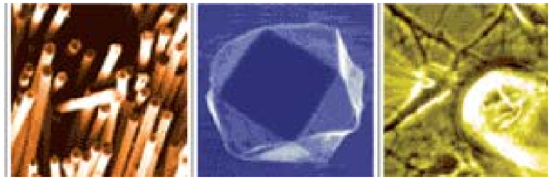
Nanostructured Interfaces and Surfaces
Centre of Excellence



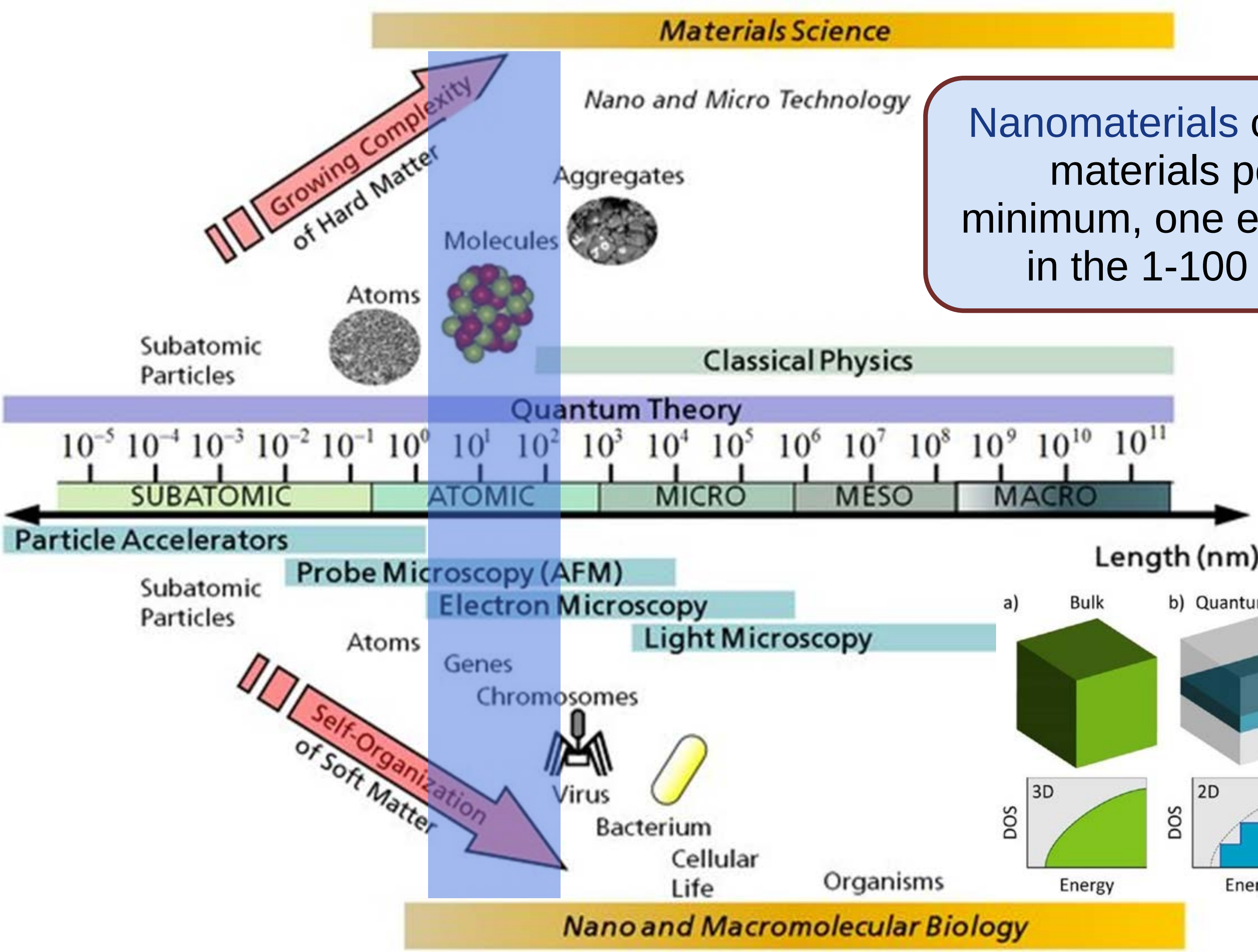
Watching nanomaterials with X-ray eyes: probing different length scales by combining scattering with spectroscopy

Lorenzo Mino

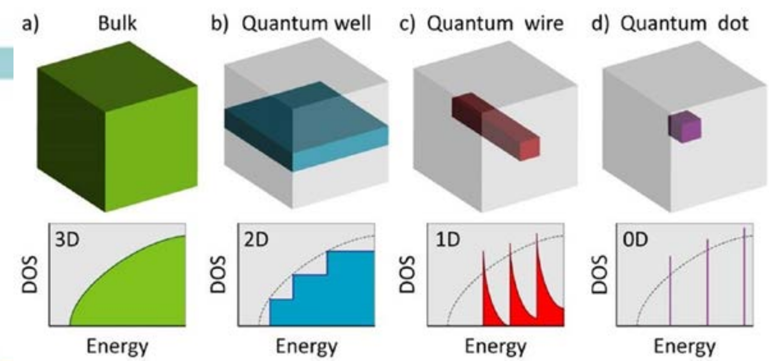
Department of Chemistry and NIS, University of Torino

School on Synchrotron Radiation "Gilberto Vlaic", 13-17 September 2021

Nanomaterials

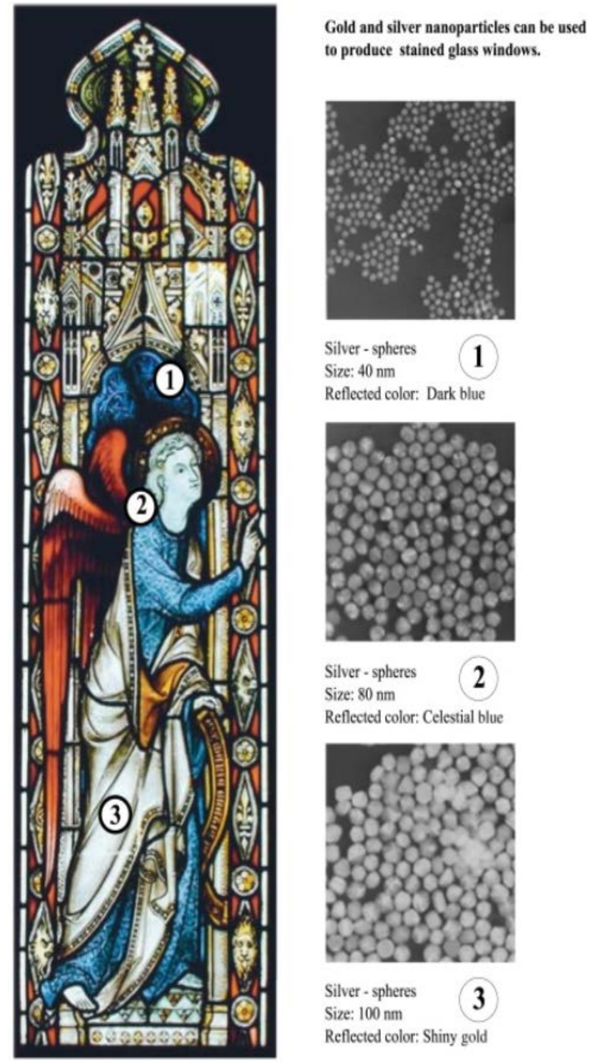


Nanomaterials can be defined as materials possessing, at minimum, one external dimension in the 1-100 nm size range



Nanotechnology: unintentional beginning

Lycurgus Cup
(4th-century)



Medieval stained glass

Nanotechnology: conceptual origins

There's Plenty of Room at the Bottom

29 December 1959, annual meeting of the American Physical Society, California Institute of Technology (Caltech)

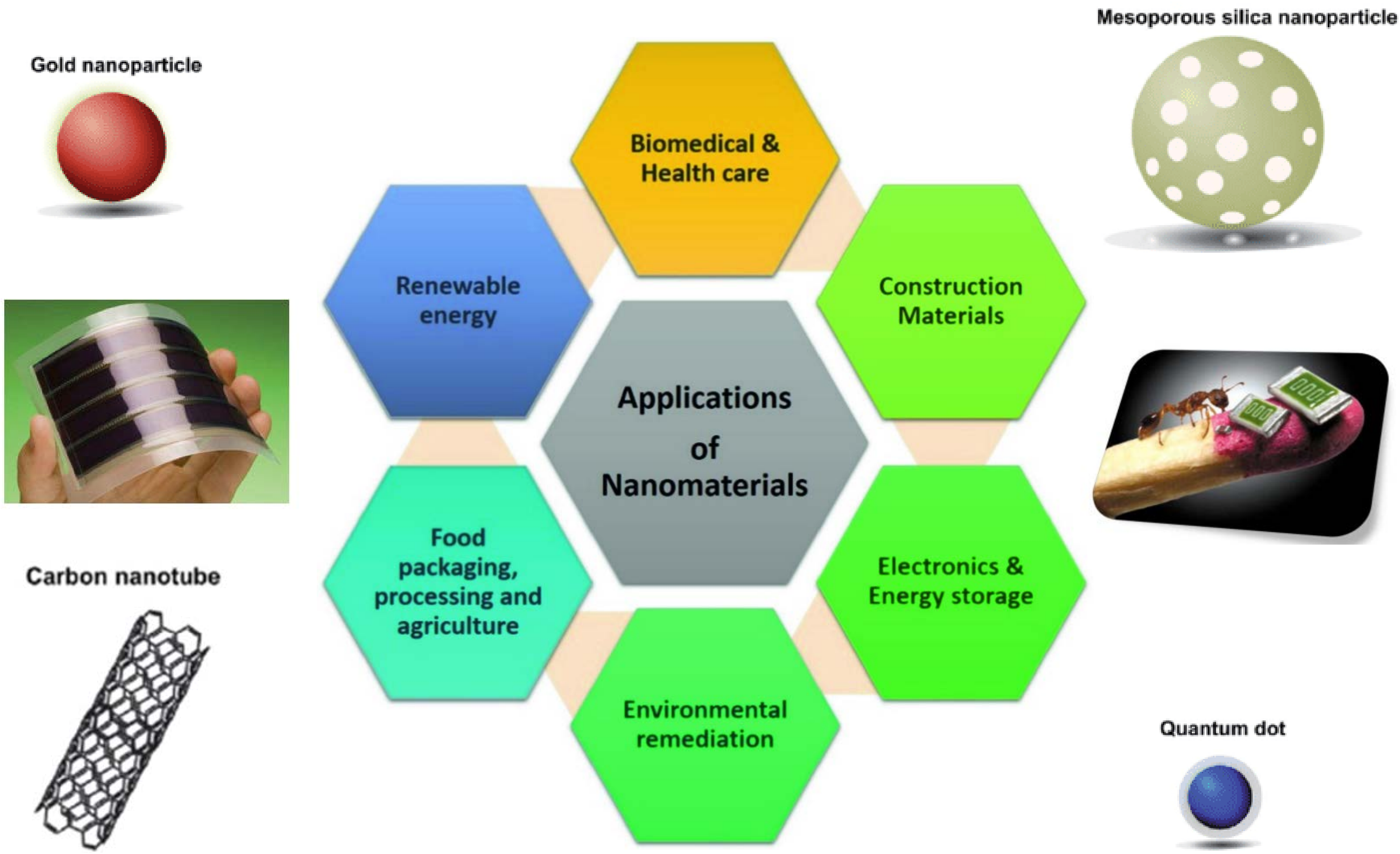
Richard Feynman

(Nobel Prize in Physics 1965)

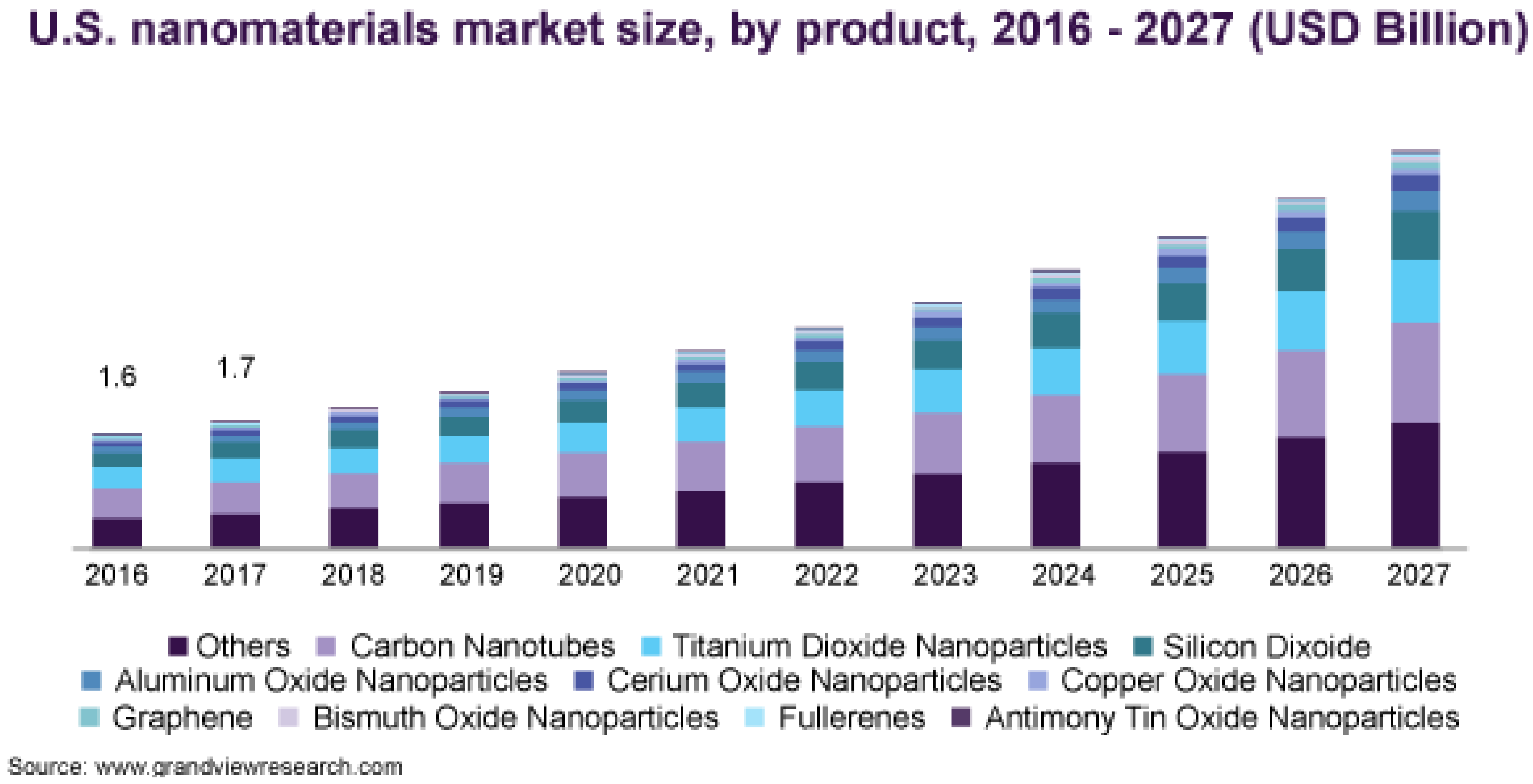
Norio Taniguchi

Coined the term «nano-technology» in 1974 referring to «ultra precision materials processing technologies»

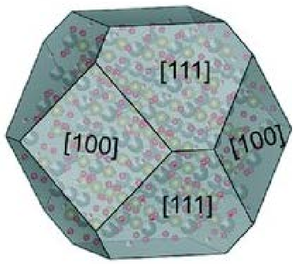
Nanomaterials applications

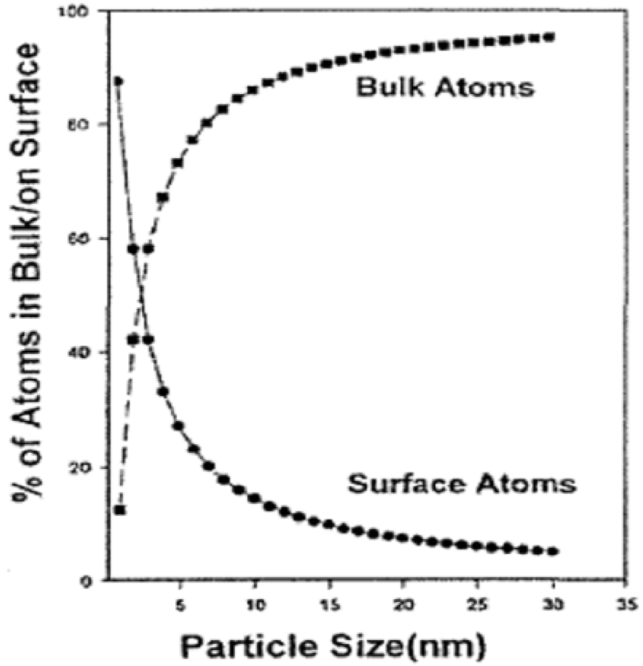


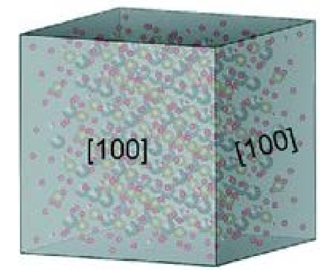
Nanomaterials market

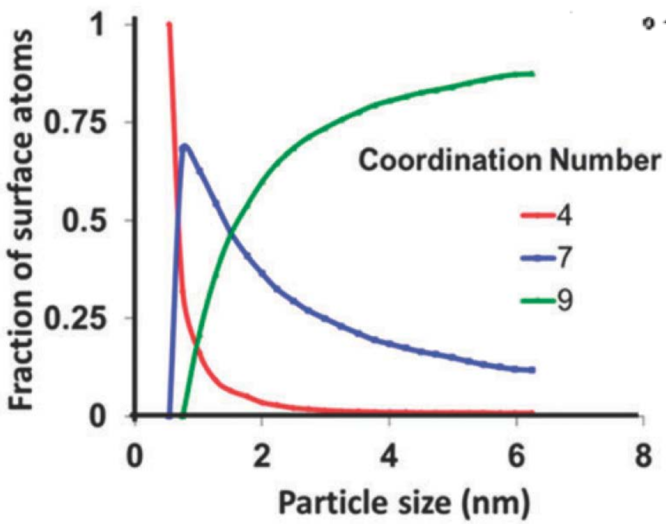


Nanomaterials properties

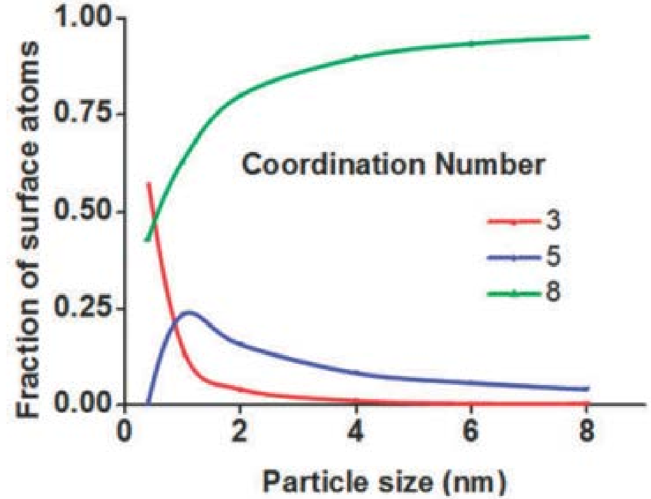








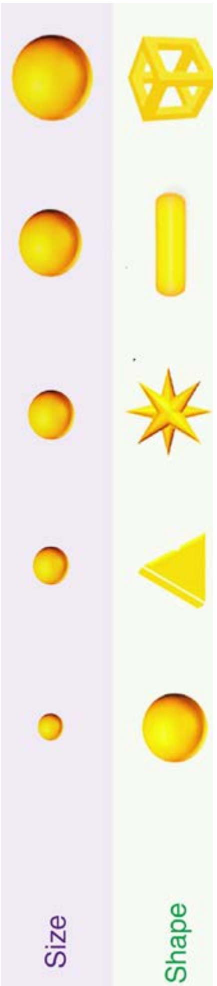
Catalytic activty is strongly shape and size dependent



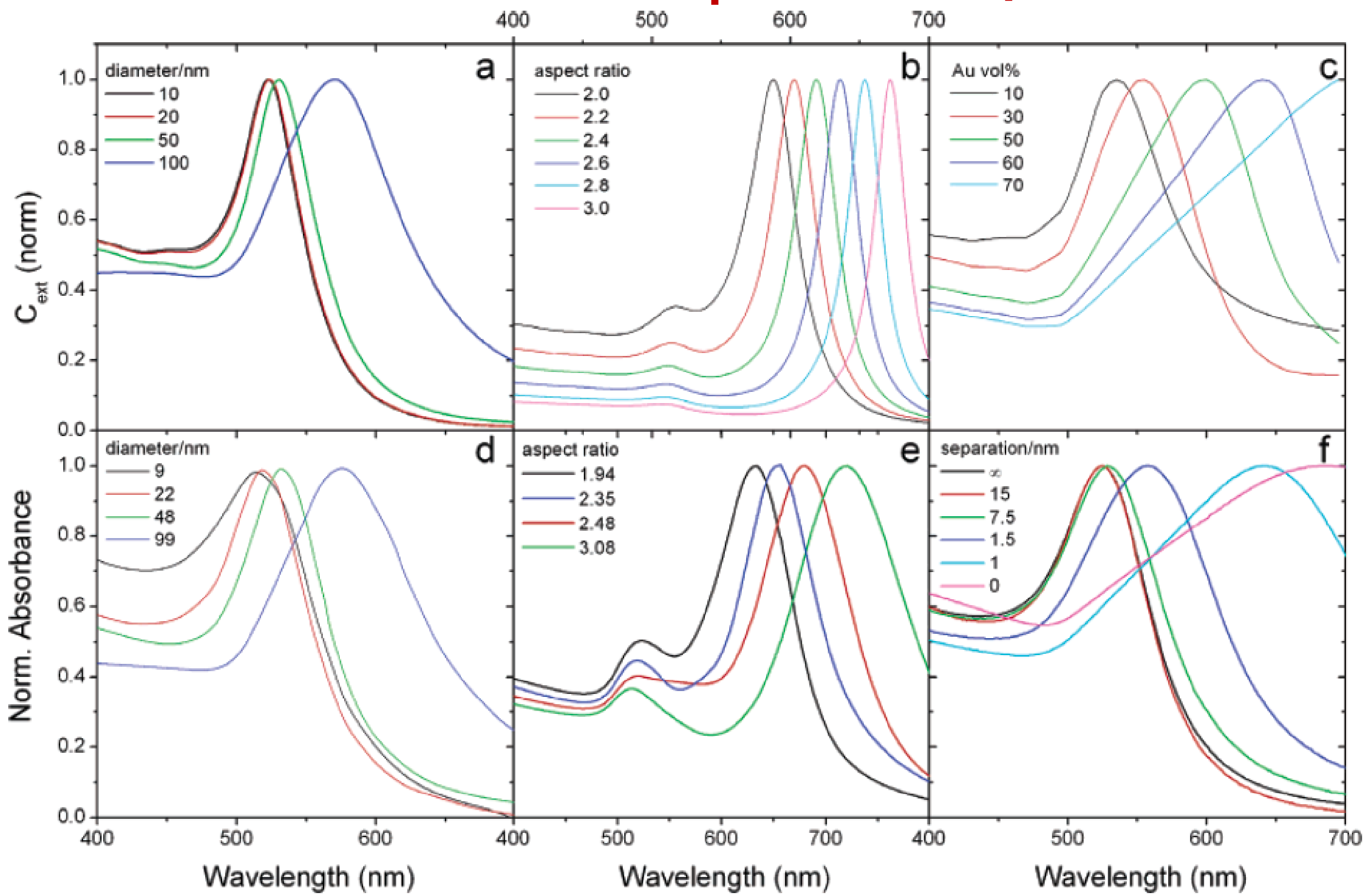
S.Cao et al., Chem. Soc. Rev., 2016, 45, 4747--4765

Nanomaterials properties

Au NPs optical properties

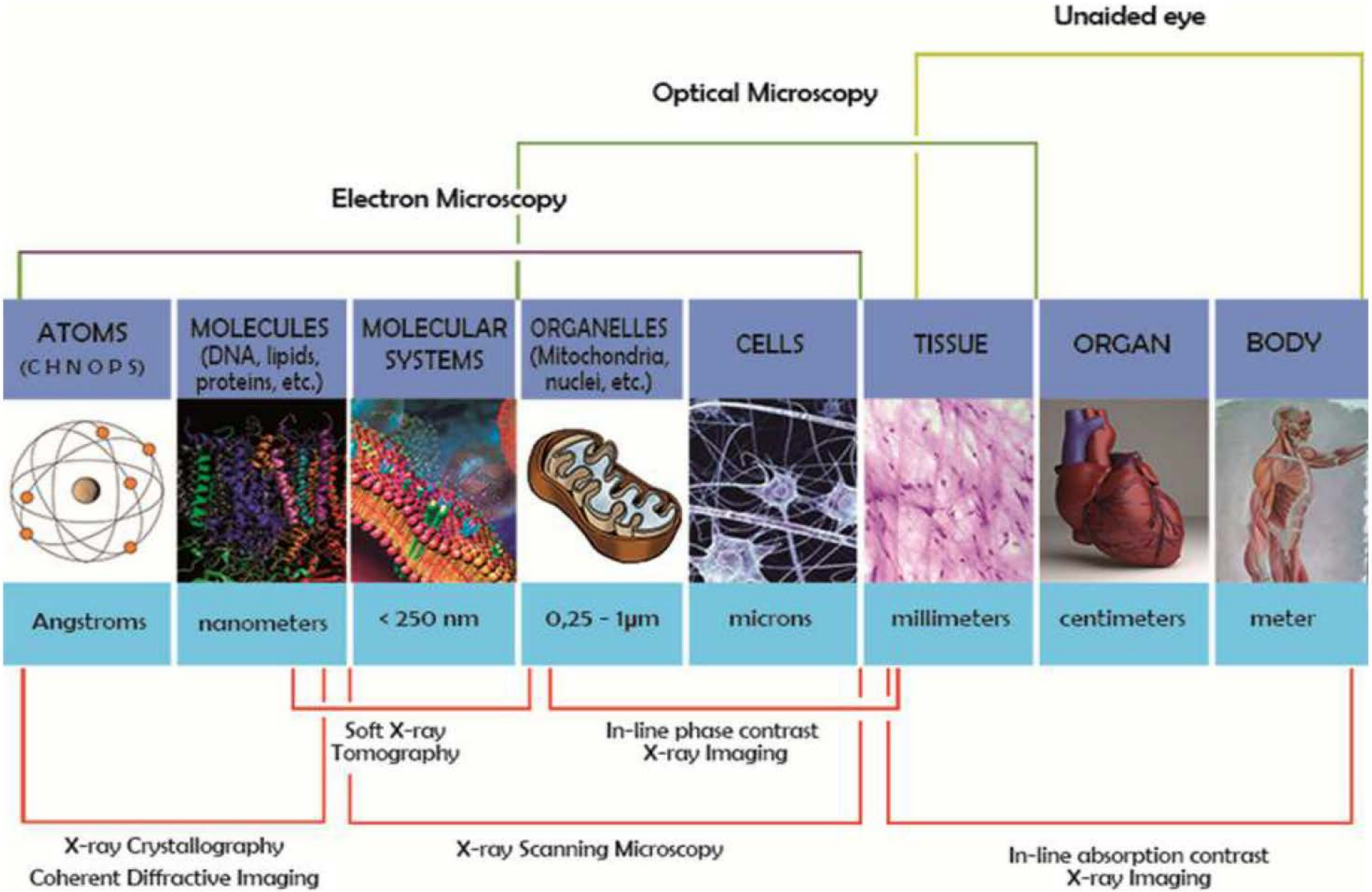


Size **Shape** **Interparticle distance**



Top: Calculated UV−visible spectra for (a) Au spheres with varying diameters, (b) Au ellipsoids of varying aspect ratio, and (c) thin glass films loaded with increasing Au nanoparticle volume fractions. Bottom: Experimental spectra for (d) Au spheres,[40] (e) Au nanorods, and (f) multilayer films of glass-coated Au spheres with varying interparticle distance.

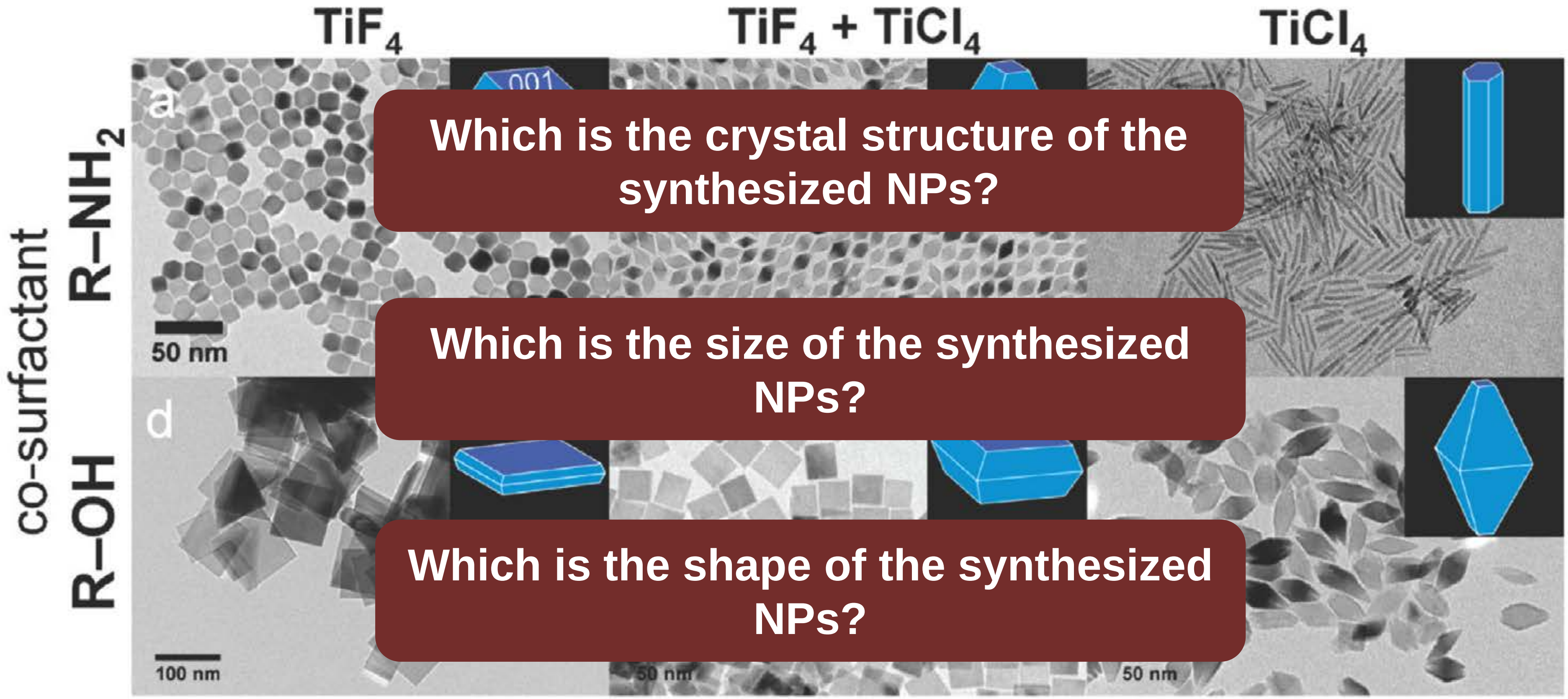
Probing different lenght scales



Let’s start with a simple case: nanoparticles…

X-ray techniques in nanoparticles characterization

TiO_2 nanoparticles



Which is the crystal structure of the synthesized NPs?

Which is the size of the synthesized NPs?

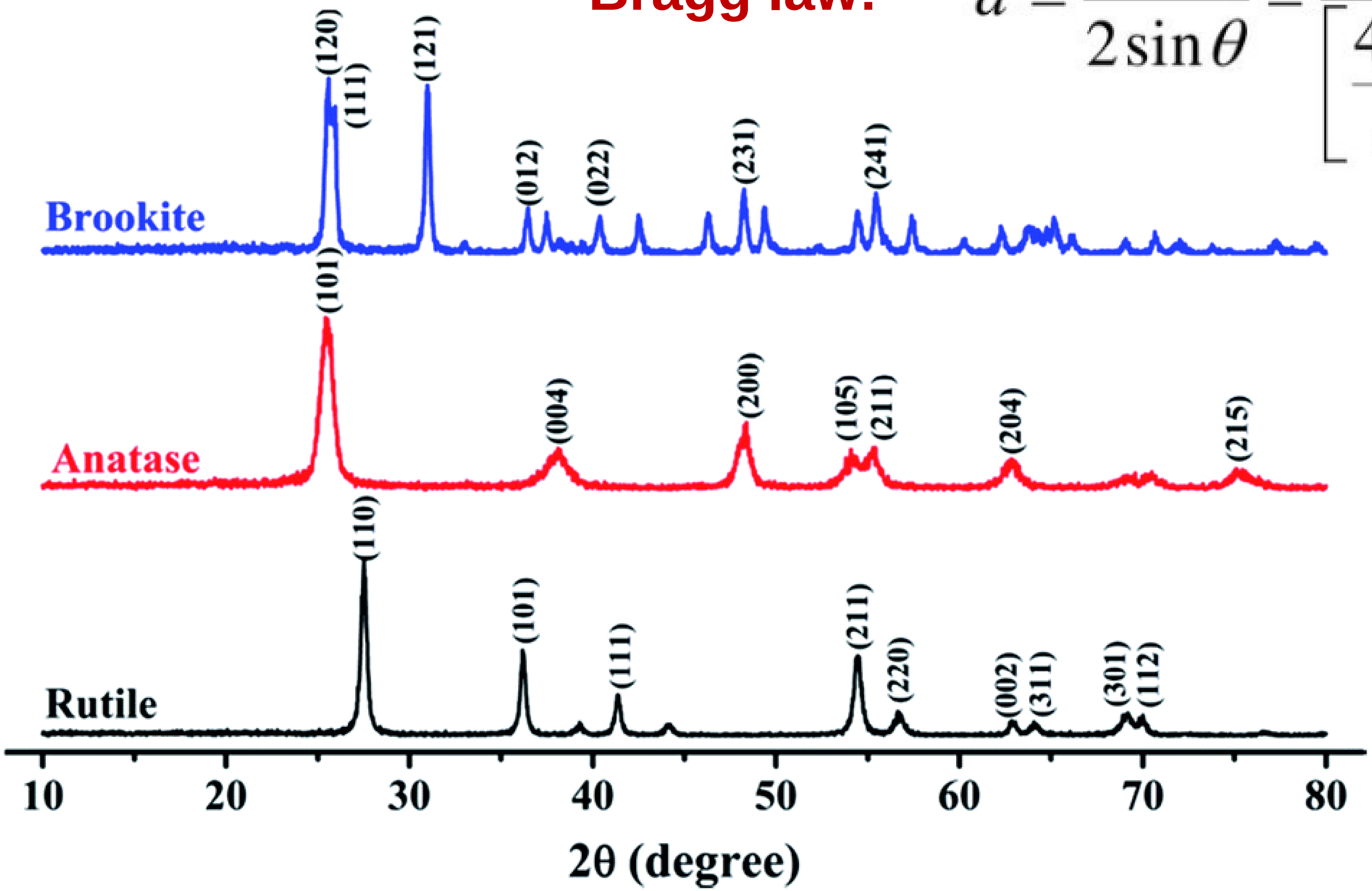
Which is the shape of the synthesized NPs?

T.. Gordon et al., J. Am. Chem. Soc. 2012, 134, 6751 − 6761

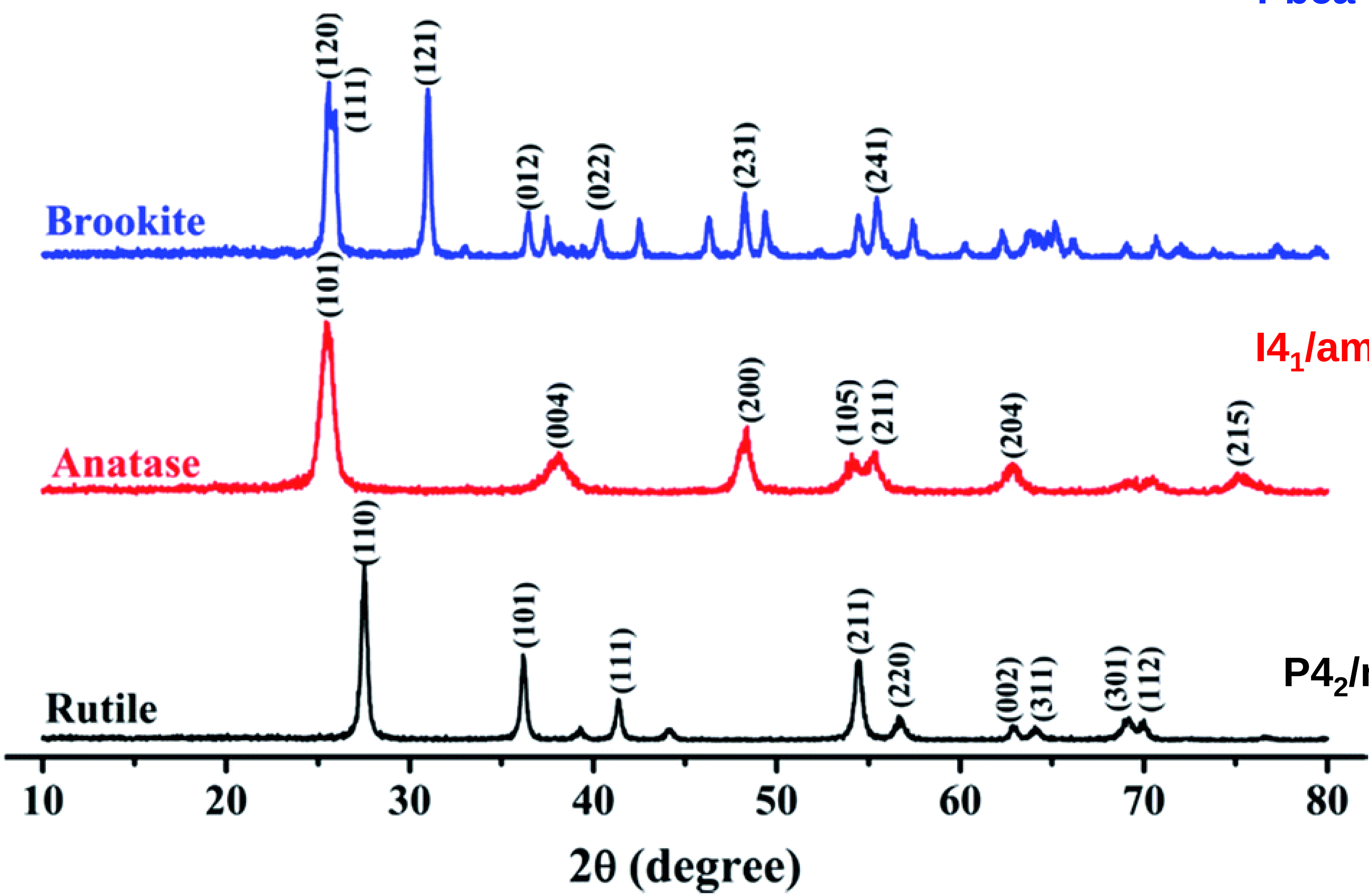
Which is the NPs crystal structure?

Bragg law:

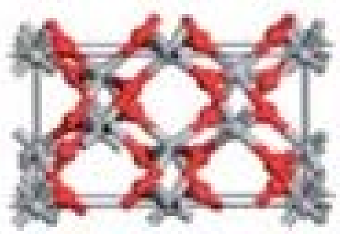
$$d = \frac{\lambda}{2\sin\theta} = \frac{2\pi}{\left[\frac{4\pi}{\lambda}\right]\sin\theta} = \frac{2\pi}{q}$$



Which is the NPs crystal structure?

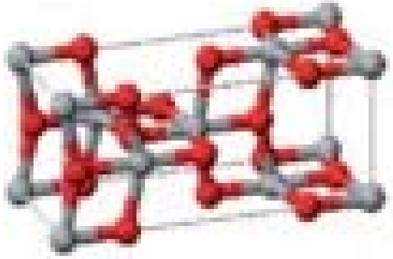


Pbca



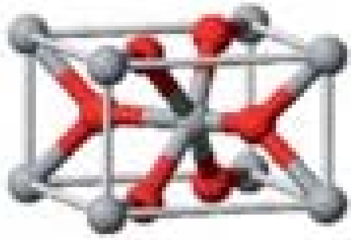
a = 5.455 Å
b = 9.181 Å
c = 5.142 Å

$I4_1/amd$



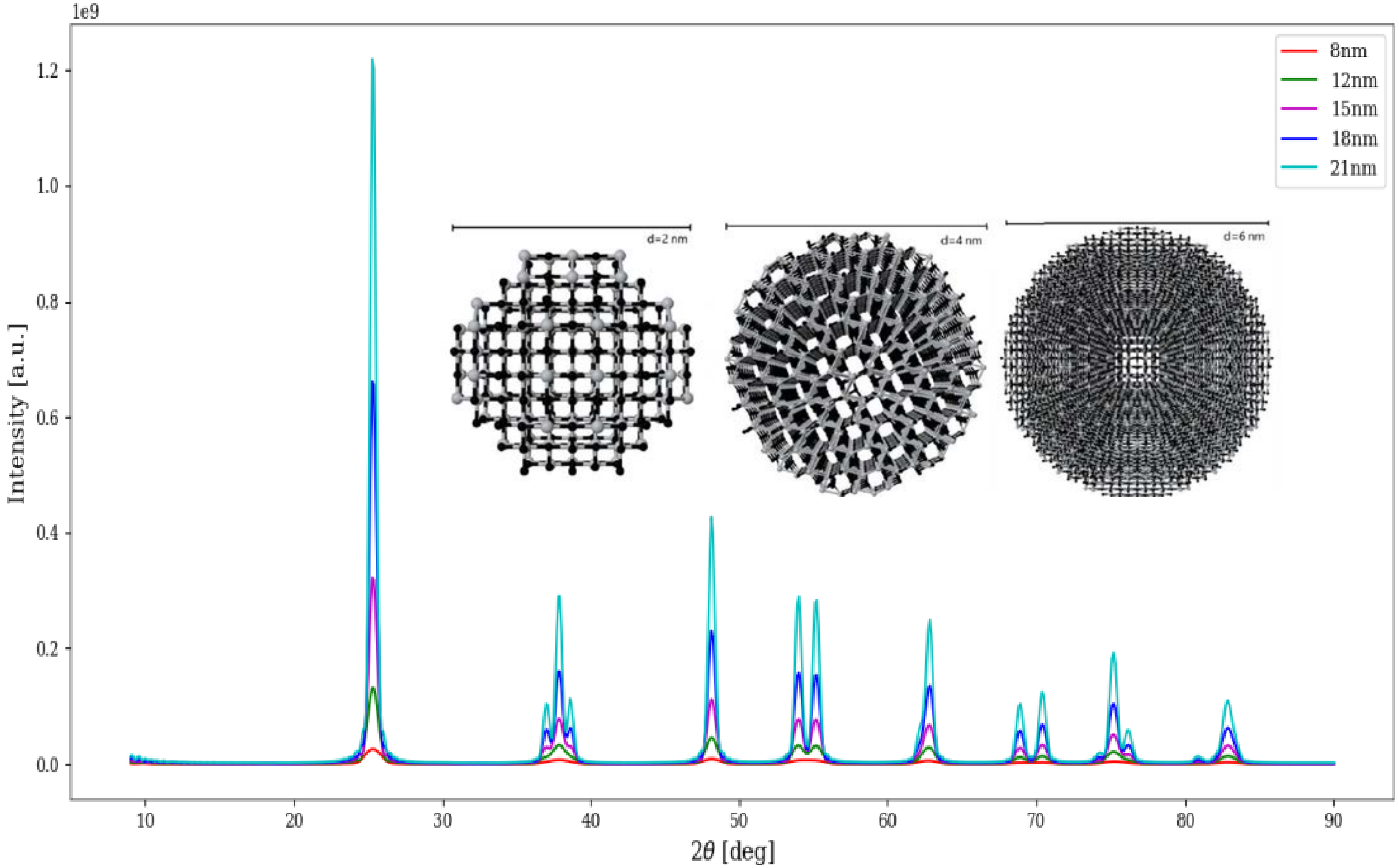
a = b = 3.785 Å
c = 9.512 Å

$P4_2/mnm$



a = b = 4.593 Å
c = 2.959 Å

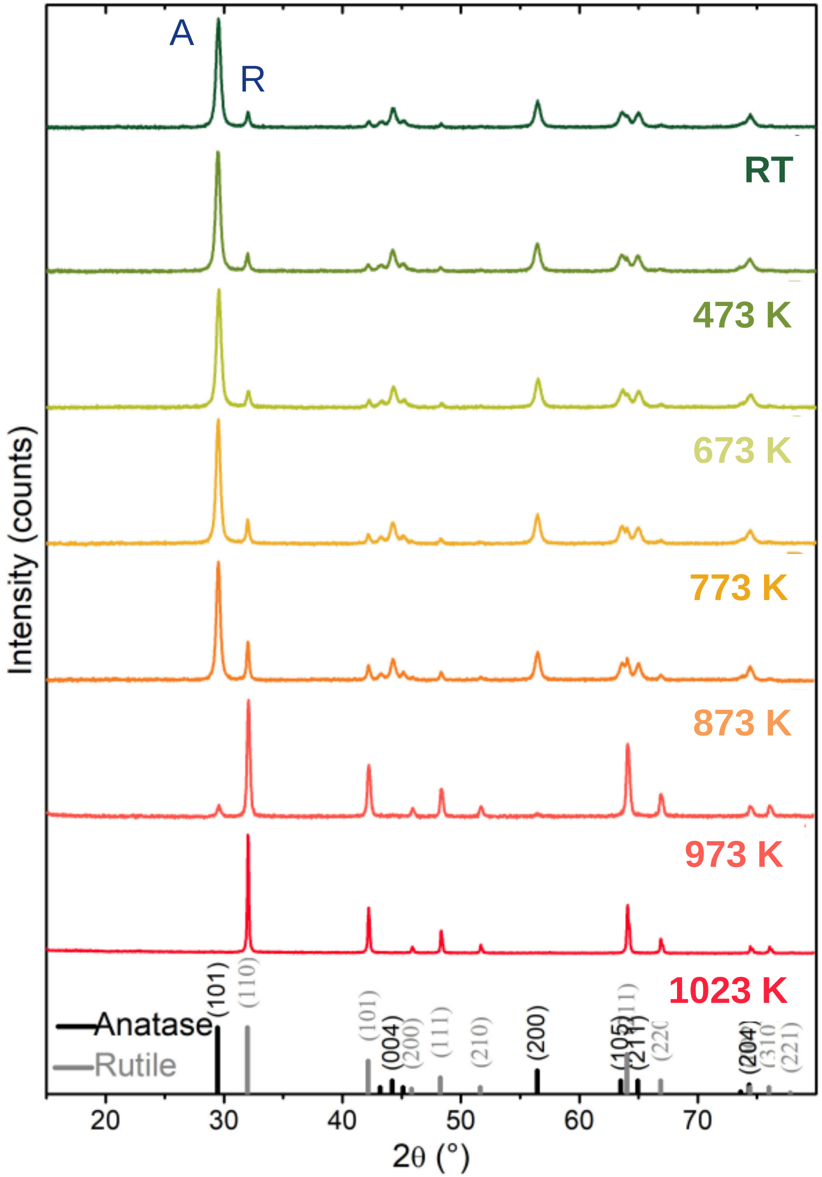
Which is the NPs size?



Scherrer equation:

$$L = \frac{K\lambda}{(\beta_{exp} - \beta_{strum})\cos\theta}$$

Monitoring NP sintering and phase transitions

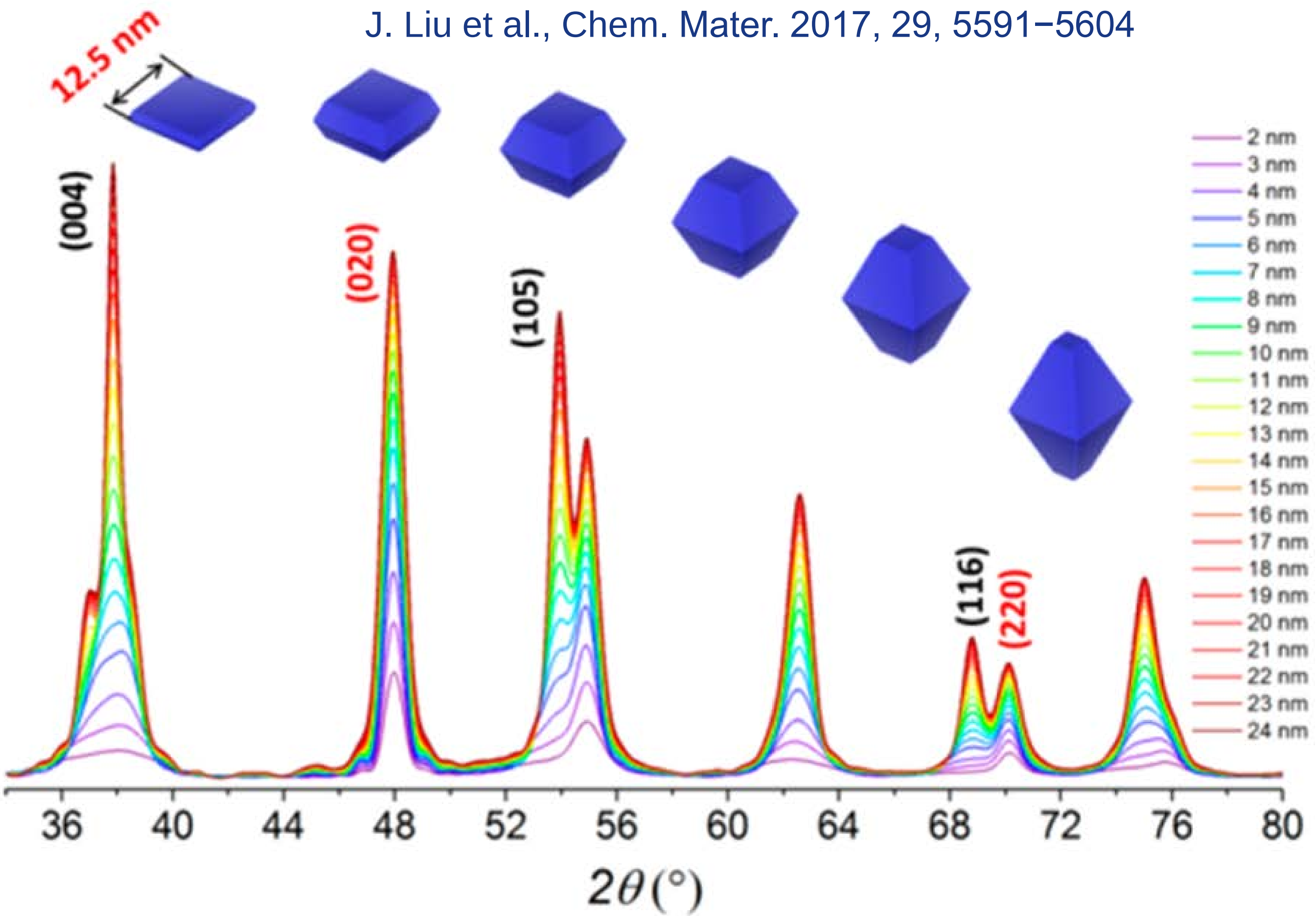


Temperature of treatments[a]	Phase composition[b]		Crystallite sizes[c]	
	Anatase (wt%)	Rutile (wt%)	Anatase (nm)	Rutile (nm)
RT	83	17	28	47
473 K	83	17	28	47
673 K	83	17	28	47
773 K	80	20	33	56
873 K	59	41	35	60
973 K	7	93	48	62
1,023 K		100		237

M. J. Uddin et al., Front. Mater. 2020, 7, 192.

Which is the NPs shape?

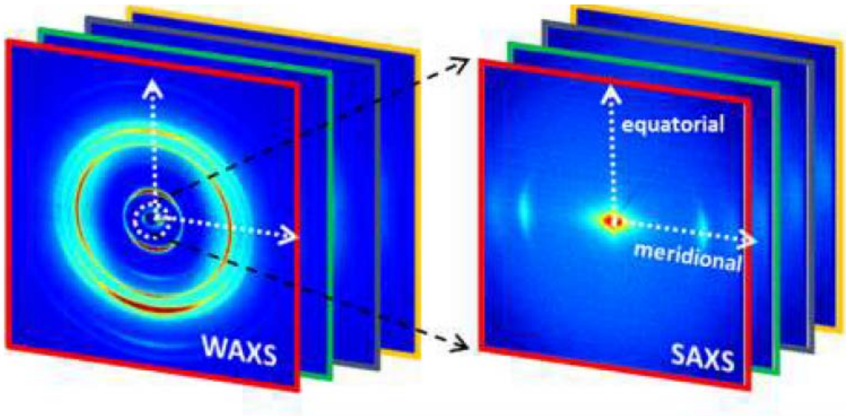
J. Liu et al., Chem. Mater. 2017, 29, 5591−5604



The relative intensity and FWHM of the XRD peaks depends on the NPs shape

Small angle X-ray scattering (SAXS)

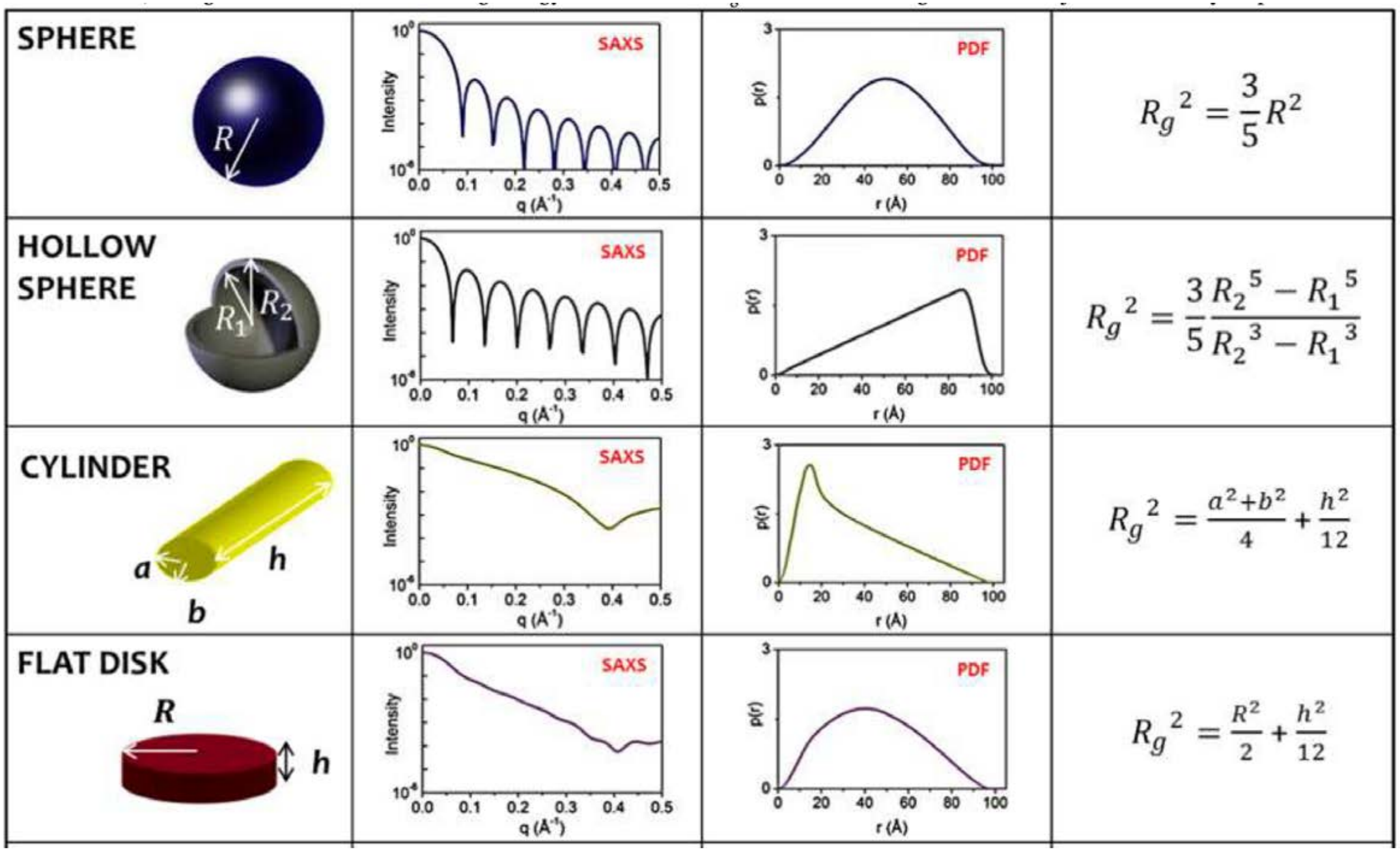
Technique	d (nm)	q (nm^{-1})	q ($Å^{-1}$)	θ(deg) for λ=1.5405Å
SAXS/SAXD	100	0.063	0.0063	0.044
SAXS/SAXD	10	0.63	0.063	0.44
WAXS/WAXD	1	6.3	0.63	4.4
WAXS/WAXD	0.1	63	6.3	50.6



$$d = \frac{\lambda}{2\sin\theta} = \frac{2\pi}{\left[\frac{4\pi}{\lambda}\right]\sin\theta} = \frac{2\pi}{q}$$

C. Giannini et al., Prog. Mater. Sci. 2020, 112, 100667

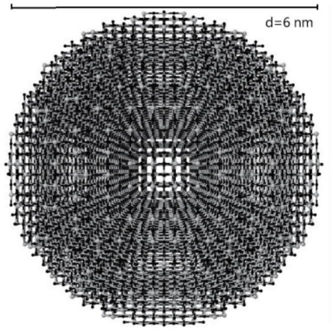
SAXS: shape and size



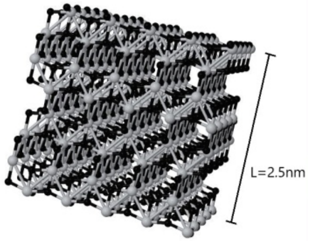
The gyration radius (R_g) can be linked to the main dimensions of the object

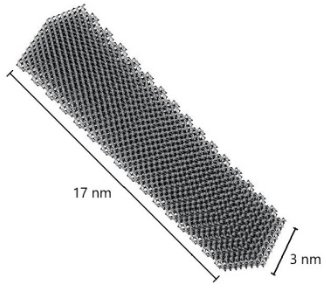
C. Giannini et al., Prog. Mater. Sci. 2020, 112, 100667

The Debye scattering equation



$$I(q) = I_0 \sum_m \sum_n F_m F_n \frac{\sin(q r_{mn})}{q r_{mn}}$$

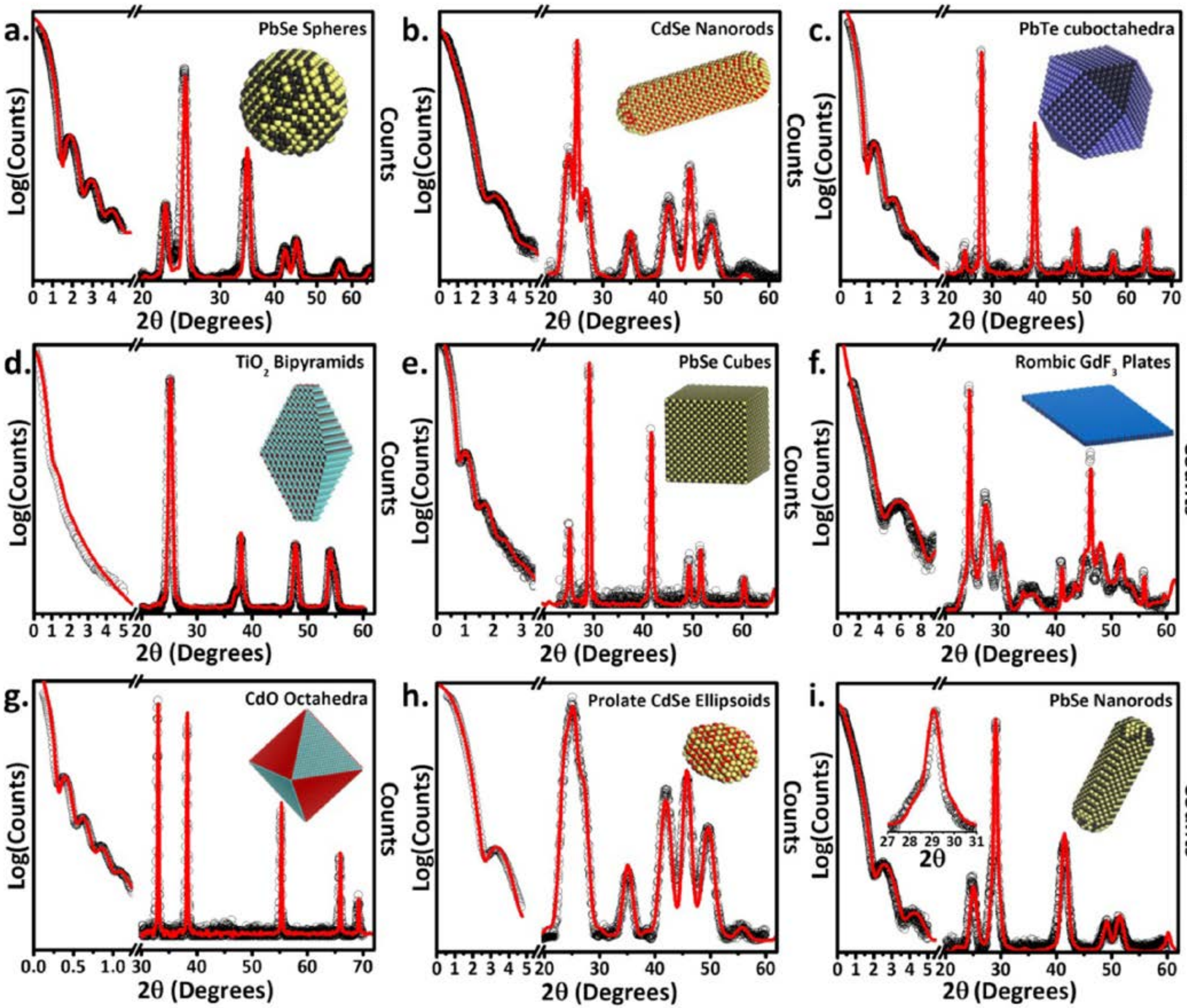




r_{mn} is the distance between atoms m and n, with atomic form factors F_m and F_n,

The Debye approach holds for both small and wide angle scattering data, and it is applicable to crystalline, partially crystalline and amorphous samples.

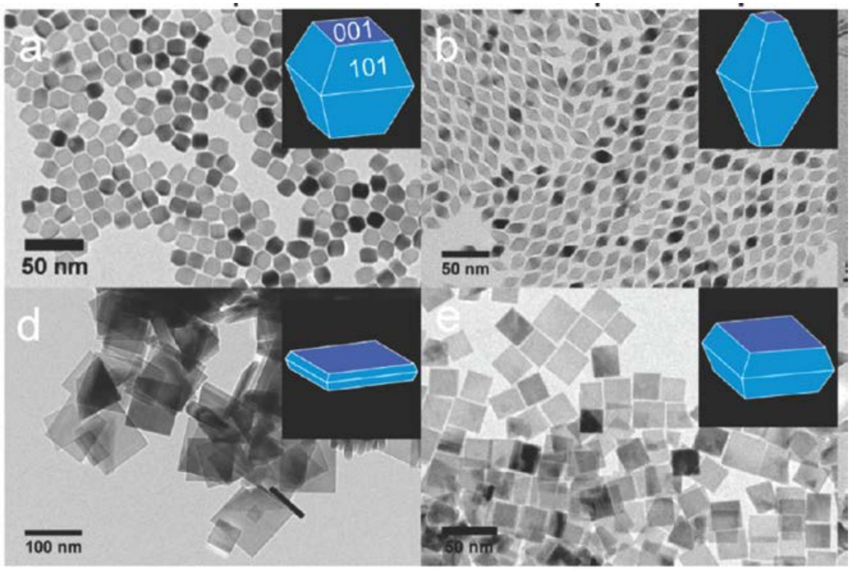
Combining SAXS and WAXS



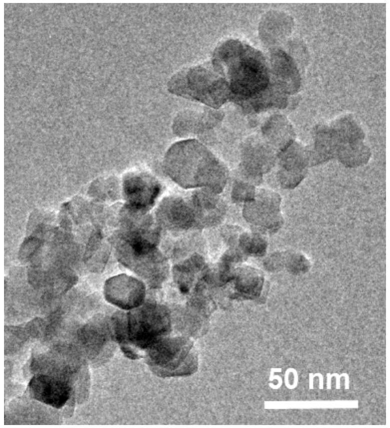
T. Gordon et al., Chem. Mater. 2015, 27, 2502−2506

Why X-rays and not electron microscopy?

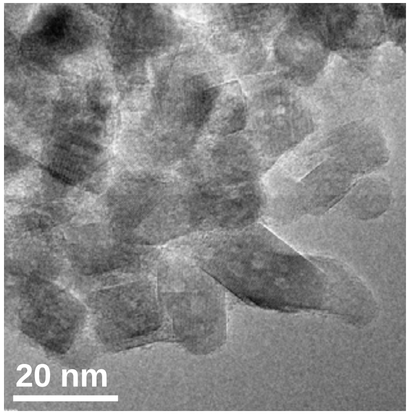
Shape-controlled NPs



Industrial commercial NPs



TiO_2 P25 (Evonik)



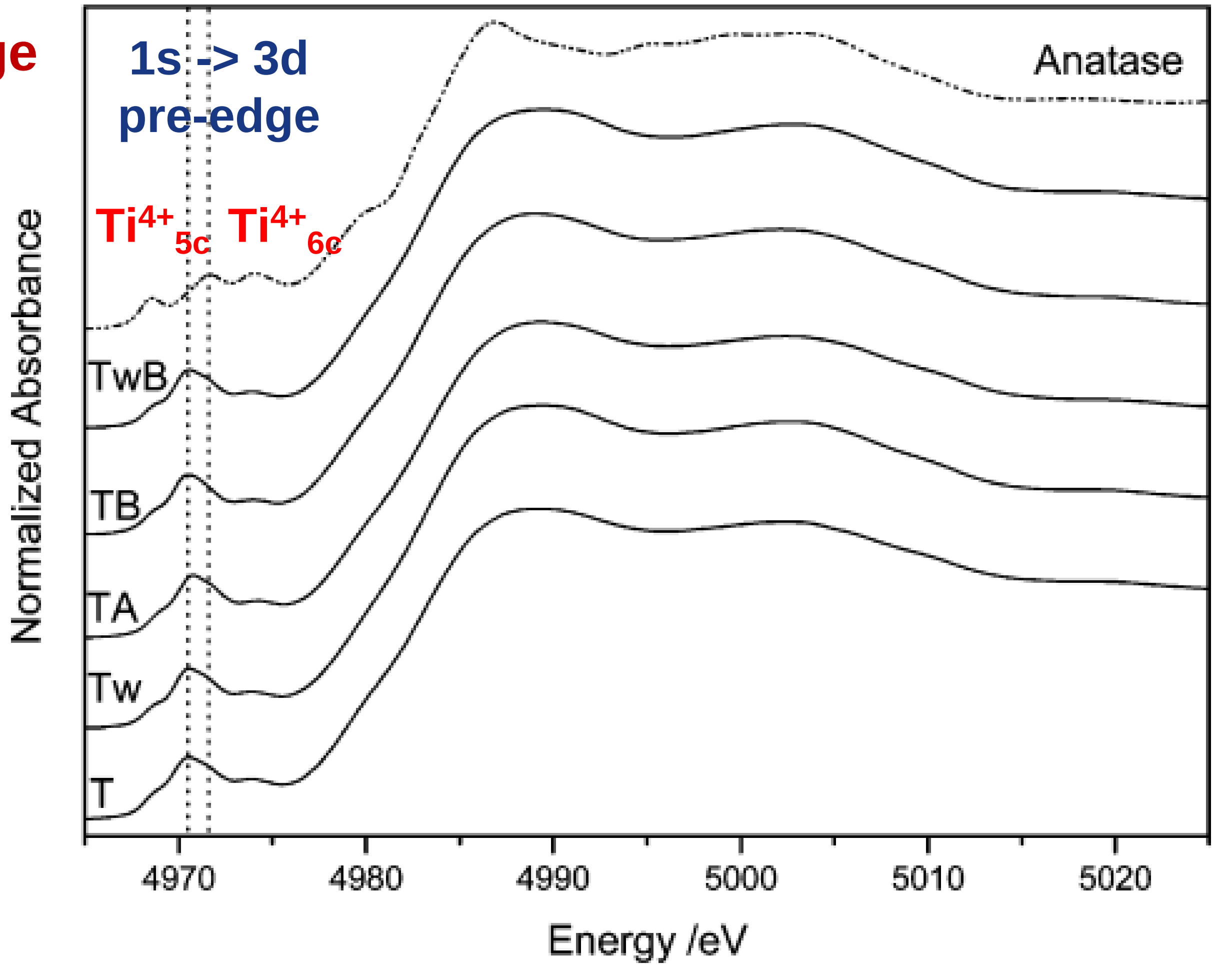
TiO_2 T-SP (Solaronix)

In «real» commercial samples the NPs heterogeneity often makes the extraction of statistically significant information from TEM images laborious and subject to bias

Combining scattering and spectroscopy

Study ot the crystallization process from amorphous TiO_2 to anatase

Ti K-edge XAS

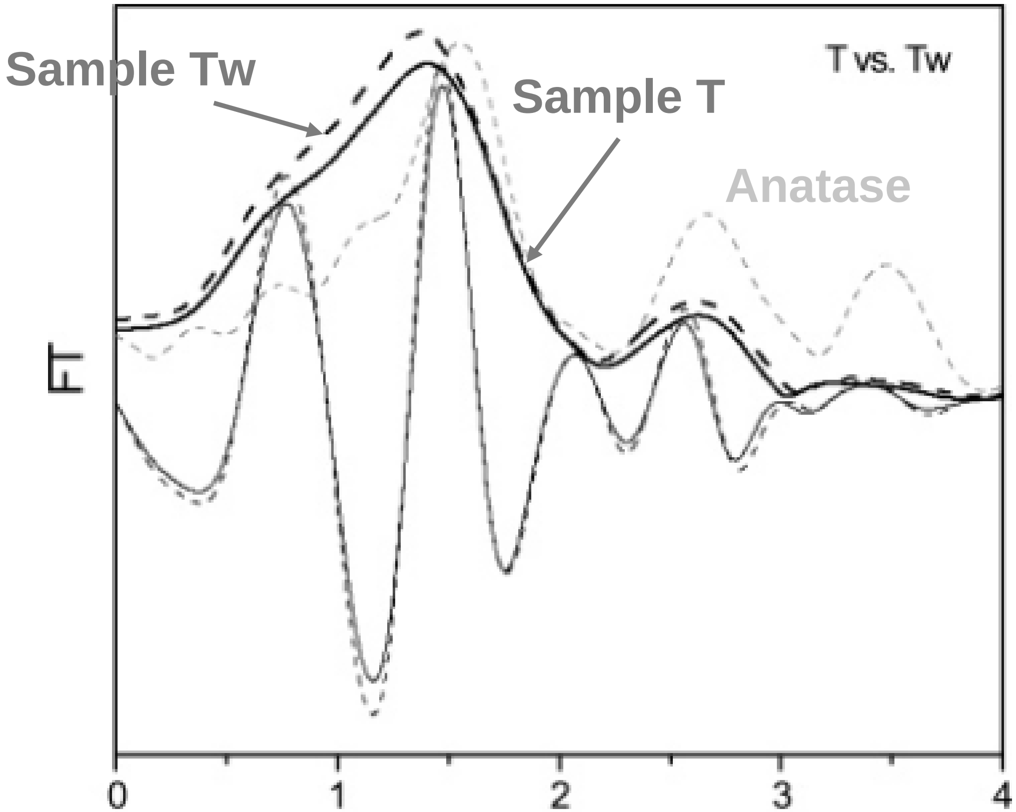


M. Fernandez-Garcia et al., J. Am. Chem. Soc. 2007, 129, 13604 - 13612

XANES highlights the presence of Ti^{4+}_{5c} in amorphous TiO_2.

Ti K-edge EXAFS analysis

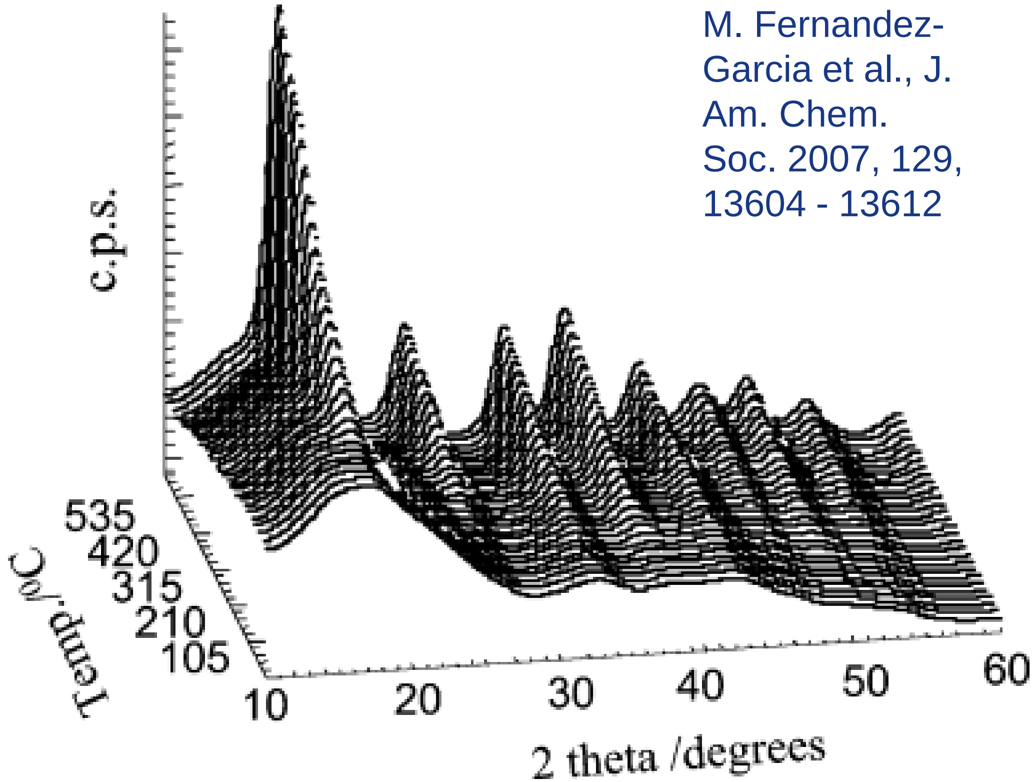
M. Fernandez-Garcia et al., J. Am. Chem. Soc. 2007, 129, 13604 - 13612



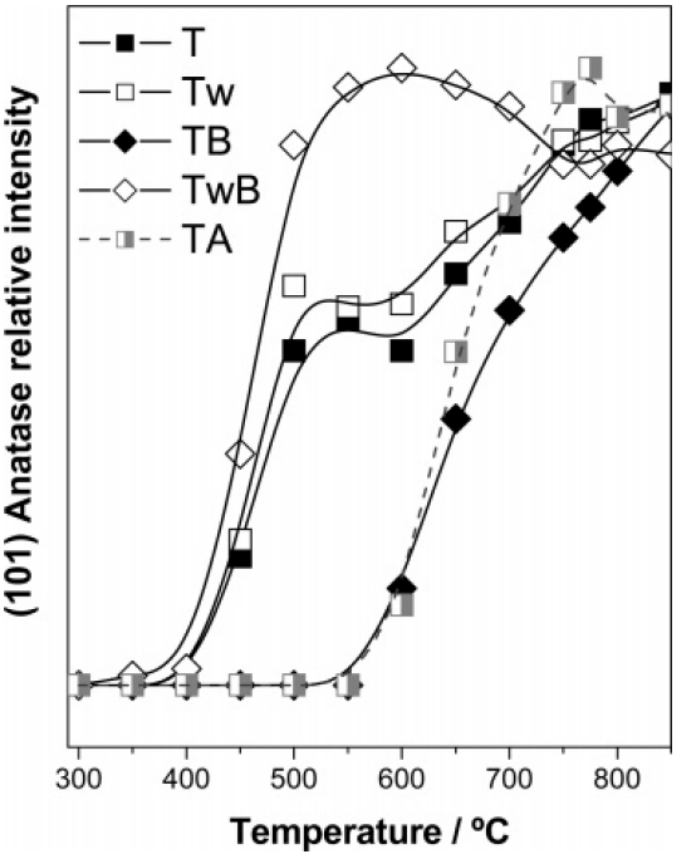
shell	N	R/Å	$\Delta\sigma/10^3 \times$ Å^2
		T; 7.7%[a]	
Ti−O	$1.2_5 \pm 0.3_5$	1.72 ± 0.02	10.1 ± 0.4
Ti−O	5.1 ± 0.6	1.91 ± 0.01	7.5 ± 0.7
Ti−Ti	1.9 ± 0.3	3.02 ± 0.01	2.0 ± 0.6
		Tw; 8.9%	
Ti−O	$1.4_5 \pm 0.4$	1.73 ± 0.02	9.0 ± 0.5
Ti−O	5.3 ± 0.7	1.90 ± 0.01	8.5 ± 0.6
Ti−Ti	2.2 ± 0.3	3.03 ± 0.01	1.7 ± 0.6
		TA, 11.1%	
Ti−O	$1.2_5 \pm 0.3_5$	1.72 ± 0.02	9.5 ± 0.3
Ti−O	5.0 ± 0.7	1.90 ± 0.01	7.0 ± 0.7
Ti−Ti	$2.3 \pm 0.3_5$	3.04 ± 0.01	1.5 ± 0.8
		TB; 8.7%	
Ti−O	1.3 ± 0.3	1.72 ± 0.02	9.0 ± 0.3
Ti−O	5.1 ± 0.7	1.90 ± 0.01	7.0 ± 0.5
Ti−Ti	2.2 ± 0.3	3.02 ± 0.01	2.4 ± 0.8
		TwB; 5.7%	
Ti−O	$1.4 \pm 0.3_5$	1.74 ± 0.02	9.1 ± 0.4
Ti−O	5.3 ± 0.7	1.92 ± 0.01	8.0 ± 0.4
Ti−Ti	2.6 ± 0.3	3.05 ± 0.01	1.0 ± 0.9

Low Ti - Ti coordination numbers (for crystalline anatase CN = 4) suggests that Ti cations have a severely restricted 3D connectivity in all samples.

In situ XRD patterns during heating



M. Fernandez-Garcia et al., J. Am. Chem. Soc. 2007, 129, 13604 - 13612

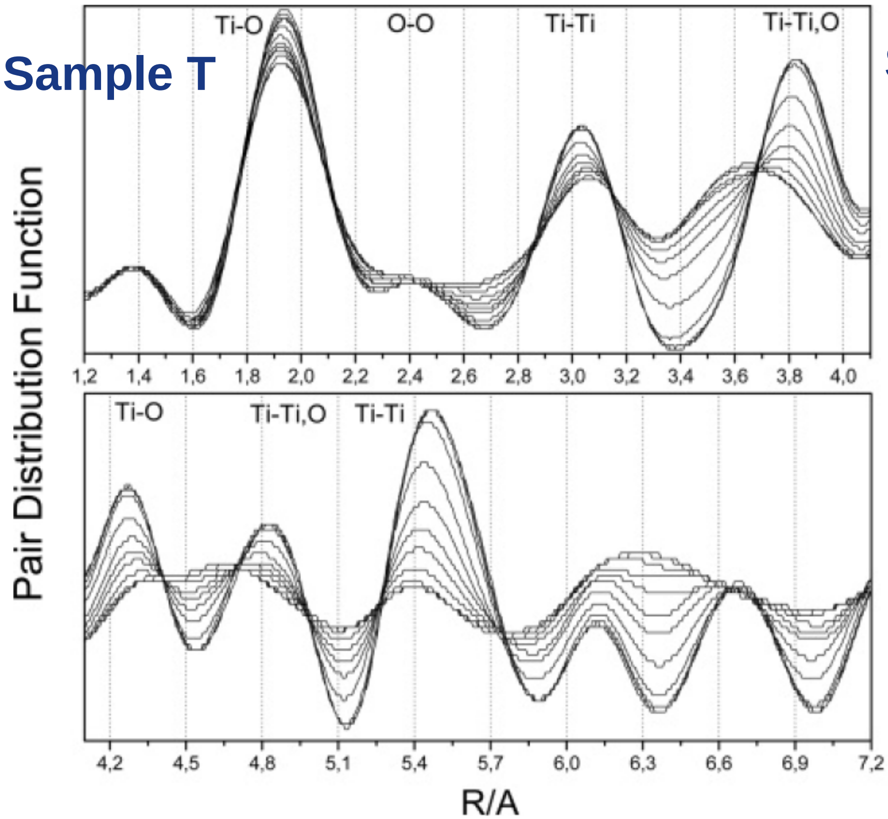


Upon heating in dry air, samples T, Tw, and TwB nucleate around 350 - 400 ˚C, samples TA and TB nucleate around 550 ˚C

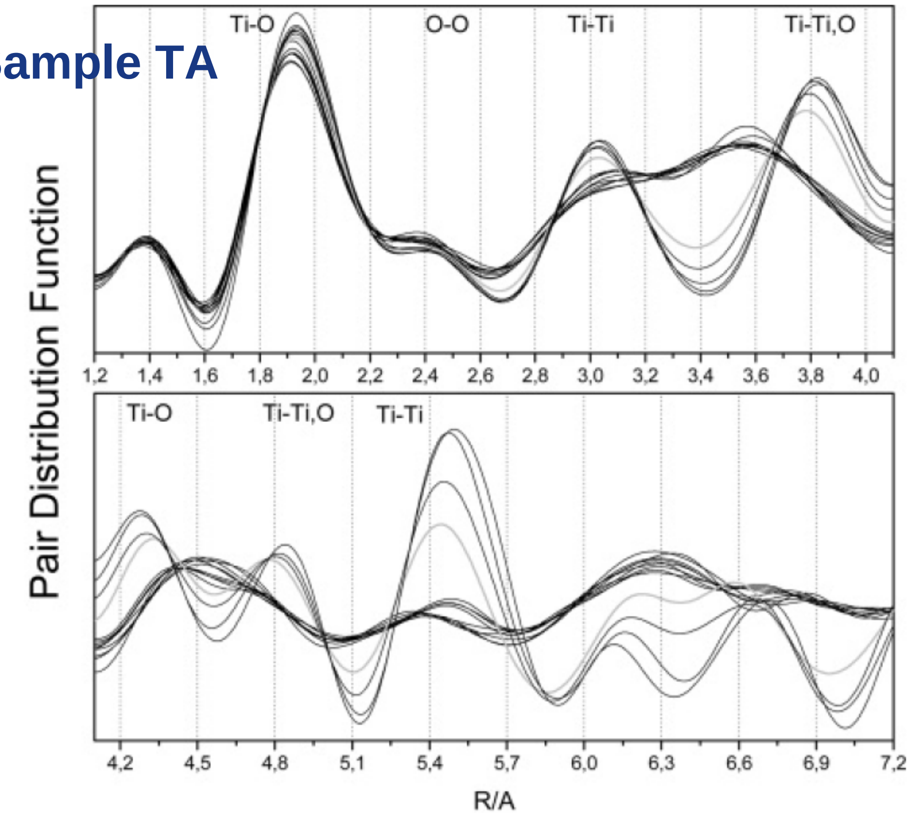
Monitoring crystallization by PDF

PDF obtained during heating in dry air in step of 50 ˚C

Sample T



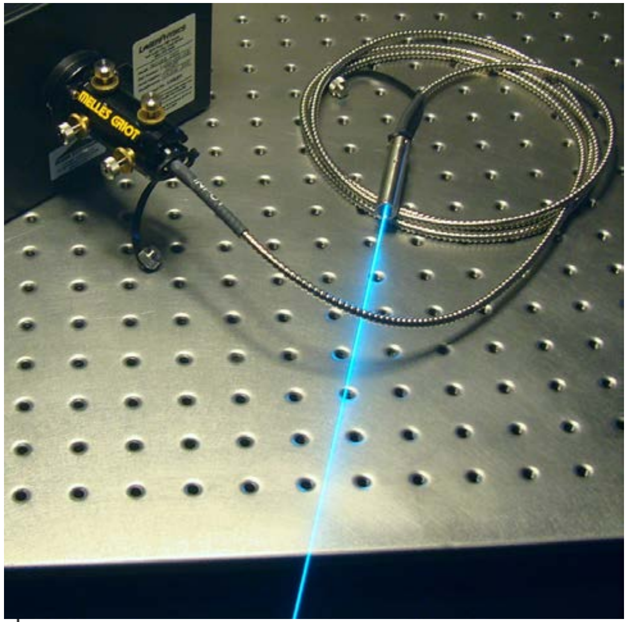
Sample TA



Crystallization onset temperature is clearly related to the local middle range order (3 - 4 Å) of the different samples

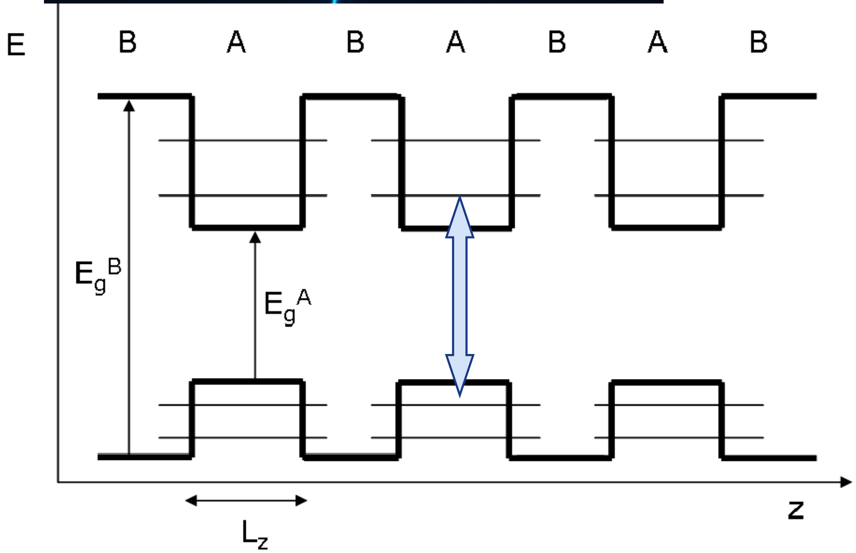
Let’s jump to a more complex case: real devices…

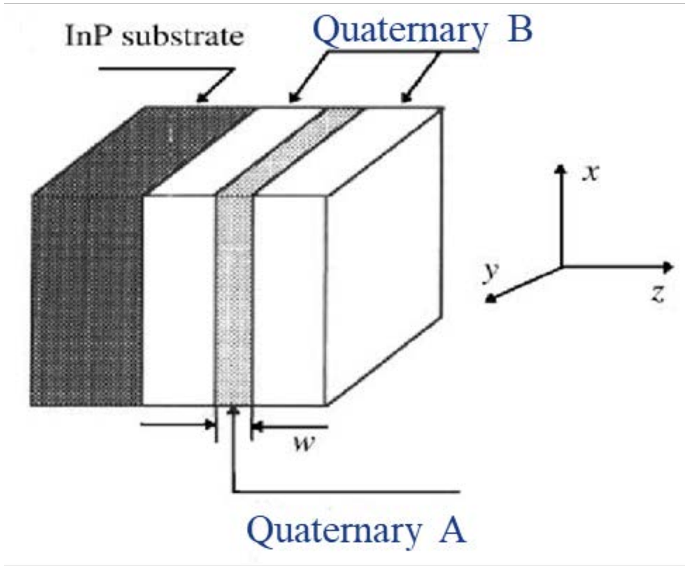
Nanostructured device characterization



Semiconductor nanostructures to realize lasers and modulators for fiber-optics communications

Both laser and modulator are $In_xGa_yAl_{1-x-y}As$ multi quantum well (MQW) heterostructures grown on InP(001)



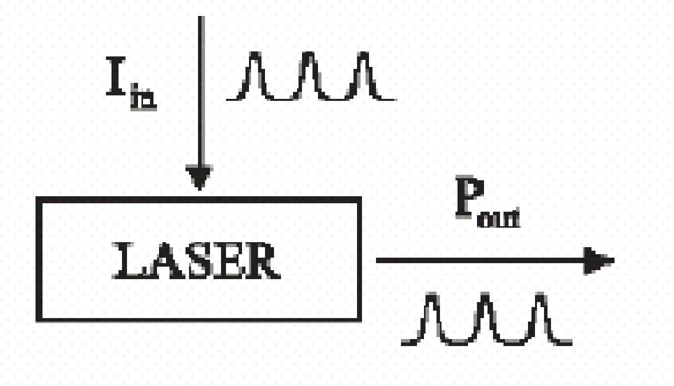


Signal modulation for fiber-optic communication

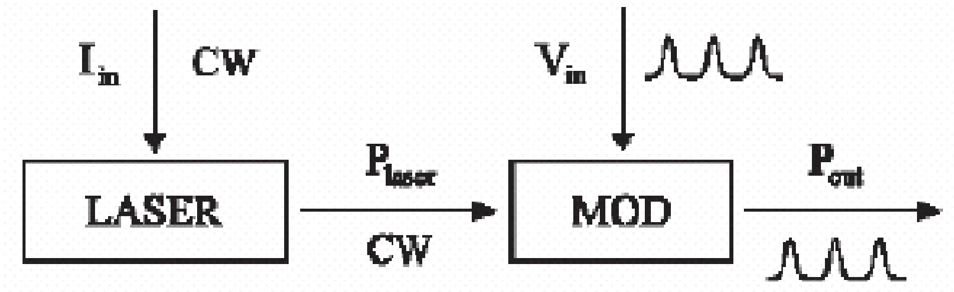
The signal can be modulated in two different ways:

- **Direct**: modulating the laser current

non equilibrium in the charge carriers causes frequency shifts in the emitted radiation

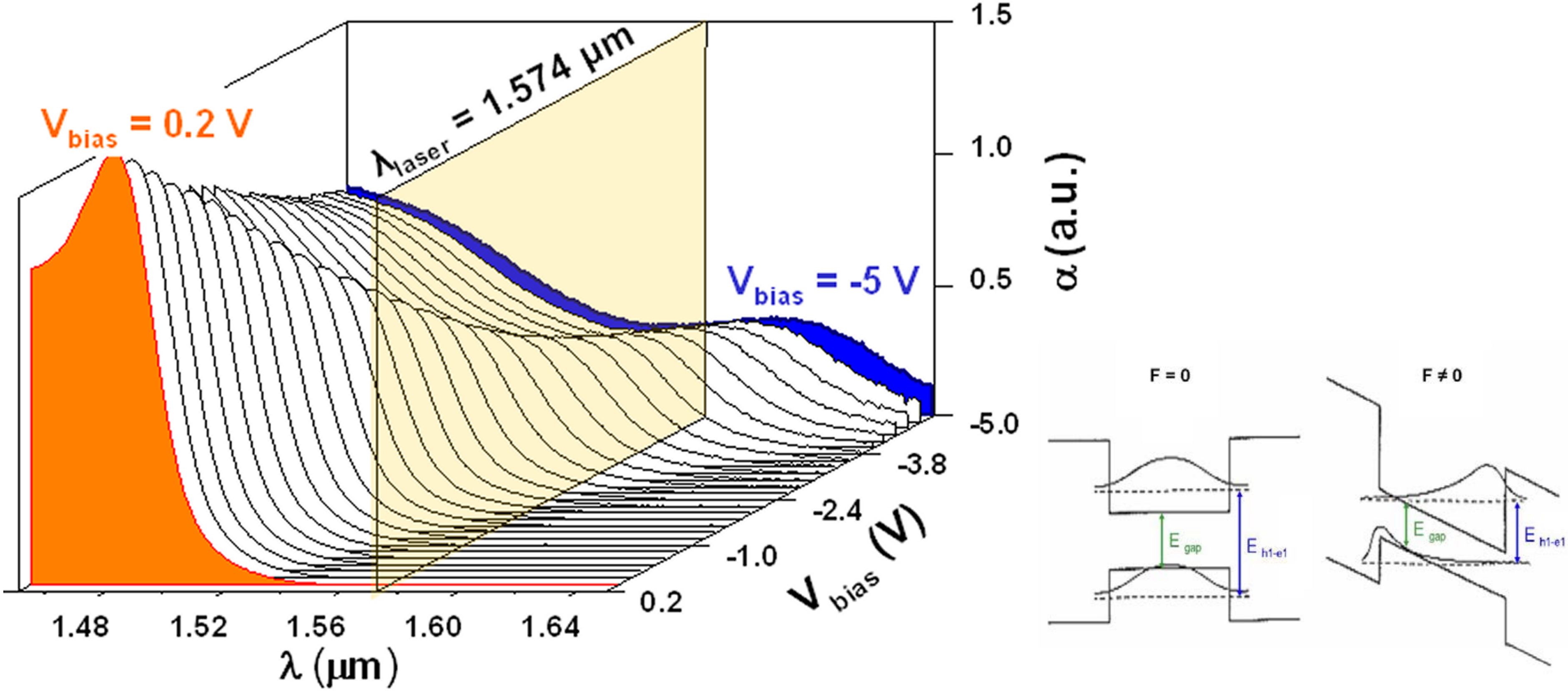


- **External:** two different devices act as laser source and signal modulator



both the frequency (Gbit/s) and transmission lengths are improved

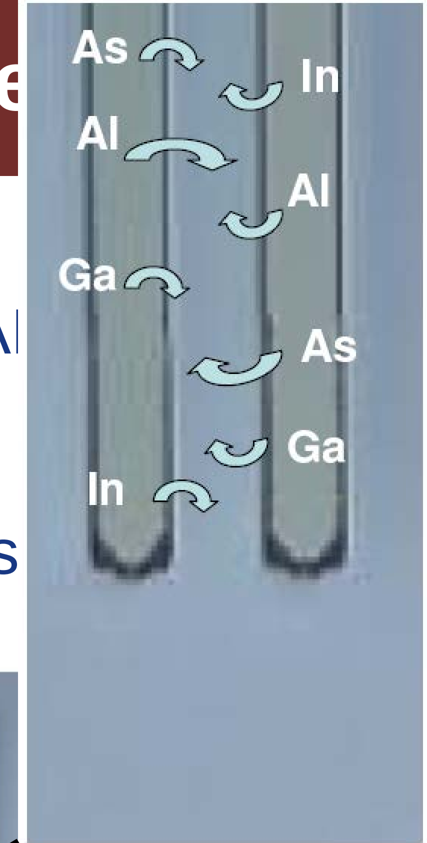
Electro-absorption modulator (EAM)



L. Mino et al., Small 2011, 7, 930-938

A suitable voltage switches the EAM from transparent to opaque (Stark effect)

Modulator (EAM)- DFB laser inte



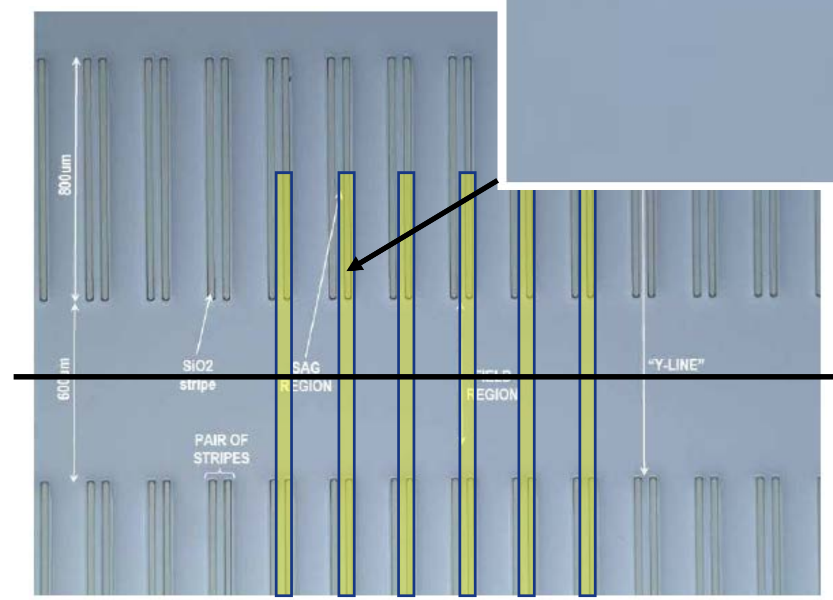
Monolithic integration of the laser and the EA

⇩

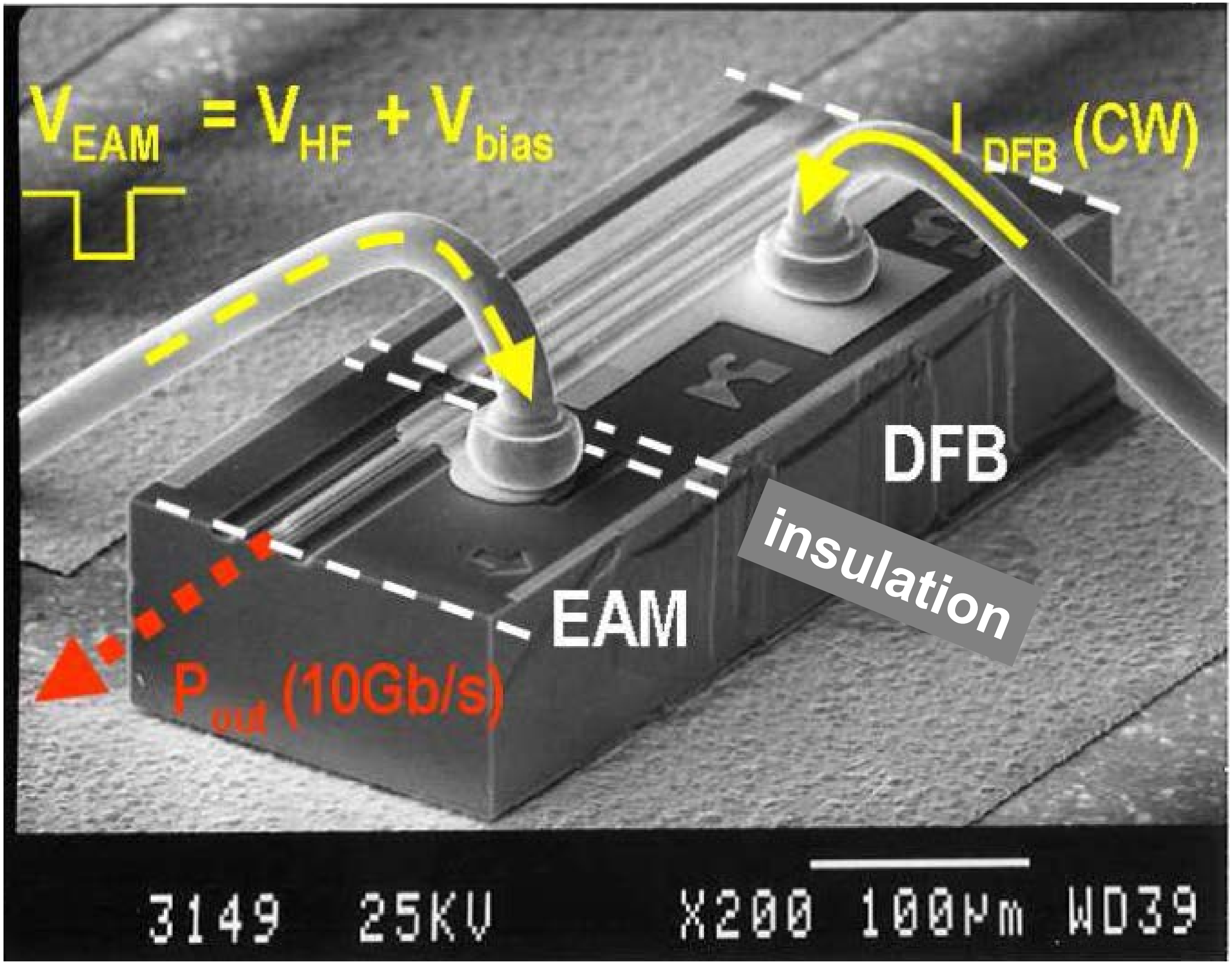
Selective Area Growth (SAG): a SiO_2 mas
the precursors flux

⇩

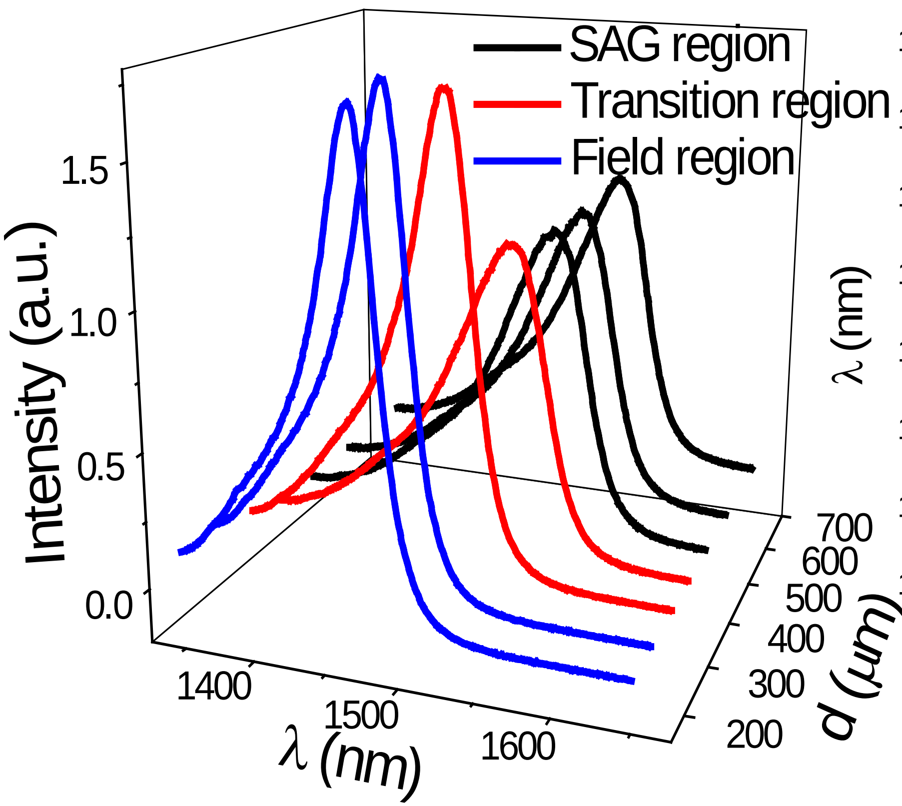
variation in composition and thickness of the material grown between the SiO_2 stripes

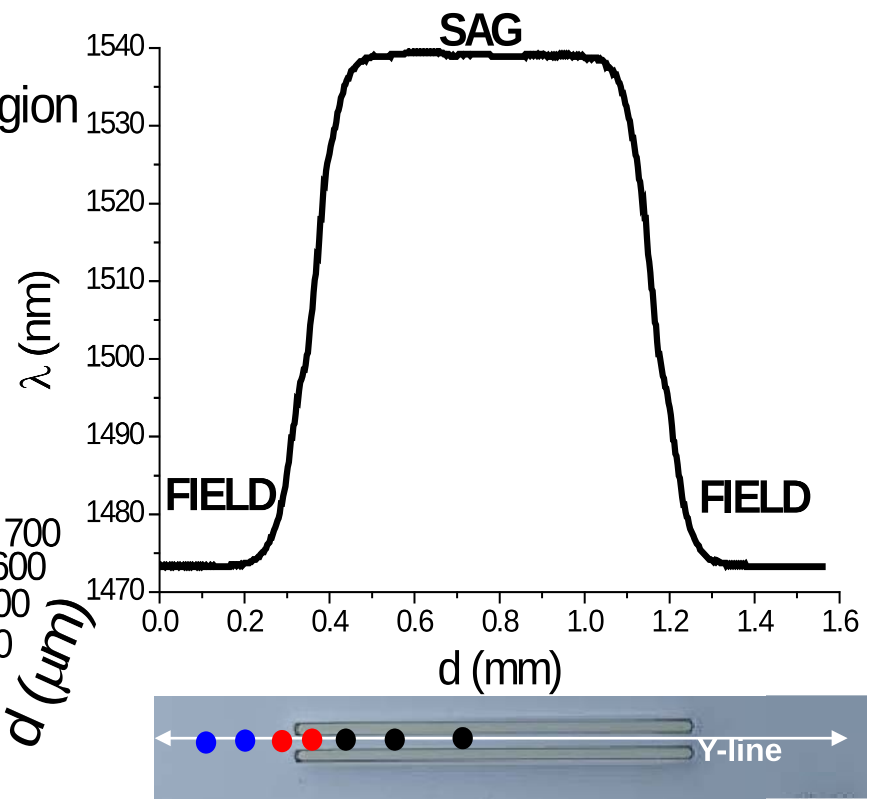


The complete modulator-laser device



Energy gap space-resolved determination

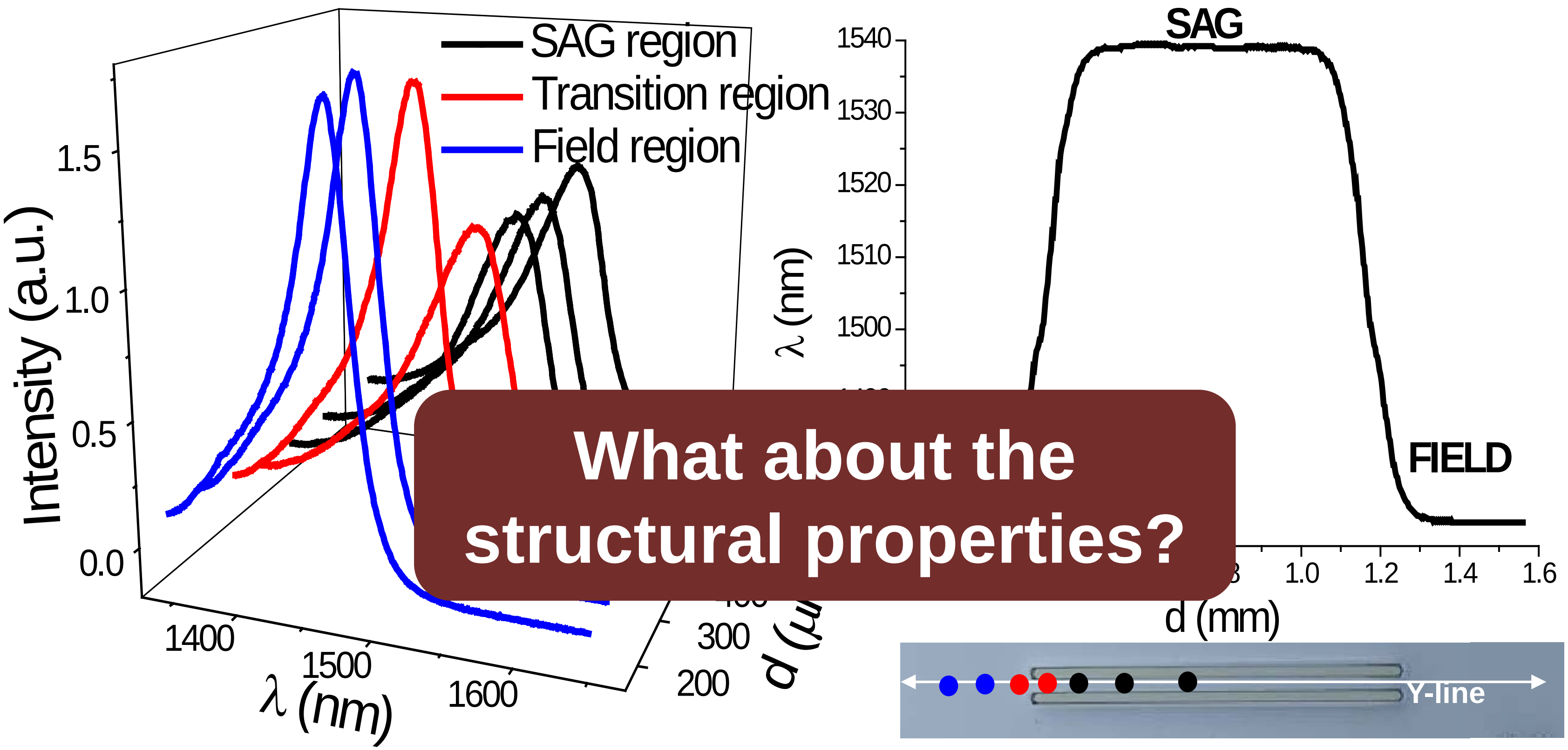




Space resolved photoluminescence (PL) study with a 15 µm resolution along a line parallel to the SiO_2 stripes (Y-line)

L. Mino et al., Adv. Mater. 2010, 22, 2050-2054

Energy gap space-resolved determination

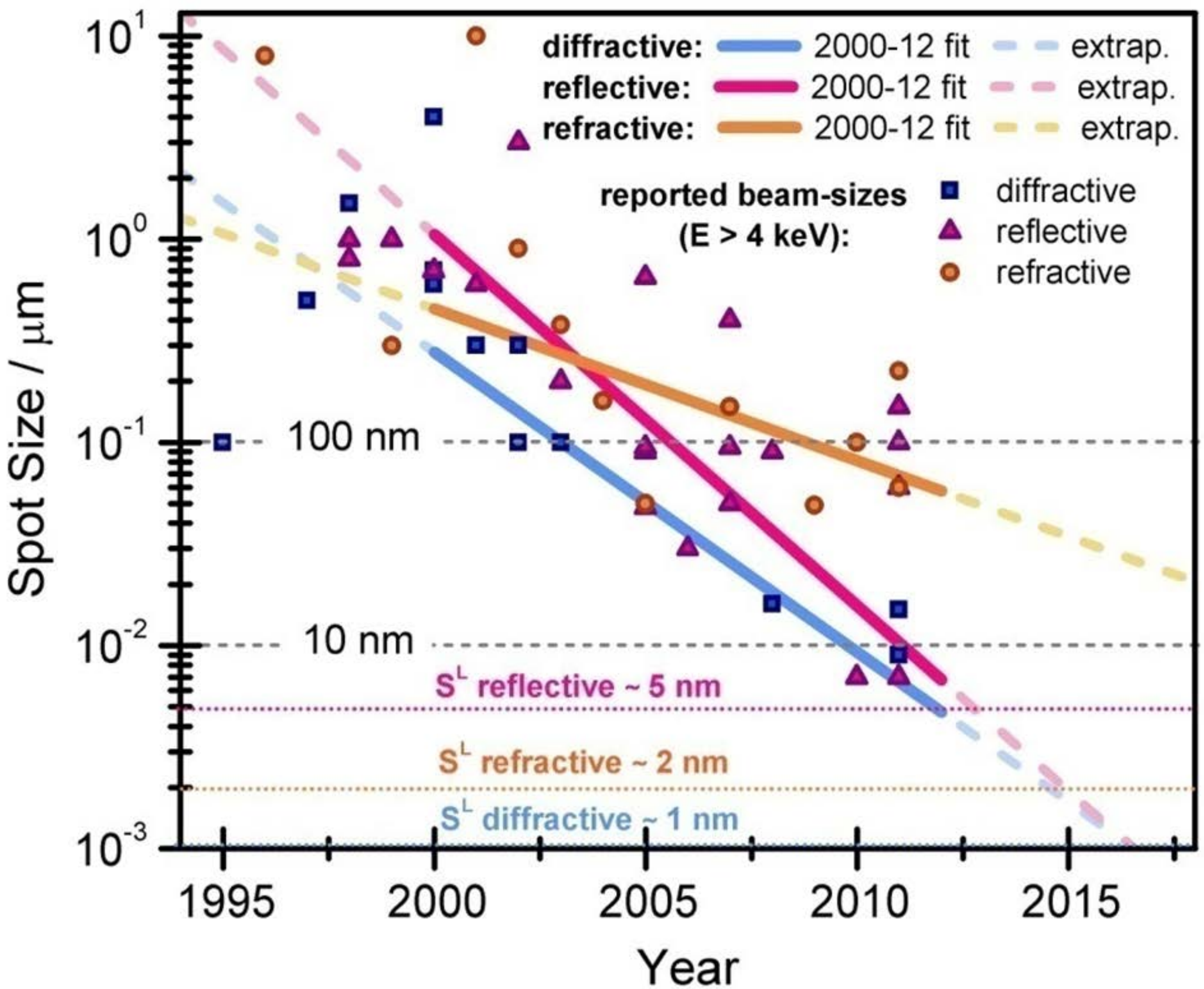


What about the structural properties?

Space resolved photoluminescence (PL) study with a 15 µm resolution along a line parallel to the SiO_2 stripes (Y-line)

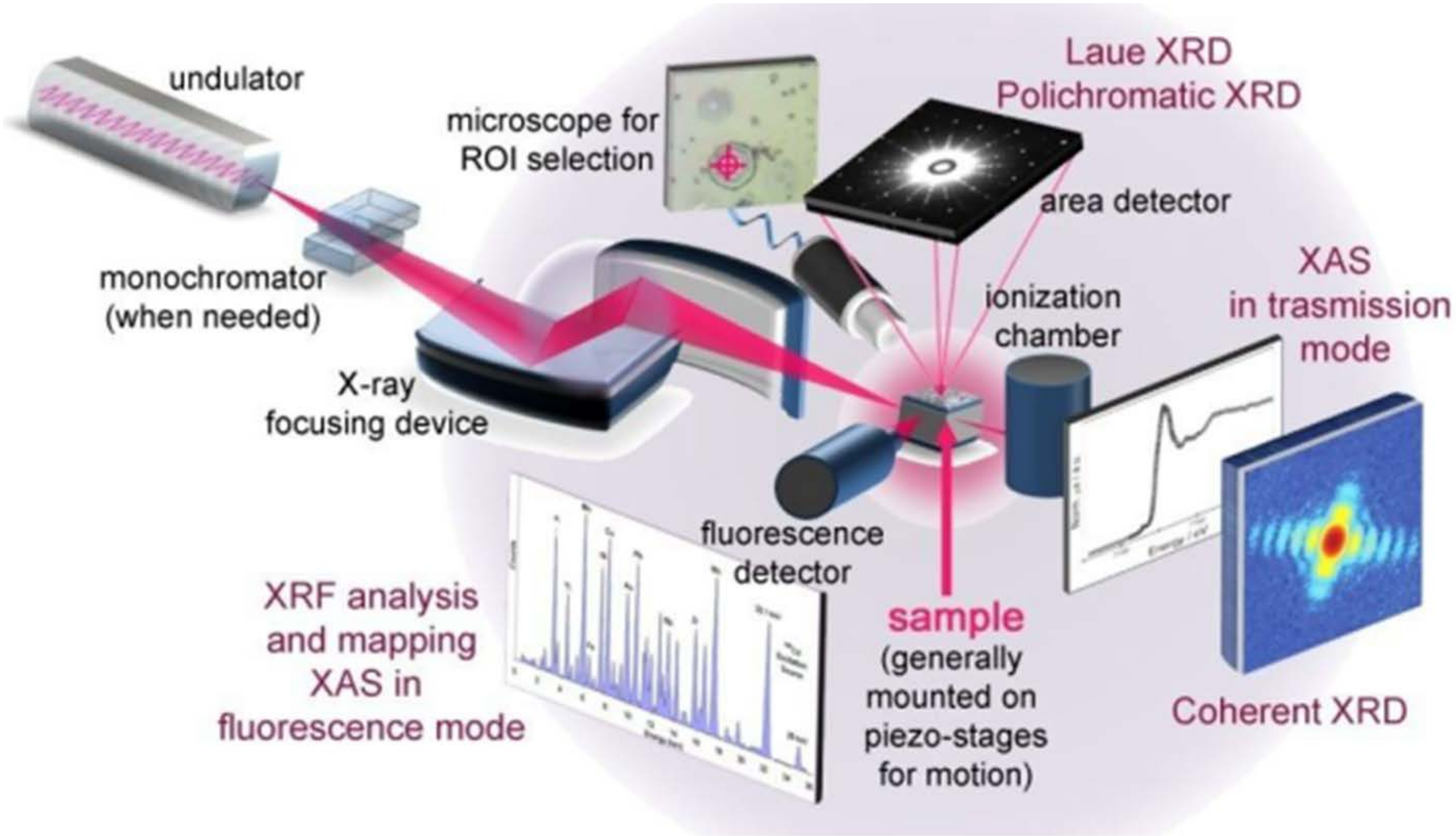
L. Mino et al., Adv. Mater. 2010, 22, 2050-2054

Synchrotron X-ray micro-/nano-beams



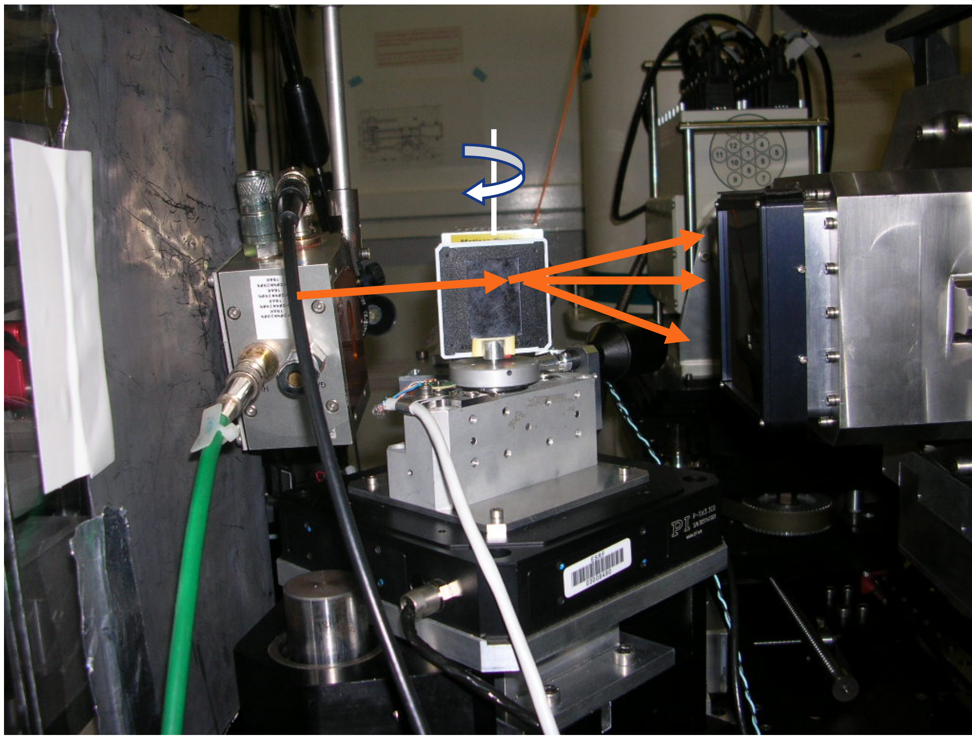
L. Mino et al., Rev. Mod. Phys. 2018, 90, 025007

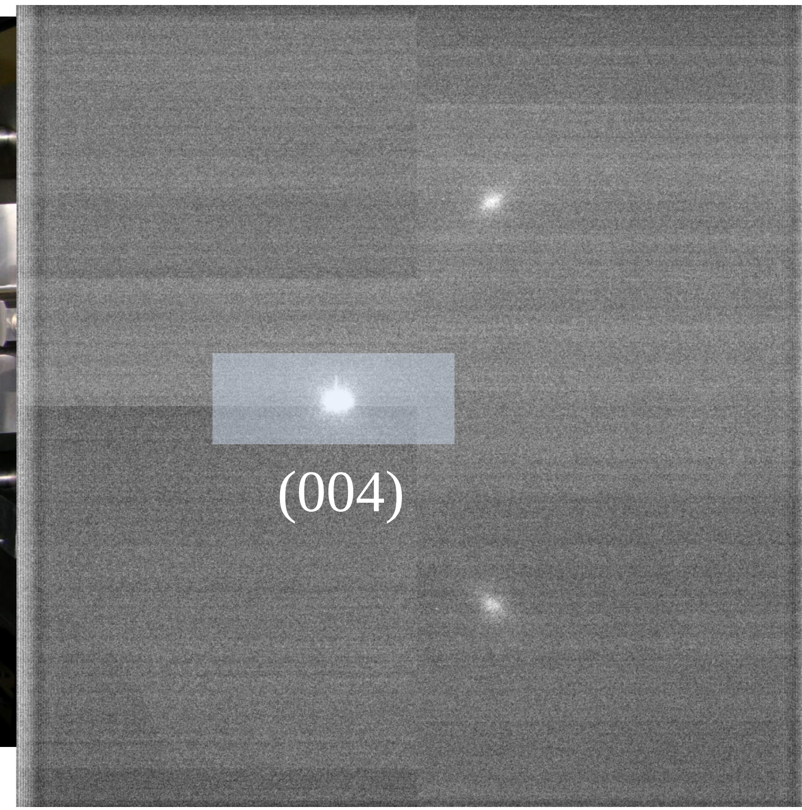
ESRF ID22 beamline (now ID16)



X-ray micro-beam: 1.7 μm × 5.3 μm

Micro-XRD experimental setup



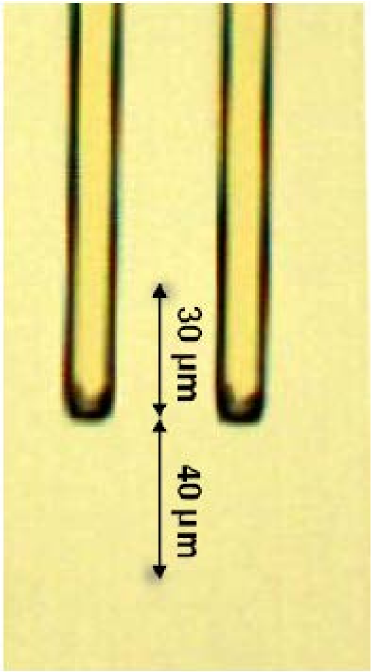


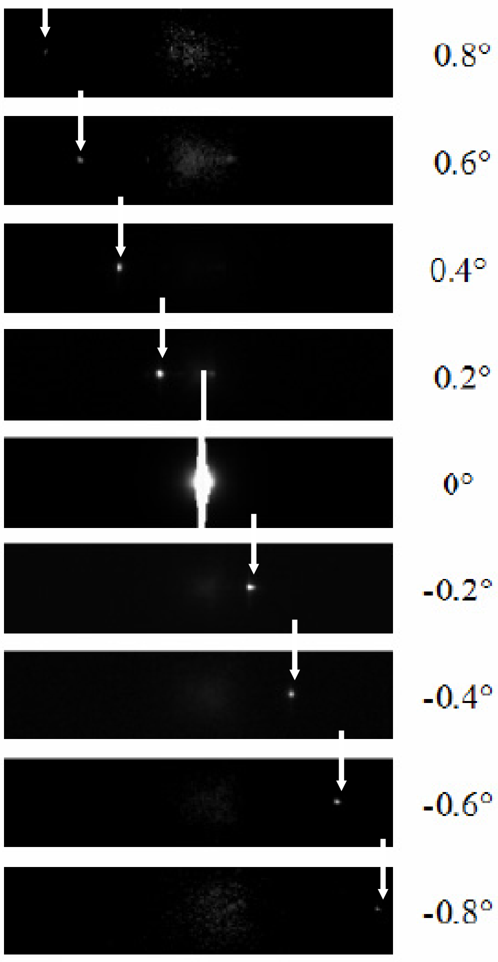
CCD image

Micro-XRD pattern acquisition

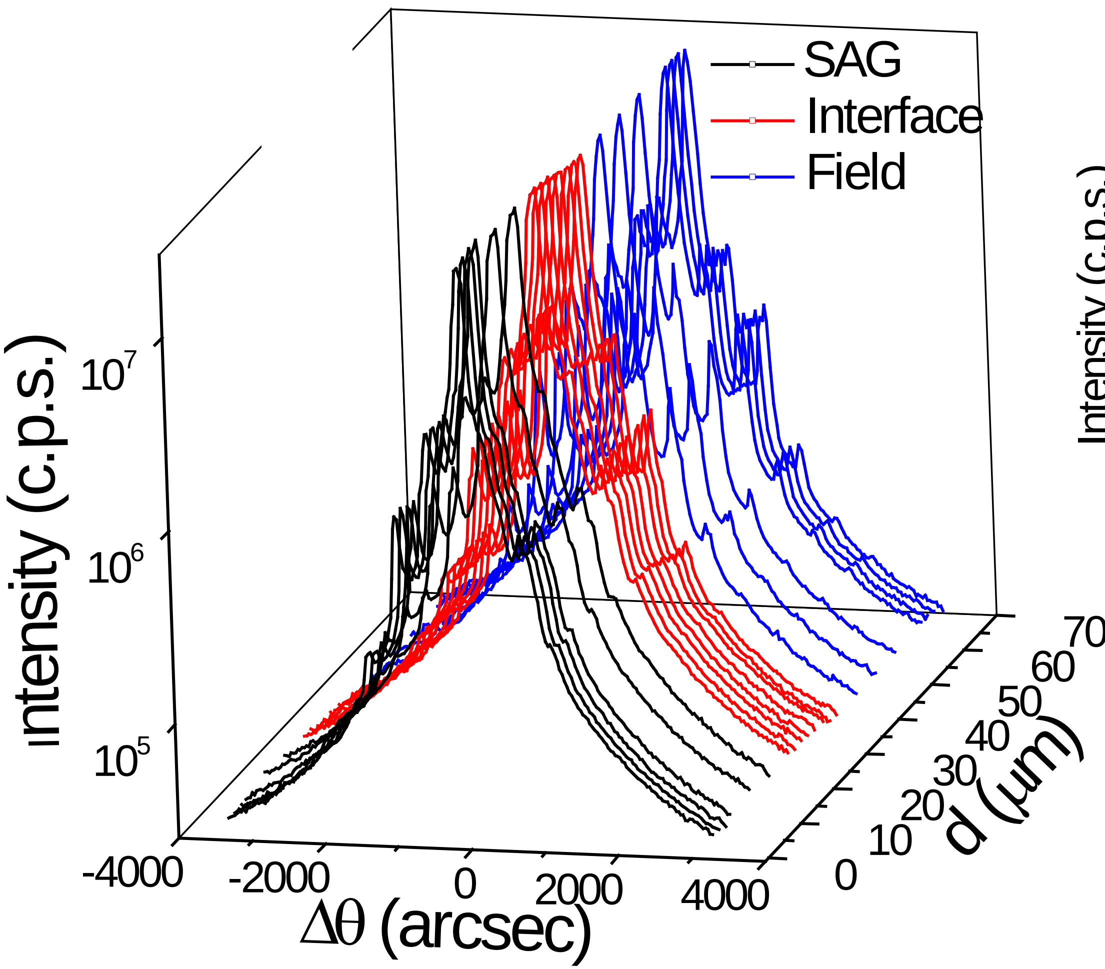
176 images covering a rotation of ± 1.1° around the InP(004) Bragg angle (θ_B = 14.359° at 17 keV)

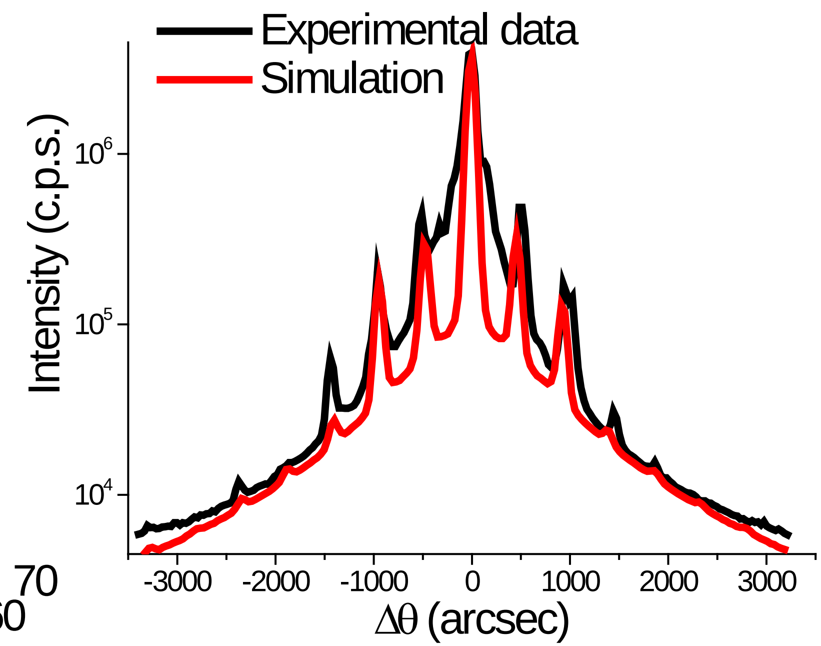
35 different points have been sampled along the Y-line with 2 μm resolution





Reconstruction of the XRD patterns

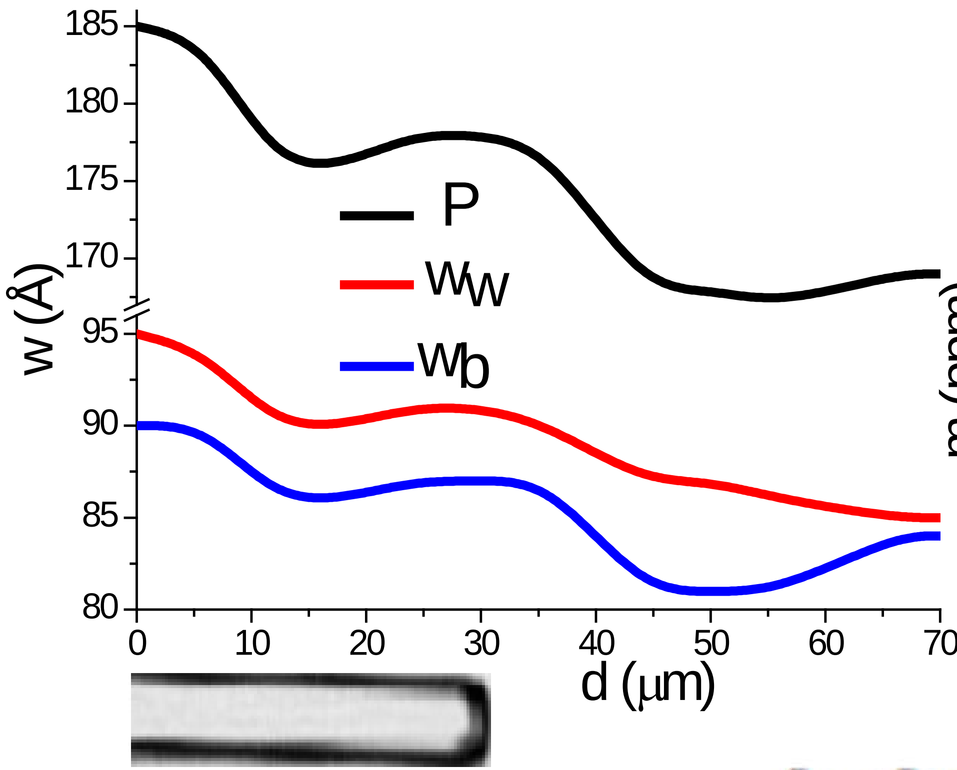


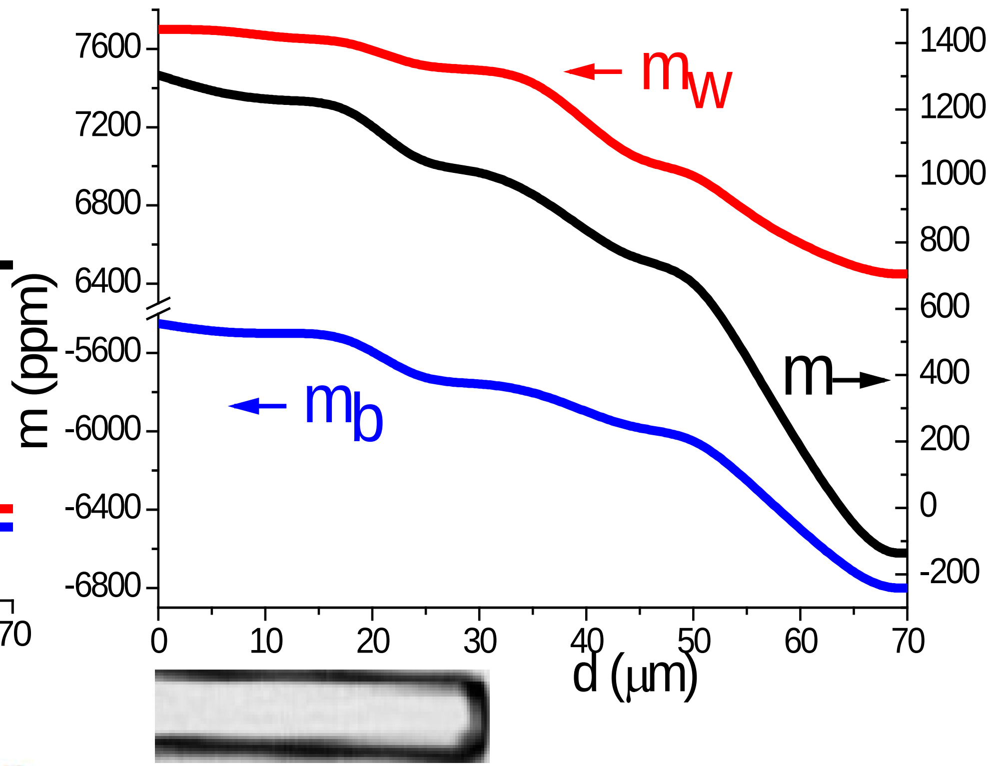


Each XRD pattern reconstructed starting from the 176 CCD images

L. Mino et al., Adv. Mater. 2010, 22, 2050-2054

Space-resoved XRD results

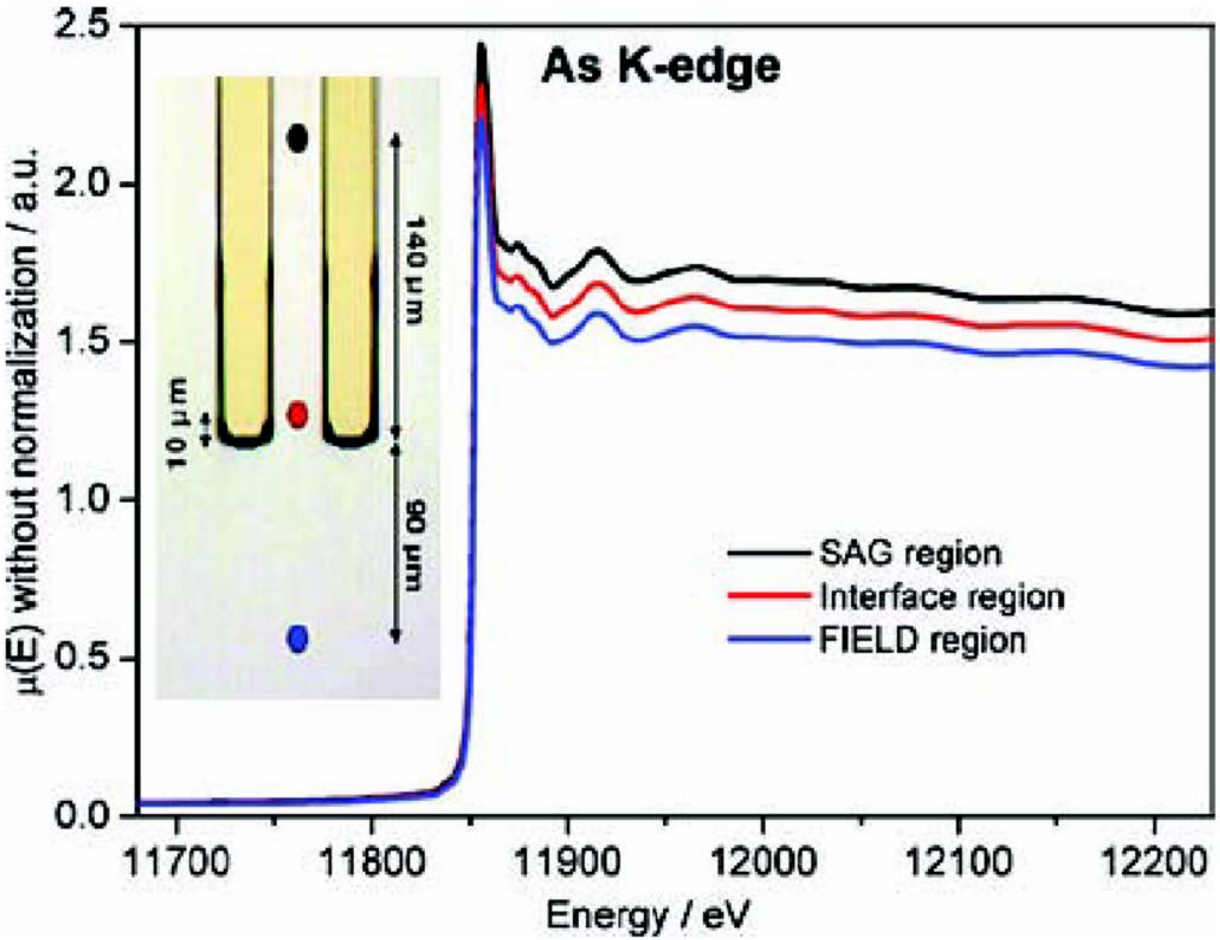




$$m = \frac{a - a_S}{a_S}$$

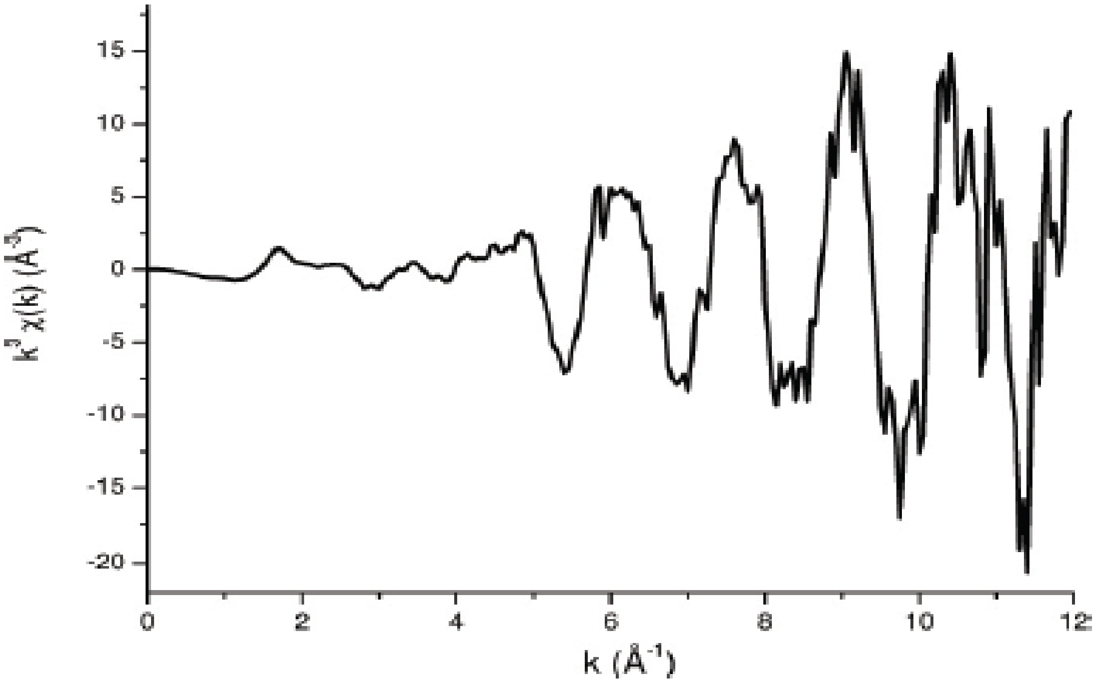
Widths (w_b, w_w) and mismatches (m_b, m_w) of the MQW barrier and of the well obtained performing a fitting of the XRD patterns

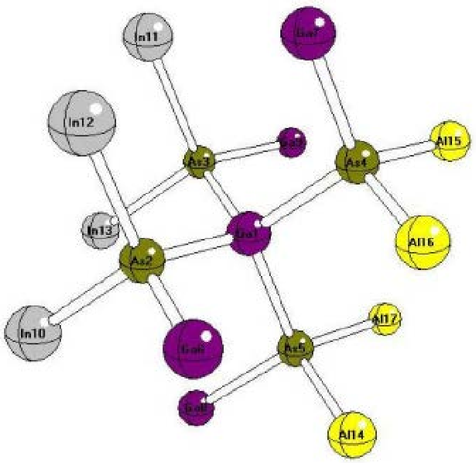
X-ray absorption spectroscopy



Local structural information on the $In_xGa_yAl_{1-x-y}As$ semiconductor combining micro-XAS at the Ga K-edge and As K-edge

EXAFS signal extraction



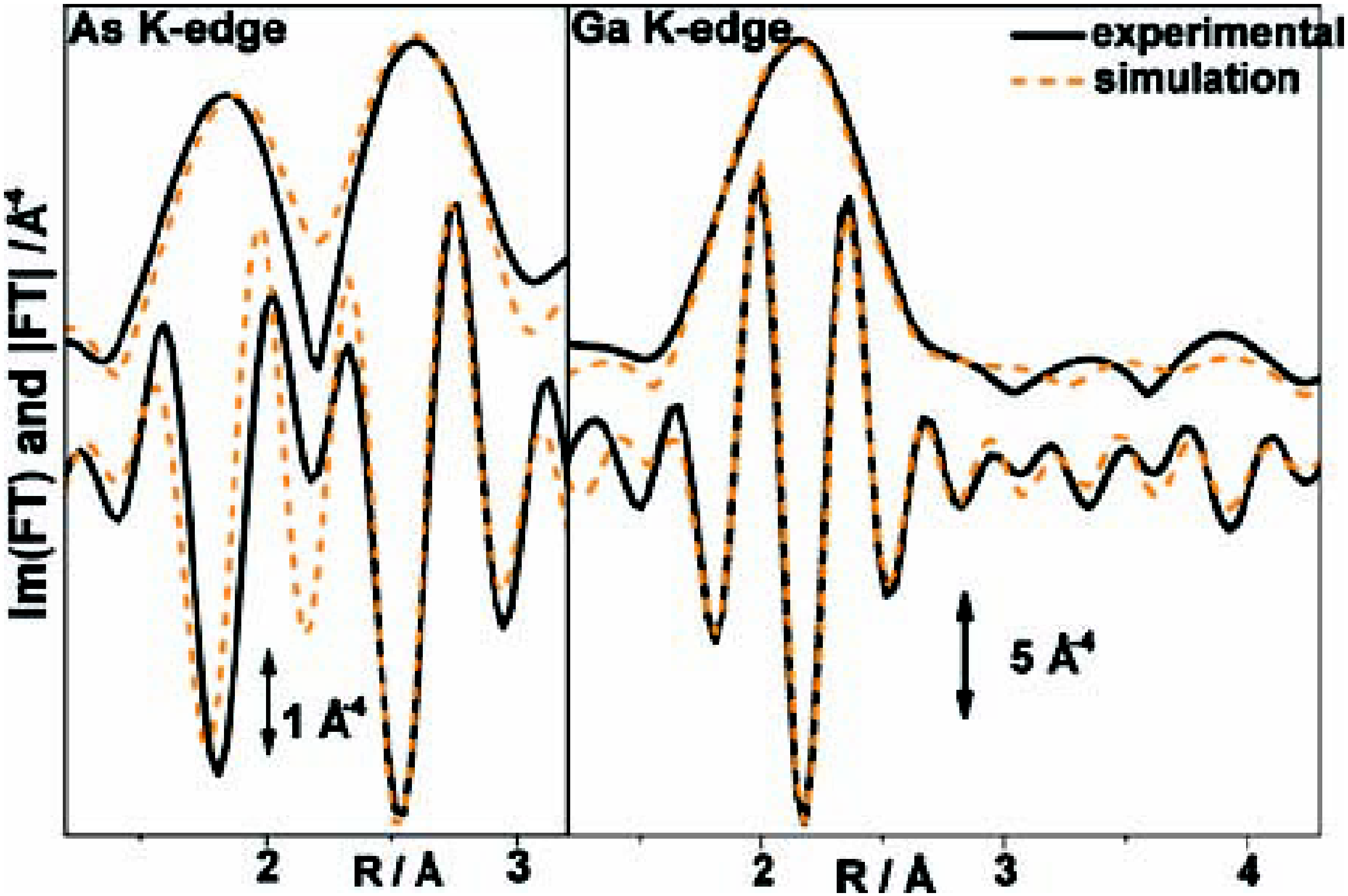


EXAFS signal:

$$\chi = \frac{\mu - \mu_0}{\mu_0}$$

$$\chi(k) = \sum_j \frac{N_j}{R_j^2} e^{-2\frac{R}{\lambda}} e^{-2k^2\sigma_j^2} A_j(k,\pi)\sin[2kR_j + \varphi(k,R_j,\pi)]$$

EXAFS data fitting



L. Mino et al., Small 2011, 7, 930-938

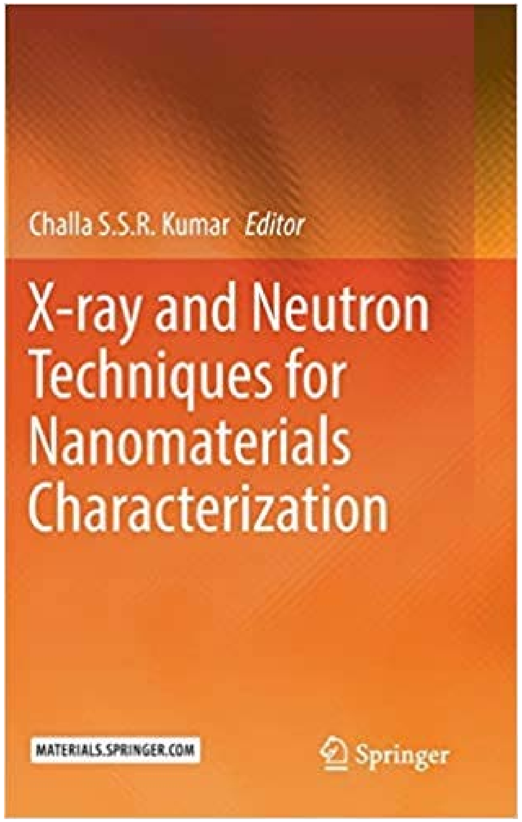
For the fit a co-refinement approach was adopted using the following intervals in k- and R-spaces: 3.0−9.0 $Å^{-1}$ and 1.0−3.2 Å for As K-edges, 3.0−10.8 $Å^{-1}$ and 1.0−4.3 Å for Ga K-edges

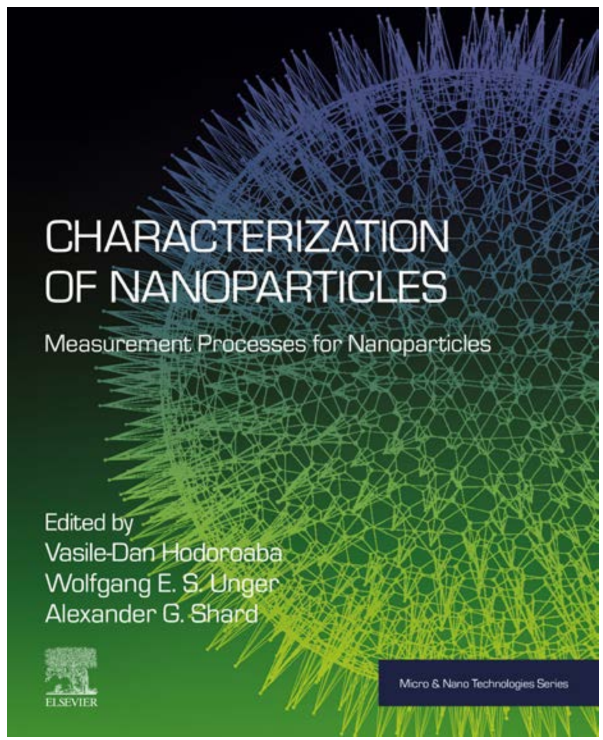
EXAFS results

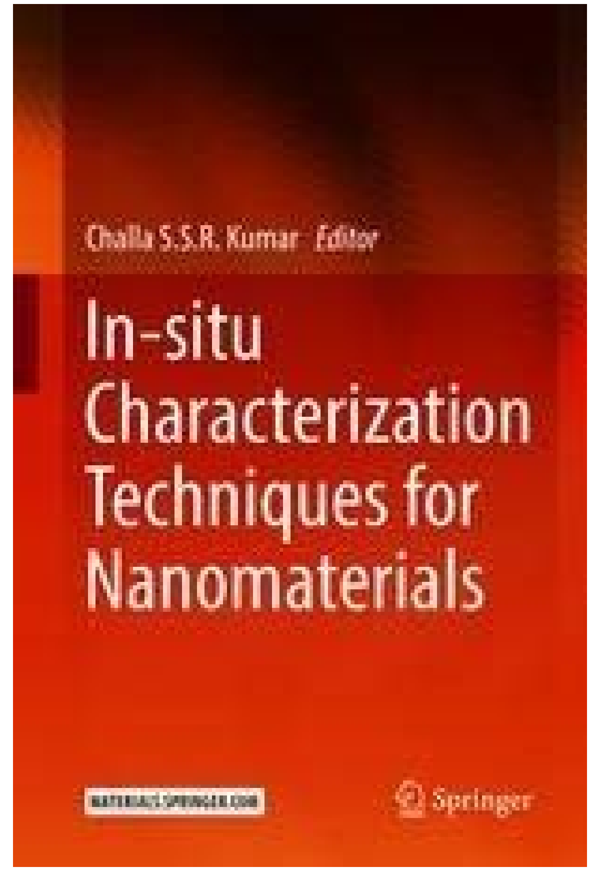
Parameter	SAG	FIELD
$R_{As\text{-}Ga}$ [Å]	2.469 ± 0.007	2.463 ± 0.005
$\Delta R_{As\text{-}Ga}$ [Å]	0.021 ± 0.007	0.015 ± 0.005
$R_{As\text{-}In}$ [Å]	2.60 ± 0.02	2.60 ± 0.02
$\Delta R_{As\text{-}In}$ [Å]	-0.02 ± 0.02	-0.02 ± 0.02
$R_{As\text{-}Al}$ [Å]	2.49 ± 0.11	2.48 ± 0.11
$\sigma^2_{As\text{-}Ga}$ [Å^2]	0.006 ± 0.002	0.005 ± 0.002
$\sigma^2_{As\text{-}In}$ [Å^2]	0.008 ± 0.003	0.007 ± 0.003
$\sigma^2_{As\text{-}Al}$ [Å^2]	0.010 ± 0.004	0.008 ± 0.004

L. Mino et al., Small 2011, 7, 930-938

Further reading







Further reading

IOP Publishing — Journal of Physics D: Applied Physics
J. Phys. D: Appl. Phys. **46** (2013) 423001 (72pp) — doi:10.1088/0022-3727/46/42/423001

TOPICAL REVIEW

Low-dimensional systems investigated by x-ray absorption spectroscopy: a selection of 2D, 1D and 0D cases

**Lorenzo Mino[1], Giovanni Agostini[1], Elisa Borfecchia[1],
Andrea Piovano[3], Erik Gallo[1,4] and Carlo Lamberti[1]**

Progress in Materials Science 112 (2020) 100667

Contents lists available at ScienceDirect

Progress in Materials Science

journal homepage: www.elsevier.com/locate/pmatsci

Watching nanomaterials with X-ray eyes: Probing different length scales by combining scattering with spectroscopy

Cinzia Giannini[a], Vaclav Holy[b,c], Liberato De Caro[a], Lorenzo Mino[d], Carlo Lamberti[e,f]

Materials characterization by synchrotron x-ray microprobes and nanoprobes

Lorenzo Mino, Elisa Borfecchia, Jaime Segura-Ruiz, Cinzia Giannini, Gema Martinez-Criado, and Carlo Lamberti

Rev. Mod. Phys. **90**, 025007 – Published 28 June 2018

Thank you for your attention!