Activated graphene: A new material for electrical energy storage

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U.S. DEPARTMENT OF ENERGY

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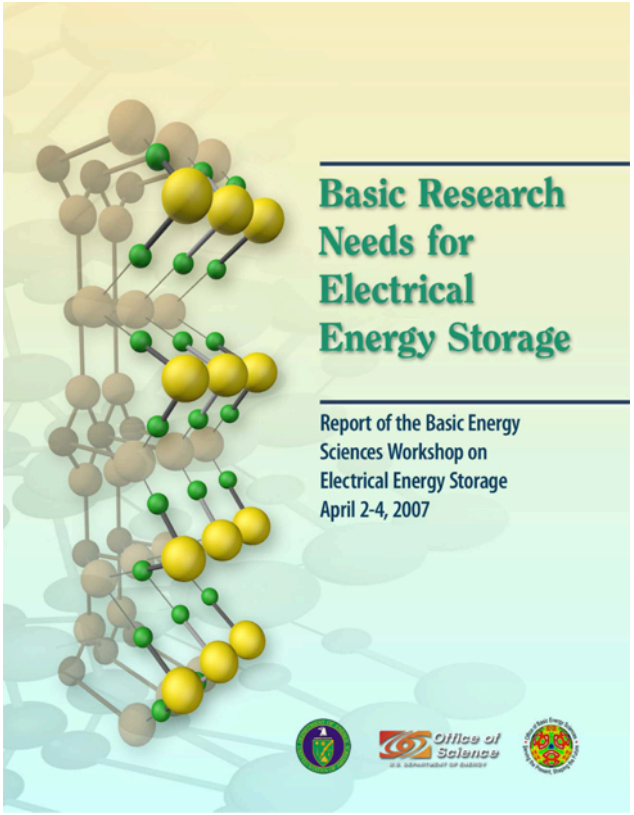
Why do we need new materials for energy storage?

- **Electrical energy Storage refers to the ability to store electrical energy in a form that is readily available for later usage**
- **It is one of the most critical energy challenges**
  - **Consumer electronics**
    - **Efficient, safe, cheaper is nice …**
  - **Transportation**
    - **Lightweight, highly-efficient, safe**
      - **Li-ion at present, what next?**
  - **Energy transmission – electric grid**
    - **Cheap, reliable, Did I mention cheap?**



"The performance of current EES technologies falls well short of requirements for using electrical energy efficiently in transportation, commercial, and residential applications."

Why do we need new materials for energy storage?

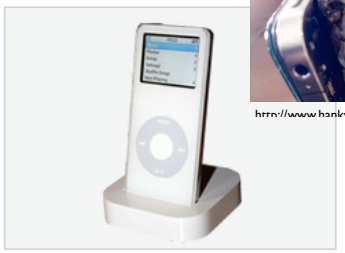
ELECTRONICS

Apple recalls first-gen iPod nano for bad batteries

Nov 14, 2011 10:15 AM

On Friday, Apple issued a recall for its first-generation iPod nano. The iconic digital music player has built-in rechargeable batteries that may overheat and pose a "safety risk."

According to Apple, the problem affects only certain iPod nanos that contain defective batteries from one specific supplier. The faulty nanos were sold between September 2005 and December 2006. Says Apple:



"While the possibility of an incident is rare, the likelihood increases as the battery ages."

http://news.consumerreports.org/safety/2011/11/apple-recalls-first-gen-ipod-nano-for-bad-batteries.html

http://www.telegraph.co.uk/news/1526424/Exploding-laptops-

17 January 2013 Last updated at 09:

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Fiery Tesla crash torpedoes stock price

Li-ion batteries in personal electronics and transportation

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GM Lithium-Battery Explosion Sparks Fire at Company Test Lab

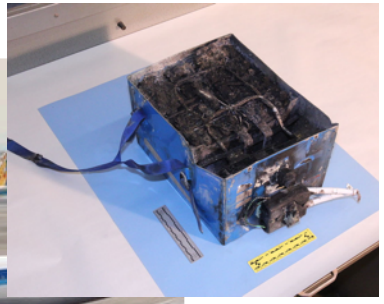
By Tim Higgins - Apr 11, 2012 4:06 PM ET

13 COMMENTS QUEUE

General Motors Co. (GM), maker of the Chevrolet Volt plug-in hybrid sedan, said a test battery exploded at a research facility near its Detroit headquarters.

http://www.bloomberg.com/news/2012-04-11/gm-lithium-battery-lab-explosion-injures-2-fire-

Dreamliner: Boeing 787 planes grounded on safety fears



There are 50 Boeing 787 Dreamliners at airlines around the world

All of Boeing's 50 flagship 787 Dreamliners have been temporarily taken out of service amid safety concerns.

Related Stories

Why do we need new materials for energy storage?

Integration of renewable energy into the 'smart grid'

- **Intermittency**

SMARTGRID.GOV

Why do we need new materials for energy storage?

Weather leads to between $18B and $33B / year in losses*

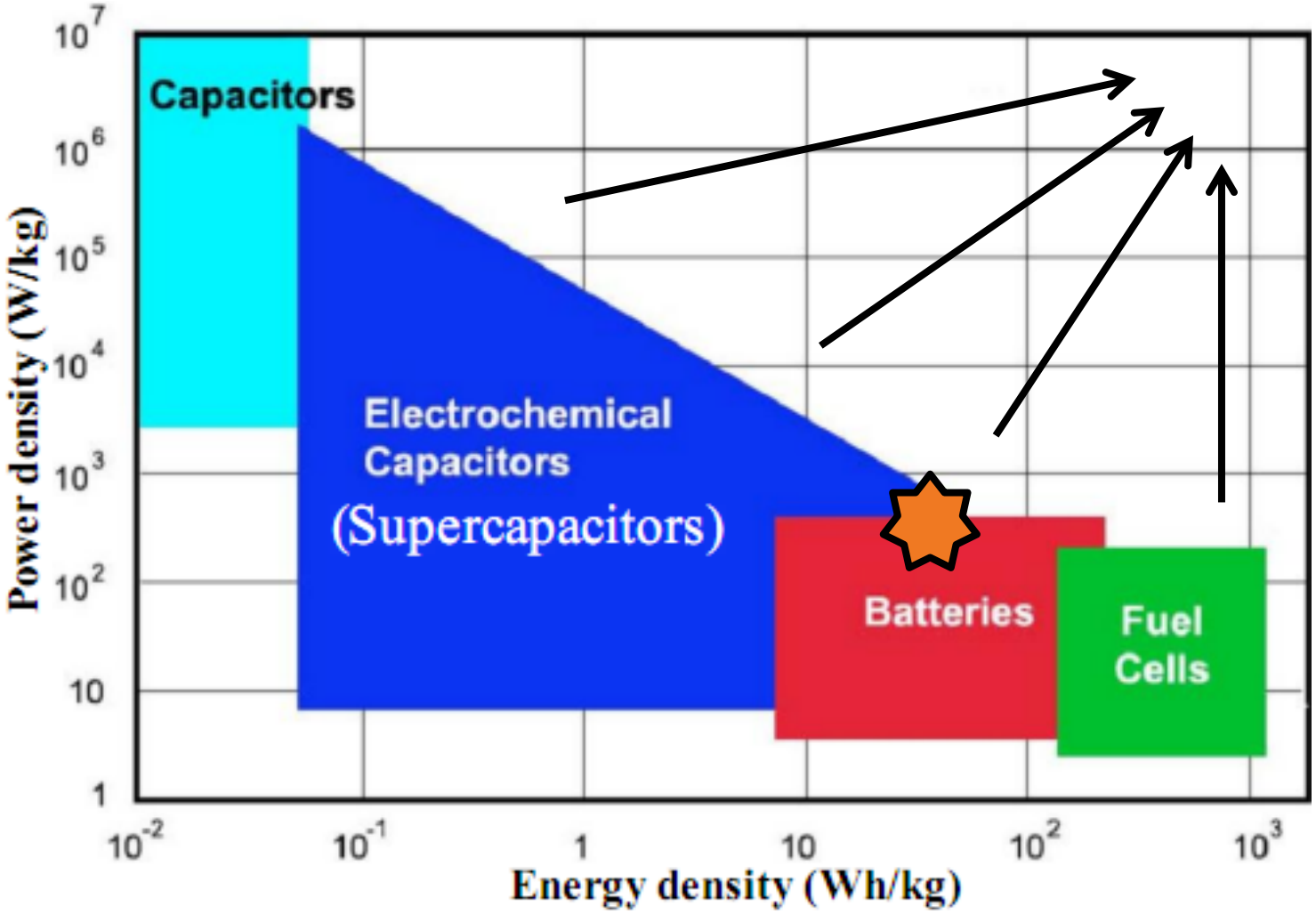
- **Hurricane Sandy: between $27B & $55B**
- **90% of Suffolk County without power**
- **50 deaths attributed to power outages**

A 'smart grid' increases the resiliency of the grid

Breezy Point, Queens after Hurricane Sandy

* ECONOMIC BENEFITS OF INCREASING ELECTRIC GRID RESILIENCE TO WEATHER OUTAGES, Executive Office of the President, August 2013
http://energy.gov/sites/prod/files/2013/08/f2/Grid%20Resiliency%20Report_FINAL.pdf

Different available technologies



Back story – Part 1

- **Rod Ruoff @ University of Texas at Austin**
- **Had synthesized a new material with "extraordinary properties" as a "supercapacitor"**
- **But what exactly was it?**

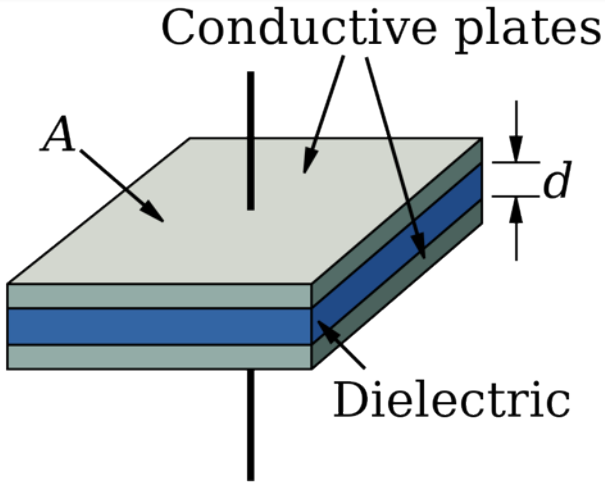
THE WHO'S WHO IN SCIENCE

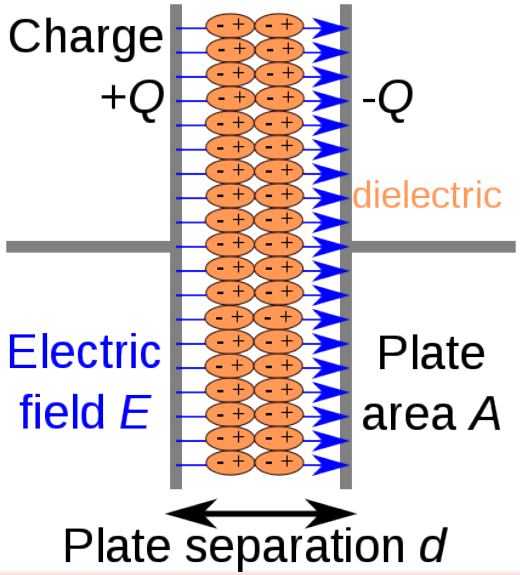
Honoring the **hottest** researchers and **hottest** research papers of 2012.

READ REPORT

Capacitors

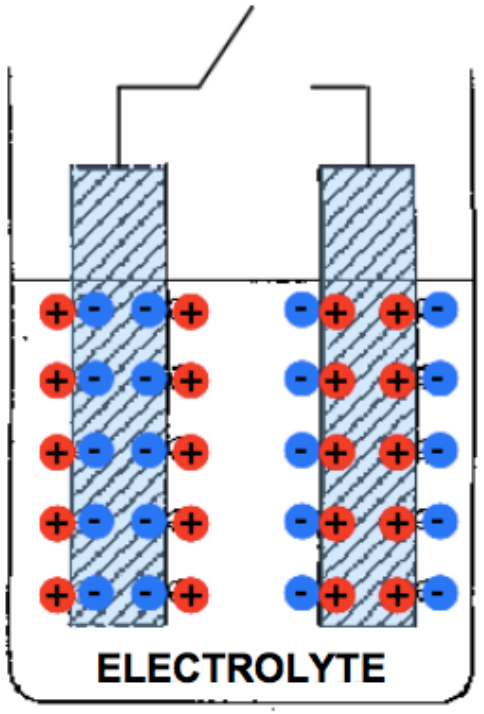
- Capacitors store electrical charge in a dielectric media
- This is conventionally a ceramic material
  - Ceramics do have electrons that move freely in the material
  - Thus they do not conduct electric charge
- Good dielectrics store charge by having electrons that can shift ("polarize") in an applied field





Electrochemical Capacitors: "Supercapacitors"

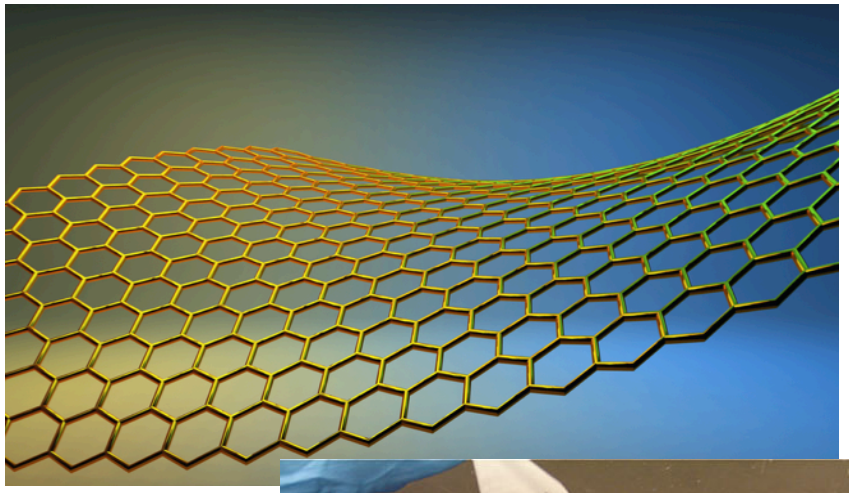
- **Batteries transfer charged ions from one electrode to a second electrode by an fluid (electrolyte).**
  - **A chemical reaction occurs at the interface to store the charge**
- **Supercapacitors store charge physically at interfaces in the material**
  - **Application of a voltage separates charge in the electrolyte to the interfaces**
  - **When voltage is removed the charge is stored**
- **Advantages:**
  - **Rapid charge & discharge**
  - **No chemical degradation – huge numbers of cycles**
- **Disadvantage:**
  - **Low energy density – can't store as much as a battery**

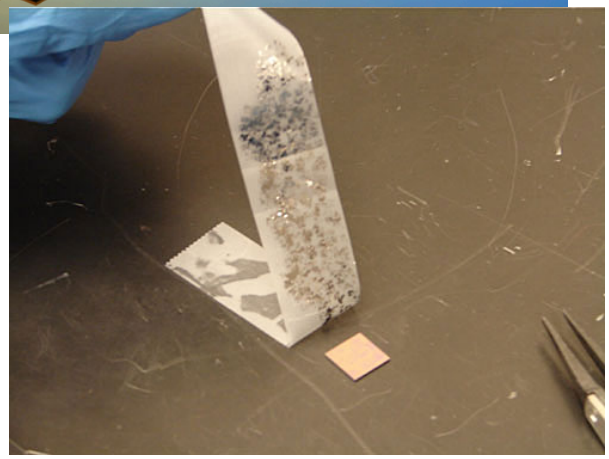


Charged double layer persists after power source is removed, providing a source of stored electric energy.

Back story – Part 2: Graphene

- **Graphene 'discovered' in 2003**
  - **A new form of carbon – a sheet of carbon atoms one atomic layer thick**
- **Amazing properties**
  - **Super strong & elastic**
  - **Highly electrically conductive**
  - **Highly thermally conductive**





The Nobel Prize in Physics 2010

Photo: U. Montan
Andre Geim

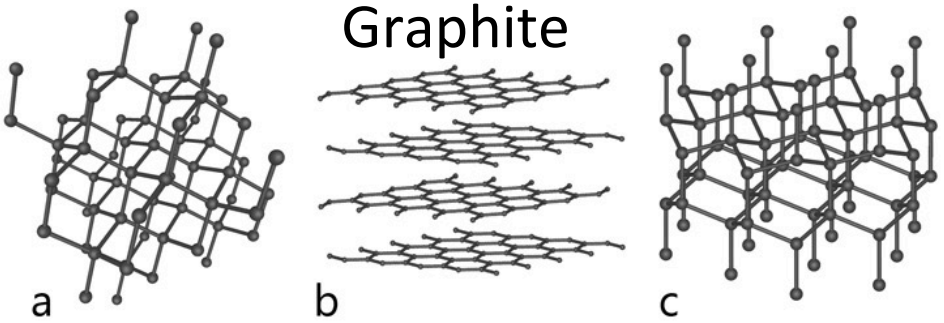
Photo: U. Montan
Konstantin Novoselov

The Nobel Prize in Physics 2010 was awarded jointly to Andre Geim and Konstantin Novoselov *"for groundbreaking experiments regarding the two-dimensional material graphene"*

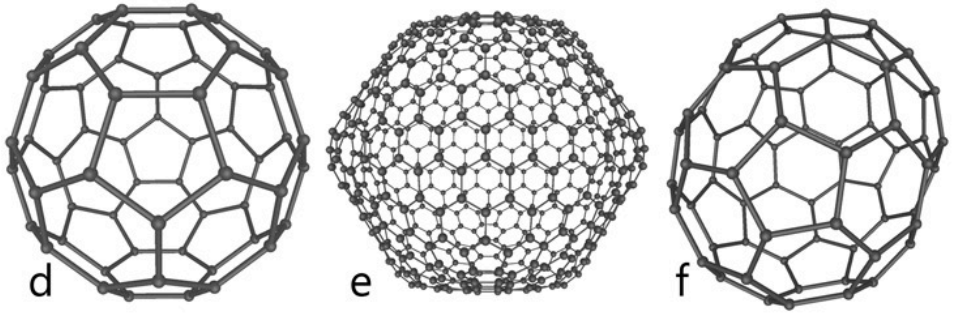
Back story – Part 2: Graphene

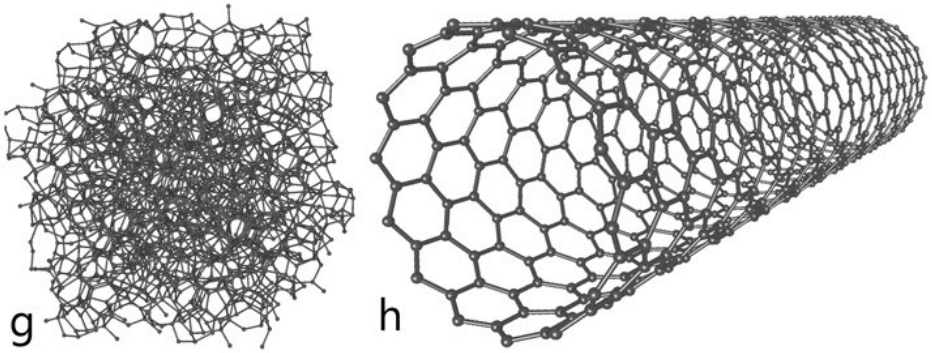
Diamond

Graphite



"Bucky-balls"
Nobel Prize in Chemistry to Smalley, Kroto and Curl in 1996

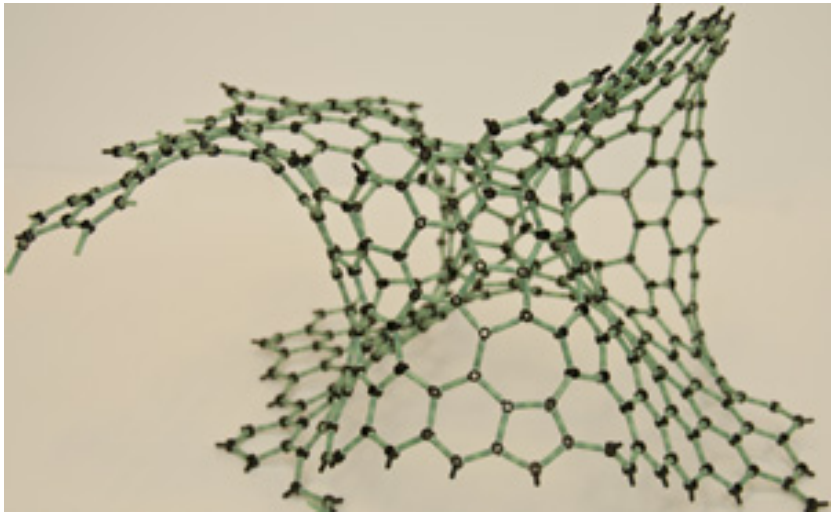


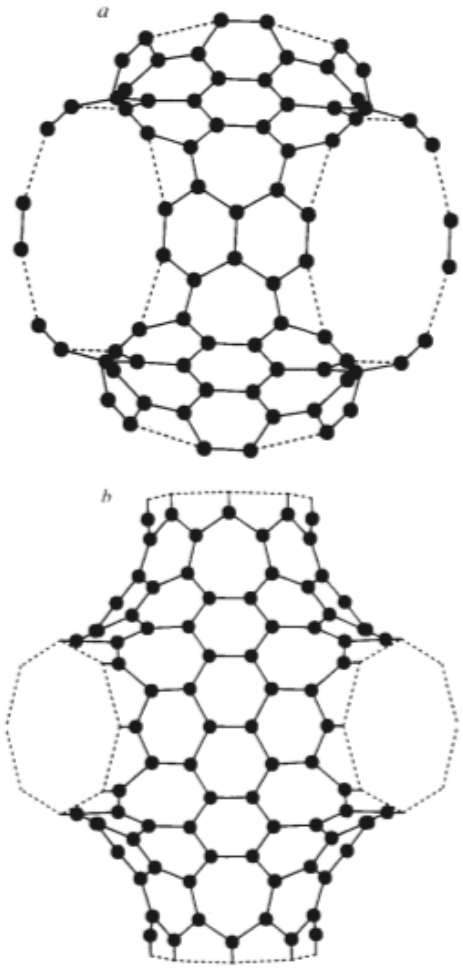


Carbon Nanotubes
Inaugural "Kavli Prize" for Nanoscience, to Sumio Iijima in 2008

Back story – Part 2: Graphene

- **Why not 'negative curvature' carbon?**
- **Theoretically predicated to be energetically favorable***
- **Despite 20+ years since predication, no prior observations**

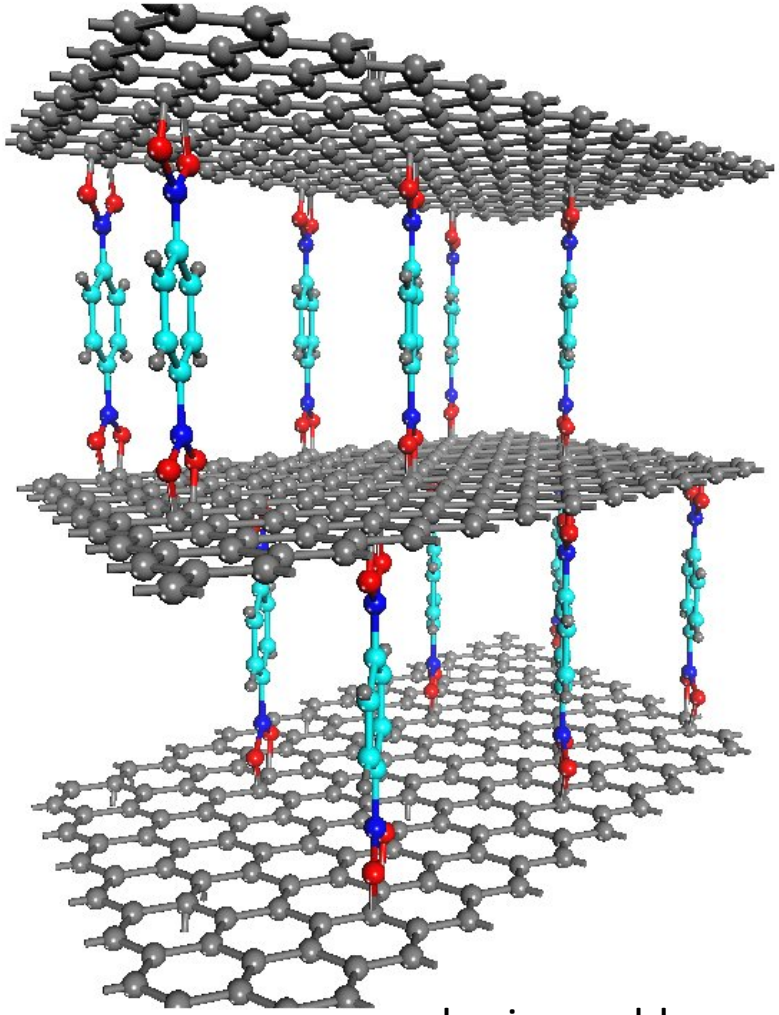




*Lenosky, et al., Nature, 355, 1992

Back story – Part 3: Graphene oxide

- Graphene oxide is a material that is available in ton qualities
- Oxygen 'linking groups' hold together graphene sheets
  - These groups can be broken through heat or chemical attack



www.physicsworld.com

Ruoff group's synthesis approach

Graphene oxide "GO"

Microwave treatment / thermal treatment

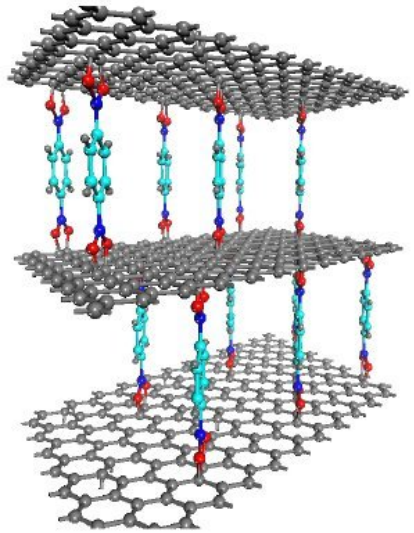
Microwave exfoliated GO "MEGO"

KOH activation

Wash, filter, dry

Heat at 800C in dry Ar

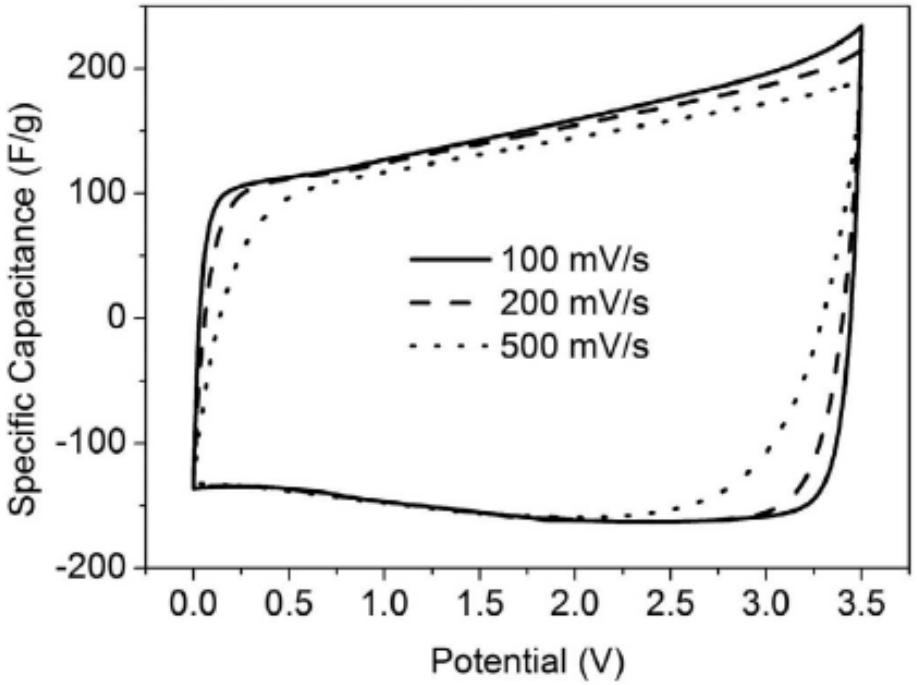
Activated microwave exfoliated GO "a-MEGO"



Manufactured in ton quantities

Electrochemical performance

- **Extraordinary performance as a supercapacitor**
  - **Estimated practical energy of a packaged device of 20 Wh/kg**
    - **4 times higher than existing supercapacitors based on activated carbons**
    - **≈ 70% of a lead-acid battery**



What did the Ruoff group make?

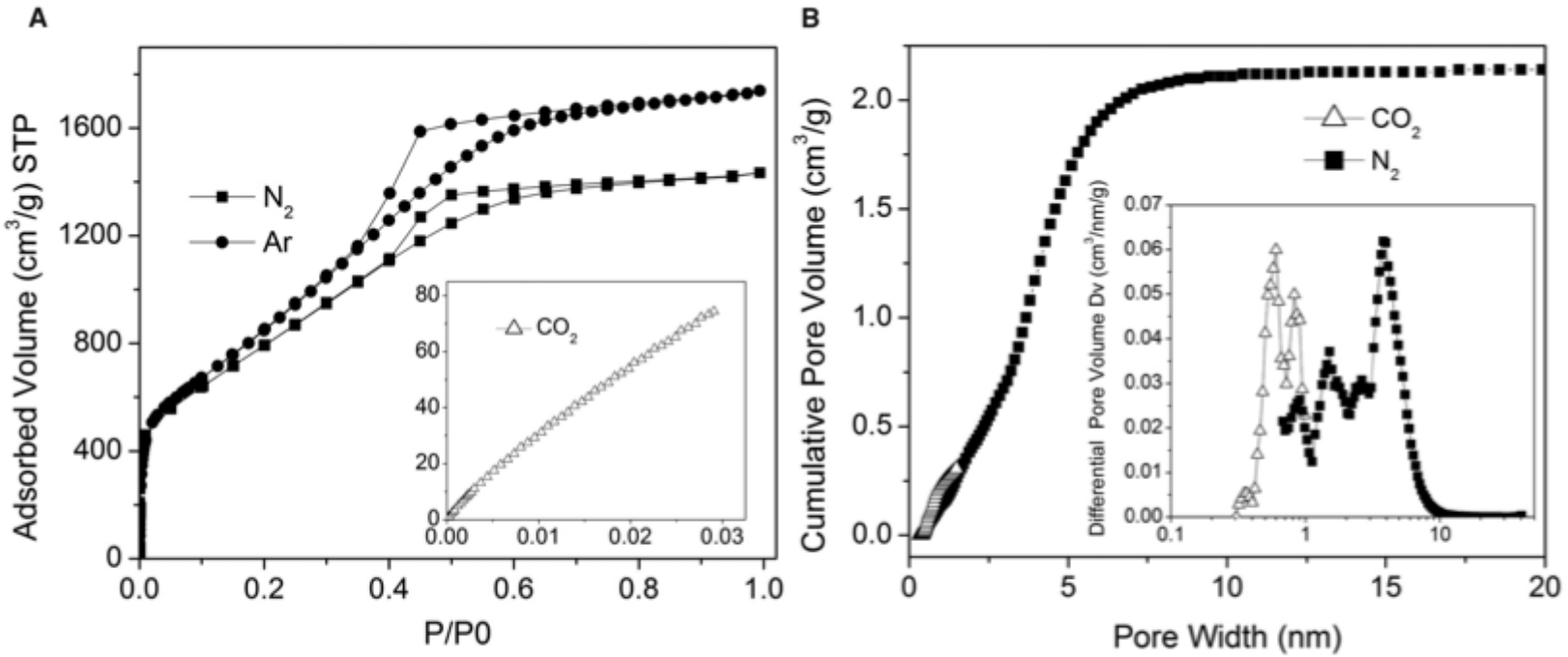


Fig. 3. Gas adsorption/desorption analysis of an a-MEGO sample (SSA ~ 3100 m^2/g). (**A**) High-resolution, low-pressure N_2 (77.4 K) and Ar (87.3 K) isotherms. (Inset) The CO_2 (273.2 K) isotherm. (**B**) Cumulative pore volume and (inset) pore-size distribution for N_2 (calculated by using a slit/cylindrical NLDFT model) and CO_2 (calculated by using a slit pore NLDFT model).

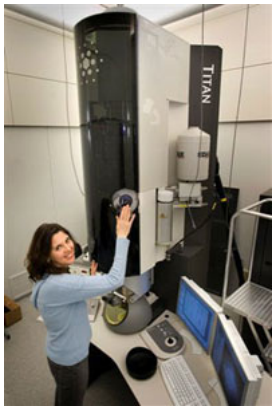
- **By measuring infiltration of N_2, Ar and CO you can determine the size of pores**
- **It was found to be a highly porous material**
  - **Distribution of pore sizes between 0.6 nm and 5 nm**

This is where BNL joined in …

- **DOE Labs have amazing resources**
  - **NSLS – bright source of x-rays**
  - **CFN – powerful electron microscopes**
  - **National Center for Electron Microscopy at Lawrence Berkeley National Lab**

National Synchrotron Light Source at BNL

Two 'aberration corrected' electron microscopes at the CFN



The TEAM instrument at the National Center for Electron Microscopy

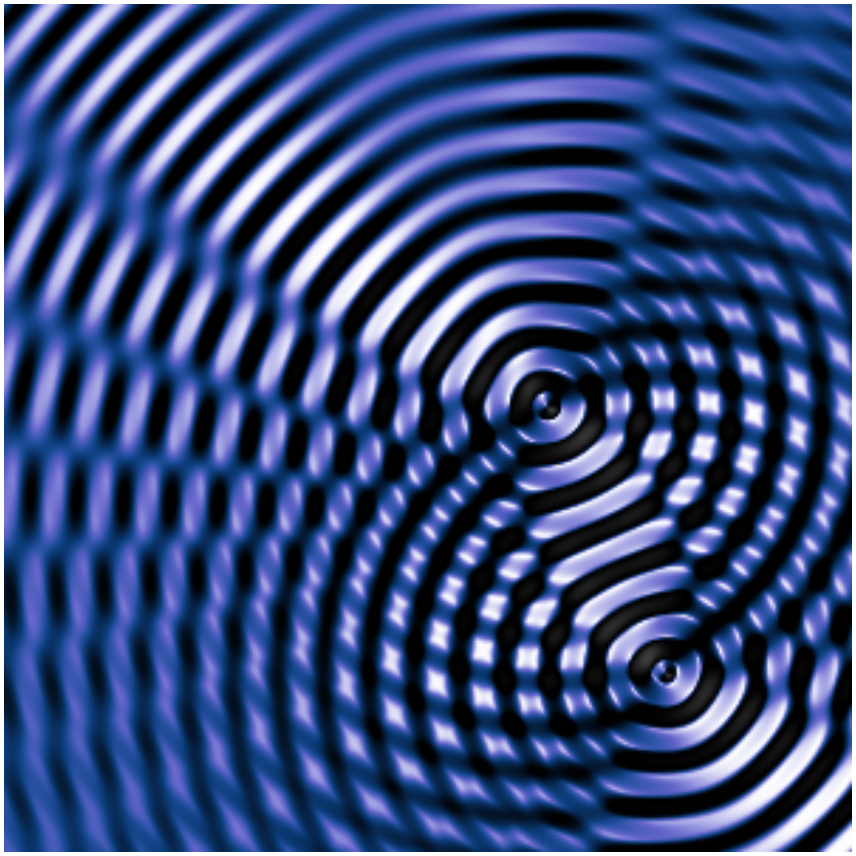
Diffraction of x-rays & electrons

- **Incident waves of x-rays / electrons bounce off of atoms.**
- **If atoms are arranged in a ordered structure there are specific angles where the waves interfere constructively**
  - **$2d \sin\theta = \lambda$**

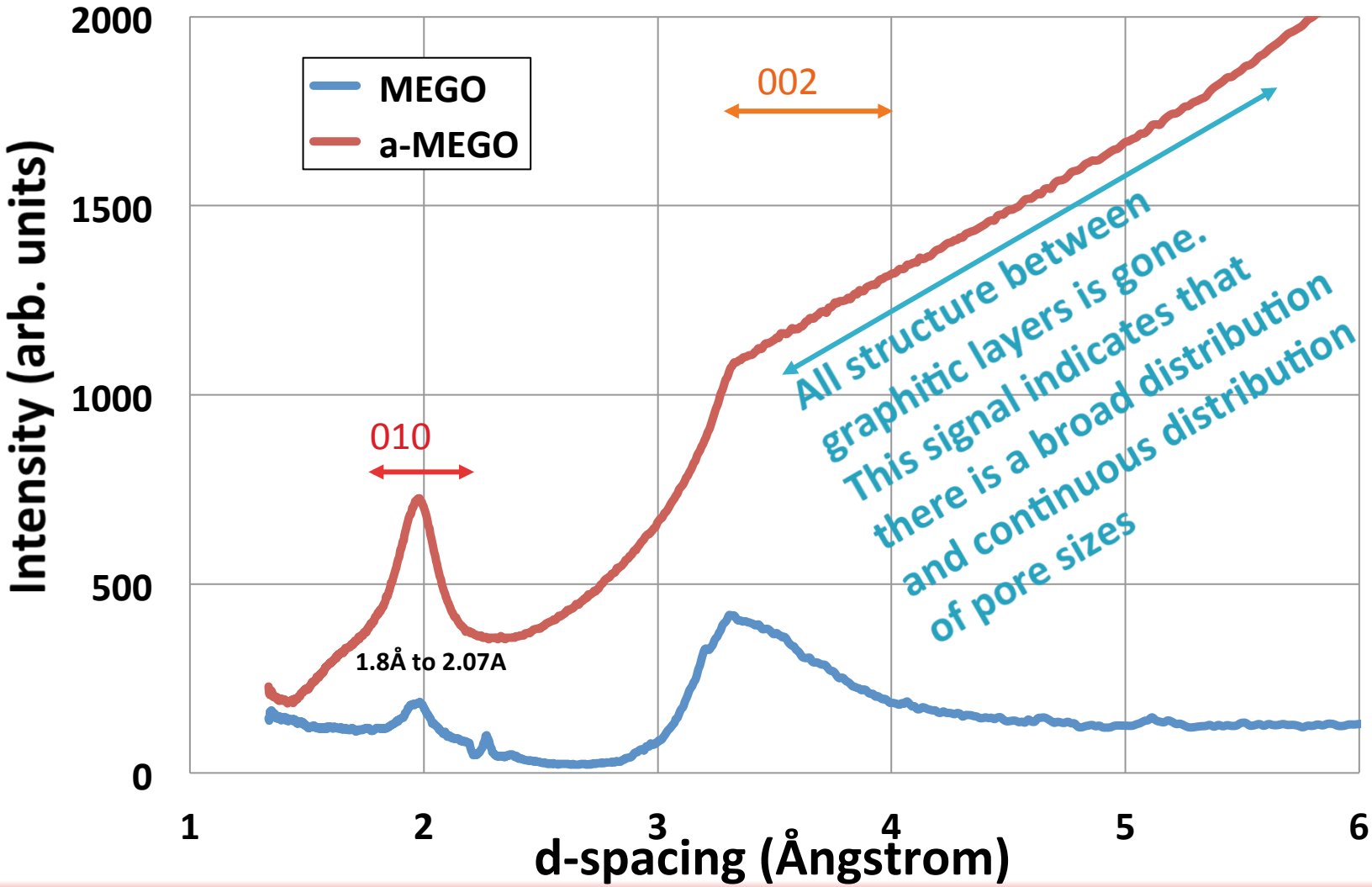
Distance between atomic planes

Angle

Wavelength

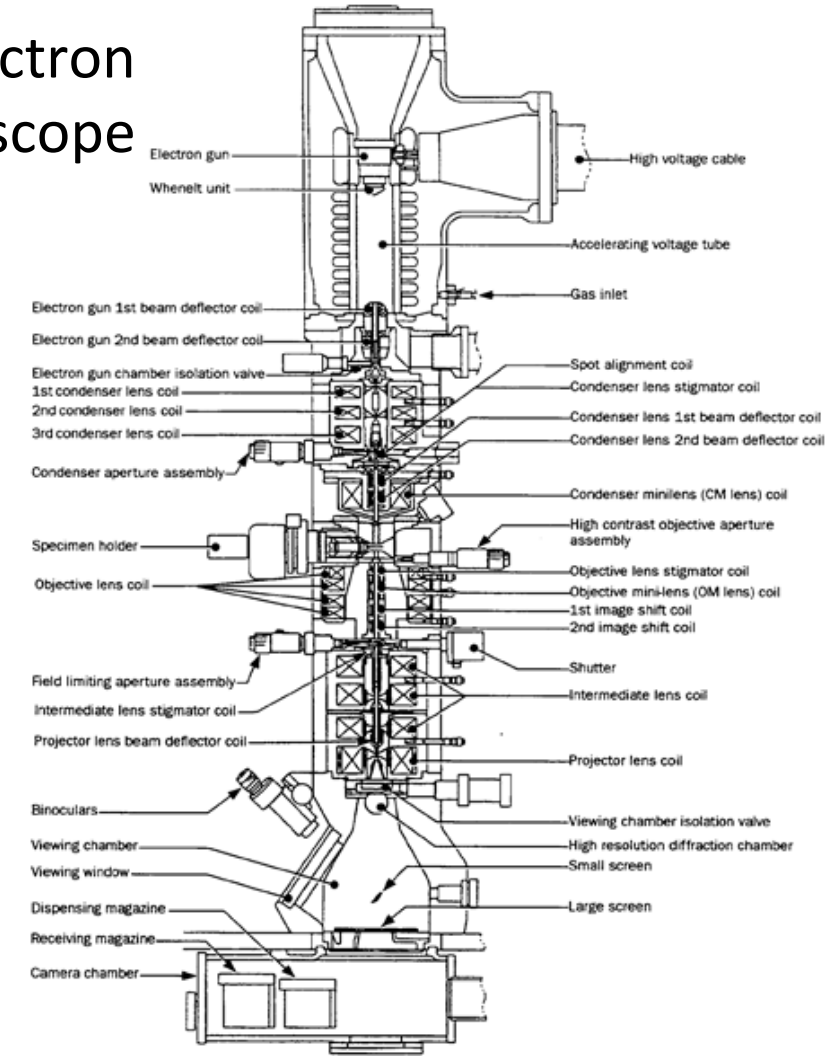


NSLS: Diffraction from MEGO & a-MEGO



Transmission electron microscope

Transmission electron microscope



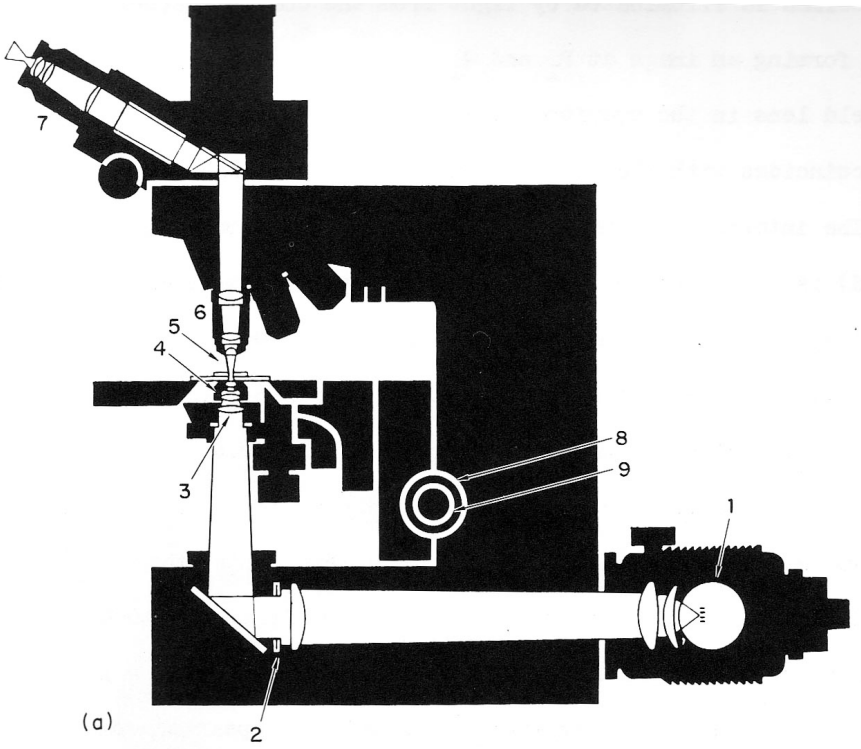
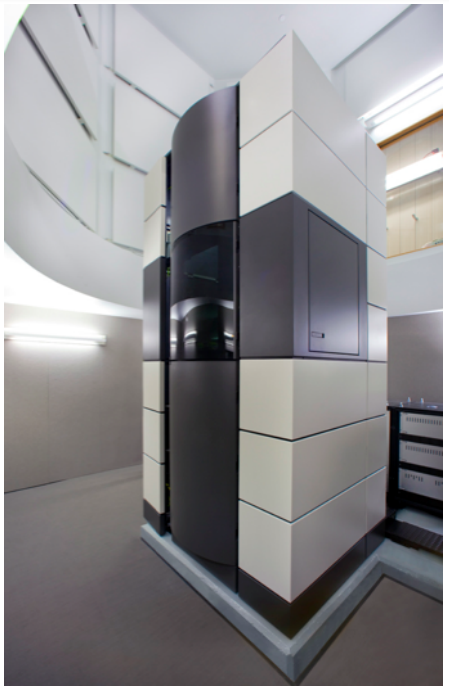


Table-top optical microscope

The best microscopes in the world …

Hitachi HD2700C STEM Probe corrector at the CFN @ BNL

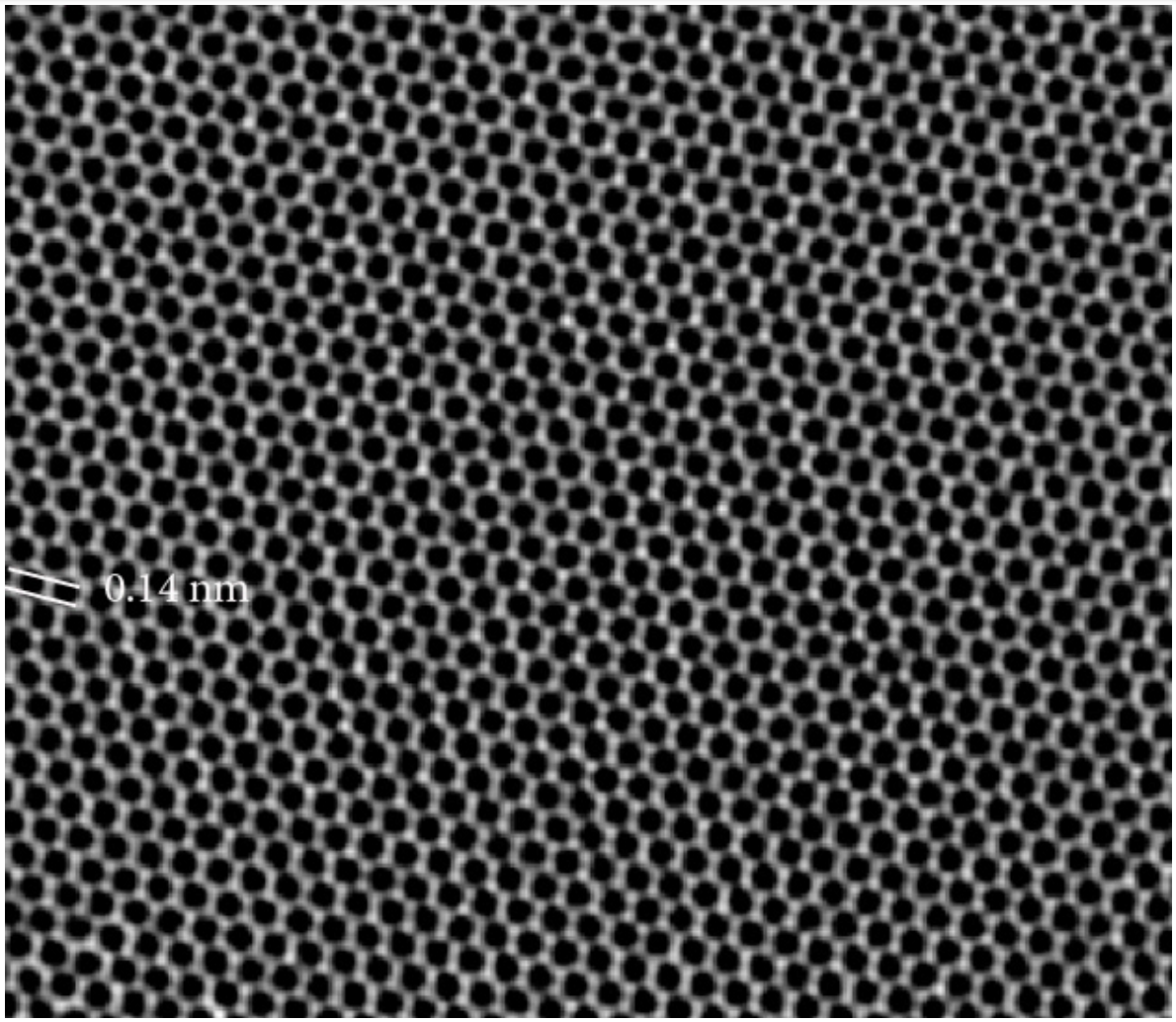
Titan 80-300 - ETEM Image corrector at the CFN @ BNL



TEAM 1.0 instrument @ the National Center for Electron Microscopy @ LBNL

"Triple-C" instrument at AIST in Tsukuba, Japan

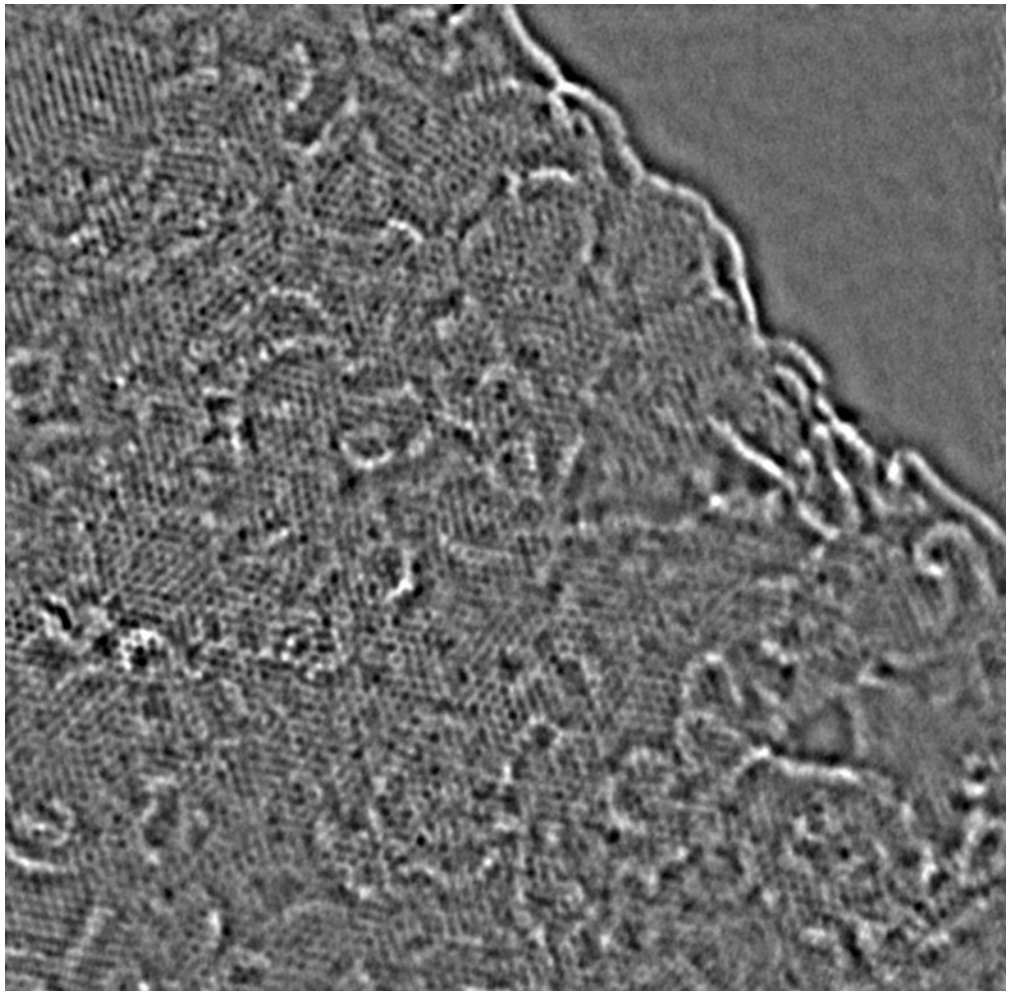
What does graphene look like in the TEM?



http://ncem.lbl.gov/frames/TEAM0.5.htm

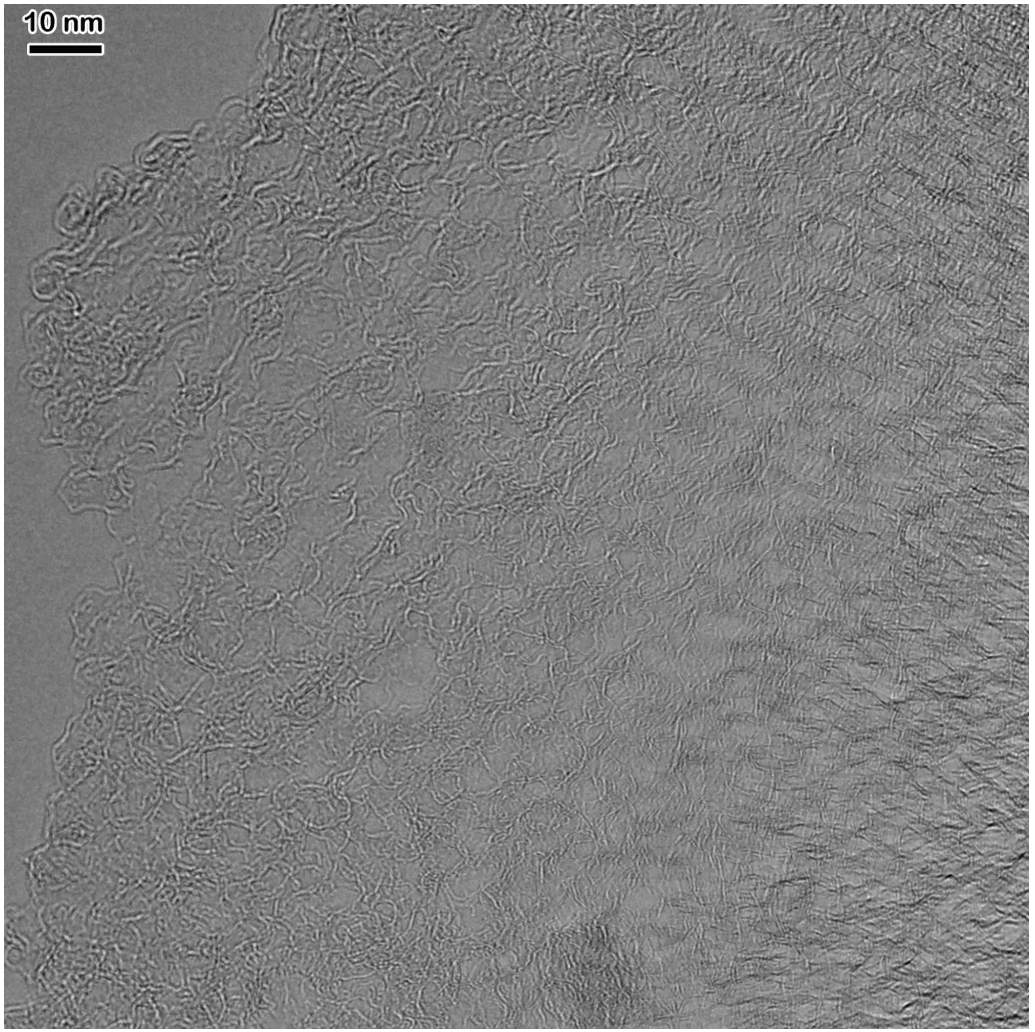
HRTEM images of MEGO

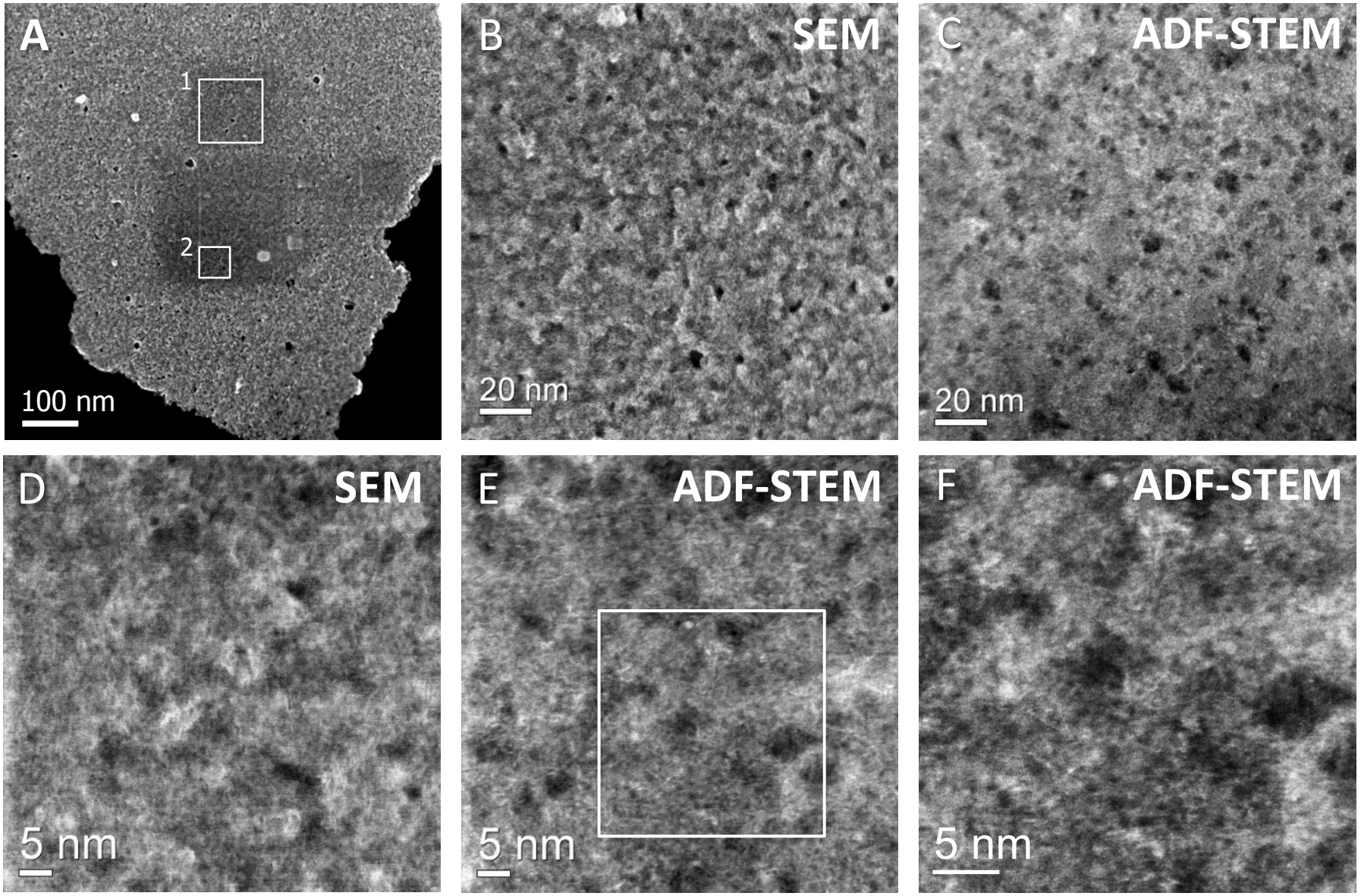
- Exit wave reconstructed image of MEGO
  - TEAM 1.0: Operated at 80kV
- Quite defective in plane
- A bit of crinkle out of plane
- Image consistent with diffraction results



Phase contrast imaging of pores

- **Movie shown is a focal series of images @ 80 kV**
  - **Taken using CFN Titan electron microscope**
- **A continuous network of pores visible**
  - **Size range from ≈ 5Å to 5 nm**
- **Consistent with BET measurements**
  - **Indicate a specific surface area of ≈ 3100 m^2/g**
    - **At the theoretical limit for flat graphene!**



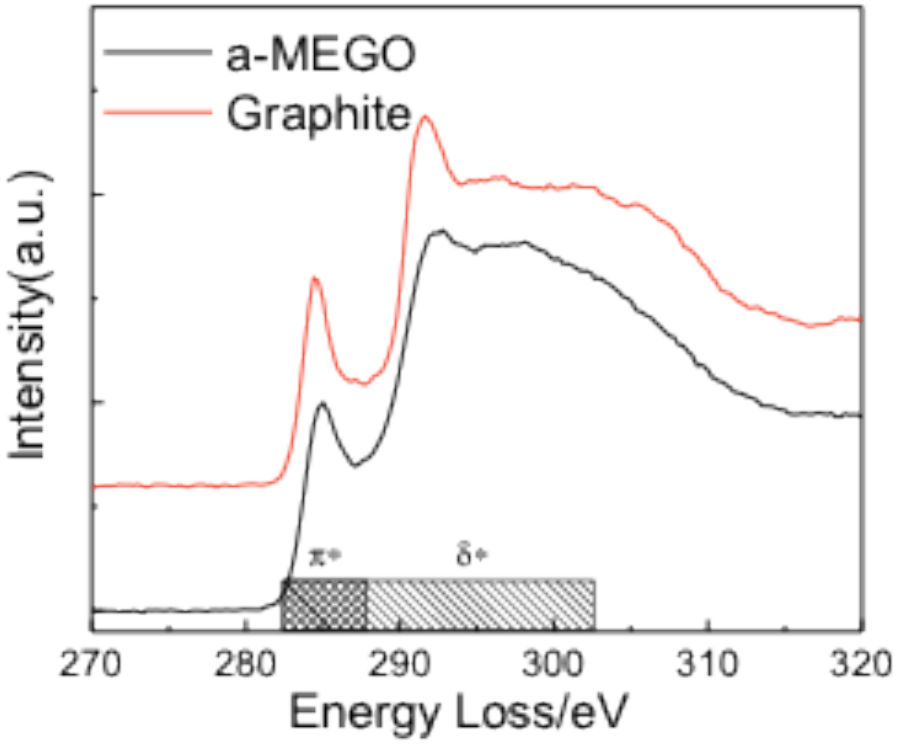


Low magnification SEM (A) and and high magnification SEM (B) and ADF-STEM (C) images of a-MEGO. (B and C) are from the region 1 in (A). Larger pores of between 2 – 10 nm are clearly resolved. Very high magnification SEM (D) and ADF-STEM (E,F) images taken from the region 2 in (A). These images indicate that the entire microstructure is composed of very small pores, of order of ≈ 1 nm in size, as is evident in the magnified portion shown as (F).

Taken using CFN Hitachi instrument

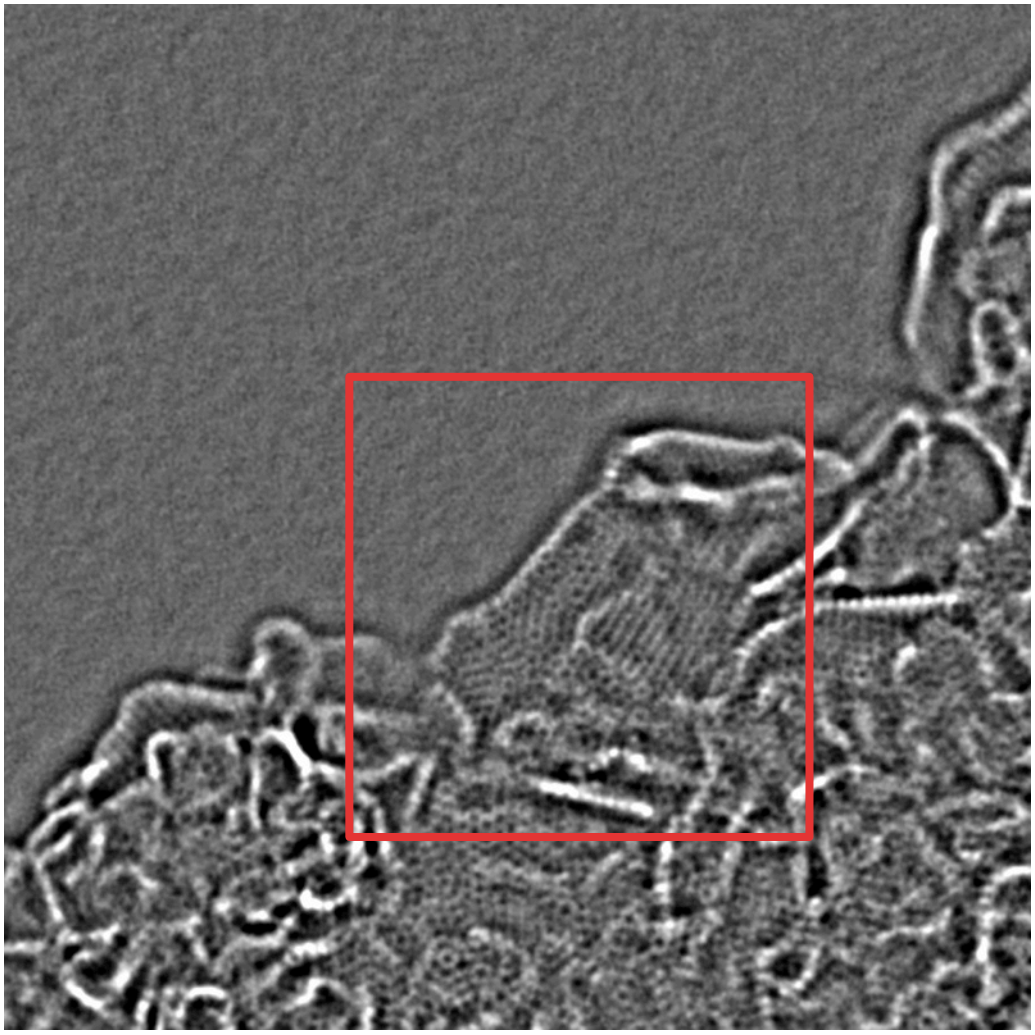
Energy loss spectroscopy from a-MEGO

- **Carbon K edge shows a-MEGO to be sp^2 bonded**
  - **Just like graphite**
- **This means that the structure has returned to a form like the graphene**
  - **At least as far as the electrons are concerned!**
  - **All the atoms are connected**

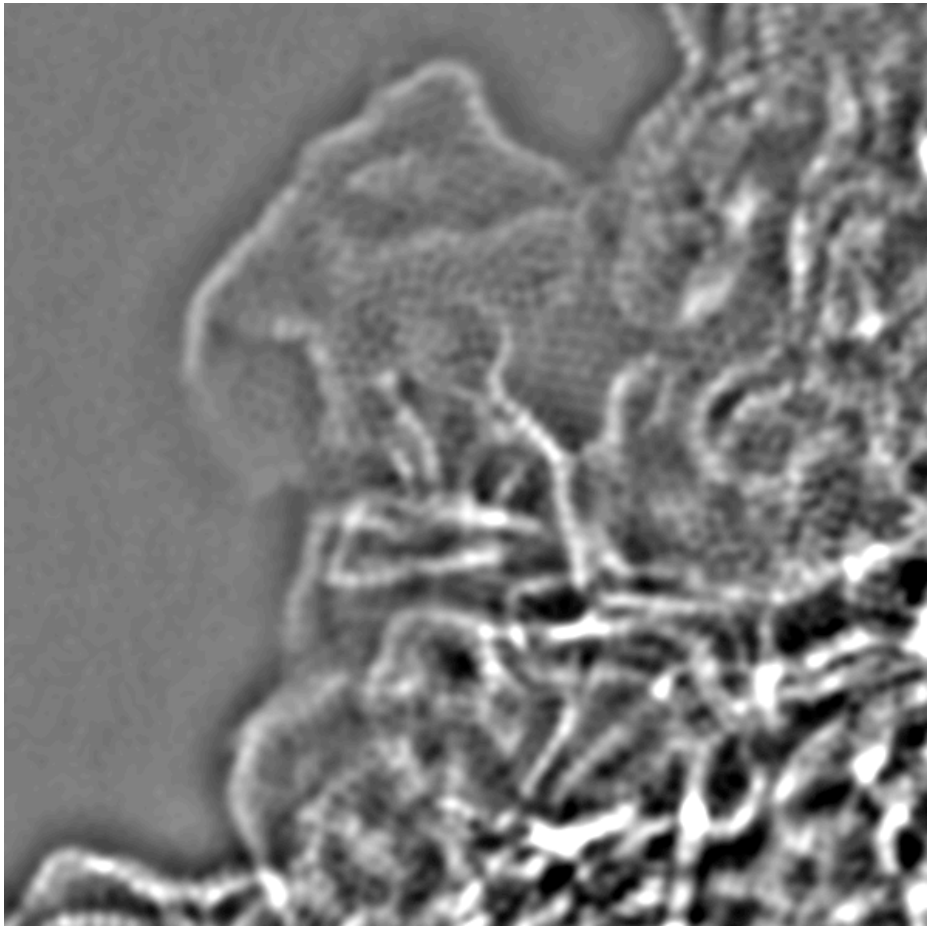


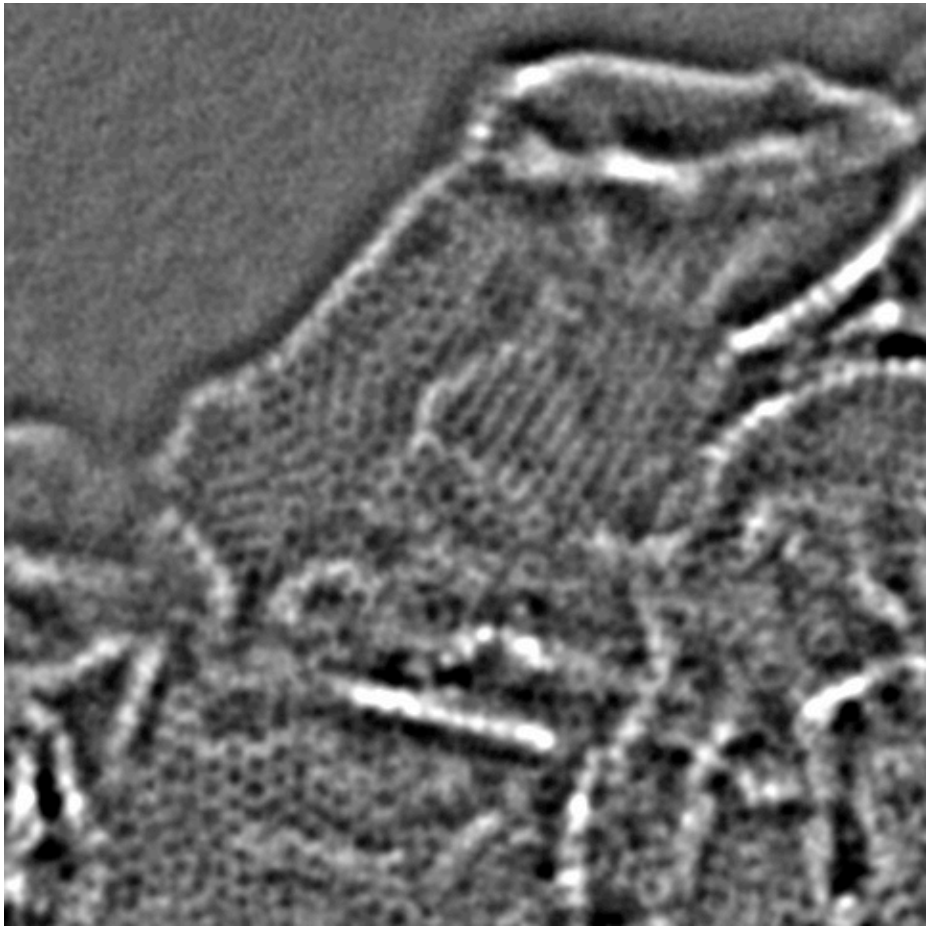
Ultrahigh-resolution images of a-MEGO

- Exit wave reconstructed image of a-MEGO from TEAM instrument
  - At low voltage = little beam damage
- A-MEGO is composed of highly curved, crystalline carbon
- Single sheet carbon, with only occasional 002 correlations



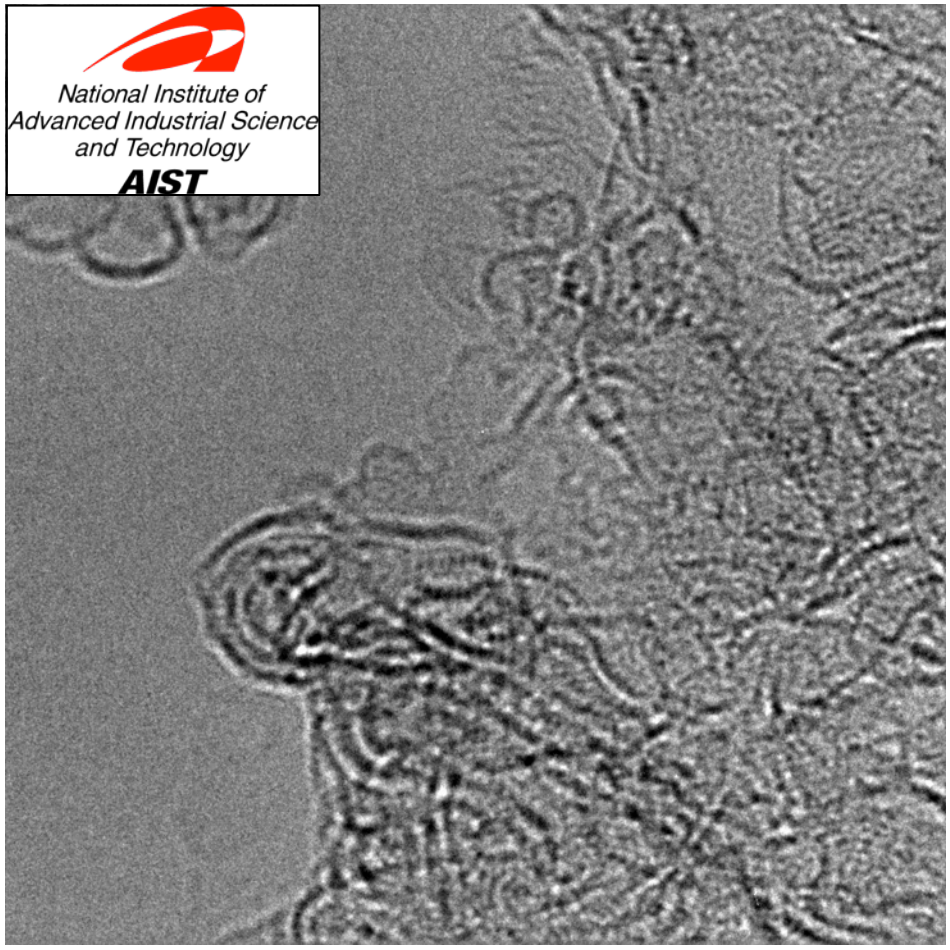
EWR images of a-MEGO



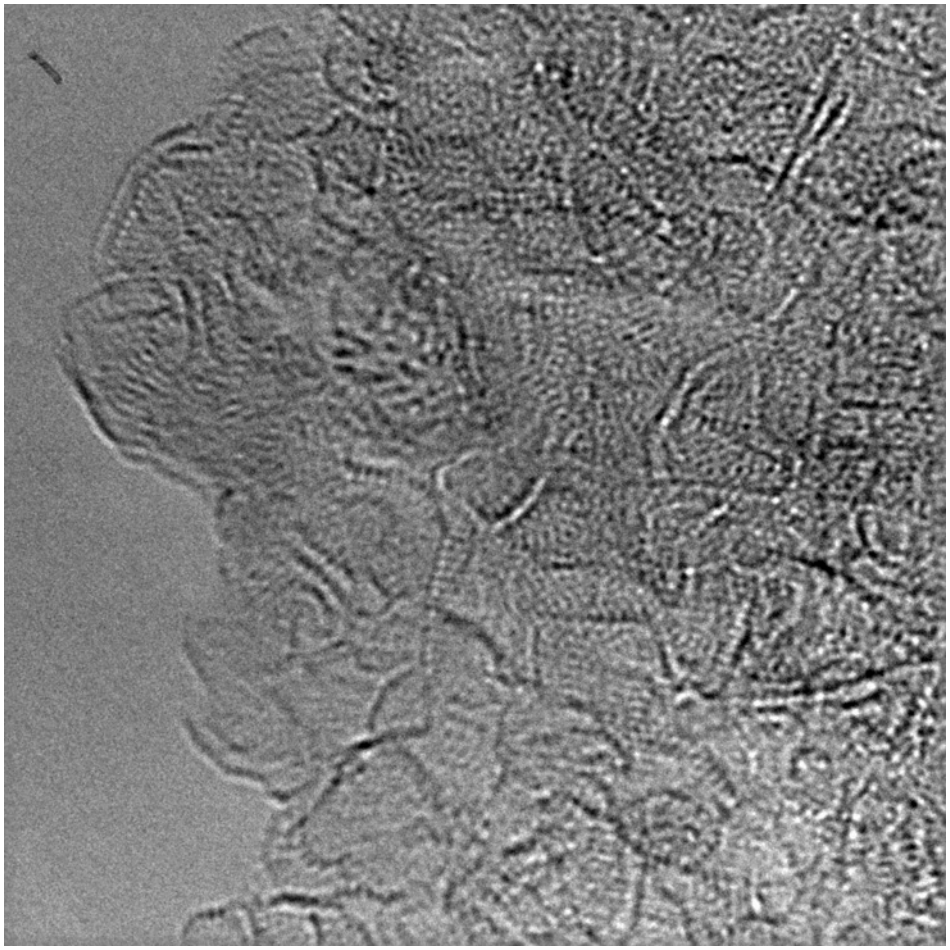


“Triple C” instrument: low dose / low voltage

National Institute of Advanced Industrial Science and Technology
AIST



20 summed images



100 summed images

With Kazu Suenaga

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Summary of a-MEGO structure

- a-MEGO is composed of individual sheets of carbon
- This carbon is sp^2 bonded – just like graphite
- These sheets are crystalline, "in-plane"
- They are composed of 5, 6, 7 and 8 membered rings of carbon atoms
- Nearly all of the atoms are bonded to other carbon atoms
- These sheets are highly curved
- They form a broadly enclosed three-dimensional network of micro- (6Å - 1nm) and mesopores (2 to 10 nm)

a-MEGO is a fundamentally new form of carbon, with extraordinary properties

Wu, et al., Science, 332, 1537, 2011.

Sciencexpress Report
May 11, 2011

> 650 Citations to date

Carbon-Based Supercapacitors Produced by Activation of Graphene

Yanwu Zhu,[1] Shanthi Murali,[1] Meryl D. Stoller,[1] K. J. Ganesh,[1] Weiwei Cai,[1] Paulo J. Ferreira,[1] Adam Pirkle,[2] Robert M. Wallace,[2] Katie A. Cychosz,[3] Matthias Thommes,[3] Dong Su,[4] Eric A. Stach,[4] Rodney S. Ruoff[1]*

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Activated Graphene Makes Superior Supercapacitors for Energy Storage

New material combines high storage capacity with quick energy release and unlimited recharge

May 12, 2011