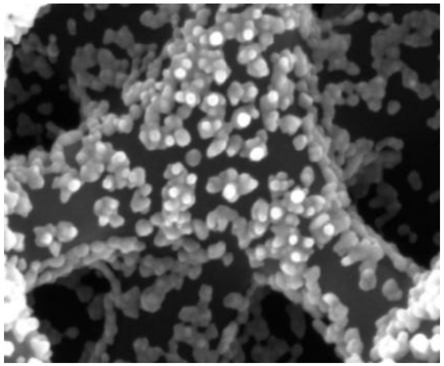


Interferometrically Patterned Carbon

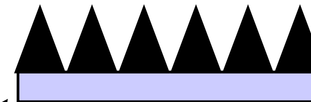
Carbon Photonics



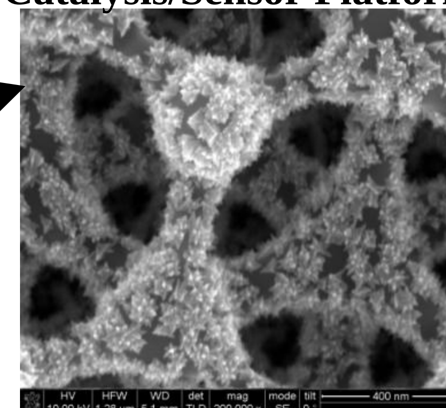
Ultra-Capacitor/Energy Storage



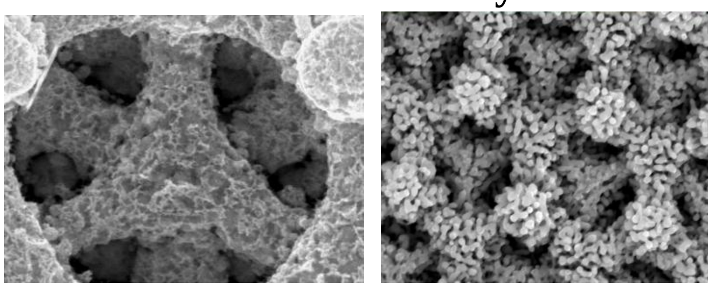
Structured Thermal Emitters



High Surface Area Catalysis/Sensor Platform

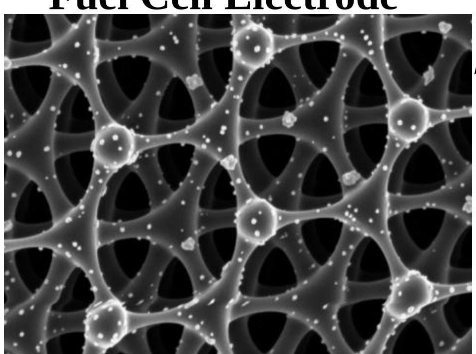


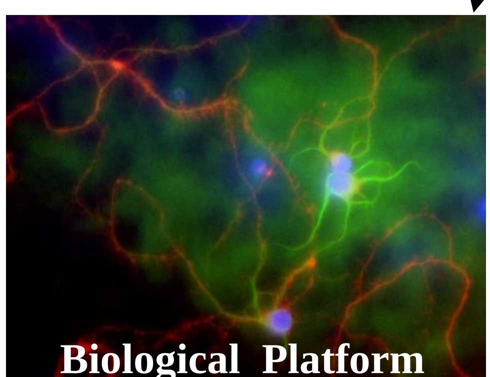
Hierarchical Porosity

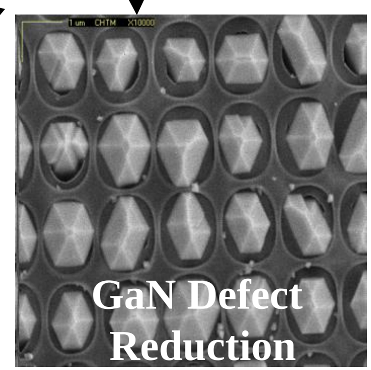


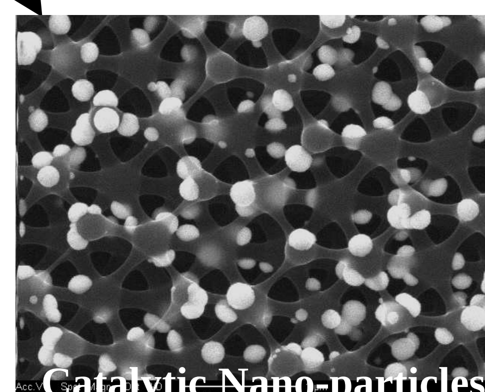
Convert 1D, 2D and 3D sub-micron photoresist patterns created with interferometric lithography into pyrolytic carbon

Fuel Cell Electrode







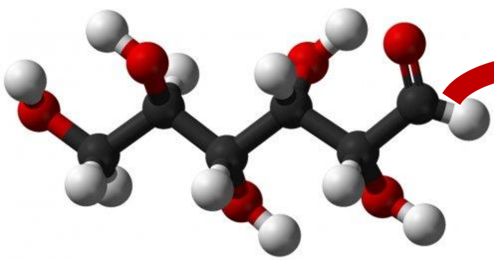


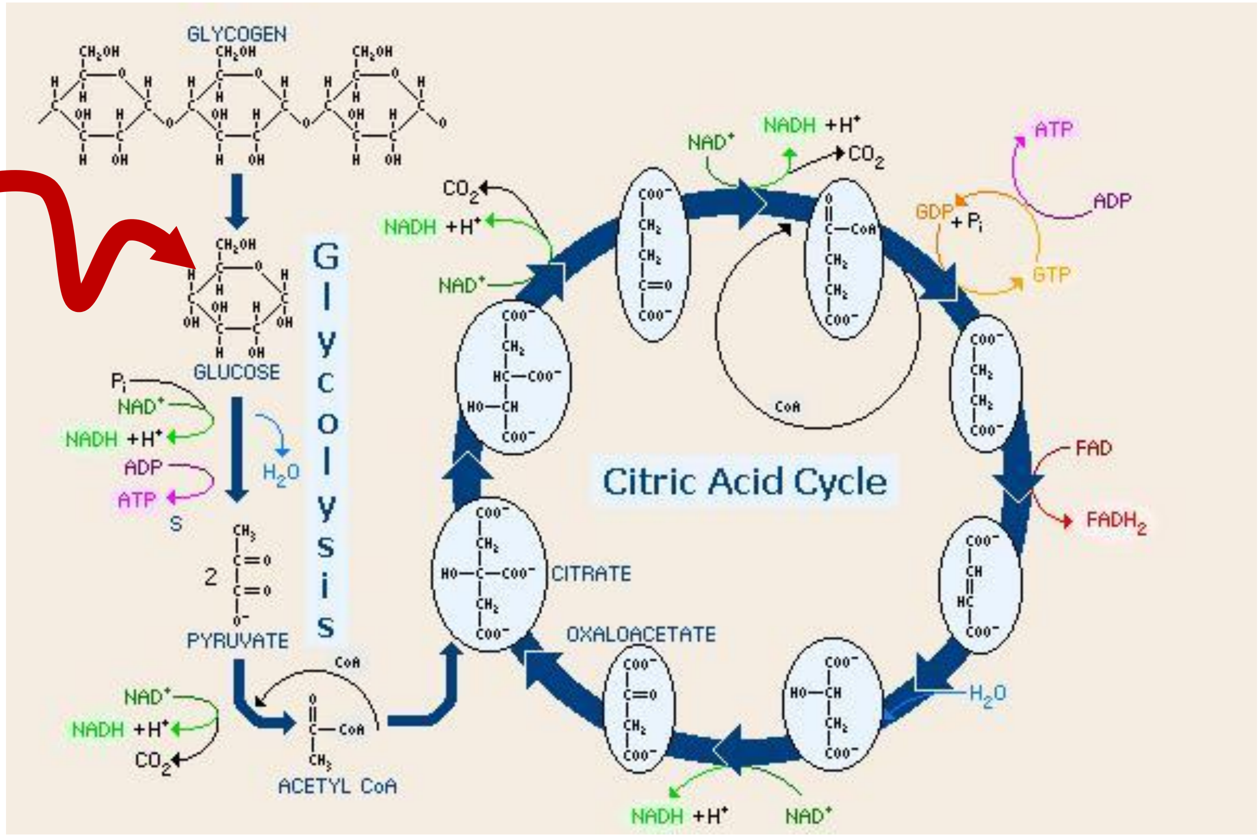
3-D Carbon Electrode Application: Non-Enzymatic Detection of Glucose

Biosensors and Bioelectronics, v. 26, pp 3641-3646 (2011)

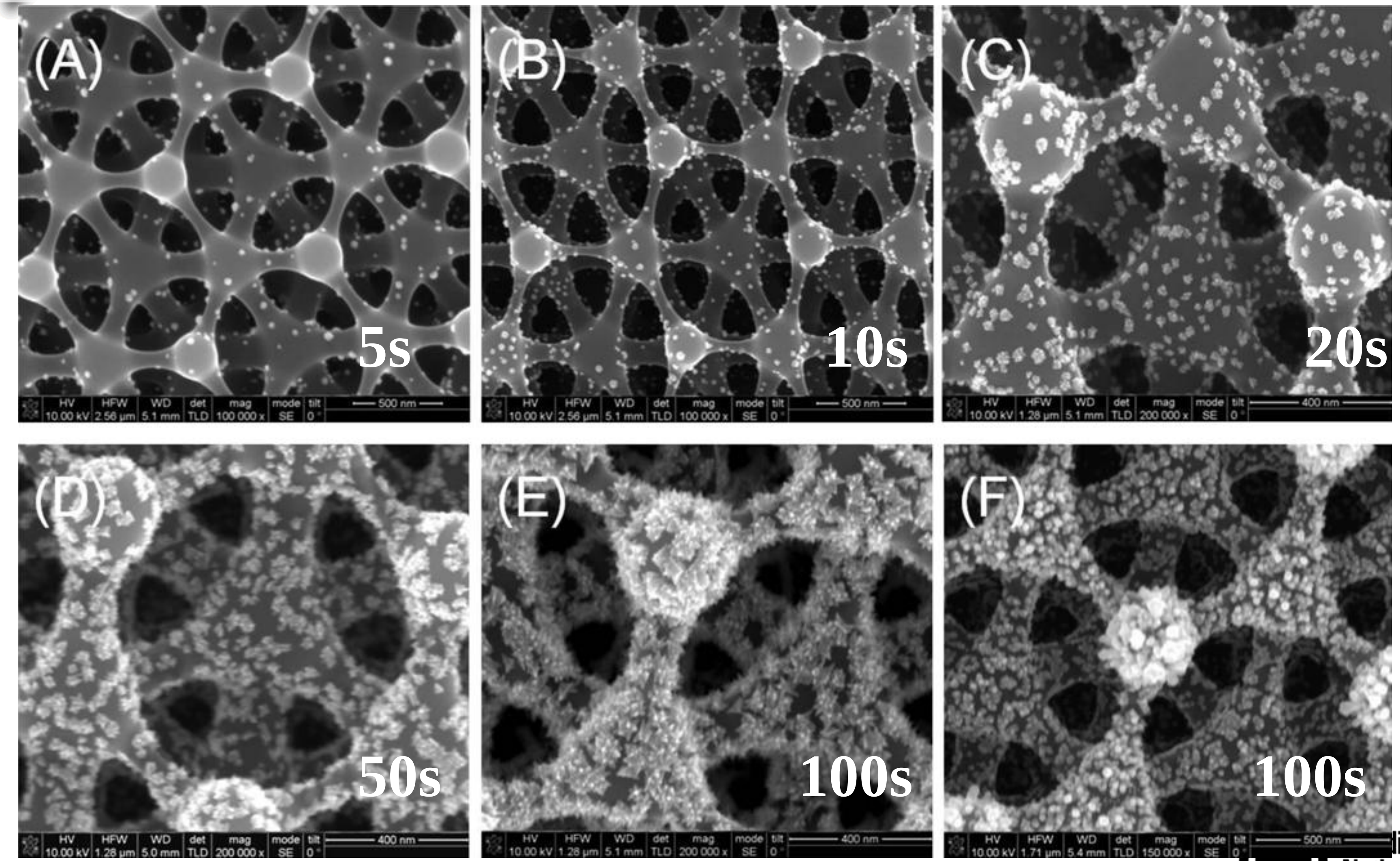
Why is Glucose Oxidation Important?

Glucose Molecule





Electrodeposition of Pd Nanoparticles



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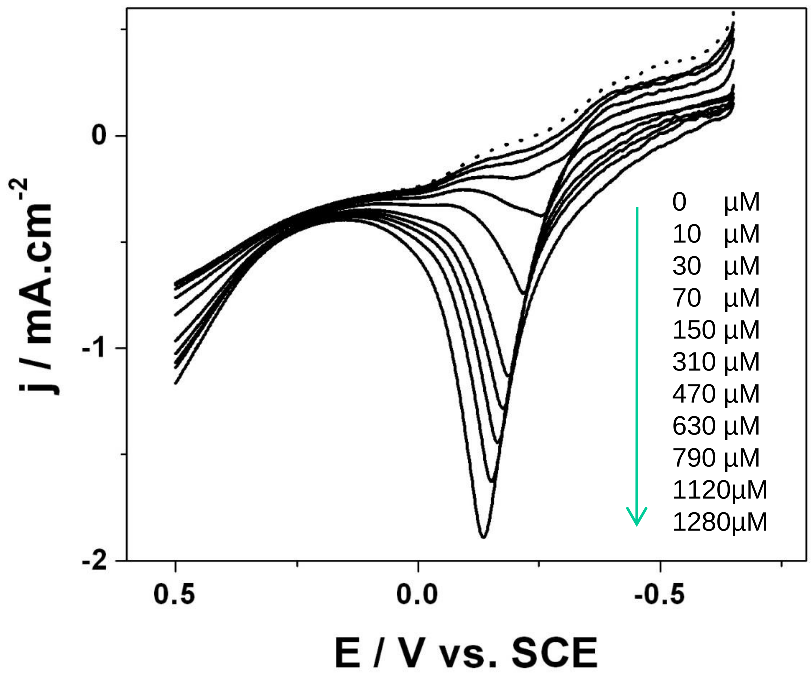
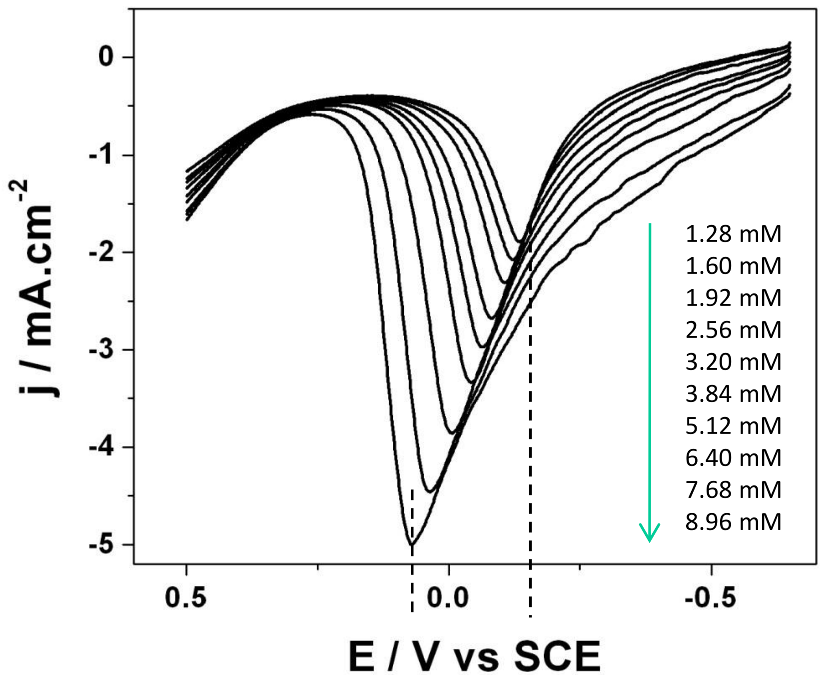
Electrode Response to Glucose Additions

μm aliquots



mm aliquots

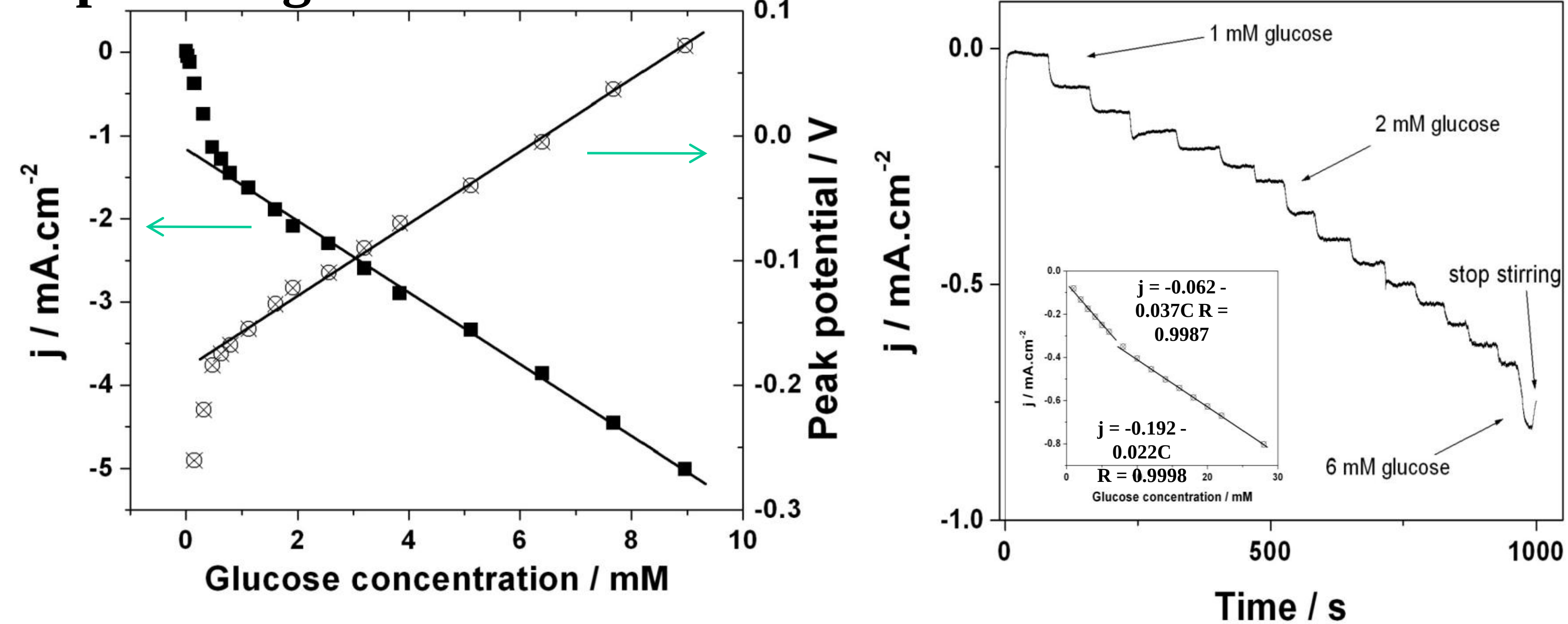


Linear scan voltammograms of Pd/Porous in 0.1 M NaOH + x M glucose. Pd deposition: 100s, Scan rate: 20 mV/s.

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

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)

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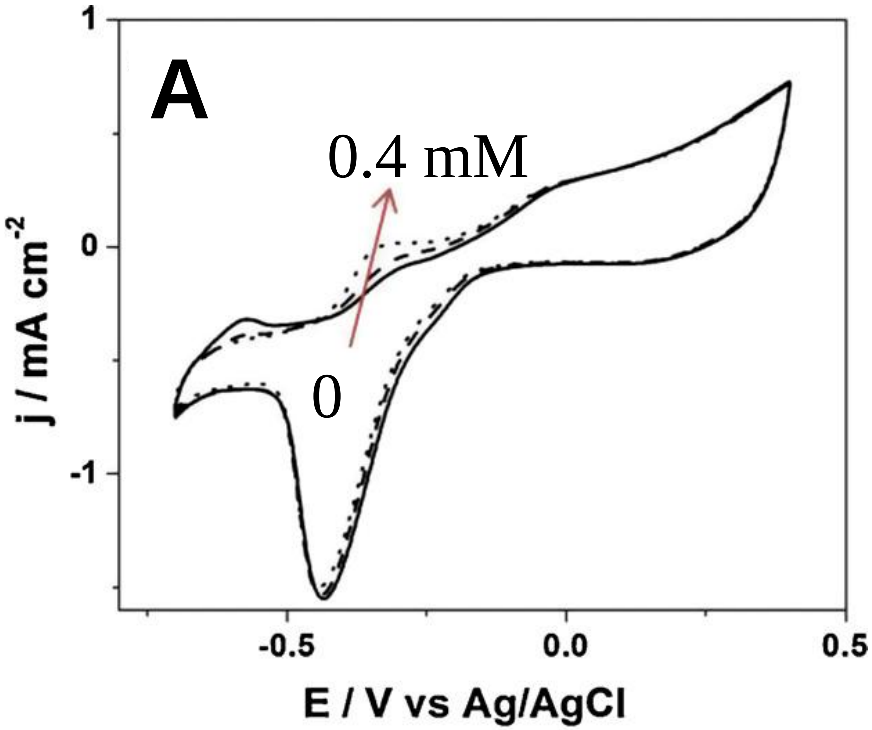
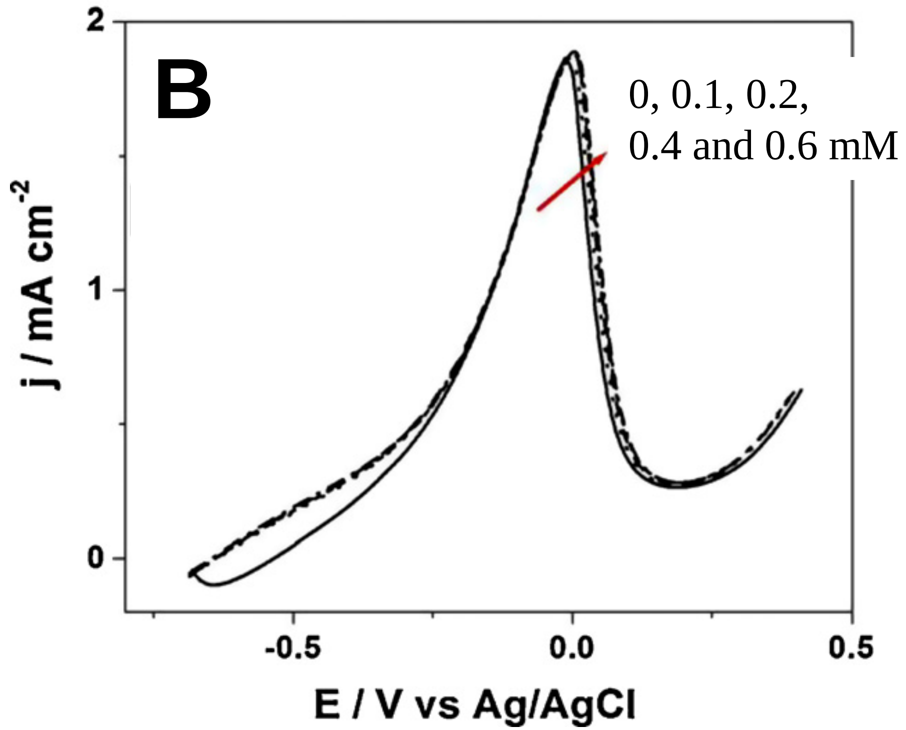
Electrode Response *vs* Ascorbic Acid

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

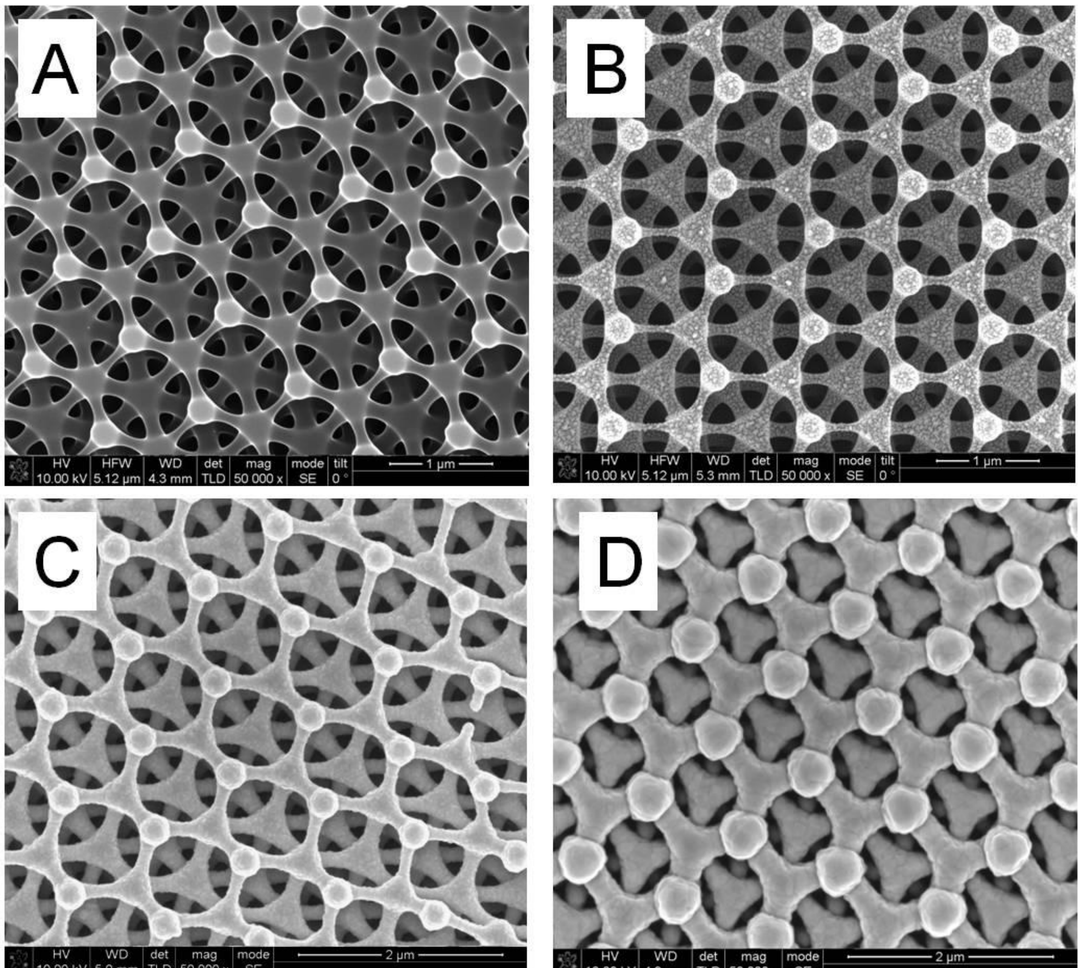
Laboratories

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

Chem. Commun., v. 47, pp. 9858-9860 (2011).

PVD Ag Scaffold Modification

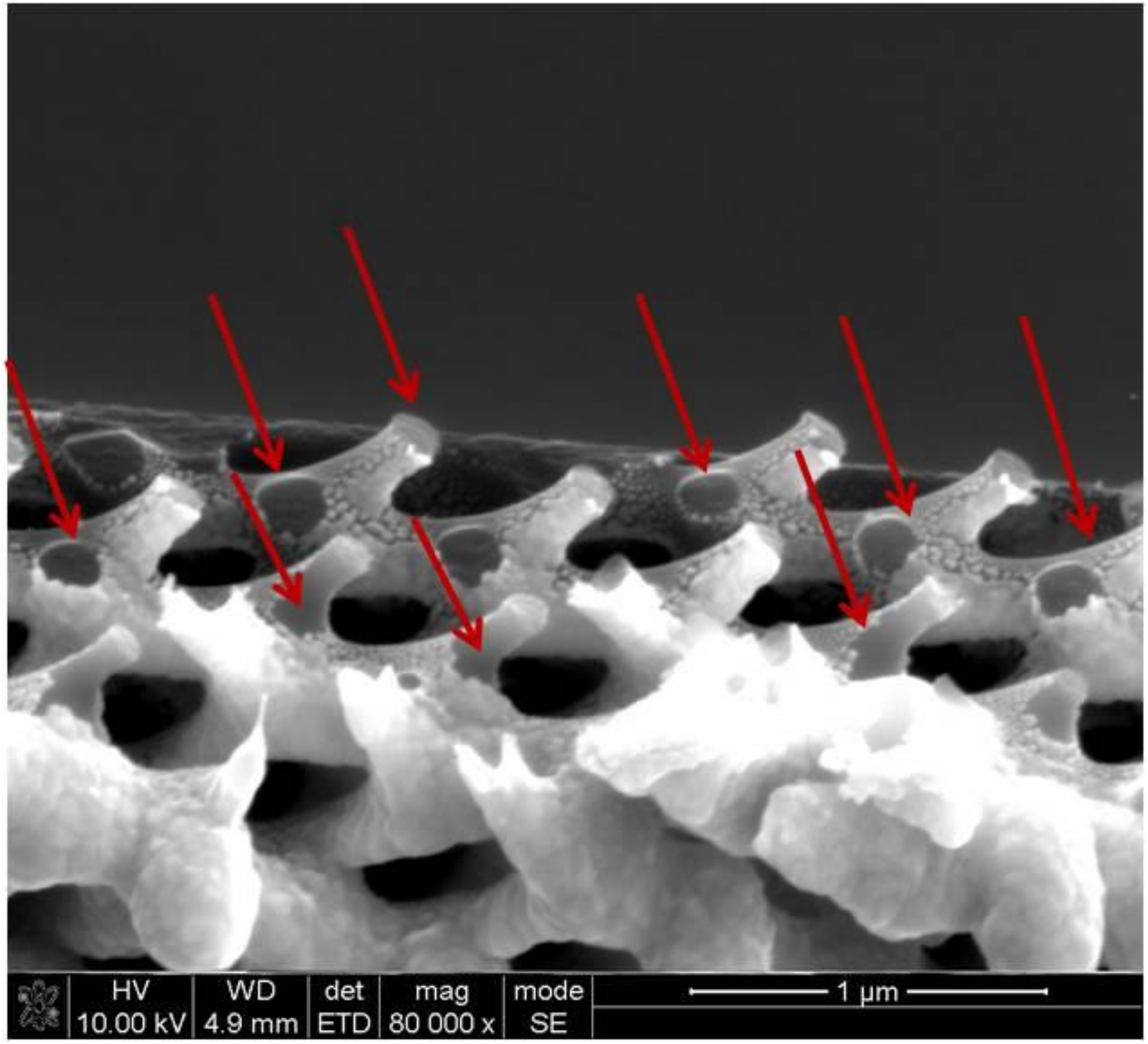
Sputtered Ag (1 Å/s)

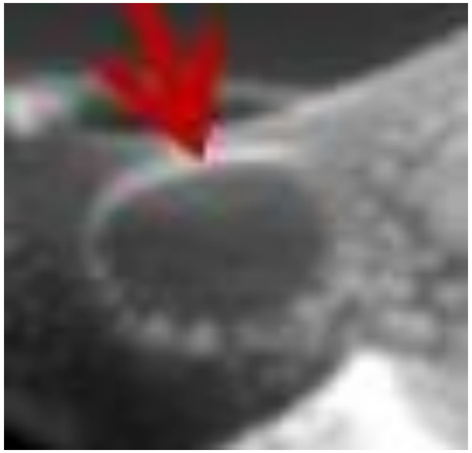


Sputtering Time

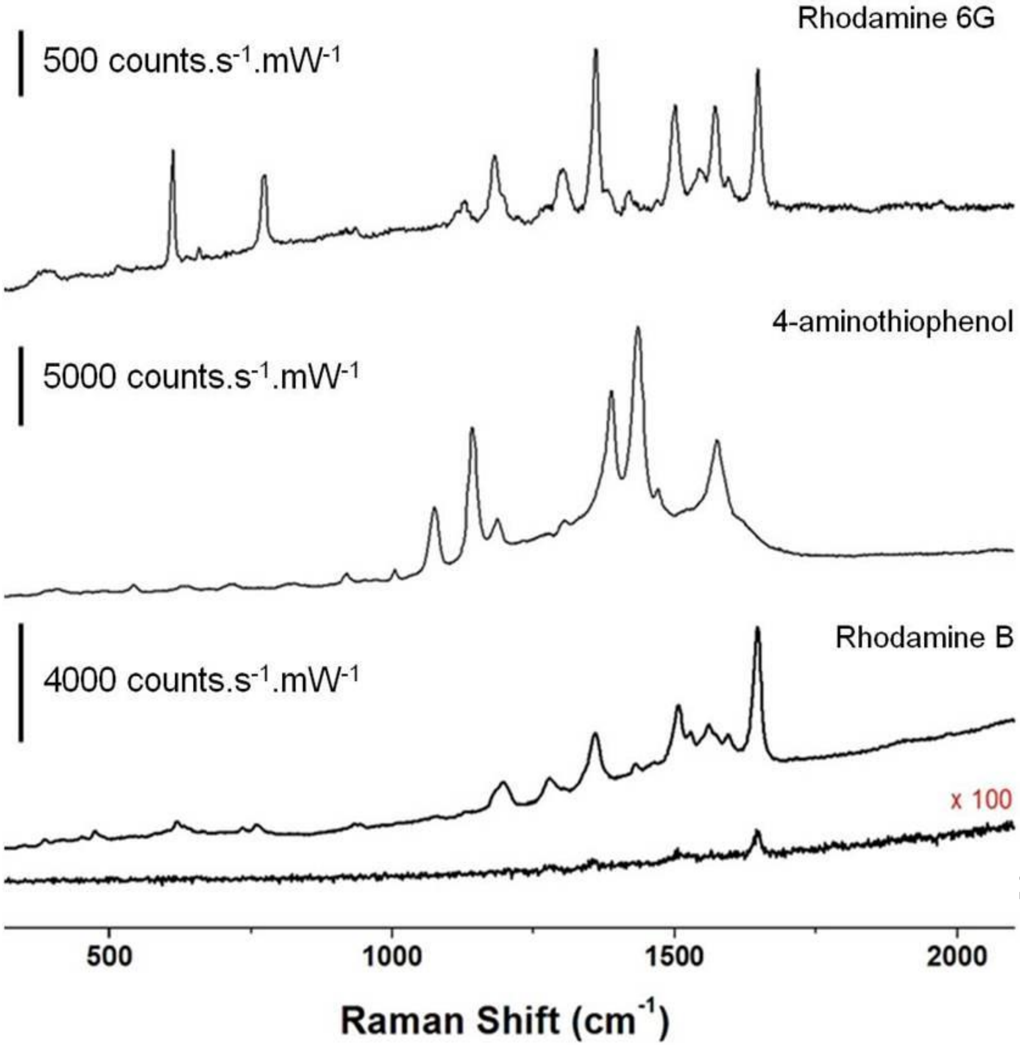
A – 0 (bare carbon)
B – 150 s
C – 1100 s
D – 3300 s

Sputtering coats bottom side too!





SERs Signals for 3 Organic Molecules

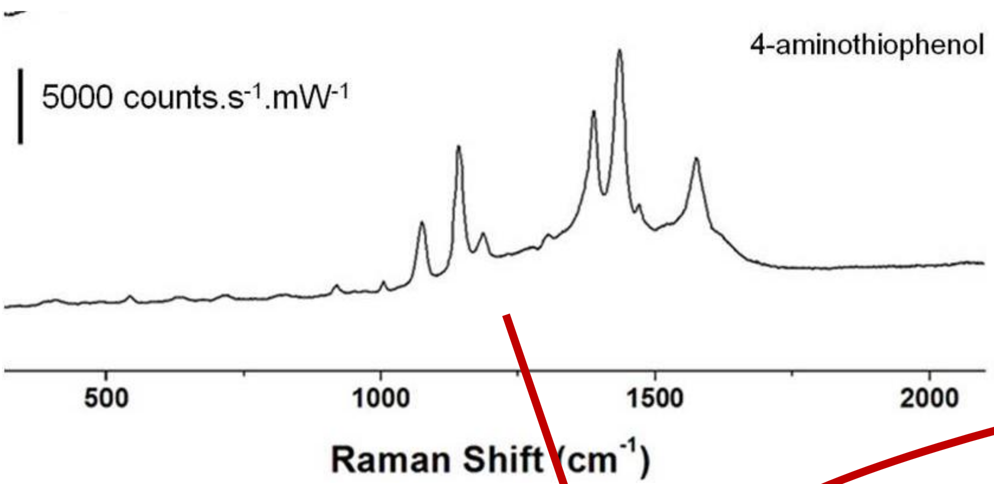


Increase in signal not due to surface area.

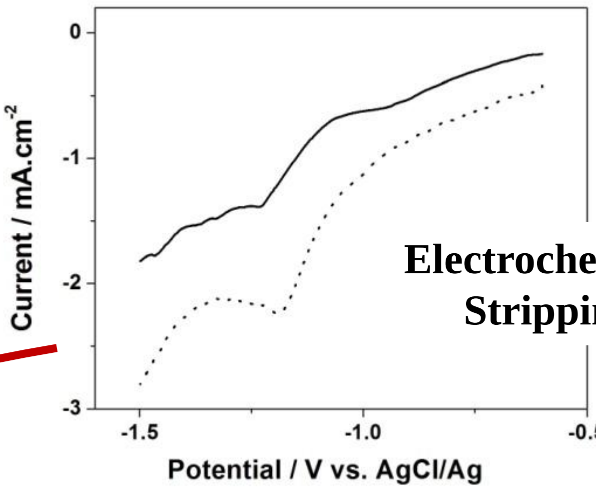
Only a 4x increase in surface area between planar carbon and 3D carbon with identical sputtering times.

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

Enhancement Factor: 4-aminothiophenol



Measure # of molecules



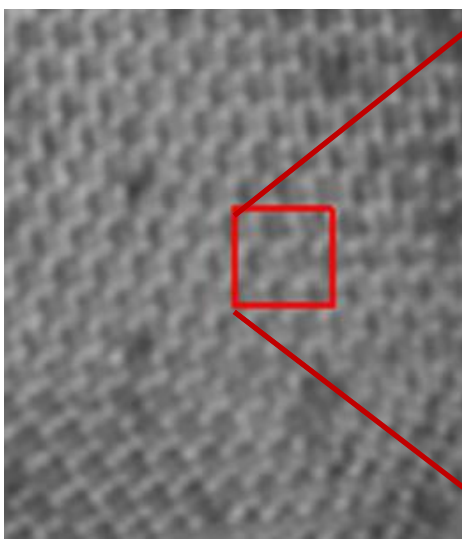
Electrochemical Stripping

Compared to response of neat control solution

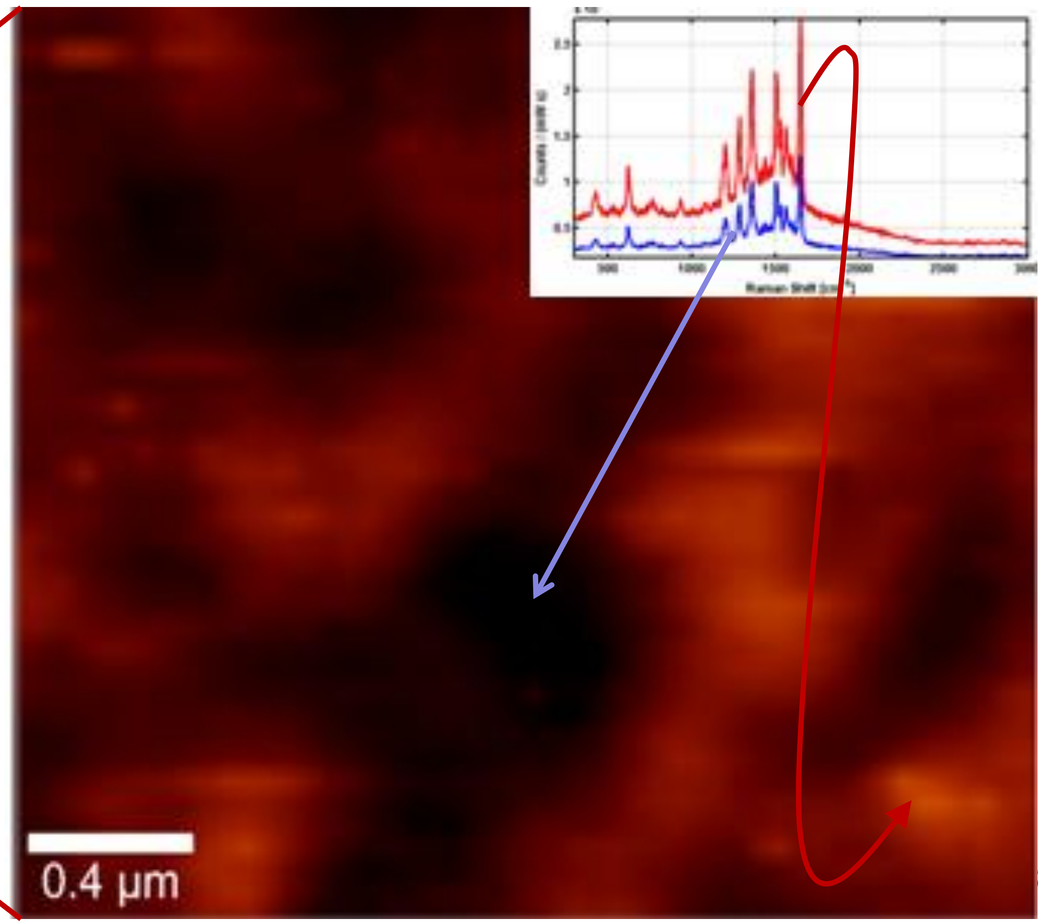
No Spatial Hotspots

Spatially resolved Raman Mapping

5 µm x 5µm Area



$$\frac{\text{Max Signal}}{\text{Min Signal}}$$ only ~ factor of 2



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.

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

- Demonstrated SERS platform with spatially homogeneous enhancement factor of ~ $5x10^9$.

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Acknowledgements

- Ronen Polsky, Xiaoyin Xiao, Cody Washburn, Thomas Beechem and Dave Wheeler (SNL)
- Alex K. Raub and Steve Brueck (UNM)

Questions?

dbburck@sandia.gov

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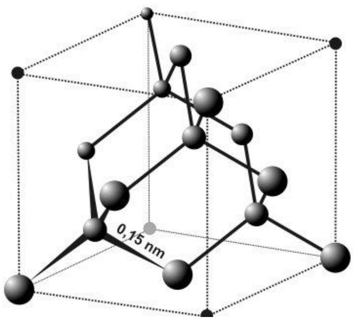
Backup Slides

Faces of Carbon

C_6

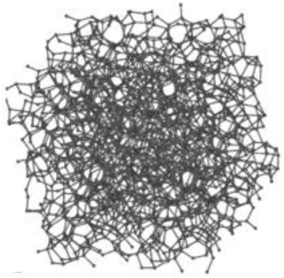
- Highest elemental melting point (sublimes at ~3900K)
- Forms ~ 10 million different compounds
- Resistant to acids, bases and all but the strongest oxidizers
- Biologically compatible

sp^3 bonds
Diamond



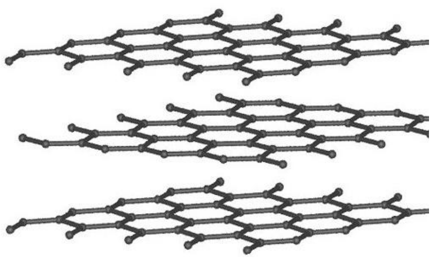
Hardest material
Good abrasive
Electrical insulator
Good thermal conductor
Optically transparent

Amorphous Carbon



High Modulus
Tunable DC Conductor
Optically Opaque

sp^2 bonds
Graphite

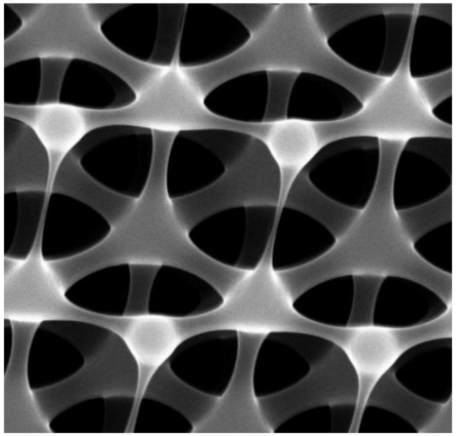


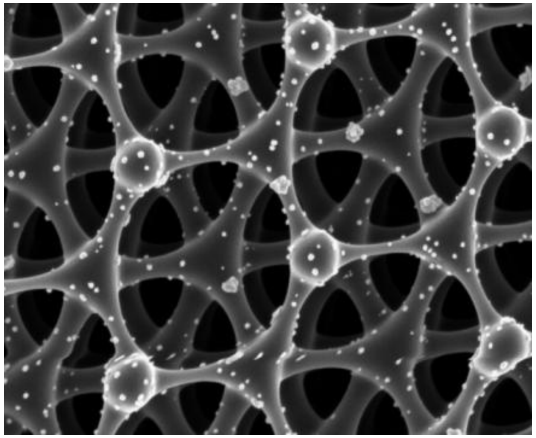
One of the softest materials
Good lubricant
Electrical Conductor
Can act as thermal insulation
Optically opaque

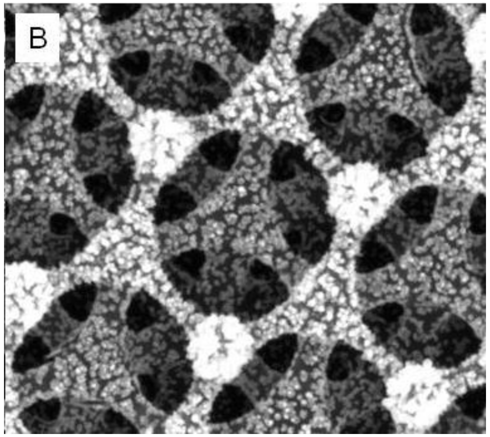
Images from Wikipedia

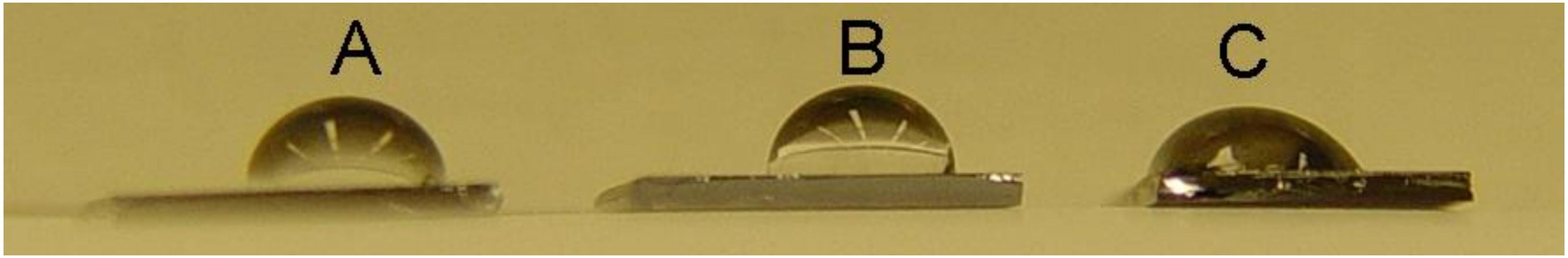
Laboratories

Lithographically Patterned Carbon



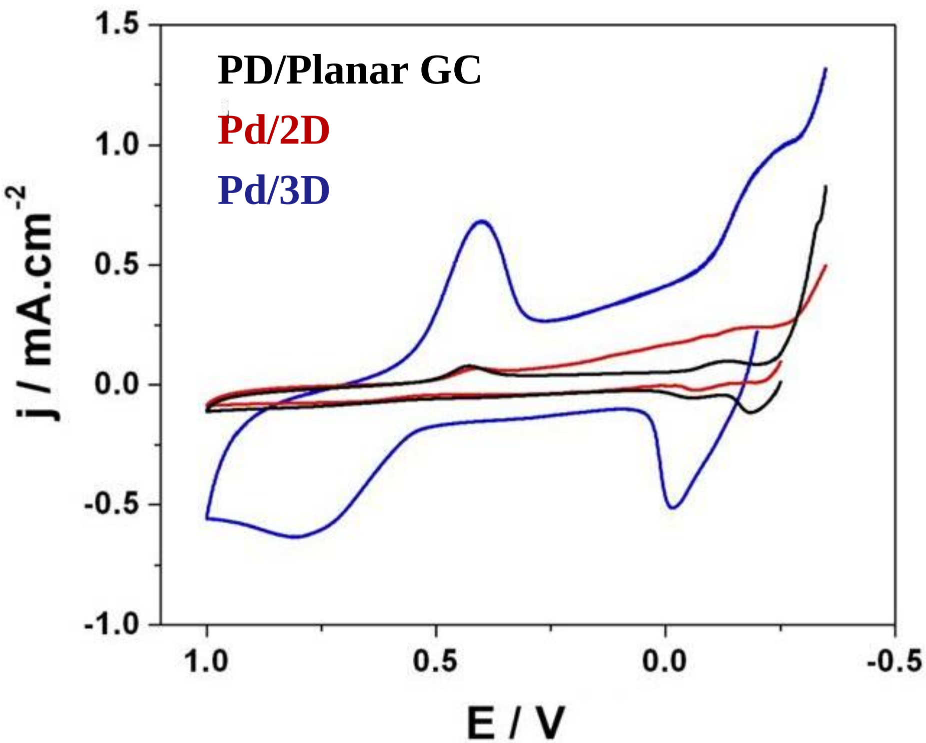






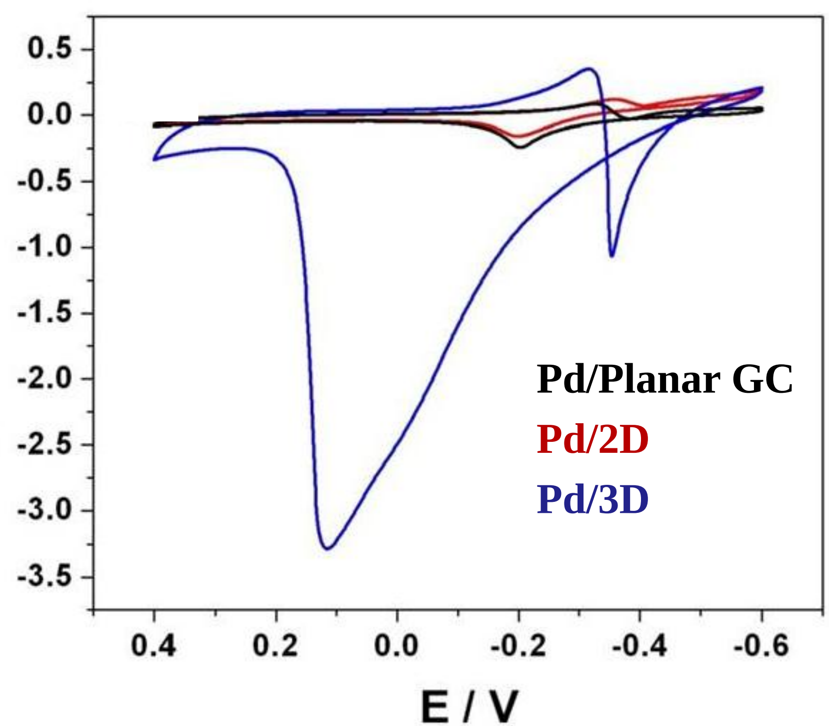
Electrode Characterization – Pd Catalytic MeOH Oxidation

Cycling in $HClO_4$



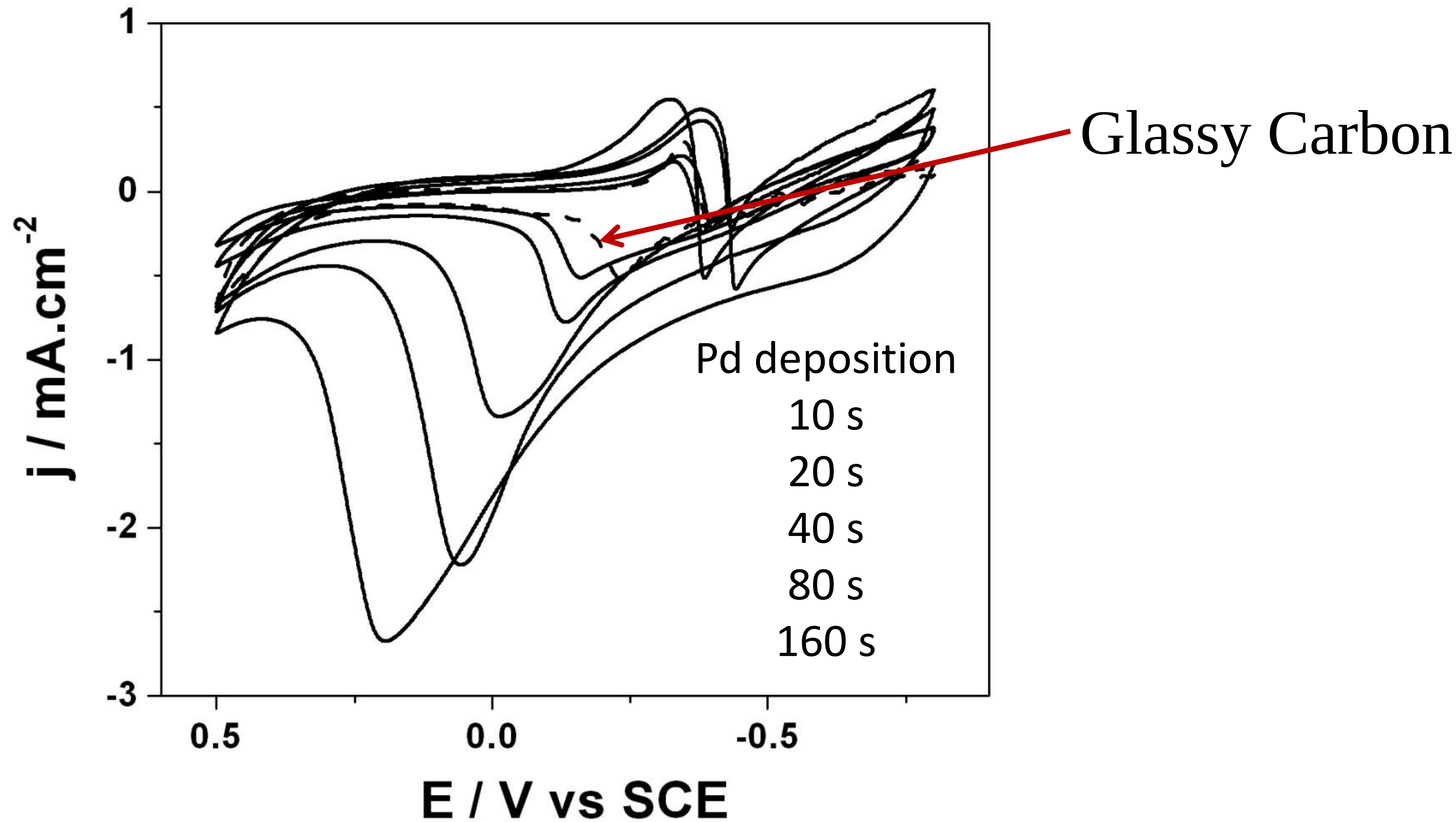
Accessible Pd surface area ~ 20x higher

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.

Sandia National Laboratories