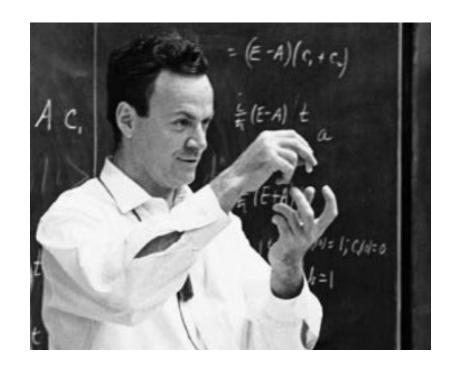


In 1959 Richard Feynman
Delivered a now famous lecture,
"There is Plenty of Room at
the Bottom."

He predicted new discoveries if one could fabricate materials and devices at the atomic scale



For this to happen, he pointed out the necessity of a new class of miniaturized instrumentation to manipulate and measure the properties of these small structures—nanostructures.

Nano = one billionth =  $10^{-9}$ 

#### One nano-Earth



Is a marble!



### Nanotechnology

Nanotechnology will build devices with structural features at the nanometer level.

Why?

Because

Nano is different than bulk

Nano is different than atomic.

Nano is something in between

Nano allows us to control the physical and chemical properties by varying the size of the structure.

### Nanogold is not golden!



Single 5nm Particles

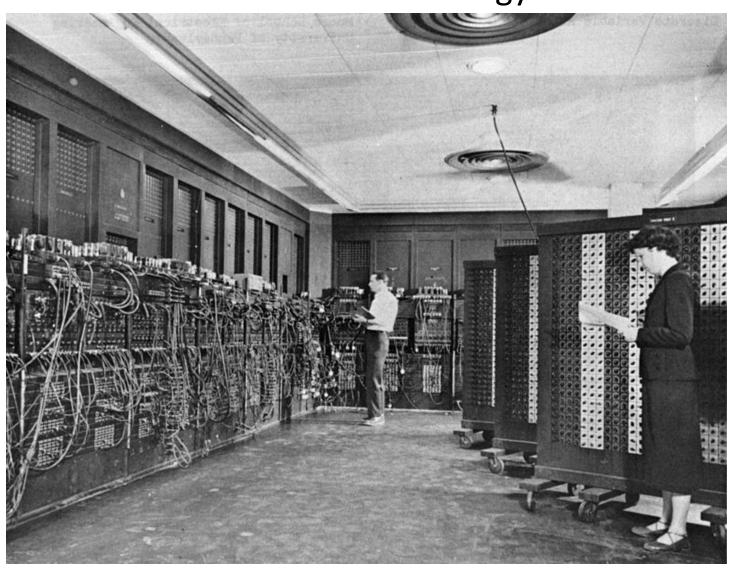
Aggregates

# Nanotechnology will build from the <u>bottom</u> <u>up</u>, rather than the top down.

# The canonical example of top down: The computer

# Electronic Numerical Integrator And Computer The ENIAC, 1946

Vacuum tube technology

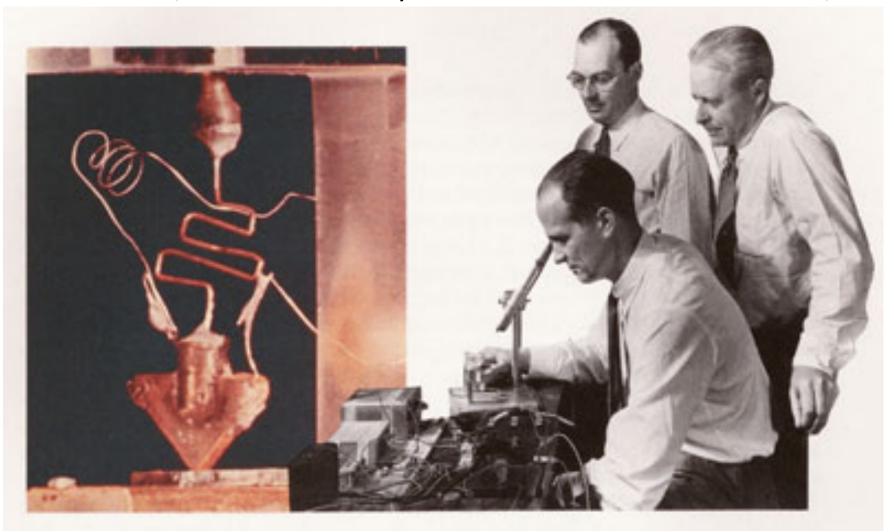


#### Electronic desktop calculator ca. 1950

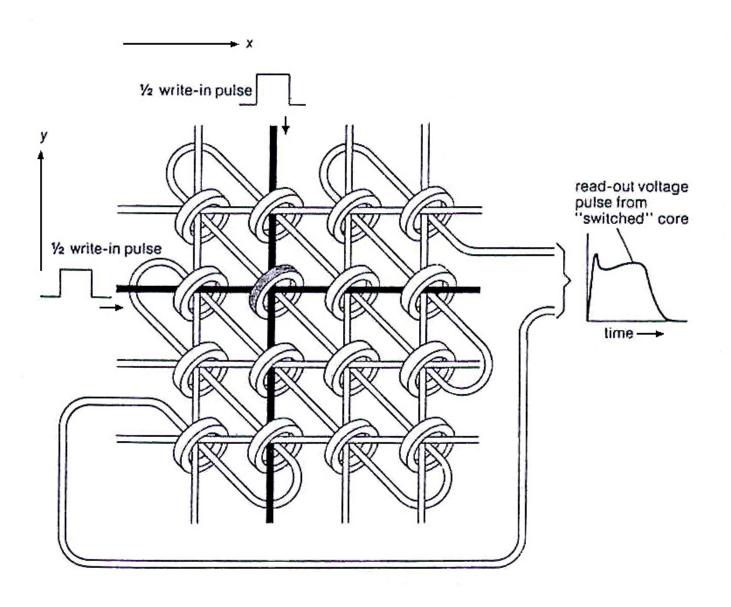


#### The transistor

John Bardeen, William Shockley and Walter Brattain at Bell Labs, 1948



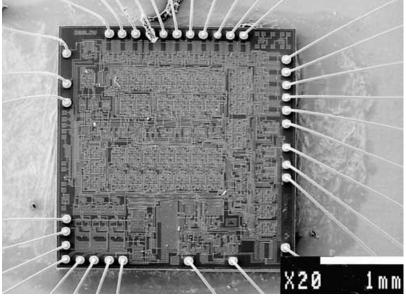
#### Magnetic core computer memory ca. 1970

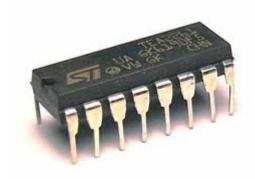


#### Jack Kilby and the integrated circuit





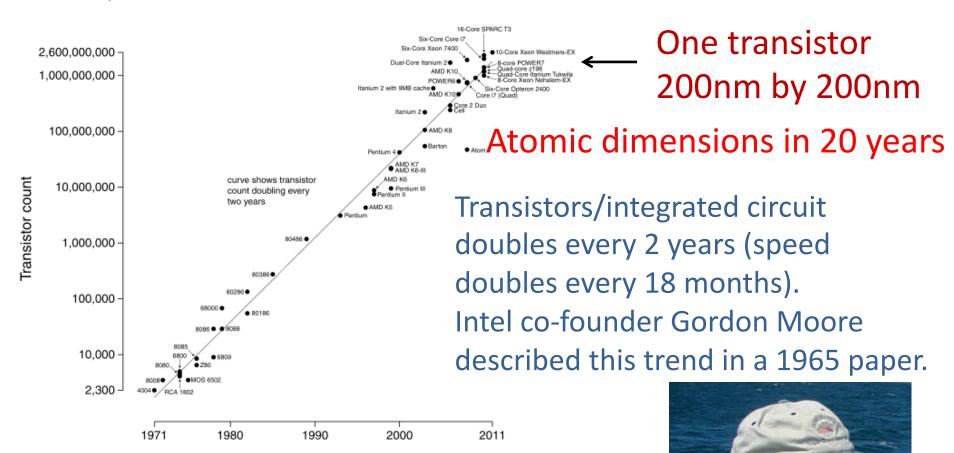




#### Moore's Law

Microprocessor Transistor Counts 1971-2011 & Moore's Law

Date of introduction

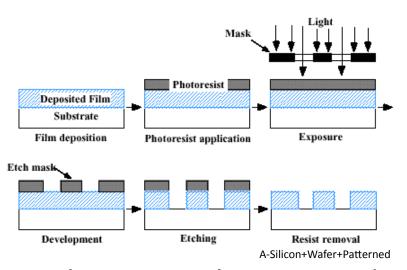


wikipedia

## Lithography

photons (light, UV, X-rays)

electrons



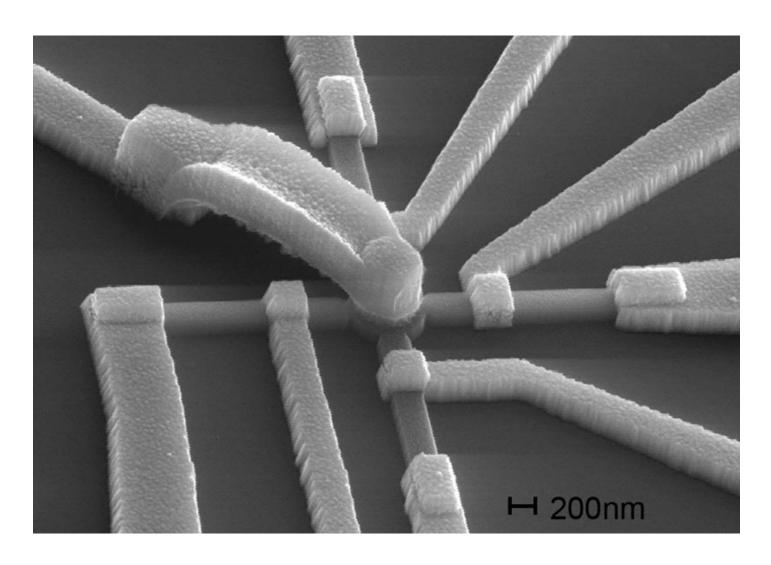


Using photons or electrons to draw a pattern in an etching resist either:

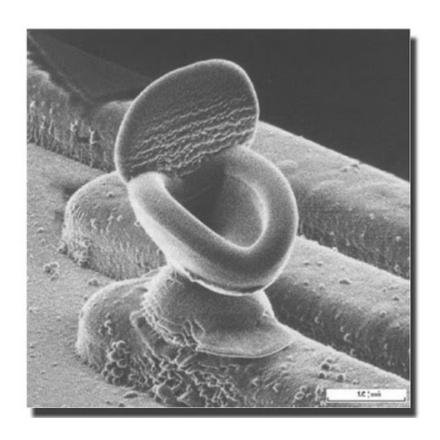
- 1. directly with a projected image, or
- 2. using an optical mask.

Extremely small patterns can be made, ~ 100 nanometers

#### Logic/memory device made via Lithography

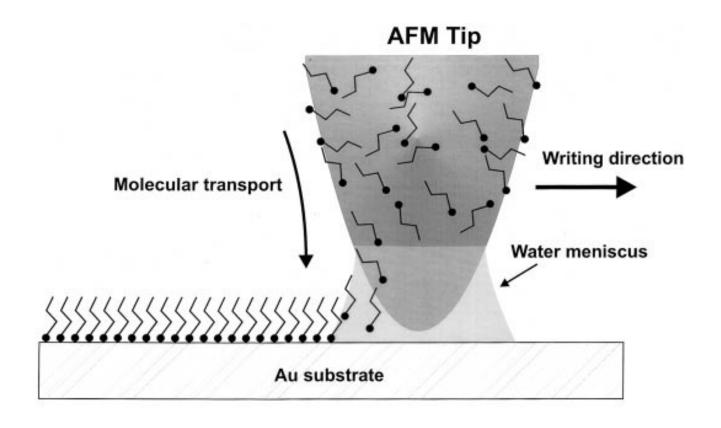


## Another important device

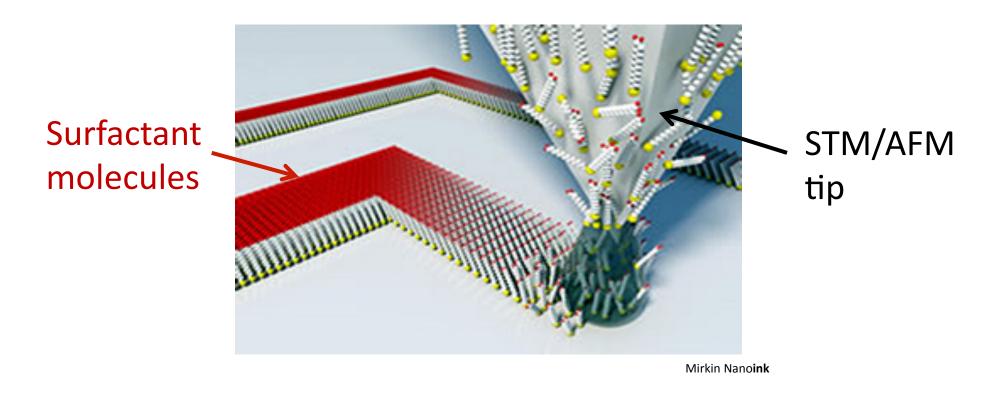


# "Bottom up" Example

Dip-Pen Nanolithography (DPN)

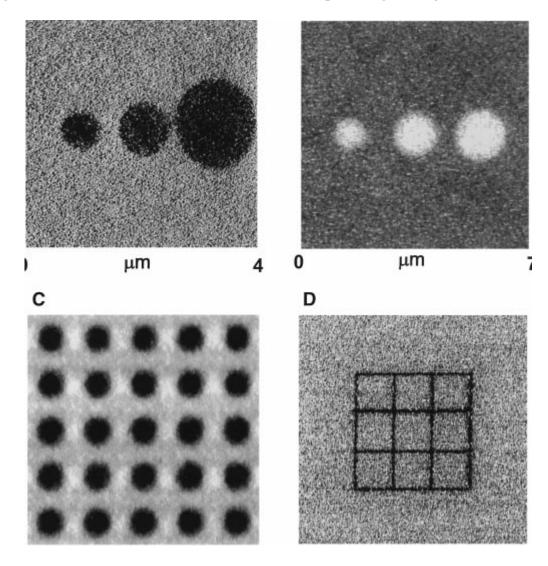


# Dip-Pen Nanolithography (DPN) "Bottom up"



Resolution to ca. 30 nm

#### Dip-Pen Nanolithography (DPN)



## Multiplexing DPN

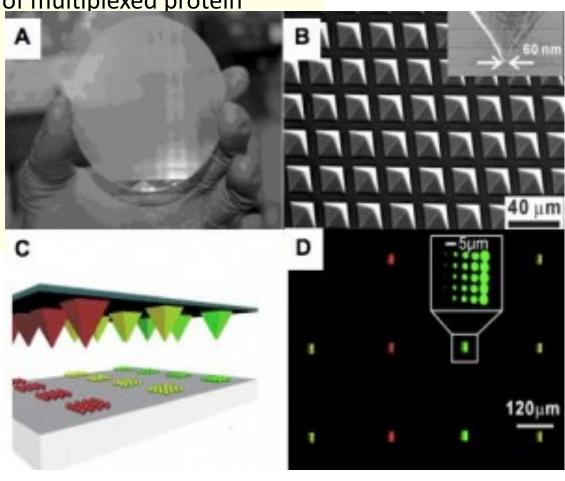
(A) Photograph of a 4-inch the Polymer-Pen Lithography (PPL) array with 11 million pens.

(B) A scanning electron micrograph image of the nanometer-scale pen tips within the array.

(C) A schematic representation of multiplexed protein

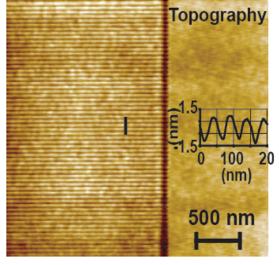
printing by PPL.

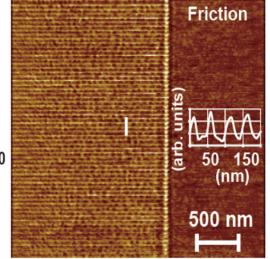
(D) A fluorescence optical micrograph image of the resultant multiplexed PPL patterns.



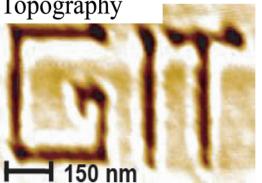
#### ThermoChemical Nanolithography (TCNL)

By locally heating a polymer with a hot AFM tip a chemical reaction is induced and nano-lines can be drawn.

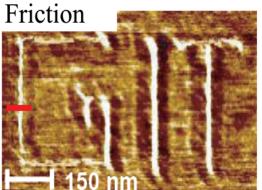


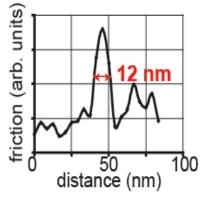




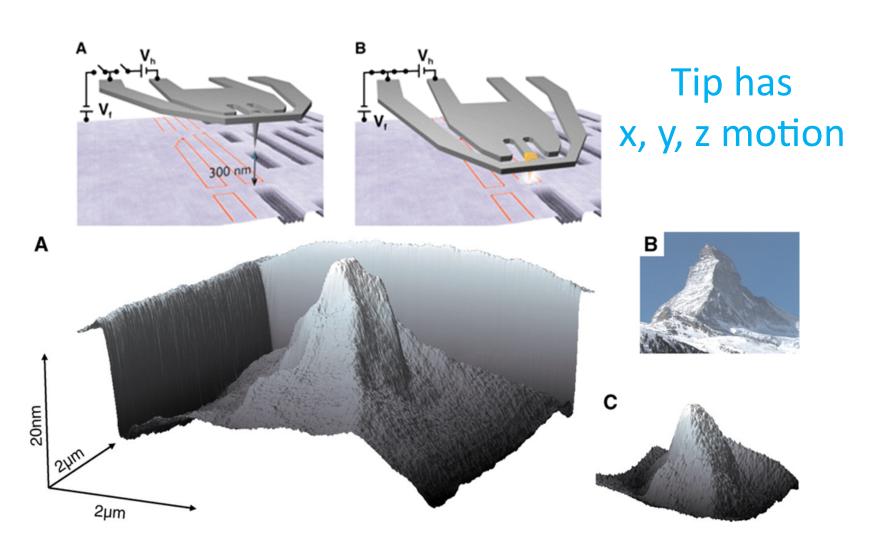


Tip Movement Direction



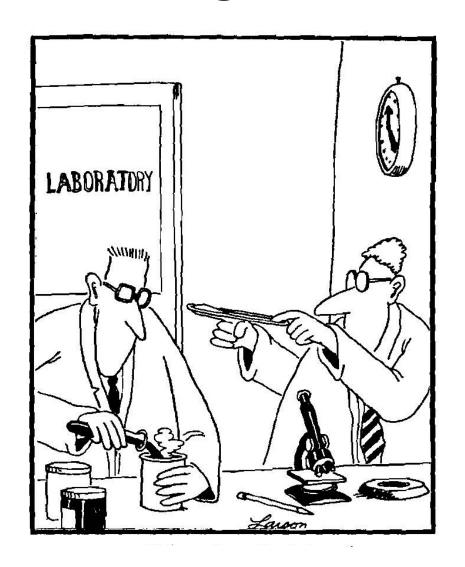


## 3D TCNL



D Pires et al., Science. 2010

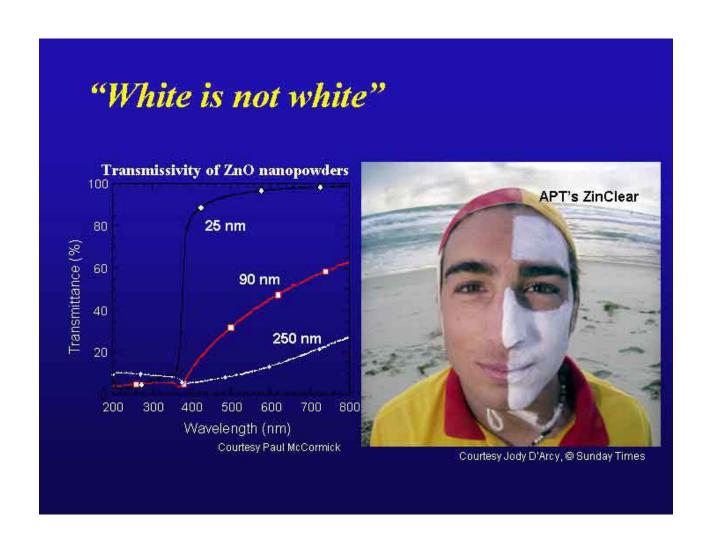
## Clever things from the lab



# **Applications of Nanoparticles**

(a small subset)

#### Invisible Sun Screen



Scat ~ NV<sup>2</sup> ~ NV·V

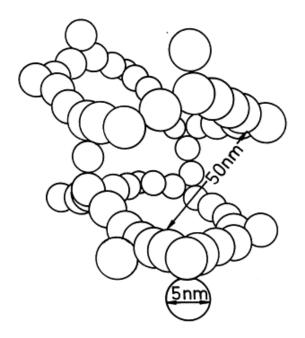
Abs ~ NV

# green



# Aerogels





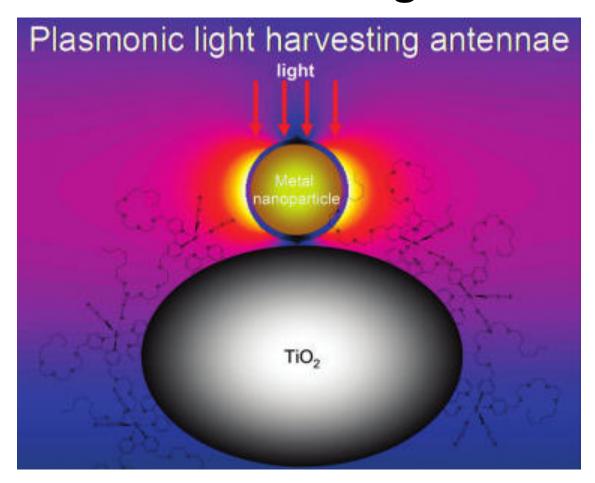
Liquid phase  $Si(OCH_3)_4 + H_2O \longrightarrow SiO_2$  particles

Particles randomly aggregate, gel forms. Density  $\sim 0.01$  g/cc, surface area  $\sim 500$  m<sup>2</sup>/g

# Aerosol Gels Gas Phase $SiH_4 + O_2 \rightarrow SiO_2$

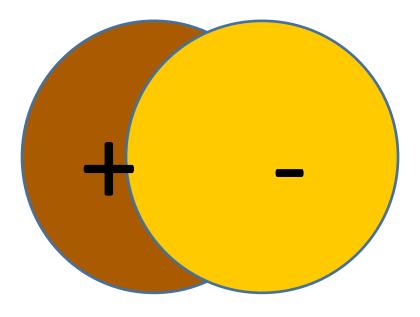


# Photocatalysis H<sub>2</sub>O to H<sub>2</sub> and O<sub>2</sub> with sunlight

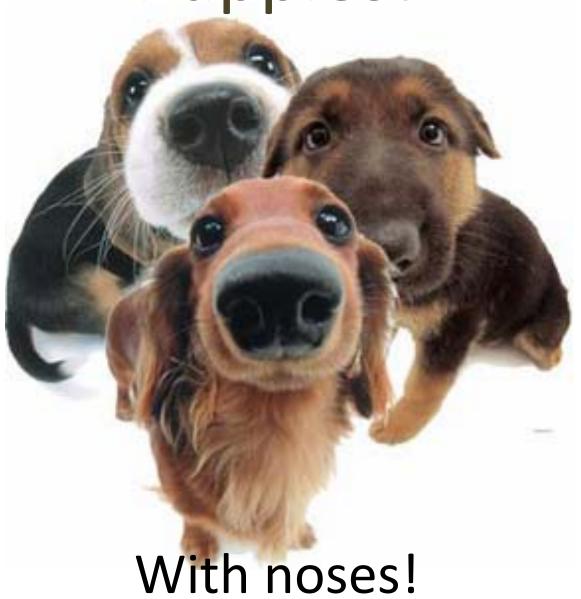


#### Plasmon resonance

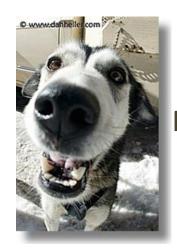
#### Ions electrons



# Puppies!



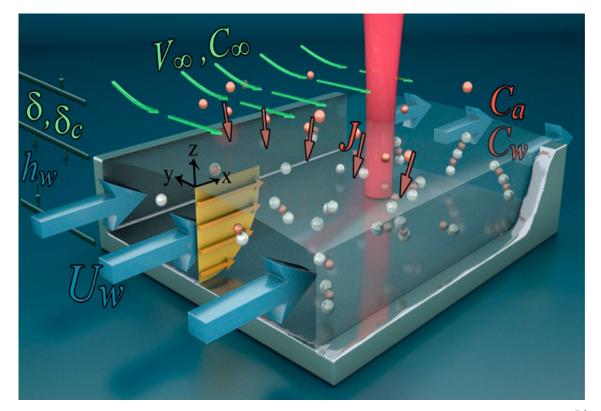




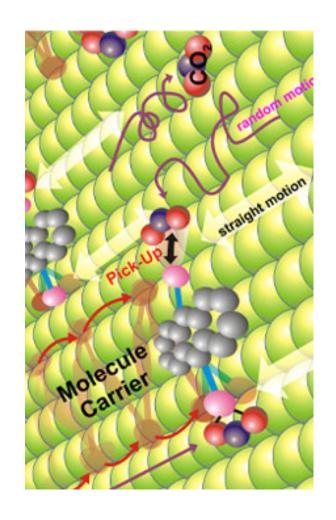
## **Artificial Dog Nose**

Nanoparticles enhance light for spectroscopy
Surface Enhanced Raman Spectroscopy
SERS





The aqueous microfluidic phase flows from left to right (blue arrows). The gas phase flows from back to front (green arrows). Analyte molecules (red spheres) diffuse from the gas into the liquid (red arrows). Nanoparticles (white spheres) in the aqueous phase adsorb analyte molecules where 658 nm laser light (red vertical beam) excites SERS.



#### Nanotruck

With STM nudging anthraquinone molecules move in a straight line on a copper surface, while carbon dioxide moves randomly. But when the two molecules get close together, the anthraquinone picks up the carbon dioxide and keeps walking.

#### anthraquinone

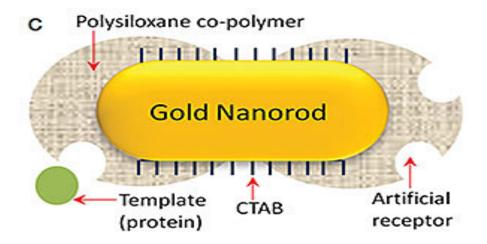
#### Nanowalker

9,10-Dithioanthracene has taken as many as 10,000 spontaneous steps on a copper surface. The thiol groups (SH) are its feet.

9,10-Dithioanthracene

#### Plasmonic biosensor/biomolecular imprinting

- Attach target proteins and polymer layer around the nanorods.
- 2. Then remove target proteins to leave cavities, which act as artificial antibodies.



When exposed to a substance, such as urine, that contains the target protein, those proteins settle into the cavities, and the nanorod changes color.

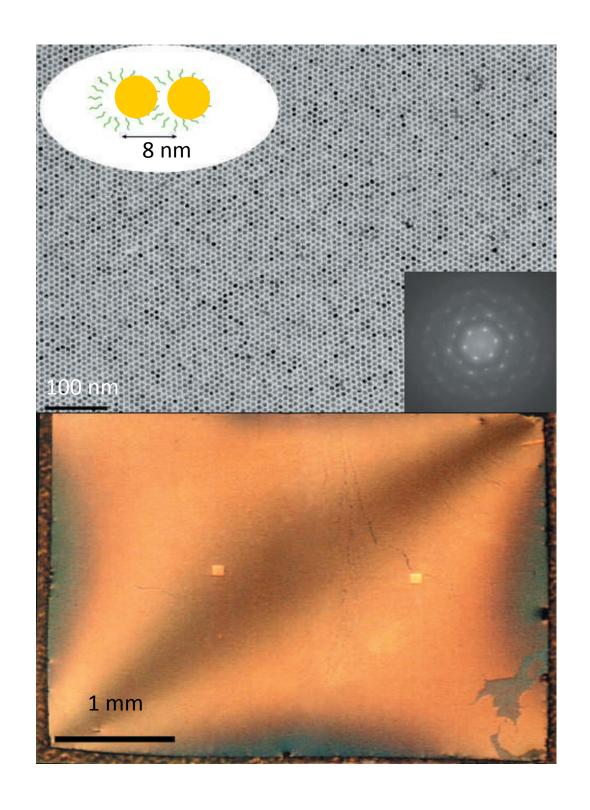
Washington University School of Medicine

# Two dimensional Superlattice Membranes

NATURE MATERIALS 5 265 (2006)



Xiao-min Lin



#### **Ultra-Fast Synthesis**

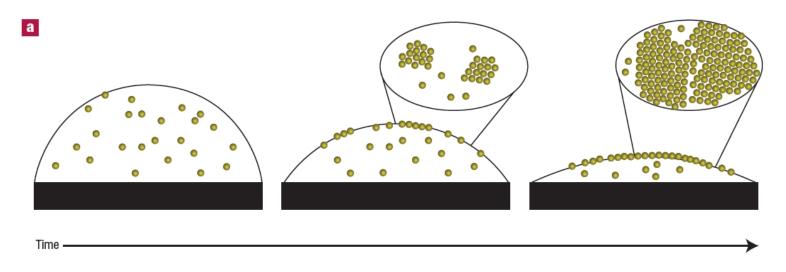
&

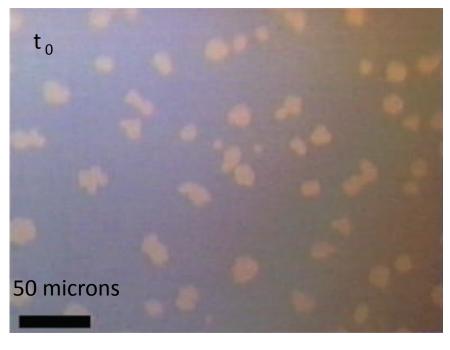
Ultra-Simple 2D Self-Assembly

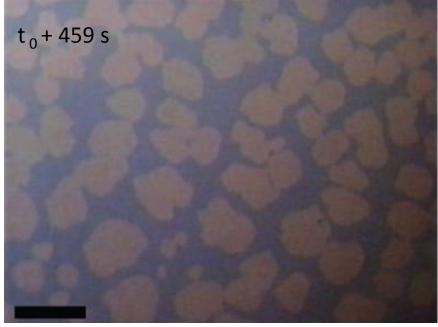
of

Monolayer-Protected Gold Nanoparticles

#### Films grow during evaporation

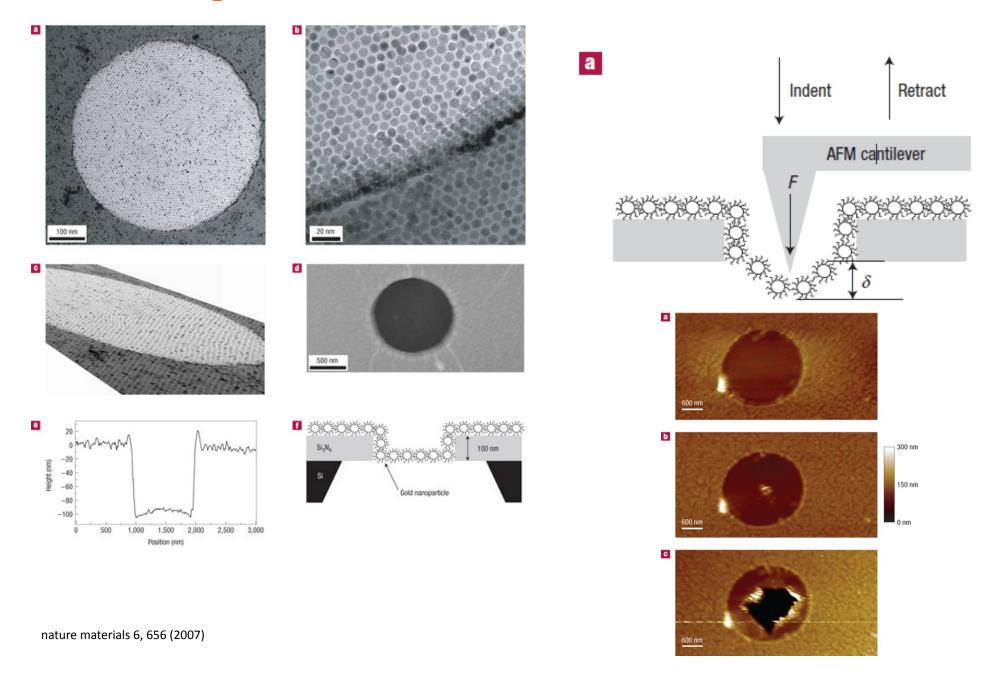






NATURE MATERIALS 5 265 (2006)

#### Tough, elastic films like drum heads

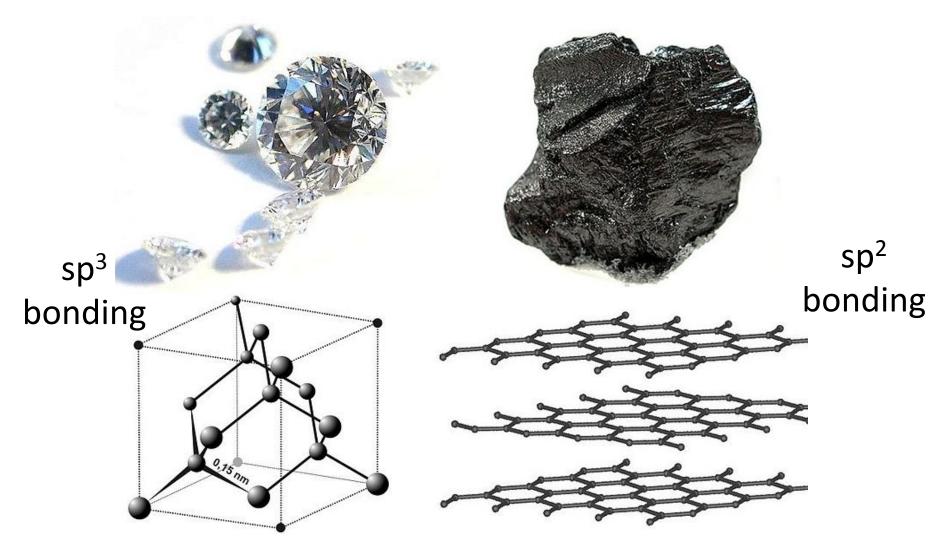


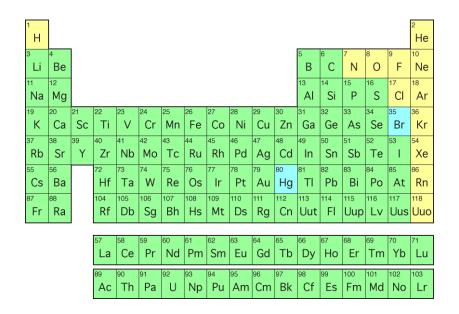


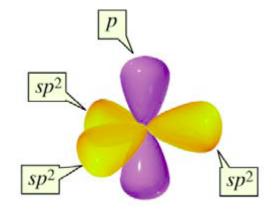
## carbon



# The allotropes of carbon Diamond and Graphite Before 1986







#### "extra" electron in the p-orbital

Graphite is a **black** conductor

#### Carbon

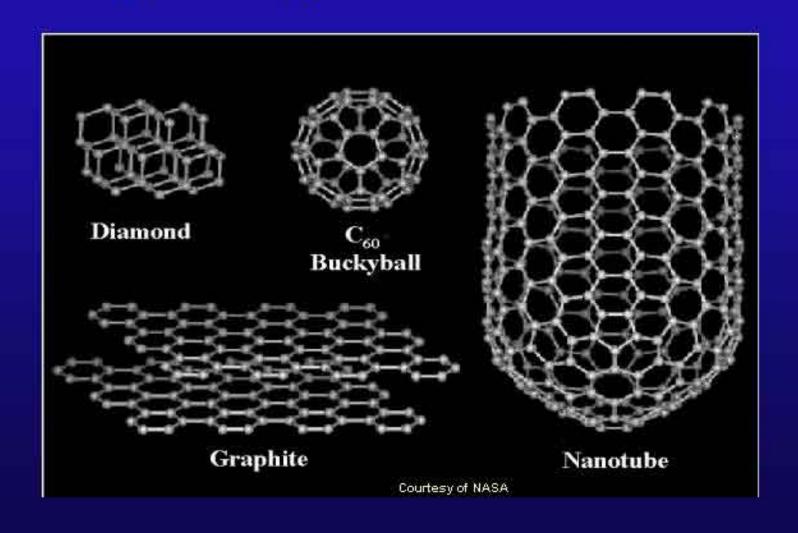
4 valence electrons
2 s-orbitals, 2 p-orbitals.
These can "hybridize" to
3 electrons in sp² hybrid, or
all 4 electrons in sp³ hybrid



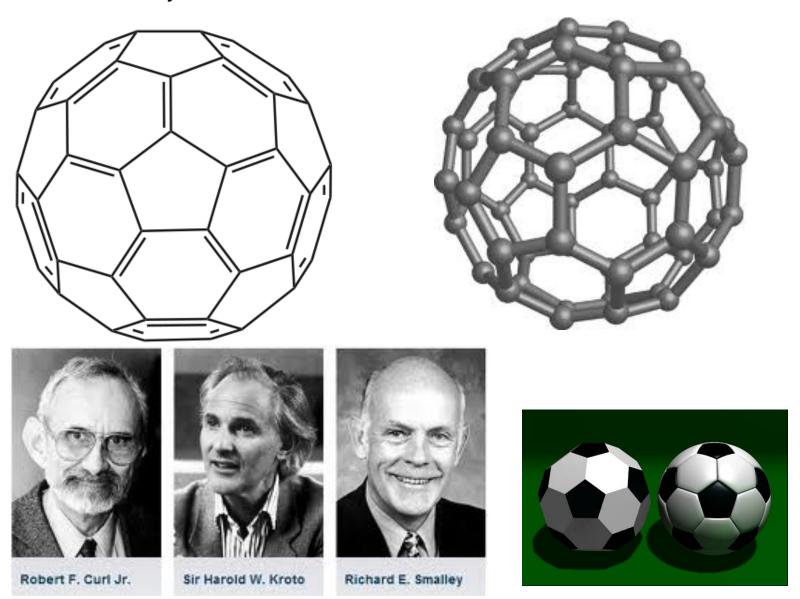
All 4 electrons are busy

Diamond is a clear insulator

## New forms of carbon

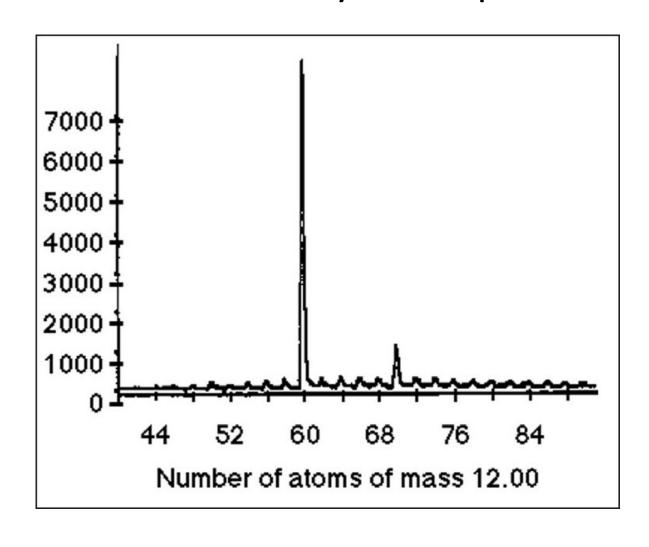


### C60, Buckminsterfullerene



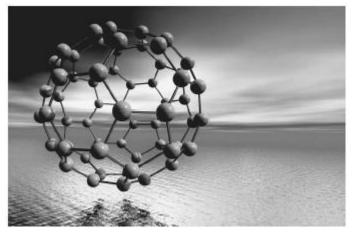
Source: Wikipedia

# Synthesis via laser ablation of graphite under low pressure He. The discovery mass spec



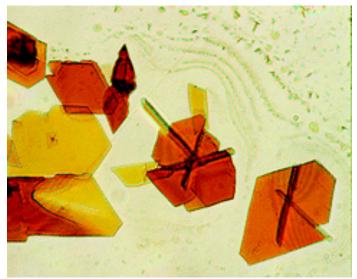
#### Krätschmer/Huffman Process

Gram quantities via the electric arc evaporation of graphite in a helium atmosphere



#### C60 developments:

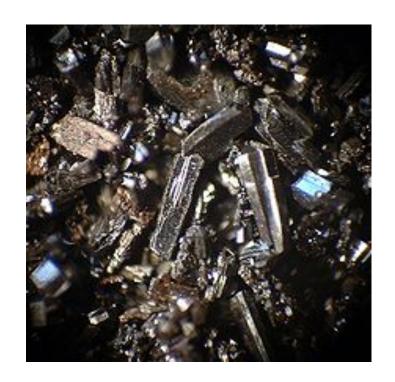
- doped solid can be made superconducting,
- large nonlinear optical effects
- room temperature conversion via nonhydrostatic compression of C60 into diamond powder.



Each of these discoveries could lead to entire fields of commercial applications in the future.

#### C60 solution (in toluene) and solid



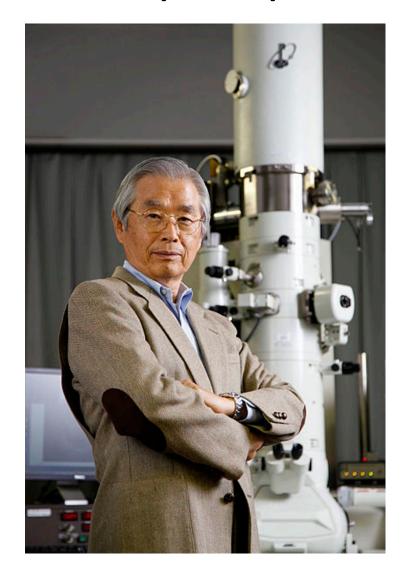


Source: Wikipedia

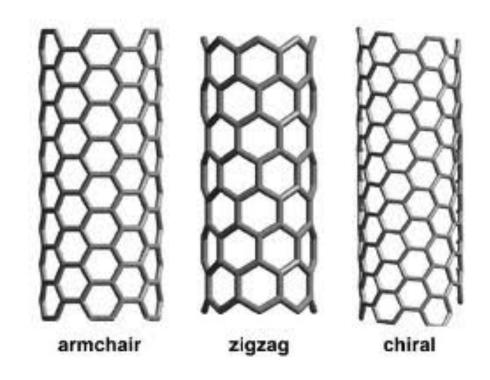
### Carbon nanotubes (CNT)



Sumio lijima, 1991

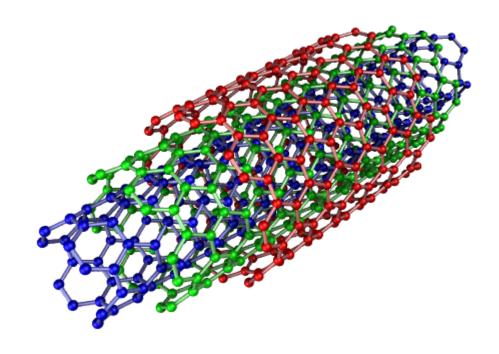


# Single-walled nanotubes (SWNT) properties controlled by helicity



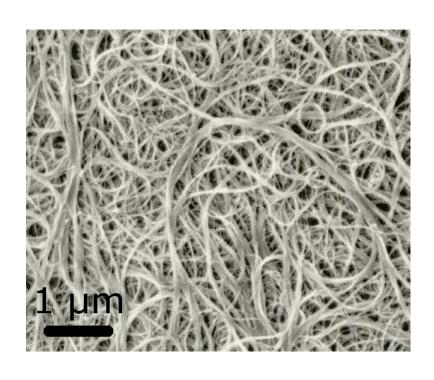
From metallic to semiconductor of various band gaps

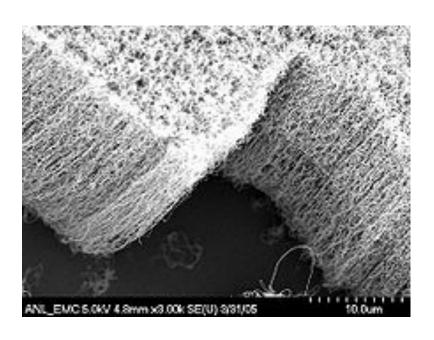
#### Multi-walled nanotubes (MWNT)



Typically metallic

#### Multi-walled nanotubes (MWNT)





#### **CNT Synthesis**

Arc discharge
Laser ablation
Chemical vapor
depostion (CVD)

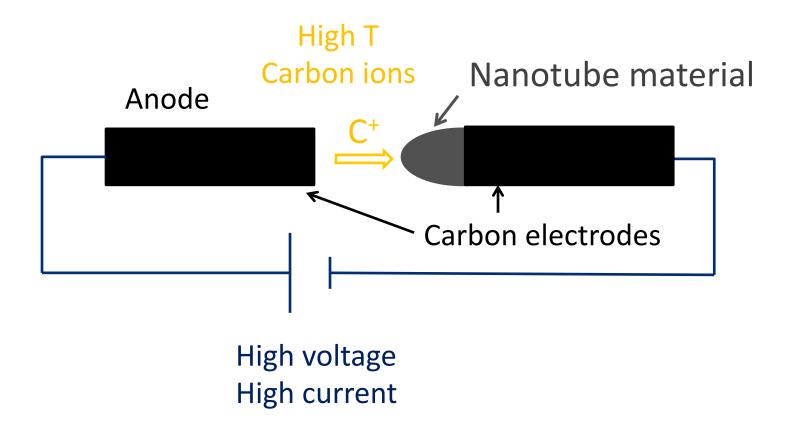
All very high T.



CVD reactor to make Carbon nanotubes

wikipedia

#### Arc Discharge Method



#### **CNT Remarkable Properties**

Variable band gap, it can be an insulator, semiconductor or a metal.

Tensile strength 10 to 100 times and elastic modulus 5 to 10 times that of steel at 1/5 the weight.

Harder than diamond, better thermal conductivity.

Black! Good absorber of electromagnetic radiation.

## Airless bicycle tire



#### Stealth

CNT coatings totally absorb and do not scatter any electromagnetic radiation e.g. light and radar

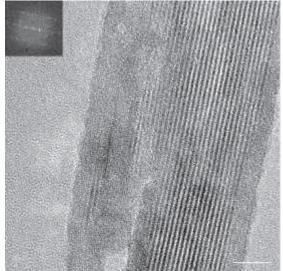


#### Damascus Steel





Detail of the "damask"



High-resolution transmission electron microscopy image of <u>carbon nanotubes</u> in a genuine Damascus sabre after dissolution in hydrochloric acid. Scale bar 5 nm.

tomastomas180.worldpress.com

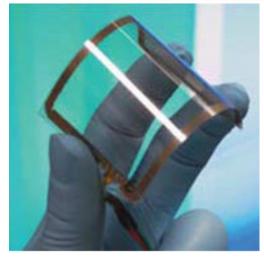
NATURE | Vol 444 | 16 November 2006

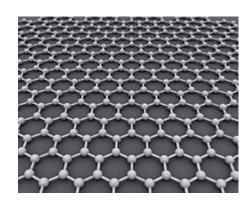
#### Graphene. A single layer of graphite

Geim and Novoselov, 2004 Nobel Prize 2010.









A lump of graphite, a graphene transistor and a tape dispenser. Donated to the Nobel museum in Stockholm by Andre Geim and Konstantin Novoselov.



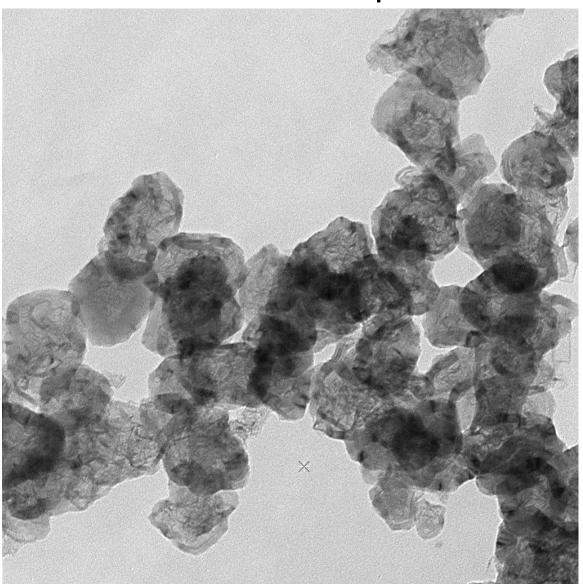
#### **Graphene Production**

- micro-mechanical exfoliation
  - Very small quantities
- Epitaxial growth on metal substrates
  - E.g. Cu, Ni with hydrocarbons, T ≈ 1000K
     Large transparent sheets, but small quantities
- Graphite oxide reduction
  - Graphite (from mines), treat with KMnO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub> to GO, then reduce with N<sub>2</sub>H<sub>2</sub> to graphene. Large quantities, but poor quality
- Detonation carbon

#### The KSU Detonator



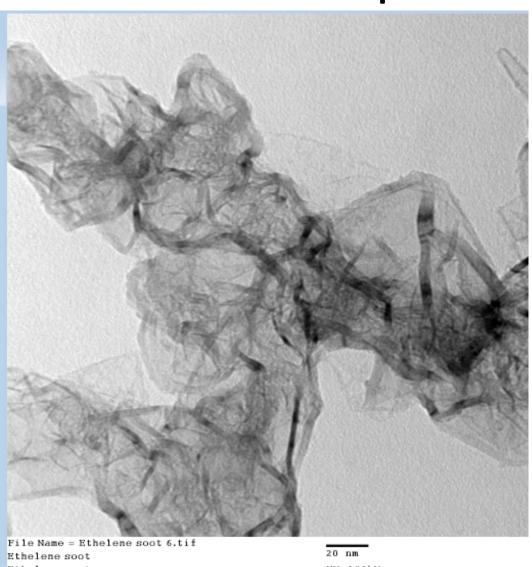
#### **Detonation Graphene**



Low vol frac 1.tif low vol frac Print Mag: 118000x@3.in 11:37 04/04/05

100 nm HV=100kV Direct Mag: 92000x AMT Camera System

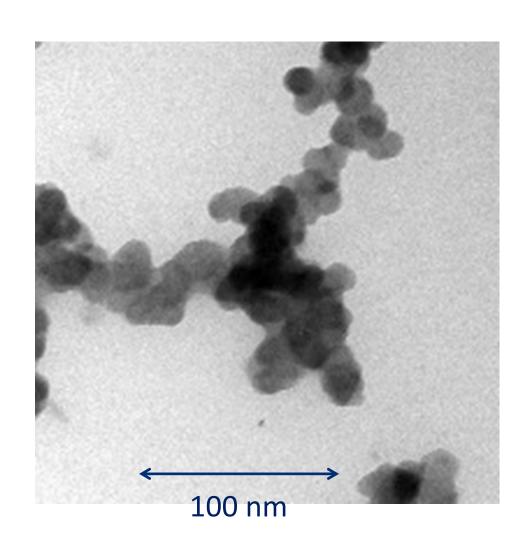
### **Detonation Graphene**



Ethelene soot Print Mag = 311959x @ 3 in

HV=100kVTEM Mag = 340000x

## TEM picture of acetylene open flame soot. $T \approx 2000K$



#### **Detonation Carbon**

Pyrometer indicates T ≈ 4000K
Simple, cheap precursors, e.g. acetylene
No catalyst needed
Eco-friendly
5 grams/detonation lab scale, easily scaled up
to metric tons.





