

Transmission Electron Microscopy

陳福榮

教科書: Transmission Electron Microscopy

David B. Williams

C. Barry Carter

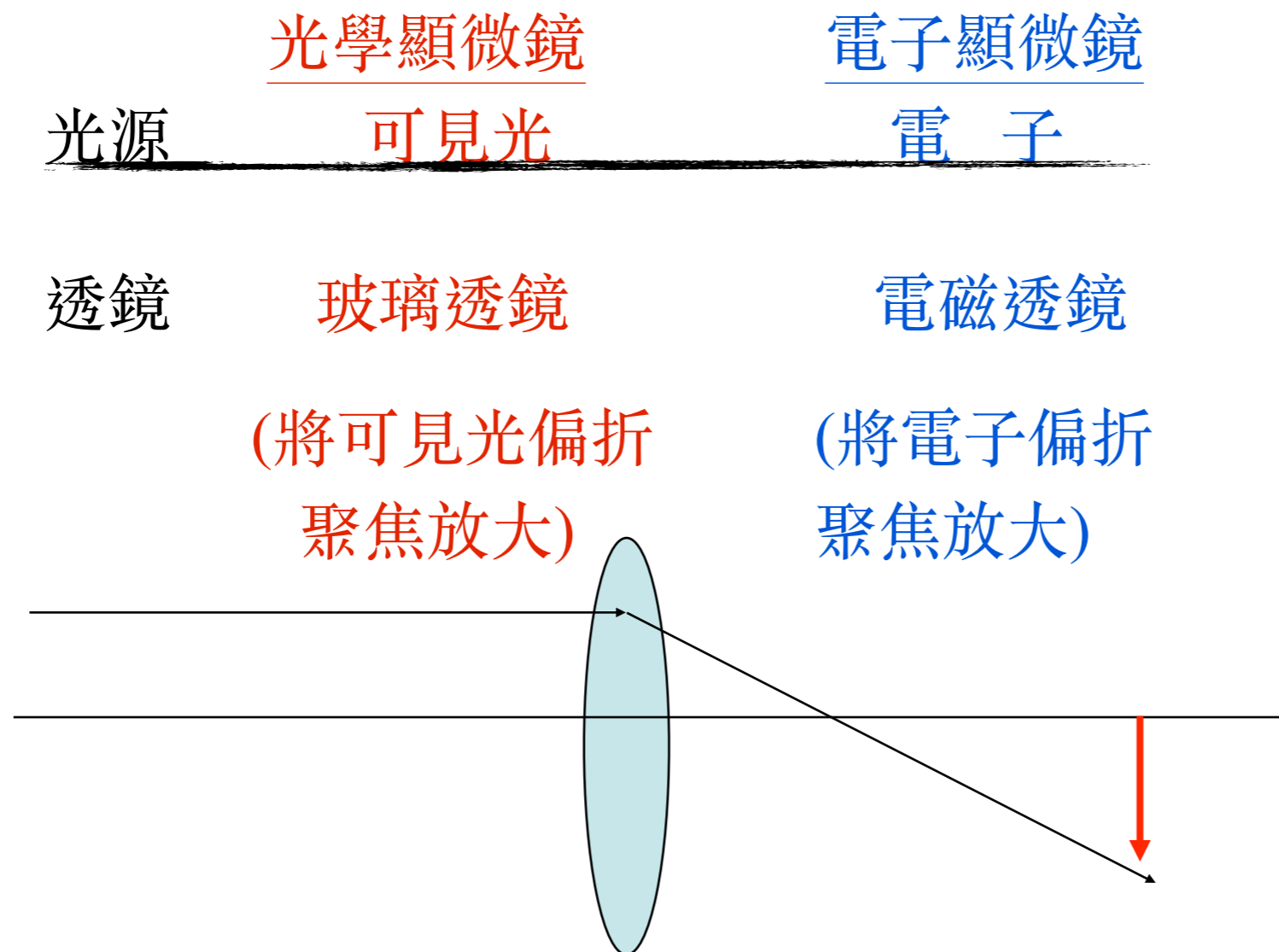
背景：固態物理
材料科學導論

Chapter 1 Overview of TEM

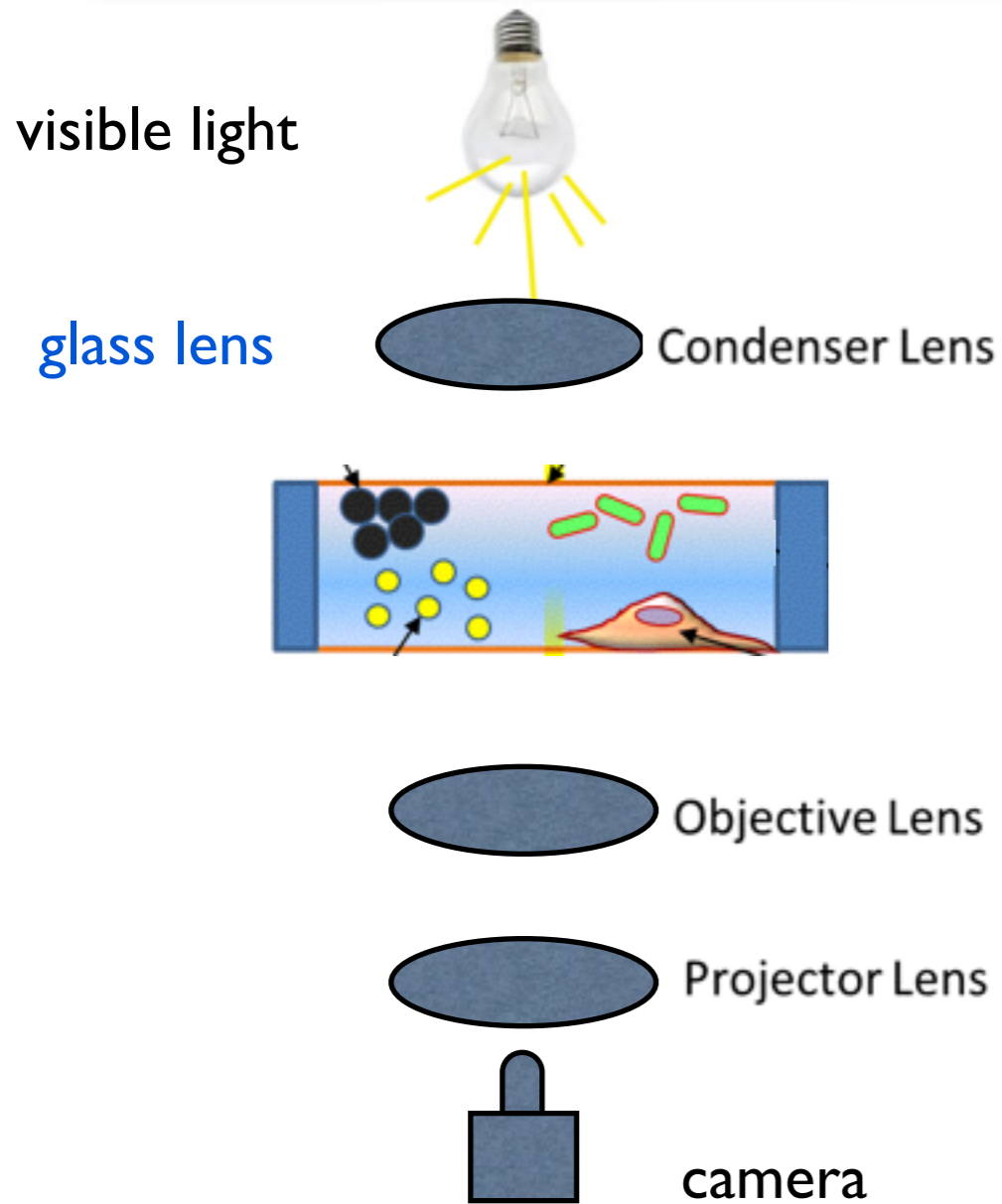
- 1. 電子光學
- 2. 電子與晶體之作用
- 3. 繞射圖形(晶體結構)/菊池圖(結晶方向)
- 4. 成像原理
- 5. 晶體缺陷(差排, 疊差, 晶界, 介面, 析出物之分析及解釋)
- 6. 原子分辨電鏡(HRTEM)
- 7. 掃描透射電鏡(STEM)
- 8. X光能譜及成份分析
- 9. 電子能量損失譜 (EELS)
- 10. 環境電鏡(Environmental TEM)
- 11. 相位電鏡(phase TEM)

1.1 為何使用“電子”顯微鏡

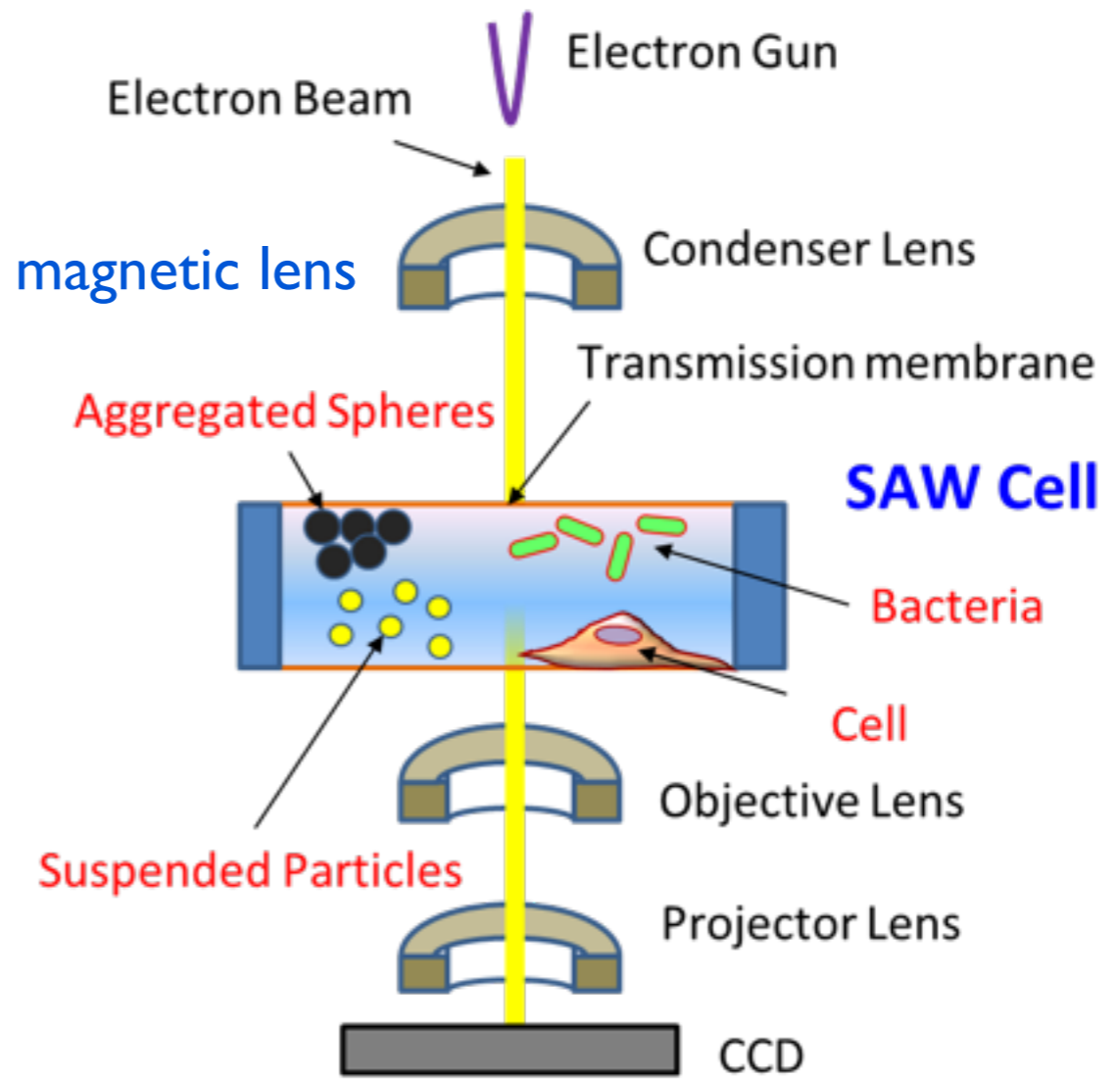
“顯微鏡”--放大人類肉眼無法觀察(分辨)出的“物體”



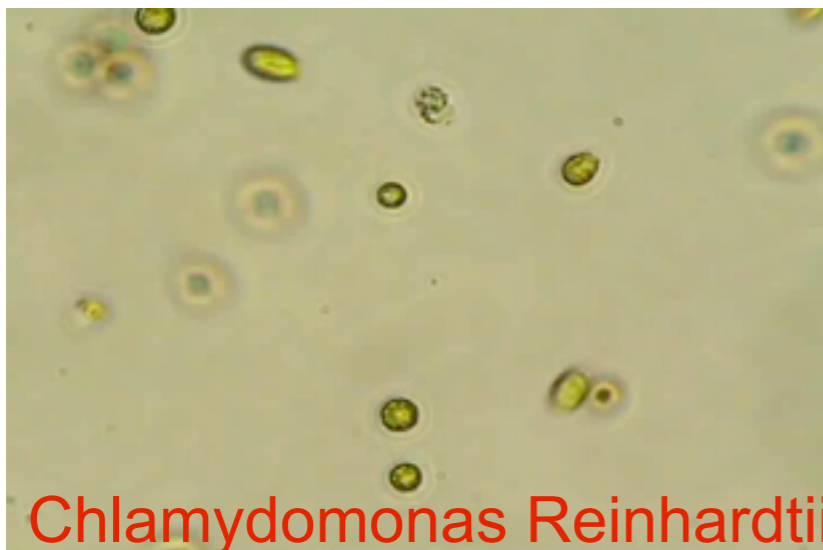
Optical Microscope



Electron Microscope

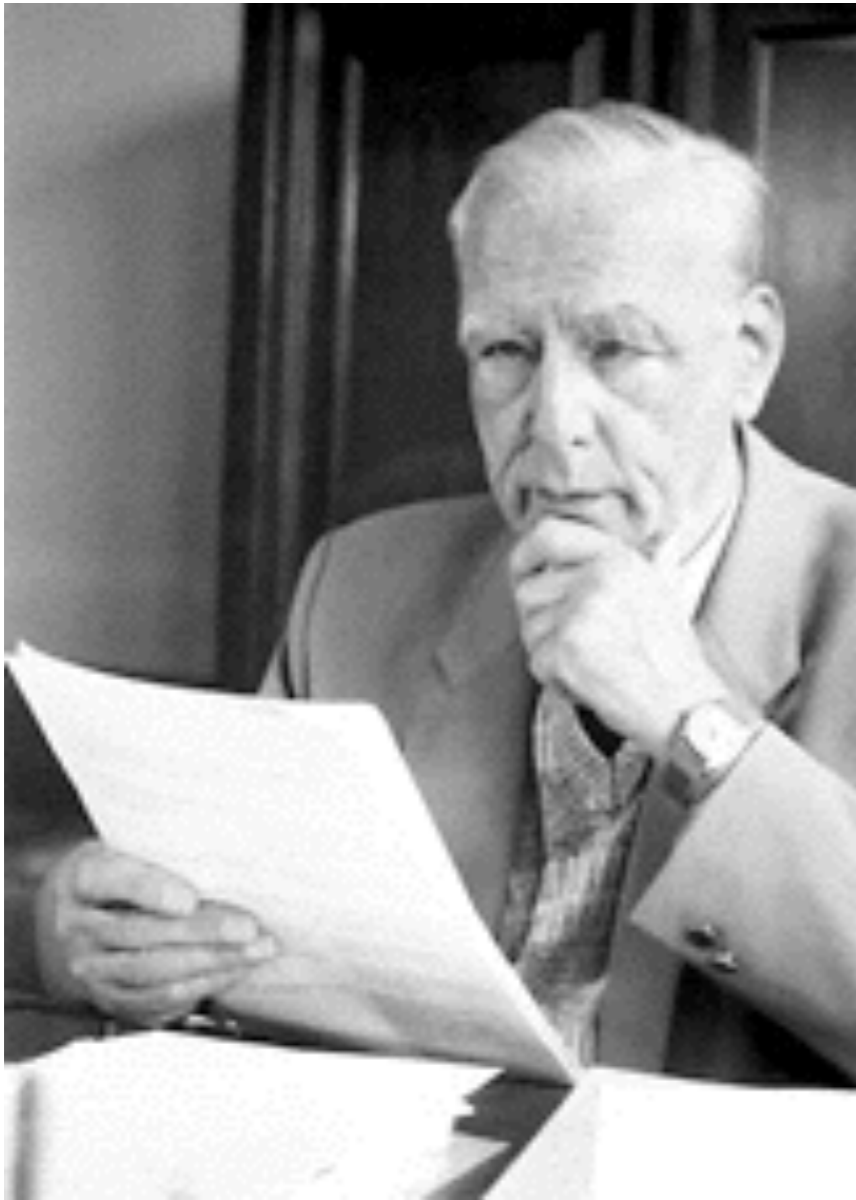


衣藻

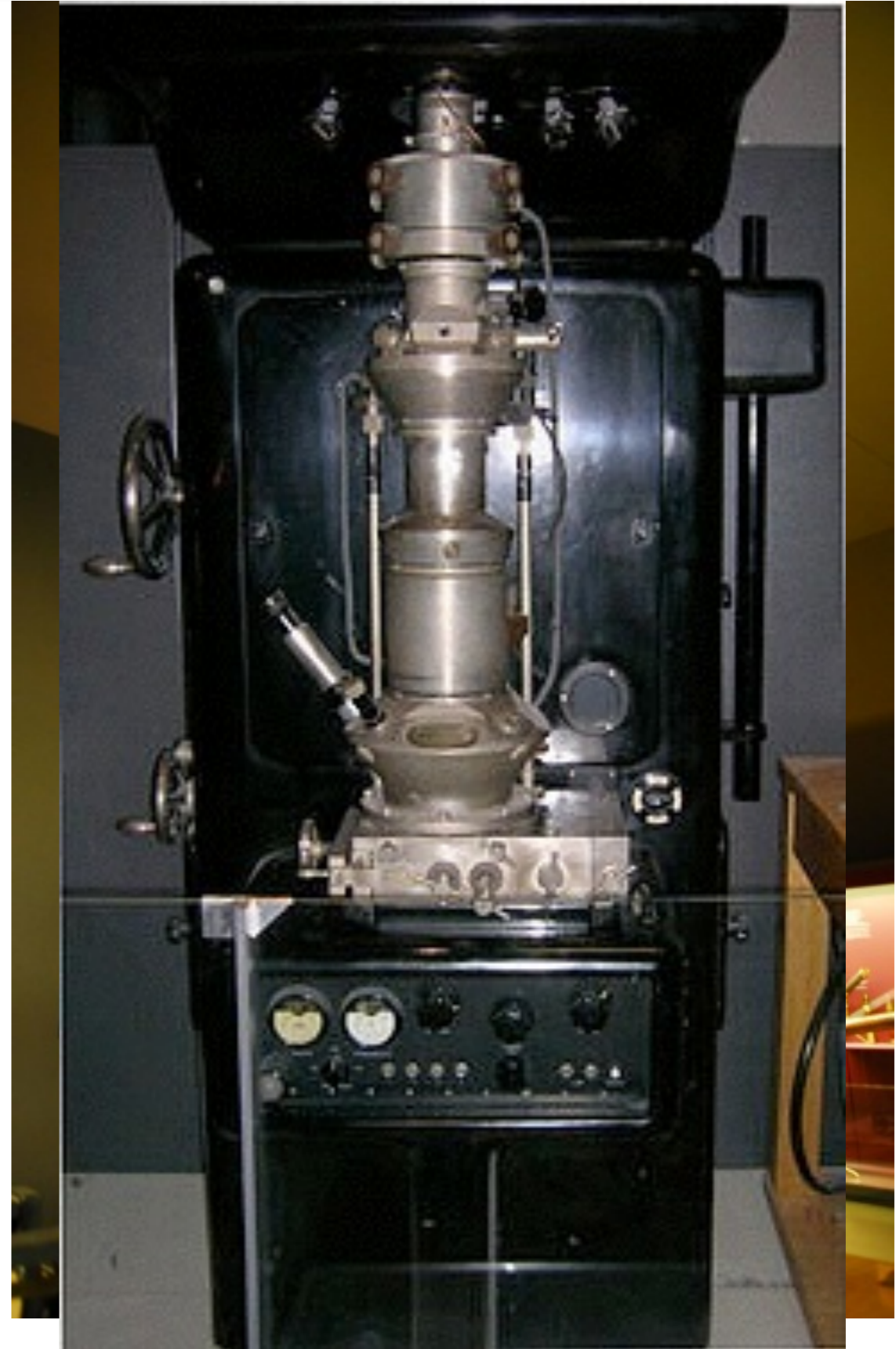


Liquid TEM image

Ernst Ruska



Nobel Prize in Physics 1986



更好的電子顯微鏡

(Better Electron Microscope)

..... 要是我們能看到**原子**在那裡，那麼分析複雜的化學物質就變得很容易

最大的困難是電子顯微鏡的能力必須要加強100倍



-Richard F. Feynman 費曼

-12.29.1959 American Physics Society, CIT



A. Resolution

(分辨最近兩點之能力)

A 因為光學顯微鏡的分辨率達到了極限。

- 幾何光學分辨率受限於光波波長($\lambda \sim 6000\text{\AA}$)

古典Rayleigh criterion 的分辨率為

$$\delta = \frac{0.61\lambda}{\mu \sin\beta} \quad (1.1)$$

δ : Rayleigh 分辨率

λ : 波長

半導體將透鏡放在油下

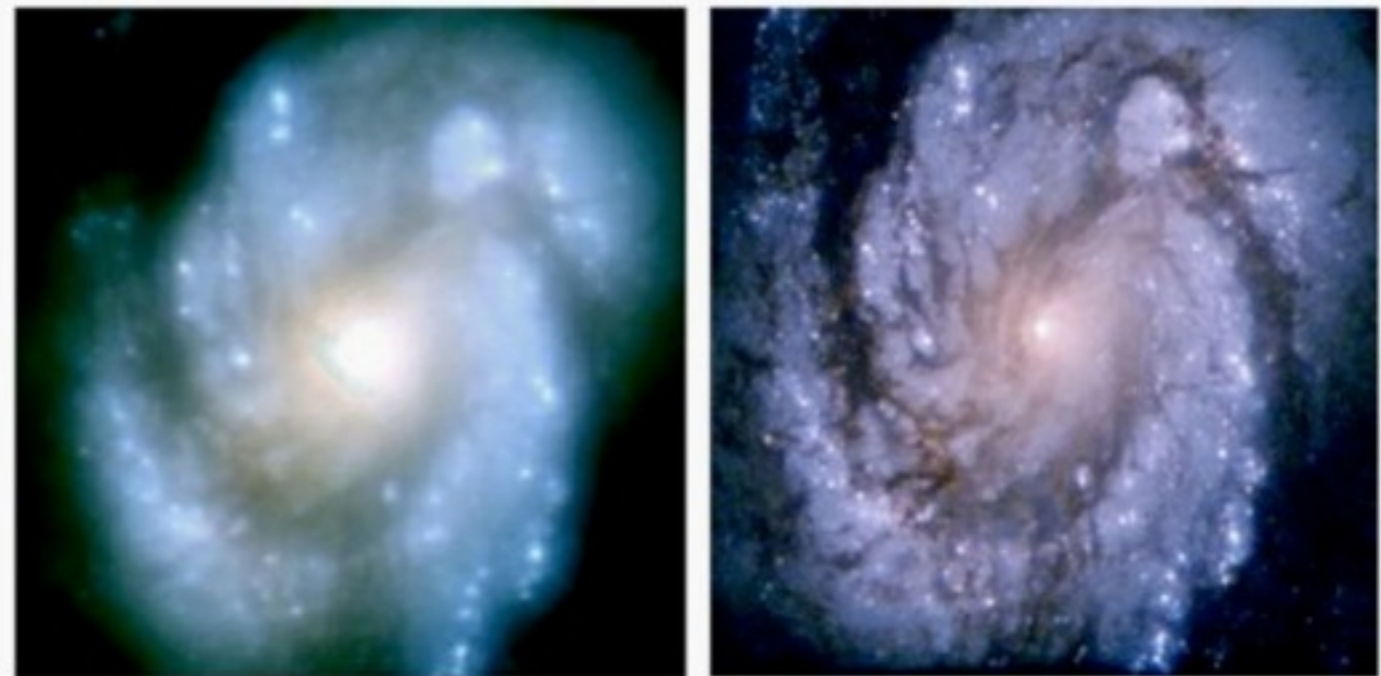
μ : 介質折射率 (refractive index)

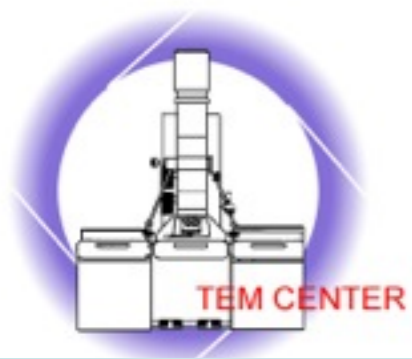
β : 透鏡之半角 和透鏡大小有關

$\mu \sin\beta$: Numerical Aperture ~ 1

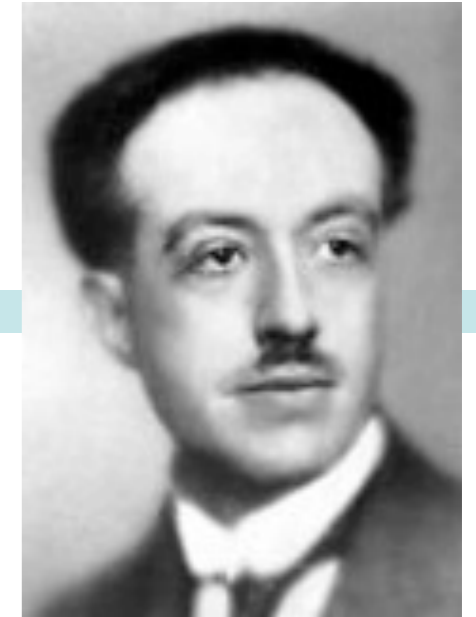
300nm

- 光學顯微鏡的分辨率約是波長之一半 $\sim 300\text{\AA}$ (1000原子)
- 人類眼睛分辨率約 $0.1 \sim 0.2\text{mm}$ (與有否近視有關)





Particle/ Wave Duality



Louis de Broglie
Nobel laureate in 1929

- 由de Broglie's物質波理論，電子同時具有粒子和波的雙重特性。

$$\lambda \sim \frac{1.22}{E^{1/2}}$$

E是電子的能量 = $1/2 m_0 v^2$

電子在電子顯微鏡內部，其“能量”最主要是由“加速電壓”

<u>E (kev)</u>	<u>$\lambda(\text{\AA})$</u>
100	0.037
200	0.025
300	0.0196
400	0.0169

**相對論修正波長必須在100KV以上引進，因這時電子的速度為~光速的一半。

原子之距離大約2~3 Å，因此使用電子當光源，理論上我們可以得到

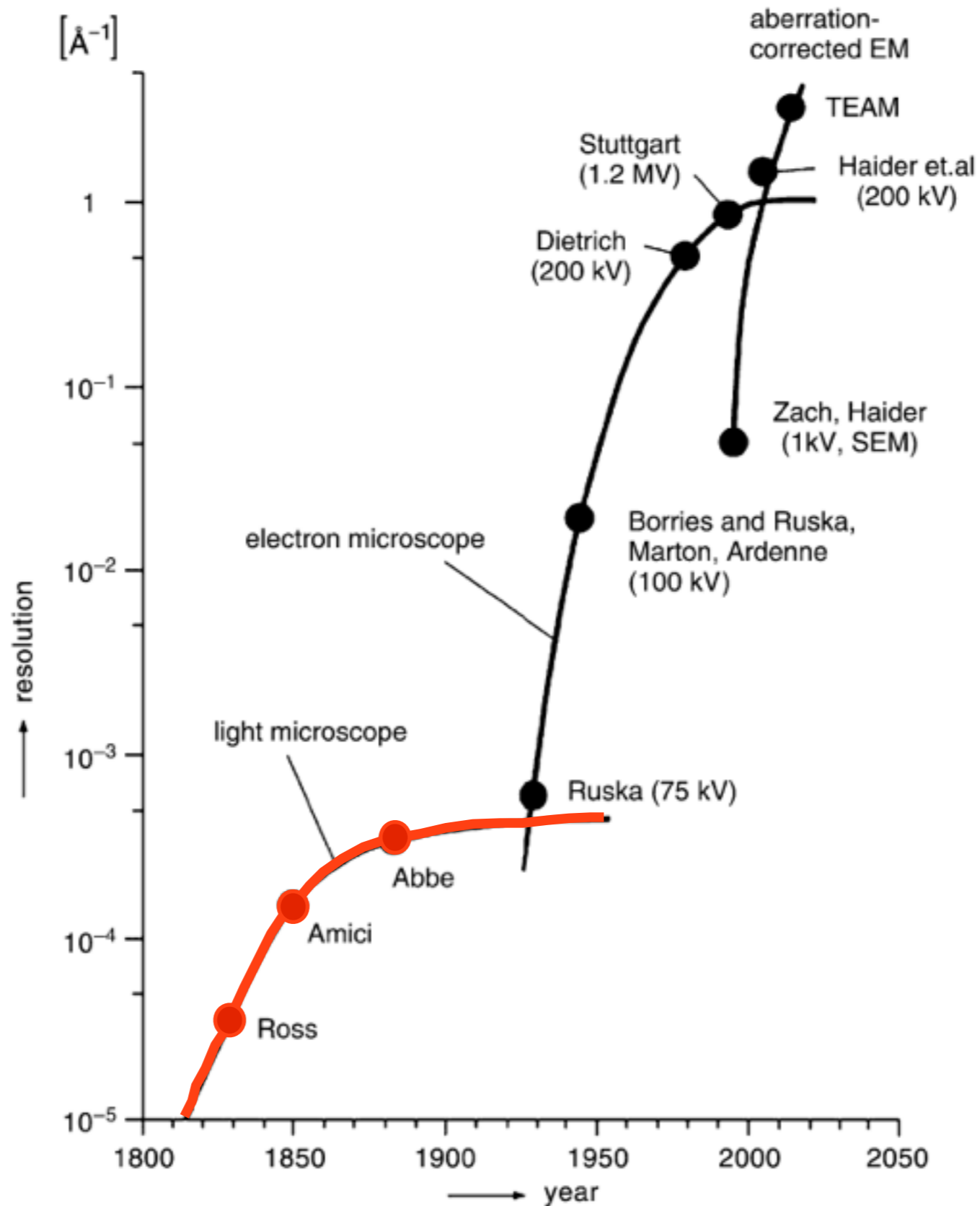
原子的影像。（這是對的，但是分辨率不是由(1.1)來預測，而必須由傅利葉光學來解釋(Fourier Optics)--也就是說

$$\delta \sim \frac{1}{E^{1/2}}$$

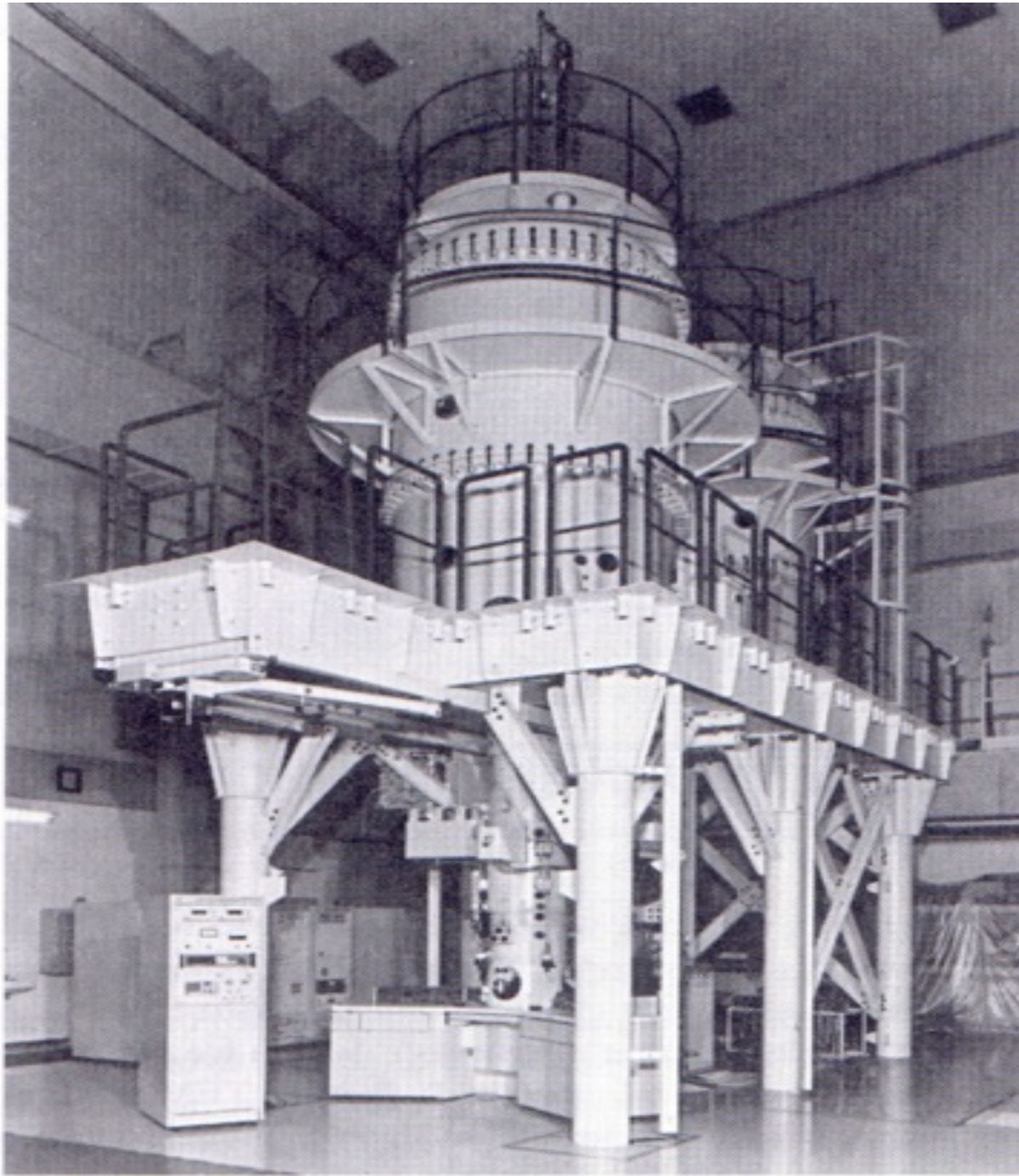
並不成立。

還受限透鏡像差

Evolution of resolution in EM



High and Median Voltage TEM



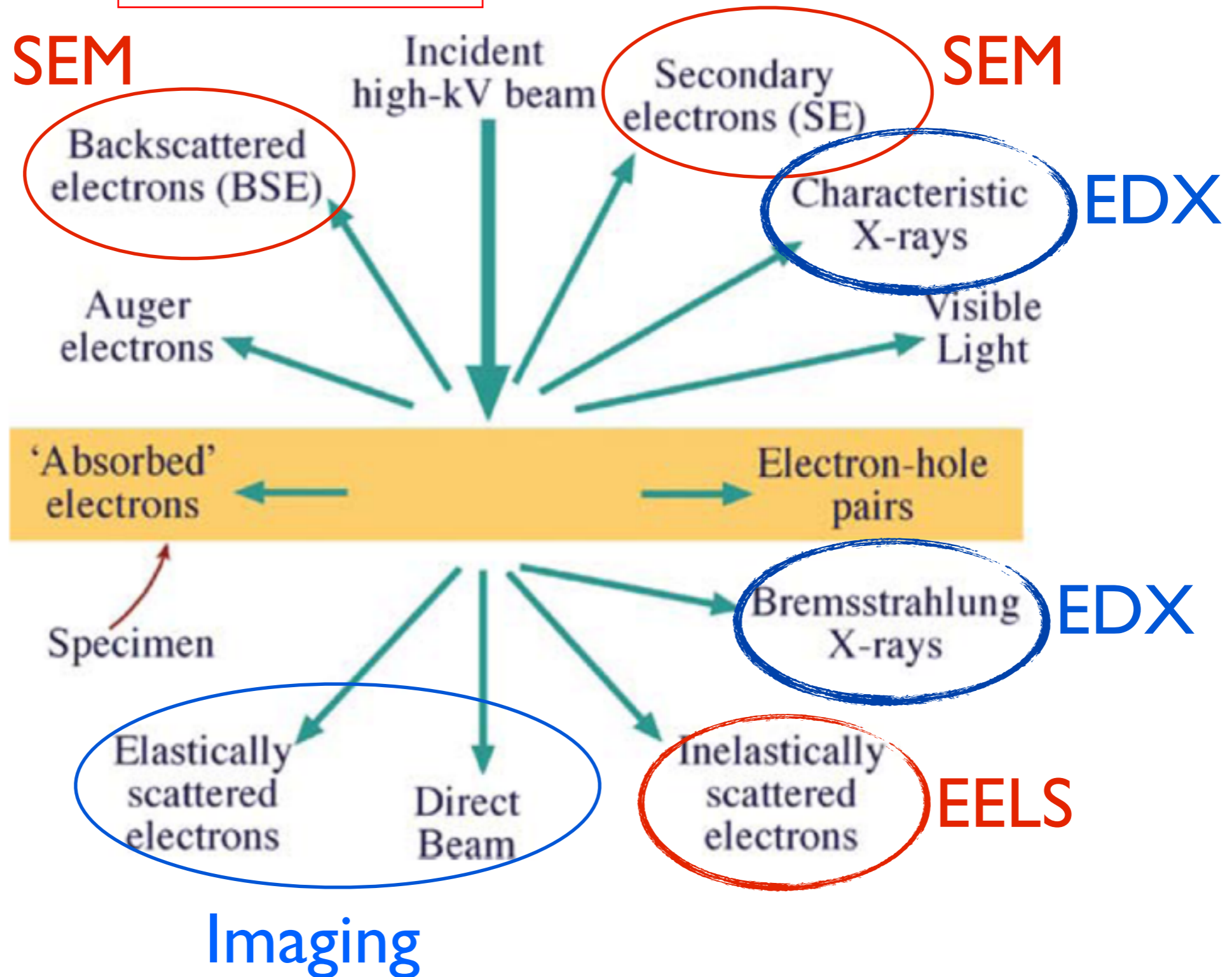
1MeV



200keV

B. 微區成份，(X-Ray)，(EELS)

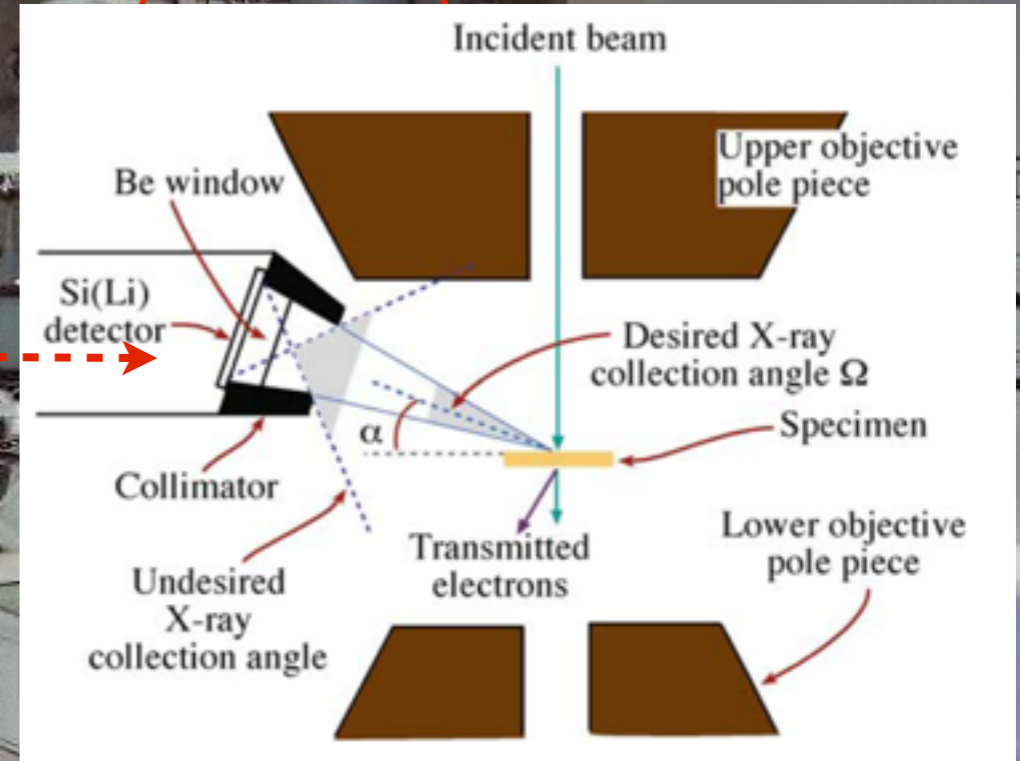
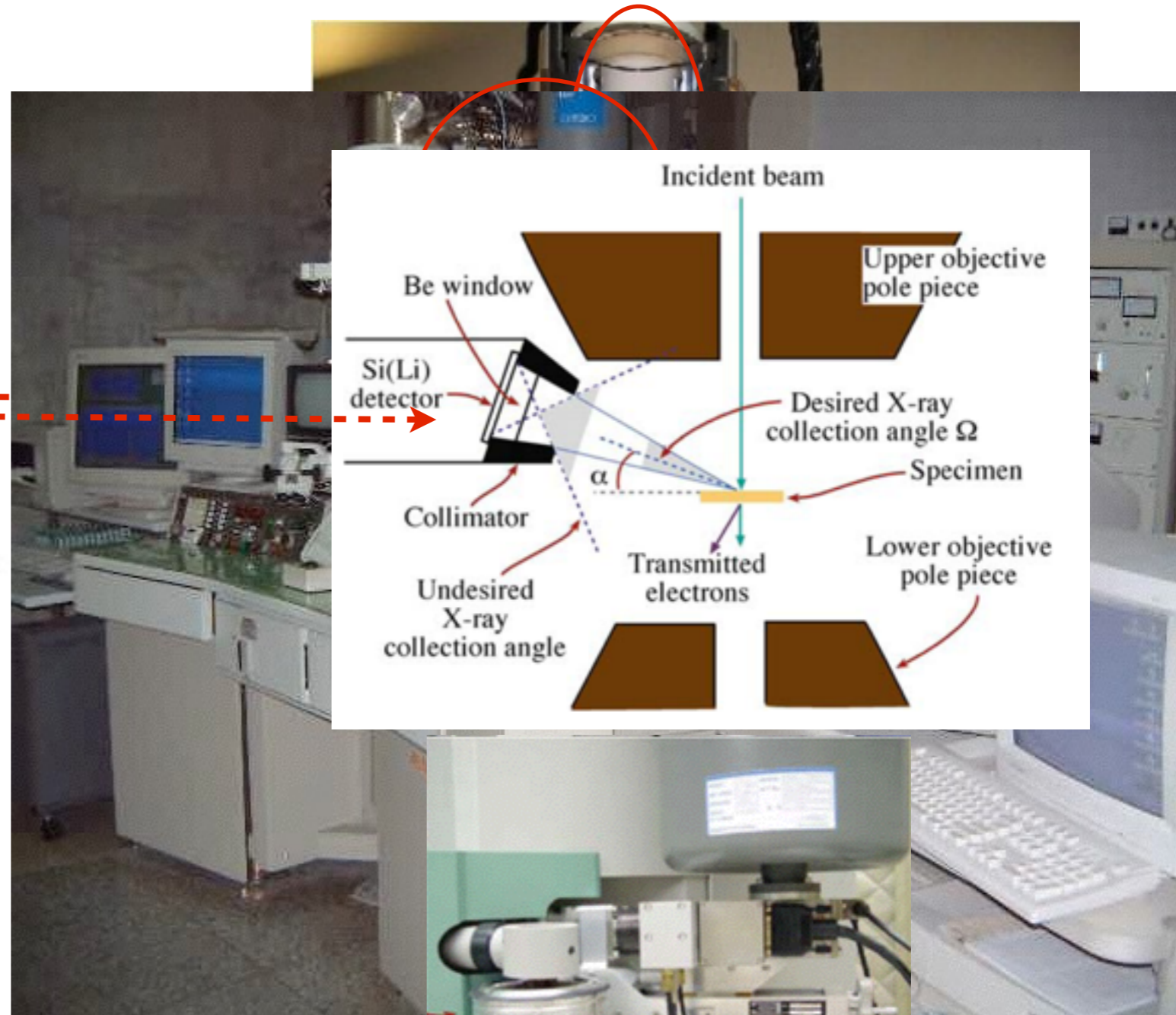
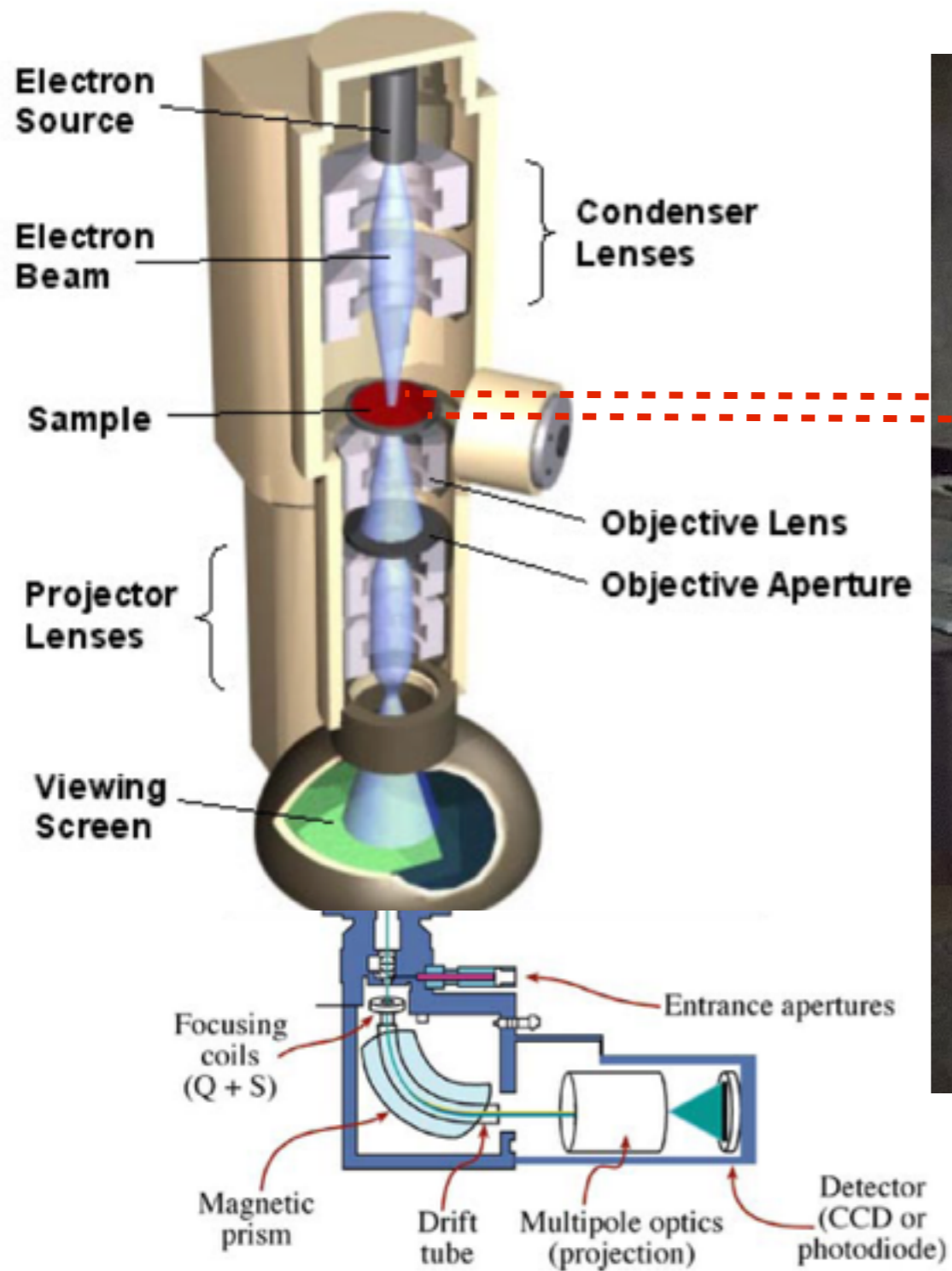
xray作用較弱



電子顯微鏡鉤構造圖

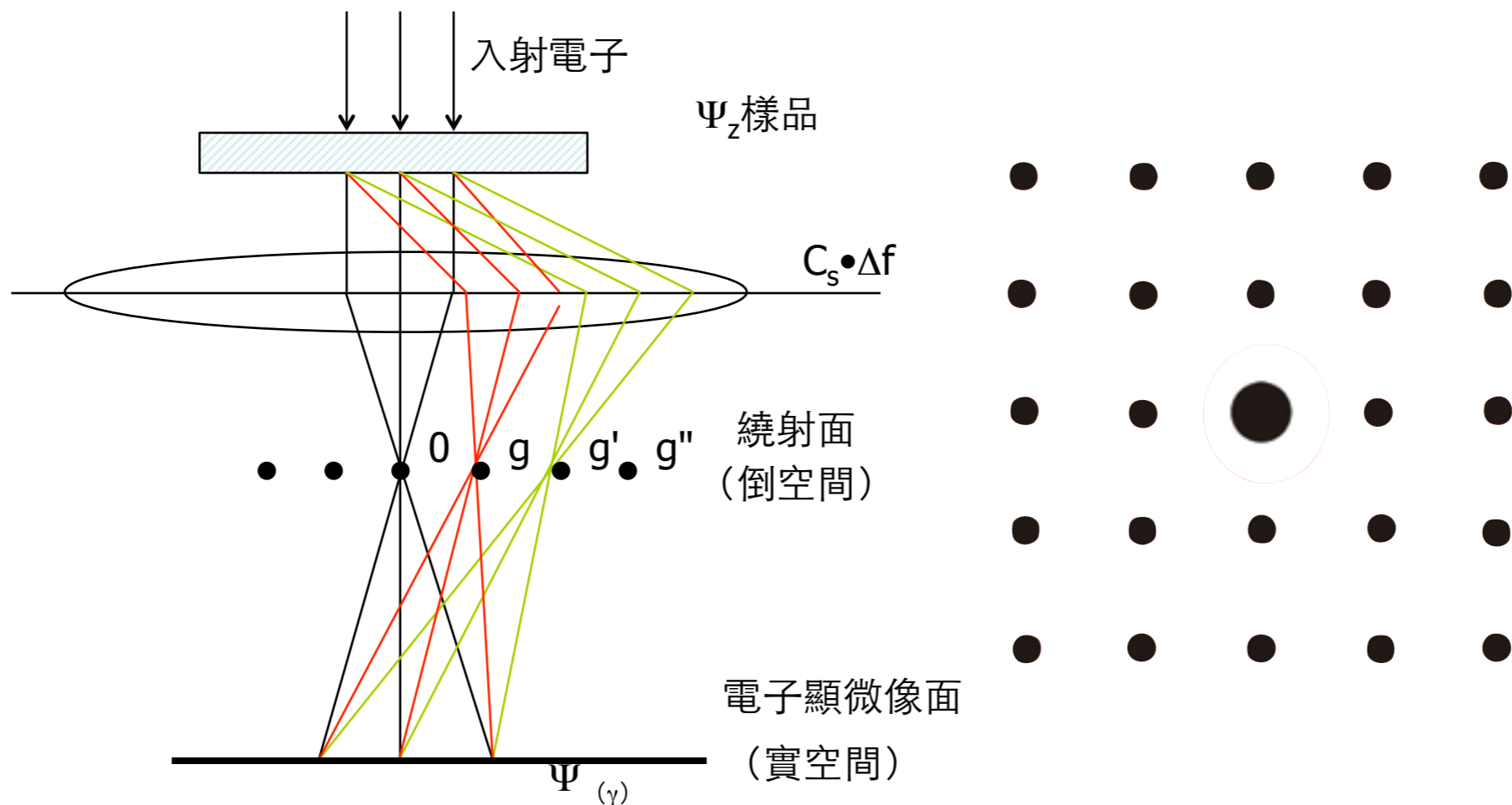


電子顯微鏡夠構造圖

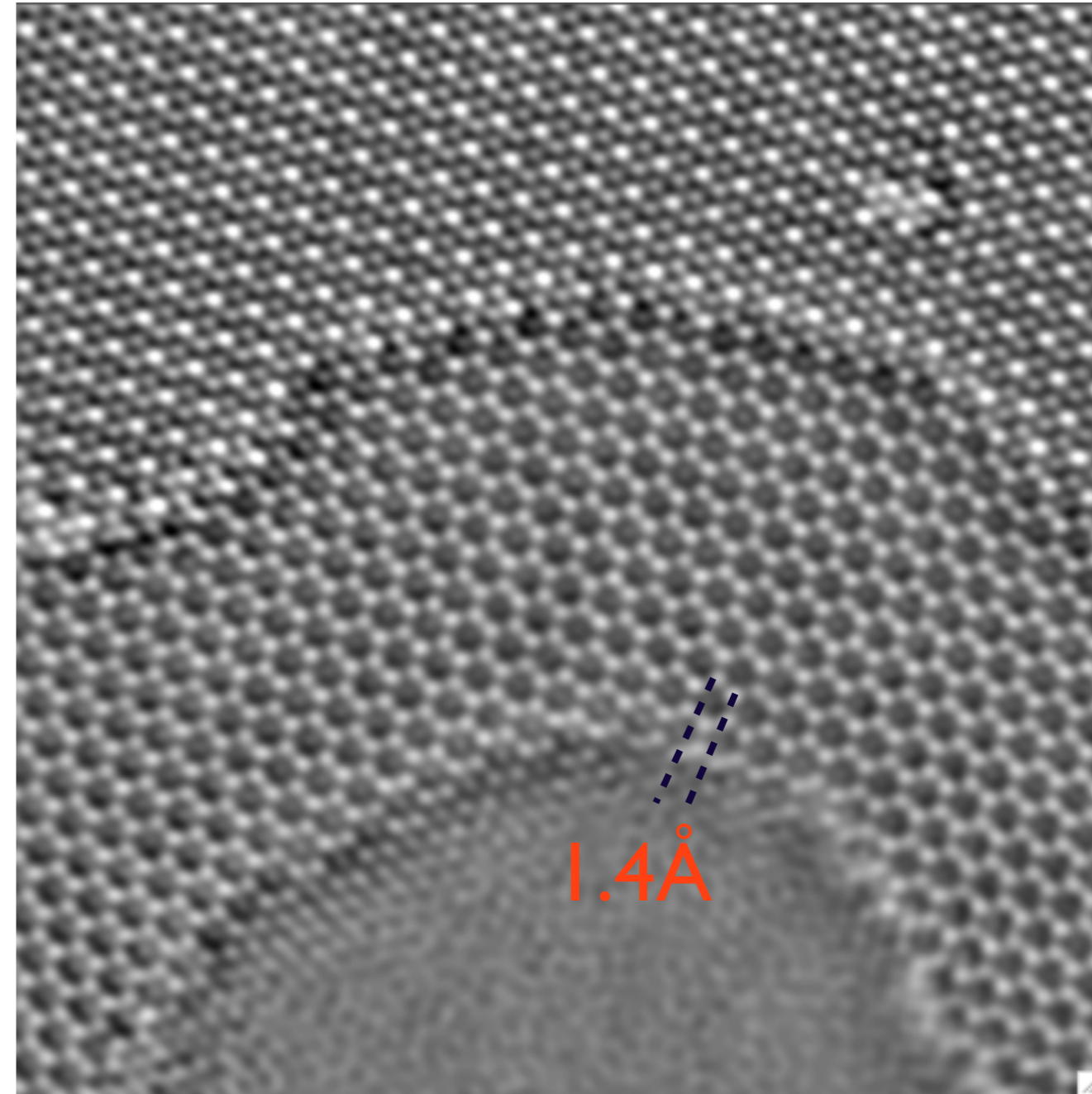
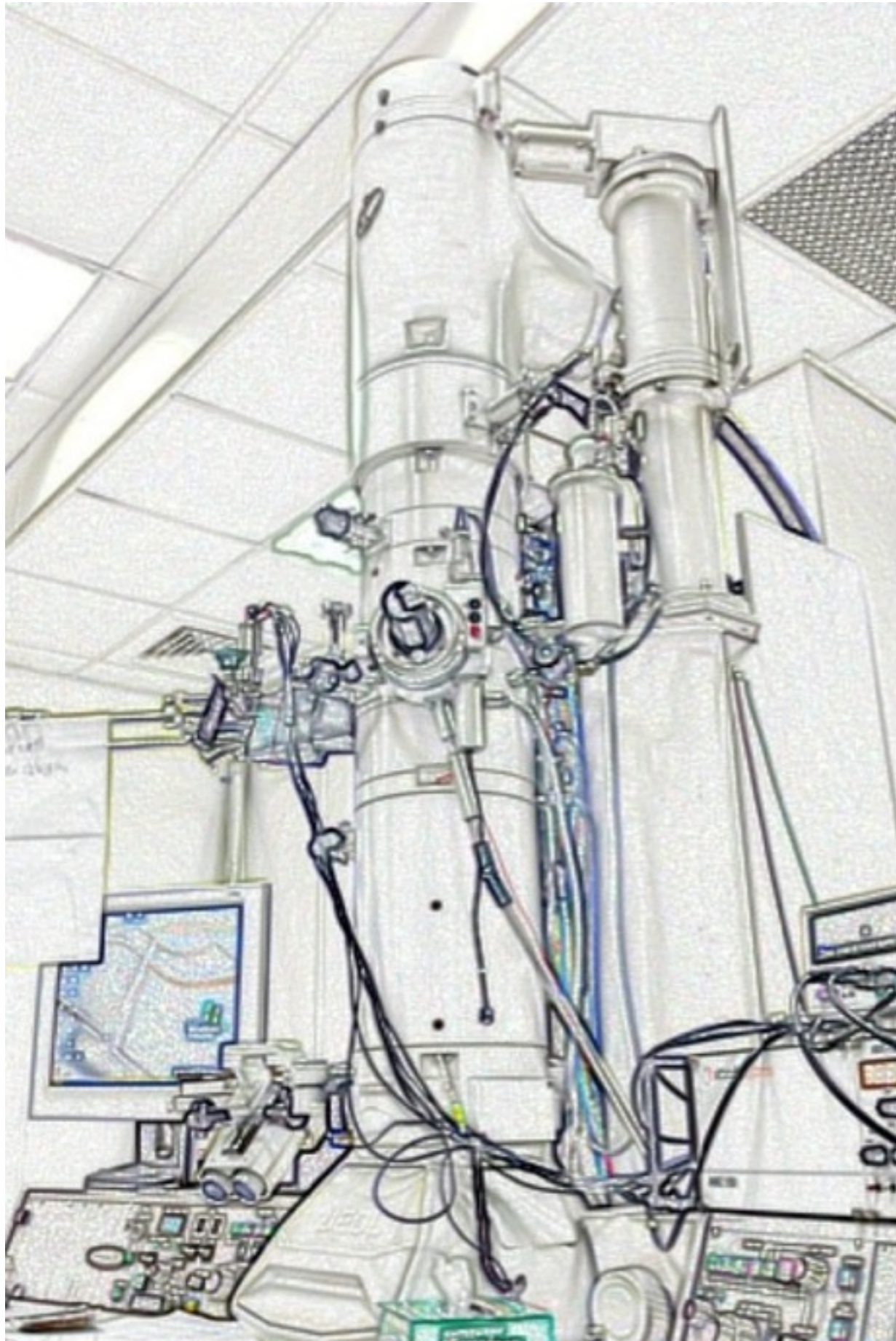


C. 繞射 (Diffraction)

- 高能電子通過週期性原子排列的晶體會產生“繞射”圖形(倒晶格 --與X-Ray光同)，繞射圖形反應出晶體的週期性和對稱性，點陣 (point group, space group)
- 電子顯微鏡一個非常有力的功能是能夠在影像和繞射圖形模式容易地相互變換。(實空間 \leftrightarrow 繞射(倒空間))

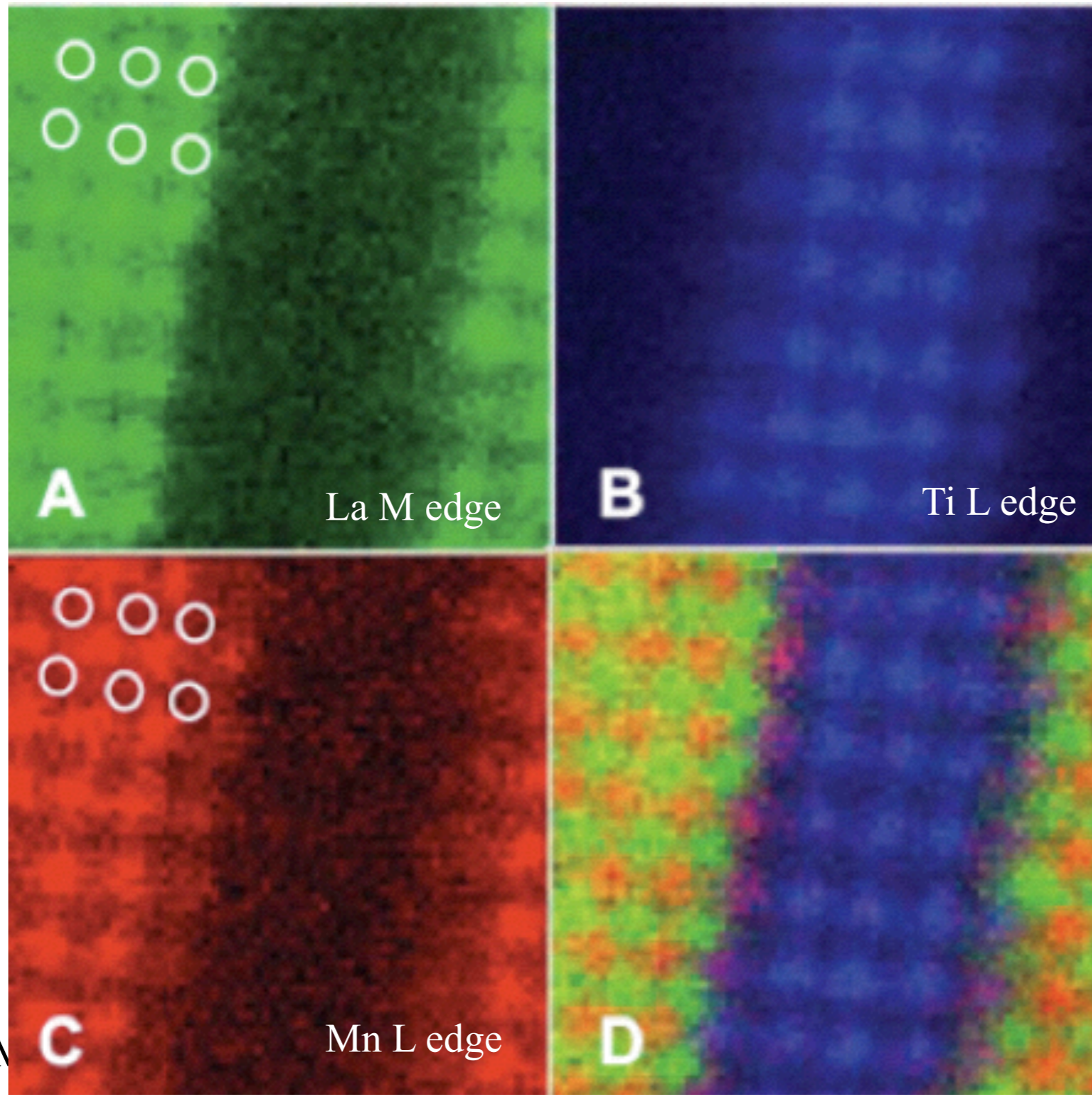


Imaging, Spectroscopy and Diffraction



Atomic Resolution

Imaging, Spectroscopy and Diffraction

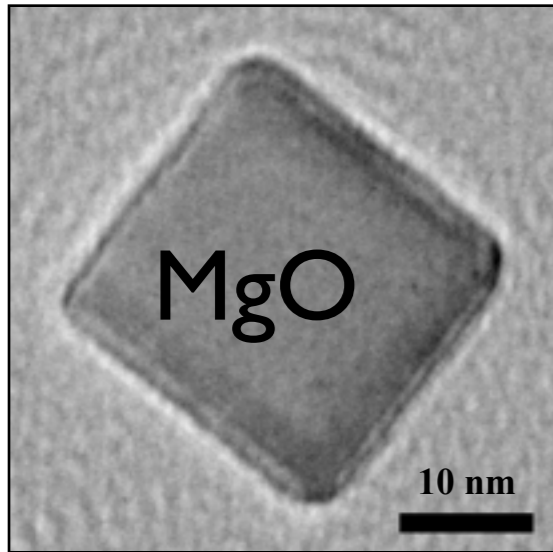


Atomic
- D. A. M

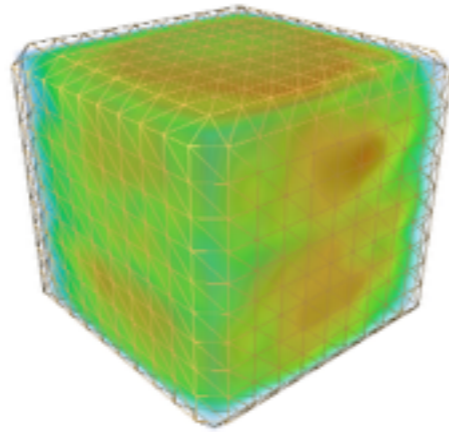
Atomic resolution compositional and bonding maps

Imaging, Spectroscopy and Diffraction

Atomic-resolution phase recovery with dynamic support

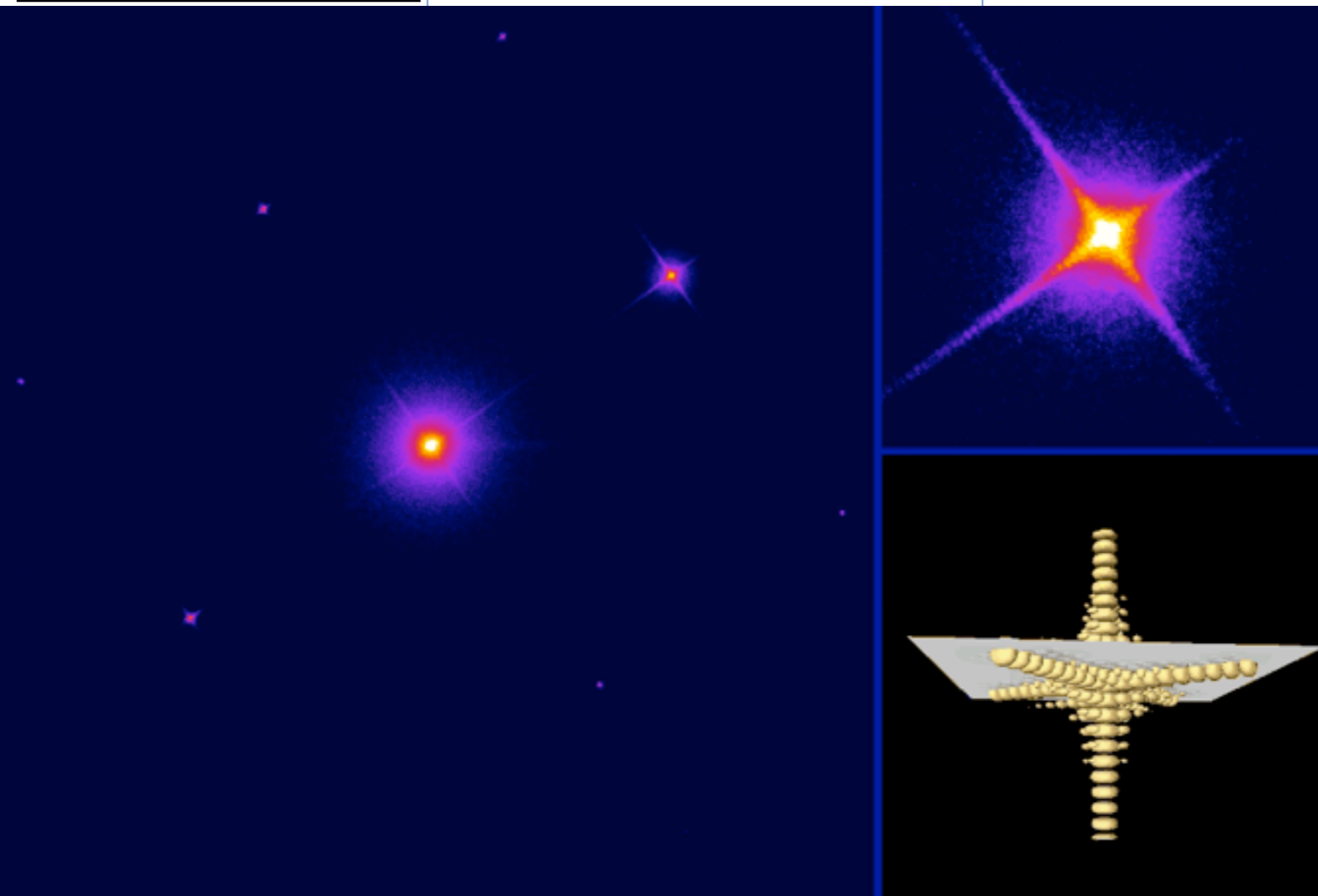
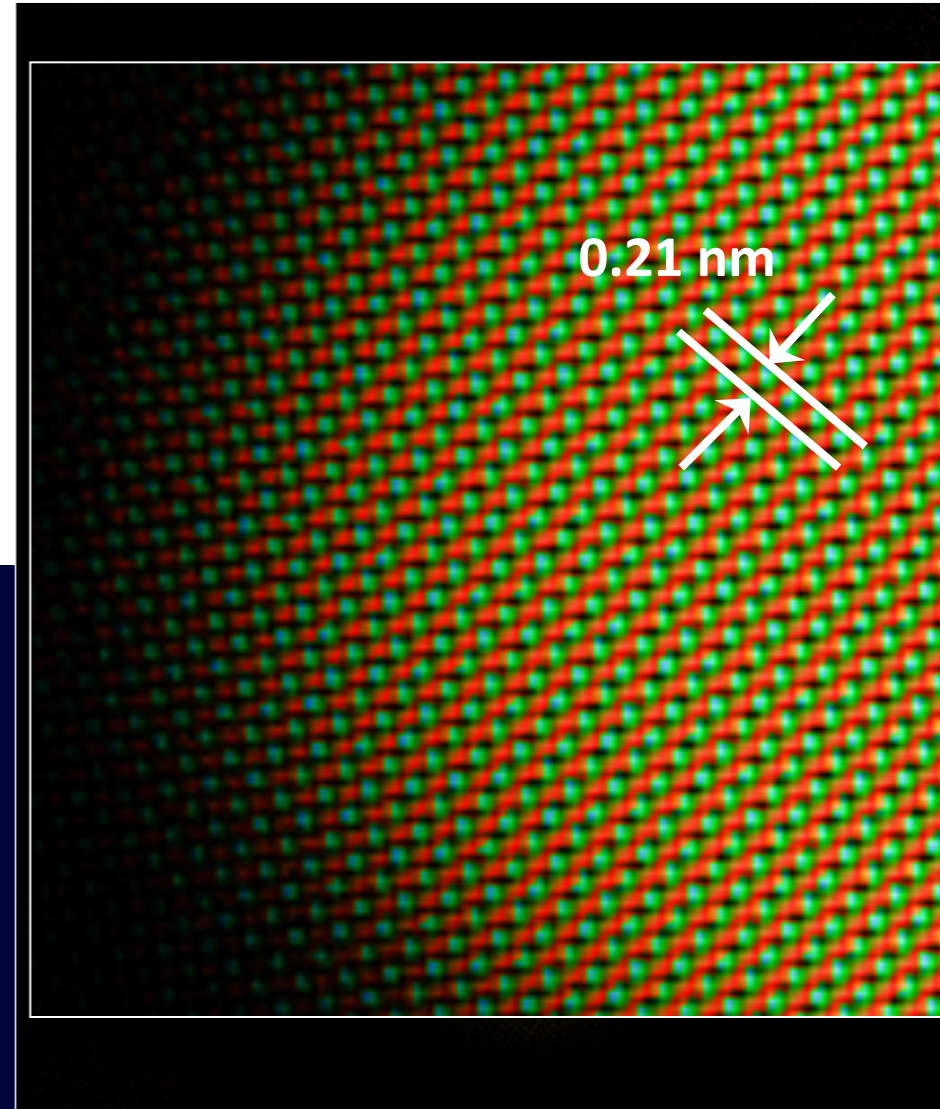


Electron Diffractive Tomography



reconstructed
wave

reconstructed
phase



1.2 電子顯微鏡的極限

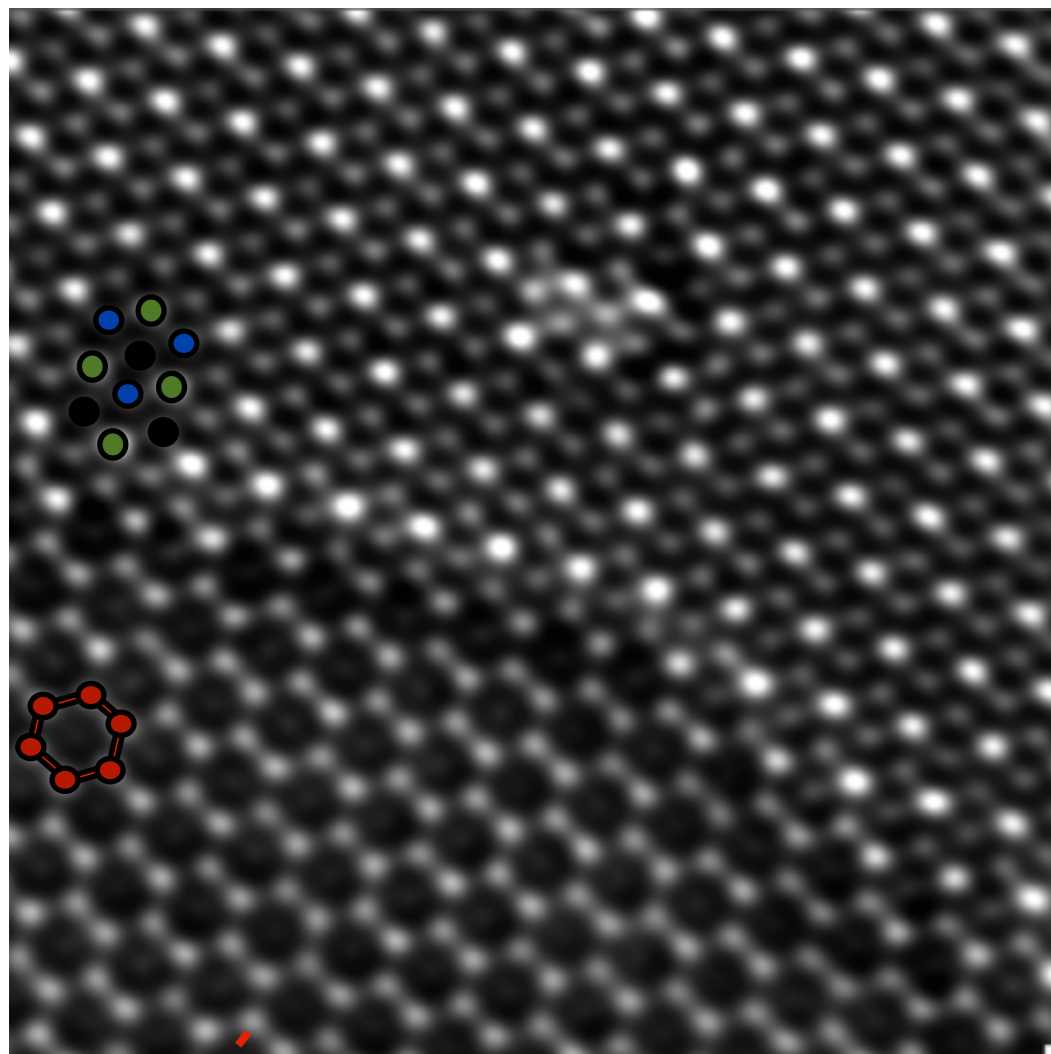
- A 電子顯微鏡所觀察的範圍比整個材料來太小了。所觀察到的結構是否能代表或推測材料的巨觀性質？（瞎子摸象）-奈米元件
- B 電子顯微鏡(以下簡稱電鏡) 提供我們的是從三維空間投影的二維訊息
(對樣品厚度投影平均) - tomography
- C 輻射損傷——尤其是對高分子及陶瓷材料而言。
造成新缺陷（不導電，電荷會累積）
- D “薄” 樣品製備困難
薄：電子透光
<50nm ~ 100nm
- E 在TEM的真空下, 只有乾燥樣品可以觀察.
- F. NO time resolved capability

The Future of TEM: 3D atomic resolution
in wet environment with time resolved

Why 3D ?

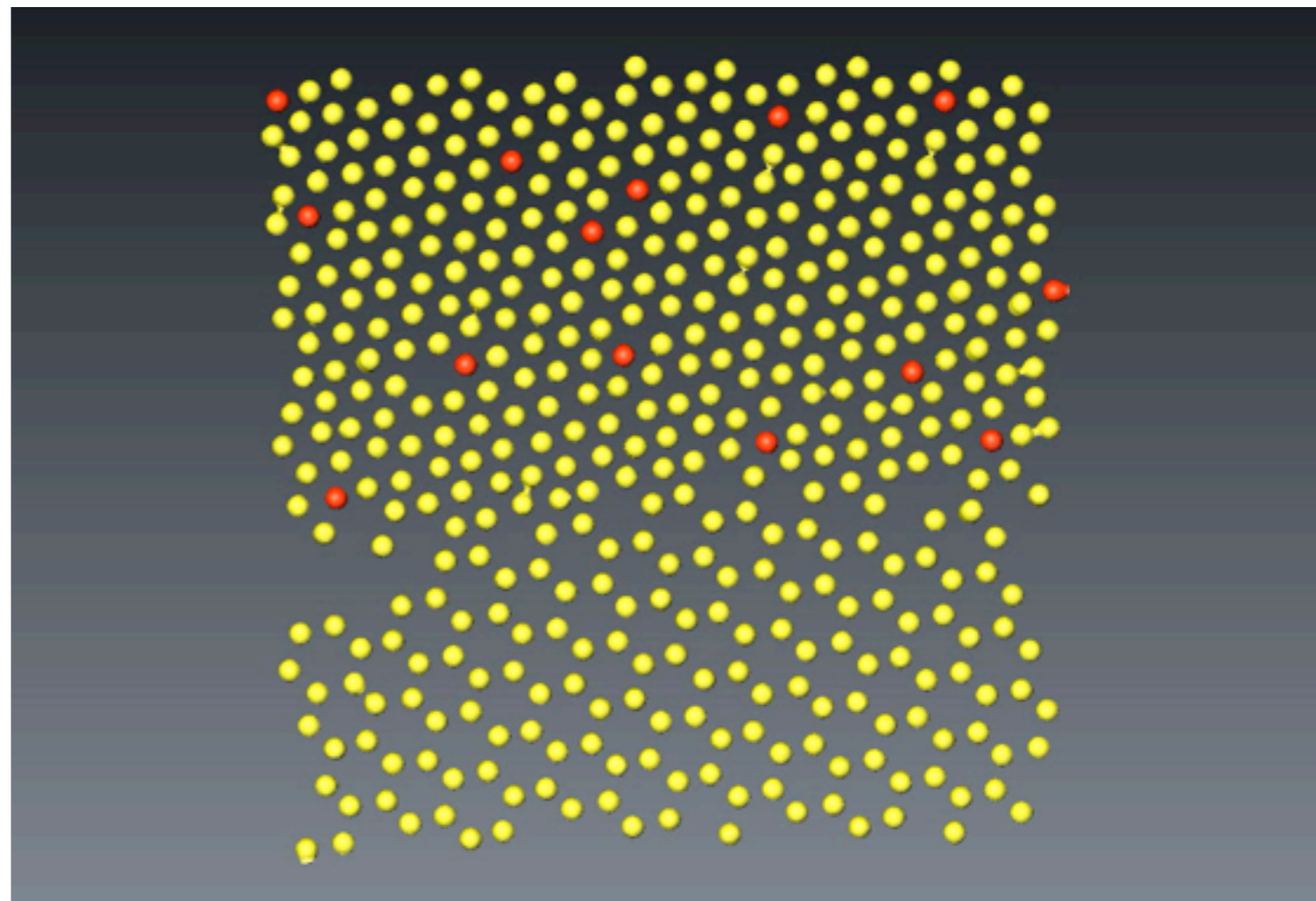


3D - 高空間分辨率



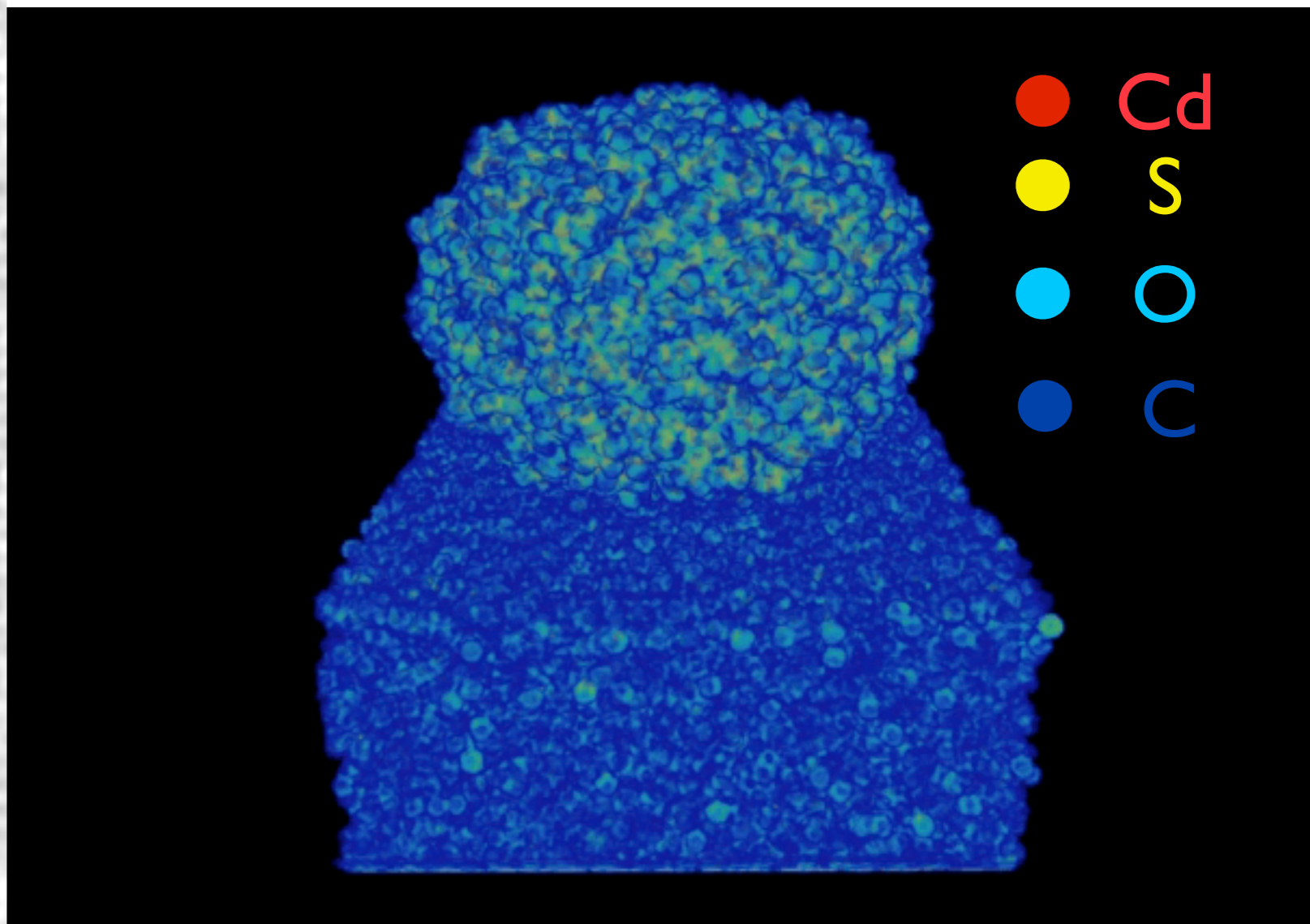
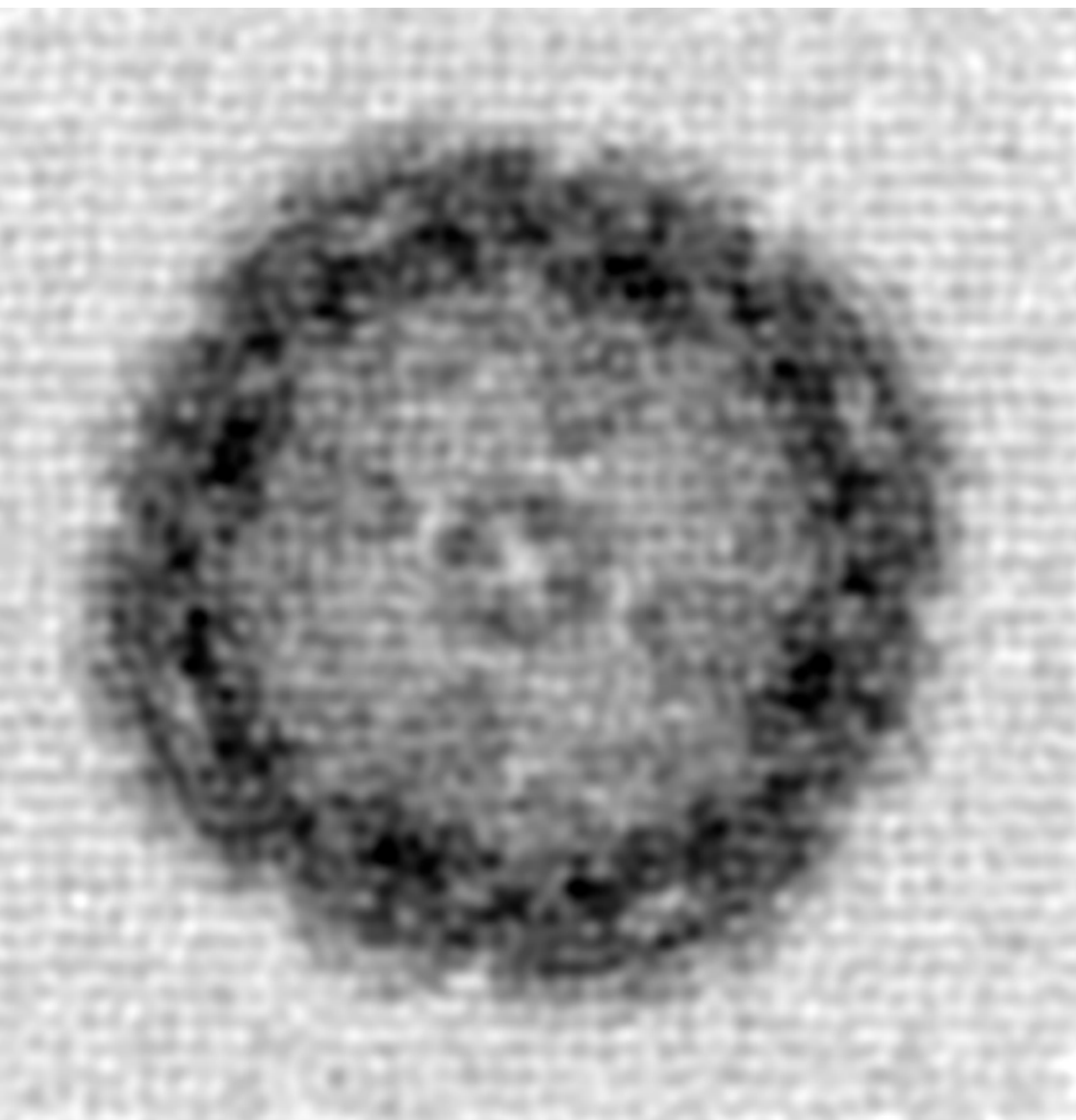
0.14nm

Two layer
Graphene

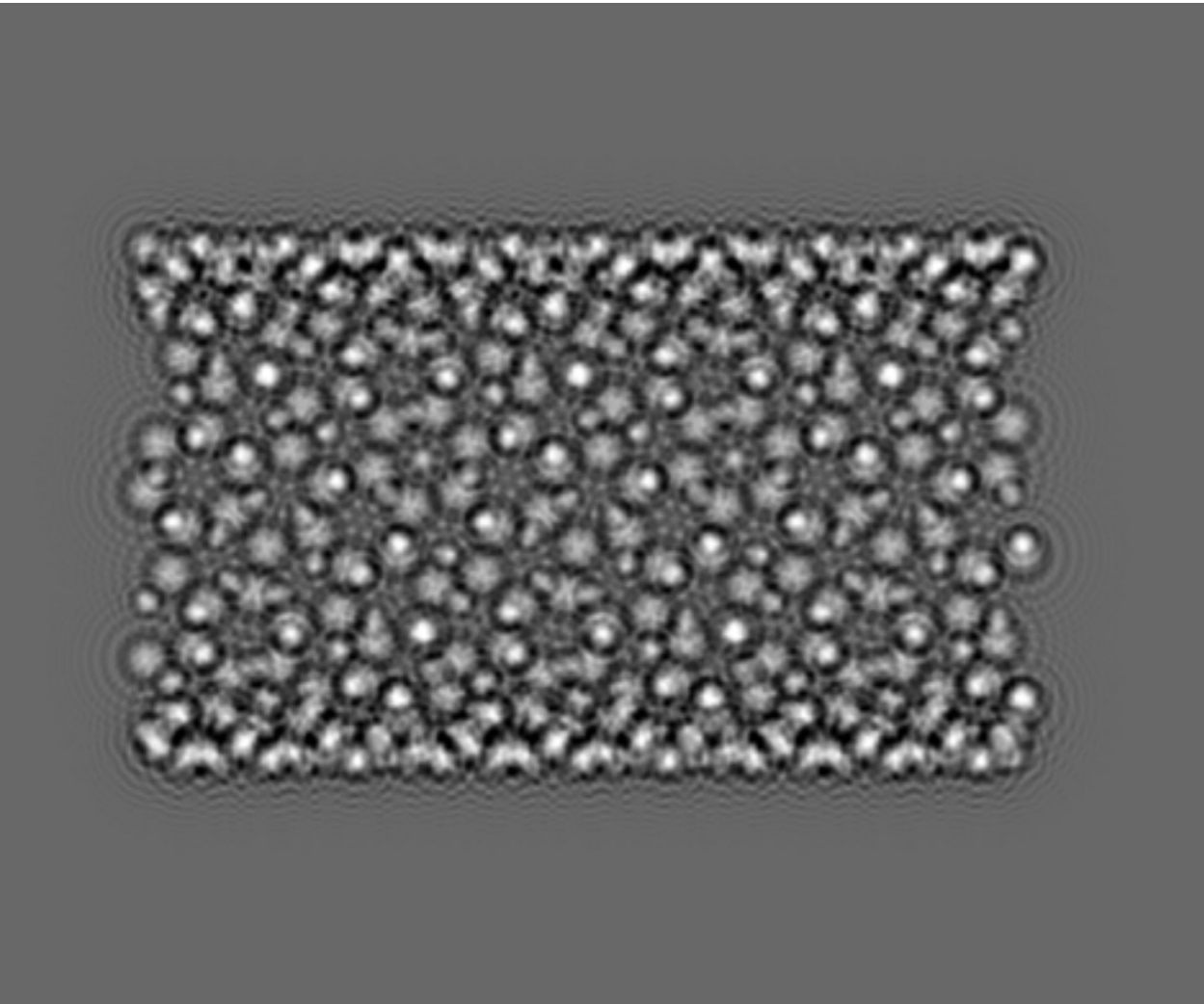


Big-Bang Tomography
原子分辨率斷層攝影學
NATURE, 14 June 2012

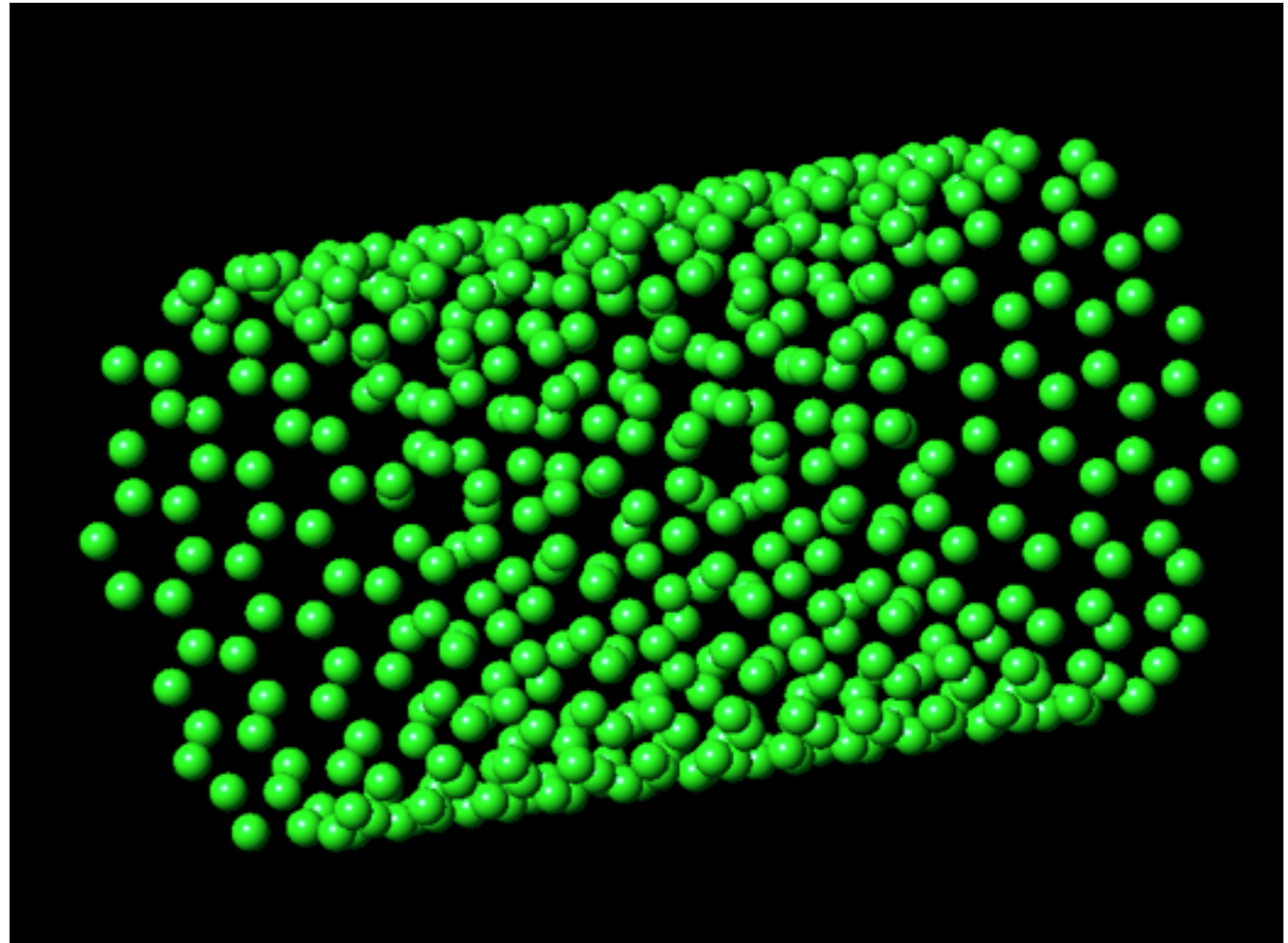
Ferritin on Carbon Film



奈米碳管 (Carbon Nanotube)

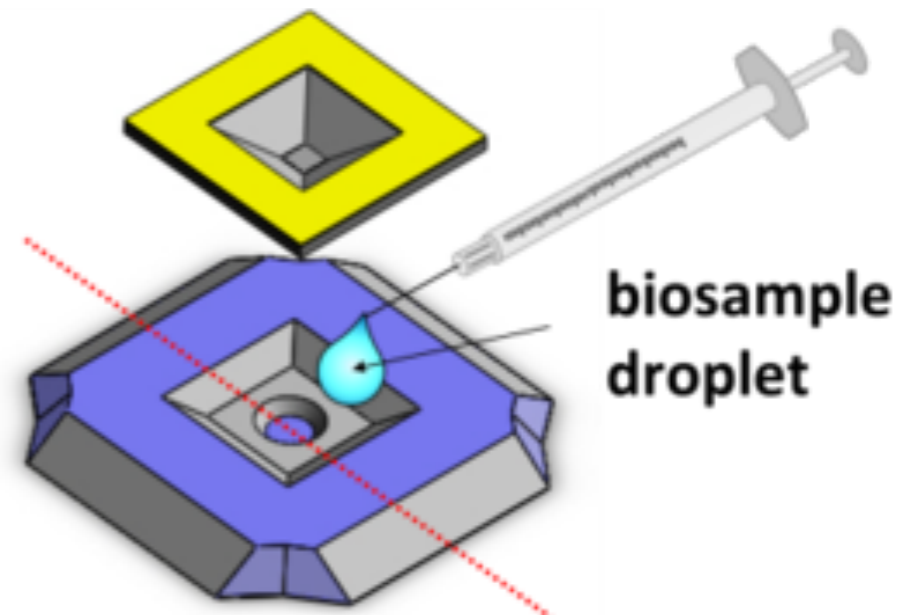
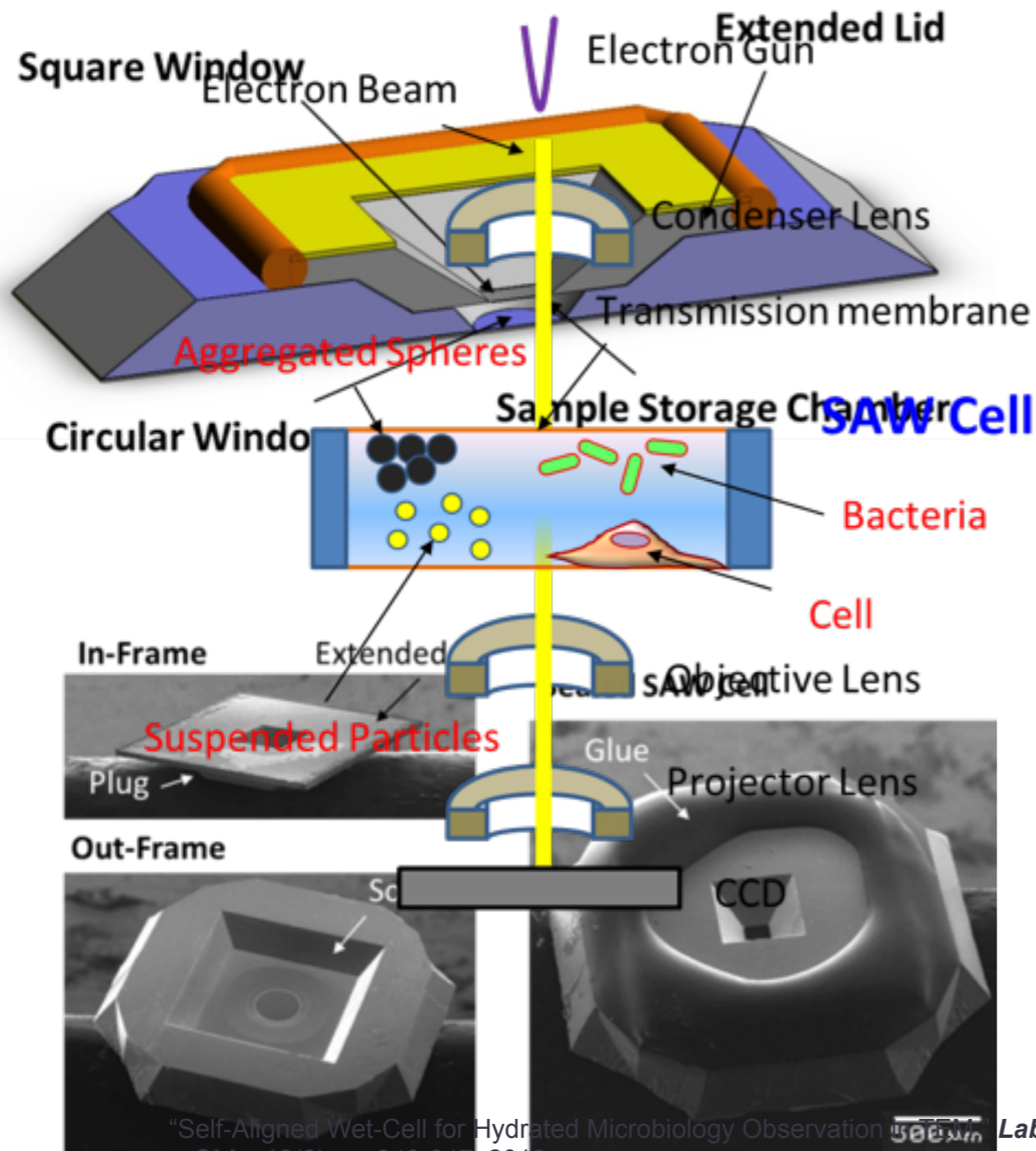


非晶



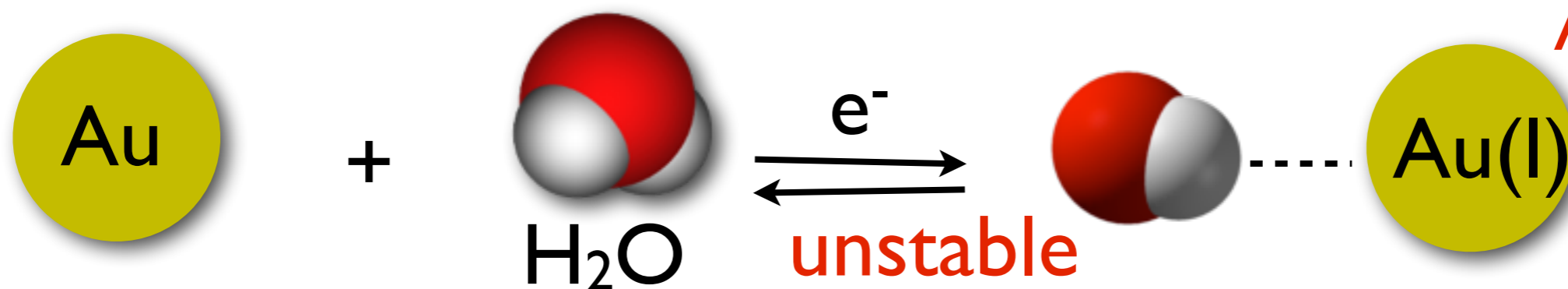
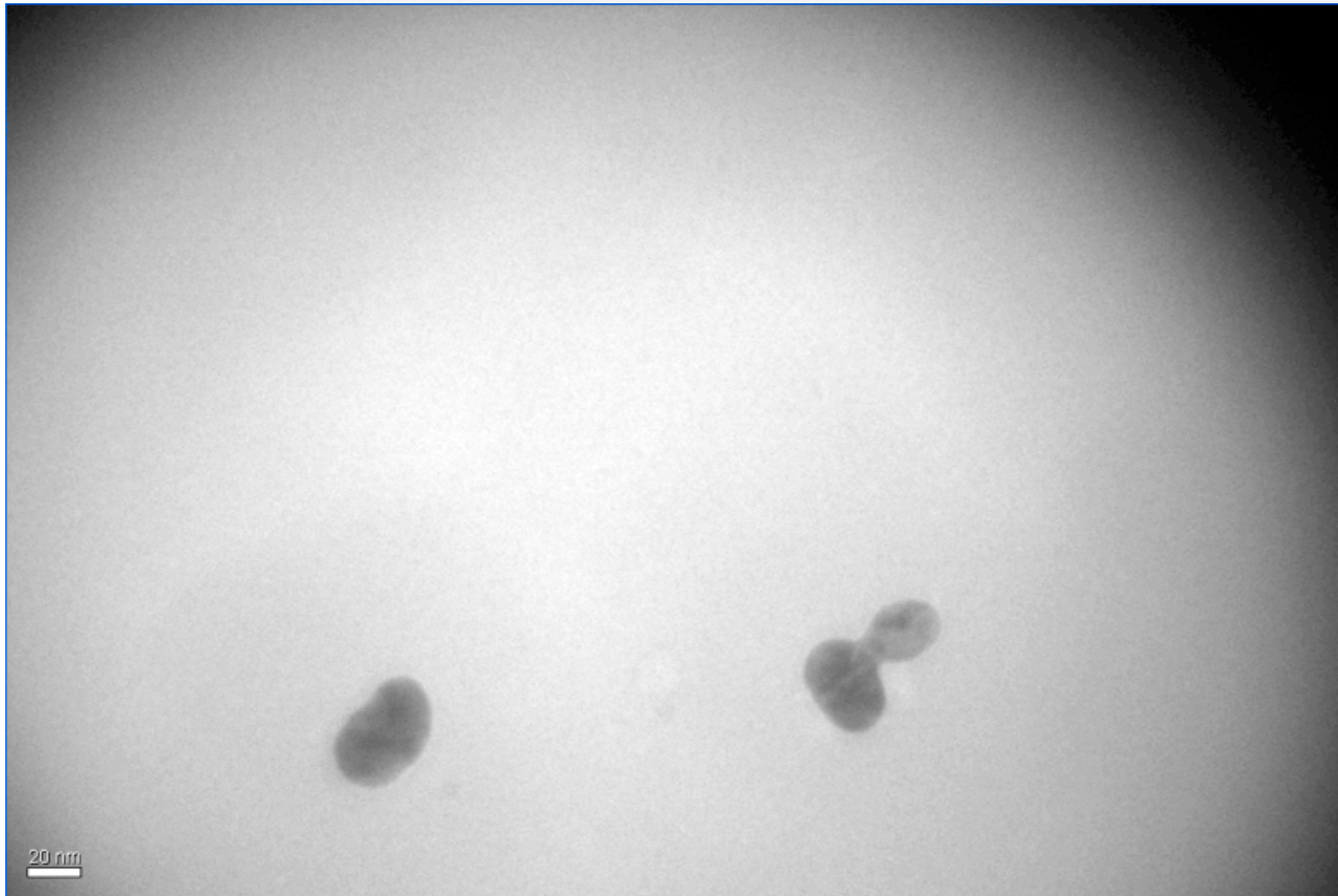
原子解析斷層攝影

Self Aligned Wet (SAW) Cell

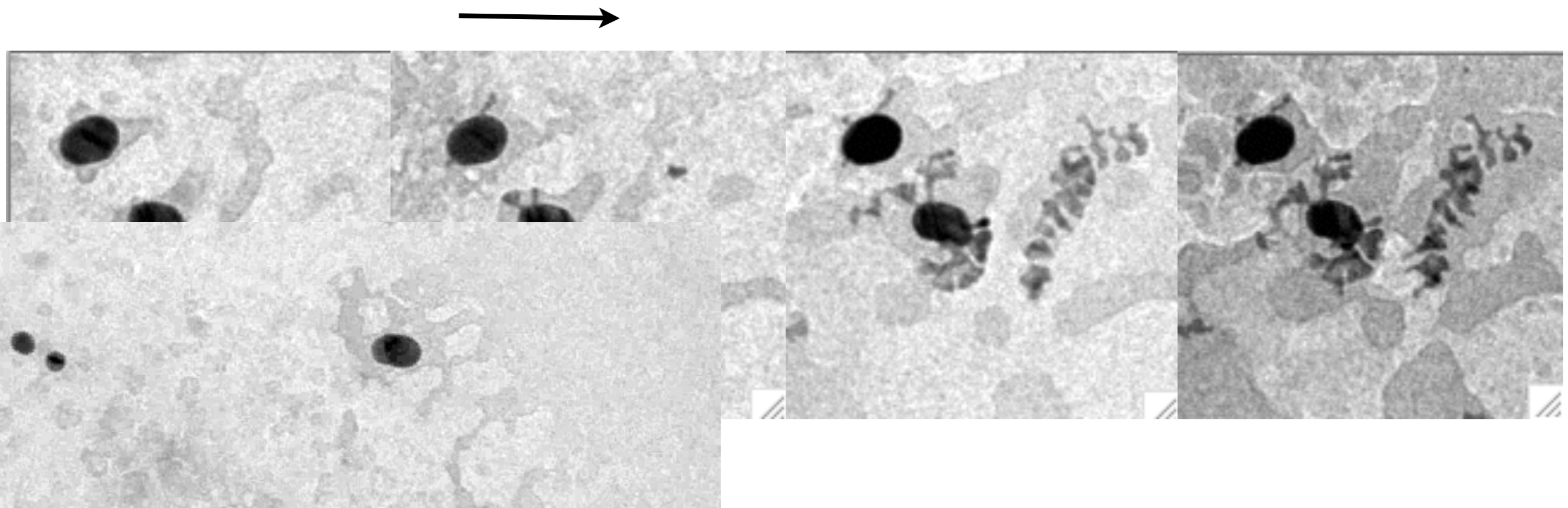
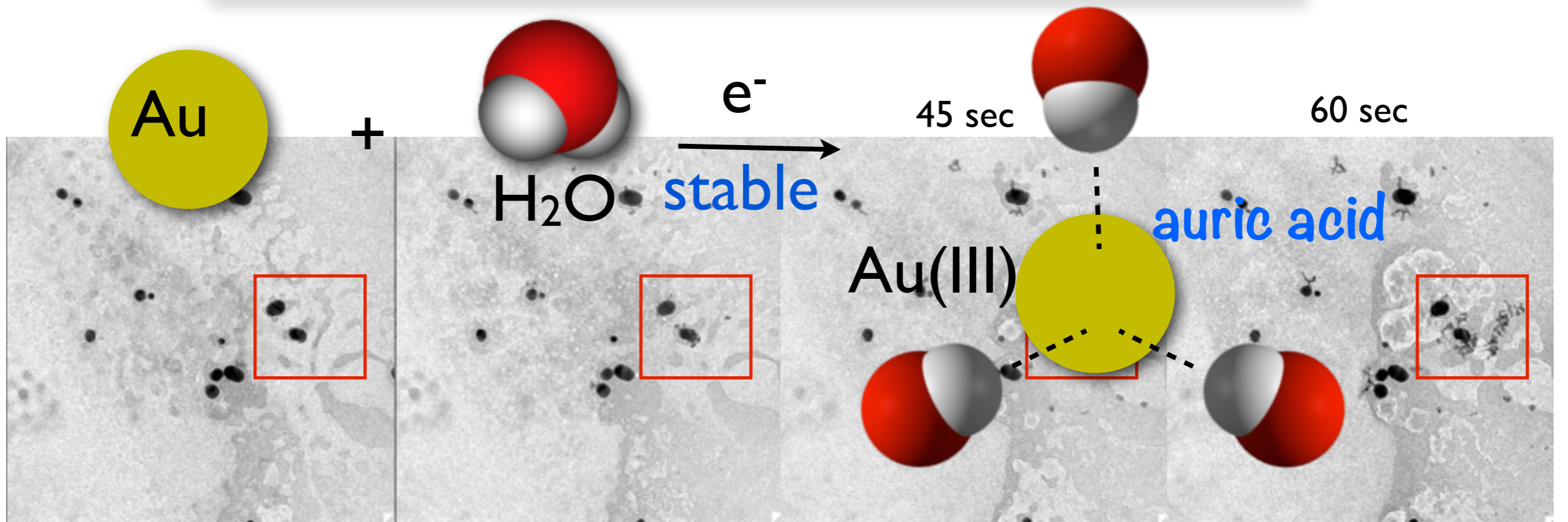


"Self-Aligned Wet-Cell for Hydrated Microbiology Observation on a Chip, 12(2), pp.340-347, 2012. Lab on a Chip

dissolution of Au nano-particles



Dynamics of NW Growth from GNPs

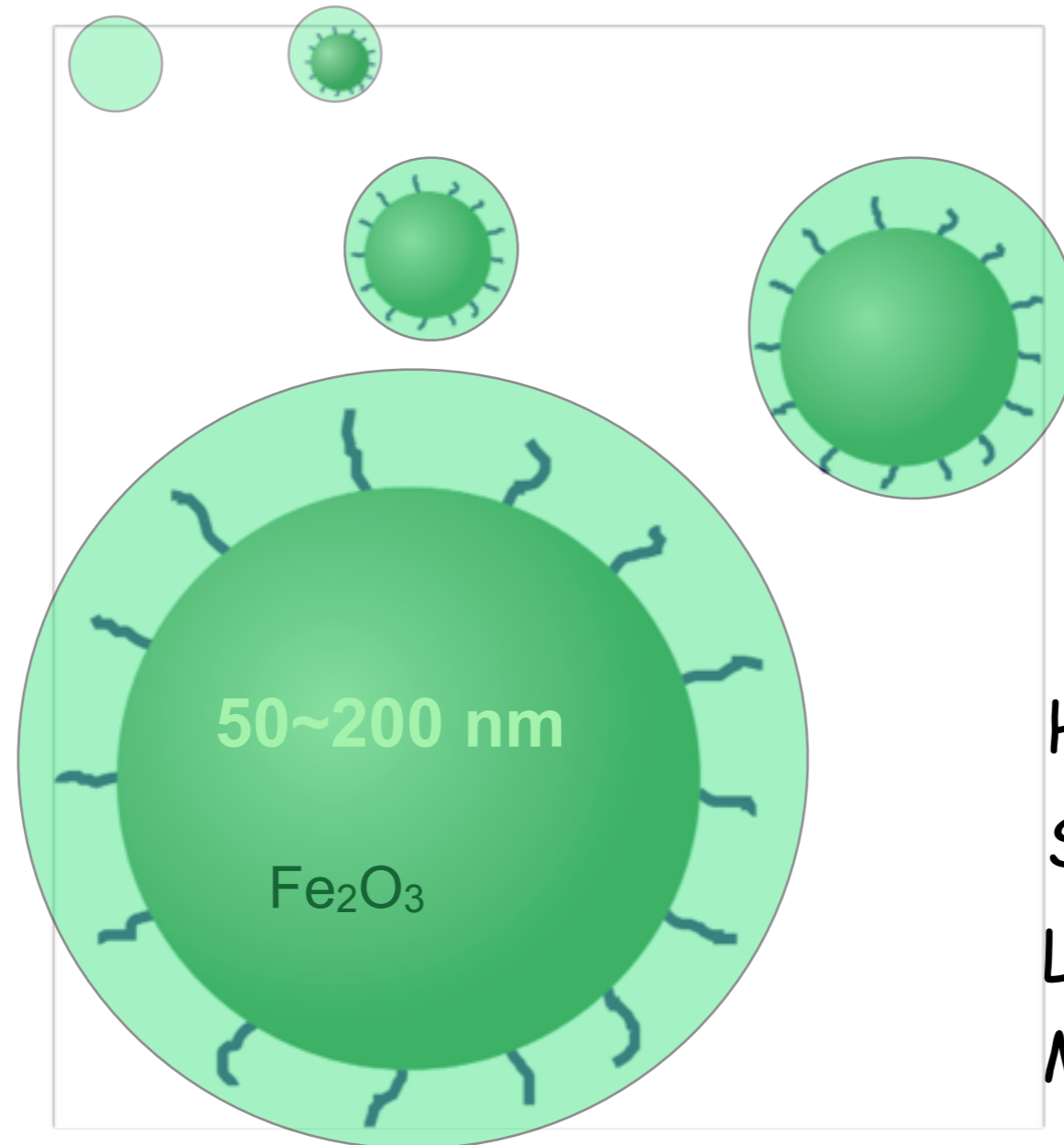


Magic Bullet: Targeting Drug

~ proposed by Nobel Prize winner (1908) Paul Ehrlich

Chitosan-SPIO: Targeting drug for MRI contrast agent

Chitosan



Easy Storage
High Drug Content
Stimuli Responsive
Large Surface Area
Modification

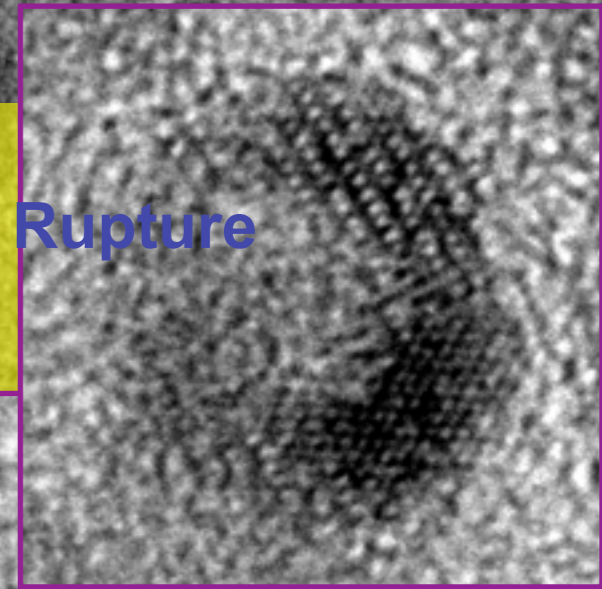
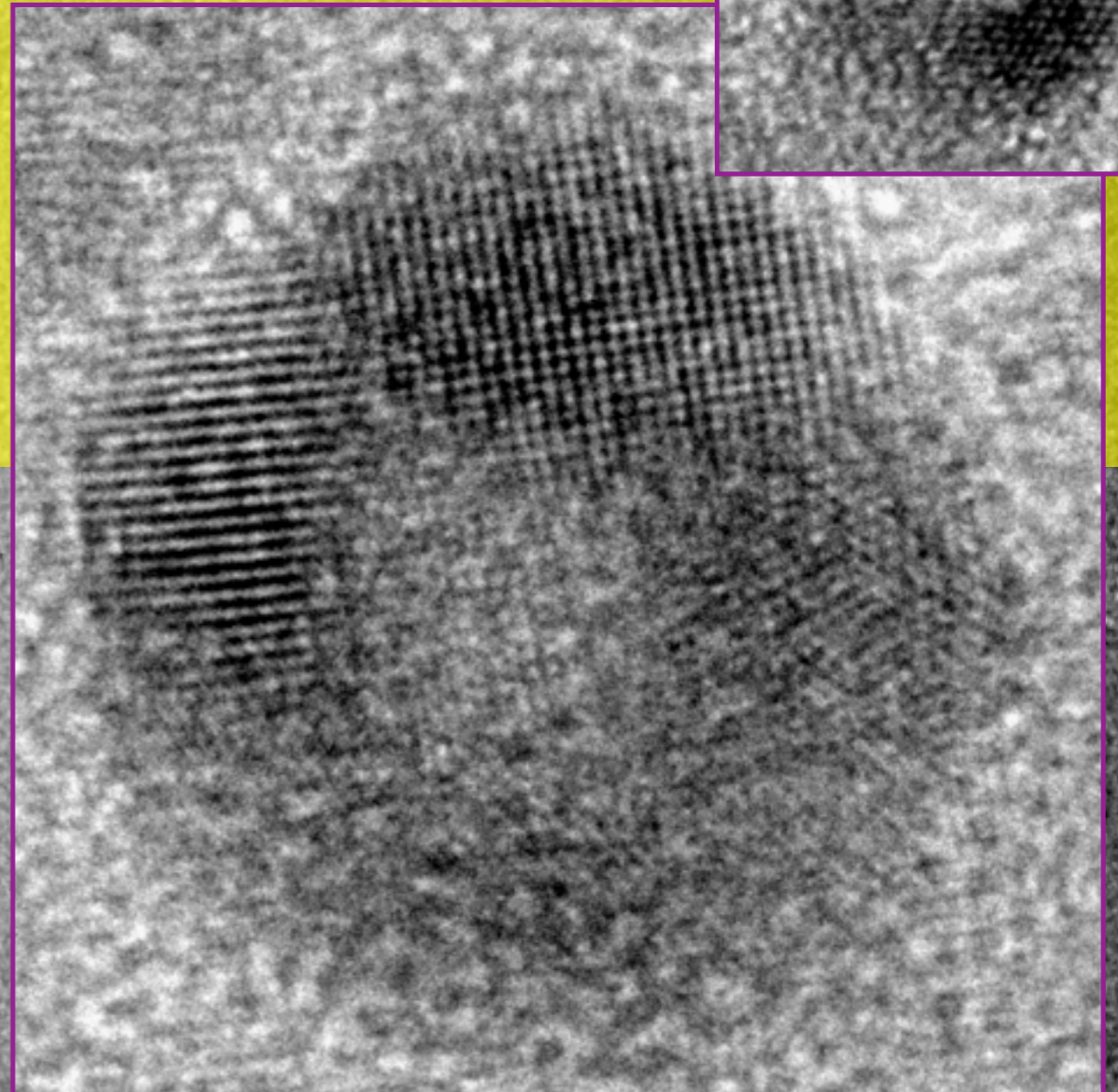
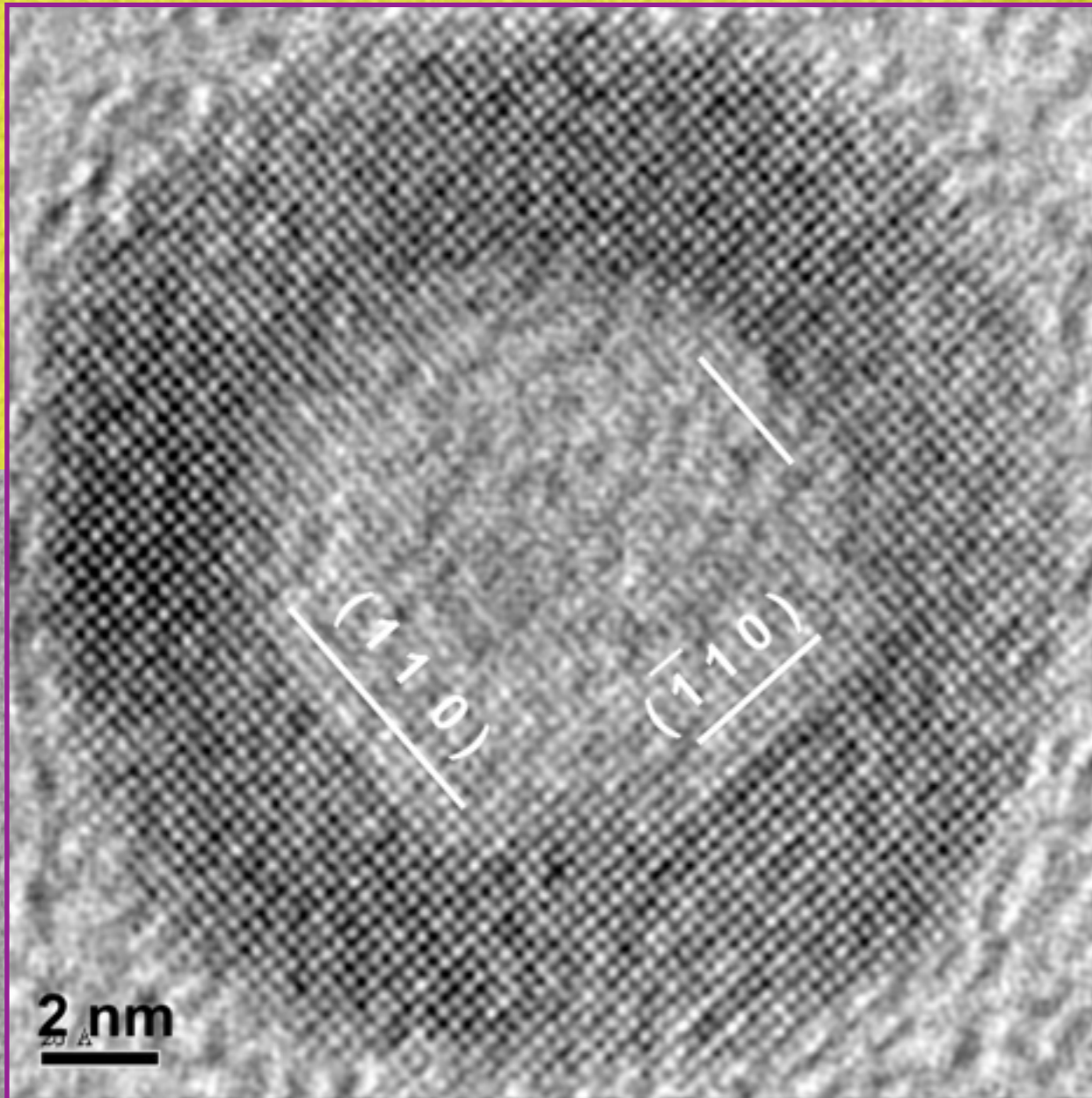
Superparamagnetic iron oxide (SPIO)

Mechanisms for core-(single crystal shells) nanospheres under HFMF

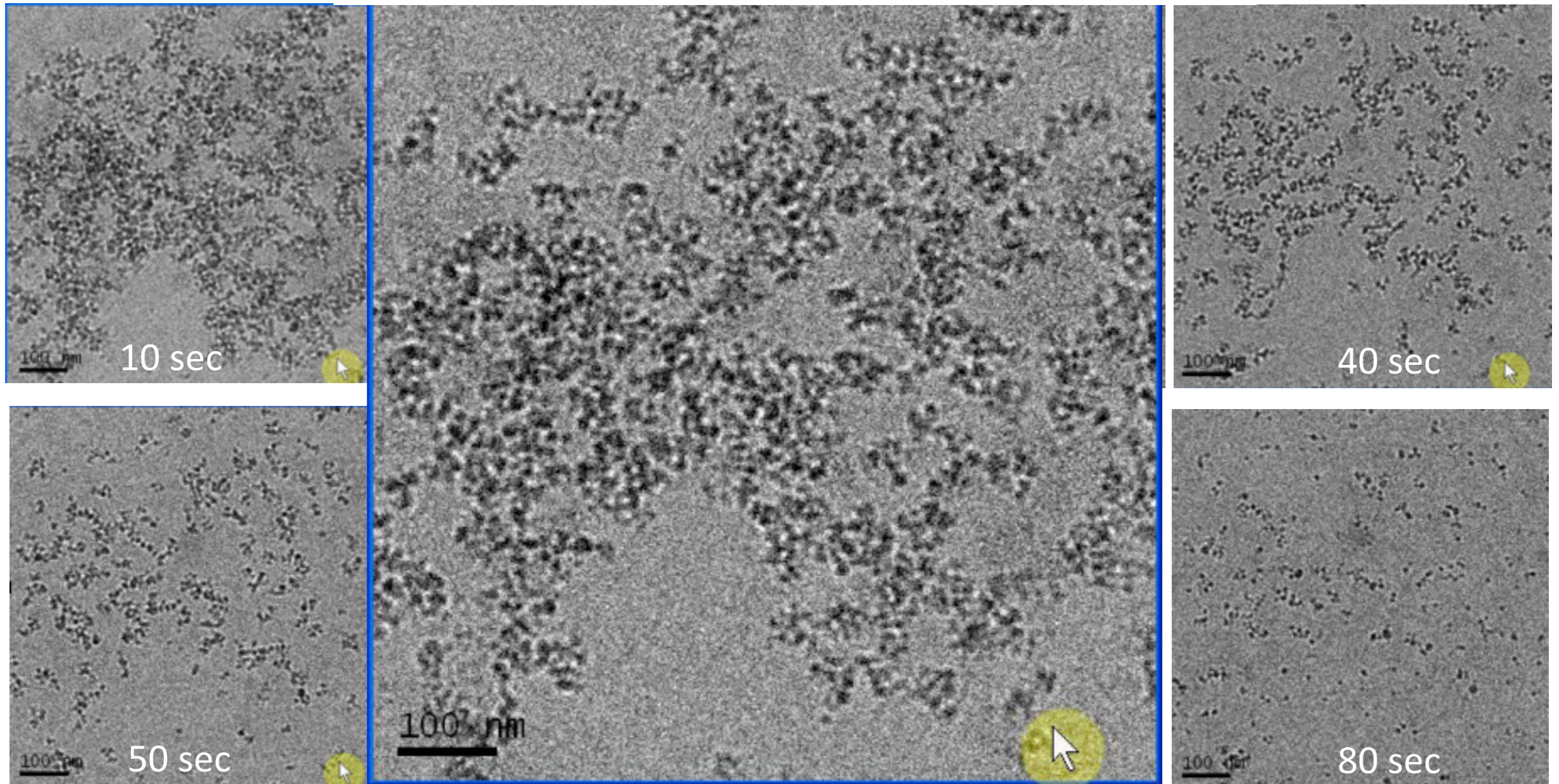
Single crsytal

Poly-crsytal

Rupture



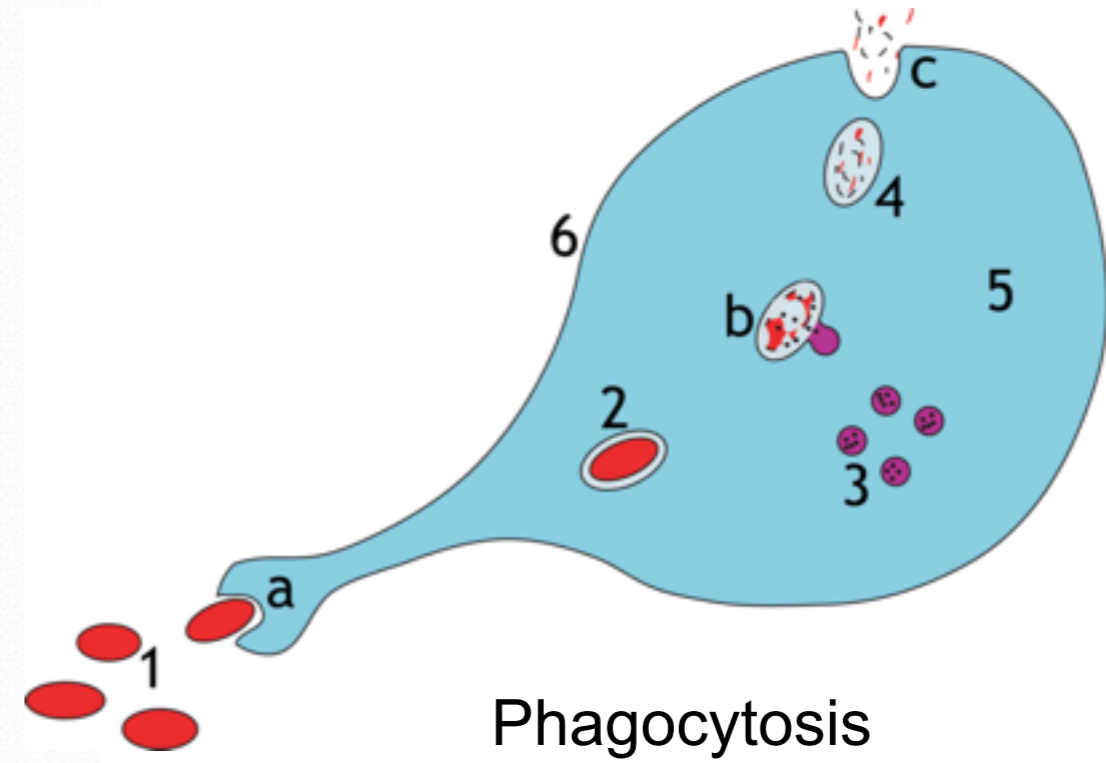
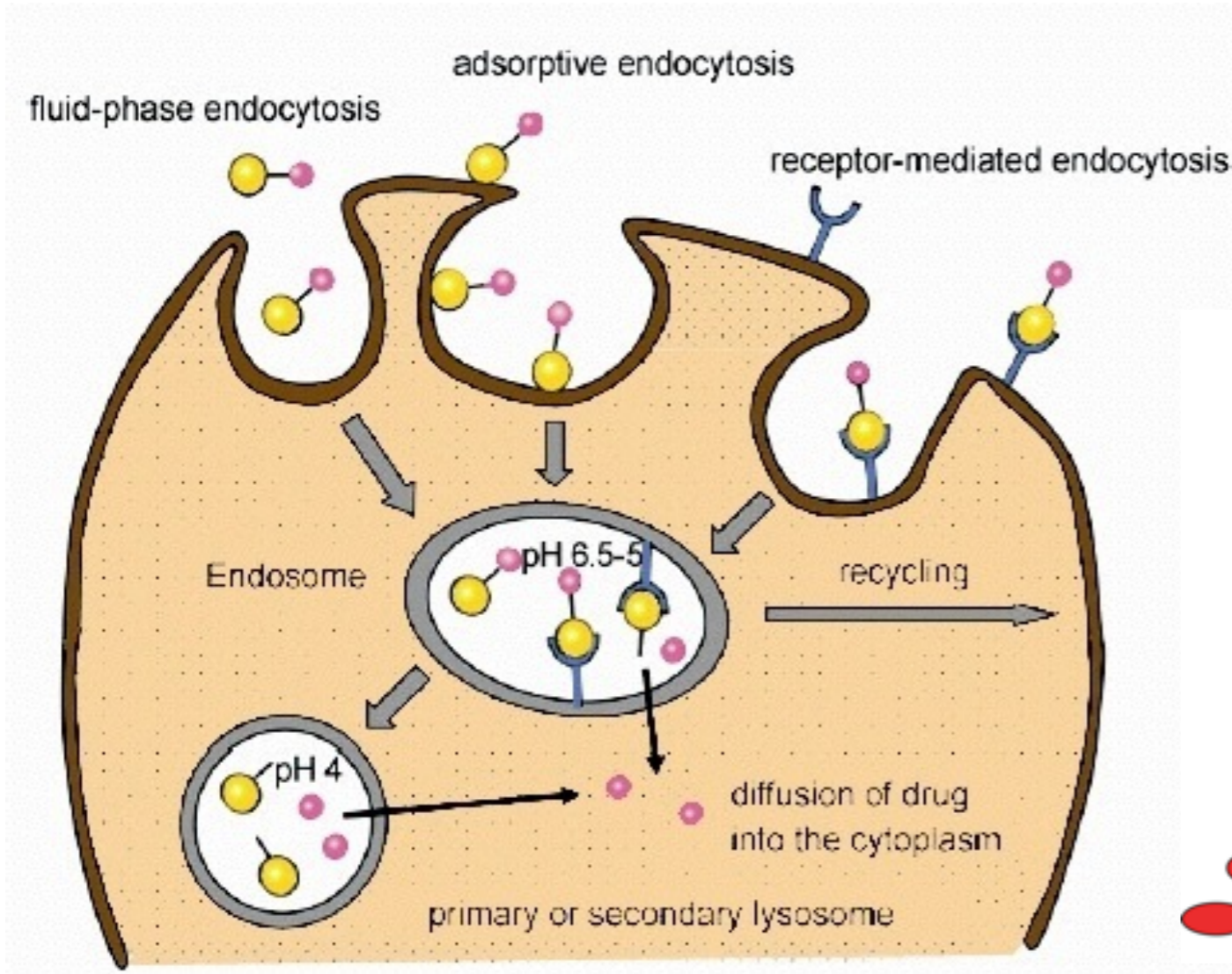
Reduction of Fe₂O₃ NPs



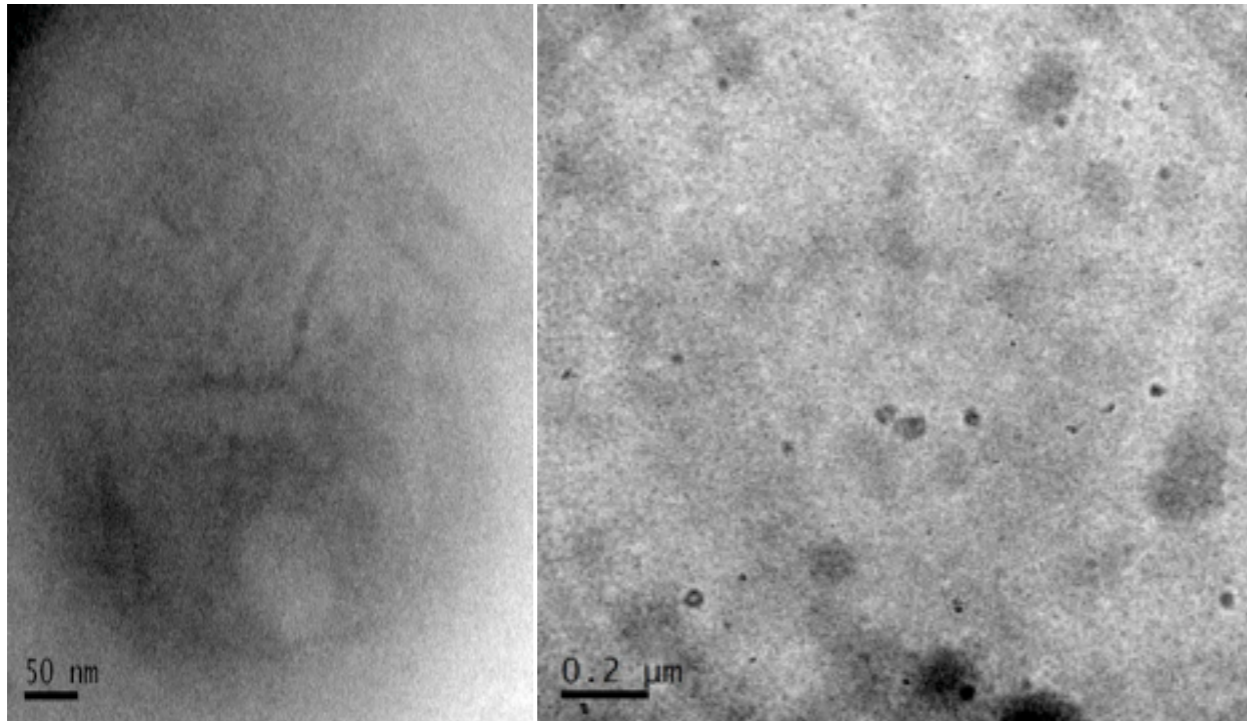
Nano-drug Tumor Targeting

MRI contrast agent

Endocytosis



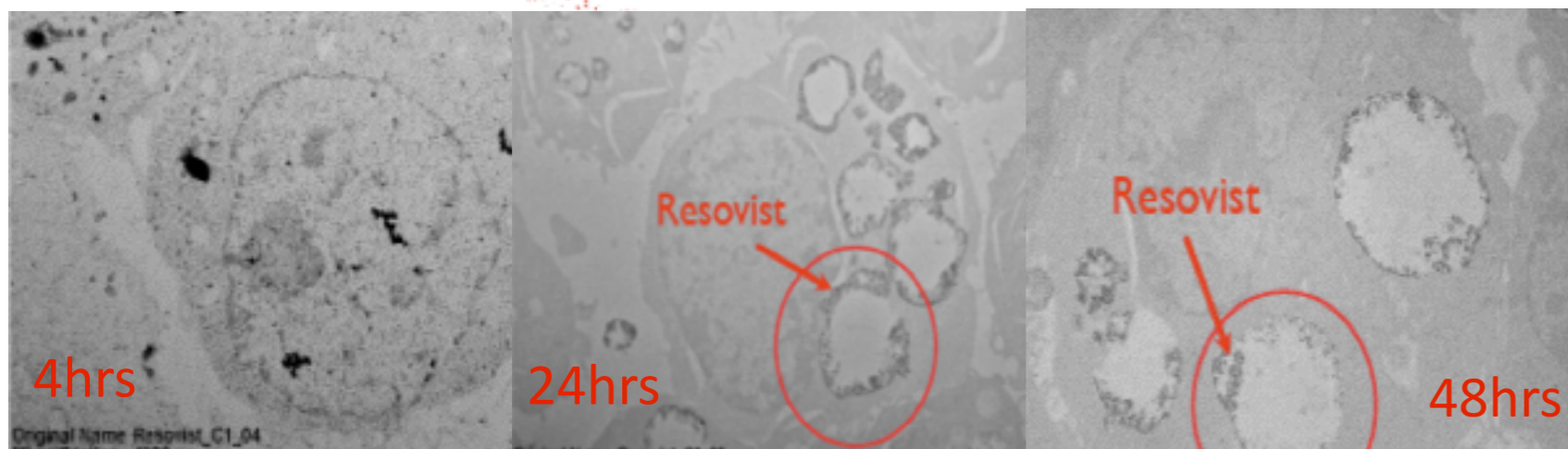
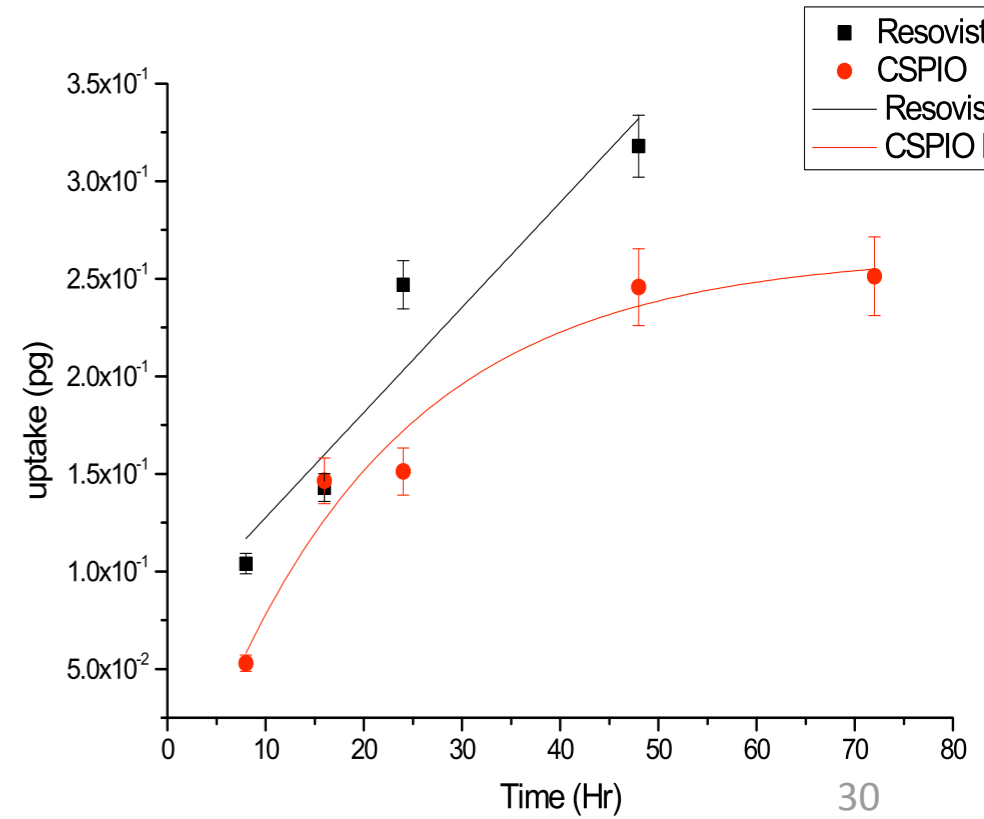
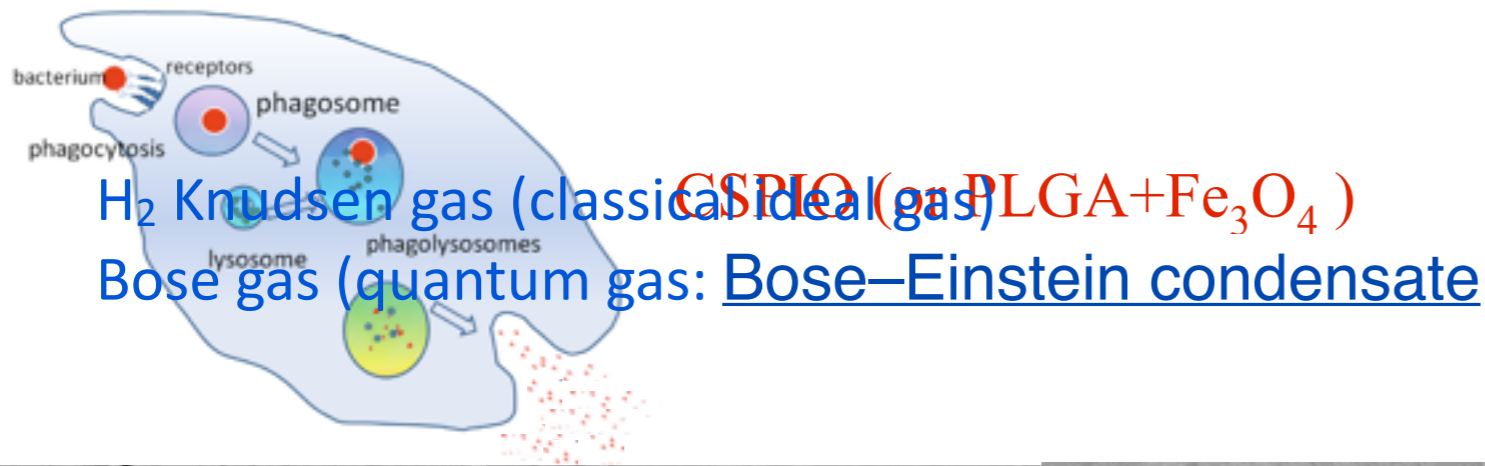
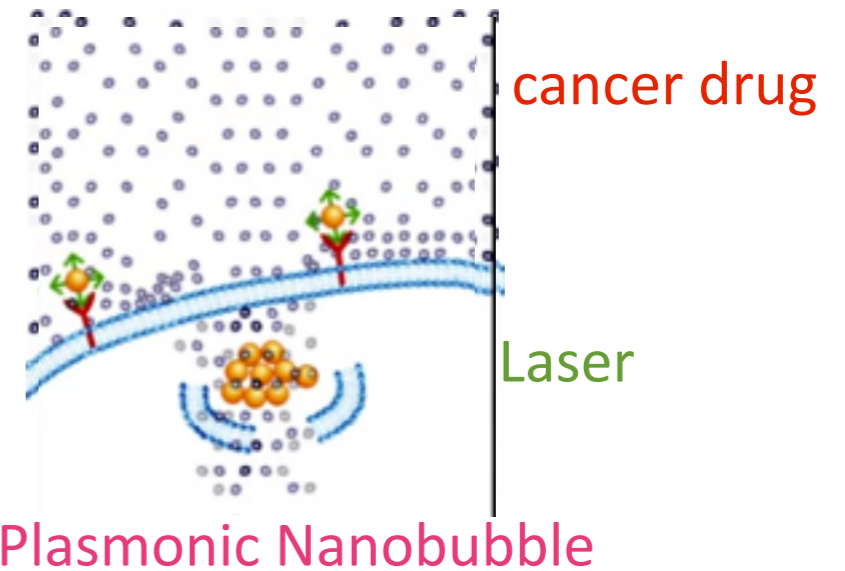
Nano-Bubbles for Cancer Therapy



Protein Liquid

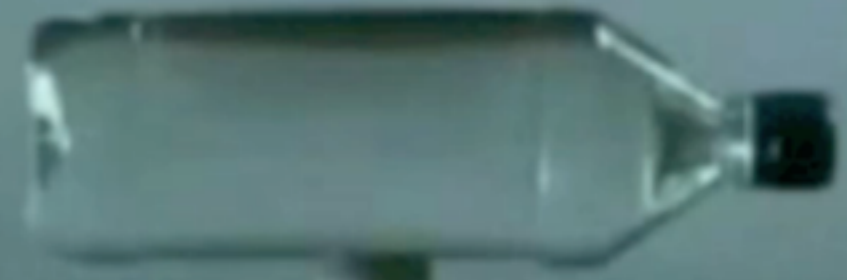
Au NPs in Protein Liquid

Au NPs with antibody



Ultra-fast Electron Microscope

High Speed Camera

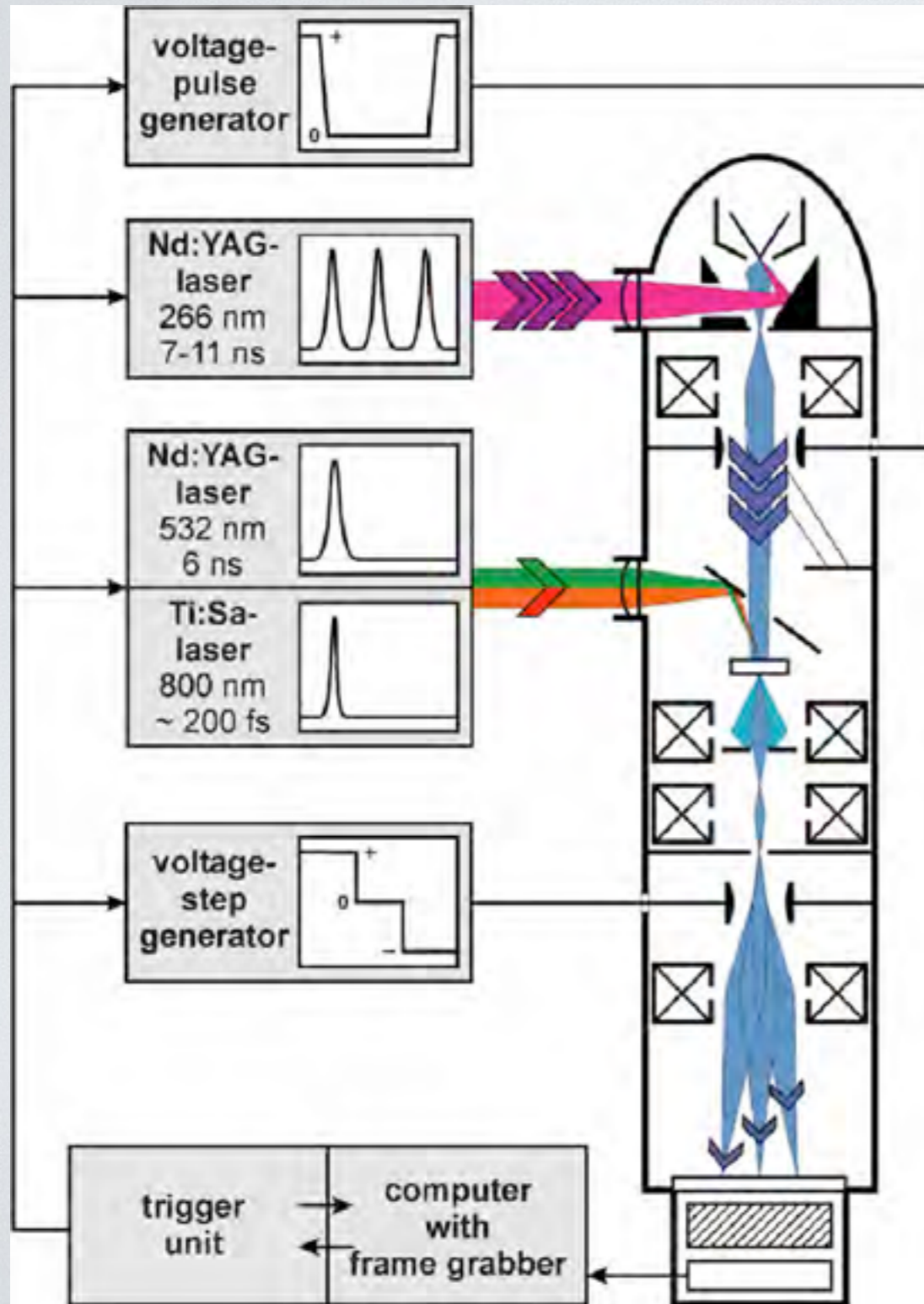


A falling apple photographed by stroboscopic illumination at intervals of $\sim 1/25$ s. The acceleration due to gravity is clear.

Time-resolved TEM was developed at TU-Berlin beginning in the late 1970's

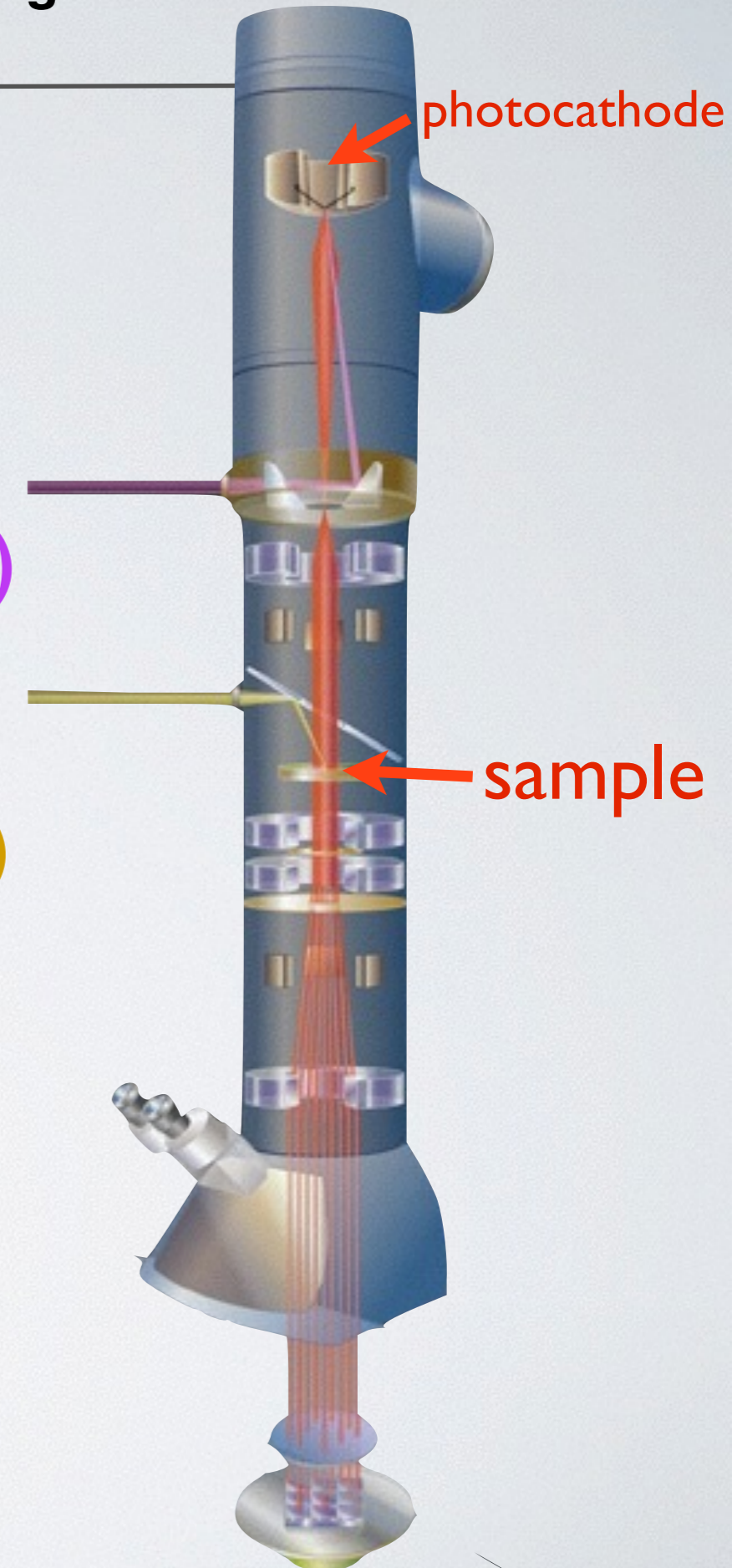
Oleg Bostanjoglo

H. Dömer and O. Bostanjoglo, Rev. Sci. Instr. 74, 4369 (2003)



Laser
(probe)

Laser
(pump)



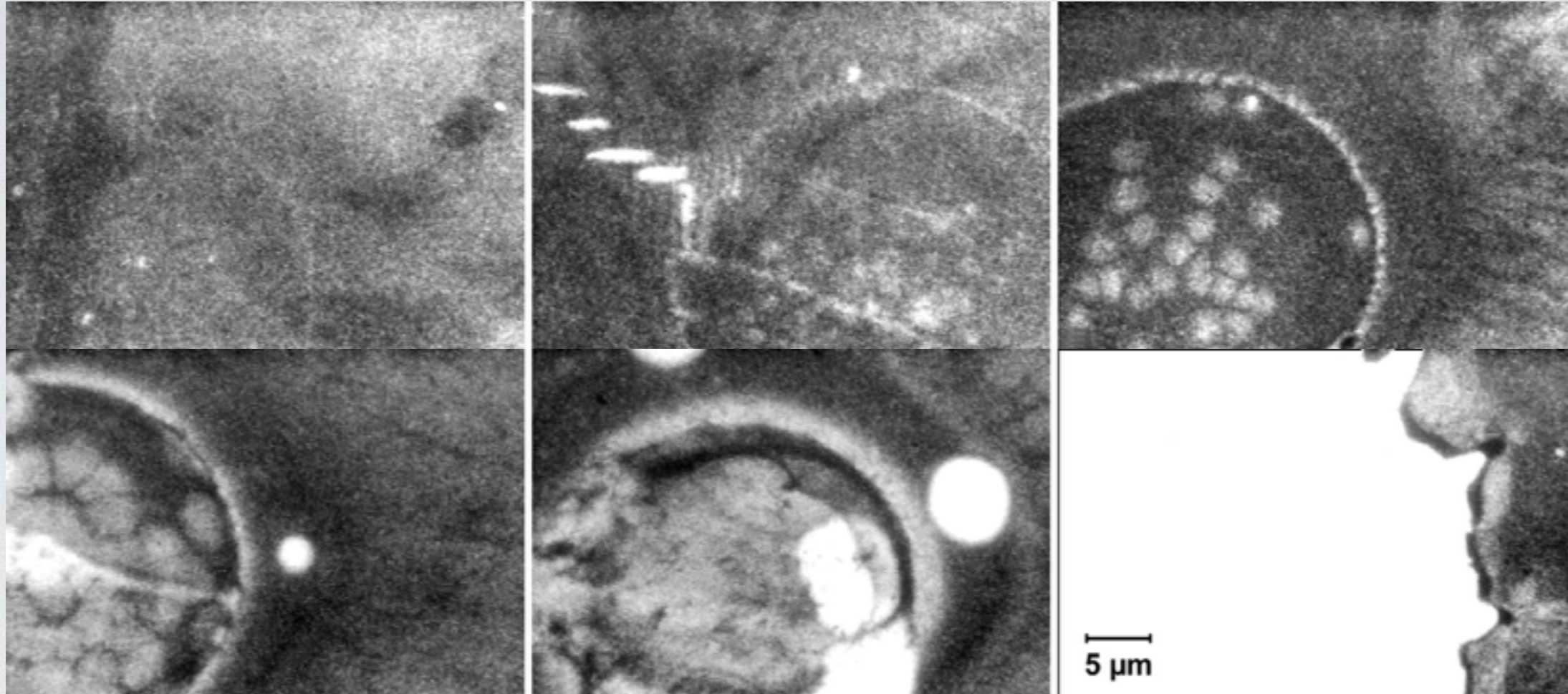
Time-resolved TEM

ablation of Ni film by ultrashort laser pulse

2.5 ns

5 ns

10 ns



20 ns

40 ns

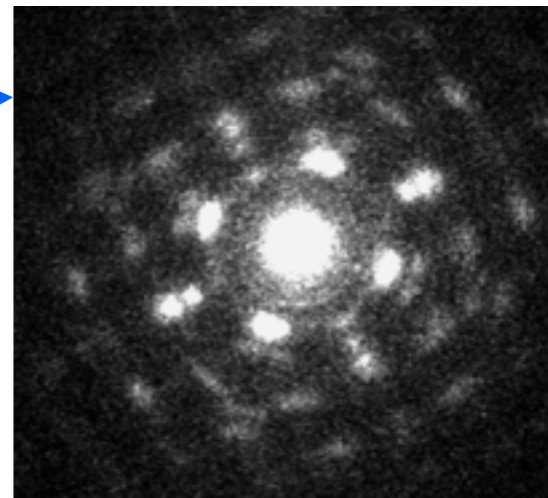
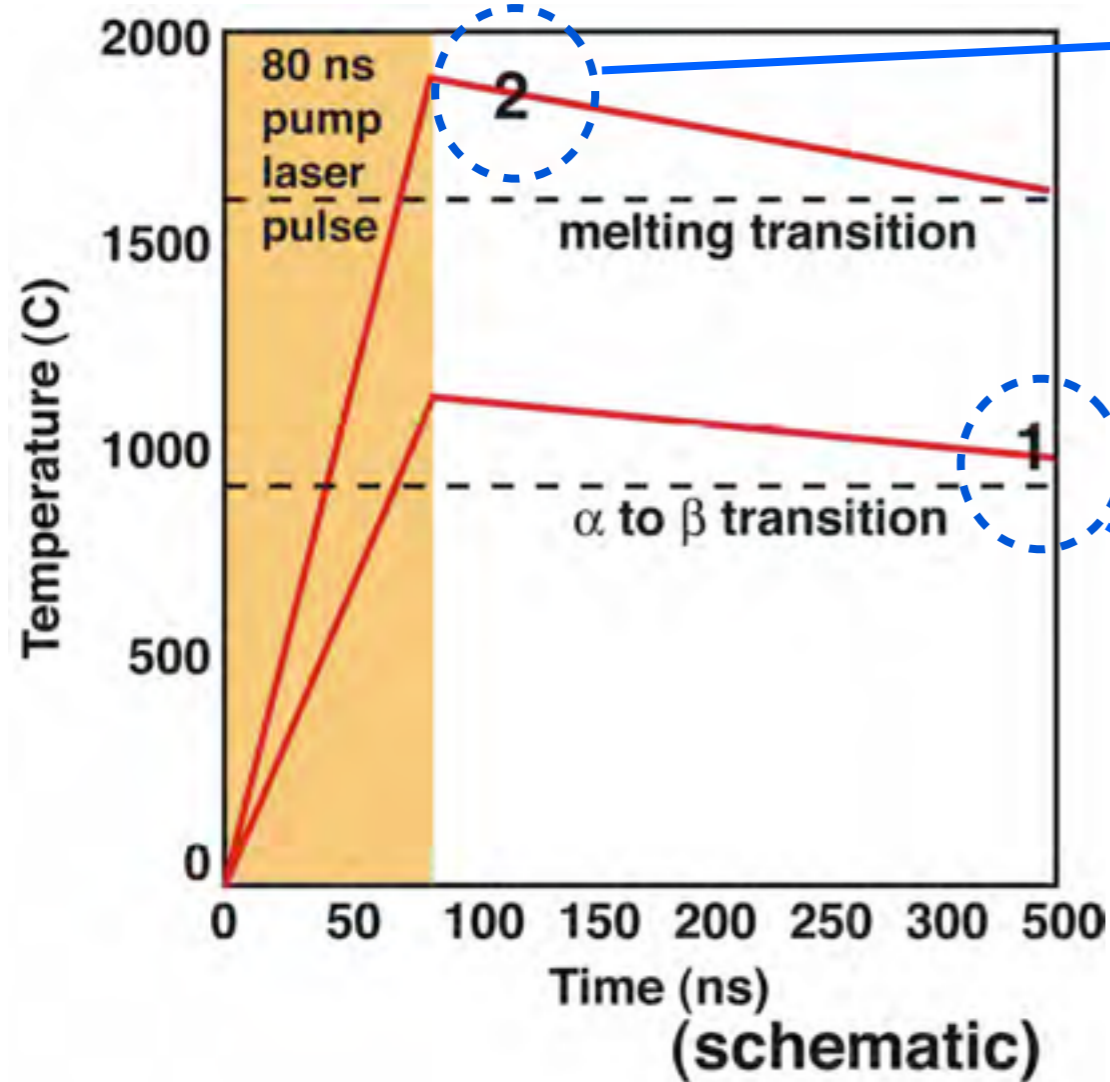
+ ∞

H. Domer and O. Bostanjoglo, Journal of Applied Physics **91**, 5462-5467 (2002).

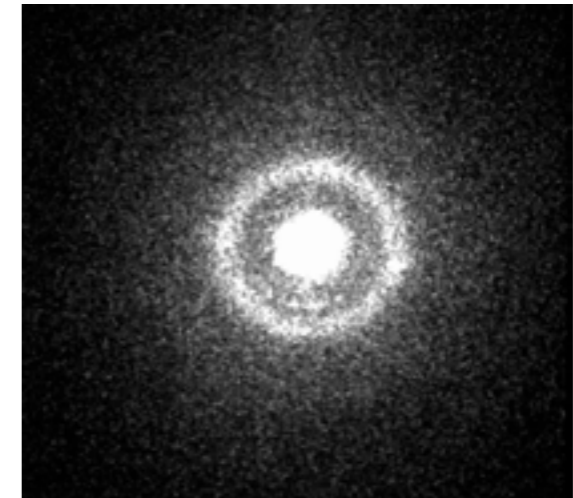
Time-resolved electron diffraction

α -Ti (hcp) \rightarrow β -Ti (bcc) martensitic transformation

Melting transition

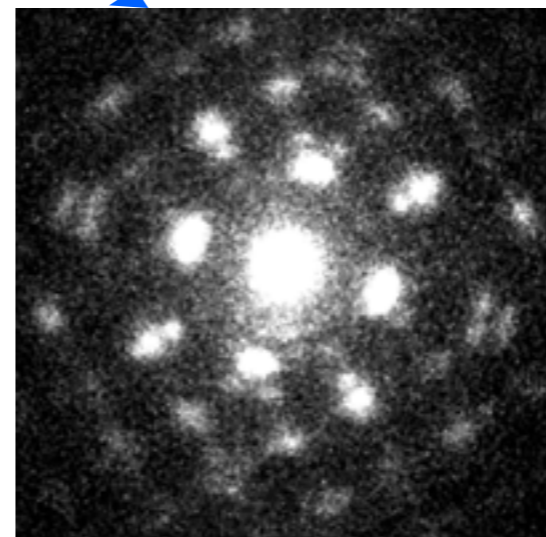


hcp Ti, α -phase

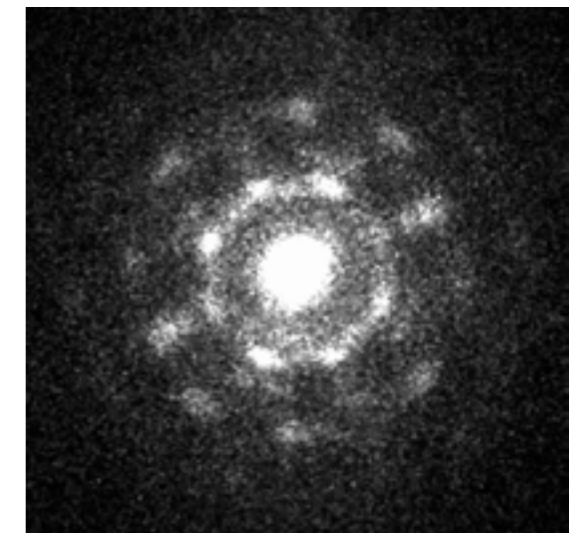


Melt structure

Phase transformation (α to β)



hcp Ti, α -phase



bcc Ti, β -phase

Bryan W. Reed, NLLB, UC, 2008

The

END