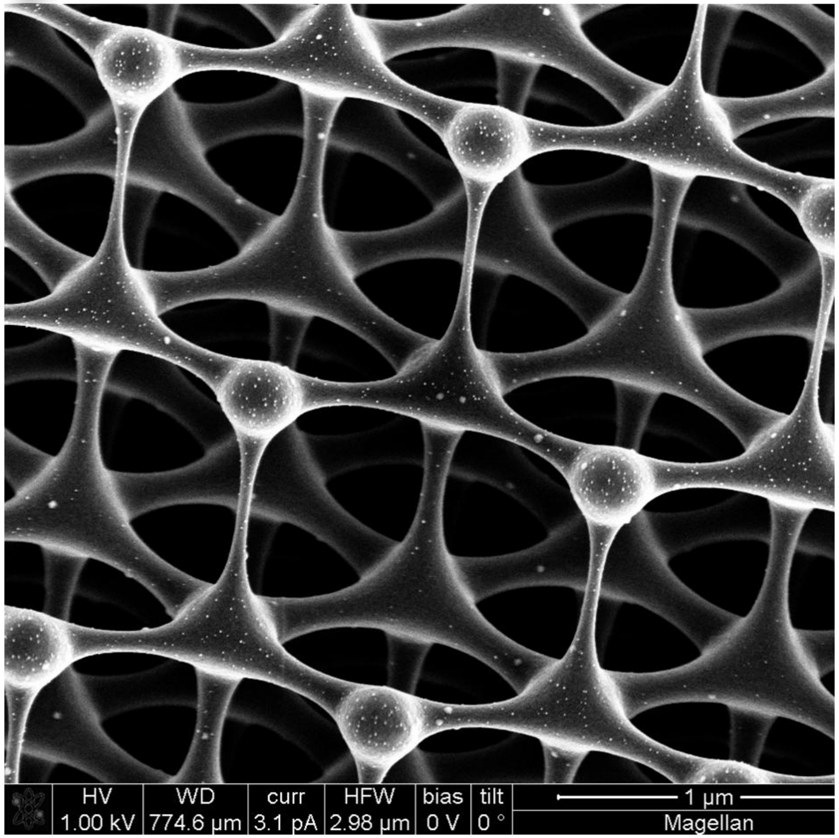
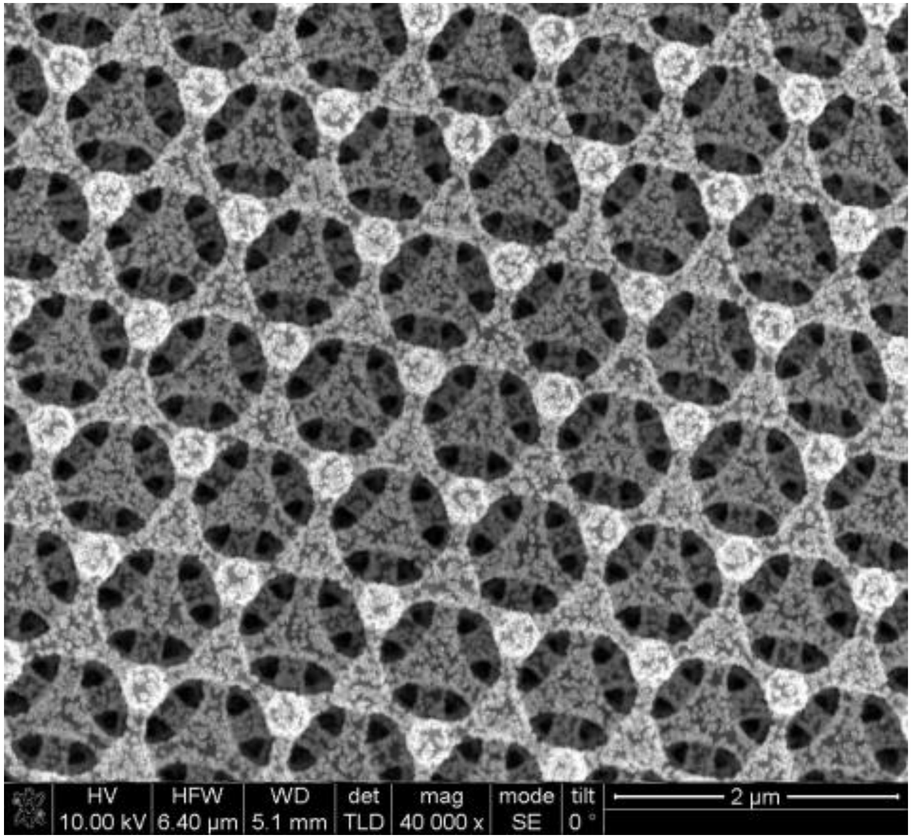
3D Pyrolyzed Carbon

SAND2012-6863C





D. Bruce Burckel, Sandia National Laboratories

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Outline

1. Formation of 3D Carbon Scaffolds

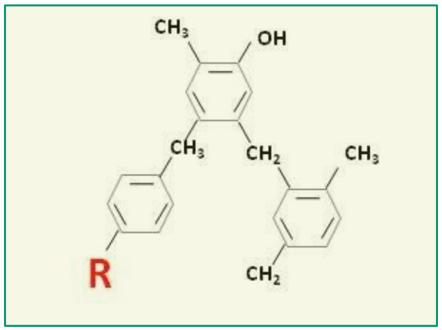
2. Physical Properties of 3D Carbon Scaffolds

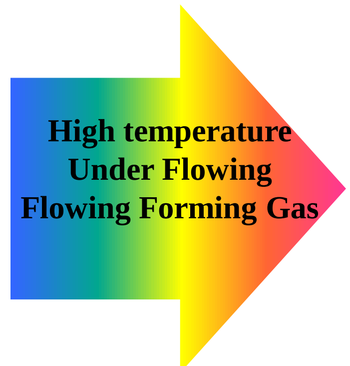
3. Application: Non Enzymatic Glucose Sensor

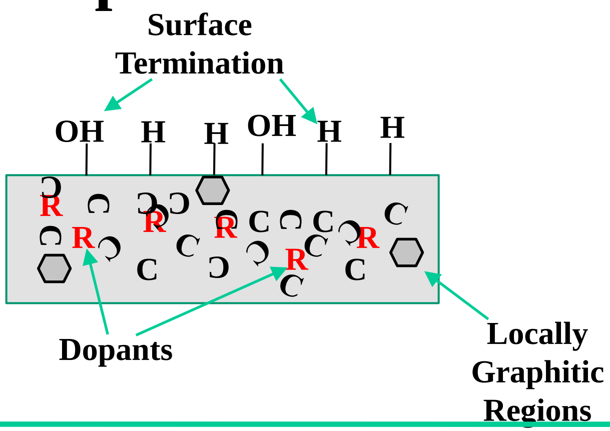
4. Application: SERS Substrate

Synthesis Route to Amorphous Carbon: Pyrolysis of Organic Polymers

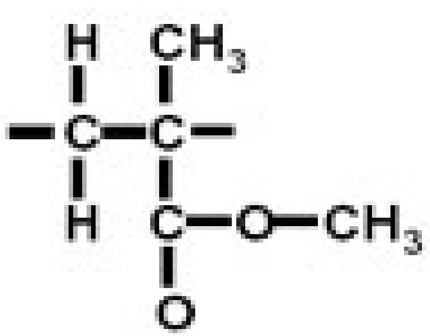
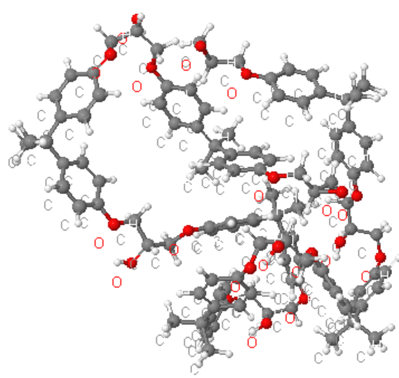
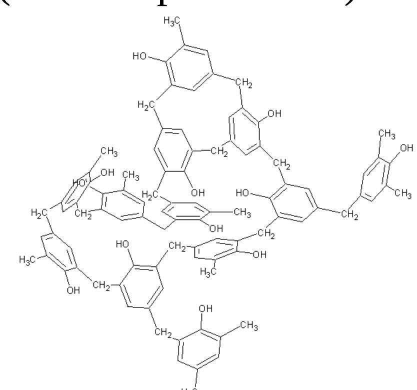
Organic Polymer → Pyrolysis → Amorphous Carbon







Typical Photopatternable Organic Polymers

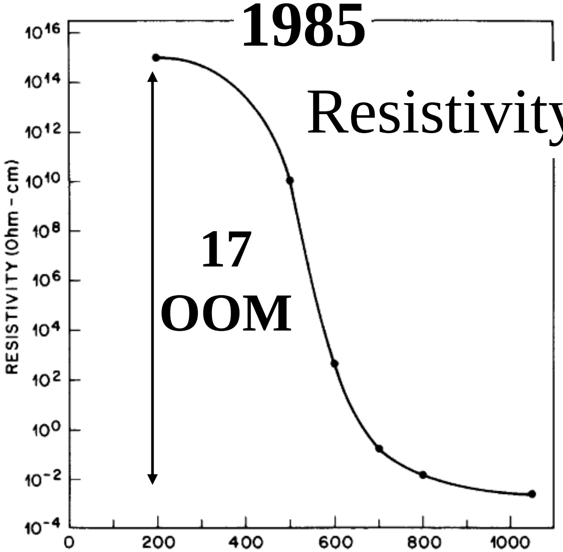
Polymethyl Methacrylate (PMMA)	Epoxide Resist (SU 8)	Phenol formaldehyde resin (novolac photoresist)
		

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

Wikipedia – Phenol fomaldehyde resin

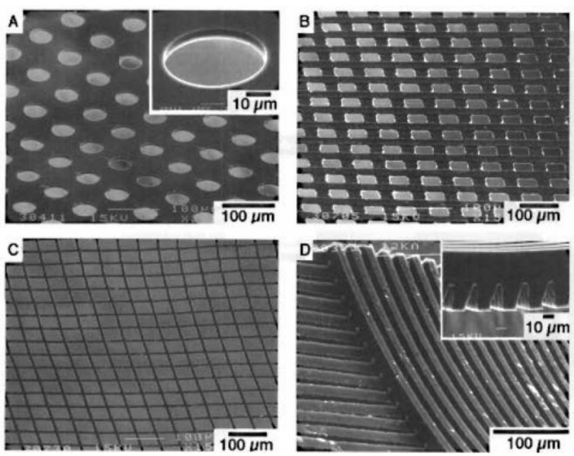
Visual History and Properties of Pyrolyzed Resist

1985



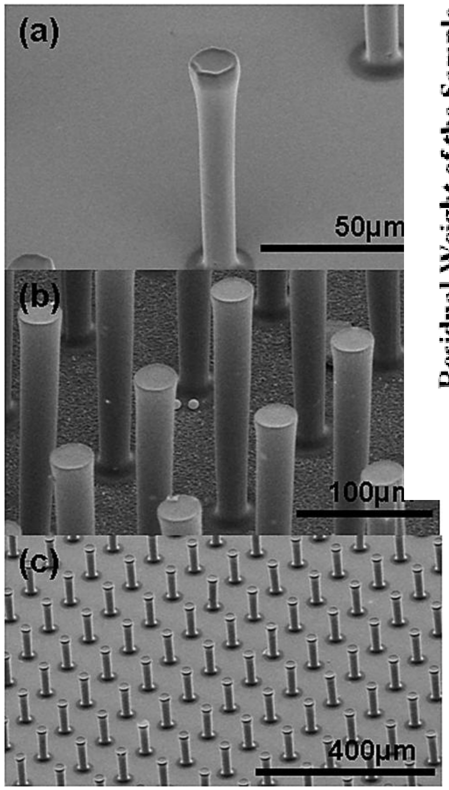
J. NonCryst Sol. **70**, 99-109 (1985)

1997

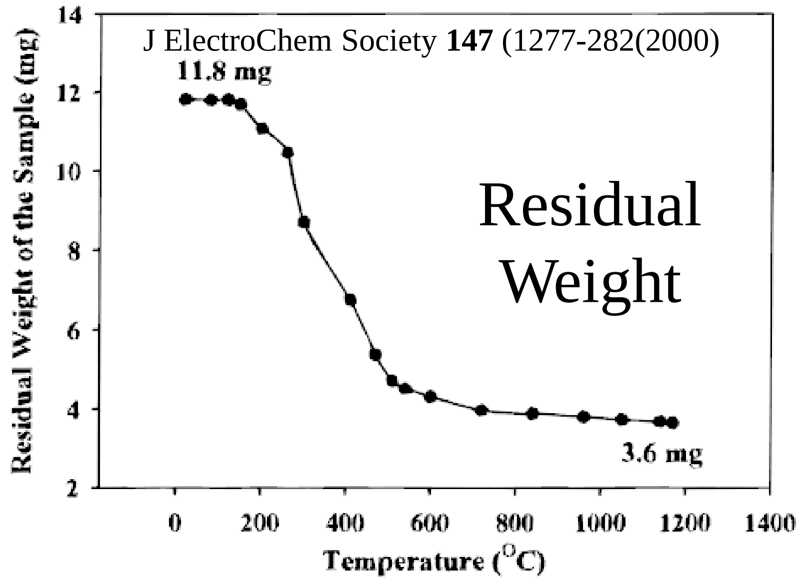


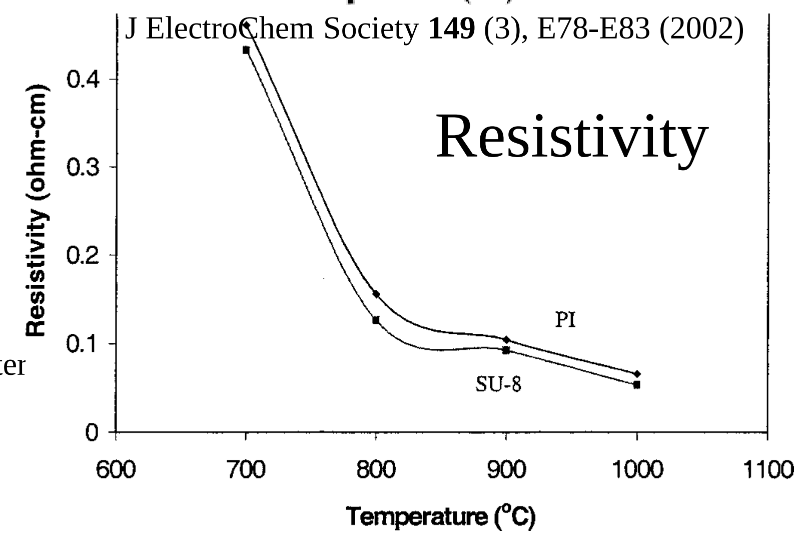
Adv. Mater. **9**, (6) 477-480 (1997)

2004



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





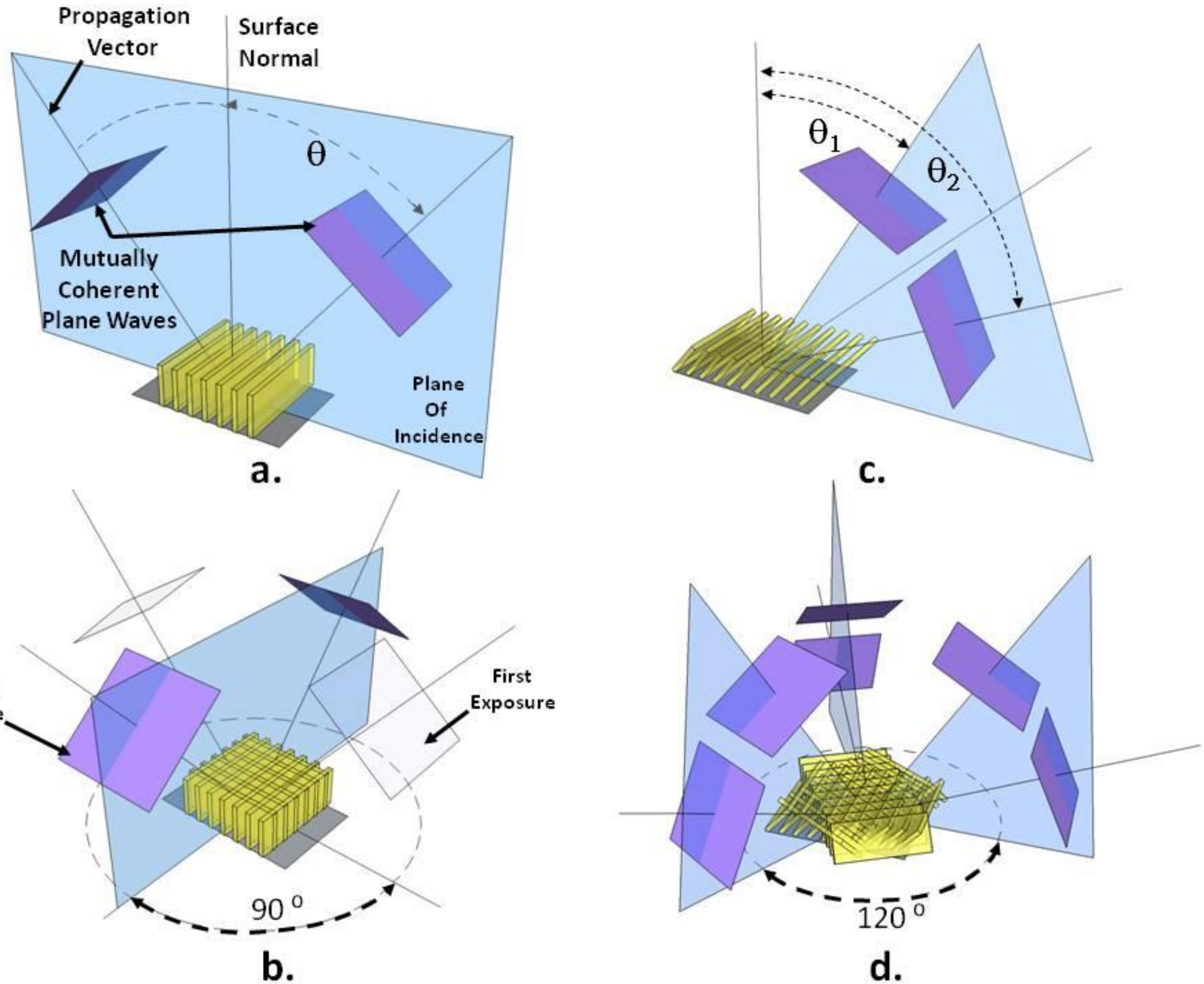
Interferometric Lithography

1-D Lines

Tilted 1-D Lines

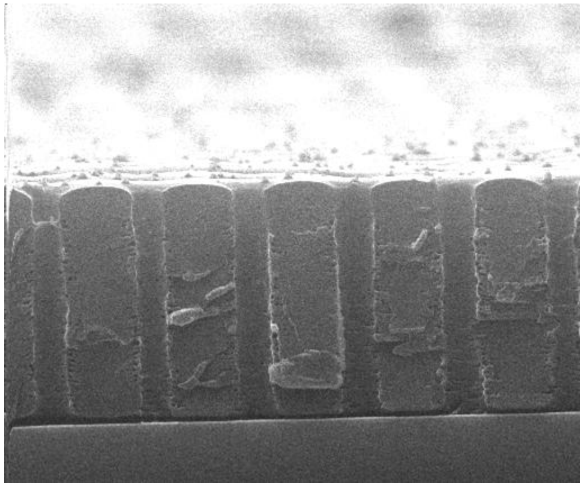
2-D Crystal

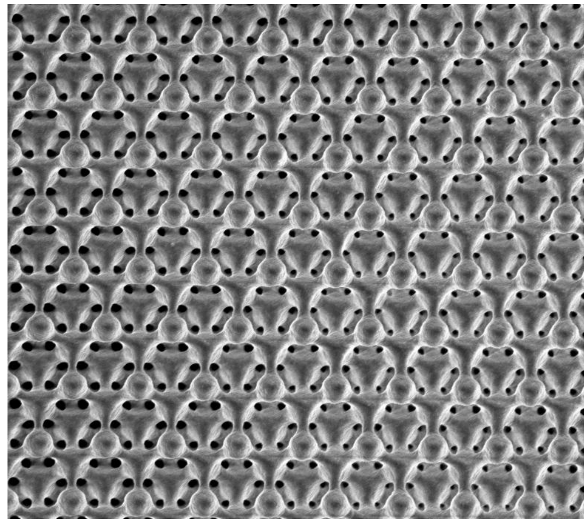
3-D Crystal

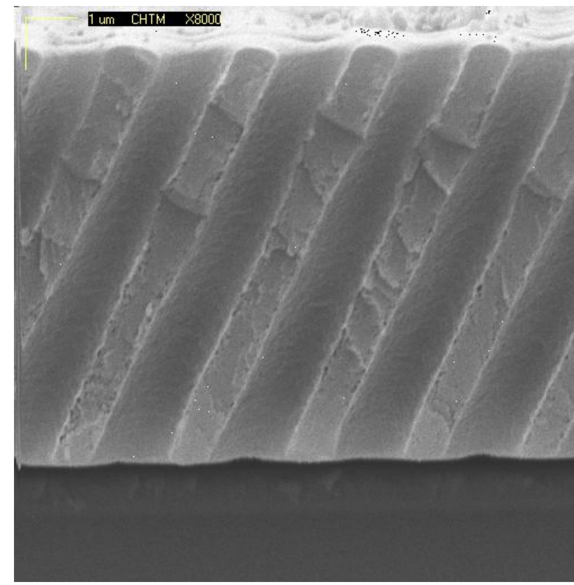


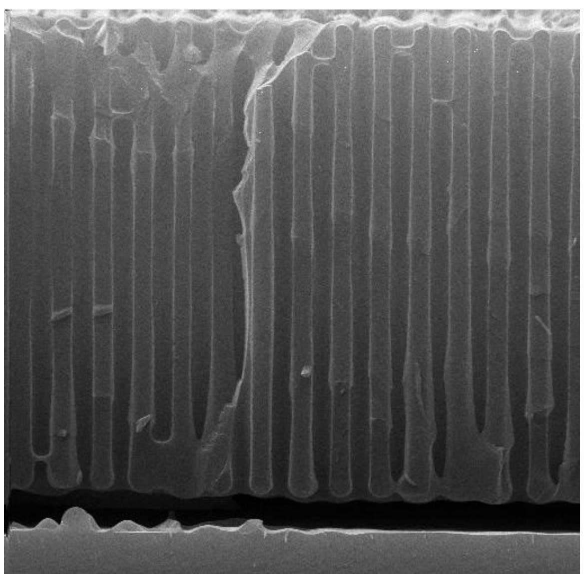
Burckel et al, *JVST B*, **28**, C6P14 (2010).

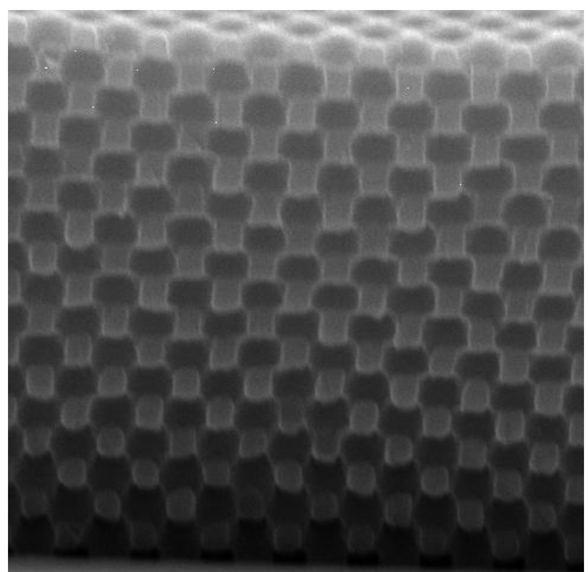
Sub-Micron 3D Resist Patterns Via Interferometric Lithography





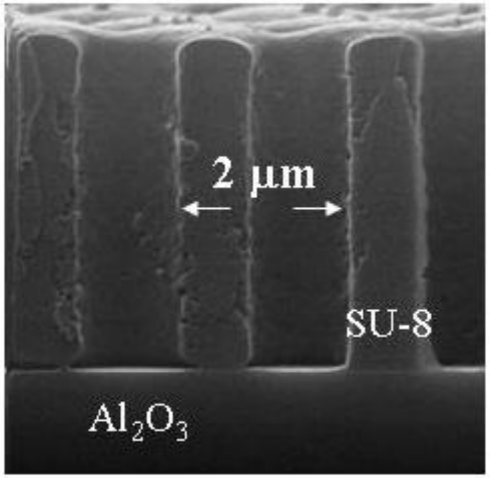


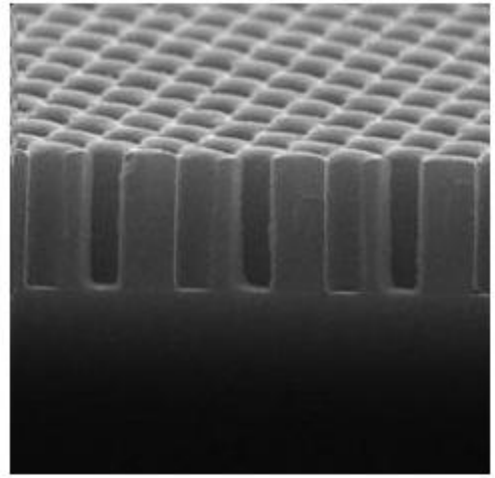


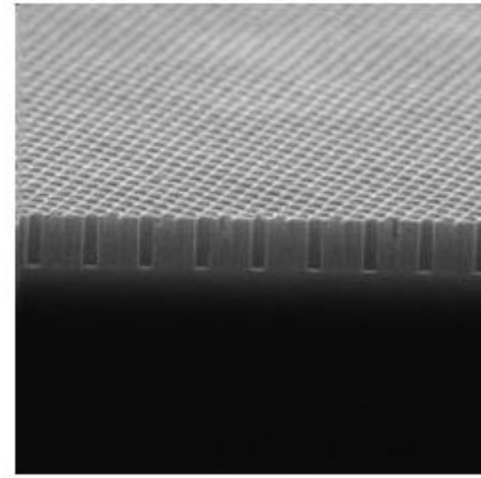


Conversion of 2-D Resist Structure to 2-D Carbon Structure

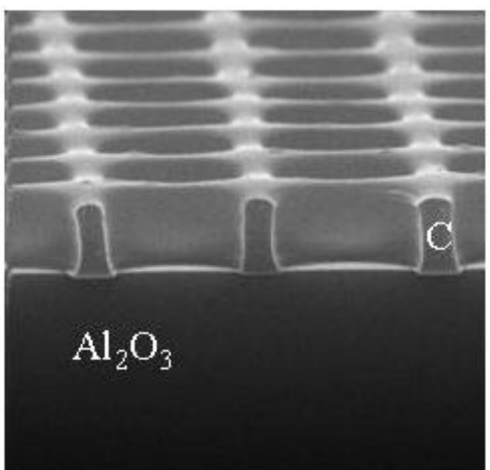
Resist

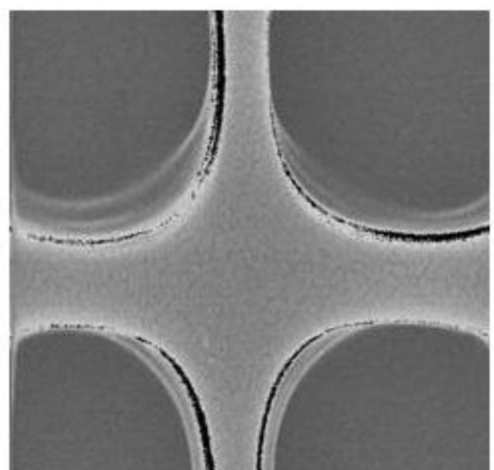


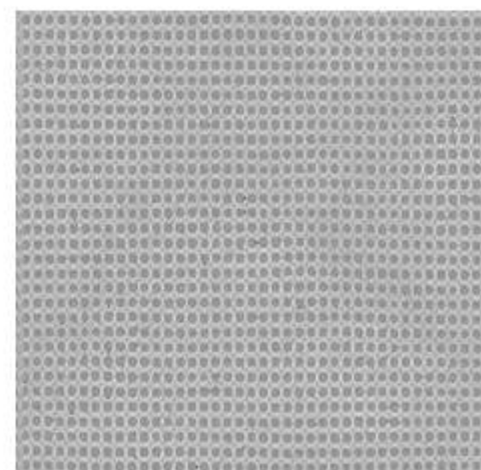




Carbon

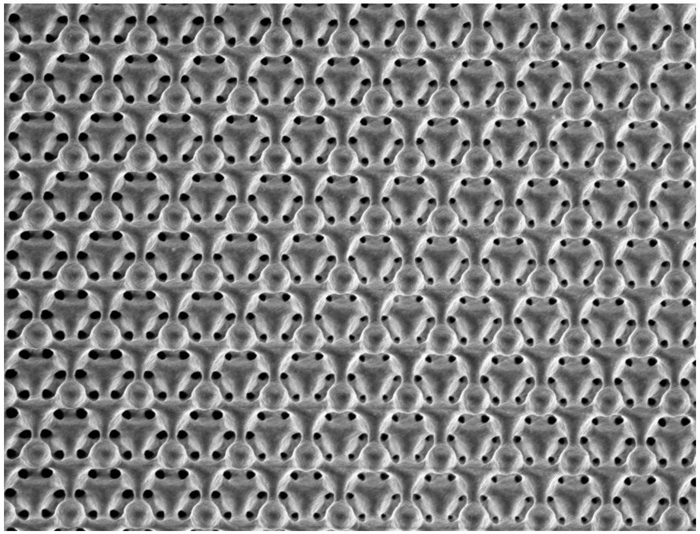


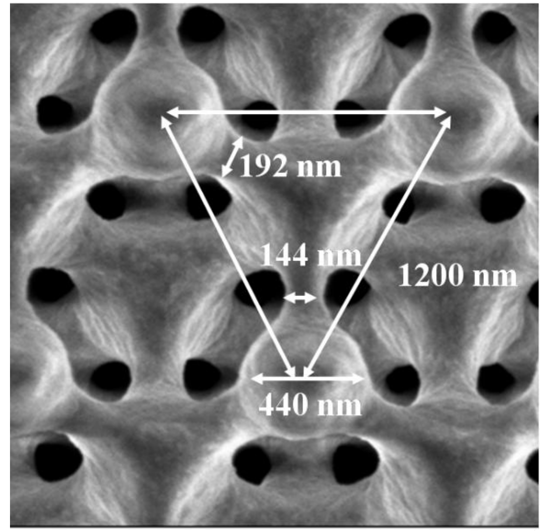




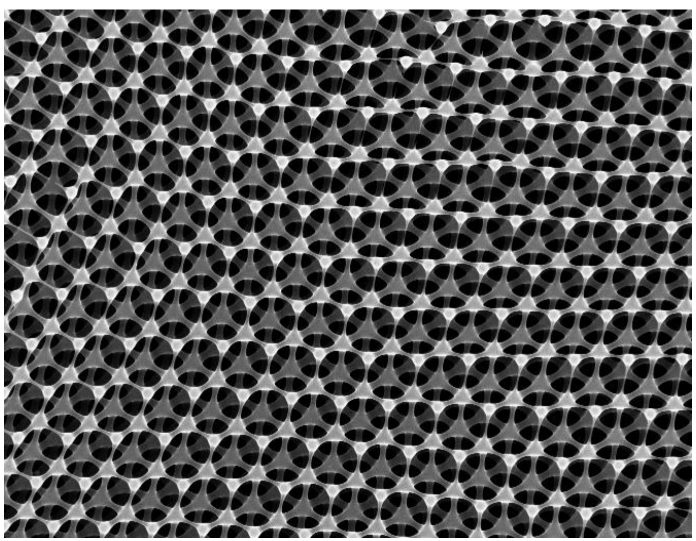
Conversion of 3-D Resist Structure to 3-D Carbon Structure

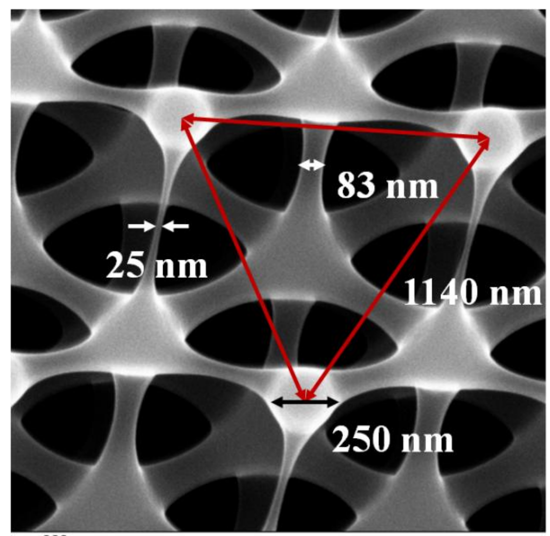
Resist





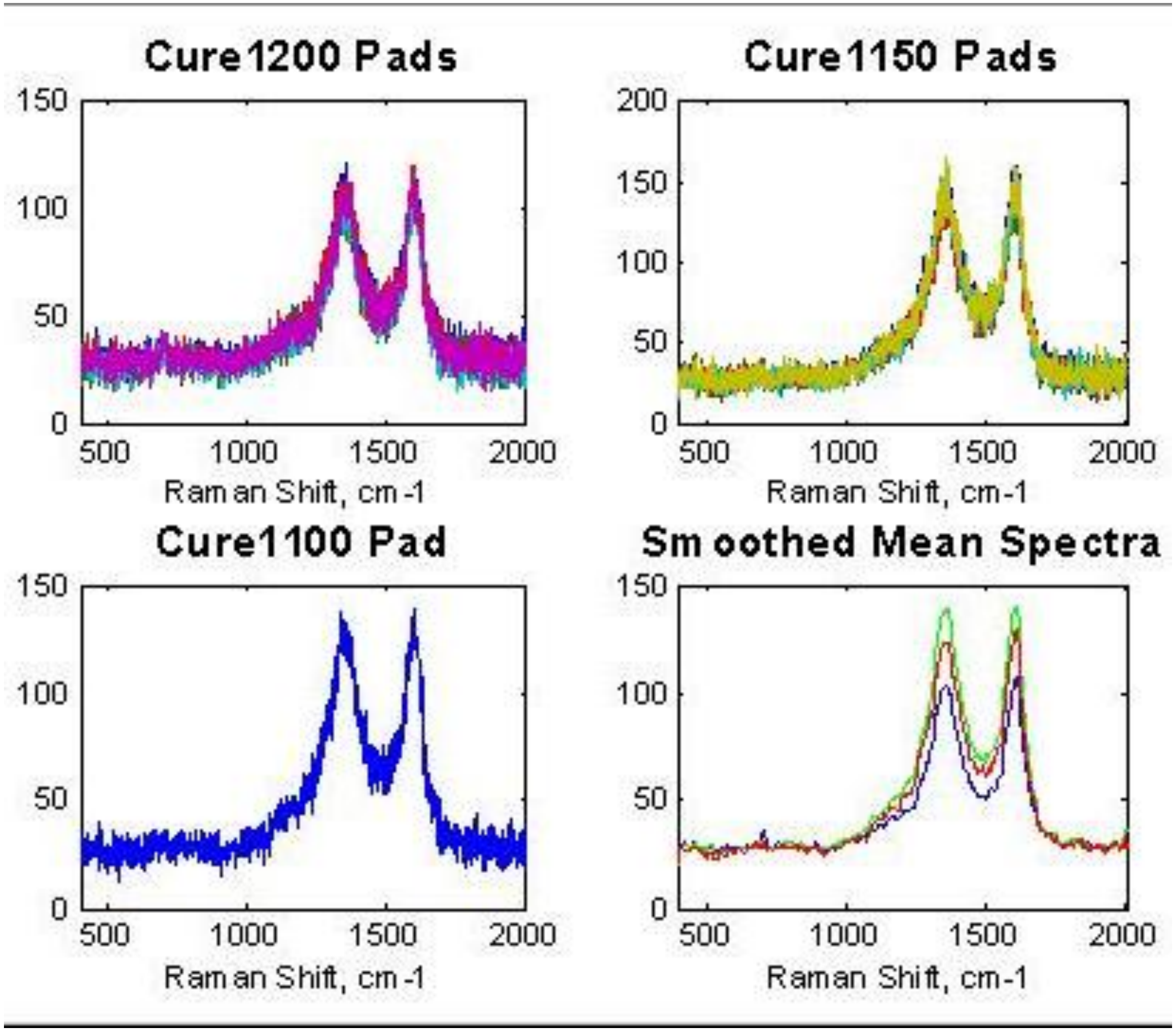
Carbon





Properties of 3-D Carbon Scaffolds

Raman Spectroscopy of Pyrolyzed Resist

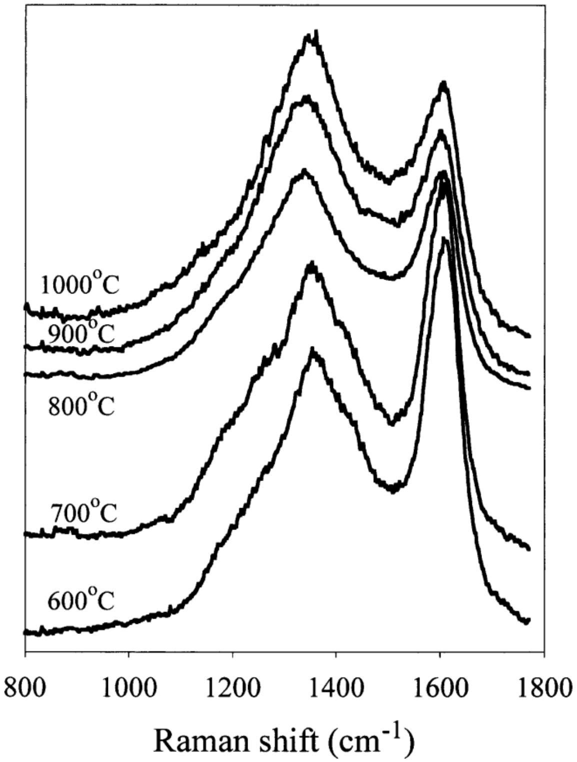


Comparison To Literature Values

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

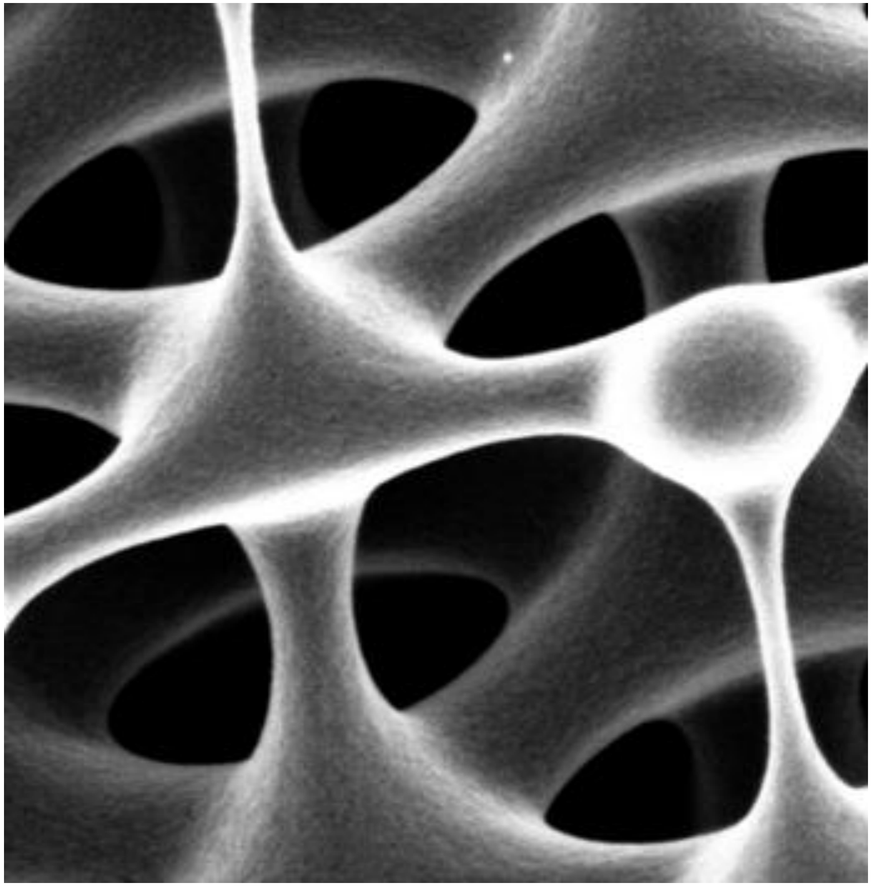
1344 cm^{-1} 1591 cm^{-1} ← **HOPG**

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

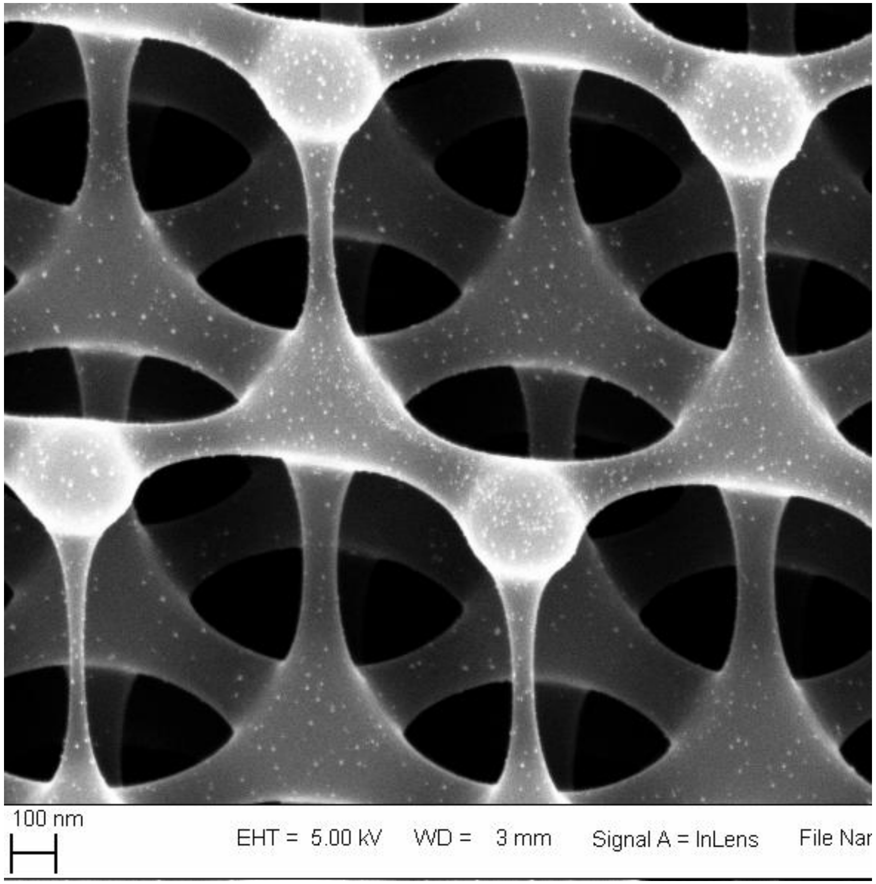


Nearly Atomically Smooth Surface

Smoothness of bare carbon – no preferential nucleation sites

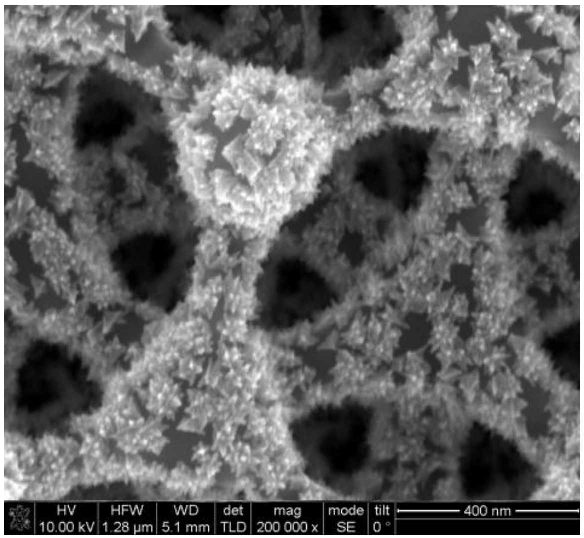


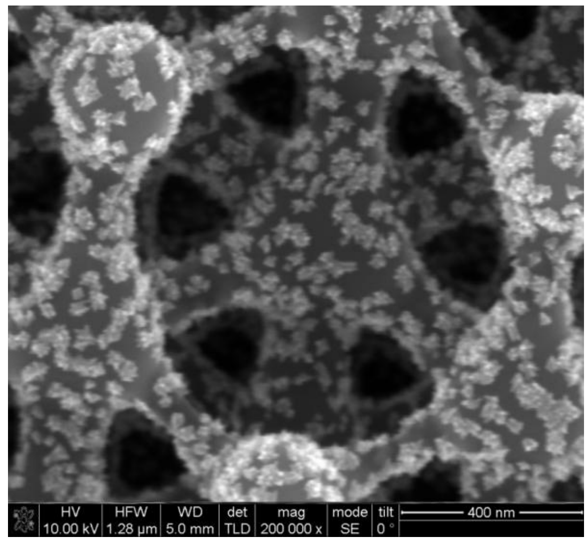
Ultra small, uniform NP formation

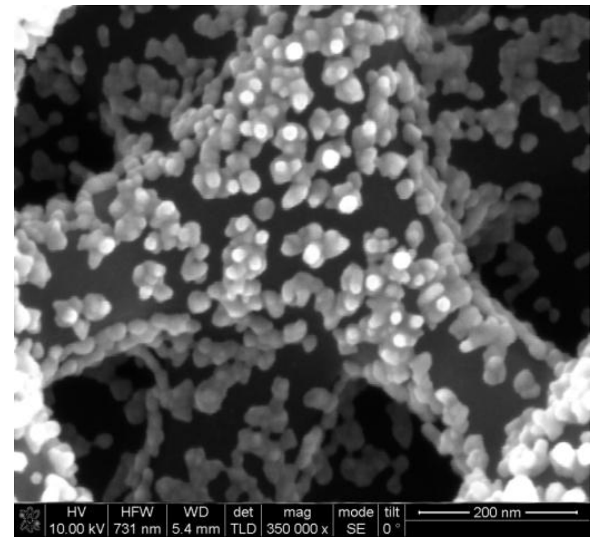


Burckel et al, *Small*, **5**, pp2792-2796 (2009).

Electrodeposition Conditions Impact Nanoparticle Morphology







100 s Deposition | 50 s Deposition | 100 s Deposition

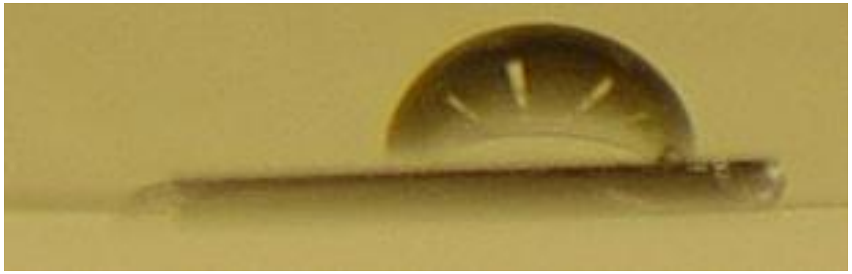
-0.65 V (100 s and 50 s Deposition)

-0.45 V (100 s Deposition)

Pd Nanocrystals

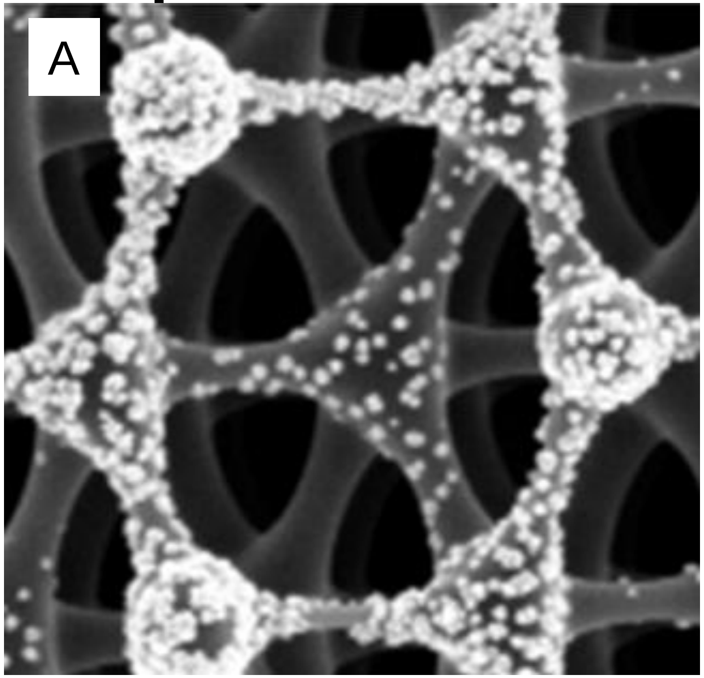
Impact of Carbon Hydrophobicity

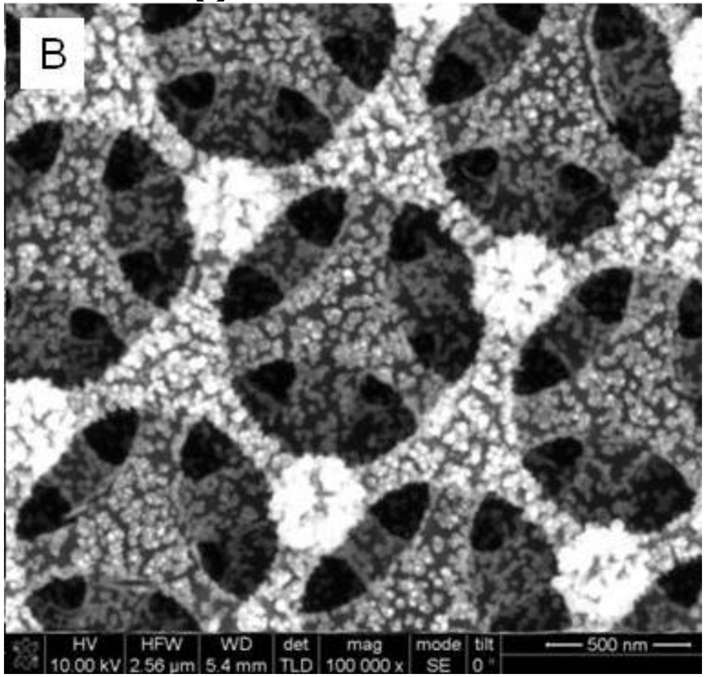
3D carbon
is hydrophobic



Deposition from Aqueous Solution

Deposition from Organic Solvent



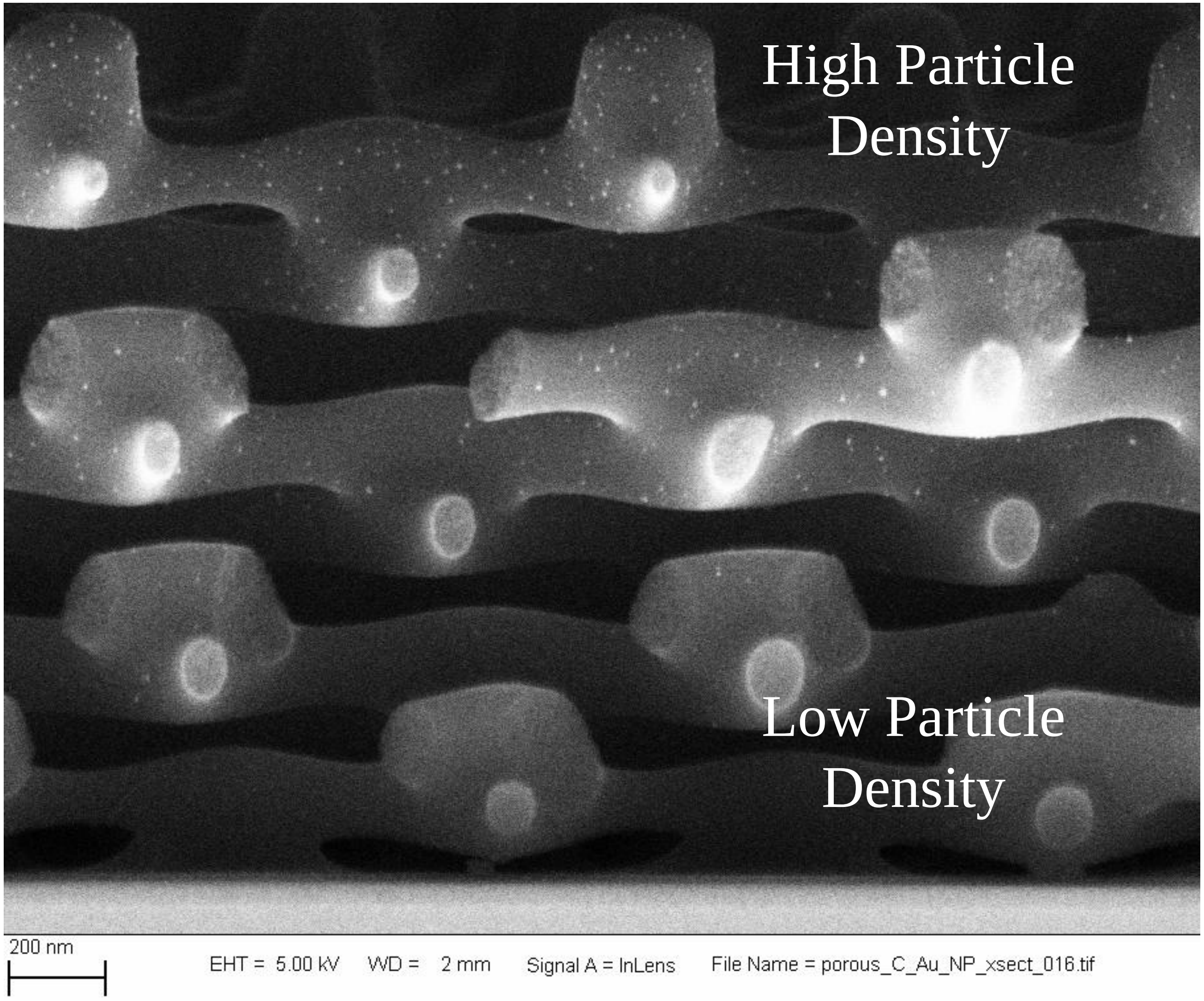


Vertical vs. Horizontal Shrinkage

Significant vertical shrinkage

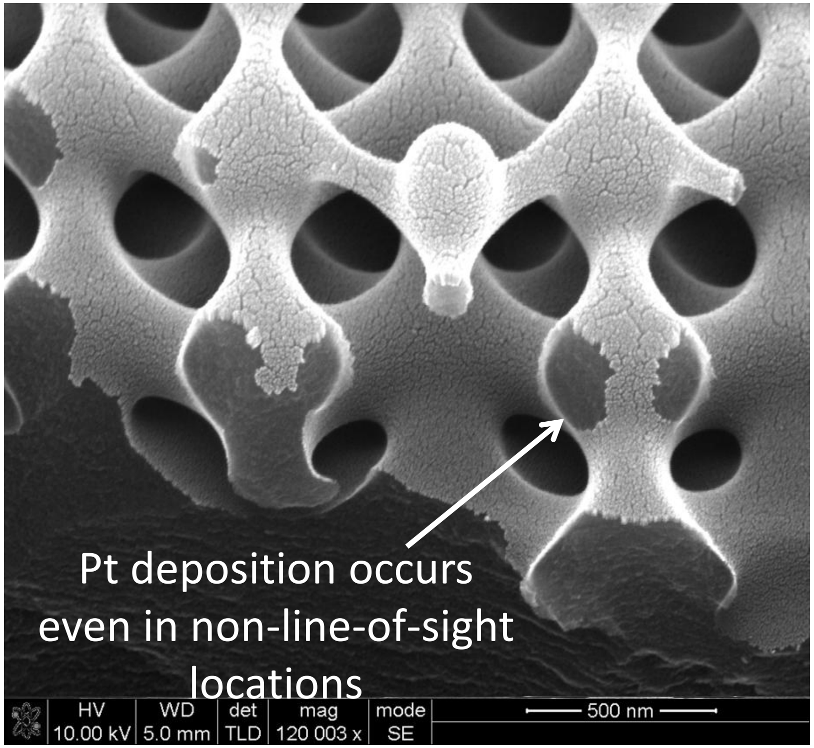
Extremely small, highly uniform NPs

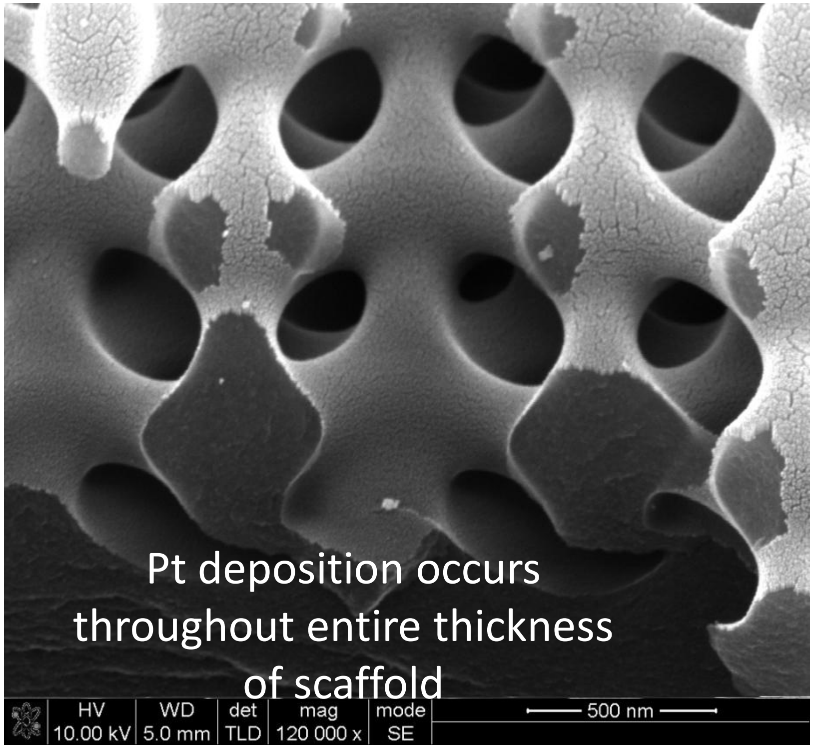
Inhomogeneous wetting



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

Modification of Carbon Scaffold: PVD

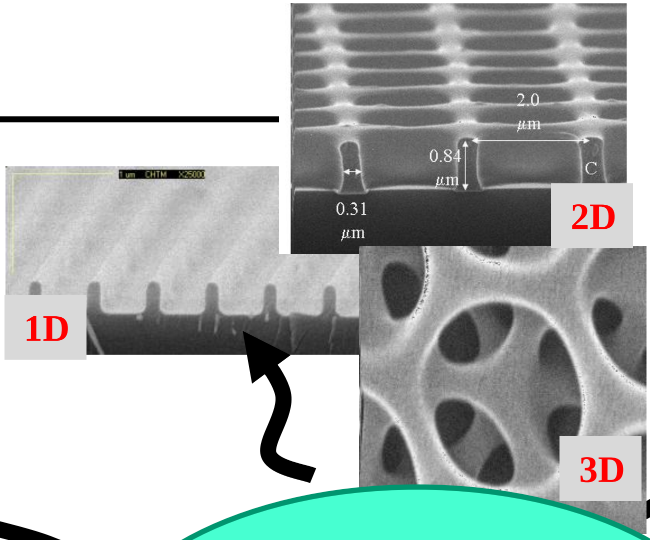




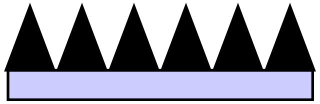
Pt sputtered @ 1A/s

Interferometrically Patterned Carbon

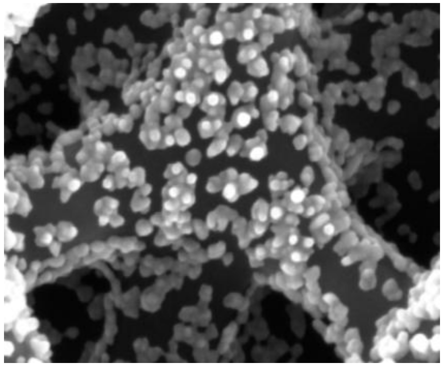
Carbon Photonics



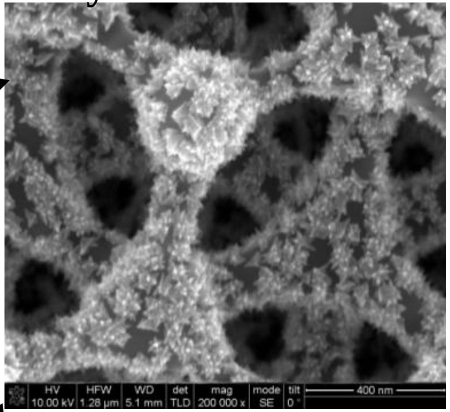
Structured Thermal Emitters



Ultra-Capacitor/Energy Storage

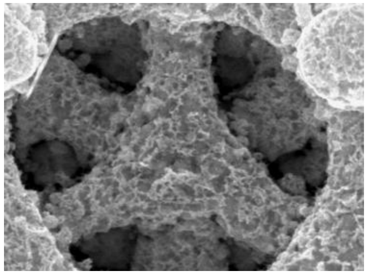


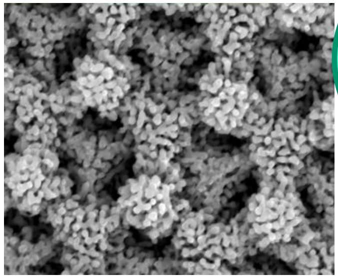
High Surface Area Catalysis/Sensor Platform



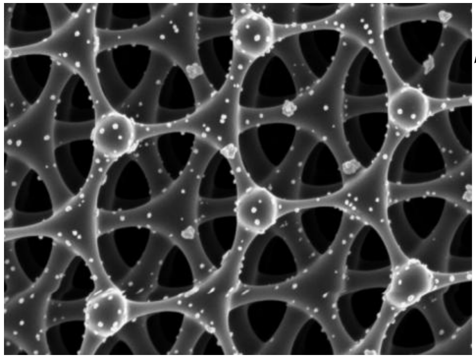
Convert 1D, 2D and 3D sub-micron photoresist patterns created with interferometric lithography into pyrolytic carbon

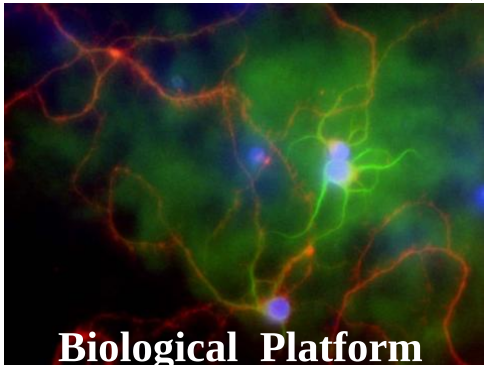
Hierarchical Porosity





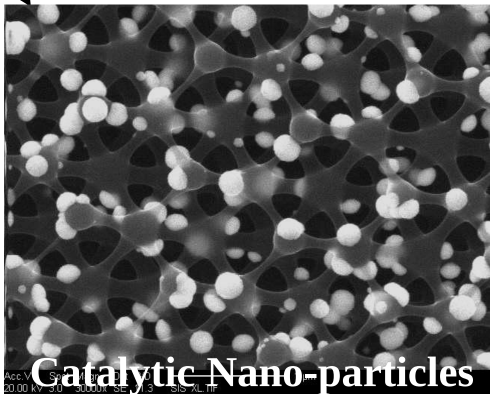
Fuel Cell Electrode





Biological Platform

GaN Defect Reduction



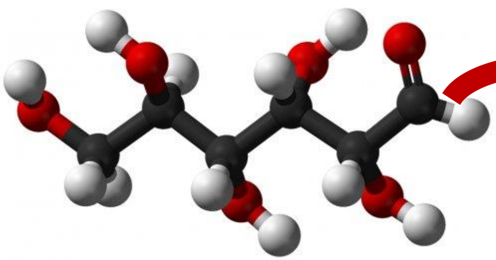
Catalytic Nano-particles

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

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

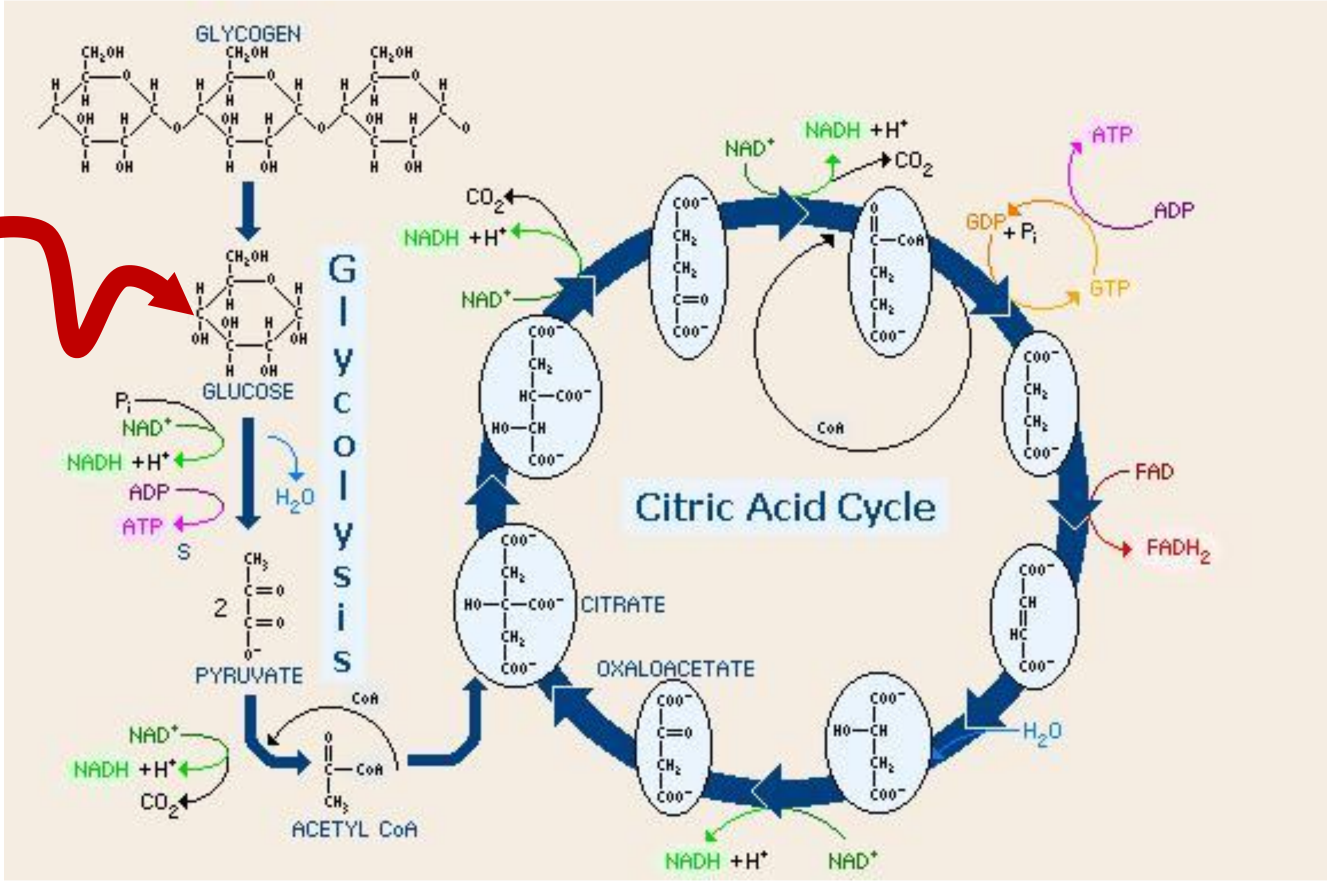
Why is Glucose Oxidation Important?

Glucose Molecule

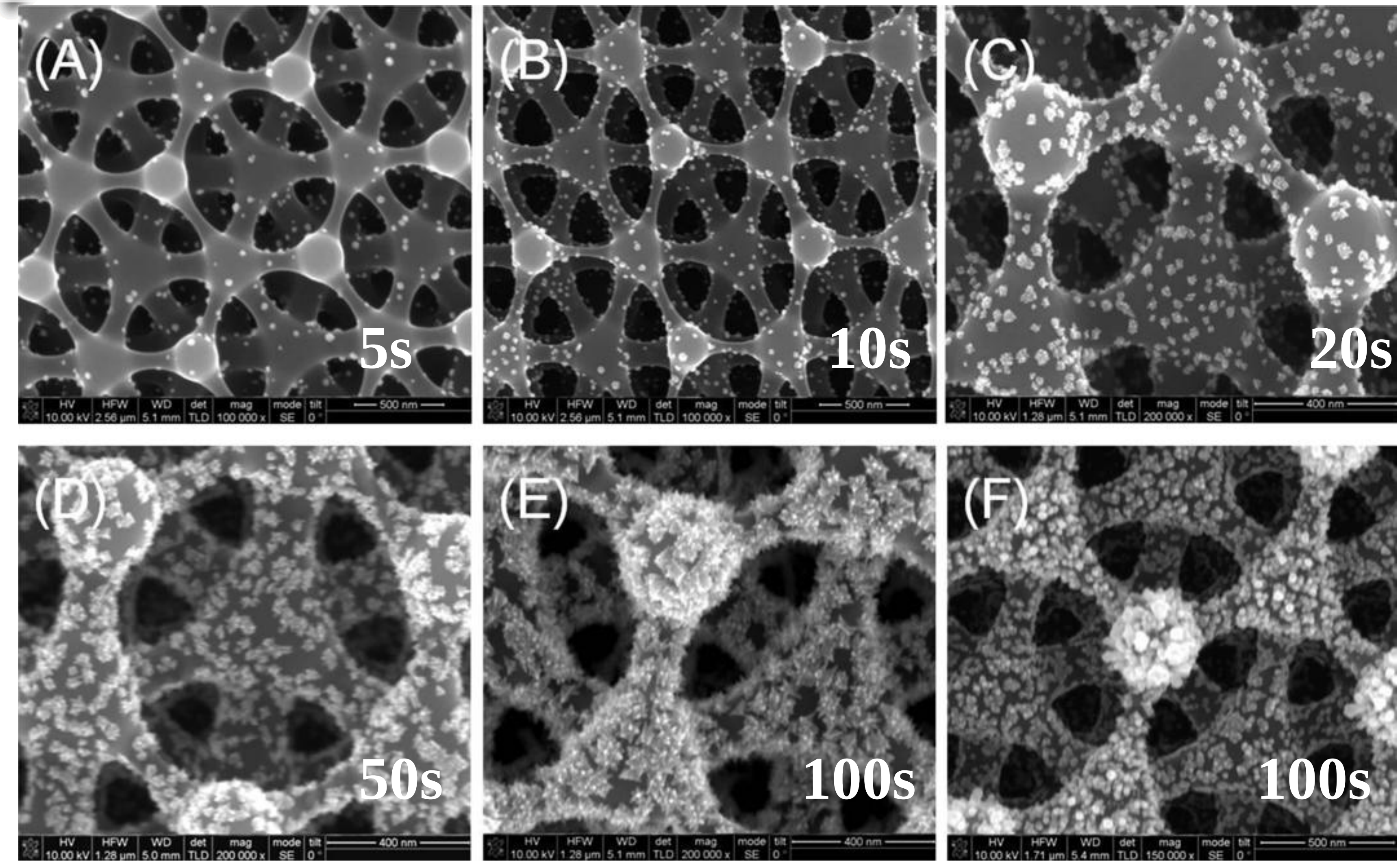


glucose oxidase

(GOx)



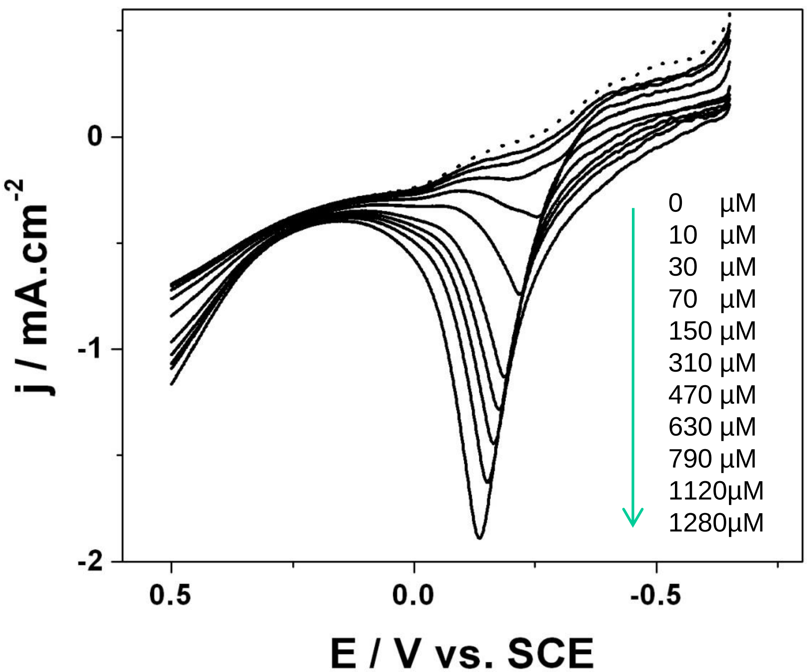
Electrodeposition of Pd Nanoparticles



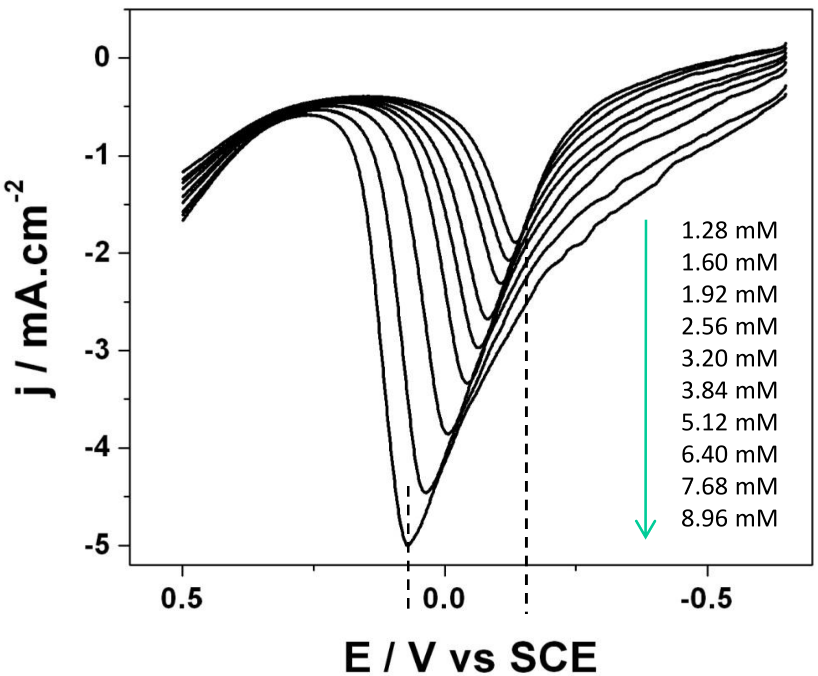
Xiao et al., Biosensors and Bioelectronics, **26**, pp 3641-3646 (2011)

Electrode Response to Glucose Additions

μm concentrations



mm concentrations

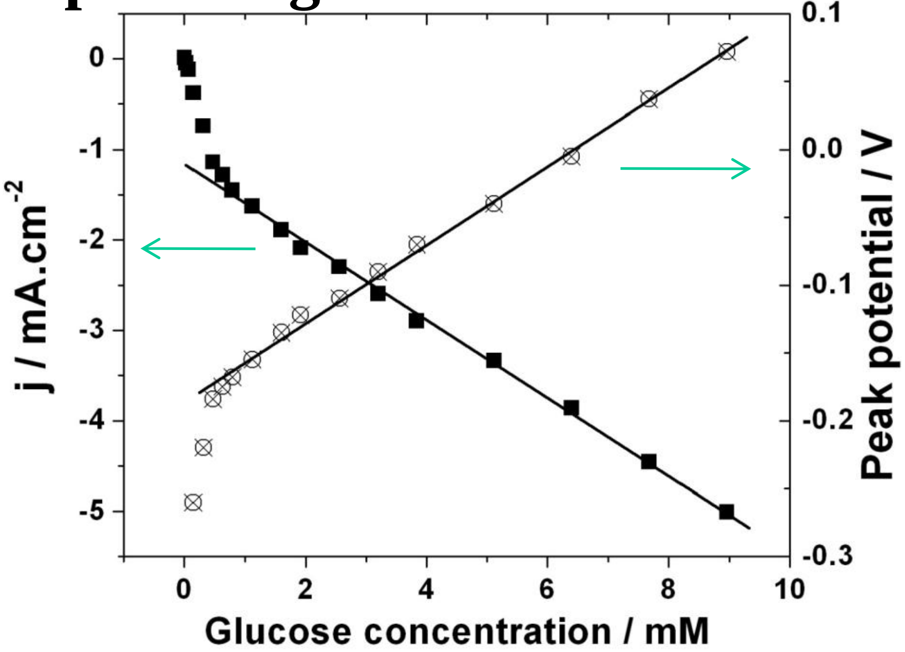


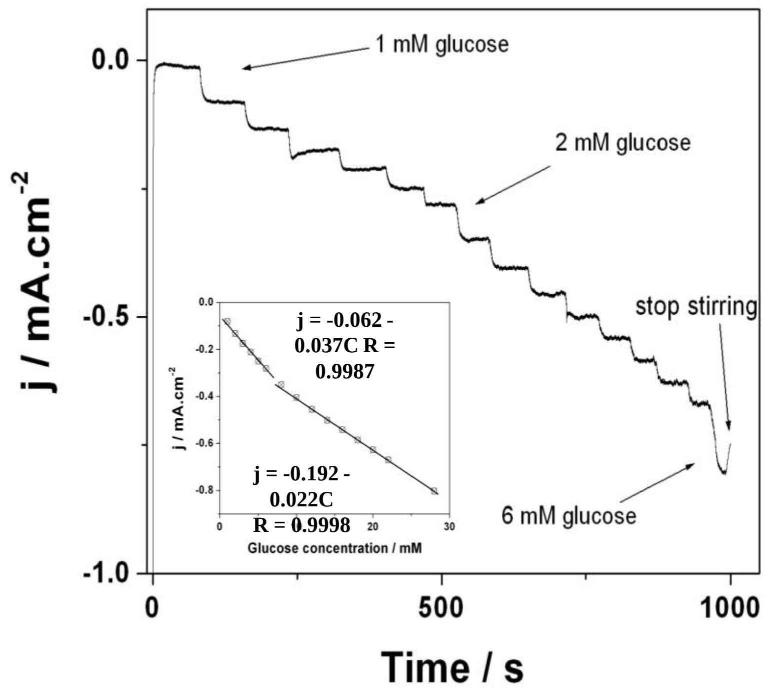
Linear scan voltammograms of Pd/Porous in 0.1 M NaOH + x M glucose. Pd deposition: 100s, Scan rate: 20 mV/s.

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

Current and Potential Response to Glucose Concentration

Both current and peak potential respond to glucose concentration



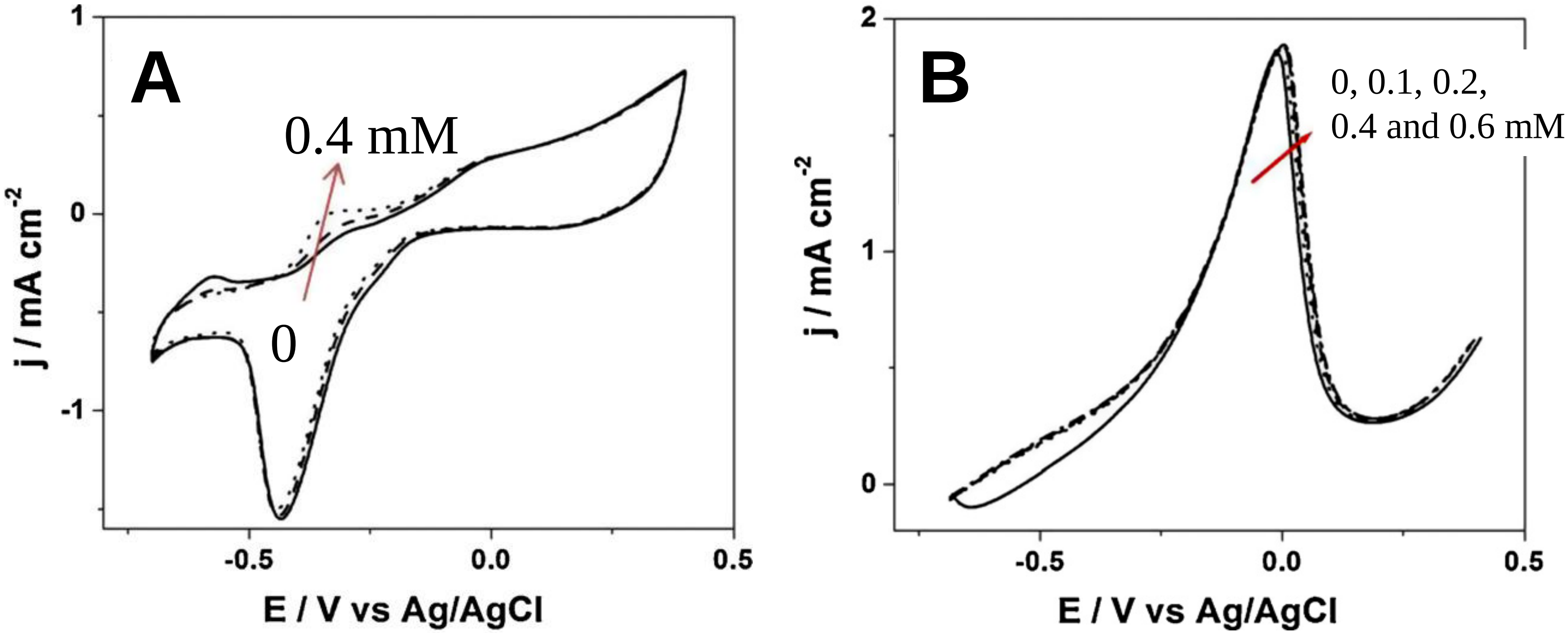


Plots of corresponding current and peak potential vs. glucose concentration. Pd deposition: 100s, Scan rate: 20 mV/s (A) and typical amperometric response of a Pd/Porous towards successive additions of glucose in 0.1 M NaOH with continuous stirring. The inset figure shows the current-concentration relationship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

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

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

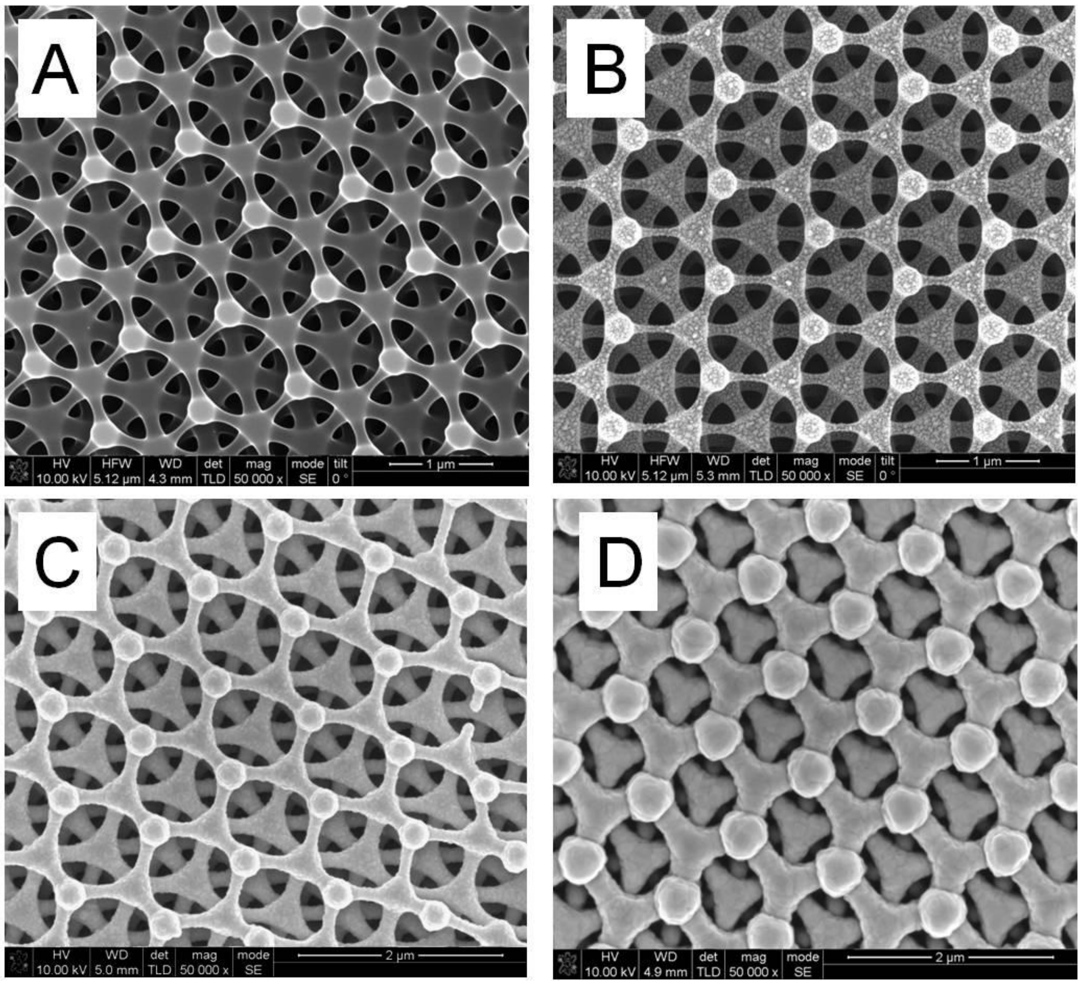
3-D Carbon Electrode Application: Surface Enhanced Raman Scattering (SERS) Sensor Platform

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

PVD Ag Scaffold Modification

Sputtered Ag (1 Å/s)

islands



Thin film

Sputtering Time

A – 0 (bare carbon)

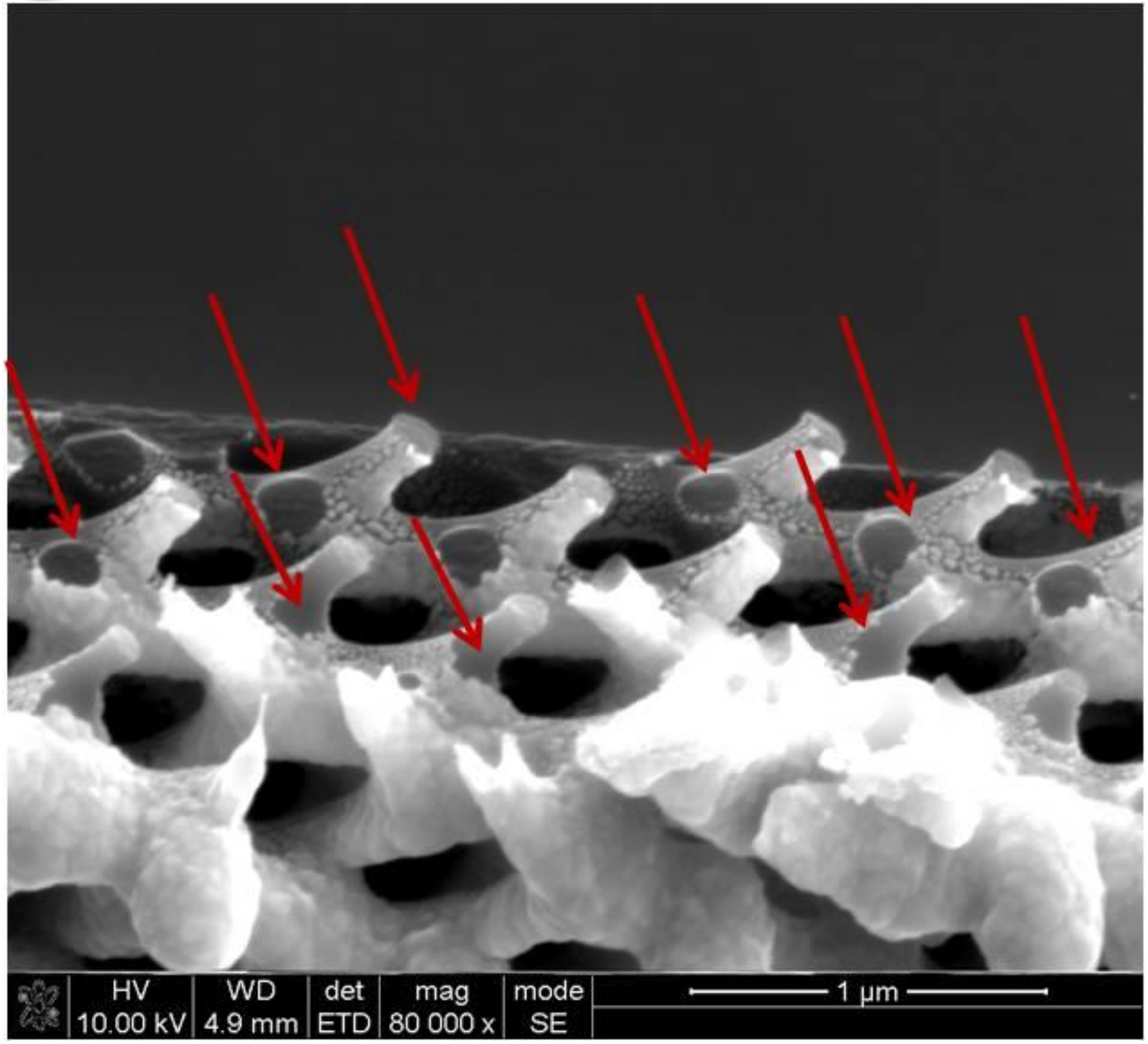
B – 150 s

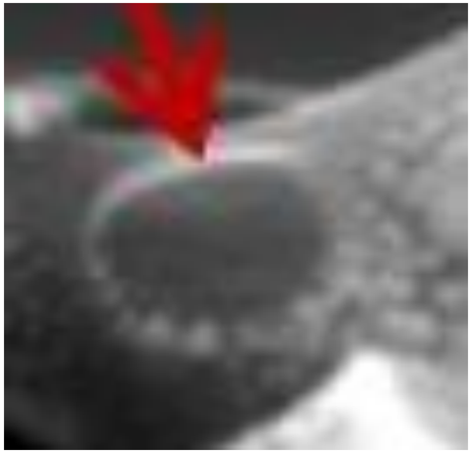
C – 1100 s

D – 3300 s

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

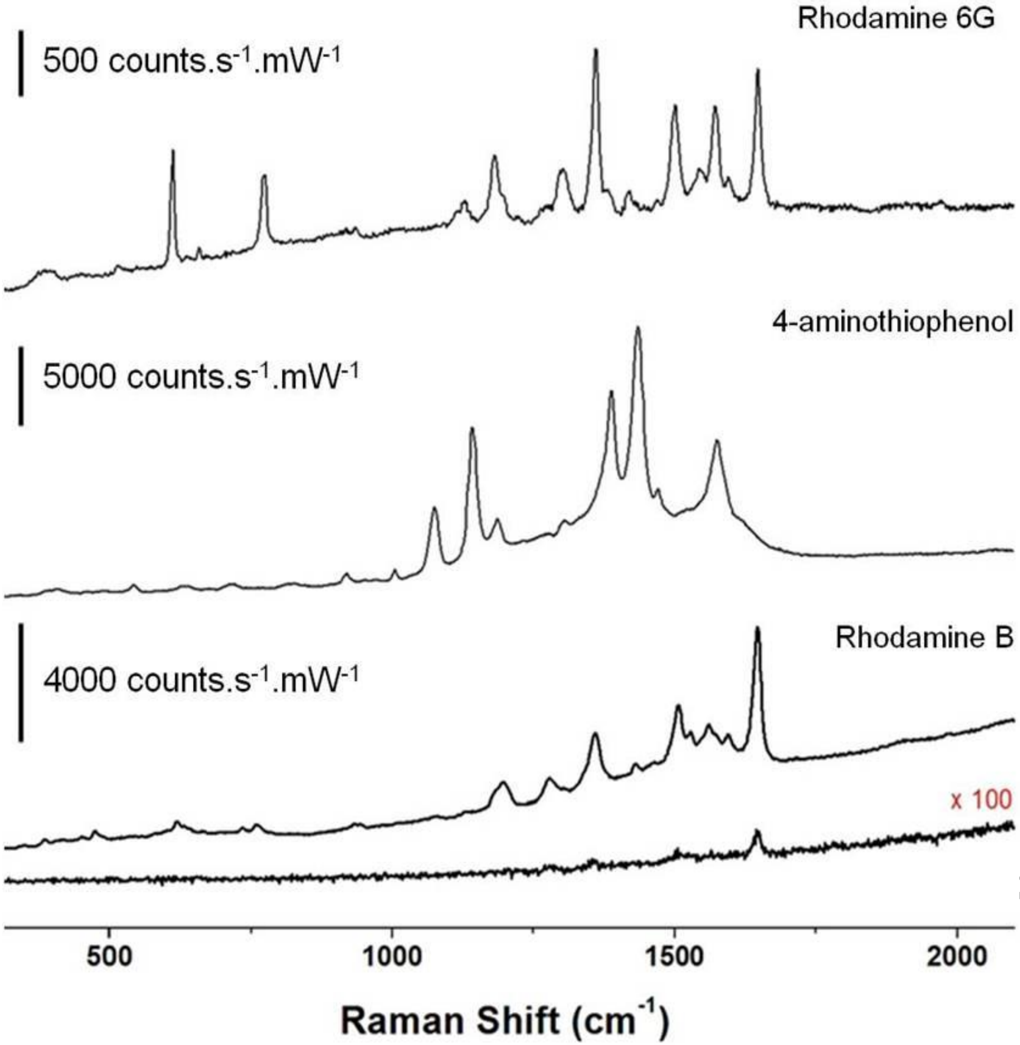
Sputtering coats bottom side too!





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

SERs Signals for 3 Organic Molecules



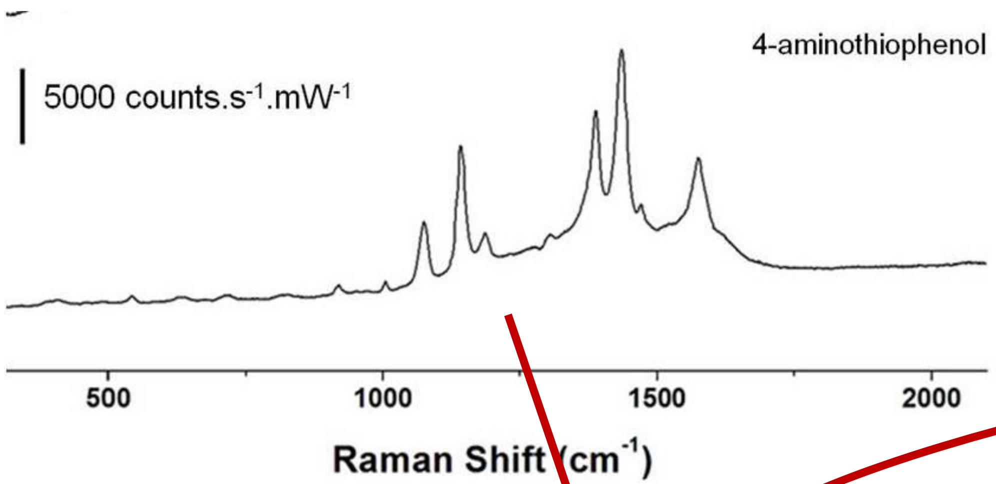
Increase in signal not due to surface area.

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

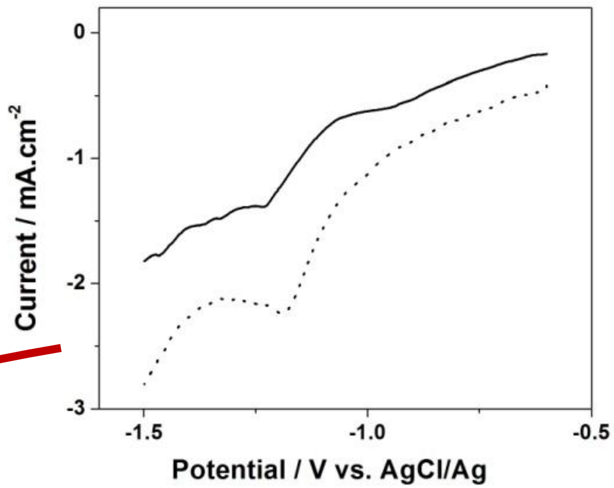
planar carbon with sputtered Ag islands **x 100**

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

Enhancement Factor: 4-aminothiophenol



Measure # of molecules



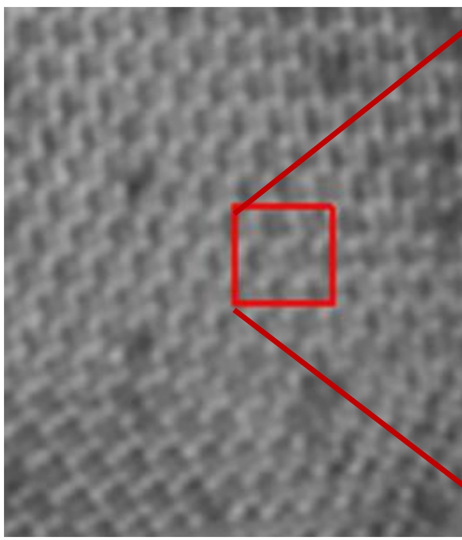
Electrochemical Stripping

Compared to response of neat control solution

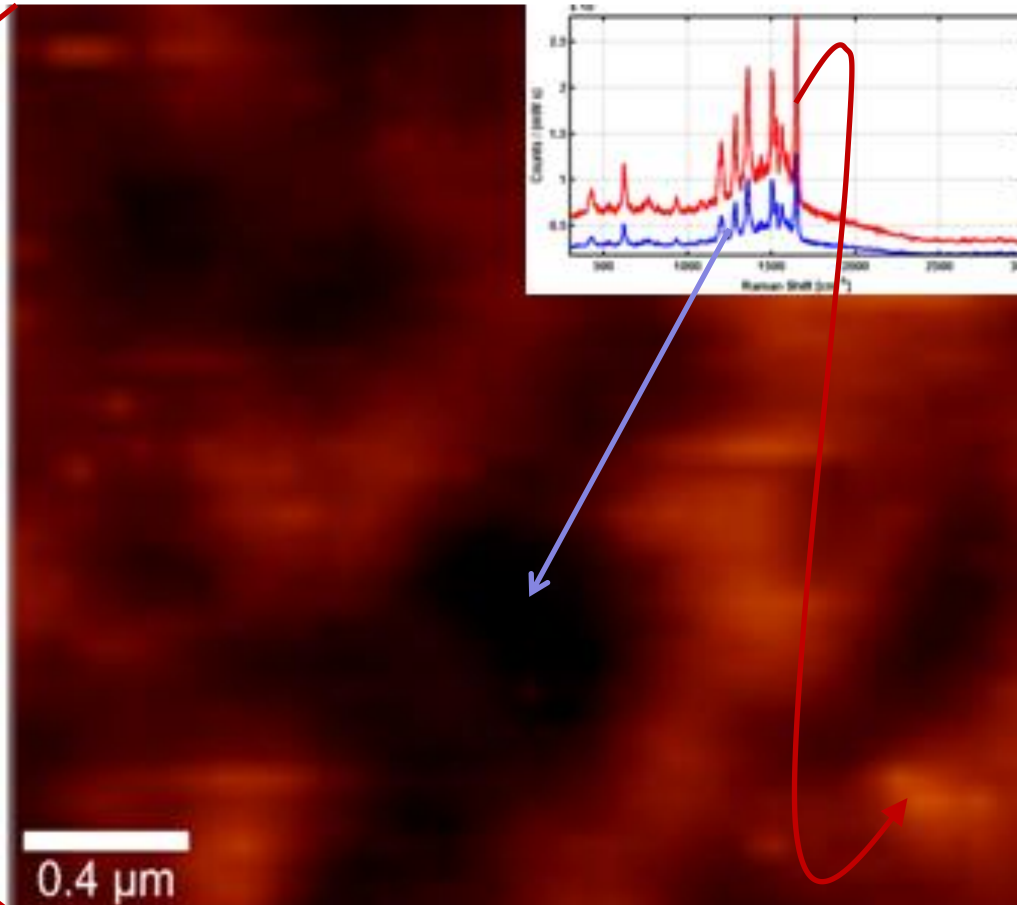
No Spatial Hotspots

Spatially resolved Raman Mapping

5 µm x 5µm Area



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



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 ~ $5x10^9$.

Acknowledgements

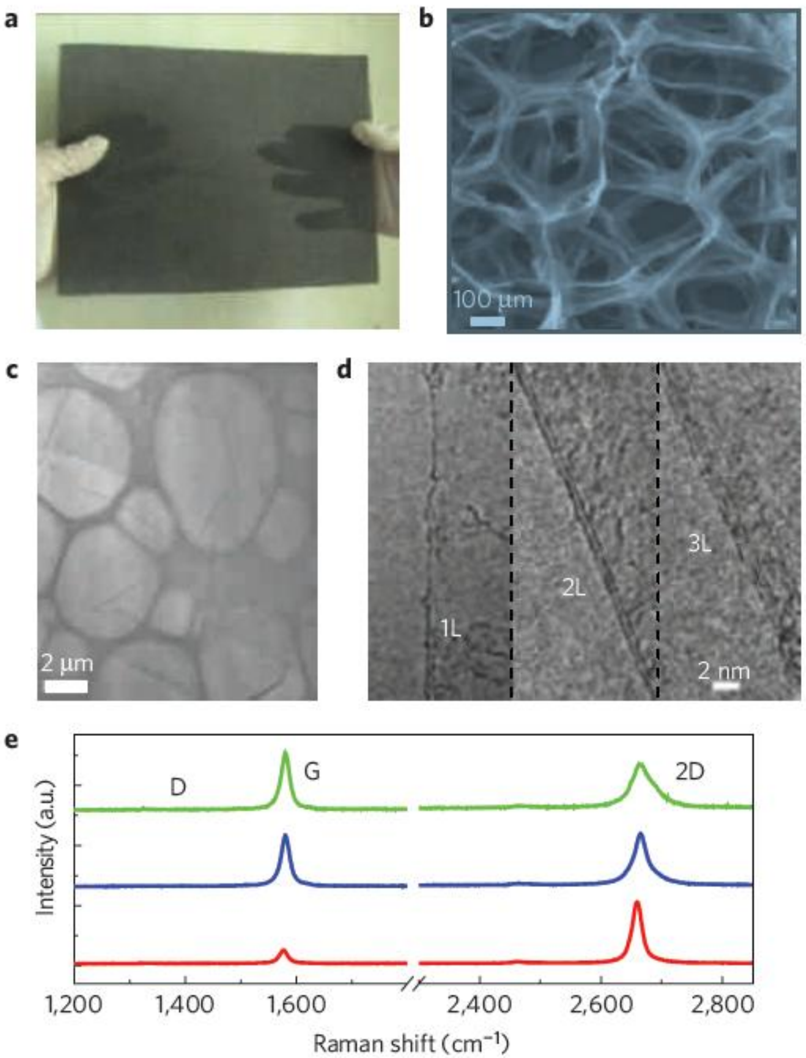
• Ronen Polsky, Xiaoyin Xiao, Cody Washburn, Thomas Beechem and Dave Wheeler (SNL)

Questions?

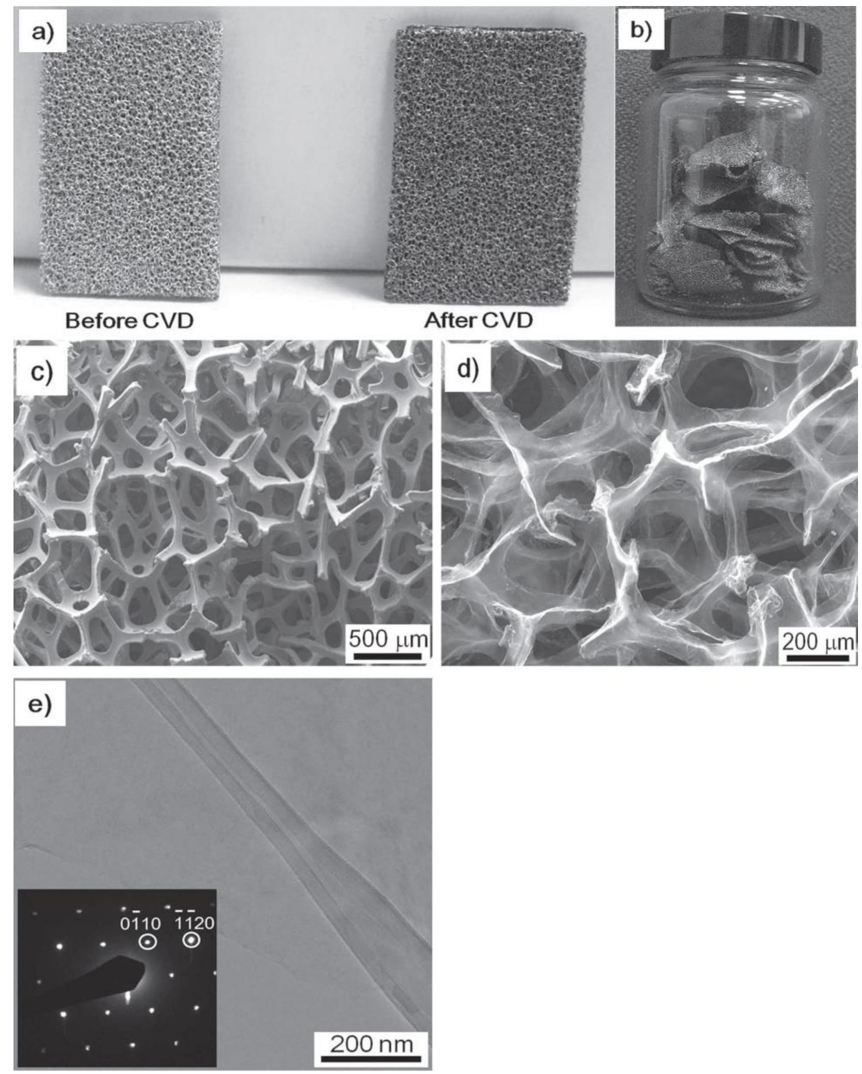
dbburck@sandia.gov

Backup Slides

3D Graphene From Nickel Foam



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

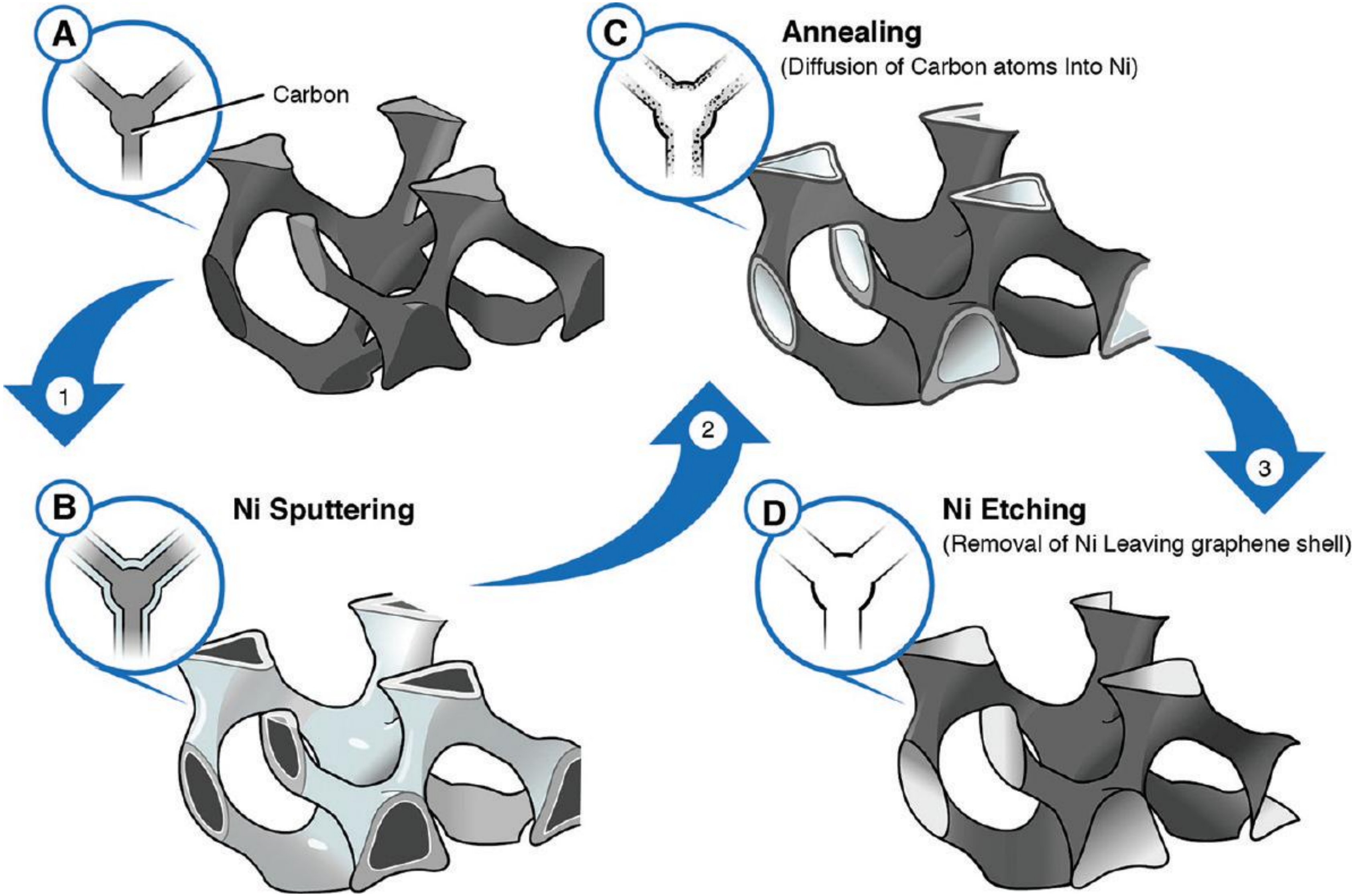


Cao et al. Small, **7**, pp 3163-3168 (2011)

3-D Few-Layer Graphene

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

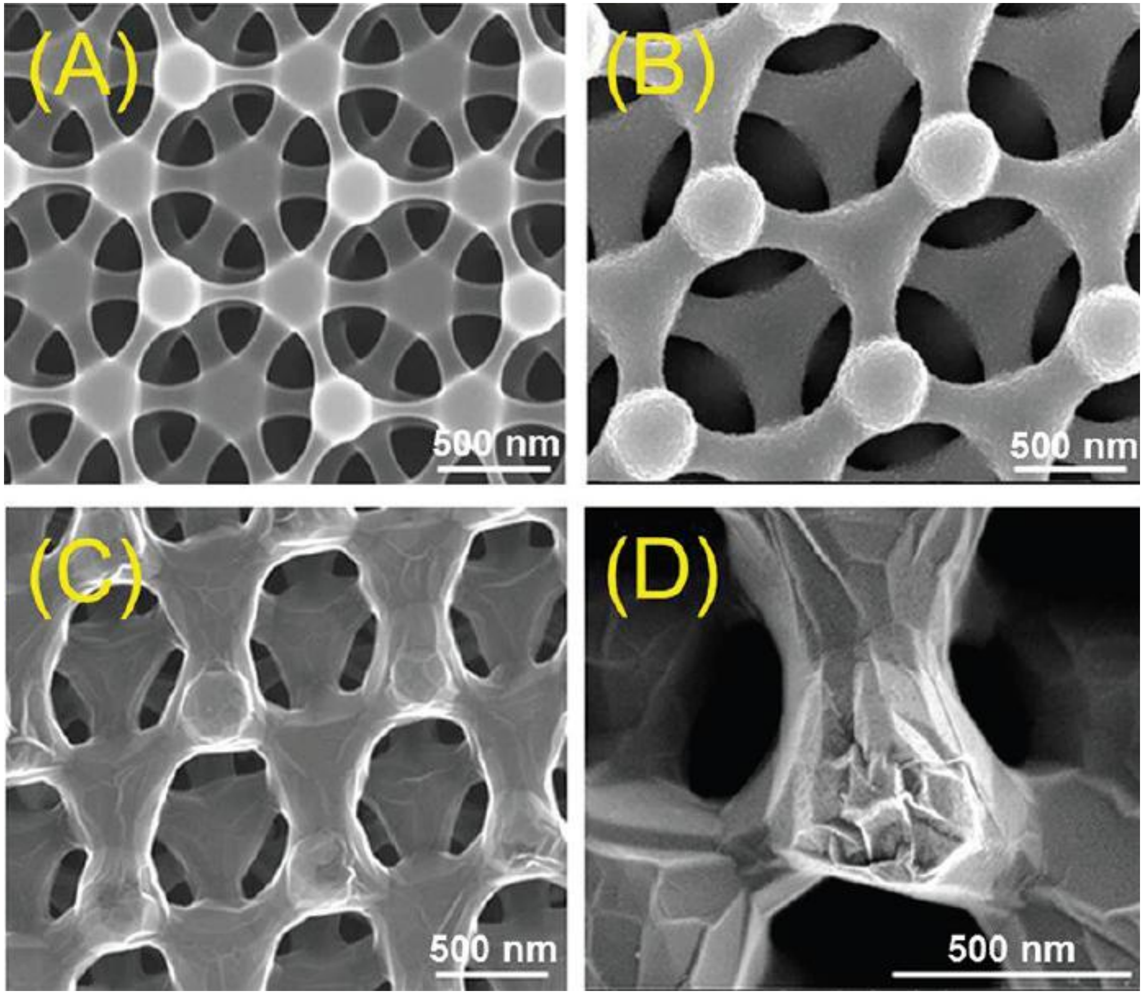
Chemical Conversion to Graphene



SEM Images of Conversion Steps

Amorphous Carbon

Conformal Sputtered Nickel

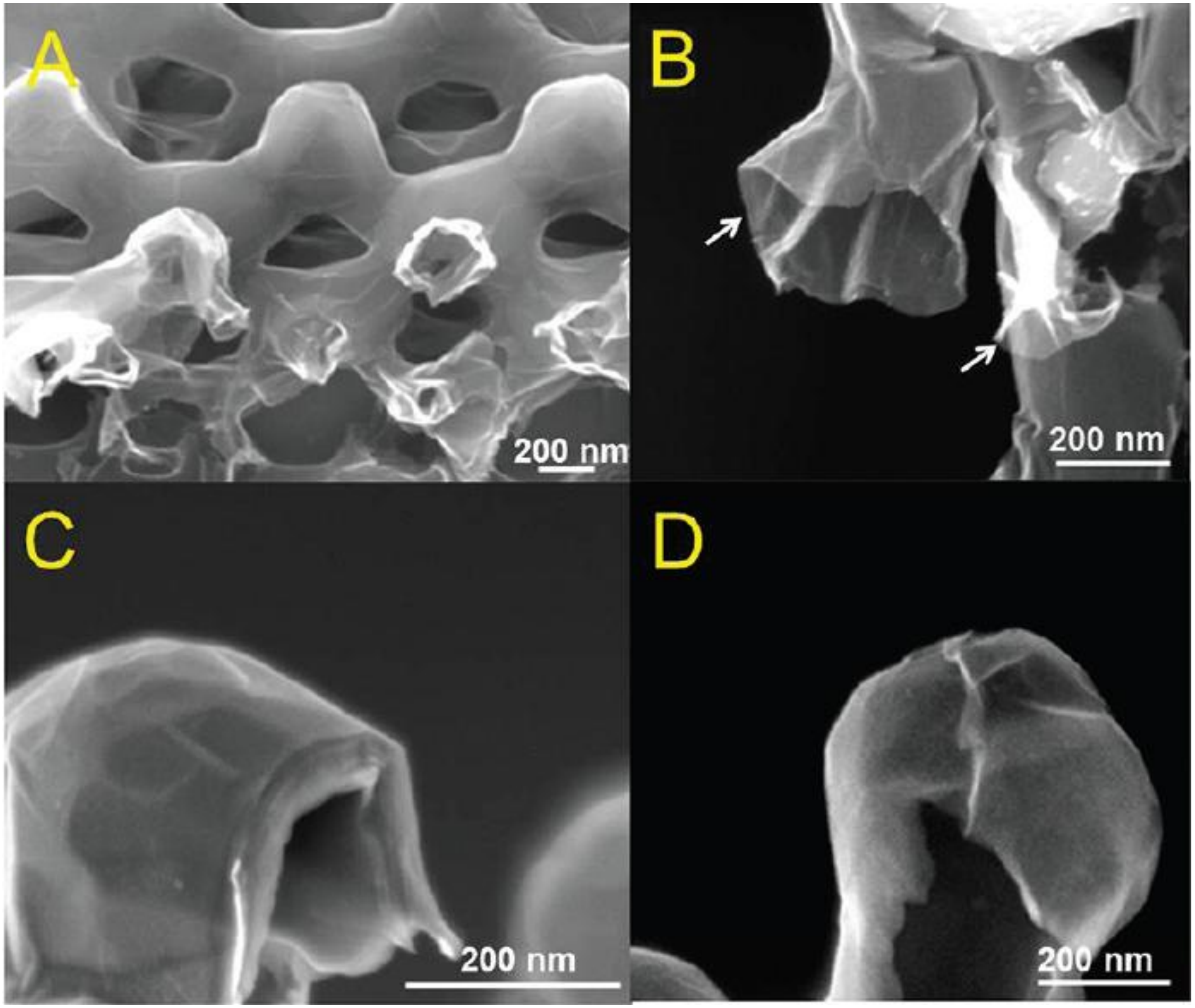


Acidic Washing Of Nickel

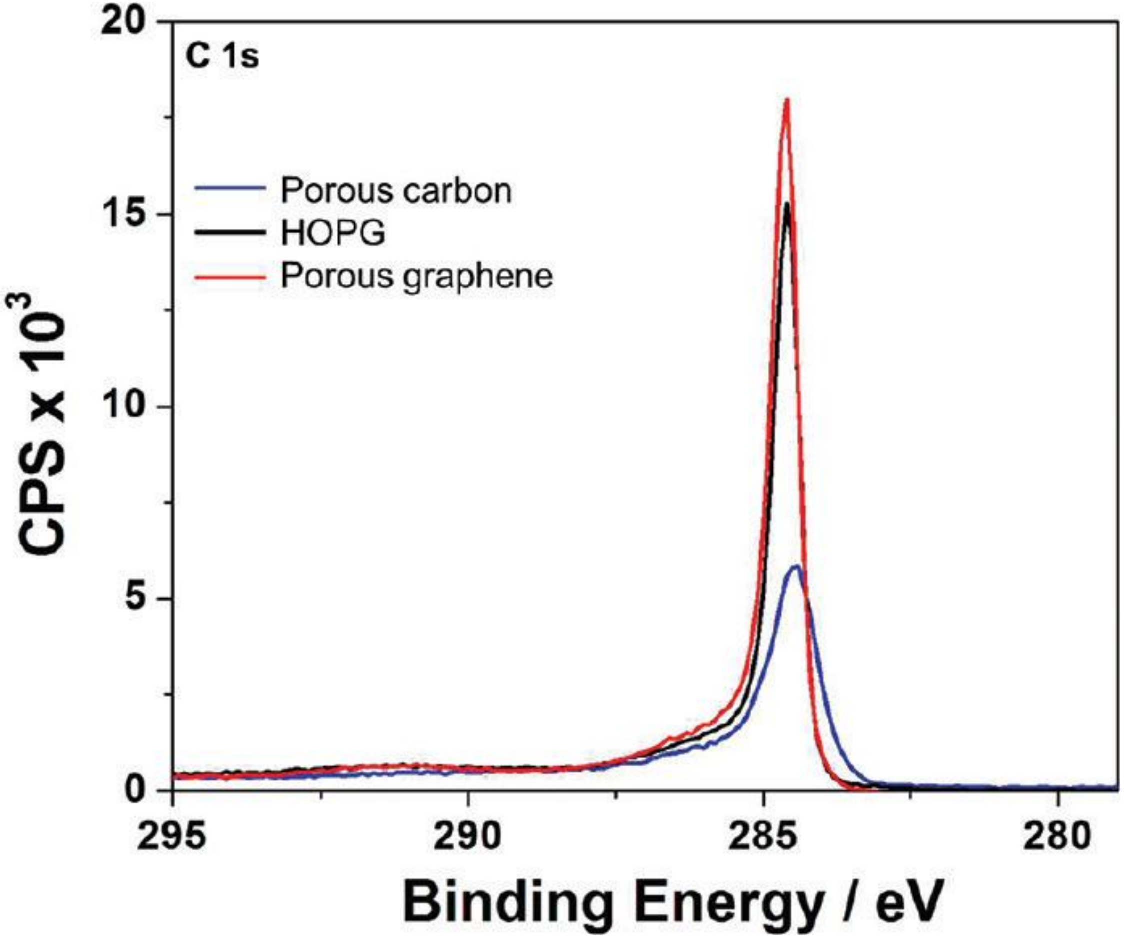
High Mag Image 3D Graphene

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

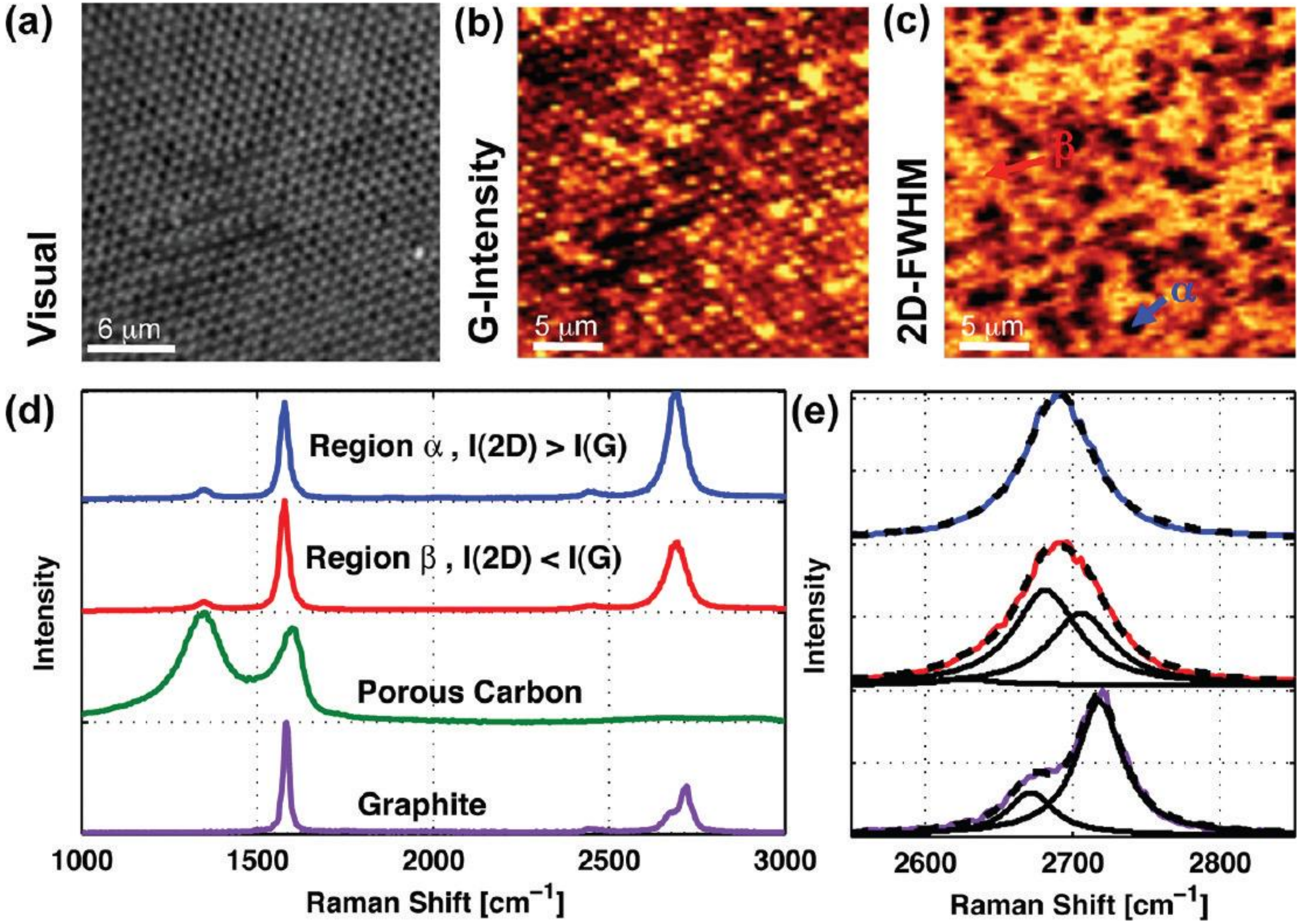
SEM Images of 3D Graphene



Confirmation 3D Graphene: XPS



3D Graphene: Micro-Raman

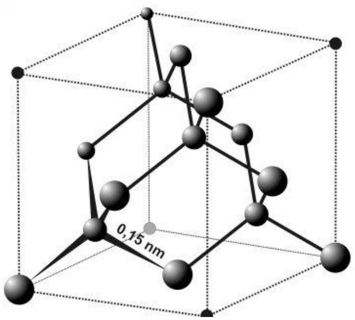


Faces of Carbon

C_6

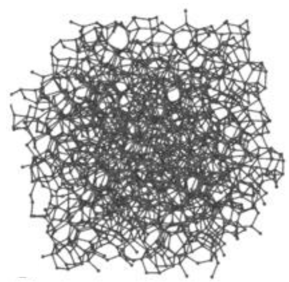
- Highest elemental melting point (sublimes at ~3900K)
- Forms ~ 10 million different compounds
- Resistant to acids, bases and all but the strongest oxidizers
- Biologically compatible

sp^3 bonds
Diamond



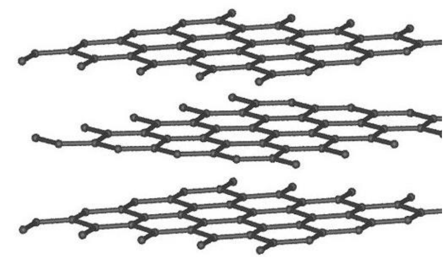
Hardest material
Good abrasive
Electrical insulator
Good thermal conductor
Optically transparent

Amorphous
Carbon



High Modulus
Tunable DC Conductor
Optically Opaque

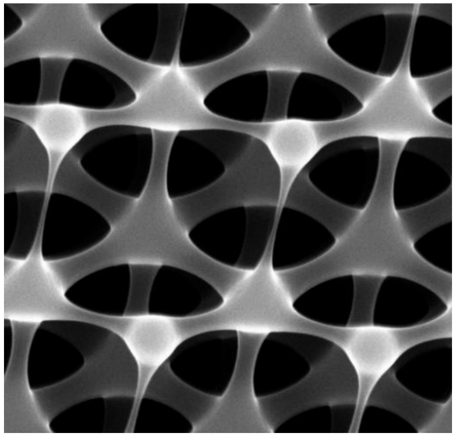
sp^2 bonds
Graphite

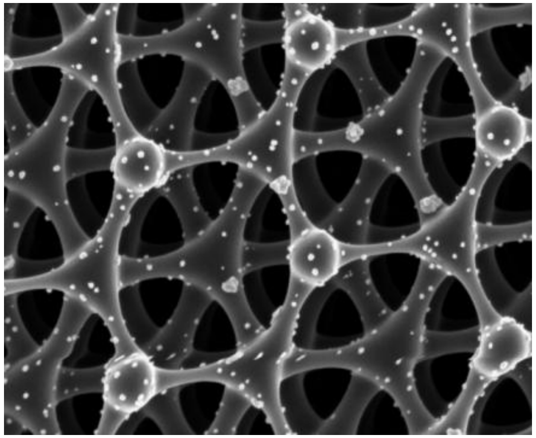


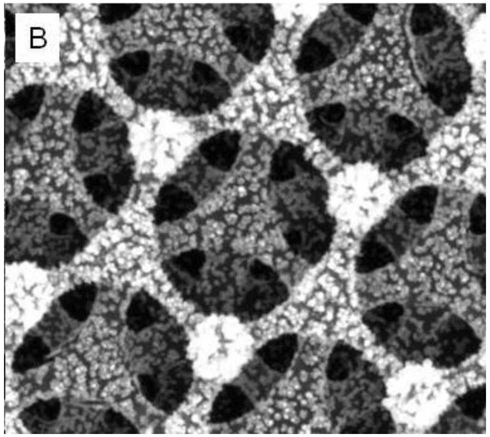
One of the softest materials
Good lubricant
Electrical Conductor
Can act as thermal insulation
Optically opaque

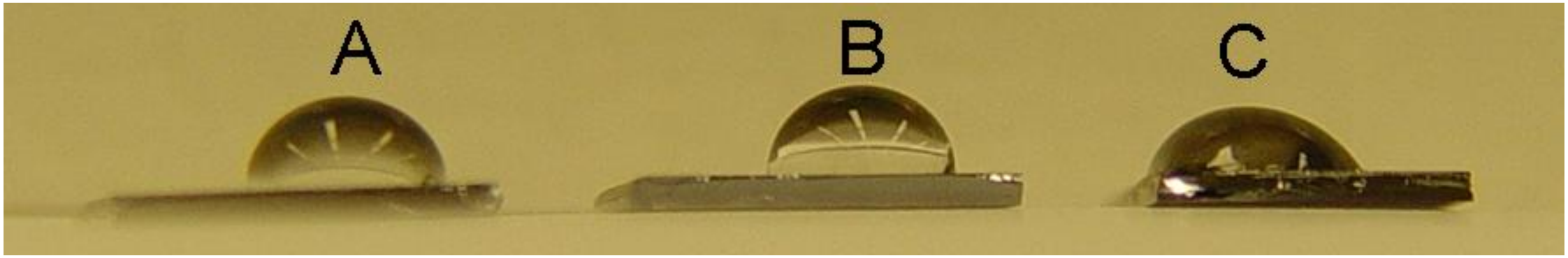
Images from Wikipedia

Lithographically Patterned Carbon



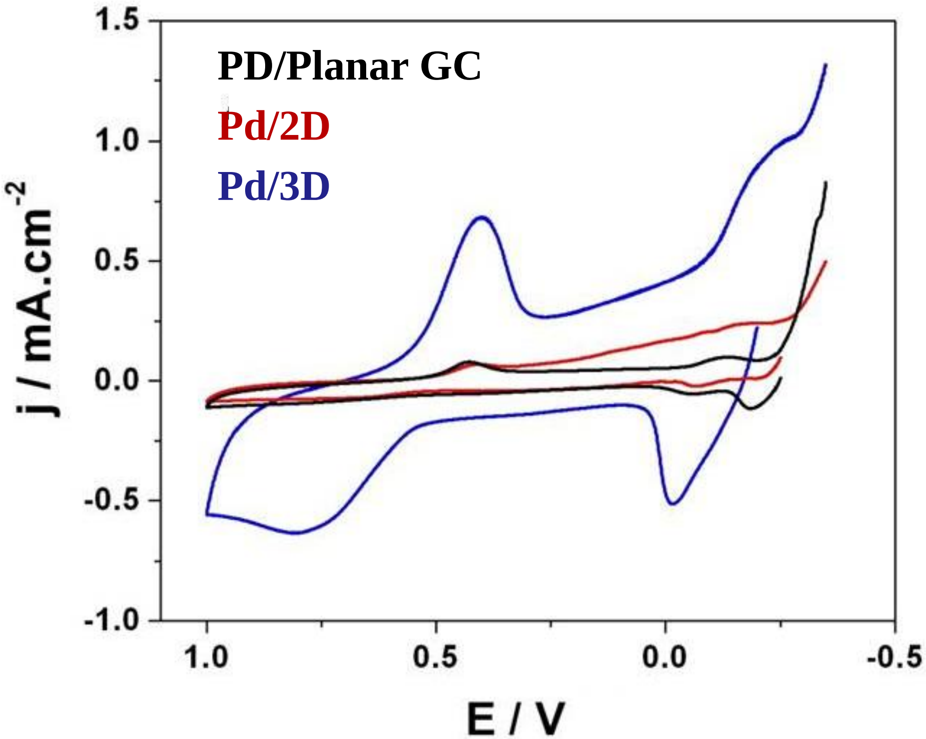






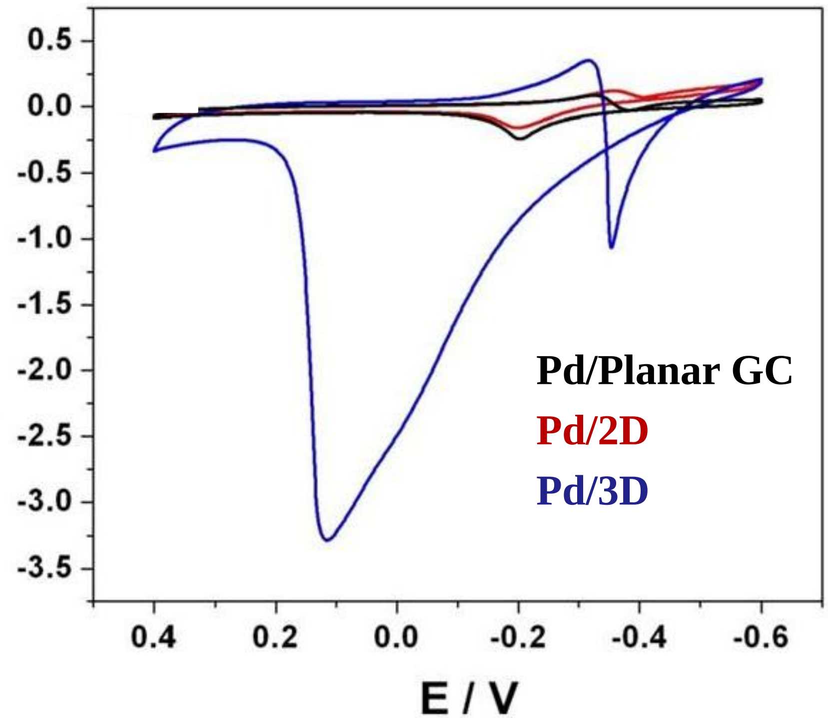
Electrode Characterization – Pd Catalytic MeOH Oxidation

Cycling in $HClO_4$



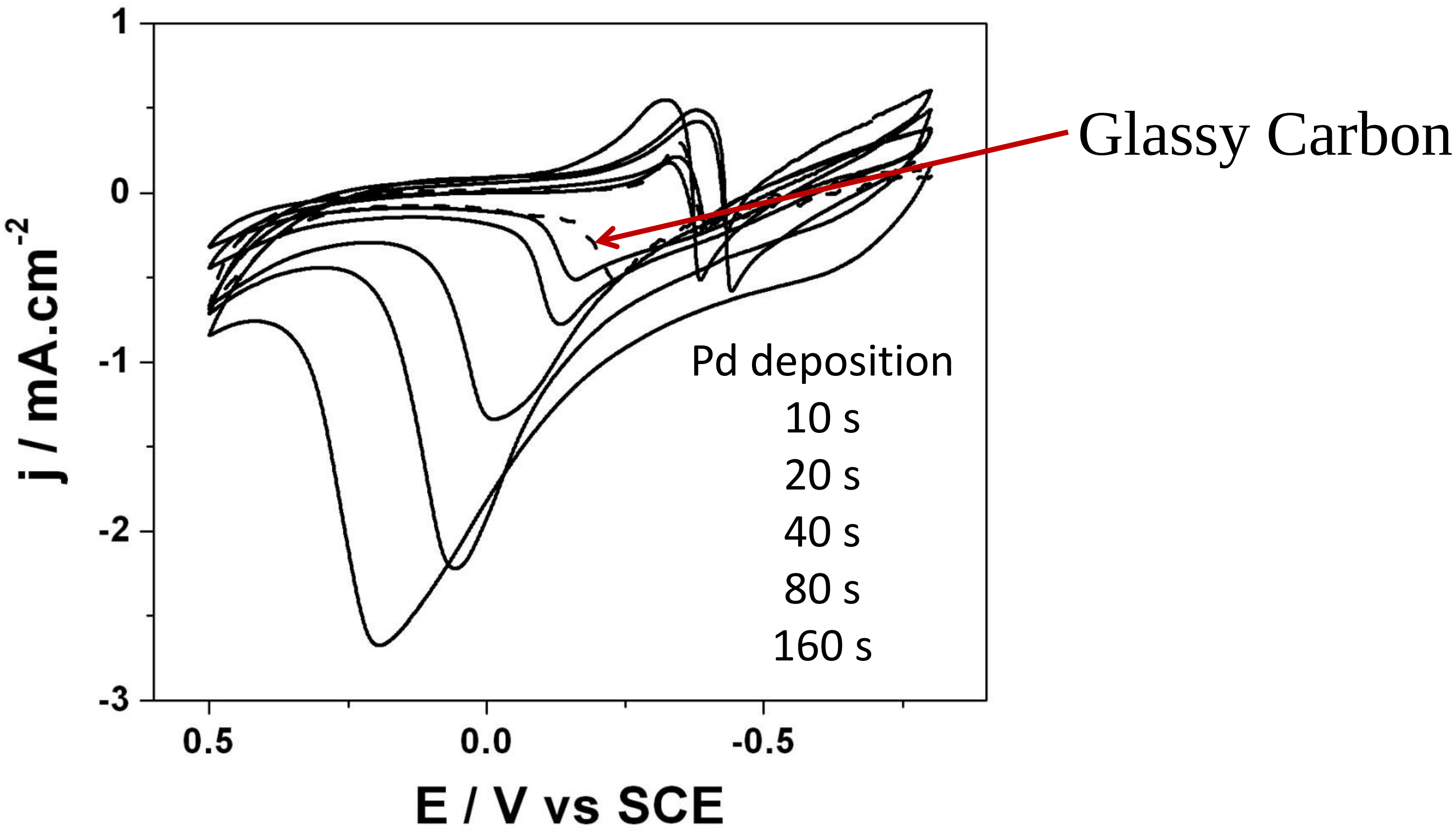
Accessible Pd surface area ~ 20x higher

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