Carbon at the Nanoscale

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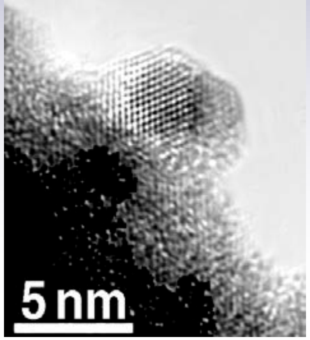
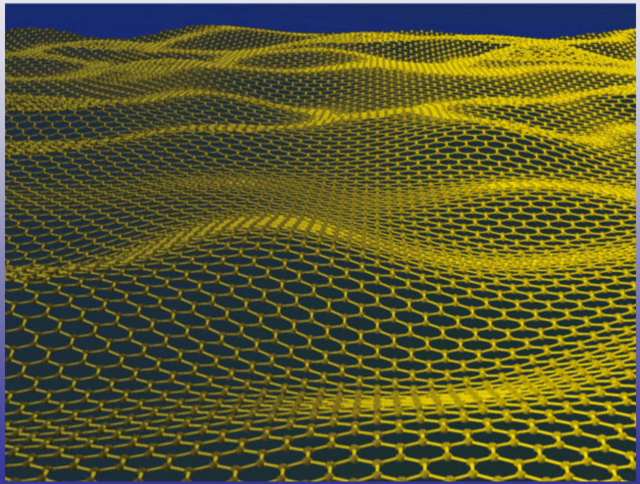
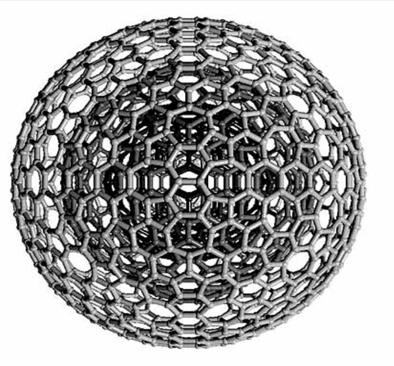
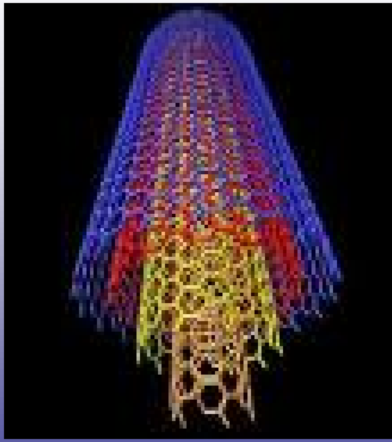
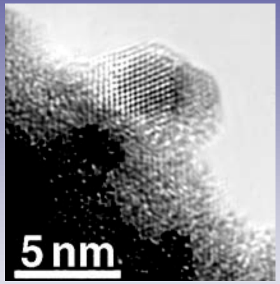


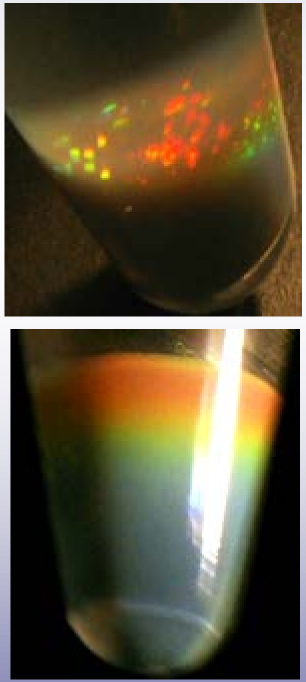






Talk Outline





- **Carbon at the Nanoscale**
- **Modern nanodiamond (ND) particles**
- **ND of dynamic synthesis (using explosives)**
  - *size, morphology*
  - *N state*
- **Recent advances in detonation ND**

Facts about Carbon

- **“Carbon" comes from Latin *carbo*, coal**

- **Carbon is the 4-th most abundant element in the universe by mass** *(after H, He, O)*

- **Carbon is abundant in the Sun, stars, comets, atmospheres of most planets and meteorites (nanodiamond)**

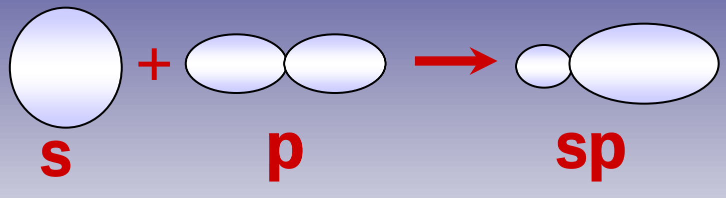
- **Carbon forms more compounds than any other element** *(~ten million organic compounds described to date)*

- **Carbon is the 2-nd most abundant element in the human body by mass (about 18.5%) after oxygen**

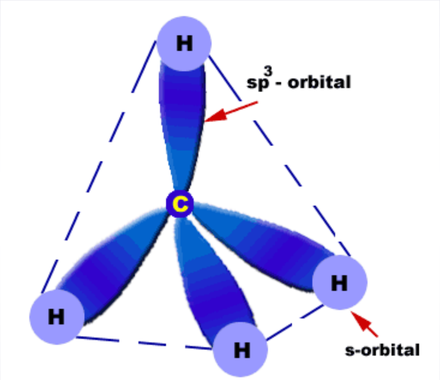
Carbon Chemistry

C	↑↓	↑↓	↑	↑	
	$1s$	$2s$	$2p_x$	$2p_y$	$2p_z$

Hybridization:



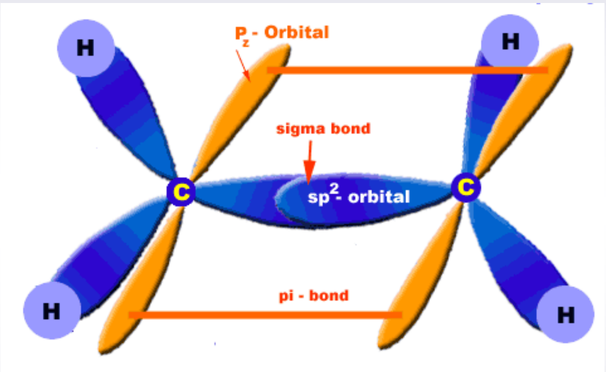
sp^3 hybrids



Orbital structure of methane

C^*	↑↓	↑	↑	↑	↑
	$1s$	sp^3	sp^3	sp^3	sp^3

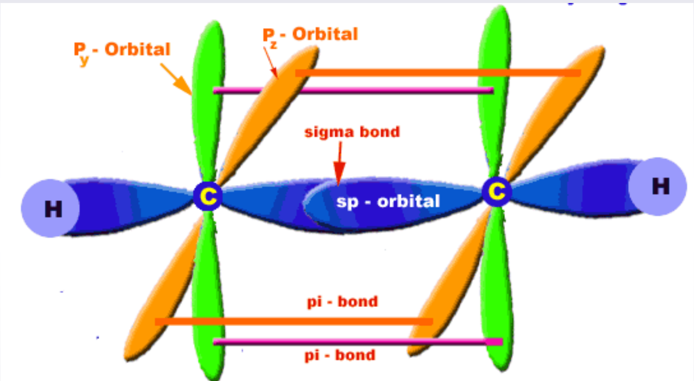
sp^2 hybrids



Orbital structure of ethene

C^*	↑↓	↑	↑	↑	↑
	$1s$	sp^2	sp^2	sp^2	$2p$

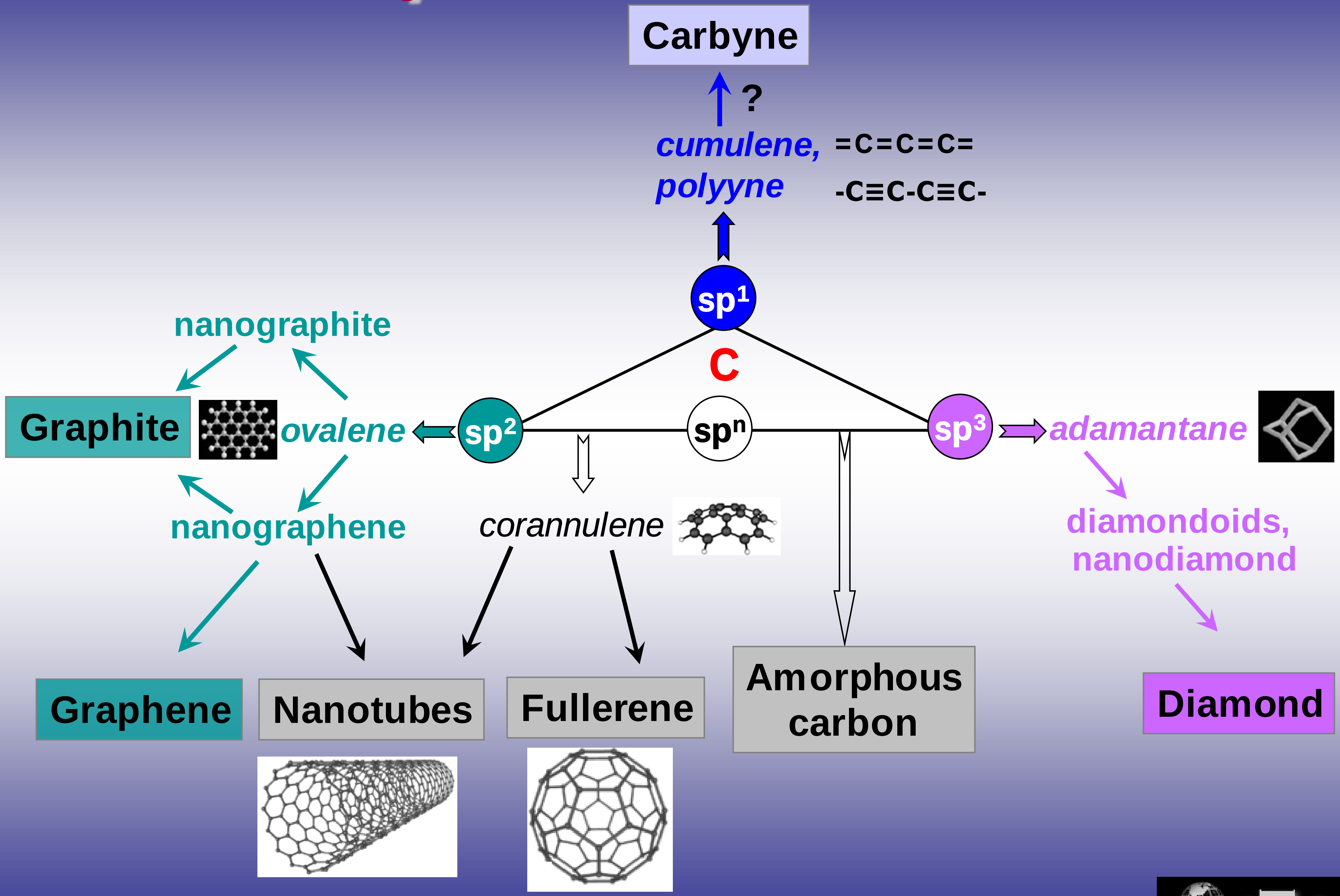
sp^1 hybrids



Orbital structure of ethyne

C^*	↑↓	↑	↑	↑	↑
	$1s$	sp	sp	p	p

Carbon Family



Carbyne

?

cumulene, =C=C=C=

polyyne -C≡C-C≡C-

sp^1

C

nanographite

Graphite

ovalene

sp^2

sp^n

sp^3

adamantane

nanographene

corannulene

diamondoids, nanodiamond

Graphene

Nanotubes

Fullerene

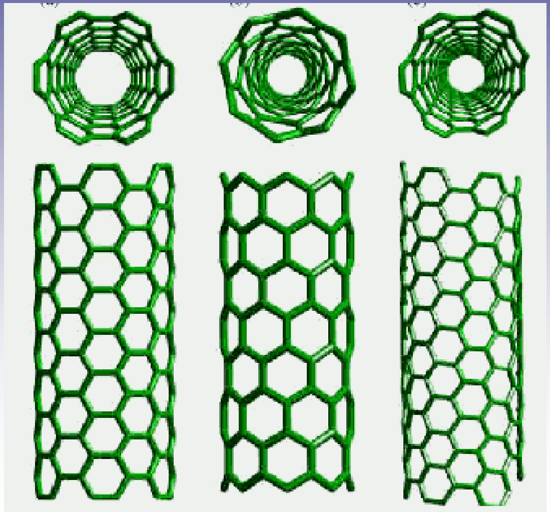
Amorphous carbon

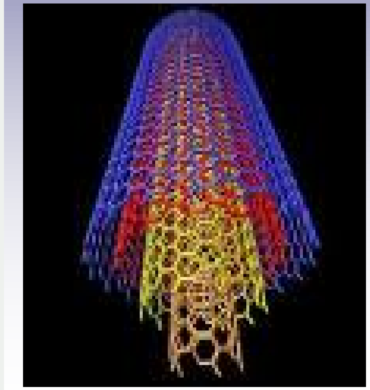
Diamond

Carbon Nanotubes

Total number of publications on Nanocarbons (in ISI):

- nanodiamonds: 2,524 papers
- fullerenes: 12,872
- carbon nanotubes: 46,568
- graphene: 6,539

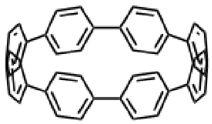




- Most cited fact of discovery of SWNT: 1991 by Iijima, but there are reports on earlier discoveries

SWNT:

- Diameter: typical 1-10nm
- Range of diameters: 0.3-100 nm
- The *thinnest* carbon nanotube is armchair (2,2) CNT with a diameter of 3 Å.)
- Length range 10 nm –50 um
- The longest: 18 cm (as of 2010)
- The shortest: cycloparaphenylene



Carbon Nanotubes

Methods of production:

- arc discharge (1991 Iijima), SWNT & MWNT
- laser ablation, (w/catalyst), SWNT
- chemical vapor deposition (CVD) (w\catalyst), SWNT & MWNT
  - high pressure CO conversion (HiPco), SWNT
  - water-assisted CVD (supergrowth)

Manufactured ~100s of tons per year
(Bayer and Showa Denko)

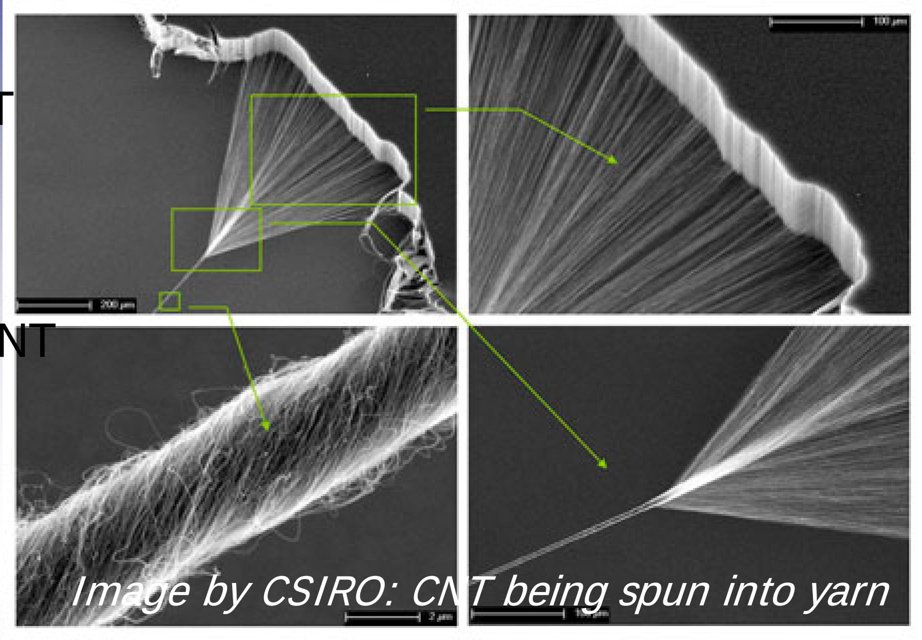


Image by CSIRO: CNT being spun into yarn

Properties:

- Band gap of SWNT: from zero to ~2 eV
- electrical conductivity of SWNTcan show metallic or semiconducting behavior
- tensile strength: ~100GPa

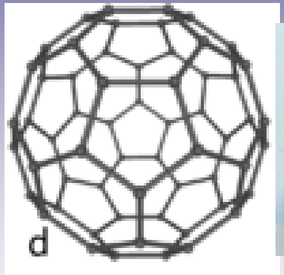
(specific strength of up to 48,000 kN·m·kg^{-1} vs. 154 kN·m·kg^{-1} for steel)

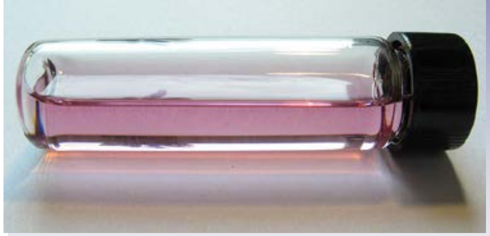
- thermal conductivity along SWNT axis ~3500 W·m^{-1}·K^{-1} (~2000 for diamond)

Cost:

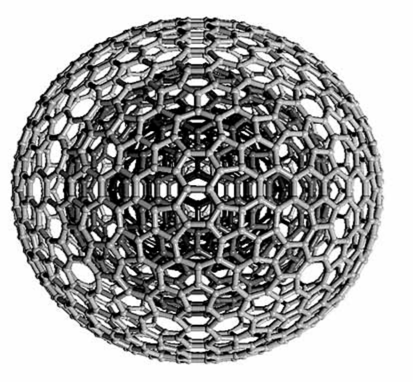
- $1500 per gram of SWNT as of 2000
- retail prices of around $50 per gram of as-produced (40–60% by weight) SWNTs as of 2010

Fullerenes (buckyballs)





- Smallest: C20
- Most abundant: C60 (buckminsterfullerene)
- endohedral fullerenes have ions inside the cage atoms



Carbon onions

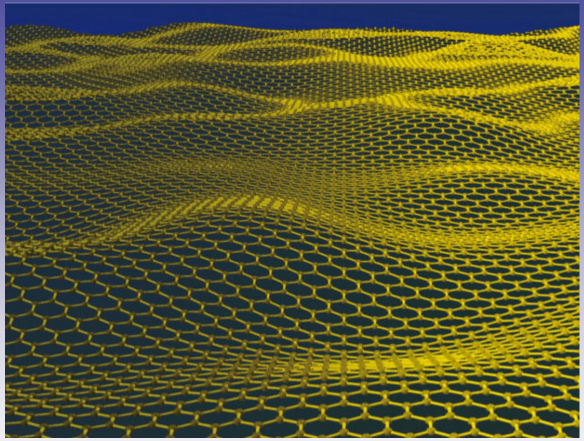
- Outer diameter: 10nm-1 um
- Inner diameter: 0.7-1 nm (~C60)

- Discovered in 1985 (laser vaporization of carbon in an inert atmosphere)
- Using arc to vaporize graphite in 1990, macroscopic quantities (Kratschmer and Huffmann)
- Arc discharge method in 1991 (Smalley group), mass production
- Nobel Prize in chemistry for 1996 (Curl, Kroto, Smalley)
- Have been detected in outer space (2010)

Properties:

- superconductivity (33K for Cs_2RbC_{60})
- C60 molecules compose a solid of weakly bound molecules (fullerites)
- C60 is well soluble in many organic solvents

Graphene



- *Produced in 2004 (scotch tape graphite exfoliation)*
- *Shown in 2005 ballistic transport of charges, large quantum oscillations, anomalous quantum Hall effect, etc. (“exotic” physics)*
- *Nobel Prize in physics for 2010 (Geim, Novoselov)*

Structural features\properties:

- “Rippling" of the flat sheet (amplitude ~1nm)
- The thinnest and the strongest material
- As a conductor of electricity it performs as well as silver
- As a conductor of heat it outperforms all other known materials
- It is almost completely transparent
- Sheets as wide as 70cm have been fabricated

Graphene

Production:

- Drawing method (mechanical exfoliation of graphite by cohesive tape)
- Epitaxial CVD growth on a substrate: SiC, metals (Ir, Ni, Cu, etc)
- Graphite oxide reduction (Boehm, 1962)
- Growth from metal-carbon melts (Ni)
- Cutting of open nanotubes (graphene ribbons)
- others

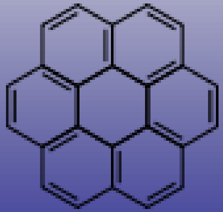
Manufactured ~tons per year *(Segal M. Nature Nanotech. 4, 612–614, 2009)*

VORBECK MATERIALS

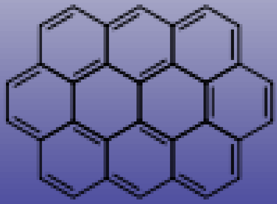
Applications: transistors, touch screens, solar panels, composite materials, etc

Nanographene: nanoplatelets, nanoribbons, etc

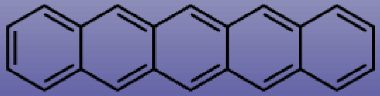
Polycyclic aromatic hydrocarbon (PAH): molecular cousins



coronene



ovalene



pentacene

Largest PAH:
10 benzene rings across

Nanocarbon in Space

Image credit: NASA/JPL-Caltech

Meteorite ND:

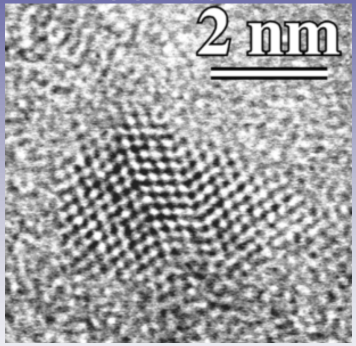


Image credit: T.Daulton, NRL

In the interstellar medium (ISM)

- Optical properties of ISM depend on the existence of silicate grains & diverse populations of carbon-based molecules:

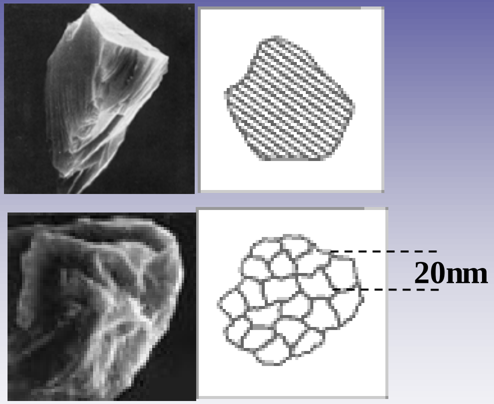
- Amorphous aliphatic hydrocarbon dust
- Polycyclic aromatic hydrocarbon
- Carbon onions (multishell fullerenes)
- Nanodiamonds (C–H vibrational emission bands from ND)

In meteorites

- Nanodiamonds found in meteorites (Lewis, 1987)
- Up to 1400ppm of ND in primitive chondritic meteorites (T.Daulton, 2006)
- They are pre-solar grains (based on isotopic anomaly analysis) (Lewis, 1987)
- Isotopically anomalous Xe and Te in NDs are associated with supernovae
- Meteoritic ND are possibly formed by low pressure C condensation similar to the CVD
- Astrophysical nanodiamonds are ~2.6 nm or less
- Diamondoids (H-terminated surface) or bucky diamonds?

Nanocrystalline Diamond Particles

Range of primary particle sizes: 10-100 nm



Monocrystalline:

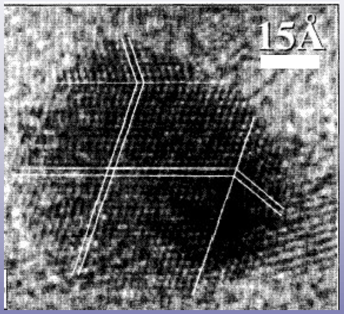
- Natural (grinding)
- Synthetic HPHT (grinding)
- Microwave plasma torch

Polycrystalline (Poly-ND):

- Shock wave compression of graphite (DuPont process)
- Detonation synthesis using carbon precursors/explosives (10-15nm grains)

Ultrananocrystalline Diamond Particles

Range of primary particle sizes: 1-10 nm



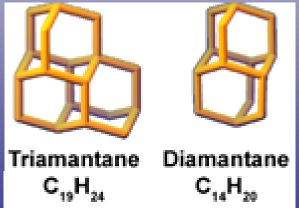
- **Detonation synthesis**
  (carbon containing explosives)
- vapor grown
- chlorination of carbide
- ion irradiation of graphite
- laser irradiation of carbon
- HPHT (2009)

Highest diamondoids

Hydrogenated molecules 1-2 nm

© 2004 Chevron U.S.A. Inc

Lower diamondoids



Adamantane

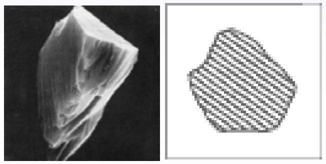
Molecule $C_{10}H_{16}$

Commercial Nanodiamond (ND) particles

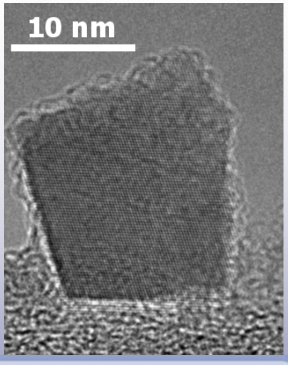
(crystal size less than 100nm)

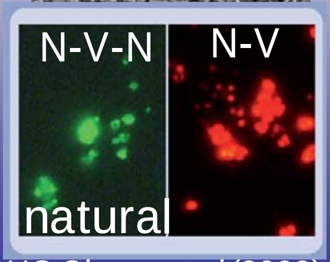
ND of Static Synthesis

(High pressure high temperature)
Grinding of microsized diamond



Smallest:
10-20nm





Type I diamond (Ia,Ib)
1-3000 ppm of N_s
PL (after irradiation)

HC Chang et al (2009)

ND of Dynamic Synthesis

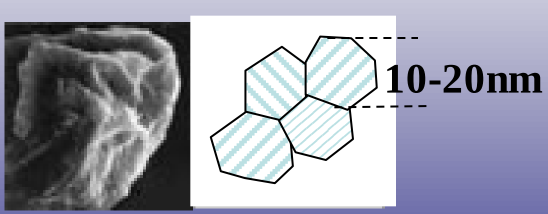
(Using explosives)

Graphite precursor

Graphite + explosive precursor

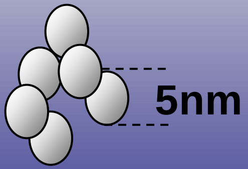
Explosives precursor

Polycrystalline ND

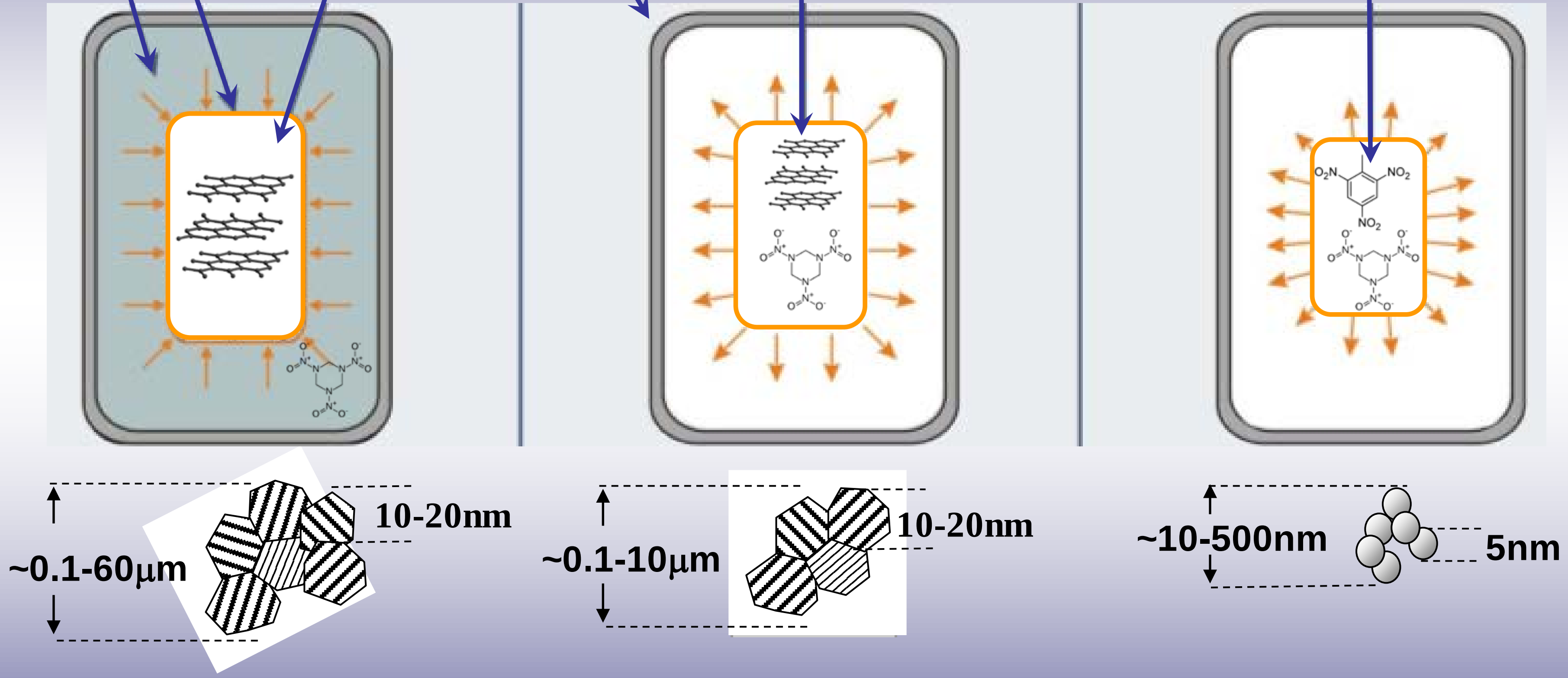


Smallest: 30-50nm
individual particles

Detonation ND
(Ultradispersed
diamond (UDD),
Cluster diamond)



Nanodiamond of Dynamic Synthesis



Metal Container

Explosive

Graphite
+metal powder

~0.1-60μm

10-20nm

Explosive Chamber

30-90% RDX + (graphite, soot)

~0.1-10μm

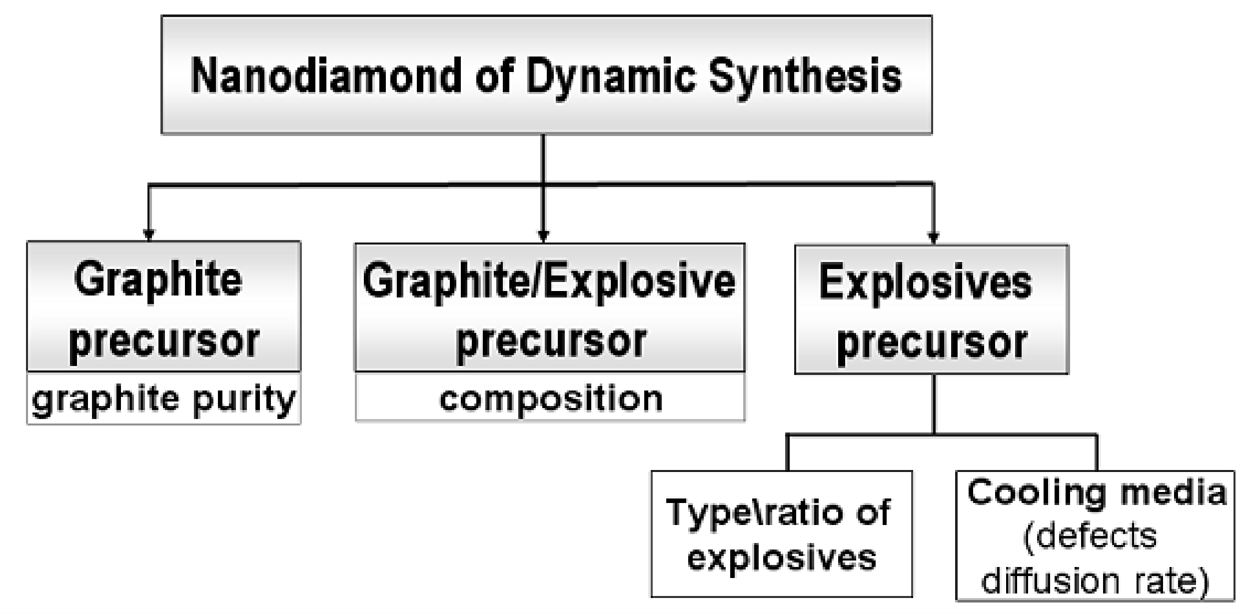
10-20nm

TNT + RDX
with negative oxygen balance

~10-500nm

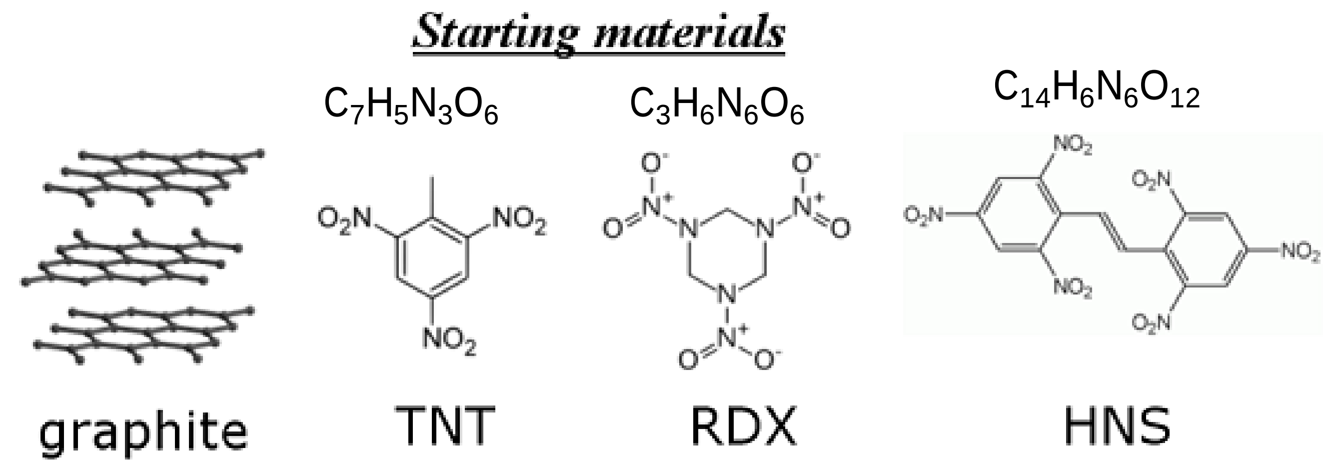
5nm

Factors influencing nitrogen content and state



Samples of ND produced from the precursors:

1. **graphite (DuPont)**
2. **graphite\RDX**
3. **TNT\RDX wet cooling**
4. **TNT\RDX dry cooling**
5. **TNT\HNS wet cooling**



Shenderova et al., J.Phys.Chem.C, 2011

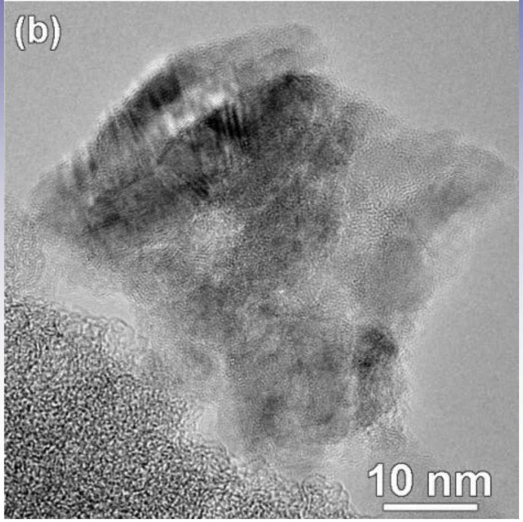
Nanodiamond produced by a shock wave conversion of graphite

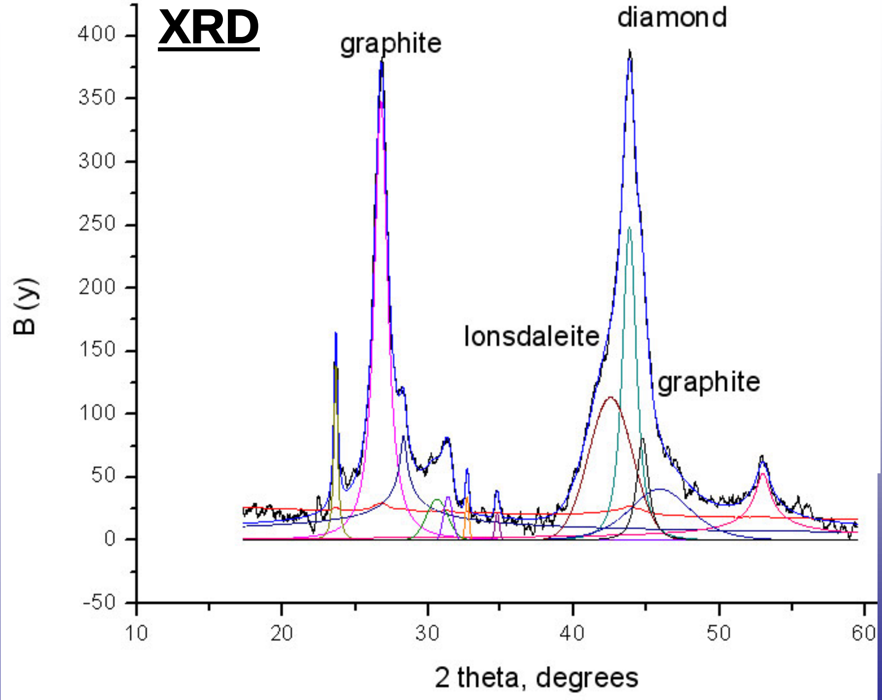
Mypolex^{TM}

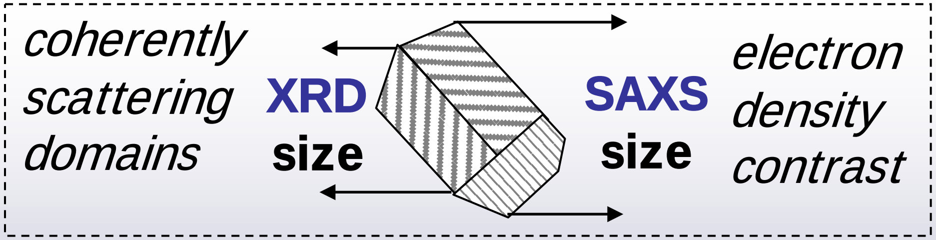
Fraction 25nm (DLS)

- **N<0.5wt%** (from CHN analysis)
- Presence of graphite
- Presence of lonsdaleite

- Crystal size from XRD:
  8nm (44°, Diam), **2.4**nm(42.5°,Lonsd.)

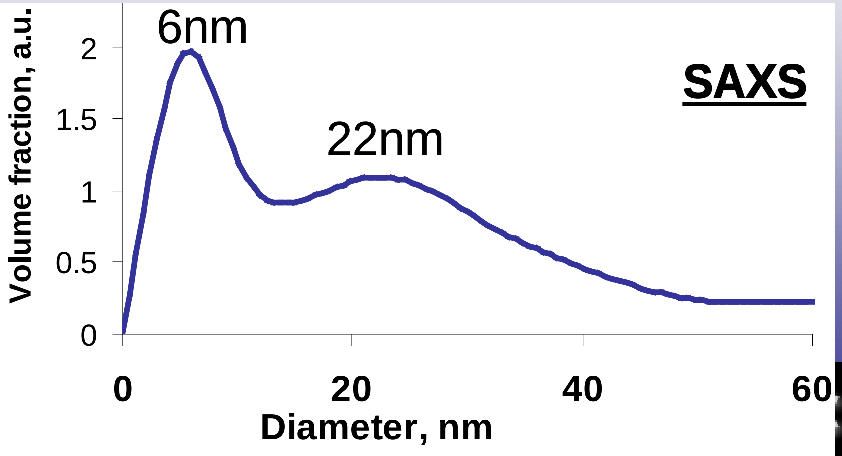




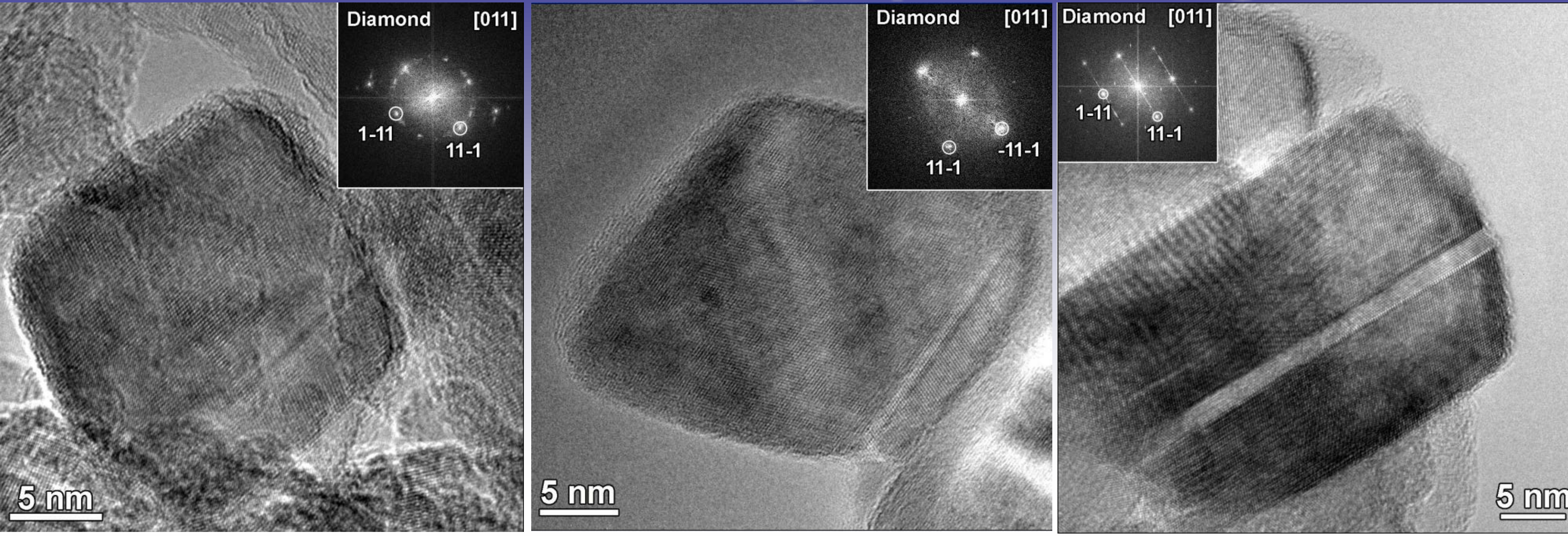


coherently scattering domains **XRD size**

SAXS size *electron density contrast*

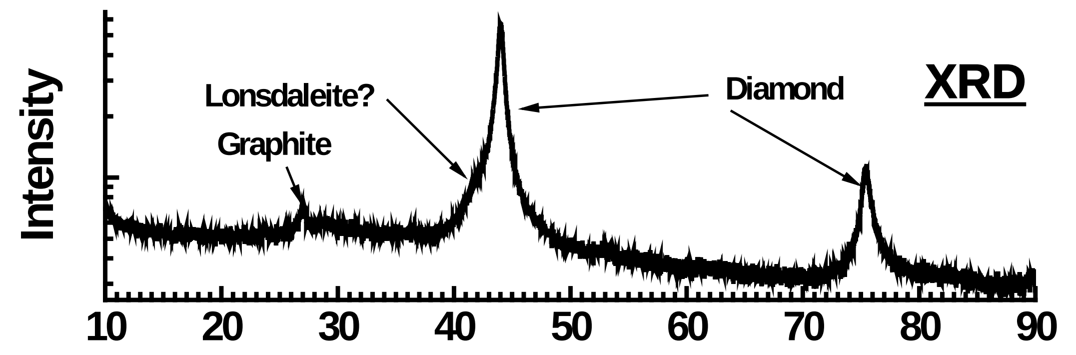


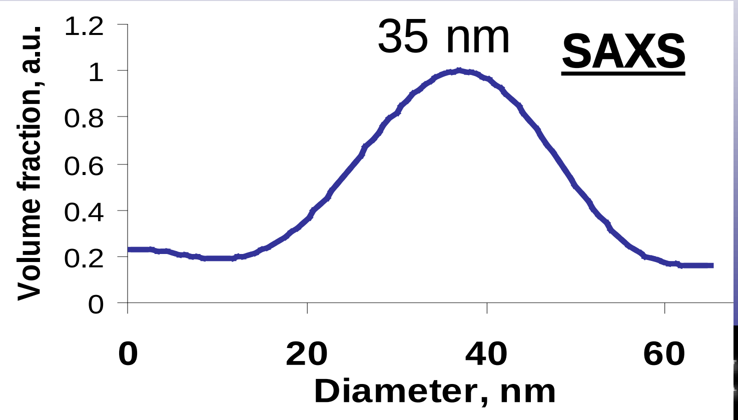
Nanodiamond from graphite\hexogen



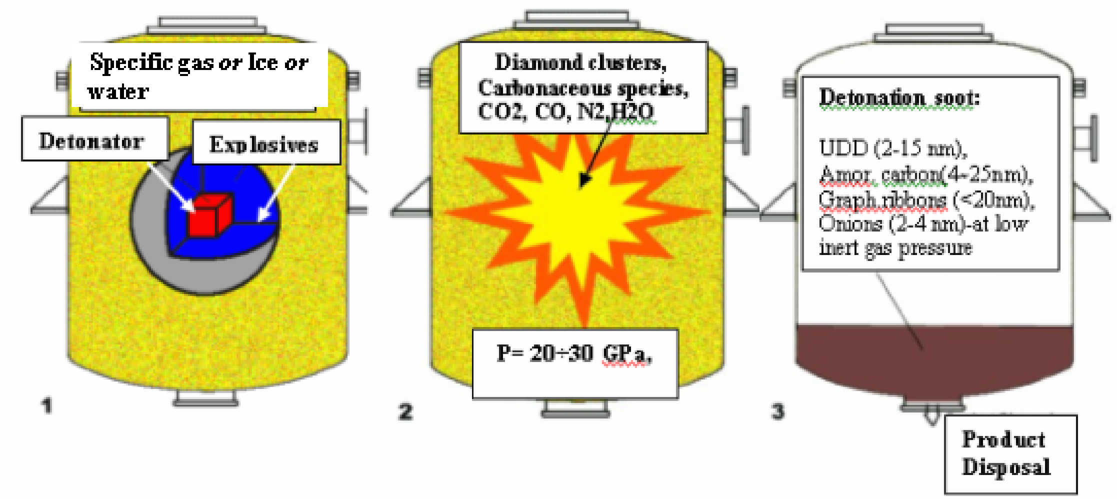
50nm fraction (DLS)

- **N <0.5wt%** (from CHN analysis)
- **Crystal size from XRD: 14.8nm** (<111>), **9.6nm**(<110>)
- **Crystal size from SAXS: 35nm**





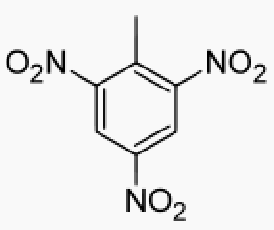
Detonation Nanodiamonds Synthesis



Nanodiamond Purification From Soot

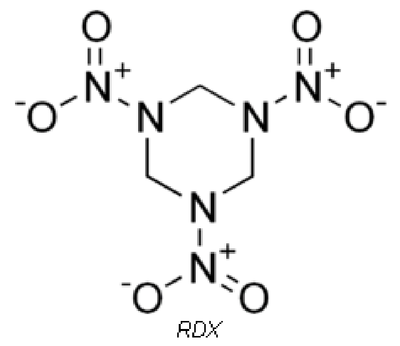
trinitrotoluene (TNT)

$C_6H_2(NO_2)_3CH_3$



cyclotrimethylene-trinitramine (hexogen or RDX)

$C_3H_6N_6O_6$



Explosion chambers:

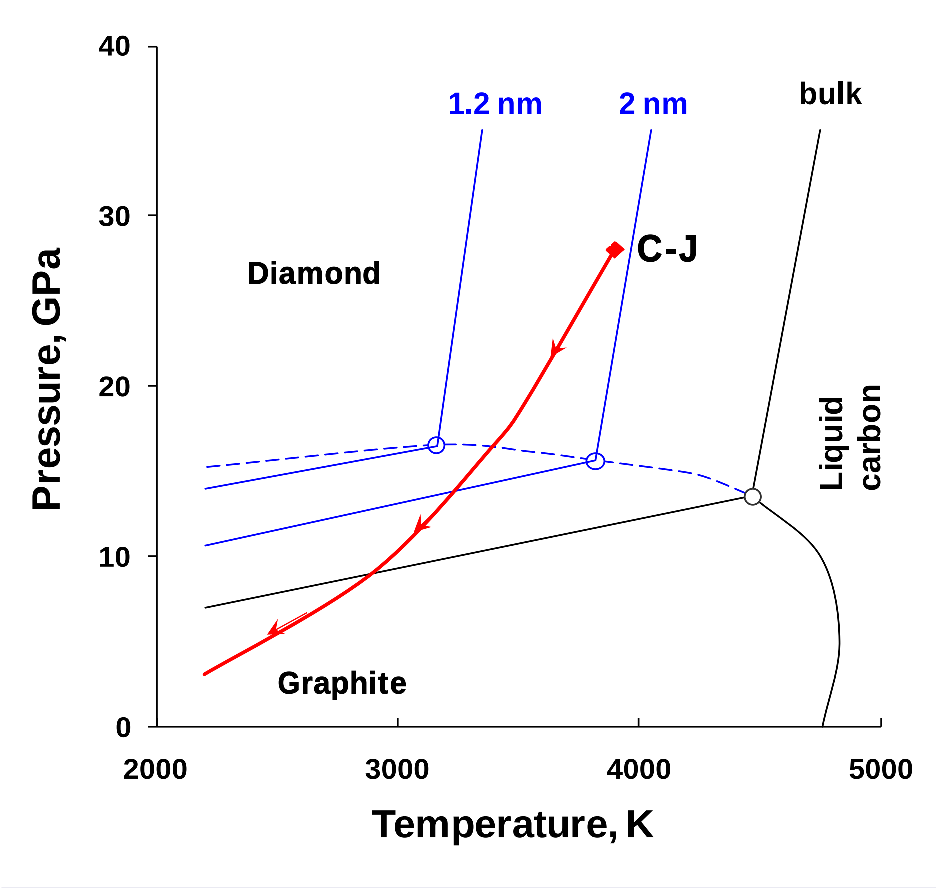
- Capacity 1-20 m^3
- Explosives 0.5-10 kg

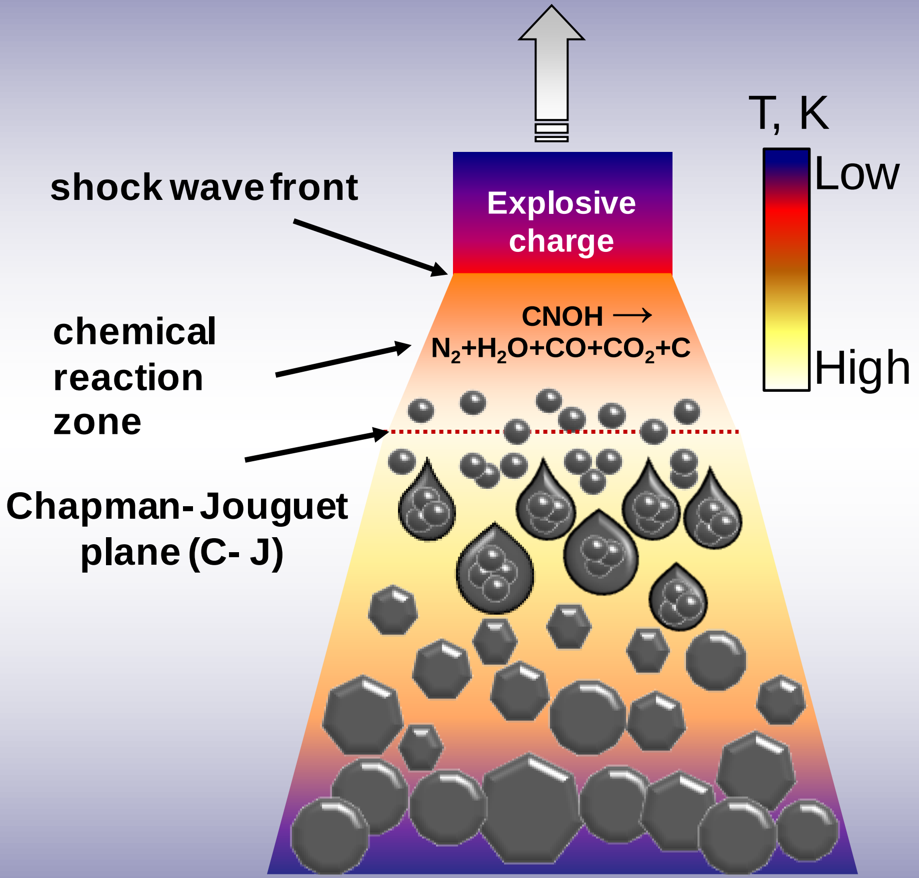
max capacity (experimental): 300m^3, 140kg (water coating)

Yield:

- 5-10wt% of soot
- 35-70% DND in soot

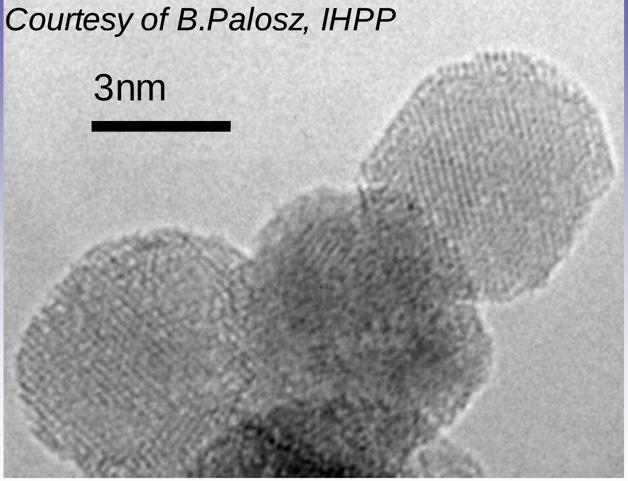
Detonation Nanodiamond Formation

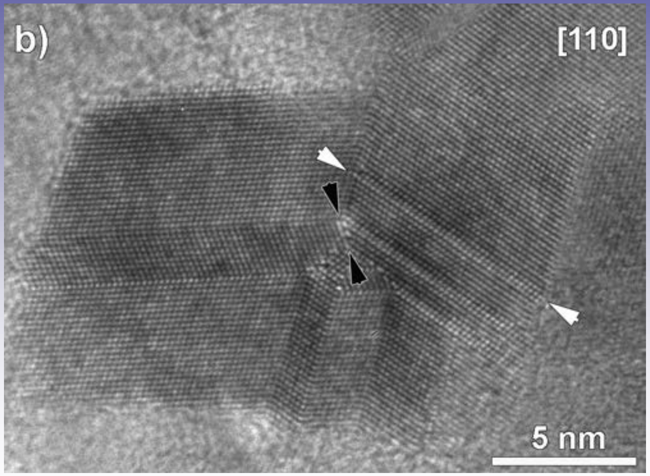


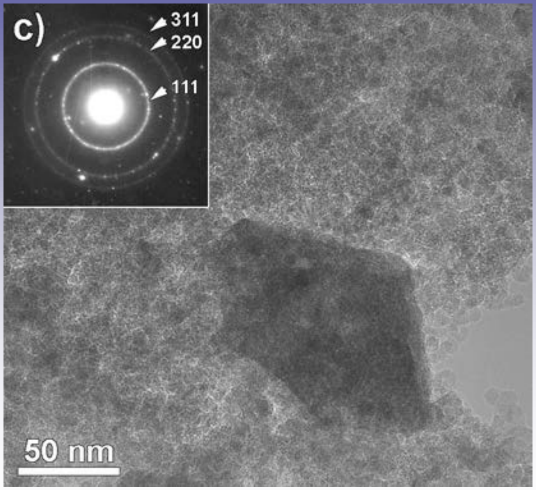


V.V.Danilenko (2005)

Detonation Nanodiamond

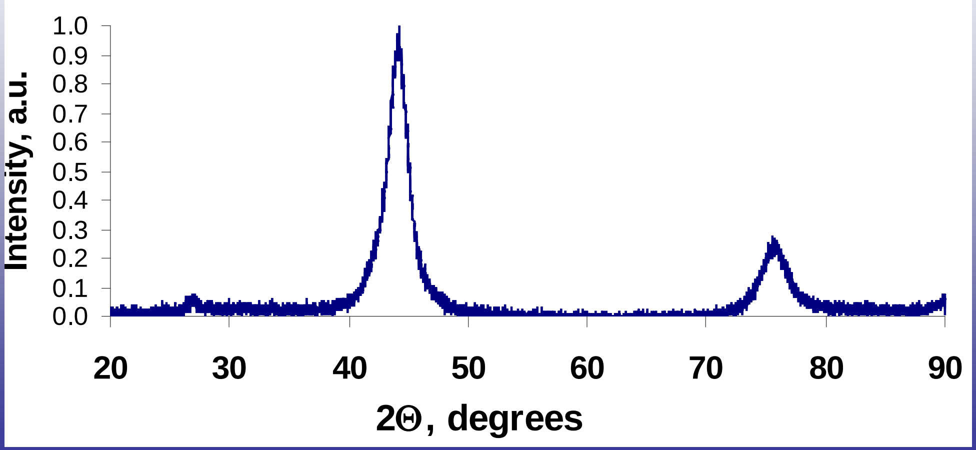

Courtesy of B.Palosz, IHPP

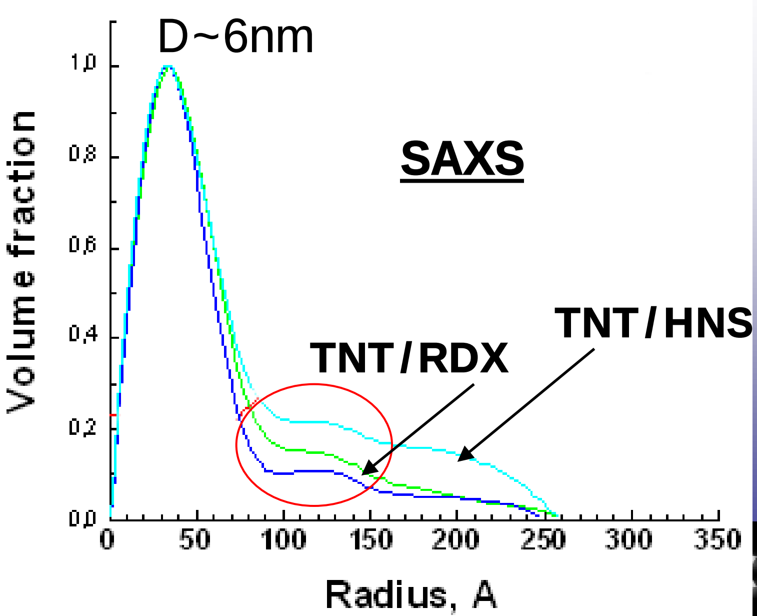




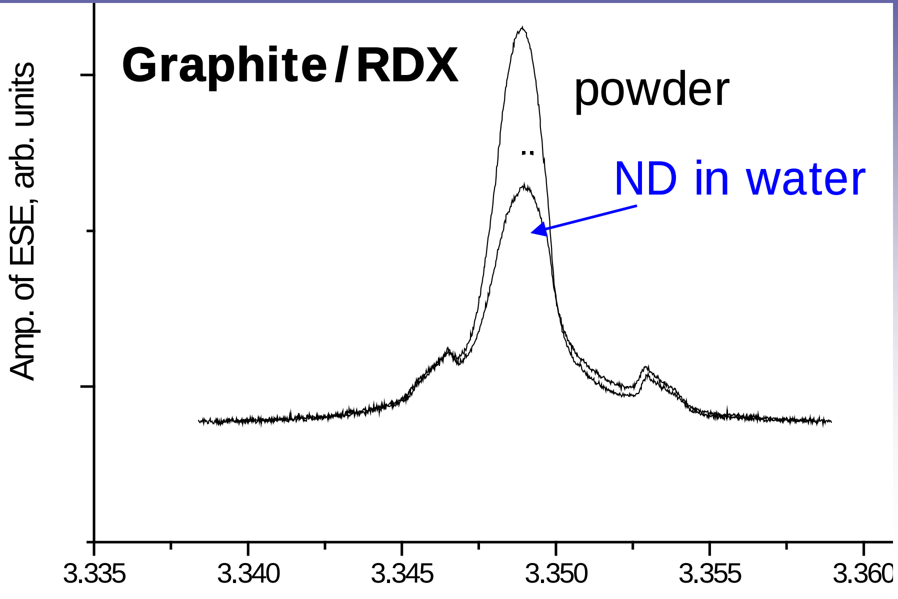
- **N ~2.4 wt%** (CHN analysis) – from TNT\RDX (21at% of N in 50\50)
- **N <1 wt%** (CHN analysis) – from TNT\HNS (hexanitrostilbene) (15at% of N)

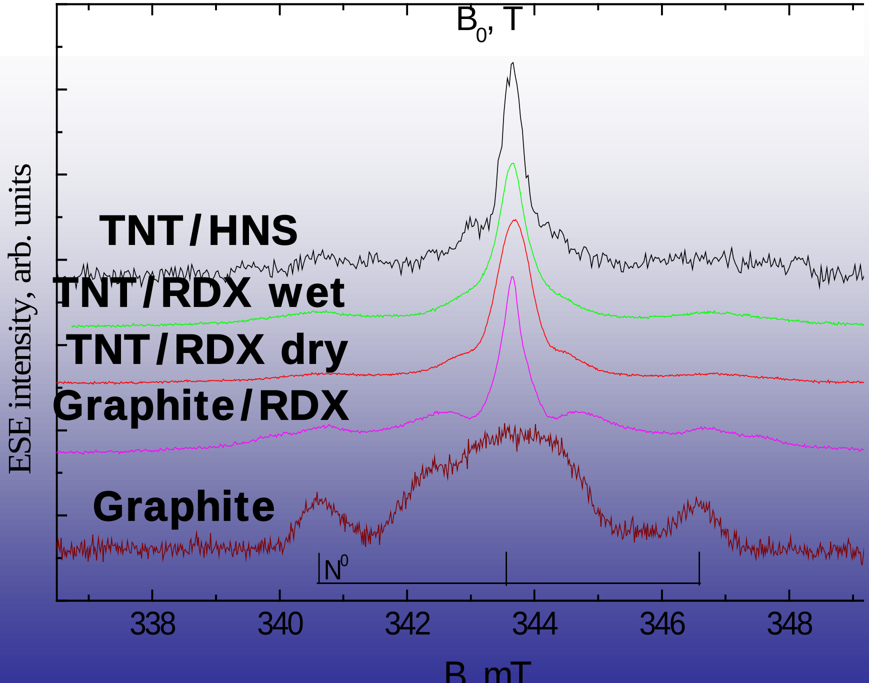
- **Crystal size from XRD: 4 nm**
- **Crystal size from SAXS: 6 nm**





Pulse EPR studies of N_s in Nanodiamond





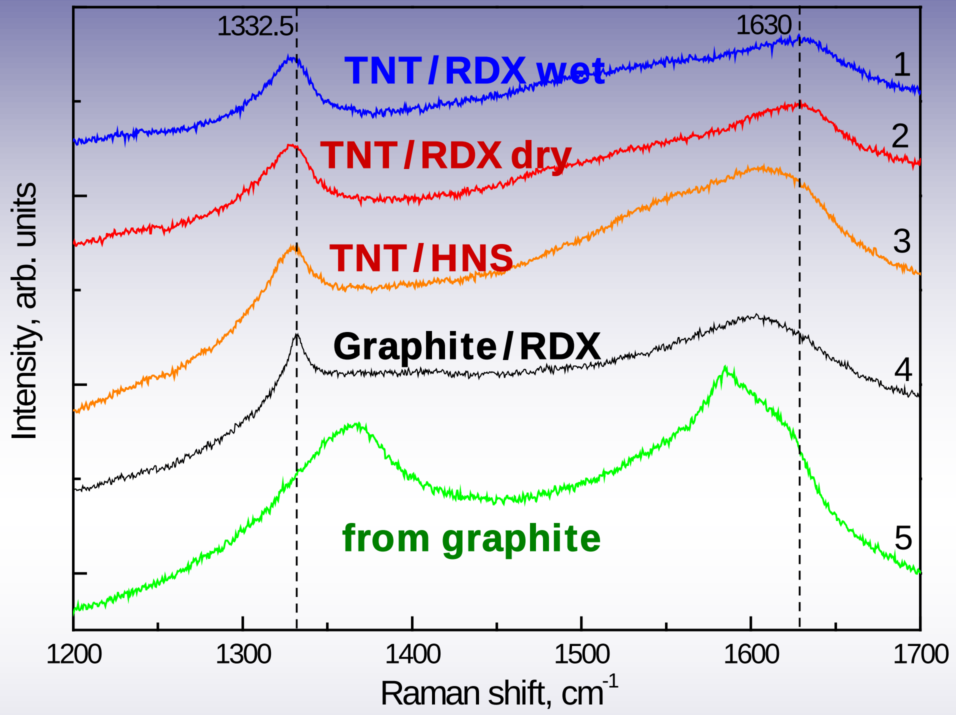
- **W-band mode (93.99 GHz) at room T and T=200K**
- **Pulse: ~00 – T - 2π/3 – τ - 2π/3, (4-3000-96-300-96 ns)**

Centers	T_2	T_1	concentration
N^0	**590 ns**	**8.0 μs**	**$6*10^{16}$ spin/g (1.2 ppm); ~1-4N^o /particle**
Surface centers	190 ns	50 μs	$7*10^{20}$ spin/g (14000 ppm)

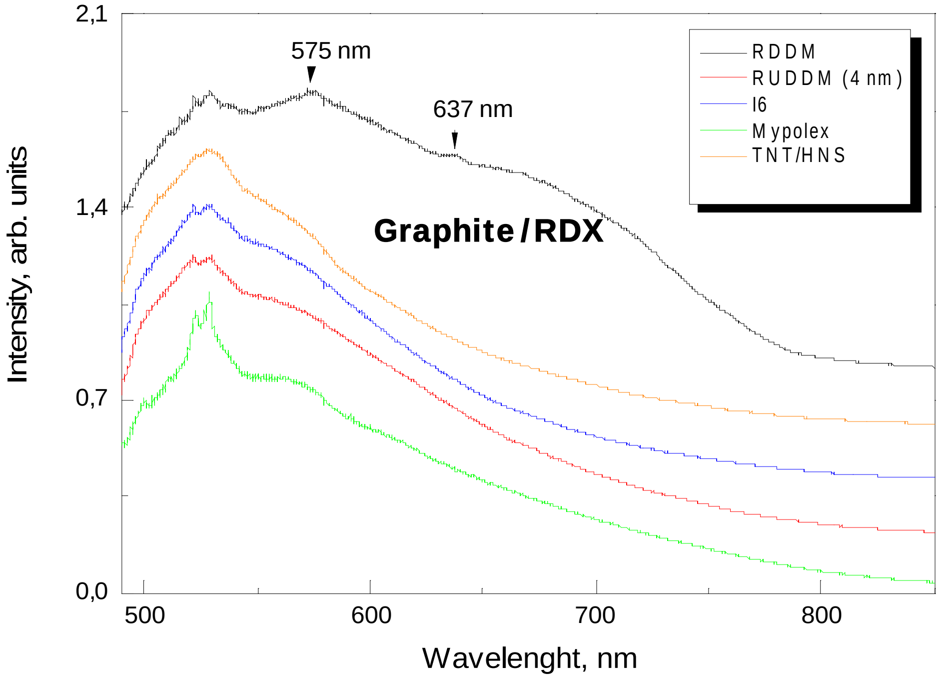
- **X-band mode (9.6 GHz) at room T**

Raman & PL Spectra of Nanodiamonds

Raman spectra



Normalized PL spectra

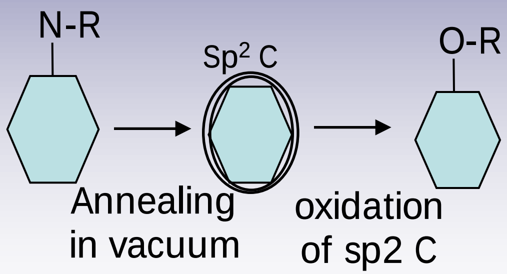


Sample	Crystal Size, SAXS (nm)	Diamond Peak pos. (cm-1)
Graphite/RDX	35	1332.5
TNT/RDX	6	1328.5
TNT/HNS	6	1328.5

Nitrogen state in Detonation Nanodiamond: “small” particles

Eliminated contribution of N from surface groups:

TNT/RDX
60/40
Wet
synthesis

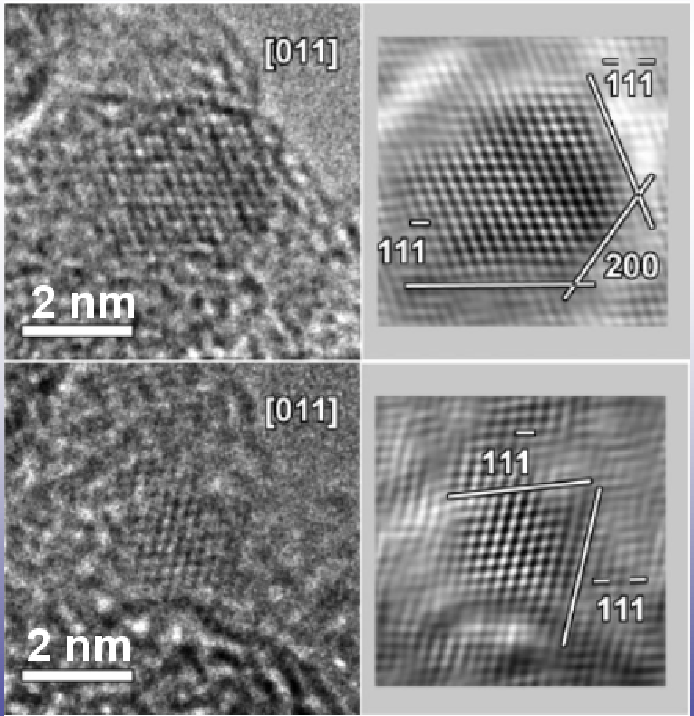

N-R

Sp^2 C

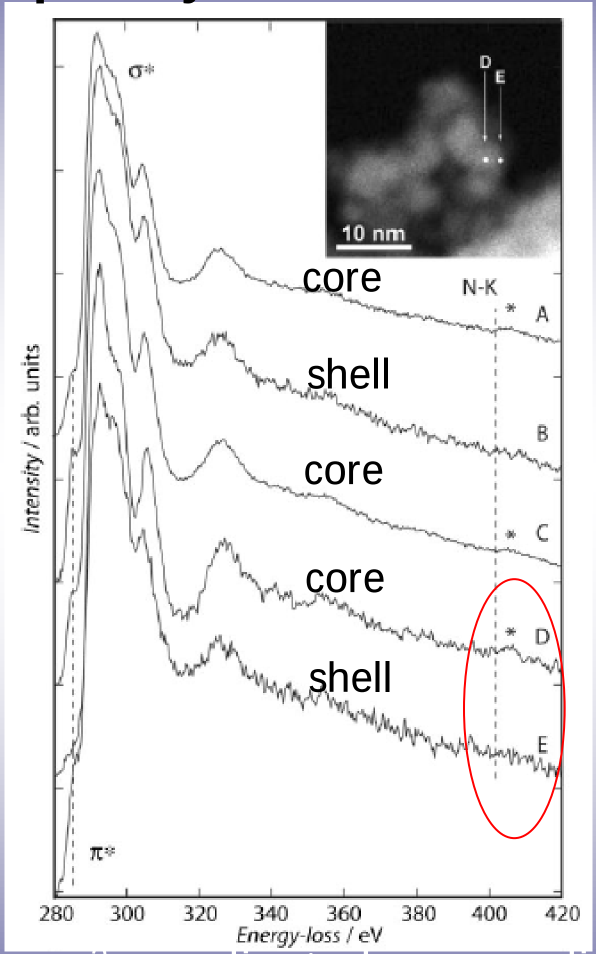
O-R

Annealing in vacuum

oxidation of sp2 C



spatially resolved EELS



core

shell

core

core

shell

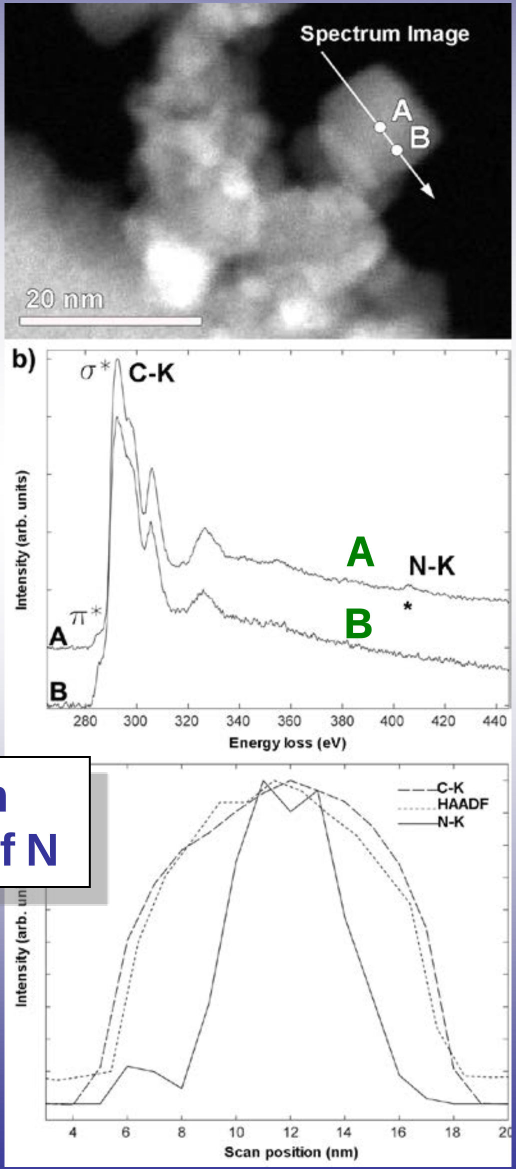
- N is in sp^3 coordinated surrounding
- ~3at% of N in 50% of 6nm particles
- N is in central part of particles

S. Turner, et al. ***Adv. Funct. Mater***. *2009, 19, 2116–2124*

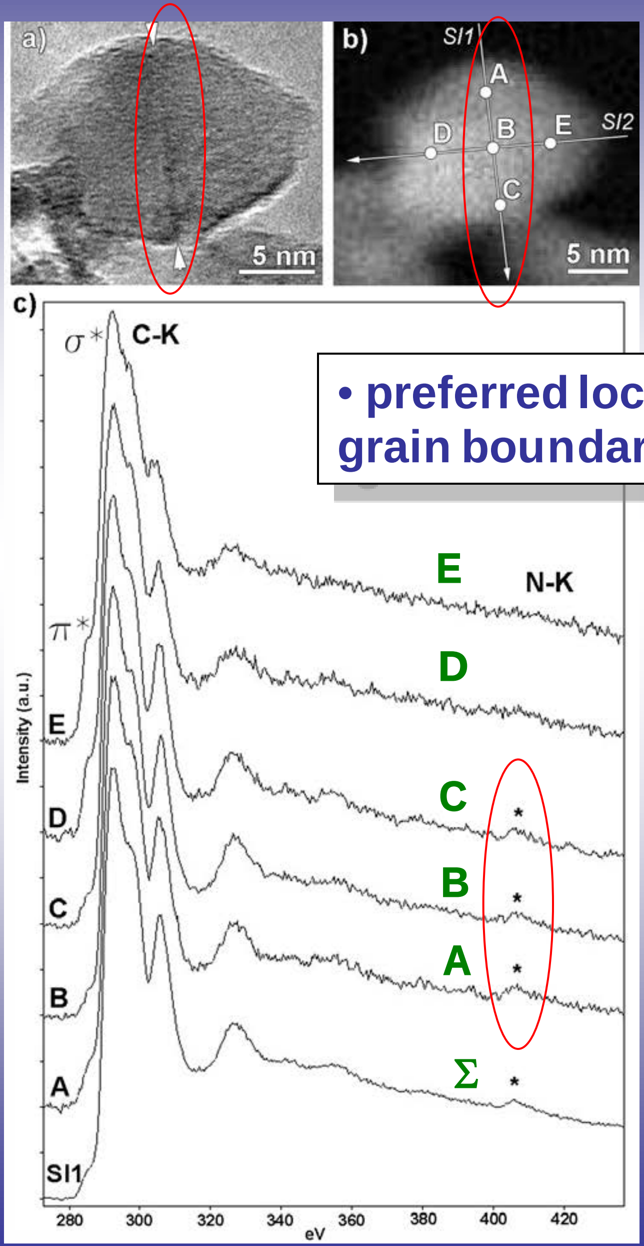
Nitrogen state in “large” particles of DND

Spatially resolved EELS

TNT/RDX
60/40
Wet
synthesis



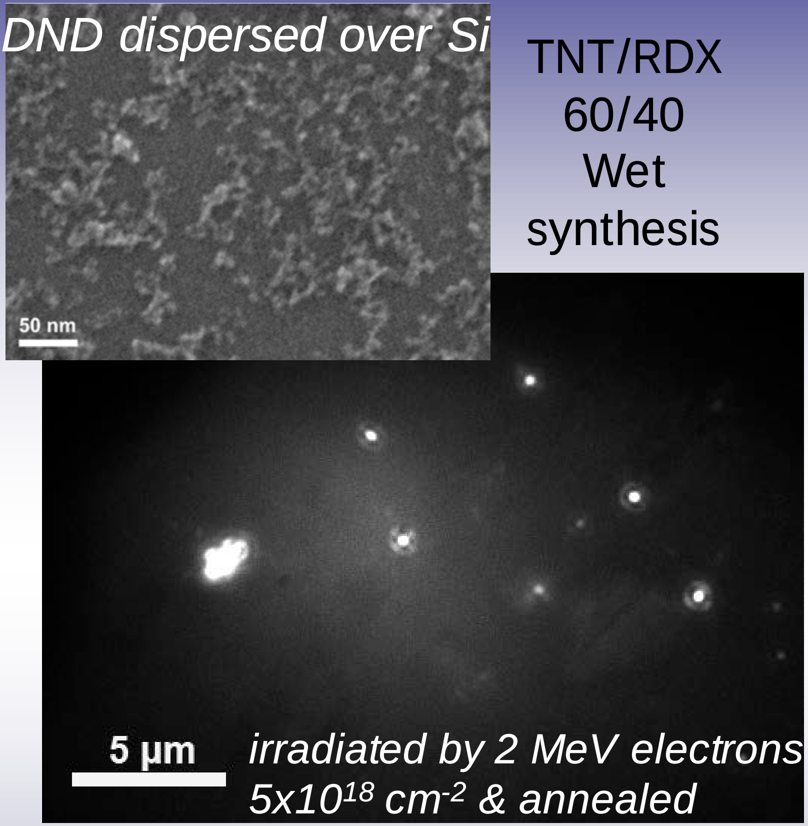
- non-uniform distribution of N



- preferred location at grain boundaries

I.Vlasov et al., ***Small***, *2010*

Nitrogen-Vacancy Centers in Detonation ND

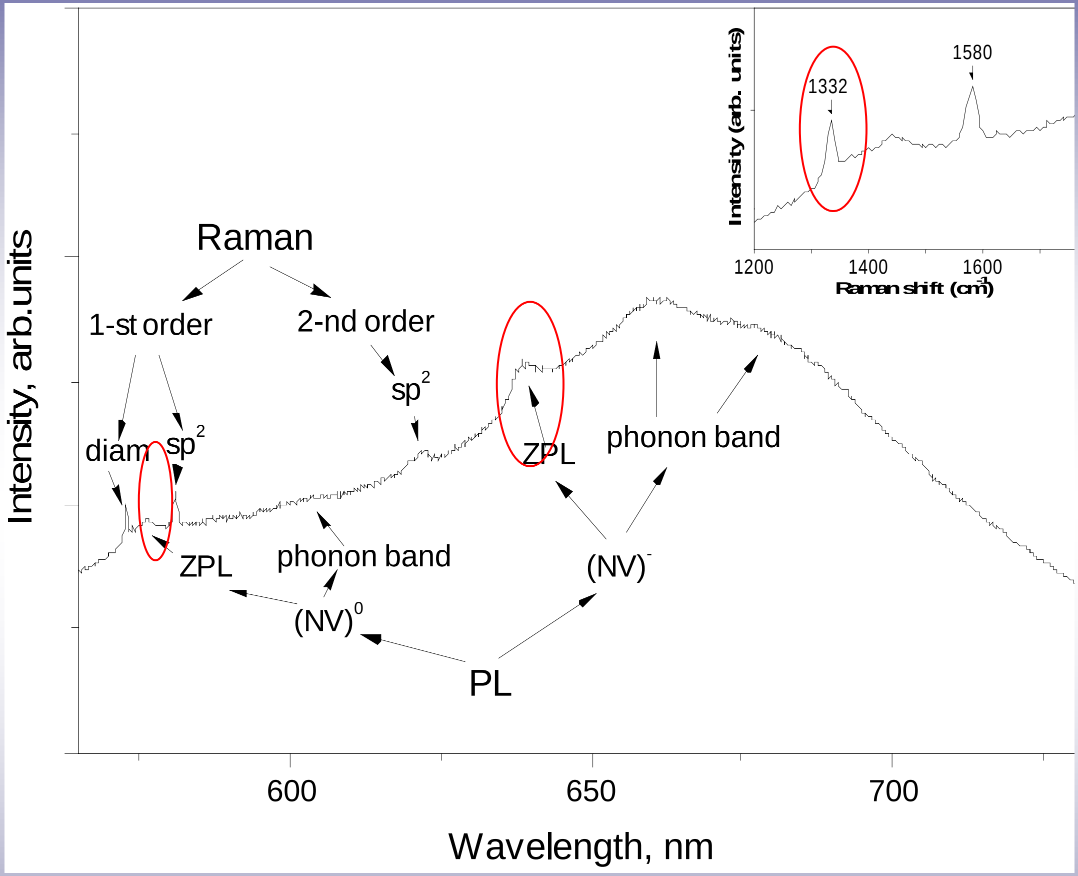


DND dispersed over Si

TNT/RDX
60/40
Wet
synthesis

irradiated by 2 MeV electrons $5x10^{18}$ cm^{-2} & annealed

- edge filter with wavelength >630 nm



Intense and stable emission from NV centers of large DND crystallites (>20-30 nm)

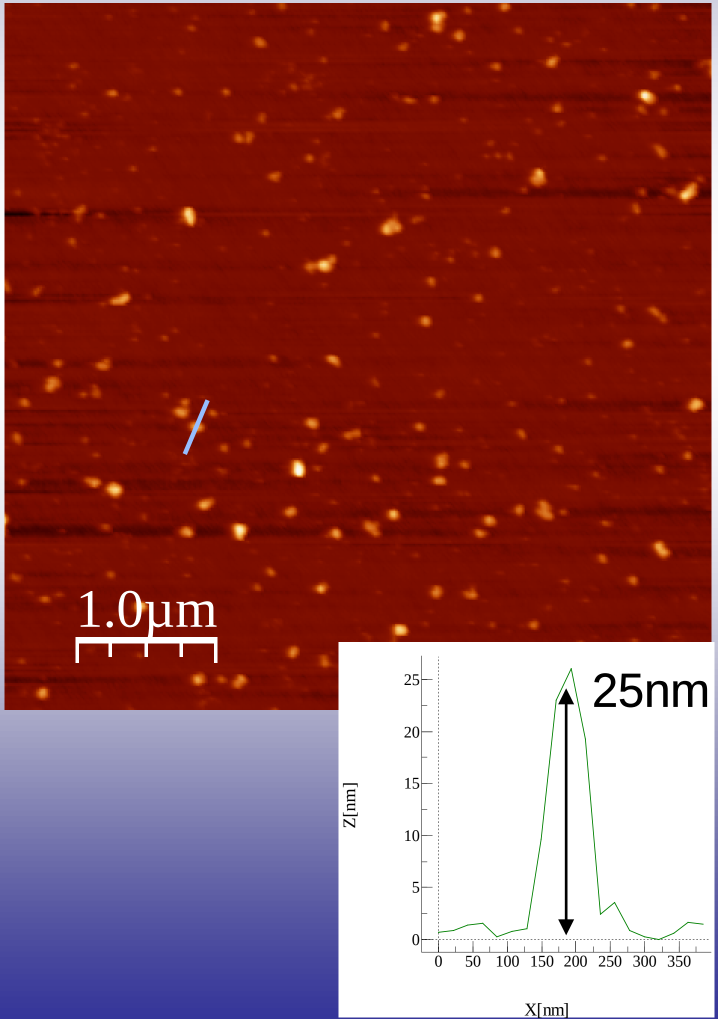
I. Vlasov, et al., ***Small****, 2010*

Nitrogen-Vacancy Centers in ND from graphite\RDX

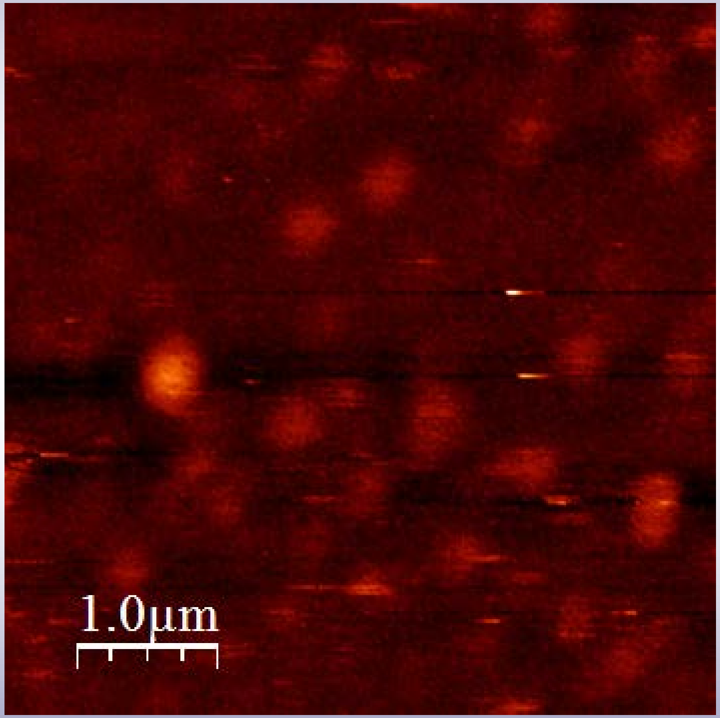
F.Zelezko
University of Stuttgart, Germany

Fraction 35nm (DLS)

AFM



Fluorescence



Luminescent <50% of particles

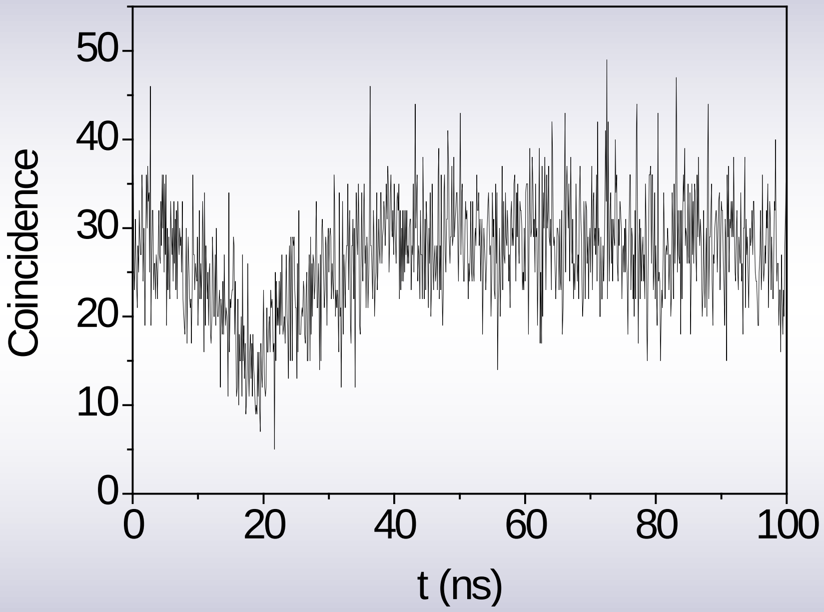
<u>Other work:</u>

Bradac et.al., Nature, 2010
1% of 5nm DND have NV;
blinking (25%)

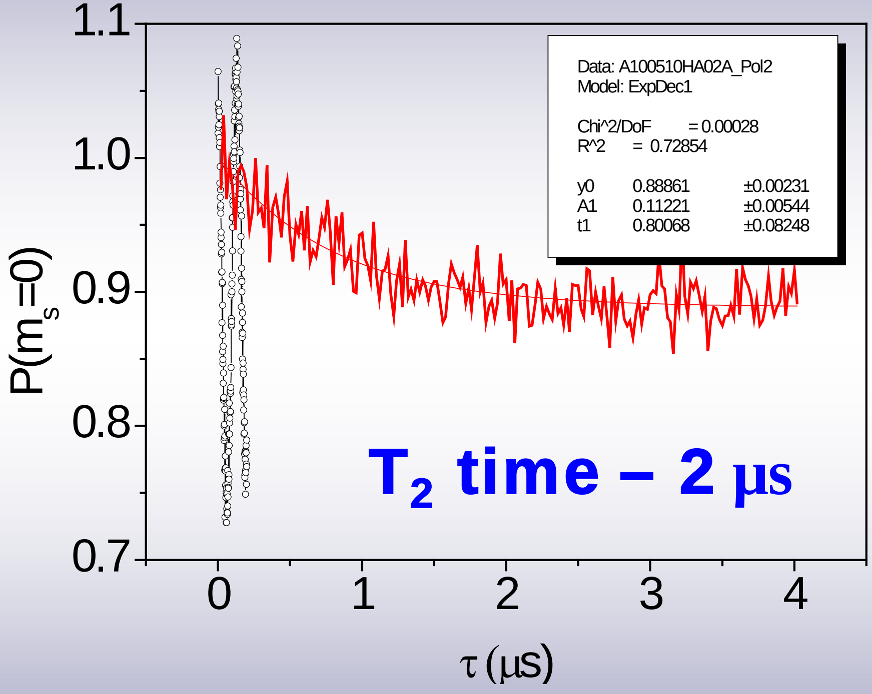
Nitrogen-Vacancy Centers in ND from graphite\RDX

F.Zelezko
University of Stuttgart, Germany

Photon antibunching



Decay of Hahn echo (Magnetic resonance measurements on single NV)



T_2 time – 2 μs

- **~3 NV centers in a particle**
- **stable (no blinking) emission from NV centers**
- **Luminescence lifetime ~10ns**

- **In ND produced from graphite (Mypolex) NV were also observed**
- **For ND from TNT\RDX NV centers were observed in ND of wet synthesis but not in ND of dry synthesis**

Conclusionson N in ND:

- By varying carbon source material in production of ND of dynamic synthesis, it is possible to control N content and state

ND	N total	N_s (EPR)	NV
graphite\RDX	<0.5 wt%	~1.2ppm	in <50% particles of ~30nm
Detonation	1÷2.5 wt%	weak	- absent in some types of DND

- as-produced ND from graphite\hexogen contain NV centers in a noticeable fraction of particles (no irradiation needed!)
- T_2 (spin-spin relaxation time) of NV centers is about 2μs, large enough to be useful for applications

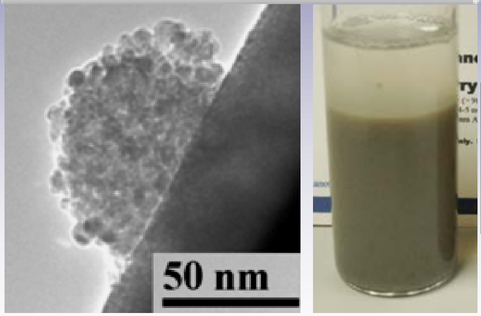
---

- Up to 1%! of nitrogen-vacancy defects can form in DND after sintering at T= 800 °C and p=6 GPa *(P.Baranov, et al. Small (2011) DOI: 10.1002/smll.201001887)*

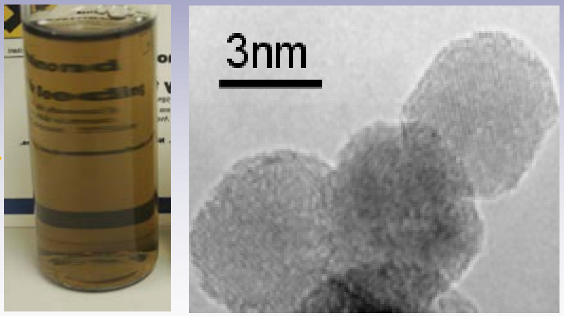
Trends in Detonation Nanodiamond

Conventional DND

Modern DND



Particle size and colloid stability



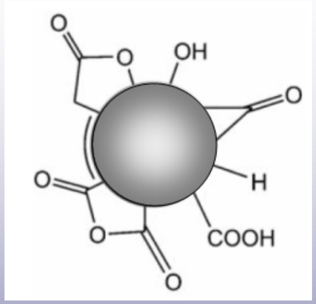
Agglomerates 200-300 nm

Stable single 4-20 nm particles

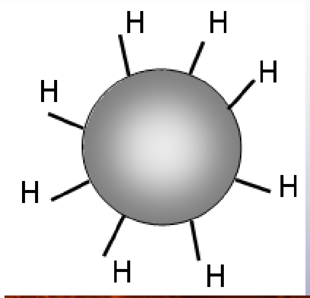
Incombustibles 0.5 – 5%
Non-diamond carbon >5%

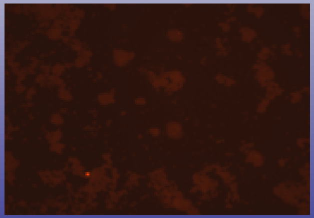
Purity

Incombustibles <0.1%
Non-diamond carbon <0.5%

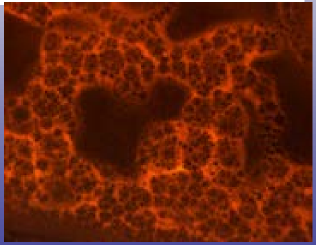


Control of Surface Chemistry

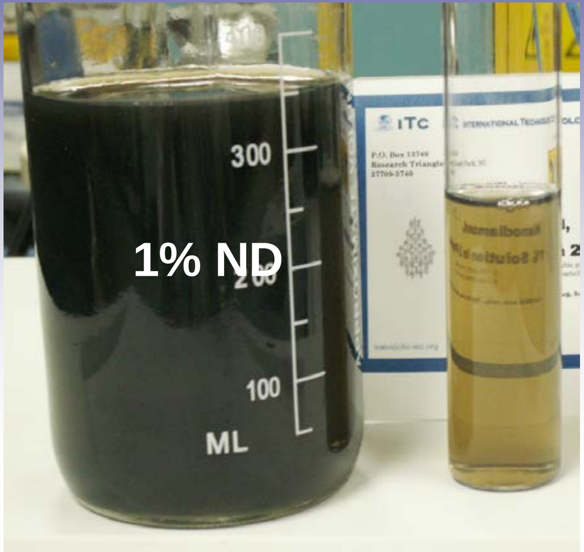


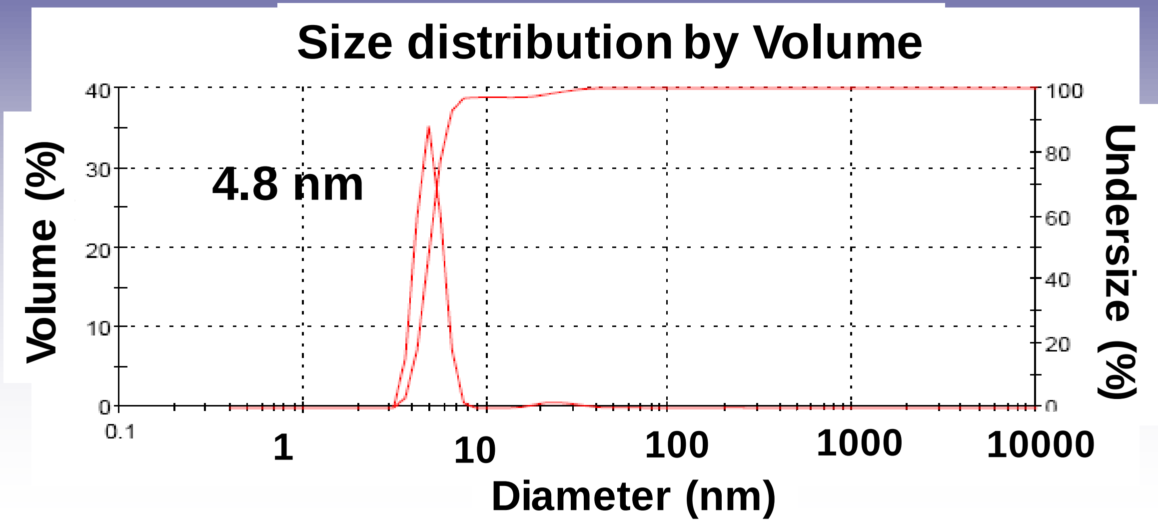


Bright Fluorescence

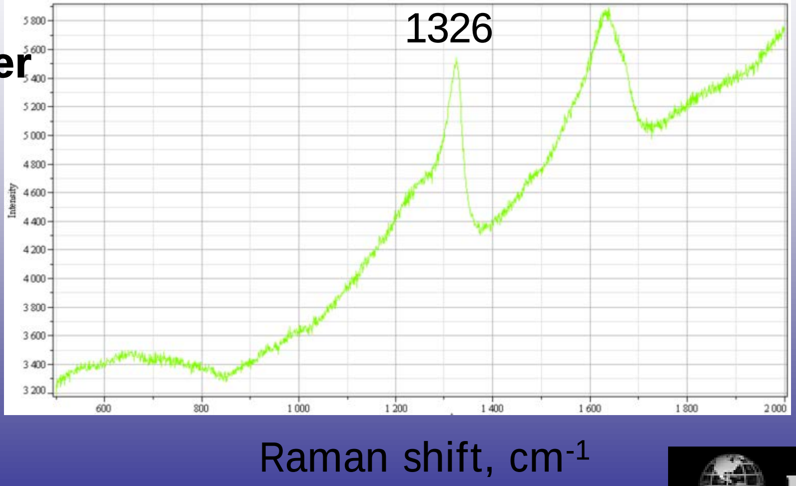


Result of Fractionation & Deagglomeration of DND




Size distribution by Volume

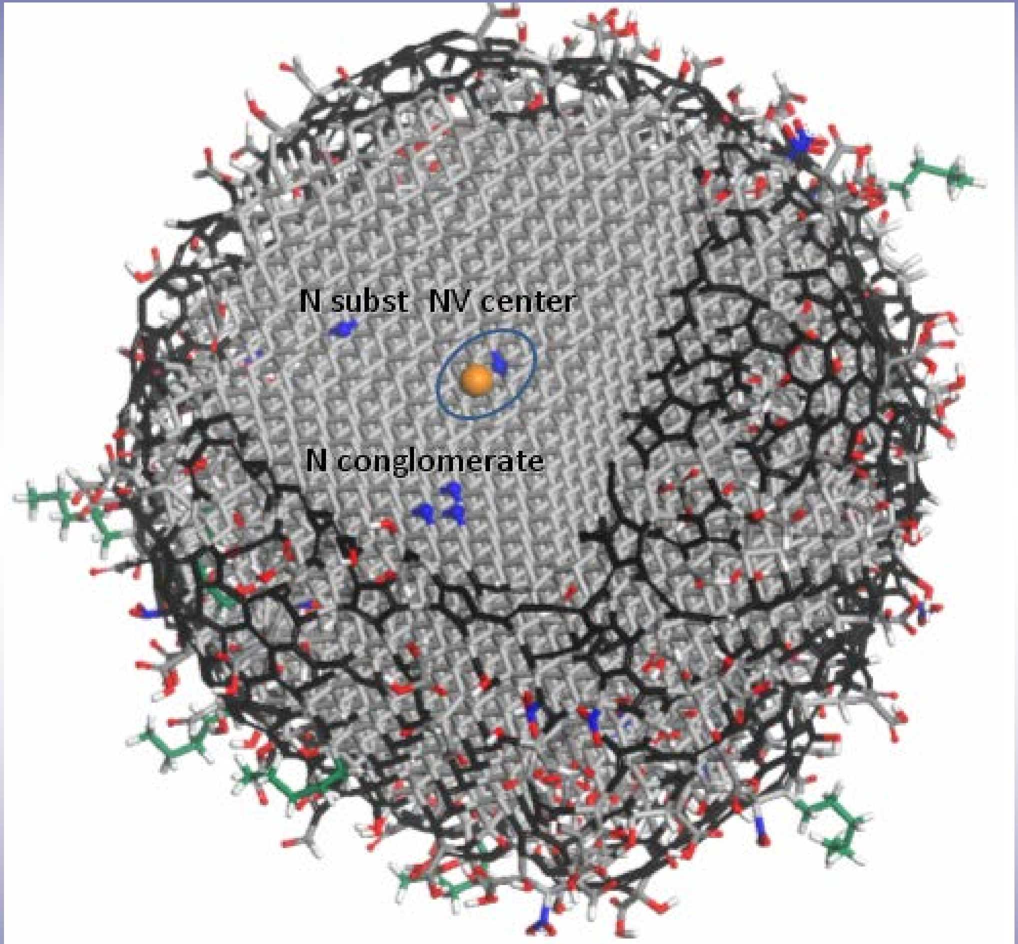
Raman spectra (excitation 442nm)



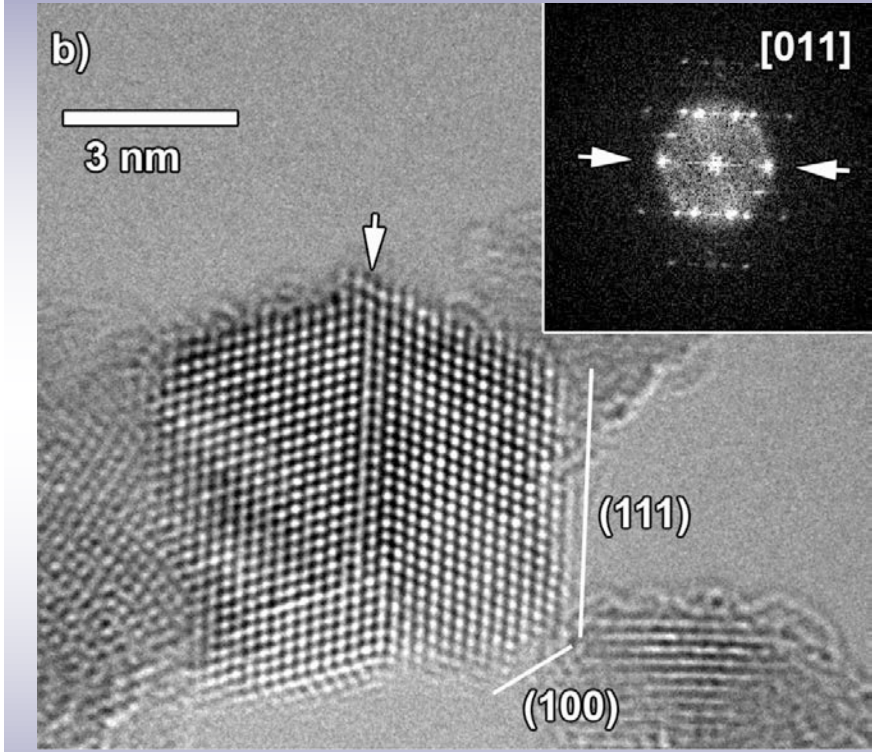
- **Can be dried and re-suspended in DI water with similar size**
- **Well purified from sp2 carbon phase**
- **Carboxylic groups prevail (zeta potential in DI water is -45mV)**
- **Size cutoff less than 30nm**

Detonation Nanodiamond Model

(theory and experiment)



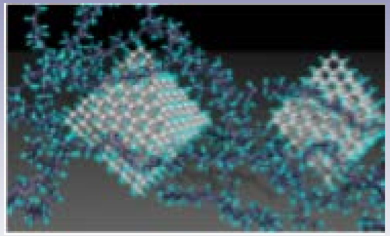
(image by V.Mochalin, O.Shenderova)



(image by S.Turner)

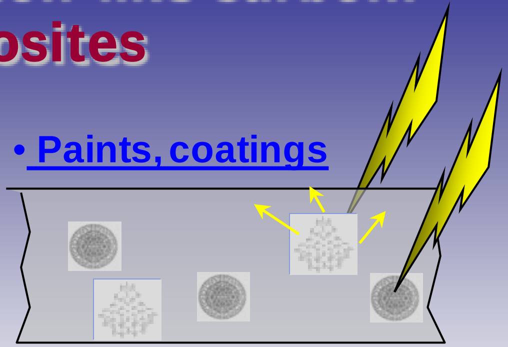
Detonation Nanodiamond & Onion-like Carbon: Applications in Composites

- **Structural polymer nanocomposites**



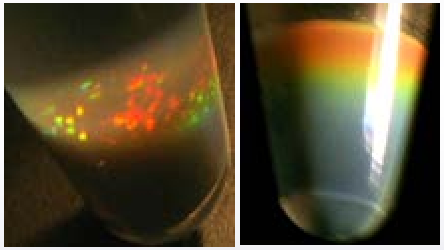
- Transparent armor

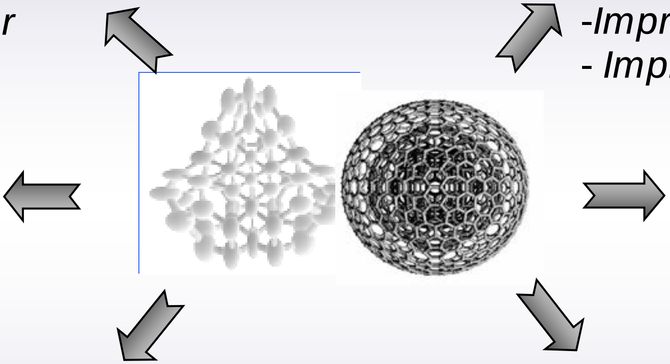
- **Paints, coatings**



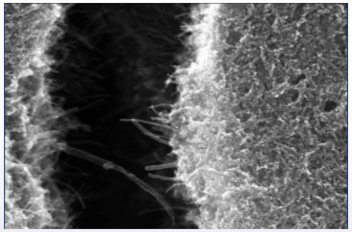
- UV protection, EMI shielding
- Wear resistant paints
-Improved thermal properties
- Improved adhesion

- **Photonic structures**

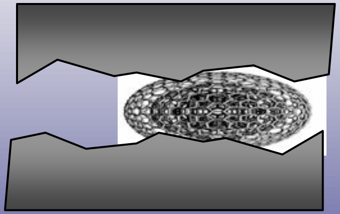




- **ND-CNT functional coatings**

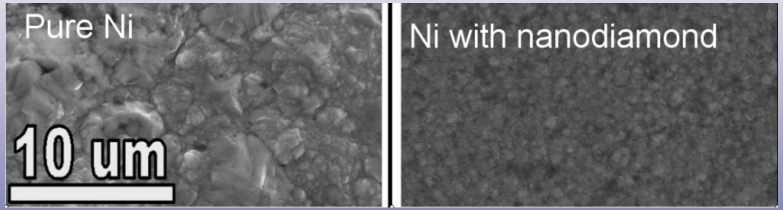


- **Motor oil additives**
- **Solid lubricants**



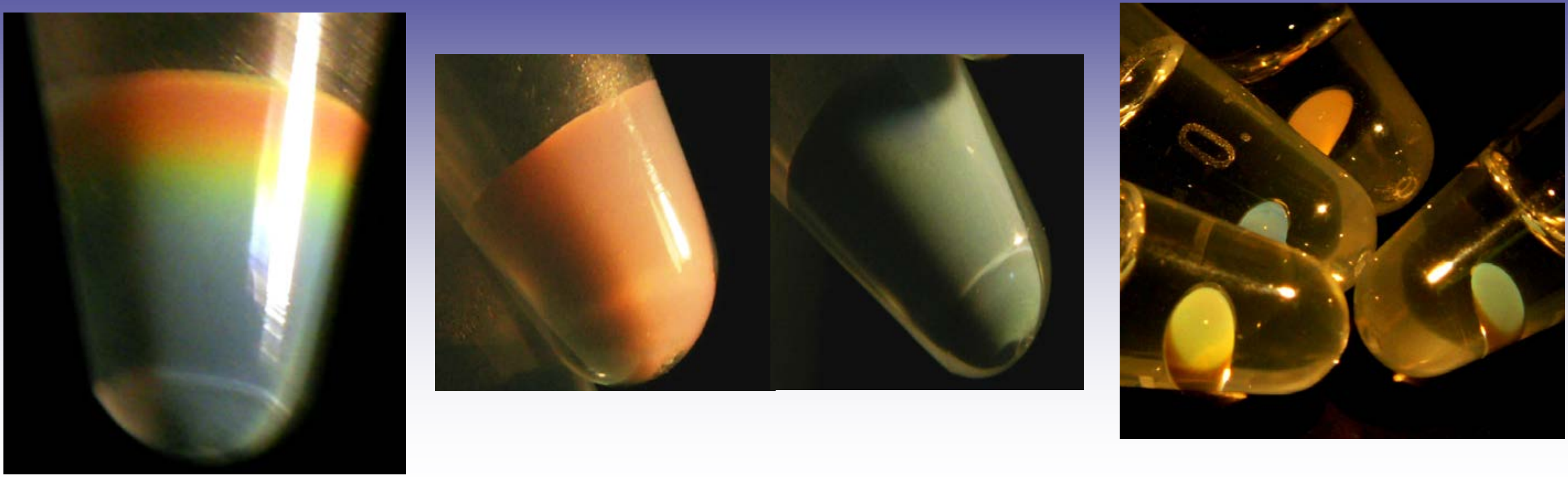
- Fuel efficiency
- Lubricant for airspace appl.

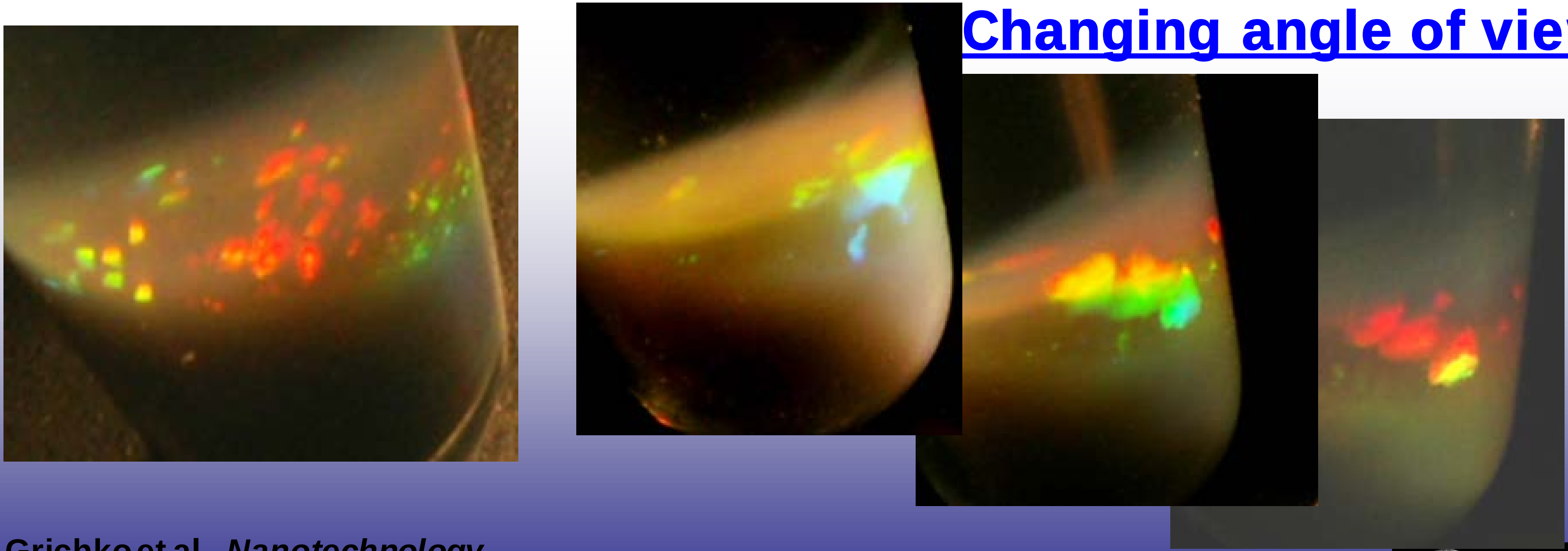
- **Metal nanocomposite coatings**



- Hexavalent Cr replacement with Ni-ND
- x8 times improvement in wear

Nanodiamond photonic structures

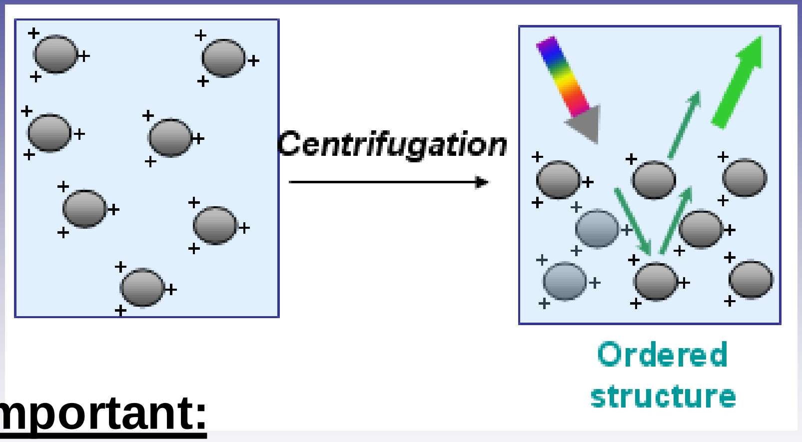


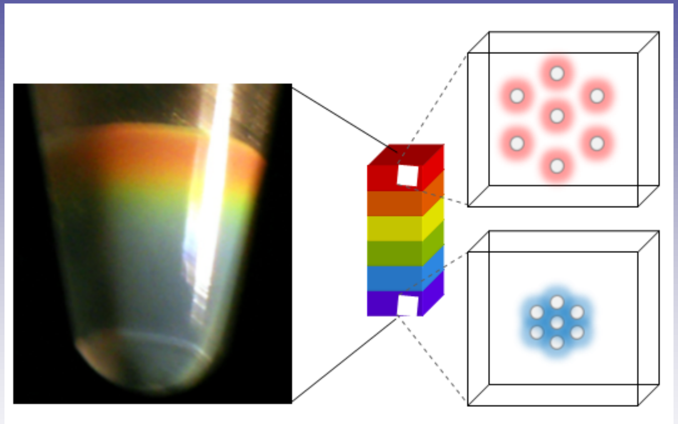


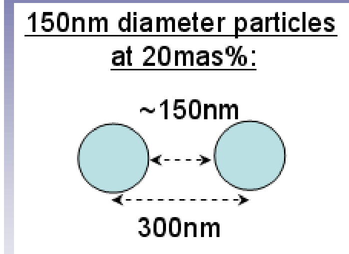
Changing angle of view

V.Grichko et al., *Nanotechnology* 19, 22, 225201 (2008)

Nanodiamond photonic structures





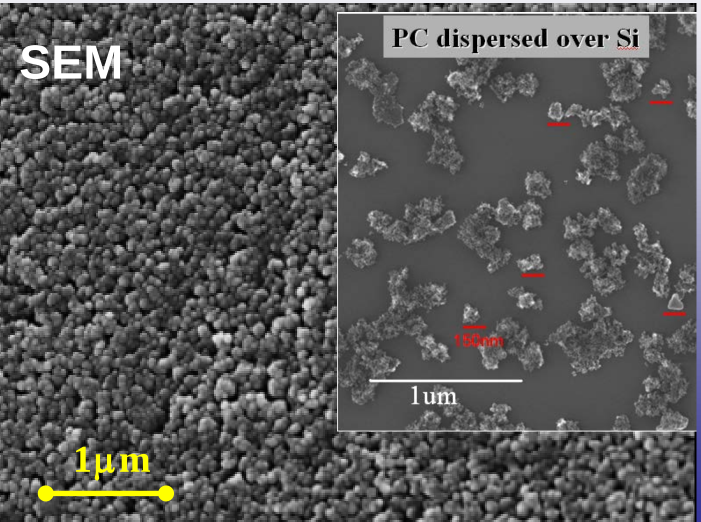


Important:

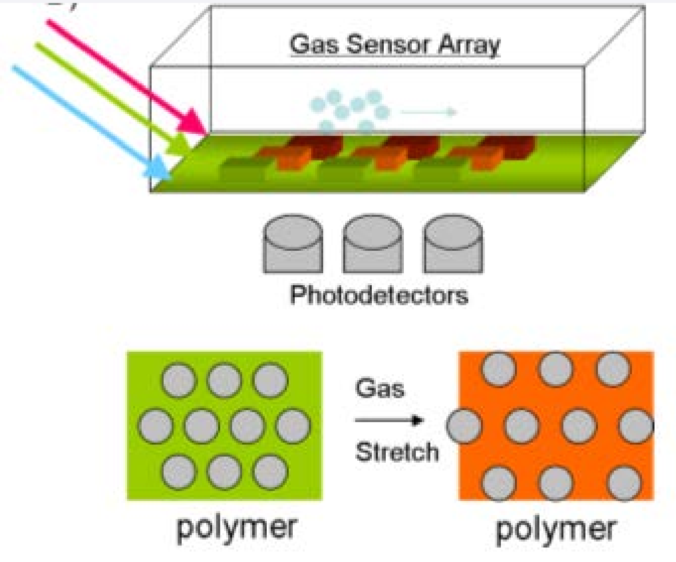
- Nanoparticles of similar sizes
- Deionization of the suspension (high surface charge on nanoparticles)

Unusual features:

Irregular shapes



Applications: chem- and biodetectors



Conclusions/Future Outlook

- Based on unique electronic structure of C, new carbon allotropes can be discovered
- Carbon nanotubes and graphene are produced at a large scale and find broad applications, while fullerenes and nanodiamond particles are not

- ➢ Further studies of ND synthesis is required
- ➢ Doping of DND with other elements during synthesis is a perspective direction
- ➢ Reduction of DND cost is needed

Acknowledgment of Colleagues/Collaborators:

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F. Jelezko, J. Wrachtrup, *Physikalisches Institut, Stuttgart, Germany*

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