SAND2018-13111PE

Lithographically Defined Electrodes

Meeting with Kingdom of Saudi Arabia Desalination Technology Research Institute (DTRI)

Sandia National Laboratories

November 15, 2018

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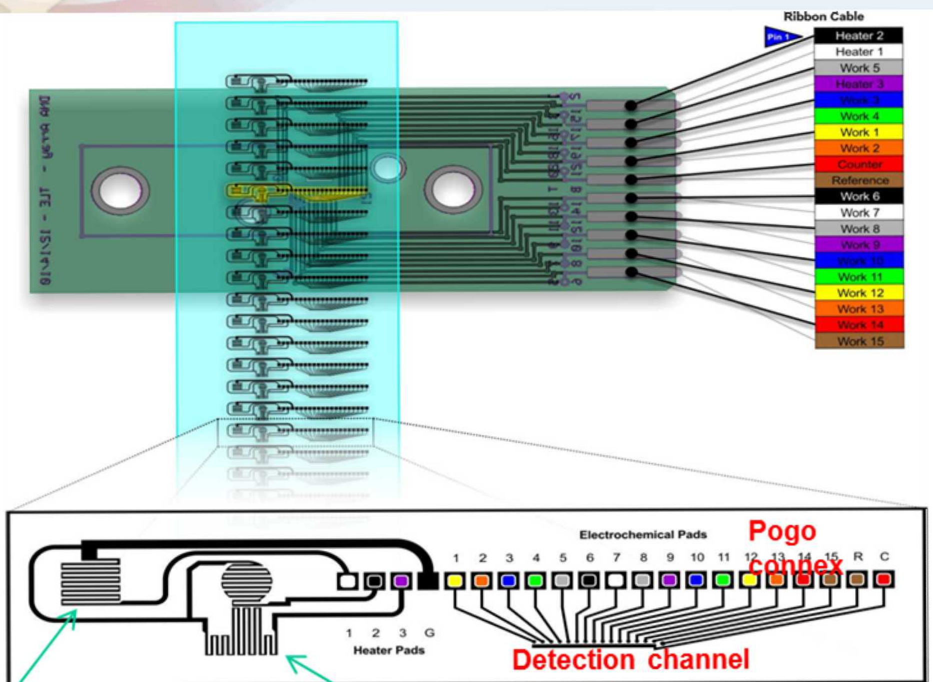
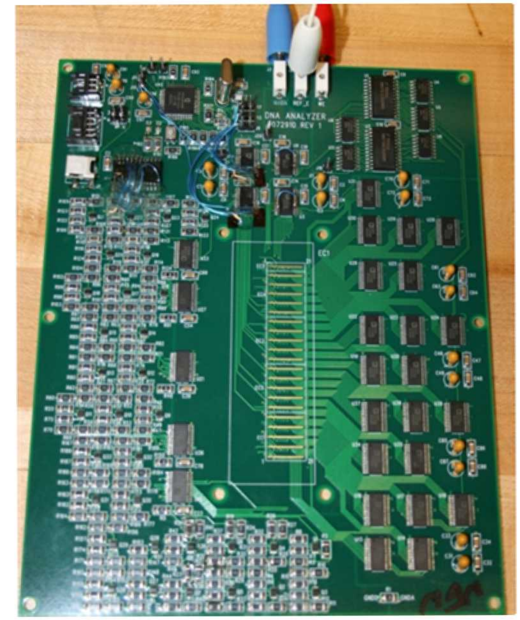
Integration of Sensors and Fluidics

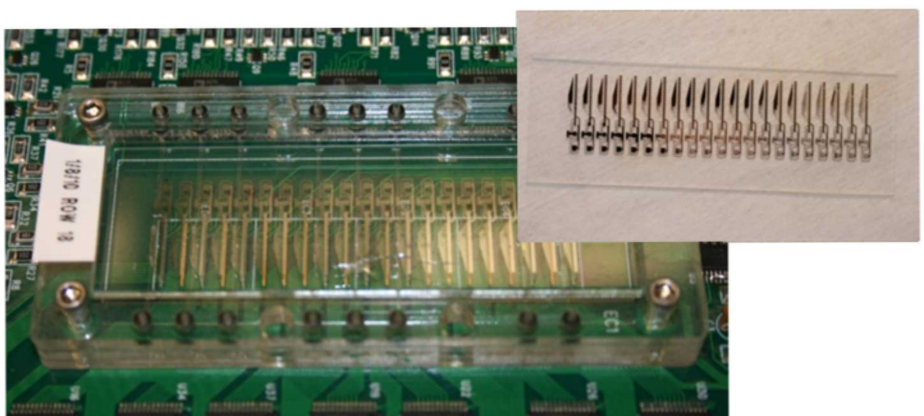


electrodes

Normally-closed valve heater

Normally-Open Valve Heaters





Electrode chip bonded to laminate channels

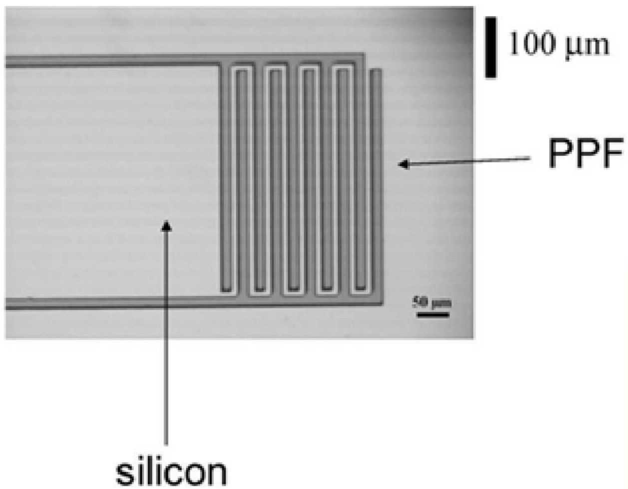
- MUX controls chip array
  - Electrodes are independently addressable
  - Reference, counter, and working electrodes plus 4 valve actuation heaters per channel
  - Low noise (<30 fA at 0.25V)
- Can be converted to an ASIC (Application Specific Circuit)

Pyrolyzed Photoresist Films

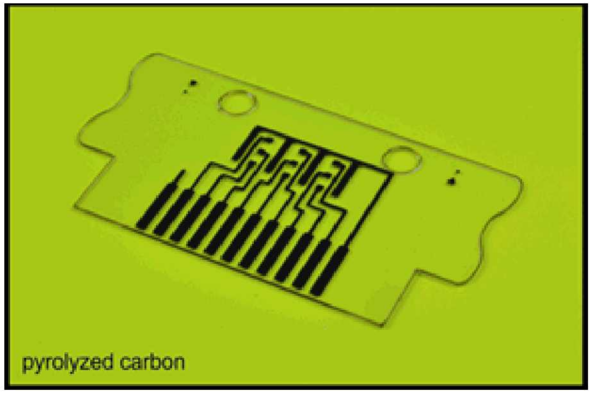
Photopatternable Surface

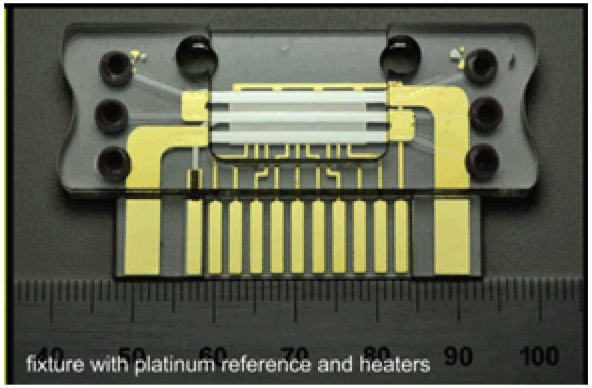
Carbon Array for Microfluidics

Interdigitated Electrode



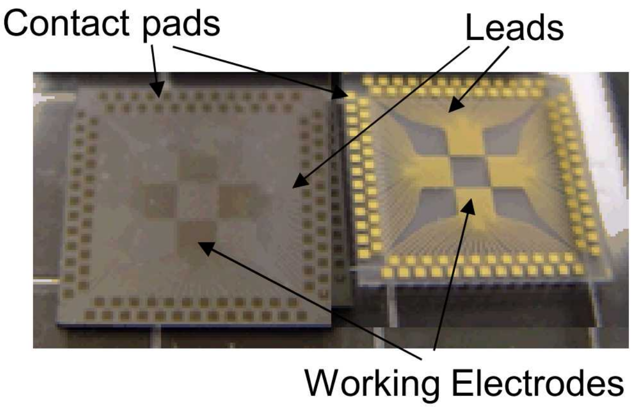
Richard McCreery
Chem Rev.,108, 2646 (2008)





Fabricated by Thayne Edwards

100 Electrode Array



Fabricated by Cody Washburn

Pyrolyzed Photoresist Films

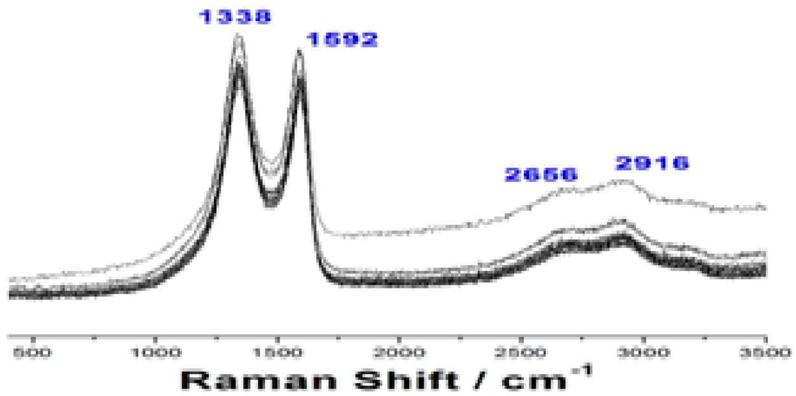
McCreery, Kinoshita, Madou et al

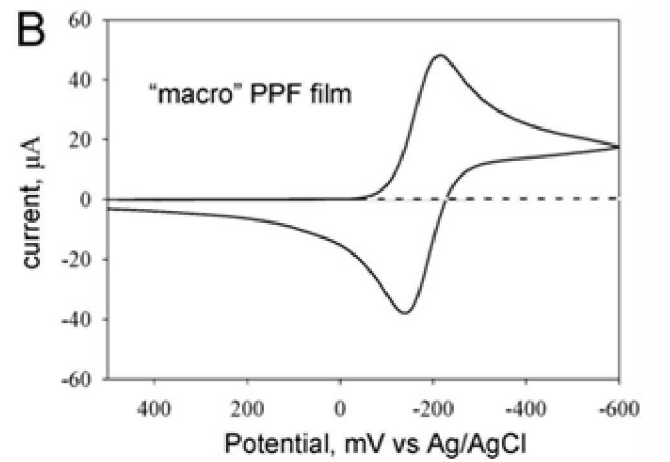
J. Of Electrochem. Soc.

145 (1998) 2314 & 147 (2000) 277

Film Preparation

Photoresist spin coated onto fused silica or quartz; Pyrolyzed at 1050 °C for 1 hour in 5% N_2 / 95% H_2 creates a predominately concucting carbon surface by driving off non-carbonaceous species with a high degree of hydrogen termination





$Sp^2 > Sp^3$ Carbon

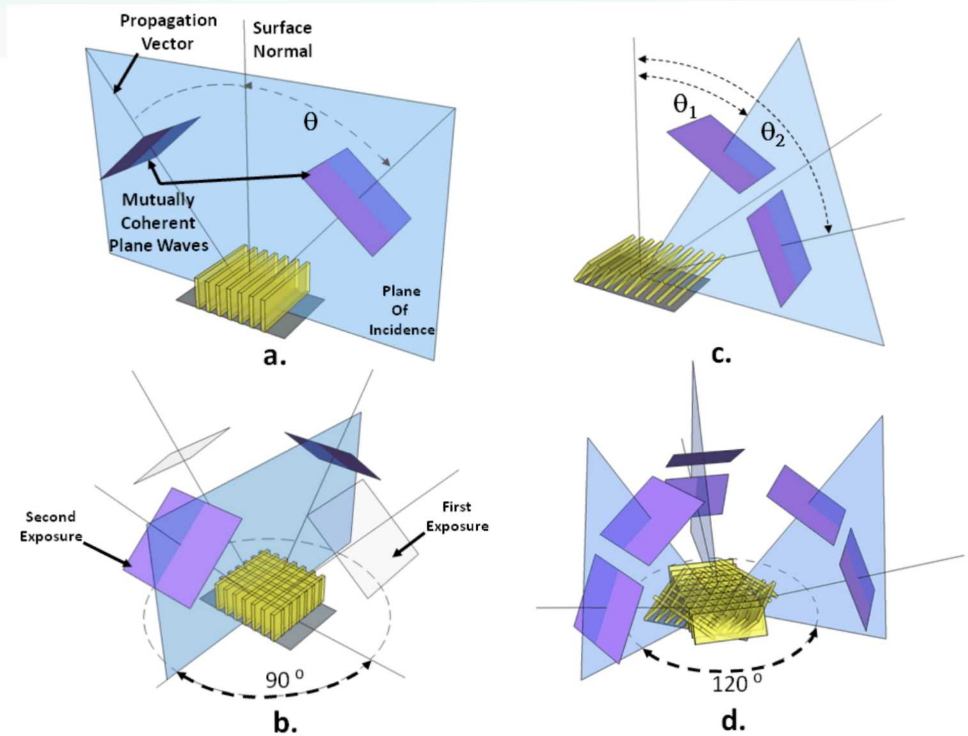
Resisitivity ~ $10^{-2} – 10^{-3}\ \Omega \cdot cm$

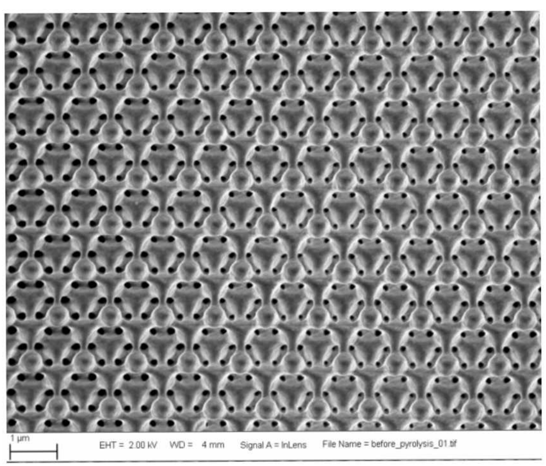
1-5 % Oxygen

Richard McCreery
Chem Rev.,108, 2646 (2008)

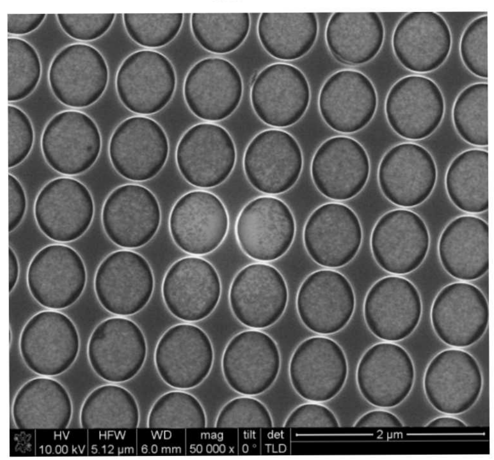
Interference Lithography
(Bruce Burckel)

By using 3-beam interference, arrays with hexagonal symmetry can be generated, while with 4 beams, arrays with rectangular symmetry are generated. Hence, by superimposing different beam combinations, different patterns are made possible.

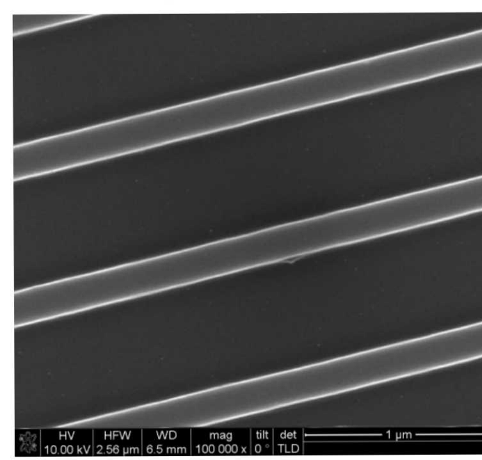




3-exposures

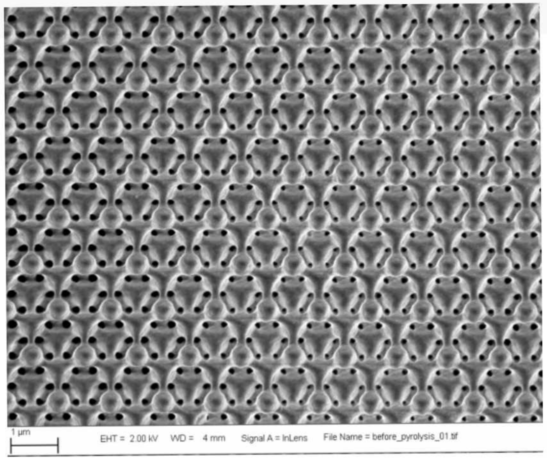


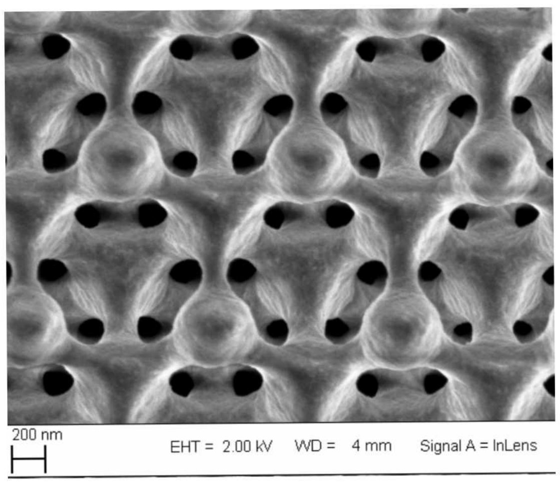
2-exposures

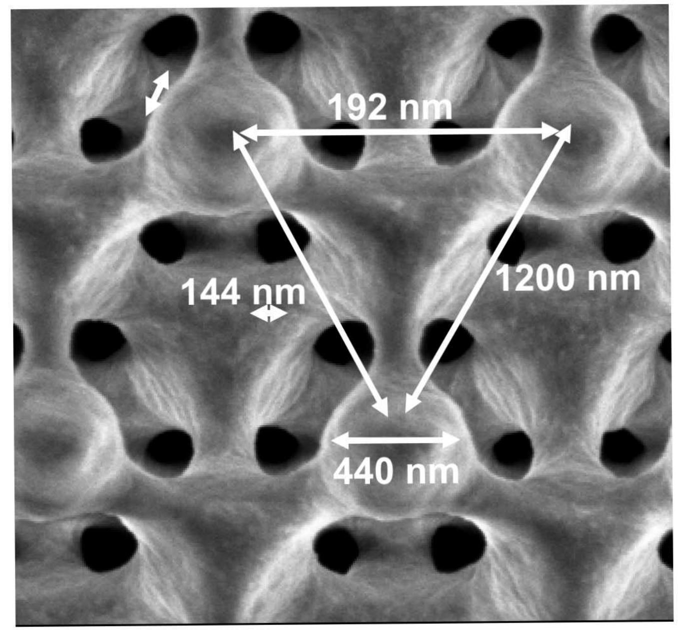


1-exposures

Interference Lithography in Photoresist







Fabricated by Bruce Burckel

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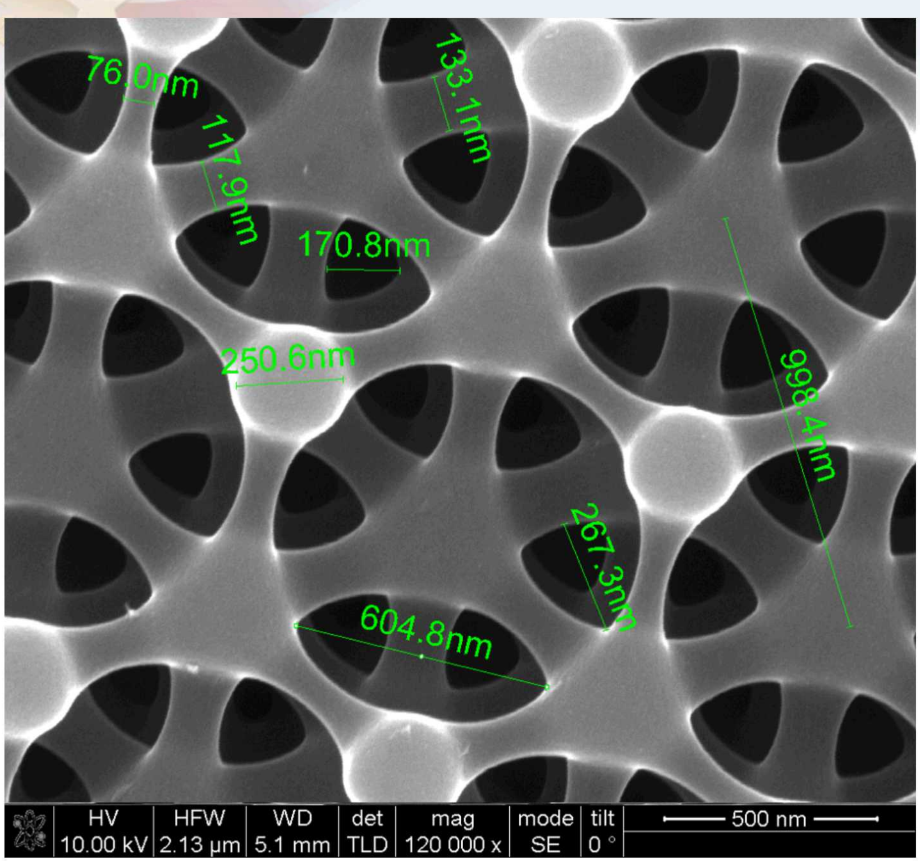
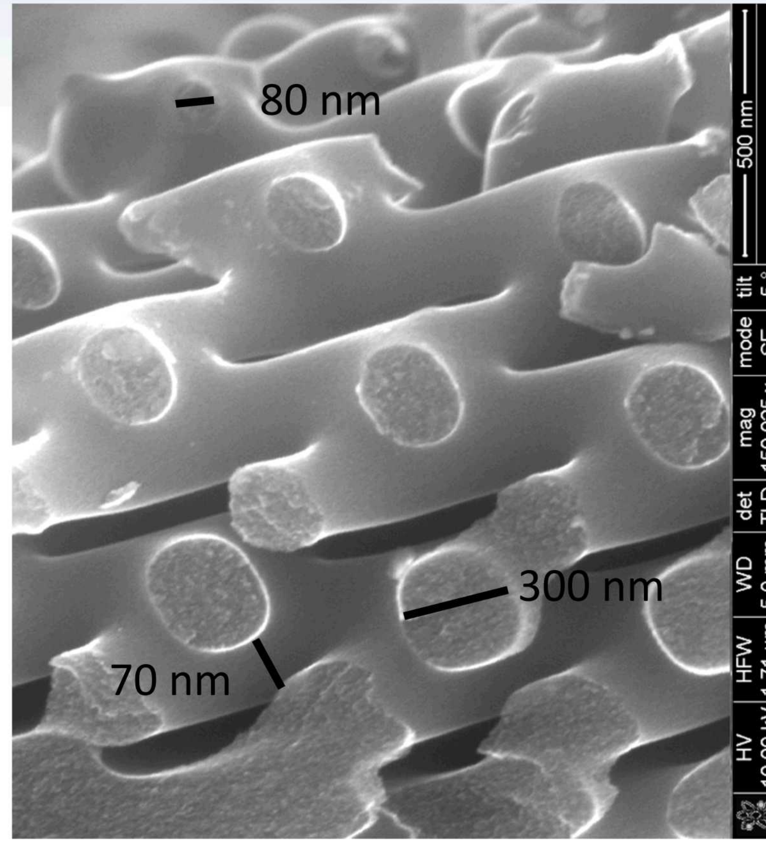
Small, 2009, 24, 2792-2796

3D Porous Carbon Electrodes





Advantages of 3D structures

- Higher surface areas
- Enhanced Diffusion of fuels and analytes

US Patent 8,349,547 B1

Small, 2009, 24, 2792-2796

Surface Area

2D

3D

	Base/ft^2	Total/ft^2
Hershey	1,189,910	1,189,910
Burj Dubai	33,600	3,700,000

Bruce Dunn et.al.
Chem. Rev. **104**, 4463 (2004),
Electrochem. and Solid-State Letts. **7**, A435 (2004)
Electrochem. Comm. **5**, 120 (2003).

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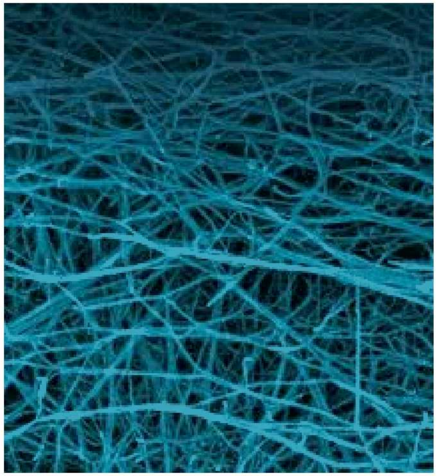
Mass Transport

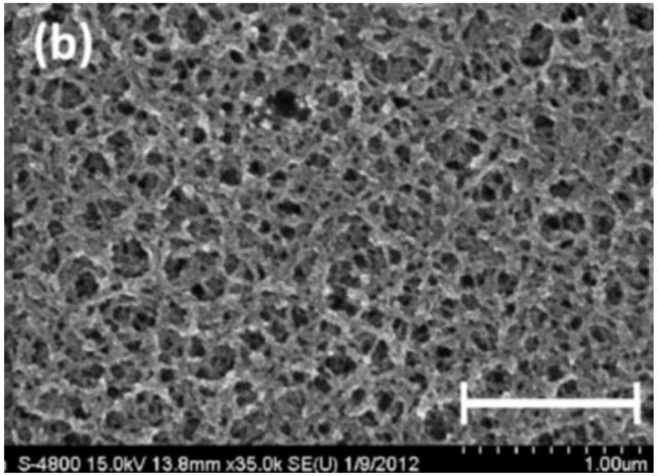
2D

3D

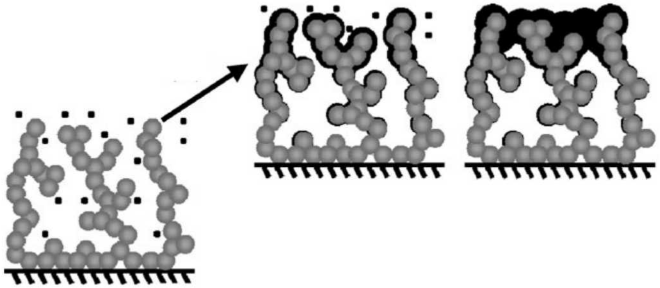
Porous Carbons

Traditional Porous Carbons





Limitations



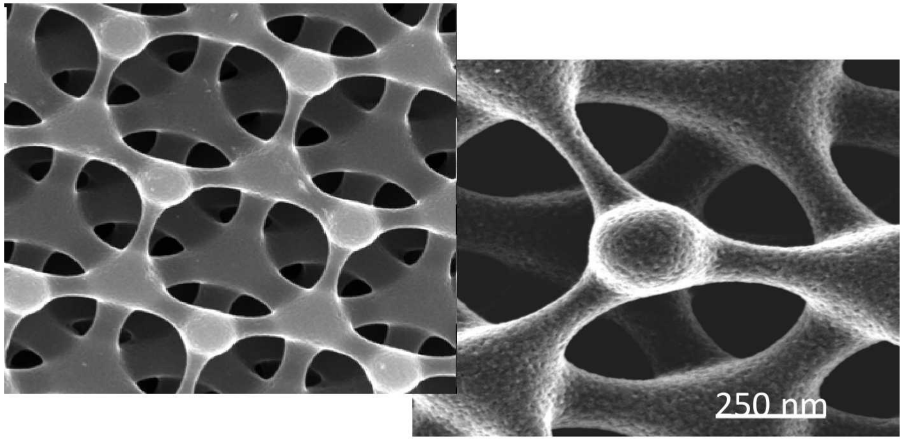
$\tau \propto \epsilon^{-1/2}$

T = tortuosity

ϵ = pore size

Bruggeman relationship

Our Porous Carbons



Advantages of our 3D structures

- High surface areas
- Enhanced Diffusion of fuels and analytes

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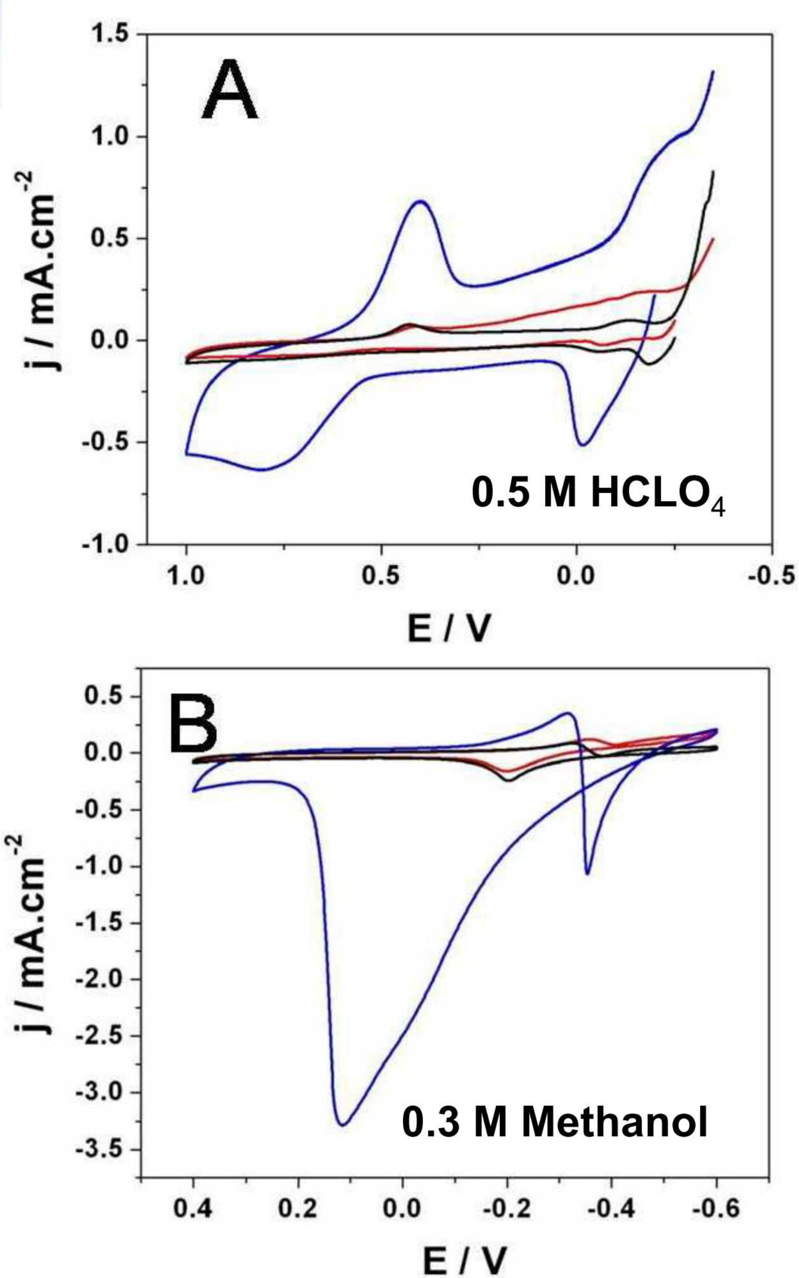
Comparison of 2D versus 3D Electrodes

Blue: Pd 3D
Red: Pd 2D
Black: Pd/GCE



3D: 3.48×10^{-3} C/cm^{-2}

2D: 1.4×10^{-4} C/cm^{-2}

20X increase in surface area

3D: 9.2×10^{-2} C/cm^{-2}

2D: 4.4×10^{-4} C/cm^{-2}

200X increase in methanol oxidation

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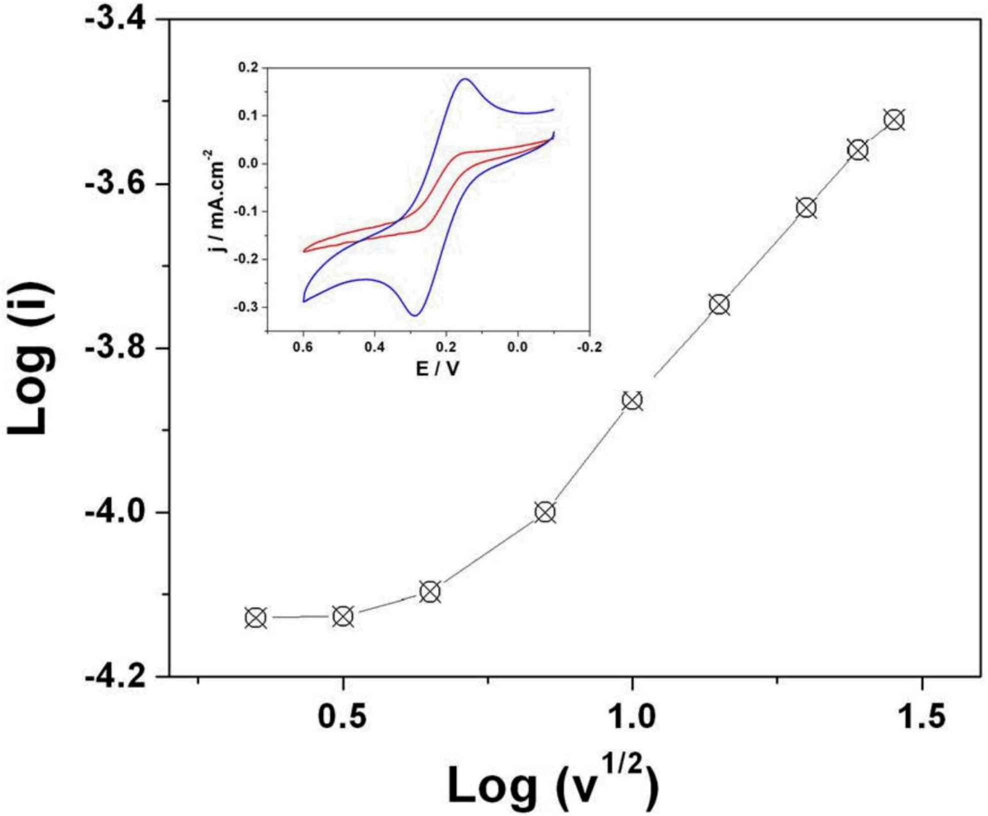
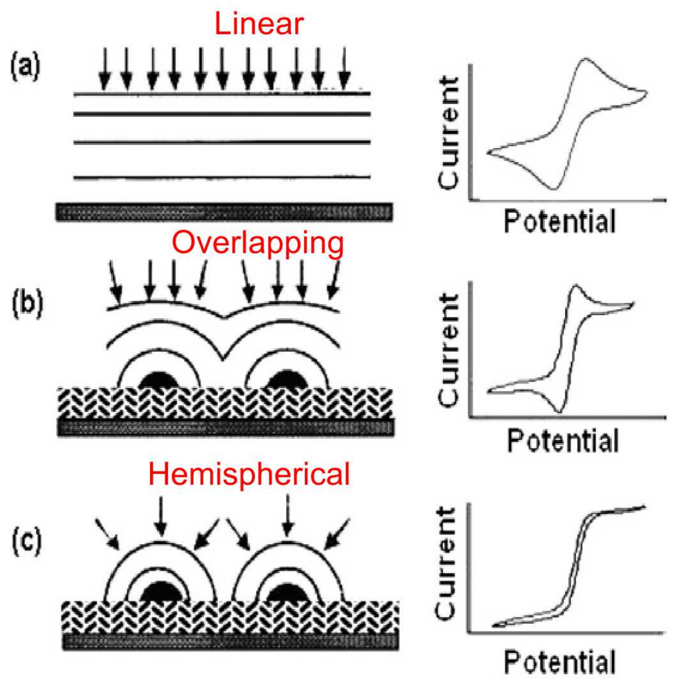
Increased Mass Transport

Microelectrode Behavior with Macroscopic Electrode!



Electrode Diffusion profiles



Hemispherical diffusion is indicative of increased mass transport kinetics.
Greater diffusion profiles throughout the 3D structures should translate to higher signals for detection of analytes and higher energy densities for power devices!

ACS Applied Materials and Interfaces 2(11): 3179-3184 (2010)

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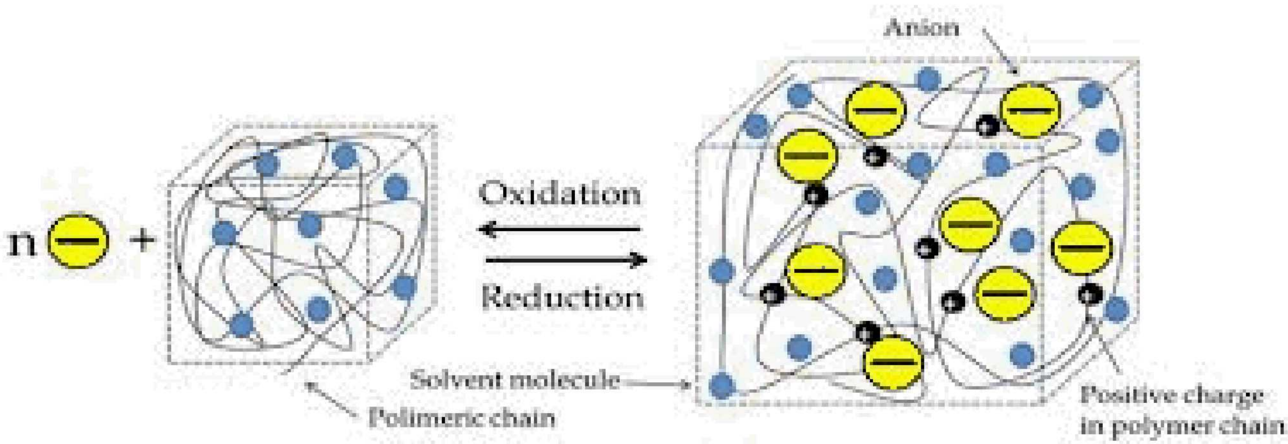
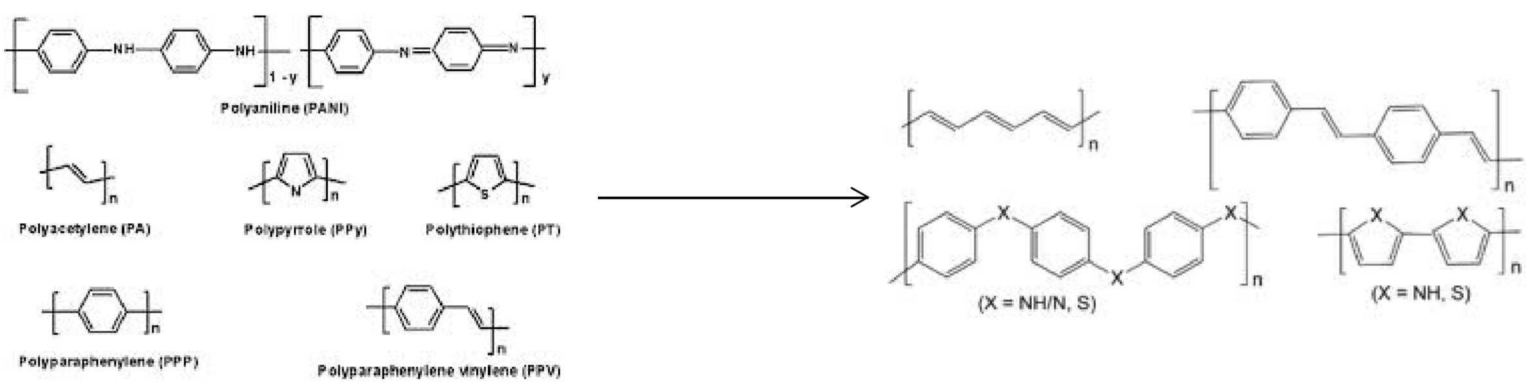
Conducting Polymers





Conducting Polymer Deposition

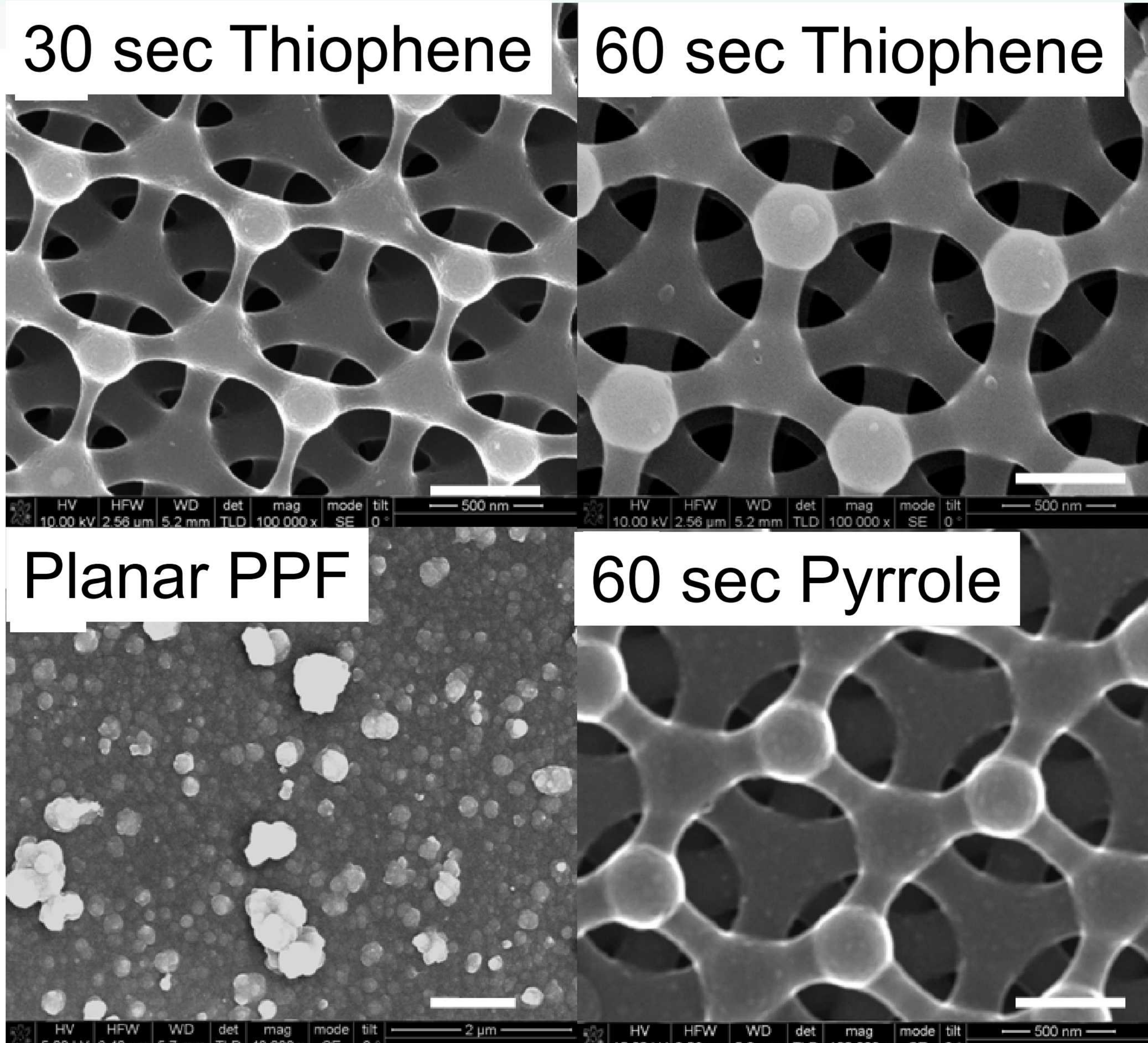
•Conducting polymers are widely used in ultracapacitors and electrochromic devices.

•The morphology of polymer films is greatly affected by mass transport during deposition

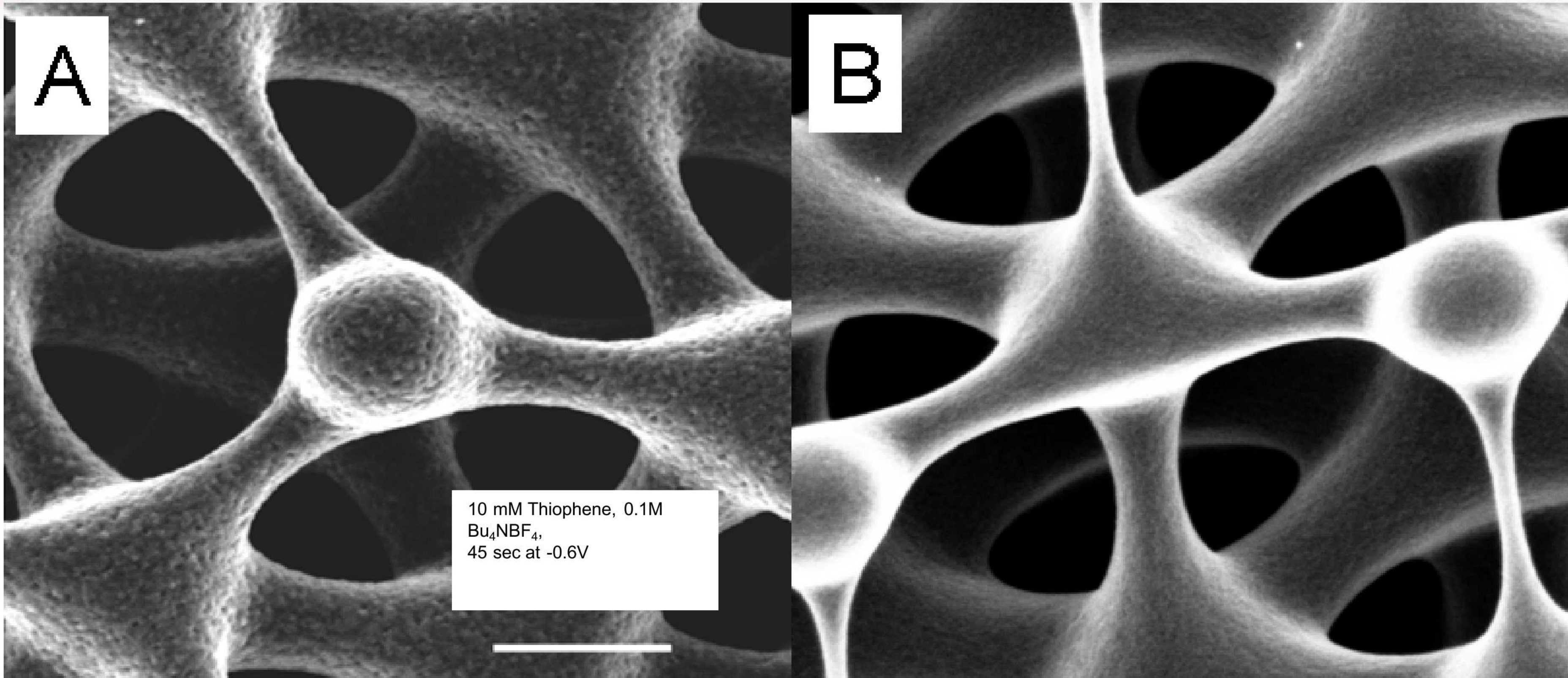
•Microelectrodes usually produce smooth uniform films

•Macroelectrodes produce highly asymmetrical aggregates

•Deposition onto the 3D porous carbon results in uncharacteristically smooth films because of the radial diffusion of monomer molecules during deposition

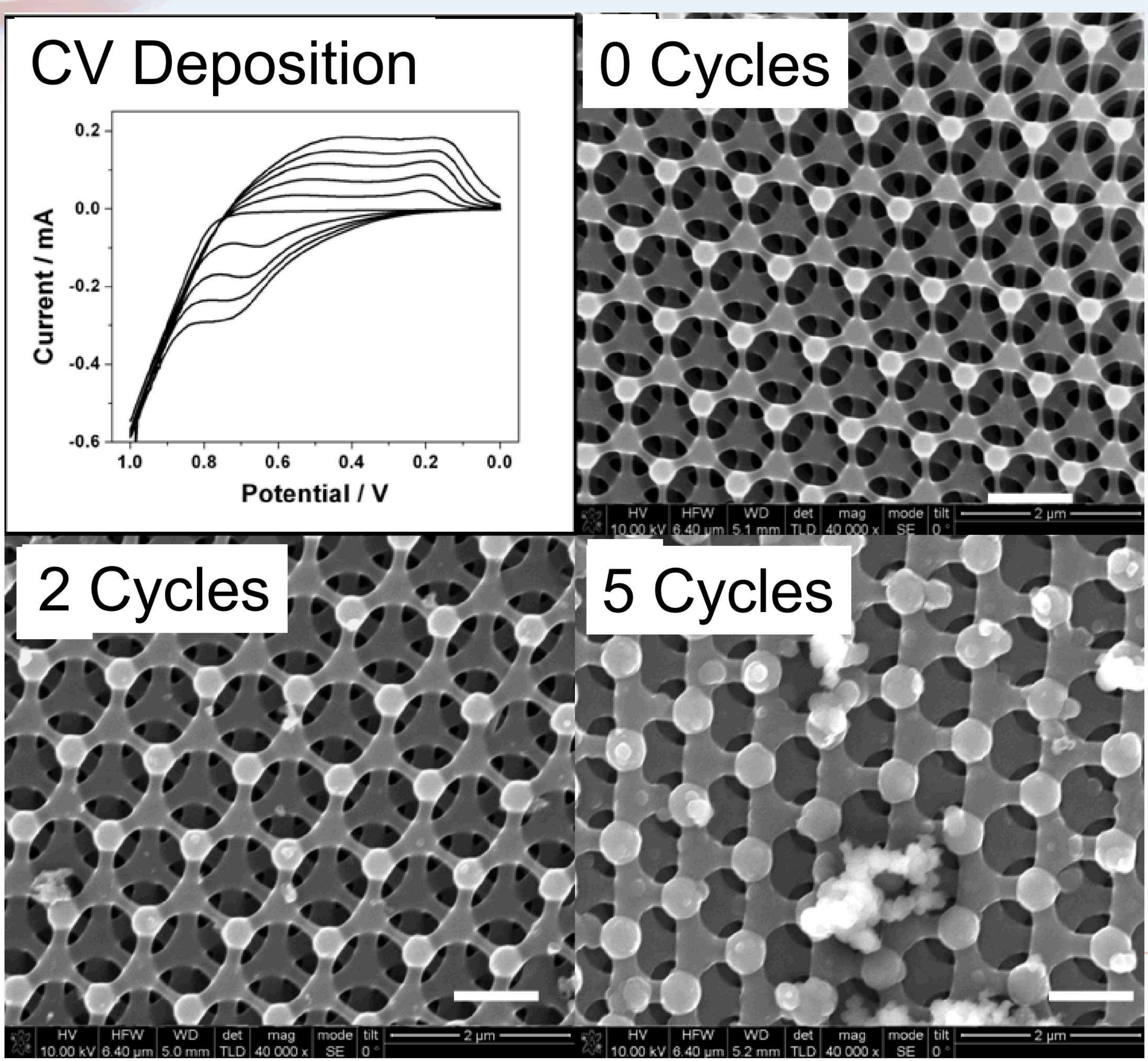


Film Morphology



Bithiophene Bare

Controlling Pore Size



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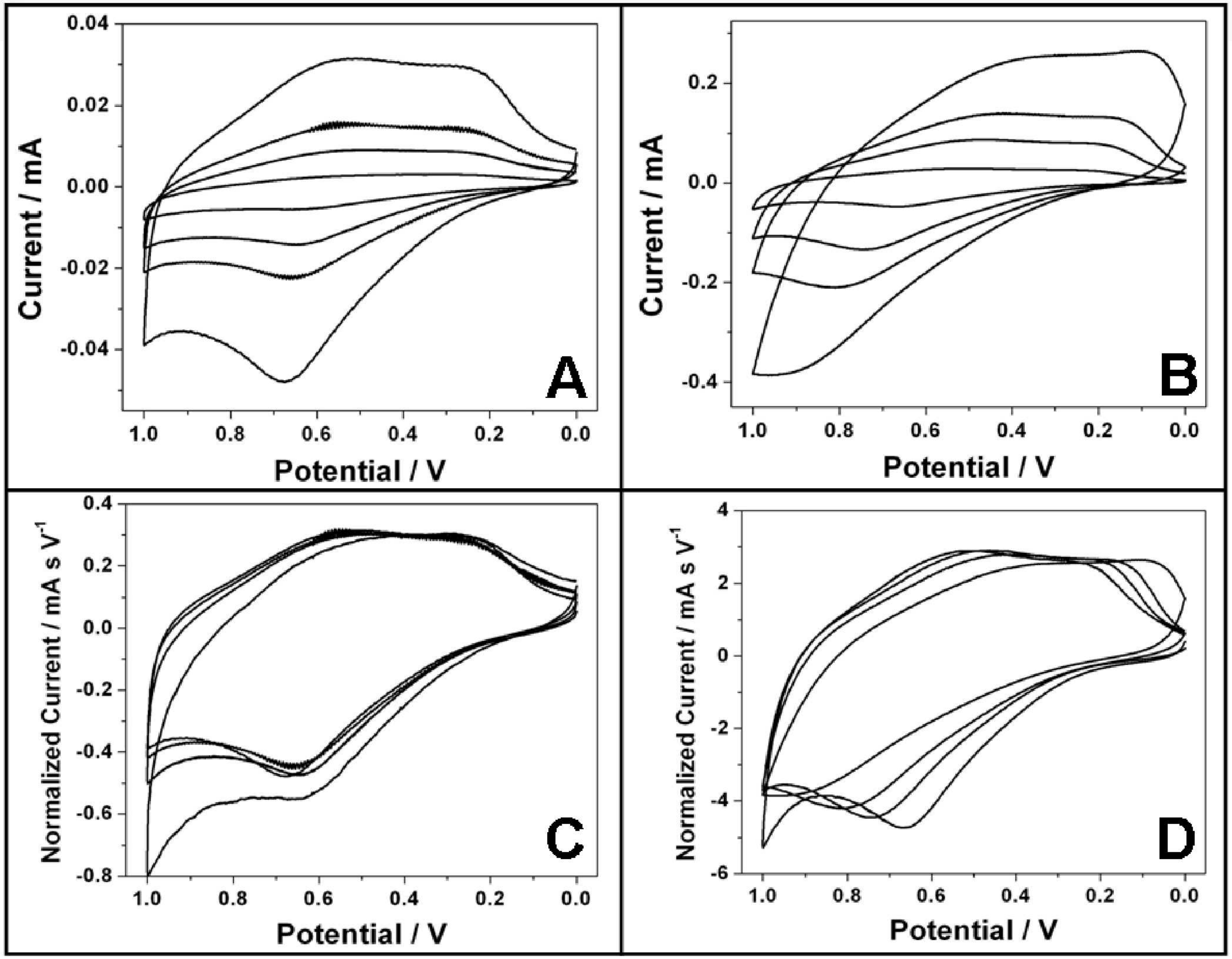
Capacitor Performance

Thin Film

Thick Film



Thin Film

Thick Film

Thin films show efficient doping-undoping properties (better performance) over thick films which experience diffusion limitations for anions to migrate through the films

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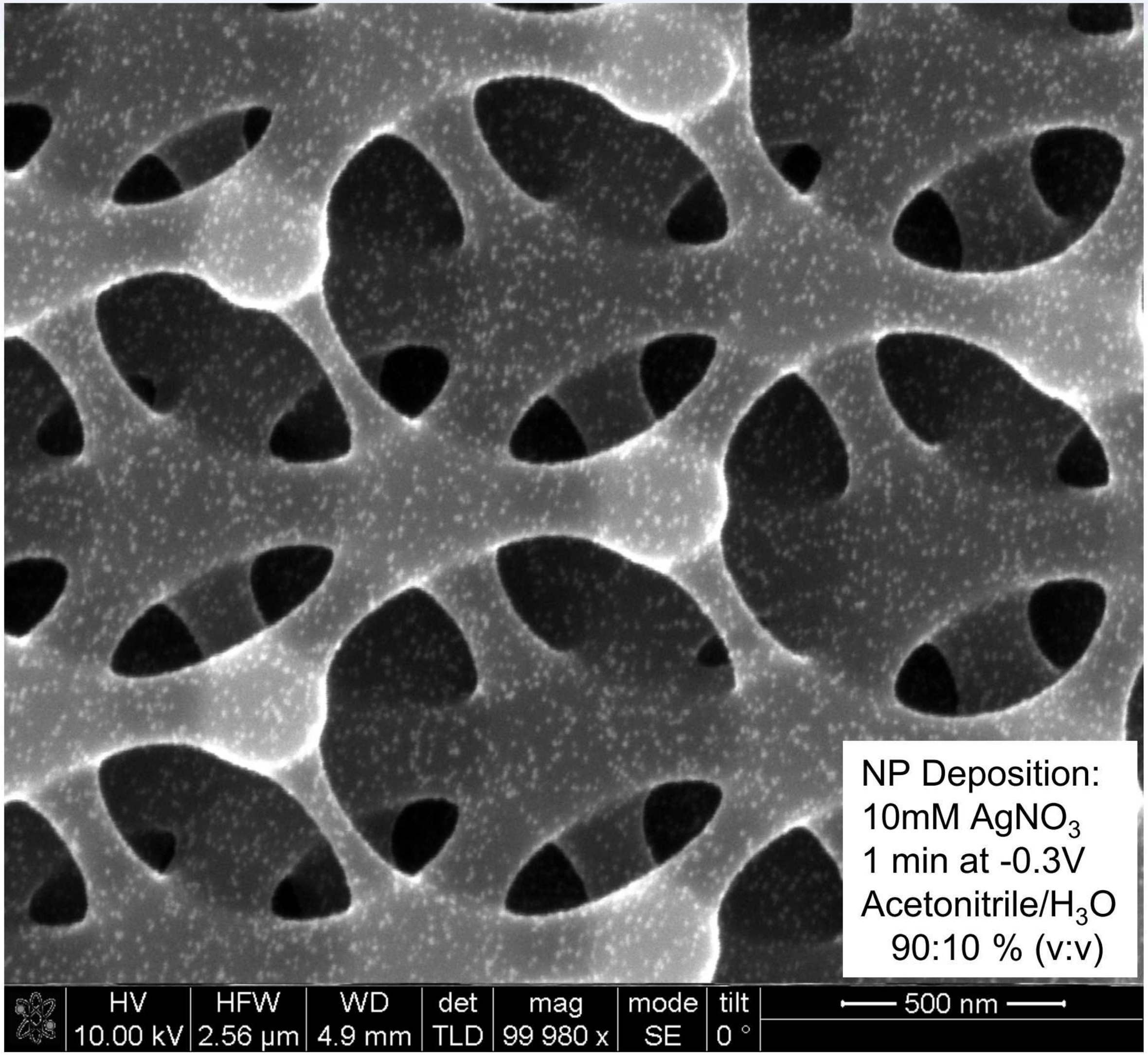
Nanoparticle Depositions



Nanoparticle modifications are used for both catalysis and biomolecular supports

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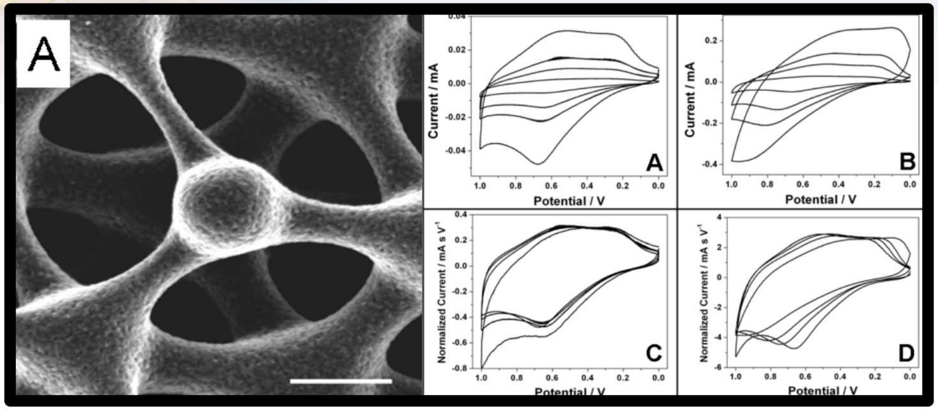
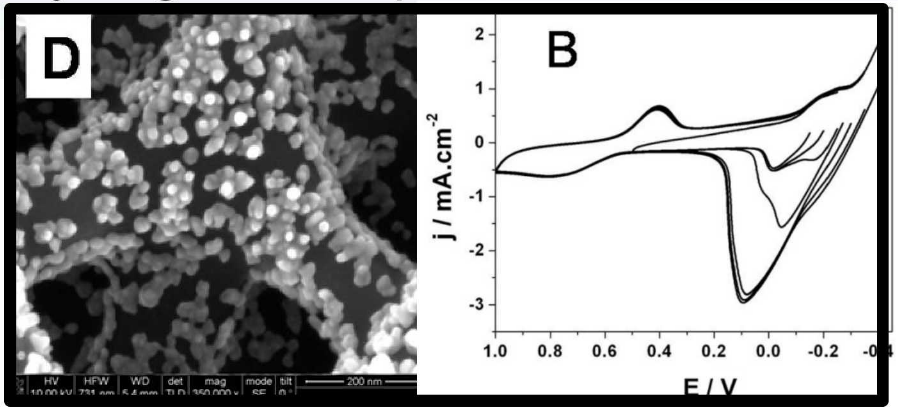
Applications

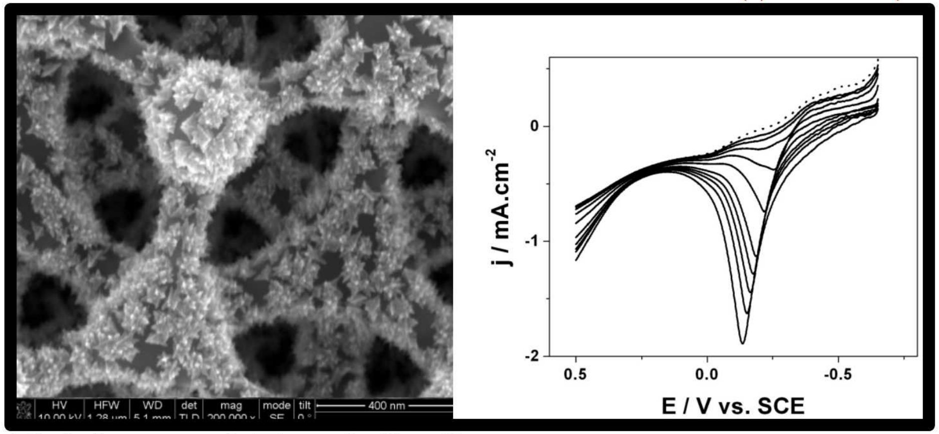
Ultracapacitors
ACS Applied Materials and Interfaces 2(11): 3179-3184 (2010)



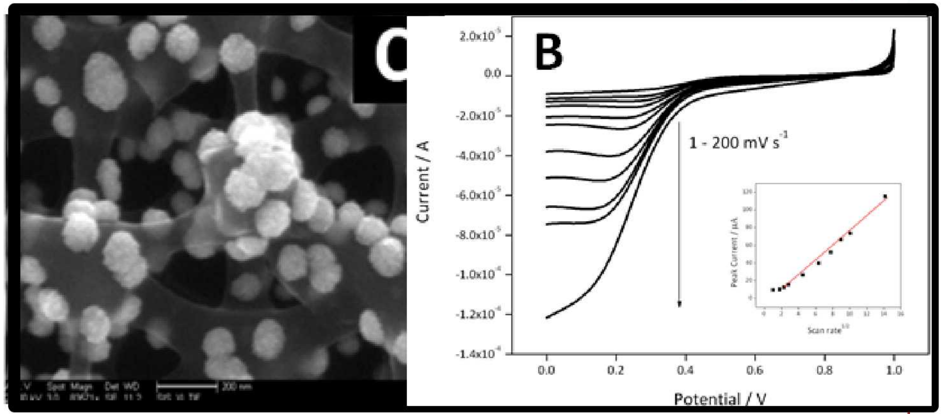
Hydrogen Adsorption
Electroanalysis 24(1): 153-157 (2012)



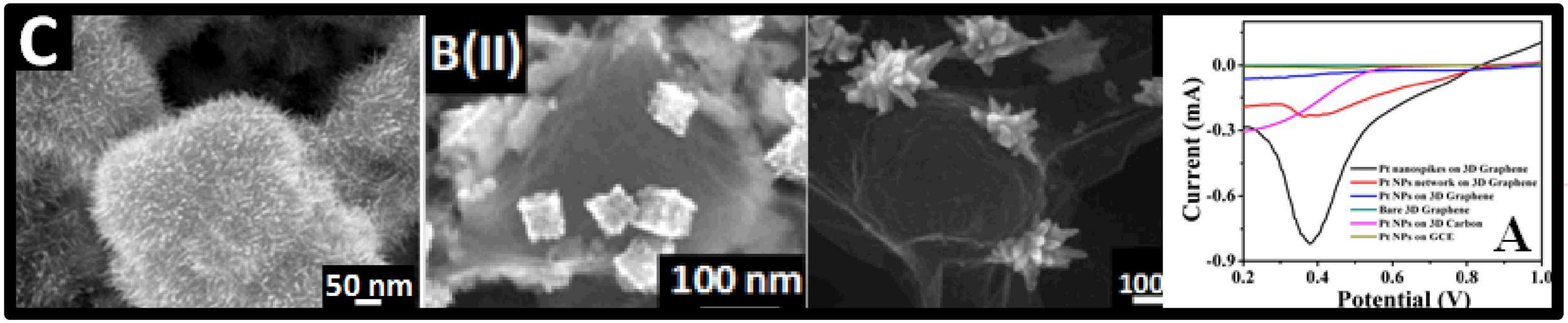
Glucose Sensors
Biosensors and Bioelectronics 26(8): 3641-3646 (2011)



Pt-based Fuel Cells
Electrochem Comm 13(8): 856-860 (2011)



Pd-based Fuel Cells
Journal of Materials Chemistry A 1 (1): 1639-1645 (2013)



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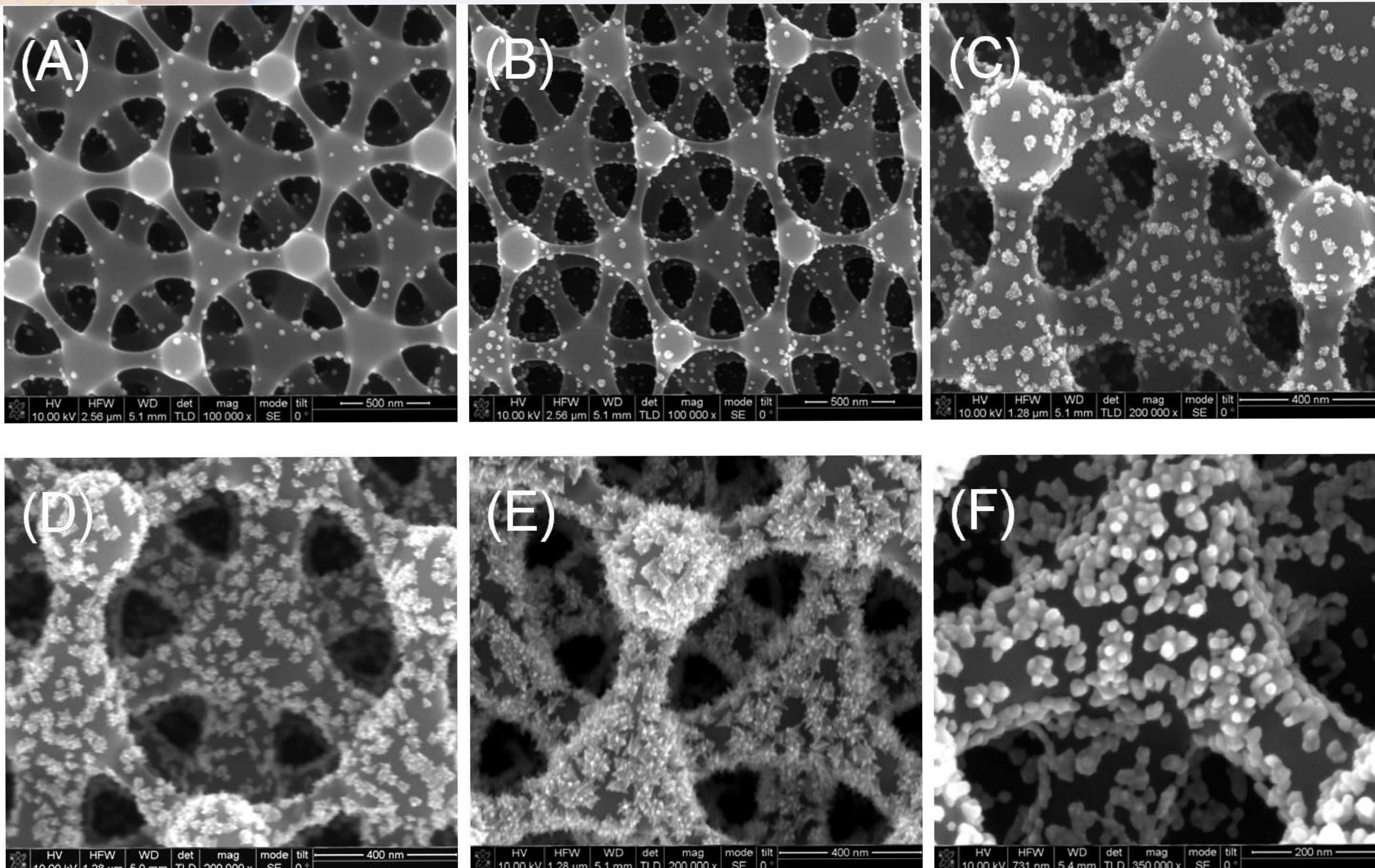
Electrochemical Control of Nanoparticle Morphology

Biosensors and Bioelectronics 26(8): 3641-3646 (2011)



Nanoparticle shape has a profound impact on its catalytic properties.
Highly faceted nanocrystals often exhibit remarkably improved catalysis

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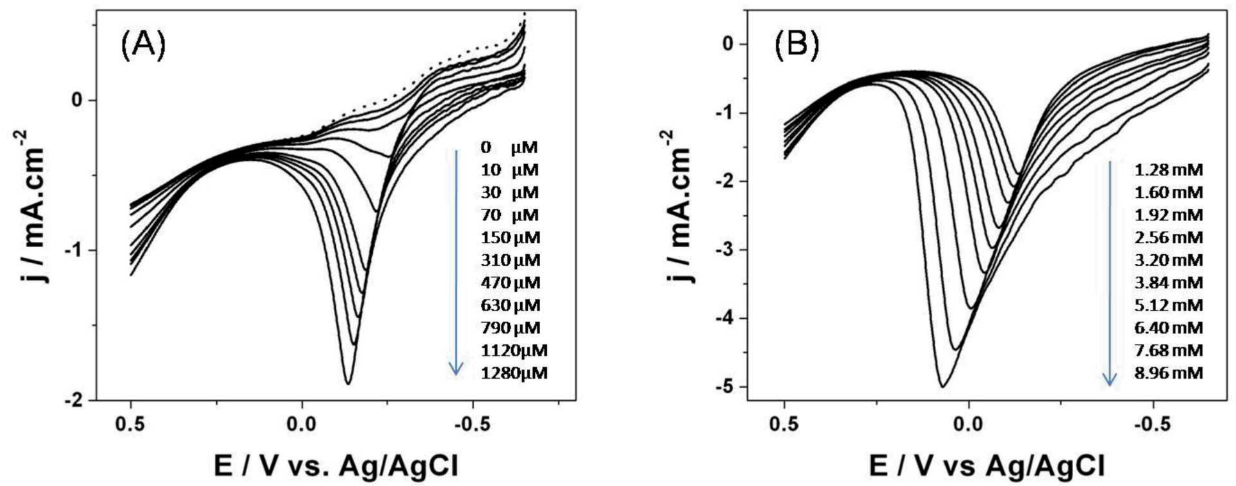
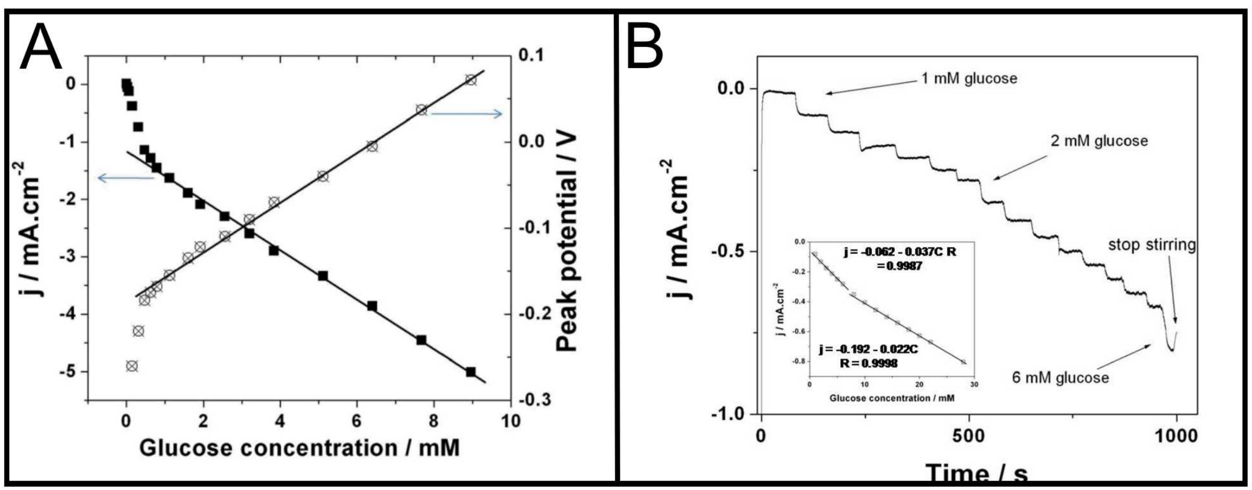
Catalytic Glucose Detection



Linear scan voltammograms of a Pd-modified 3D carbon electrode in 0.1 M NaOH + x M glucose. Pd deposition: 100s, Scan rate: 20 mV/s.

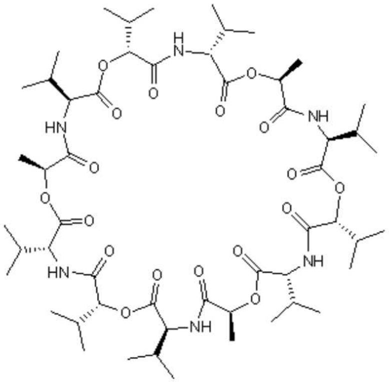


(A) Plots of corresponding current and peak potential vs. glucose concetration. Pd deposition: 100 sec, scan rate = 20 mv/sec and (B) amperometric response towards successive additions of glucose in 0.1M NaOH with continuous stirring.

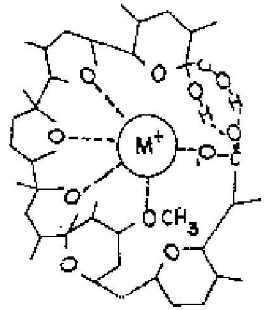
Solid State Ion Selective Electrodes

K^+ Solid State Ion Selective Electrode

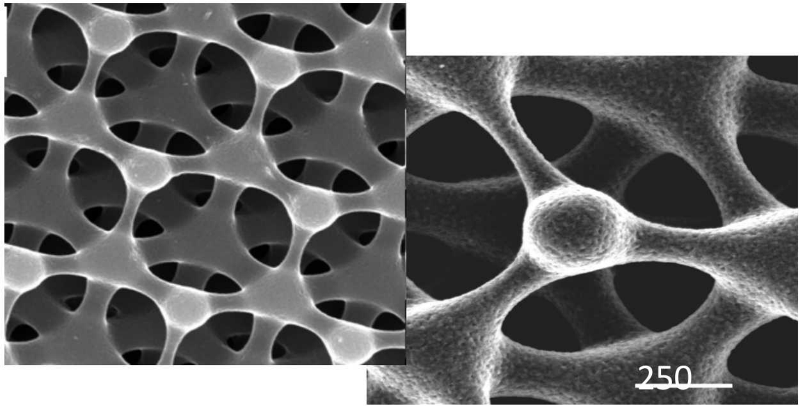
Three dips into ISE cocktail of (1% valinomycin, 32.8% PVC, 66% o-NPOE and 0.2% KTFPB) followed by 24 hours of drying. Mixture repeated from *J. Ping et al. Electrochemistry Communications 13 (2011) 1529–1532.*



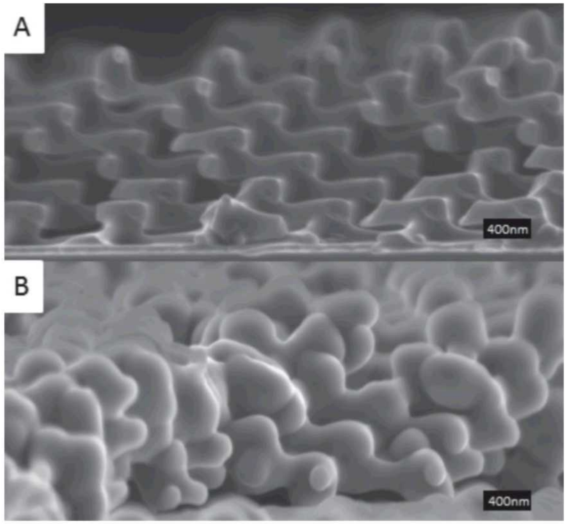
Valinomycin

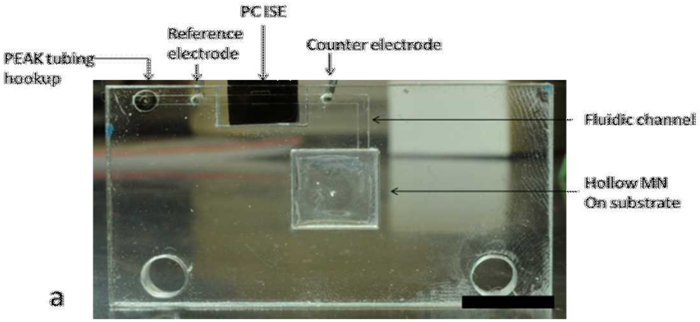


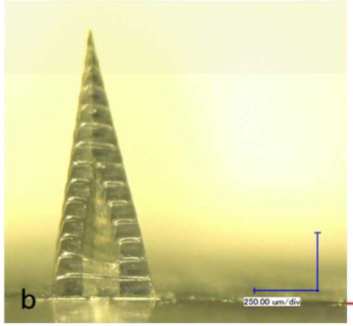
Valinomycin and K^+



Porous Carbons







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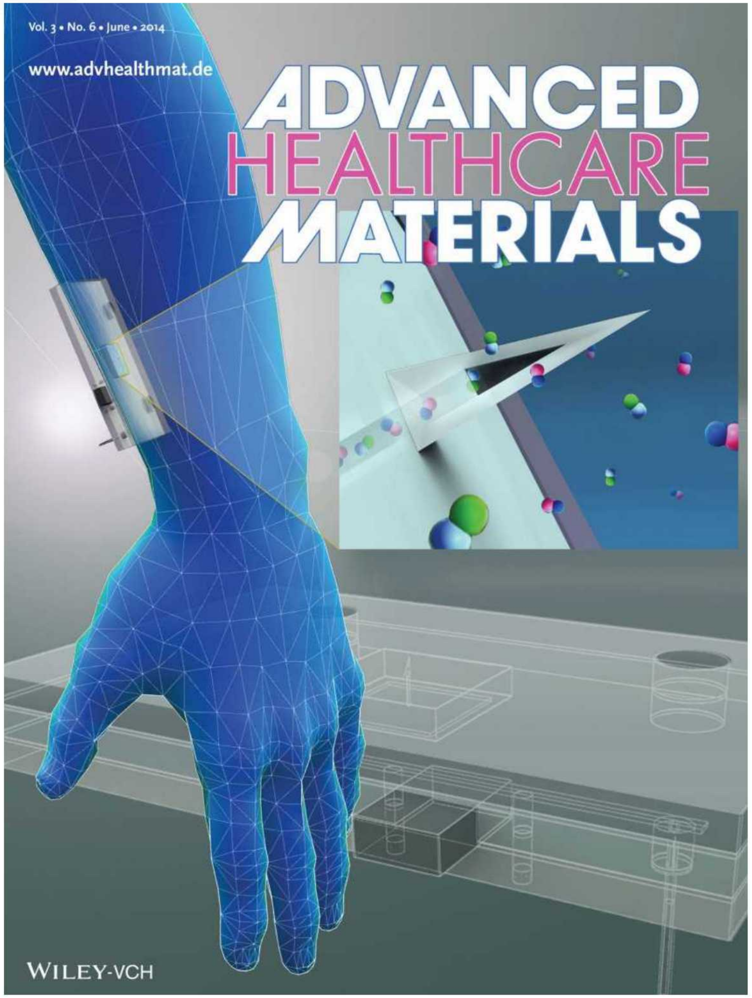
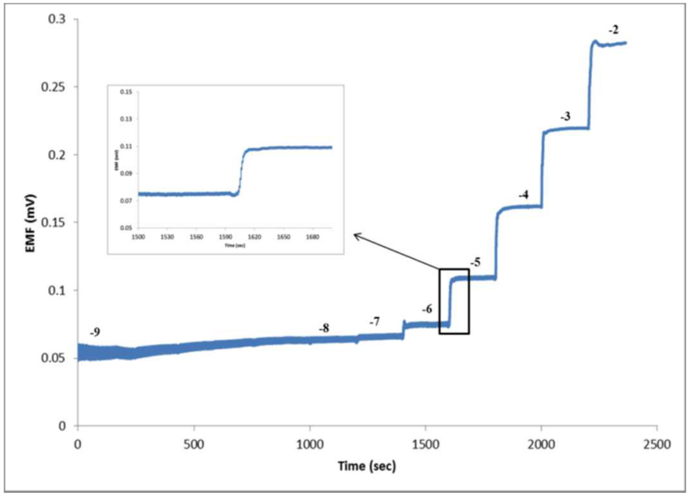
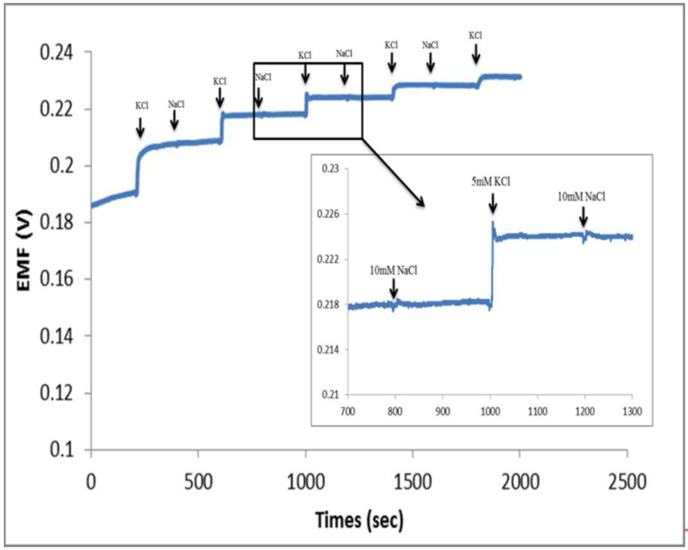
Solid State Ion Selective Electrodes







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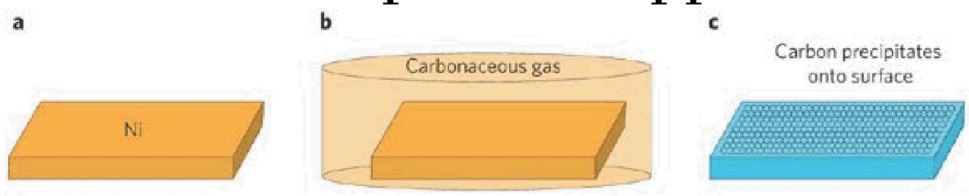
3D Graphene

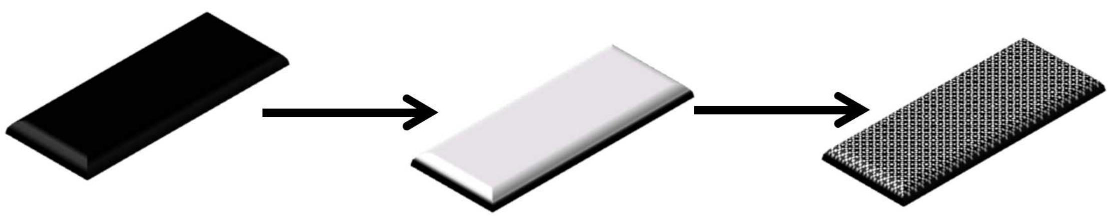
Graphene Preparation

1. Top Down Approach



(gaseous carbon source precipitates graphene onto substrate)

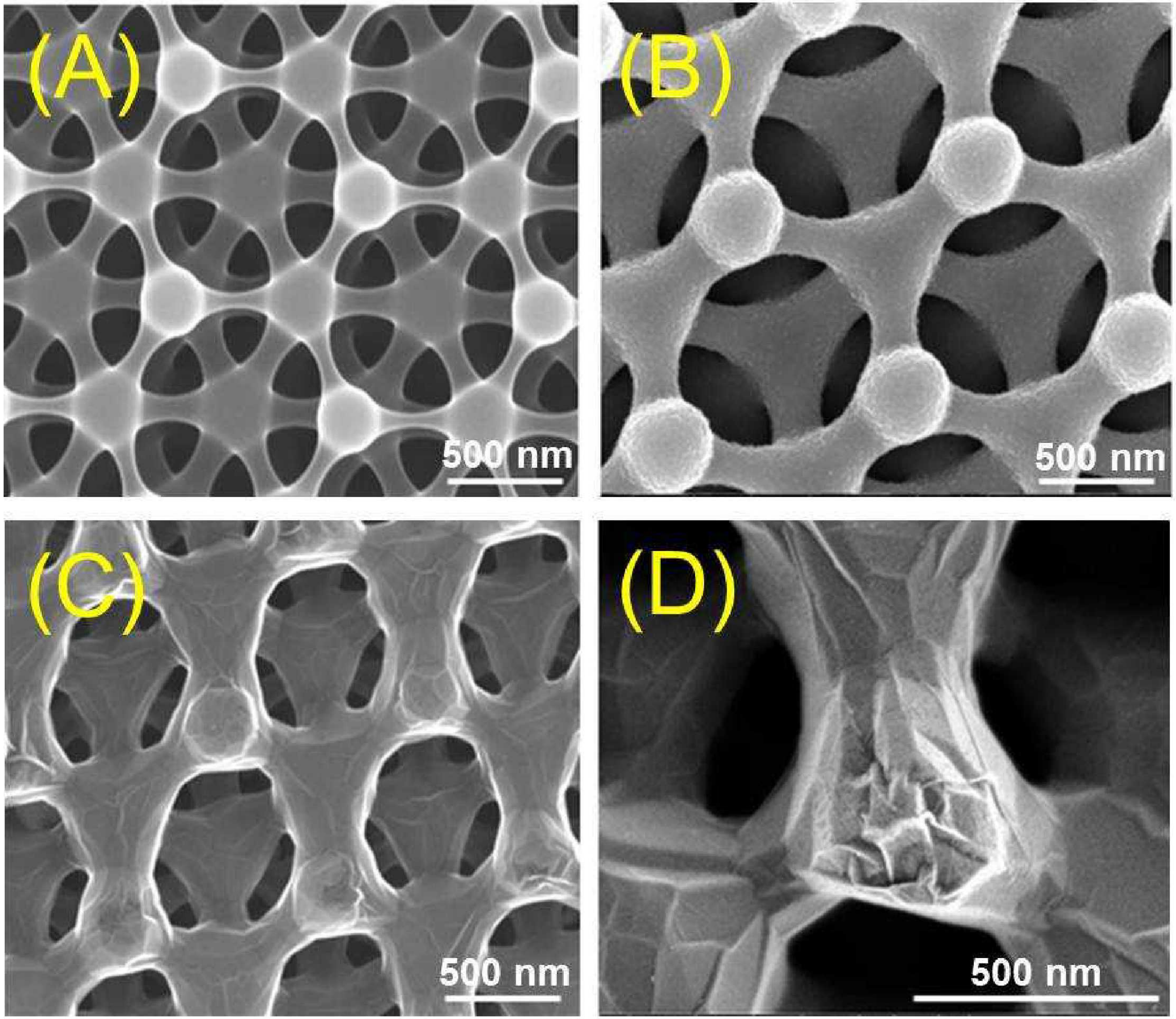
2. Bottom-Up Approach



Carbon Source   Nickel Coating   Annealing

(carbon diffuses up through metal catalyst to form graphene)

Ni-Coating and Annealing



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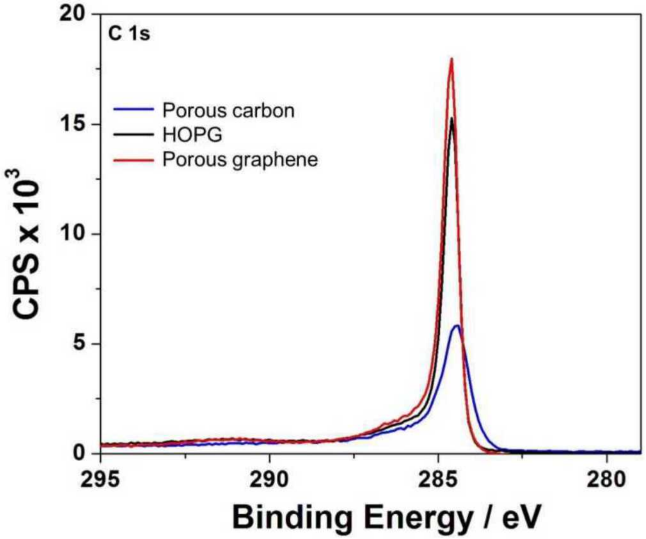
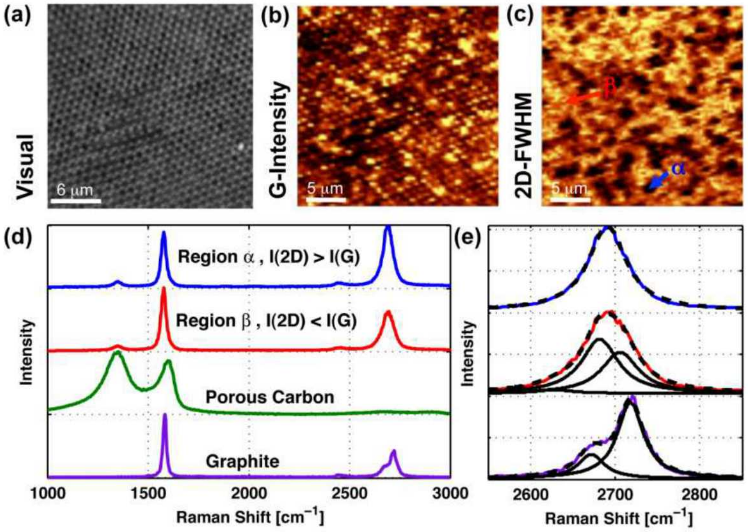
3D Graphene Structures?

XPS



Mike Brumbach

Raman



Thomas Beechem

Complete conversion from sp^3 to sp^2

ACS Nano **6(4): 35730-3579 (2012)**

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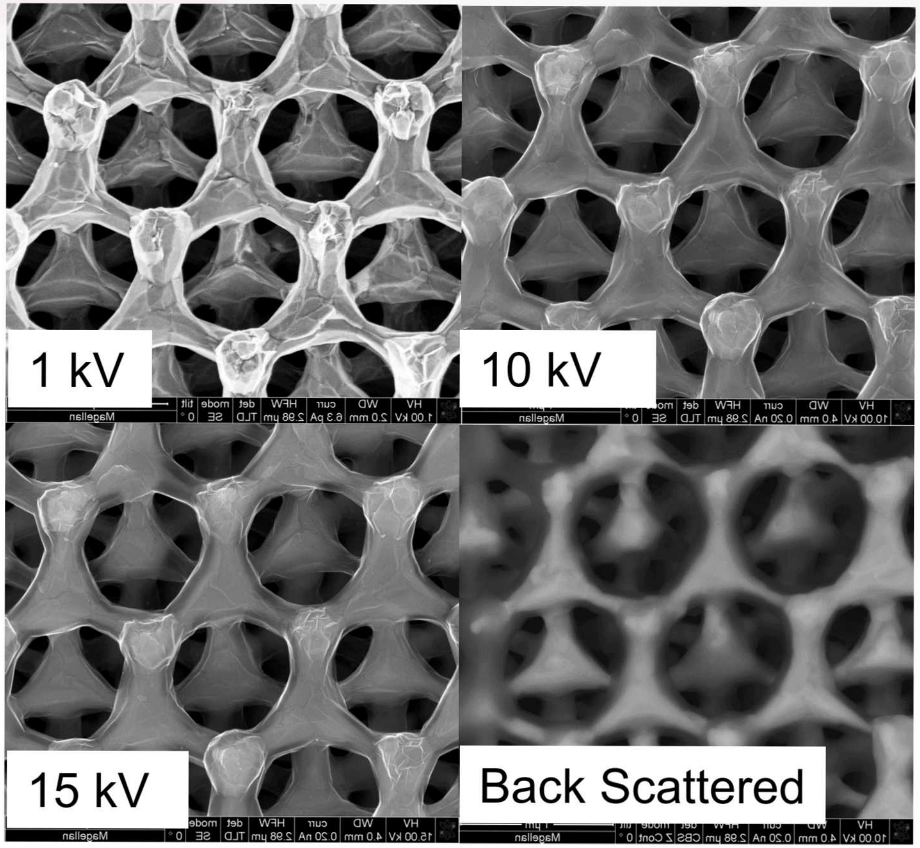
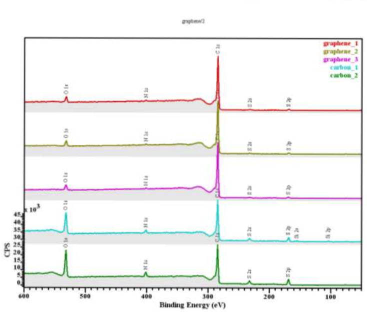
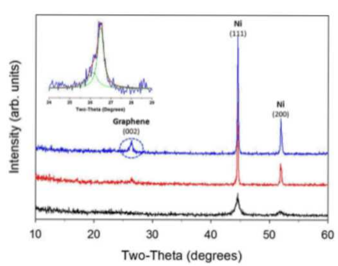
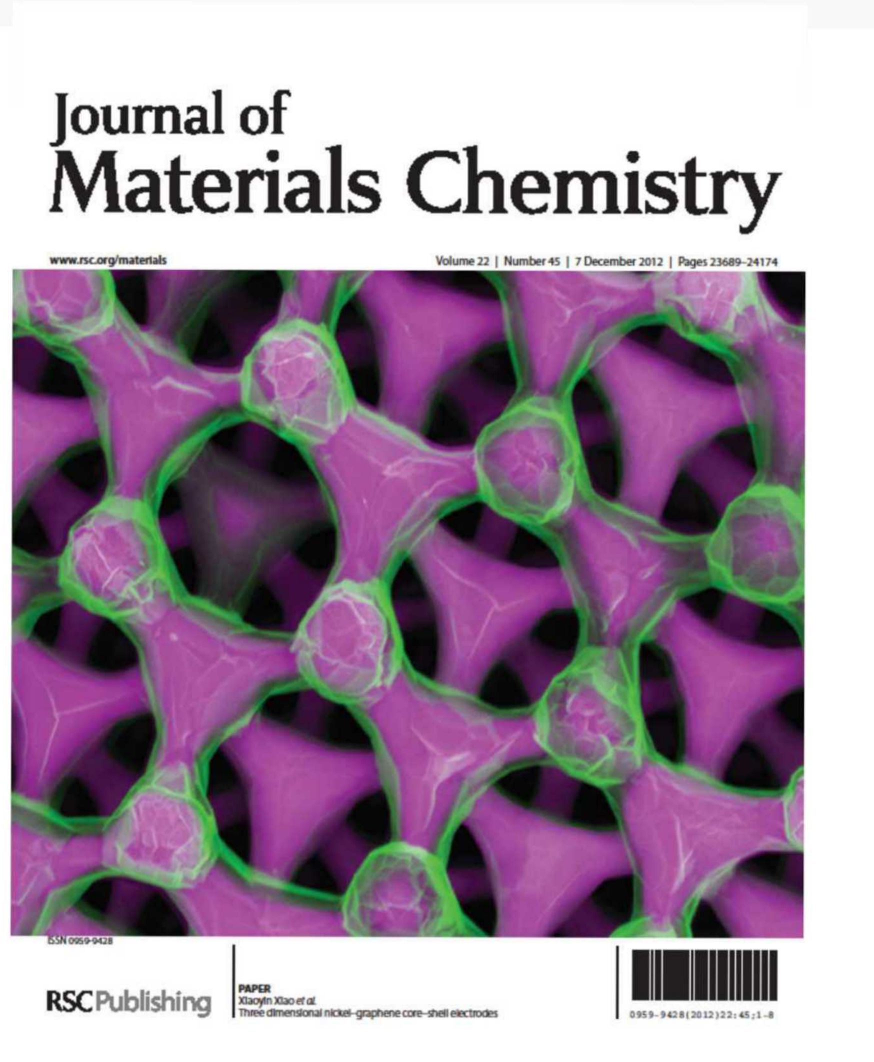
Core-Shell Structures




XPS

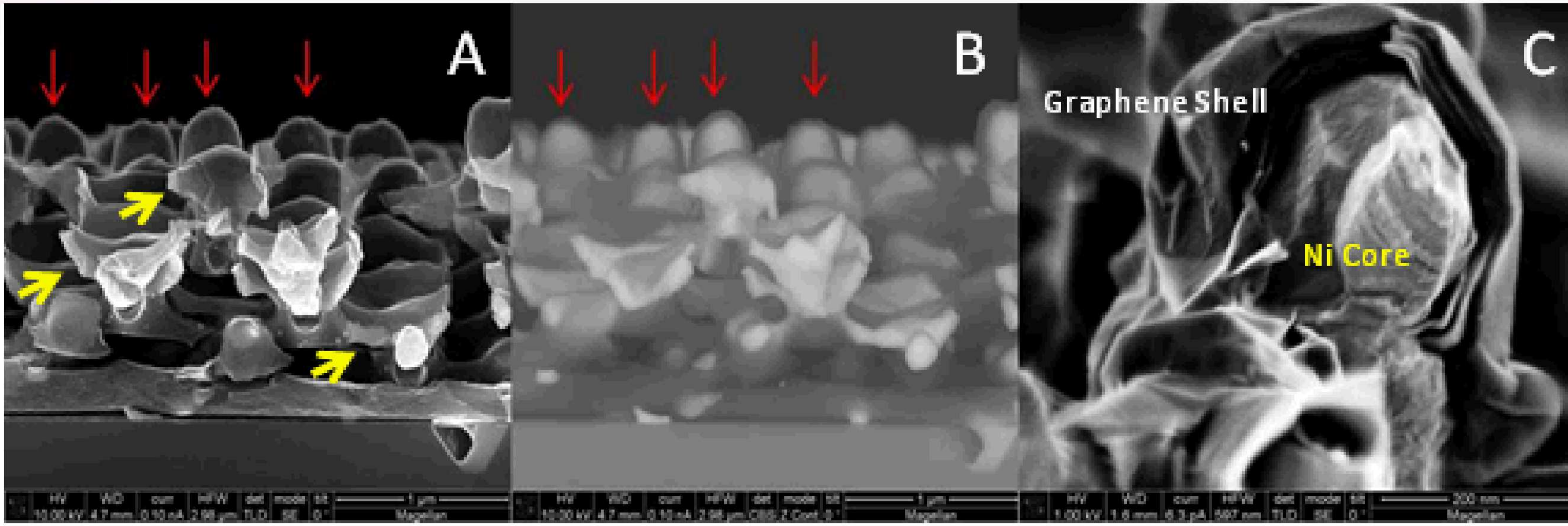


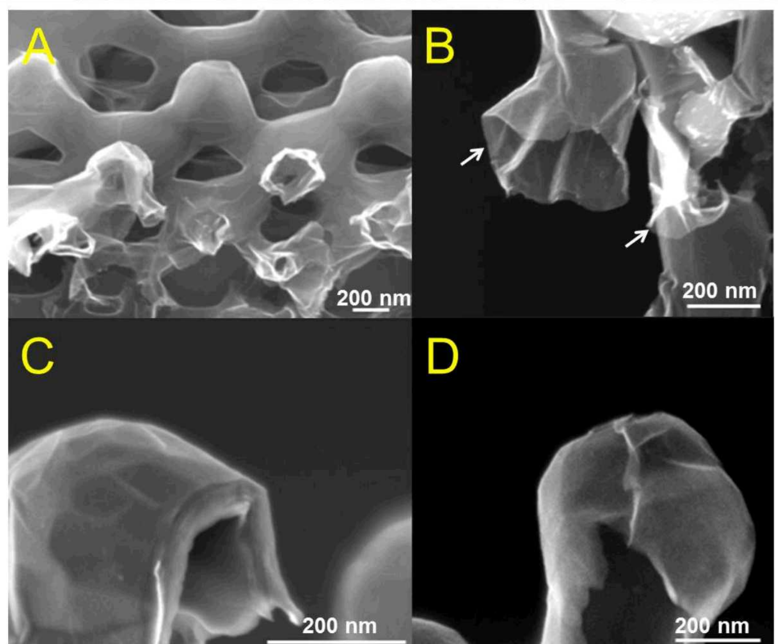
XRD


Journal of
Materials Chemistry
www.rsc.org/materials
Volume 22 | Number 45 | 7 December 2012 | Pages 23689–24174
ISSN 0959-9428
RSCPublishing
PAPER
Xiaoyin Xiao *et al.*
Three dimensional nickel–graphene core–shell electrodes

Journal of Materials Chemistry 22(45): 23749-23754 (2012)

Cross Section





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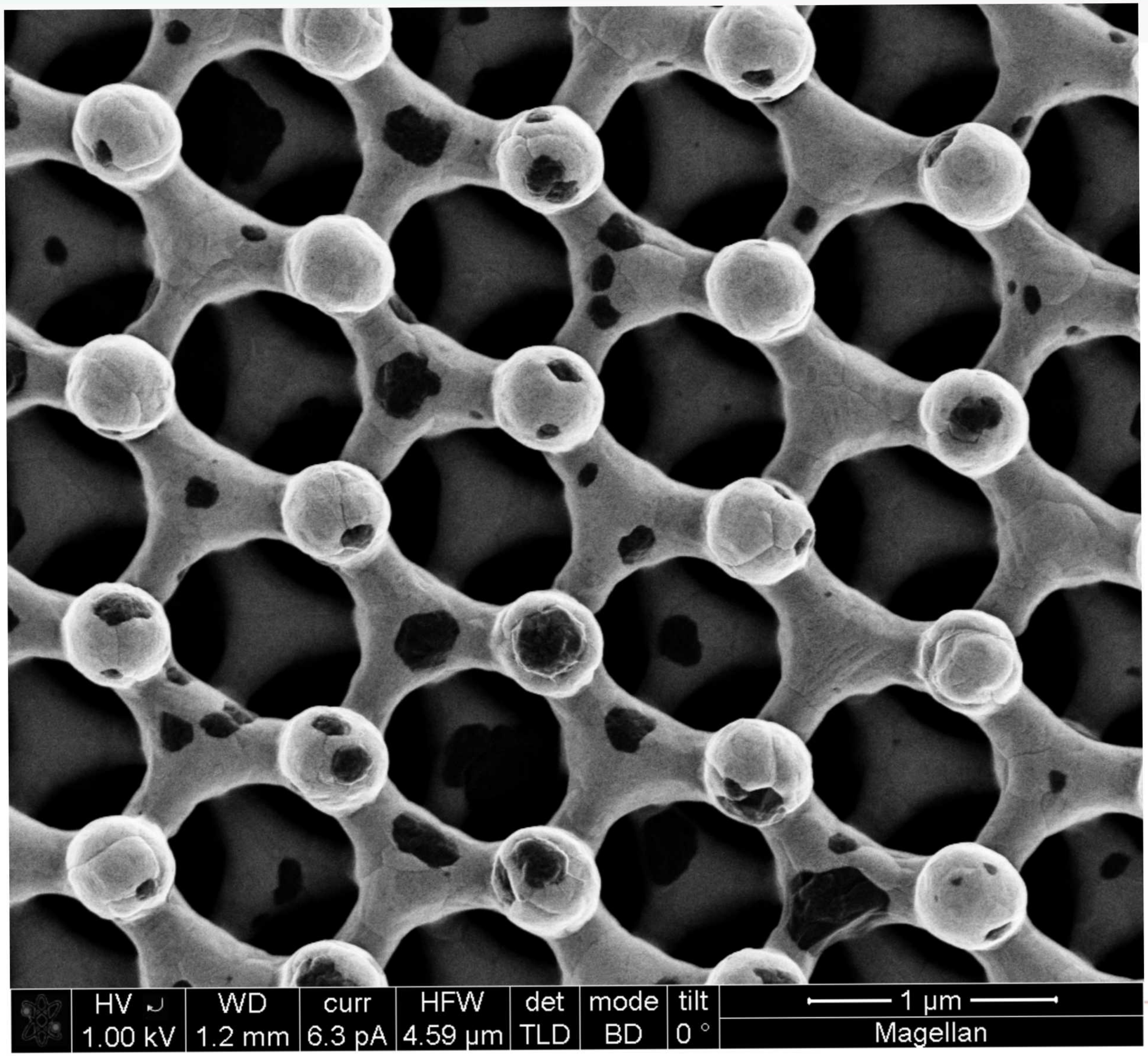
Mechanism



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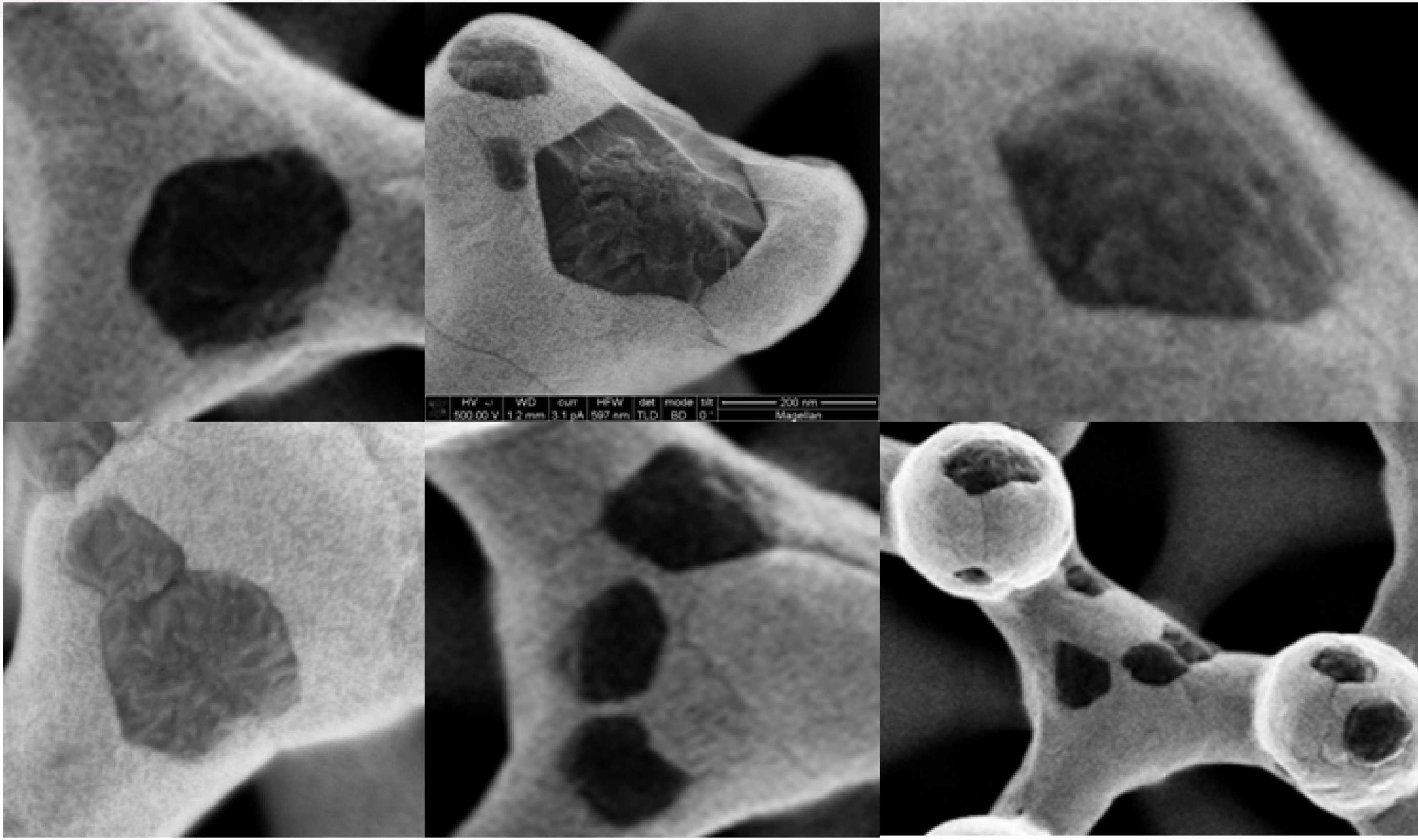
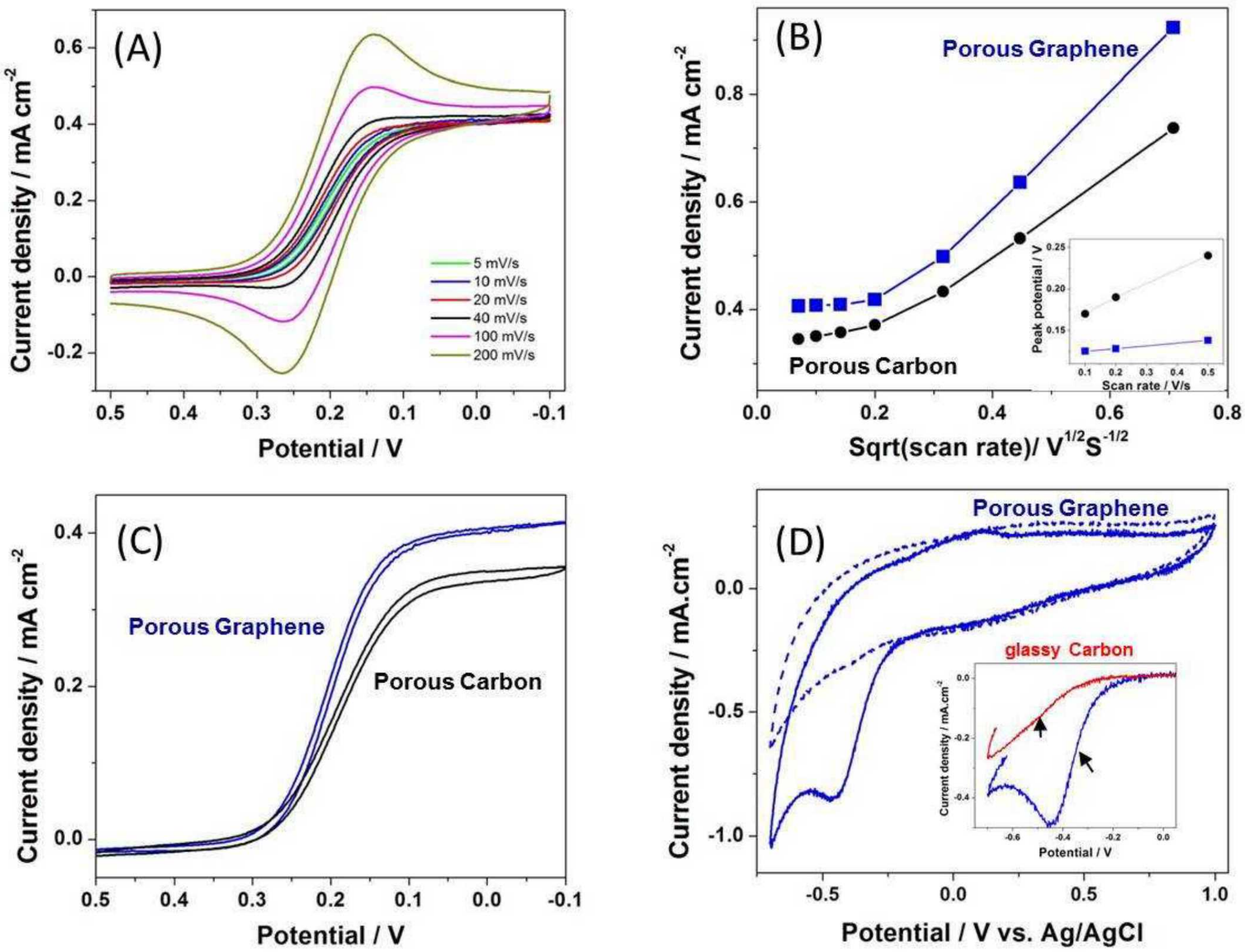
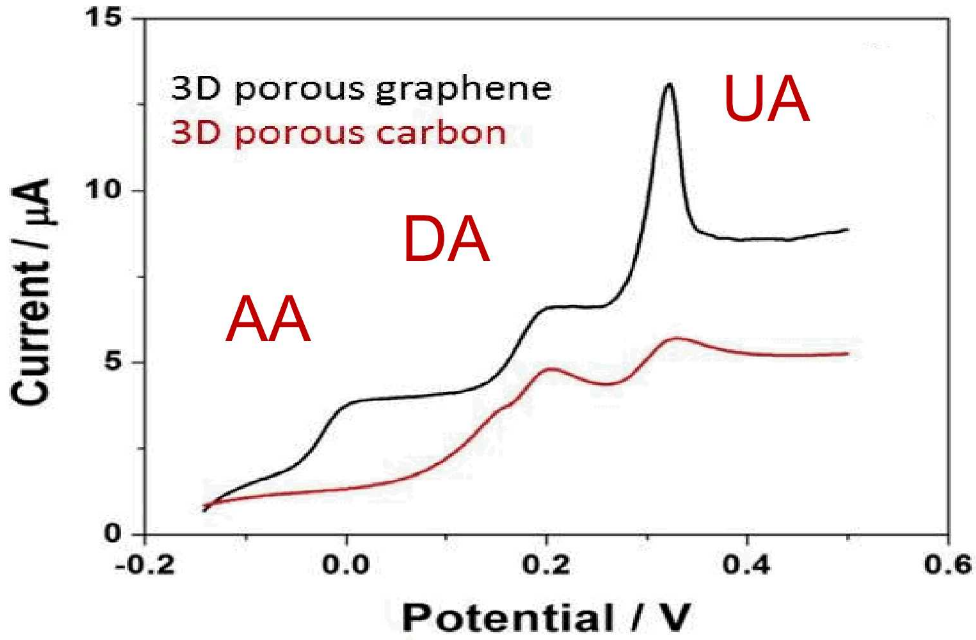
Mechanism


HV WD curr HFW det mode tilt
500.00 V 1.2 mm 3.1 pA 597 nm TLD BD 0 °
200 nm
Magellan

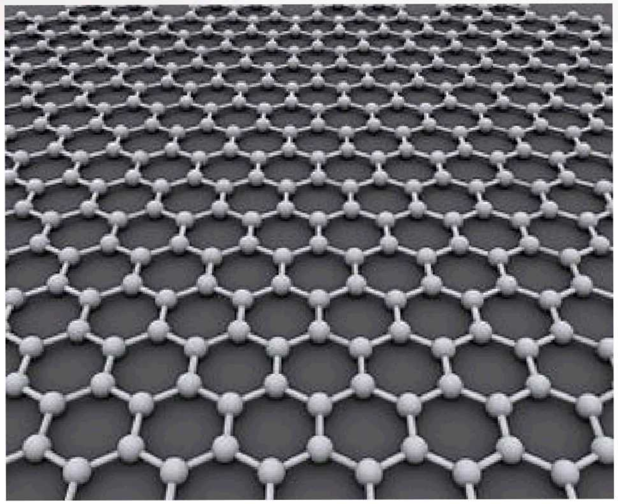
Electrochemical Results

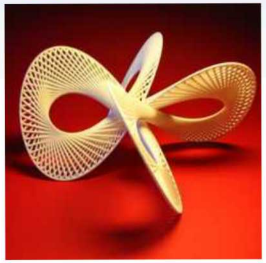


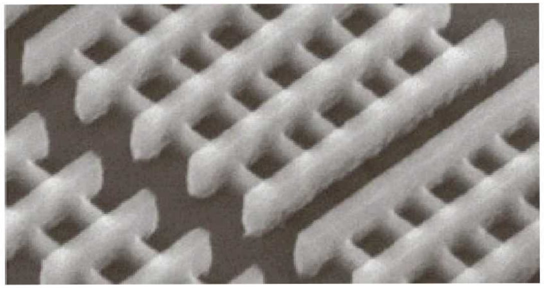
Detection of ascorbic acid, uric acid, and dopamine

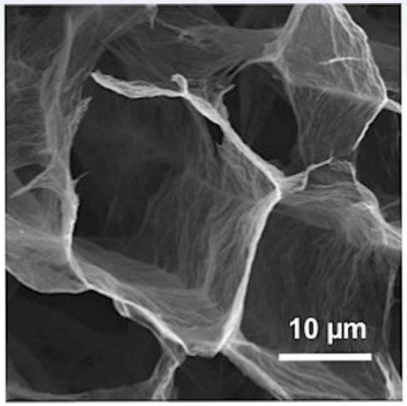


3D Graphene









Can we make graphene into functional three dimensional shapes that preserve/enhance its inherent benefits or result in new beneficial properties?

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Summary

- 3D porous carbon electrodes can be used to enhance mass transport of fuels and analytes for improved sensors and battery applications
- 3D graphene opens the door for a new generation of novel materials that can impact sensors, batteries, and electronics

Lithographically Defined Three Dimensional Graphene Electrodes

X. Xiao, D.B. Burckel, Thomas Beechem, Joseph Michaels, C.M. Washburn, S.M. Brozik, D.R. Wheeler

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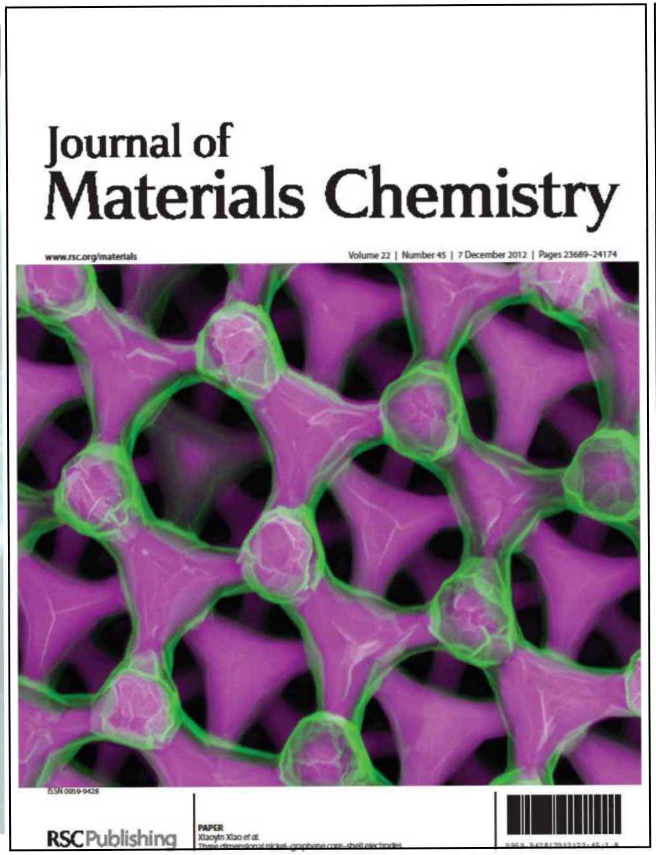

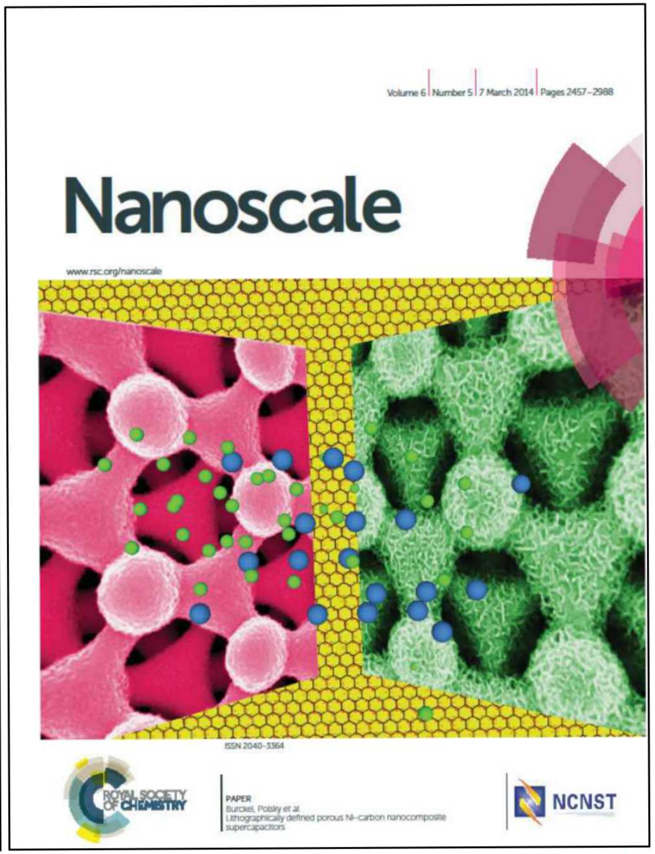

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