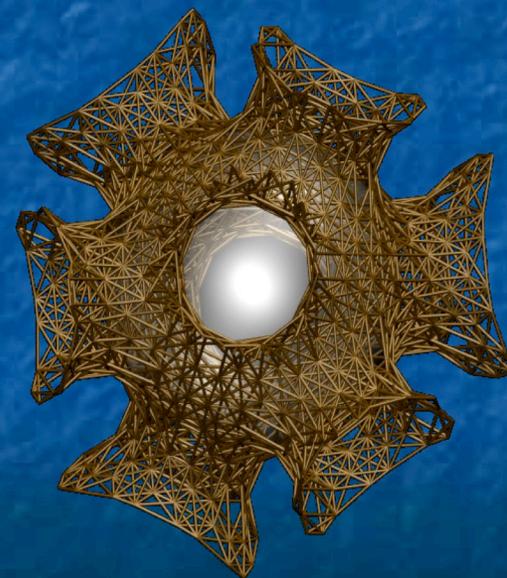


Using Computational Science to Optimize Carbon Supercapacitors

a step toward efficient energy storage

Vincent Meunier

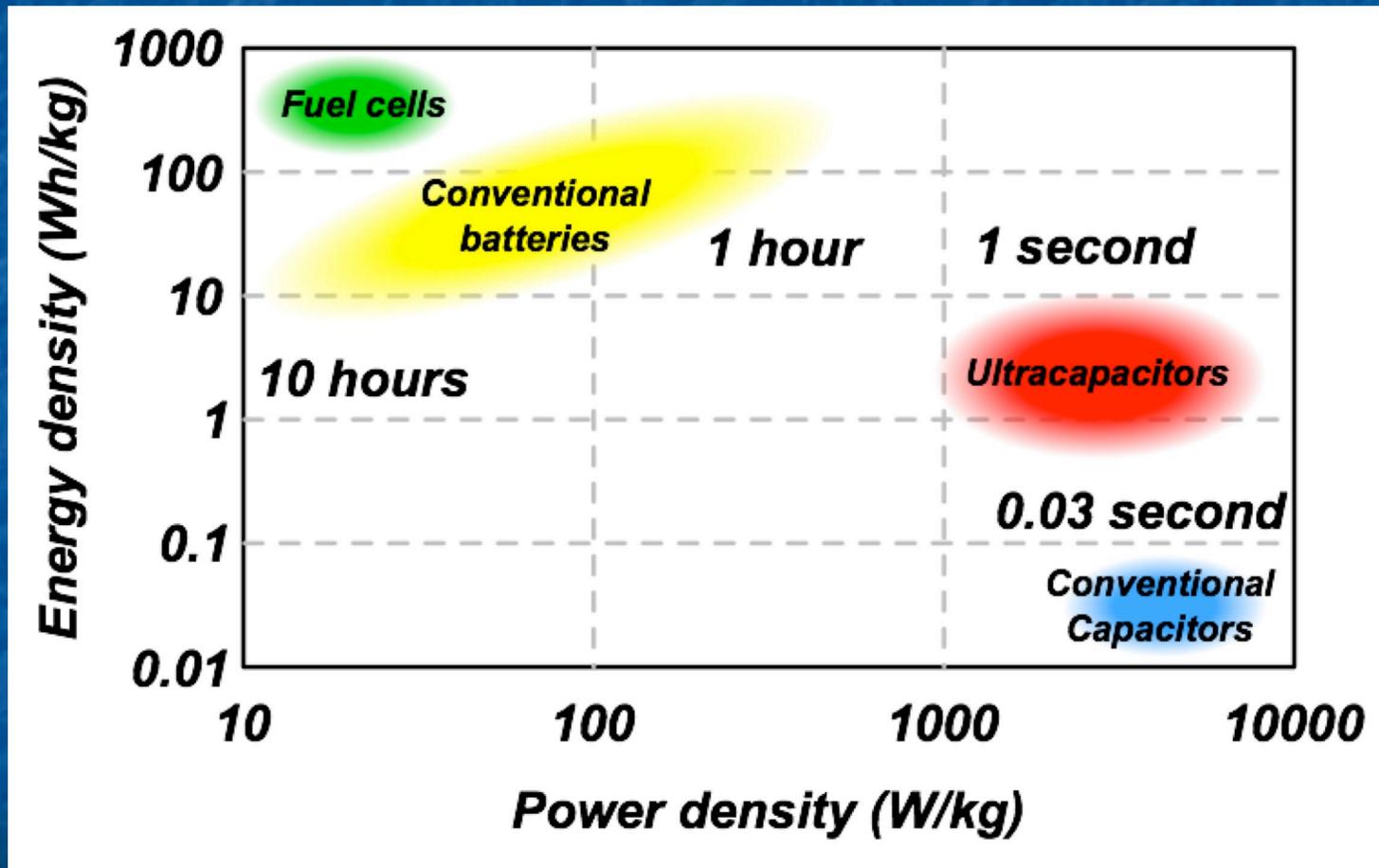
Oak Ridge National Laboratory



Managed by UT-Battelle for
the Department of Energy



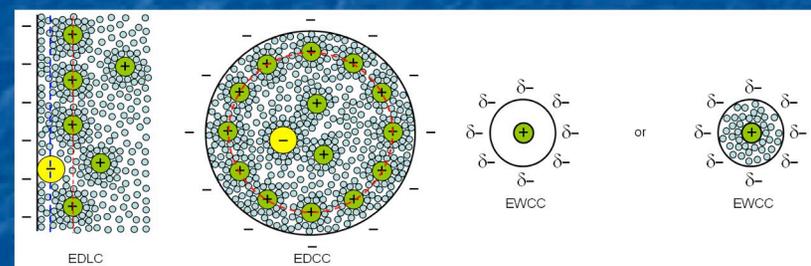
Need for Energy Storage Devices



Ragone Chart

Outline

- **Energy storage in supercaps**
 - Carbon-based supercapacitors
 - Anomalous increase



- **2D and 3D meshes : pore engineering and design.**
 - Carbon -based covalent network
 - Realistic systems

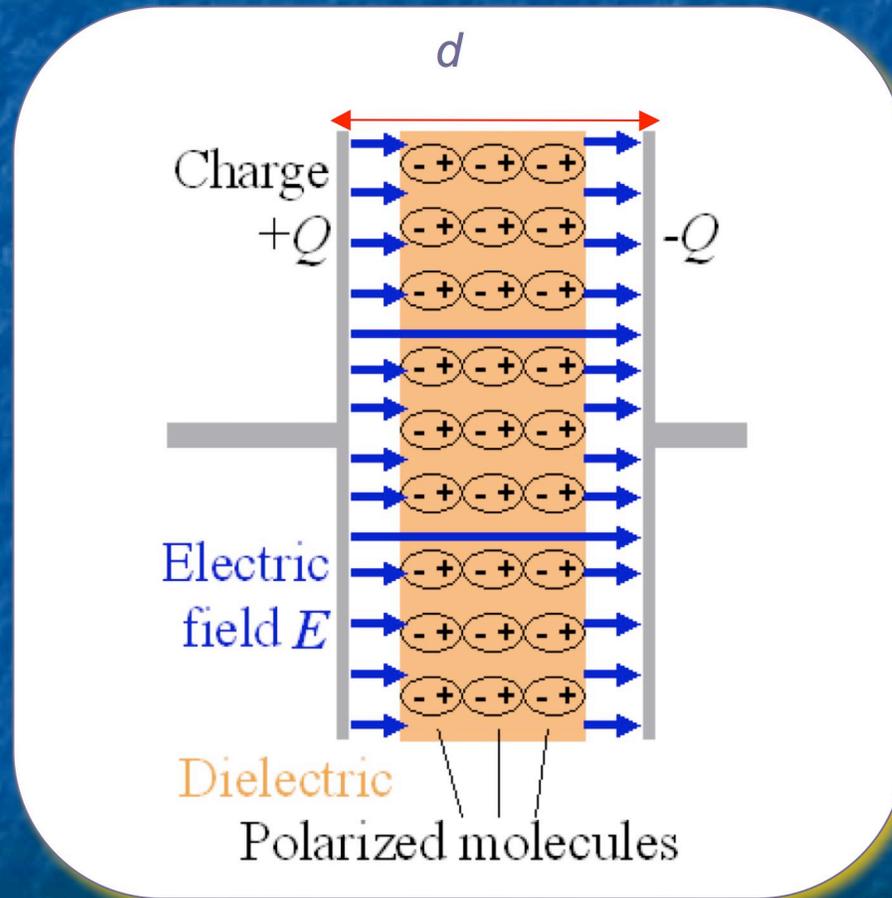


Part I: Understanding Nanoporous Carbon Supercapacitors

References:

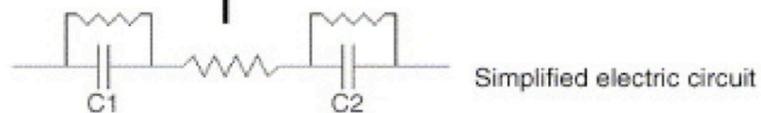
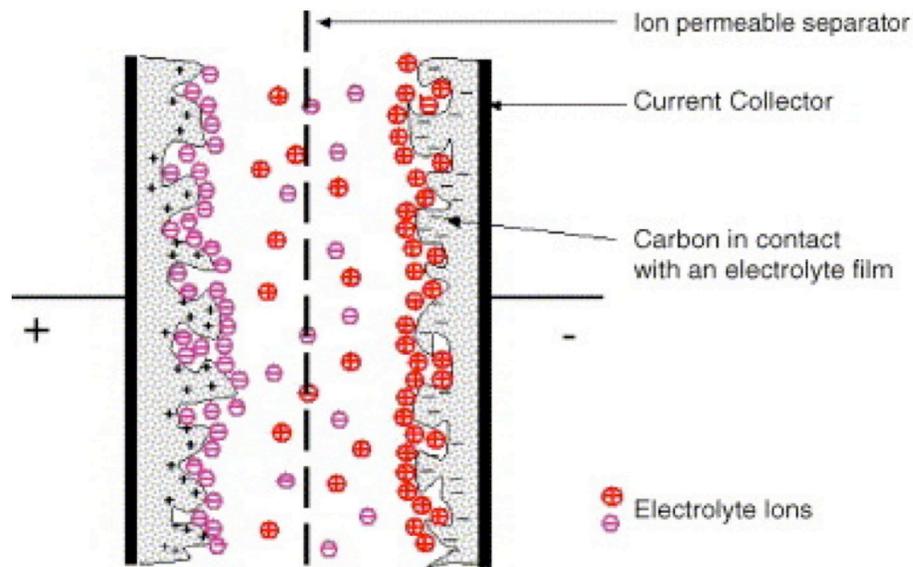
- *Nanoporous carbon supercapacitors: from double layer, to double cylinder, to wire in cylinder*, J. Huang, B.G. Sumpter, and V. Meunier, *Angew. Chem.* **120**, 3440 (2008)
- *A Universal Model for Nanoporous Carbon Supercapacitors Applicable to Diverse Pore Regimes, Carbon Materials, and Electrolytes*, J. Huang, B.G. Sumpter, and V. Meunier, *Chem. Eur. J.* (2008)

What is a supercapacitor?



$$C = \frac{\epsilon A}{d}$$

Conventional capacitor



$$\frac{1}{C_{cell}} = \frac{1}{C_{cathode}} + \frac{1}{C_{anode}}$$

$$C = \frac{\epsilon A}{d}$$

Electric double-layer capacitors

Early success



This "early stage" experiments commenced in Shanghai, China with a new form of electric bus powered by energy stored in large onboard supercapacitors.

Initial testing suggested that when fully charged the capacitors could be able to supply enough power for a bus to travel **a total distance of 5 km at 44km/h (a little over 27mph), but for practicality it was proposed that recharging stations should be located approximately every 3 stops.** Recharging was through a railway-style pantograph fitted to the buses' roof that made contact with an overhead power supply.



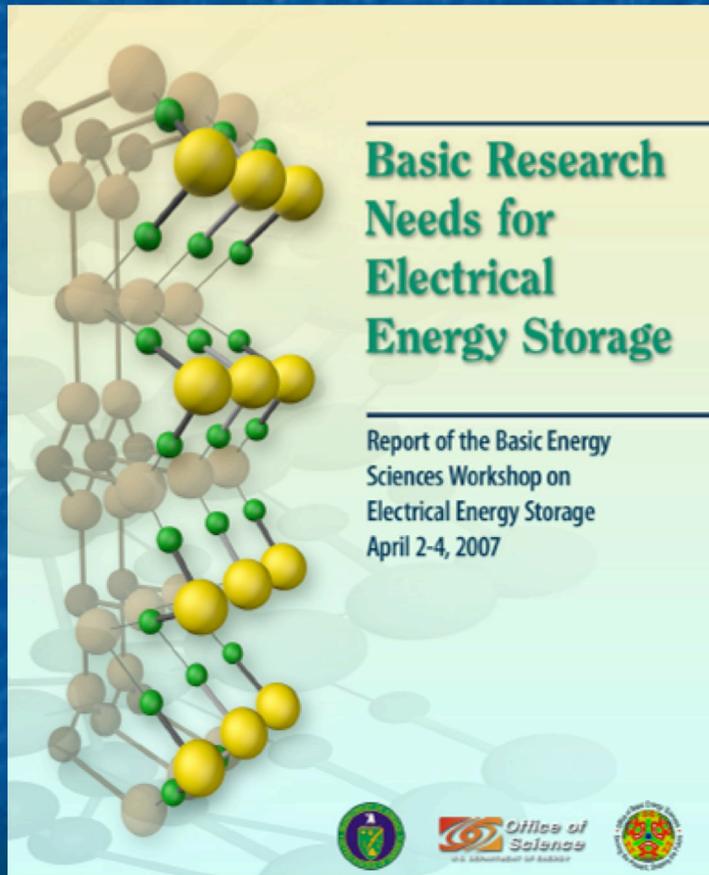
This new technology of supercapacitor is bringing another environment-friendly power into our daily lives. As of May 2007, this supercapacitor bus has passed over 10,000 km trial-run in a wide temperature ranging from sizzling summer to freezing winter.

Automobile Supercapacitors

Shanghai Aowei Technology
Development Co., Ltd.

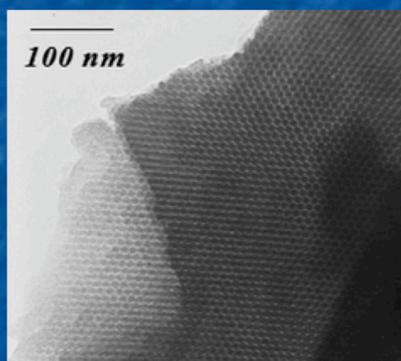
FCF - 2008

Need for Electrical Energy storage

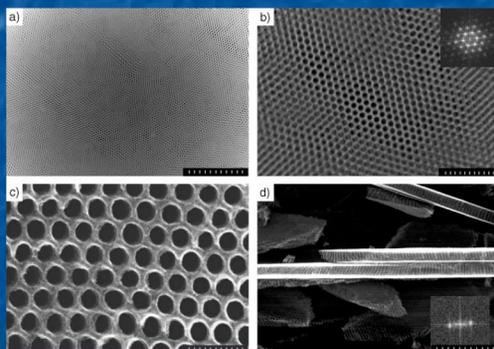


1. Chemical Storage
2. Capacitive Storage

Classification of Nanoporous Materials



Carbon, 2005, 43, 1293.



Courtesy of Dr. Sheng Dai at ORNL

IUPAC classification for nanoporous materials (2-100nm)

50-100nm

2-50nm

<2nm

macropore

mesopore

micropore

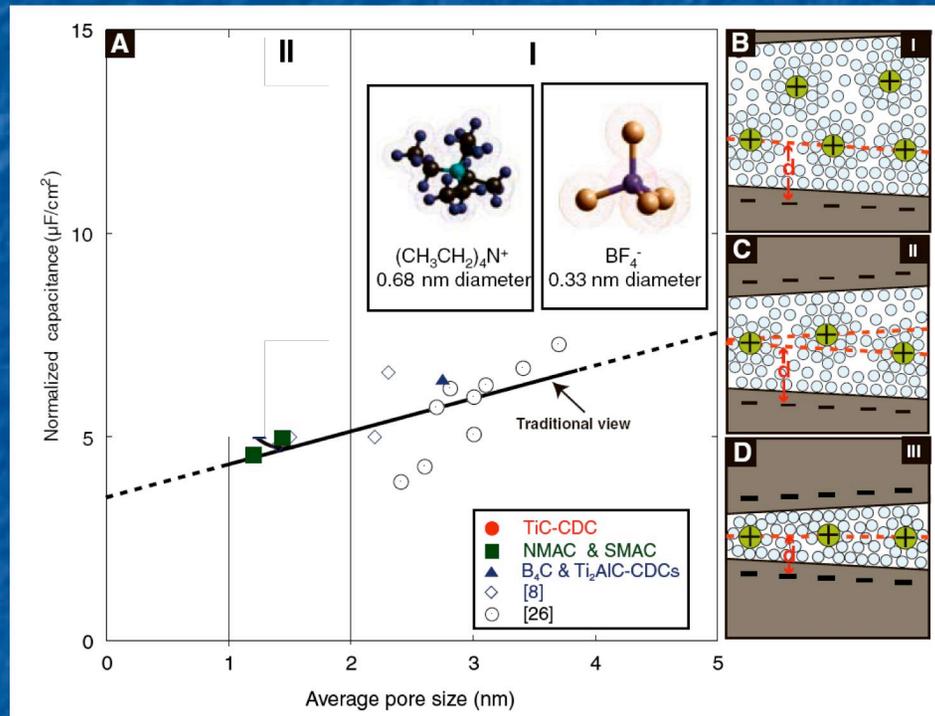
Double layer

Double cylinder

Wire in cylinder

- Pores can be approximated by cylinders because of the worm hole structures.
- Cylindrical pores are usually the assumption for theoretical treatments for physical adsorption of gases and impedance spectroscopy.
- If cross-section of pores are not completely circles, the movements of ions in pores should see the average. Therefore, an average effect of a polygon should be a circle.
- With double layer formed in the pores, it should be a double cylinder capacitor, not a parallel plate capacitor.
- If the pores are too small to allow the inner cylinder, ions enter pores and form a wire-in-cylinder capacitor.
- The nano-confinement probably reduces a lot of vibration modes of the ions, but rotation and translation along the pore should still exist.

Nanoporous carbon supercapacitors

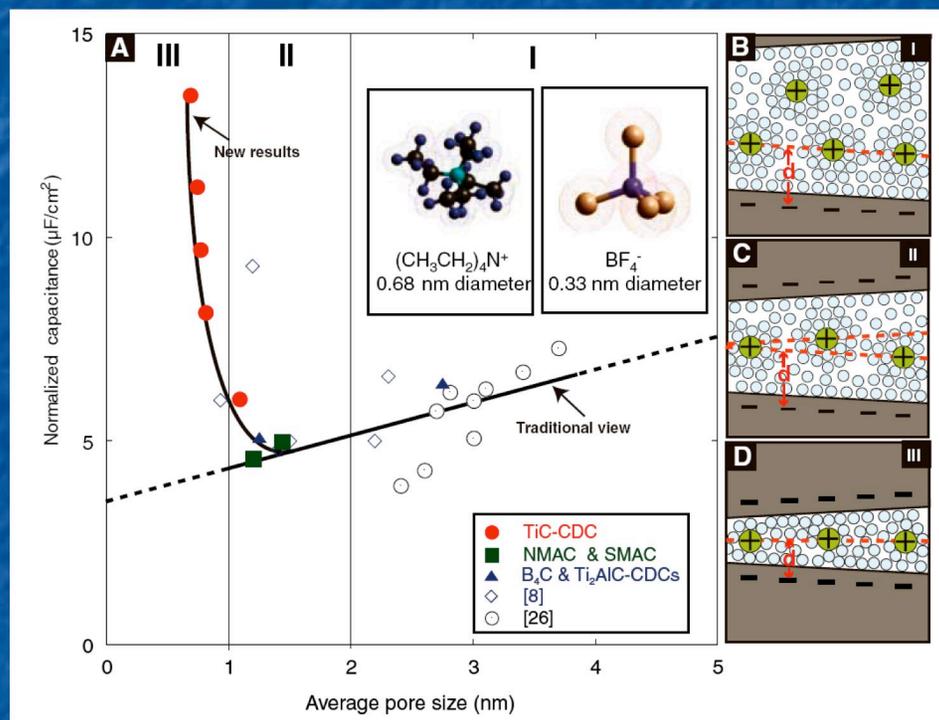


Chmiola, J.; Yushin, G.; Gogotsi, Y.; Portet, C.; Simon, P.; Taberna, P. L. *Science*, **2006**, *313*, 1760.

- Traditional belief is that nanopores with a small diameter may not be accessible to electrolyte solution;
- There is a lack of model to explain the effects of A and d on C . The model for parallel-plate capacitor has been still used for EDLCs until now.
- The model for parallel-plate capacitor has been still used for EDLCs. Our interest is what is happening in the micropore region under 1 nm.

$$C / A = \frac{\epsilon}{d}$$

Nanoporous carbon supercapacitors



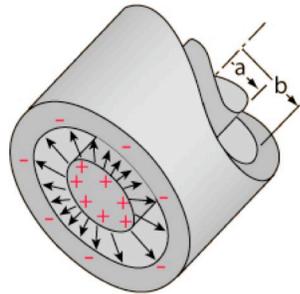
Chmiola, J.; Yushin, G.; Gogotsi, Y.; Portet, C.; Simon, P.; Taberna, P. L. *Science*, **2006**, *313*, 1760.

- Traditional belief is that nanopores with a small diameter may not be accessible to electrolyte solution;
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- The model for parallel-plate capacitor has been still used for EDLCs. Our interest is what is happening in the micropore region under 1 nm.

$$C / A = \frac{\epsilon}{d}$$

Beyond the parallel plate model

Finding an alternative to the Electrical Double Layer Capacitor



$$C = \frac{2\pi\epsilon_r\epsilon_0L}{\ln(b/a)}$$

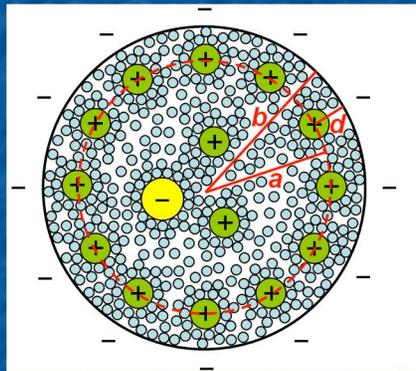
Capacitance of a cylindrical capacitor

$$\begin{aligned} & \ln(b/a) \\ &= \ln((a+d)/a) \\ &= \ln(1+d/a) \\ &\approx d/a \end{aligned}$$

Taylor expansion of Logarithm
($d \ll a$)

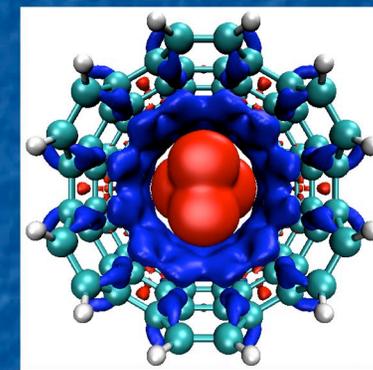
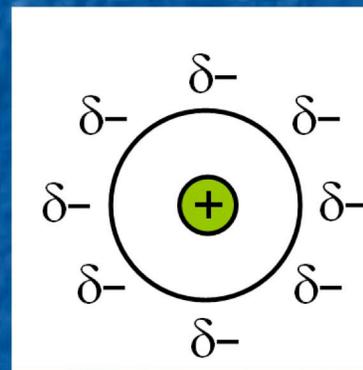
Beyond the parallel plate model: EWCC vs EDCC

Electric double-cylinder capacitor (EDCC)



$$C/A = \frac{\epsilon_r \epsilon_0}{b \ln(b/(b-d))}$$

Electric wire-in-cylinder capacitor (EWCC)

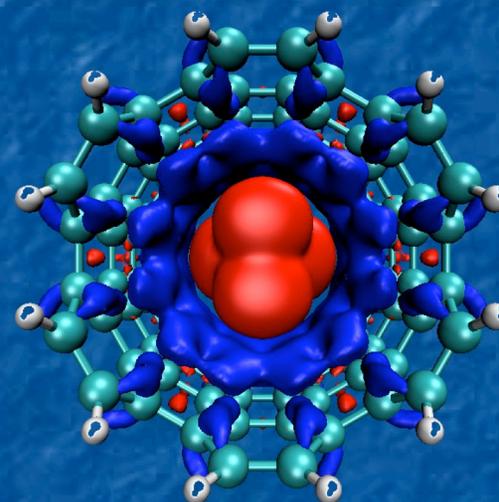
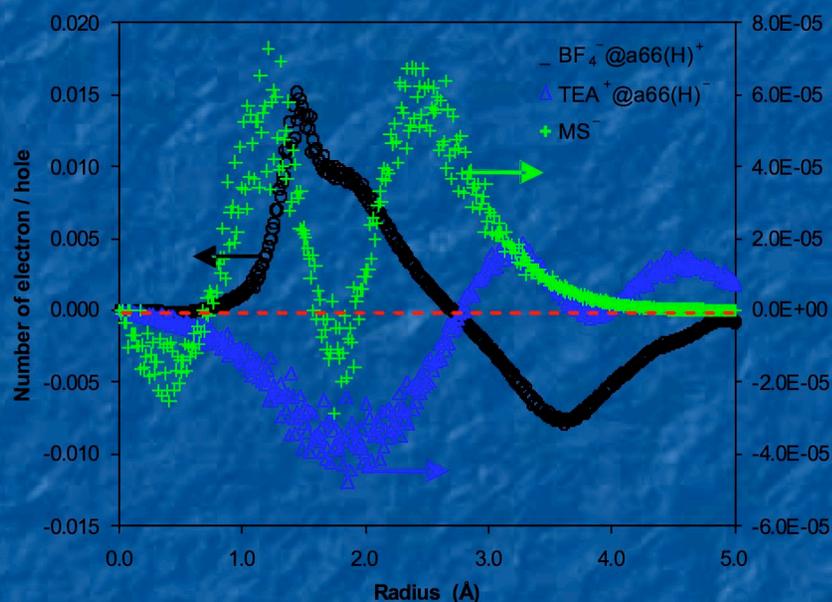


$$C/A = \frac{\epsilon_r \epsilon_0}{b \ln(b/a_0)}$$

Computational Methods

- **Atomic-scale** methods provide information on the structure, dynamics and thermodynamics
 - Molecular dynamics (MD), mechanics (MM),
 - Large-scale normal-mode analysis (NMA),
 - Advanced Monte Carlo Methods (MC)
- **Ab Initio methods** are used to compute electronic and molecular structure, and to obtain interaction potentials, activation energies for transitions, and electronic spectra as input into MD, kinetic MC, course grain approaches, etc.
 - NWChem, Gamess, Plane wave codes, new Wavelet based methods, Multi-scale methods
- Heuristic methods provide complementary ways to perform efficient optimization and modeling based on experimental or simulation data
 - Computational neural networks, evolutionary algorithms
- **All codes are implemented in parallel and run on ORNL/NCCS resources**

Computational Studies: finding d and a₀



	a_0	$BF_4^-@a66 (H-term)$	$TEA^+@ a66(H-term)$	MS^-
Radii (Å)	2.30	2.22, ^a 2.31^a	2.38^a	3.13^a
		2.3 ^{b,c}	3.4^{c,d}	---

^a Huang, J.; Sumpter, B. G.; Meunier, V. *Angew. Chem. Int. Ed.* **2008**, *47*, 520. ^b Jenkins, H. D. B.; Thakur, K. P. *J. Chem. Educ.* **1979**, *56*, 577. ^c Ue, M. *J. Electrochem. Soc.* **1994**, *141*, 3336. ^d Fawcett, W. R.; Fedurco, M.; Opallo, M. *J. Phys. Chem.* **1992**, *96*, 9959.

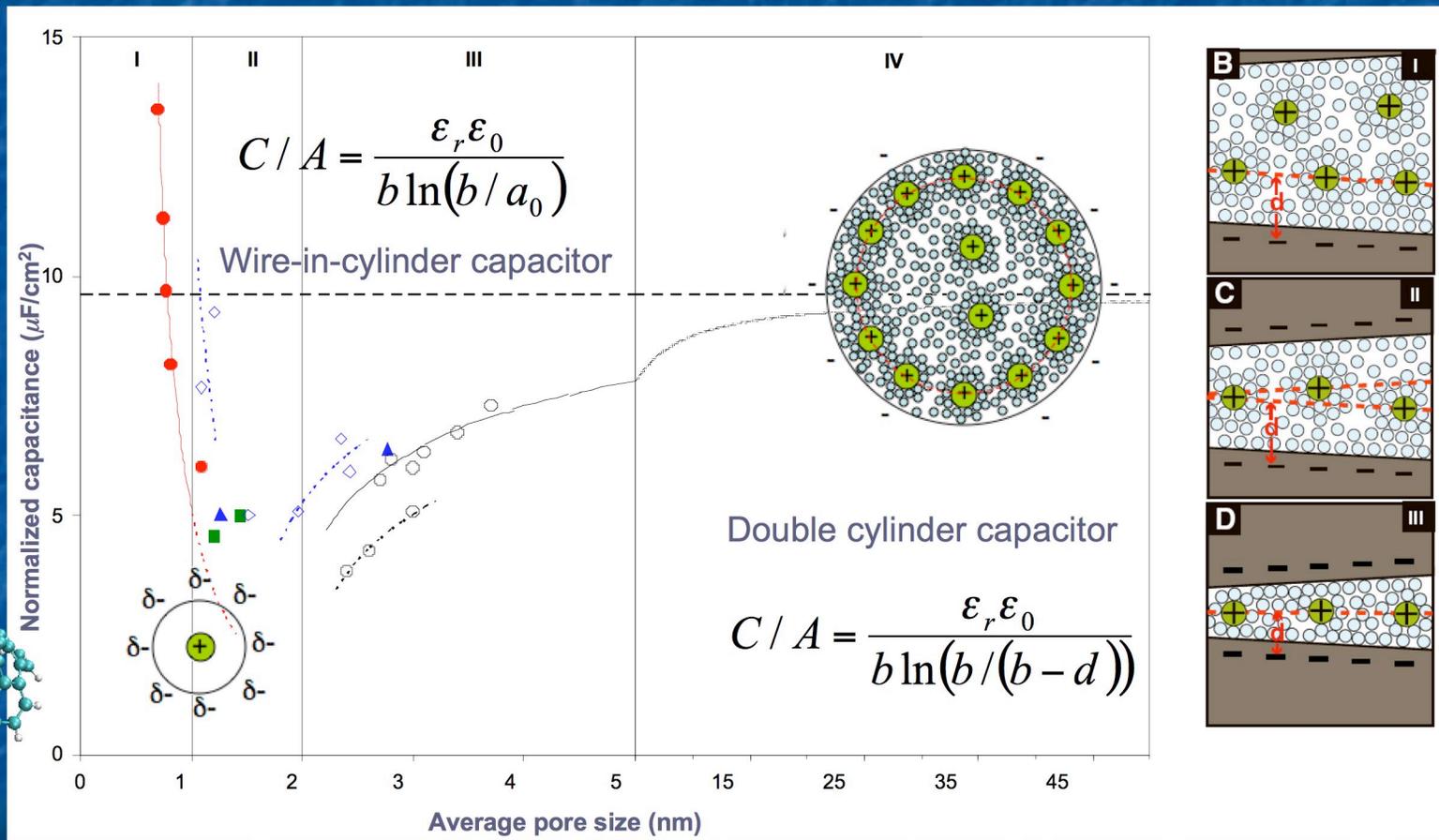
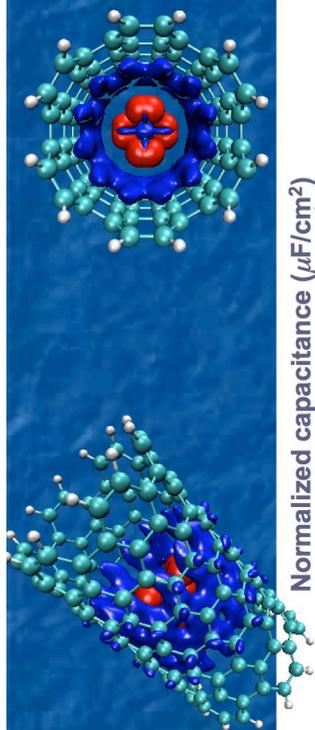
Evaluating the capacitance from first-principles

Pores	Carbon materials	Electrolytes	R^2	ϵ_r	d [Å]	a_0 [Å]	Ionic radii [Å]	
Micropores	CDC	EMI-TFSI	0.944	1.12 (0.26)	-	2.91 (0.16)	EMI ⁺ : 2.15, ^[a] 3.80 ^[b]	TFSI ⁻ : 1.45, ^[a] 3.85 ^[b]
Micropores	CDC, activated C	H ₂ SO ₄ (1M)	0.889	27.1 (18.7)	-	0.05 (0.17)	H ⁺ : 0.28 ^[c]	SO ₄ ²⁻ : 2.40, 2.58 ^[c]
Mesopores	Template C		0.328	17.4 (6.3)	9.77 (1.92)	-		
Micropores	Activated C	KOH (6M)	0.921	7.76 (3.06)	-	1.64 (0.83)	K ⁺ : 1.38 ^[c]	OH ⁻ : 1.33 ^[c]
Mesopores	Activated C		0.618	13.4 (3.2)	6.72 (1.03)	-		

^a Along the short dimension. ^b Along the long dimension. ^c See the literature results in Huang, J.; Sumpter, B. G.; Meunier, V. *Chem. Eur. J.* **2008**, in press.

Calculations: DFT + B3LYP/cc-pVDZ

Evaluating the capacitance from first-principles (II)



Experiments from; *Science*, 2006, 313, 1760.

Multimodal samples

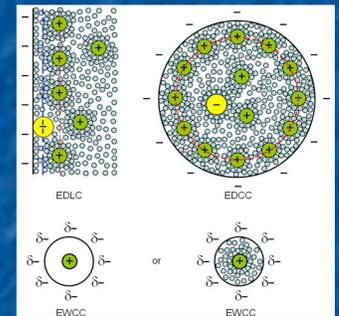
Multimodal pore size distribution:

$$C = \sum_i \frac{\epsilon_{r,micro} \epsilon_0 A_{i,micro}}{b_i \ln(b_i / a_0)} + \sum_j \frac{\epsilon_{r,meso} \epsilon_0 A_{j,meso}}{b_j \ln[b_j / (b_j - d)]} + \sum_k \frac{\epsilon_{r,macro} \epsilon_0 A_{k,macro}}{d}$$

Bimodal pore size distribution:

$$C = \frac{\epsilon_{r,micro} \epsilon_0 A_{micro}}{b_{micro} \ln(b_{micro} / a_0)} + \frac{\epsilon_{r,meso} \epsilon_0 A_{meso}}{b_{meso} \ln[b_{meso} / (b_{meso} - d)]}$$

$$C = C_{micro} A_{micro} + C_{meso} A_{meso} \quad \text{or} \quad \frac{C}{A_{meso}} = C_{meso} + C_{micro} \frac{A_{micro}}{A_{meso}}$$



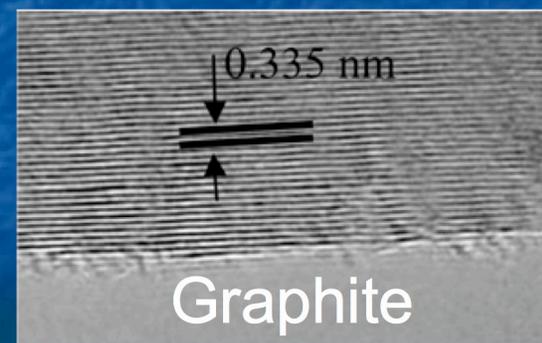
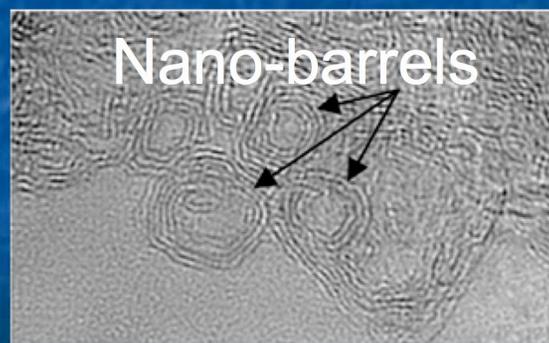
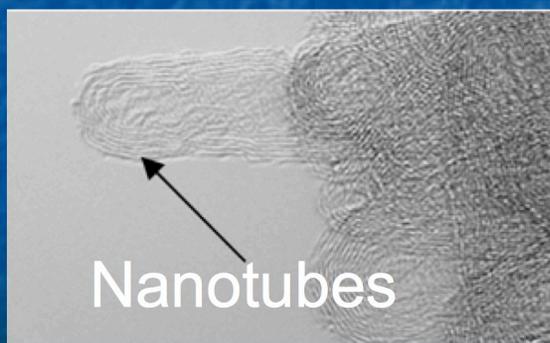
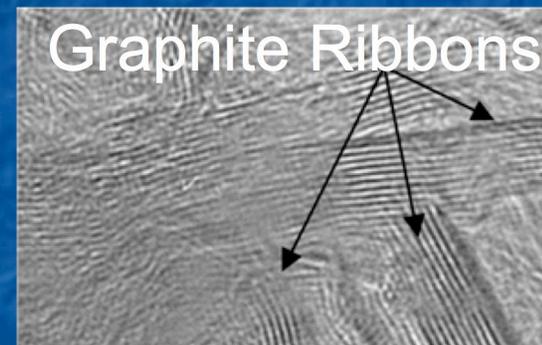
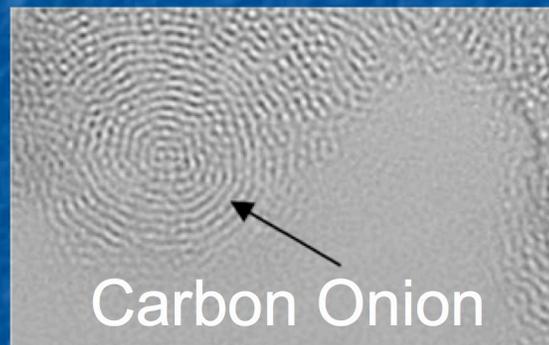
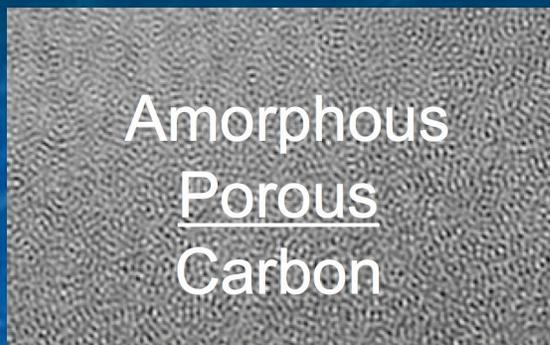
Part II:

Modelling realistic systems

References:

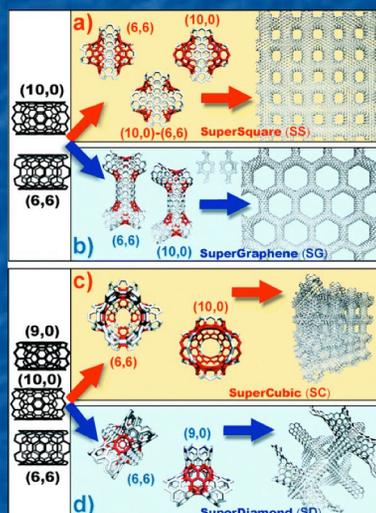
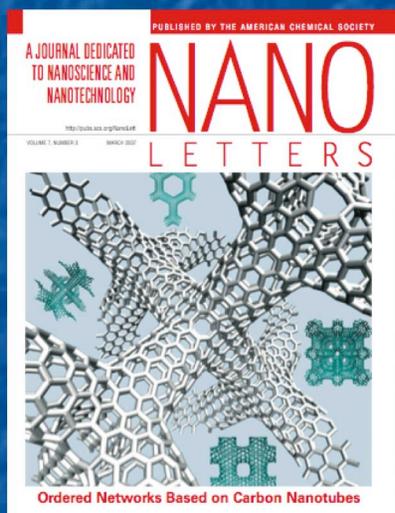
- *An Atomistic Branching Mechanism for Carbon Nanotubes: Sulfur as triggering agent*, J.M. Romo-Herrera, B.G. Sumpter, D.A. Cullen, H. Terrones, E. Cruz, D.J. Smith, V. Meunier, and M. Terrones, *Angewandte Chemie*, **47**, 2948 (2008)
- *Electron transport properties of ordered networks using carbon nanotubes*, Jose Romo-Herrera, H. Terrones, M. Terrones, and V. Meunier, *Nanotechnology*, **19**, 315704 (2008)
- *Guiding electronic current through Organic Nanocircuits: Defects engineering in ON-CNTs*, J.M. Romo-Herrera, M. Terrones, H. Terrones, and Vincent Meunier, *submitted to Nature Nanotechnology* (2008)
- *Covalent 2D and 3D Networks from 1D Nanostructures: Designing New Materials*, Jose Romo-Herrera, Mauricio Terrones, Humberto Terrones, Sefa Dag, and Vincent Meunier, *Nano Letters*, **7**(3), 570 - 576 (2007)

Actual Structures (TEM)



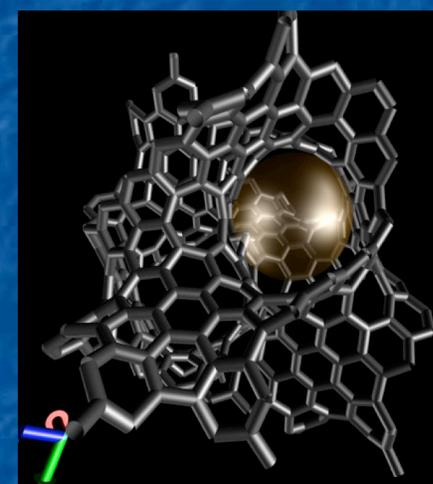
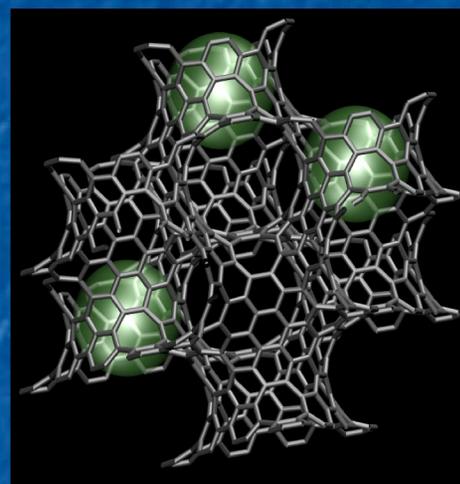
G. Yushin, Y. Gogotsi, and A. Nikitin, *Carbide Derived Carbon*, in *Nanomaterials Handbook.*, Y. Gogotsi, Editor, 239-282, CRC Press (2006)

Beyond the cylindrical model



“Hierarchy algorithm”

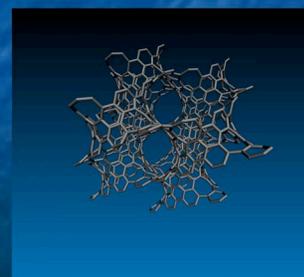
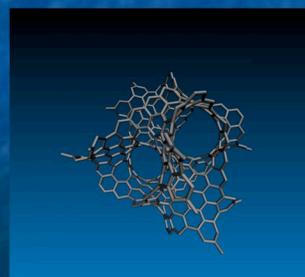
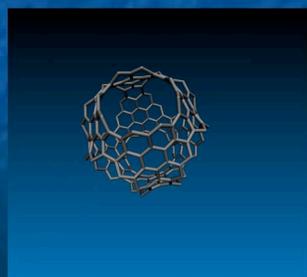
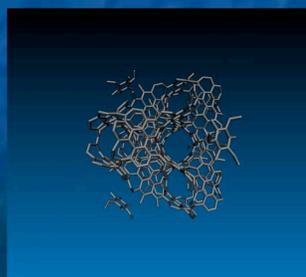
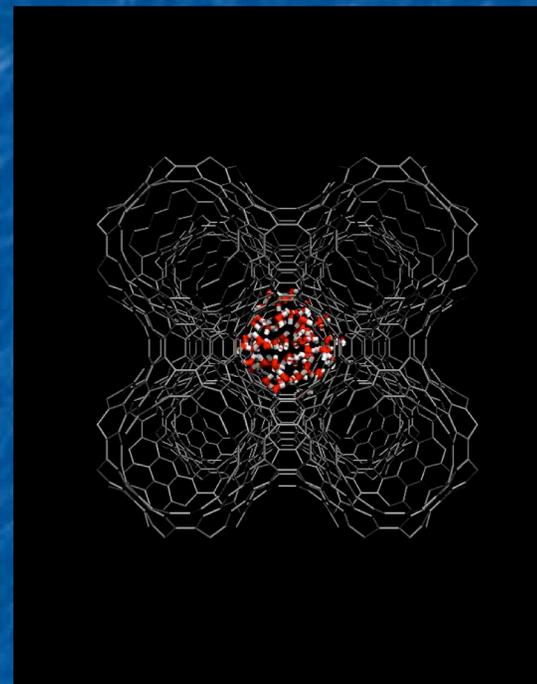
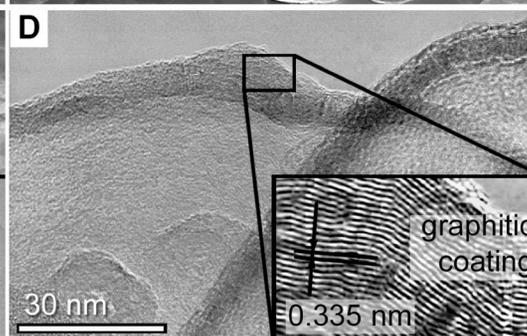
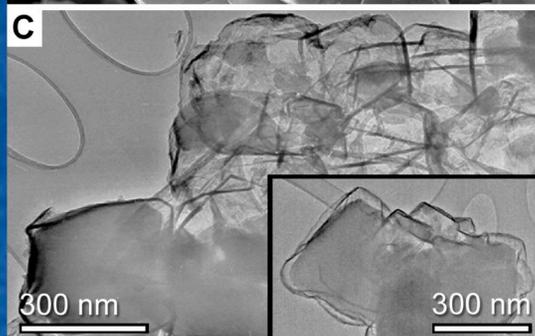
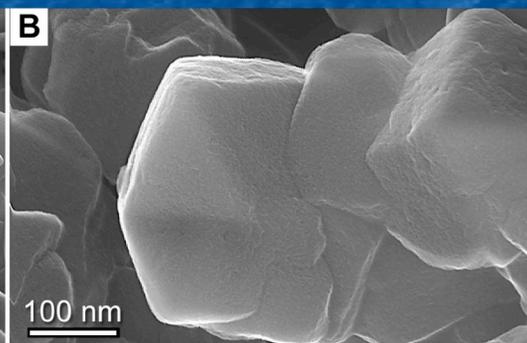
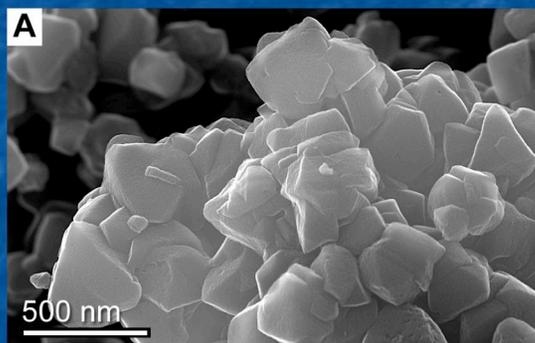
J. M. Romo, M. Terrones, H. Terrones, S. Dag,
and V. Meunier, Nano Lett., 7 (3), 570 -576, 2007



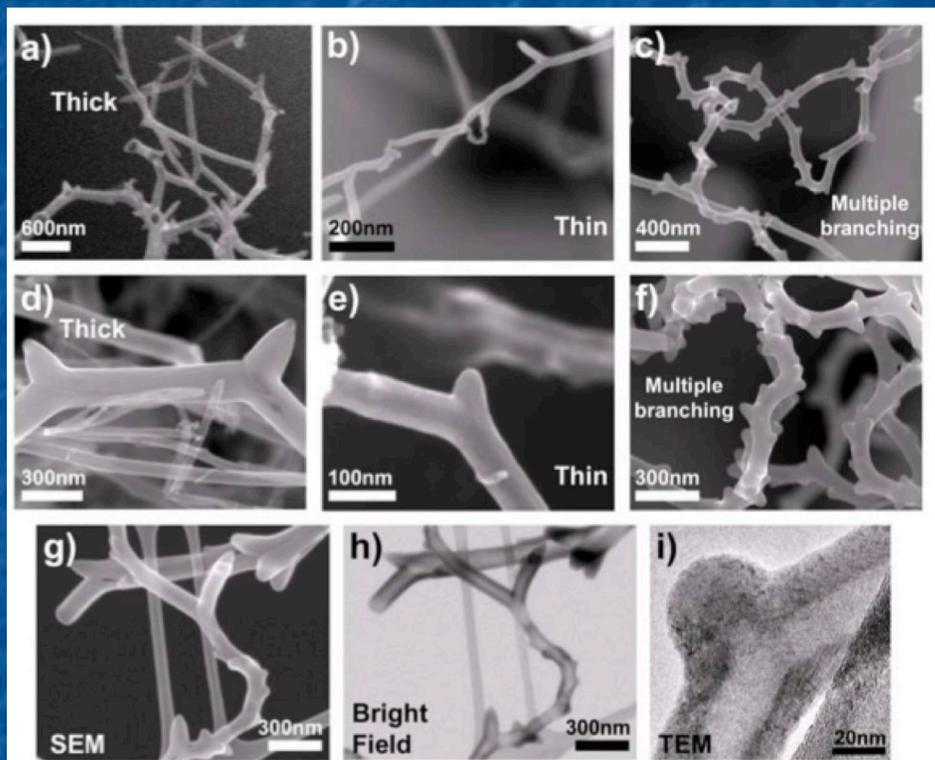
“Negative curvature surfaces”

F Valencia, A H Romero, E Hernández, M Terrones
and H Terrones, New J. Phys. 5 (2003) 123

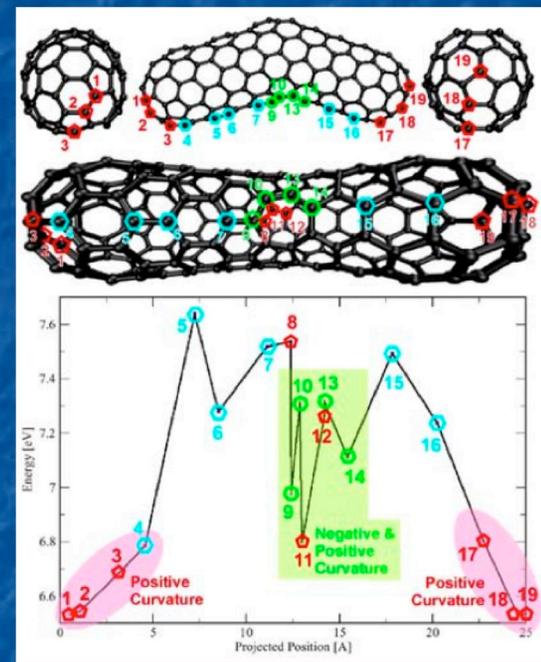
More realistic models



Nanomeshes and nanonetworks



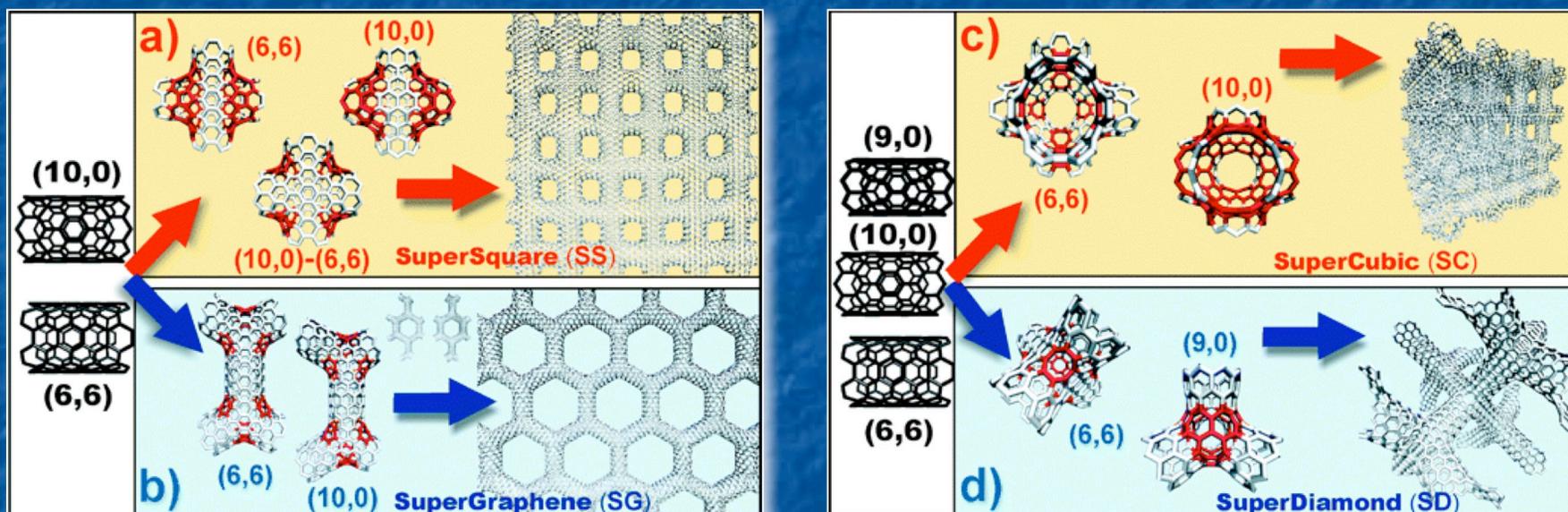
SEM evidence of nanonetwork creation



Calculations showing the triggering role of S

An Atomistic Branching Mechanism for Carbon Nanotubes: Sulfur as triggering agent, J.M. Romo-Herrera, B.G. Sumpter, D.A. Cullen, H. Terrones, E. Cruz, D.J. Smith, V. Meunier, and M. Terrones, *Angewandte Chemie*, (2008)

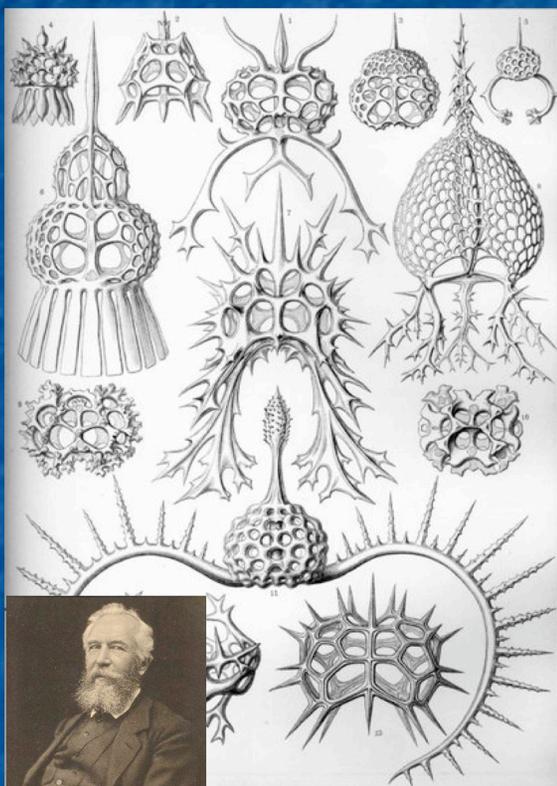
Hierarchical Algorithm for the construction of supramolecular nanonetworks



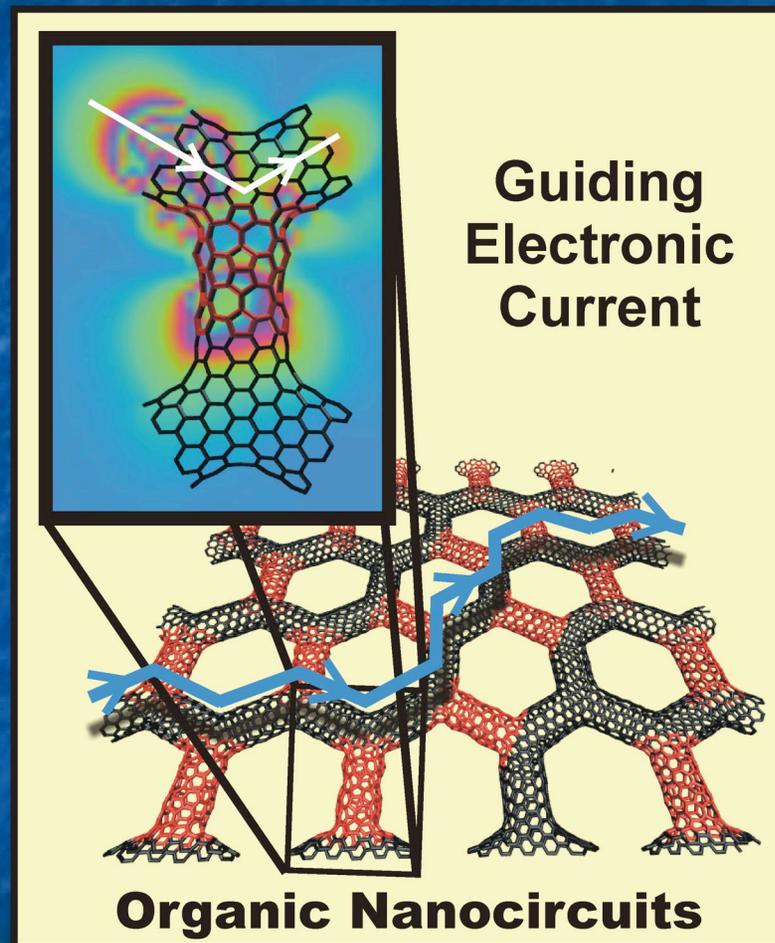
Hierarchy concept for four different architectures of ordered networks based on CNTs (1D nanostructures). (a and b) super-square and super-graphene correspond to 2D networks, whereas (c and d) super-cubic and super-diamond represent 3D network examples. The four families are constructed from either armchair or zigzag CNTs in order to study the chirality effects. The red rings point out the nonhexagonal carbon rings in each node.

J. M. Romo-Herrera, M. Terrones, H. Terrones, S. Dag, and V. Meunier, *Nano Lett.*, 7 (3), 570 -576, 2007

Guiding Electrical Current in 2D nanomeshes



**Inserting defects to
guide electrons
(Haeckel)**

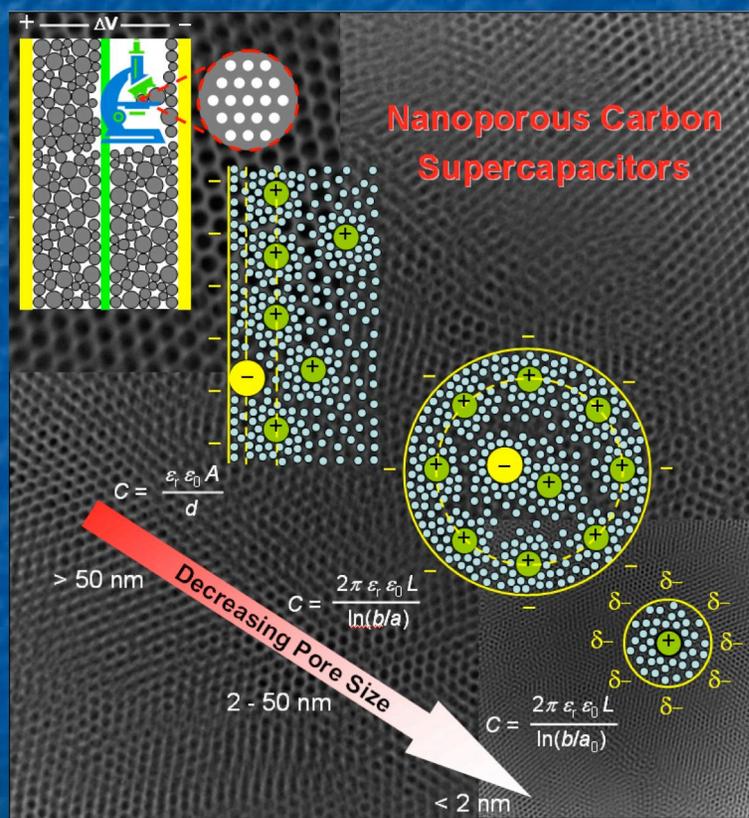


**Guiding
Electronic
Current**

Organic Nanocircuits

J. M. Romo-Herrera, M. Terrones, H. Terrones, and V. Meunier, submitted (2008)

Carbon Supercapacitors: work so far

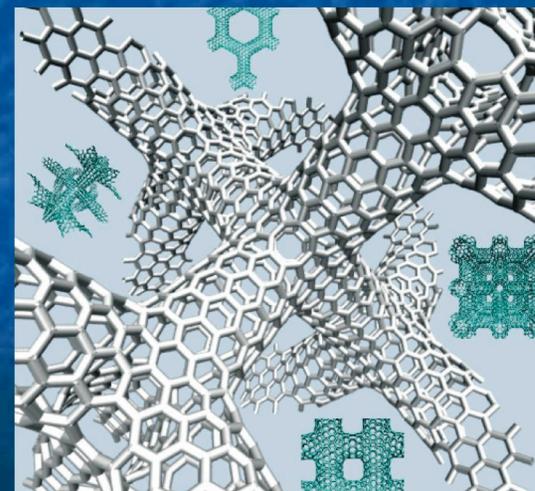
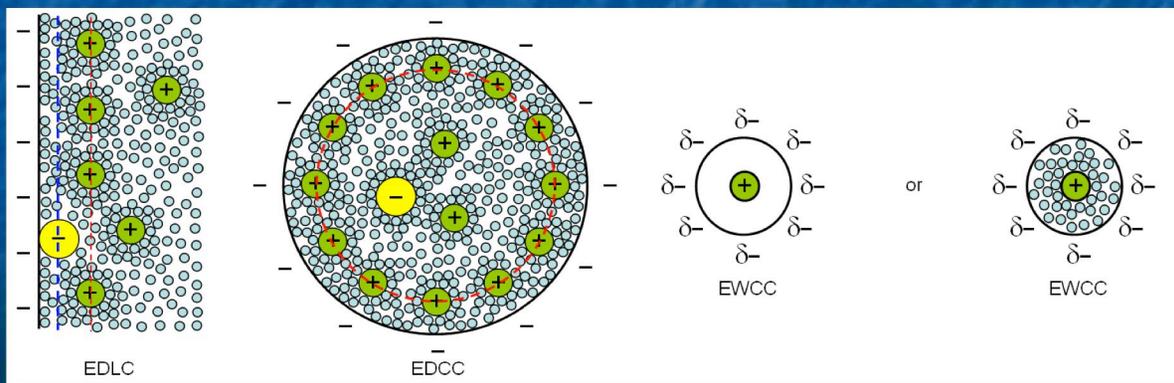
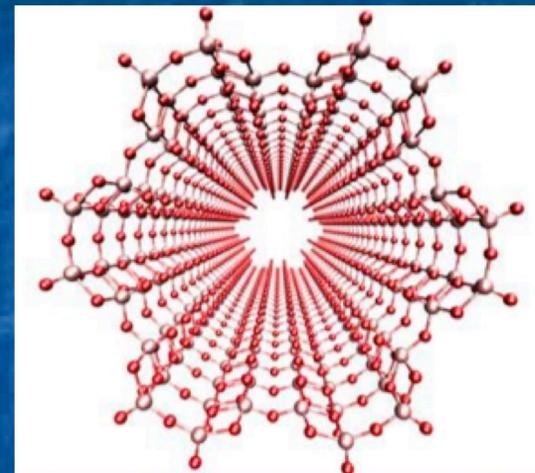


➤ **Our analysis does clearly show the significance of pore curvature.** Our results indicate that curvature has significant effect on the capacitance of carbon materials with mesopores and micropores. For macropores, curvature is not important any more-it has a plate-like behavior.

➤ **The proposed model is universal for carbon supercapacitors with diverse pore regions, carbon materials, and electrolytes.** It allows the capacitance properties to be correlated with the total specific surface area (SSA) and pore size, pointing a direction for optimization of supercapacitor materials.

Future and current work

- **Role of pore size and shapes**
 - effect on energetics of the adsorption
 - Exhoedral vs endohedrals?
- **Dynamics of the solvation/desolvation process**
- **Role of pore chemistry; beyond carbon nanopores**
 - Effects of functionalization,
 - Other types of elements, including oxides.



References

Supercapacitors:

- *Nanoporous carbon supercapacitors: from double layer, to double cylinder, to wire in cylinder*, J. Huang, B.G. Sumpter, and V. Meunier, *Angew. Chem.* **120**, 3440 (2008)
- *A Universal Model for Nanoporous Carbon Supercapacitors Applicable to Diverse Pore Regimes, Carbon Materials, and Electrolytes*, J. Huang, B.G. Sumpter, and V. Meunier, *Chem. Eur. J.* (2008)

Nanomeshes:

- *An Atomistic Branching Mechanism for Carbon Nanotubes: Sulfur as triggering agent*, J.M. Romo-Herrera, B.G. Sumpter, D.A. Cullen, H. Terrones, E. Cruz, D.J. Smith, V. Meunier, and M. Terrones, *Angewandte Chemie*, **47**, 2948 (2008)
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