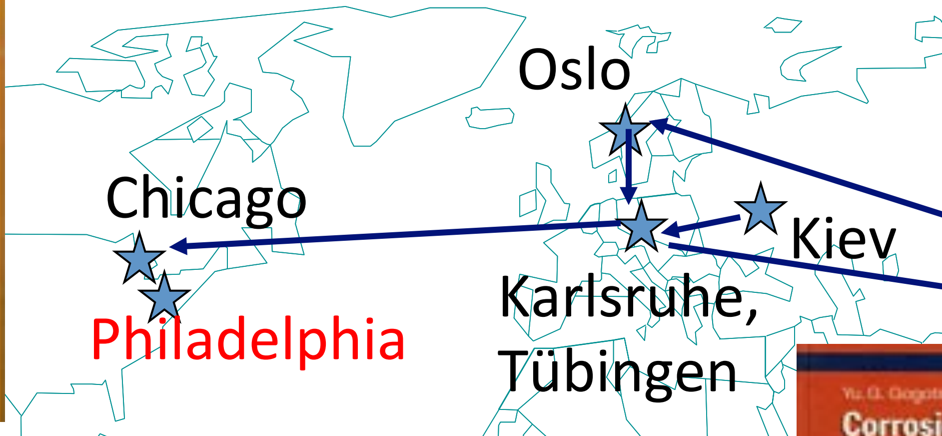
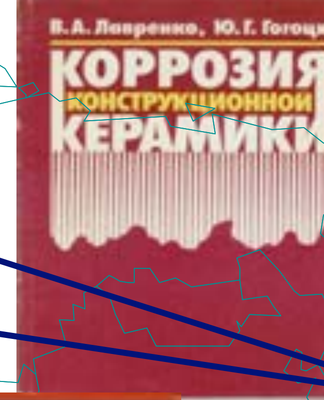
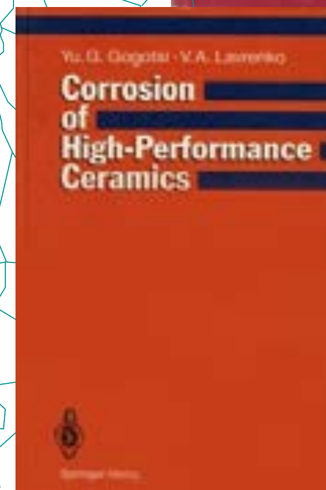
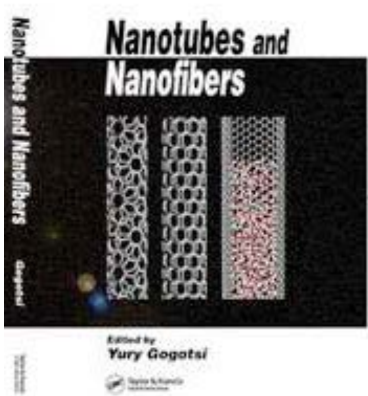
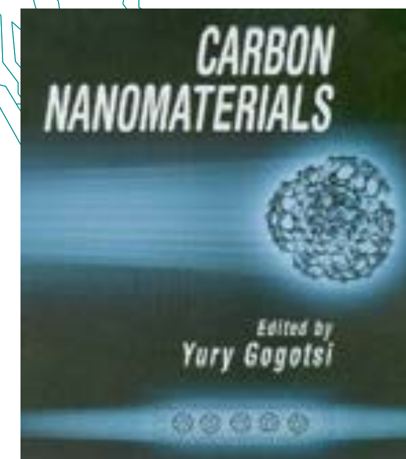










Yury Gogotsi

Distinguished University Professor and Trustee Chair
Department of Materials Science and Engineering
Director, A.J. Drexel Nanomaterials Institute

RASA-USA Annual Meeting, Cambridge, MA, November 9, 2014

Углеродный наномир: новые материалы, от открытия до применения

Yury Gogotsi

Director, A.J. Drexel Nanomaterials Institute
Distinguished University Professor and Trustee Chair

Department of Materials Science & Engineering
Drexel University, Philadelphia, Pennsylvania, USA

Drexel University:
A Vibrant Urban University

- Established in 1891
- Co-op program is one of the nation's oldest, largest, and best-known cooperative education programs
- 26,132 students – **15th largest** student population in the U.S.
- Colleges & schools: Engineering, Business, Law, Medicine, Arts & Sciences, Media Arts and Design, Education, Information Science & Technology
- Dept. of Materials Science & Engineering ranks **11th** out of 88 programs in the U.S. (National Research Council S-Rankings, Sept. 2010)
- Highlighted as one of the top 10 “Up-and-Comers” in *U.S. News and World Report’s* 2012 edition of “America’s Best Colleges.”

Bossone building (home to College of Engineering labs)

Current Research Activities - Gogotsi Group

Carbon Nanotubes – composites, single cell probes

Science (2000), ***Science*** (2010), ***Nature Nano*** (2011), ***Scientific Reports*** (2012)

Nanodiamond – nanocomposites, drug delivery

J. American Chemical Society (2006, 2009); ***Nature Nano*** (2012)

Nanoporous Carbons – gas (H_2, CH_4) storage, , protein sorption supercapacitors, water desalination

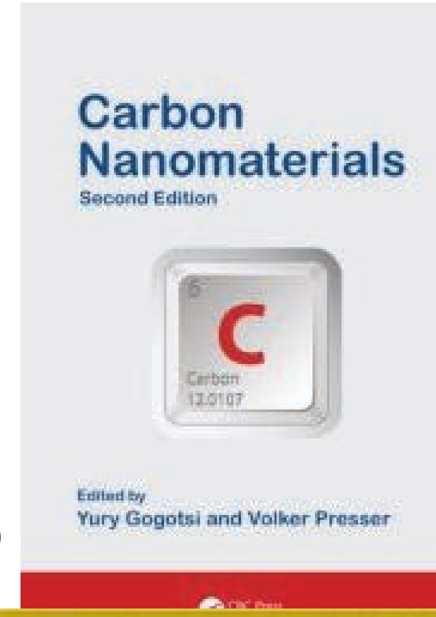
Nature (1994), ***Nature*** (2001), ***Science*** (2006, 2010)

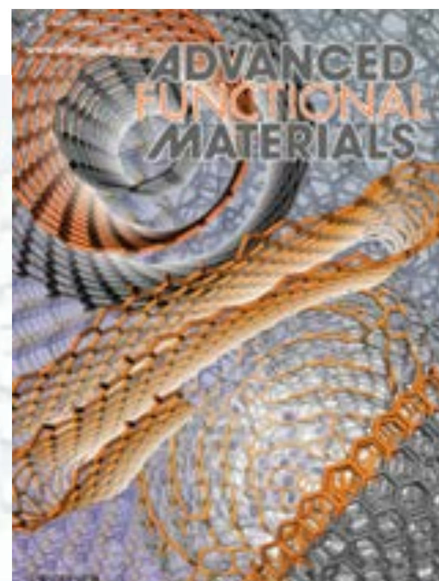
Carbon Materials for Electrical Energy Storage

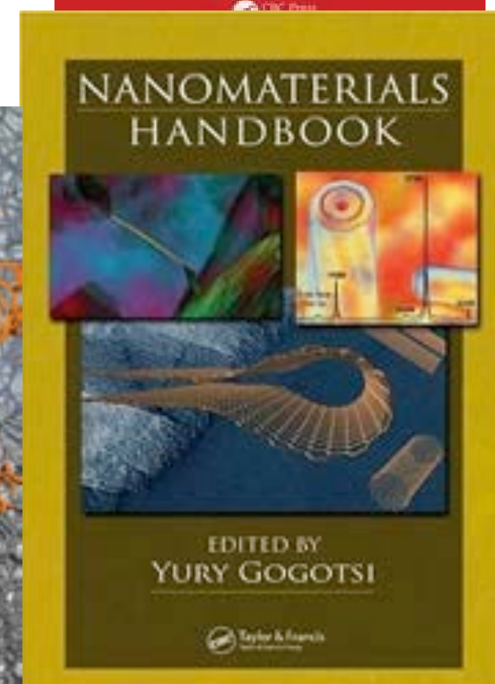
Nature Materials (2008, 2012); ***Nature Nano*** (2010); ***Nature*** (2014) ***Science*** (2011, 2014)

Two-Dimensional Carbides and Nitrides

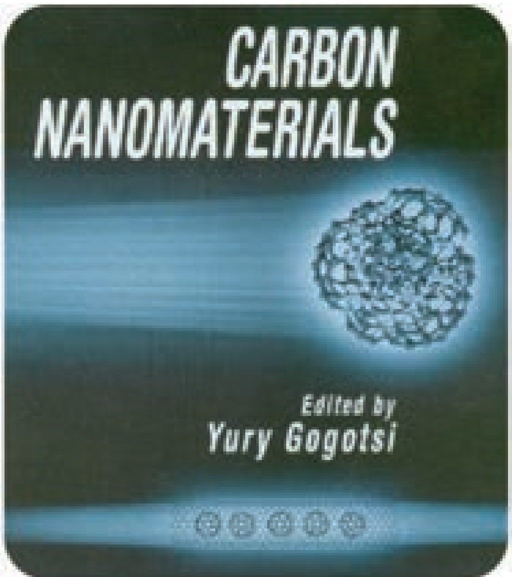
Adv. Mater (2011, 2014), ***Nature Comm***., ***Science*** (2013), ***Nature***, ***PNAS*** (2014)



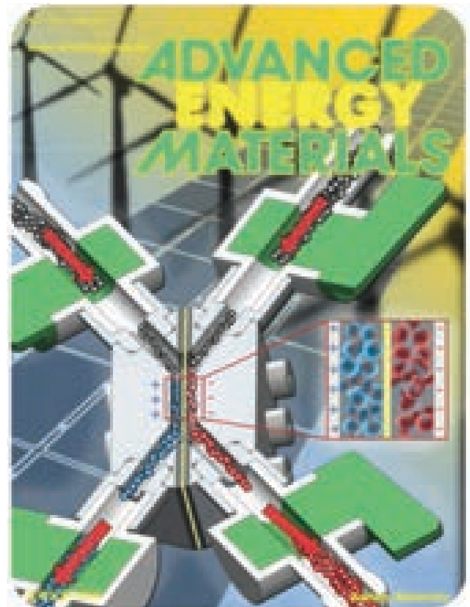




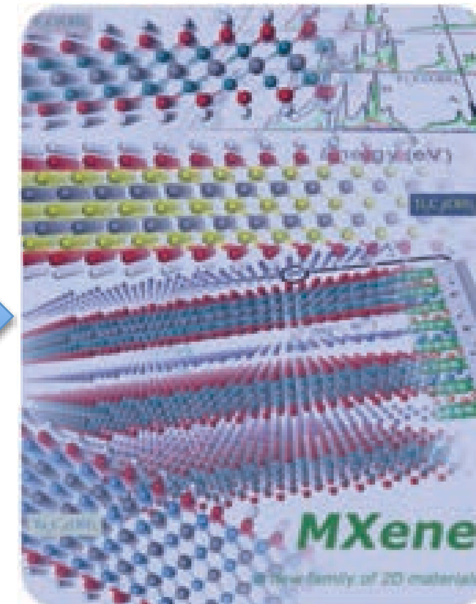
Outline



Rich World of Carbon Nanomaterials



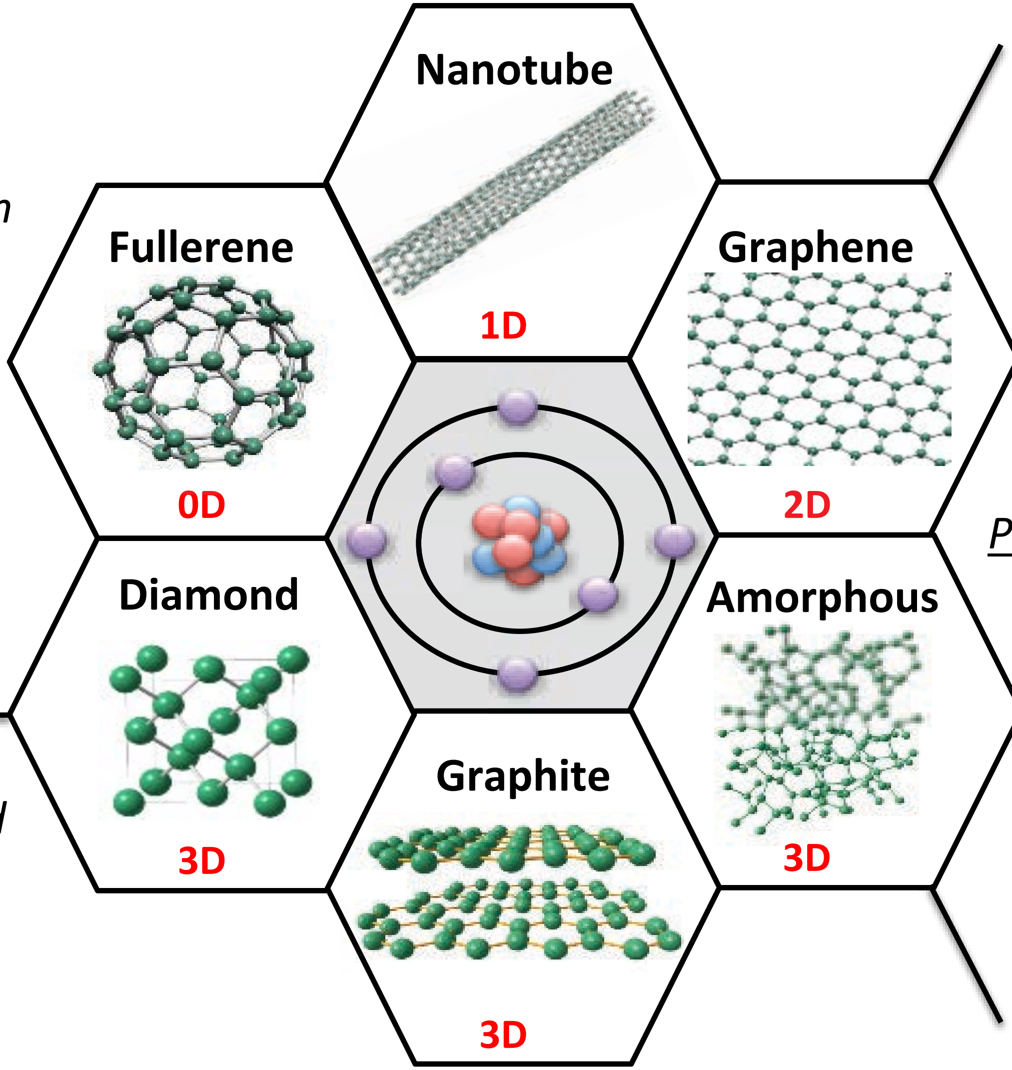
Case Study: Supercapacitor Electrodes



From Pure Carbon to Carbides

Carbon Nanomaterials

***sp*-bonded:**
Carbynes
(linear carbon
chains)

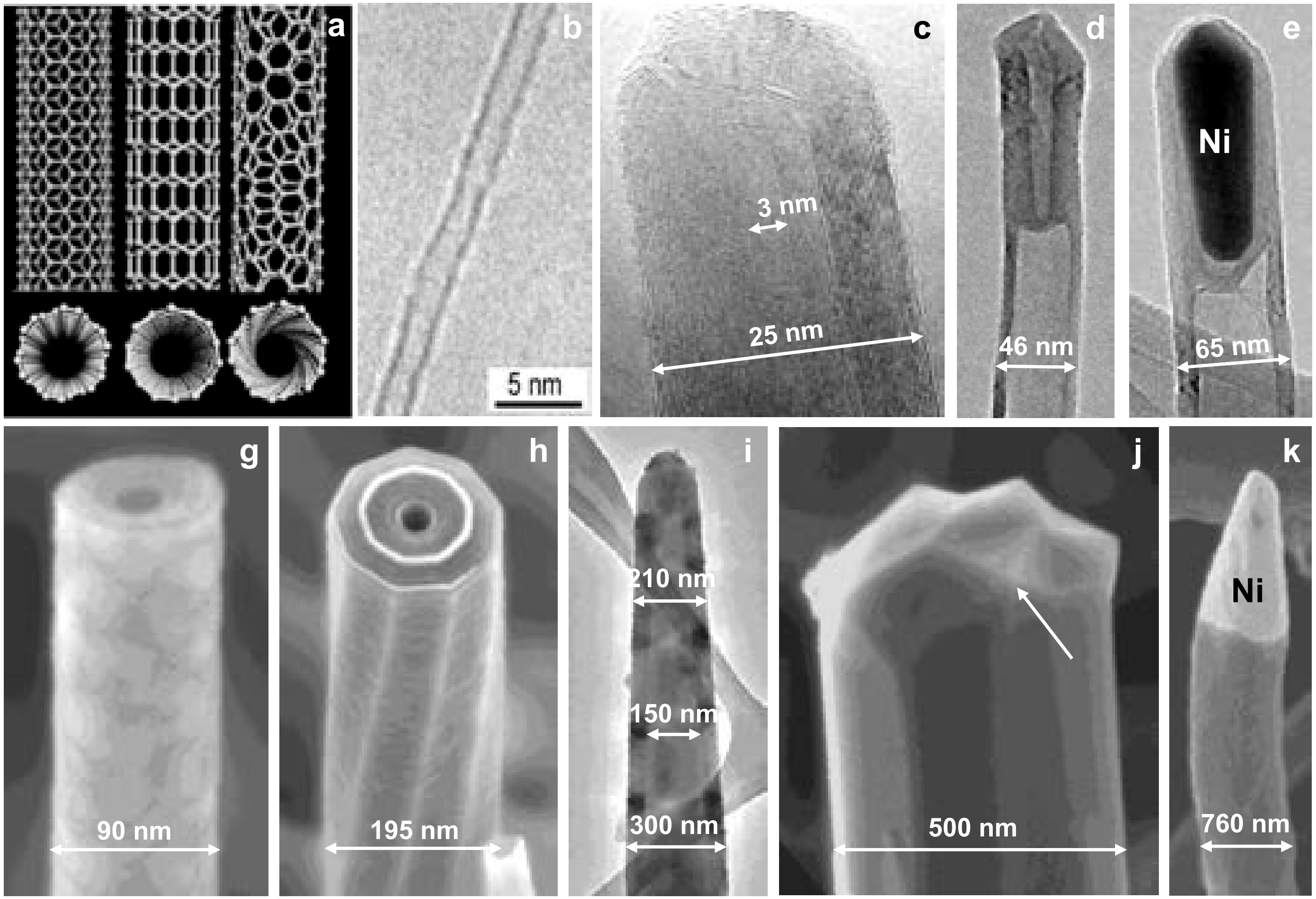


***sp*³-bonded:**
Nanodiamond
Diamondoids

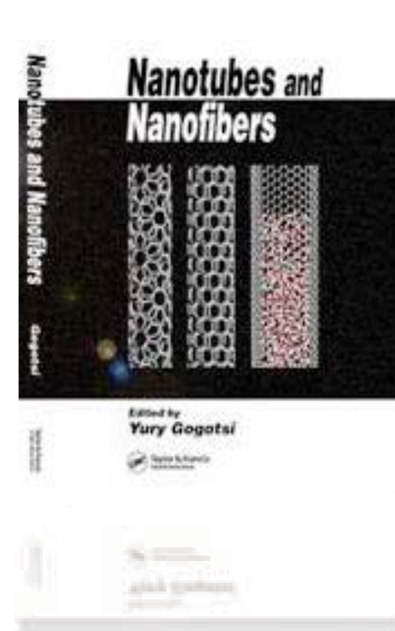
***sp*²-bonded:**
Graphene
Nanotubes
Fullerenes
Carbon onions
Nanohorns
Nanocones

Porous/disordered carbons:
Activated carbon
Carbon fibers
Carbide-derived carbon
Templated carbon
Aerogels

Carbon Nanotube/Nanofiber Family



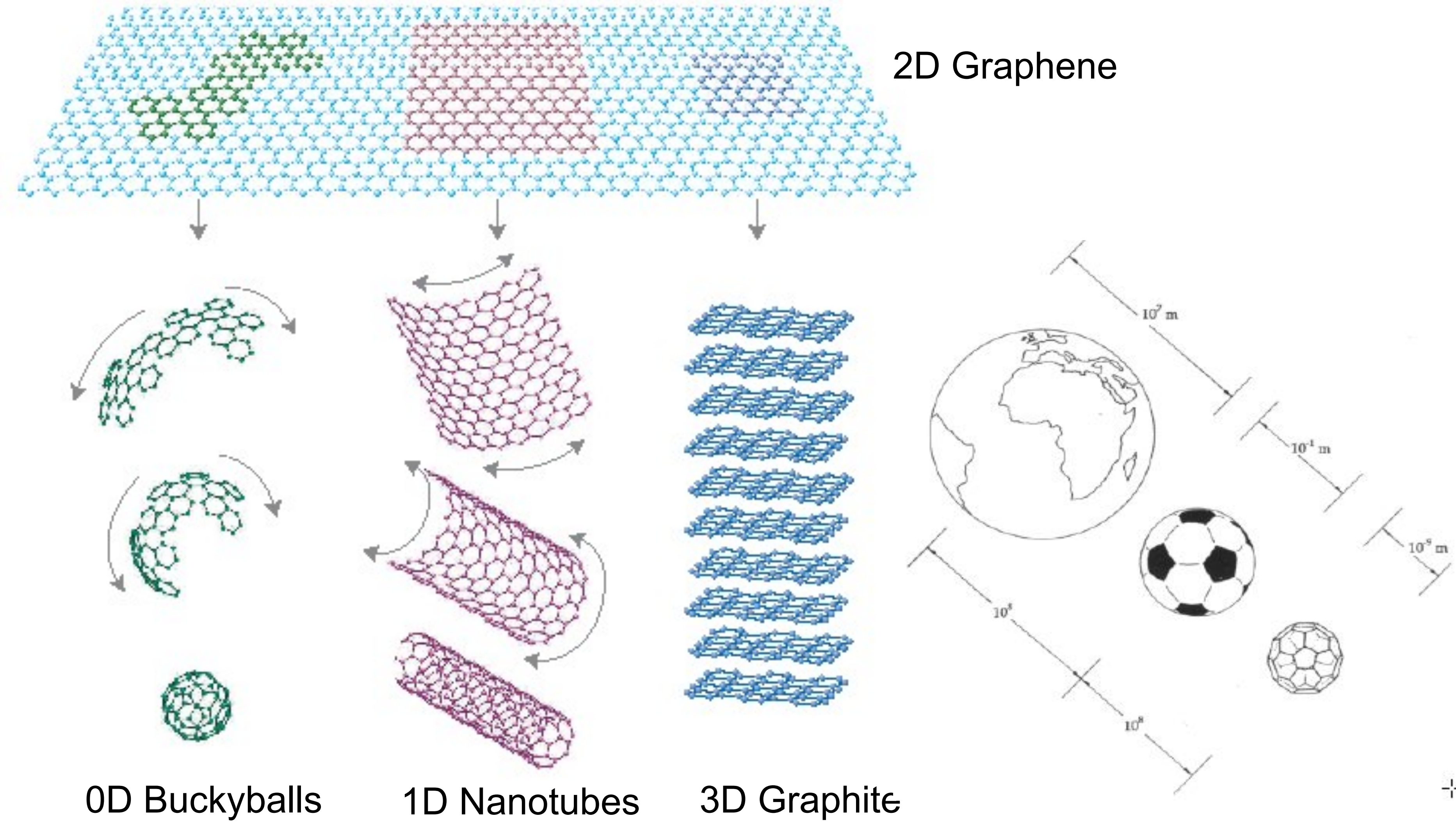
Large volume production of nanotubes in China Europe, Japan and the US



A few representatives of a large family of carbon nanotubes, which form structures ranging from <1 nm to hundreds of nanometers in diameter. They can be purchased as powders, paper, or aligned arrays on conducting (Al, Ti, steel, etc.) substrates.

Y. Gogotsi, ***Materials Research Innovations***, *7*, 192 (2003)

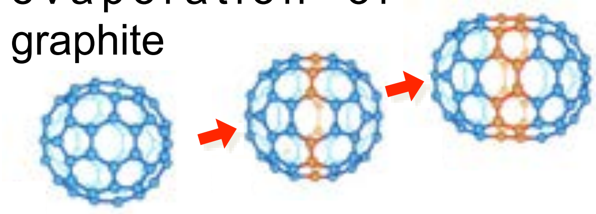
Graphene: Mother of All Graphitic Materials

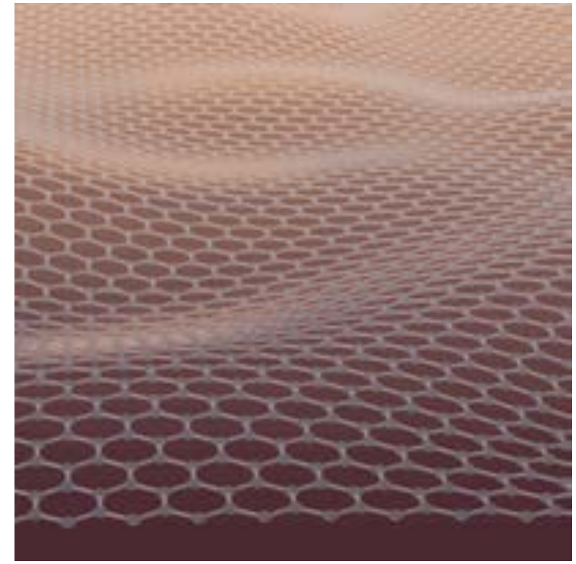


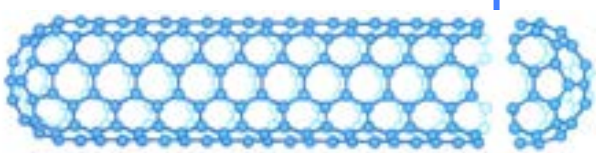
A. K. Geim, K. S. Novoselov, ***Nature Materials***, *6*, 183 (2007)
Y. Gogotsi, ***J. Physical Chemistry Lett***., *2*, 2509 (2011)

Carbon Nanomaterials Timetable

1985 – Kroto and Smalley: fullerenes from pulsed laser evaporation of graphite







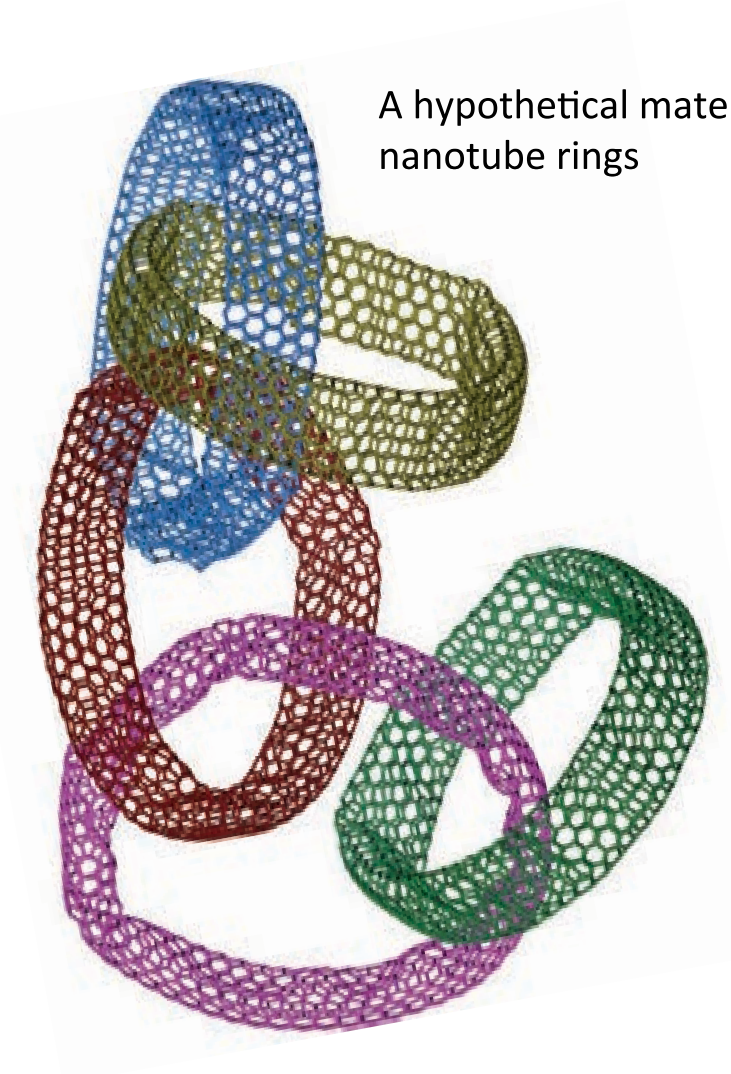
1991 – Iijima: multi-wall nanotubes on electrodes during arc discharge

1993 – Iijima: synthesis of single-wall carbon nanotubes from soot of arc discharge with iron

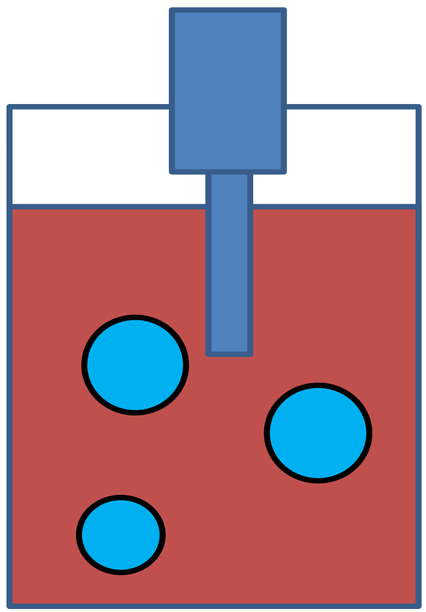
2004 – Geim and Novoselov: show a unique electronic structure of a graphene sheet

Y. Gogotsi, Carbon Nanomaterials, CRC Press, 2006

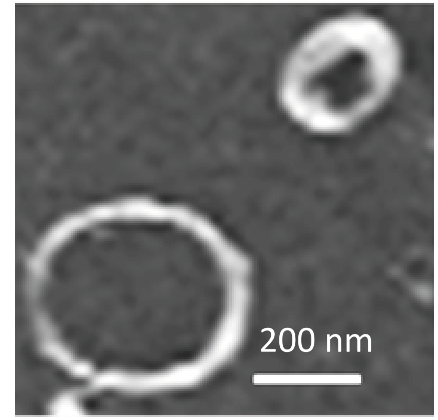
Carbon Rings

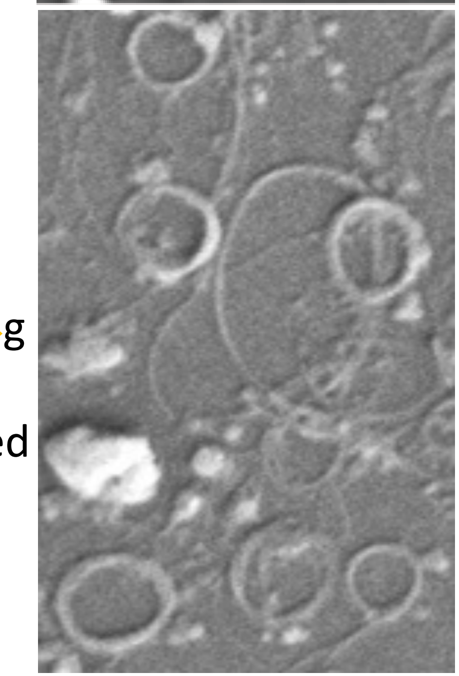


A hypothetical material consisting of interlocking nanotube rings



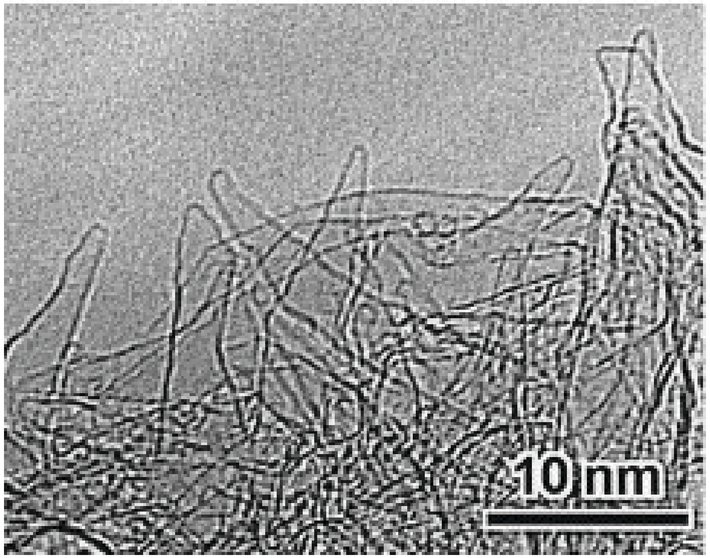
SWCNT nanorings produced using a Pickering emulsion-based process

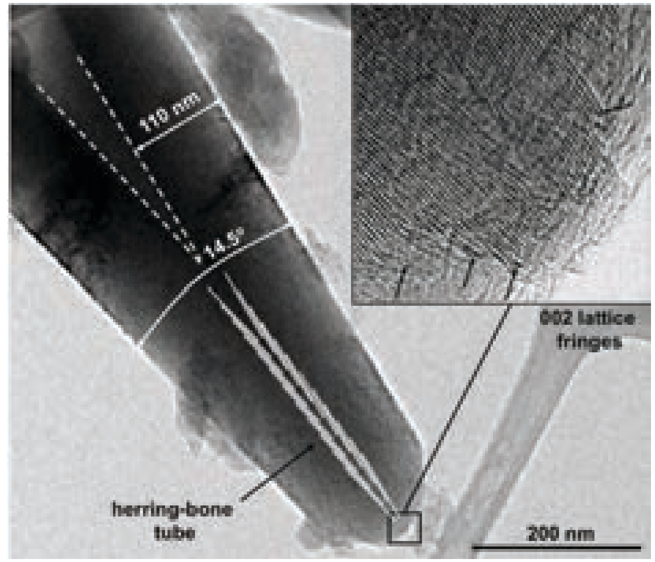


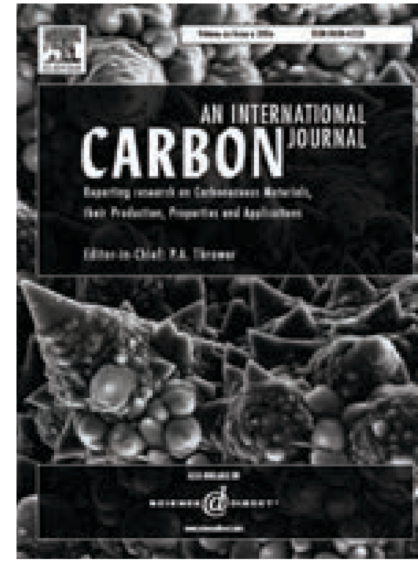


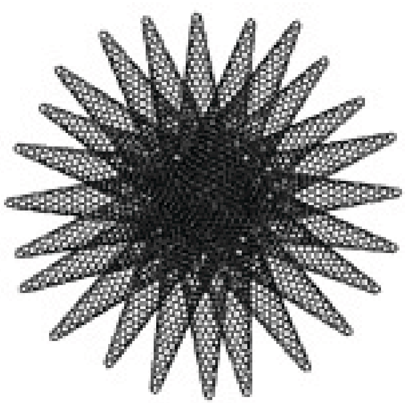
W. Wang, et al, ***Carbon***, *50*, 1769 (2012)
Y. Gogotsi, ***Science***, *330*, 1332 (2010)

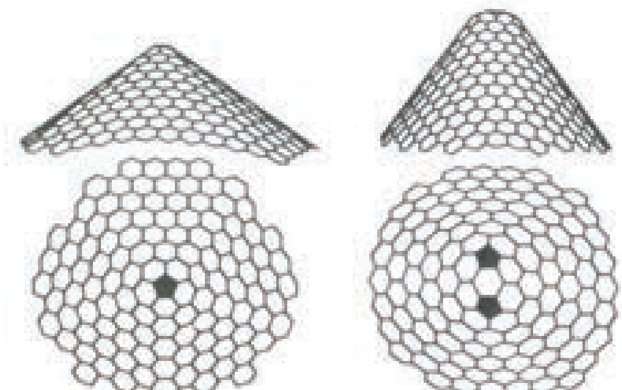
Carbon Nanohorns, Nanocones and Cones



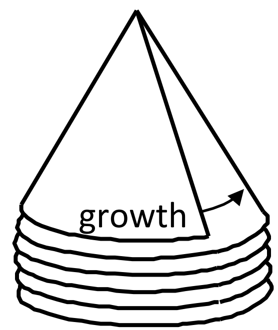


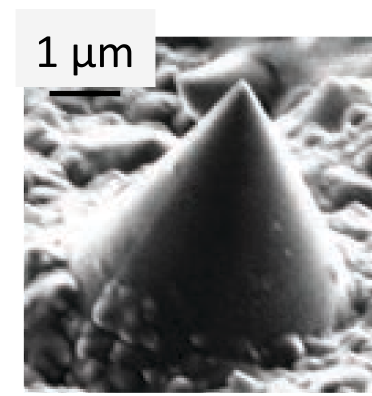






Pentagons

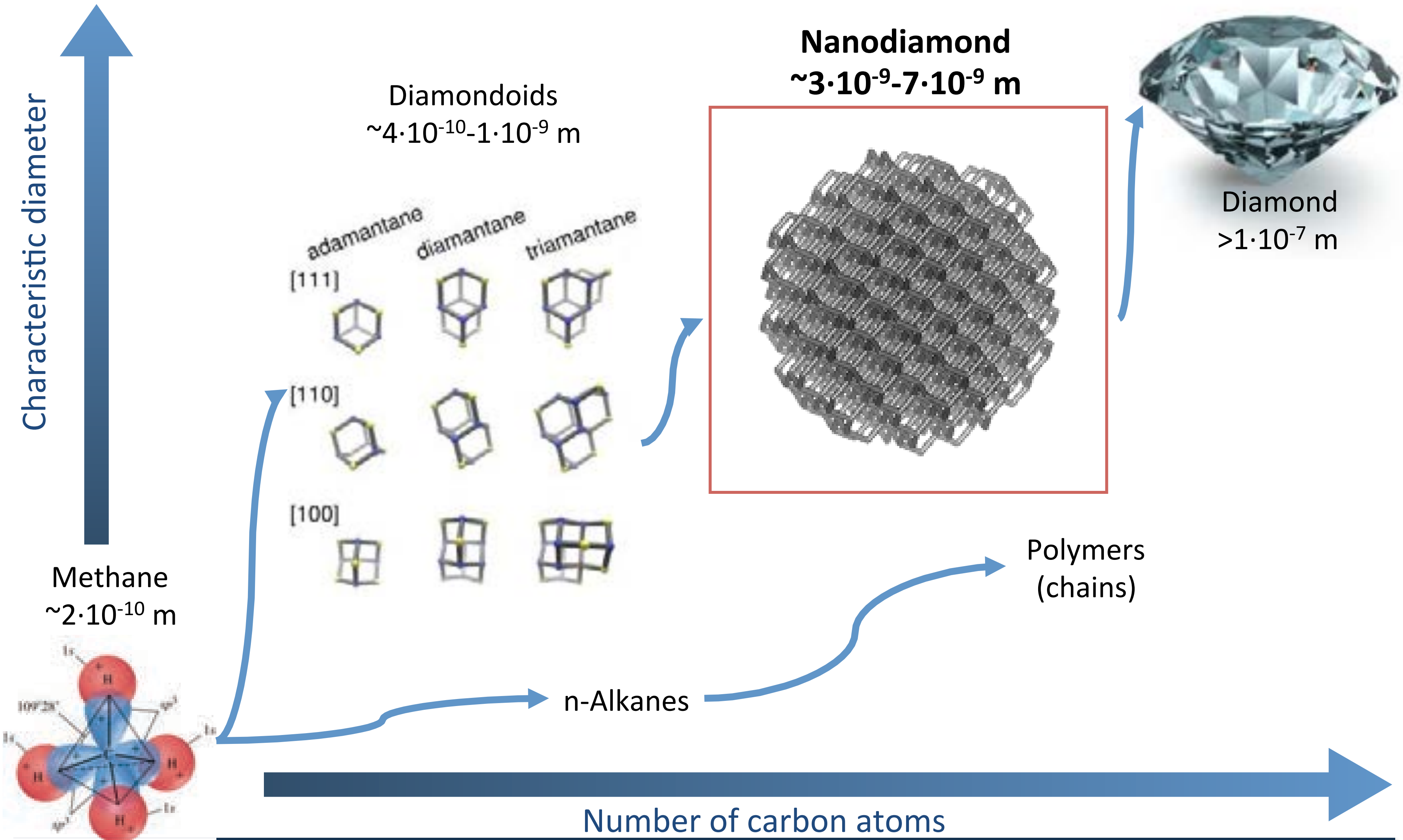




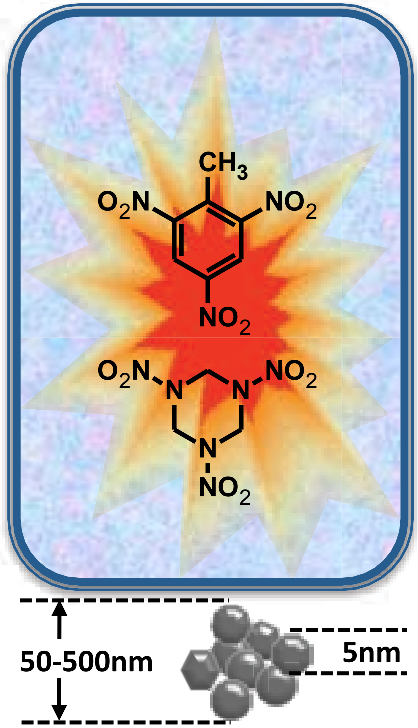
Disclination

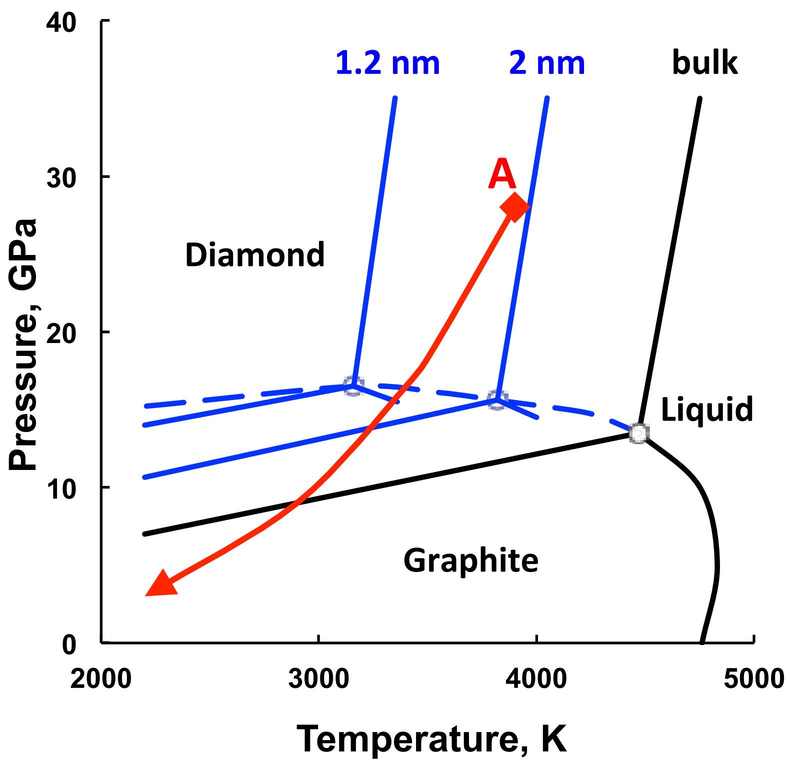
S. Iijima et al., ***Chem. Phys. Lett***., *309,* 165 (1999)
Y. Gogotsi, et al, ***Carbon***, 40, 2263 (2002)
J.A. Jaszczak, et al. ***Carbon***, *41*, 2085 (2003)

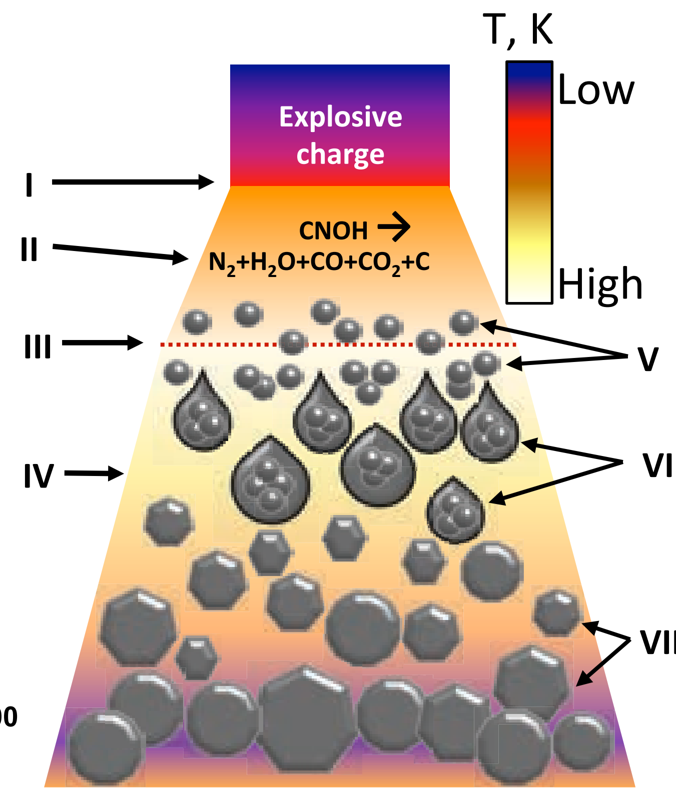
sp^3 Carbon Structure Evolution



Detonation Synthesis of Nanodiamond

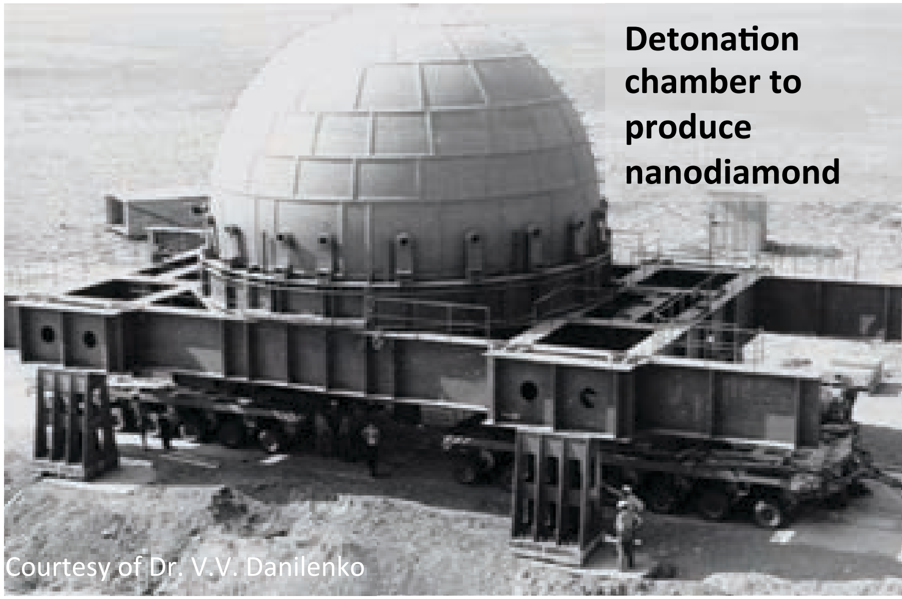


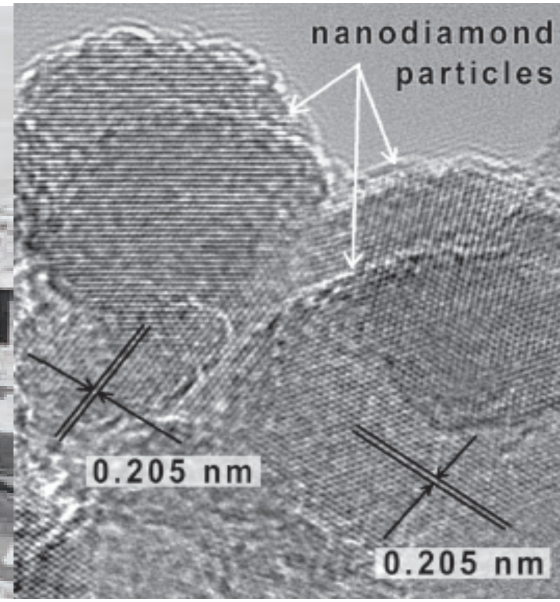


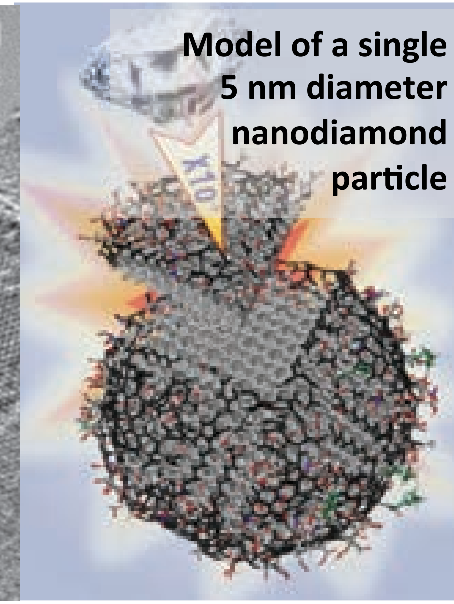


V. Danilenko, *Phys. Solid State* **46,** 595-599 (2004)
V. N. Mochalin, et al., *Nature Nanotechnol.* **7**, 11 (2012)

What is Nanodiamond?



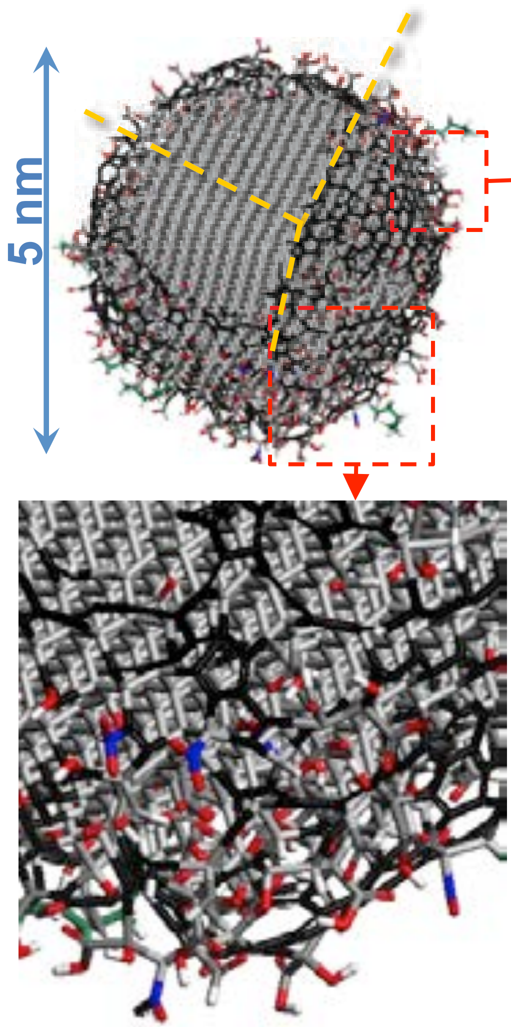


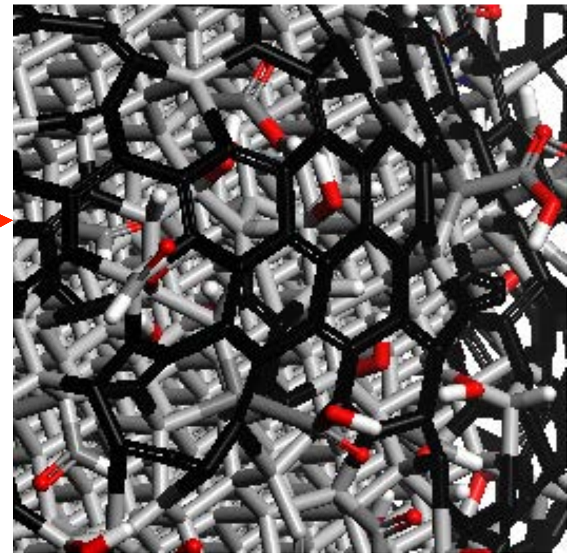


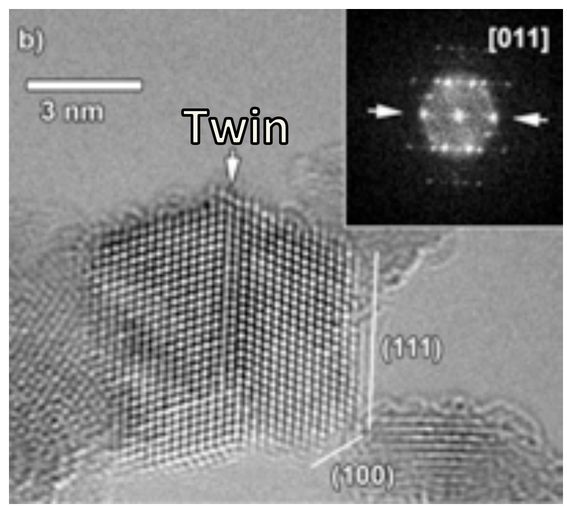
- Inexpensive
- Available commercially
- Excellent mechanical properties
- Small particle size
- Biocompatible
- Rich surface chemistry

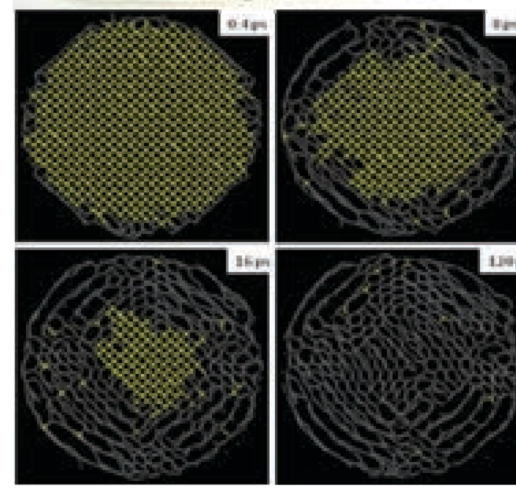
V. N. Mochalin, et al. ***Nature Nanotechnol. 7***, 11-23 (2012)
S. Osswald, et al. ***J. American Chemical Society***, 128, 11635 (2006)

Detonation Nanodiamonds





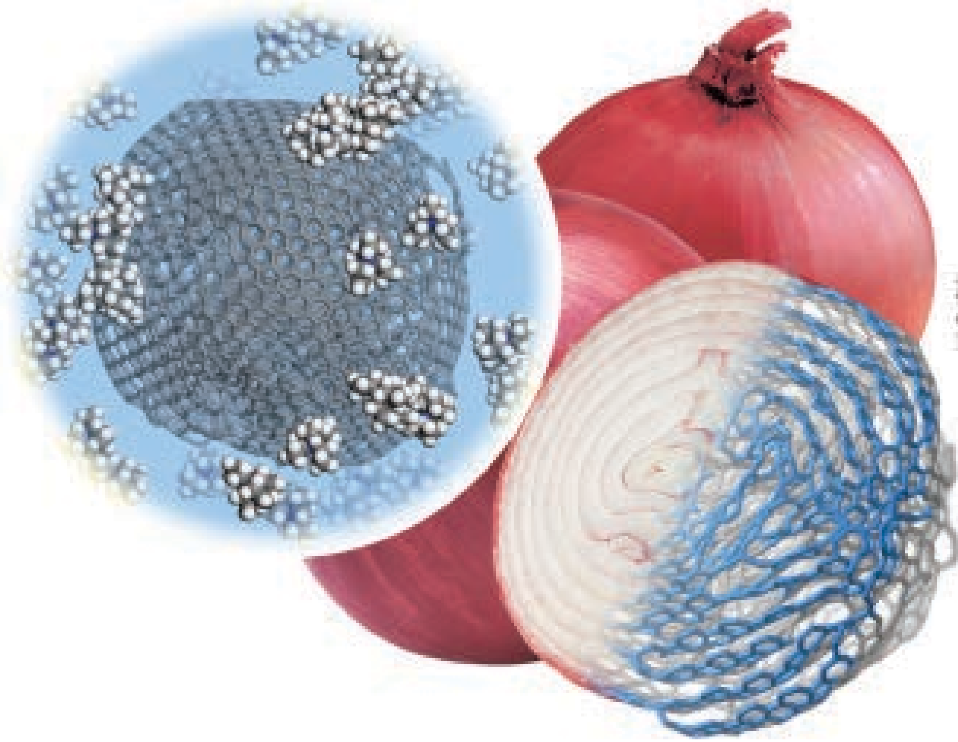


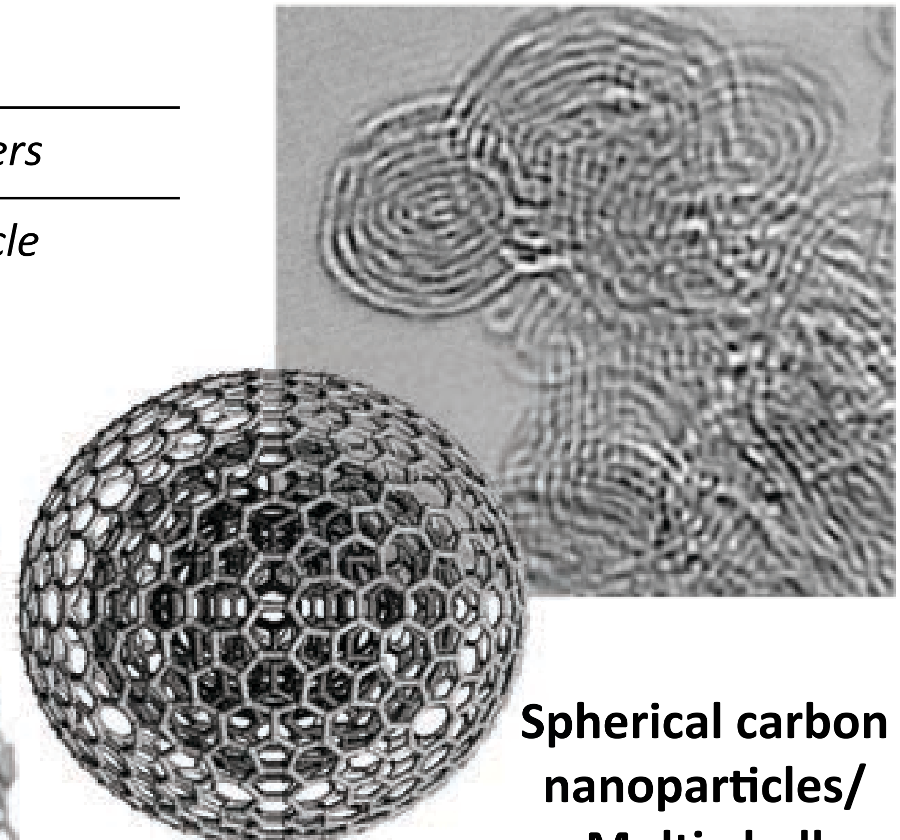


V. N. Mochalin, et al, ***Nature Nano***, *7*, 11 (2012)
D. Pech, et al, ***Nature Nano,*** *5*, 651 (2010)

Onion-Like Carbon

Specific surface area	*400 – 600 m^2/g*
Particle size	*Several nanometers*
Pore size	*>2 nm, interparticle*



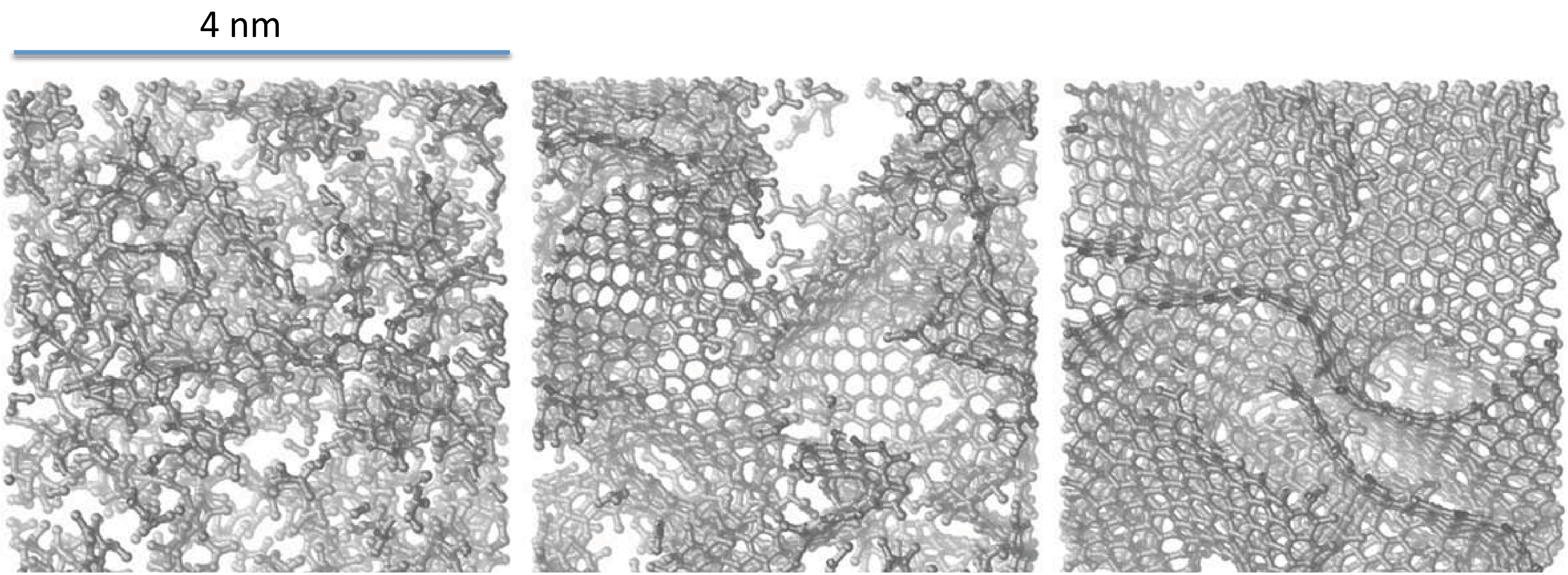


Spherical carbon nanoparticles/ Multi-shell fullerenes

Model: H. Terrones & M. Terrones

D. Pech, et al**, *Nature Nano,*** *5*, 651 (2010)
J. McDonough, et al, ***Carbon,*** 50, *3298* (2012)
C. Portet, et al**, *Carbon***, *45,* 2511 (2007)
R. Lin, et al, ***J. Physical Chemistry Lett.***, *2,* 2396 (2011)

Structure of Porous Carbons



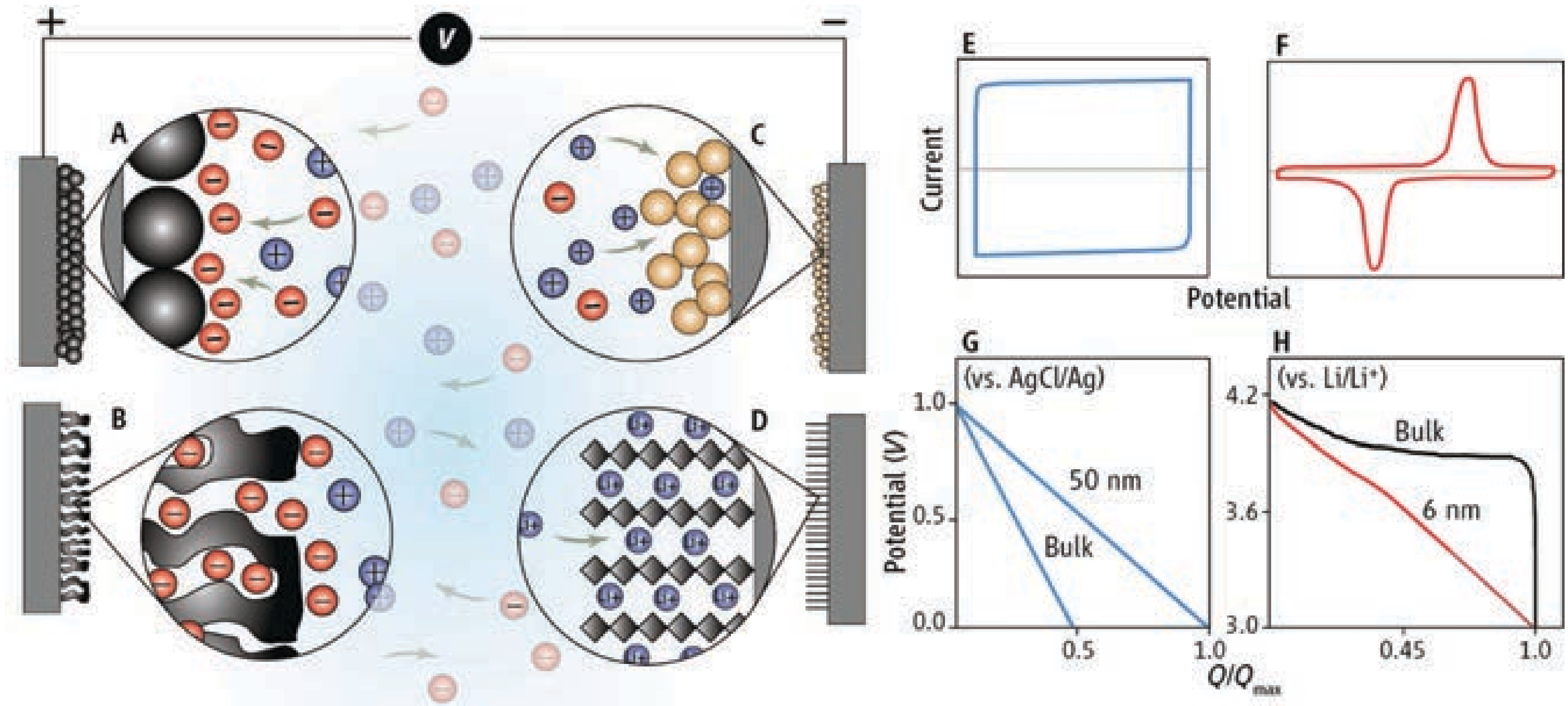
Fast quenching = 600°C   Medium rate = 800°C   Slow quenching = 1200°C

- Quenched Molecular Dynamics (QMD) snapshots of the model structures of Ti-CDC. Surface termination has not been taken into account.
- Hybrid Reverse Monte Carlo and QMD modeling performed using neutron scattering data (RDF) and verified by HRTEM.

J. C. Palmer, et al, ***Carbon***, *48,* 1116 (2010)

Case Study:
Supercapacitor Electrodes

Mechanisms of Charge Storage

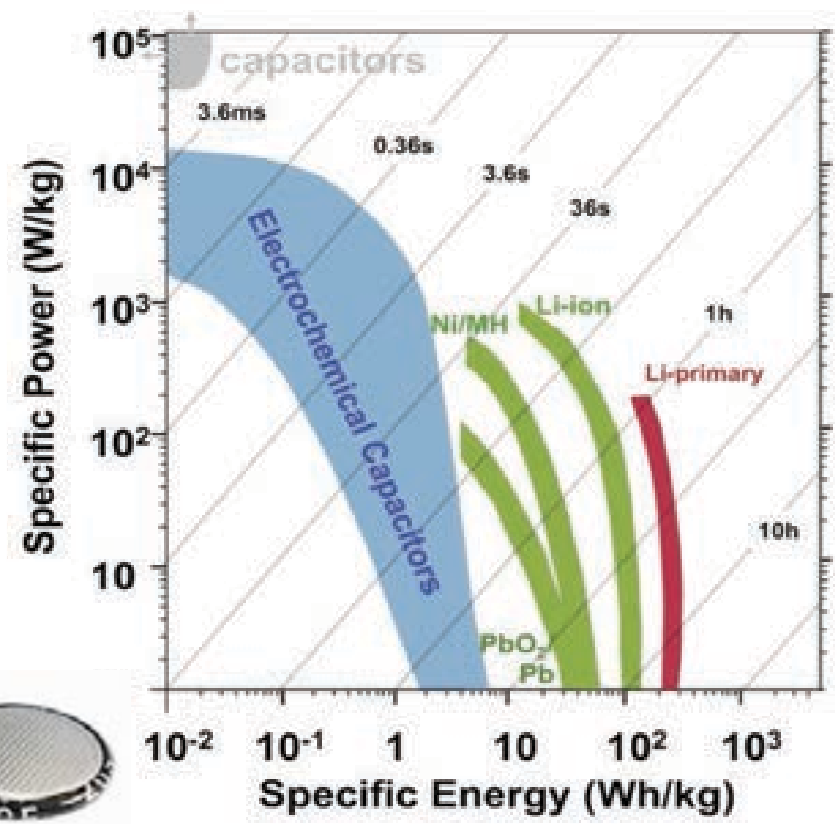


Supercapacitors (ultracapacitors, double-layer capacitors, electrochemical capacitors) differ in their electrical and electrochemical characteristics from batteries.

Electrochemical Storage of Energy

Affordable and **efficient** electrical energy storage is needed to **enable widespread use of renewable energy sources** and provide energy security for our future

Properties of supercapacitors:
Long cycling: up to 1,000,000,
High power,
Higher energy density for up to 10-30 s discharge or harvesting



Possible to make the entire device from easily **recyclable materials**

P. Simon, Y. Gogotsi, ***Nature Materials***, 7, 845 (2008)
B. Dyatkin, et al., ***ChemSusChem***, *6*, 2269 (2013)

Applications of Supercapacitors


Energy Quarterly ·

Super-capacitors take charge in Germany

By Philip Ball
Feature Editor Yury Gogotsi

The yellow-and-white Stadtbahn trams criss-crossing the streets of Mannheim in southern Germany look unremarkable, but some of them are lit-

(dielectric) layer. But a supercapacitor (sometimes called an ultracapacitor) holds its charge a little differently. Typically it contains two conductive porous electrodes—usually made of carbon—immersed in a liquid electrolyte and separated by a very thin insulating film, usually made of a porous polymer. The charge is stored by adsorption of ions onto the high-surface-area electrodes. When the electrodes are charged, this produces a layer of oppositely charged ions on their surfaces: a so-called electrical double-layer, which is why this type of supercapacitor is often called a double-layer capacitor.

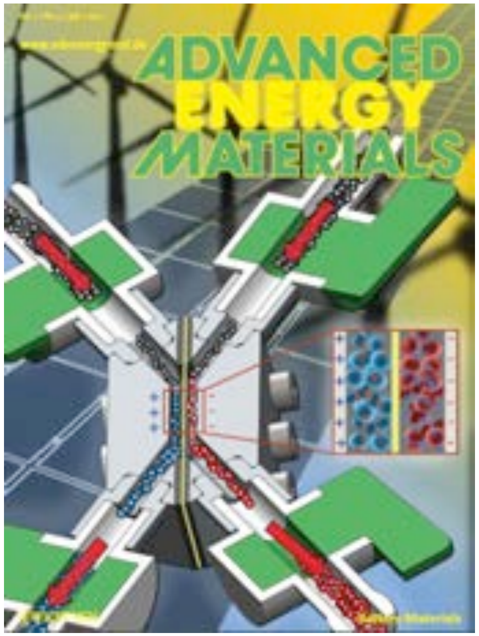
Trams in Germany, powered by supercapacitors, use 30% less energy than their equivalents in other regions.

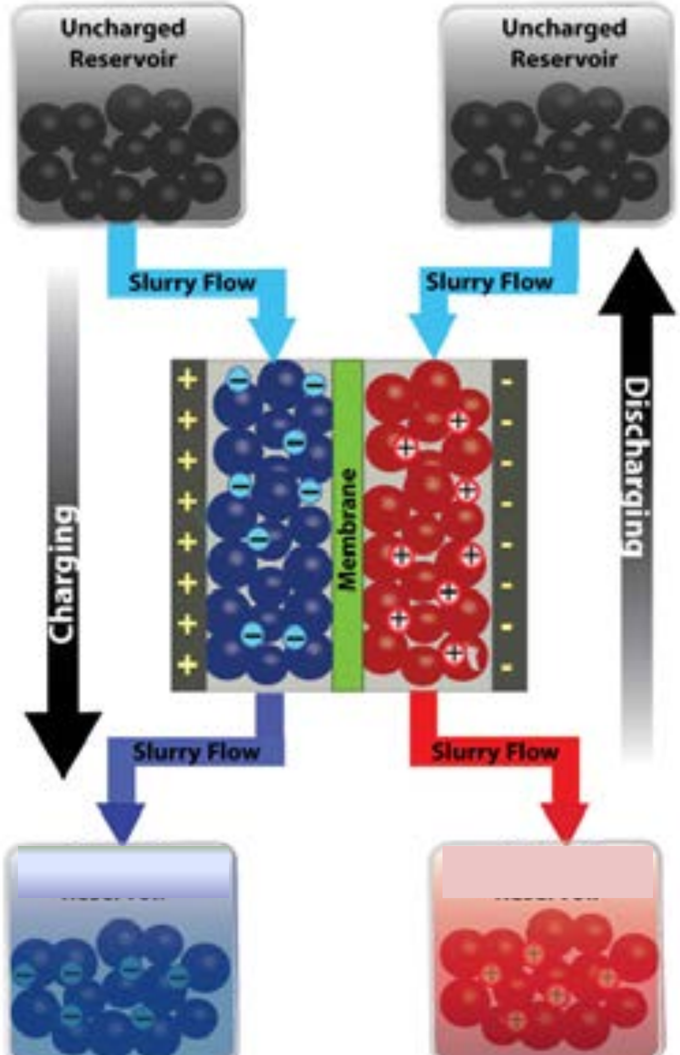
- 2 x 15W LED
- Charging time = 2-6 hrs, depending on weather
- The street lamp (LED and solar panels) developed by Nippon Chemi-Con and Kyocera Corporation

skyscrapercity.com

P. Ball (ed. Y. Gogotsi), ***MRS Bulletin*,** Sept. 2012
P. Ball (ed. Y. Gogotsi), ***MRS Bulletin***, Nov. 2012

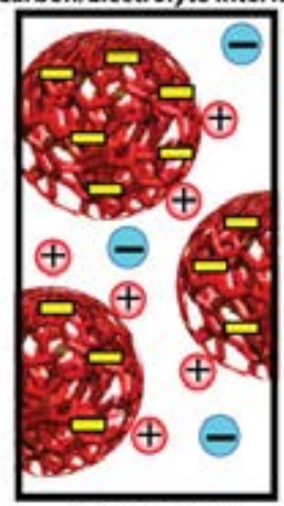
The Electrochemical Flow Capacitor



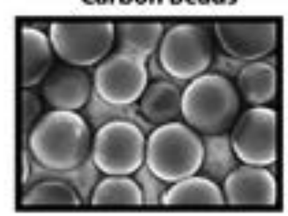


Slurry=Activated Carbon Beads and Electrolyte

Carbon/Electrolyte Interface



Carbon Beads



Flowable Capacitive Slurry

Charge Storage in Electric Double Layer

Spherical Carbon Beads

Scalable Architecture

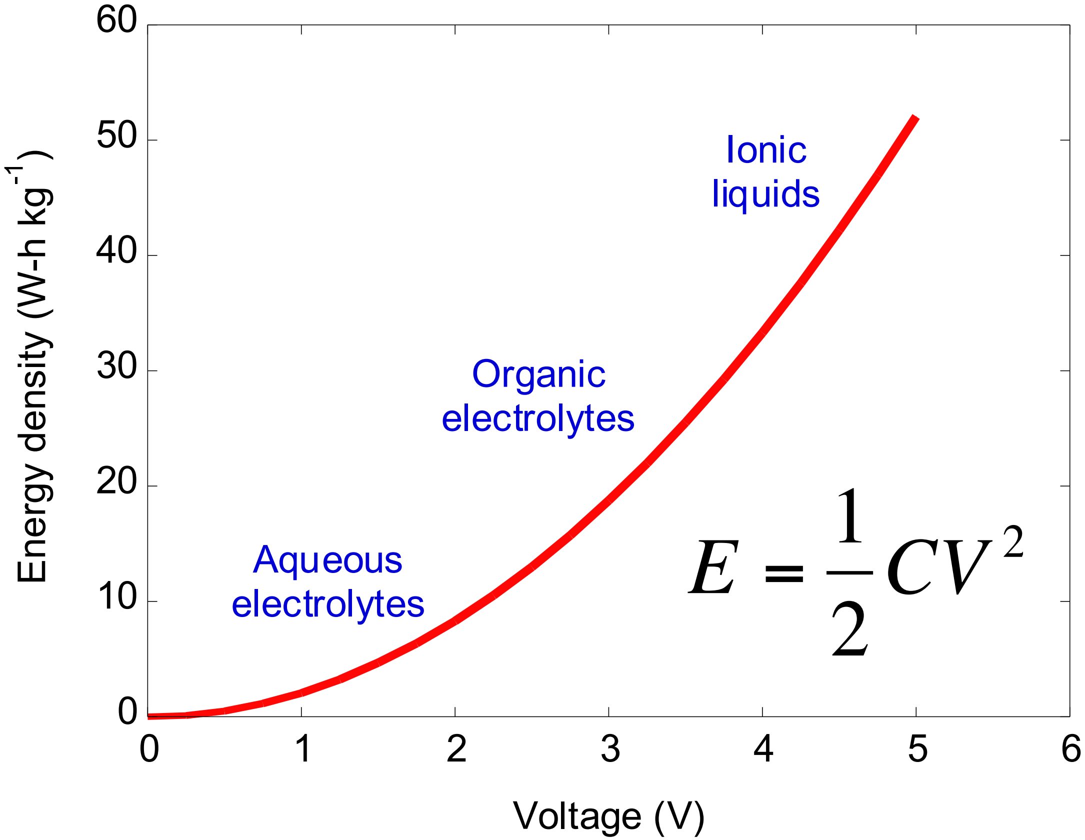
V. Presser et al, ***Advanced Energy Materials***, 2, 895 (2012)
K. B. Hatzell, et al., ***Electrochimica Acta***, 111, 888 (2013)
J. W. Campos, ***Electrochimica Acta***, 98, 123 (2013)

Winner of the International Science & Engineering Visualization Challenge

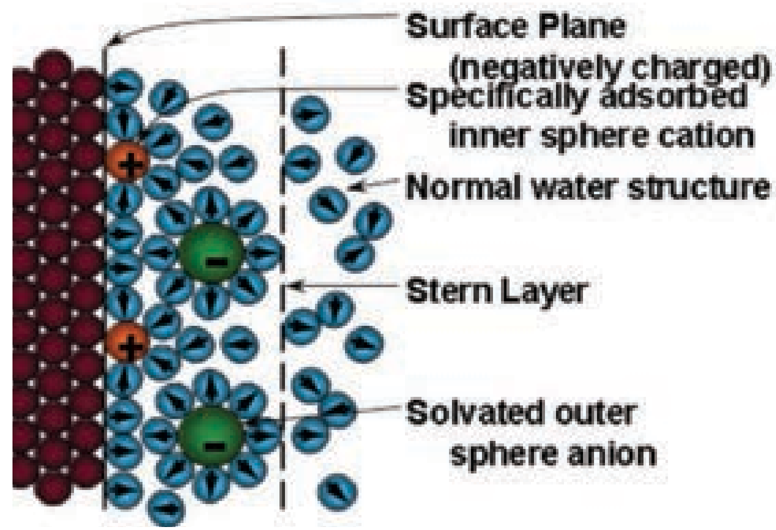
K. Jost, B. Anasori, M. Beidaghi, G. Dion, Y. Gogotsi

K. Jost, et al., ***Science***, *343*, 602 (2014)

Electrolytes for Supercapacitors



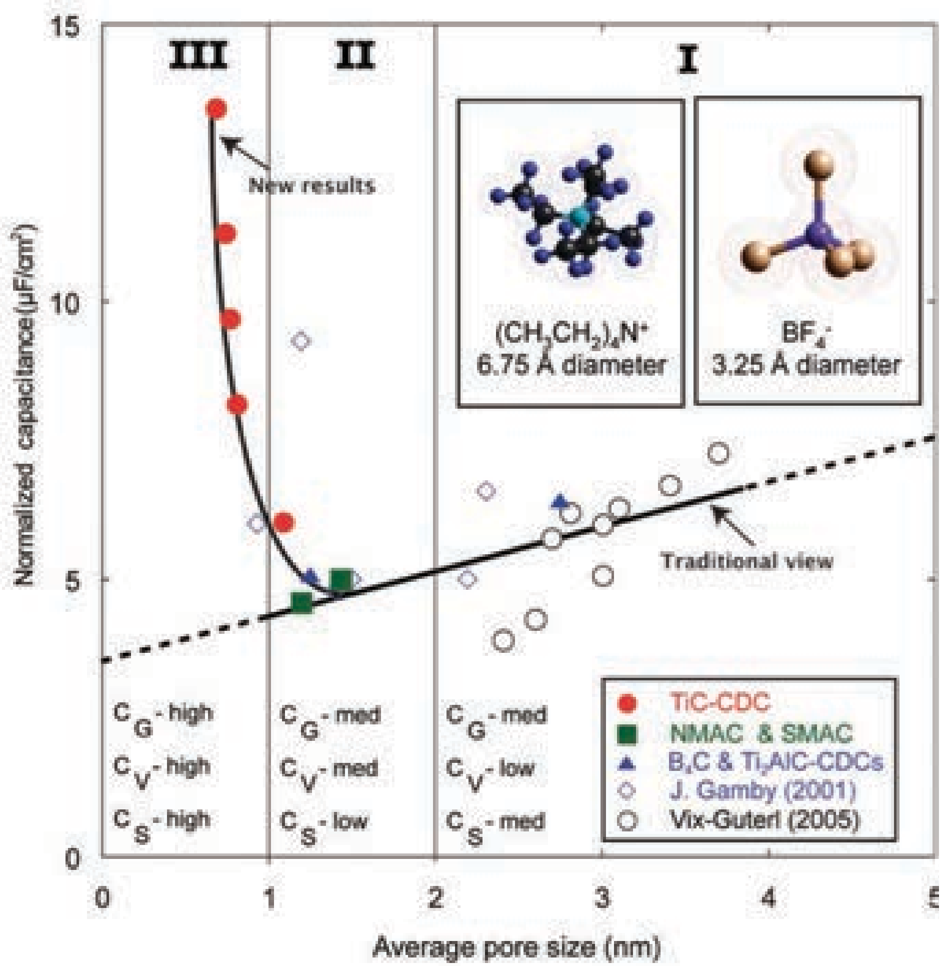
Question: How to match a carbon electrode with an electrolyte (thousands of combinations!)

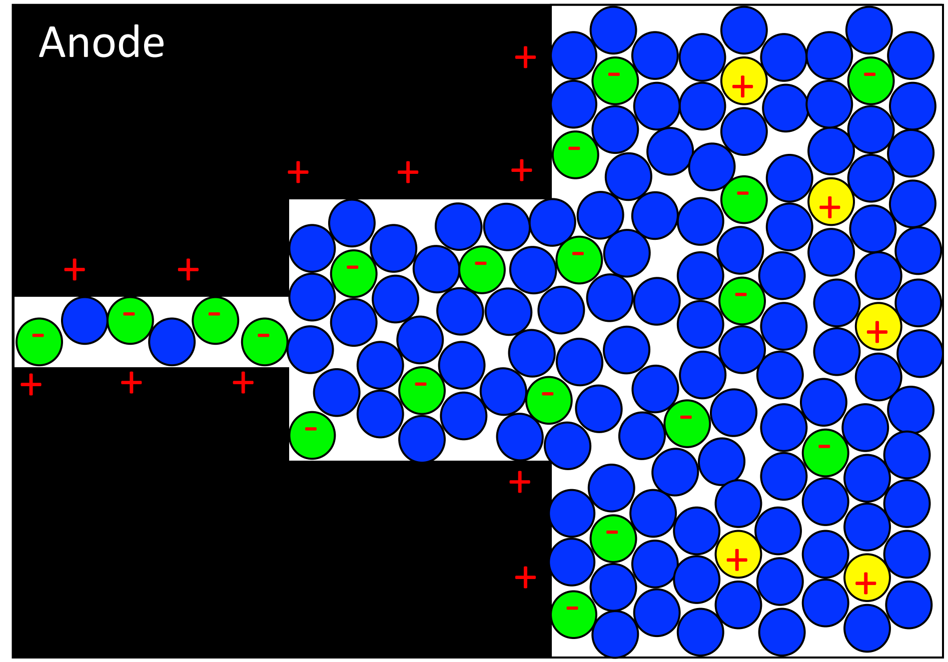


- Need to increase energy (>100 W-h kg^{-1}) to directly compete with batteries
- Ionic liquids offer a larger voltage window than traditional electrolytes, providing a much greater energy density

P. Simon, Y. Gogotsi, ***Phil. Trans. Royal Soc. A***, *368*, 3457 (2010)

Ion desolvation in subnanometer pores





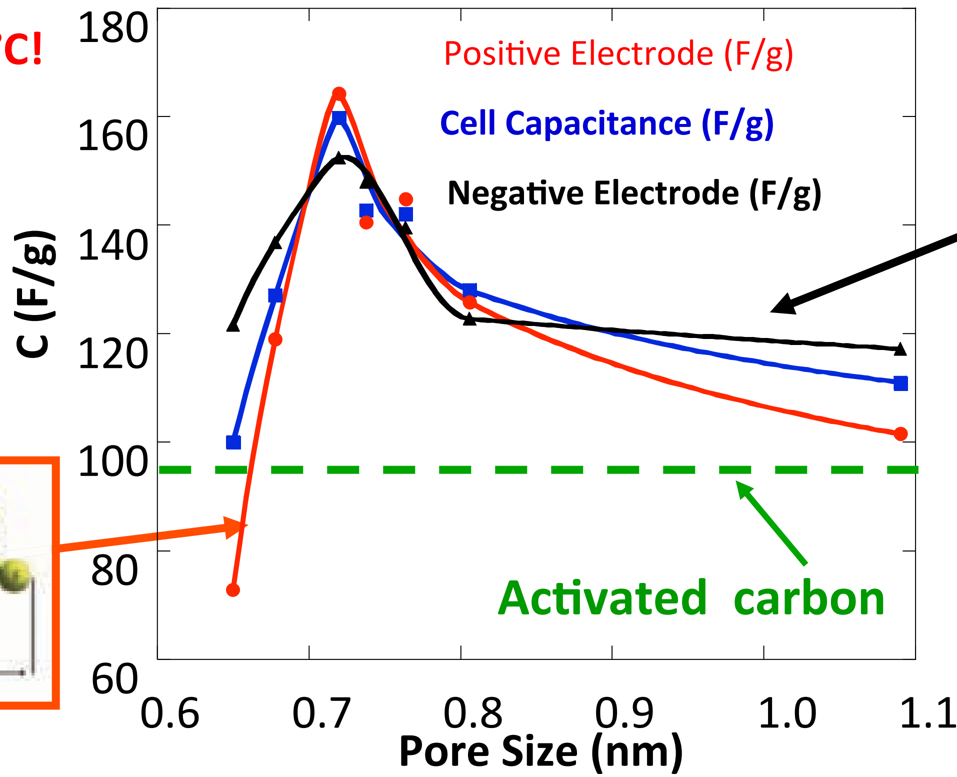
Ions MUST be desolvated!

Capacitance increases as pore size decreases below 1 nm (this value depends on the electrolyte ion size).

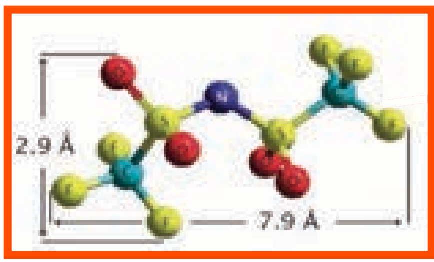
J. Chmiola, et al., ***Science***, *313*, 1760 (2006)

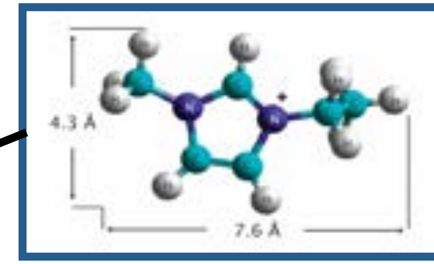
Matching the Pore Size to the Ion Size

Note testing at 60°C!



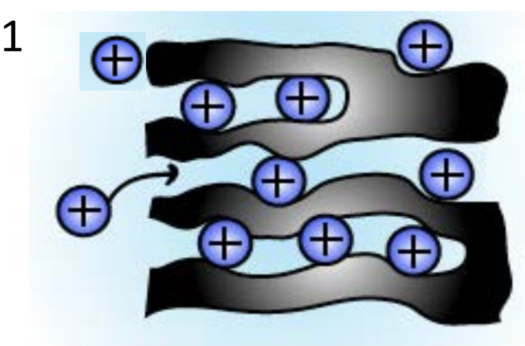
TFSI⁻





EMI⁺

3-Electrode Cell in EMI-TFSI

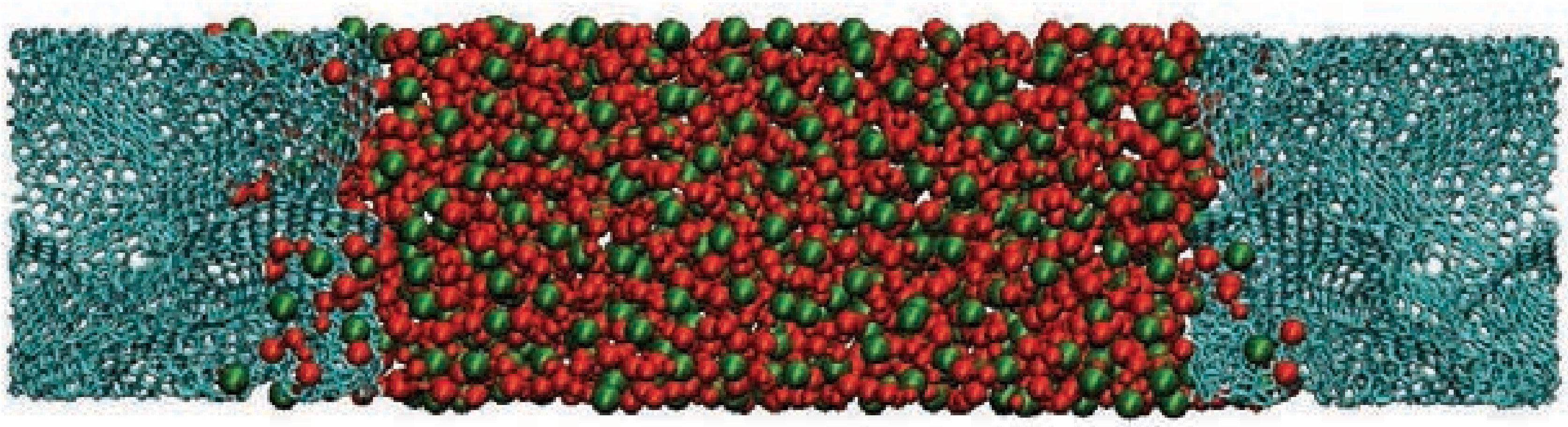


50% capacitance increase vs activated carbon
Maximum at approx. 0.7 nm → when ion size ~ pore size!!!

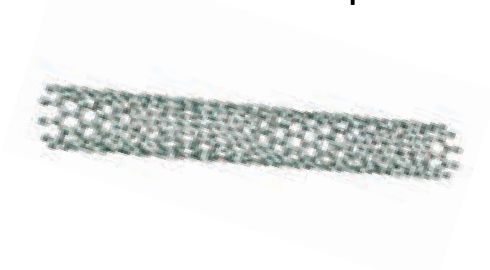
→ Ions are confined in pores

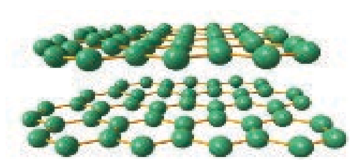
C. Largeot, et al., ***J. Am. Chem. Soc.***, *130*, 2730 (2008)
R. Lin, et al., ***Electrochimica Acta***, 54, 7025 (2009)

Ion Adsorption in Carbon Pores



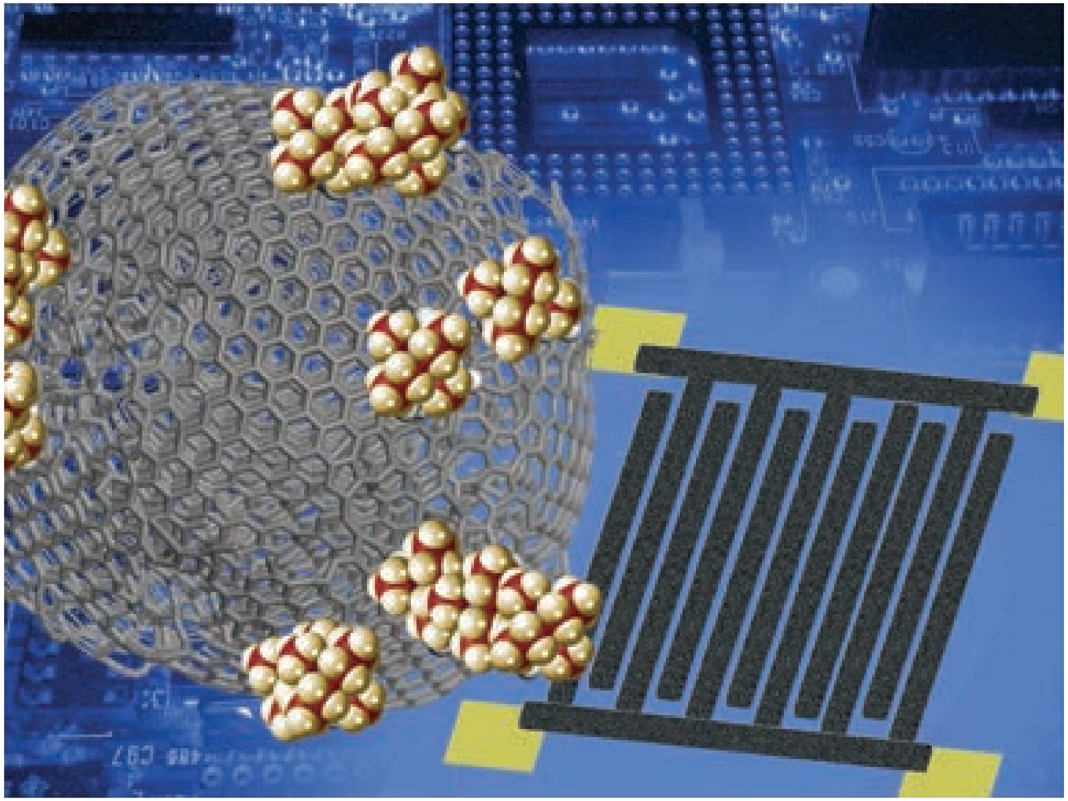
- Molecular dynamics (MD) simulation of diffusion of ions from ionic liquid into pores of 1200°C-CDC.
- The non-idealized MD model of CDC structure used led to the most realistic simulation and quantitatively accurate prediction on capacitance.

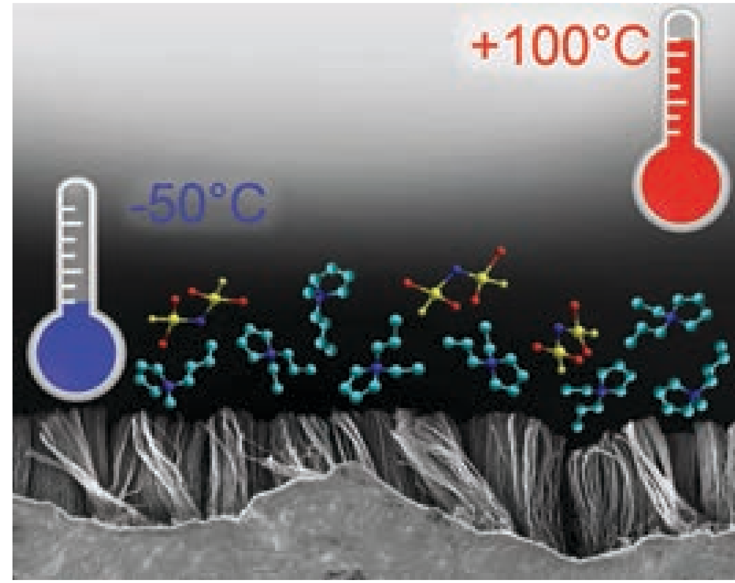




J. C. Palmer, et al., ***Carbon***, *48*, 1116 (2010)
C. Merlet, et al., ***Nature Materials***, *11*, 306 (2012)

Design of Interdigital Micro-supercapacitors with OLC, CDC and CNT Electrodes





R. Lin, et al., ***JPC Lett.***, *2,* 2396 (2011)

A volumetric power density of up to 1 kW cm^{-3} was obtained with a thickness of the deposited layer in the ~10 µm, not the nm range.

D. Pech, et al., ***Nature Nano***, *5,* 651 (2010)
M. Beidaghi, Y. Gogotsi, ***Energy Env. Science***, *7*, 867 (2014)

The Future

K. Jost

From pure carbon to carbides

Graphene is important, but there are many other exciting and useful carbon (and not only carbon) nanomaterials

COMMENT

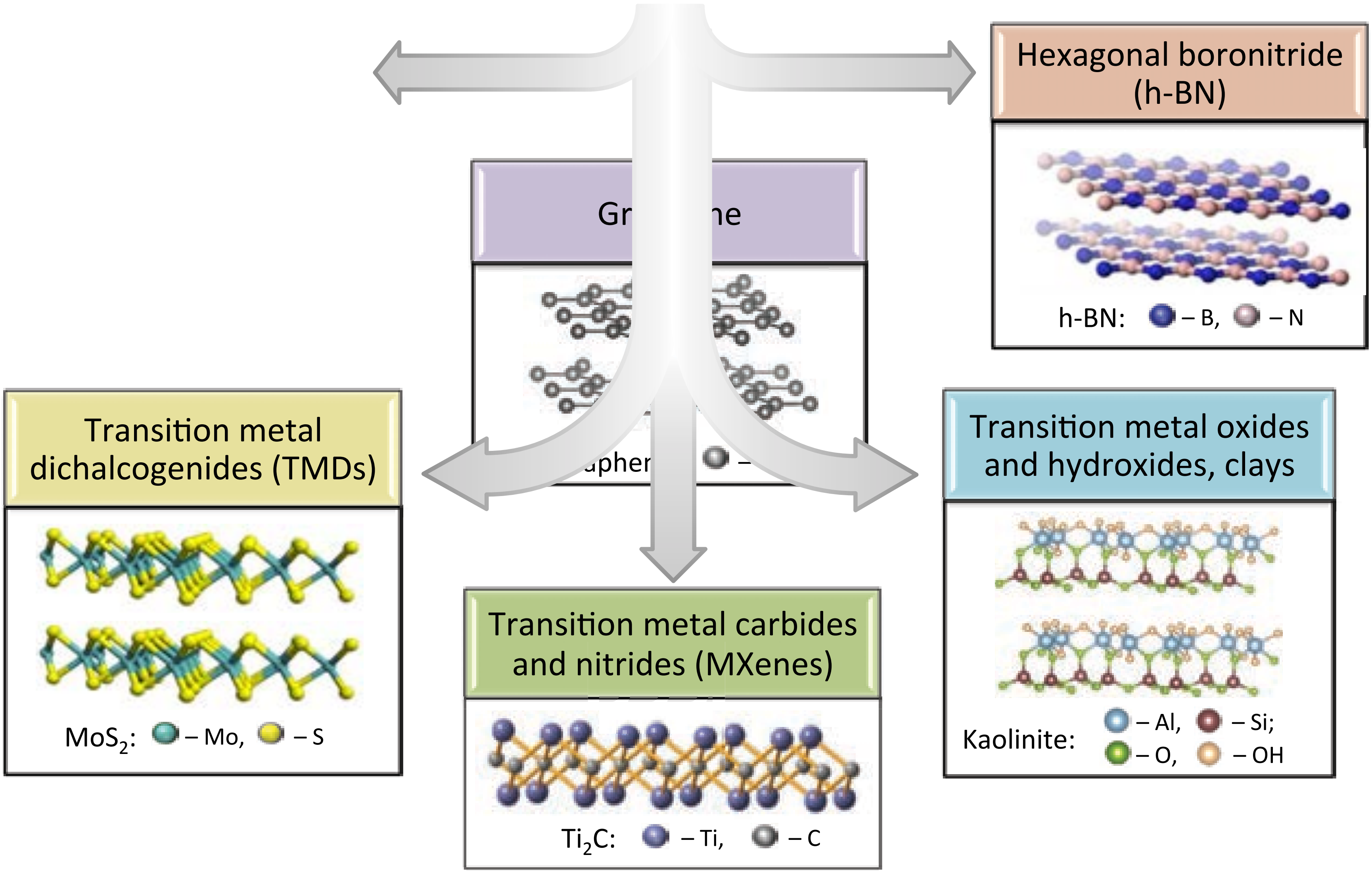
Not just graphene

Read the news, flick through a journal, or browse the internet: it's impossible to ignore a certain hexagonal monolayer. But there's more to carbon than just graphene.

Yury Gogotsi | *Drexel University, Pennsylvania, USA* | Gogotsi@Drexel.Edu

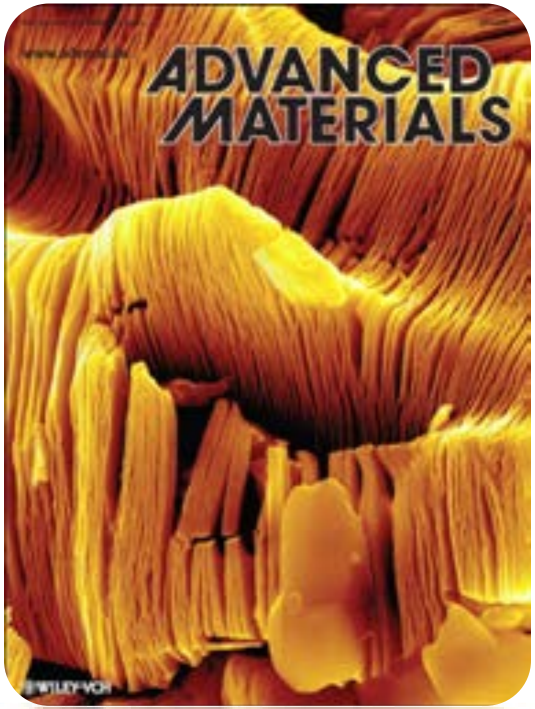
When one thinks of carbon, graphite is probably the first thing that comes to mind; and there are good reasons for this. I have been drawing and writing with pencils, leaving traces of multilayer graphene on bonding: diamond-like carbon, a -C:H, and hard carbon films. Carbon nanomaterials that have been attracting a great deal of attention in the past 20+ years include fullerenes (also polymerized, endohedral, and exohedral or graphene ribbons can be tuned. Thus, virtually any combination of mechanical, electrical, or chemical properties can be achieved by controlling carbon structure and surface chemistry. This is why we need

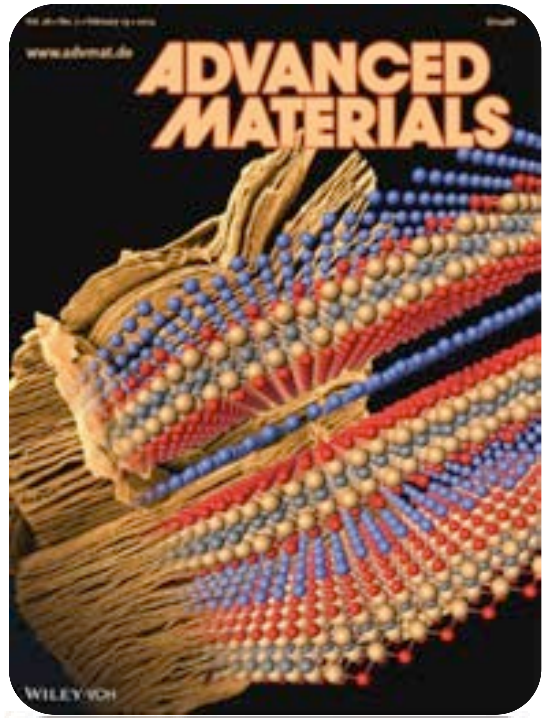
2D World Beyond Graphene



V. Nicolosi, *et al*., ***Science*** 340, 1420 (2013)

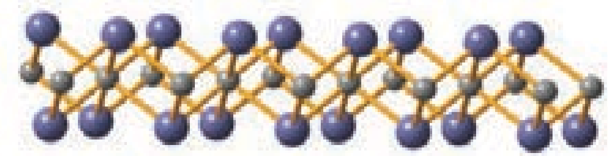
MXene – A New Family of 2D Materials



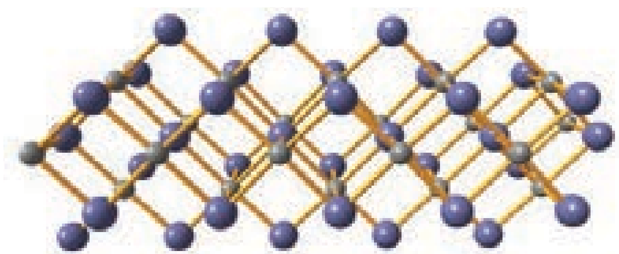


Two-Dimensional Transition Metal Carbides, Oxycarbides and Carbonitrides – 13 synthesized (9 published), dozens more predicted

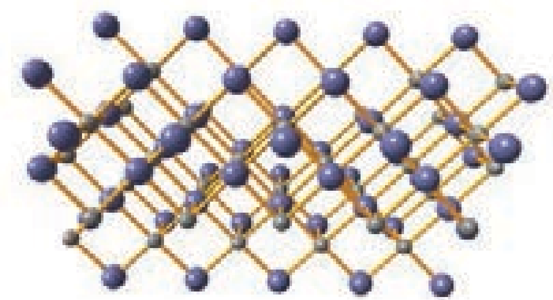
M_2X



M_3X_2



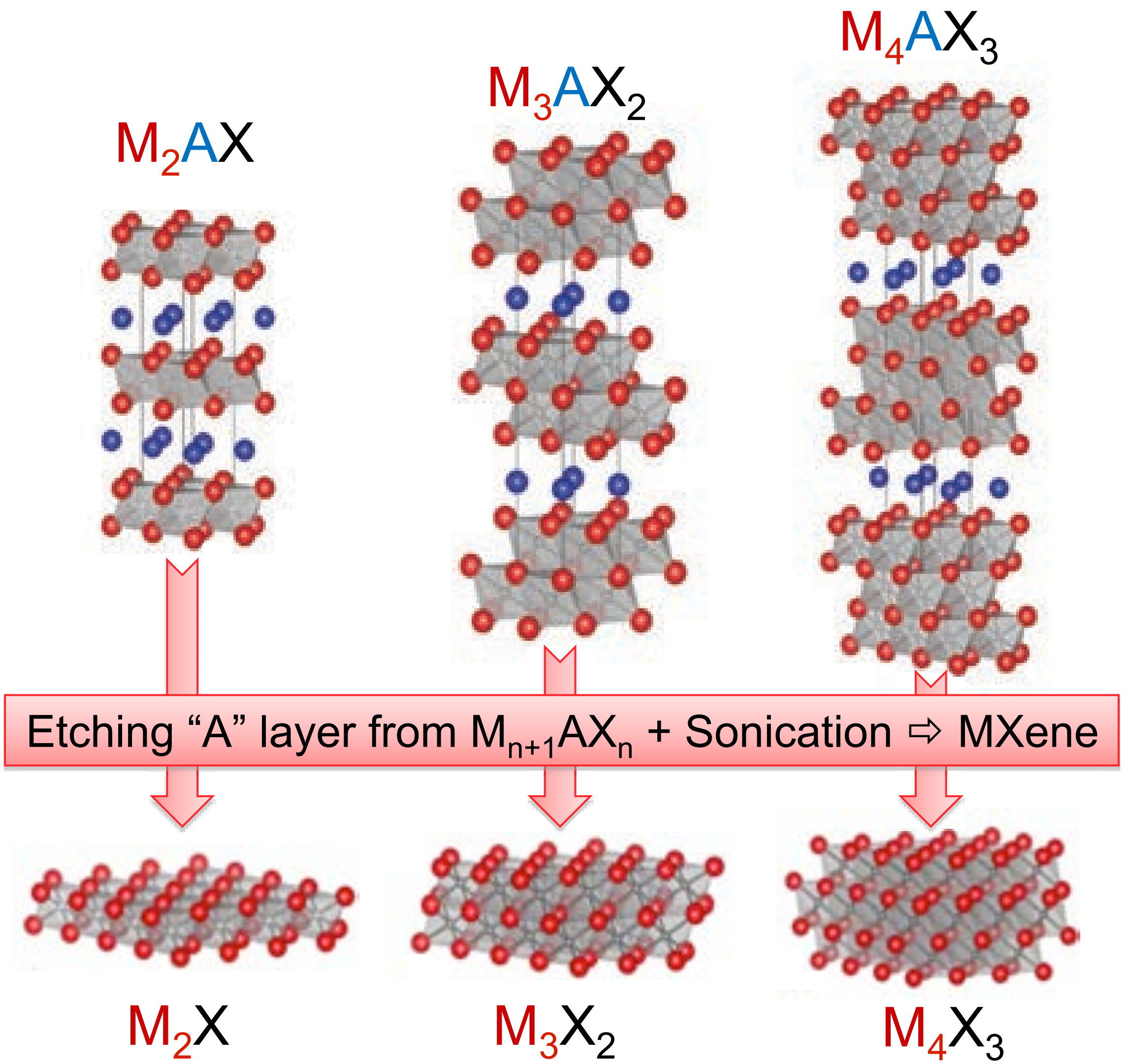
M_4X_3



M. Naguib, et al., ***Advanced Materials*** (2011)
M. Naguib, et al., ***ACS Nano*** (2012)
O. Mashtalir, et al., ***Nature Comm.*** (2013)
M. Lukatskaya, et al., ***Science*** (2013)
M. Naguib et al., ***Advanced Materials*** (2014)

Drexel UNIVERSITY

MXenes: 2D Transition Metals Carbides and Nitrides



Metallic conductivity

Hydrophilic

Tunable band gap

Paper, films, composites

Intercalation of organics

Cations intercalated:

H^+, NH_4^+, Li^+, Na^+, K^+, Cs^+, TMA^+

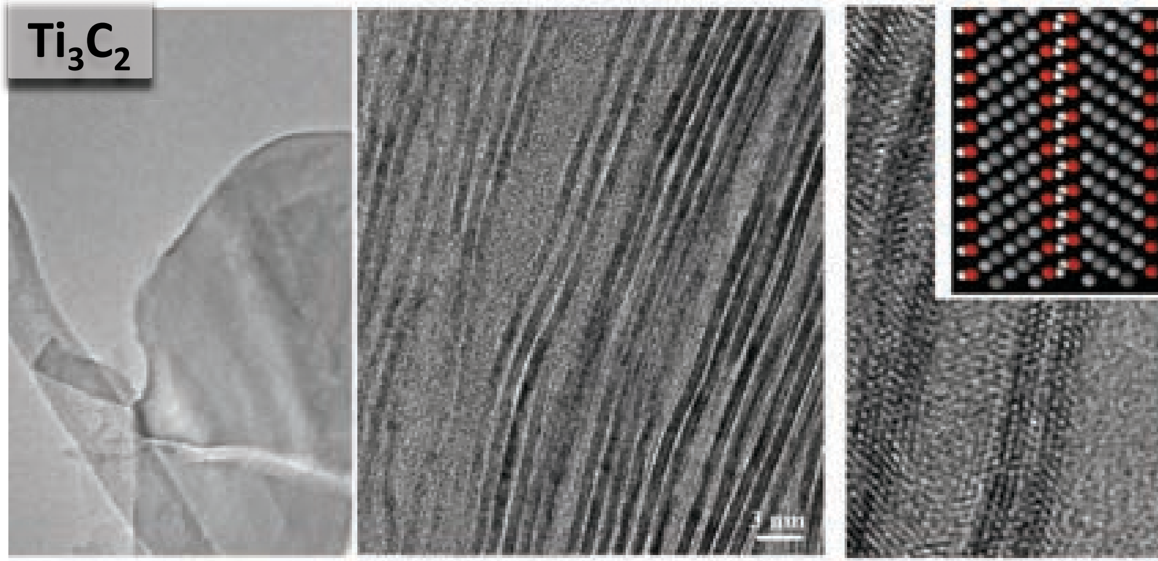
Mg^{2+}, Al^{3+}

Pb^{2+} (Q. Peng, *JACS*, 2014)

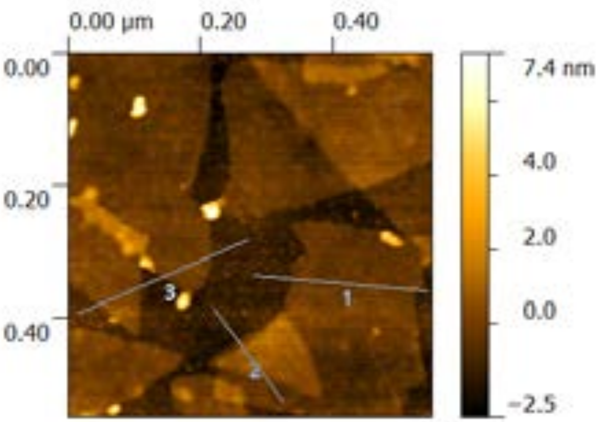
Eleven 2D carbides and carbonitrides produced in about 3 years

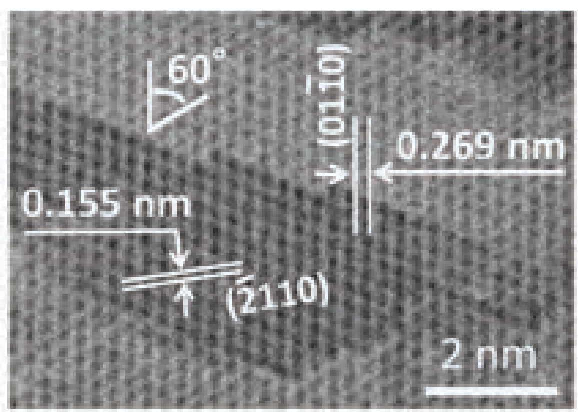
MXene Nanosheets

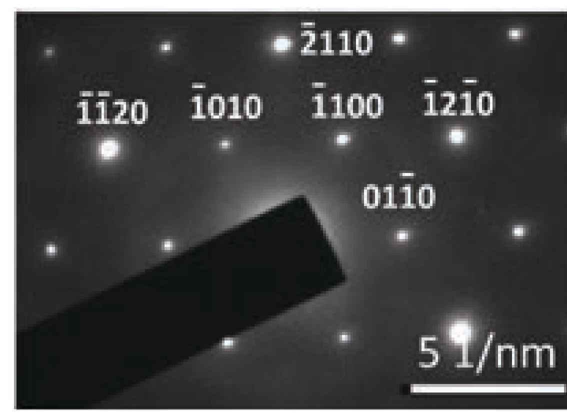
Optically transparent



TEM and SAED characterization



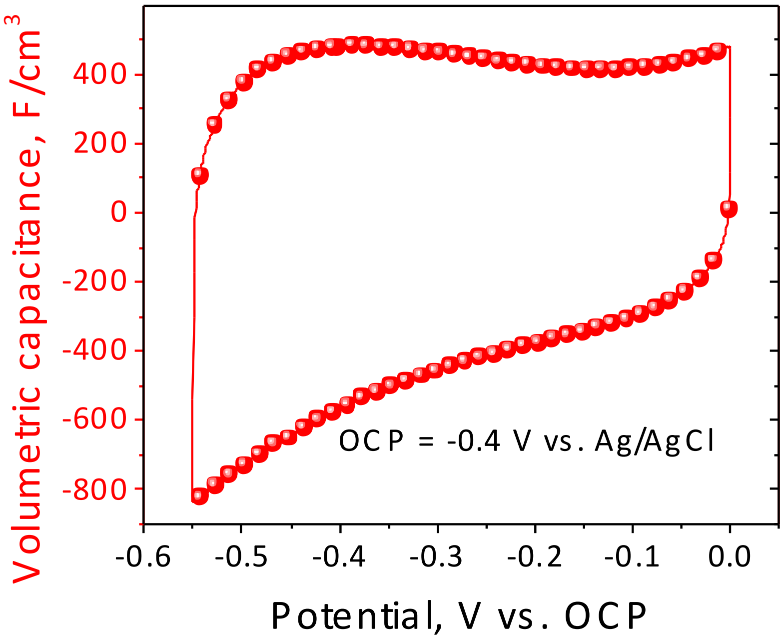


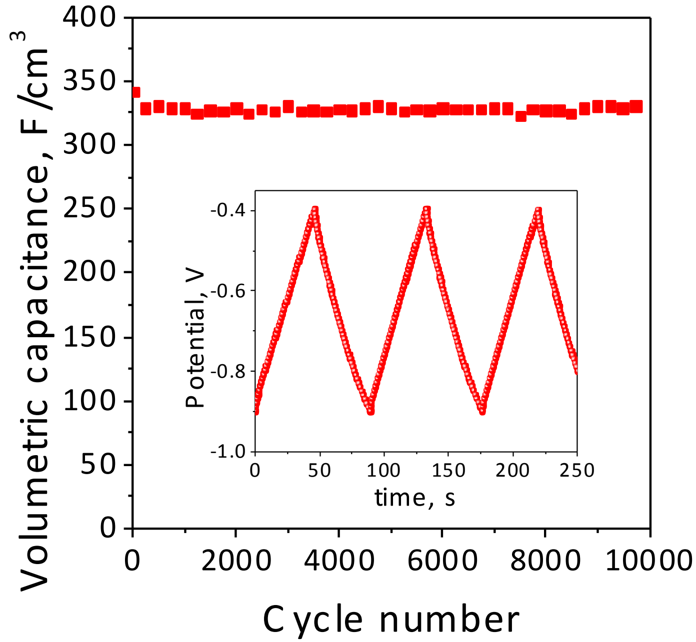


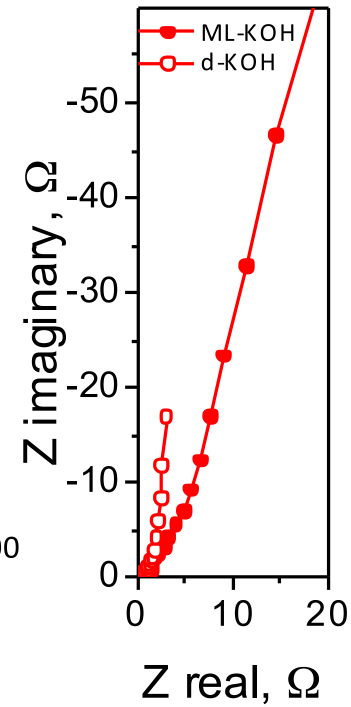
AFM shows ~1 nm flake thickness

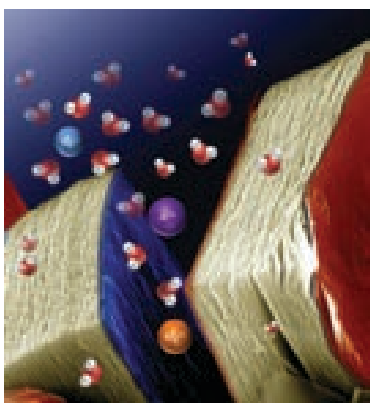
M. Naguib, et al., ***Advanced Materials,*** 23, 4248 (2011)
M. Naguib, et al., ***ACS Nano,*** 6, 1322 (2012)
J. Halim et al., ***Chem. Mater***., (2014)

Electrochemistry of Delaminated Ti_3C_2







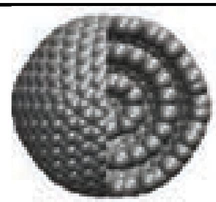
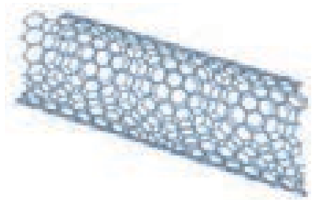
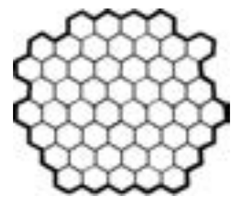
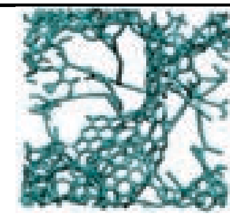
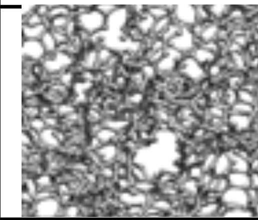
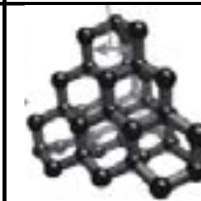


- Very high volumetric capacitance in KOH, Mg_2SO_4 and other aqueous electrolytes
- Intercalation capacitance – new science to be explored
- Excellent cyclability
- Low electronic resistance – additive free, flexible "paper" electrodes

M. Lukatskaya, *et al.*, ***Science***, *341*, 1502 (2013)

M. Lukatskaya, *et al.*, ***Nature***, Nov. 2014

Summary of Carbon-based Nanomaterials for Energy Storage

Material	Carbon onions	Carbon nanotubes	Graphene	Activated carbon	Carbide derived carbon	Templated carbon
Dimensionality	0-D	1-D	2-D	3-D	3-D	3-D
Conductivity	High	High	High	Low	Moderate	Low
Volumetric Capacitance	Low	Low	Moderate	High	High	Low
Cost	High	High	Moderate	Low	Moderate	High
Structure						

- We can **design carbon nanostructures** for specific applications. Pore size, surface area, accessibility, conductivity, surface chemistry and other parameters can be controlled.
- Carbon allows truly **nanoscale engineering** of materials for sorption of ions, gases, biomolecules, etc.
- New carbon-containing low-dimensional materials further broaden the palette.

P. Simon, Y. Gogotsi, ***Accounts Chem. Res.***, *46*, 1094 (2013)

Acknowledgement

National Science Foundation
WHERE DISCOVERIES BEGIN

U.S. DEPARTMENT OF
ENERGY

FIRST Center
Catalysis for Energy
Fundamental Interface Science
Electrical Energy Storage
Fluid-Solid Interface Models
Nanotextured & Reactive Substrates
Fluid-Mediated Surface Reactions

puf
PARTNER
UNIVERSITY
FUND

DARPA

BES, EERE-BATT

OFFICE OF
ELECTRICITY DELIVERY &
ENERGY RELIABILITY

Thank You!

The edge of the two-dimensional world

B. Anasori et al, ***Science*** 335, 526 (2012)