

Application of Low Voltage Cs-corrected TEM for Nanocarbon Materials

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Donostia - San Sebastian

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Dubna, 27.08.2012





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Data SIO, NOAA, U.S. Navy, NGA, GEBCO

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45°37'09.89" N 0°47'57.75" E elev 549 ft

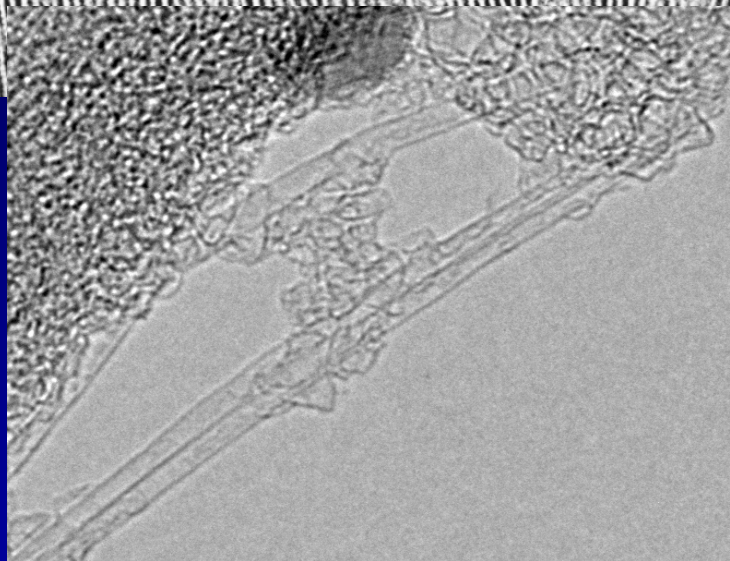
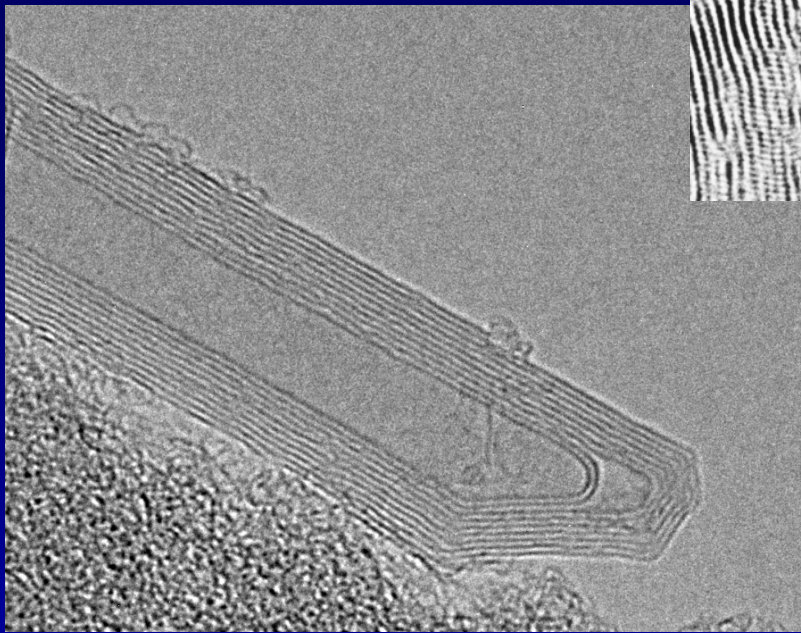
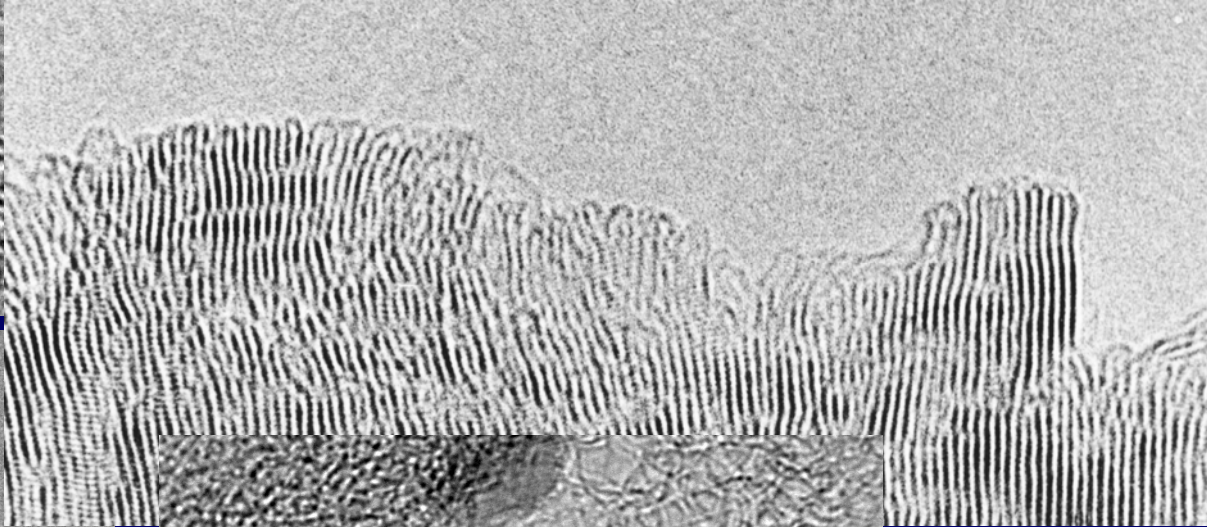
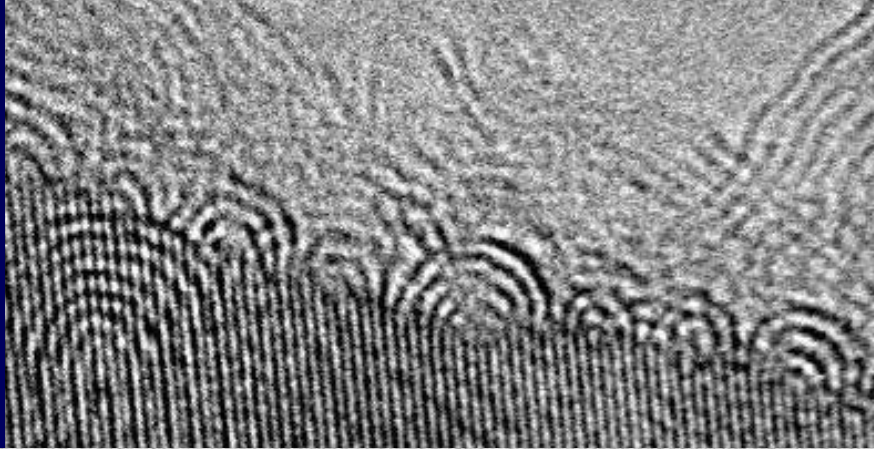
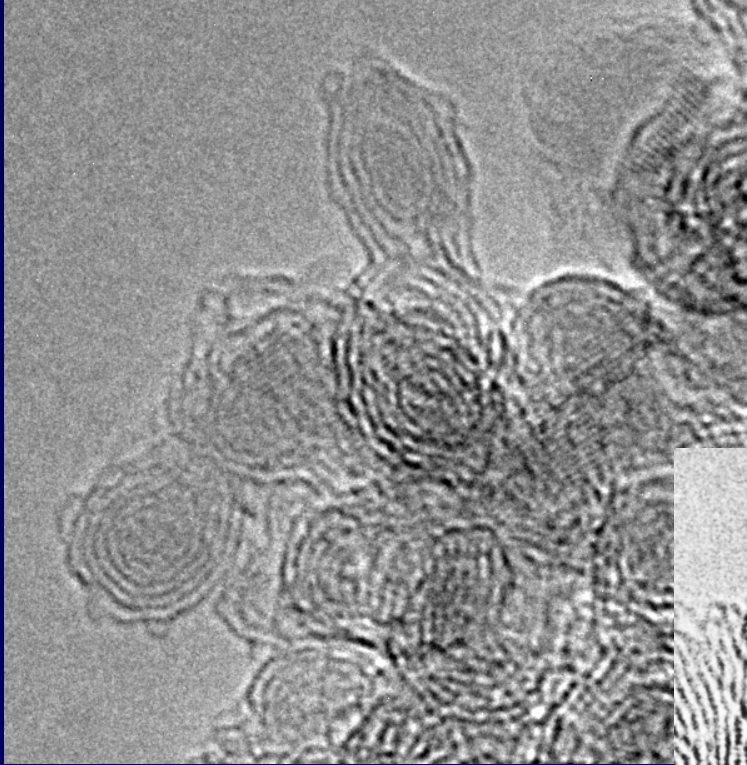


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Nanoscience Cooperative Research Center



Outline:

- Factors limiting resolution in TEM
 - Optics
 - Signal-to-Noise Ratio
 - Radiation damage
- Cs correction
 - What is it?
 - What do we have out of it?
- Application examples
 - (Dy@C82)@SWNT
 - Monoatomic carbon chains
 - Fullerene formation
 - Carbon nanoribbons
 - High resolution tomography
 - Visualization of chemical bond



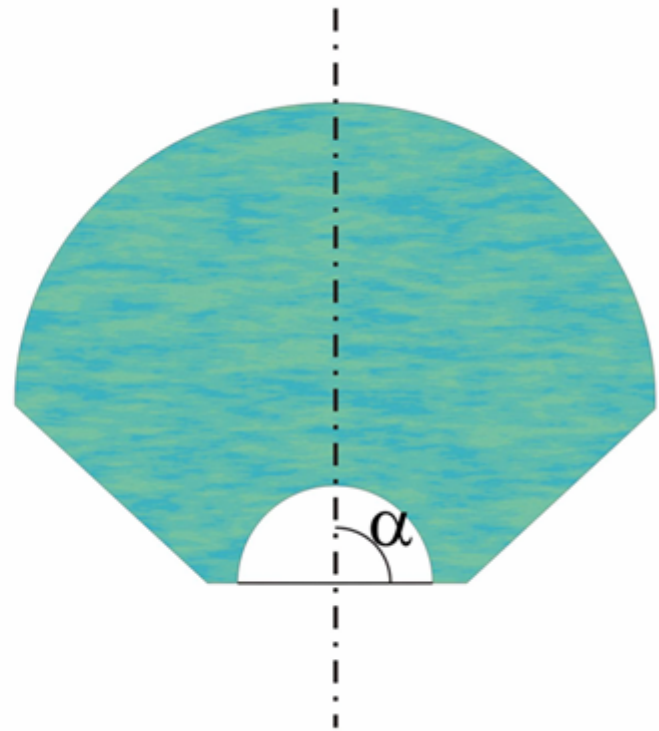
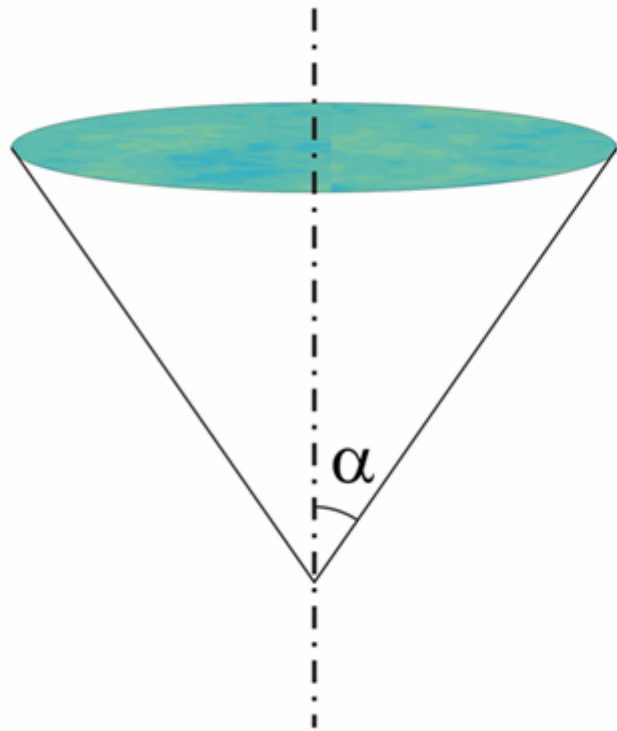
Resolution limited by electron optics



$$d = 1.22 \frac{\lambda}{NA_c + NA_o}$$

$$d \cong \frac{\lambda}{\sin \alpha}$$

Resolution limited by electron optics



Resolution limited by electron optics

Scherzer O, *Über einige Fehler von Elektronenlinsen*. Z. Phys. **101** (1936) 593-603

Otto Scherzer



Über einige Fehler von Elektronenlinsen.

Von O. Scherzer in Darmstadt.

Mit 3 Abbildungen. (Eingegangen am 4. Juni 1936.)

Unmöglichkeit des Achromaten. Die Bildfehler dritter Ordnung. Unvermeidbarkeit der sphärischen Aberration.

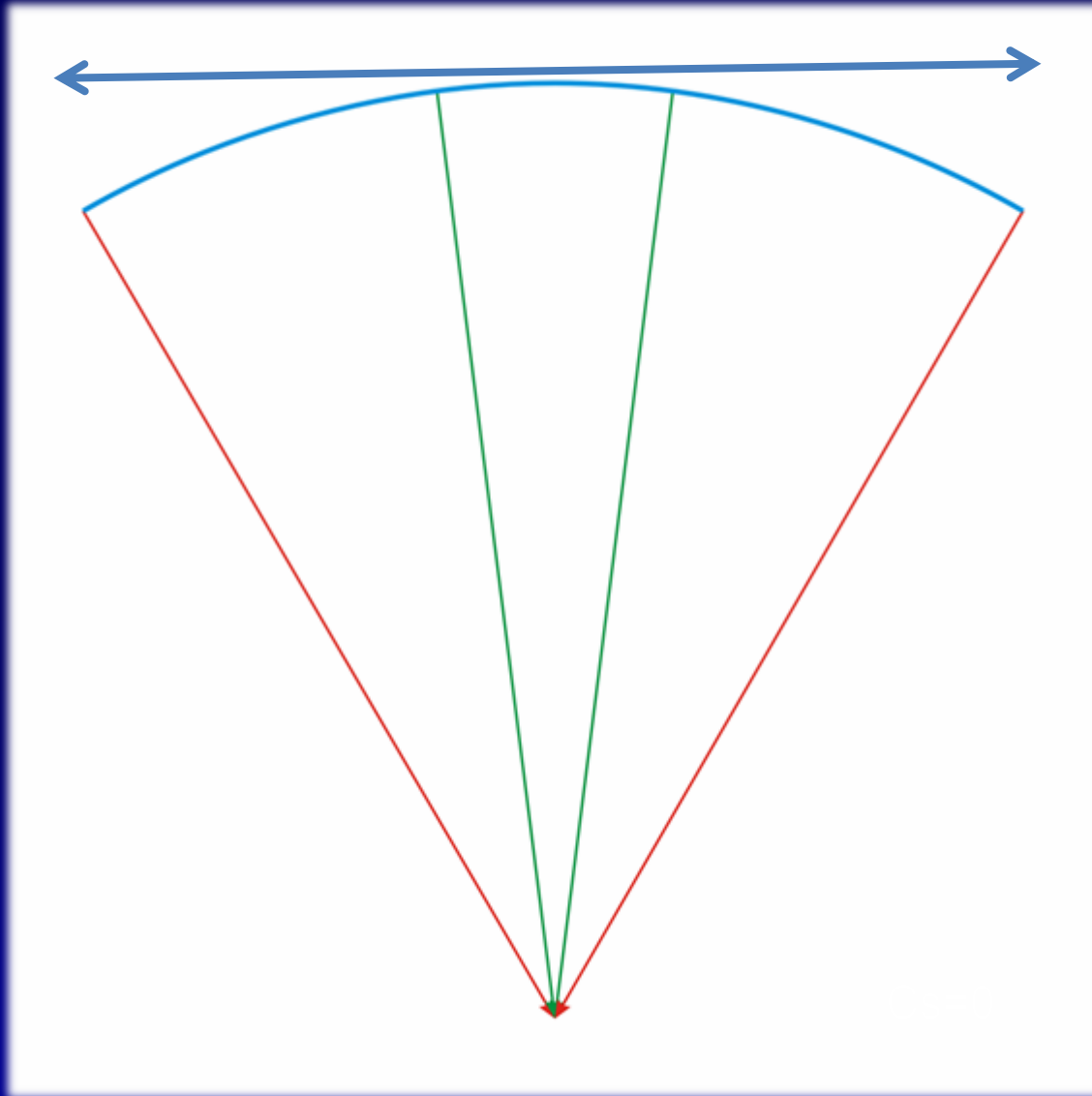
1. Unmöglichkeit des Achromaten.

Die wichtigste Forderung, die ein chromatisch korrigiertes Linsensystem erfüllen muß, ist die, daß zwei Strahlen benachbarter Farbe, die von der Objektmitte unter kleinem Winkel gegen die optische Achse ausgehen, sich in der Bildmitte treffen; bei Elektronenlinsen tritt an die Stelle der „Farbe“ die Elektronengeschwindigkeit. Wir werden zeigen, daß sich diese Forderung bei raumladungsfreien Elektronenlinsen niemals in Strenge erfüllen läßt.

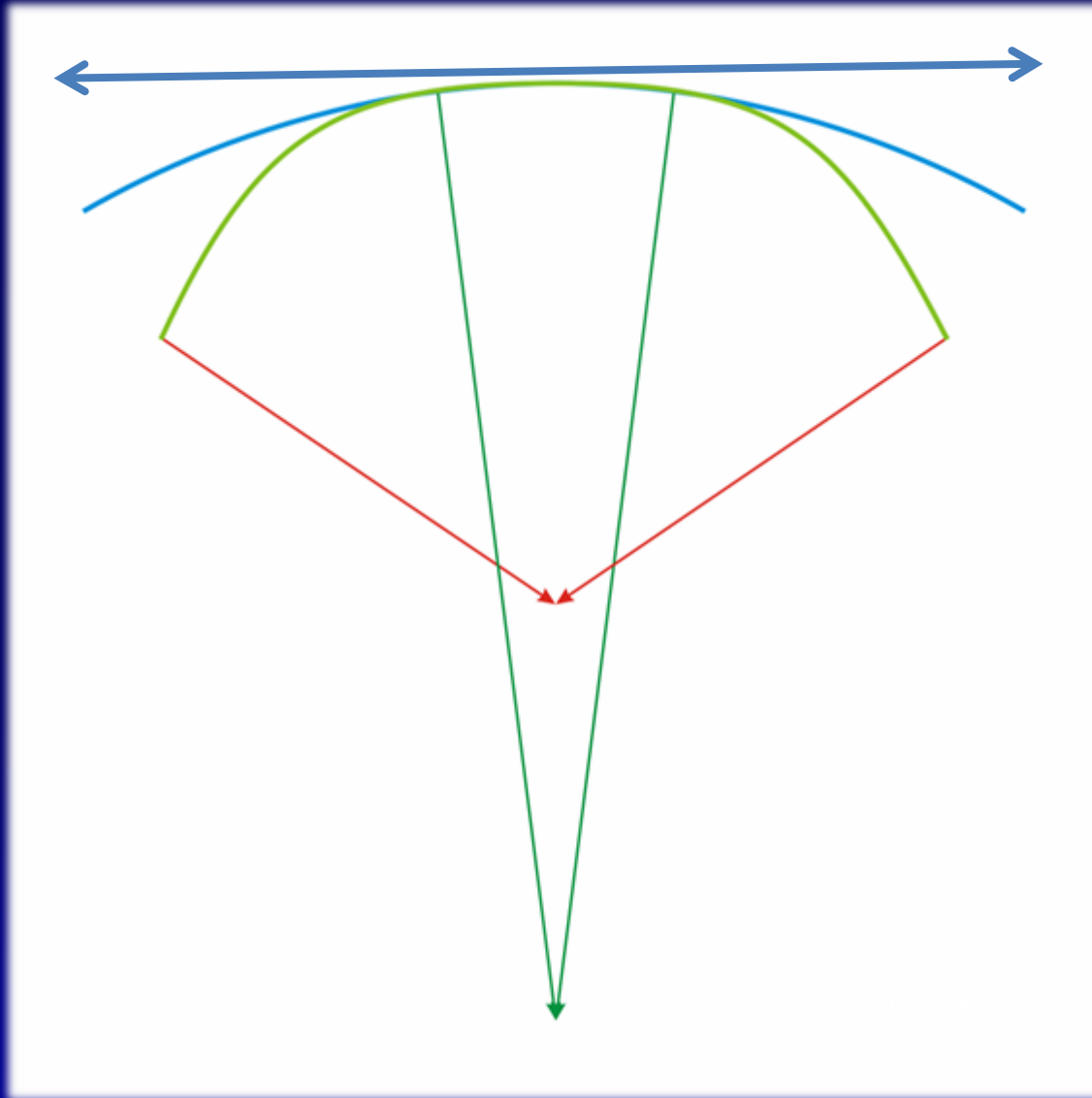
Die Bewegung der achsennahen Elektronen (Gaußscher Strahlengang) genügt bekanntlich der Gleichung

$$\Phi r'' + \frac{1}{2} \Phi' r' = -\frac{r}{4} \Phi'' - \frac{er}{8m} \mathfrak{S}^2. \quad (1)$$

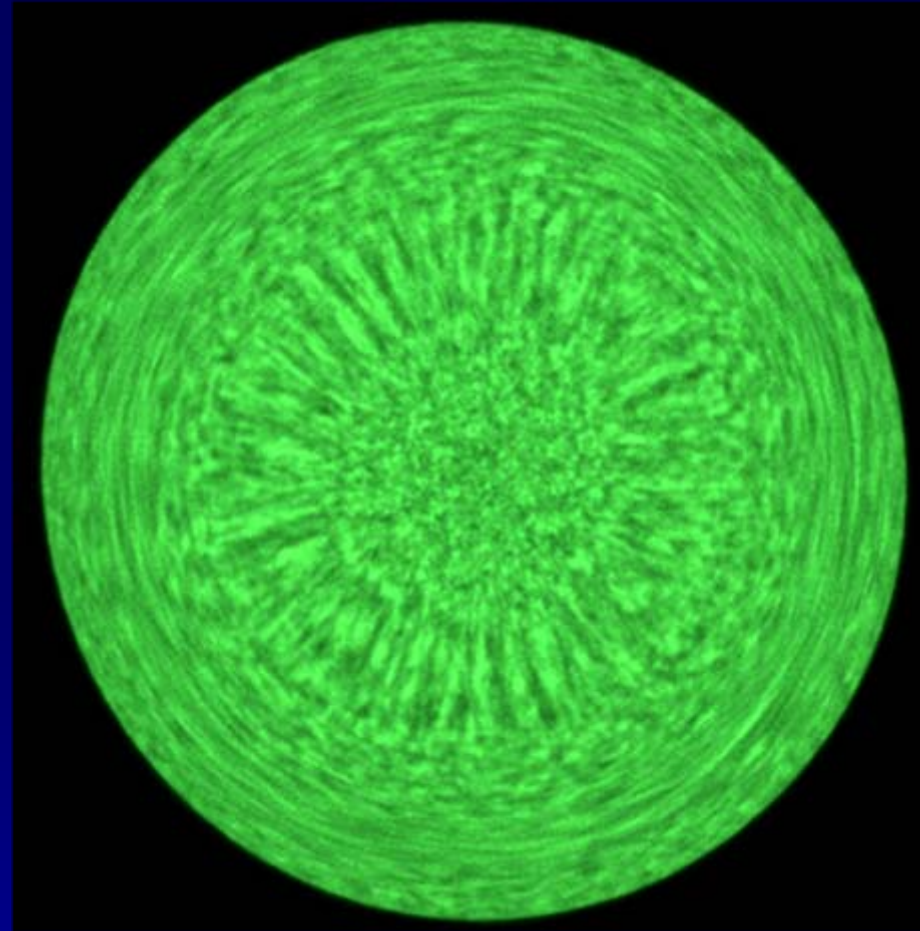
Resolution limited by electron optics



Resolution limited by electron optics



Resolution limited by electron optics



Resolution limited by electron optics

Typical values:

$C_s = 0.5 - 2.5$ mm

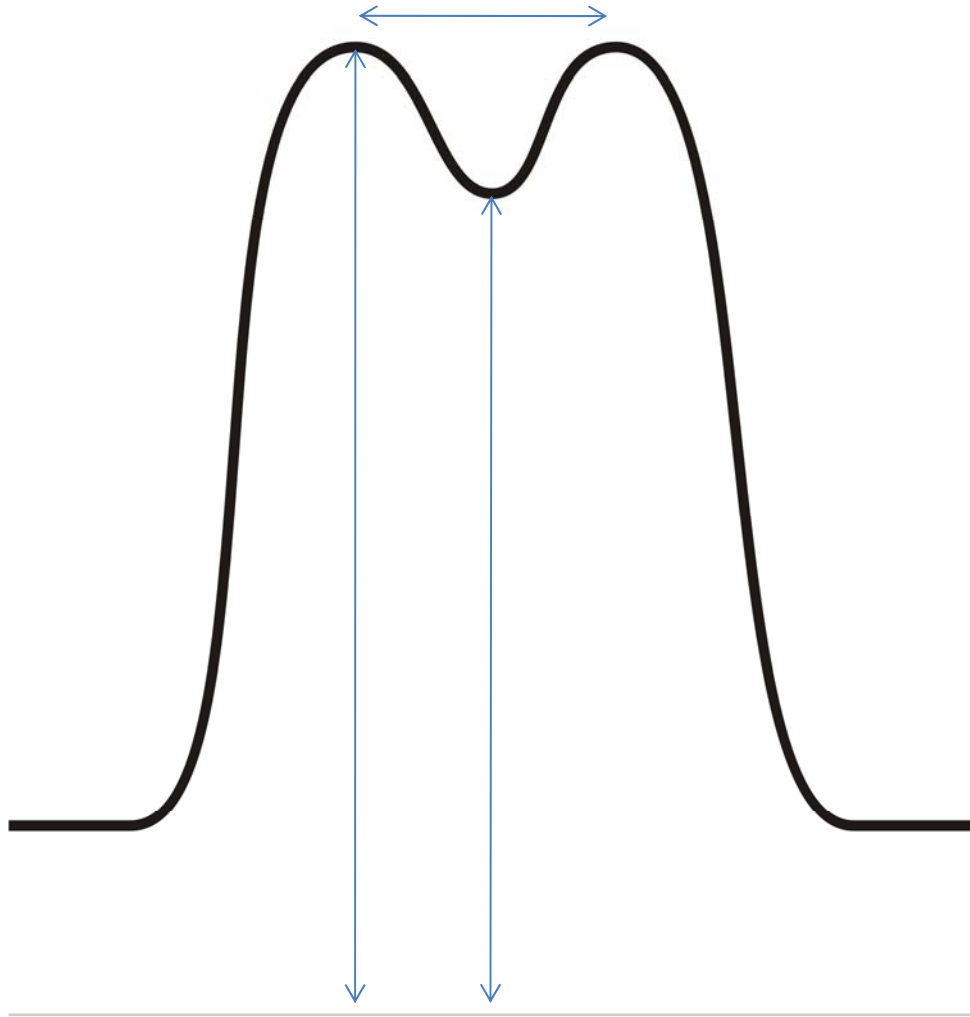
5-10 mrad

$NA_o \sim 0.01$

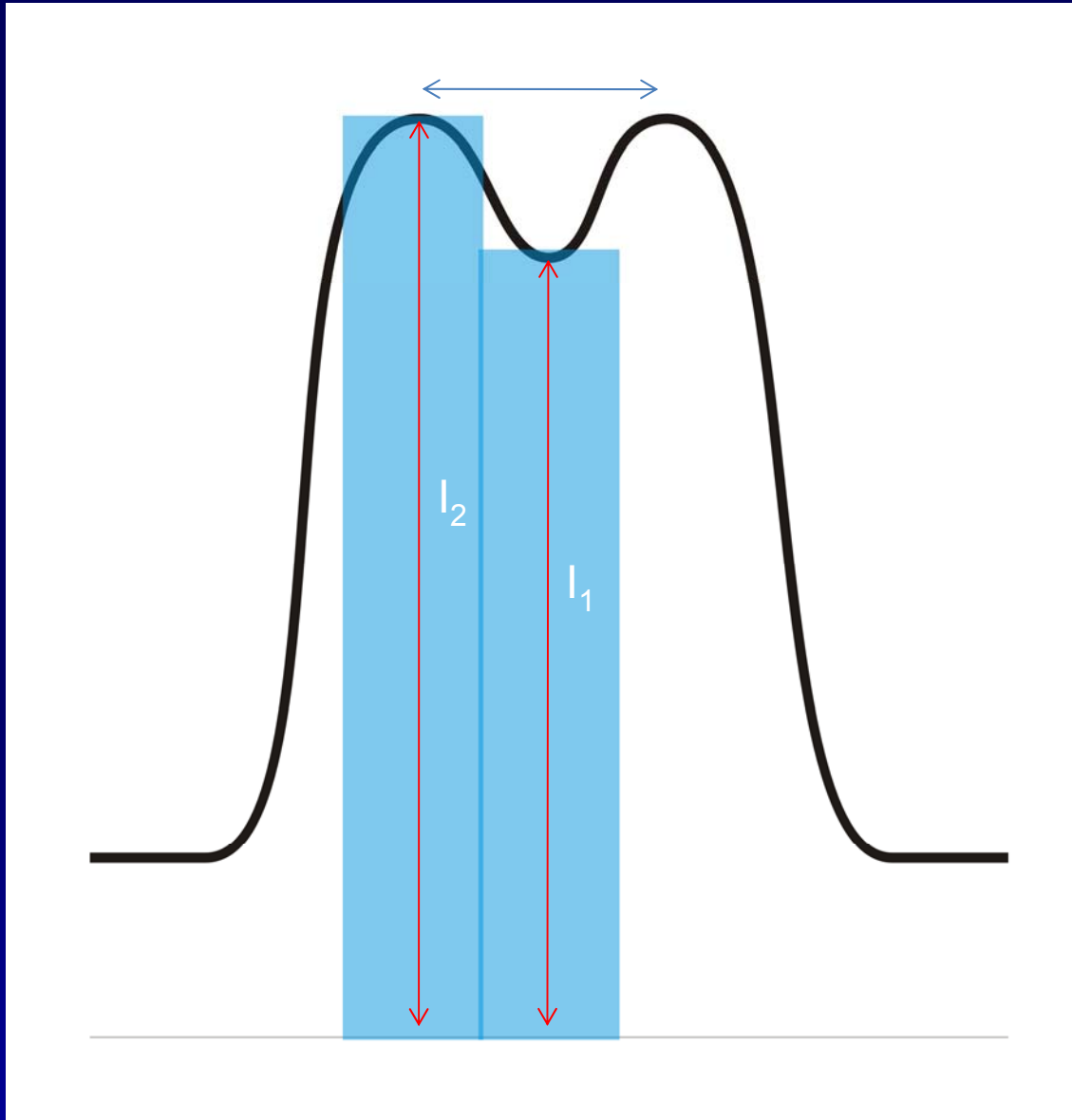
$$d_o = 0.6 \sqrt[4]{C_s \lambda^3}$$

HT [kV]	[nm]	d_o [nm]
1500	0.0006	0.084
400	0.0016	0.171
300	0.0020	0.196
200	0.0025	0.235
100	0.0037	0.315
80	0.0042	0.345
60	0.0049	0.387
40	0.0060	0.454
20	0.0086	0.592

Resolution limited by SNR



Resolution limited by SNR



$$C = \frac{I_2 - I_1}{I_2 + I_1} = \frac{N_2 - N_1}{N_2 + N_1} = \frac{S}{B}$$

$$S = (N_2 - N_1)/2$$

$$B = (N_2 + N_1)/2$$

$$\Delta N = \sqrt{B}$$

$$S > SNR_{lim} * \Delta N$$

$$B > \frac{SNR_{lim}^2}{C^2}$$

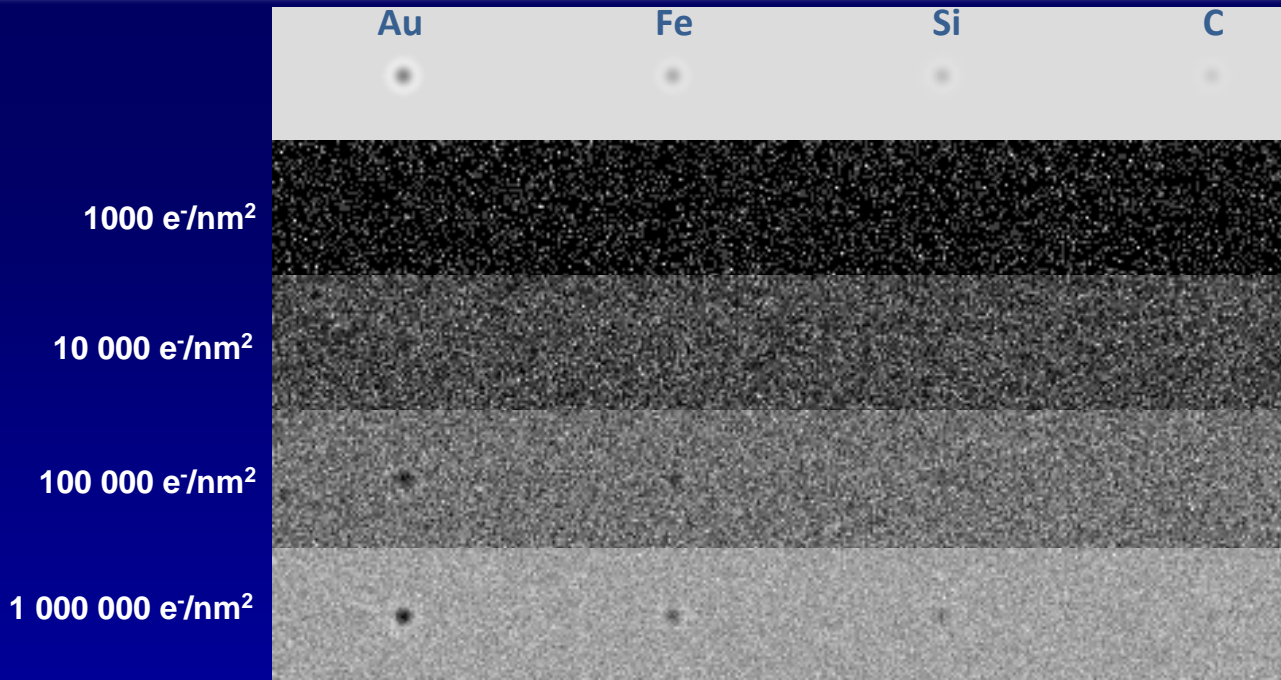
$$D > \frac{SNR_{lim}^2}{C^2 * \left(\frac{d_n}{2}\right)^2}$$

Resolution limited by SNR

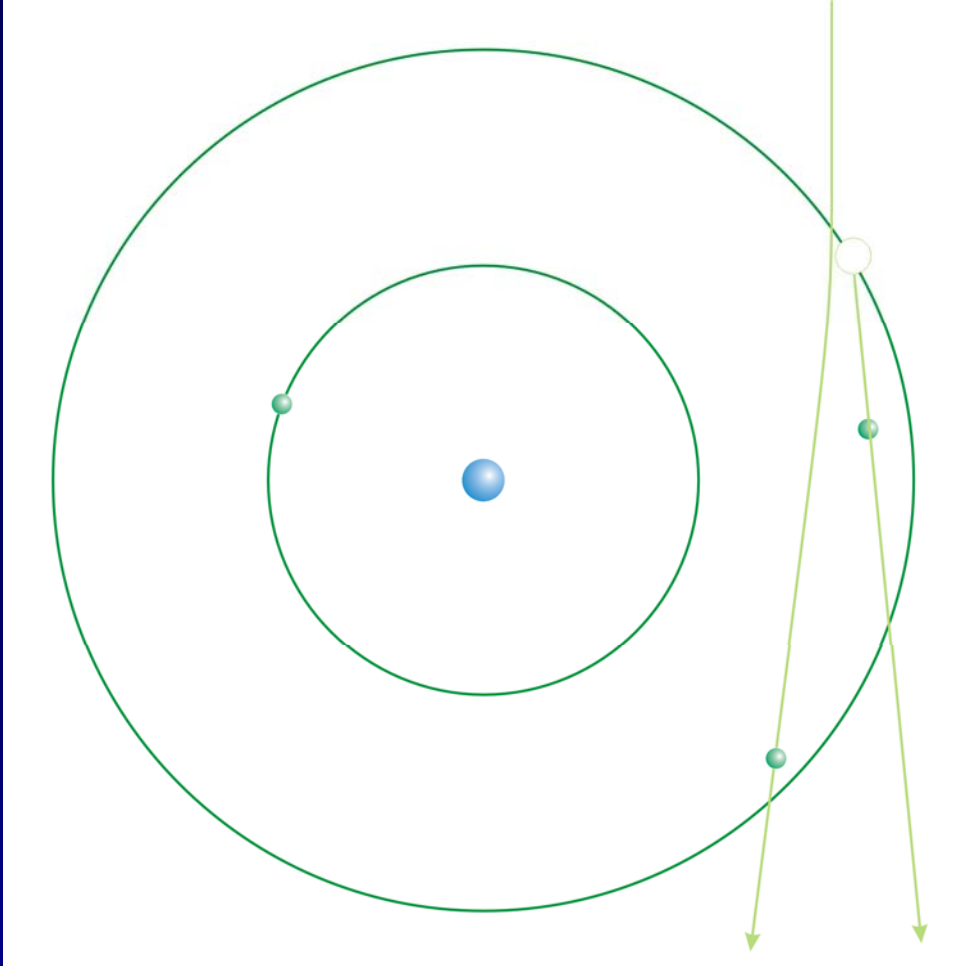
Contrast	Electron dose [e^-/nm^2]				
	100	1000	10000	100000	1000000
Au 0.18	5.47	1.73	0.55	0.17	0.05
Fe 0.08	12.75	4.03	1.28	0.40	0.13
Si 0.05	19.95	6.31	2.00	0.63	0.20
C 0.03	32.85	10.39	3.28	1.04	0.33

Noise limited resolution [nm]

HT - 300kV, instrumental resolution - 0.1 nm

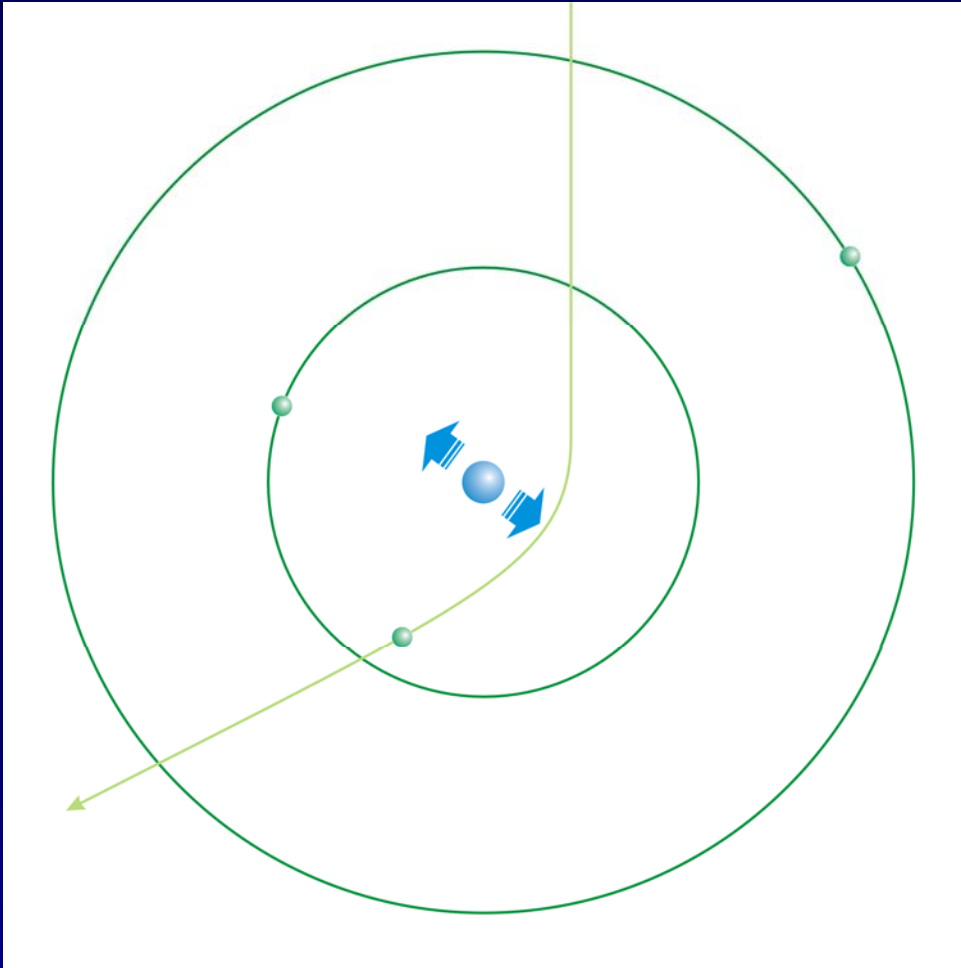


Radiation damage



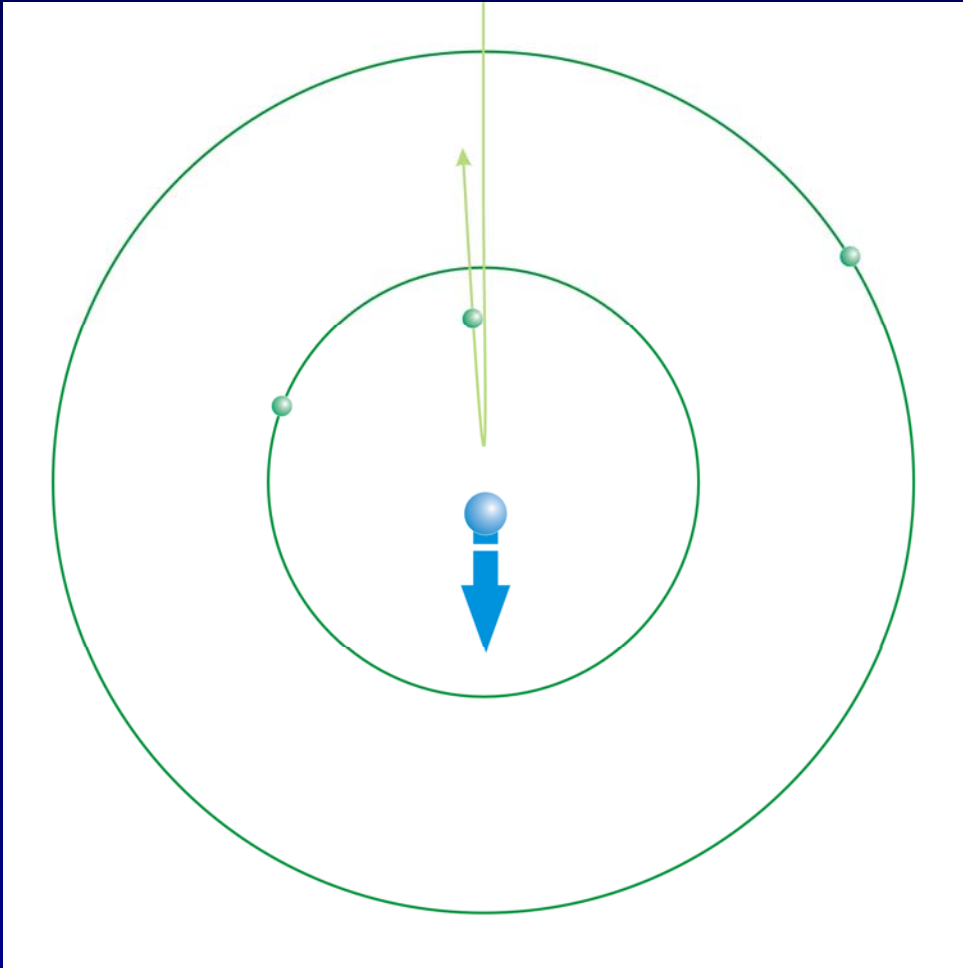
- ionisation

Radiation damage



- ionisation
- heating

Radiation damage



- ionisation
- heating
- knock-on damage

$$\Delta E \cong \frac{E_e}{450 * A_m}$$

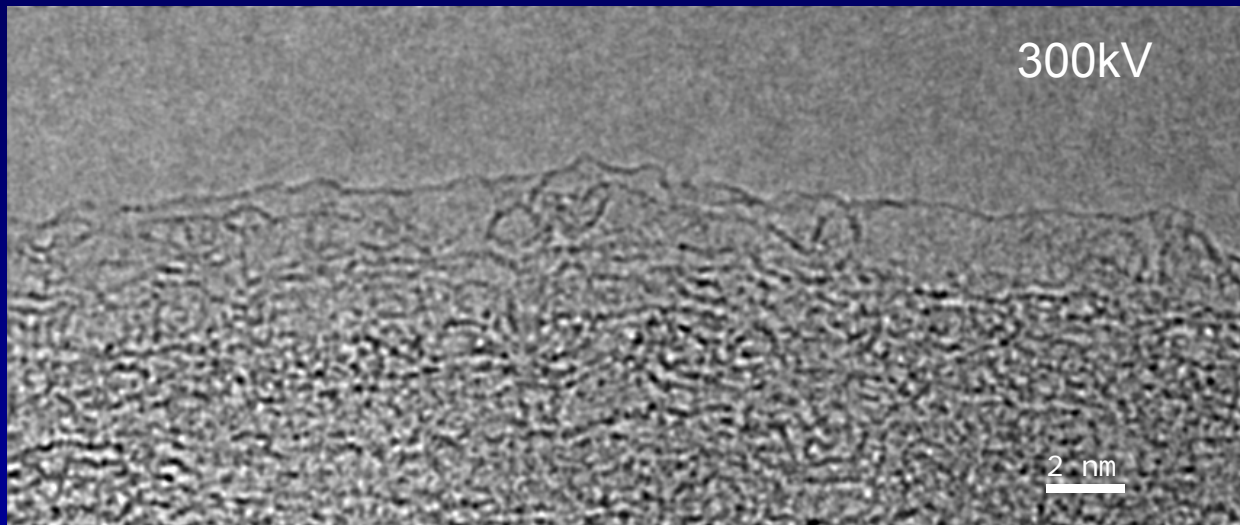
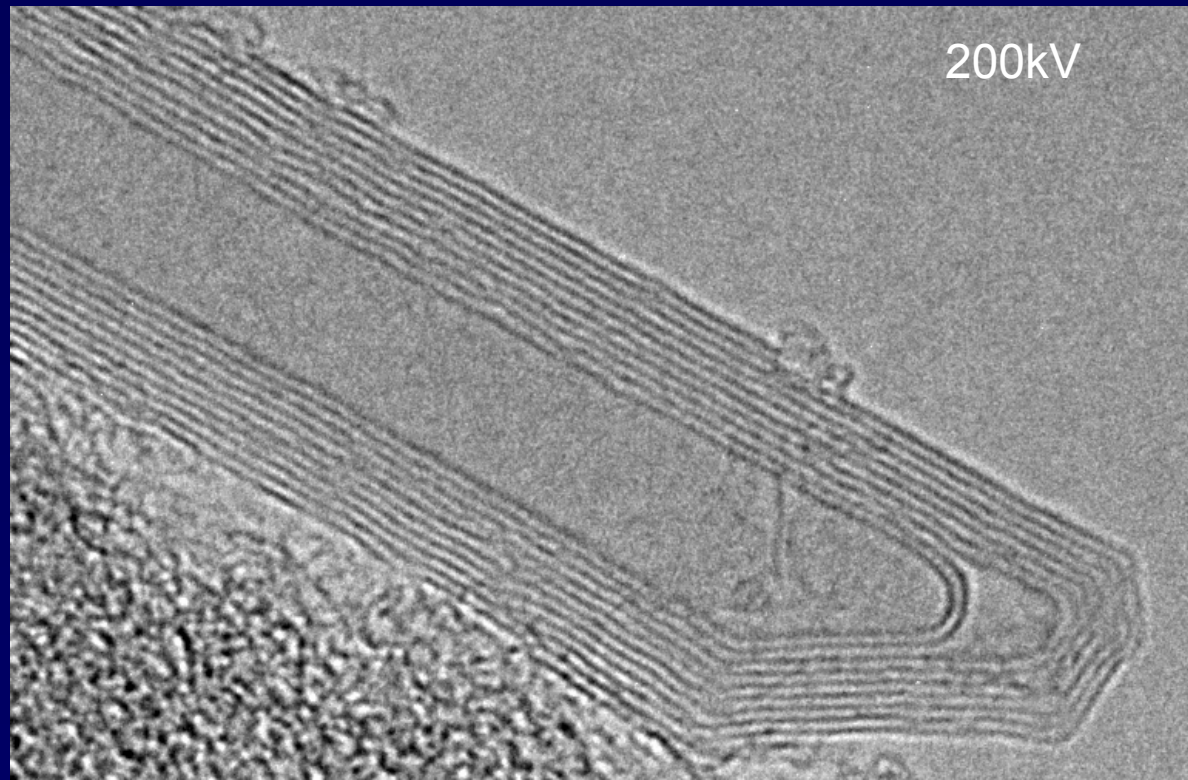
$$\Delta E > E_{bond}$$

$$\Delta E < E_{bond}$$

$$E_e < 450 * E_{bond} * A_m$$

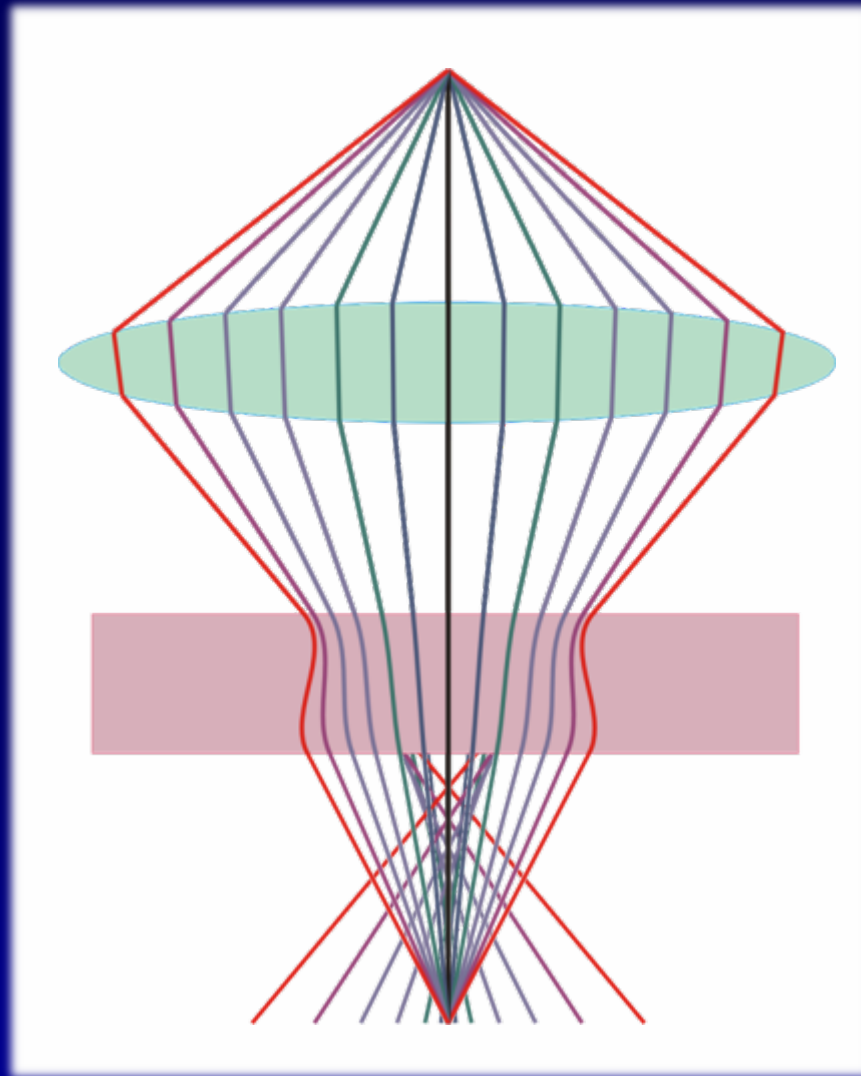
$$C_{graphene} \Rightarrow \sim 79 \text{keV}$$

Radiation damage



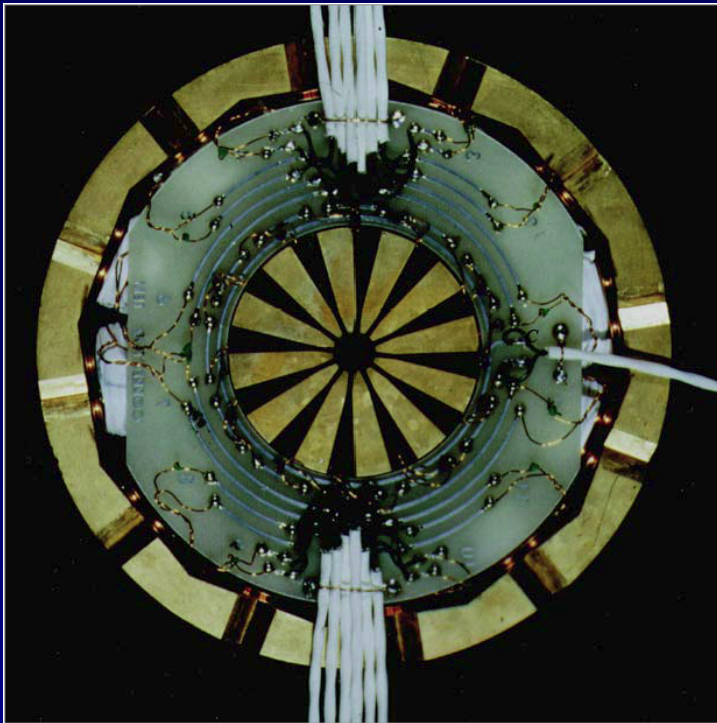
Cs correction

Correction of spherical aberration



Correction of spherical aberration

*Aberrations of **round** static **space-charge-free** electromagnetic lenses are unavoidable and their coefficients are always positive.*



Scherzer, 1947, Optik 2, 114

Seeliger, 1949, Optik 5, 490

Rose, 1990, Optik 85, 19

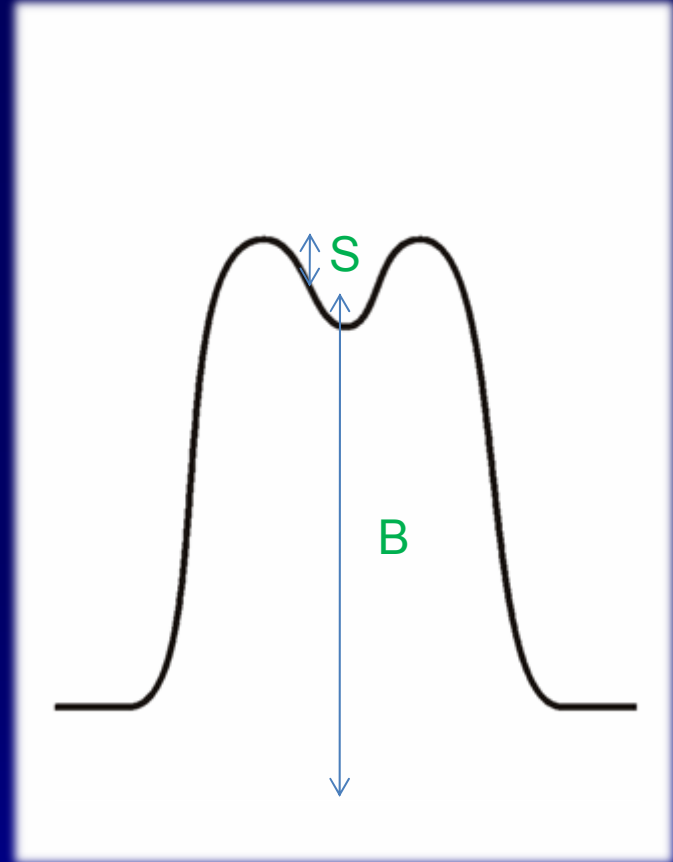
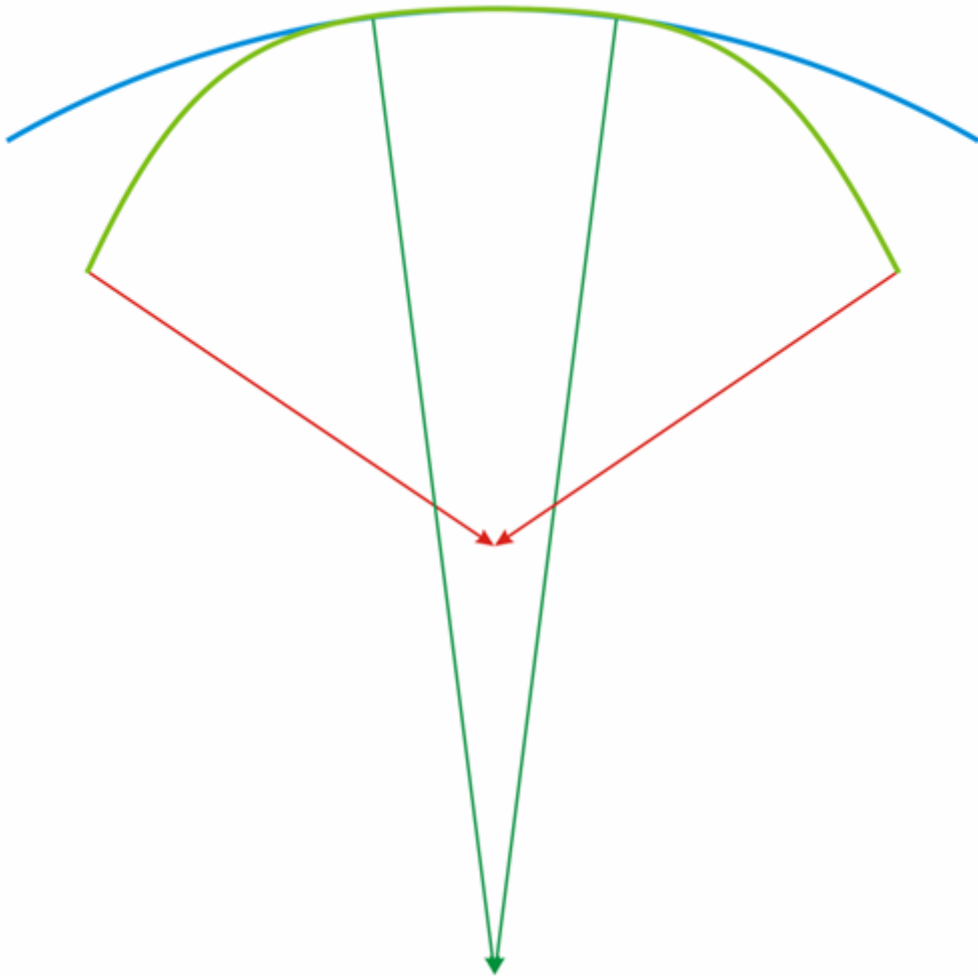
Haider et al. 1998, Nature 392, 768

CEOS

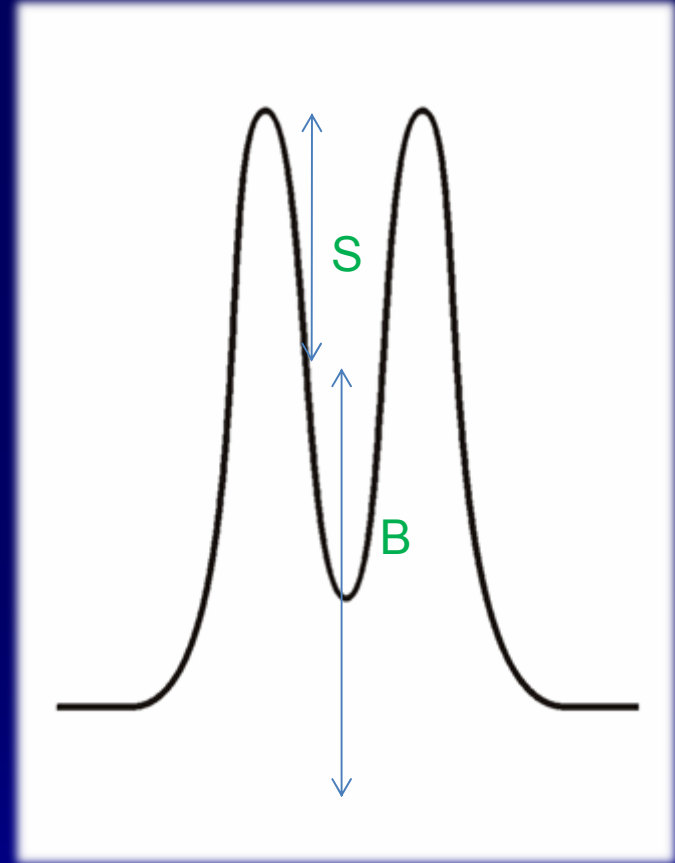
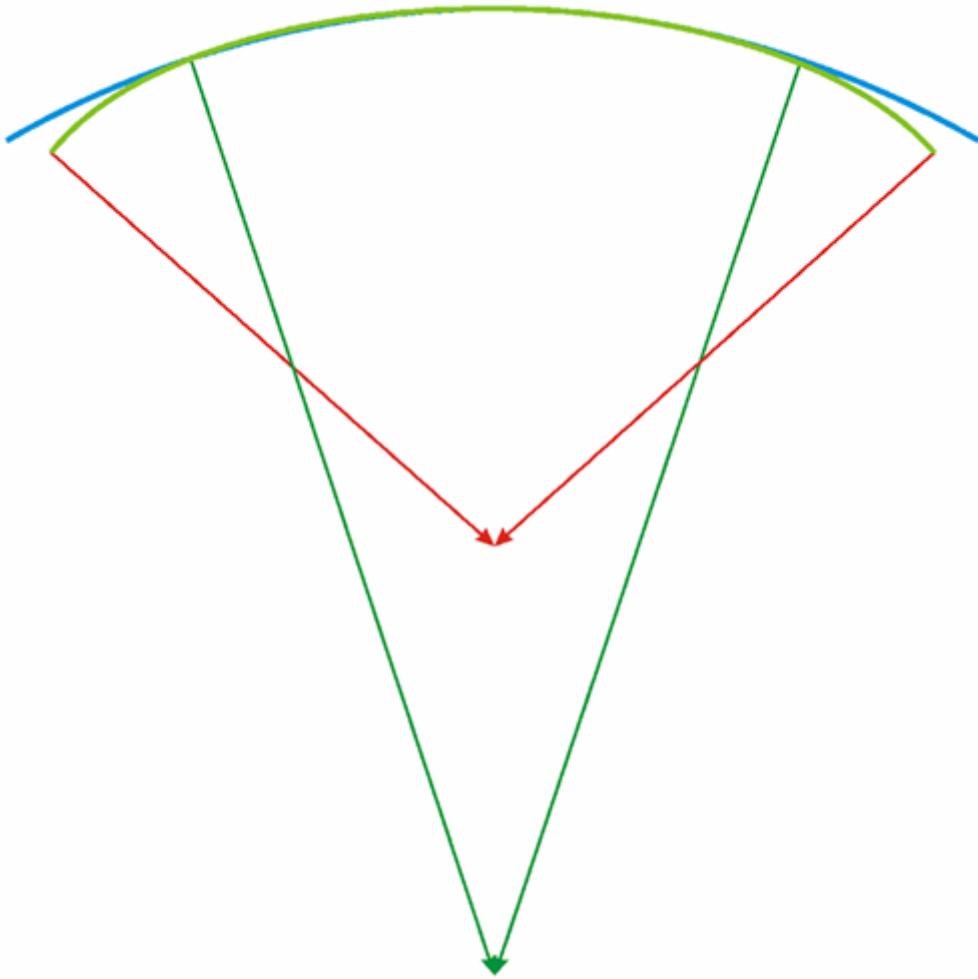
Corrected Electron Optical
Systems GmbH



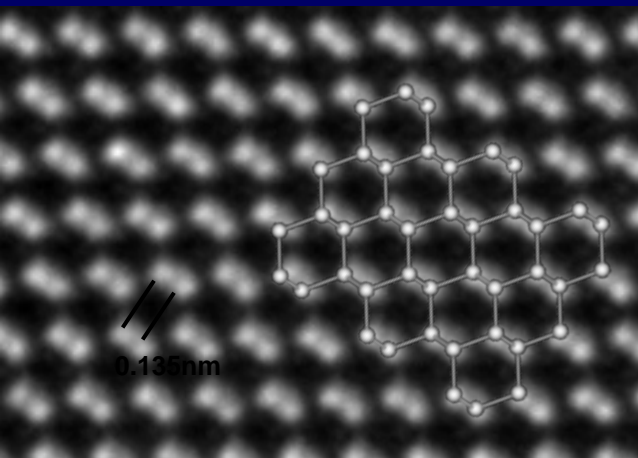
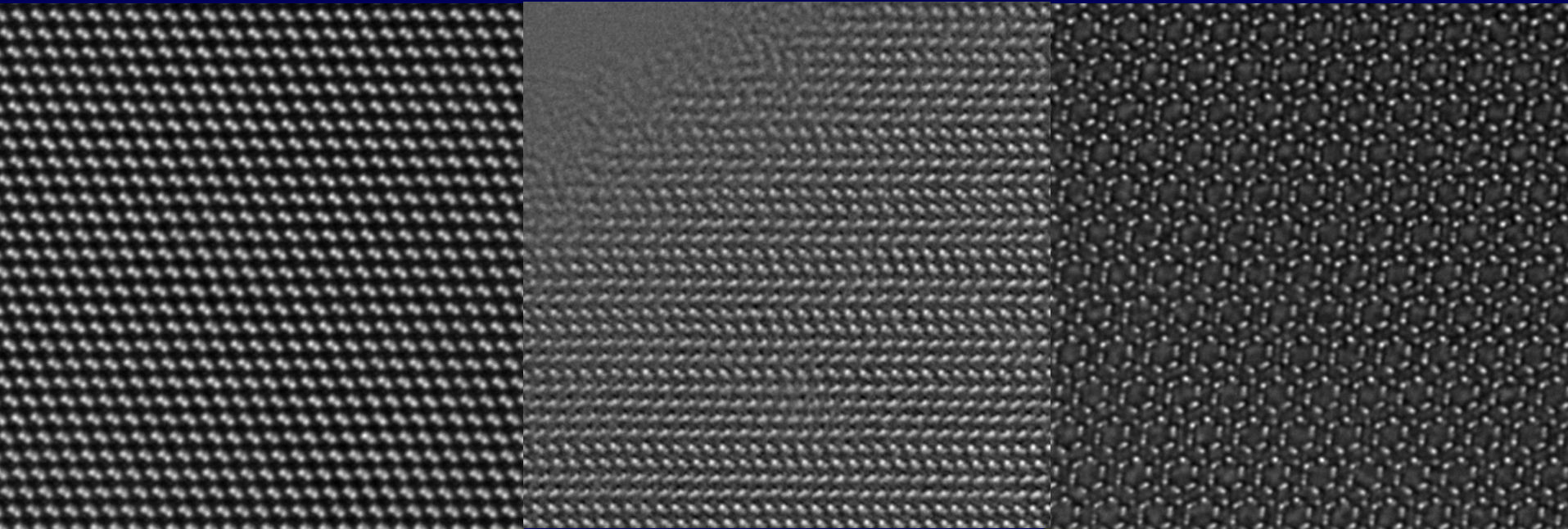
Correction of spherical aberration



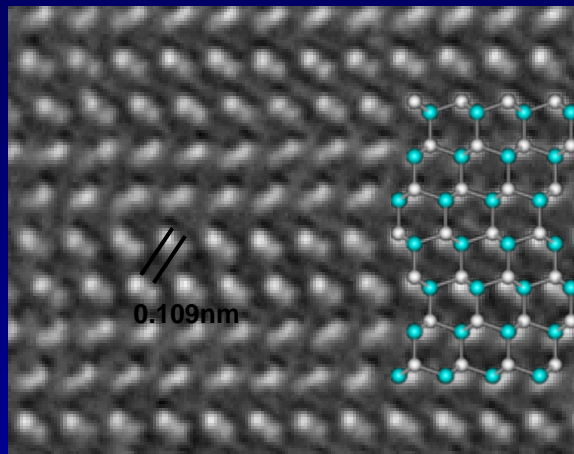
Correction of spherical aberration



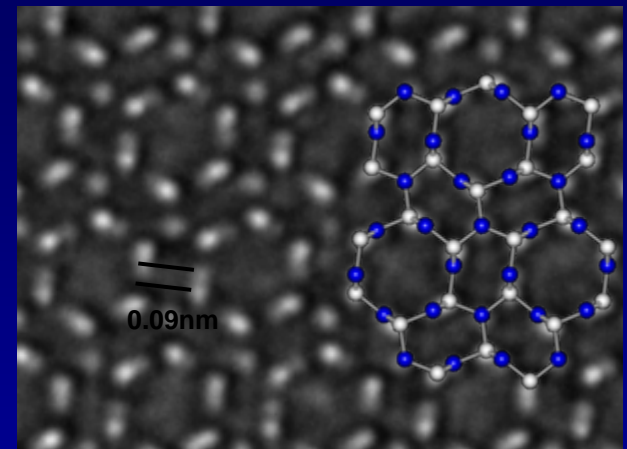
HRTEM images obtained at Cs-corrected 300kV TEM



Si



4H-SiC



Si₃N₄

Correction of spherical aberration

- instrumental resolution increase
- possibility to decrease HT
- contrast increase
- dose decrease

HT [kV]	[nm]	d_o [nm]
1500	0.0006	0.084
400	0.0016	0.171
300	0.0020	0.196 0.05
200	0.0025	0.235
100	0.0037	0.315
80	0.0042	0.345 0.1
60	0.0049	0.387
40	0.0060	0.454
20	0.0086	0.592

Microscope Control - TEM1

TEM CsCorrector GUI log file - c3mteservicegui

```

# 7 C1: -376.8nm A1: 43.4nm / -63deg signal mean: 1320cnts
# 8 C1: -370.7nm A1: 35.4nm / -13deg signal mean: 1320cnts
# 9 C1: -363.9nm A1: 21.7nm / +46deg signal mean: 1327cnts
#10 C1: -351.0nm A1: 20.5nm / +13deg signal mean: 1330cnts
#11 C1: -337.3nm A1: 52.6nm / -10deg signal mean: 1332cnts
#12 C1: -331.9nm A1: 63.1nm / -11deg signal mean: 1335cnts
#13 C1: -324.3nm A1: 76.8nm / -6deg signal mean: 1337cnts
#14 C1: -41.6nm A1: 35.5nm / -36deg signal mean: 1320cnts
#15 C1: -439.7nm A1: 13.6nm / -60deg signal mean: 1321cnts
#16 C1: -441.1nm A1: 32.8nm / -36deg signal mean: 1320cnts
#17 C1: -415.6nm A1: 10nm / -9deg signal mean: 1320cnts
#18 C1: -456.8nm A1: 27.2nm / -36deg signal mean: 1320cnts
#19 C1: -456.8nm A1: 27.2nm / -36deg signal mean: 1320cnts
#20 C1: -456.8nm A1: 27.2nm / -36deg signal mean: 1320cnts
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#100 C1: -456.8nm A1: 27.2nm / -36deg signal mean: 1320cnts

```

TEM CsCorrector GUI (service) V2.9p10 built by...

Config Analysis

Exported Controls

Single Channel control

em_data Supervisor

Microscope Control - TEM1

CCD/TV Camera

Controller: Gaston Ccd

Camera: CCD

Integration time (s): 1024 x 1024

Image time: 1024 x 1024

Binning: 1

Search Preview Acquire

Insert

Stigmator

Condenser Objective Diffraction

None Condenser 3

Step size: 2

Image Settings

Reset shift Reset Def Contrast

MF Knobs

Step size: 3

0.00000 0.00000 0.00000

0.00000 0.00000 0.00000

Image K

Type: Inager 2 Signed

Size: 1024 x 1024

X: 554

Y: 164

Value: 3331

Acquisition Status

Control

Cormax at: 1254, 1250

Cormax at: 1252, 1255

Cormax at: 1252, 1257

Cormax at: 1252, 1250

Cormax at: 1260, 1252

Cormax at: 1256, 1253

Cormax at: 1259, 1255

Cal: Thread ended

Analysis correlated 1.5

number top, left, bottom, right, width, height

number expTime: 0.5

image timestamp

image resTime

image setTime, corseal

number firstTime: 1, isRunning: 0, is

TITAN

HT: 80 kV

SA 620 kx TEM

Focus step: 2 C1 Lens: 21.218 % X -2.16 μ m A 0.01 deg

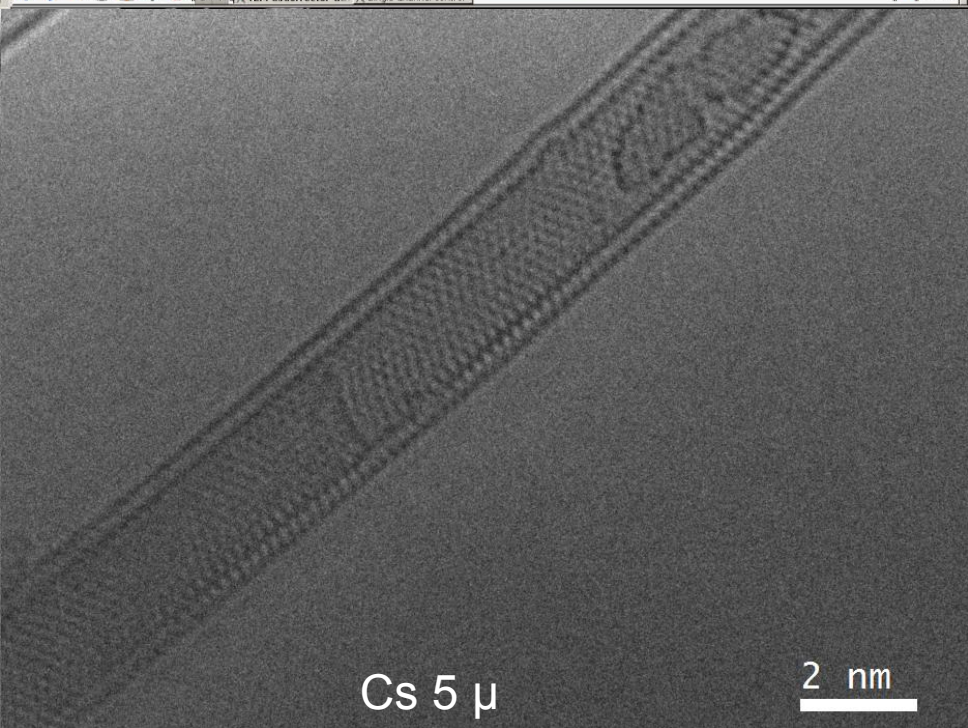
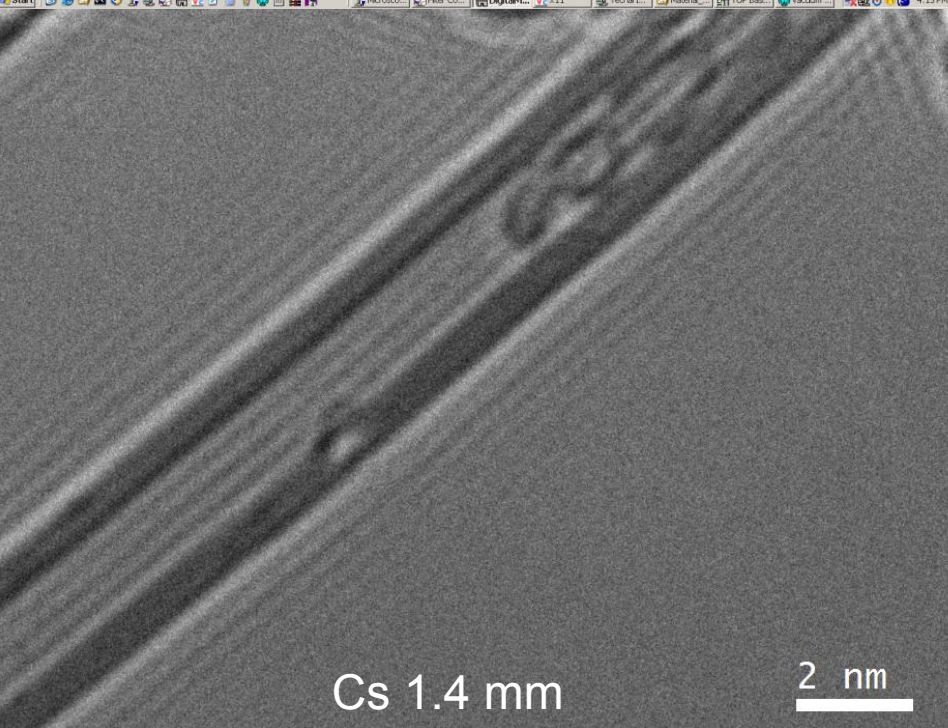
Spot size: 1 C2 Lens: 0.000 % Y -22.18 μ m

Defocus: -67.39 nm C3 Lens: 30.110 % Z -165.35 μ m B -0.05 deg

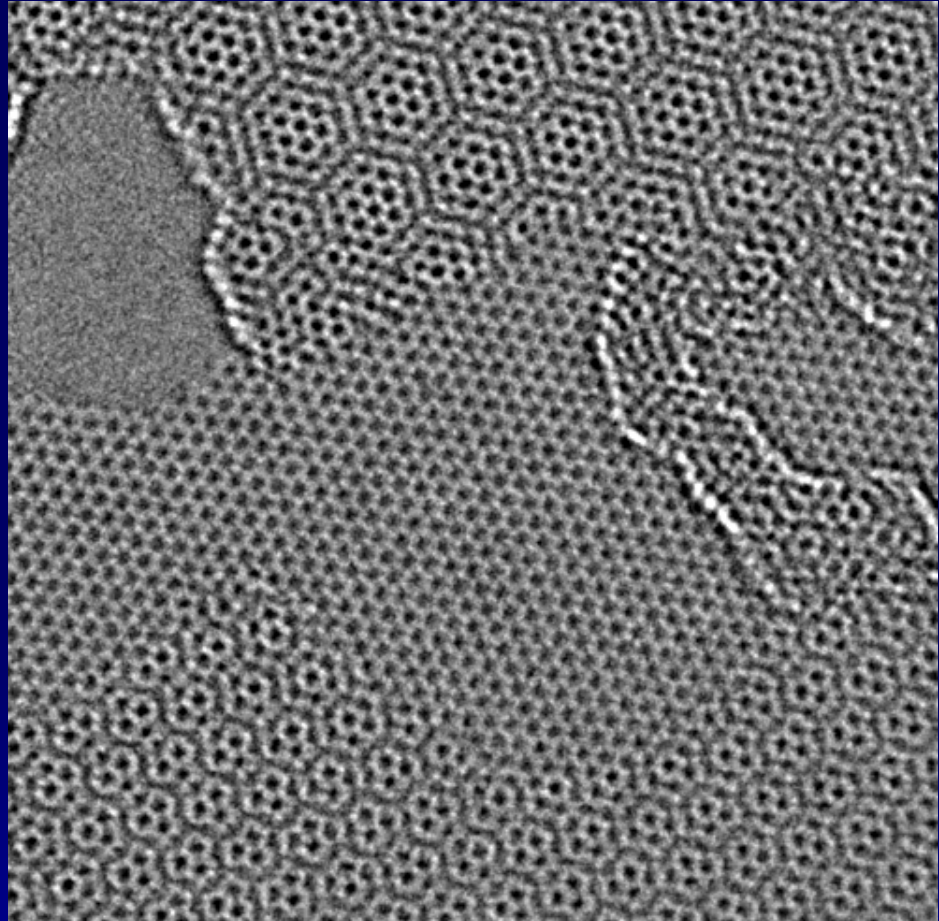
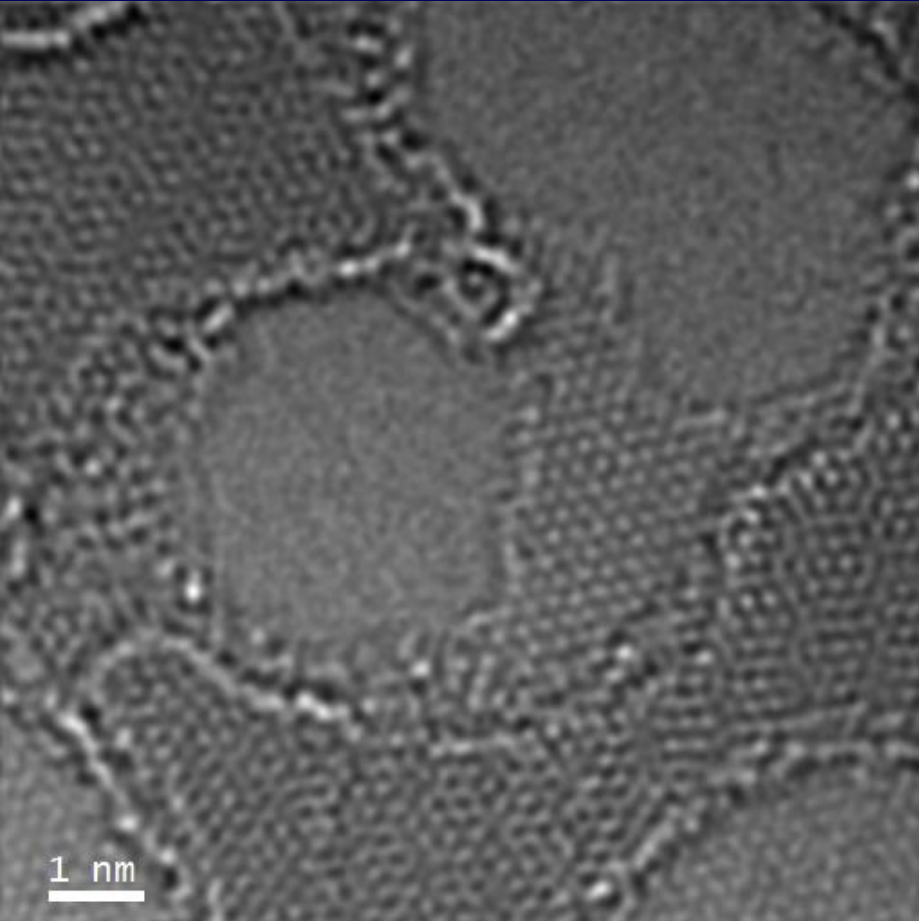
Exposure time: 0.85 s Diff Lens: 60.279 %

Conv.: 0.00 mrad Obj Lens: 77.3442 %

4:13 PM



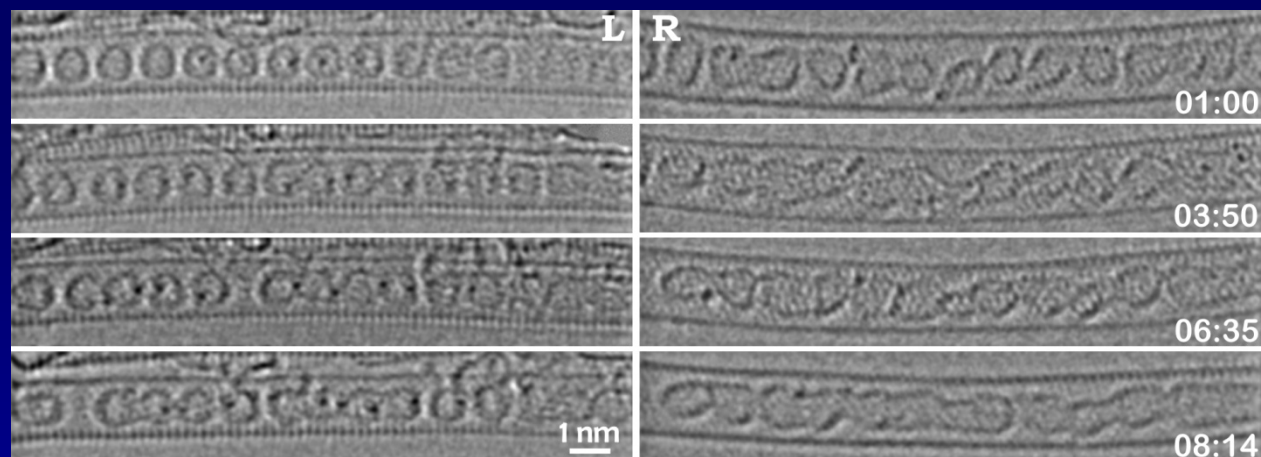
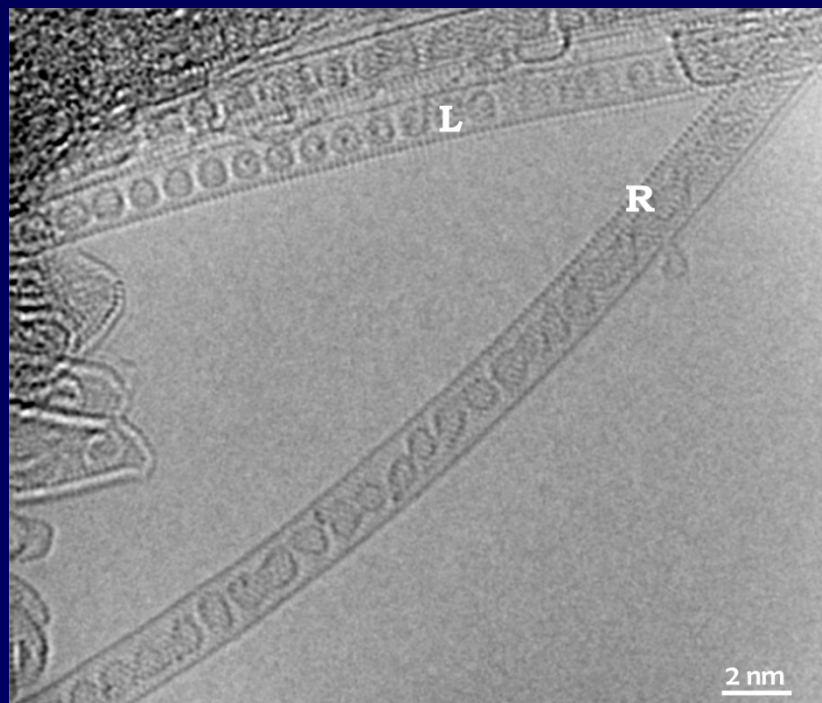
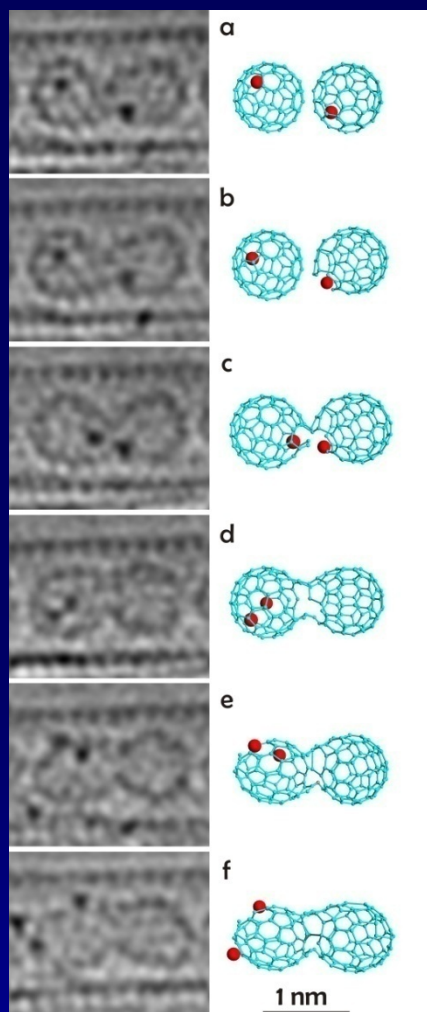
Applications



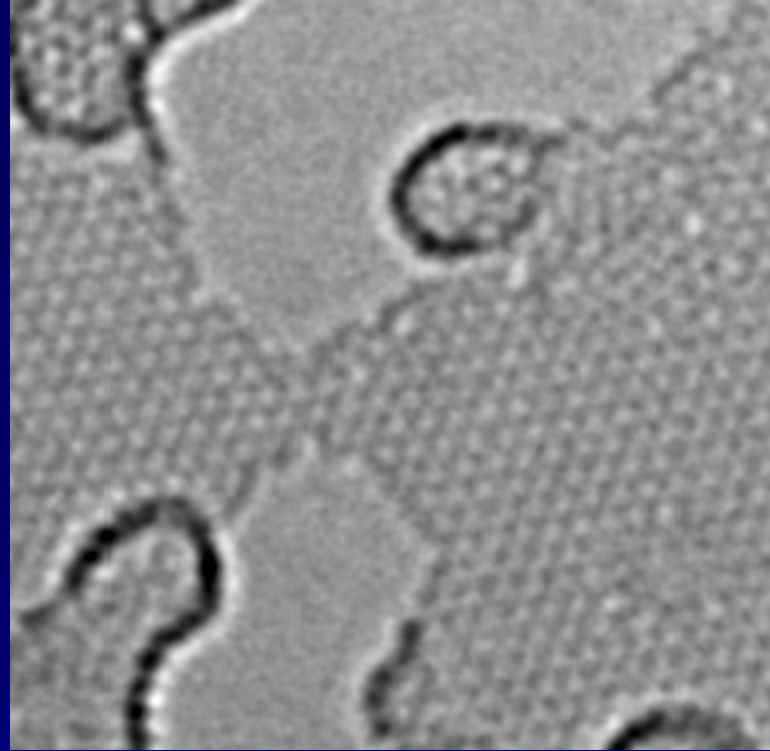
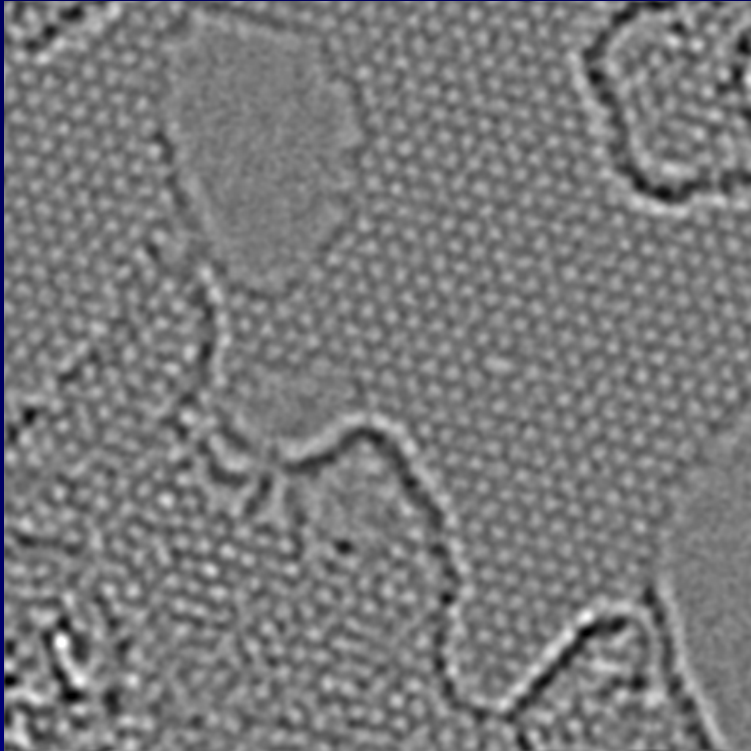
(Dy@C82)@SWNT



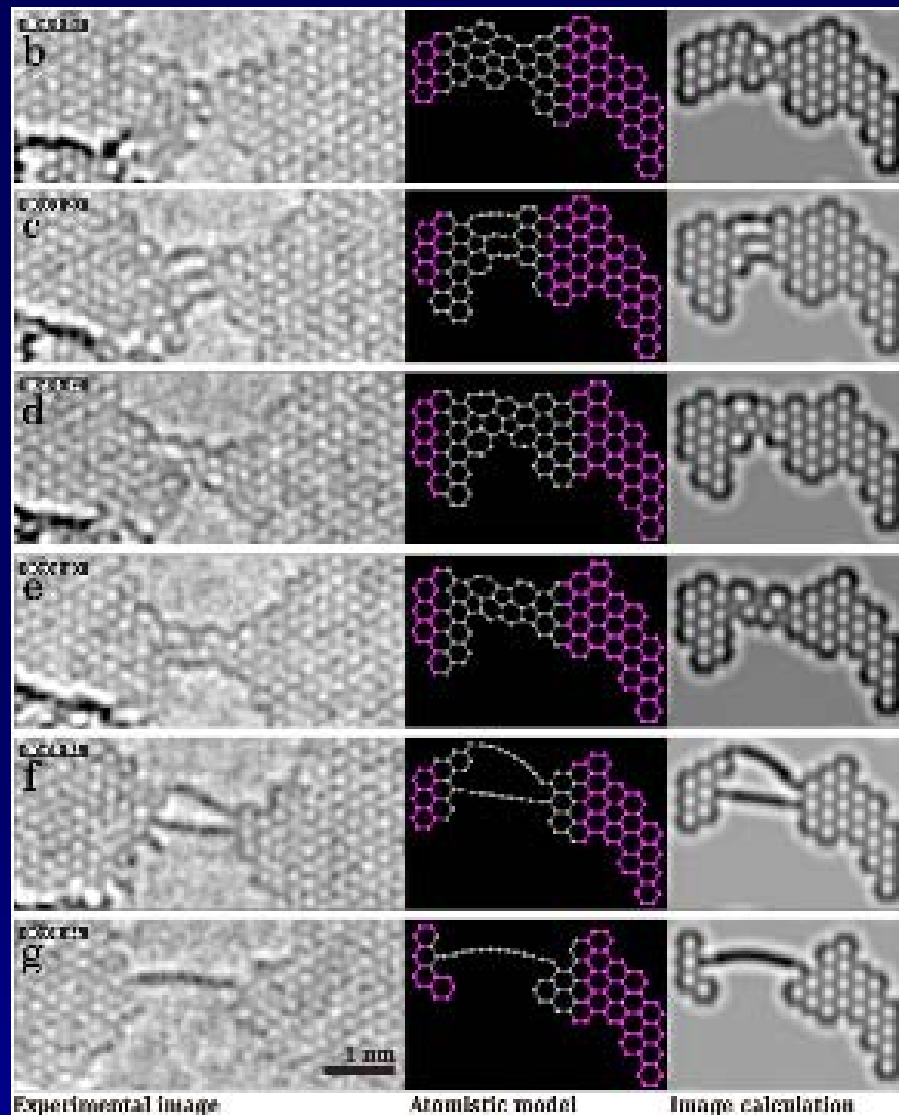
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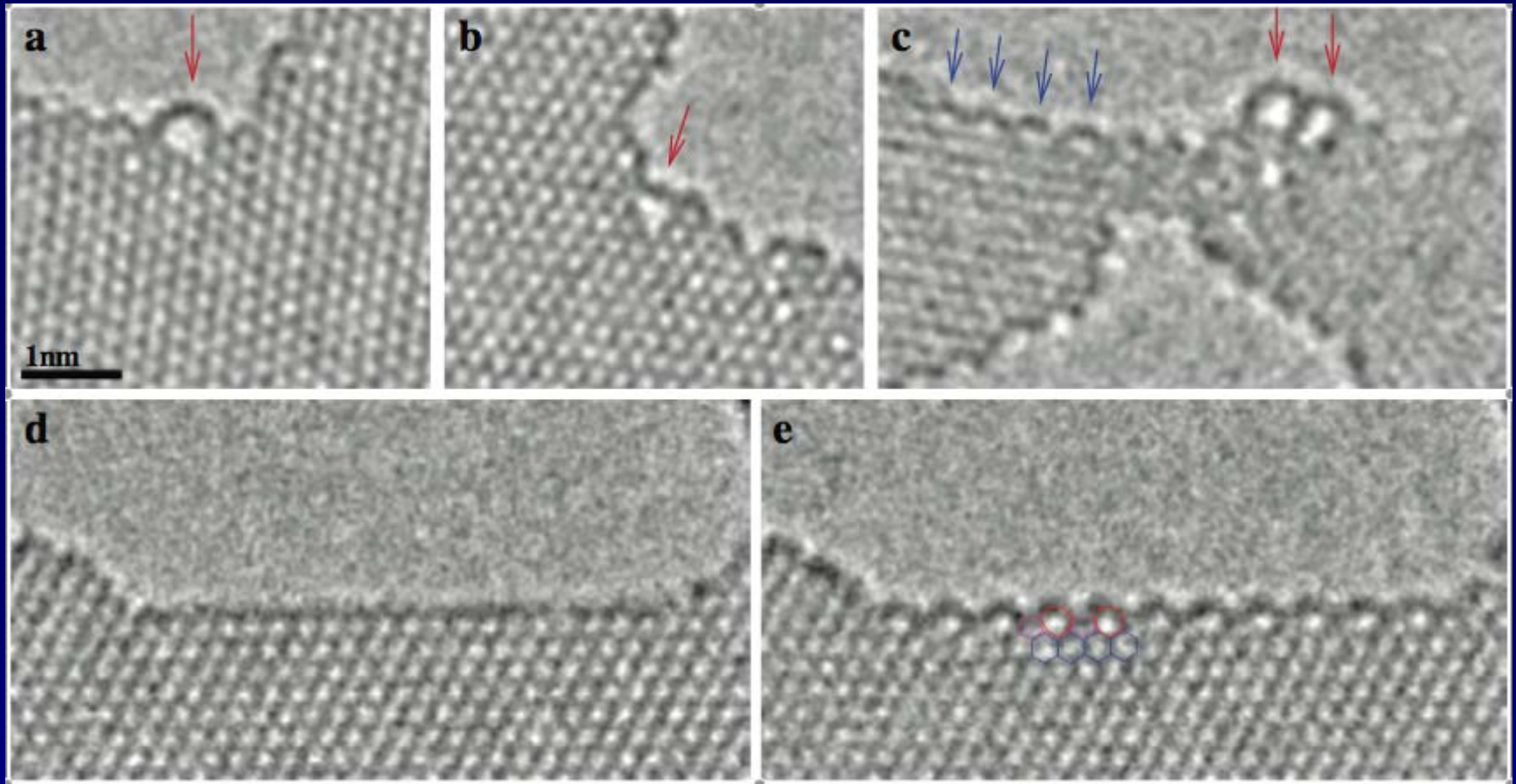
Monocarbon chains



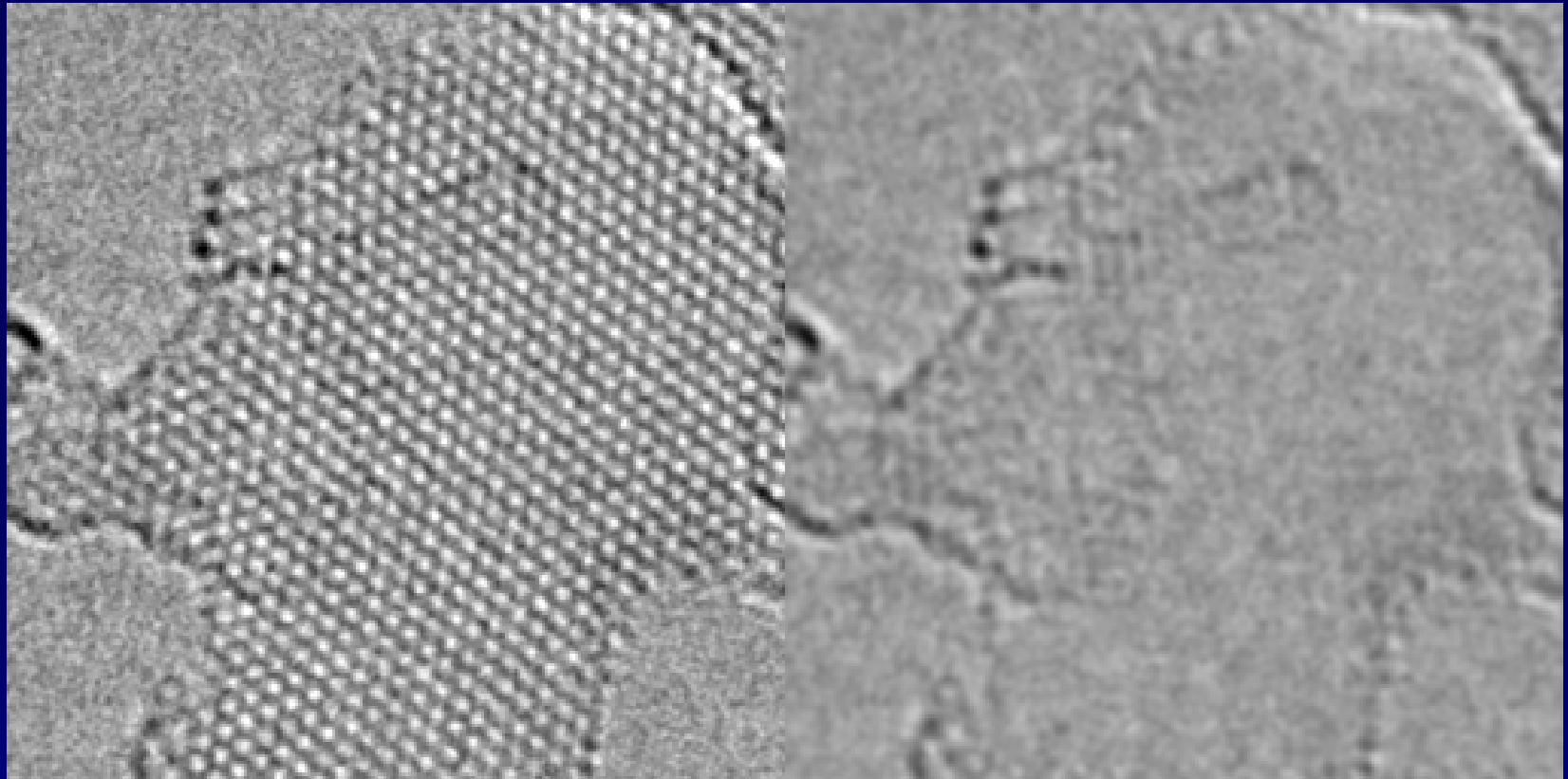
Monocarbon chains



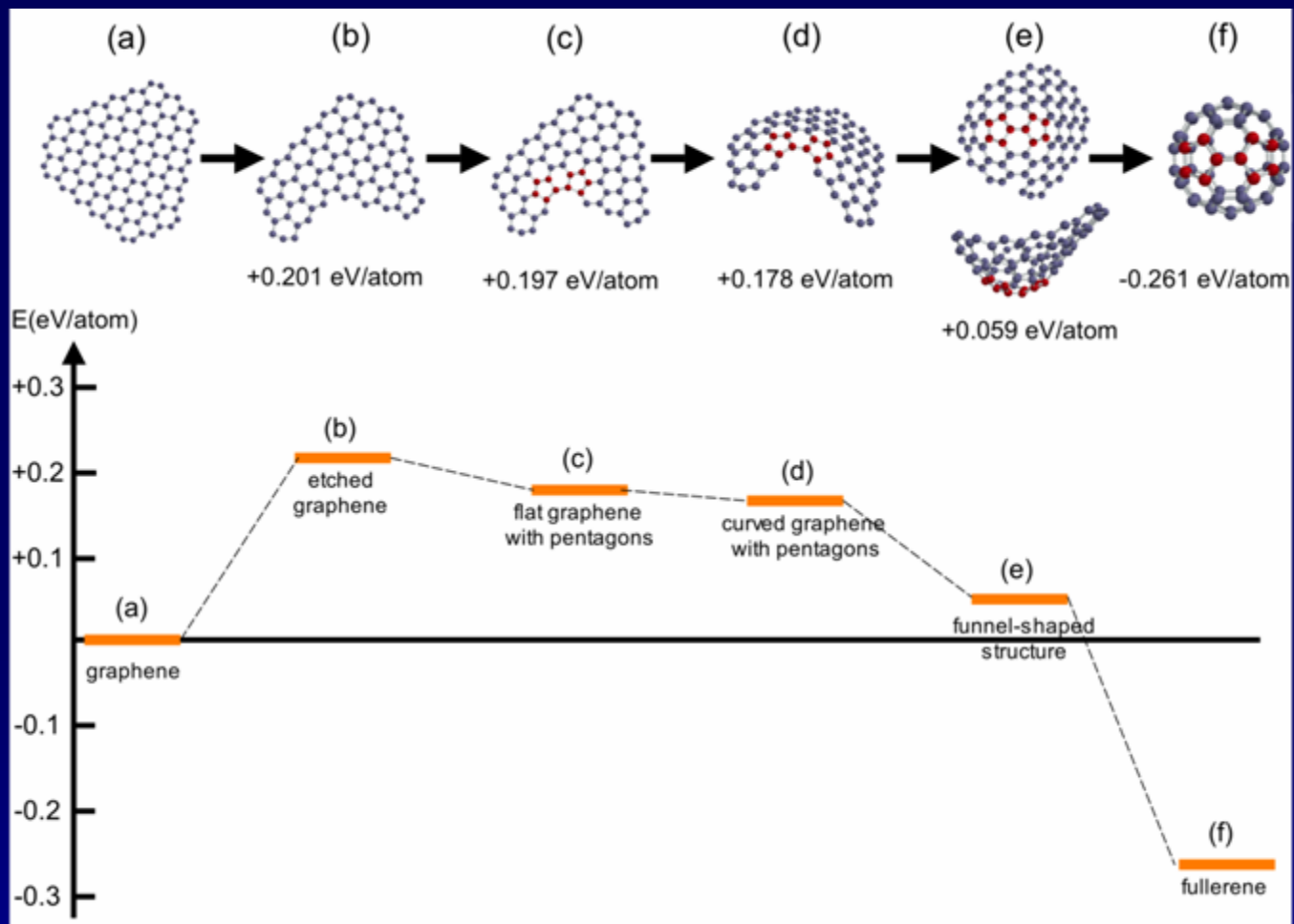
Monocarbon chains



Top-down mechanism of fullerene formation



Top-down mechanism of fullerene formation



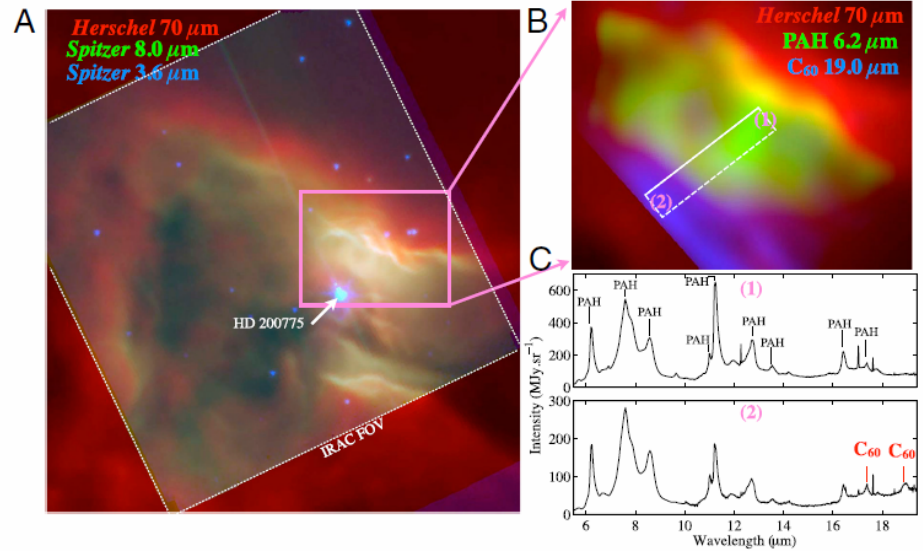
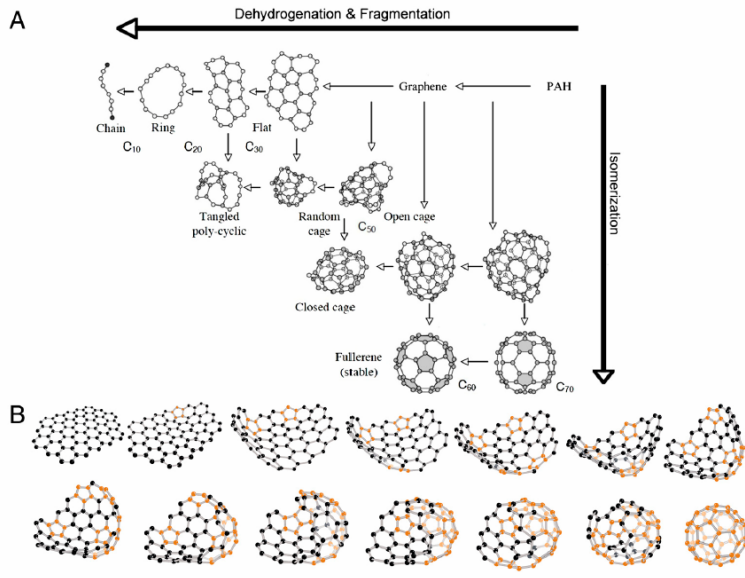
Top-down mechanism of fullerene formation

Formation of buckminsterfullerene (C₆₀) in interstellar space

Olivier Berné¹ and A. G. G. M. Tielens

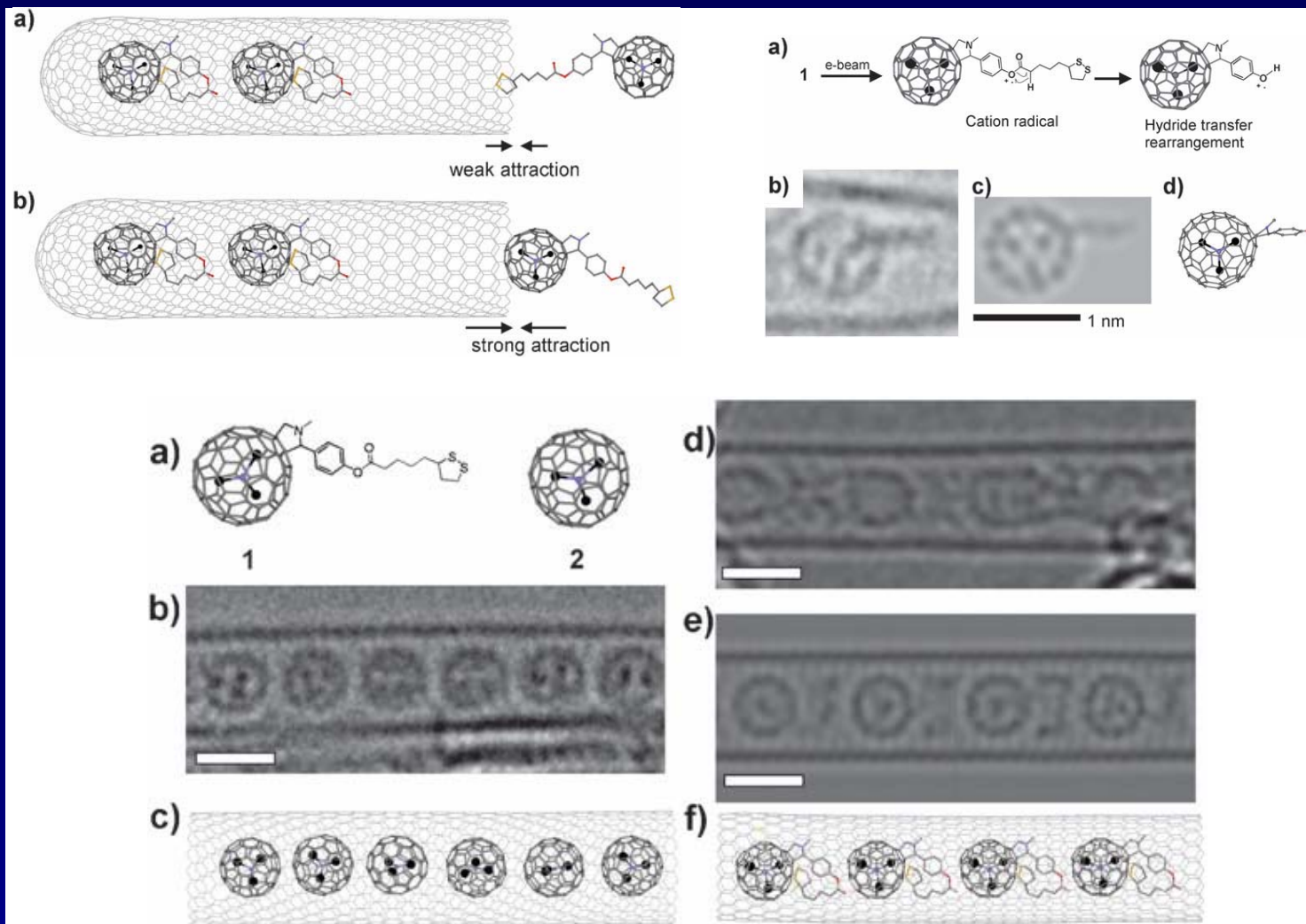
Leiden Observatory, Leiden University, P.O. Box 9513, NL- 2300 RA Leiden, The Netherlands

PNAS | January 10, 2012 | vol. 109 | no. 2 | 401–406

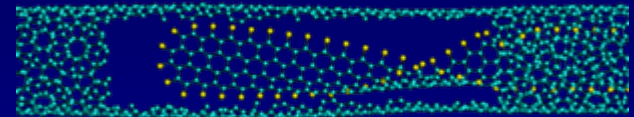
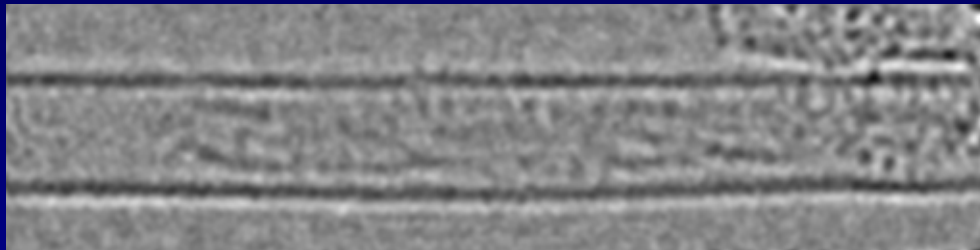
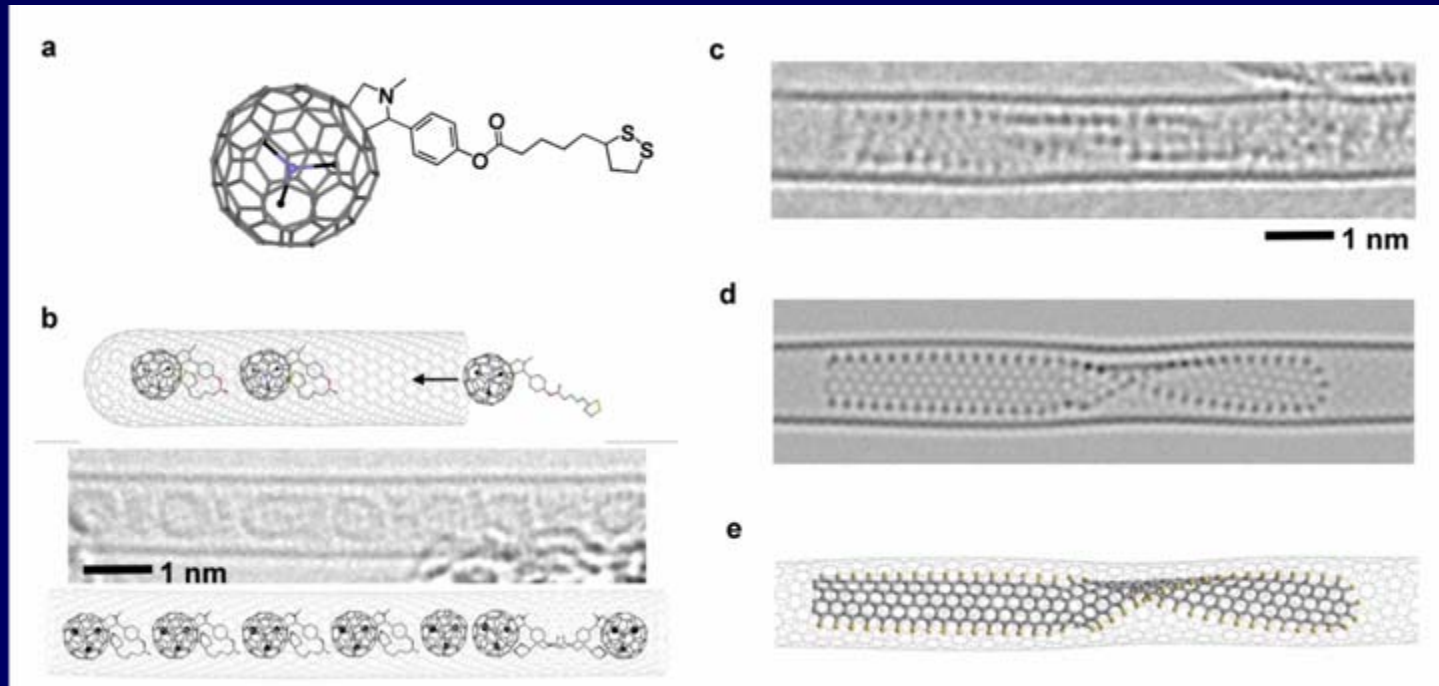


As shown in laboratory experiments (31), graphene sheets larger than about 70 C atoms can be transformed into fullerene, but in space this is driven by UV photons rather than energetic electrons. We surmise that fullerene formation is initiated by single

Peapods with functionalized fullerenes

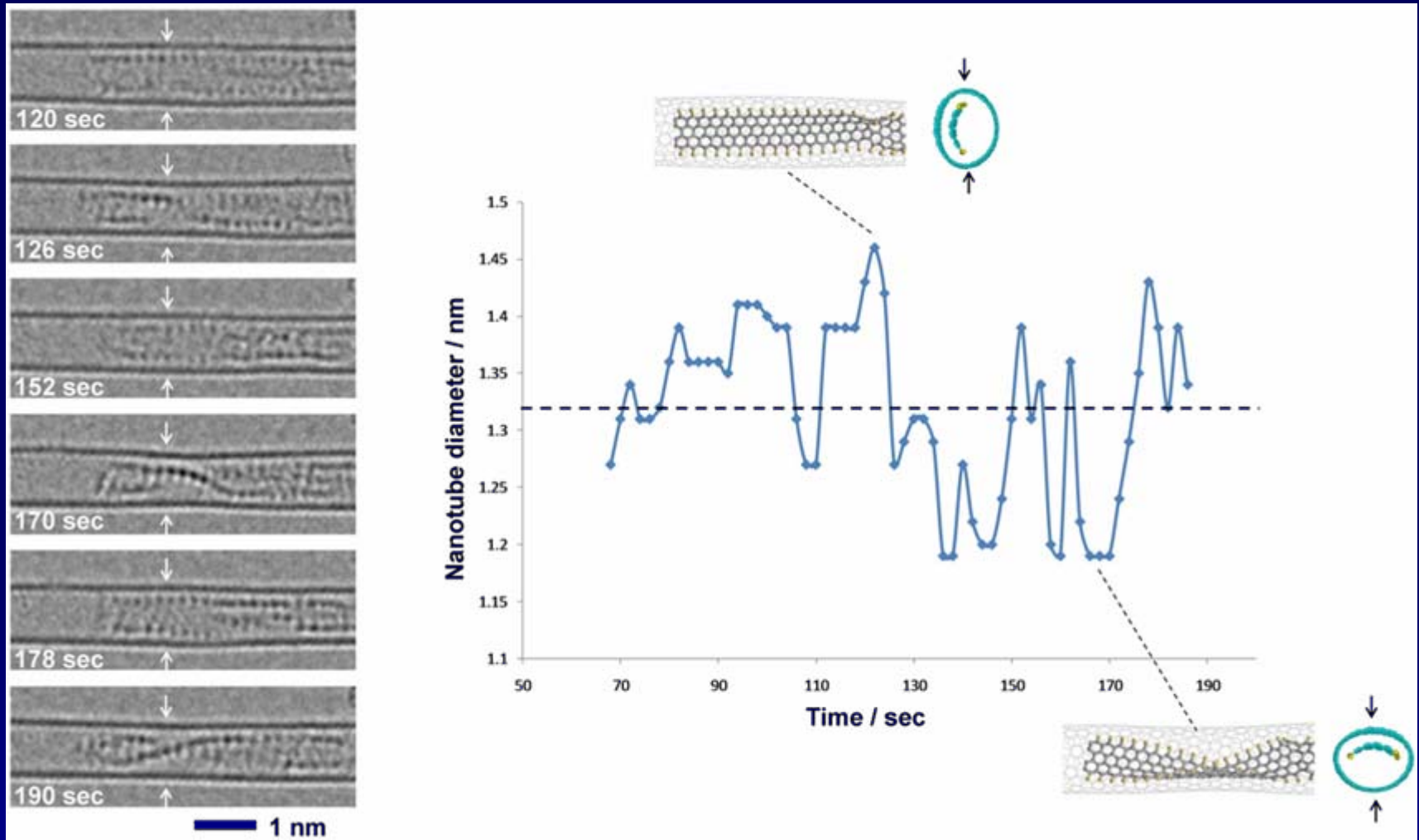


Synthesis of carbon nanoribbons



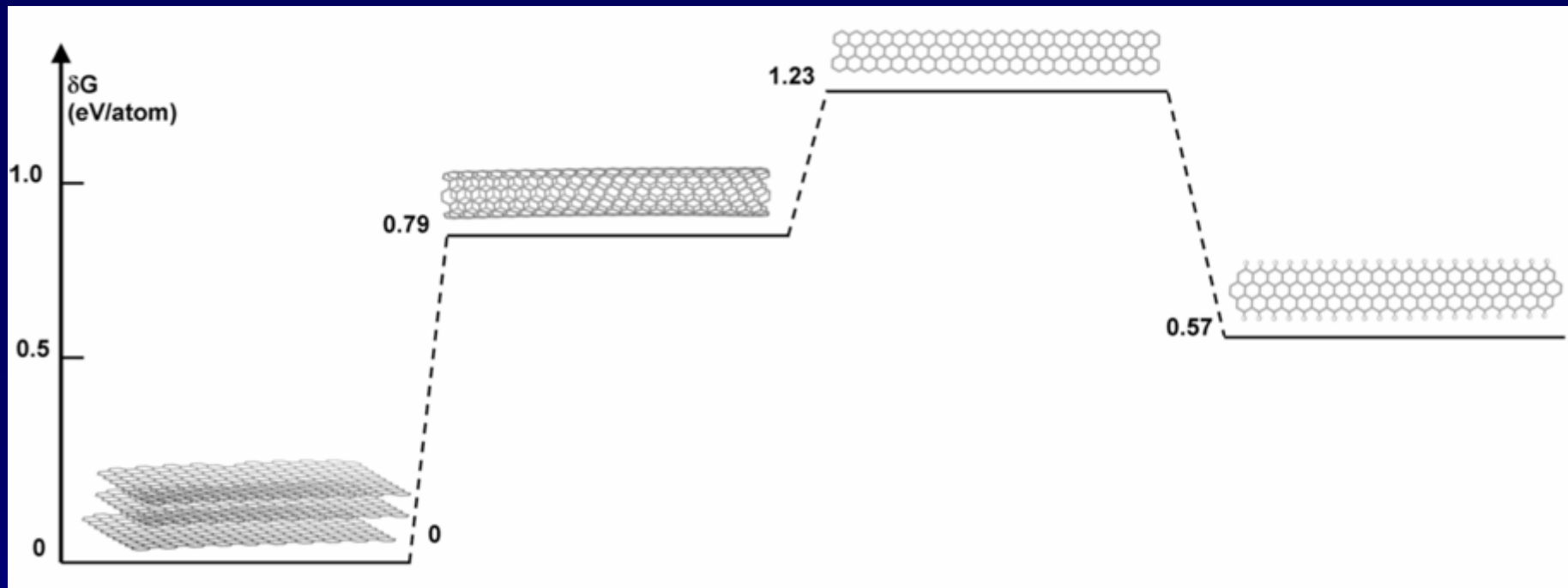
Self-assembly of a sulphur-terminated graphene nanoribbon within a single-walled carbon nanotube
A.Chuvilin, E. Bichoutskaia, M. C. Gimenez-Lopez, T.W. Chamberlain, G. A. Rance,
B. N. Kuganathan, J. Biskupek, U. Kaiser, A. N. Khlobystov
Nature Materials 10 (2011) 687-692

Synthesis of carbon nanoribbons



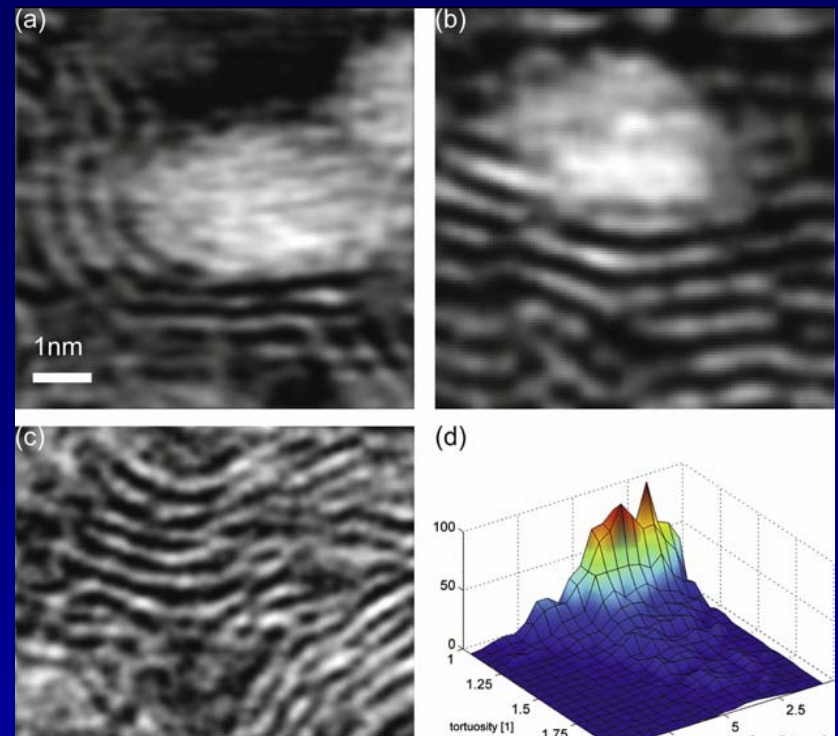
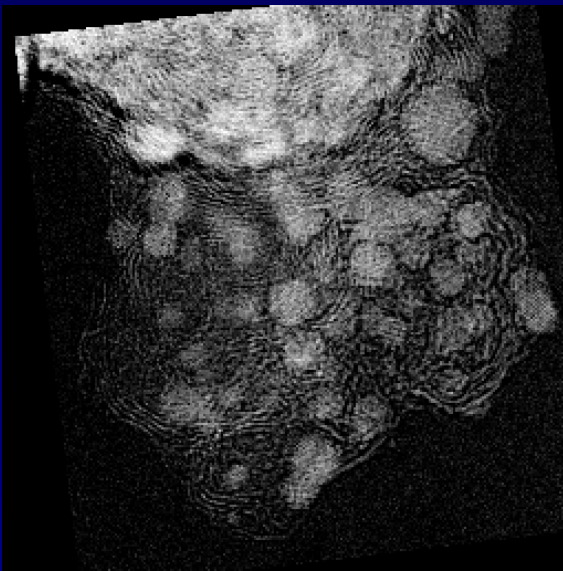
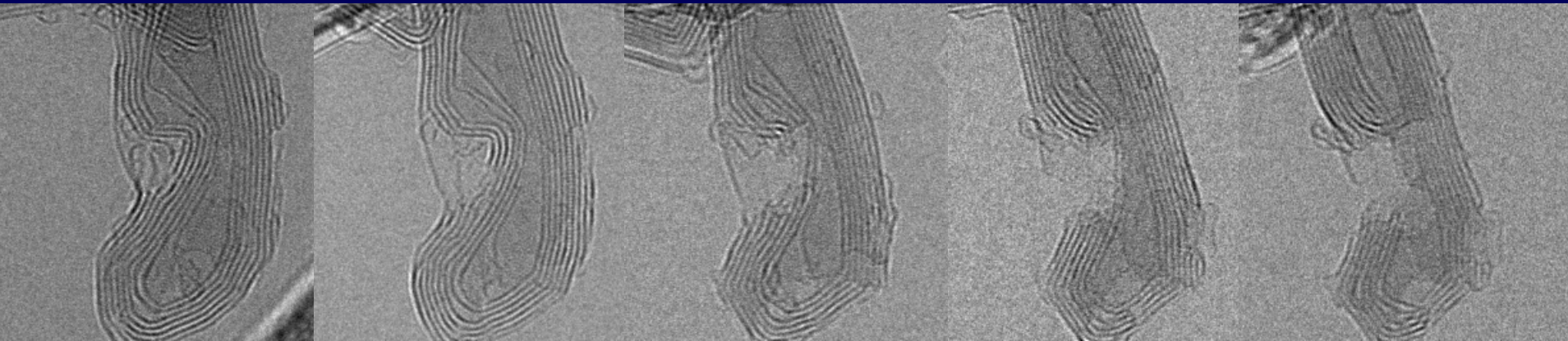
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Synthesis of carbon nanoribbons



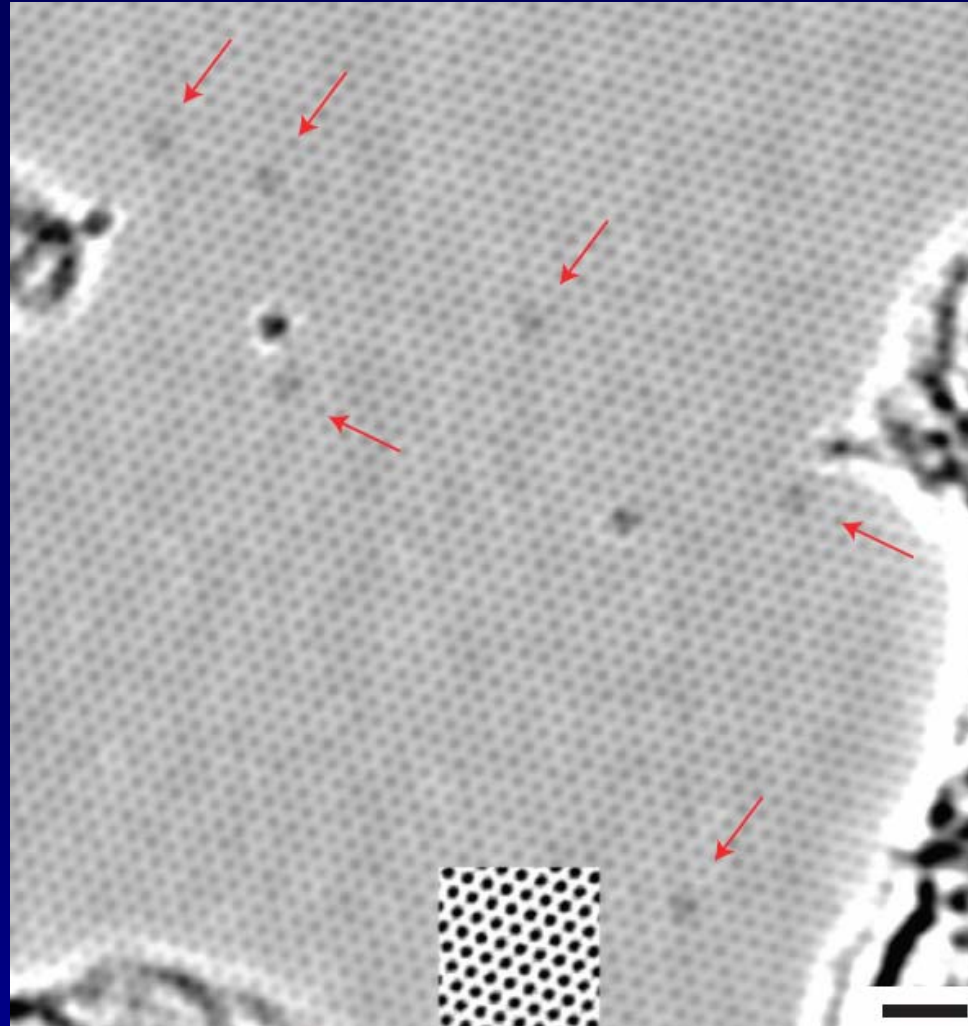
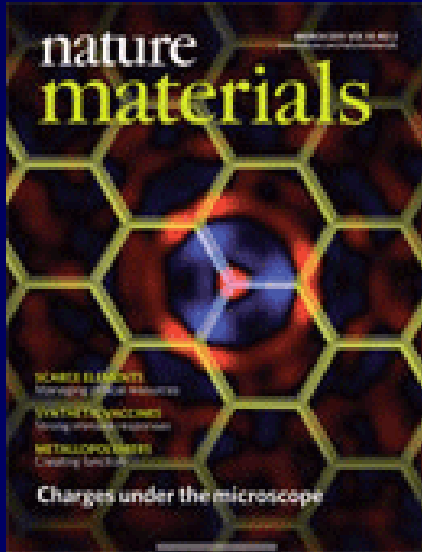
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B. N. Kuganathan, J. Biskupek, U. Kaiser, A. N. Khlobystov
Nature Materials 10 (2011) 687-692

Tomography of nanocarbons



J.Leschner, J.Biskupek, A.Chuvilin, U.Kaiser
Accessing the local three-dimensional structure of carbon materials
sensitive to an electron beam
Carbon 48 (2010) 4042-4048

Chemical bonds in TEM



Jannik C. Meyer, Simon Kurasch, Hye Jin Park, Viera Skakalova, Daniela Künzel, Axel Groß, Andrey Chuvilin, Gerardo Algara-Siller, Siegmund Roth, Takayuki Iwasaki, Ulrich Starke, Jurgen H. Smet, Ute Kaiser
Experimental analysis of charge redistribution due to chemical bonding by high-resolution transmission electron microscopy
Nature Materials 10, 209–215 (2011)

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Prof. Ute Kaiser

Dr. Jannik Meyer

Gerardo Algara-Siller

Electron Microscopy Group of Materials Science, University of Ulm, Germany

Dr. Elizaveta Nikulina

Electron Microscopy Lab, nanoGUNE

Thank you
for your
attention

1 μm

Mag = 26.41 K X

EHT = 2.00 kV

WD = 5.0 mm

Signal A = InLens

Mix Signal = 0.5526

System Vacuum = 7.67e-007 mbar

Collector Bias = 300 V

ESB Grid = 217 V

Aperture Size = 30.00 μm

User Name = LIZA

Date :26 Jan 2009

File Name = Thank9_11.tif

FIB Lock Mags = No

