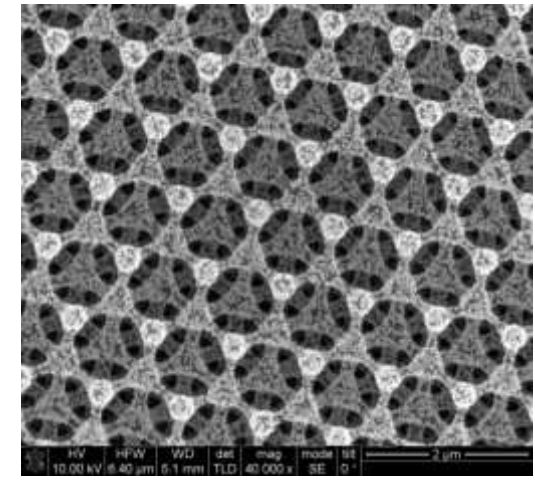
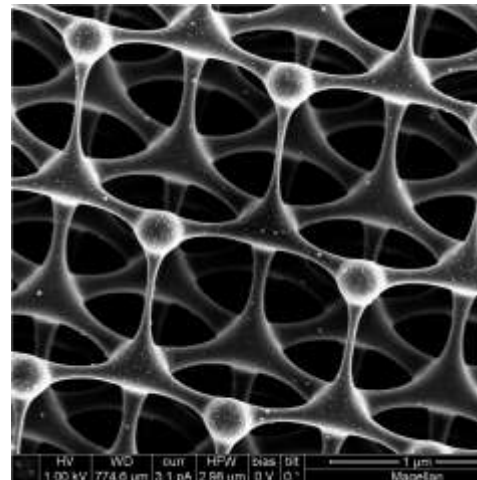
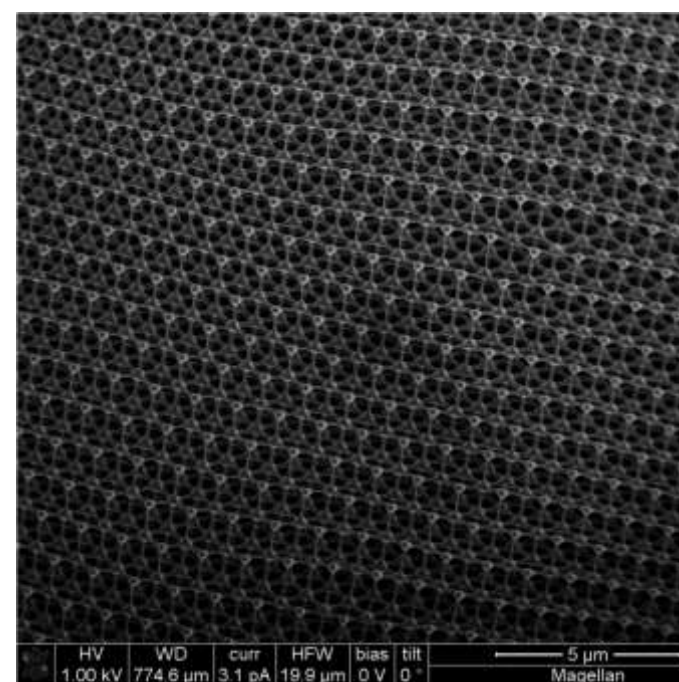


Interferometrically Defined 3D Carbon

SAND2013-0817C

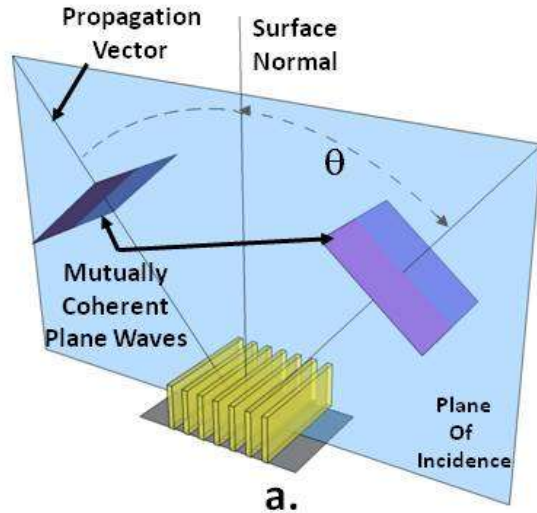


D. Bruce Burckel, Sandia National Laboratories

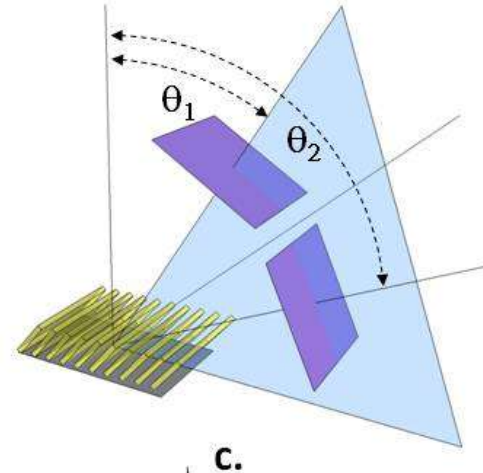
Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Interferometric Lithography

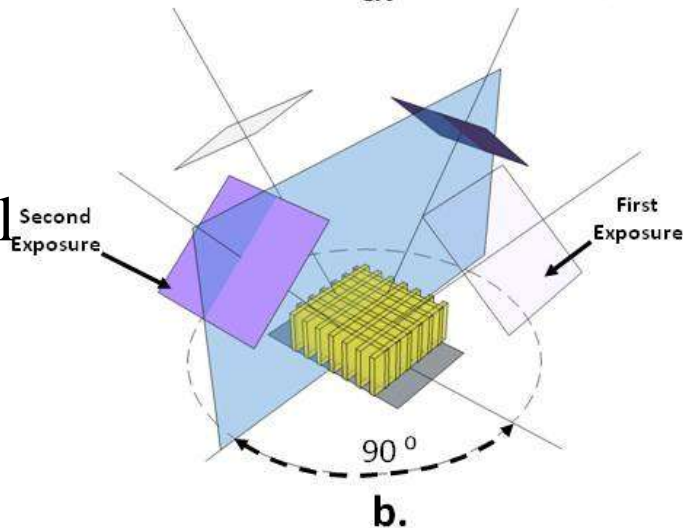
1-D
Lines



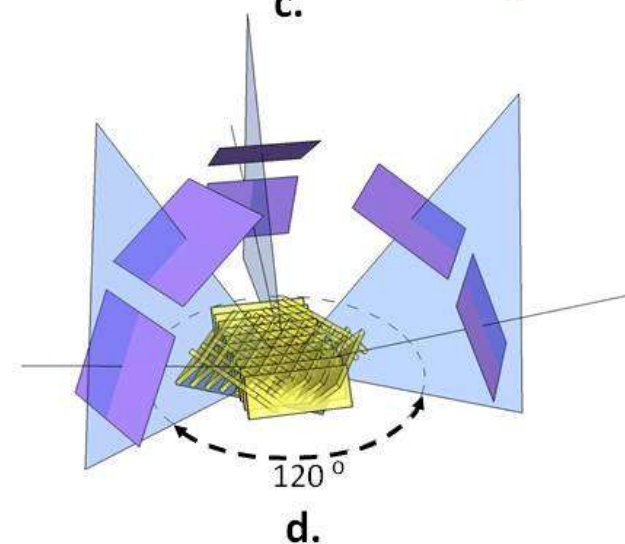
Tilted
1-D
Lines



2-D
Crystal

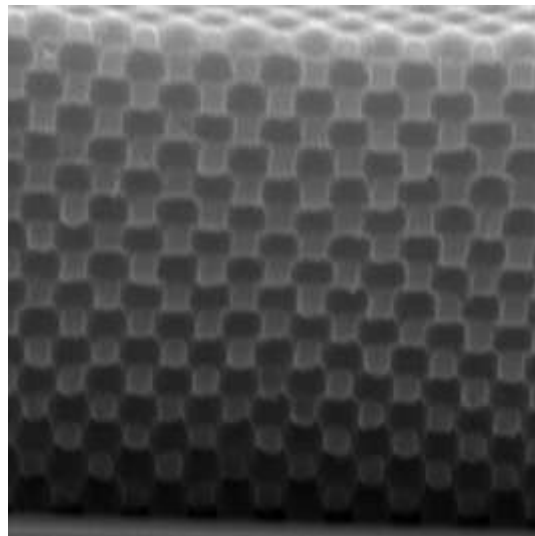
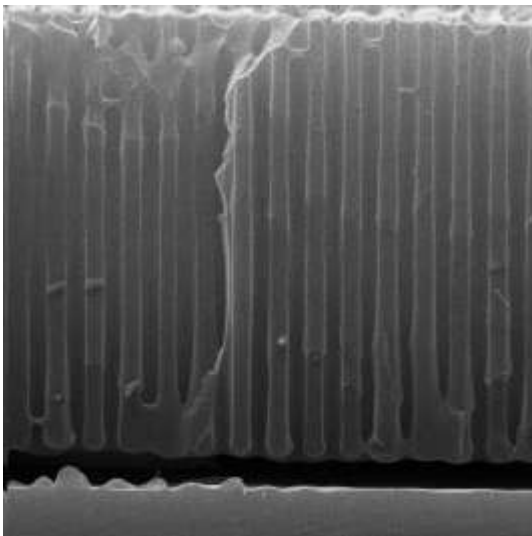
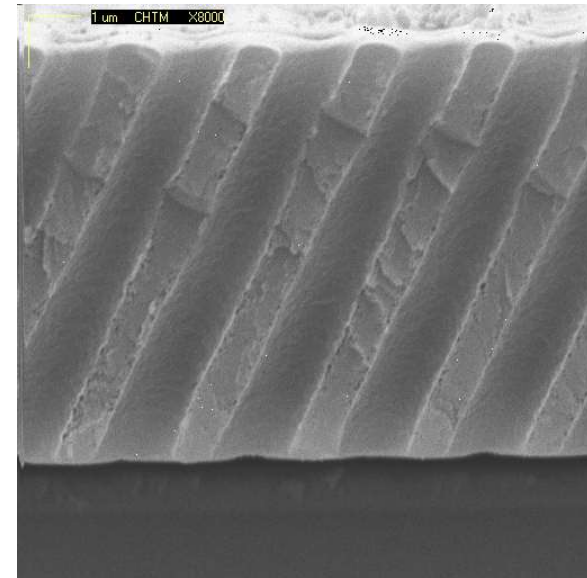
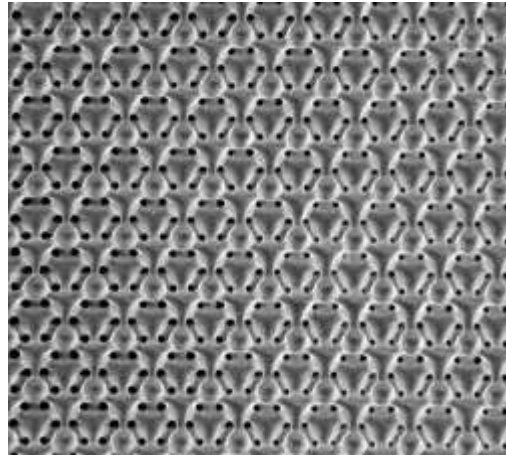
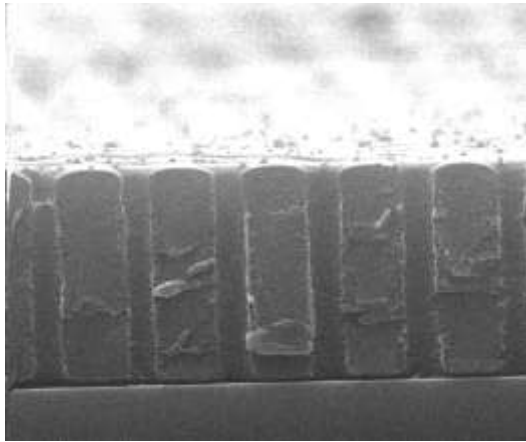


3-D
Crystal



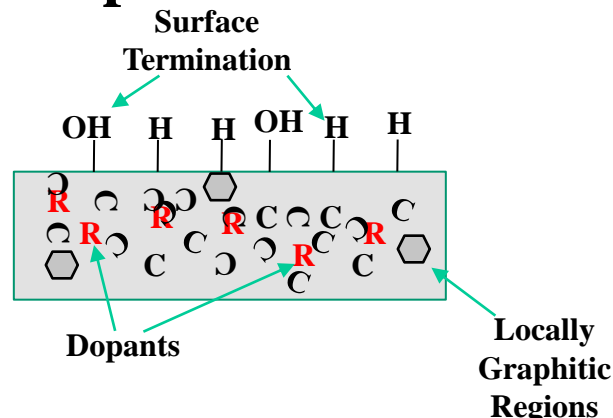
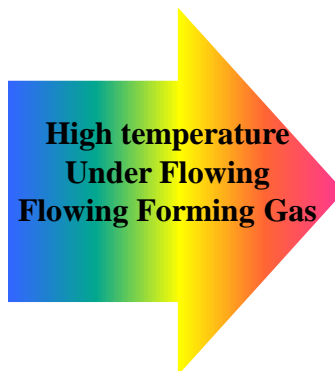
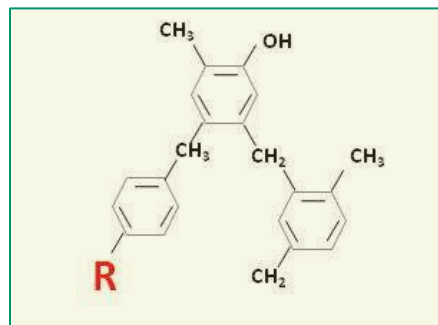
Burckel et al, *JVST B*, 28, C6P14 (2010).

Sub-Micron 3D Resist Patterns Via Interferometric Lithography



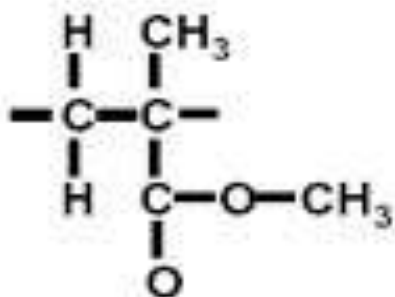
Synthesis Route to Amorphous Carbon: Pyrolysis of Organic Polymers

Organic Polymer → Pyrolysis → Amorphous Carbon

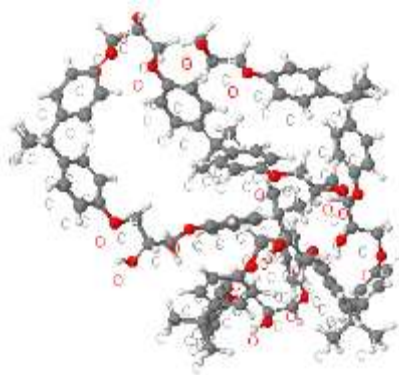


Typical Photopatternable Organic Polymers

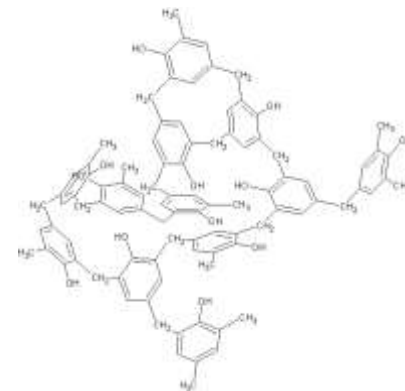
Polymethyl Methacrylate
(PMMA)



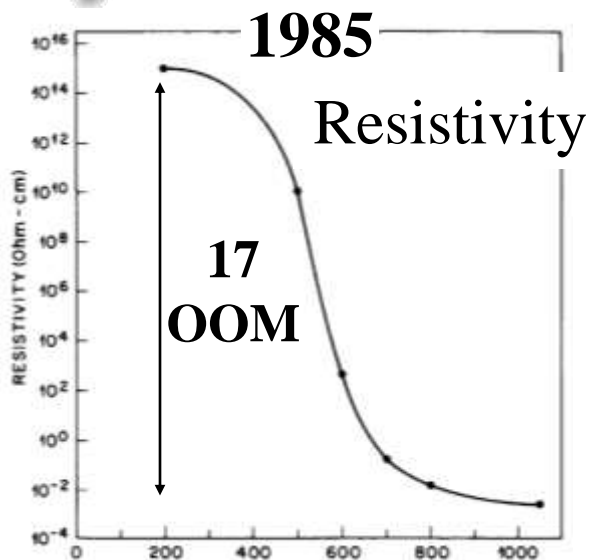
Epoxide Resist
(SU 8)



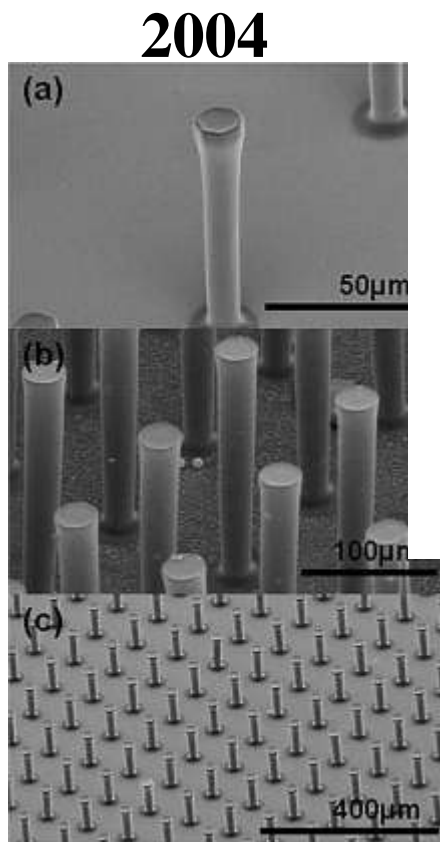
Phenol formaldehyde resin
(novolac photoresist)



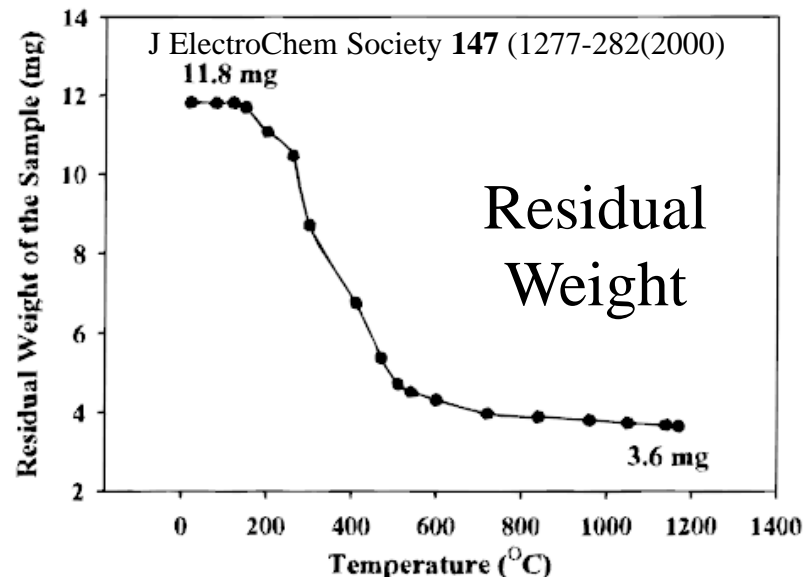
Visual History and Properties of Pyrolyzed Resist



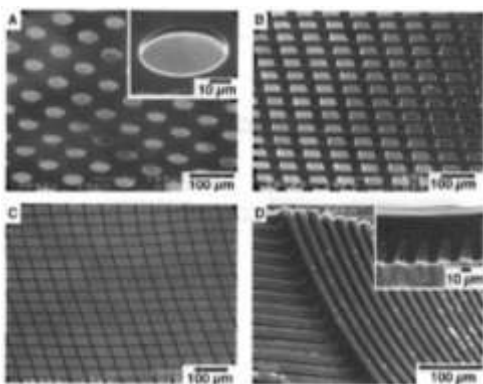
J. NonCryst Sol. **70**, 99-109 (1985)



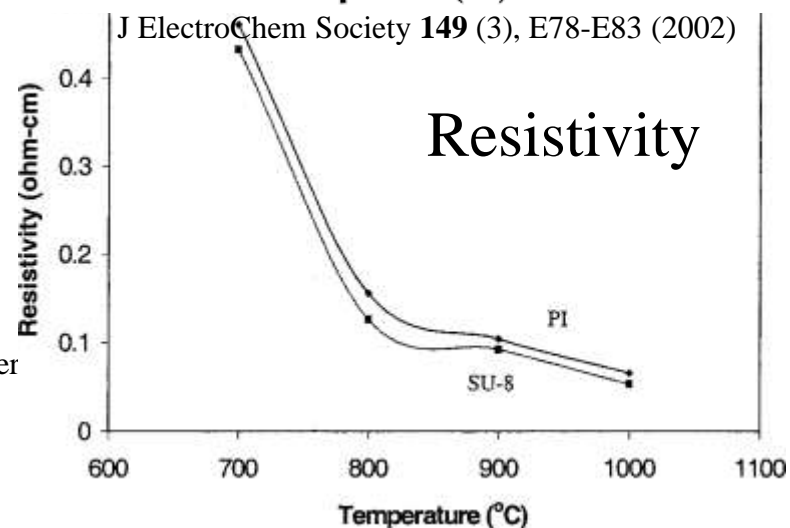
Electrochemical and Solid State Letter **7**, (11) A435-A438 (2004)



1997

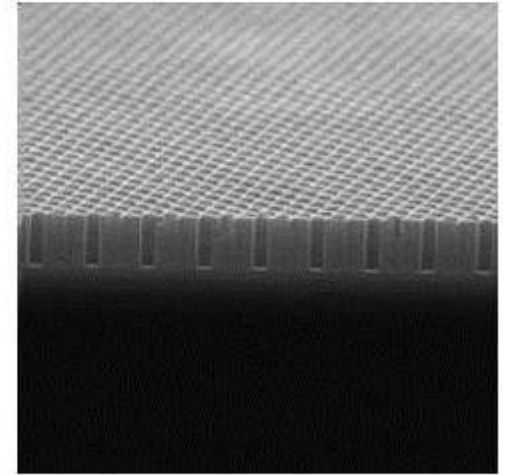
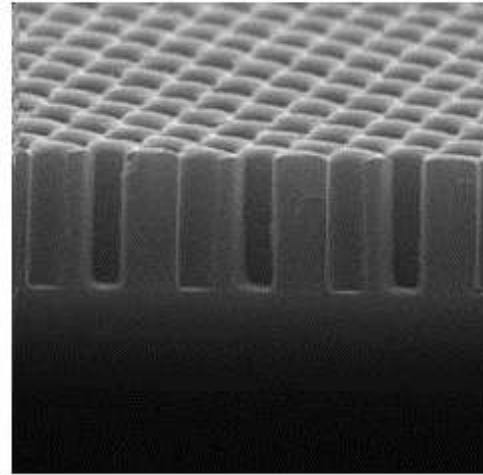
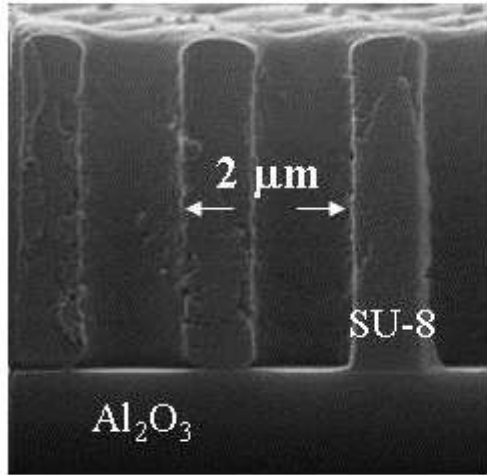


Adv. Mater. **9**, (6) 477-480 (1997)

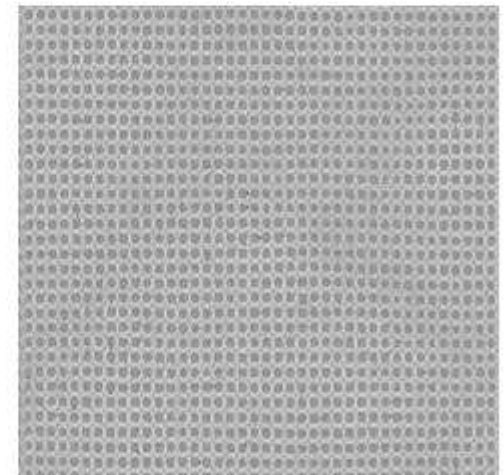
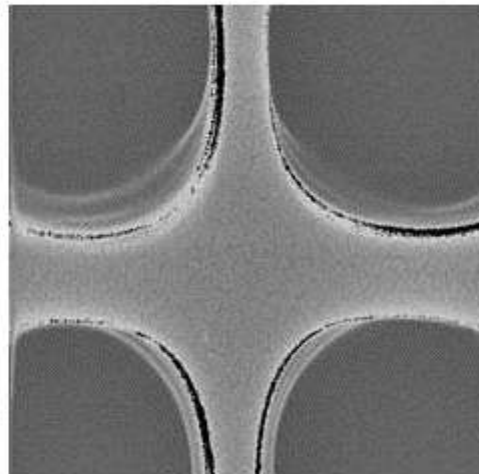
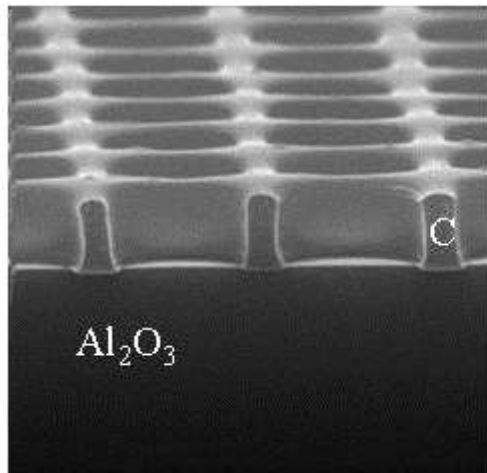


Conversion of 2-D Resist Structure to 2-D Carbon Structure

Resist

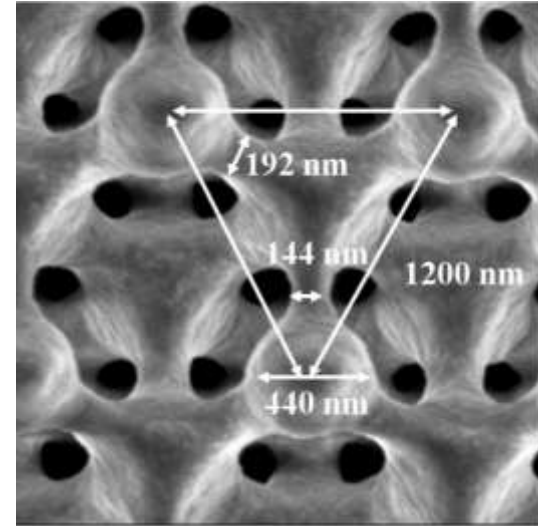
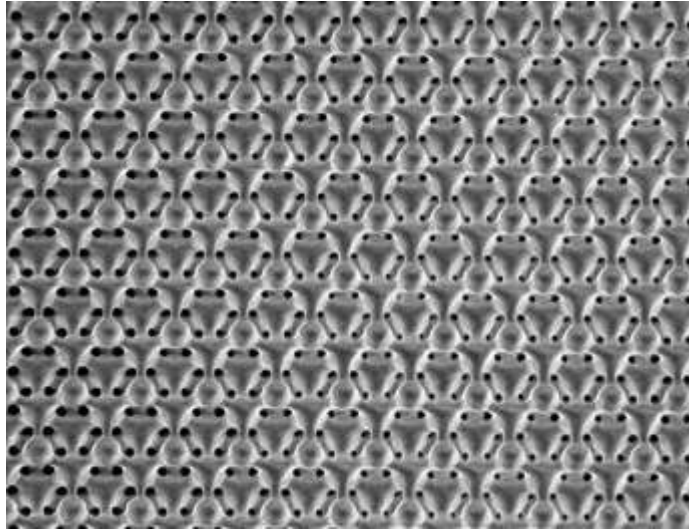


Carbon

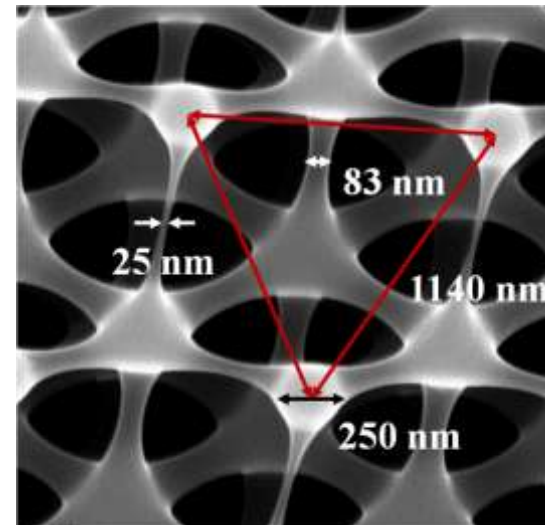
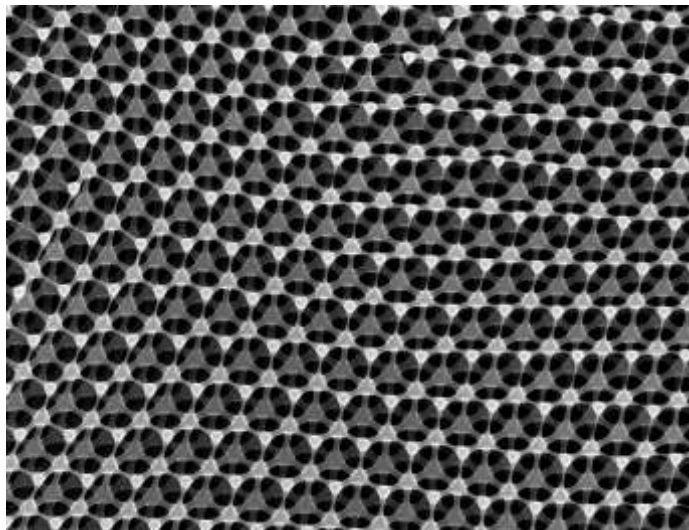


Conversion of 3-D Resist Structure to 3-D Carbon Structure

Resist



Carbon

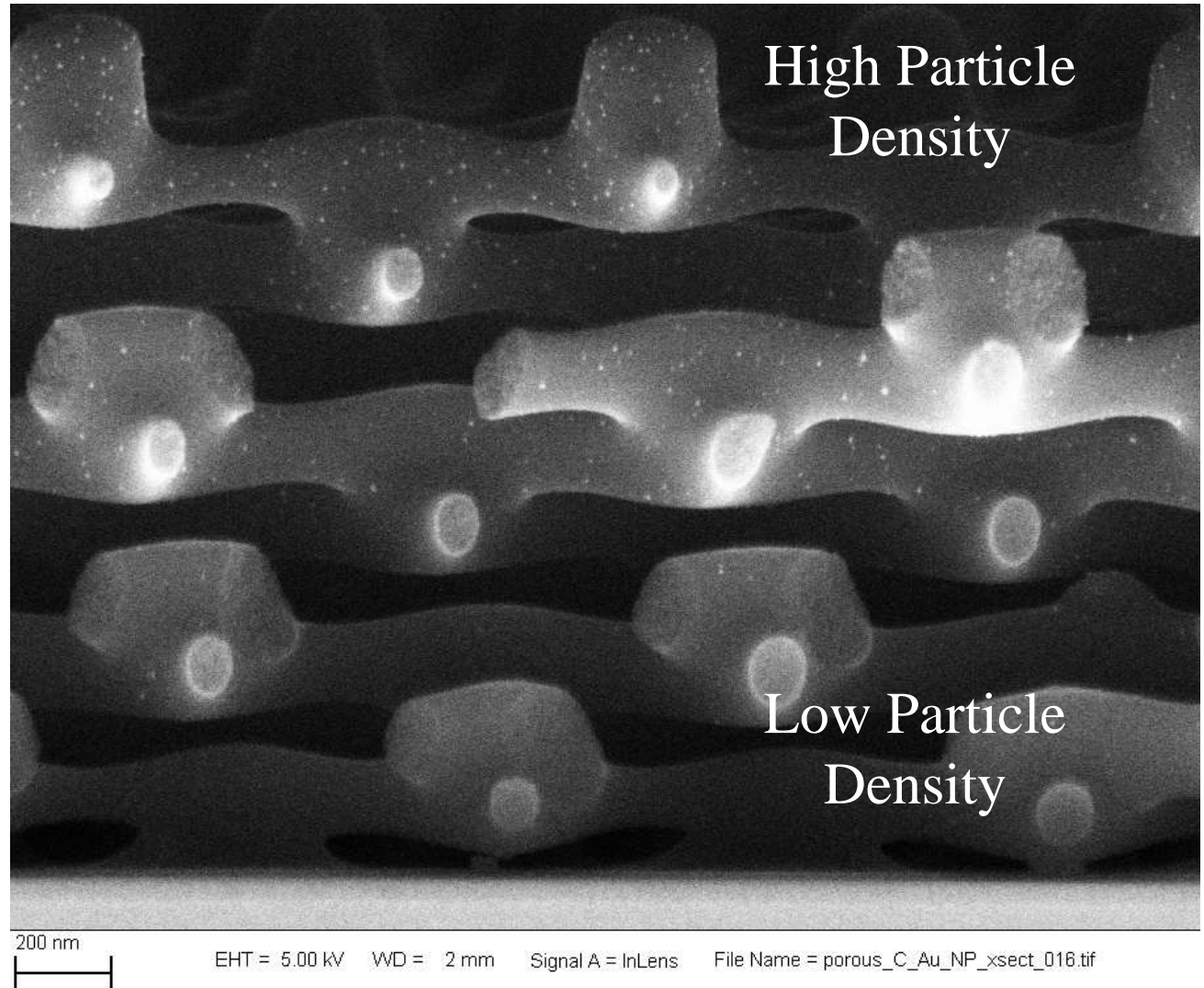


Vertical vs. Horizontal Shrinkage

Significant
vertical
shrinkage

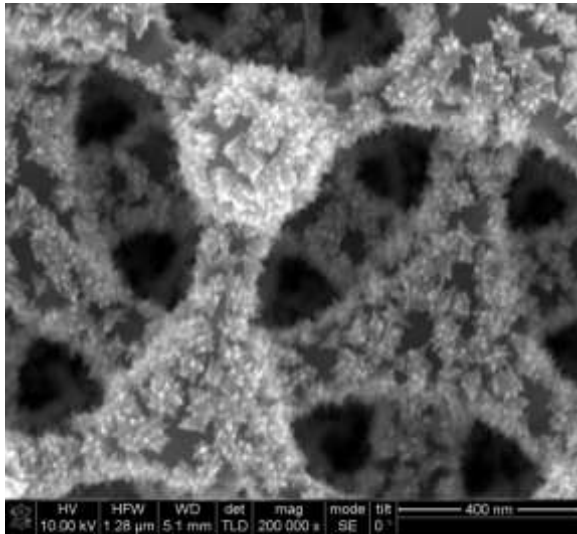
Extremely small,
highly uniform
NPs

Inhomogeneous
wetting

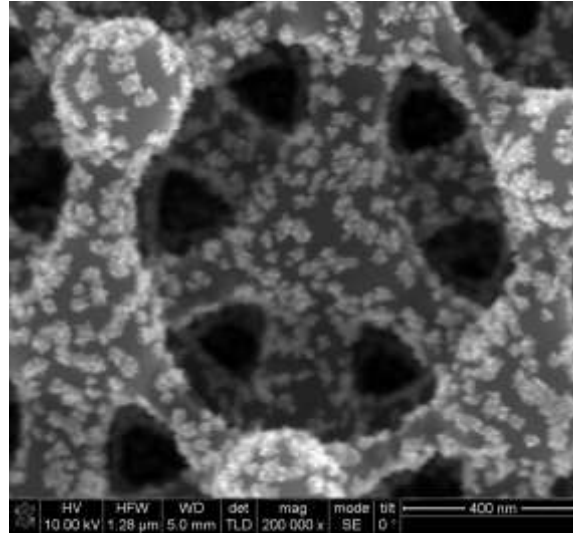


Burckel et al, *Small*, **5**, pp2792-2796 (2009).

Electrodeposition Conditions Impact Nanoparticle Morphology

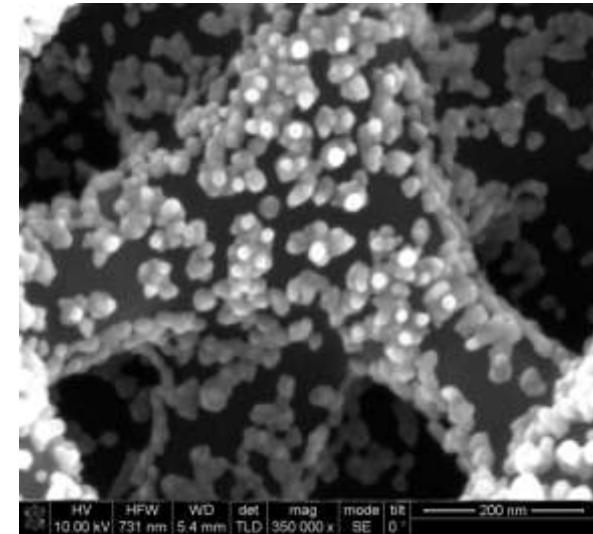


100 s Deposition



50 s Deposition

-0.65 V



100 s Deposition

-0.45 V

Pd Nanocrystals

Interferometrically Patterned Carbon

Carbon
Photonics

Structured
Thermal
Emitters

High Surface Area
Catalysis/Sensor Platform

GaN Defect
Reduction

Catalytic Nano-particles

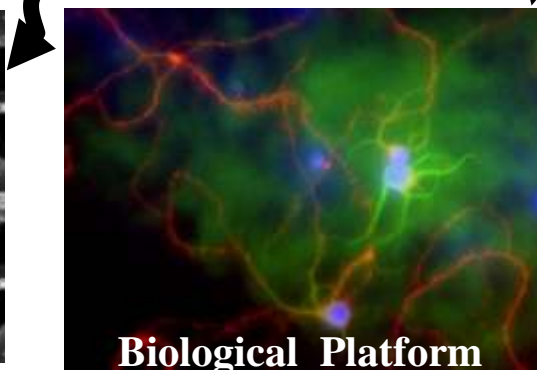
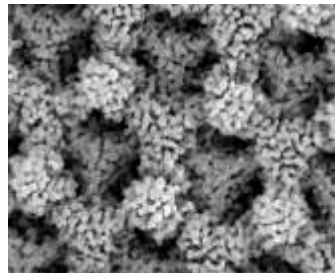
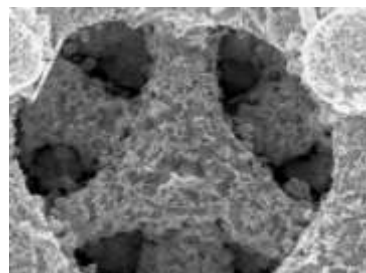
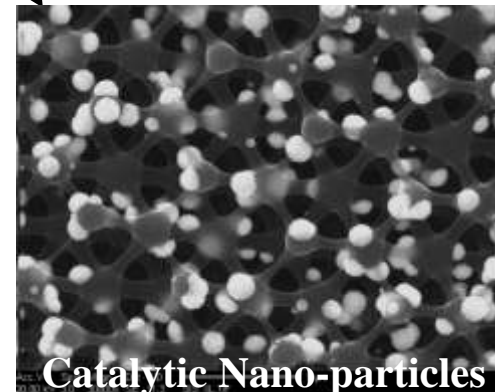
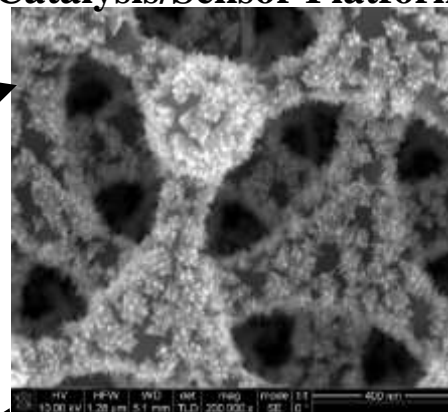
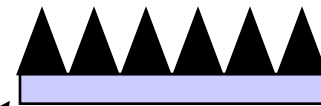
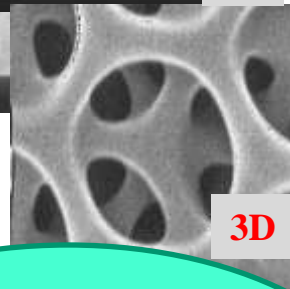
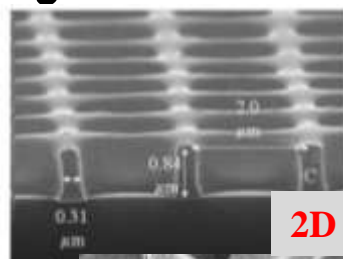
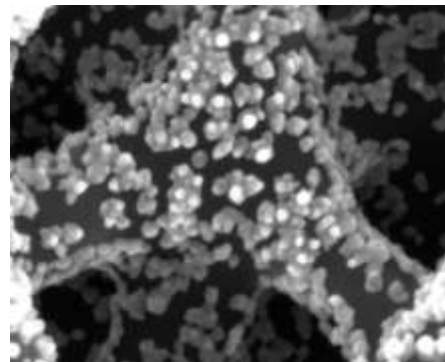
Convert 1D, 2D and 3D
sub-micron photoresist patterns
created with interferometric
lithography into
pyrolytic carbon

Ultra-Capacitor/Energy Storage

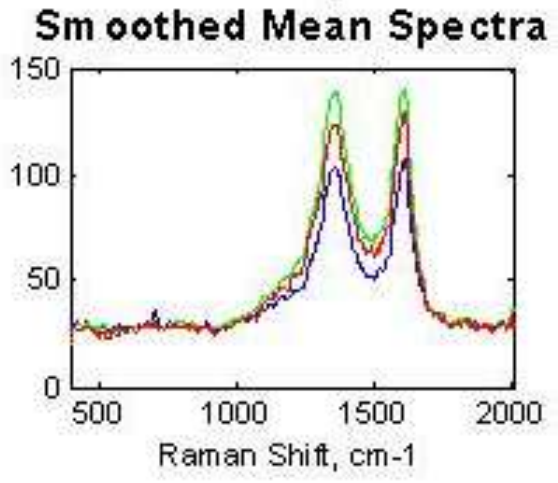
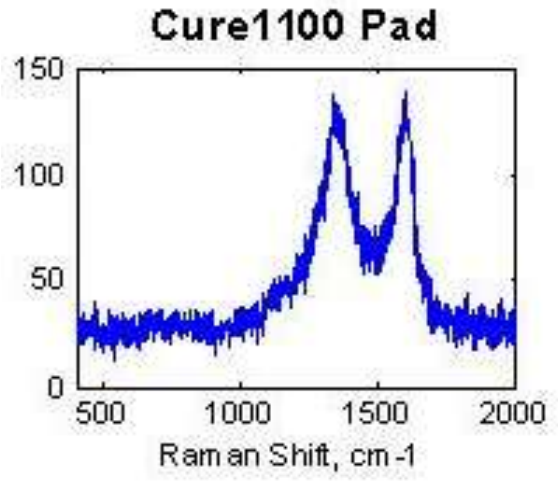
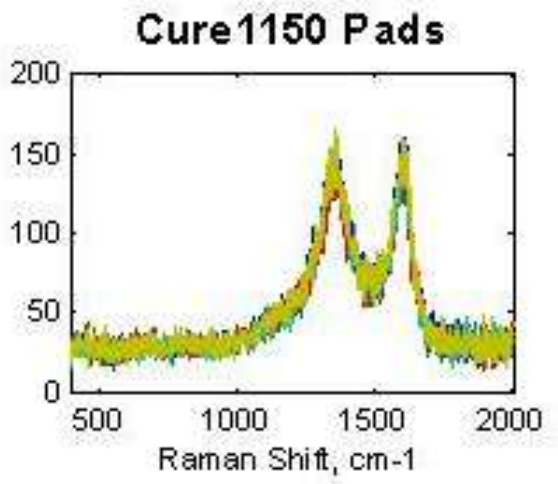
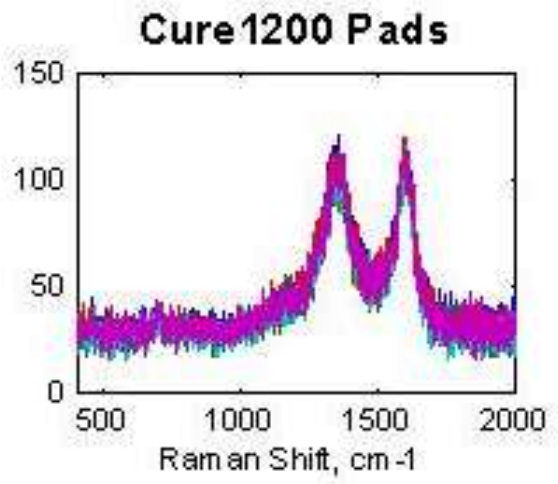
Hierarchical Porosity

Fuel Cell Electrode

Biological Platform

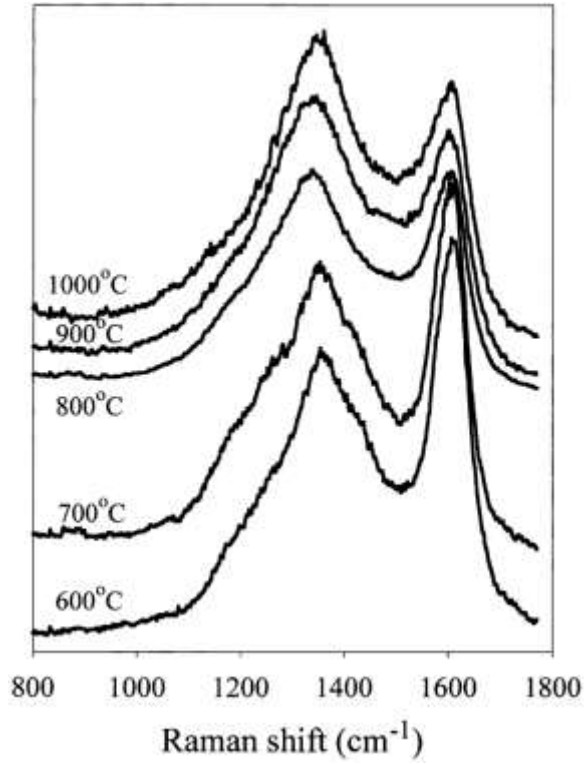


Raman Spectroscopy of Pyrolyzed Resist

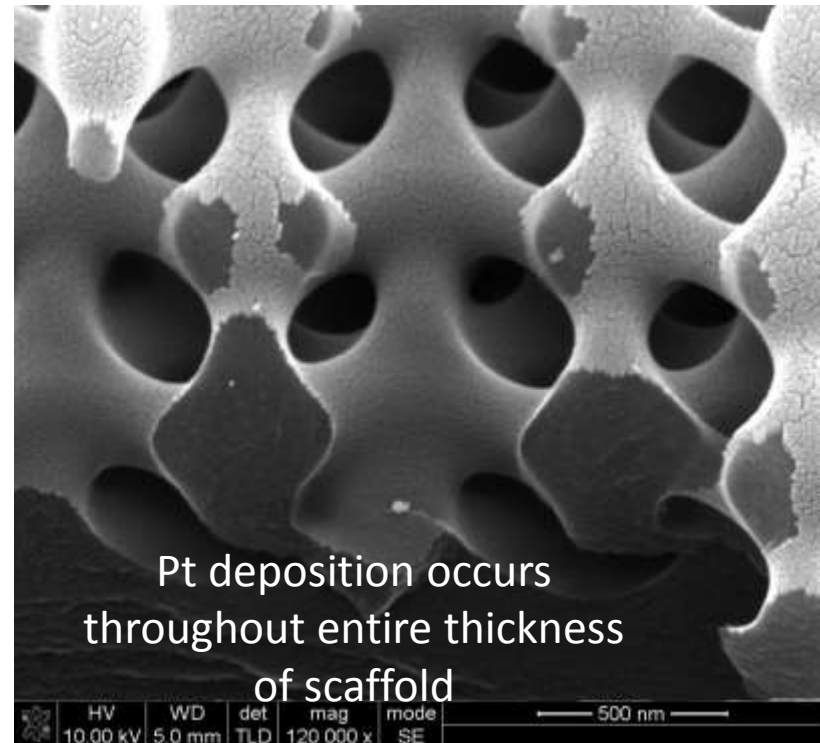
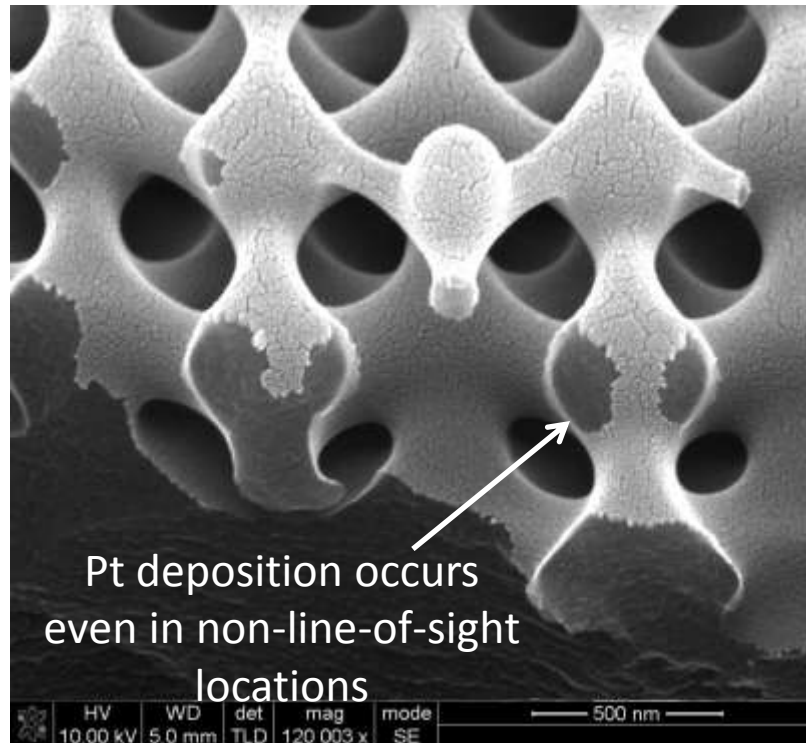


Comparison To Literature Values

J. Non Cryst Solids 396 (2001) 36-43
1344 cm⁻¹ 1591 cm⁻¹ ← HOPG
1367 cm⁻¹ 1622 cm⁻¹ ← Disordered C



Modification of Carbon Scaffold: PVD



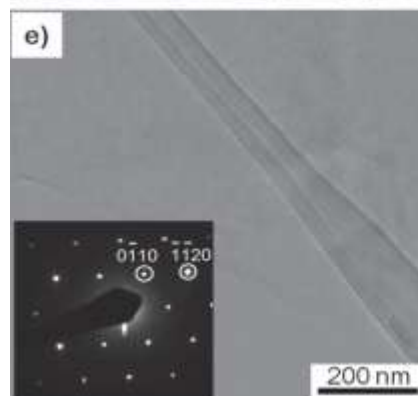
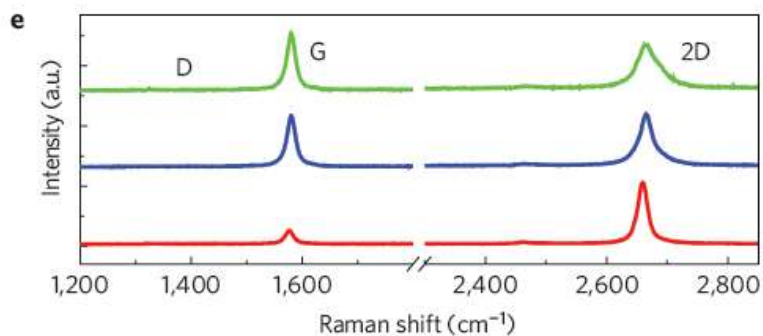
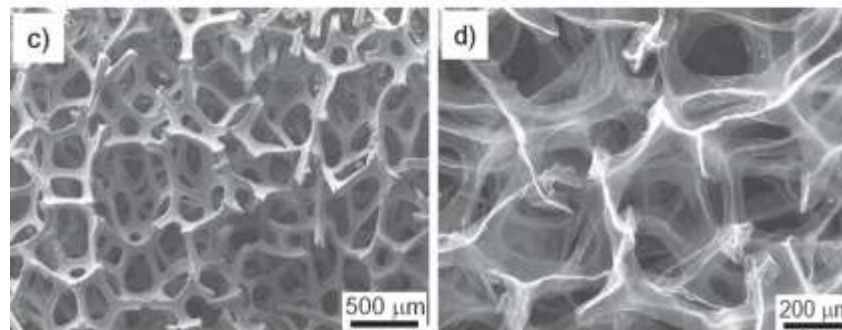
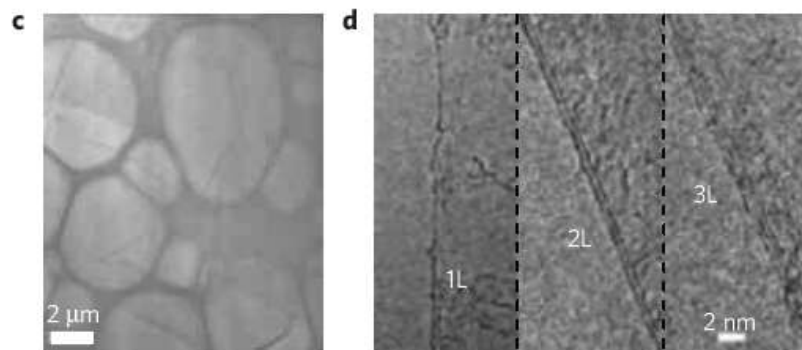
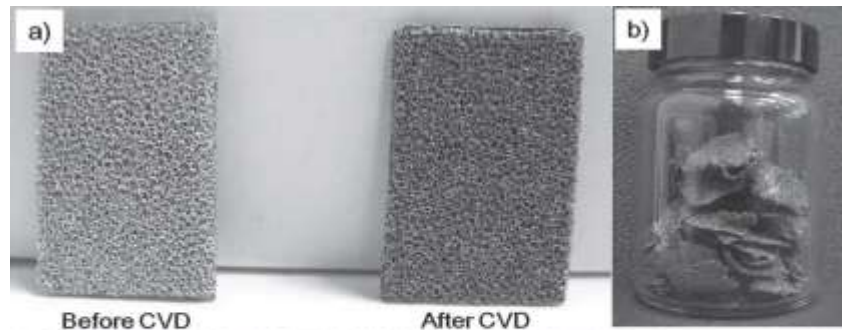
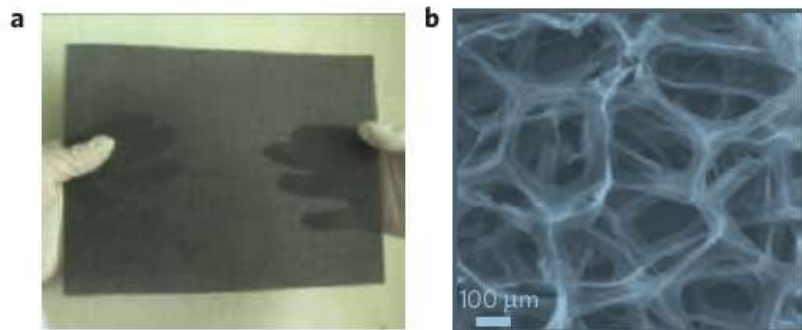
Pt sputtered @ 1A/s



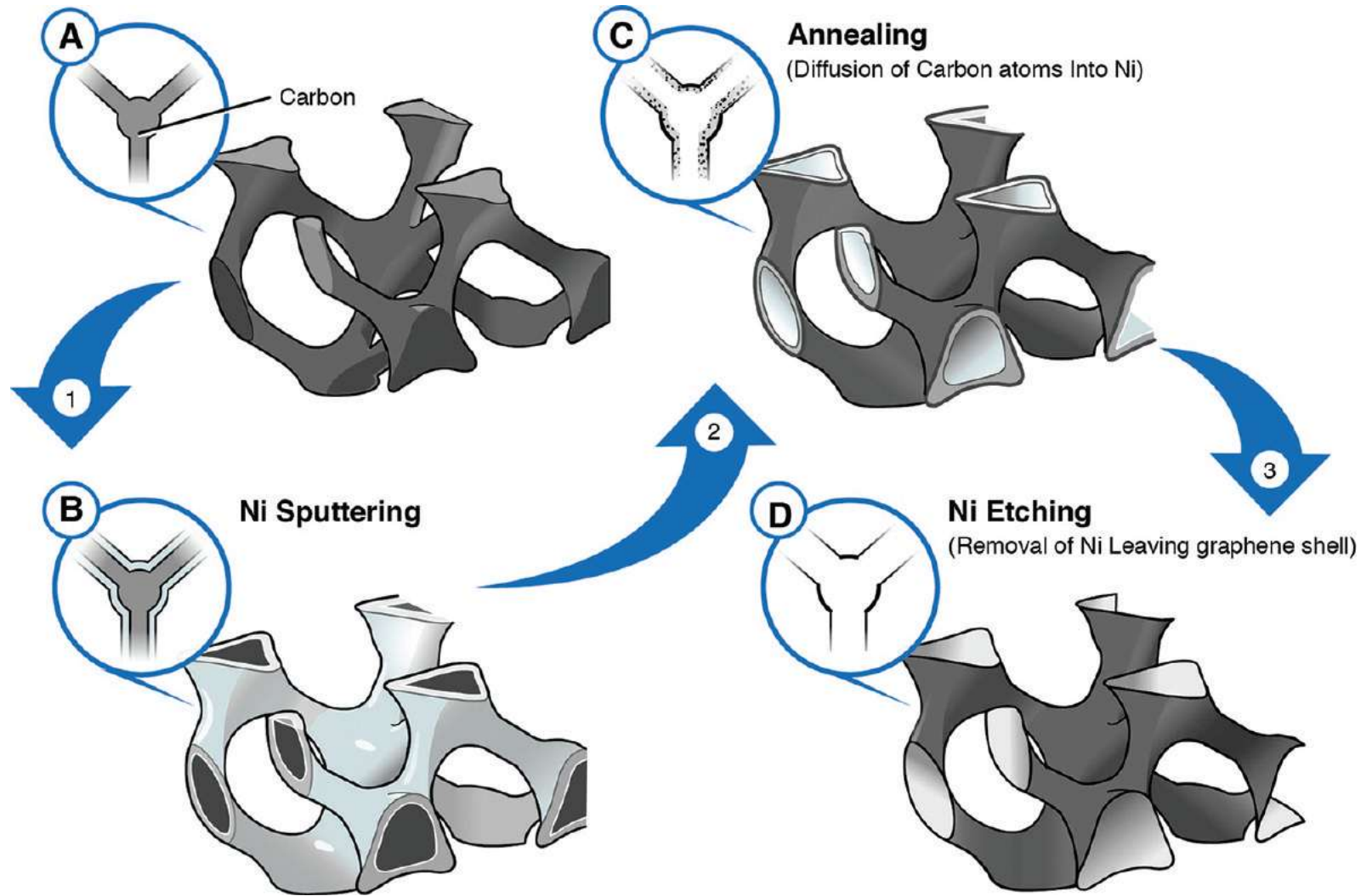
3-D Few-Layer Graphene

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

3D Graphene From Nickel Foam

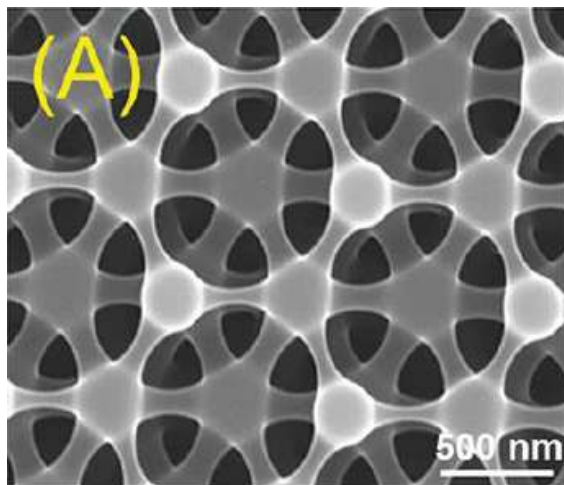


Chemical Conversion to Graphene

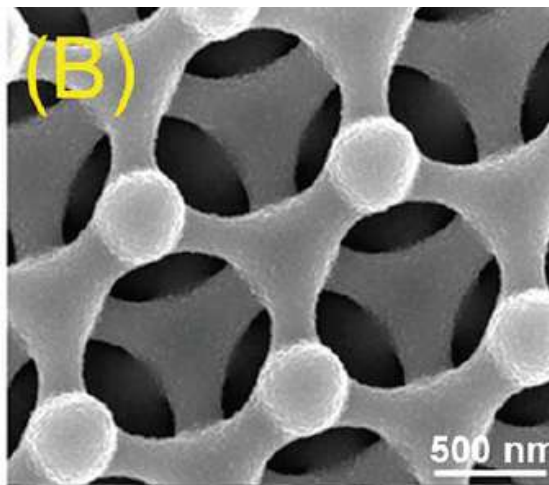


SEM Images of Conversion Steps

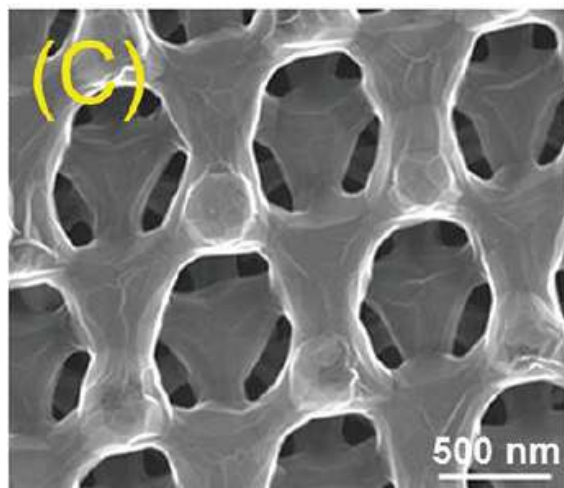
**Amorphous
Carbon**



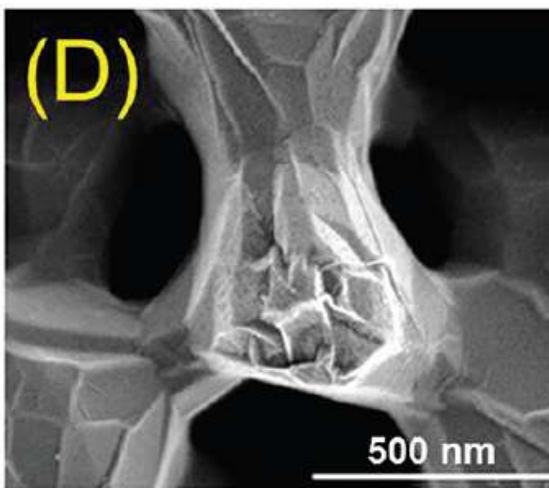
**Conformal
Sputtered
Nickel**



**Acidic
Washing
Of Nickel**

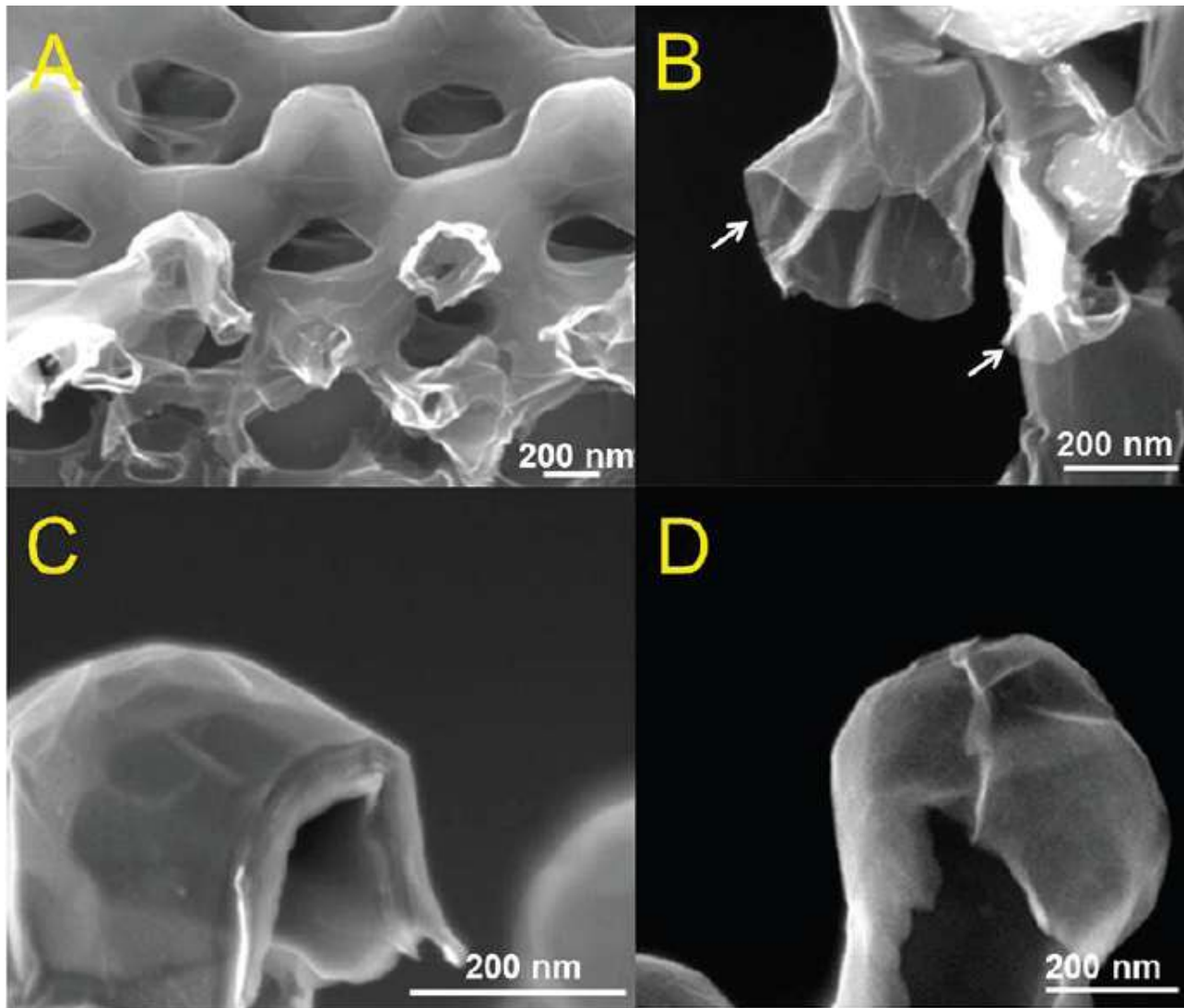


**High
Mag
Image
3D Graphene**

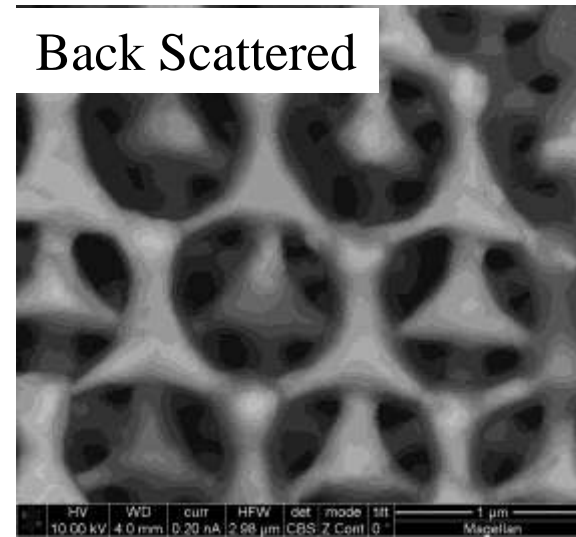
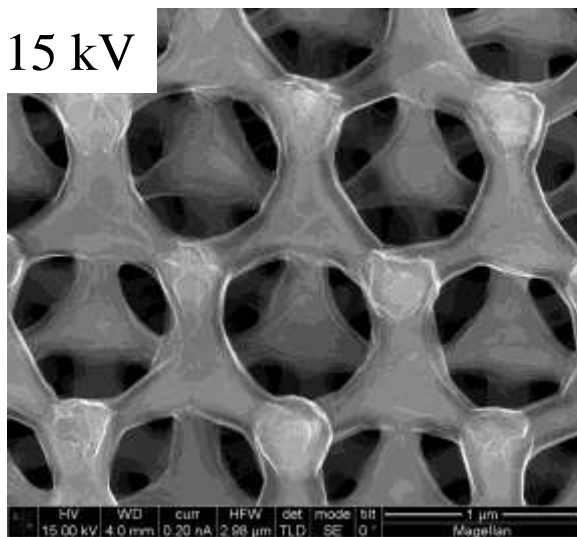
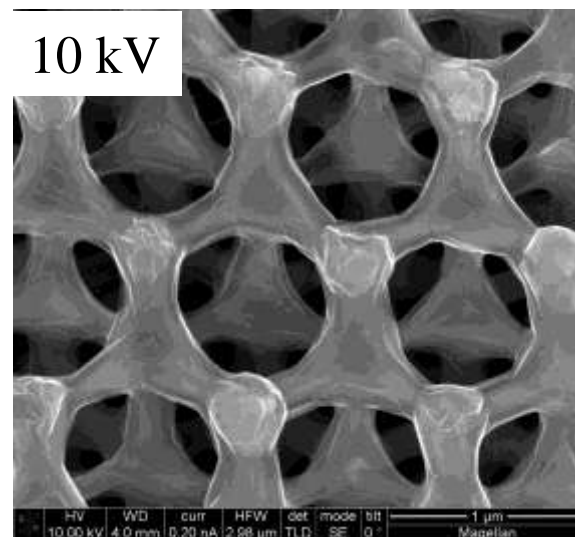
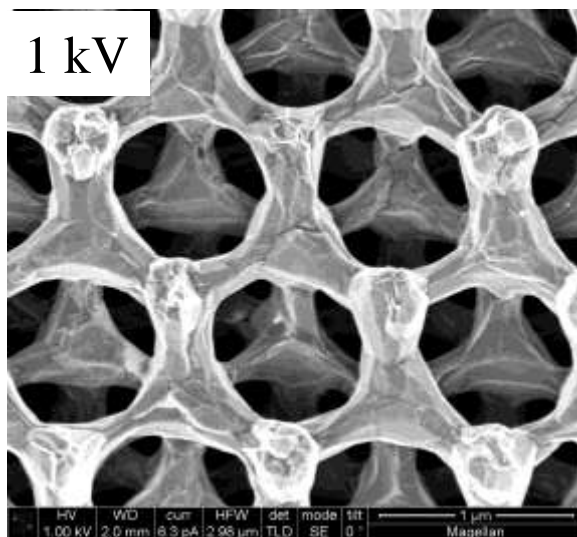


Xiao et al, ACS Nano, **6**, pp. 3573-3579 (2012).

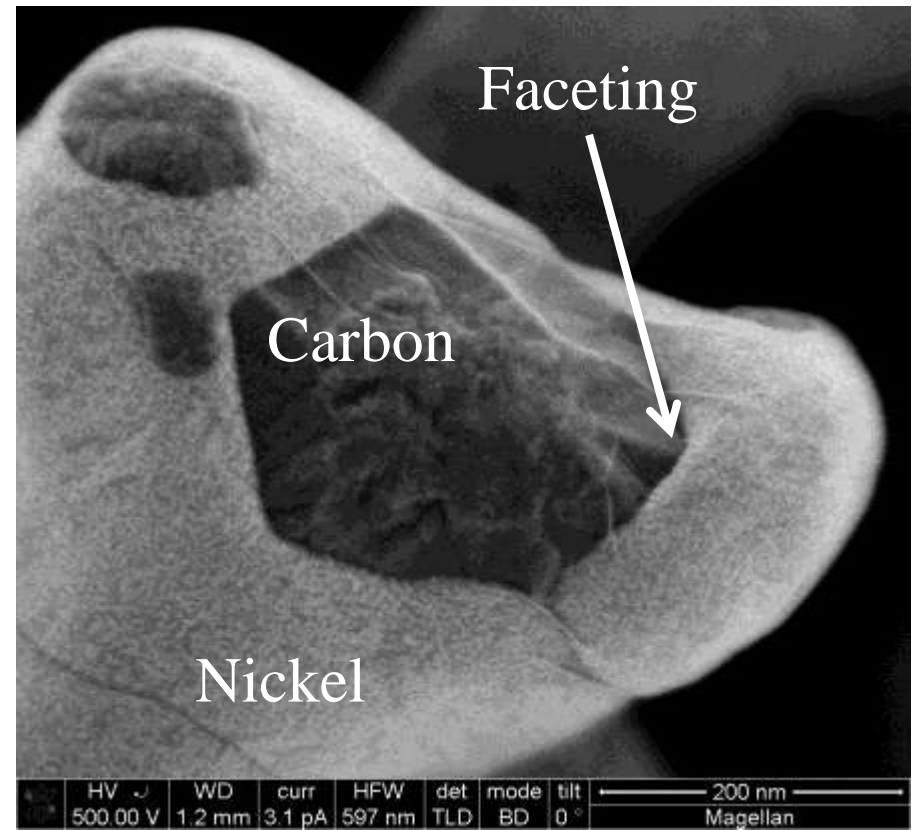
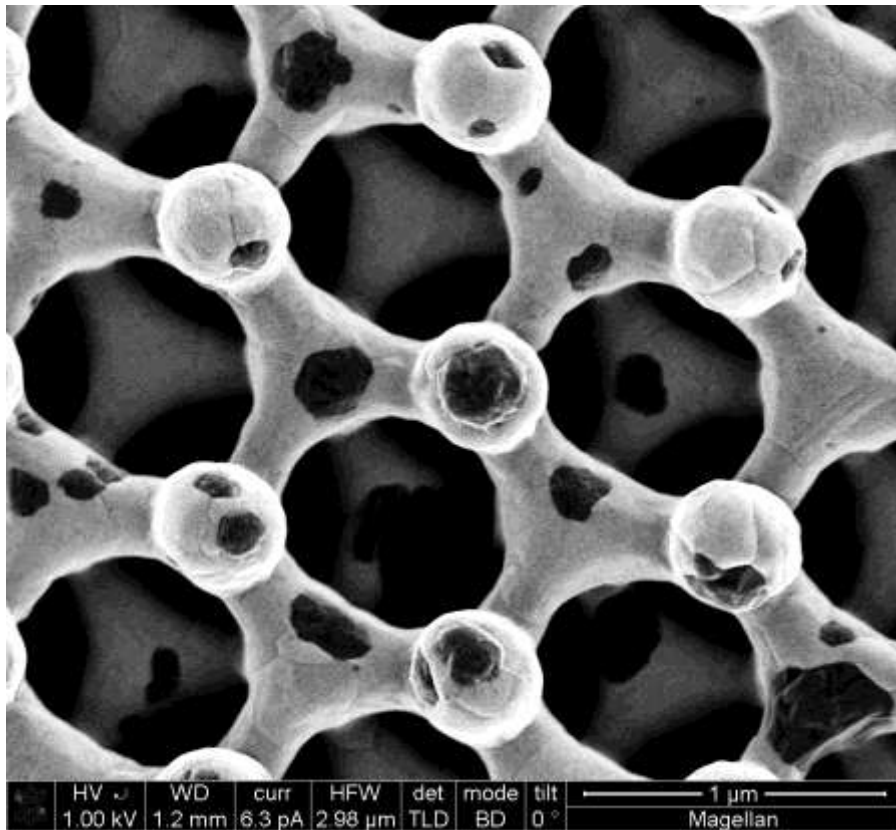
SEM Images of 3D Graphene



SEM Images of 3D Graphene

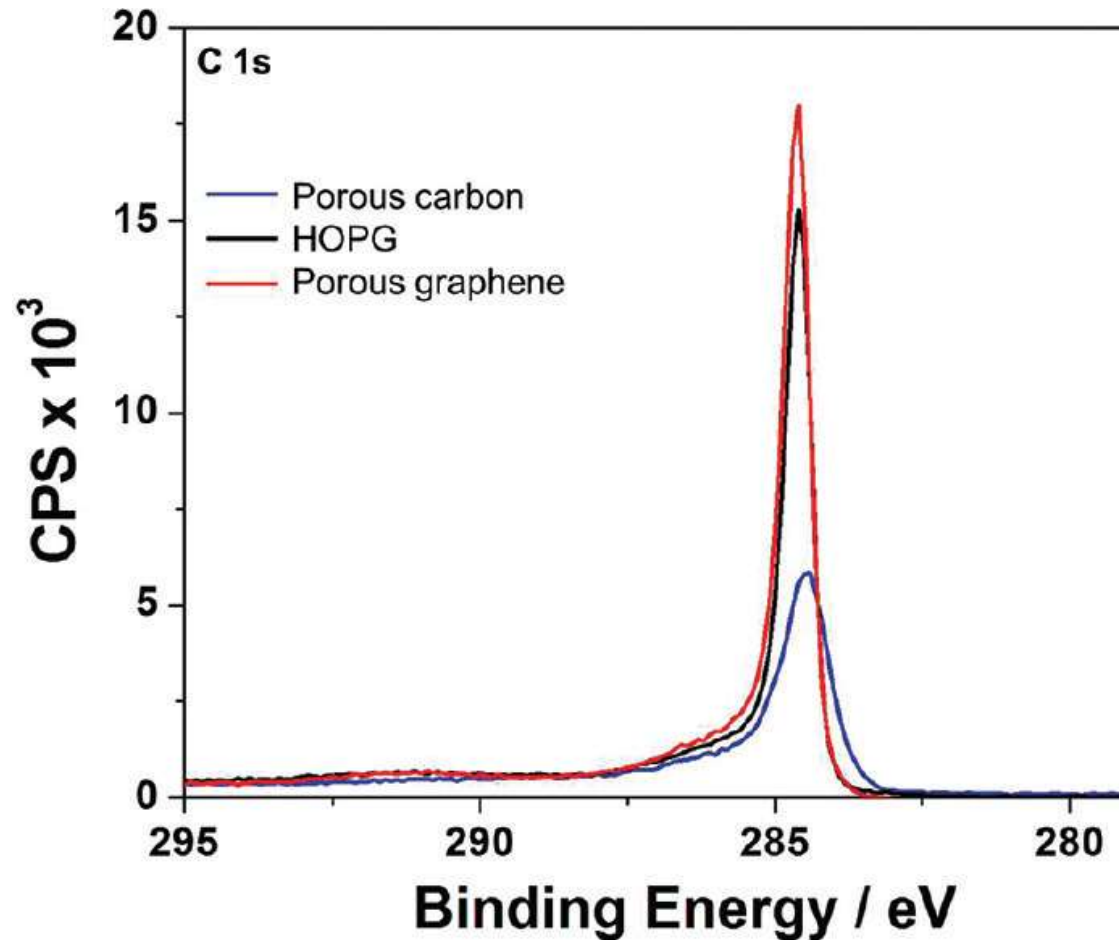


Intermediate Chemical Conversion

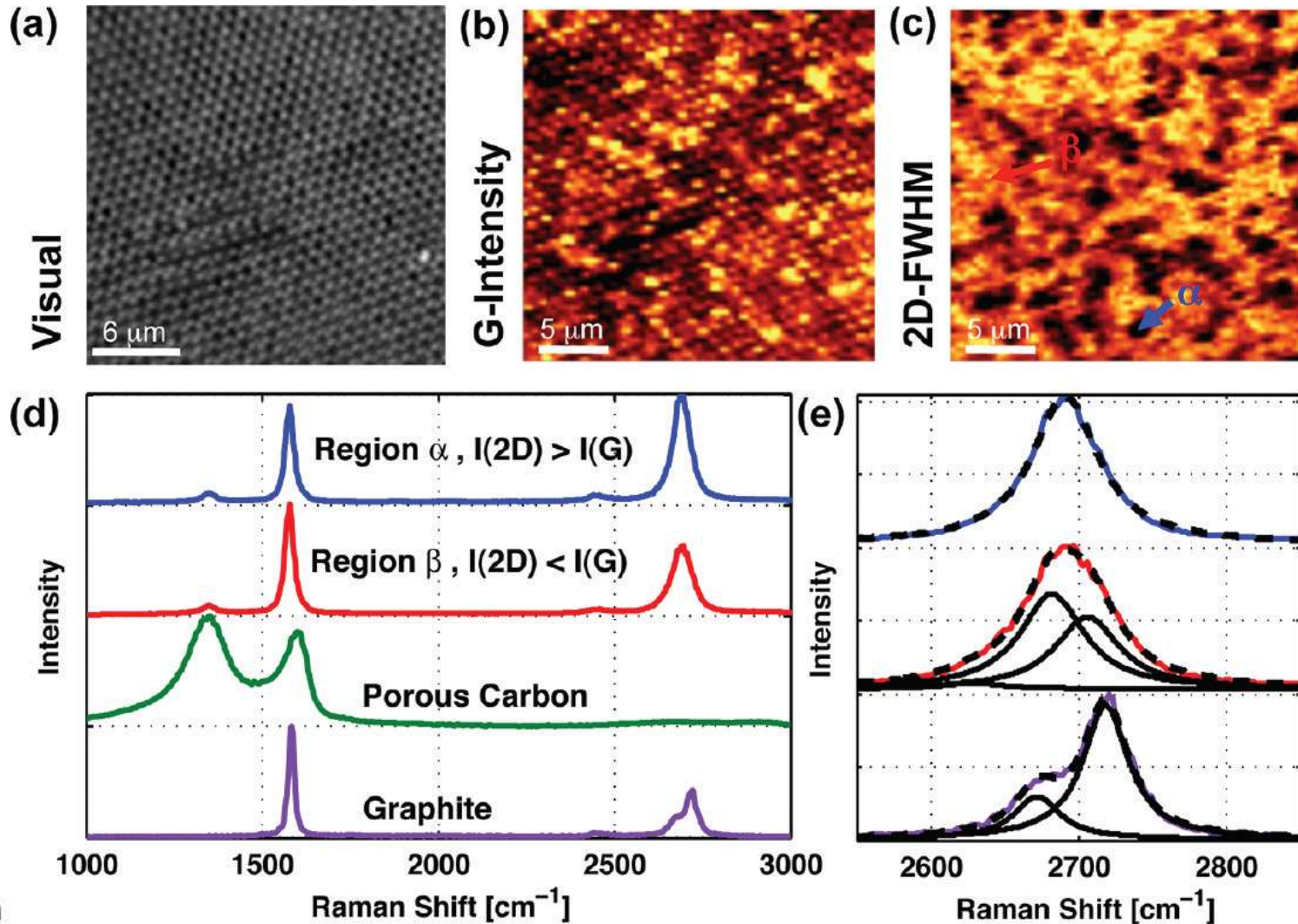


Atmospheric pressure RTA

Confirmation 3D Graphene: XPS



3D Graphene: Micro-Raman



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
- Carbon diffuses through nickel shell, completely trading places, and reorients from sp^3 bonded carbon into sp^2 bonded carbon.



Acknowledgements

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

Questions?

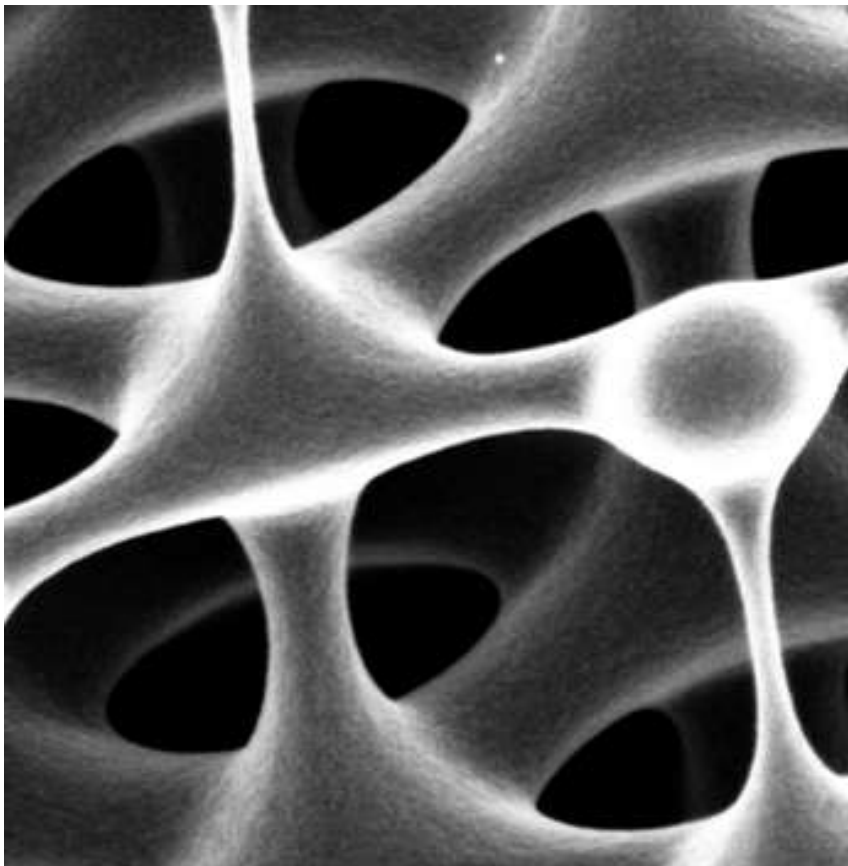
dbburck@sandia.gov



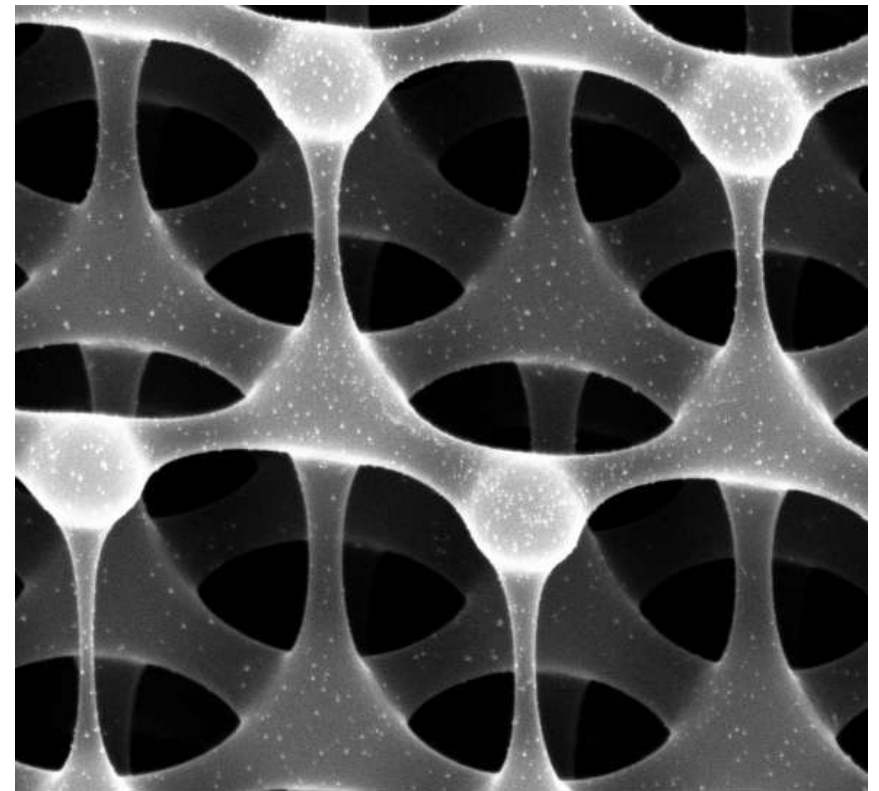
Backup Slides

Nearly Atomically Smooth Surface

Smoothness of bare carbon –
no preferential nucleation sites



Ultra small, uniform NP formation

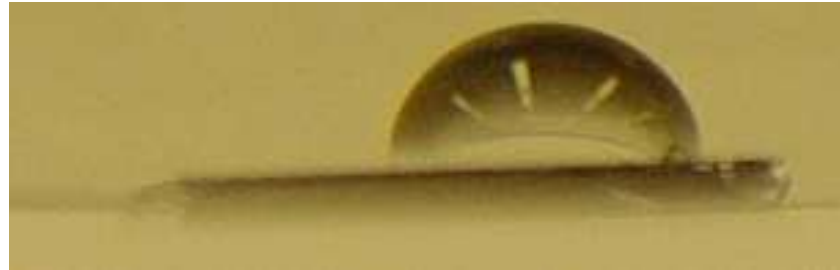


100 nm
H

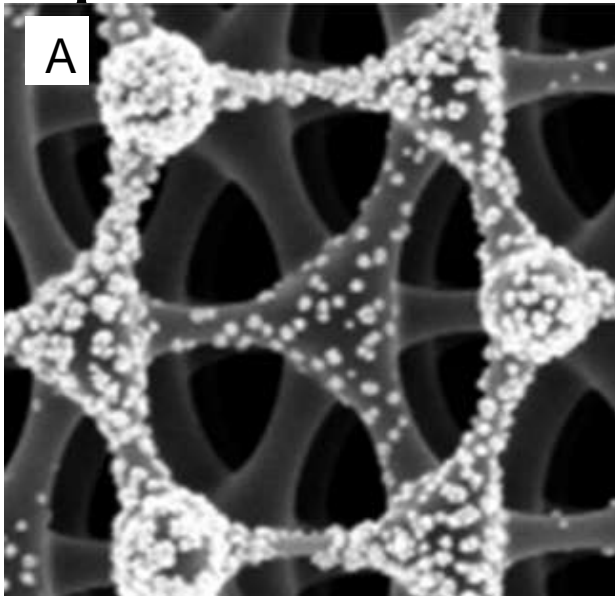
EHT = 5.00 kV WD = 3 mm Signal A = InLens File Nar

Impact of Carbon Hydrophobicity

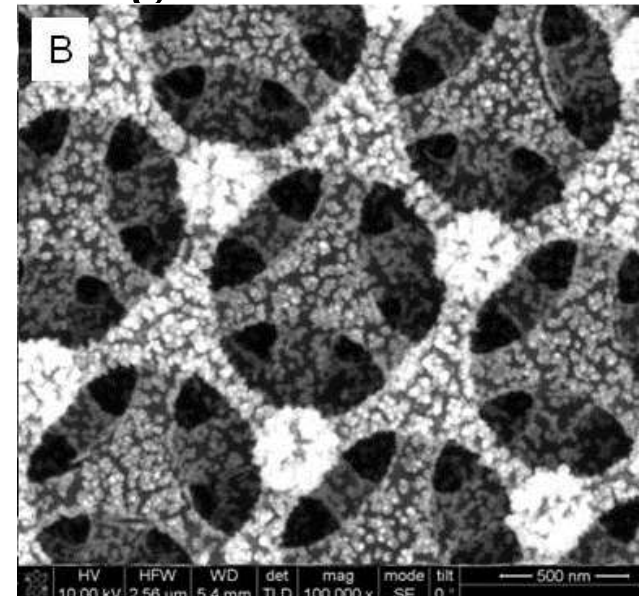
3D carbon
is hydrophobic



**Deposition from
Aqueous Solution**

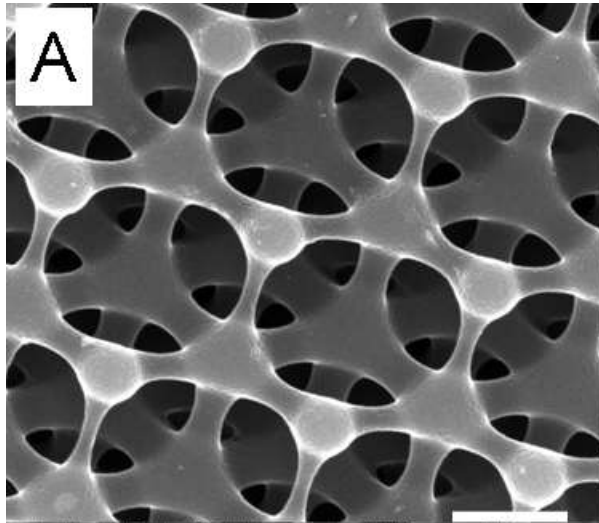


**Deposition from
Organic Solvent**

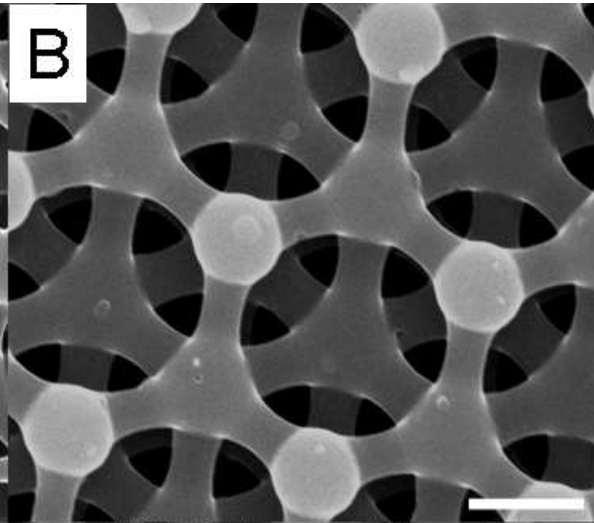


Composite Electrodes: Coating Carbon Scaffold w/ Conducting Polymers

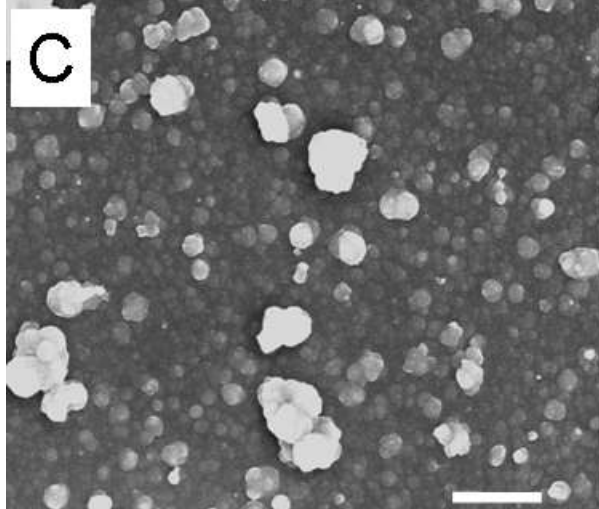
poly(bithiophene)
850mV 30 sec



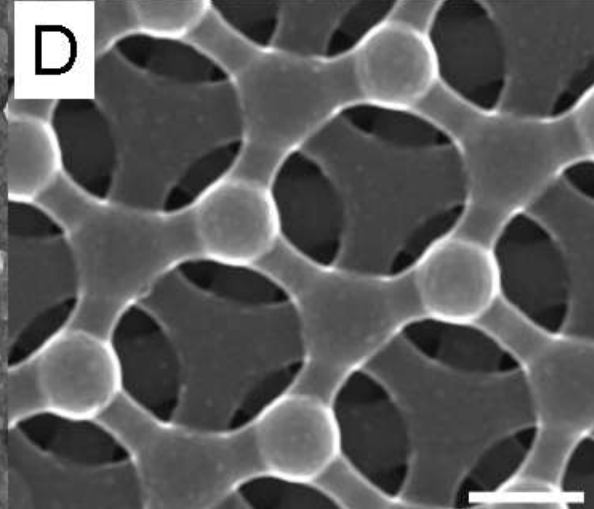
Poly(bithiophene)
850mV 60 sec



Planar pyrolyzed
Carbon
850 mV 60sec



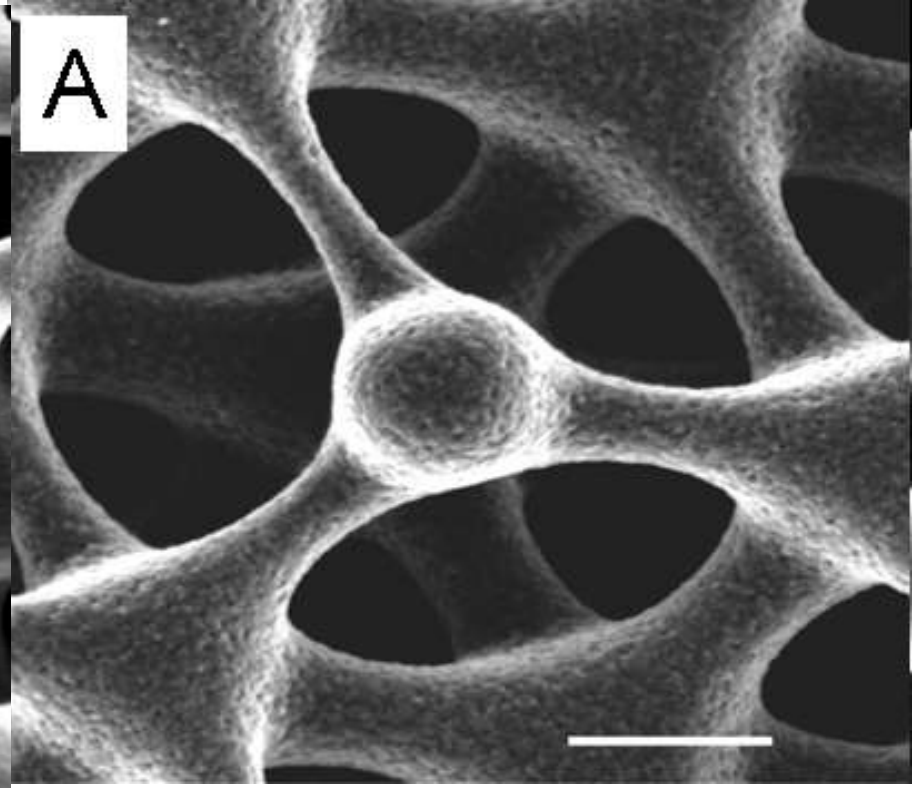
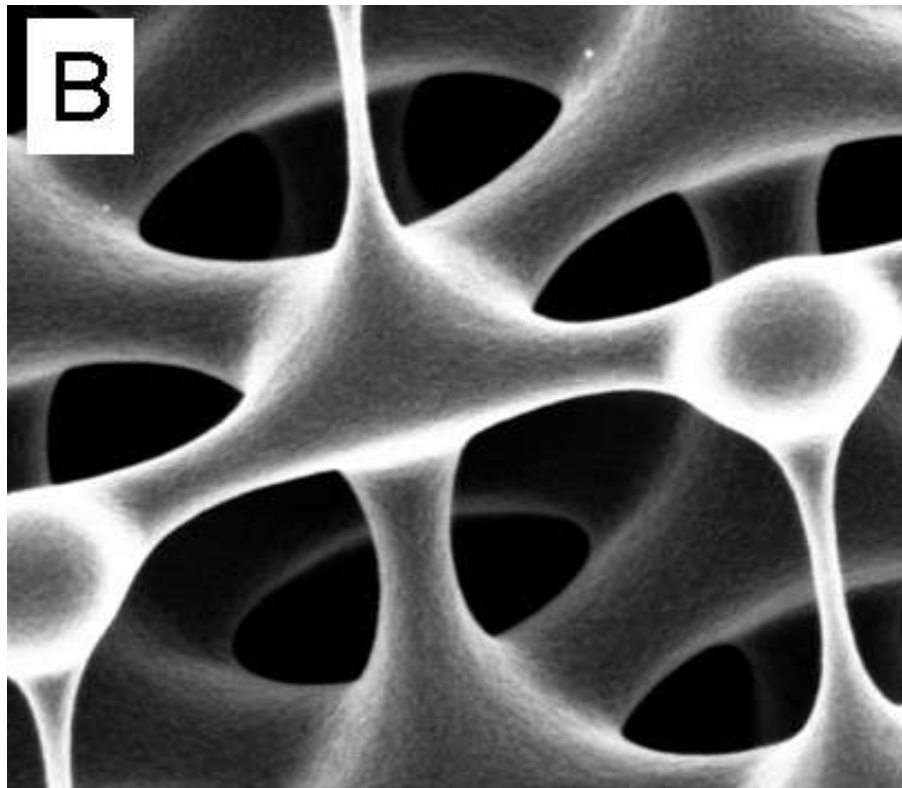
poly(pyrrole)



Deposition of Bithiophene

Bare Carbon

BTP Coated



Scale Bar = 250 nm