Advanced materials for electrochemical capacitors

A proposed contribution to a CU capacitor consortium

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Also, Dr. Oleg Borodin, University of Utah

Steve Creager
Electrochemistry & Carbon

Darryl DesMarteau
Fluoropolymers;
ionic liquid electrolytes

Dennis Smith
Polymers & Carbon

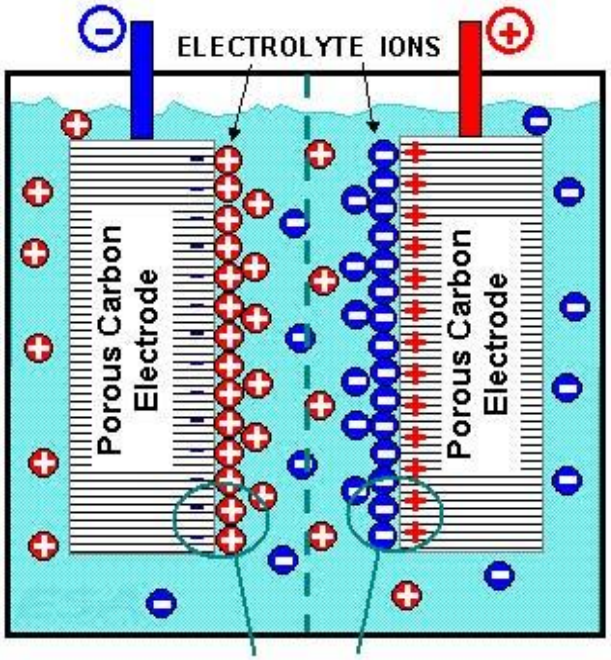
Luis Echegoyen
Fullerenes; Carbon
Nano-onions

Oleg Borodin
Research Professor, U Utah.
Computational approaches to
liquid structure / dynamics

Supercapacitors / Ultracapacitors

Electrode requirements:

- High electrical conductivity
- High surface area (for high capacitance)
- High porosity (for electrolyte penetration and fast response)
- Wide voltage stability window



Double Layer Capacitors
(Adsorbed layers of ions and solvated ions)

Photo Courtesy of ESMA

Electrolyte requirements:

- High ionic conductivity
- Low viscosity
- Low volatility / flammability
- Wide voltage stability window

Photo Courtesy of Maxwell Technologies

Images from the Energy Storage Association, California

http://www.electricitystorage.org/technologies.htm

Accessed July 2, 2003

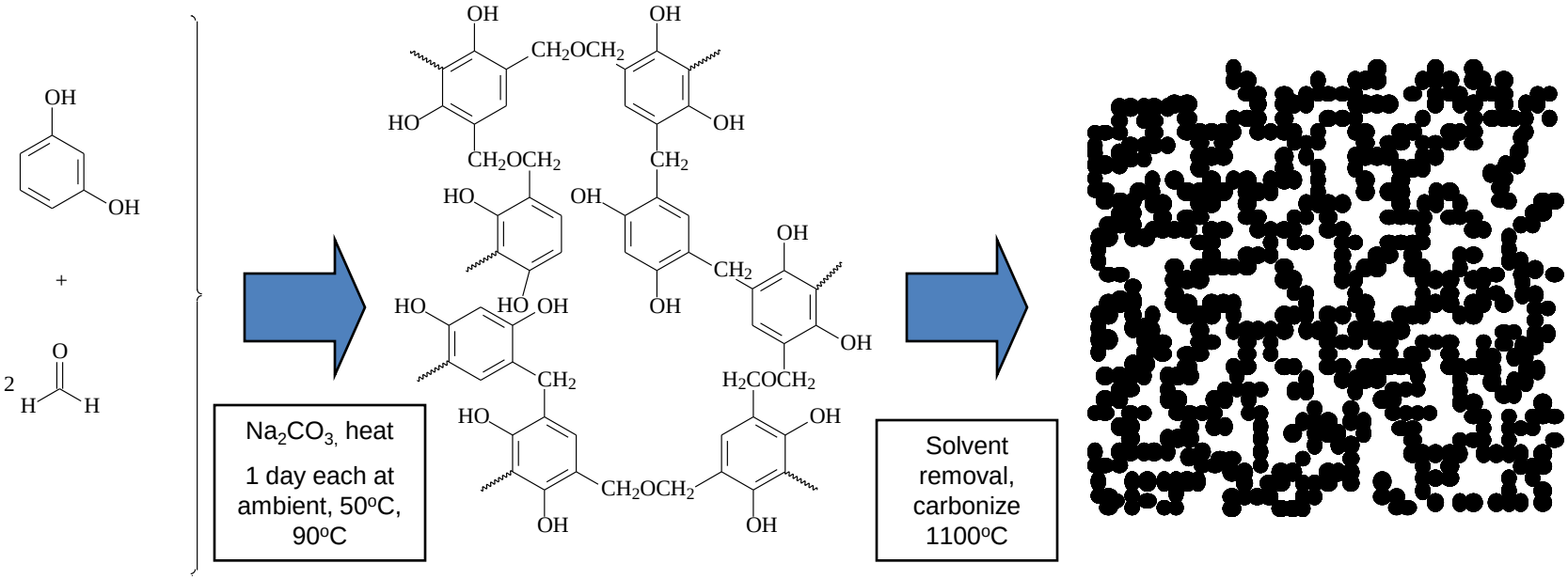
Advanced Materials for Electrochemical Capacitors

- Electrode materials; Nanoporous / nanostructured carbon
  - Carbon aerogels (e.g. resorcinol / formaldehyde)
  - Fullerenes / Nanotubes / Carbon Nano-Onions
  - Hi-carbon-yield glassy carbon precursors (“BODA”).

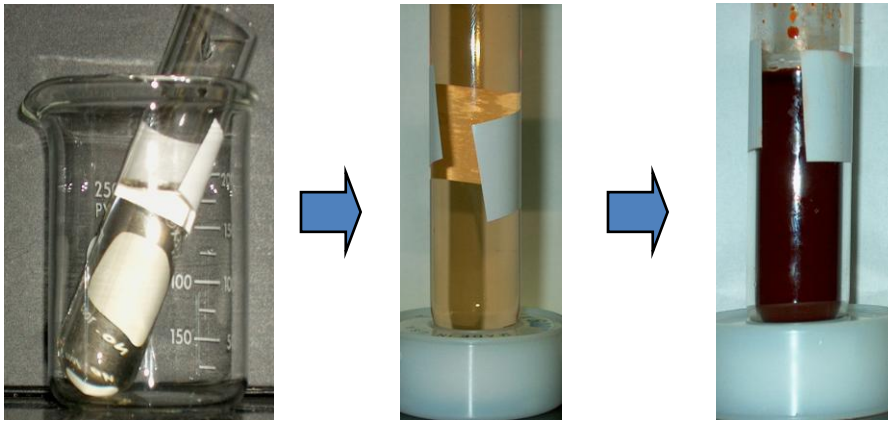
- Electrolyte materials; Room-temperature ionic liquids (RTILs)
  - Ammonium / phosphonium cations
  - Fluorosulfonimide anions
  - No solvent

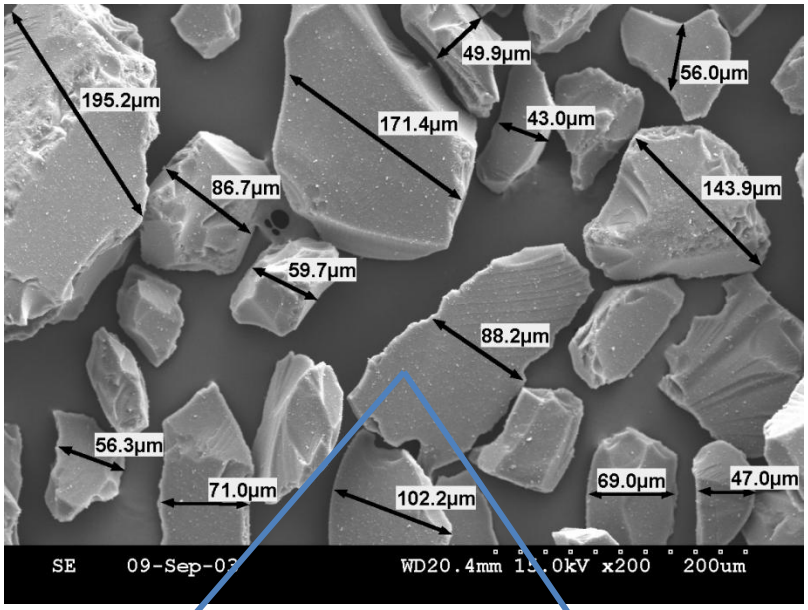
- Small-scale testing
  - Three-electrode cells / potentiostatic control
  - Voltammetry / impedance spectroscopy
  - Galvanostatic charging / discharging

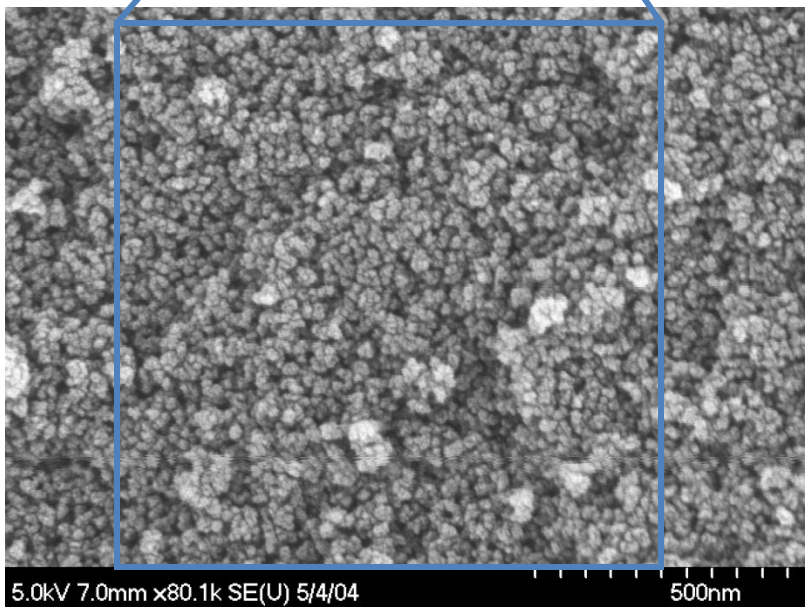
Carbon aerogels via the resorcinol / formaldehyde (RF) method

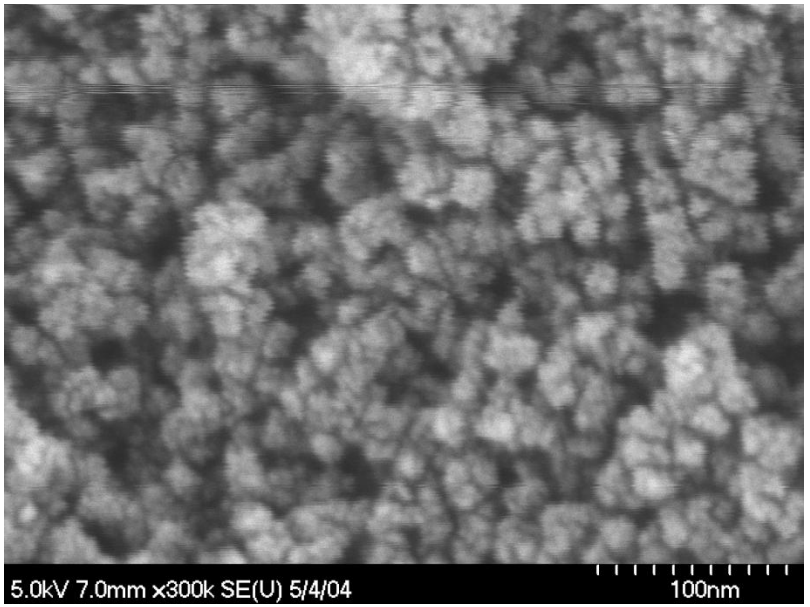


Monomers | Crosslinked polymer (sol) | Nanoporous carbon aerogel





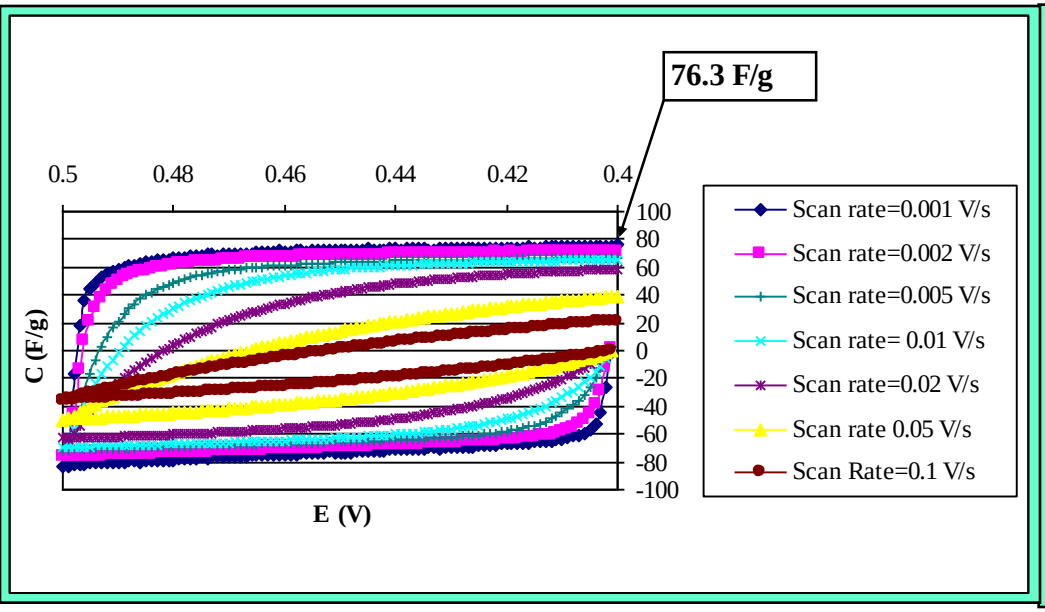


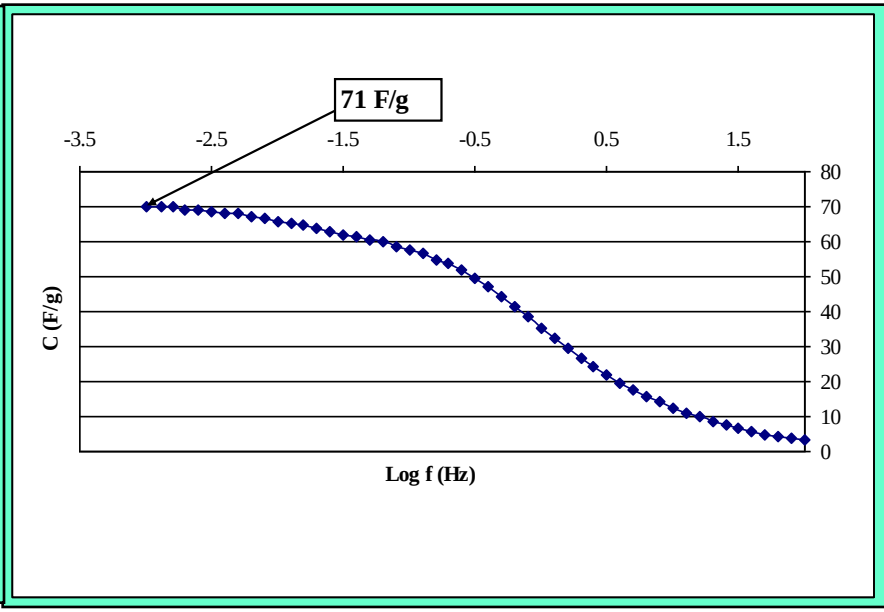


Carbon aerogel typical properties:

- Surface area 500 – 600 m^2/g (BET)
- Pore sizes 0.3 – 20 nm (BHJ)
- Macroscopic density after pyrolysis, approx. 0.5 g / cm^3
- Free volume, approx. 70 %

Specific capacitance of non-templated CAG materials





Left, cyclic voltammograms of 2.0 mg of large particle (~90 micrometer) of RF 30 carbon aerogel (sample S-12) on sticky carbon electrode, plotted as a dependence of specific capacitance on different scan rates vs. voltage profiles. The electrolyte was aqueous 1M H_2SO_4.

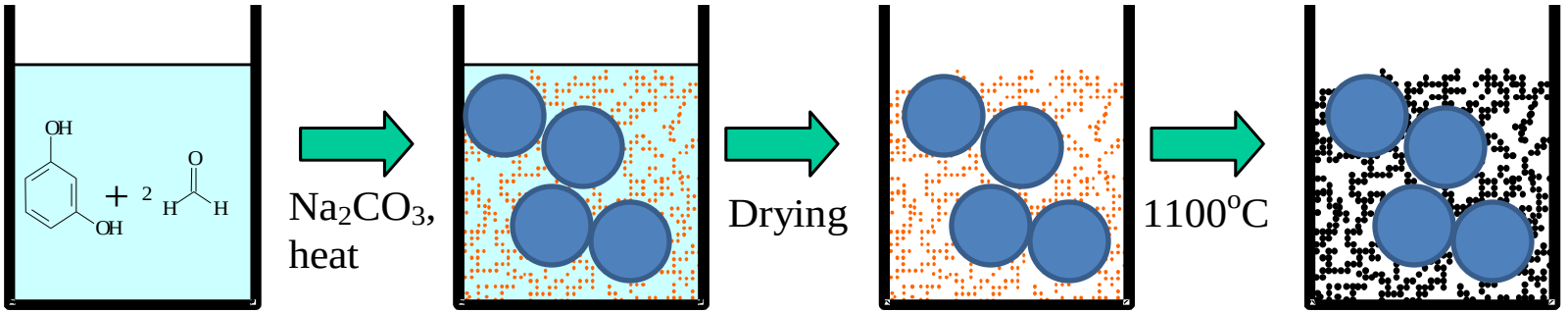
Right, frequency dependence of 2.0 mg of RF 30 carbon aerogel large particle (~90 micron) in 1 M of H_2SO_4 electrolyte, at DC potential of 0.4 V, AC amplitude of 80 mV, and frequency range from 100 to 0.001 Hz.

Specific capacitance (*C*) values were calculated from the imaginary part of Nyquist impedance plots according to the equation; $C = -1/(2\pi f * Z_{im})$, where *f* is the frequency and Z_{im} is the imaginary (out-of-phase) portion of the impedance.

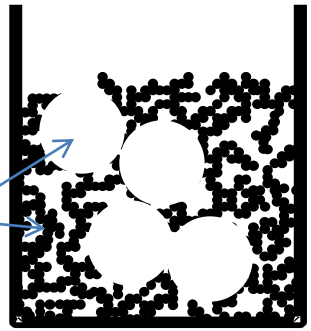
Preparation of templated carbon aerogels via the RF method

Q: Why templating?

A: To promote rapid electrolyte access to the full interior surface area of the carbon electrode!

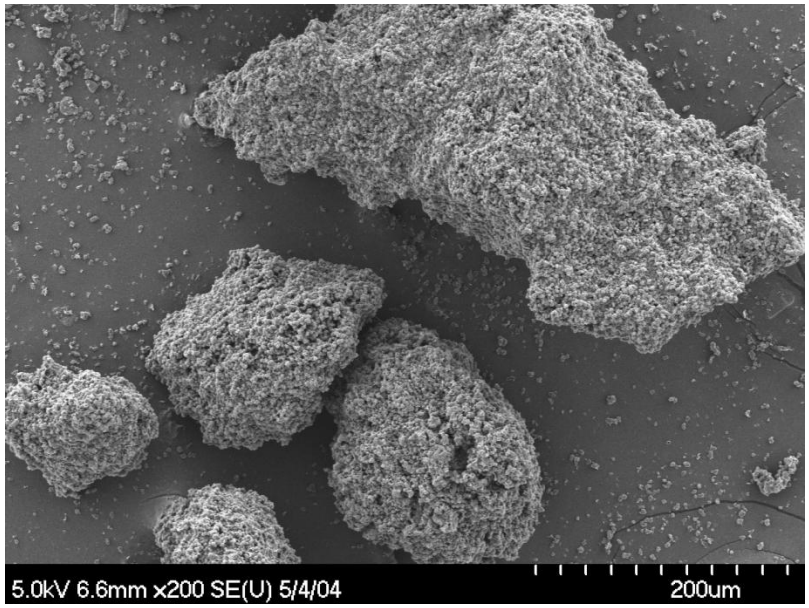


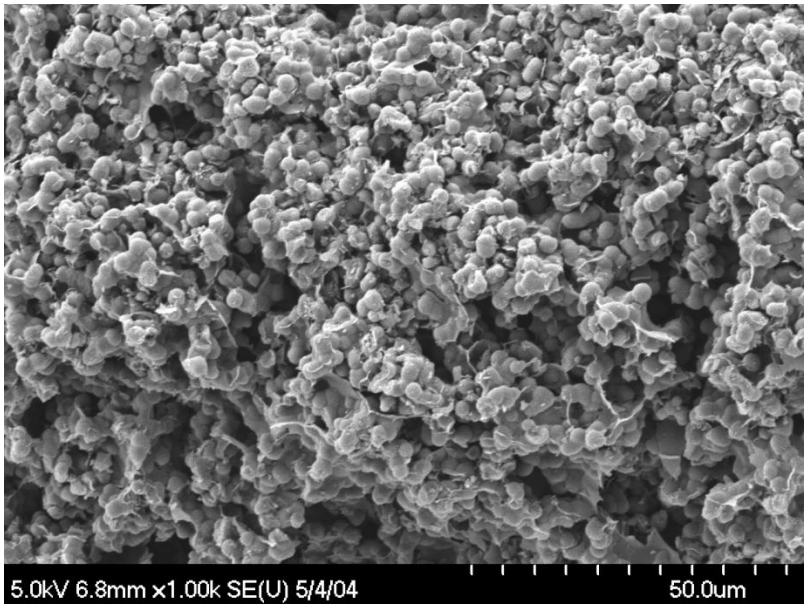
Hierarchical porosity;
Large pores & small pores

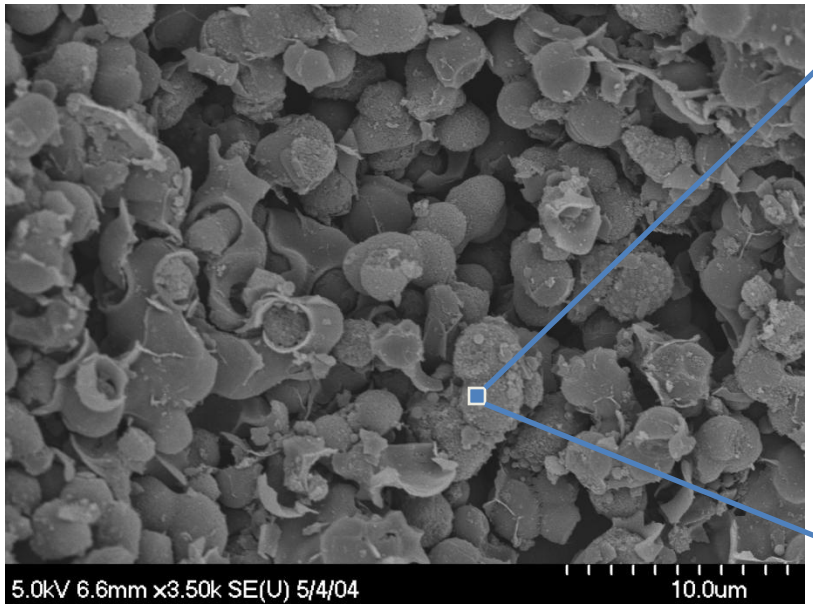


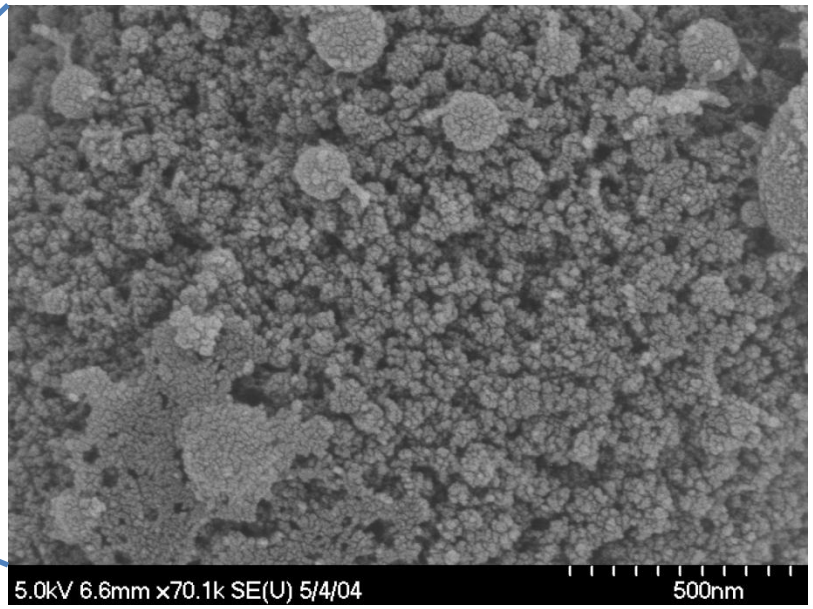
Templated Carbon Aerogel

Etching to remove templating agent



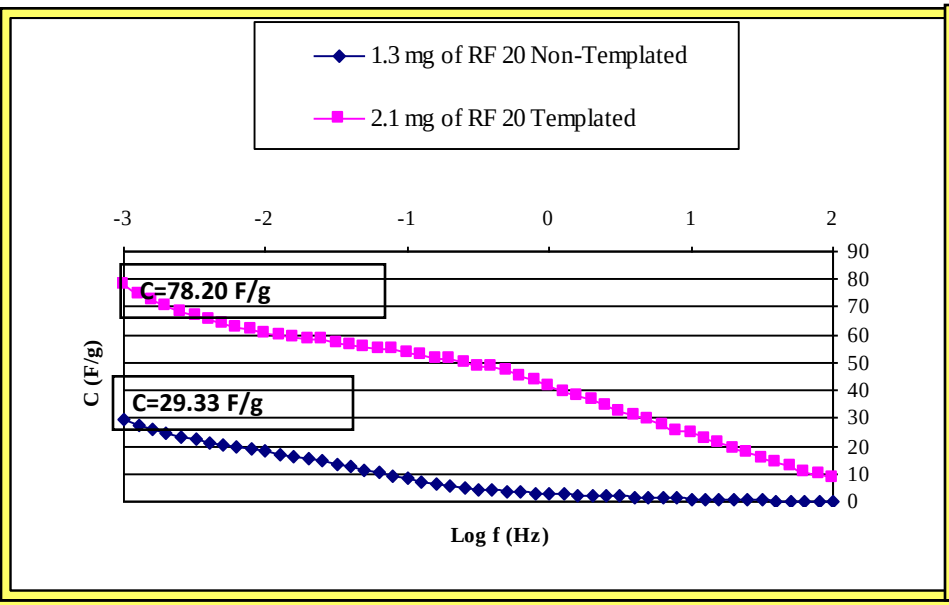


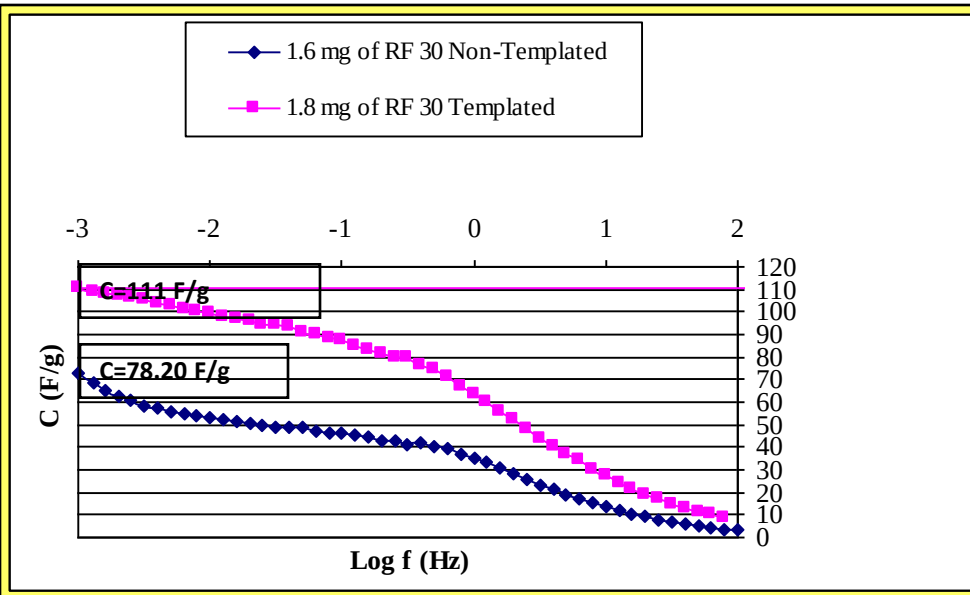


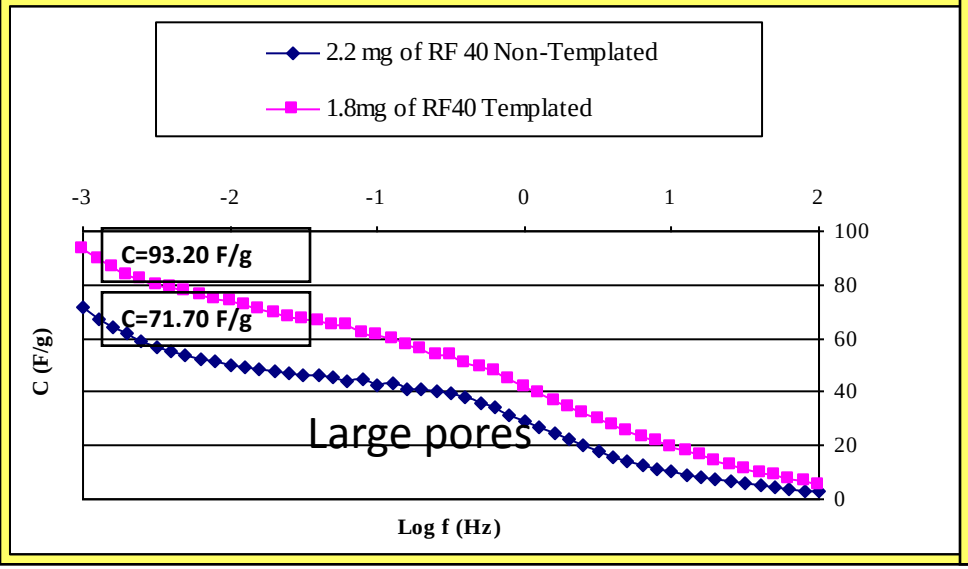


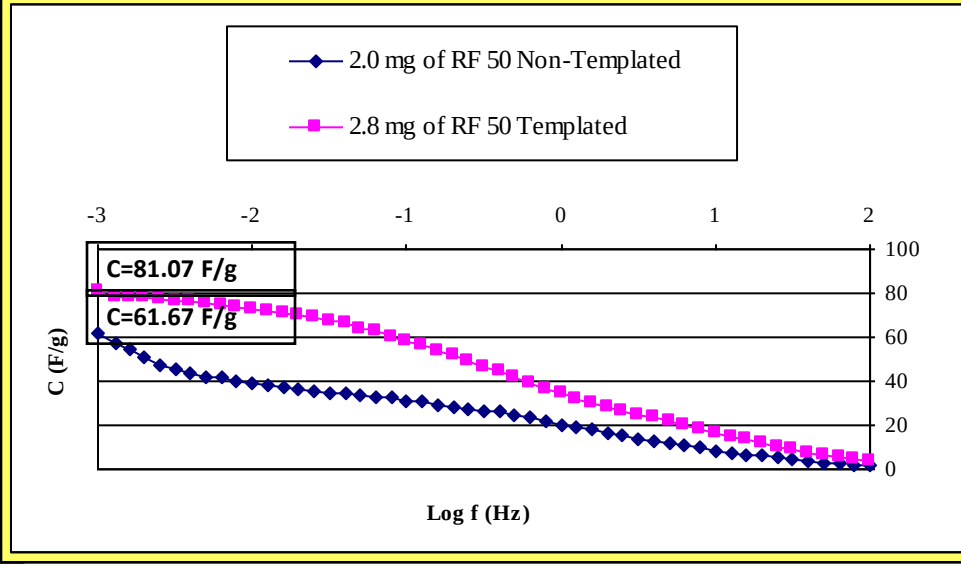
FE-SEM of Templated RF 20 CAG after carbonization and etching with 30 % HF to remove silica template.

Specific capacitance of templated CAG samples by impedance spectroscopy



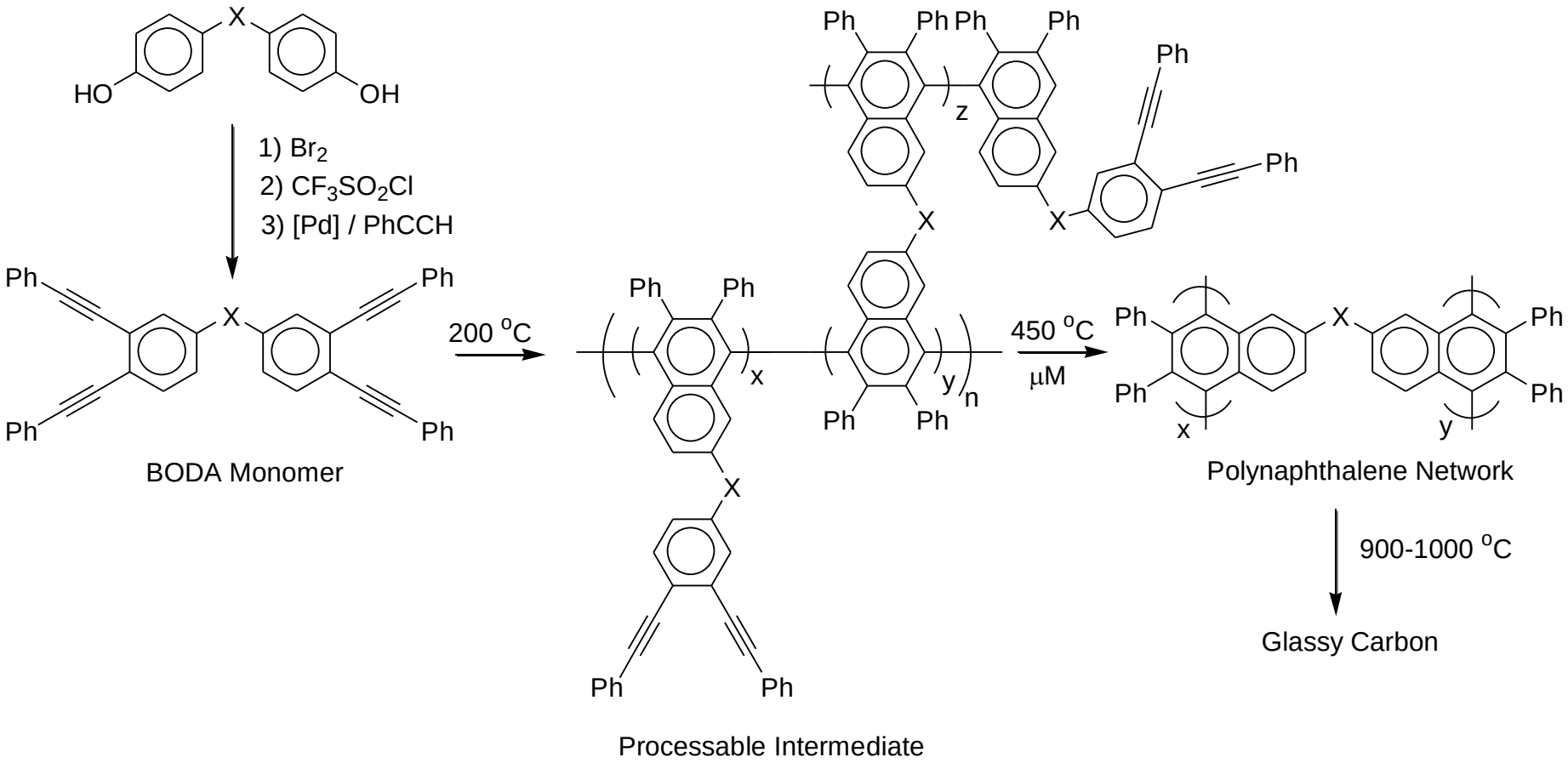






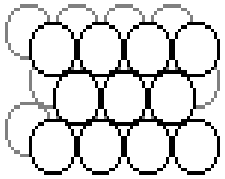
Frequency dependence of Templated (S20-23) and Non-Templated (S16-19) CAG in 1 M H_2SO_4, at DC potential of 0.4 V, AC amplitude of 80 mV, and frequency range from 100 to 0.001 Hz. Capacitance was evaluated at the lowest frequency of 0.001 Hz.

BIS-ORTHO-DIYNYL-ARYLENE (BODA)-DERIVED POLYNAPHTHALENES AND GLASSY CARBON

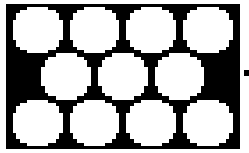


Adv. Funct. Mater. **2007**, *17*, 1237–1246; *Carbon* **2007**, *45(5)*, 931-935;
Chem. Mater. **2007**, *19*, 1411-1417.

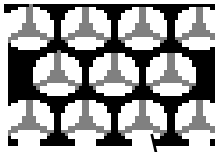
Polymer (BODA) Derived Inverse Carbon Opal Photonic Crystal

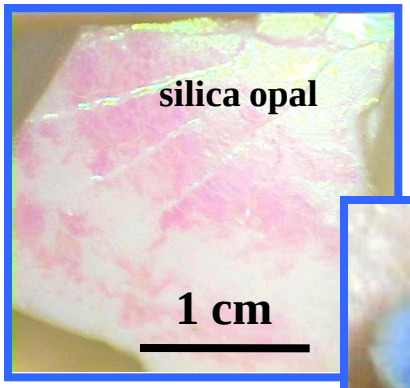


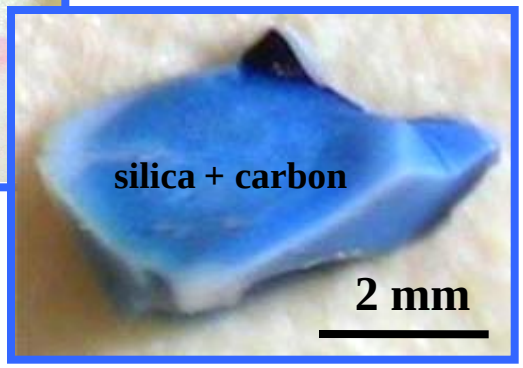
1) BODA melt 103 °C
2) Cure 265 °C
3) Pyrolyze 900 °C



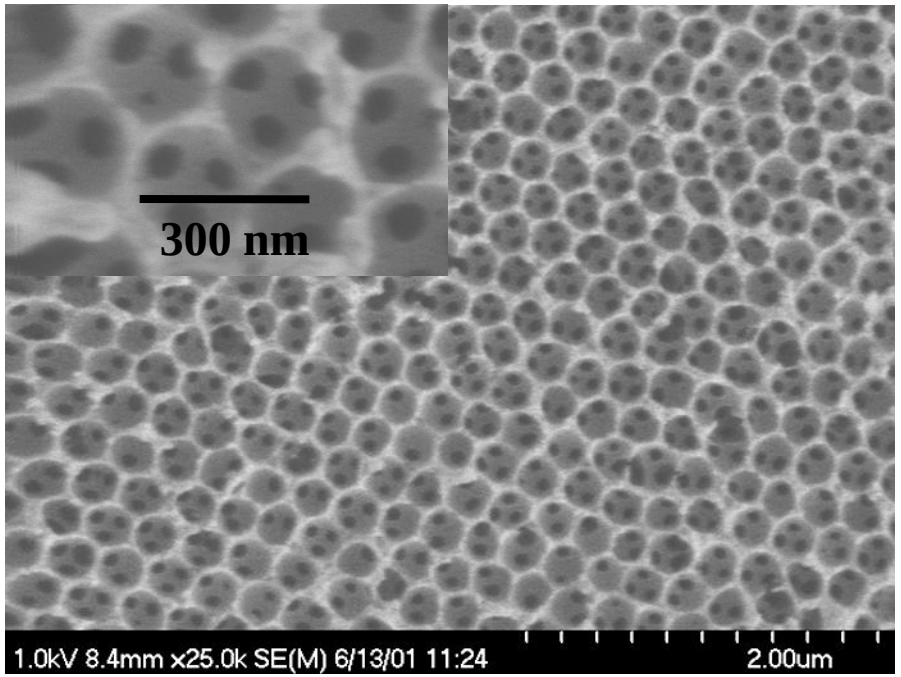
4) HF Etch







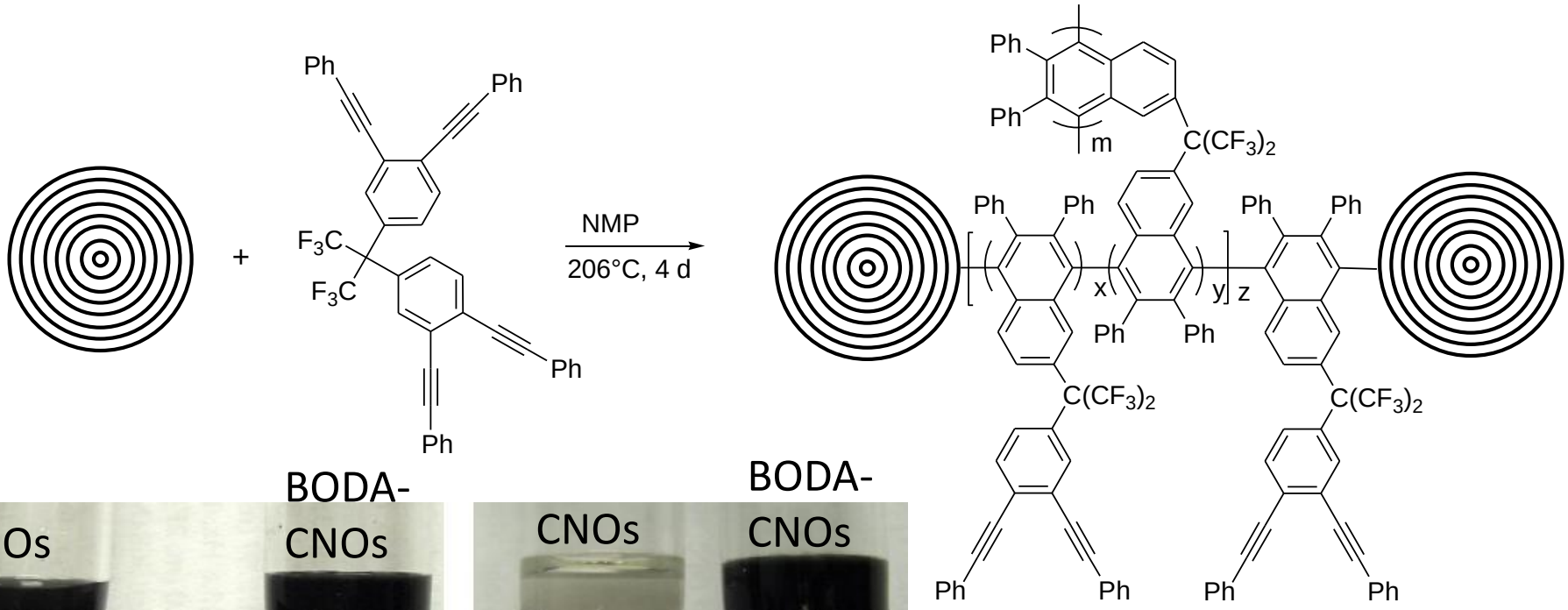
Sol-gel prepared closed packed colloidal silica impregnated with processable polymer and carbonized

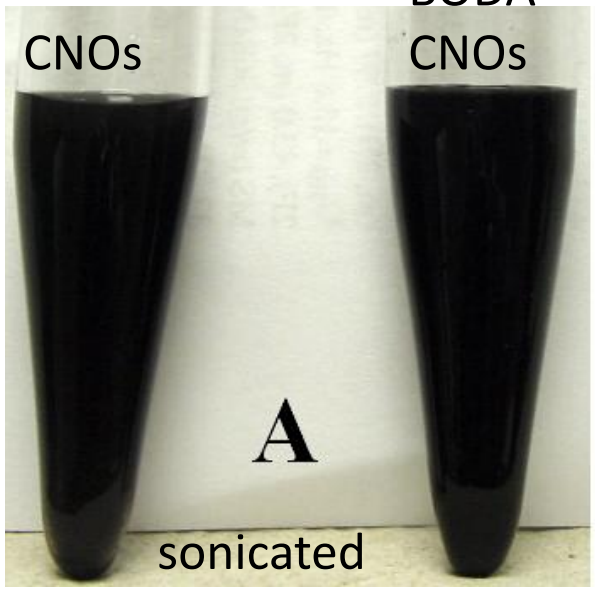


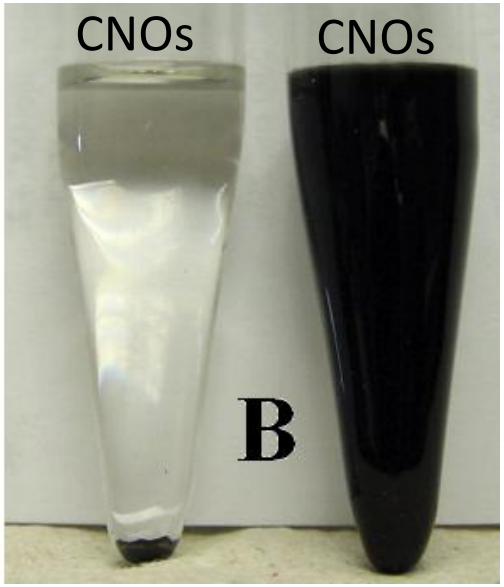
Etch with HF giving 3-D (SEM) periodic array of holes surrounded by carbon.

Langmuir **2003**, *19*, 7153.

BODA-co-CNOs (Carbon Nano-onions)





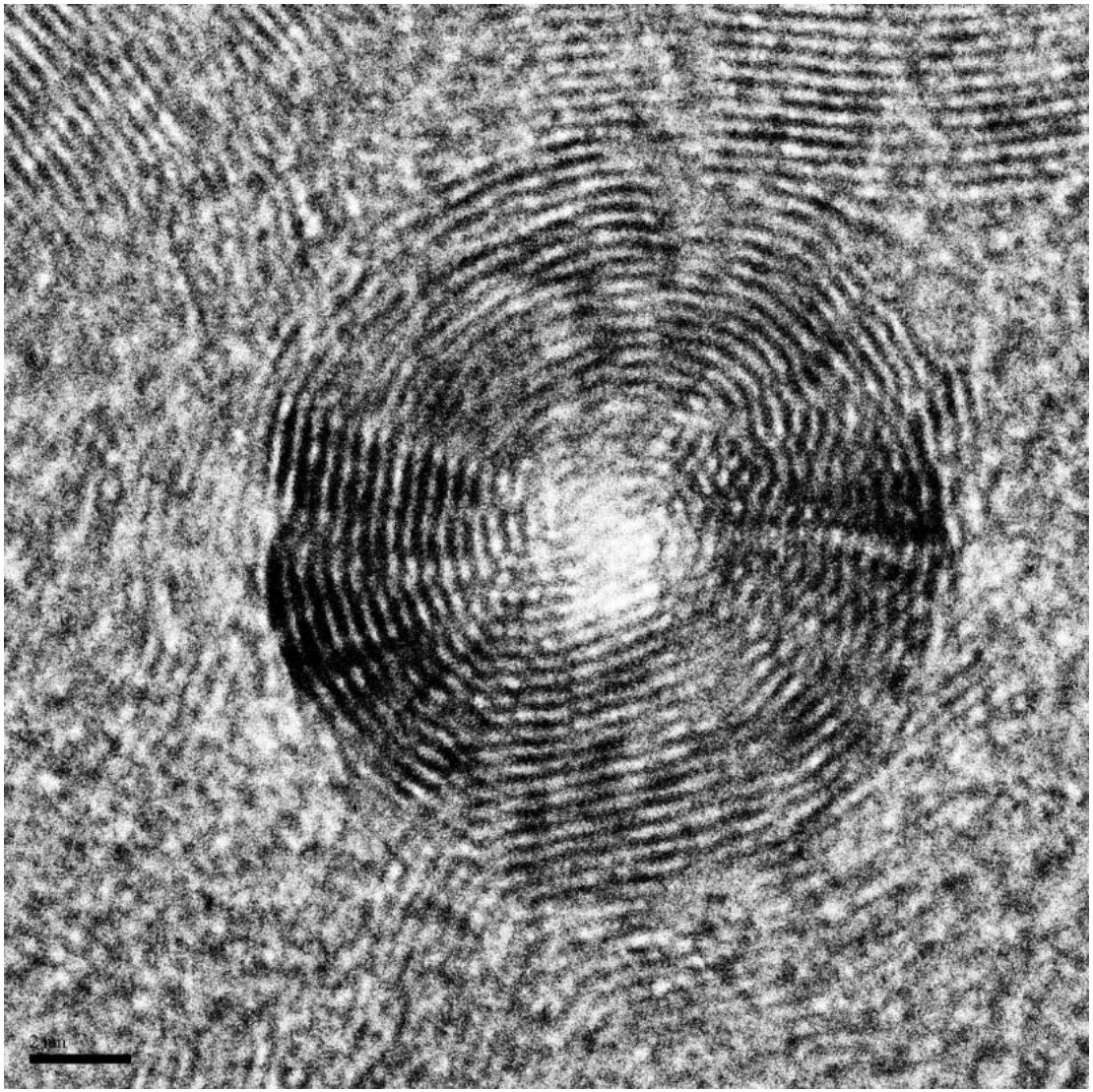


Solubilized CNOs

Arno Rettenbacher

Chem. Mater. **2007**, *19*, 1411-1417.

High Resolution TEM of Soluble BODA-Carbon Onions



HRTEM (300 keV) image of BODA-CNO copolymer (from $CHCl_3$ solution), scale bar represents 2 nm.

The first radical addition to CNO also provides a route to purify and resolve CNOs sizes by thermal-oxidative de-functionalization.

Chem. Mater. **2007**, *19(6)*, 1411

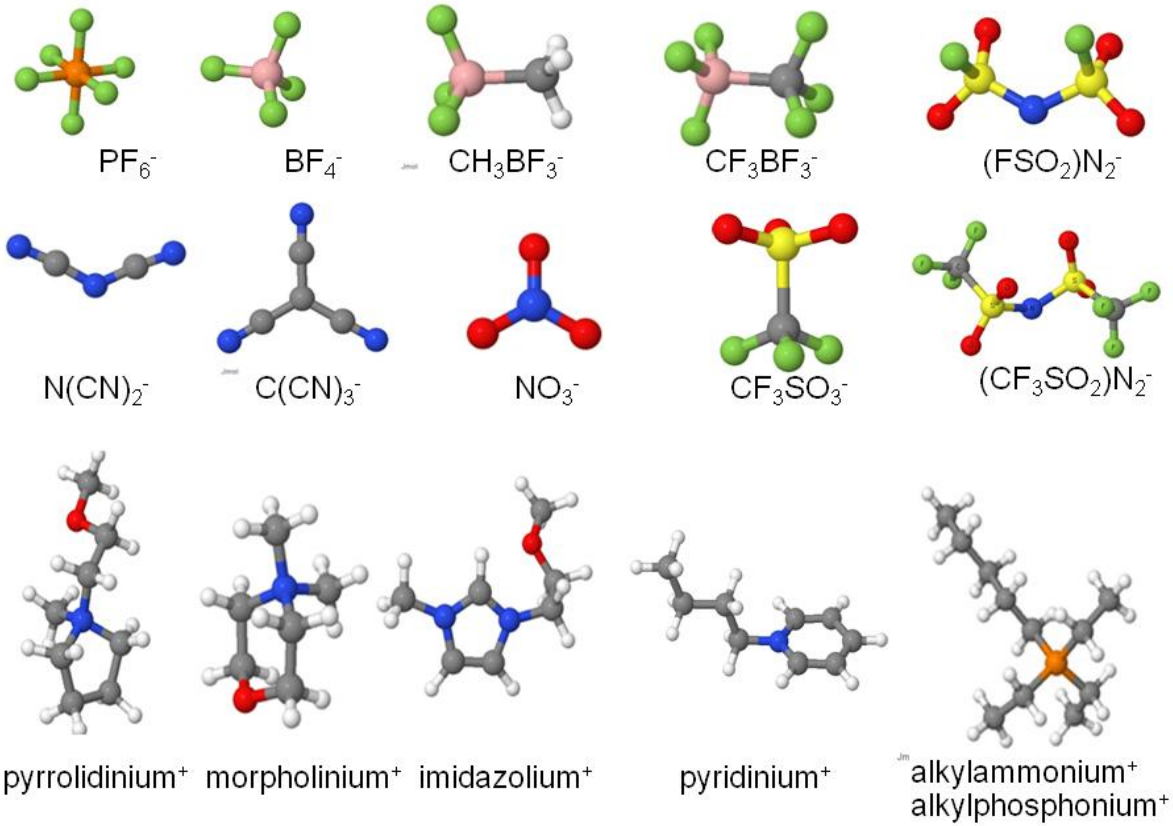
Adv. Funct. Mater. **2007**, *17*, 1237

RTIL electrolytes

1. Cation 2. A

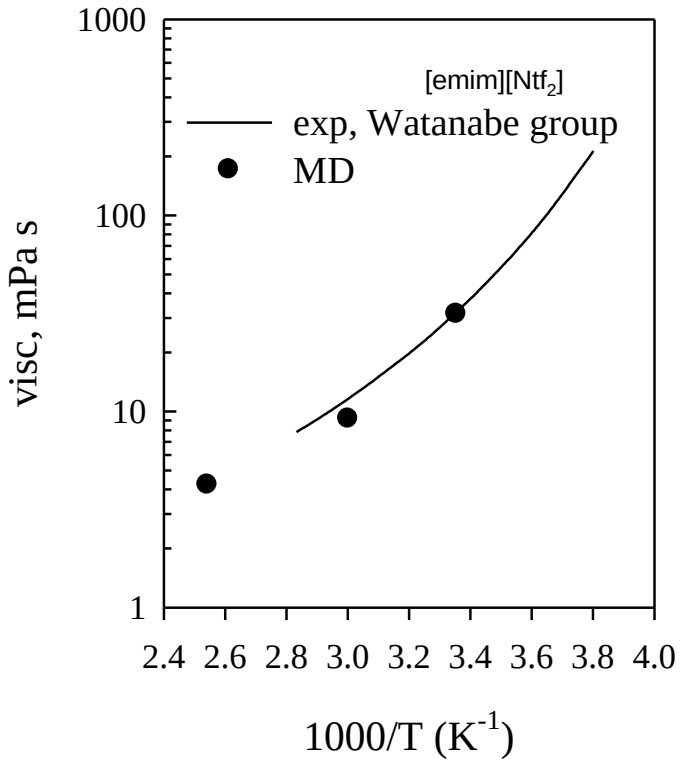
- Certain combinations of cations and anions (often organic) produce salts which remain liquid at ambient temperature.
- These materials have low volatility and flammability, relatively high conductivity, and can have a very wide voltage window.
- They are well suited for use as electrolytes in electrochemical capacitors.
- Clemson has experience in making and characterizing such electrolytes, with special focus on fluorinated materials having high stability, low viscosity, and high ionic conductivity.

Simulated Ionic Liquids; Work of Dr. Oleg Borodin, University of Utah



A set of anions and cations for which many-body polarizable force field has been developed in Phase I of the project. Note, that while pyrrolidinium$^+$ and imidazolium$^+$ cations are shown only with oligoether modifying groups, the force field has been tested for these cations with both oligoether and alkane modifying groups. Different attachment positions of alkyl chains to the imidazolium$^+$ ring have also been tested. N-alkyl-N-methyl-piperidinium cation has also been simulated (not shown)

Viscosity; from Borodin, Utah



IL	T, K	Viscosity (mPa s)	
		MD	exp
[emim][Ntf_2]	393	4.2	4.4
[C_5O_2im][Ntf_2]	303	51.8	48.4
[C_7 mim][Ntf_2]	303	65.5	63-66.8

Viscosity of selected ILs from MD simulations using Lees-Edwards boundary conditions and experiments from Smith, G. D.; Borodin, O.; Li, L.; Kim, H.; Liu, Q.; Bara, J. E.; Jin, D. L., A Comparison of Ether- and Alkyl-Derivatized Imidazolium-Based Room-Temperature Ionic Liquids: A Molecular Dynamics Simulation Study. *Phys. Chem. Chem. Phys. (2008)*

Other attributes which can be addressed by simulation are as follows: Liquid density, heat of vaporization, ion diffusion, ionic conductivity, and especially, ***ion polarization and dynamics in electric fields at and away from polarized interfaces.***

Proposed project scope

- **Synthesize** new high-voltage-limit high-conductivity ionic liquid electrolytes.
- **Characterize** WRT conductivity, voltage limits and specific capacitance using templated carbon aerogel electrodes.
- Co-ordinate experimental efforts with **modeling** efforts focusing on polarization of ionic liquid electrolytes
- As progress dictates, work with private-sector partner(s) to **scale up** materials for larger-scale testing in functional capacitors.

Summary

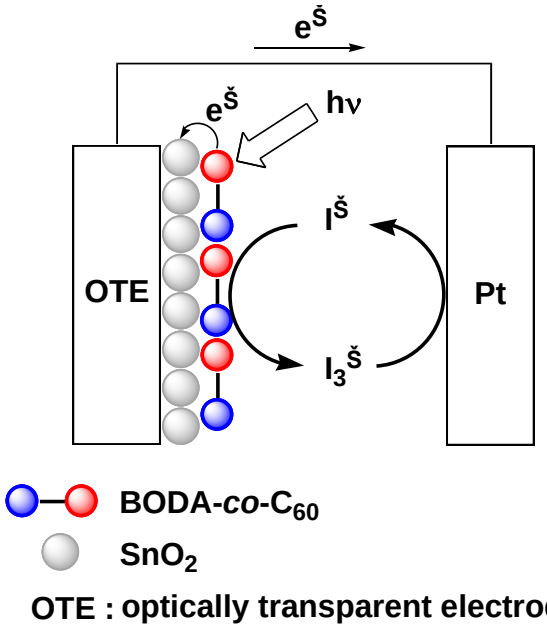
- Clemson has experience in making and characterizing a wide range of nanoporous carbon materials and RTIL electrolytes suitable for use in electrochemical capacitors

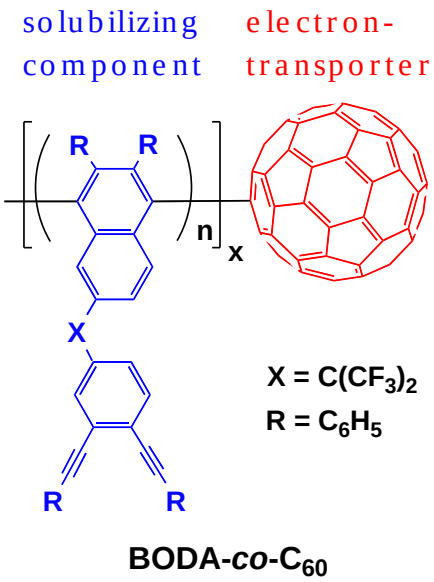
- Specific projects could leverage this experience in ways that could enable new capacitor technologies and improve existing technologies.

Extra Slides....

Photo-Voltaic Devices with BODA-C_{60} Films

(with Prof. S. Fukuzumi, Osaka University)





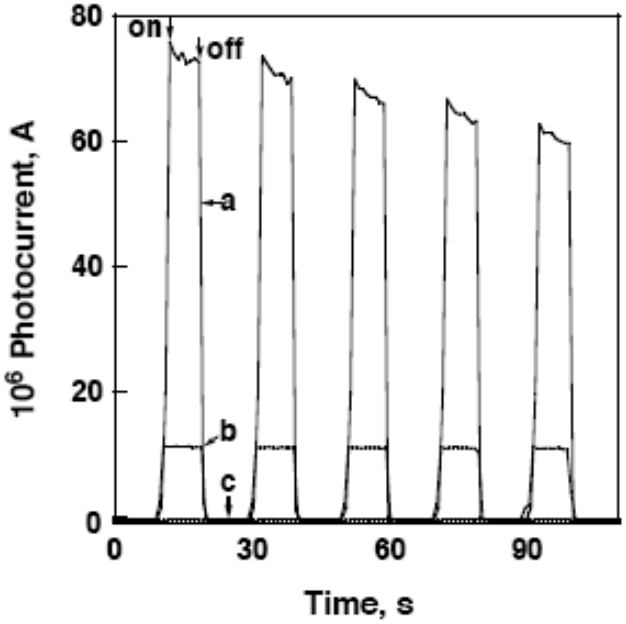


Illustration of photoelectrochemical cell and the structure of BODA-*co*-C_{60}

Photocurrent of (a) OTE/SnO2/BODA-*co*-C60, (b) OTE/SnO2, and (c) OTE/BODA-*co*-C60 electrodes under visible light illumination (l > 380 nm) in the absence of any applied bias. Electrolyte: 0.5 M NaI and 0.01 M I2 in acetonitrile. Input power: 100 mW cm–2.

J. Mater. Chem. **2008**, *18*, 3237–3241

Electrochemical characterization

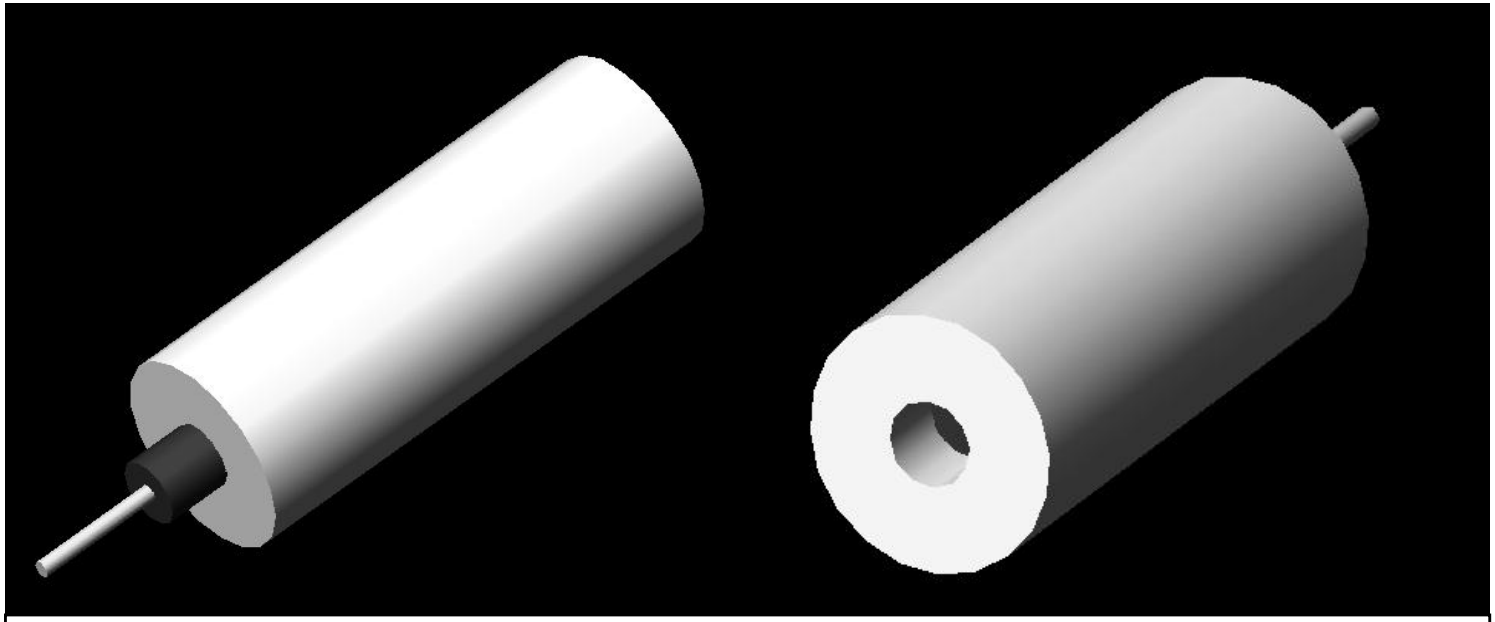
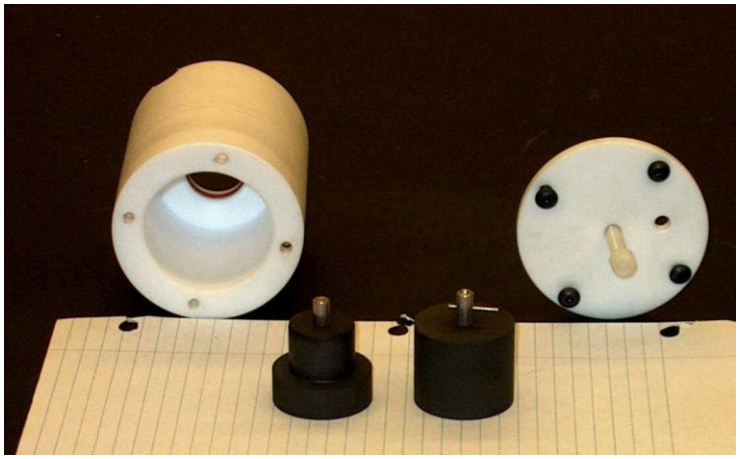


Figure 1. The geometric shape of sticky carbon electrode used for primary measurements of the RF aerogel capacitance.

Second-generation supercapacitor cell



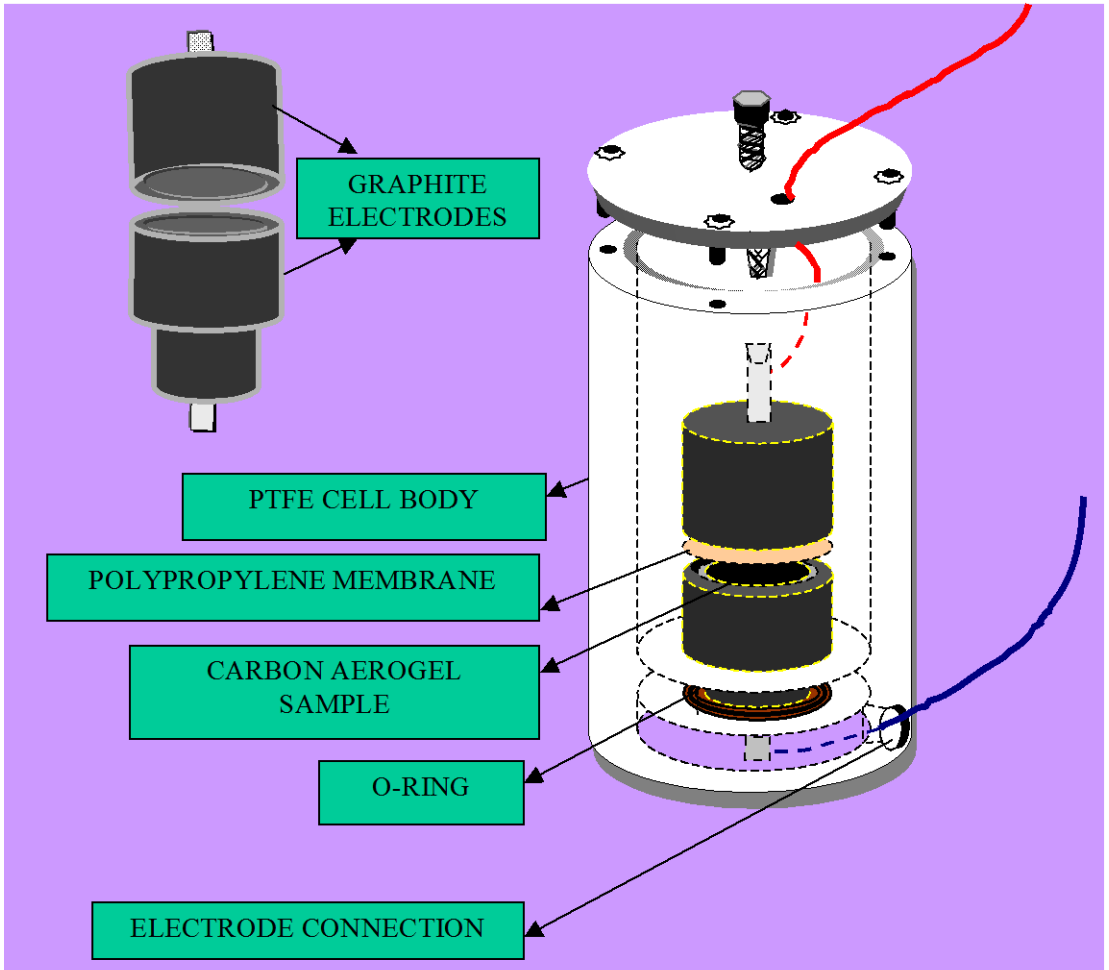


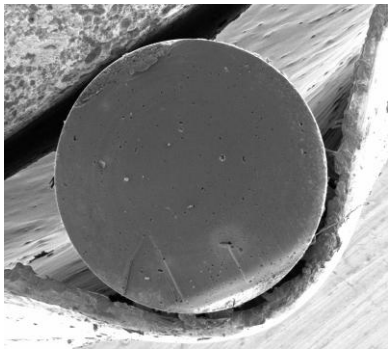
Figure 2. Measurement cell for the RF aerogel double layer capacitor characterization.

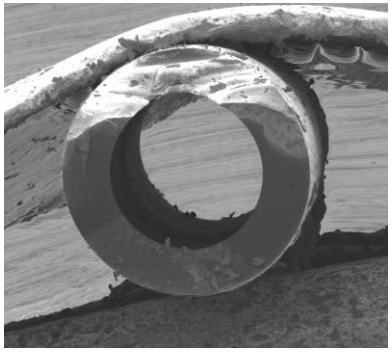
Specific capacitance and surface area for the S12-S15 series of carbon aerogels, in 1 M H_2SO_4

Table 5. Specific capacitance results for the S12 - S15 series.

Sample	S13	S12	S14	S15
RF value	20	30	40	50
Specific capacitance from slow-scan CV, 1 mV/sec in 1 M H_2SO_4, Farads / gram	49	76	30	31
Specific capacitance from low-frequency impedance, 10^{-3} Hz in 1 M H_2SO_4, Farads / gram	50	71	37	30
BET specific surface area, measurements made October 2003 (m^2/g)	482	709	494	558
Capacitance/area from low-frequency impedance, microFarads / cm^2	10.4	10.0	7.5	5.4

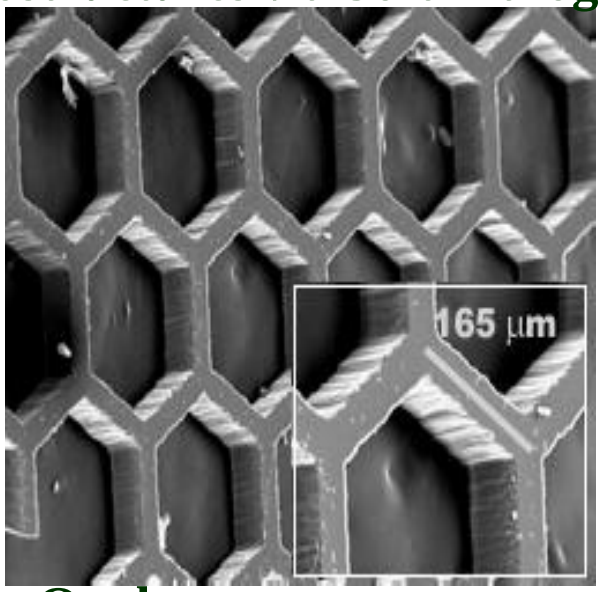
BODA Derivved Carbon Fibers





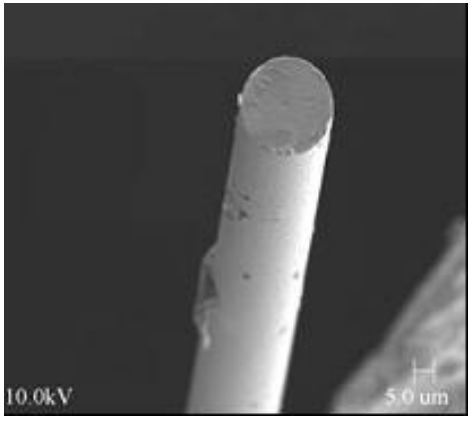
diameter = 604 μm and (right) hollow fiber (O.D. = 612 μm, I.D. = 375 μm) carbonized at 1000 °C.

Microstructures via Soft Lithography

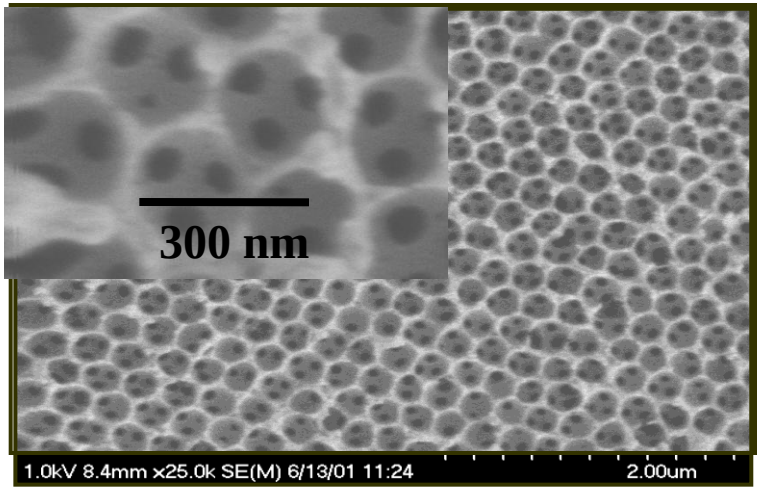


Pre-carbonized processable resin cured at 250 °C
&
pyrolyzed 800-1000 °C

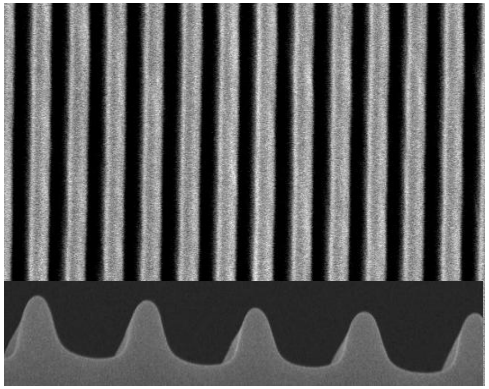
Edwards AFB
15-25 μm diameter fibers



Inverse Carbon Opal



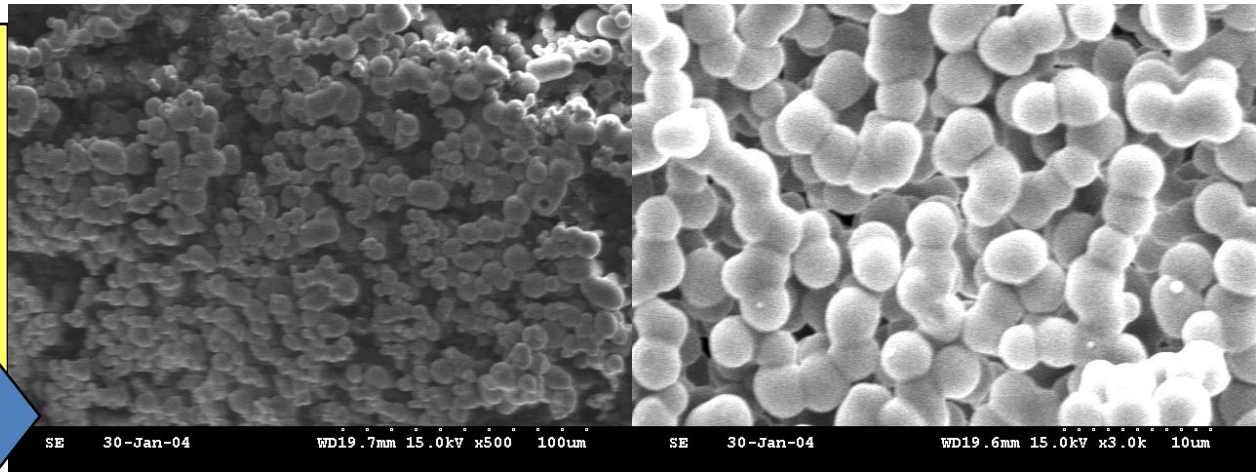
Microtransfer molded grating with 0.5 μm lines



Shah, H.V.; Brittain, S.T.; Huang, Q.; Hwu, S.-J.; Whitesides, G.M., Smith, Jr. D.W *Chem. Mater.* **1999,** *11*, 2623.
Perpall, M.W.; Smith, Jr., D.W.; et al. *Langmuir* **2003**, *19*, 7153.

Use of a porous silica monolith as the templating phase

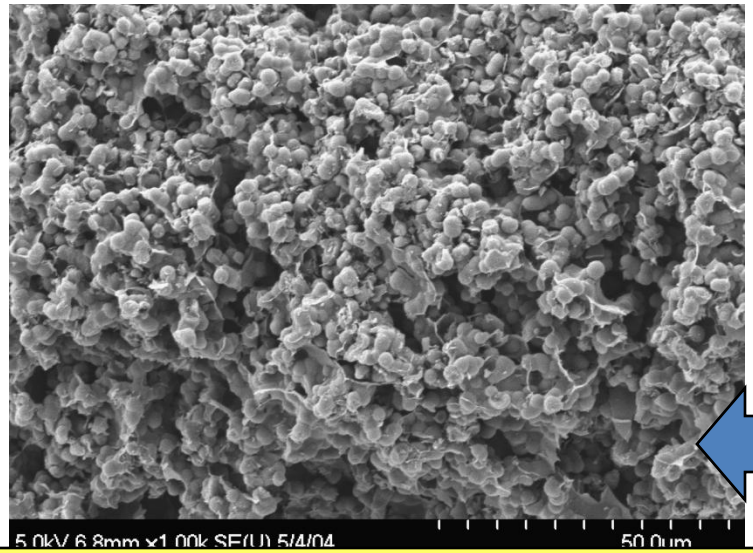
1. Gelation accomplished by mixing 4 mL TMOS + 10 mL 0.01 M acetic acid + 0.84 g PEG (MW = 10K), heating to 40°C. (Thanks to Jamie Norton, Clemson)



2. Backfill with wet RF sol followed by thermal program (1, 1, 1) and Heat 50°C, 48 hrs.

3. Carbonize at 1050°C, 8 hrs.

4. Etch with 30% HF to remove silica template.



Templated RF-20 carbon aerogel