Application of Low Voltage Cs-corrected TEM for Nanocarbon Materials

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CIC nanoGUNE Consolider
Donostia - San Sebastian
Basque Country, Spain

Dubna, 27.08.2012


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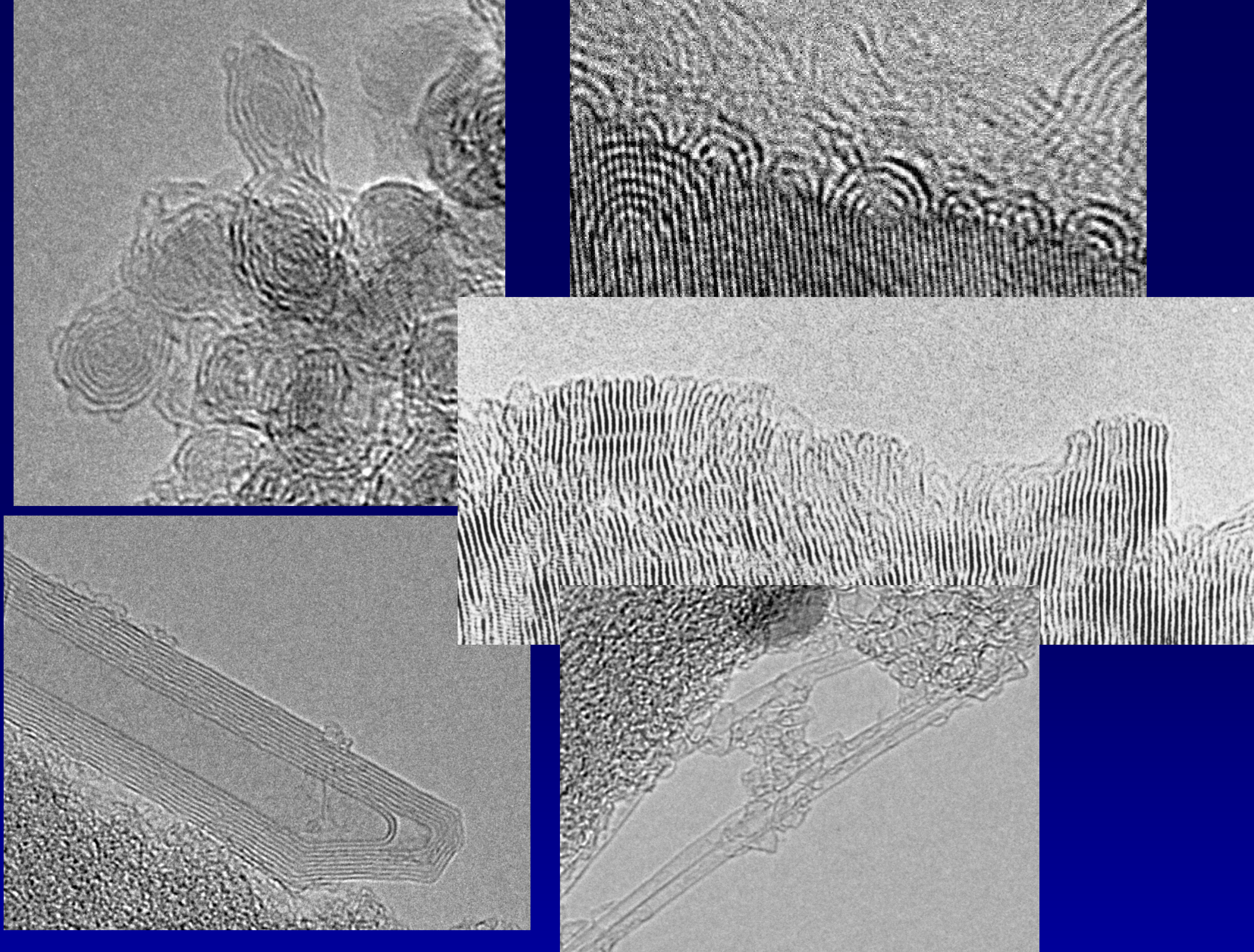
Outline:

- 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

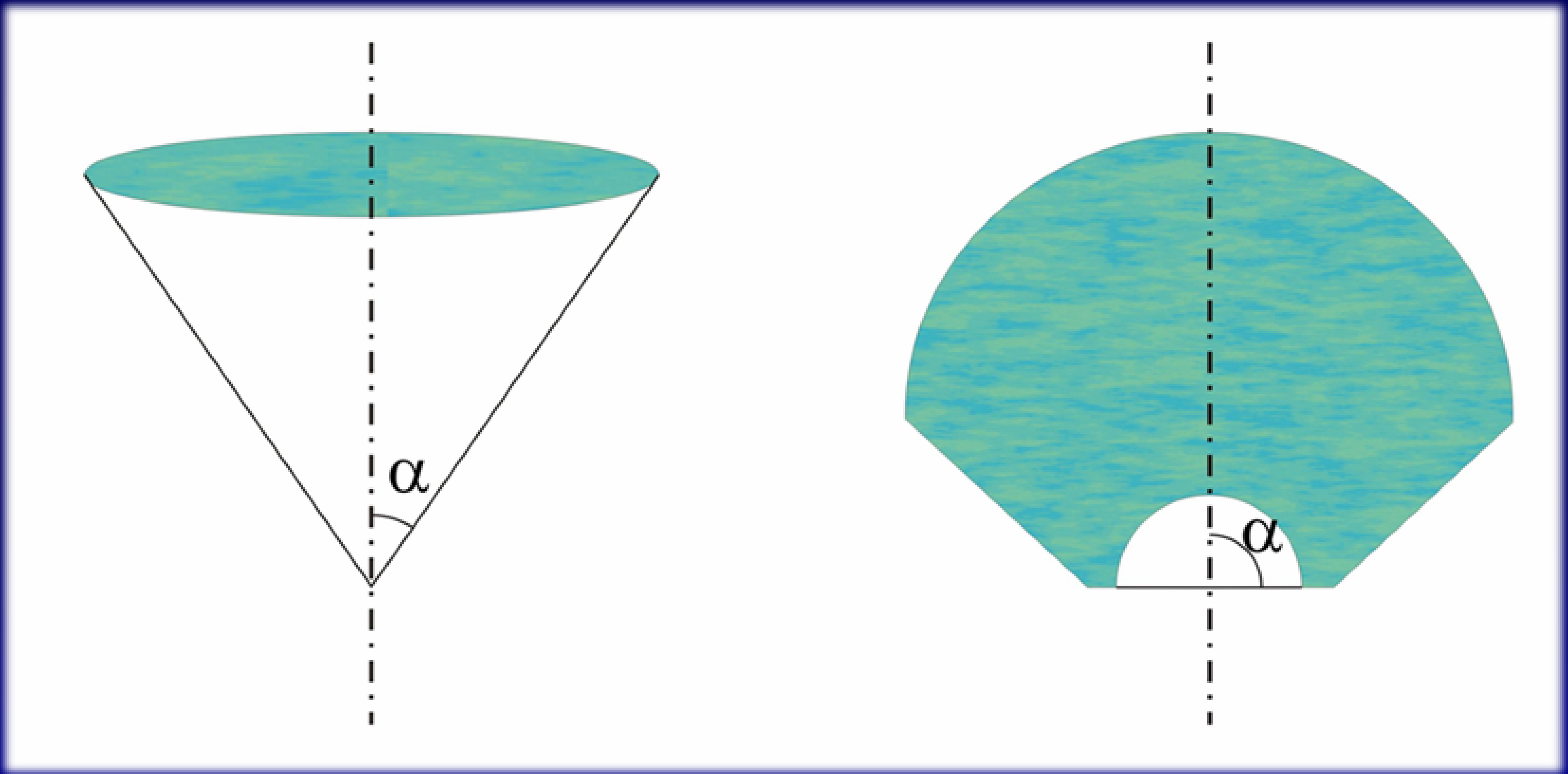


Resolution limited by electron optics

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

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

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.

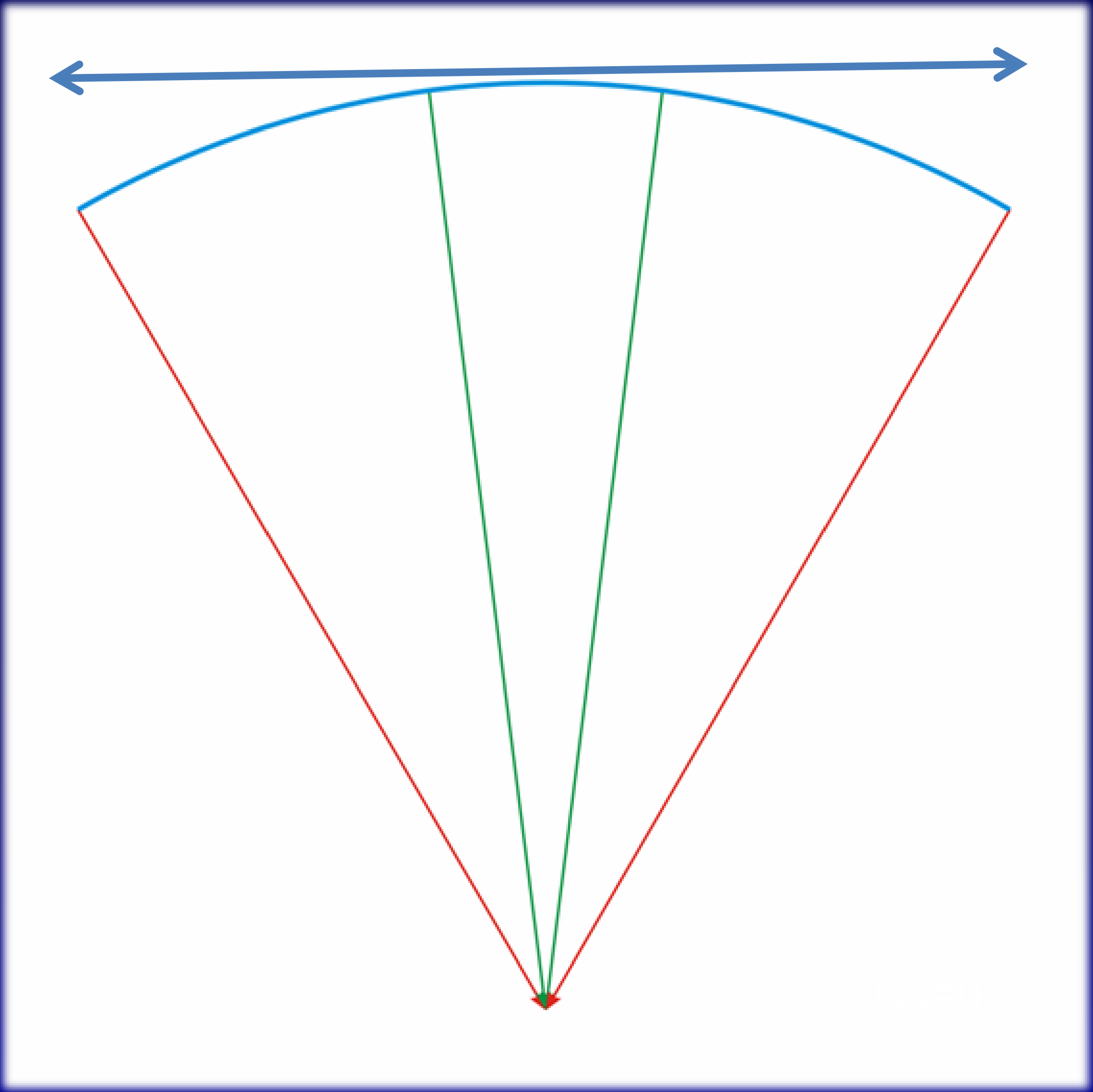
1. Unmöglichkeit des Achromaten.

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.

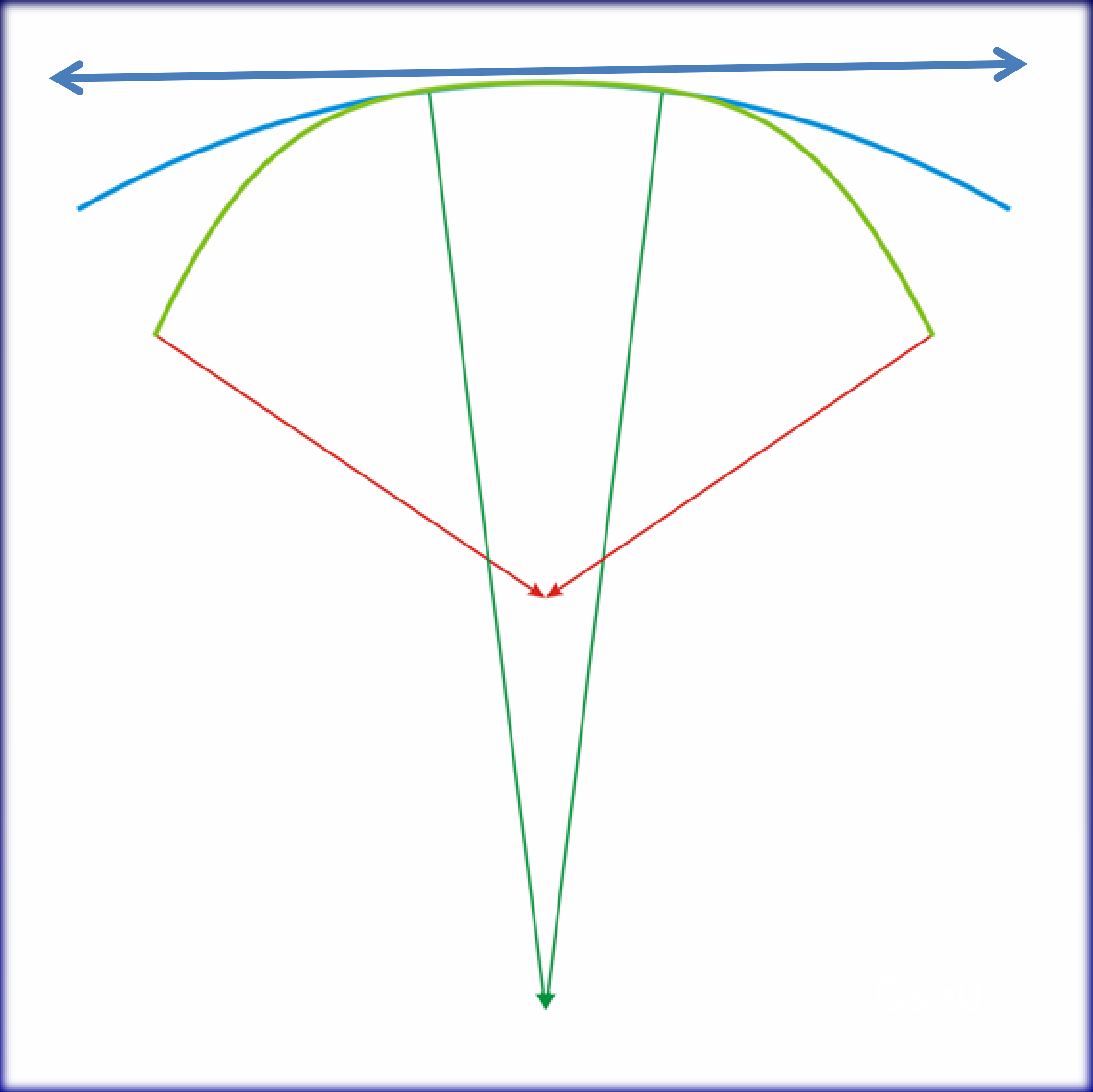
Die Bewegung der achsennahen Elektronen (Gaußscher Strahlengang) genügt bekanntlich der Gleichung

$$\Phi r'' + \frac{1}{2}\Phi' r' = -\frac{r}{4}\Phi'' - \frac{e r}{8 m}\mathfrak{H}^2. \qquad (1)$$

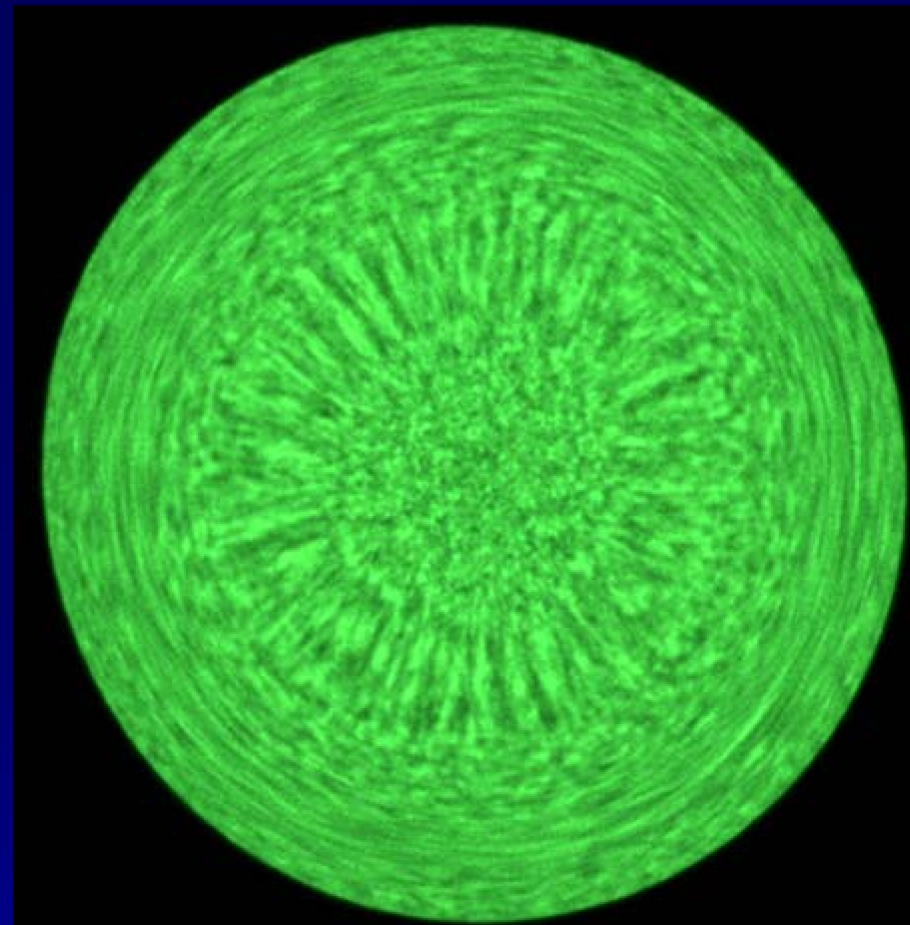
Resolution limited by electron optics



Resolution limited by electron optics



Resolution limited by electron optics



Resolution limited by electron optics

Typical values:

C_s = 0.5 - 2.5 mm

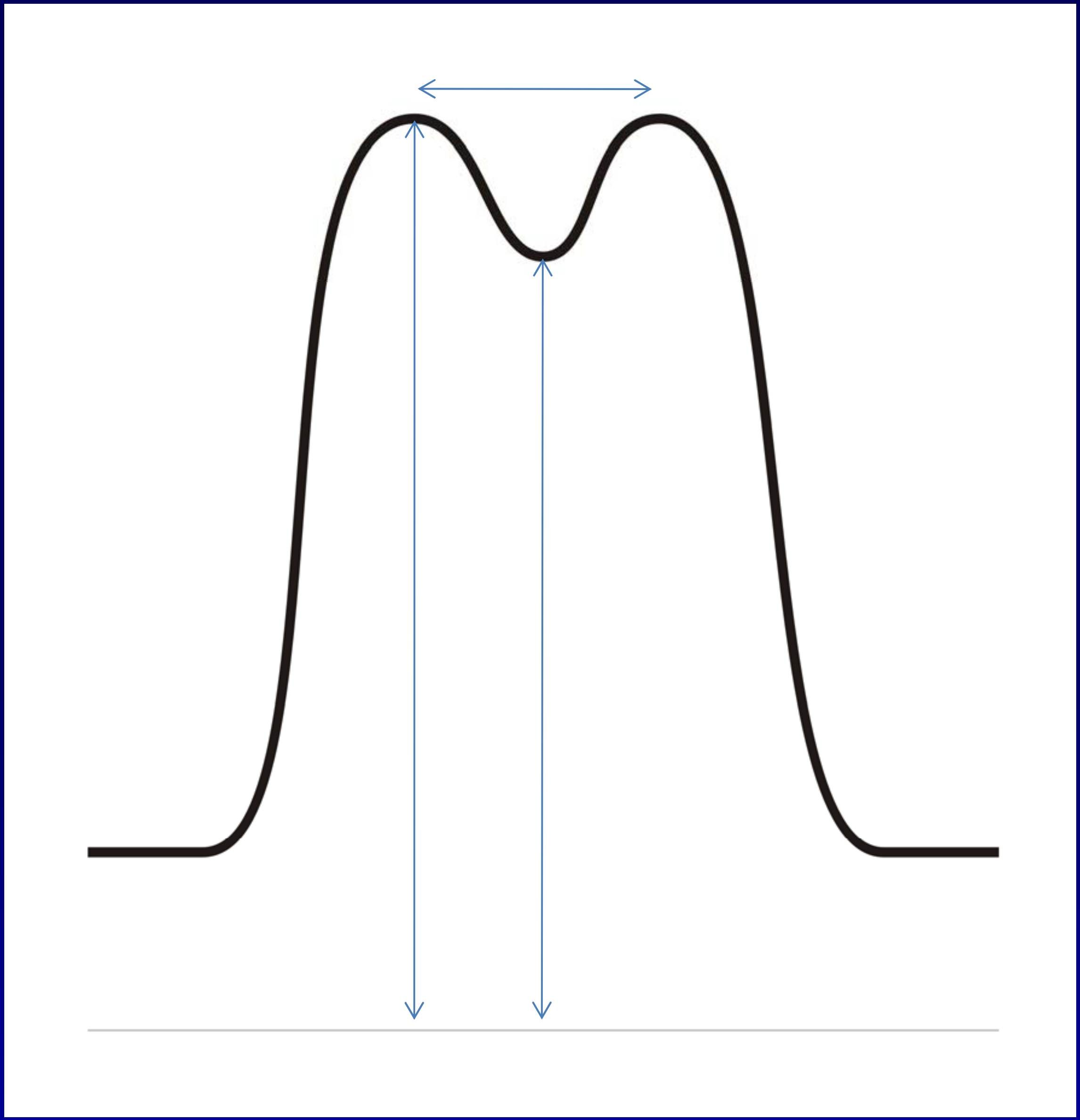
5-10 mrad

NA_o ~ 0.01

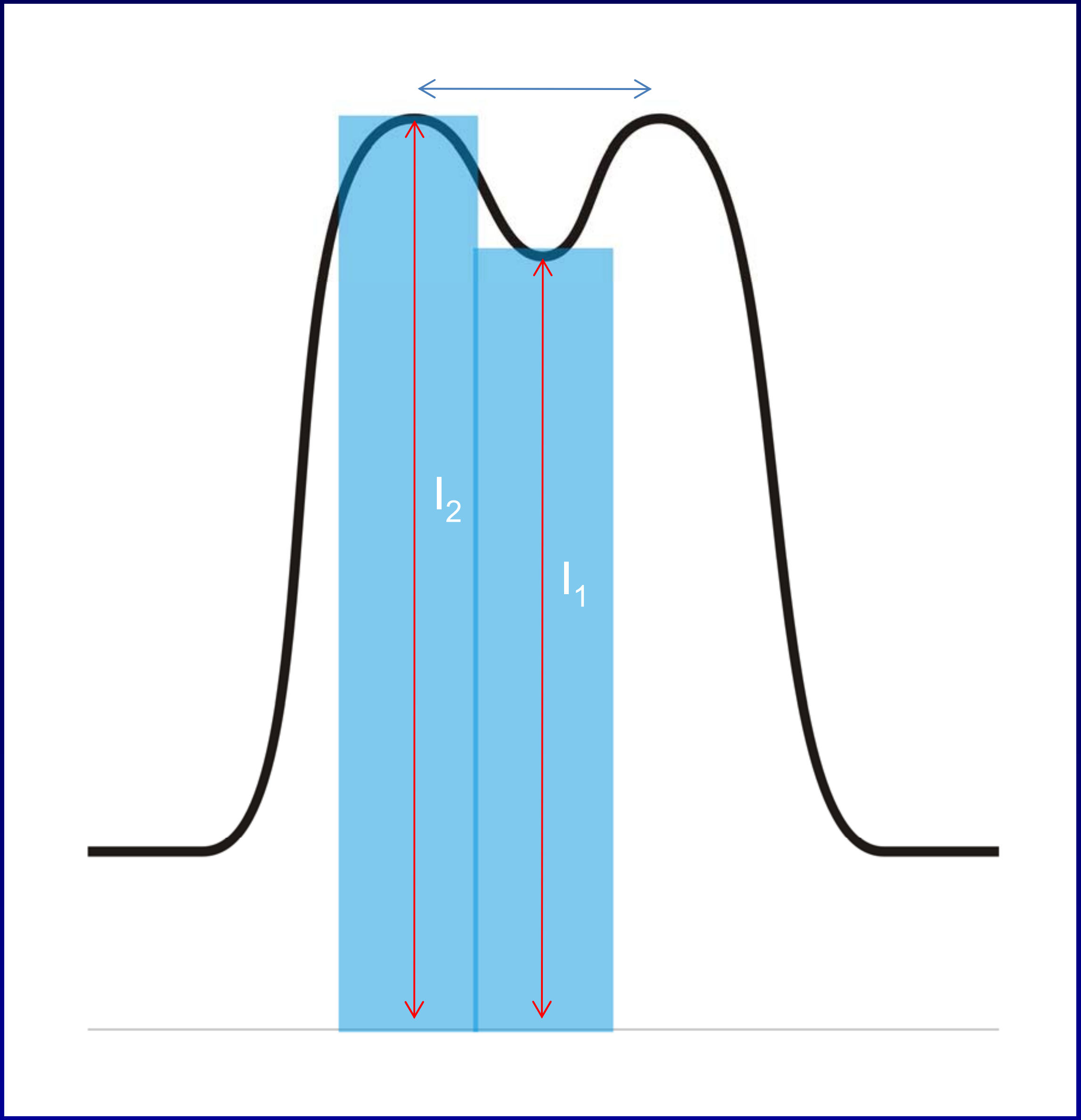
$$d_o = 0.6\sqrt[4]{C_s\lambda^3}$$

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



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

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

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

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

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

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

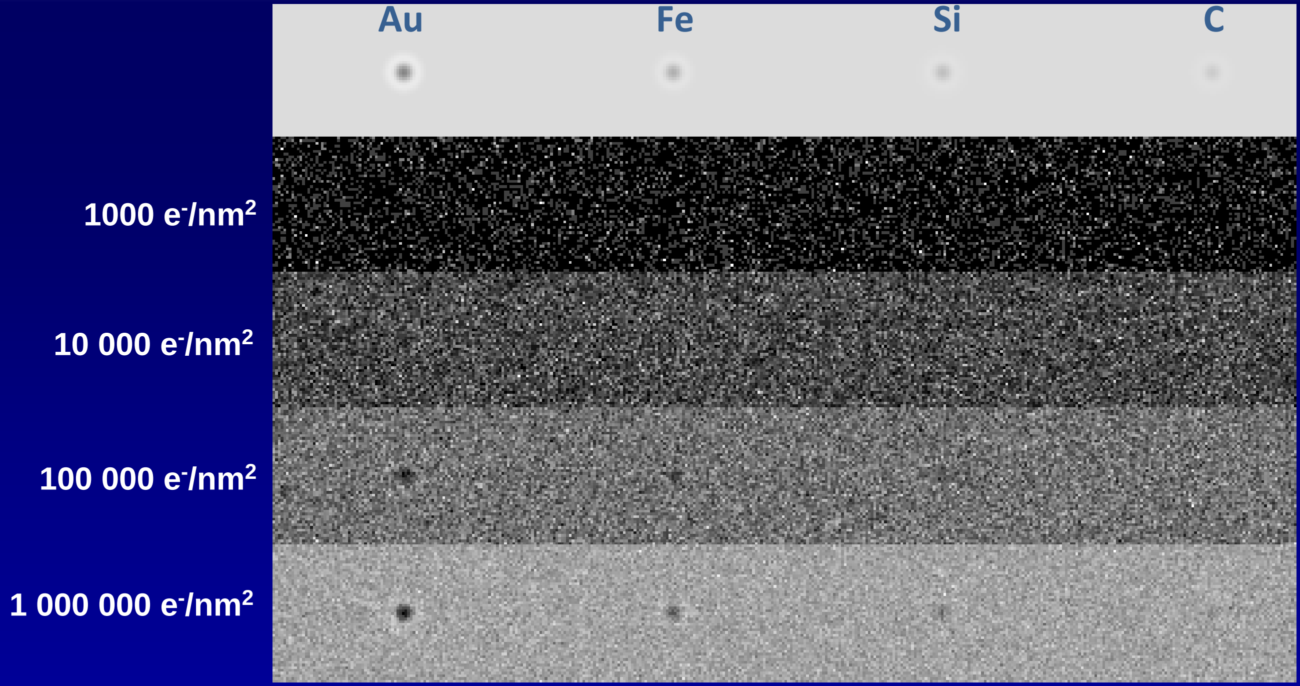
$$D > \frac{SNR_{lim}^2}{C^2 * \left(\frac{d_n}{2}\right)^2}$$

Resolution limited by SNR

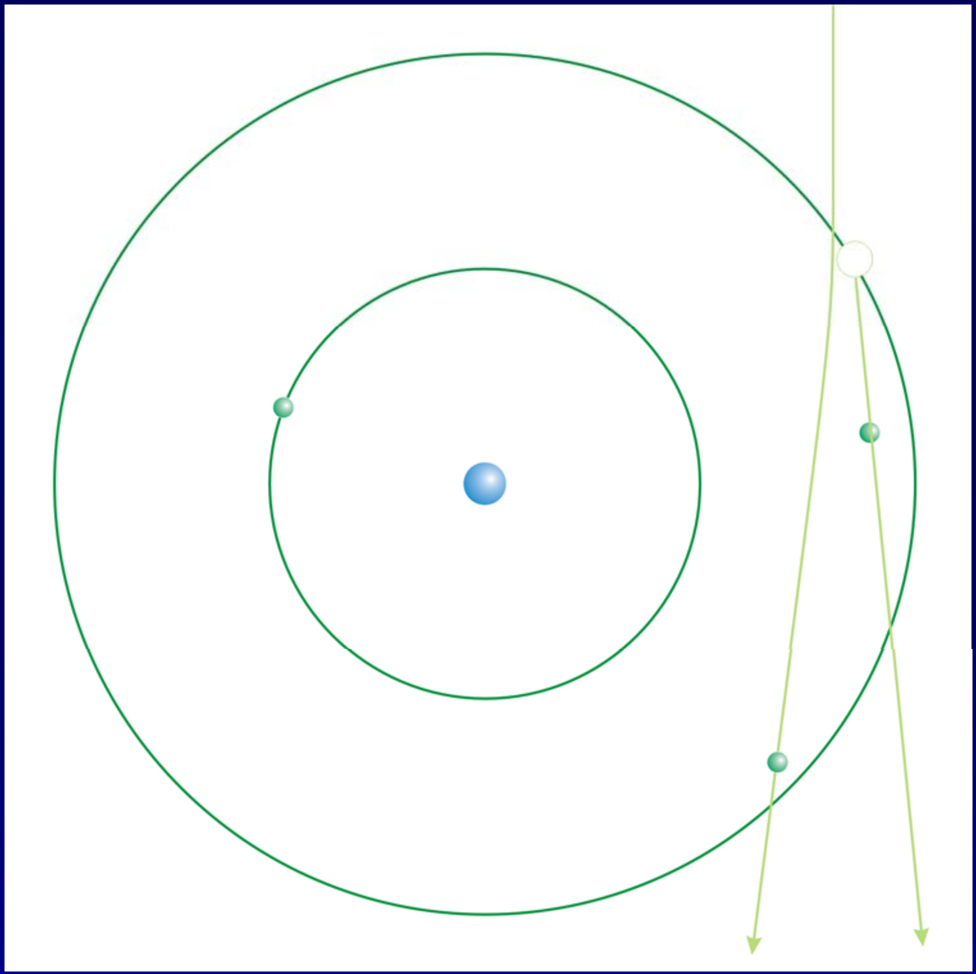
		Electron dose [e^-/nm^2]				
	Contrast	100	1000	10000	100000	1000000
Au	0.18	5.47	1.73	0.55	0.17	0.05
Fe	0.08	12.75	4.03	1.28	0.40	0.13
Si	0.05	19.95	6.31	2.00	0.63	0.20
C	0.03	32.85	10.39	3.28	1.04	0.33

Noise limited resolution [nm]

HT - 300kV, instrumental resolution - 0.1 nm

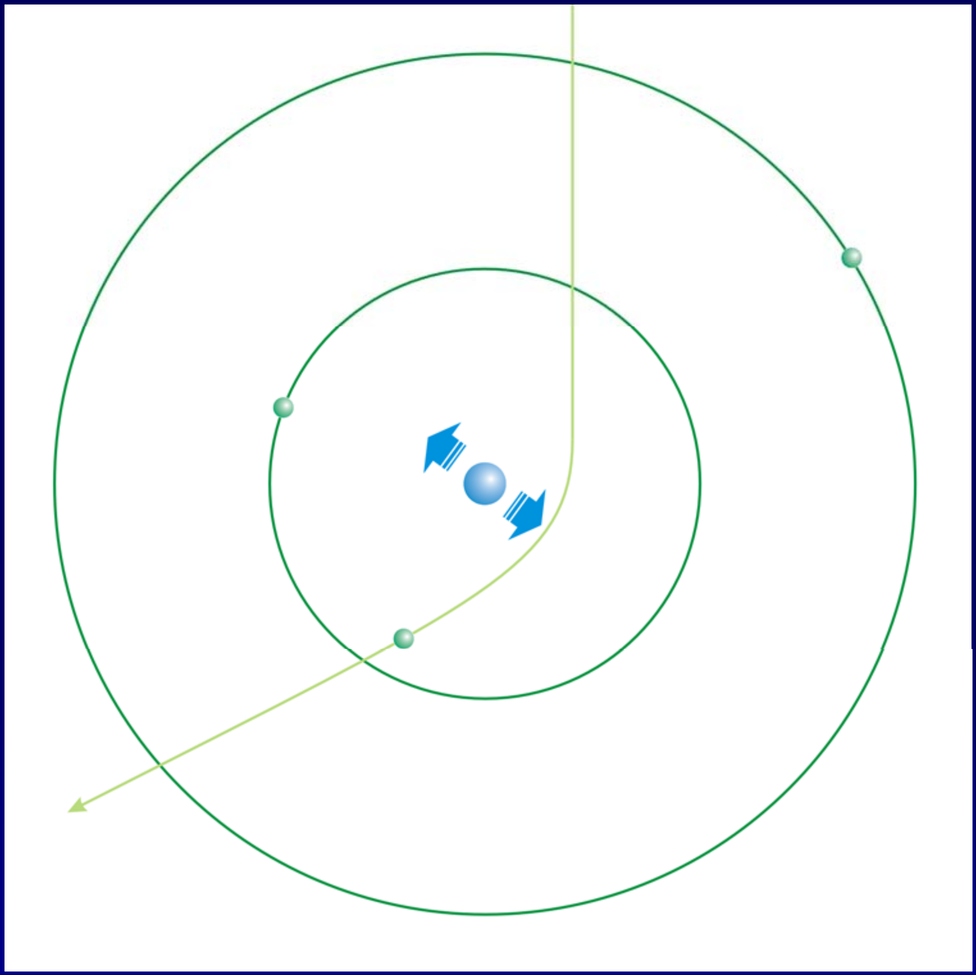


Radiation damage



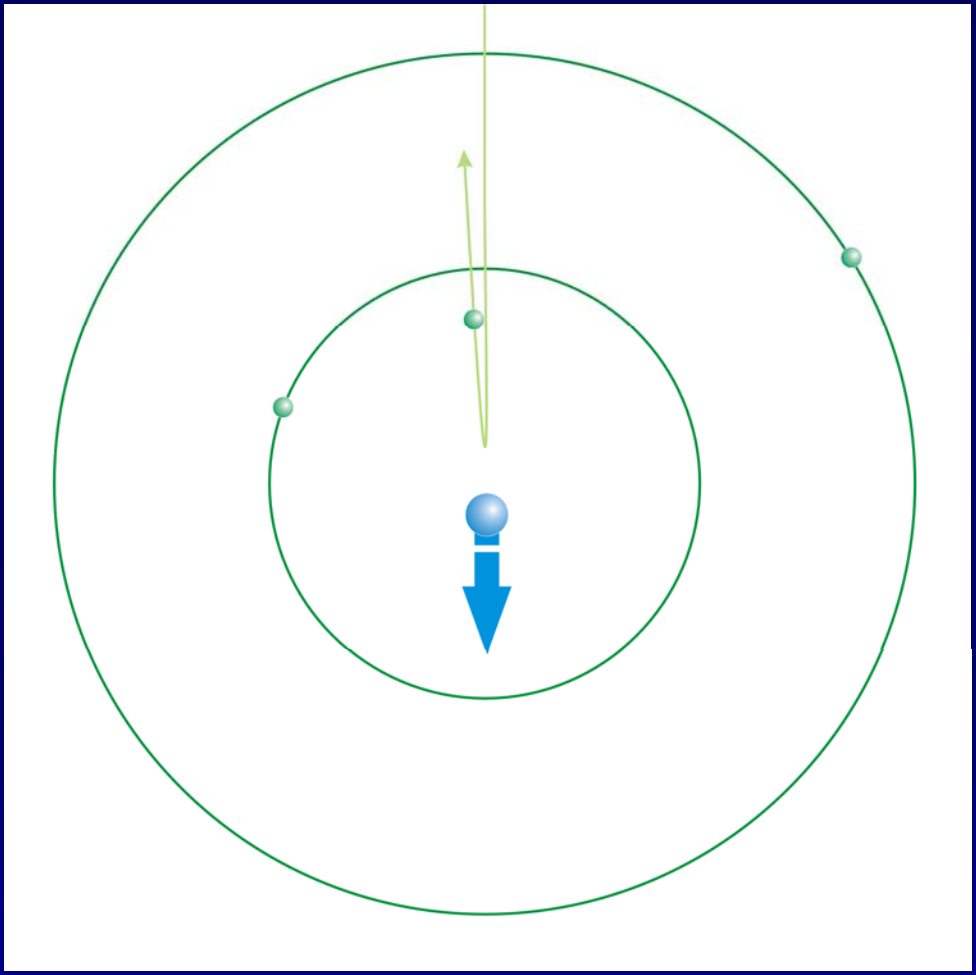
- ionisation

Radiation damage



- ionisation
- heating

Radiation damage



- ionisation
- heating
- knock-on damage

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

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

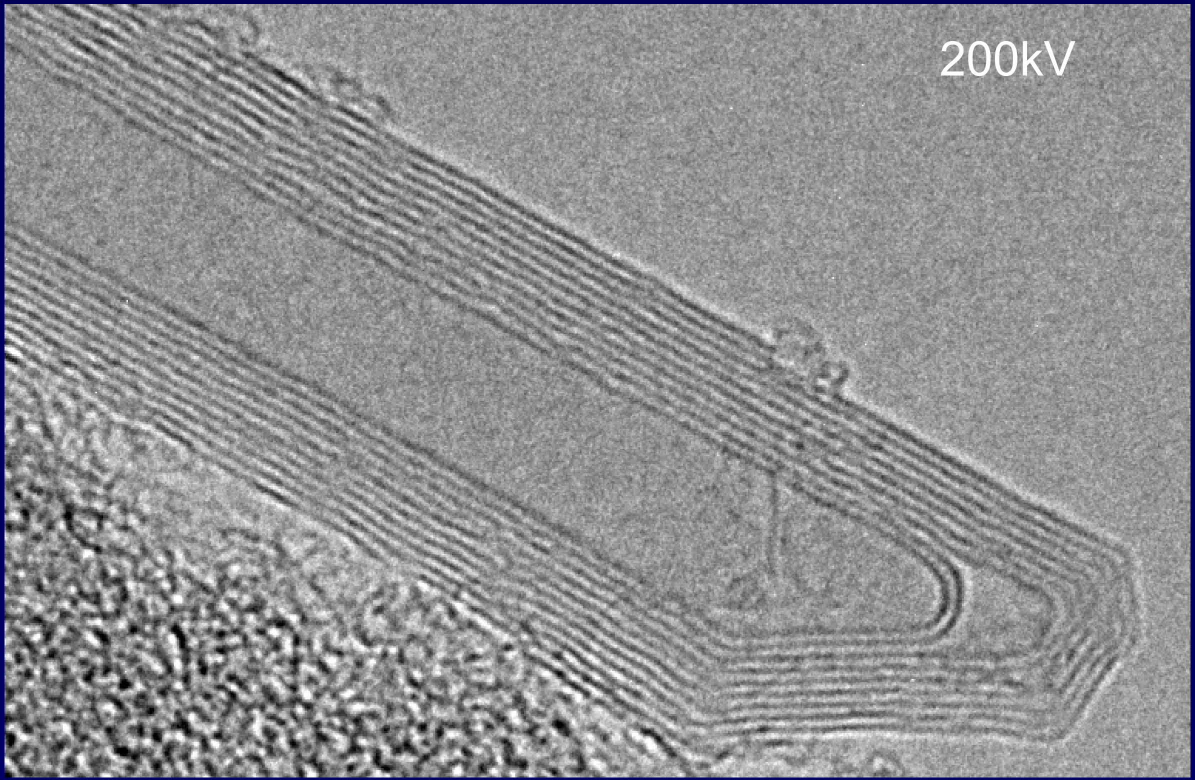
$$\Delta E < E_{bond}$$

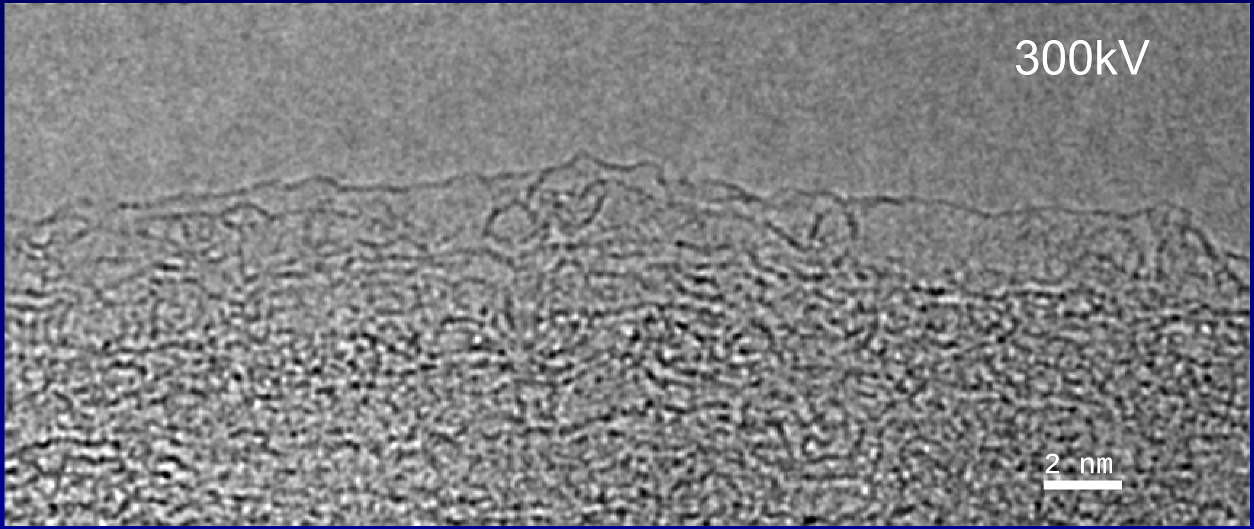
$$E_e < 450 * E_{bond} * A_m$$

$$C_{graphene} \Longrightarrow \sim 79keV$$

A. Zobelli, A. Gloter, C. P. Ewels, G. Seifert, C. Colliex, PhysRev B 75, 245402 (2007)

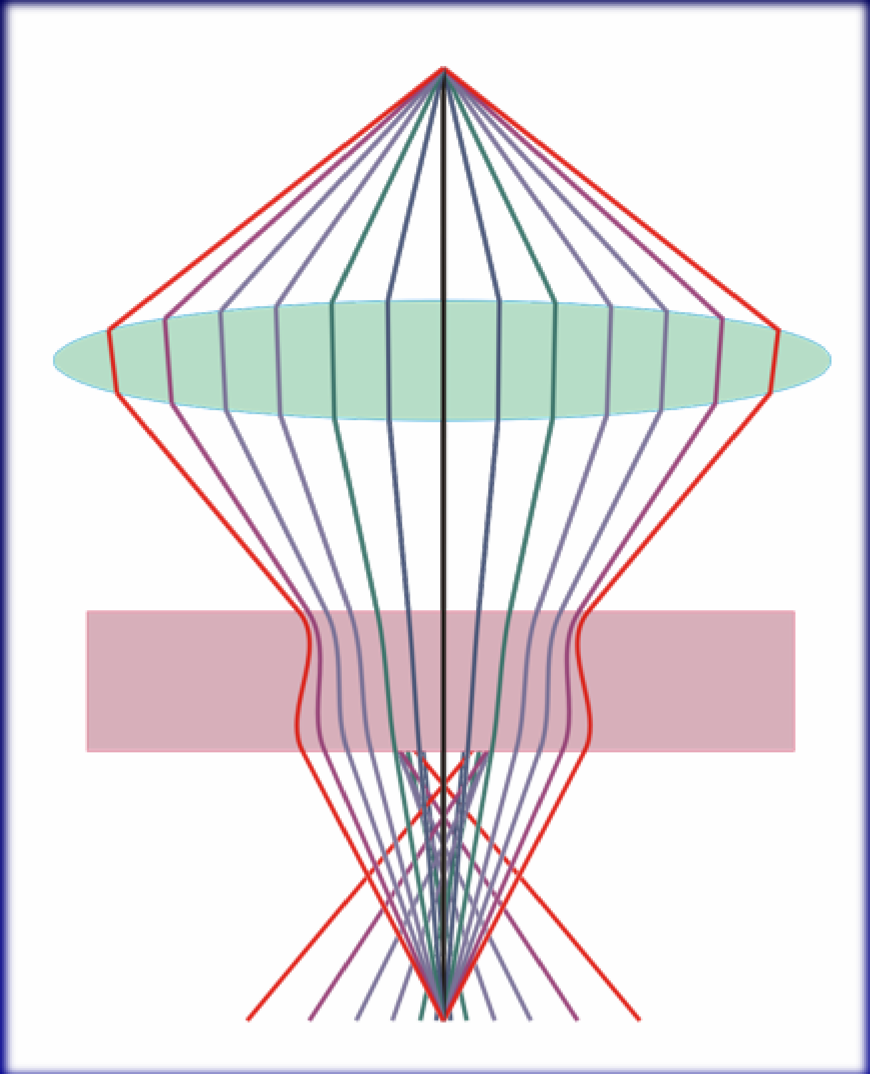
Radiation damage





Cs correction

Correction of spherical aberration



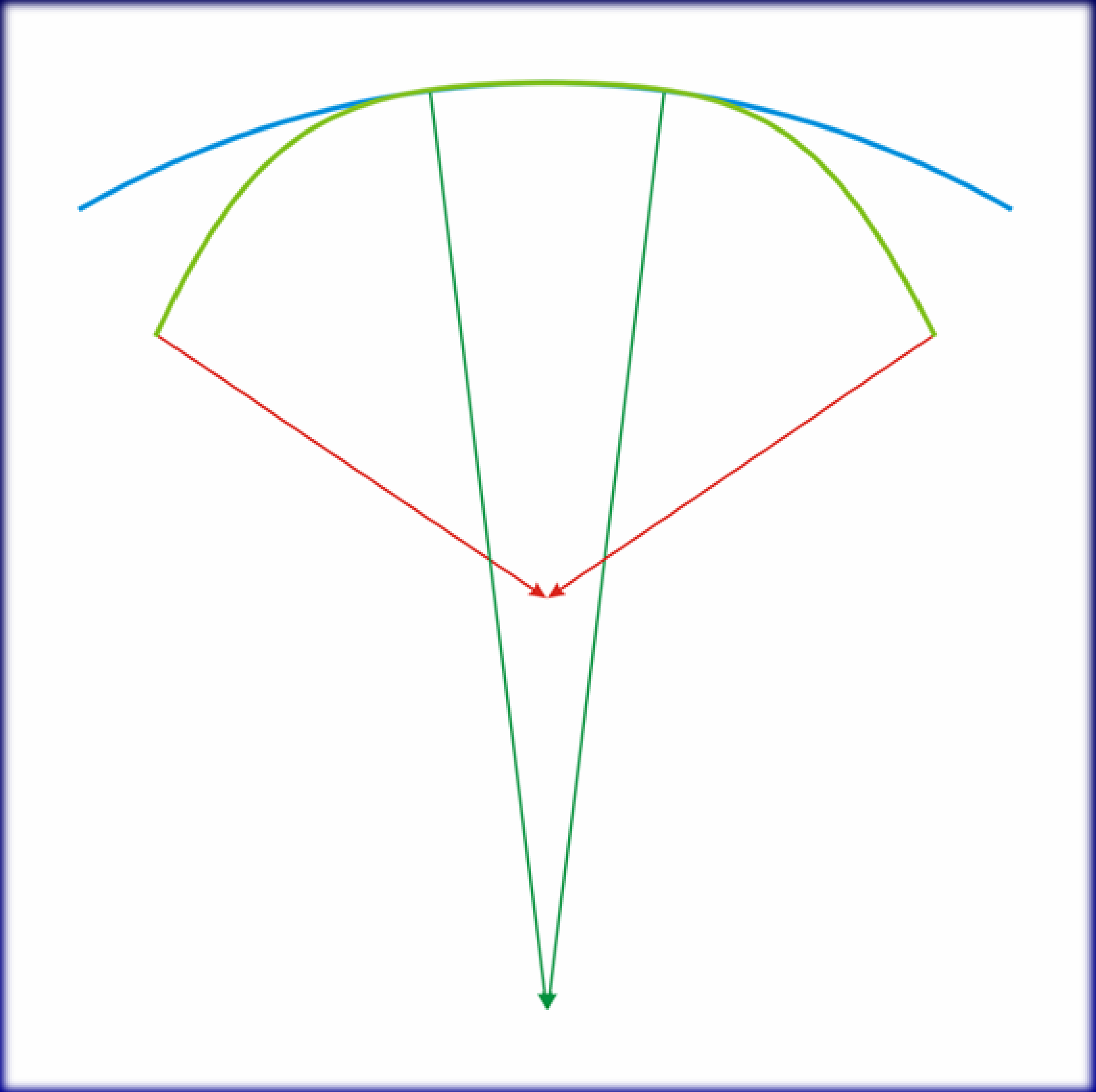
Correction of spherical aberration

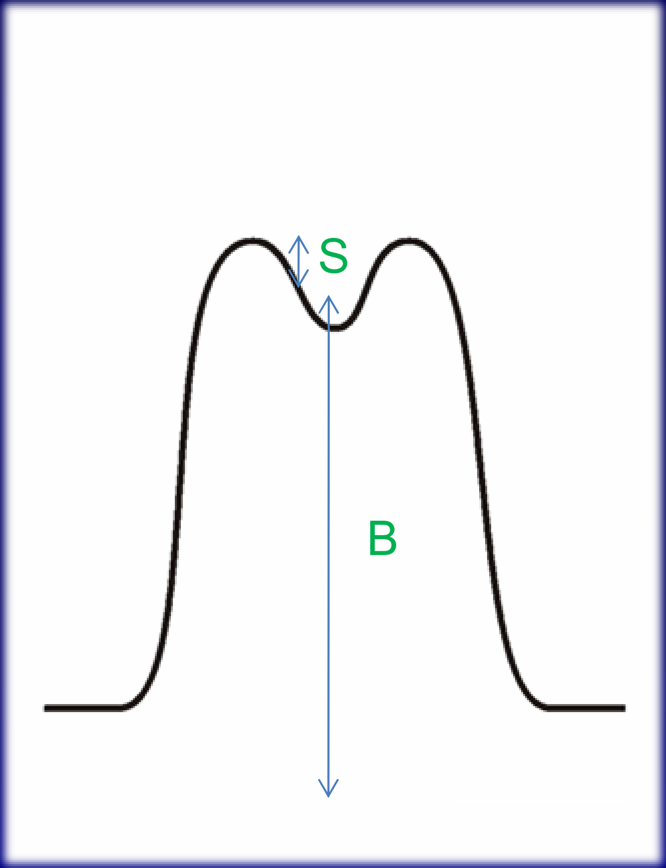
Aberrations of round static space-charge-free electromagnetic lenses are unavoidable and their coefficients are always positive.

CEOS
Corrected Electron Optical Systems GmbH

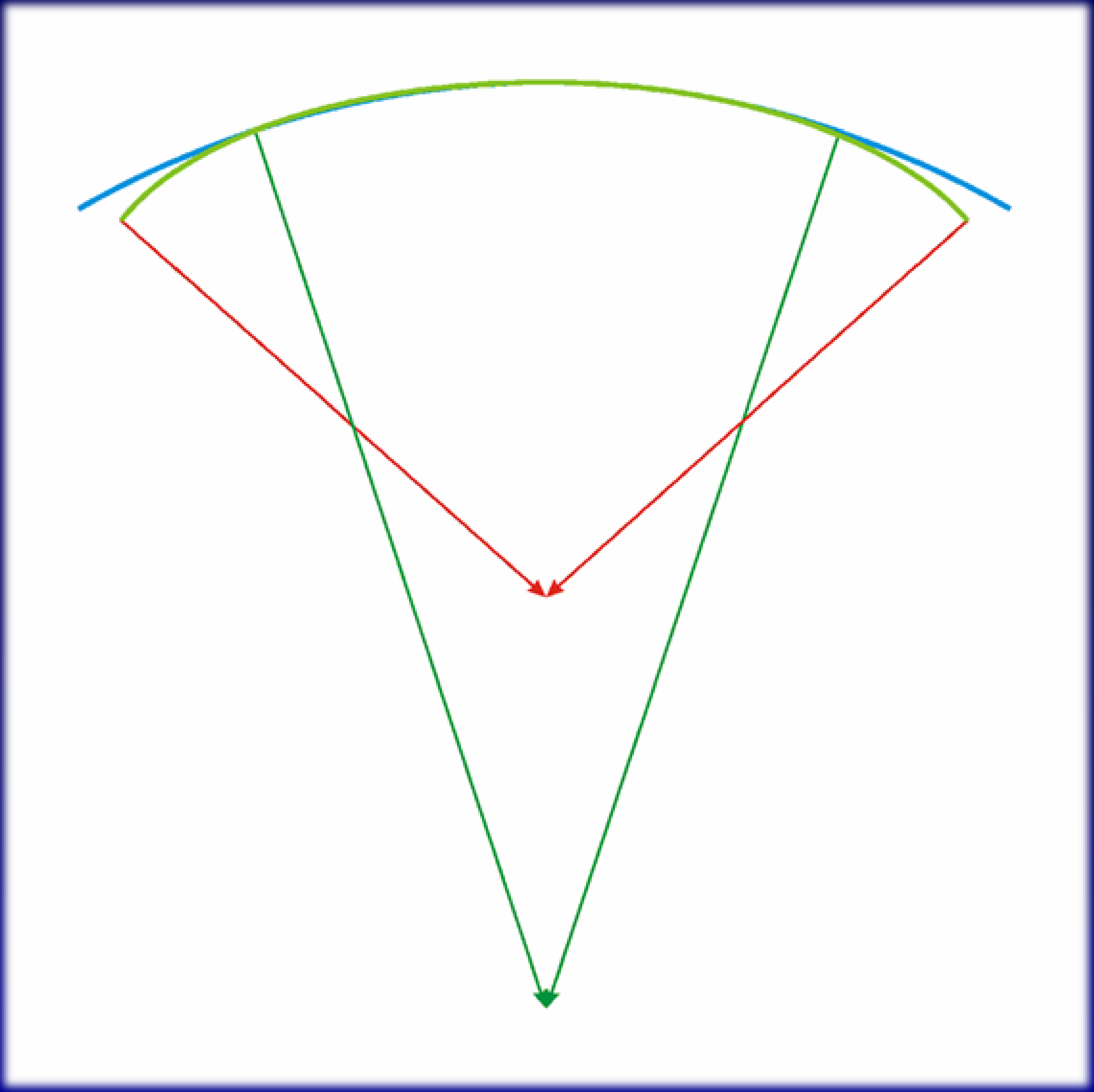
Scherzer, 1947, Optik 2, 114
Seeliger, 1949, Optik 5, 490
Rose, 1990, Optik 85, 19
Haider et al. 1998, Nature 392, 768

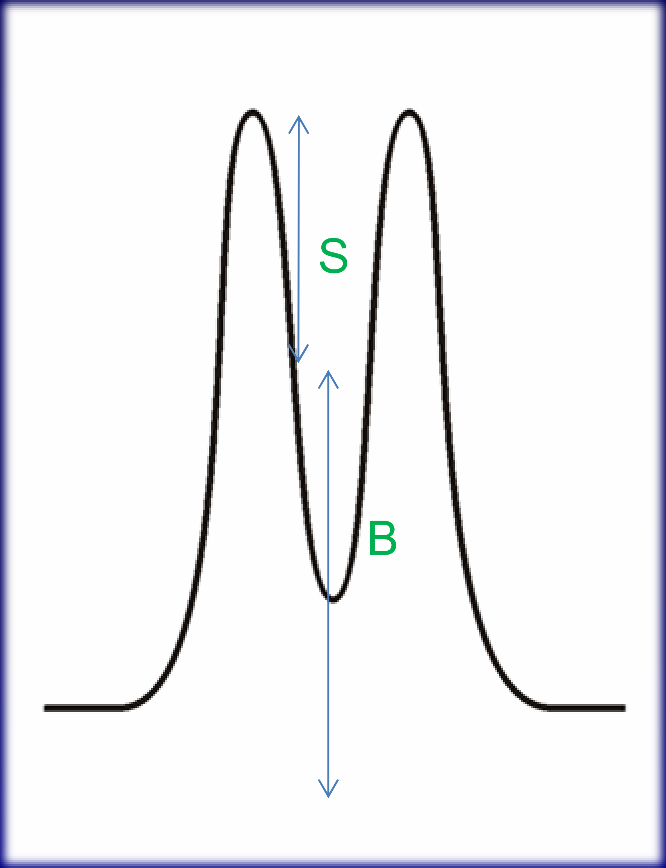
Correction of spherical aberration



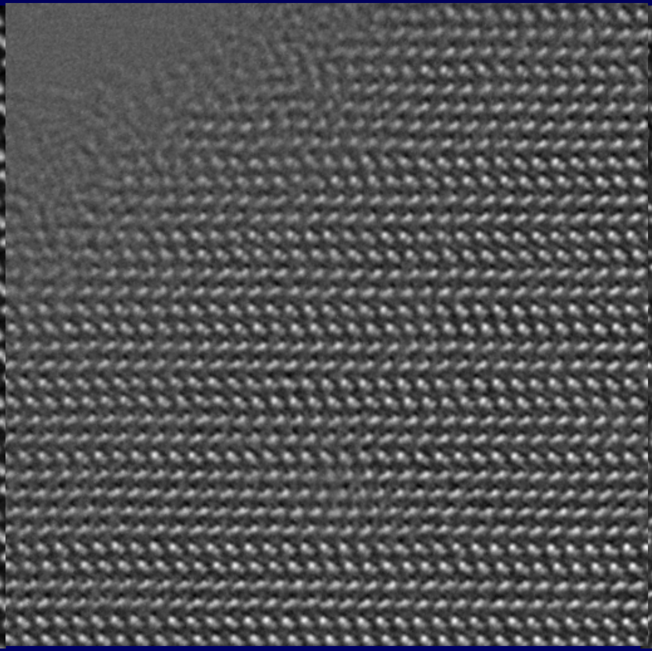


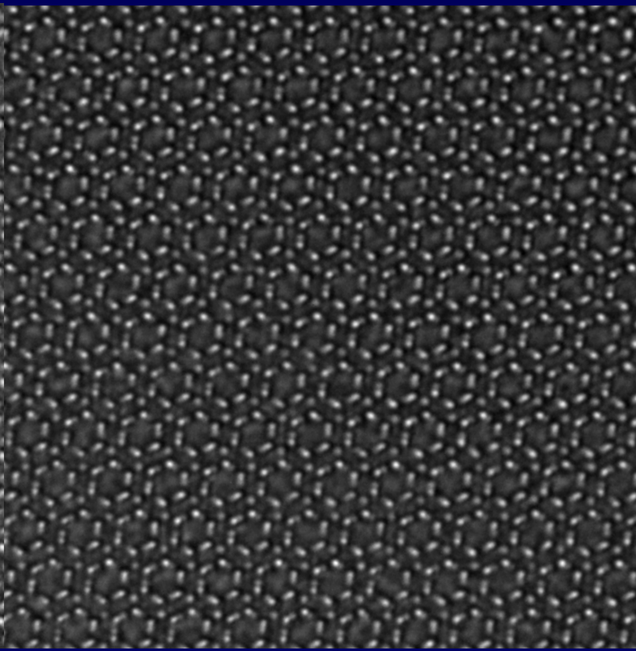
Correction of spherical aberration

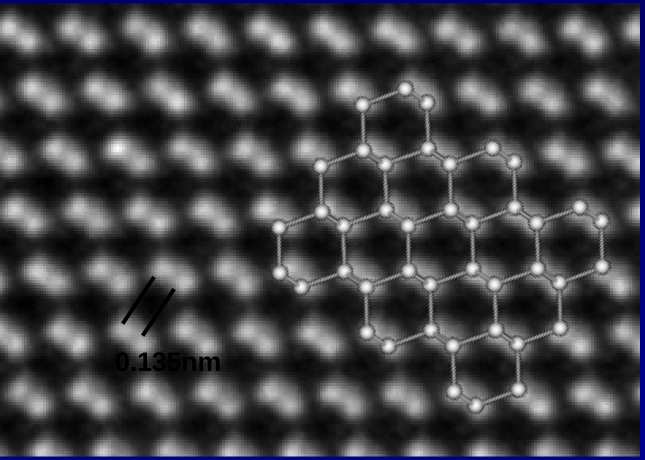




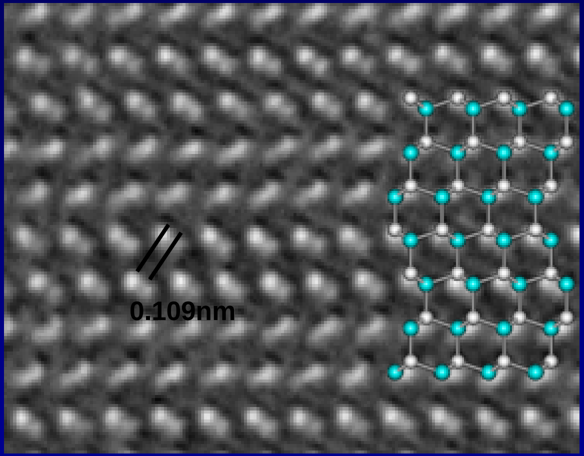
HRTEM images obtained at Cs-corrected 300kV TEM



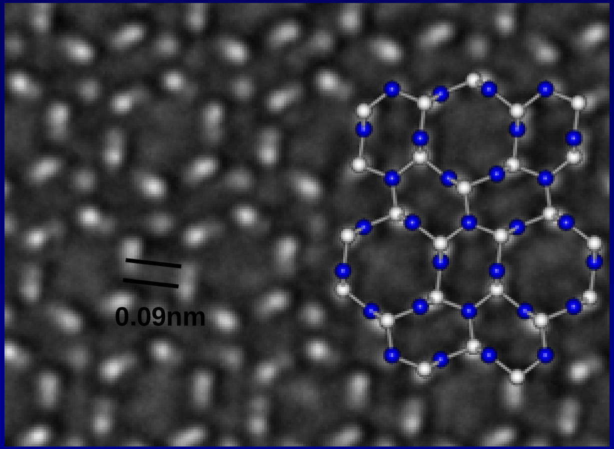




Si



4H-SiC

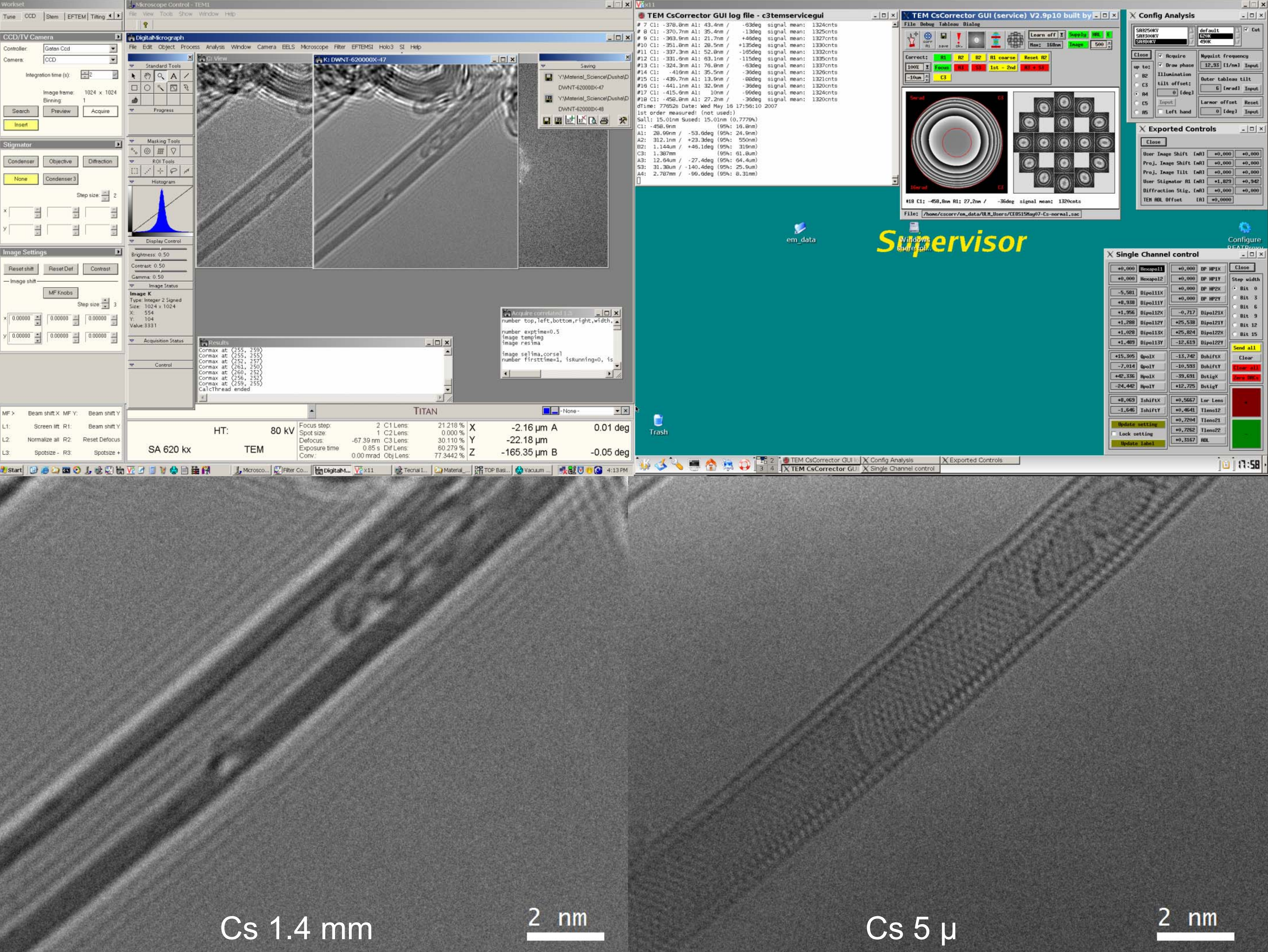


Si_3N_4

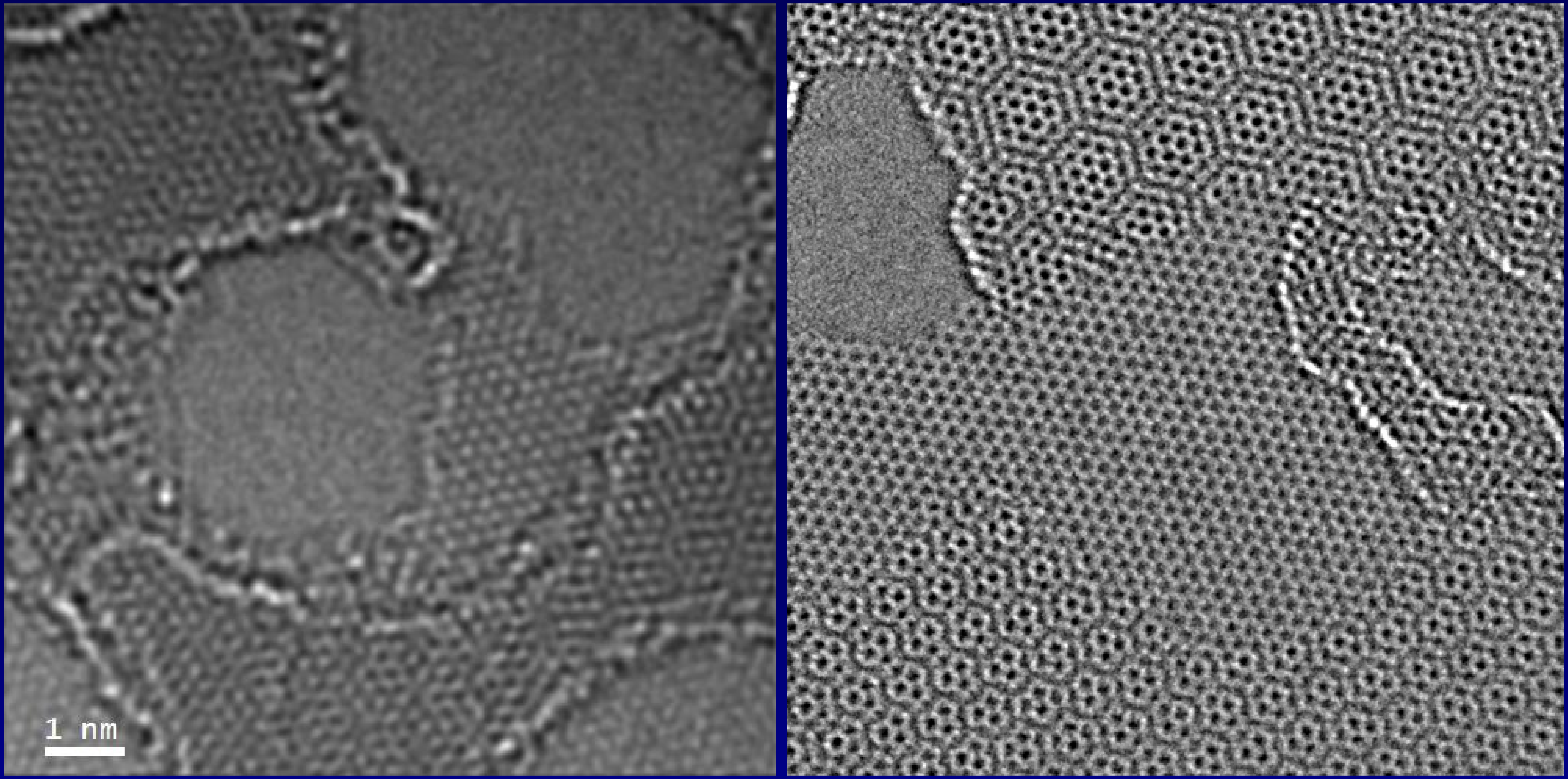
Correction of spherical aberration

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

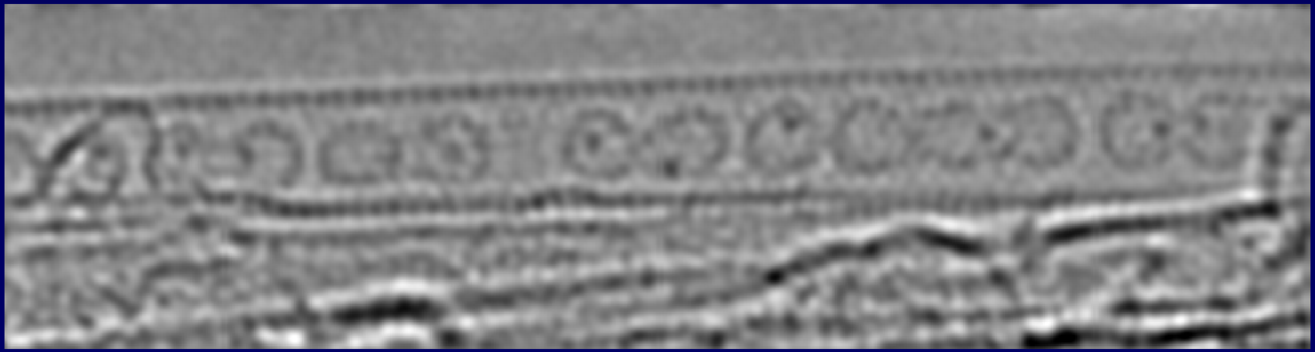
HT [kV]	[nm]	d_o [nm]	
1500	0.0006	~~0.084~~	
400	0.0016	~~0.171~~	
300	0.0020	~~0.196~~	0.05
200	0.0025	~~0.[illegible]35~~	
100	0.0037	~~0.[illegible]15~~	
80	0.0042	~~0.345~~	0.1
60	0.0049	~~0.387~~	
40	0.0060	~~0.454~~	
20	0.0086	~~0.592~~	


Supervisor
TITAN
HT: 80 kV
SA 620 kx
TEM
Cs 1.4 mm
2 nm
Cs 5 µ
2 nm

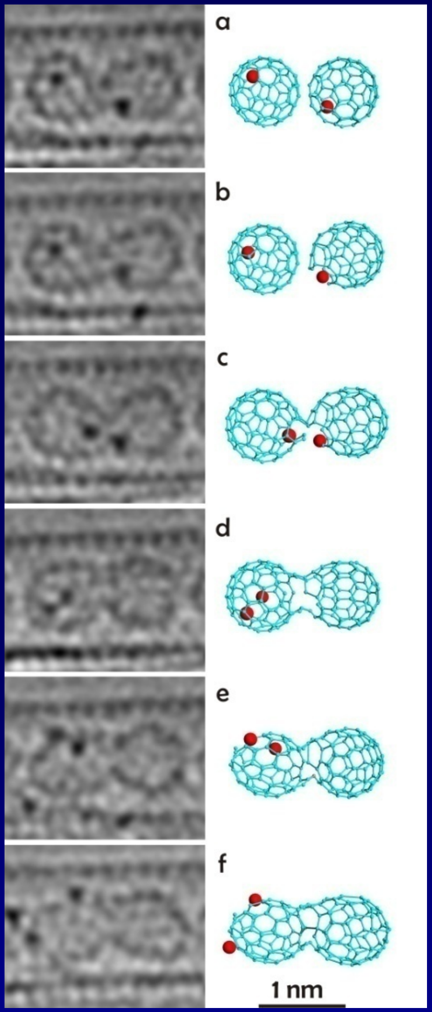
Applications

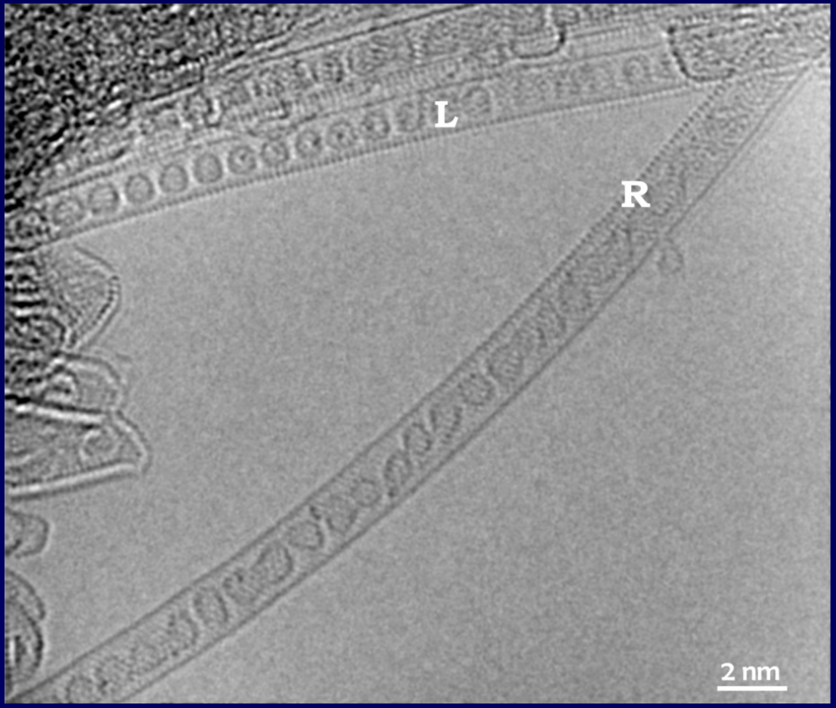

1 nm

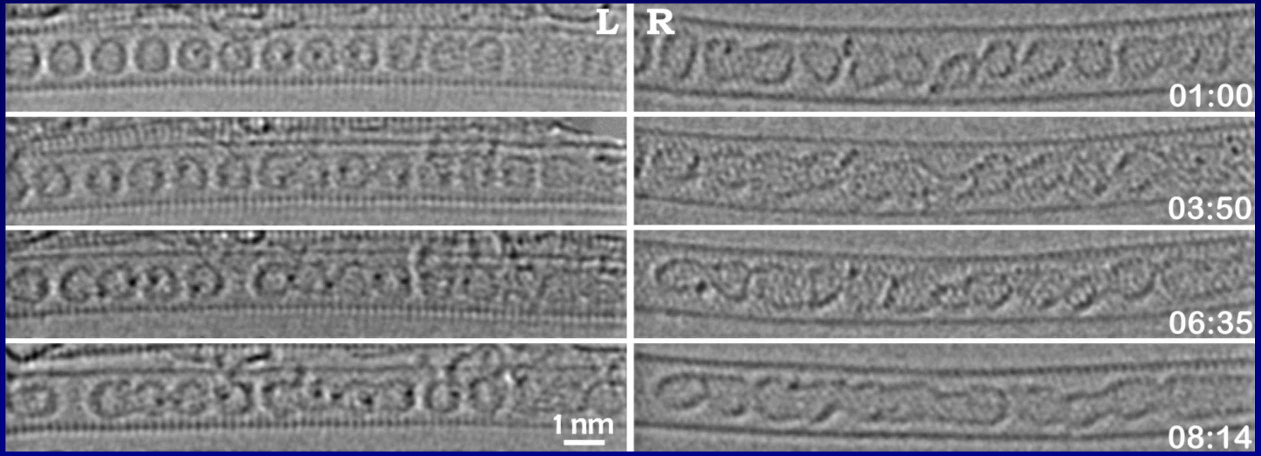
$(Dy@C_{82})@SWNT$



(Dy@C82)@SWNT

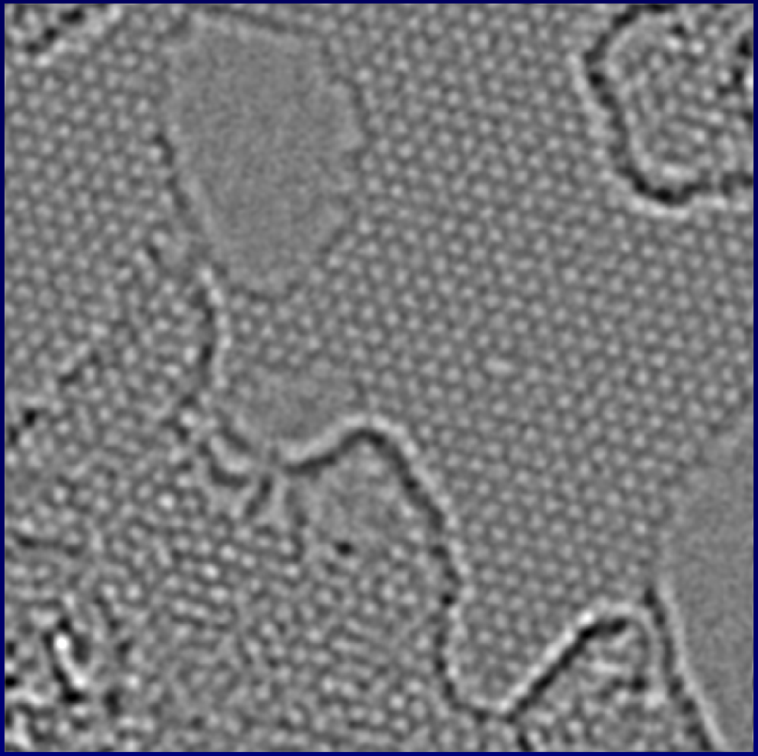


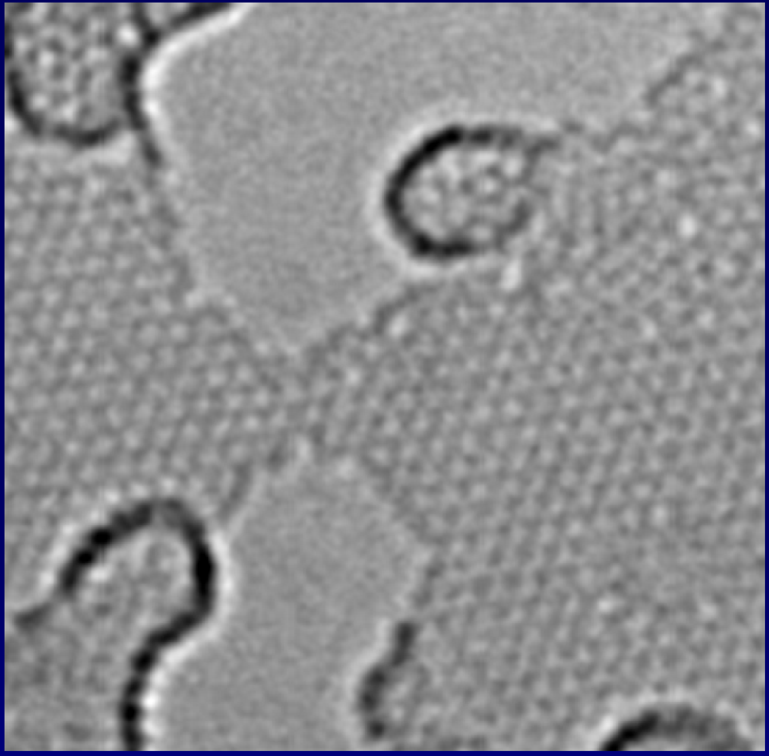




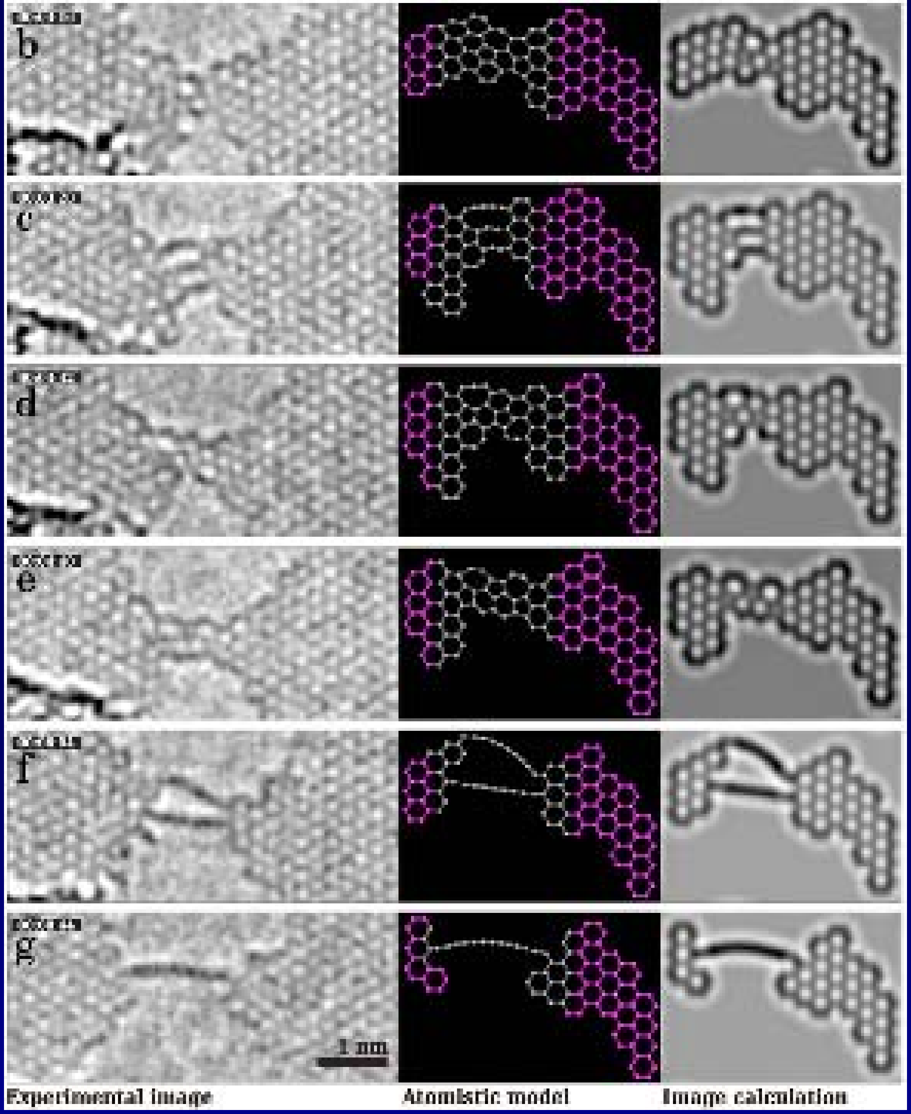
A. Chuvilin, A. Khlobystov, D. Obergfell, M. Haluska, S. Yang, S. Roth, U. Kaiser
Observations of Chemical Reactions at the Atomic Scale : Dynamics of Metal-Mediated Fullerene Coalescence and Nanotube Rupture
Angewandte Chemie (2010) 49, 193

Monocarbon chains



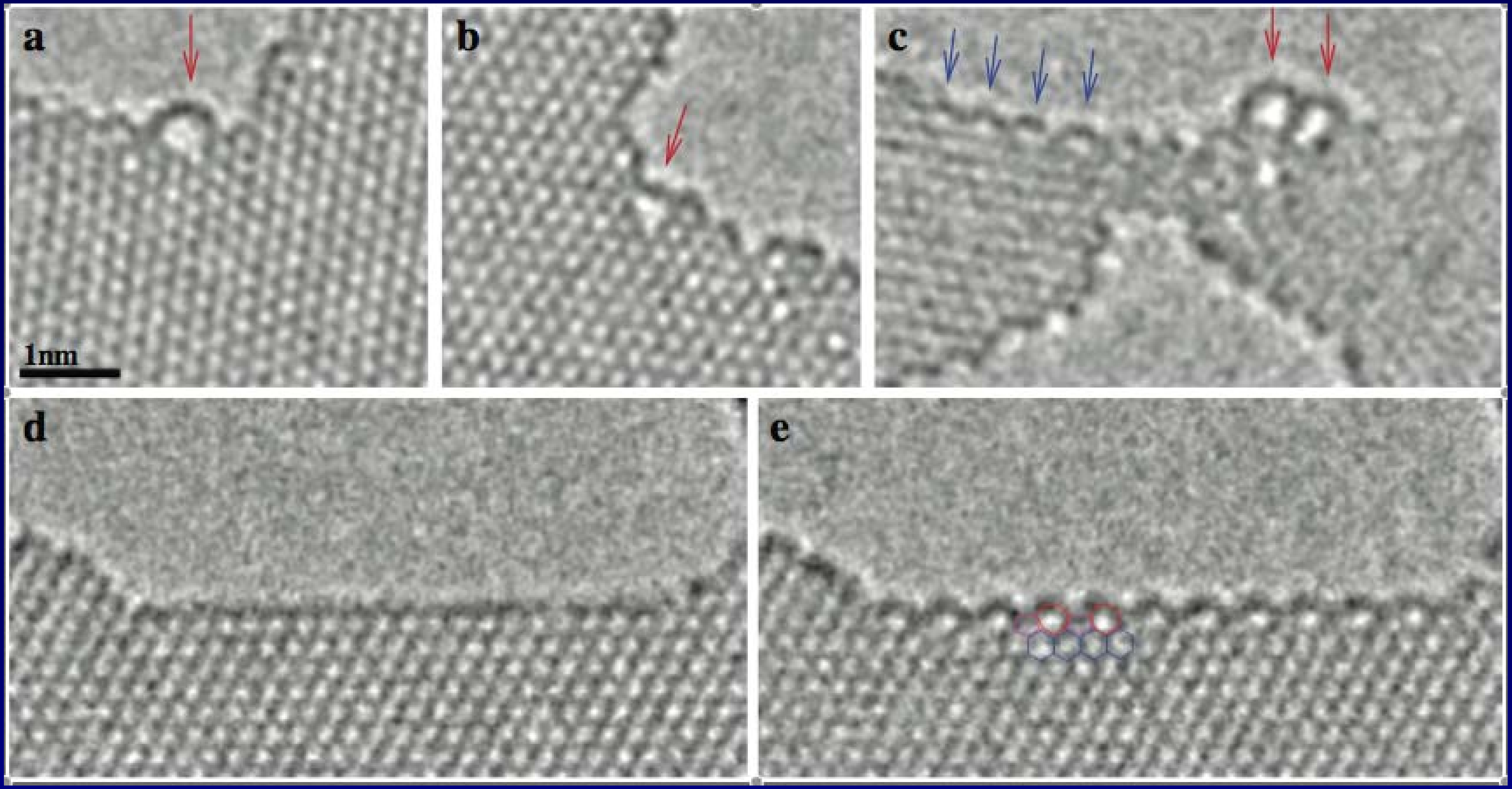


Monocarbon chains



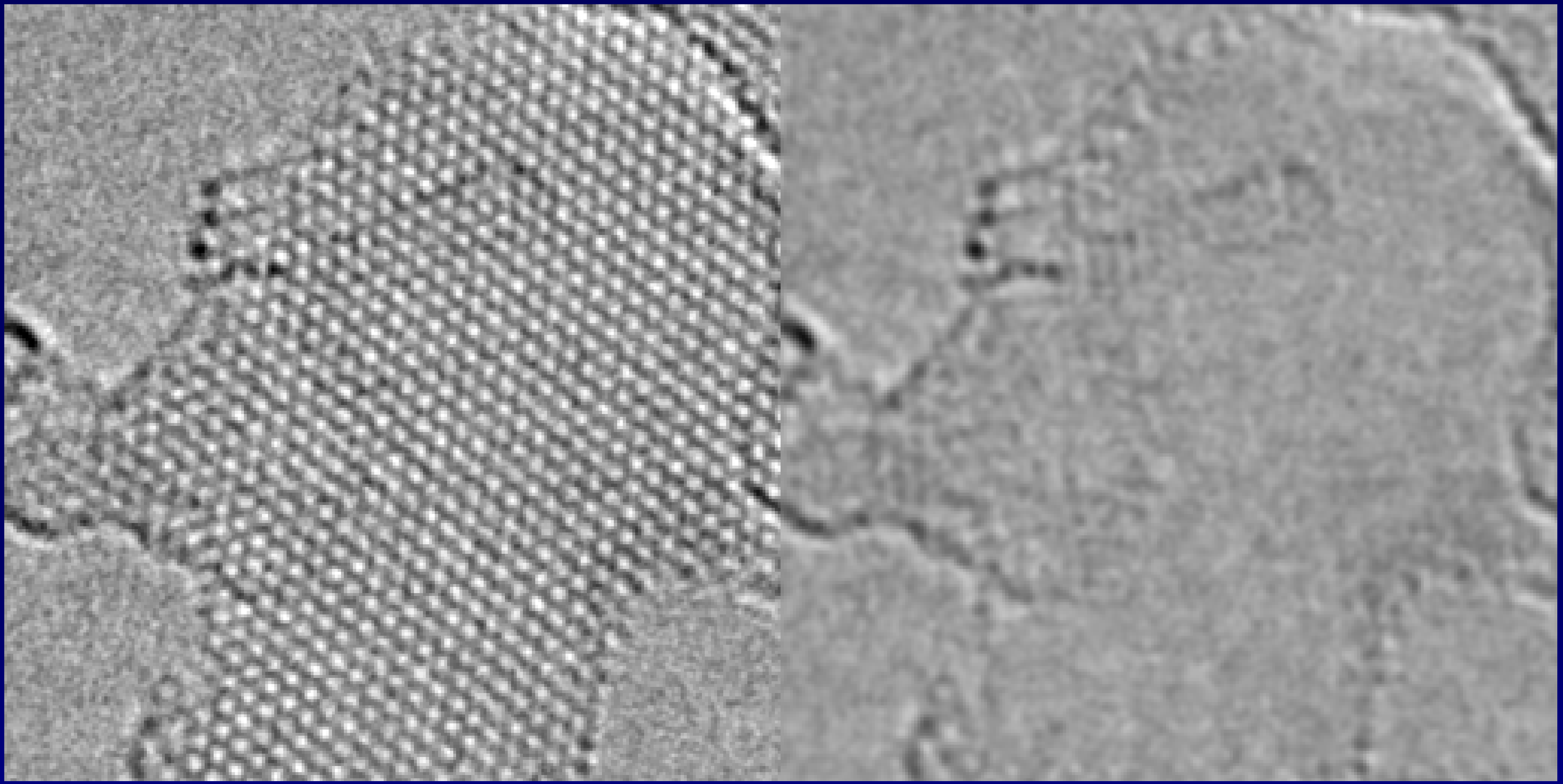
A. Chuvilin, J.C. Meyer, G. Algara-Siller, U. Kaiser
From graphene constrictions to single carbon chains
New Journal of Physics 11 (2009) 083019

Monocarbon chains



A. Chuvilin, J.C. Meyer, G. Algara-Siller, U. Kaiser
From graphene constrictions to single carbon chains
New Journal of Physics 11 (2009) 083019

Top-down mechanism of fullerene formation



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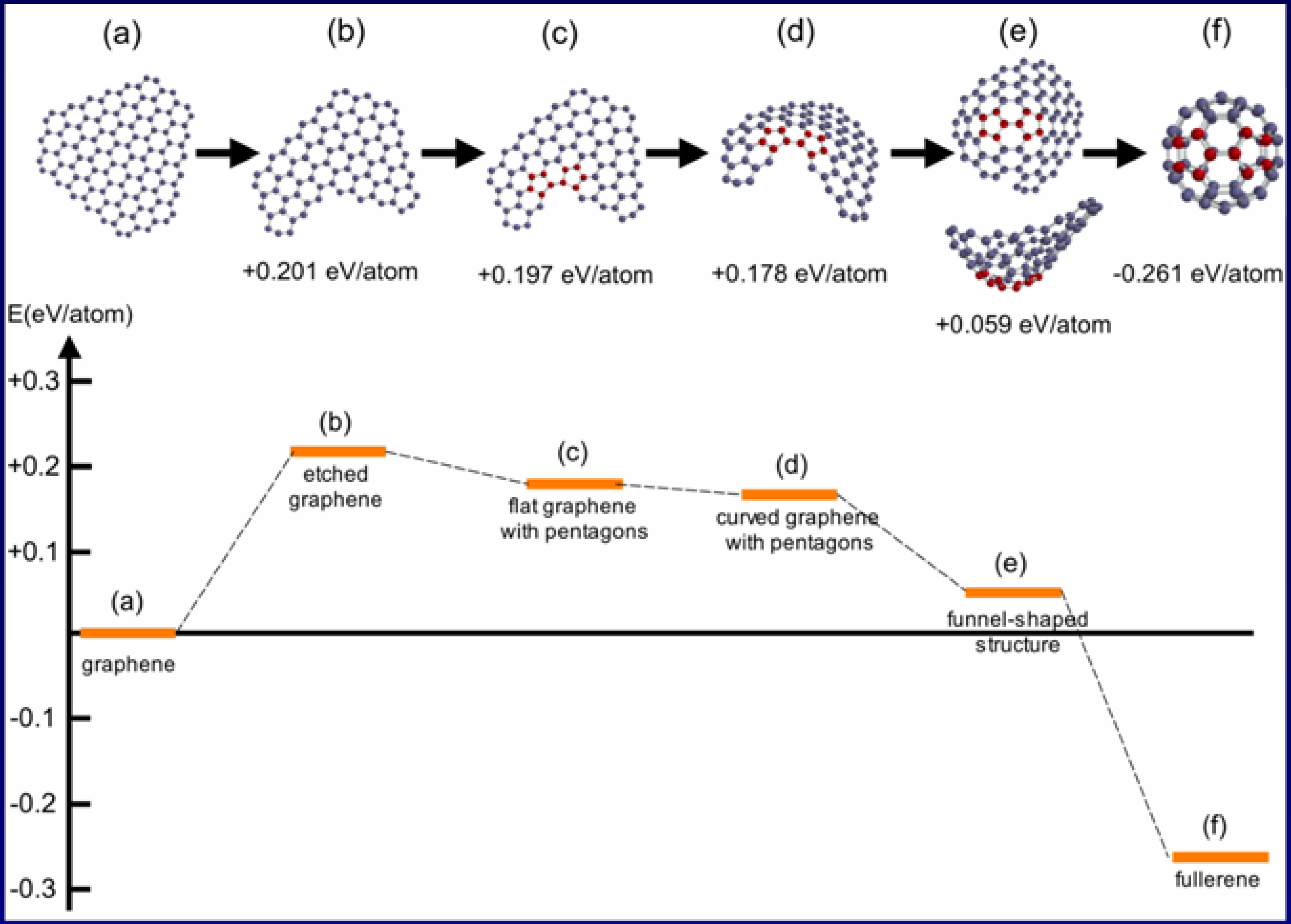


A. Chuvilin, U. Kaiser, E. Bichoutskaia, N.A. Besley, A.N. Khlobystov
Direct Transformation of Graphene to Fullerene
Nature Chemistry, 2 (2010) 450-453

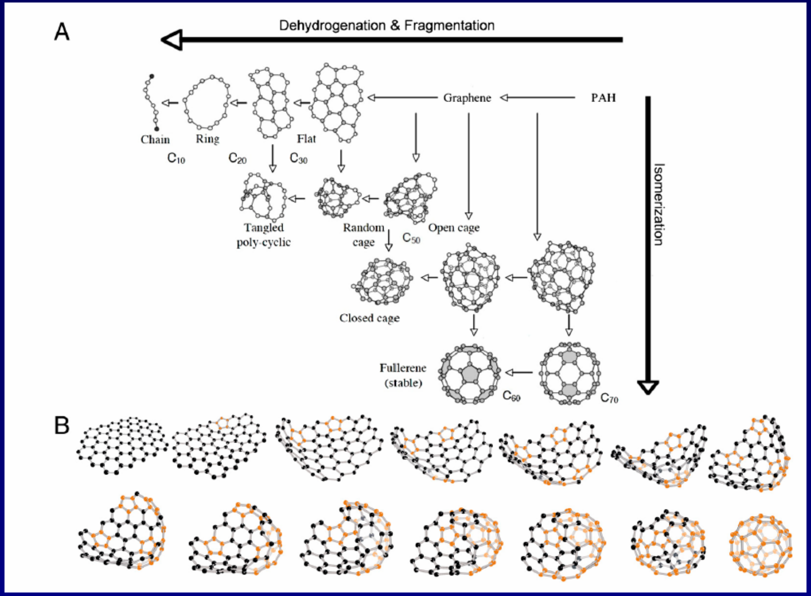
Top-down mechanism of fullerene formation

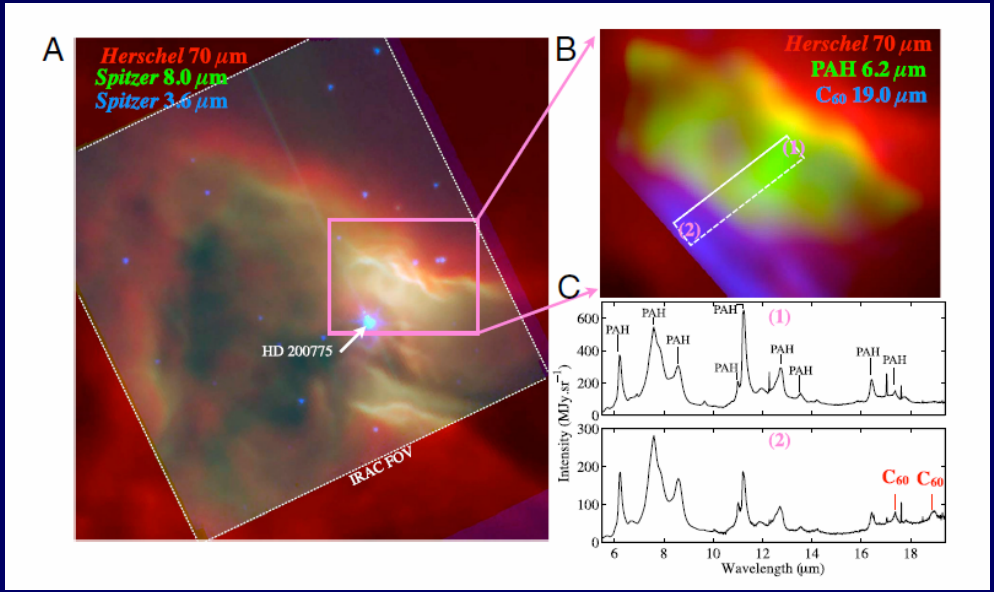
Formation of buckminsterfullerene (C_{60}) in interstellar space

Olivier Berné[1] and A. G. G. M. Tielens

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

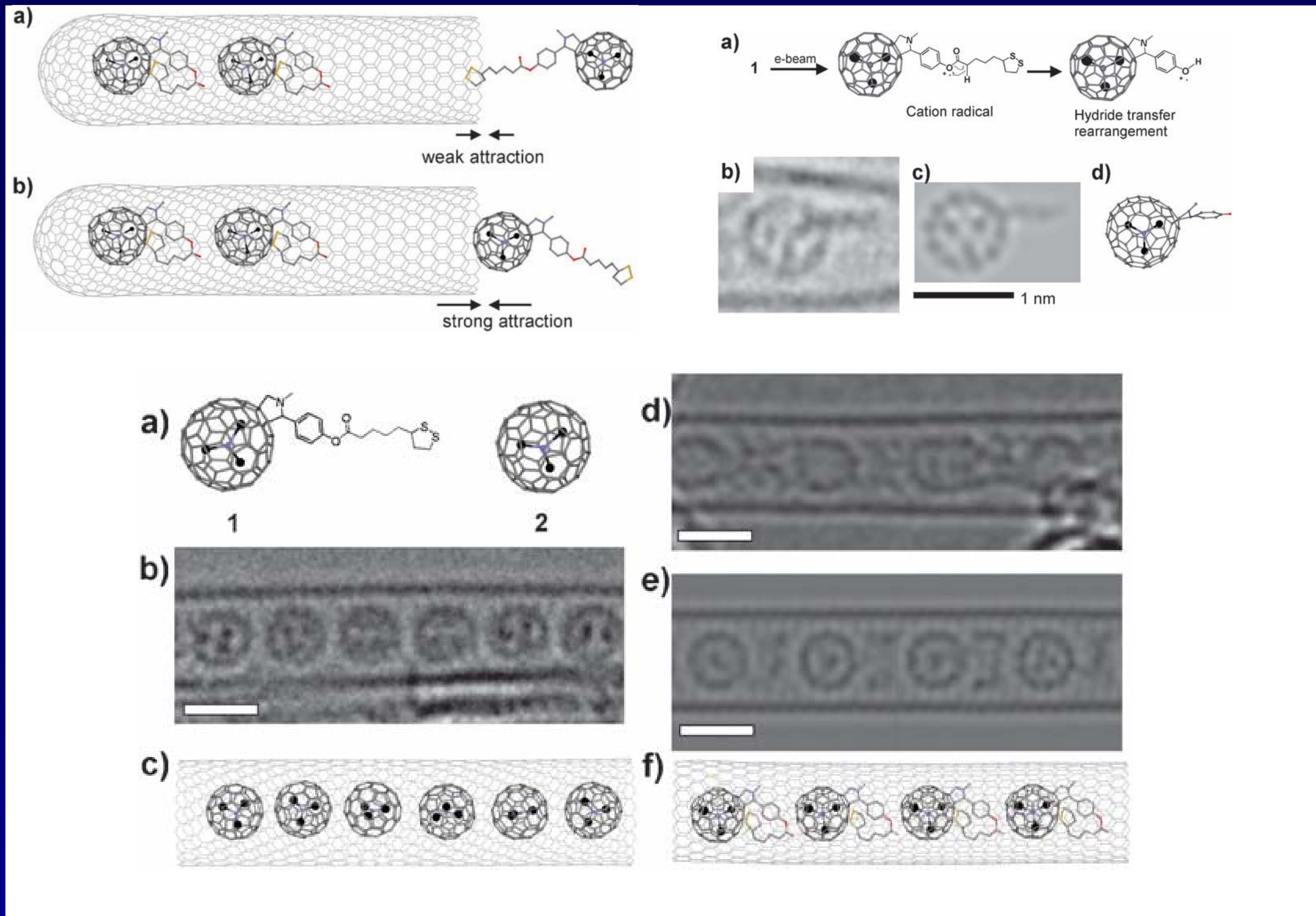
PNAS | January 10, 2012 | vol. 109 | no. 2 | 401–406





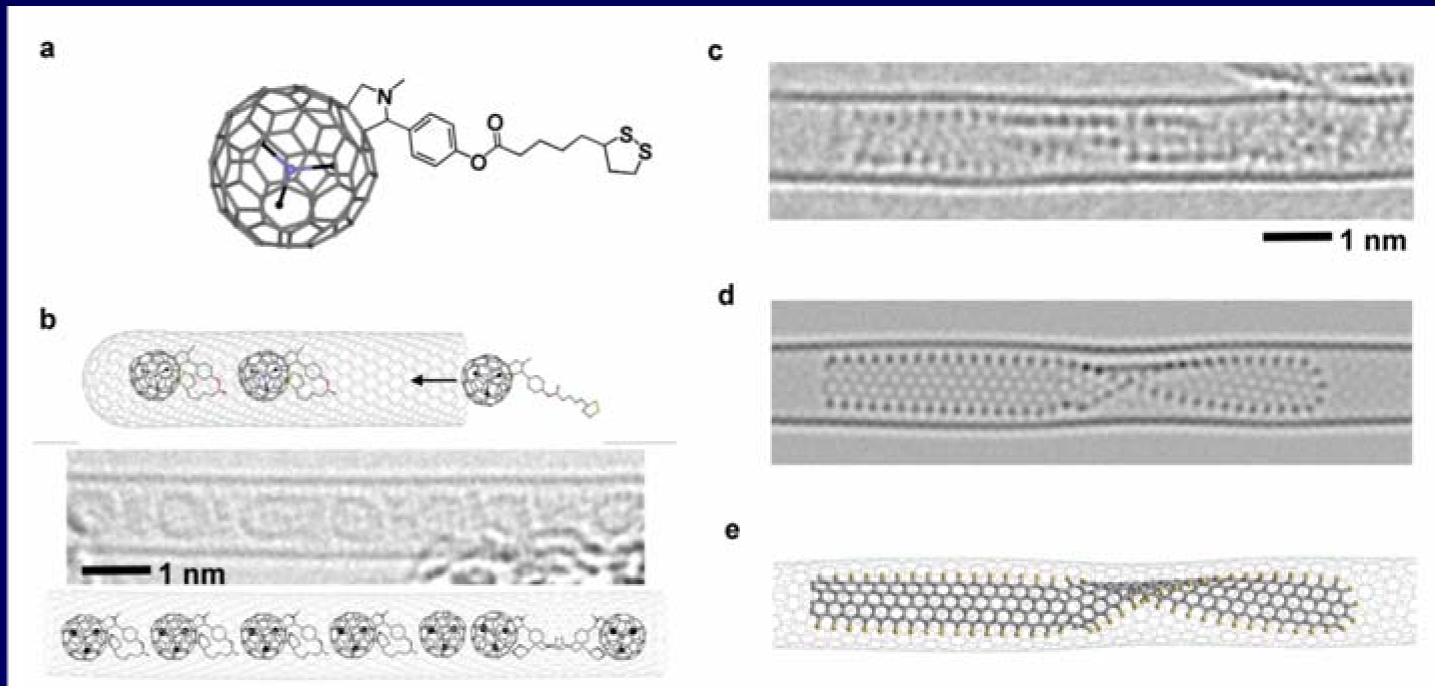
As shown in laboratory experiments (31), graphene sheets larger than about 70 C atoms can be transformed into fullerene, but in space this is driven by UV photons rather than energetic electrons. We surmise that fullerene formation is initiated by single

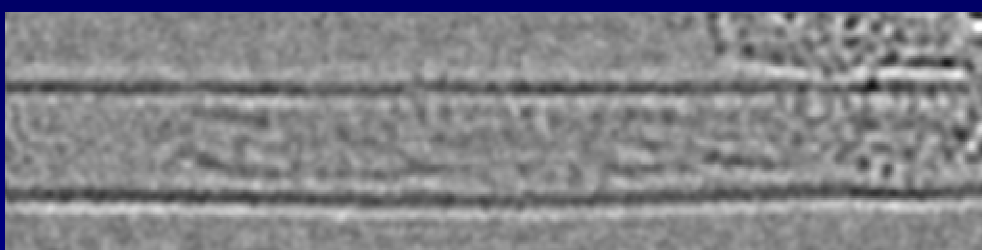
Peapods with functionalized fullerenes

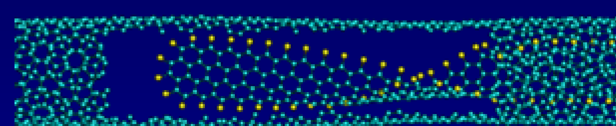


M.C. Gimenez-Lopez, A. Chuvilin, U. Kaiser, A.N. Khlobystov
Functionalised endohedral fullerenes in single-walled carbon nanotubes
Chem. Commun., 2011, 47, 2116–2118

Synthesis of carbon nanoribbons

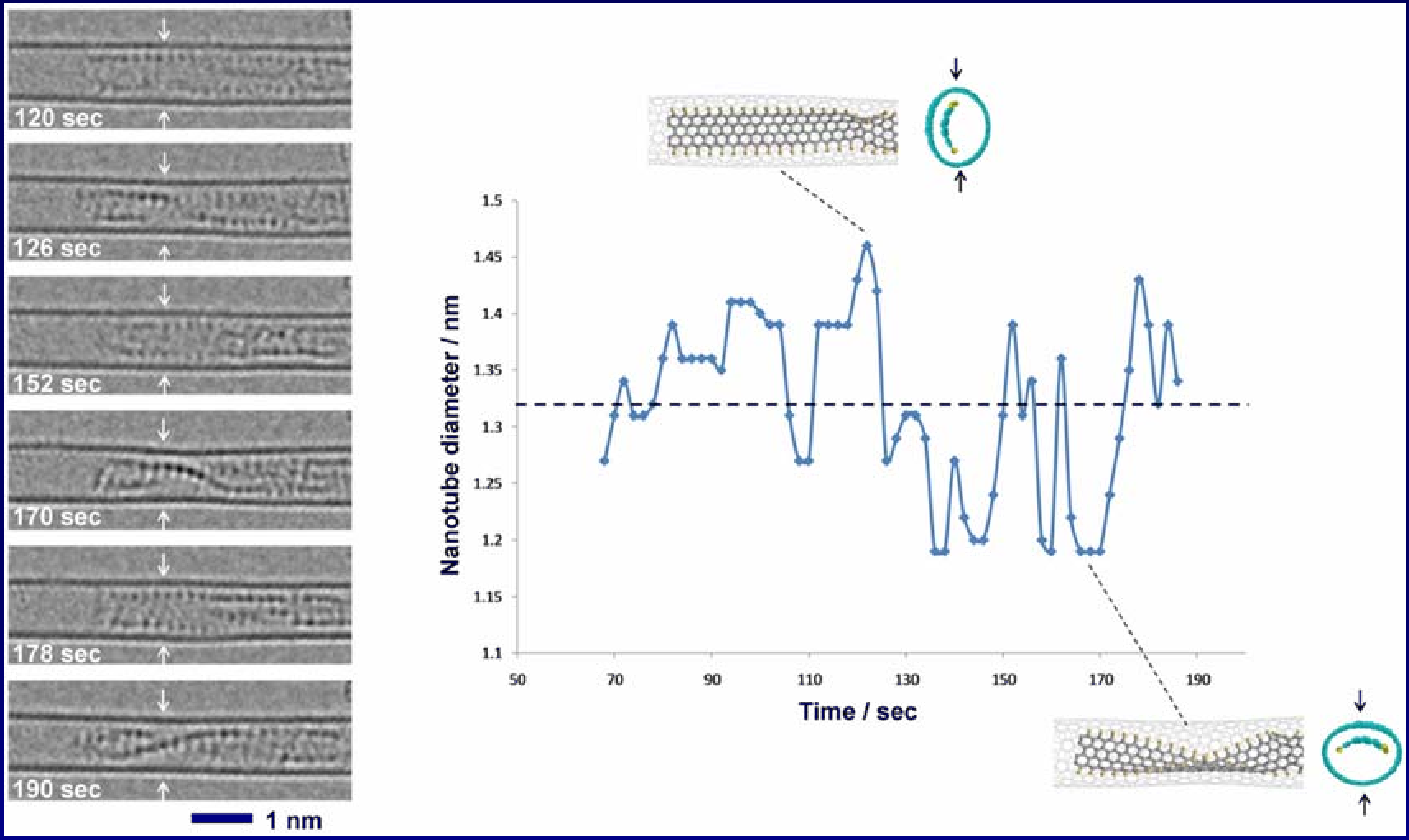






Self-assembly of a sulphur-terminated graphene nanoribbon within a single-walled carbon nanotube
A.Chuvilin, E. Bichoutskaia, M. C. Gimenez-Lopez, T.W. Chamberlain, G. A. Rance,
B. N. Kuganathan, J. Biskupek, U. Kaiser, A. N. Khlobystov
Nature Materials 10 (2011) 687-692

Synthesis of carbon nanoribbons



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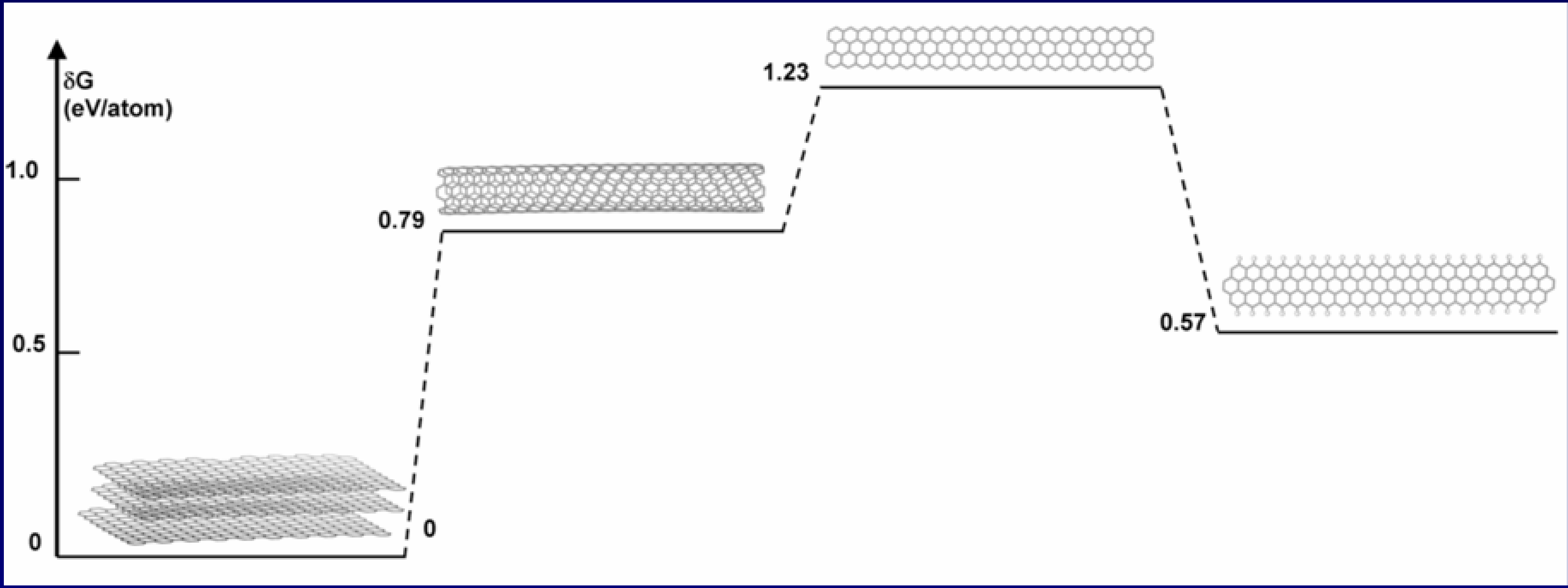
Synthesis of carbon nanoribbons



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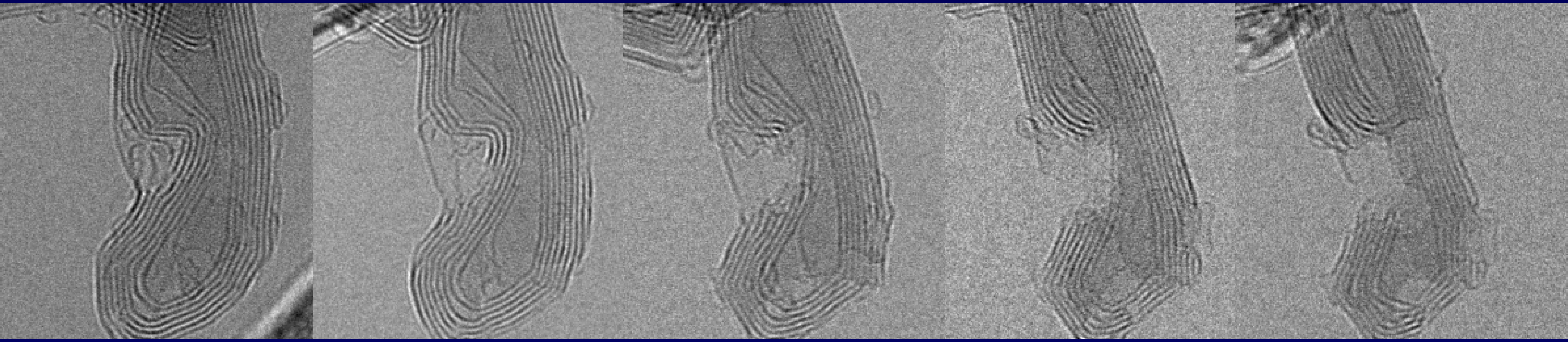
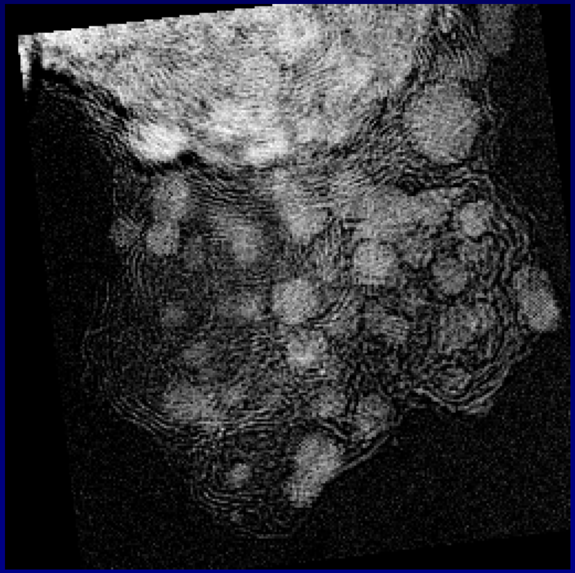
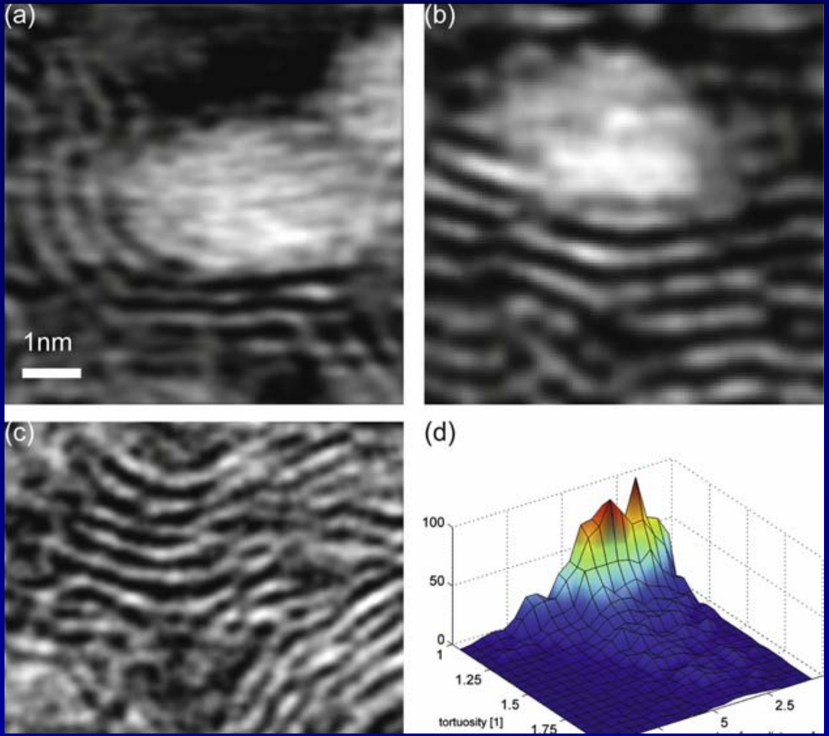
B. N. Kuganathan, J. Biskupek, U. Kaiser, A. N. Khlobystov
Nature Materials 10 (2011) 687-692

Tomography of nanocarbons

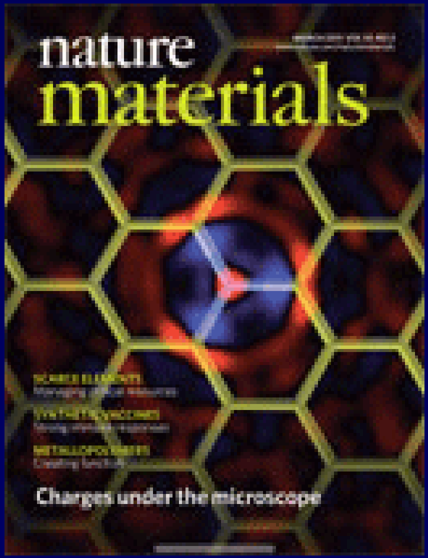


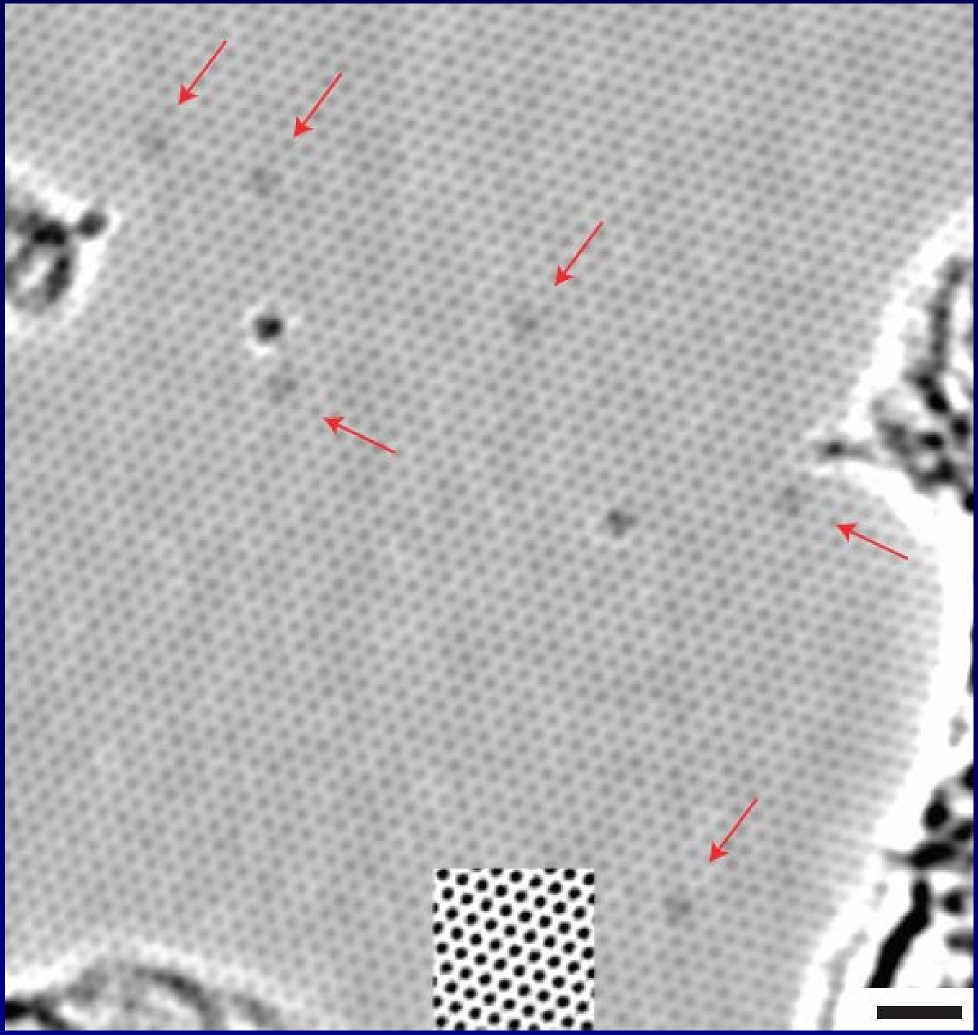




J.Leschner, J.Biskupek, A.Chuvilin, U.Kaiser
Accessing the local three-dimensional structure of carbon materials sensitive to an electron beam
Carbon 48 (2010) 4042-4048

Chemical bonds in TEM





Jannik C. Meyer, Simon Kurasch, Hye Jin Park, Viera Skakalova, Daniela Künzel, Axel Groß, Andrey Chuvilin, Gerardo Algara-Siller, Siegmar 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)

Acknowledgements

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Dr. Siegmar Roth
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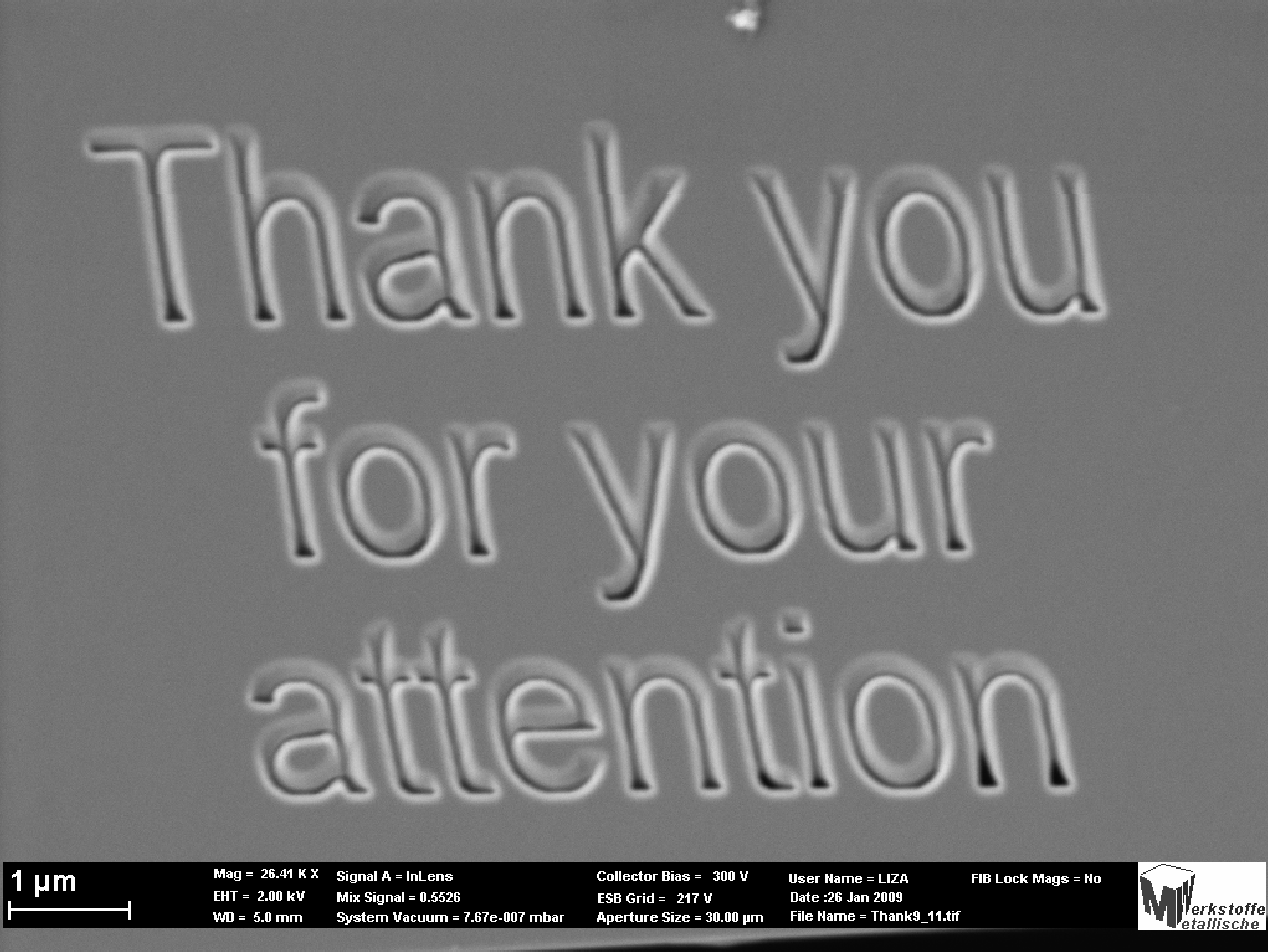
Dr. Elena Bichoutskaia
School of Chemistry, University of Nottingham, UK

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