Consiglio Nazionale delle Ricerche

Coherent diffractive imaging of non-periodic self-assembled colloidal nanocrystals

Cinzia Giannini

cinzia.giannini@ic.cnr.it
+39 080 5929167

IC CNR Istituto di Cristallografia

xmi l@b

Colloidal Nanomaterials

2D Materials Engineering

Nanotechnology for Precision Medicine

Printed and Molecular Electronics

NanoChemistry

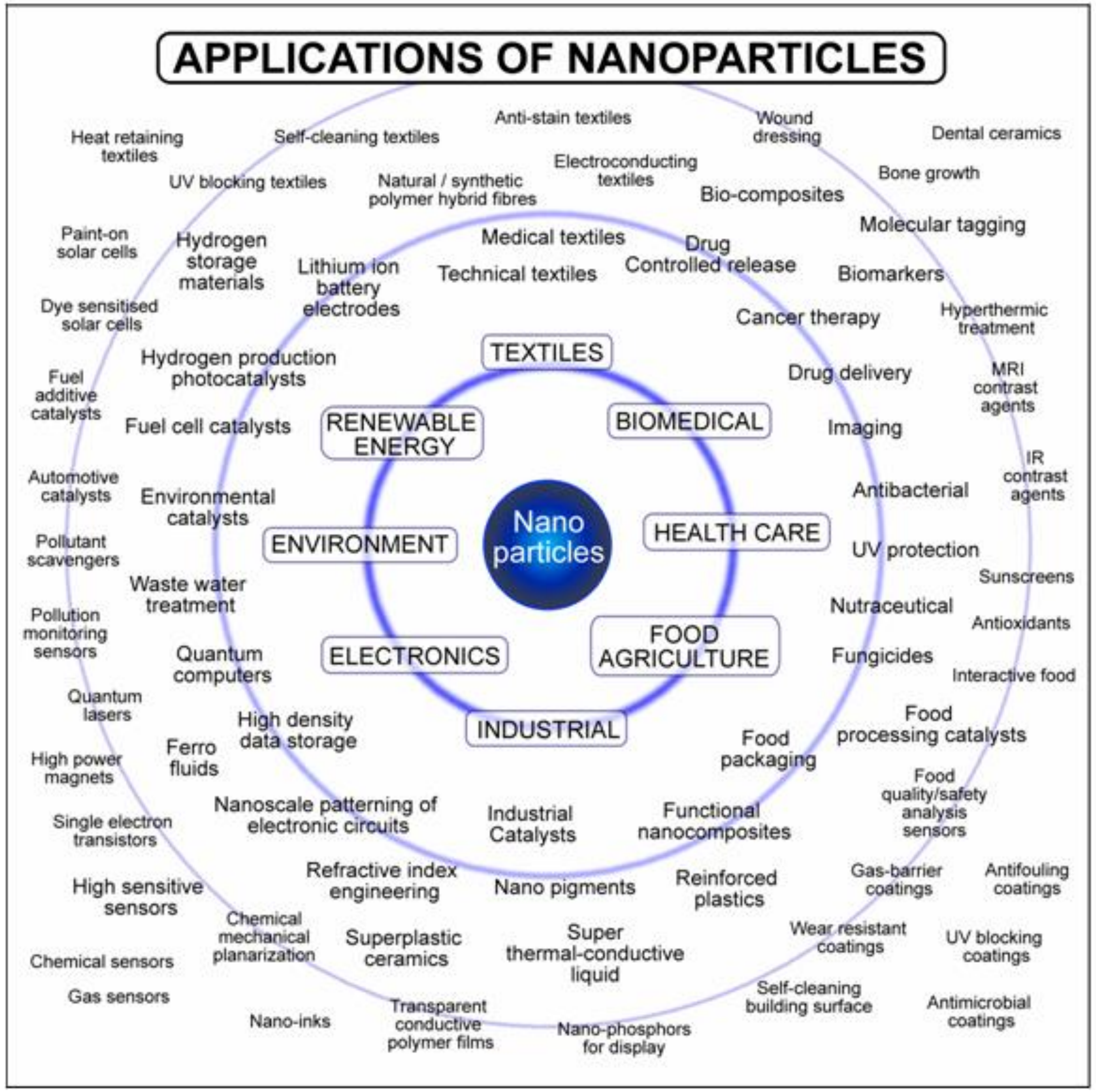
✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167

IC CNR | Istituto di Cristallografia

xmi l@b

Outline

- Colloidal nanocrystals can be prepared with high degree of control in size, shape and composition. Colloidal nanocrystals are used as building blocks to prepare hydrid systems or Superlattices (SL)
- (GI)WAXS – (GI)SAXS
- cSAXS and scanning cSAXS (ptychography)
- perspectives

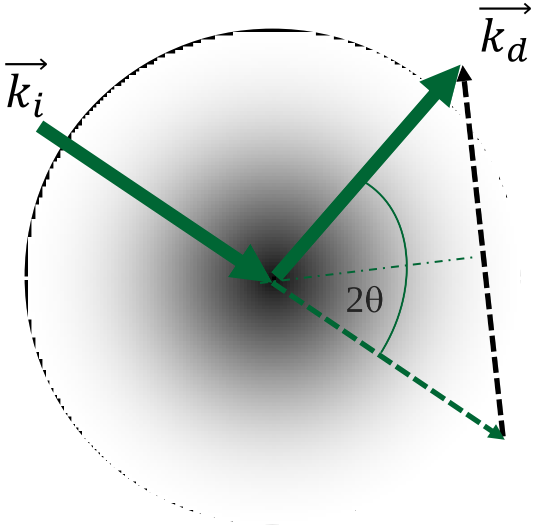


cinzia.giannini@ic.cnr.it
+39 080 5929167
CNR Istituto di Cristallografia

Length scales

$$q = \frac{4\pi}{\lambda}\sin(\theta) = \frac{2\pi}{d}$$

$$\vec{q} = \overrightarrow{k_d} - \overrightarrow{k_i}$$



Technique	d (nm)	q (Å^{-1})	θ(deg) for λ=1.5405Å
uSAXS/uSAXD	1000	0.00063	0.0044
SAXS/SAXD	100	0.0063	0.044
SAXS/SAXD	10	0.063	0.44
WAXS/WAXD	1	0.63	4.4
WAXS/WAXD	0.1	6.3	50.6

ID02 - TIME-RESOLVED ULTRA SMALL-ANGLE X-RAY SCATTERING

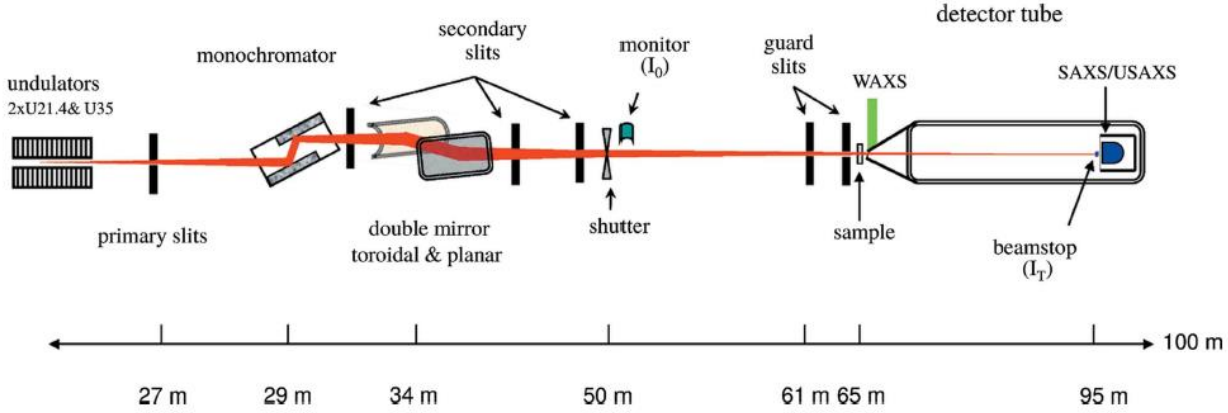


Figure 1

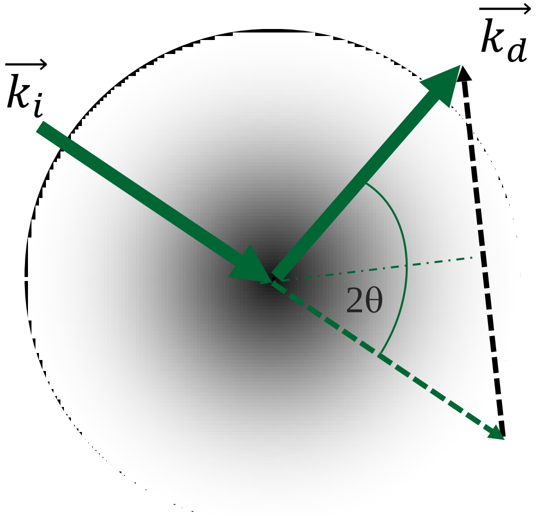
✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167

CNR | Istituto di Cristallografia

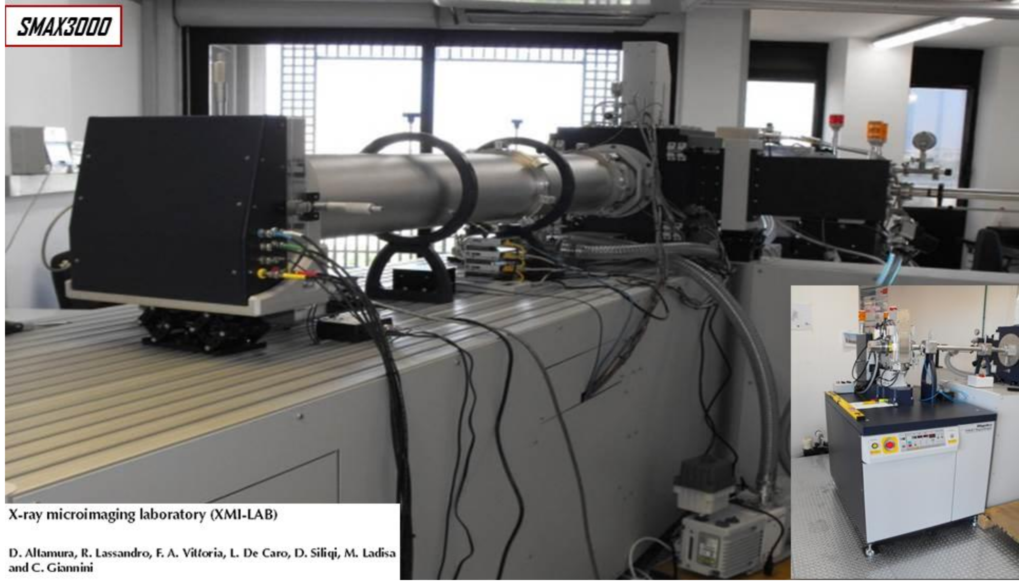
xmi l@b

Length scales

$$q = \frac{4\pi}{\lambda}\sin(\theta) = \frac{2\pi}{d}$$



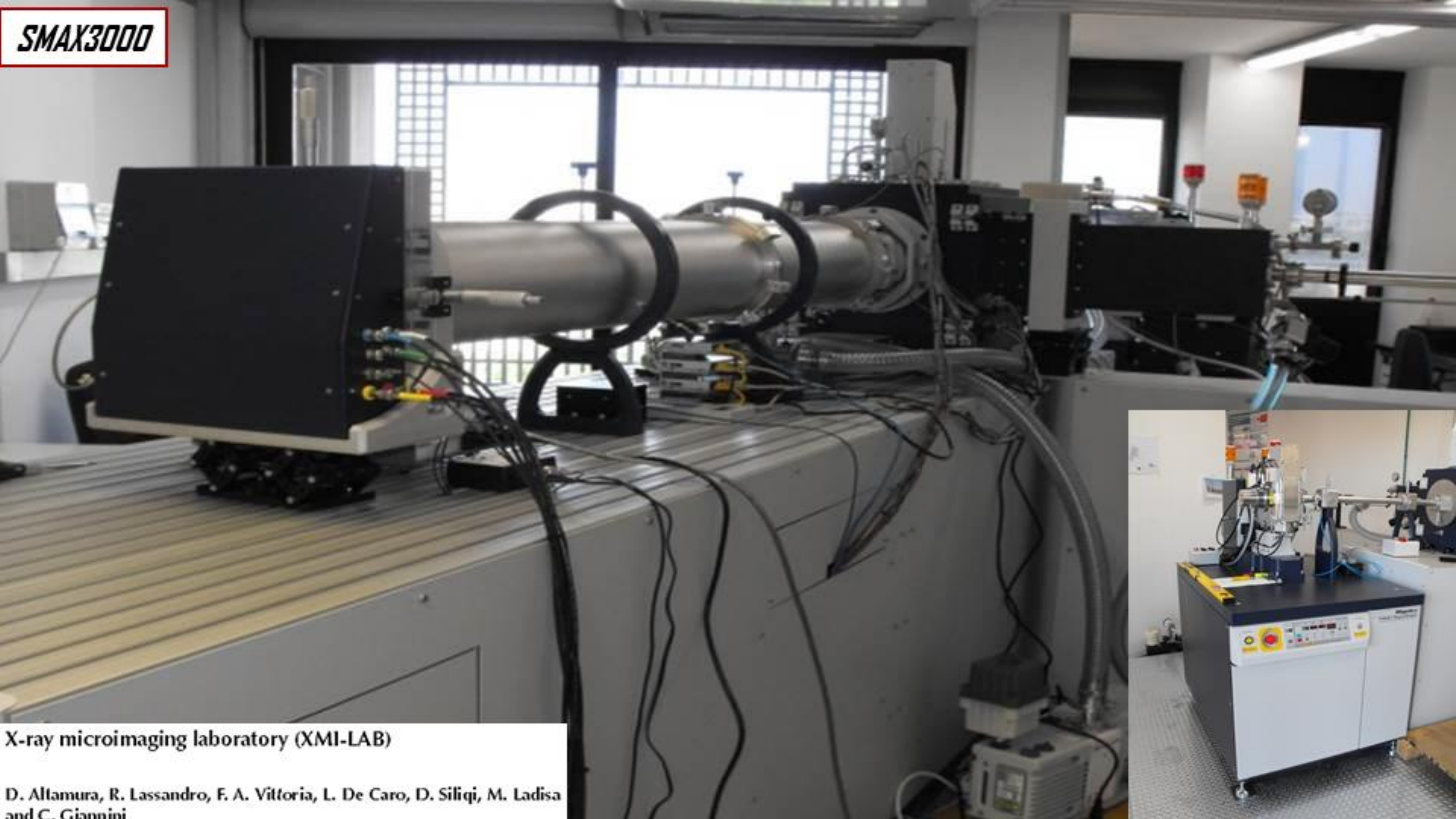
$$\vec{q} = \vec{k_d} - \vec{k_i}$$



Technique	d (nm)	q (nm^{-1})	q ($Å^{-1}$)	θ(deg) for λ=1.5405Å
~~uSAXS/uSAXD~~	~~1000~~	~~0.0063~~	~~0.00063~~	~~0.0044~~
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

✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167
CNR | Istituto di Cristallografia

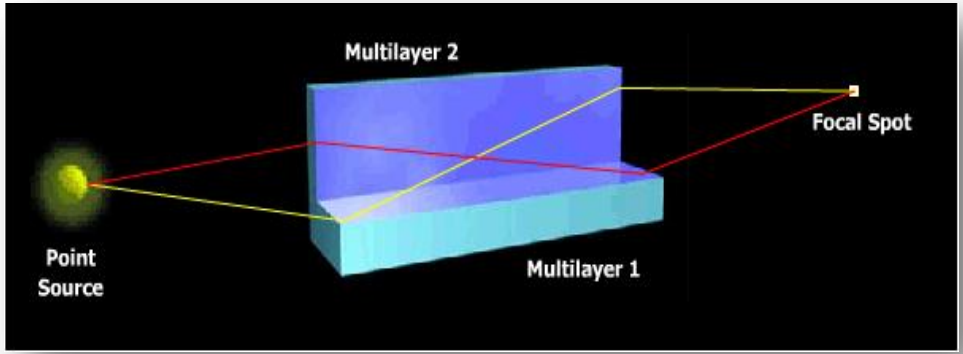
SMAX3000

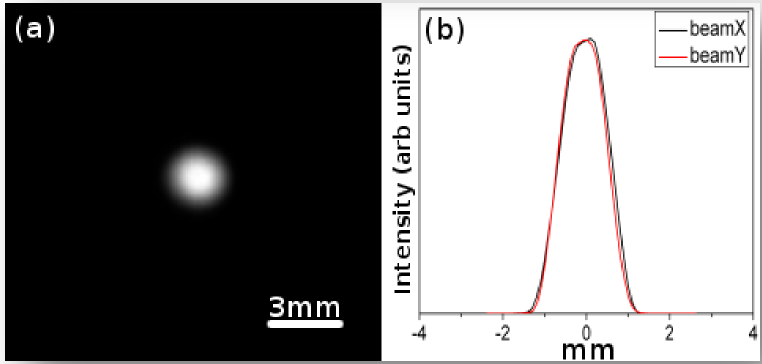


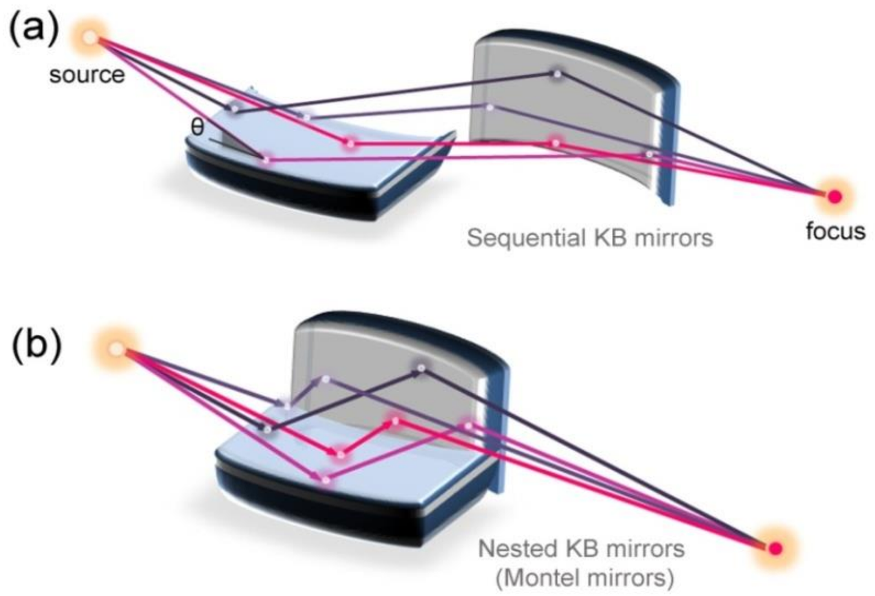
X-ray microimaging laboratory (XMI-LAB)

D. Altamura, R. Lassandro, F. A. Vittoria, L. De Caro, D. Siliqi, M. Ladisa and C. Giannini

X-ray MicroImaging L@b







X-ray microimaging laboratory (XMI-LAB)

D. Altamura, R. Lassandro, F. A. Vittoria, L. De Caro, D. Siliqi, M. Ladisa and C. Giannini

J. Appl. Cryst. (2012). 45, 869–873

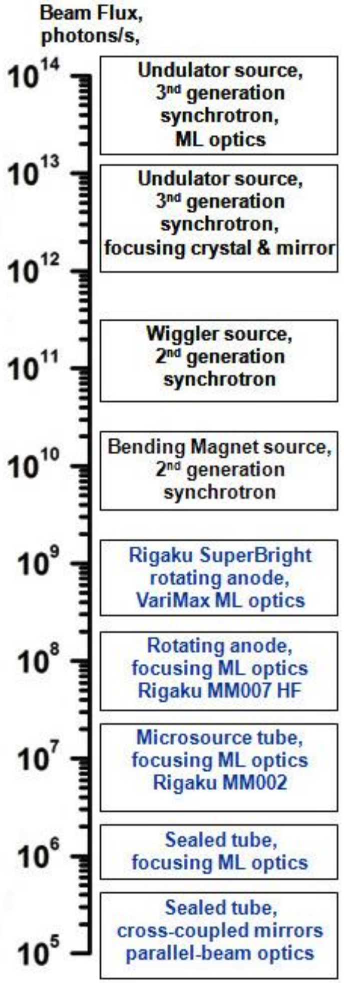
cinzia.giannini@ic.cnr.it
+39 080 5929167

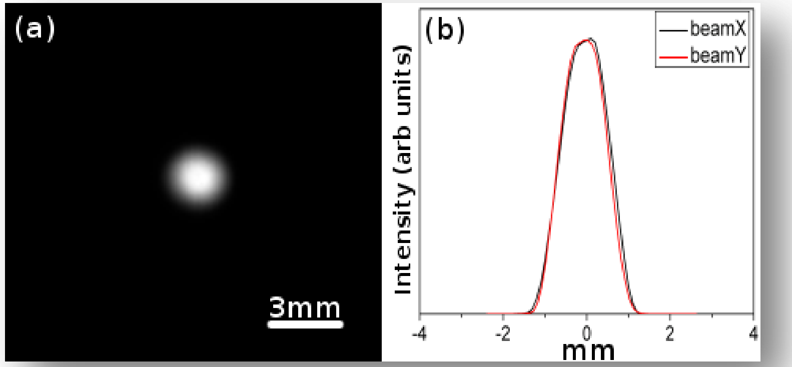
IC CNR Istituto di Cristallografia

xmi l@b

X-ray MicroImaging L@b

FR-E+ SuperBright





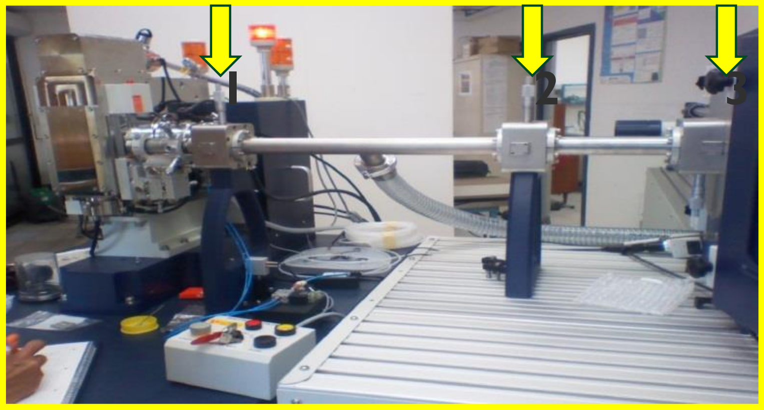
X-ray microimaging laboratory (XMI-LAB)

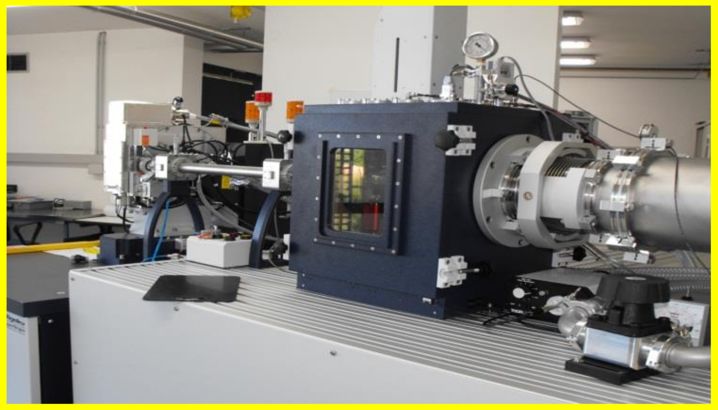
D. Altamura, R. Lassandro, F. A. Vittoria, L. De Caro, D. Siliqi, M. Ladisa and C. Giannini

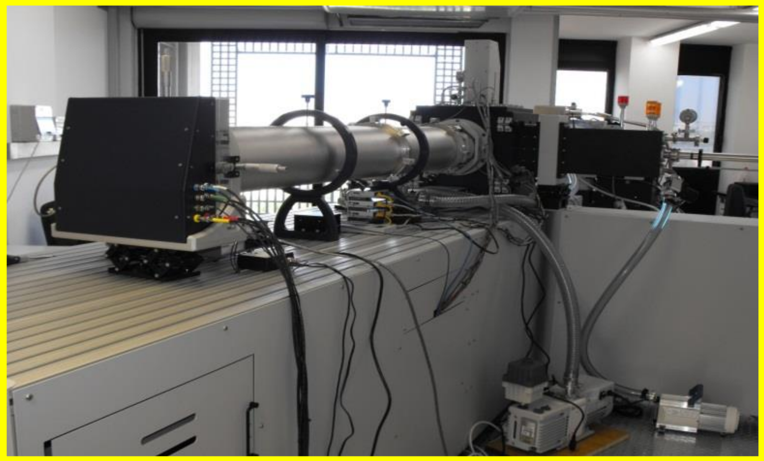
J. Appl. Cryst. (2012). 45, 869–873

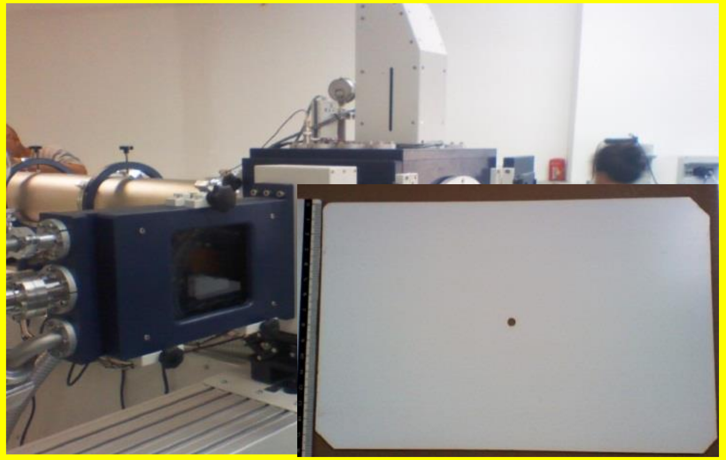
✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167
IC CNR | Istituto di Cristallografia
xmi l@b

three pinholes camera
Rigaku Smax 3000









SAXS: Triton™20 detector, a 20cm diameter multi-wire gas-filled proportional counter

WAXS: RAXIA Image Plate with off line reader

X-ray microimaging laboratory (XMI-LAB)

D. Altamura, R. Lassandro, F. A. Vittoria, L. De Caro, D. Siliqi, M. Ladisa and C. Giannini

J. Appl. Cryst. (2012). 45, 869–873

cinzia.giannini@ic.cnr.it
+39 080 5929167

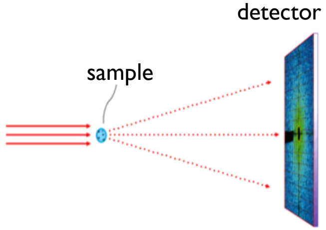
IC CNR | Istituto di Cristallografia

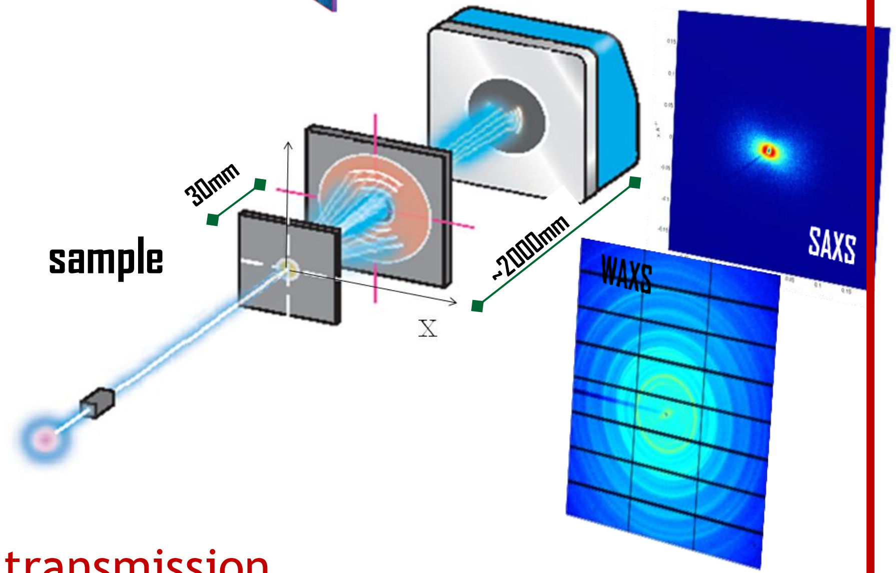
XMI L@b

Transmission VS Reflection

SAXS/WAXS

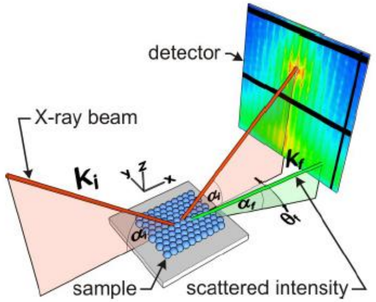
- ❑ liquids
- ❑ Biopsies / tissues



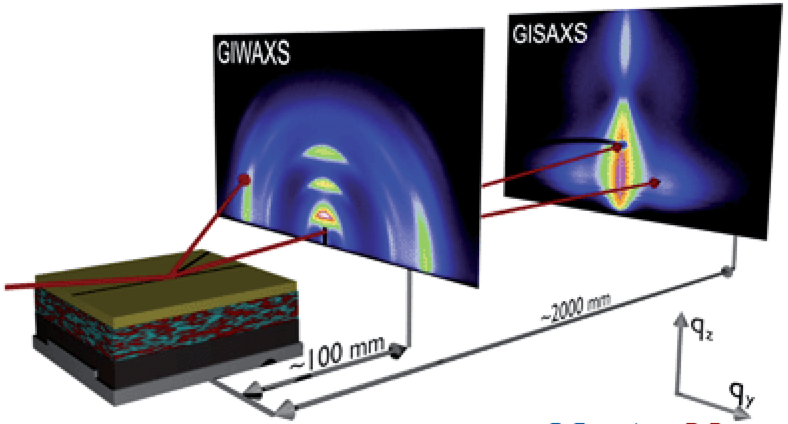


transmission

GISAXS/GIWAXS



- ❑ Planar devices
- ❑ Nanostructured surfaces



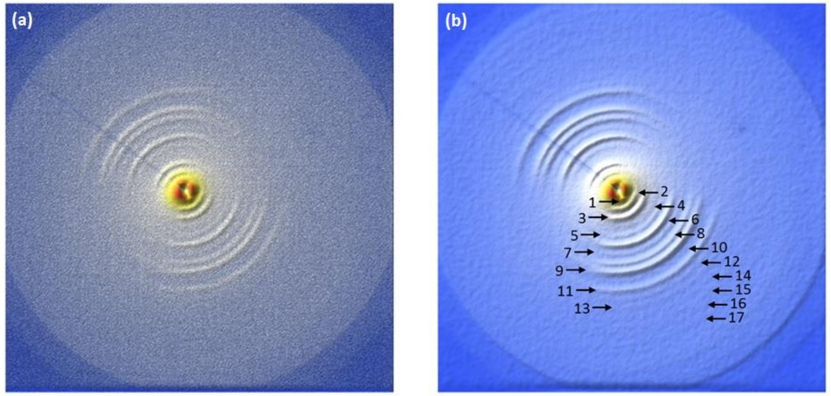
reflection

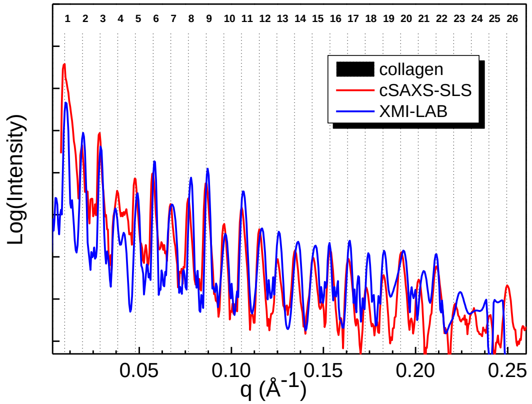
CNR | Istituto di Cristallografia

✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167

Lab VS Synch

SAXS – rat tail tendon





research papers

Journal of
Applied
Crystallography
ISSN 0021-8898

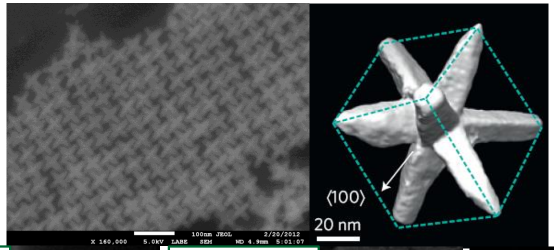
Received 24 December 2012
Accepted 20 March 2013

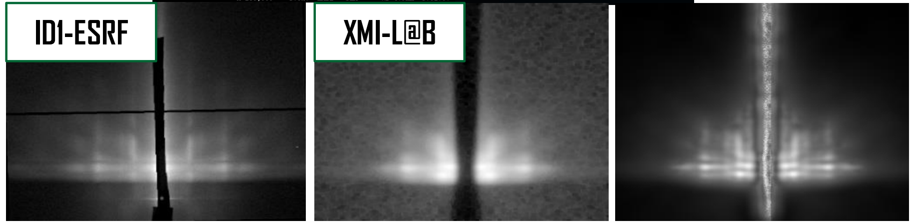
Rat-tail tendon fiber SAXS high-order diffraction peaks recovered by a superbright laboratory source and a novel restoration algorithm

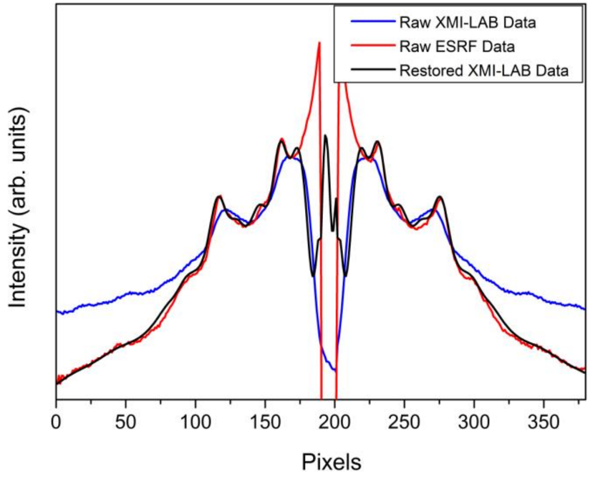
Liberato De Caro,[a] Davide Altamura,[a] Teresa Sibillano,[a] Dritan Siliqi,[a] Giovanni Filograsso,[a] Oliver Bunk[b] and Cinzia Giannini[a]*

[a]Istituto di Cristallografia (IC-CNR), via Amendola 122/O, Bari, 70126, Italy, and [b]Paul Scherrer Institut, Swiss Light Source, Villigen PSI, 5232, Switzerland. Correspondence e-mail: cinzia.giannini@ic.cnr.it

GISAXS in nano-assembled crystal







Journal of
Applied
Crystallography
ISSN 0021-8898

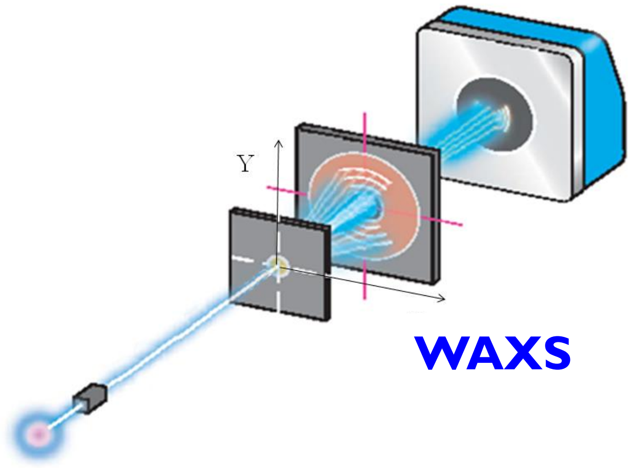
Received 9 July 2012
Accepted 8 October 2012

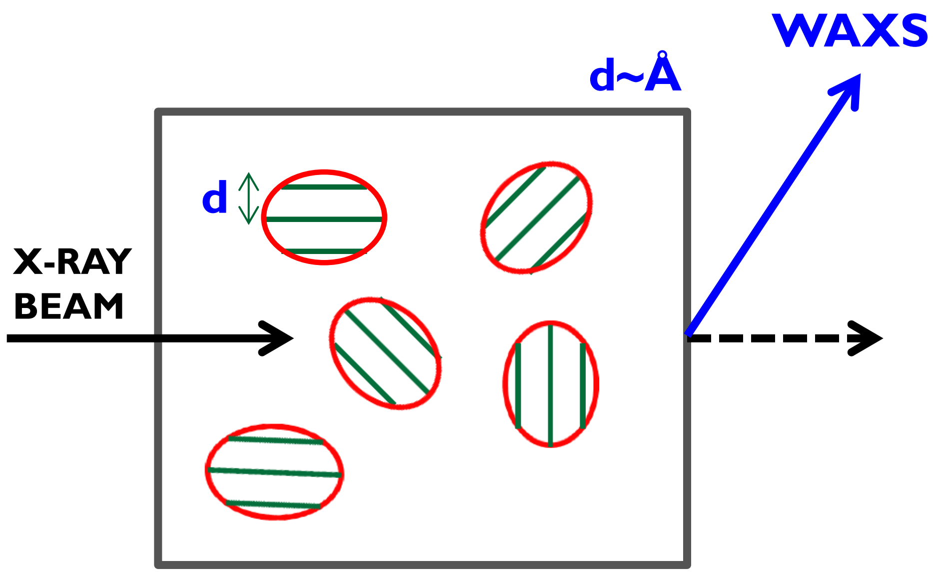
A superbright X-ray laboratory microsource empowered by a novel restoration algorithm

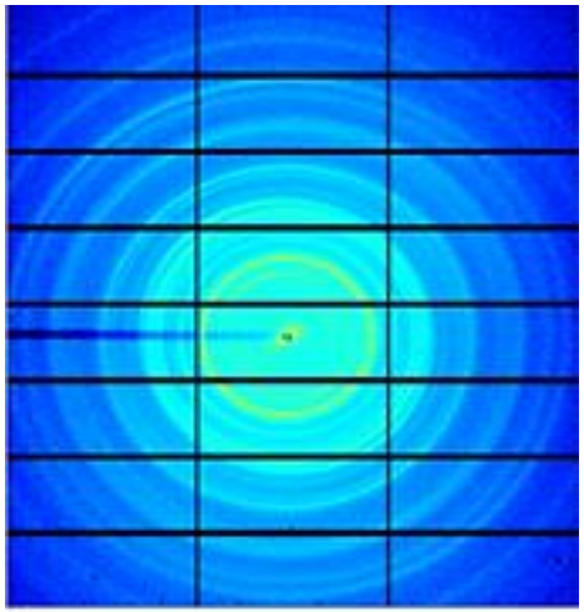
Liberato De Caro,[a] Davide Altamura,[a] Fabio Alessio Vittoria,[a] Gerardina Carbone,[b] Fen Qiao,[c] Liberato Manna[c] and Cinzia Giannini[a]*

✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167

WAXS







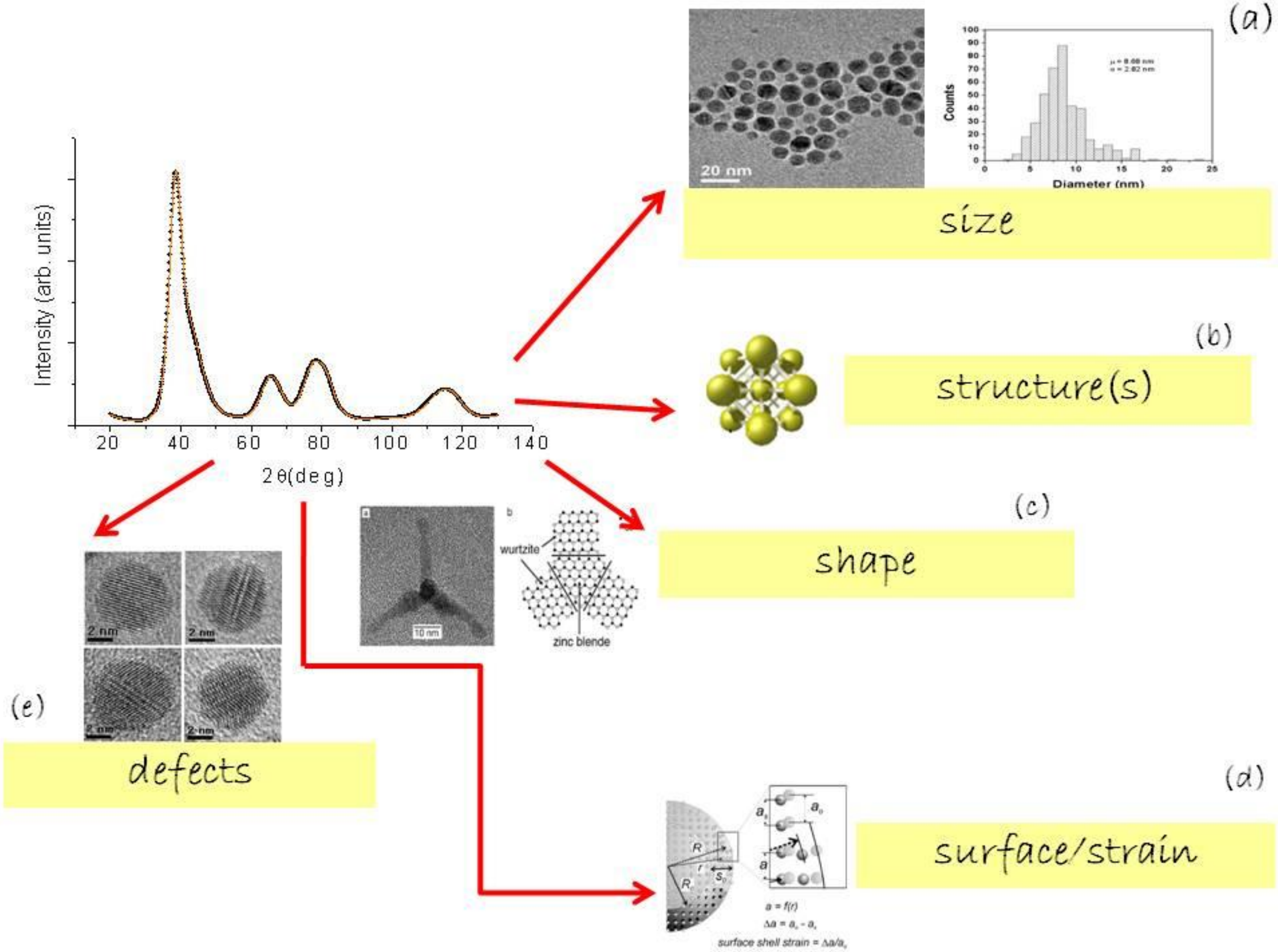
$\sin\theta = \lambda / 2d$

Large θ → small d
Small θ → large d

✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167

CNR Istituto di Cristallografia

WAXS



1.08 Quantum Dots: Synthesis and Characterization

D Dorfs, R Krahne, A Falqui, and L Manna, Istituto Italiano di Tecnologia, Genoa, Italy
C Giannini, CNR-Istituto di Cristallografia (IC), Bari, Italy
D Zanchet, Laboratório Nacional de Luz Síncrotron, Campinas-SP, Brazil

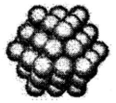
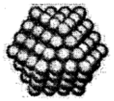
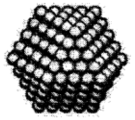
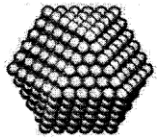
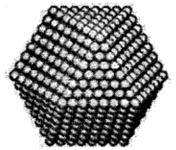
✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167
CNR Istituto di Cristallografia

Main information

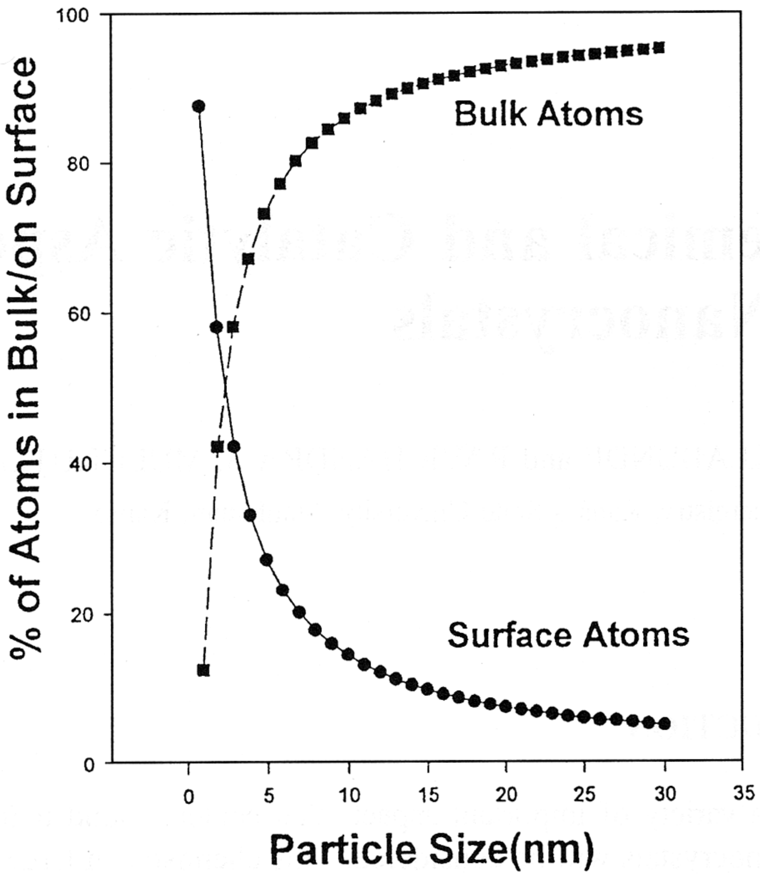
- Crystal structure determination (single phase)
- Phase Identification – pure crystalline phases or mixtures
- Quantitative Phase Analysis (QPA)
- Preferred Orientation (texture)
- Crystalline domain size/shape and lattice defects
- Residual Stress Field

✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167
CNR Istituto di Cristallografia

Nanocrystals

Full-shell Clusters		Total Number of Atoms	Surface Aton (%)
1 Shell		13	92
2 Shells		55	76
3 Shells		147	63
4 Shells		309	52
5 Shells		561	45
7 Shells		1415	35

Nanoscale Materials in Chemistry,
Ed. K.J. Klabunde, Wiley, 2001



Kenneth J. Klabunde et al,
Nanocrystals as Stoichiometric Reagents
with Unique Surface Chemistry
J. Phys. Chem. 1996, 100, 12142-12153

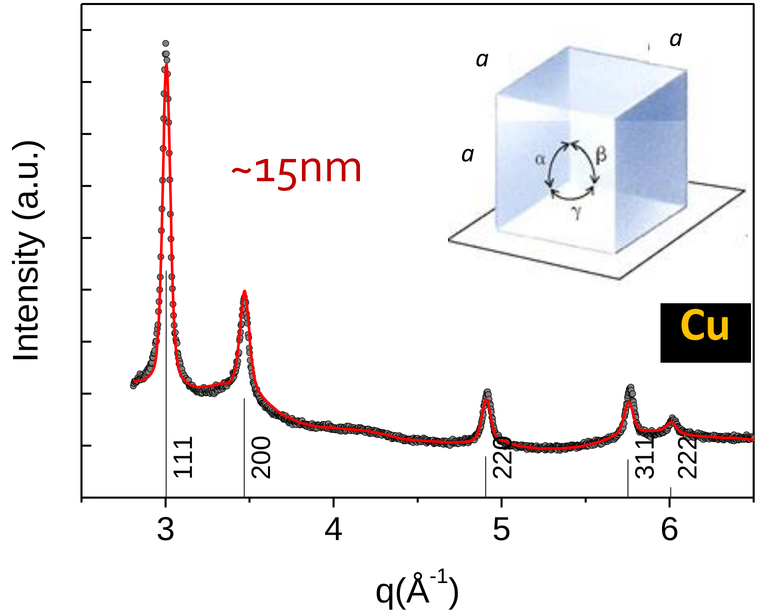
CNR Istituto di Cristallografia

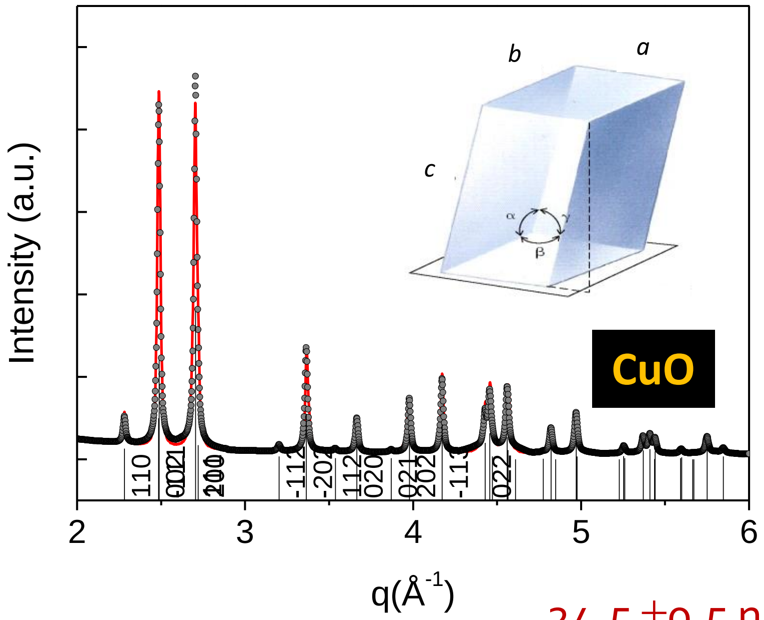
✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167

What is the structure?

✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167
IC CNR Istituto di Cristallografia
xmi l@b

Structure: single phase

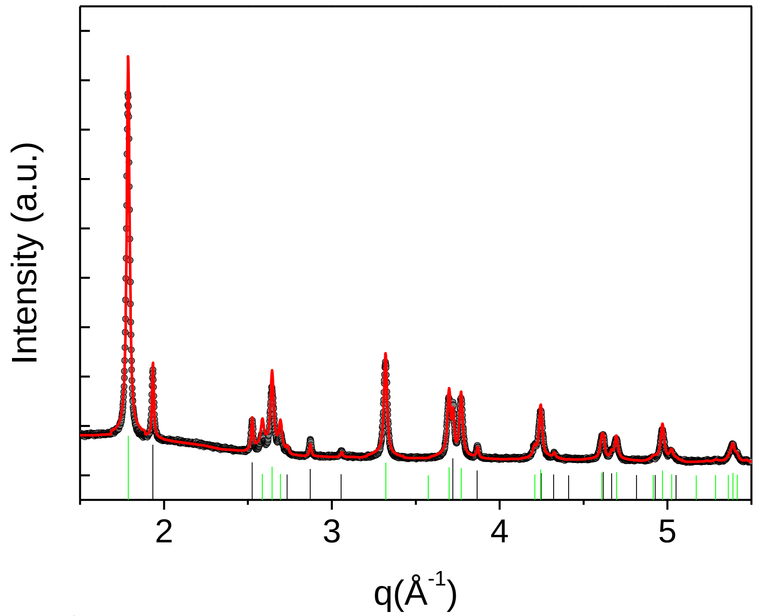




24.5 ±0.5 nm

✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167
CNR Istituto di Cristallografia

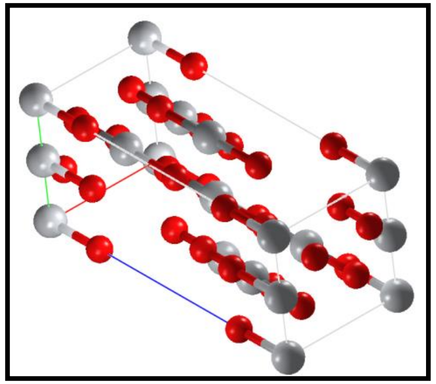
Stucture mixture



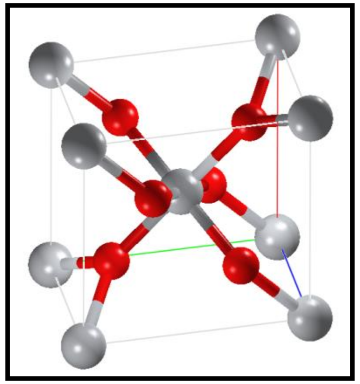
TiO_2

21±0.5 nm

35 ±0.5 nm



Anatase [91%]



Rutile [9%]

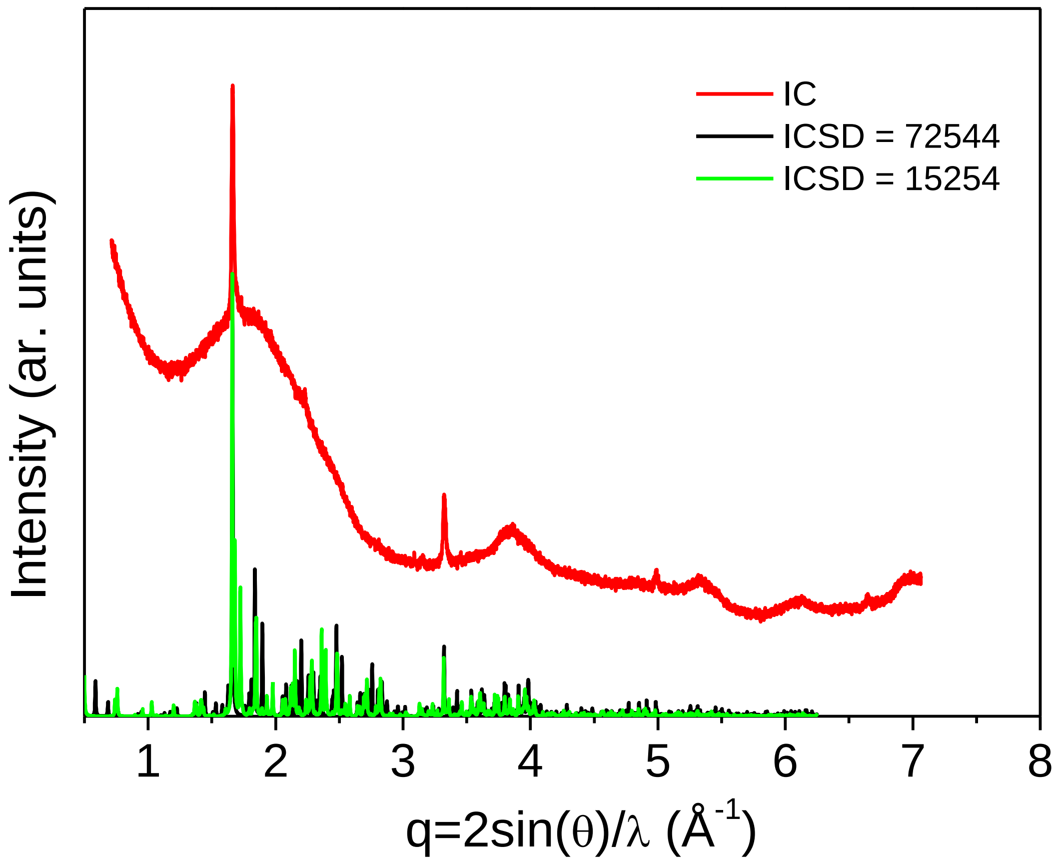
O

Identifier	7206075
Literature Reference	Rezaee, Masih, Mousavi Khoie, Seyyed Mohammad, Liu, Kun Hua, *CrystEngComm* (2011), **13**, 5055
Formula	O_2 Ti
Compound Name	Titanium oxide **- anatase**
Synonym	
Space Group	I 4_1/a m d
Cell Lengths	**a** 3.7850 **b** 3.7850 **c** 9.5196
Cell Angles	**α** 90 **β** 90 **γ** 90
Cell Volume	136.38

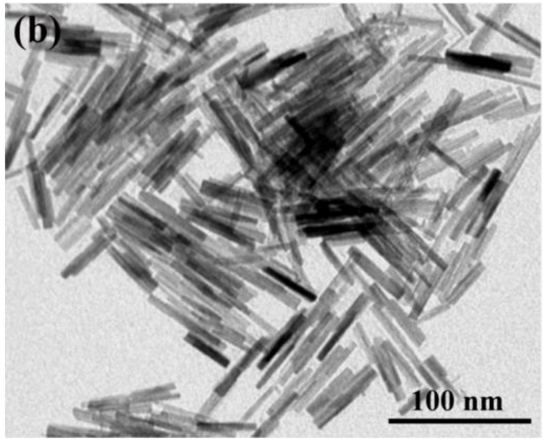
Identifier	9007432
Literature Reference	Baur, W. H., *Acta Crystallographica* (1956), **9**, 515
Formula	O_2 Ti
Compound Name	**rutile**
Synonym	
Space Group	P 4_2/m n m
Cell Lengths	**a** 4.594 **b** 4.594 **c** 2.959
Cell Angles	**α** 90 **β** 90 **γ** 90
Cell Volume	62.4492

✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167
IC CNR Istituto di Cristallografia

Structure of WOx nanocrystalline powders

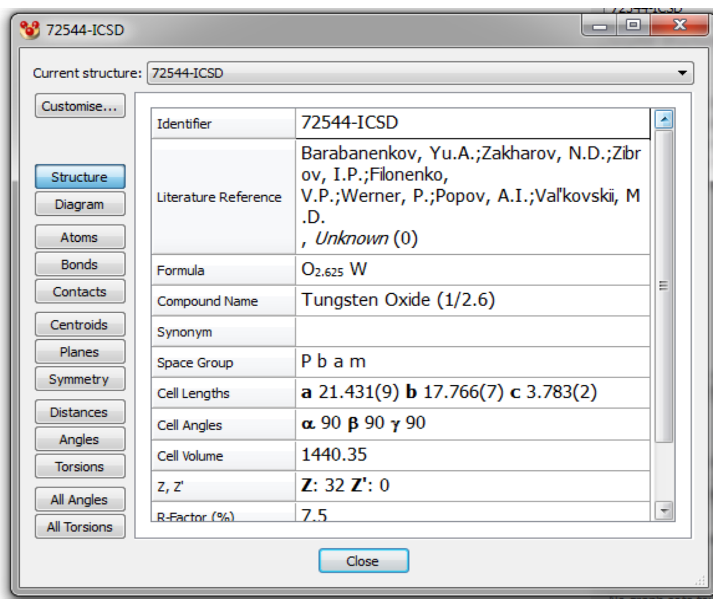


Data can be explained either as:
$W_{18}O_{49}$(ICSD=15254)
or
$WO_{2.626}$ (ICSD=72544)
phases.



✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167

CNR Istituto di Cristallografia

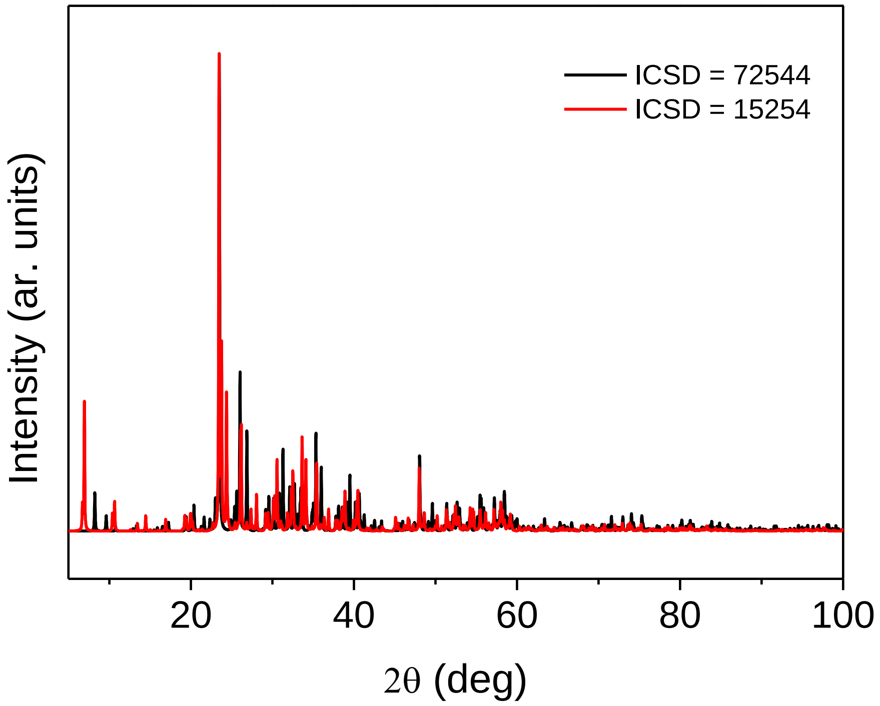


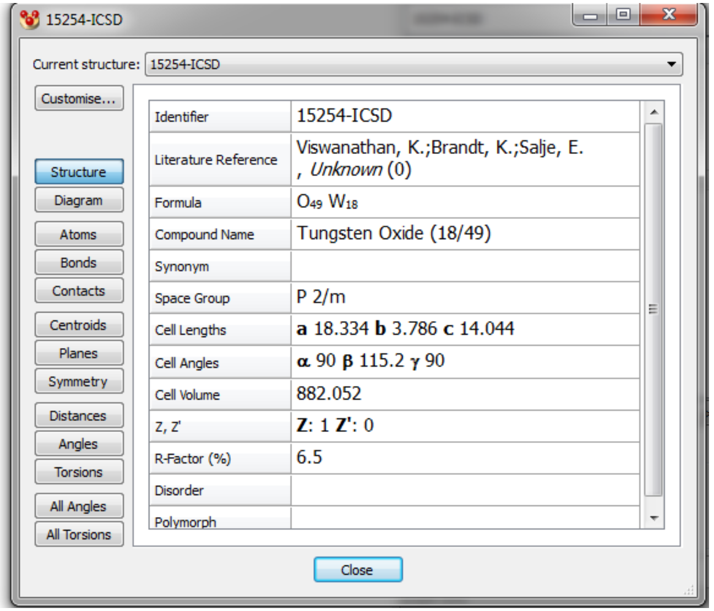
72544-ICSD

Current structure: 72544-ICSD

Identifier	72544-ICSD
Literature Reference	Barabanenkov, Yu.A.;Zakharov, N.D.;Zibrov, I.P.;Filonenko, V.P.;Werner, P.;Popov, A.I.;Val'kovskii, M.D. , *Unknown* (0)
Formula	$O_{2.625}$ W
Compound Name	Tungsten Oxide (1/2.6)
Synonym	
Space Group	P b a m
Cell Lengths	**a** 21.431(9) **b** 17.766(7) **c** 3.783(2)
Cell Angles	**α** 90 **β** 90 **γ** 90
Cell Volume	1440.35
Z, Z'	**Z**: 32 **Z'**: 0
R-Factor (%)	7.5

WO$_{2.626}$ (ICSD=72544)
orthorhombic





15254-ICSD

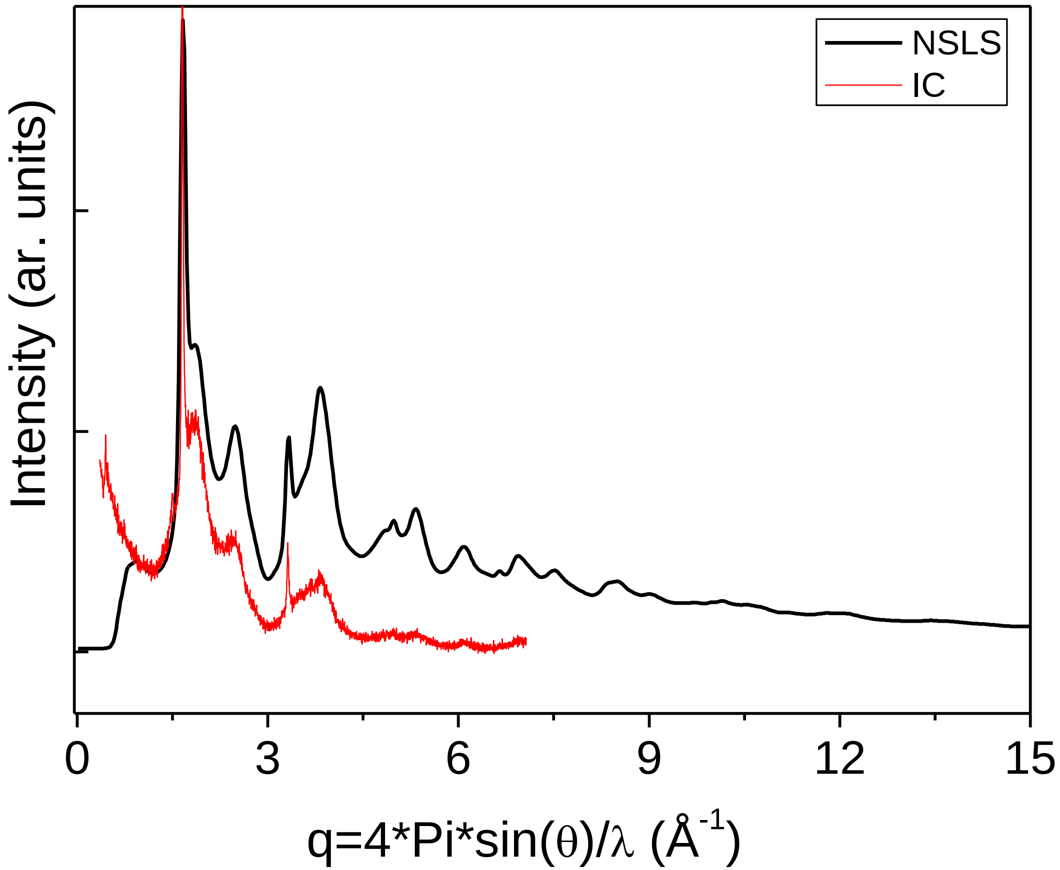
Current structure: 15254-ICSD

Identifier	15254-ICSD
Literature Reference	Viswanathan, K.;Brandt, K.;Salje, E. , *Unknown* (0)
Formula	O_{49} W_{18}
Compound Name	Tungsten Oxide (18/49)
Synonym	
Space Group	P 2/m
Cell Lengths	**a** 18.334 **b** 3.786 **c** 14.044
Cell Angles	**α** 90 **β** 115.2 **γ** 90
Cell Volume	882.052
Z, Z'	**Z**: 1 **Z'**: 0
R-Factor (%)	6.5
Disorder	
Polymorph	

$W_{18}O_{49}$ (ICSD=15254)
monoclinic

✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167
IC CNR Istituto di Cristallografia

Higher resolution data



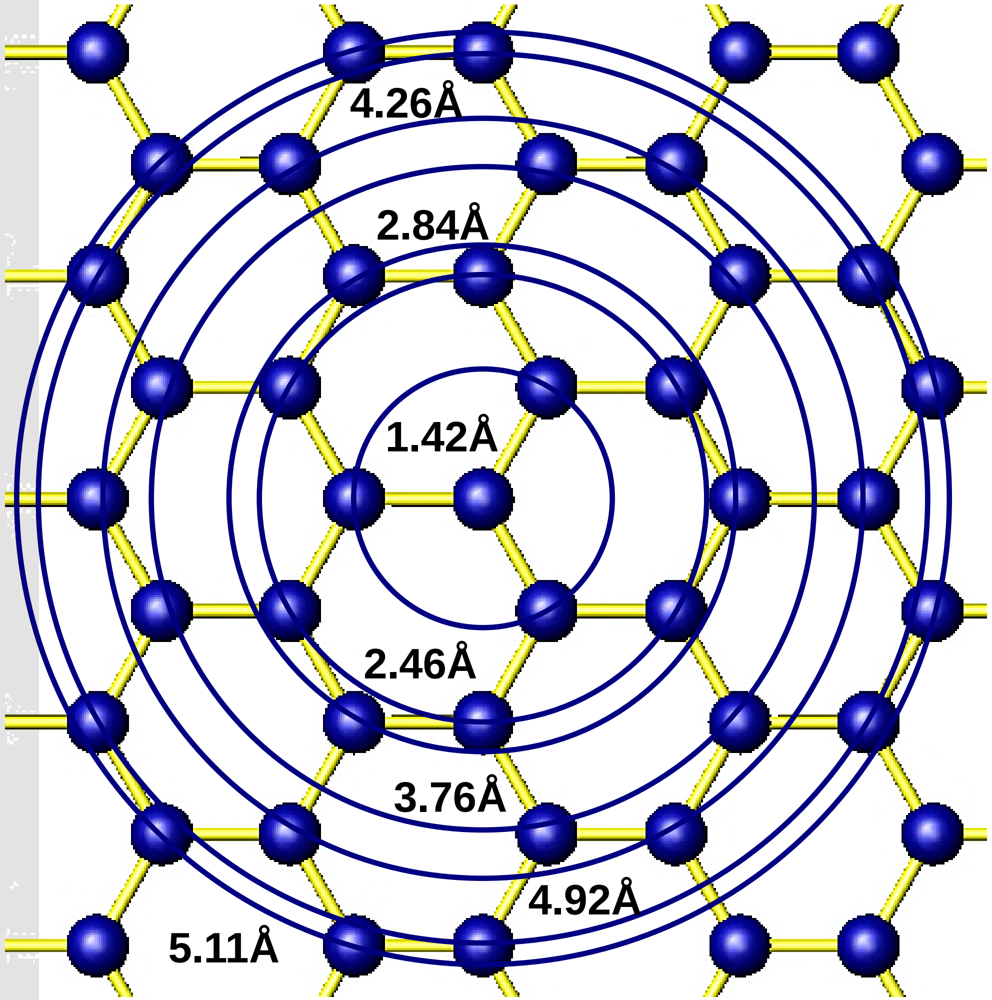
The XPD data collected at IC (IC-XPD) were acquired with a Bruker D8-Discover (3.3 kW) diffractometer equipped with a Cu source (8KeV, λ=1.540562 Å)

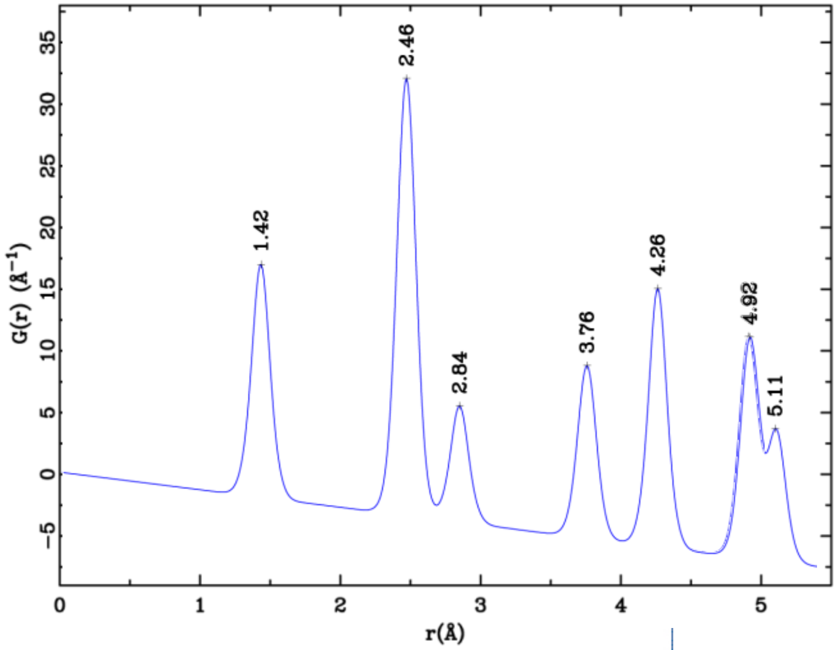
The NSLS data (NSLS-XPD) were measured using X-ray radiation with an energy of 66.7 keV (λ=0.18597 Å).

✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167

CNR | Istituto di Cristallografia

Pair Distribution Function



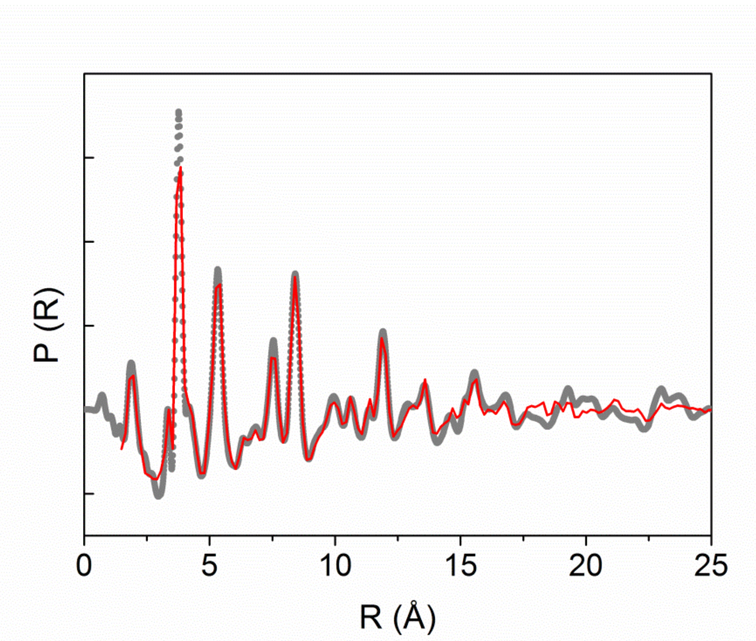


Pair distribution function (PDF) gives the probability of finding an atom at a distance “r” from a given atom.

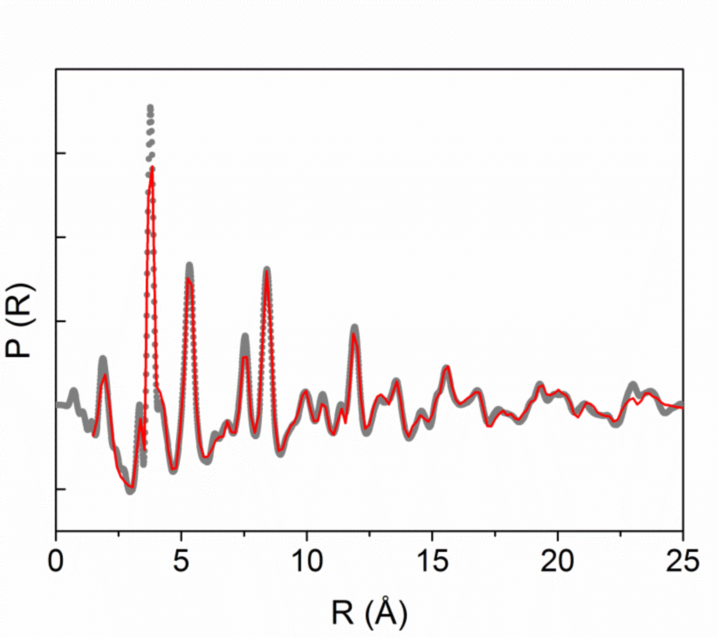
✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167

CNR | Istituto di Cristallografia

Structure of WOx nanocrystalline powders



$W_{32}O_{84}$ (ICSD=72544)



$W_{18}O_{49}$ (ICSD=15254)


ChemPubSoc Europe
DOI: 10.1002/cphc.201501175
CHEMPHYSCHEM Articles

Static and Dynamical Structural Investigations of Metal-Oxide Nanocrystals by Powder X-ray Diffraction: Colloidal Tungsten Oxide as a Case Study

Rocco Caliandro,*[a] Teresa Sibillano,[a] B. Danilo Belviso,[a] Riccardo Scarfiello,[b, c, f] Jonathan C. Hanson,[d] Eric Dooryhee,[e] Michele Manca,[c] P. Davide Cozzoli,[b, f] and Cinzia Giannini*[a]

Results of the PDF data allowed to identify the **monoclinic $W_{18}O_{49}$ crystal phase** (ICSD # 15254); fitting proved that the actual stoichiometry was **$W_{16\pm0.4}O_{45\pm3}$**

✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167

IC CNR | Istituto di Cristallografia

XMI L@b

What is the size/shape?

✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167

CNR Istituto di Cristallografia

Size/Shape

γ-Fe_2O_3 spheres

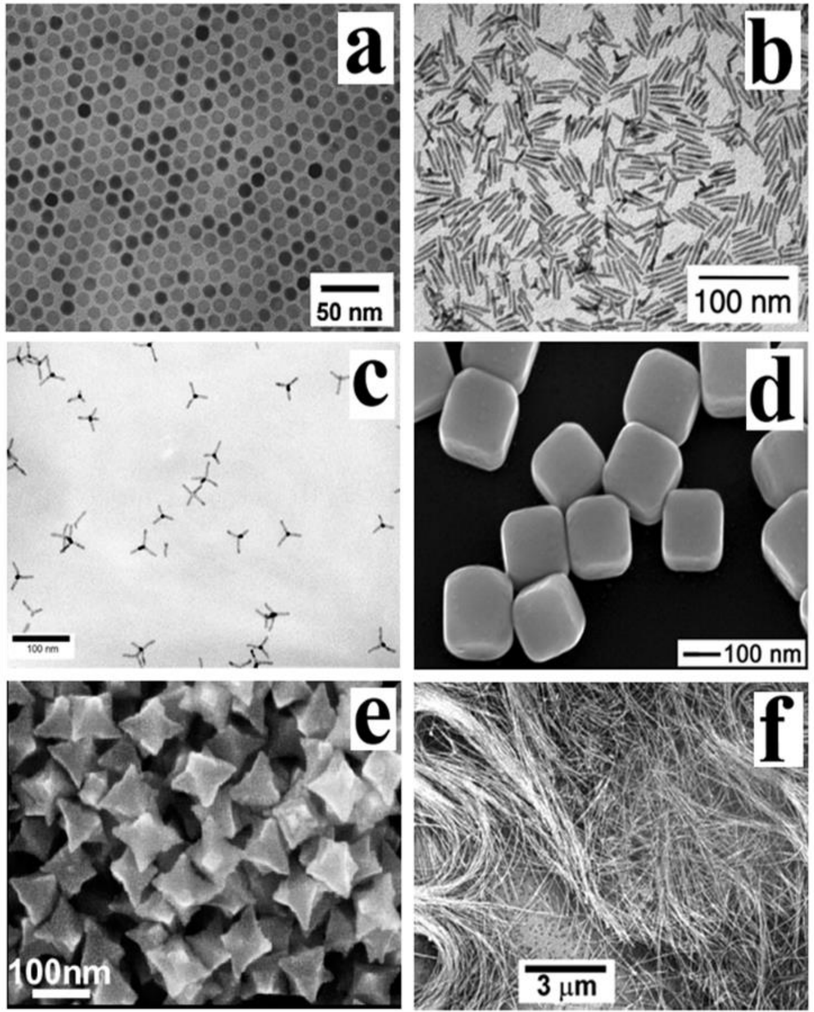
CdSe nanorods

CdTe tetrapods

Ag nanocubes

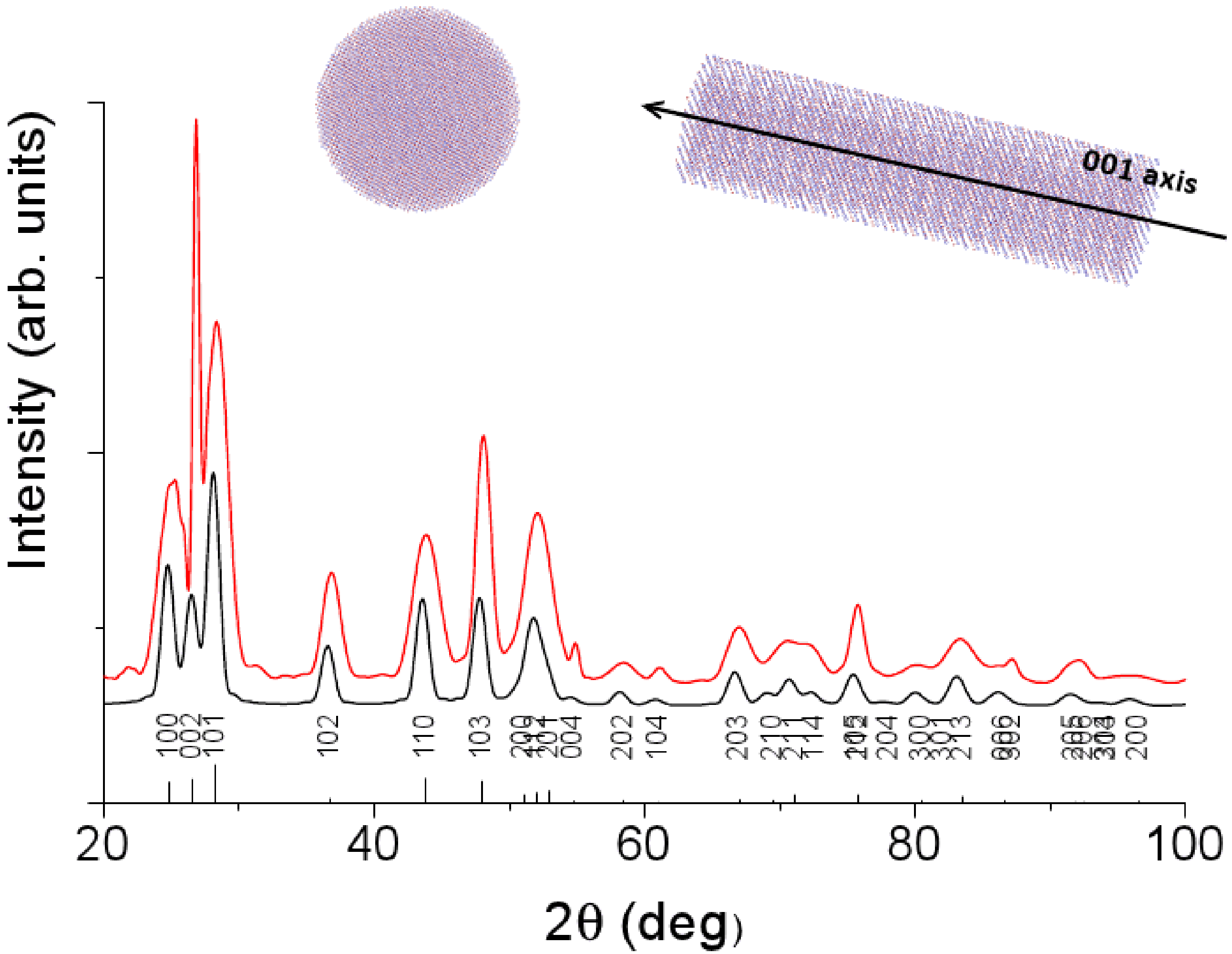
PbSe stars

PbSe nanowires



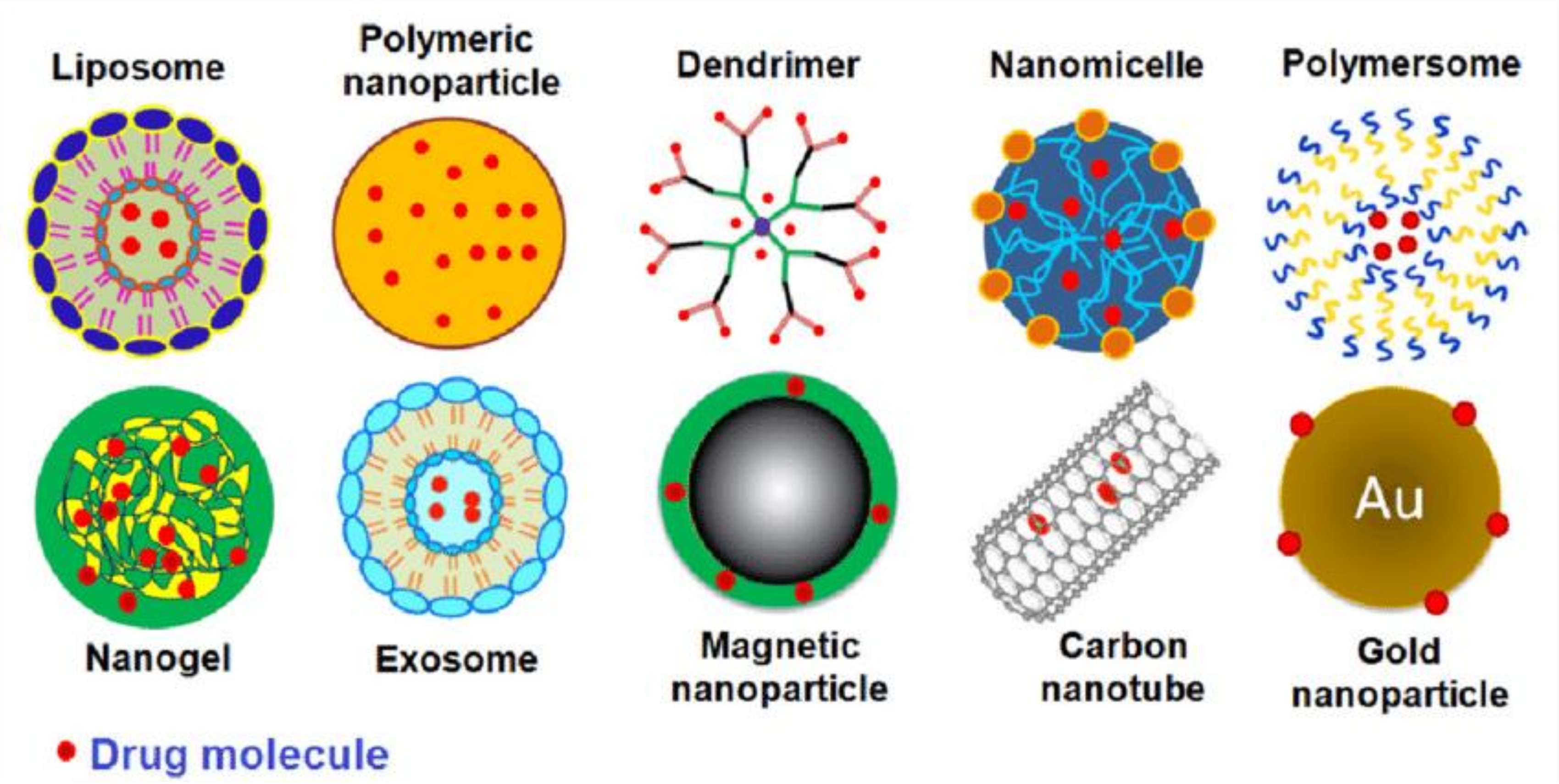
✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167
CNR Istituto di Cristallografia

Size/Shape



✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167
CNR Istituto di Cristallografia

nano carries for drug delivery



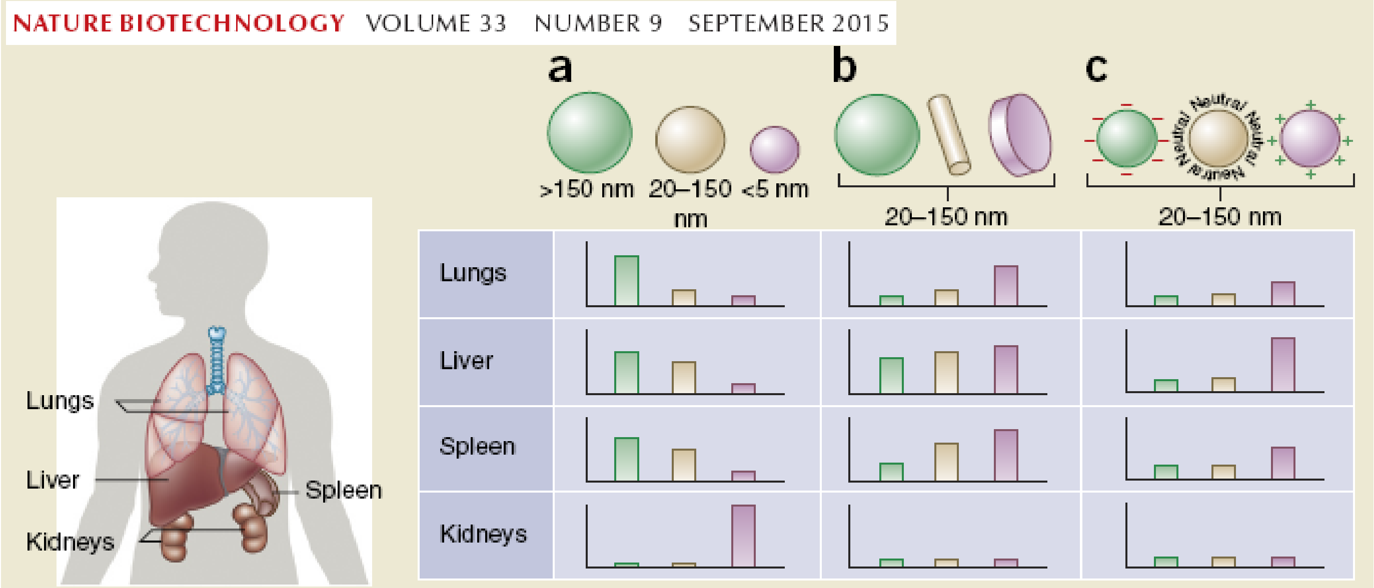
cinzia.giannini@ic.cnr.it
+39 080 5929167
CNR Istituto di Cristallografia

nano carries for drug delivery

(a) **Spherical**: d >2,000 nm accumulate readily within spleen and liver, as well as in the capillaries of the lungs. d~100–200 nm extravasate through vascular fenestrations of tumors and escape filtration by liver and spleen. d>150 nm, more and more nanoparticles are entrapped in liver and spleen. d<5 nm are filtered out by the kidneys;

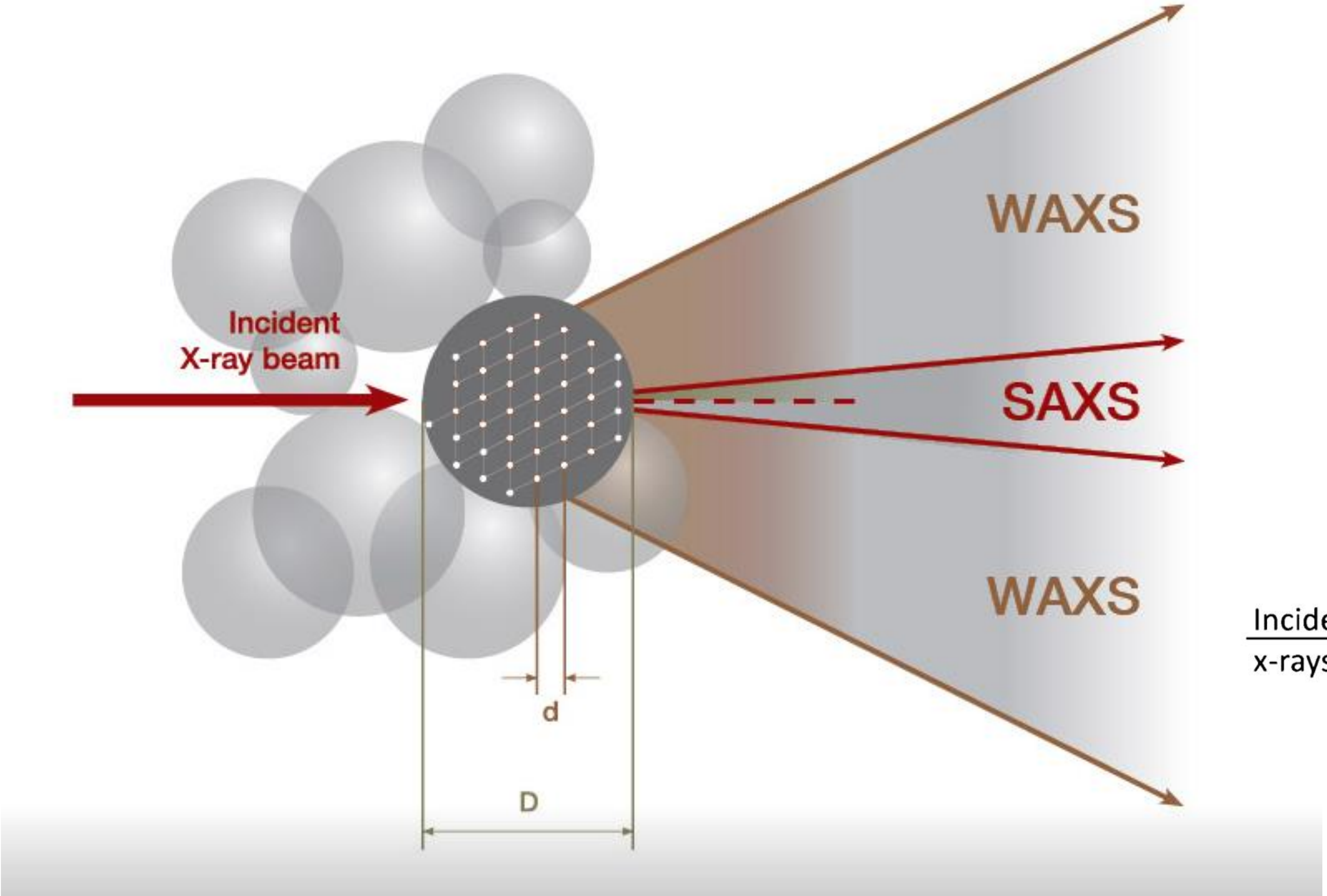
(b) **Non-spherical:** Different shapes exhibit unique flow characteristics that substantially alter circulating lifetimes, cell membrane interactions and macrophage uptake, which in turn affect biodistribution among the different organs;

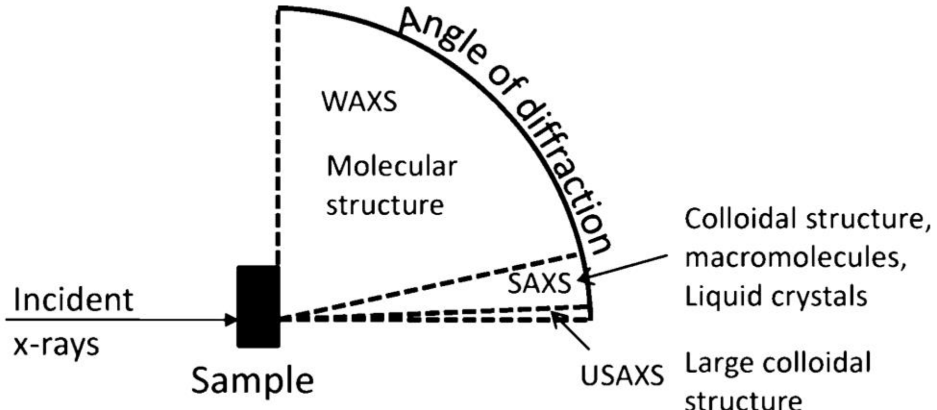
(c) **Charge** influences circulation times and interaction with resident macrophages of organs, with positively charged particles more prone to sequestration by macrophages in the lungs, liver and spleen.



✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167
CNR | Istituto di Cristallografia

SAXS



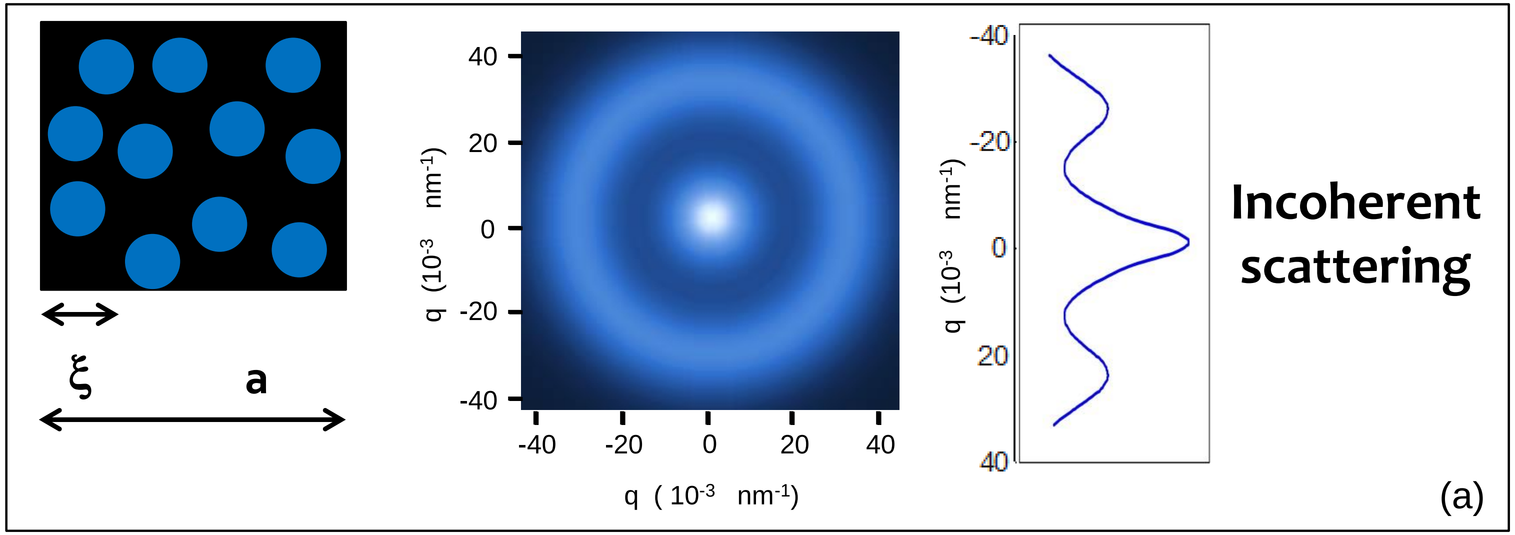


cinzia.giannini@ic.cnr.it
✆ +39 080 5929167

ICCNR Istituto di Cristallografia

xmi l@b

Incoherent scattering assembly

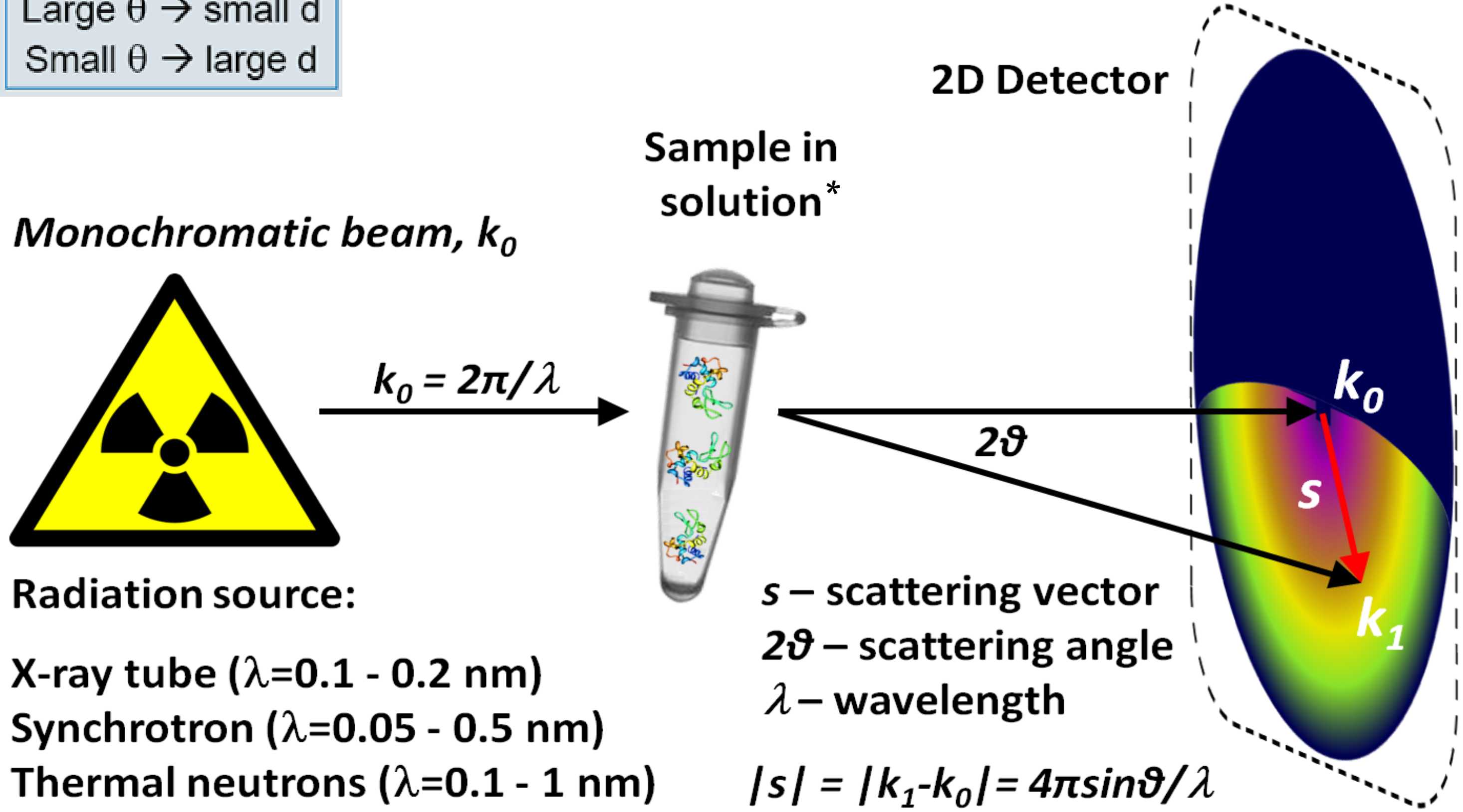


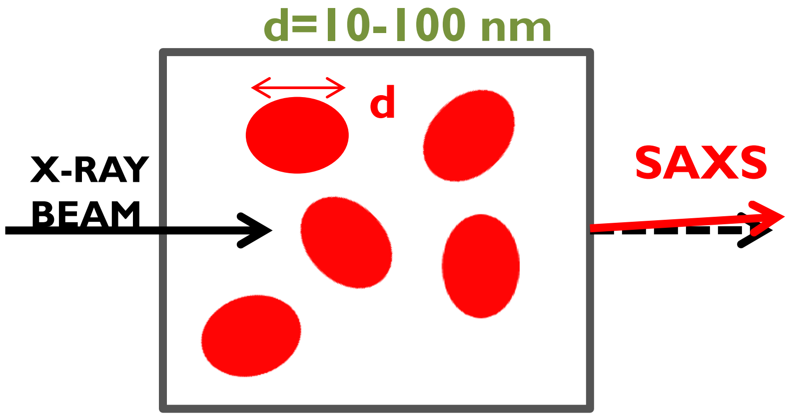
cinzia.giannini@ic.cnr.it
+39 080 5929167
CNR Istituto di Cristallografia

SAXS

$\sin\theta = \lambda / 2d$

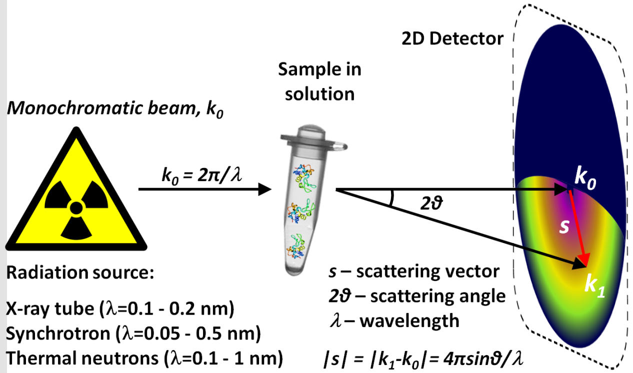
Large θ → small d
Small θ → large d





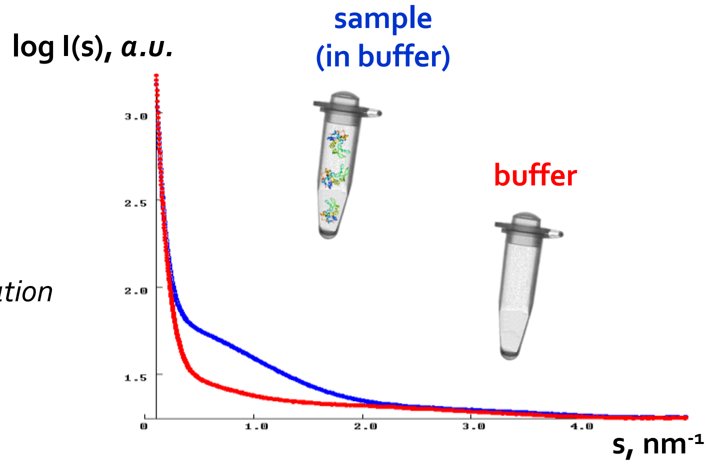
✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167
CNR Istituto di Cristallografia

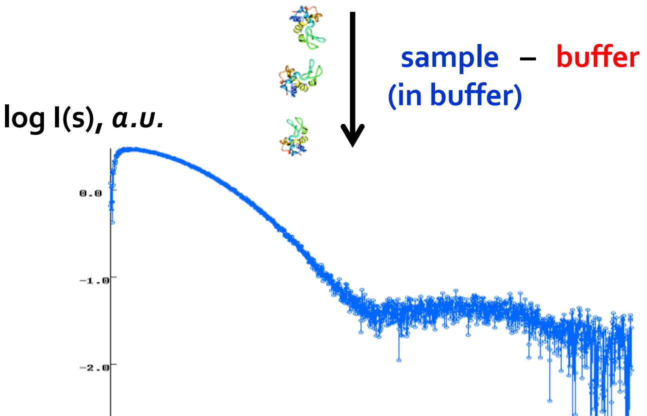
SAXS

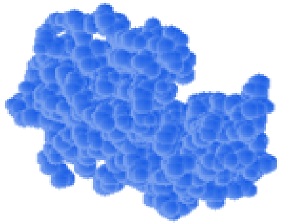


radially averaged

normalized:
sample concentration
incoming beam
exposure time





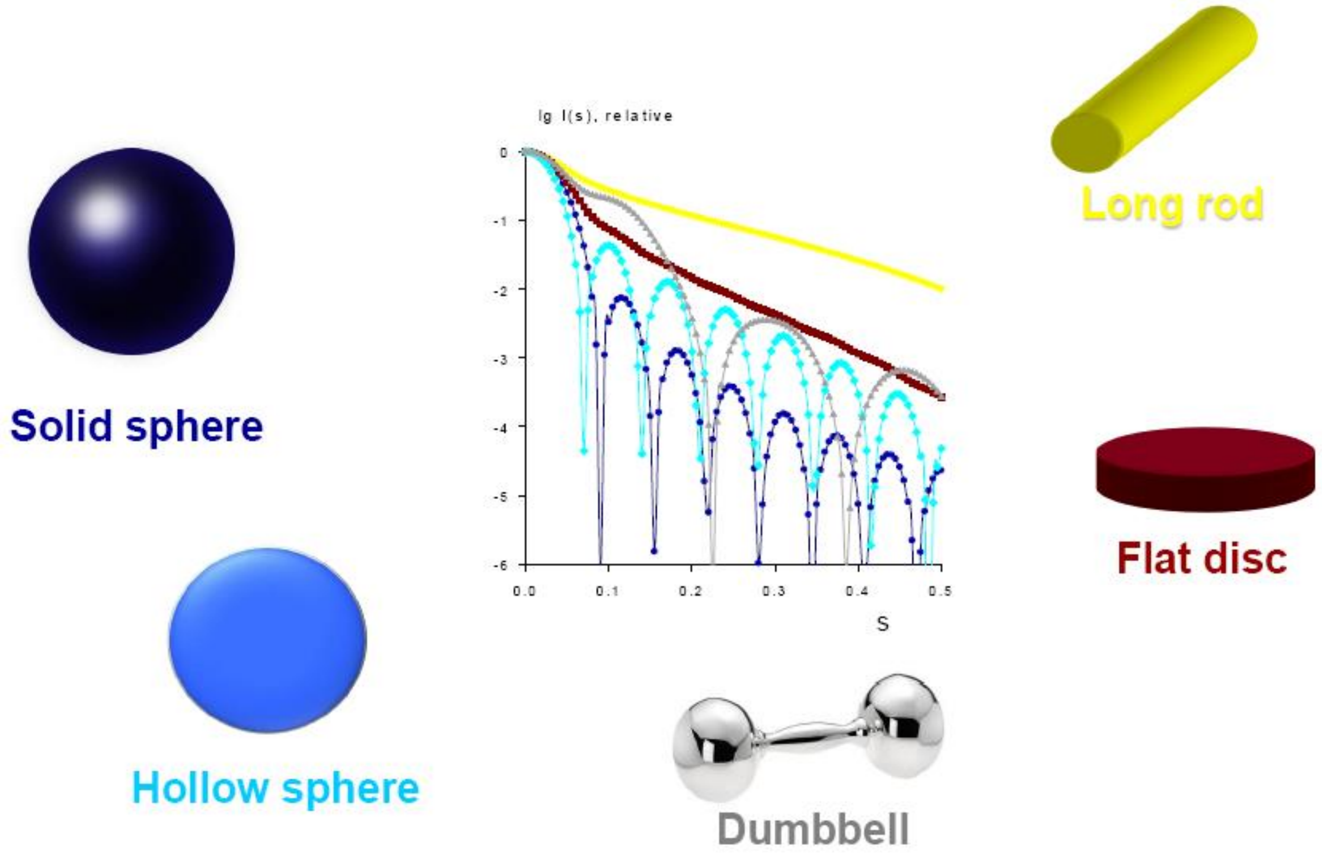


$$I(s) = 4\pi \int_0^D p(r) \frac{\sin sr}{sr} dr$$

for *monodisperse* systems the scattering is proportional to that of a single particle

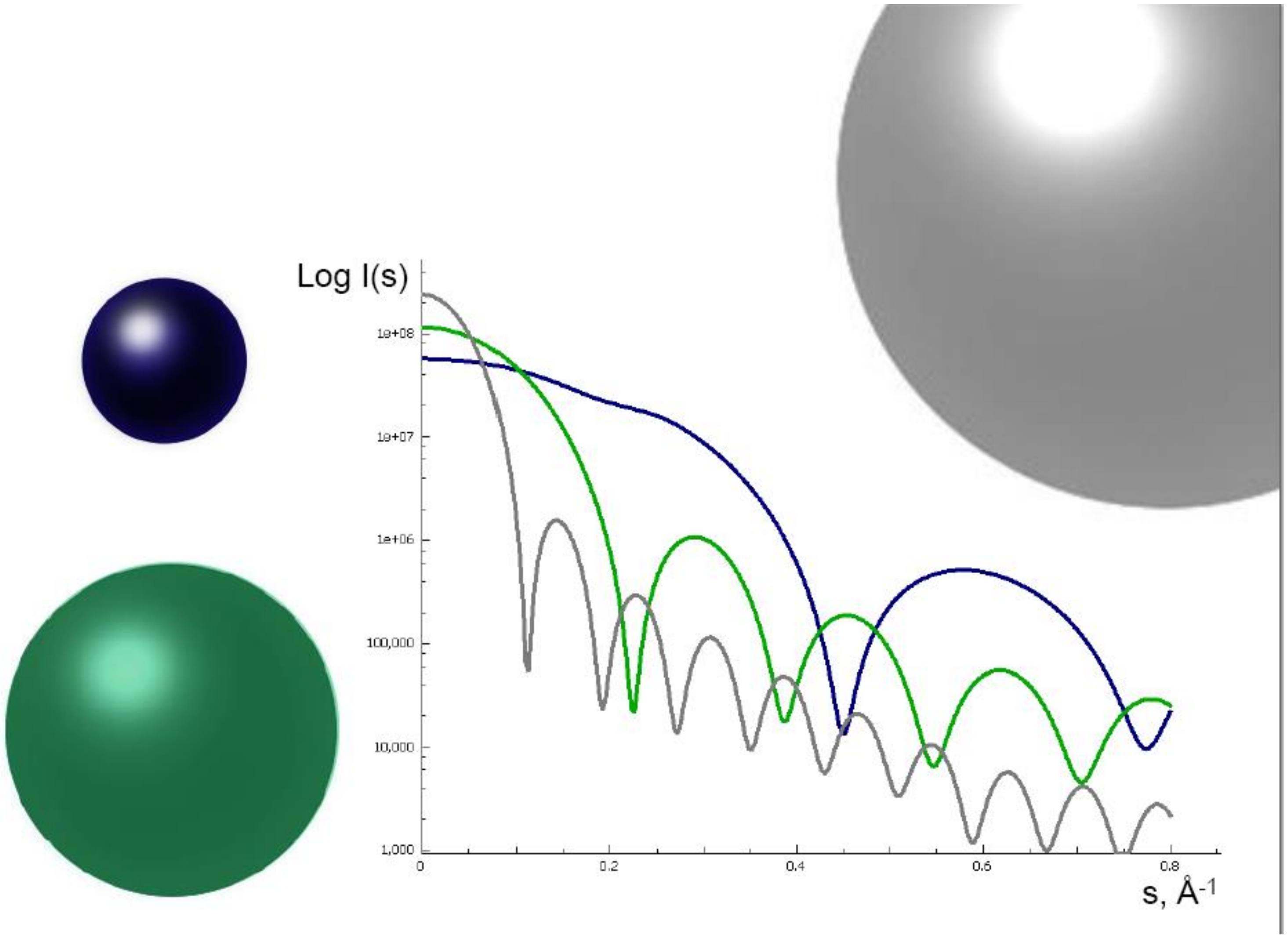
✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167

SAXS



✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167
IC CNR Istituto di Cristallografia
xmi l@b

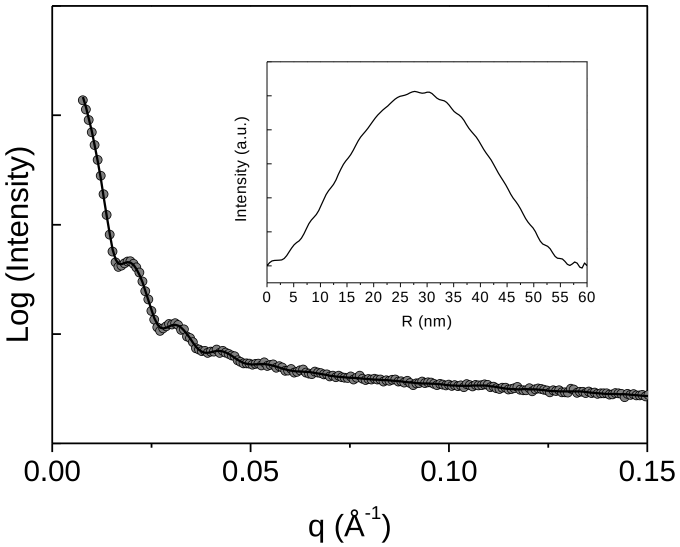
SAXS - size

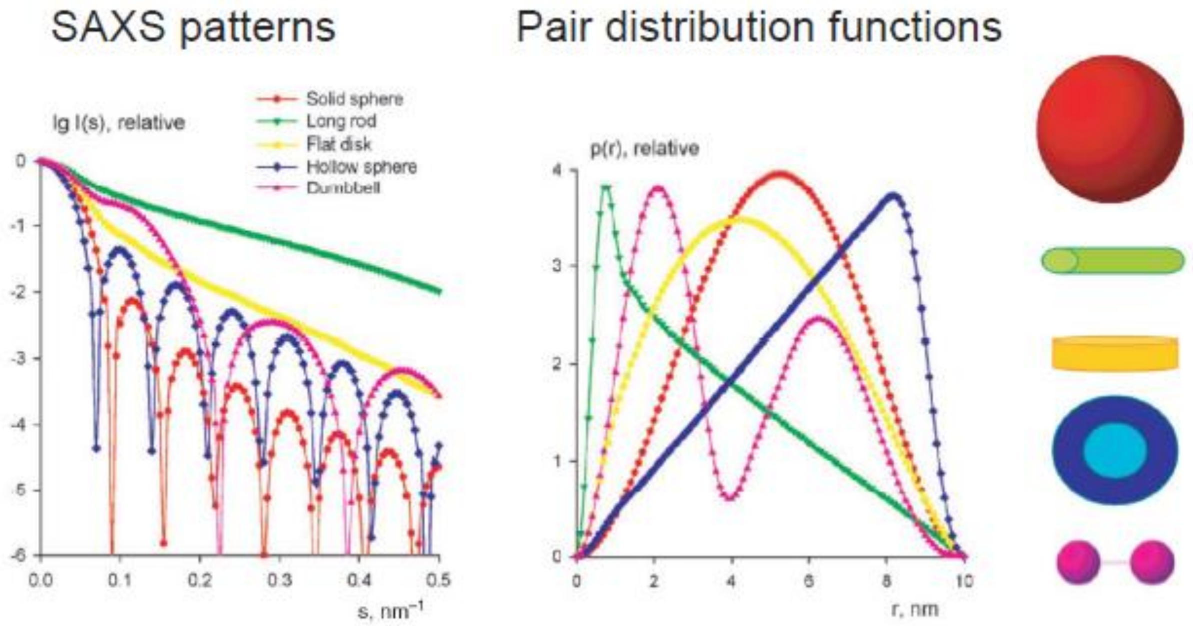


✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167

CNR Istituto di Cristallografia

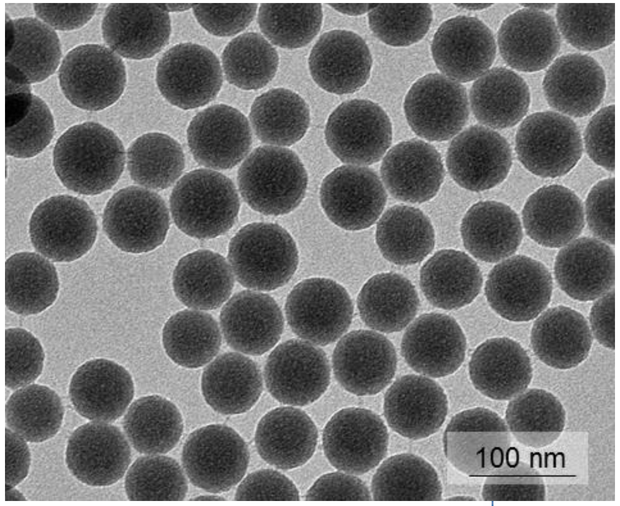
SAXS of non-crystalline particles





R_g=21.7 nm → D = 2*√5/3R_g ~ 56±1 nm →

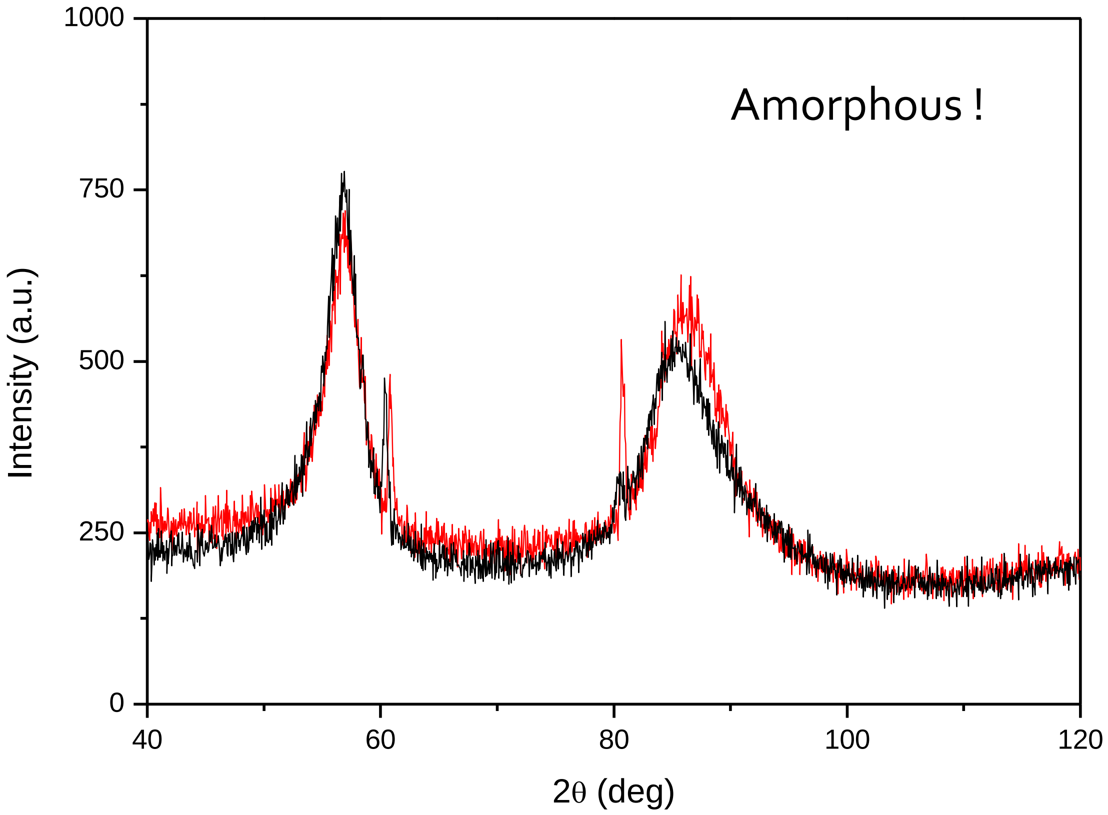
Spherical particle with D~55 nm



TEM

✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167
CNR Istituto di Cristallografia

SAXS/WAXS

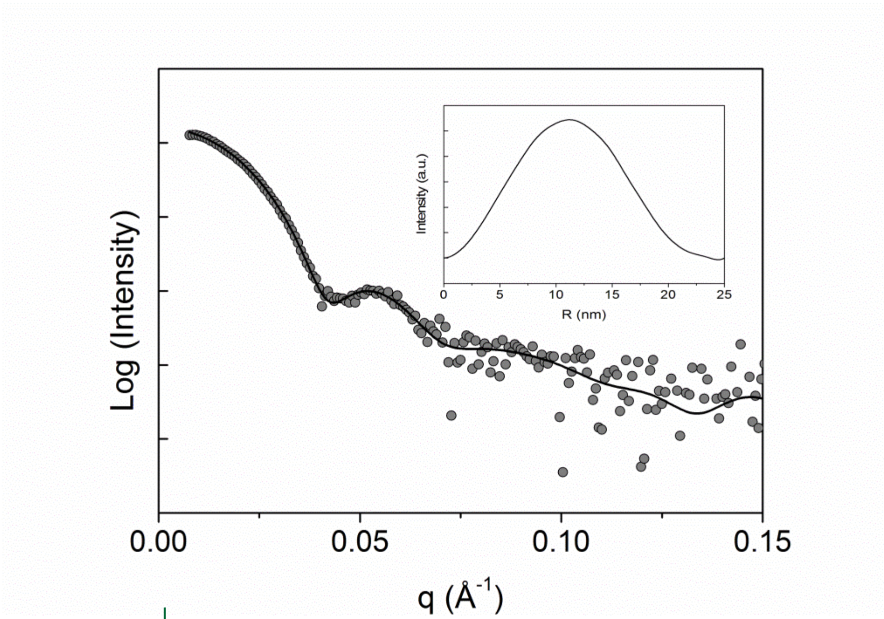


cinzia.giannini@ic.cnr.it
+39 080 5929167

IC CNR Istituto di Cristallografia

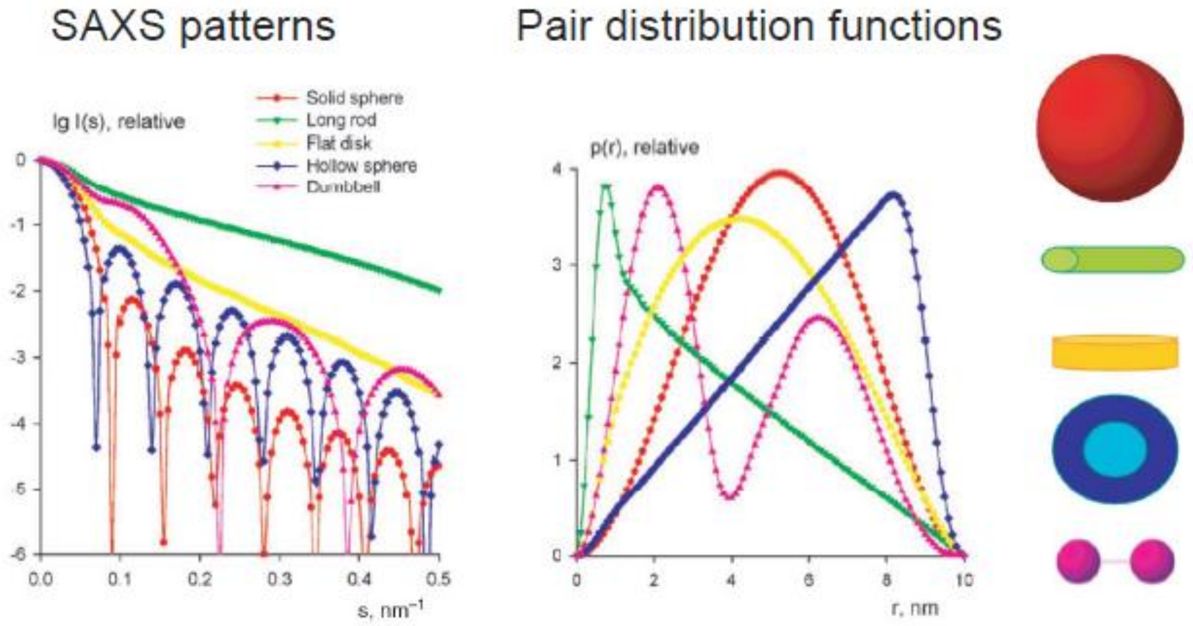
xmi l@b

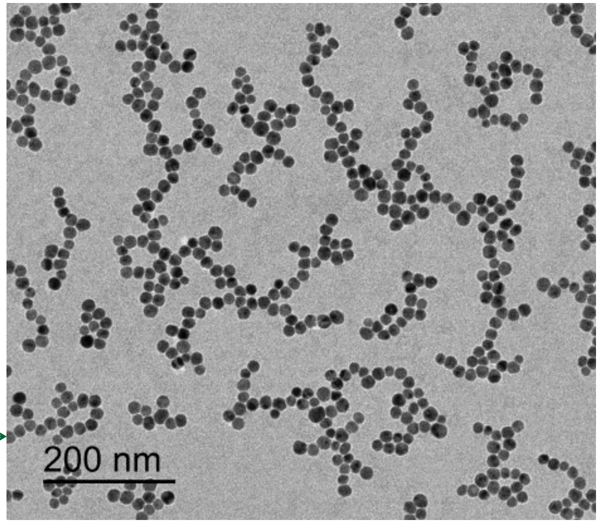
SAXS
of crystalline particles



R_g=8.6 nm → $D = 2*\sqrt{5/3}R_g \sim 22\pm1$ nm →

Spherical particle with D=22 nm

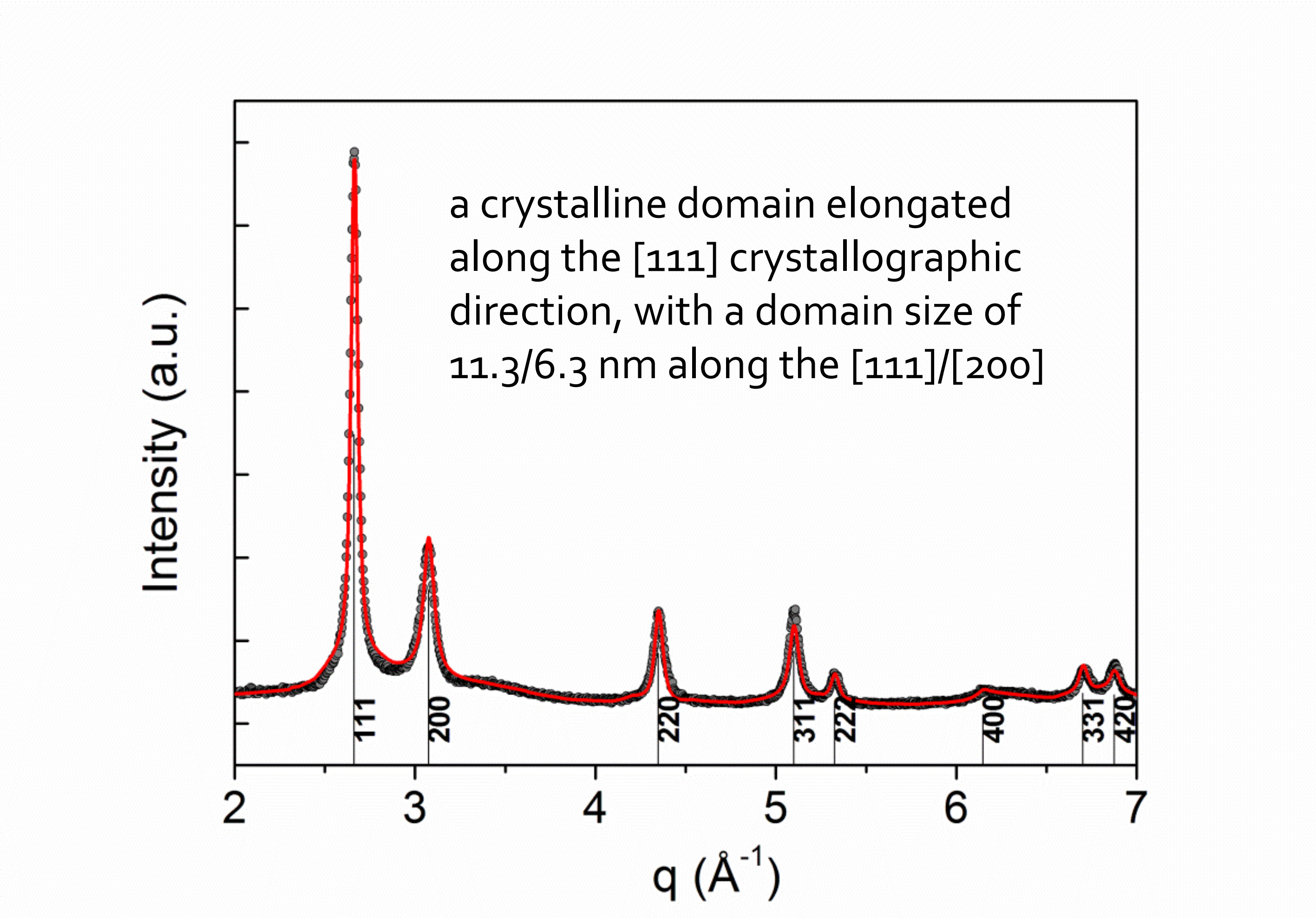


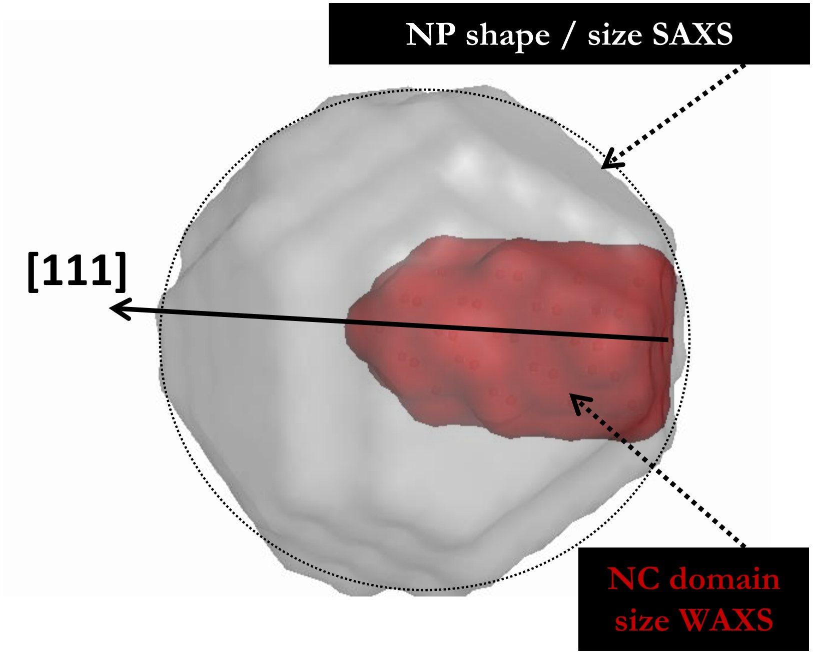


TEM

✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167
CNR | Istituto di Cristallografia

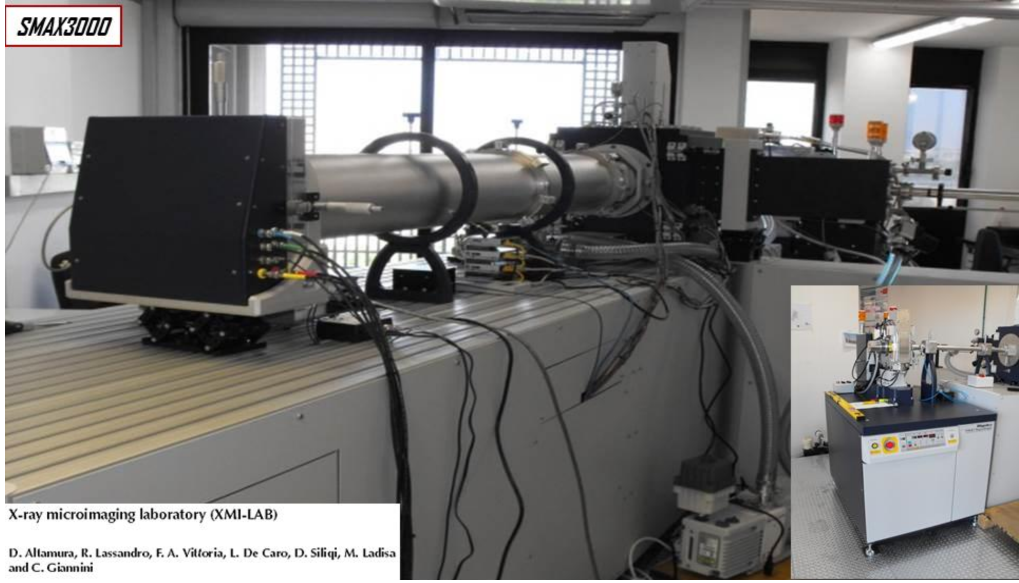
SAXS/WAXS

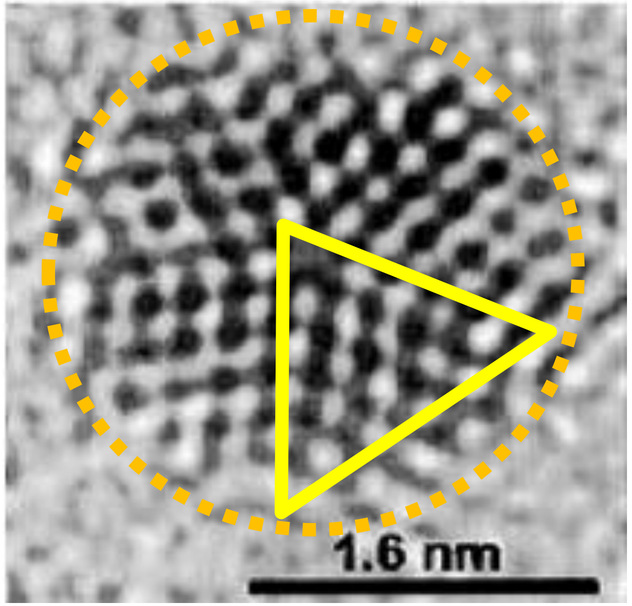




✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167
IC CNR | Istituto di Cristallografia
xmi l@b

SAXS/WAXS





crystalline domain - WAXS

NP shape / size SAXS

cinzia.giannini@ic.cnr.it
+39 080 5929167

IC CNR Istituto di Cristallografia

xmi l@b

What is the size/shape for nanoparticles on surfaces?

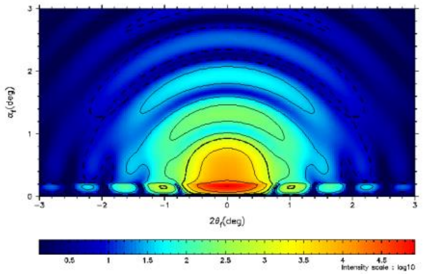
✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167

IC CNR Istituto di Cristallografia

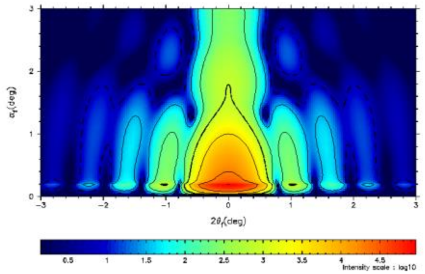
xmi l@b

GISAXS

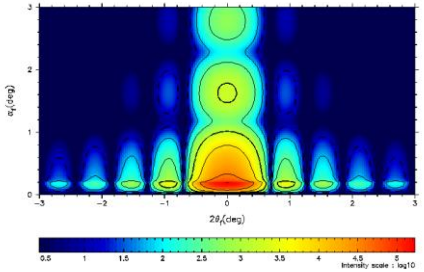
FULL SPHERE



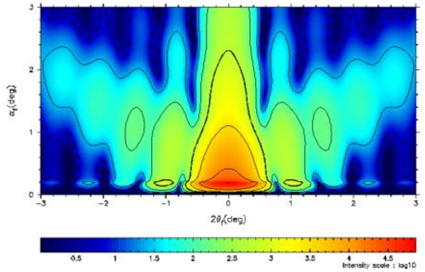
HALF SPHERE



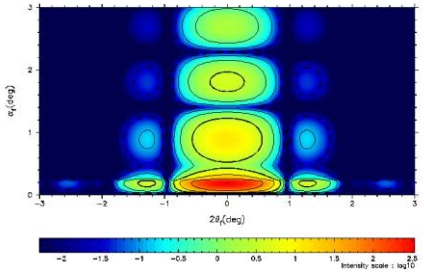
CYLINDER



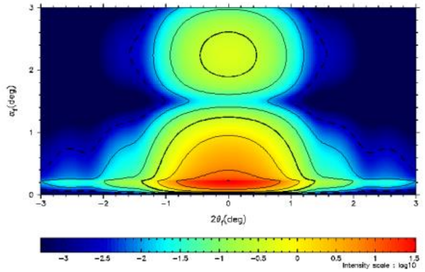
PYRAMID

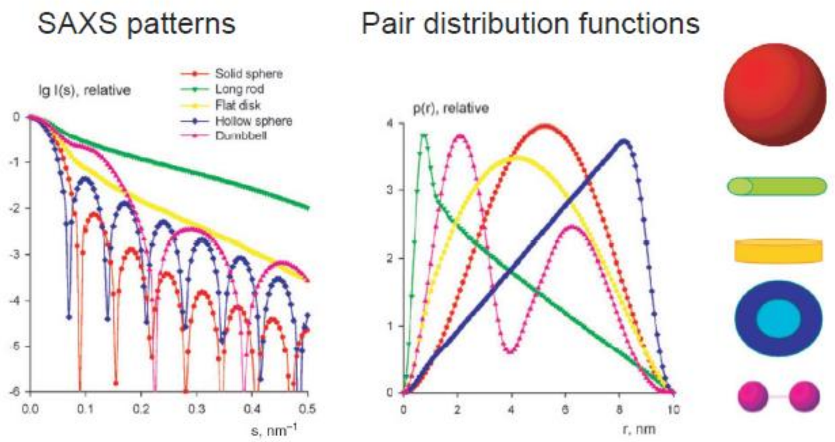


CUBOCTAHEDRON



TETRAHEDRON





INTECH
open science | open minds

OPEN ACCESS ARTICLE

Nanomaterials and Nanotechnology

Assembled Nanostructured Architectures Studied By Grazing Incidence X-Ray Scattering

Invited Feature Article

Davide Altamura[1], Teresa Sibillano[1], Dritan Siliqi[1], Liberato De Caro[1] and Cinzia Giannini[1,*]

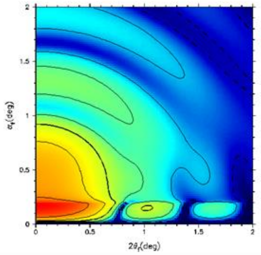
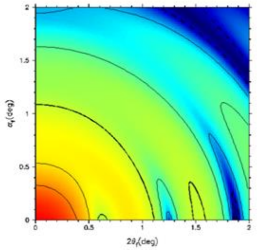
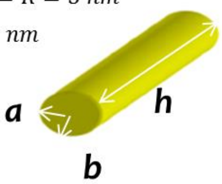
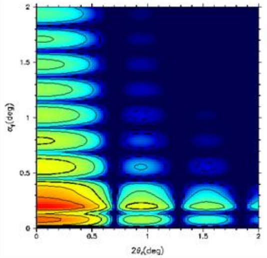
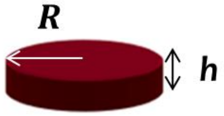
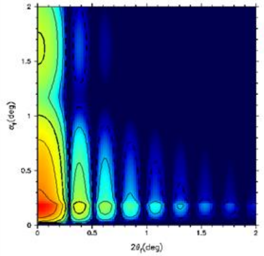
1 Istituto di Cristallografia, Sede di Bari, Bari, Italy
* Corresponding author: cinzia.giannini@ic.cnr.it

cinzia.giannini@ic.cnr.it
+39 080 5929167

CNR | Istituto di Cristallografia

xmi l@b

GISAXS

SPHERE $R = 5\ nm$ 	 FORM FACTOR		
HOLLOW SPHERE  $R_2 - R_1 = 1\ nm$	 FORM FACTOR		
CYLINDER $a = b = R = 5\ nm$ $h = 25\ nm$ 	 FORM FACTOR		
FLAT DISK $R = 12.5\ nm$ $h = 5\ nm$ 	 FORM FACTOR		

INTECH open science | open minds

OPEN ACCESS ARTICLE

Nanomaterials and Nanotechnology

Assembled Nanostructured Architectures Studied By Grazing Incidence X-Ray Scattering

Invited Feature Article

Davide Altamura[1], Teresa Sibillano[1], Dritan Siliqi[1], Liberato De Caro[1] and Cinzia Giannini[1,*]

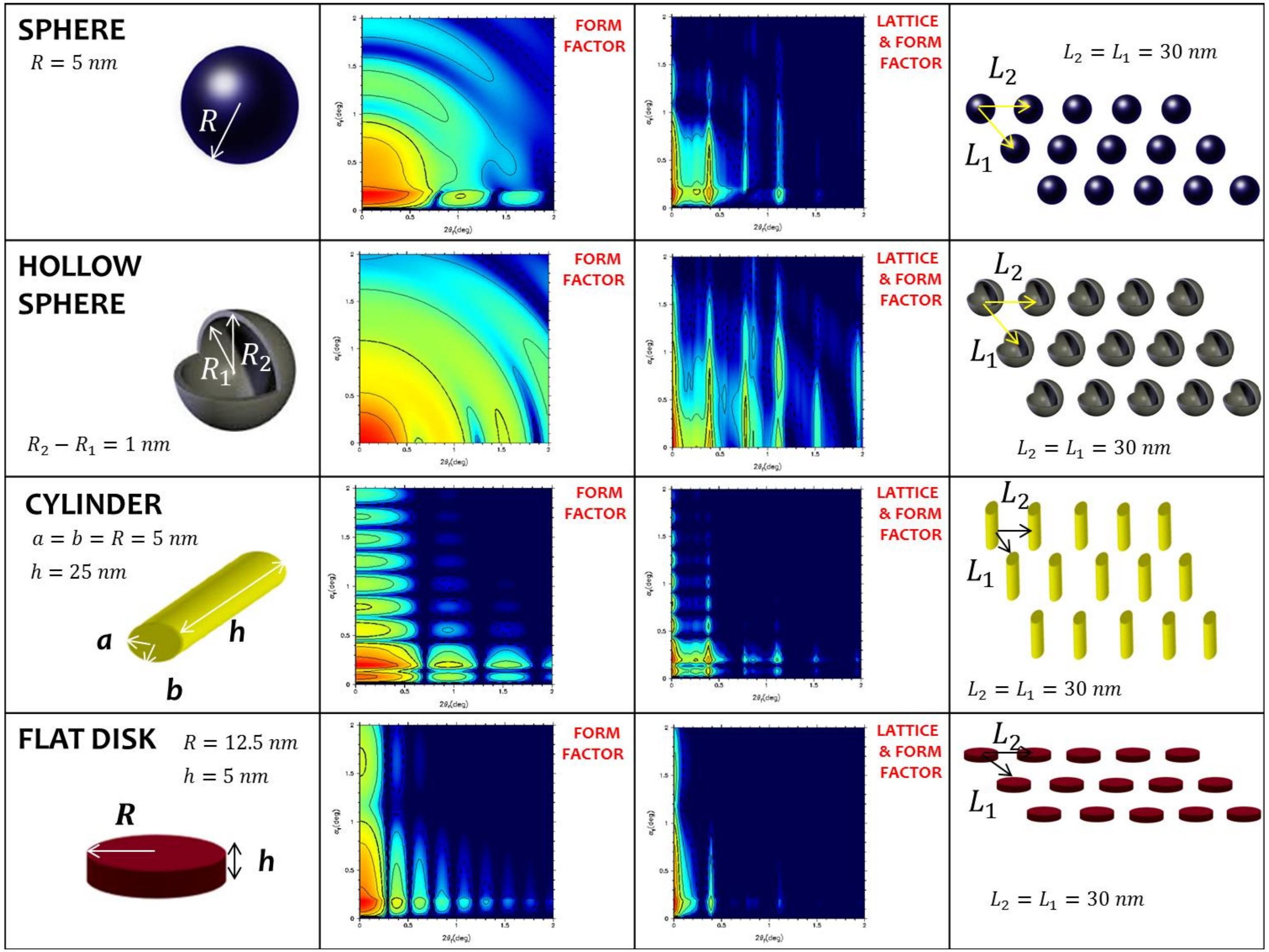
1 Istituto di Cristallografia, Sede di Bari, Bari, Italy
* Corresponding author: cinzia.giannini@ic.cnr.it

cinzia.giannini@ic.cnr.it
+39 080 5929167

IC CNR Istituto di Cristallografia

xmi l@b

GISAXS



INTECH
OPEN ACCESS ARTICLE
Nanomaterials and Nanotechnology

Assembled Nanostructured Architectures Studied By Grazing Incidence X-Ray Scattering

Invited Feature Article

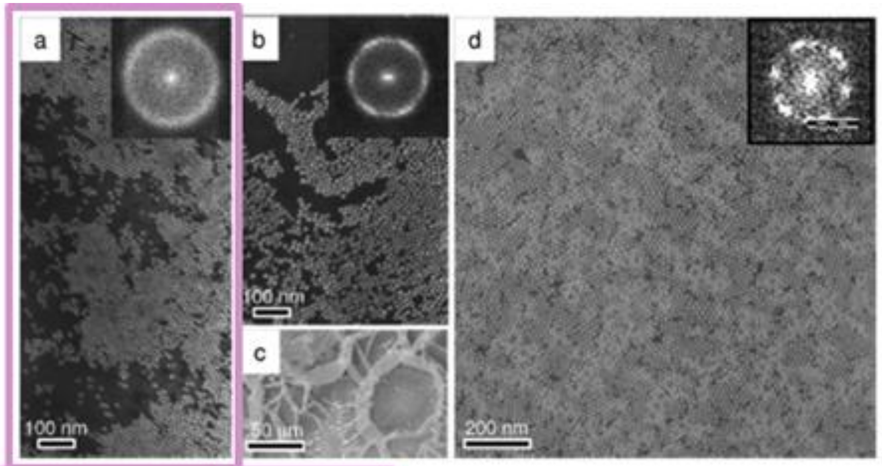
Davide Altamura[1], Teresa Sibillano[1], Dritan Siliqi[1], Liberato De Caro[1] and Cinzia Giannini[1,*]

1 Istituto di Cristallografia, Sede di Bari, Bari, Italy
* Corresponding author: cinzia.giannini@ic.cnr.it

cinzia.giannini@ic.cnr.it
+39 080 5929167

CNR Istituto di Cristallografia

GISAXS on Au nanoparticles on substrates



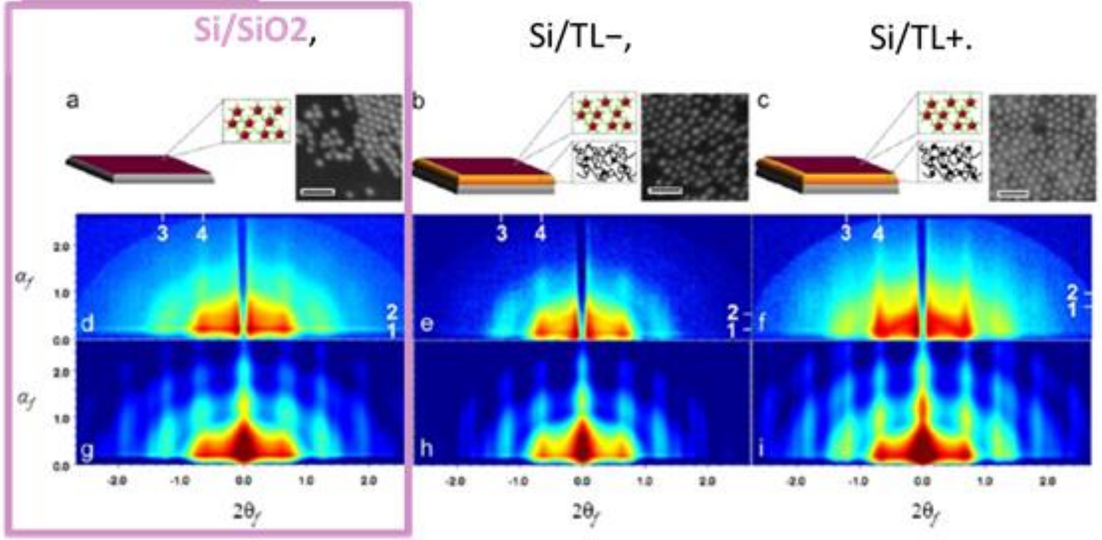


Table 1. Experimental Conditions Used for the Realization of the Two Different Teflon-like Films

	Si/TL−	Si/TL+
C_3F_6 flow rate	20 sccm	20 sccm
Ar flow rate	10 sccm	20 sccm
pressure	200 mTorr	200 mTorr
discharge power	200 W	250 W

THE JOURNAL OF PHYSICAL CHEMISTRY C
Article
pubs.acs.org/JPCC

Two-Dimensional Plasmonic Superlattice Based on Au Nanoparticles Self-Assembling onto a Functionalized Substrate

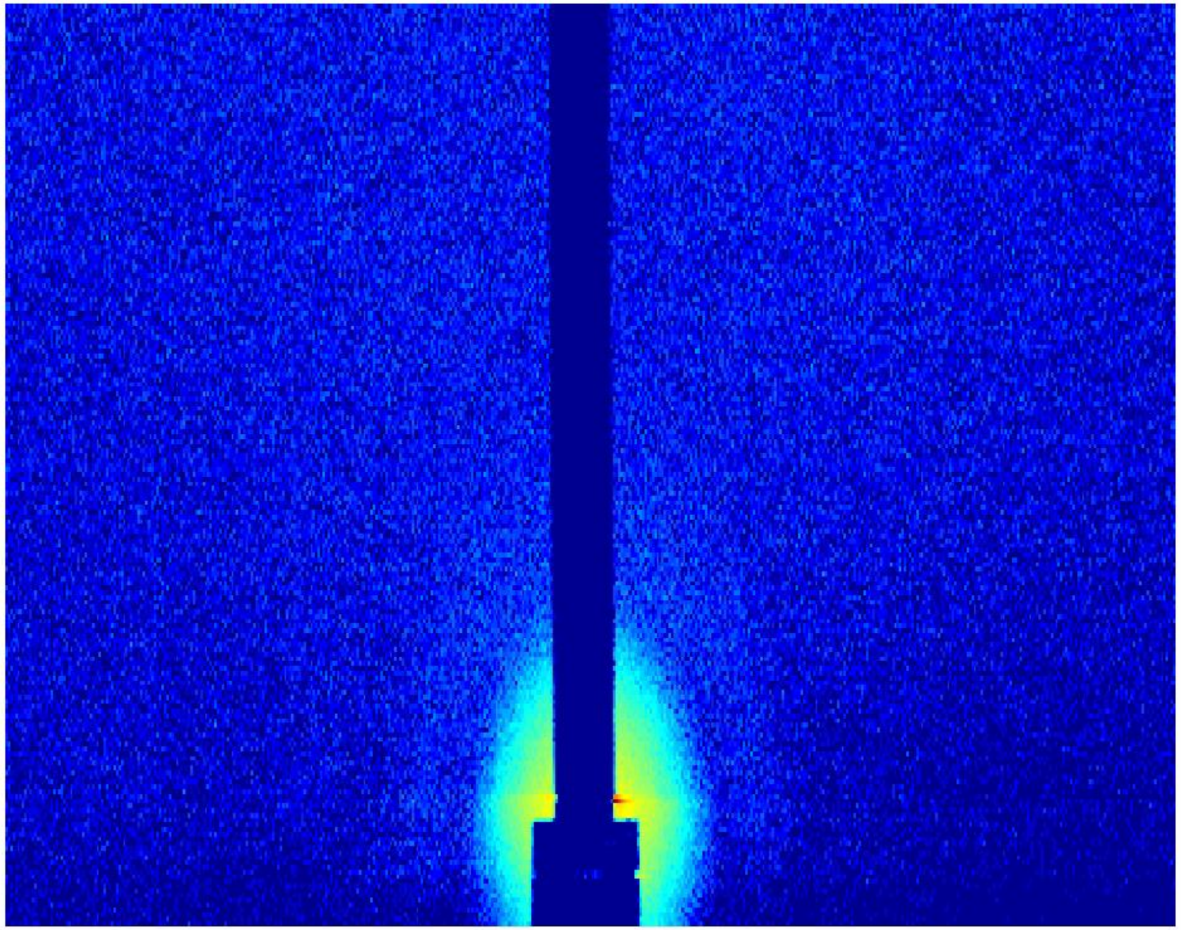
Michela Corricelli,[†,‡] Nicoletta Depalo,[†] Elisabetta Fanizza,[†,‡] Davide Altamura,[§] Cinzia Giannini,[§] Dritan Siliqi,[§] Rosa Di Mundo,[‡] Fabio Palumbo,[⊥] Vasily G. Kravets,[∥] Alexander N. Grigorenko,[∥] Angela Agostiano,[†,‡] Marinella Striccoli,[†] and M. Lucia Curri*[,†]

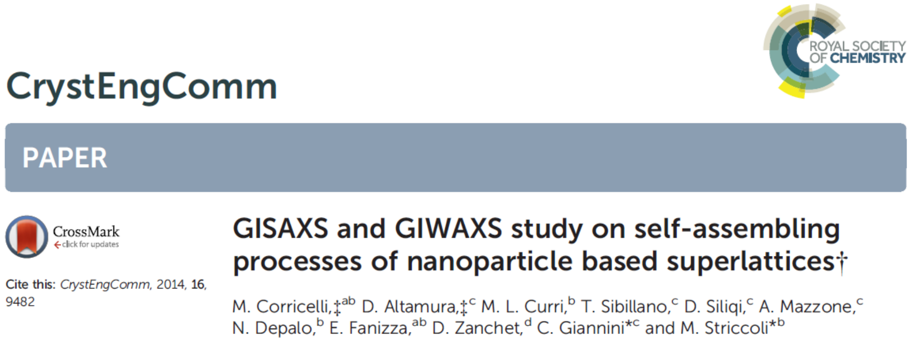
[†]Istituto per i Processi Chimico Fisici (IPCF-CNR) Bari, c/o Dipartimento di Chimica and [‡]Dipartimento di Chimica, Università degli Studi di Bari, Via Orabona 4, Bari I-70126, Italy
[§]Istituto di Cristallografia (CNR-IC), Via Amendola 122/O, Bari I-70126, Italy
[⊥]CNR-IMIP, Istituto di Metodologie Inorganiche e Plasmi, Via Orabona 4, Bari I-70126, Italy
[∥]School of Physics and Astronomy, the University of Manchester, Manchester M13 9PL, United Kingdom

✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167

CNR | Istituto di Cristallografia

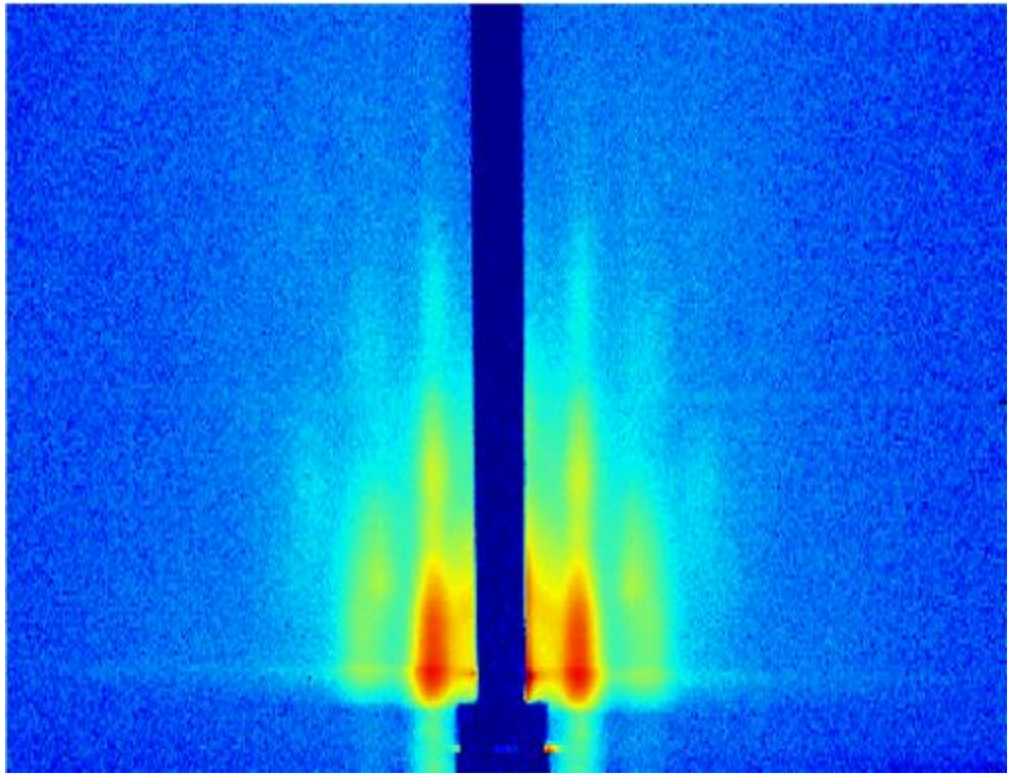
GISAXS on Au nanoparticle 2D superlattices





cinzia.giannini@ic.cnr.it
+39 080 5929167
CNR Istituto di Cristallografia

GISAXS on Au nanoparticle 2D superlattices



CrystEngComm

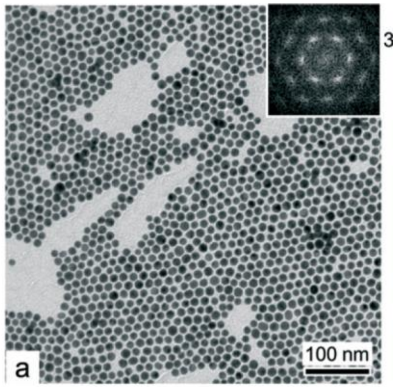
PAPER

Cite this: *CrystEngComm*, 2014, 16, 9482

GISAXS and GIWAXS study on self-assembling processes of nanoparticle based superlattices†

M. Corricelli,‡[ab] D. Altamura,‡[c] M. L. Curri,[b] T. Sibillano,[c] D. Siliqi,[c] A. Mazzone,[c] N. Depalo,[b] E. Fanizza,[ab] D. Zanchet,[d] C. Giannini*[c] and M. Striccoli*[b]

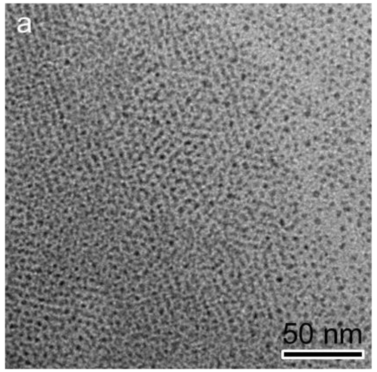
Vertical lateral streaks indicates a 2D layer of Au nanoparticles



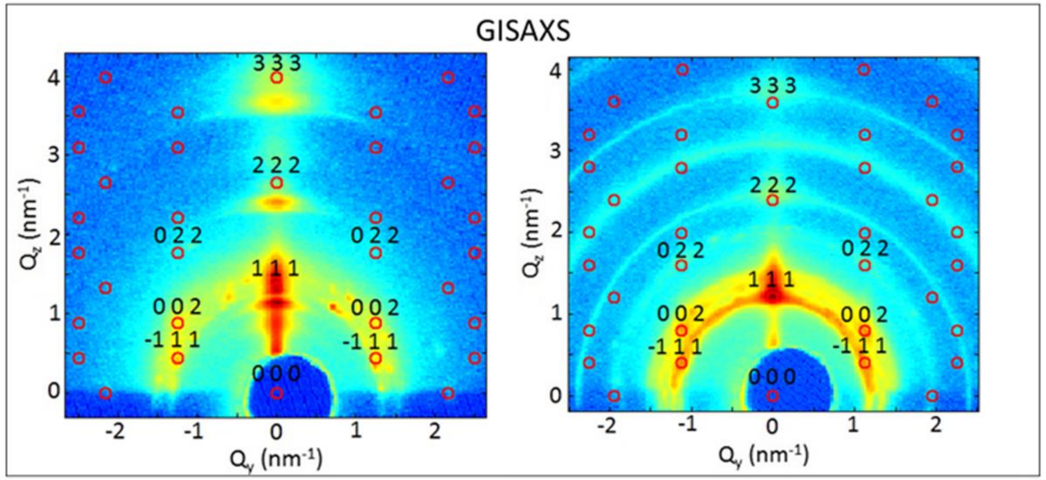
cinzia.giannini@ic.cnr.it
+39 080 5929167

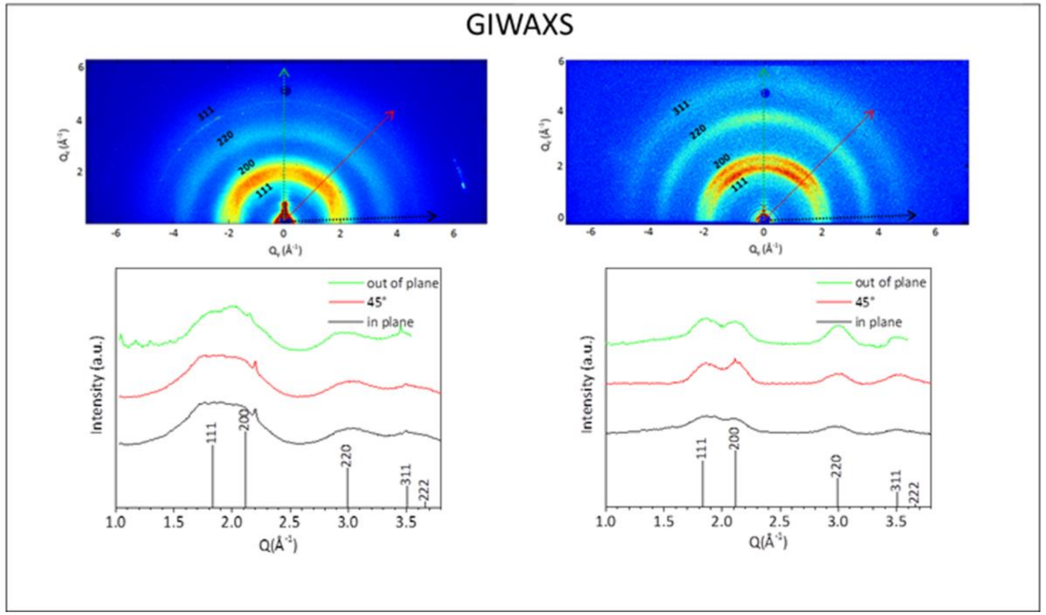
CNR Istituto di Cristallografia

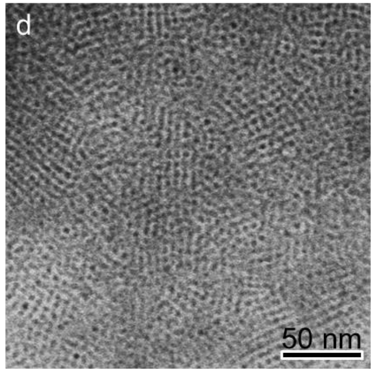
GISAXS/GIWAXS on PbS nanoparticle 3D superlattices



2.7 nm PbS NC







3.3 nm PbS NC

CrystEngComm
Design and understanding of solid-state and crystalline materials
Impact Factor 3.879 48 Issues per Year

Paper
GISAXS and GIWAXS study on self-assembling processes of nanoparticle based superlattices

Michela Corricelli, Davide Altamura, Maria Lucia Curri, Teresa Sibillano, Dritan Siliqi, Annamaria Mazzone, Nicoletta Depalo, Elisabetta Fanizza, daniela Zanchet, Cinzia Giannini and Marinella Striccoli

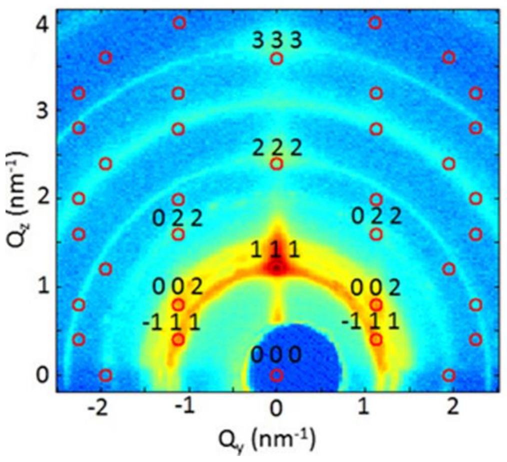
CrystEngComm, 2014, Accepted Manuscript
DOI: 10.1039/C4CE01291G
Received 25 Jun 2014, Accepted 13 Aug 2014
First published online 13 Aug 2014

✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167

IC CNR Istituto di Cristallografia
XMI L@b

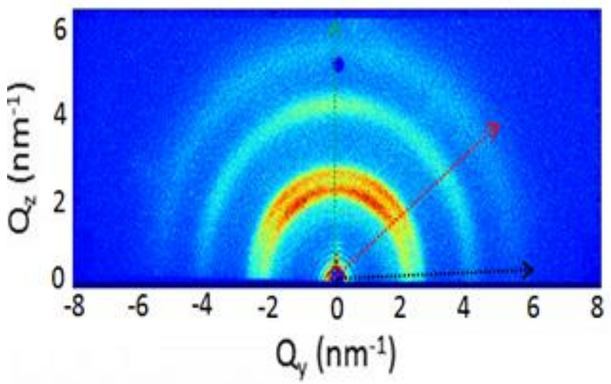
GISAXS/GIWAXS on 3D assembly

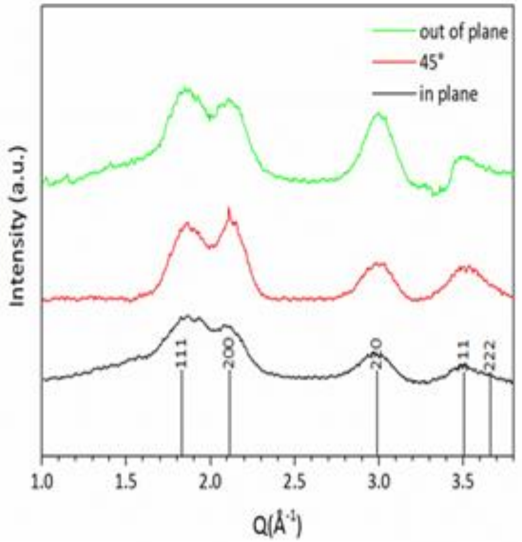
GISAXS



indexed as (111)-oriented fcc superlattice.

GIWAXS





GIWAXS measurements were performed, to account for a possible QD orientational order. This comparison does not show relevant differences for PbS2.7 sample, either in terms of peak intensity and FWHM and evidences an isotropic almost spherical shape and no preferential orientation of the QDs.
Conversely, comparing the FWHM of the (111) and (220) peaks for the PbS3.3 sample, they are slightly different as in the case of not fully isotropic QD shape.

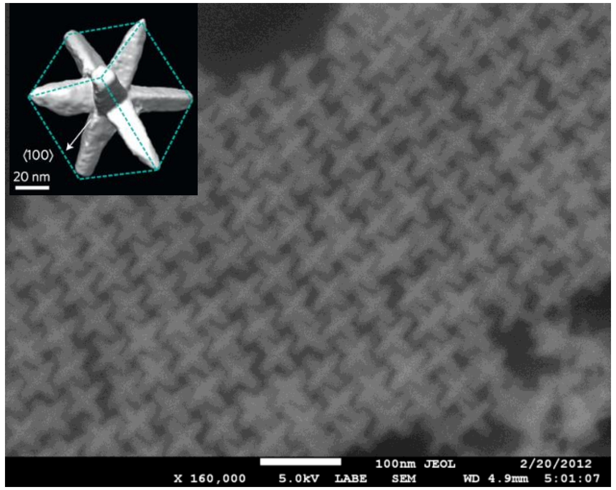
QDs hold a slight orientational order in this sample, with the (220) planes preferentially oriented parallel to the substrate.

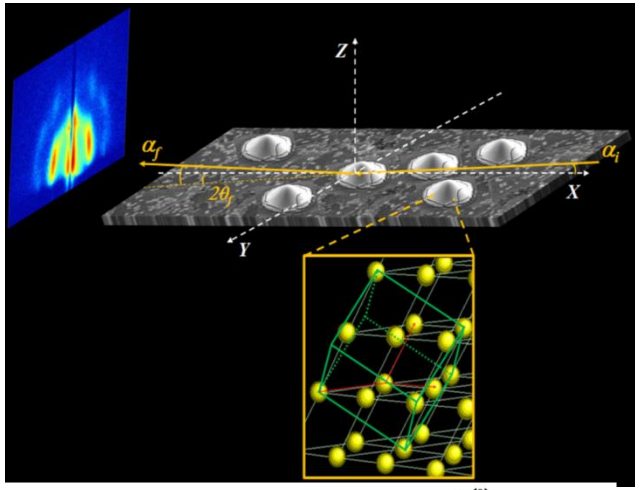
PbS-3.3 nm sample
QD superlattice is 111-oriented and its QD building blocks are 110-preferentially oriented

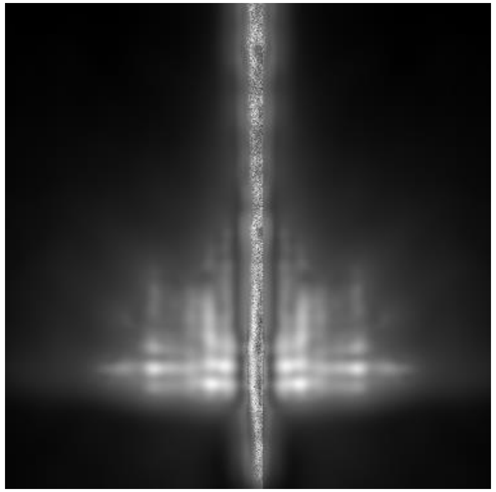
✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167

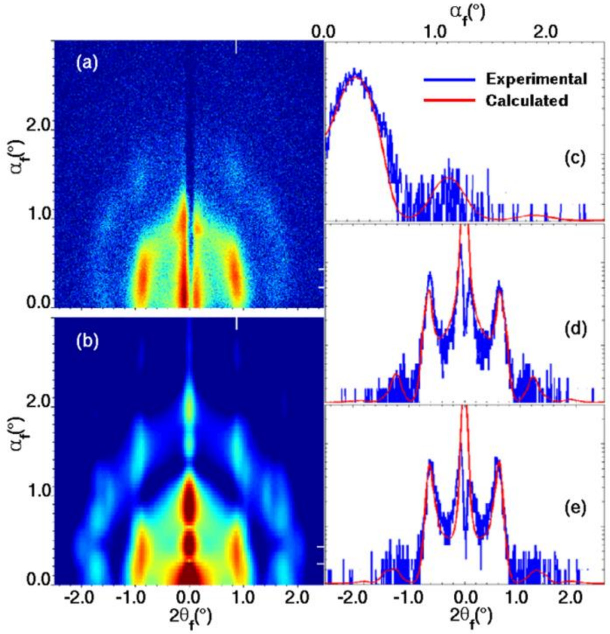
CNR | Istituto di Cristallografia

nanoparticle
3D superlattices









A superbright X-ray laboratory microsource empowered by a novel restoration algorithm

Liberato De Caro, Davide Altamura, Fabio Alessio Vittoria, Gerardina Carbone, Fen Qiao, Liberato Manna and Cinzia Giannini

J. Appl. Cryst. (2012). 45, 1228–1235

CRYSTAL GROWTH & DESIGN
Article
pubs.acs.org/crystal

Exploiting GISAXS for the Study of a 3D Ordered Superlattice of Self-Assembled Colloidal Iron Oxide Nanocrystals

Davide Altamura,† Václav Holý,‡ Dritan Siliqi,† Indira Chaitanya Lekshmi,§ Concetta Nobile,§ Giuseppe Maruccio,§,∥ P. Davide Cozzoli,§,∥ Lixin Fan,⊥ Fabia Gozzo,# and Cinzia Giannini*,†

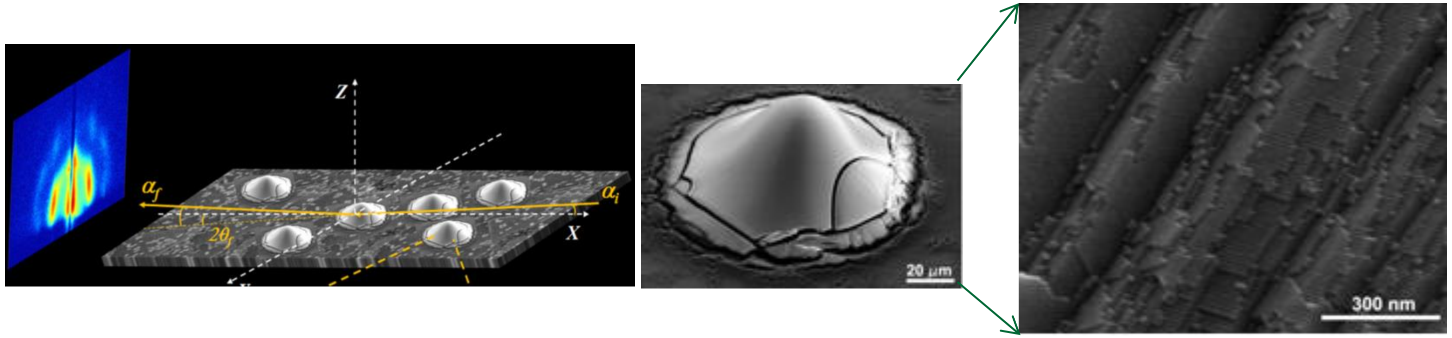
†Institute of Crystallography (CNR-IC), V. Amendola 122/O, 70126-Bari, Italy
‡Faculty of Mathematics and Physics, Charles University, Ke Karlovu 5, 121 16 Prague, Czech Republic
§National Nanotechnology Laboratory (NNL), CNR Istituto Nanoscienze , c/o Distretto Tecnologico, via per Arnesano km 5, 73100 Lecce, Italy
∥Dipartimento di Matematica e Fisica "E. De Giorgi", Università del Salento, via per Arnesano, 73100 Lecce
⊥Rigaku Innovative Technologies (RIT), 1900 Taylor Road, Auburn Hills, Michigan 48326, United States
#Paul Scherrer Institut, Swiss Light Source, 5232 Villigen PSI, Switzerland

cinzia.giannini@ic.cnr.it
+39 080 5929167

CNR Istituto di Cristallografia

xmi l@b

nanoparticle 3D superlattices

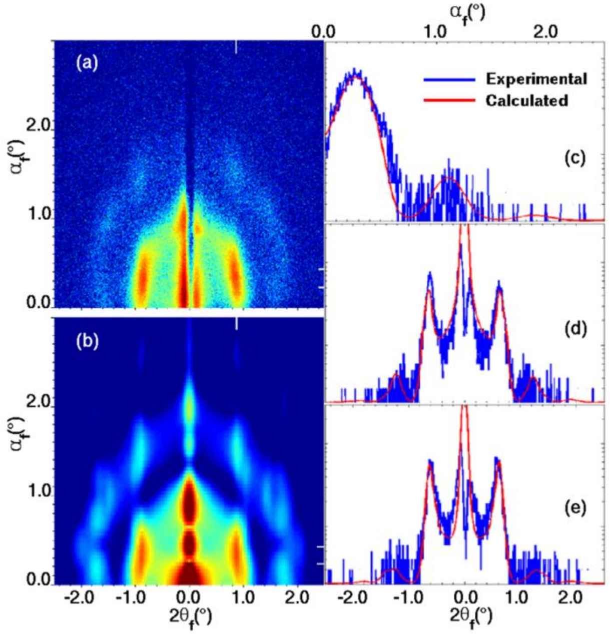


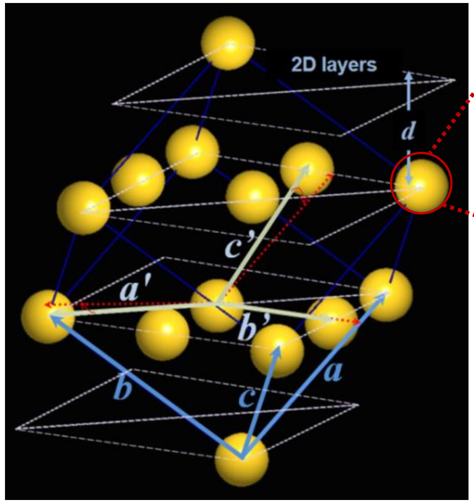
CRYSTAL GROWTH & DESIGN
Article
pubs.acs.org/crystal

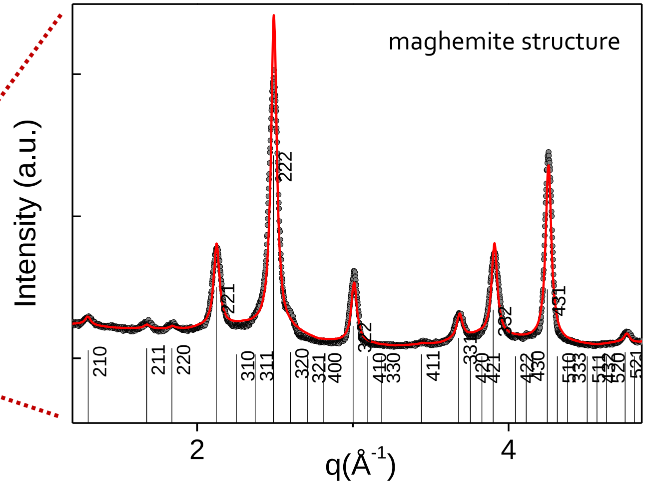
Exploiting GISAXS for the Study of a 3D Ordered Superlattice of Self-Assembled Colloidal Iron Oxide Nanocrystals

Davide Altamura,[†] Václav Holý,[‡] Dritan Siliqi,[†] Indira Chaitanya Lekshmi,[§] Concetta Nobile,[§] Giuseppe Maruccio,[§,∥] P. Davide Cozzoli,[§,∥] Lixin Fan,[⊥] Fabia Gozzo,[#] and Cinzia Giannini*,[†]

[†]Institute of Crystallography (CNR-IC), V. Amendola 122/O, 70126-Bari, Italy
[‡]Faculty of Mathematics and Physics, Charles University, Ke Karlovu 5, 121 16 Prague, Czech Republic
[§]National Nanotechnology Laboratory (NNL), CNR Istituto Nanoscienze , c/o Distretto Tecnologico, via per Arnesano km 5, 73100 Lecce, Italy
[∥]Dipartimento di Matematica e Fisica "E. De Giorgi", Università del Salento, via per Arnesano, 73100 Lecce
[⊥]Rigaku Innovative Technologies (RIT), 1900 Taylor Road, Auburn Hills, Michigan 48326, United States
[#]Paul Scherrer Institut, Swiss Light Source, 5232 Villigen PSI, Switzerland





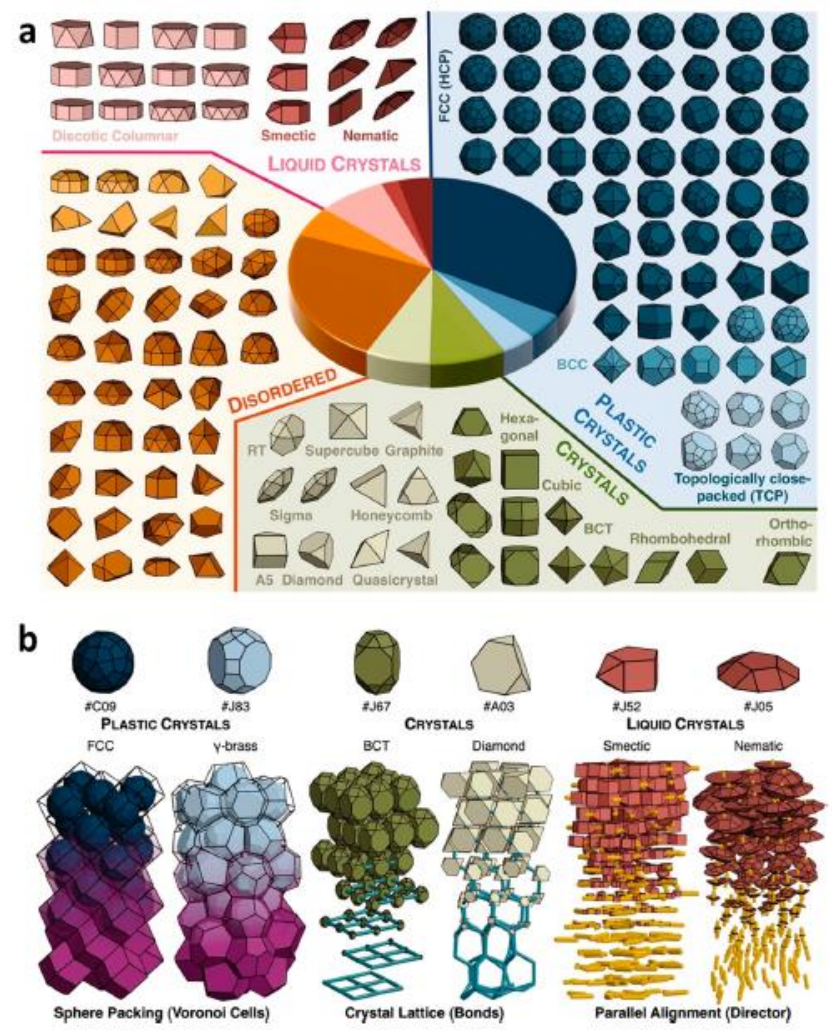


✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167

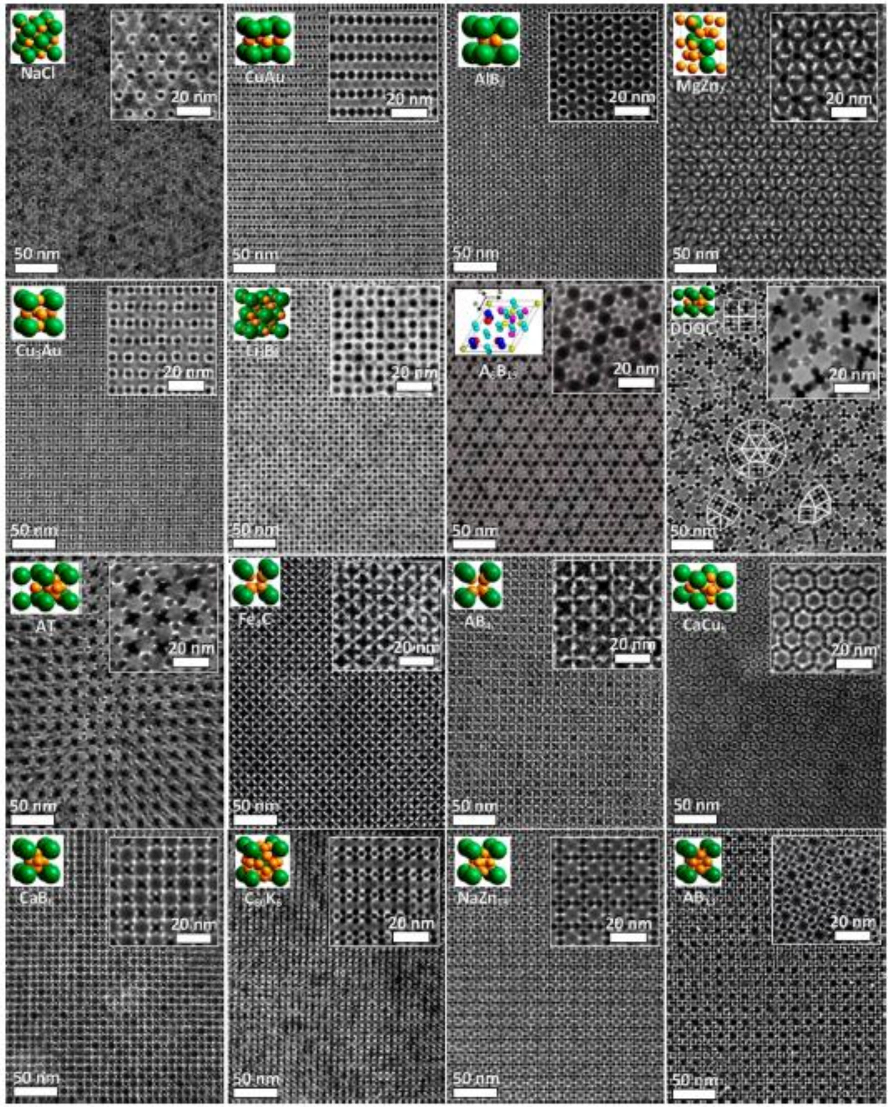
CNR | Istituto di Cristallografia

XMI L@b

Assembly of colloidal nanocrystals in ordered super-structures is well advanced (both experimentally and theoretically):



Damasceno, P. F., et al. Science 2012, 337 (6093), 453−457



Boles, M A.. Et al., Chem.Rev.2016,116, 11220−11289

✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167

CNR | Istituto di Cristallografia

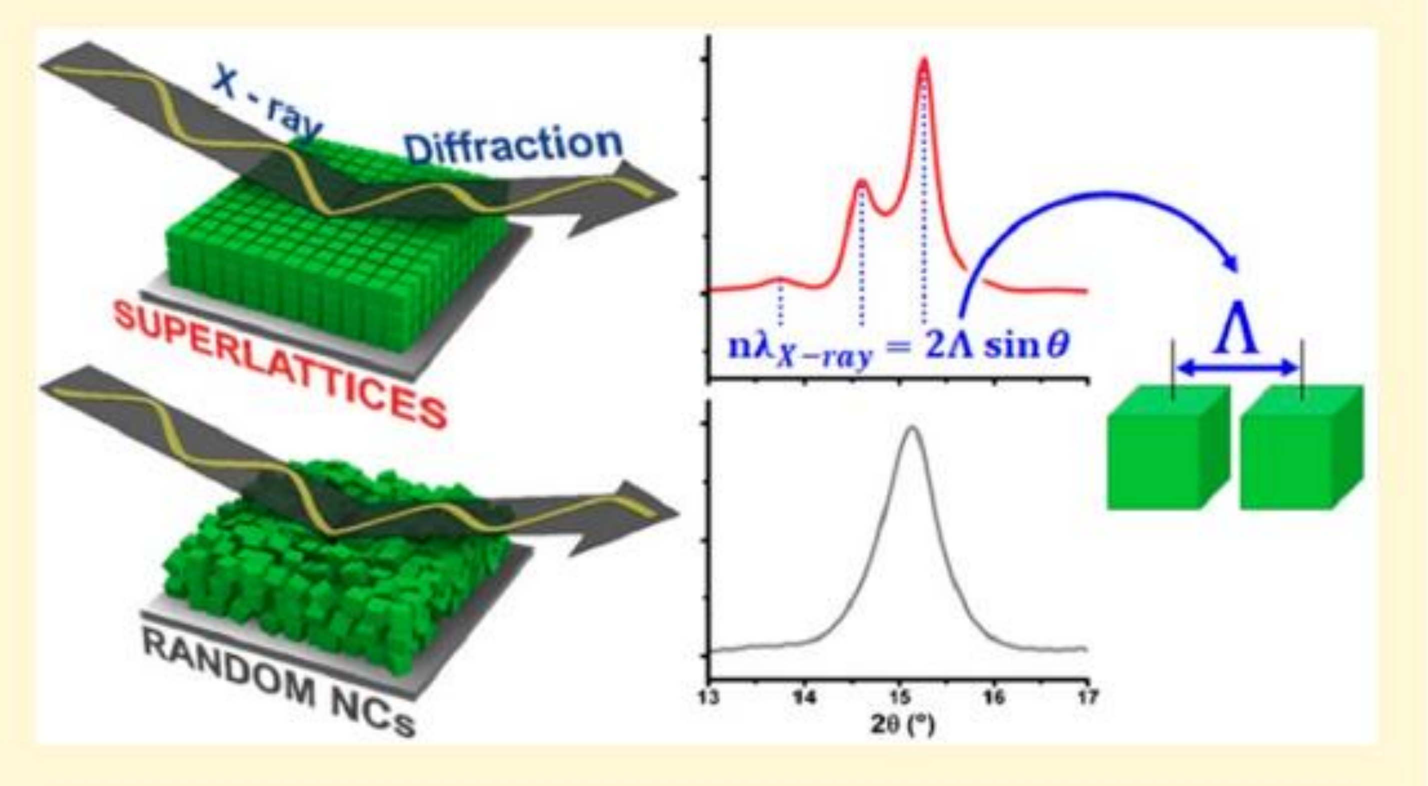
Highly coherent SL of perfect nanocrystals

ACS MATERIALS LETTERS
Cite This: ACS Materials Lett. 2019, 1, 272–276
www.acsmaterialslett.org

Wide-Angle X-ray Diffraction Evidence of Structural Coherence in $CsPbBr_3$ Nanocrystal Superlattices

Stefano Toso,[†] Dmitry Baranov,[*,†] Cinzia Giannini,[*,‡] Sergio Marras,[†] and Liberato Manna[*,†]

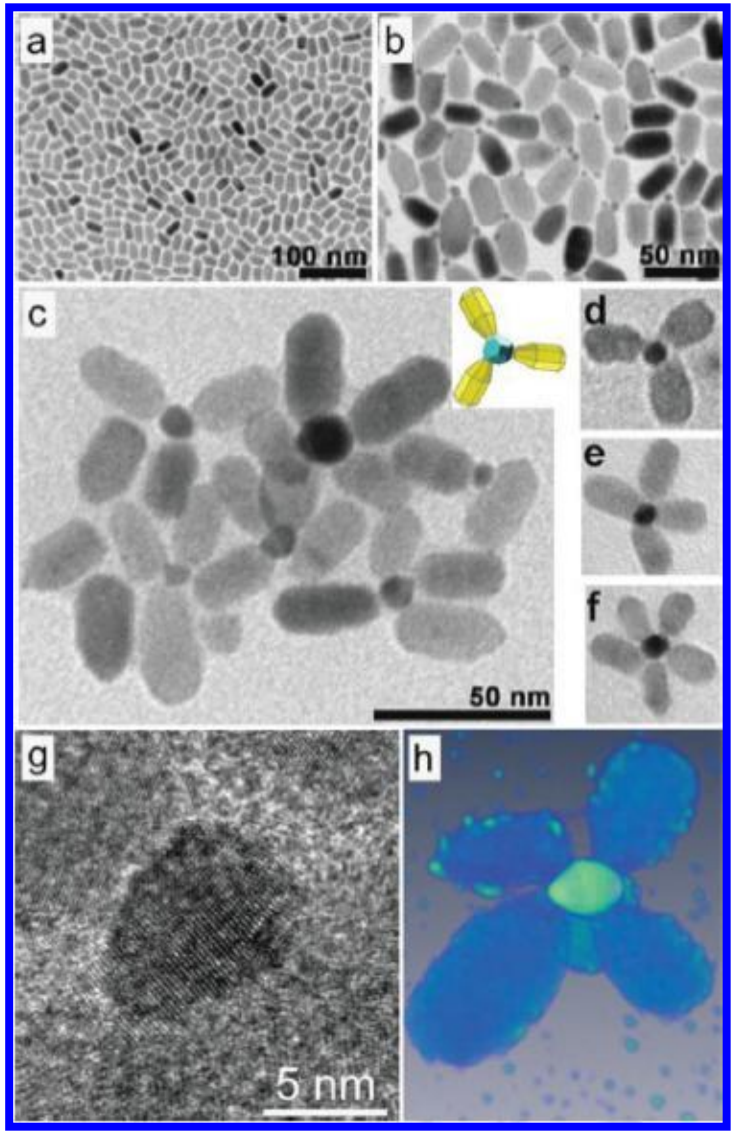
[†]Nanochemistry Department, Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy
[‡]Istituto di Cristallografia - Consiglio Nazionale delle Ricerche (IC-CNR), via Amendola 122/O, I-70126 Bari, Italy



cinzia.giannini@ic.cnr.it
+39 080 5929167

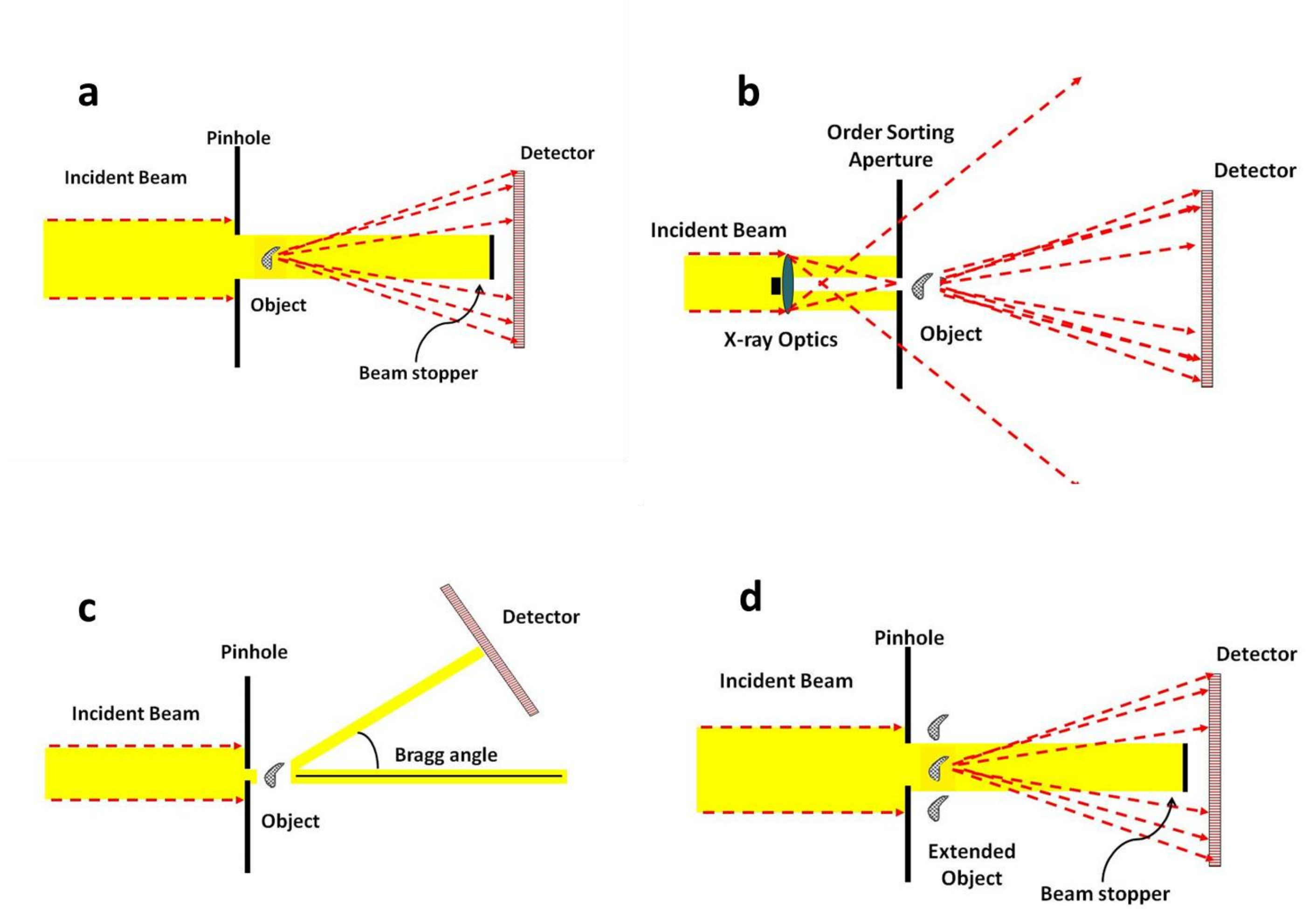
CNR | Istituto di Cristallografia

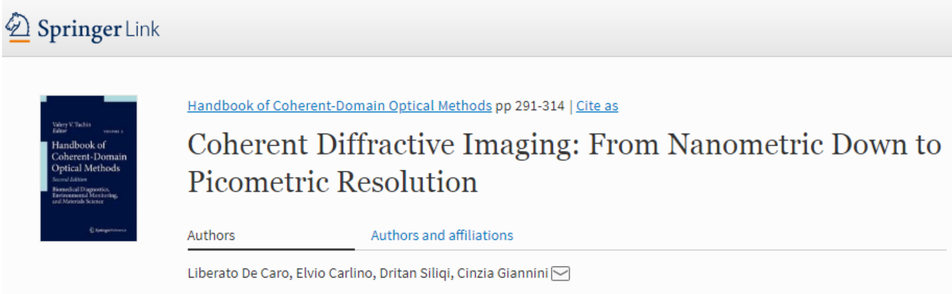
NANOCRYSTALS **NON PERIODICALLY** ASSEMBLED ON TOP OF SURFACES



✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167
CNR Istituto di Cristallografia

Different geometries

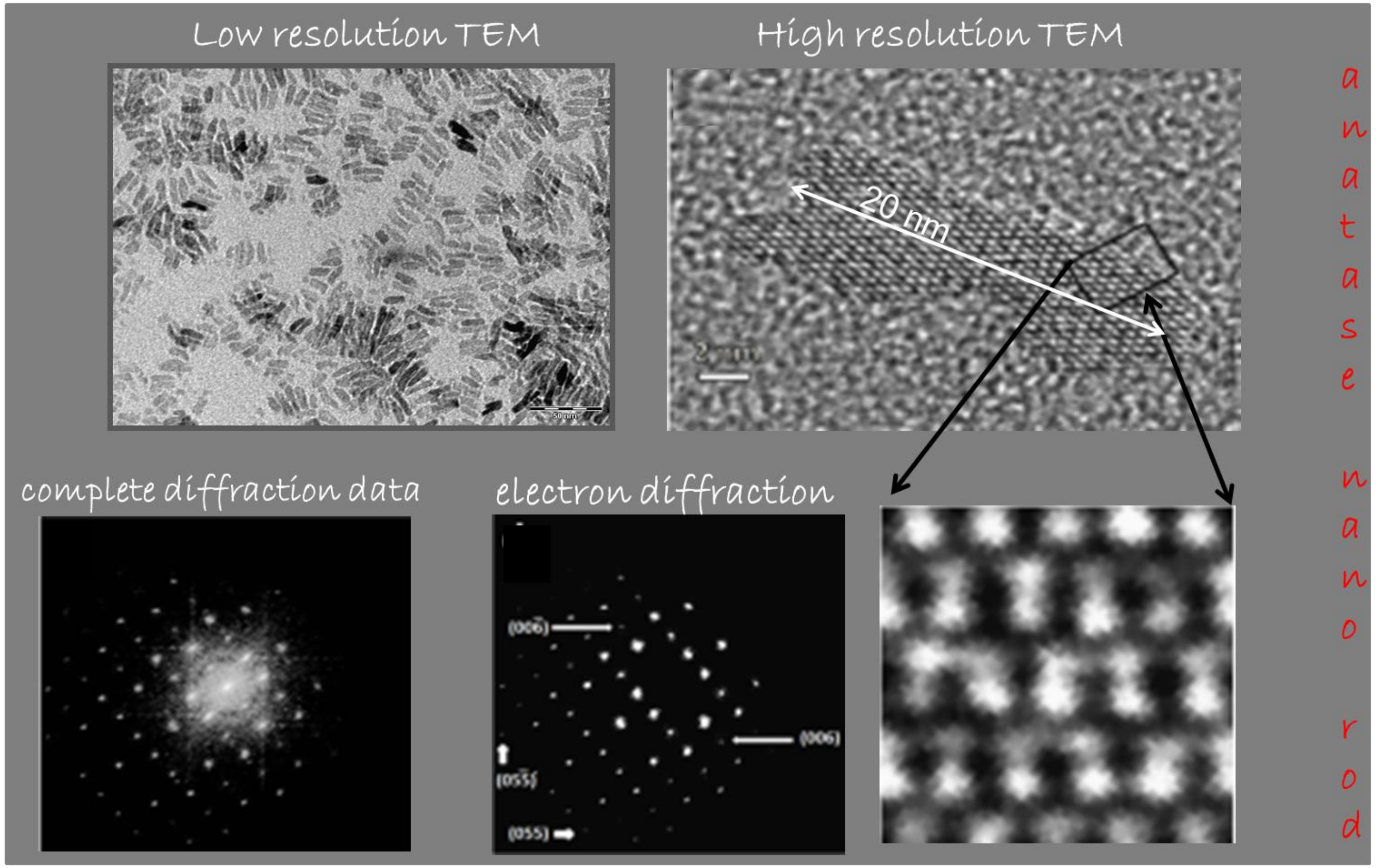


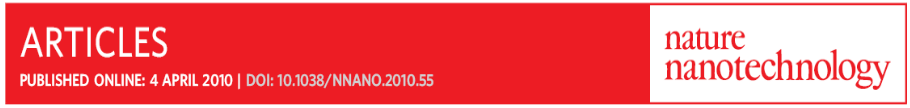

SpringerLink
Handbook of Coherent-Domain Optical Methods pp 291-314 | Cite as
Coherent Diffractive Imaging: From Nanometric Down to Picometric Resolution
Authors
Authors and affiliations
Liberato De Caro, Elvio Carlino, Dritan Siliqi, Cinzia Giannini

✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167

CNR Istituto di Cristallografia

TEM of a nanocrystal




ARTICLES
PUBLISHED ONLINE: 4 APRIL 2010 | DOI: 10.1038/NNANO.2010.55
nature nanotechnology

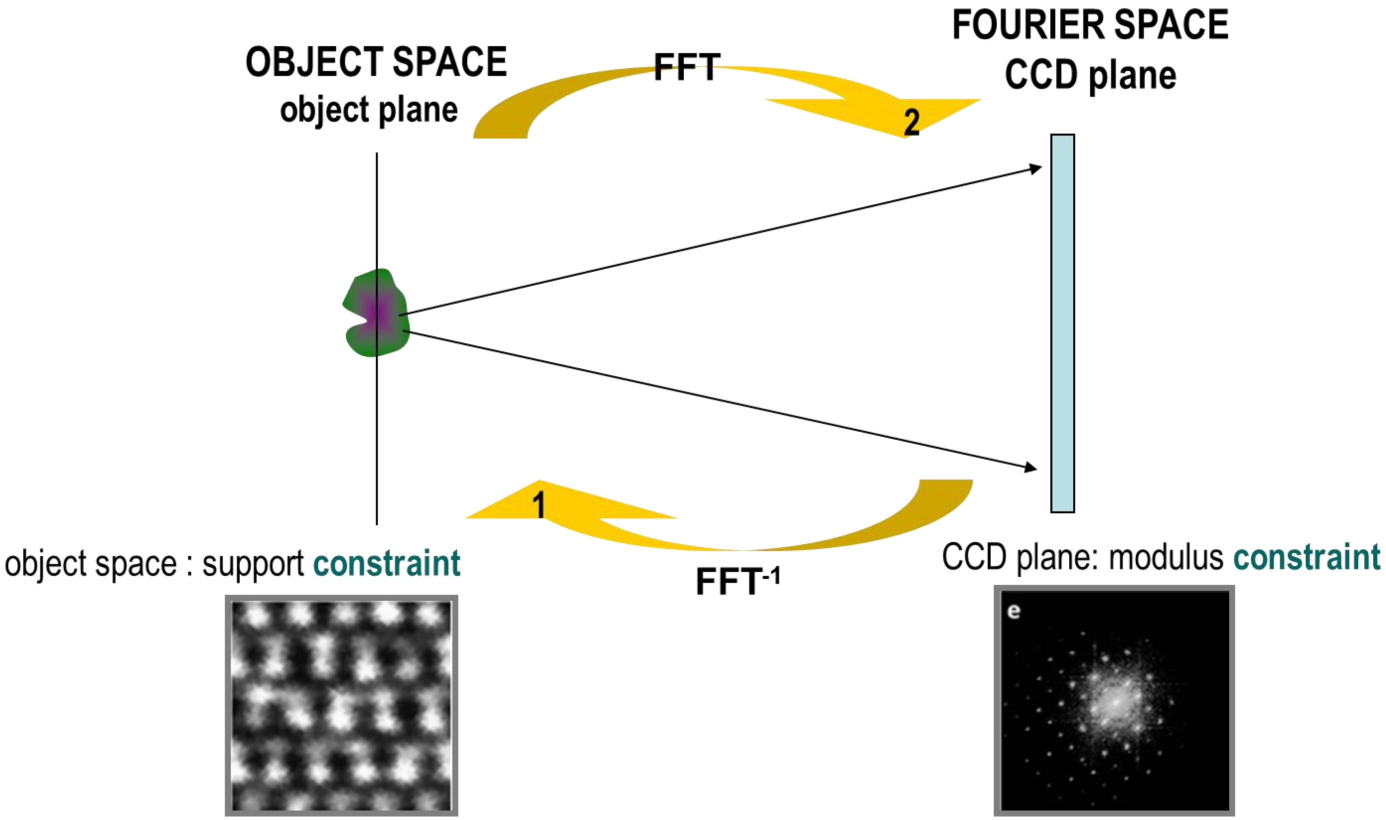
Electron diffractive imaging of oxygen atoms in nanocrystals at sub-ångström resolution

Liberato De Caro[1], Elvio Carlino[2], Gianvito Caputo[3,4], Pantaleo Davide Cozzoli[3,4] and Cinzia Giannini[1*]

✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167

IC CNR Istituto di Cristallografia
xmi l@b

Phase retrieval of a EDI pattern



ARTICLES
PUBLISHED ONLINE: 4 APRIL 2010 | DOI: 10.1038/NNANO.2010.55
nature nanotechnology

Electron diffractive imaging of oxygen atoms in nanocrystals at sub-ångström resolution

Liberato De Caro[1], Elvio Carlino[2], Gianvito Caputo[3,4], Pantaleo Davide Cozzoli[3,4] and Cinzia Giannini[1]*

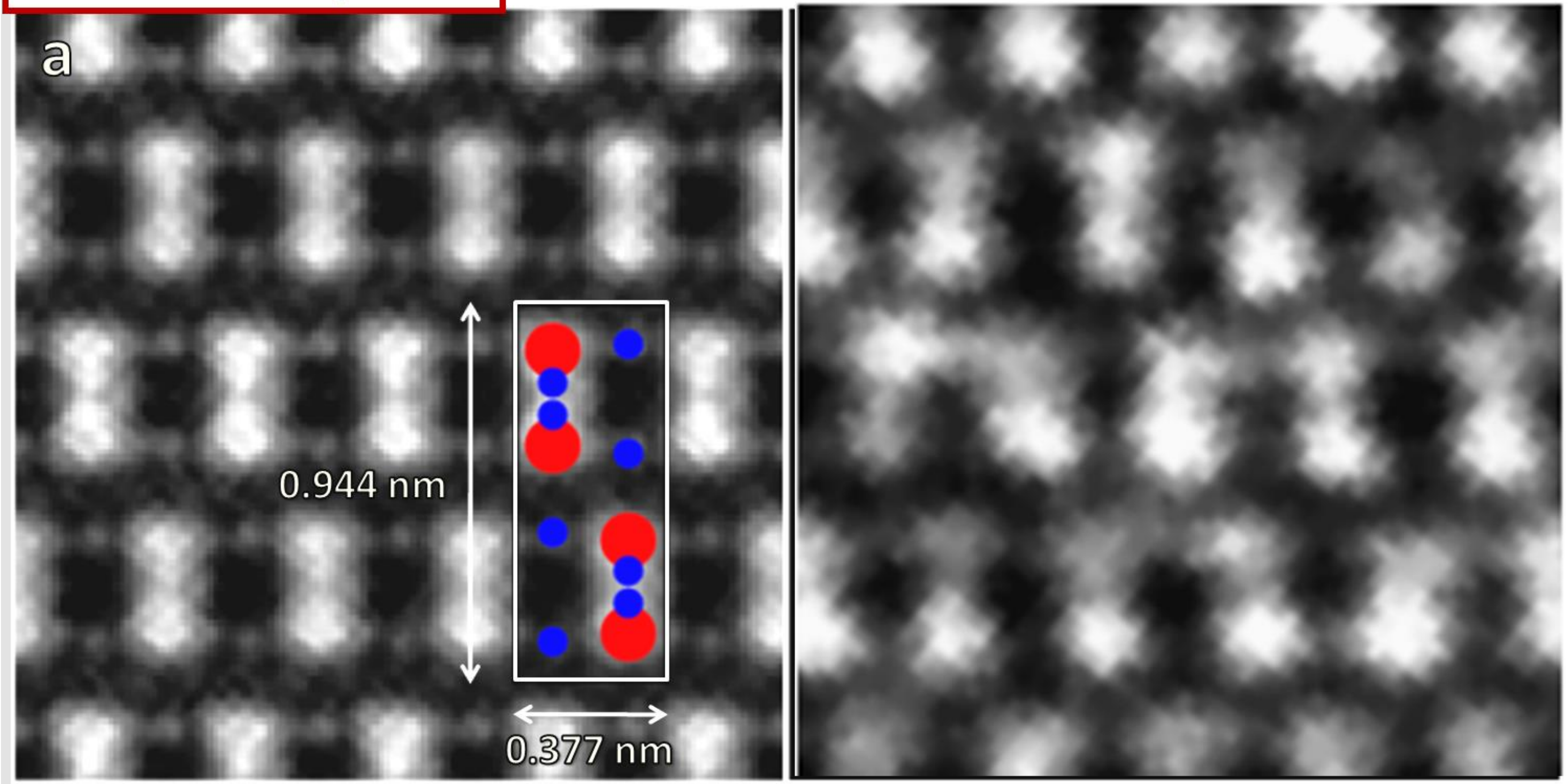
✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167

IC | CI
CNR | Istituto di Cristallografia

xmi l@b

Phase retrieval of a EDI pattern
resolution = 70 pm (0.7 Å)

TiO_2 anatase nanocrystals
Resolution = 0.7 Å



ARTICLES
PUBLISHED ONLINE: 4 APRIL 2010 | DOI: 10.1038/NNANO.2010.55
nature nanotechnology

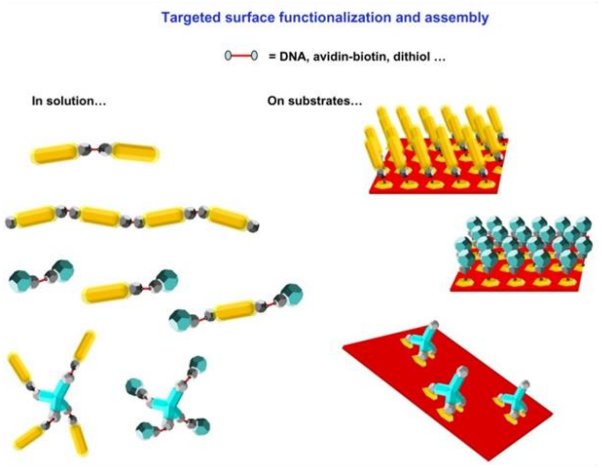
Electron diffractive imaging of oxygen atoms in nanocrystals at sub-ångström resolution

Liberato De Caro[1], Elvio Carlino[2], Gianvito Caputo[3,4], Pantaleo Davide Cozzoli[3,4] and Cinzia Giannini[1]*

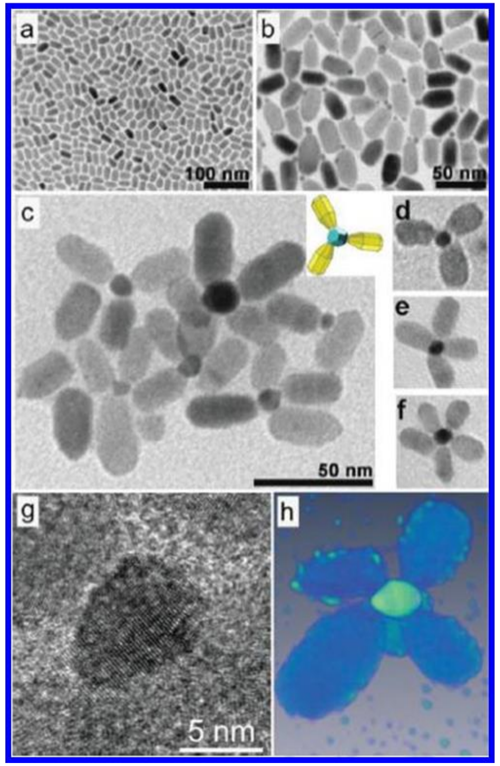
✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167

CNR | Istituto di Cristallografia

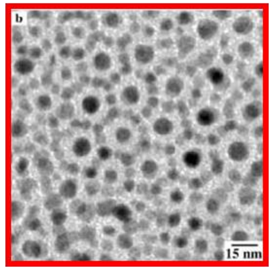
Nanocrystal Assembly



end-to-end assembly



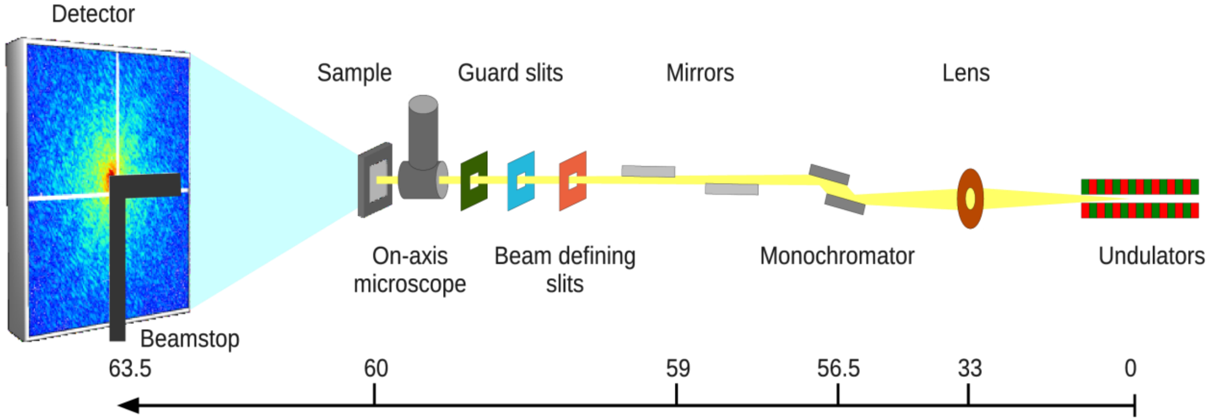
self-assembly



✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167

CNR Istituto di Cristallografia

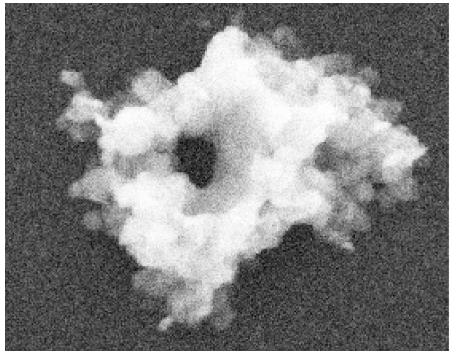
CDI experiment



CDI data collected at the ID10 beamline in ESRF

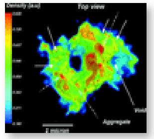
Fe_2P nanorods

38 ± 12 nm / 4 ± 1 nm)



RESEARCH PAPERS

J. Synchrotron Rad. (2014). **21**, 594-599
https://doi.org/10.1107/S1600577514003440
Cited by 8



Three-dimensional coherent diffractive imaging on non-periodic specimens at the ESRF beamline ID10

Y. Chushkin, F. Zontone, E. Lima, L. De Caro, P. Guardia, L. Manna and C. Giannini

The progress of tomographic coherent diffractive imaging with hard X-rays at the ID10 beamline of the European Synchrotron Radiation Facility is presented. The performance of the instrument is demonstrated by imaging a cluster of Fe_2P magnetic nanorods at 59 nm 3D resolution by phasing a diffraction volume measured at 8 keV photon energy. The result obtained shows progress in three-dimensional imaging of non-crystalline samples in air with hard X-rays.

Keywords: **coherent diffraction imaging**; **phase-retrieval**; **randomly assembled nanostructures**.

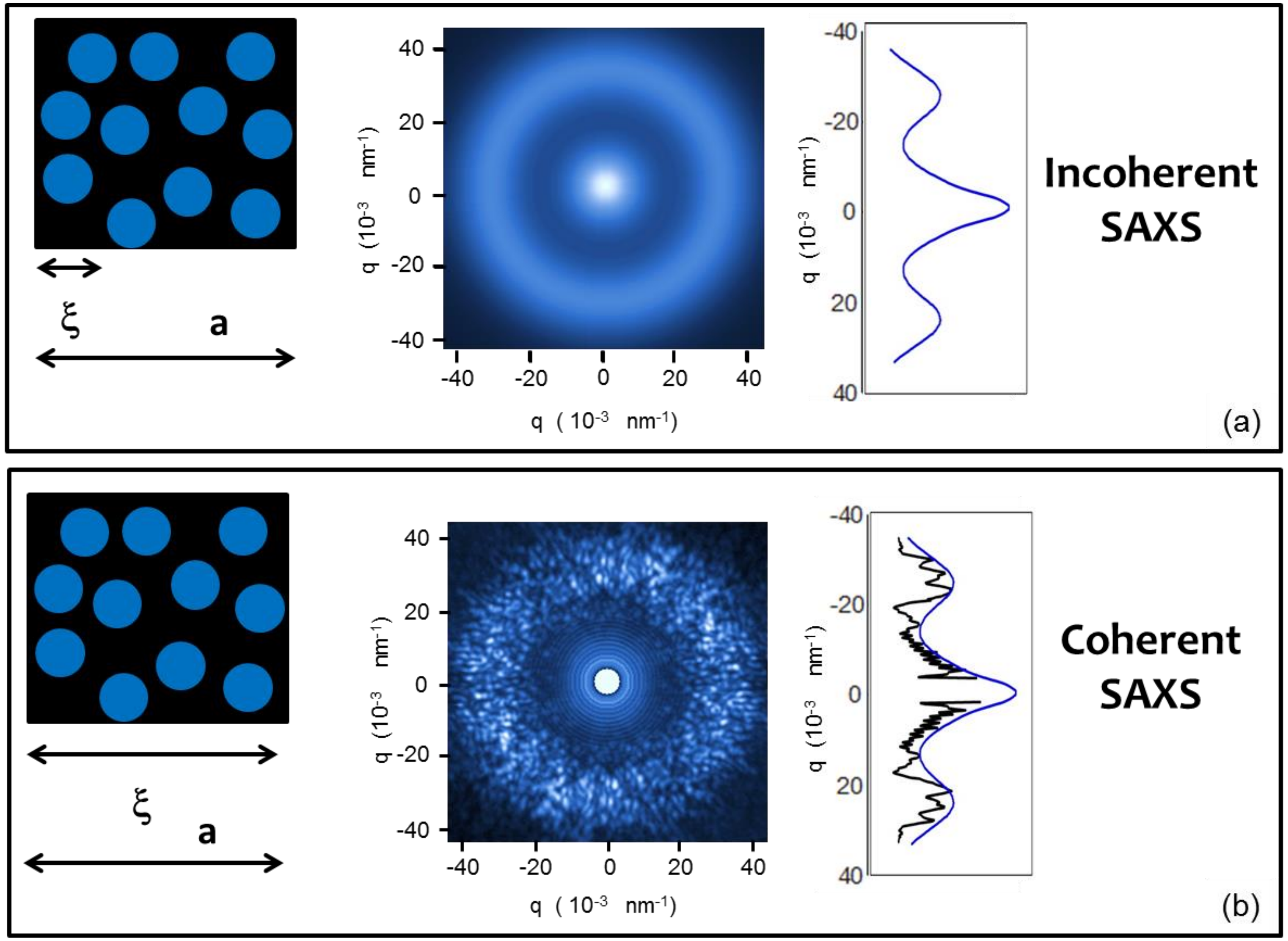
Object of the work:
investigate the assembly of magnetic rods of Fe2P nanocrystals by Coherent Diffractive Imaging (CDI), aiming at a 3D reconstruction of the electron density

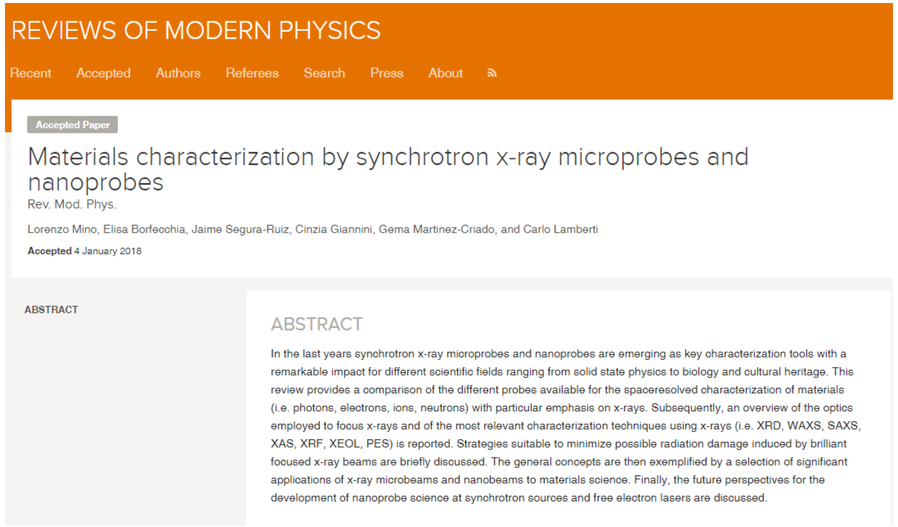
cinzia.giannini@ic.cnr.it
+39 080 5929167

IC CNR | Istituto di Cristallografia

xmi l@b

Coherence





REVIEWS OF MODERN PHYSICS

Recent Accepted Authors Referees Search Press About

Accepted Paper

Materials characterization by synchrotron x-ray microprobes and nanoprobes

Rev. Mod. Phys.

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

Accepted 4 January 2018

ABSTRACT

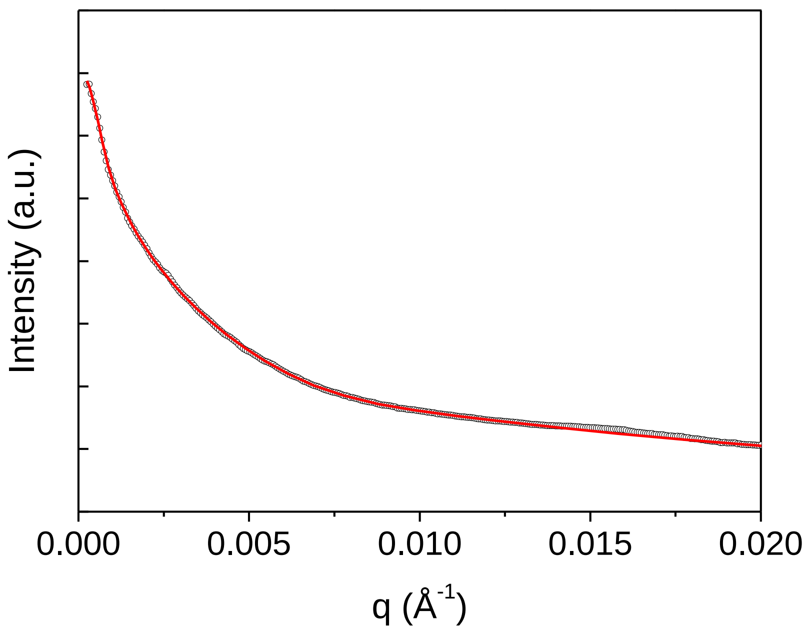
ABSTRACT

In the last years synchrotron x-ray microprobes and nanoprobes are emerging as key characterization tools with a remarkable impact for different scientific fields ranging from solid state physics to biology and cultural heritage. This review provides a comparison of the different probes available for the spaceresolved characterization of materials (i.e. photons, electrons, ions, neutrons) with particular emphasis on x-rays. Subsequently, an overview of the optics employed to focus x-rays and of the most relevant characterization techniques using x-rays (i.e. XRD, WAXS, SAXS, XAS, XRF, XEOL, PES) is reported. Strategies suitable to minimize possible radiation damage induced by brilliant focused x-ray beams are briefly discussed. The general concepts are then exemplified by a selection of significant applications of x-ray microbeams and nanobeams to materials science. Finally, the future perspectives for the development of nanoprobe science at synchrotron sources and free electron lasers are discussed.

cinzia.giannini@ic.cnr.it
+39 080 5929167

CNR Istituto di Cristallografia

Incoherent SAXS

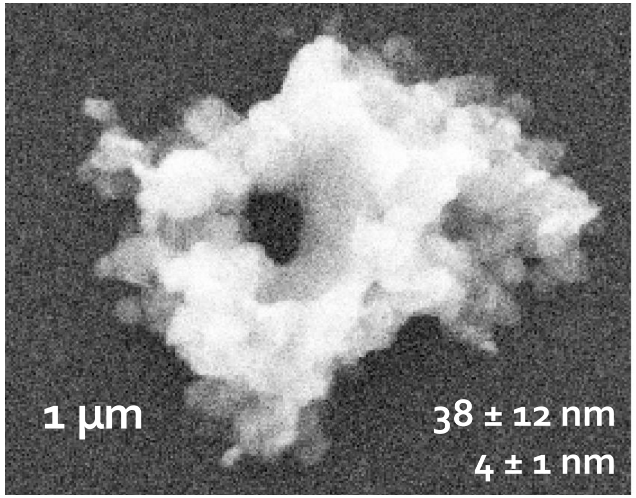


two scattering length scales in the sample:

Rg1 = (431.6 ± 4.1) nm
P1 = 3.44 ± 0.06 (mass fractal)

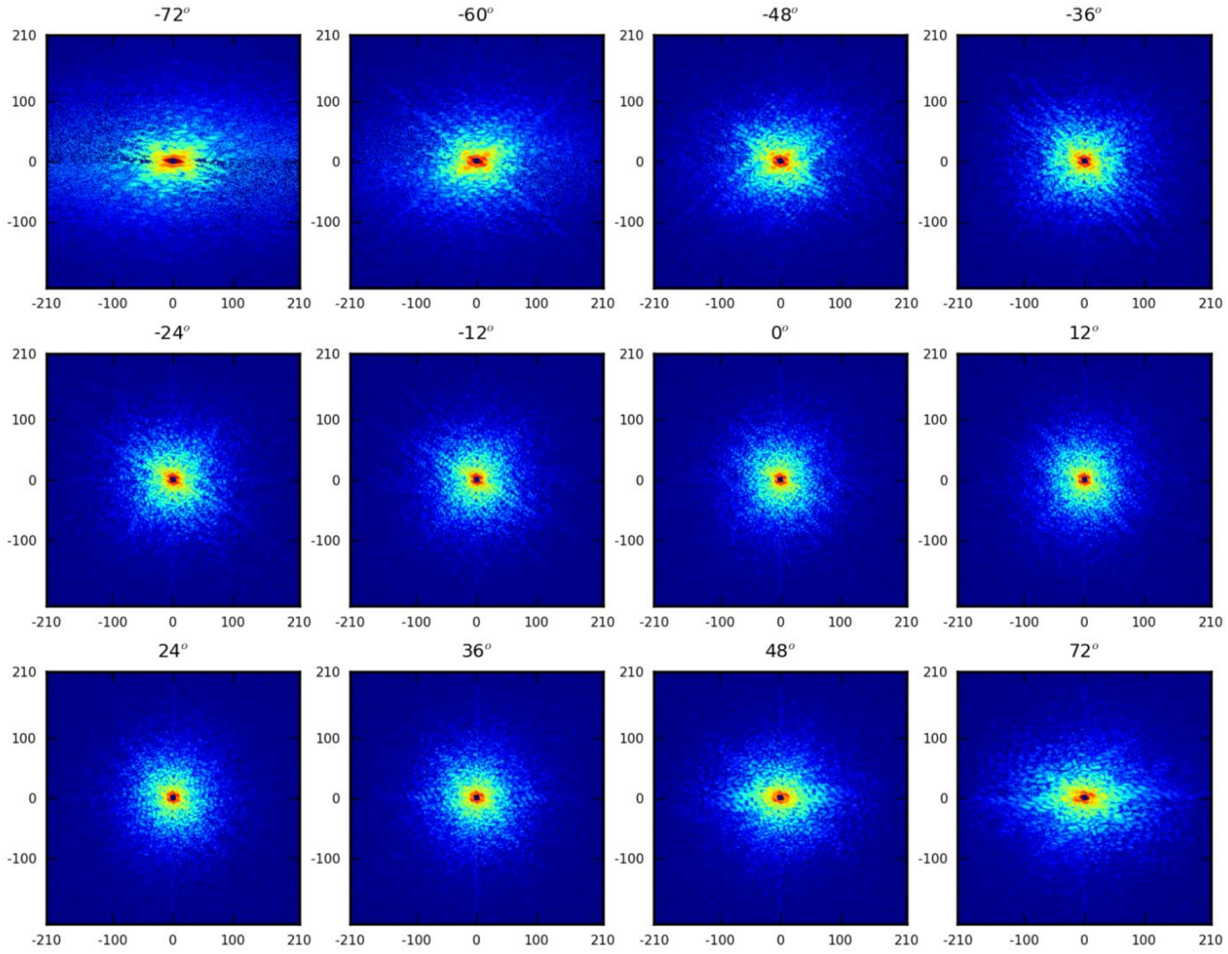
Rg2 = (39.8 ± 5.5) nm
P2 = 1.9 ± 0.12 (surface fractal)

Rg gyration radius
P power law exponent



cinzia.giannini@ic.cnr.it
+39 080 5929167
CNR Istituto di Cristallografia

Coherent SAXS



The diffraction patterns and the background were measured for 300 s each;

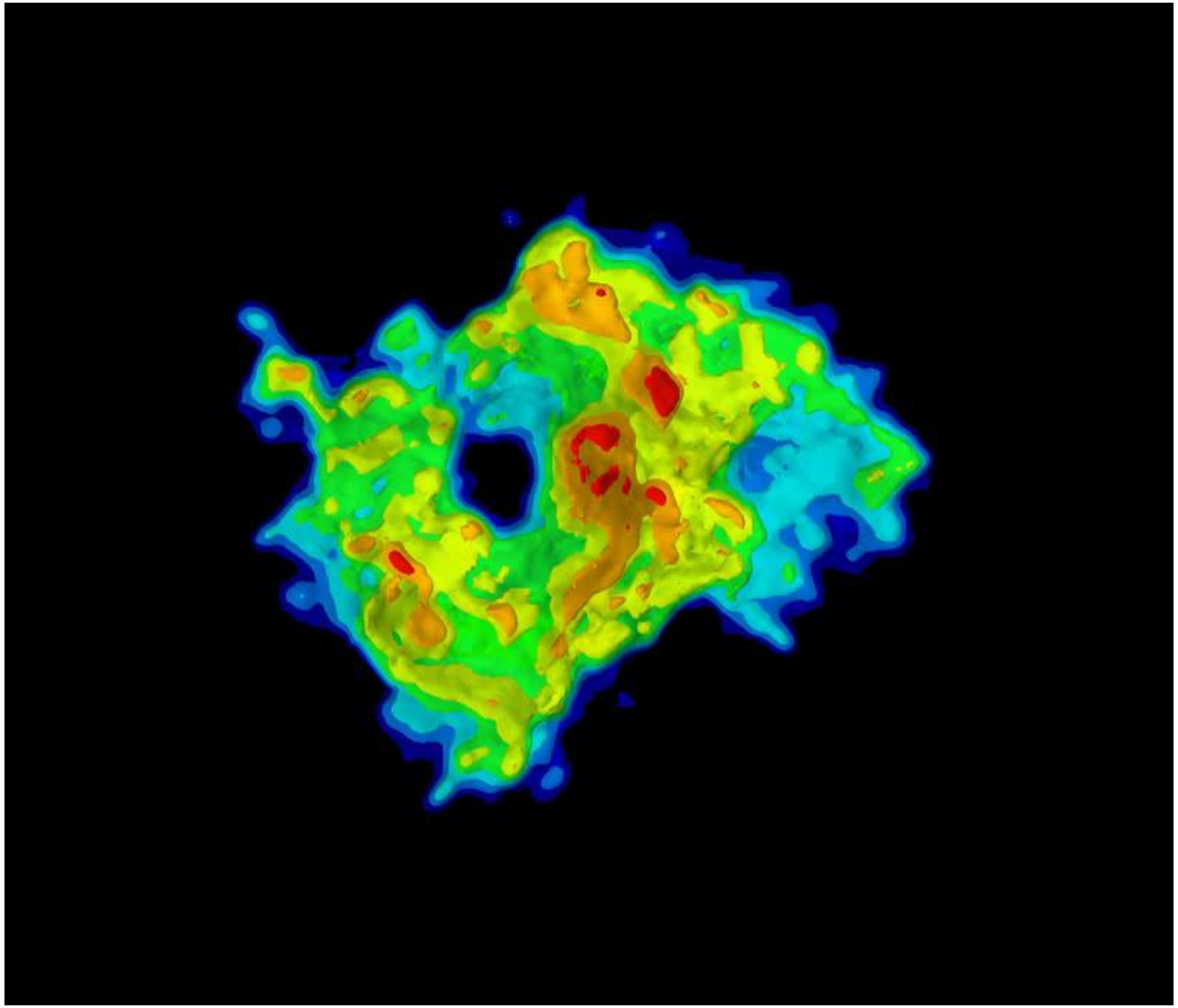
The collection of 73 2D diffraction patterns taken for sample tilts between -72° and +72° with a step of 2° required 24 h

✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167

IC CNR Istituto di Cristallografia

xmi l@b

Imaging 3D of the «object»

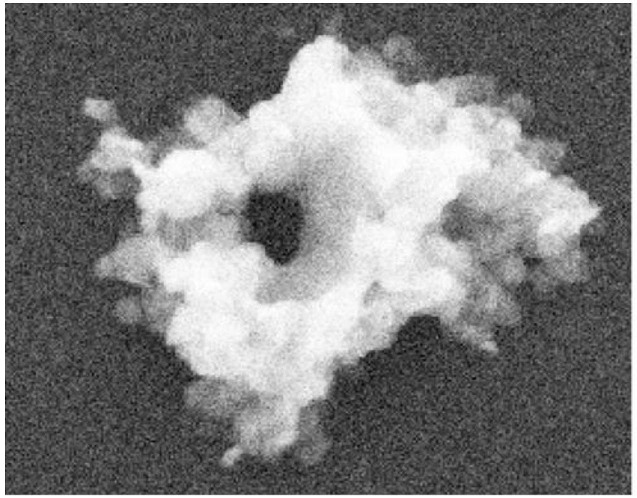


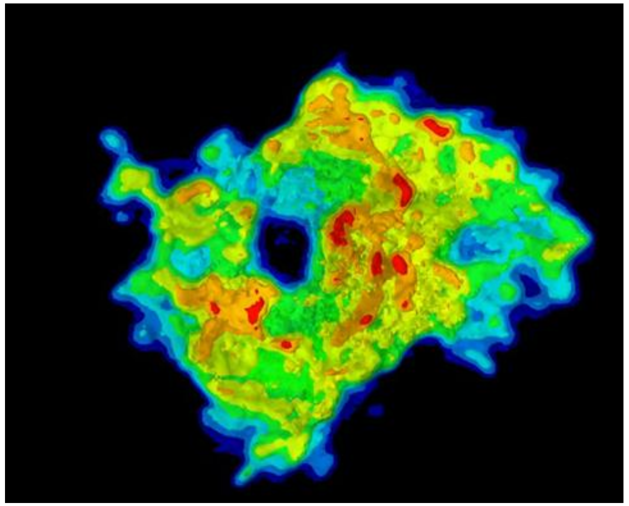
✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167

IC CNR Istituto di Cristallografia

xmi l@b

2D comparison to SEM



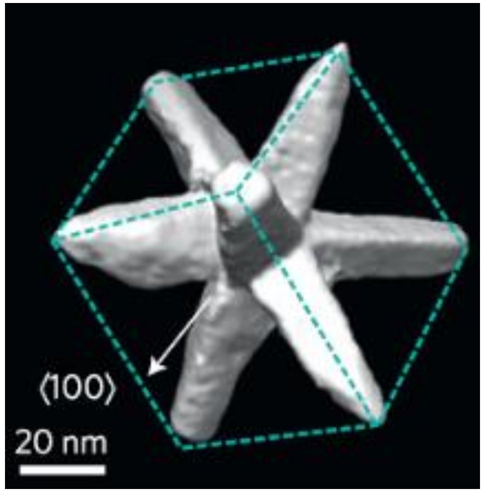


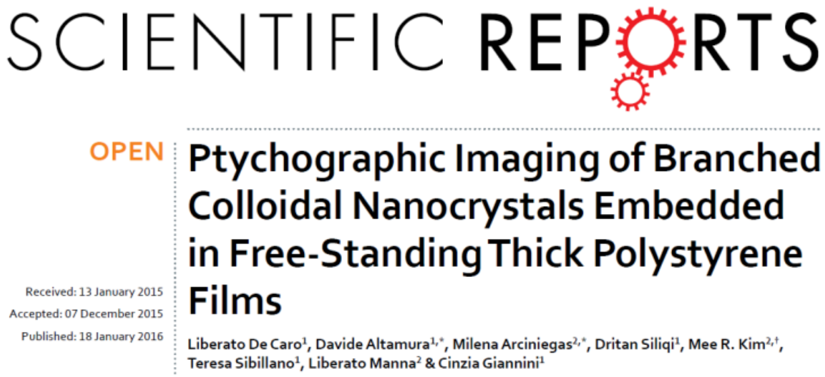
imaging a cluster of Fe_2P magnetic nanorods at 59 nm 3D resolution by phasing a diffraction volume measured at 8 keV photon energy

cinzia.giannini@ic.cnr.it
+39 080 5929167
IC CNR Istituto di Cristallografia
xmi l@b

Ptychography experiment

- Object of the work: investigate the dispersion of octapod-shaped NCs (made of a CdSe core and eight CdS arms) embedded in ~25 µm thick polystyrene (PS) free-standing films.
- A reliable non-destructive high resolution imaging technique with the capability to penetrate µm-thick samples and with the necessary resolution to visualize nanometre-scale structures is needed. This stringent requirement rules out any electron-based microscopic technique, as they are not suited for the observation of µm thick films.





SCIENTIFIC REPORTS
OPEN

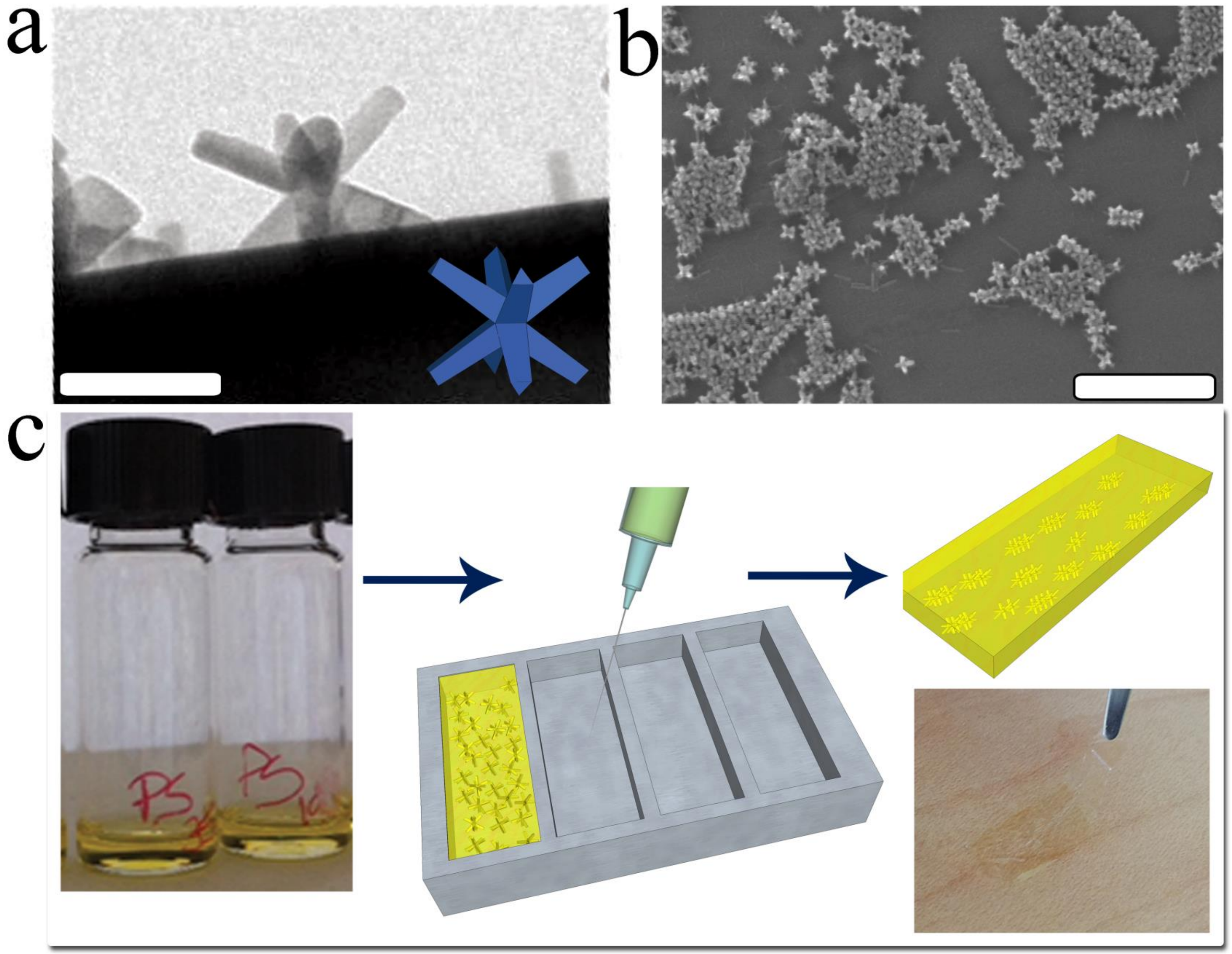
Ptychographic Imaging of Branched Colloidal Nanocrystals Embedded in Free-Standing Thick Polystyrene Films

Received: 13 January 2015
Accepted: 07 December 2015
Published: 18 January 2016

Liberato De Caro[1], Davide Altamura[1,*], Milena Arciniegas[2,*], Dritan Siliqi[1], Mee R. Kim[2,†], Teresa Sibillano[1], Liberato Manna[2] & Cinzia Giannini[1]

✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167
CNR | Istituto di Cristallografia

Ptychography experiment



SCIENTIFIC REPORTS

OPEN

Ptychographic Imaging of Branched Colloidal Nanocrystals Embedded in Free-Standing Thick Polystyrene Films

Received: 13 January 2015
Accepted: 07 December 2015
Published: 18 January 2016

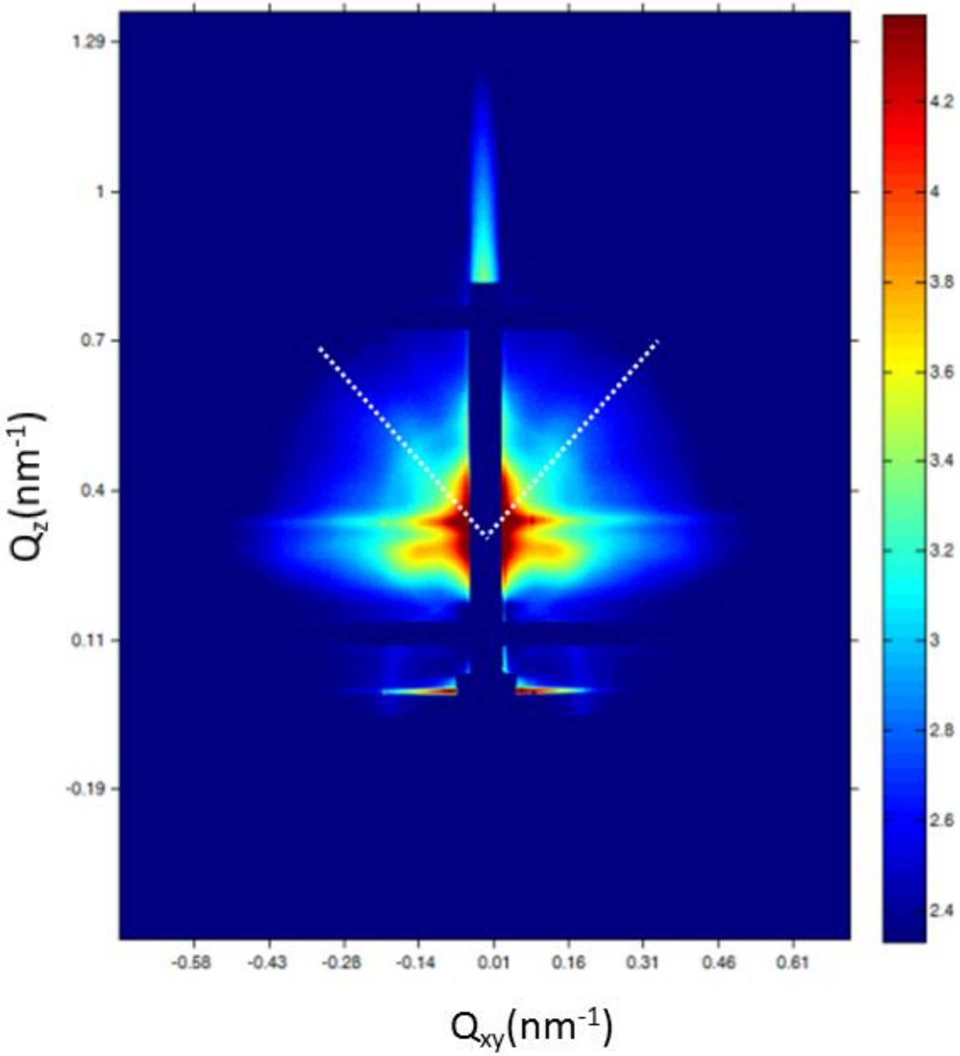
Liberato De Caro[1], Davide Altamura[1,*], Milena Arciniegas[2,*], Dritan Siliqi[1], Mee R. Kim[2,†], Teresa Sibillano[1], Liberato Manna[2] & Cinzia Giannini[1]

✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167

IC CI
CNR | Istituto di Cristallografia

xmi l@b

GISAXS



GISAXS investigation ruled out any possible organization of the octapods into ordered arrays for the thin polymer films; periodic arrays were found only for the sample made from a repeatedly-washed octapod solution (no polymer), drop-casted on top of a Si_3N_4 membrane

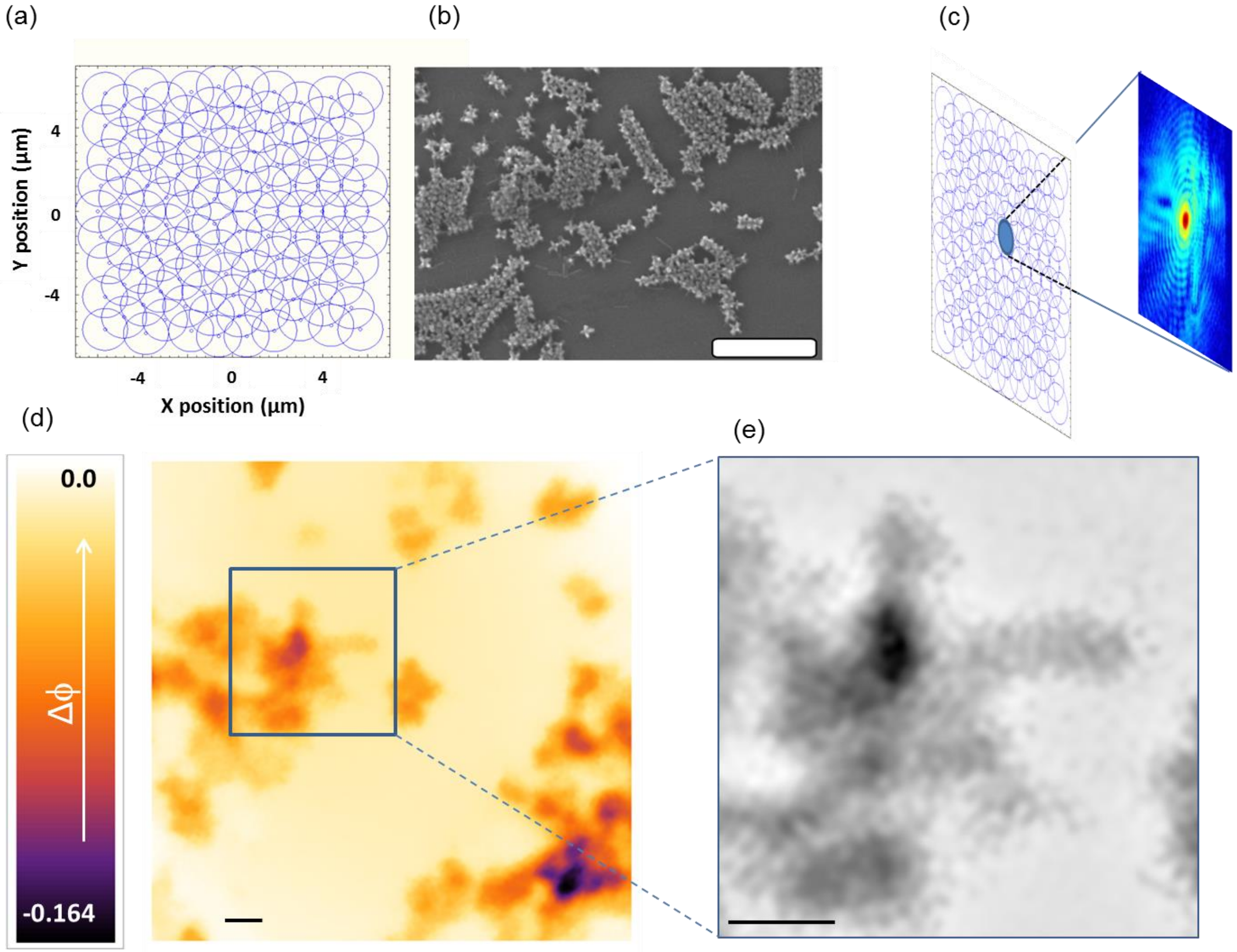
✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167

IC CNR Istituto di Cristallografia

xmi l@b

Ptychography experiment

PCDI data collected at the cSAXS beamline in SLS



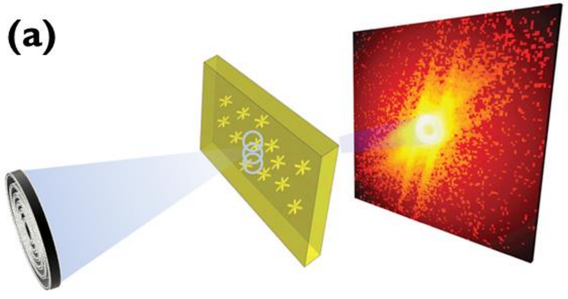
Ptychography allowed visualizing the self-assembly of octapods into linear and interconnected structures.

This result is in agreement with the octapod configuration observed by TEM/SEM on nanometric thin polymer samples, but never experimentally demonstrated for free-standing thick films.

✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167
CNR | Istituto di Cristallografia

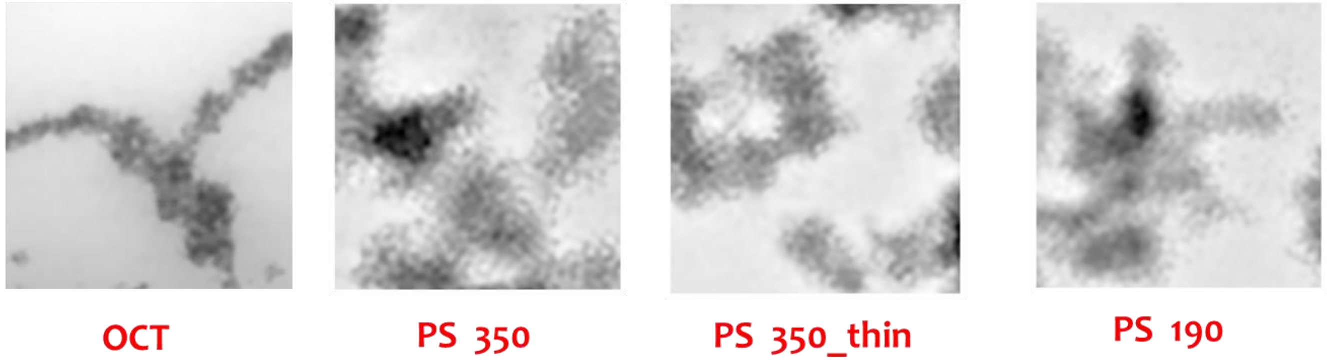
Ptychography experiment

(a)



Sample	$\Delta\phi$	M_w	t_{PS} [μm]
OCT	0.044	---	0
PS 350	0.089	350	24±4
PS 350_thin	0.133	350	0.307±0.010
PS 190	0.164	190	24±4

(b)



We explored the effect on the octapod aggregation of: *i*) different polymer film thickness for the same polymer molecular weight in the PS350_thin and PS350 samples; and *ii*) different molecular weights, for the same thickness of the polymer film in the PS350 and PS190 samples.

✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167

IC CNR Istituto di Cristallografia

xmi l@b

Ptychography experiment

Sample	<Δϕ>	t_{PS} [μm]	$\rho_{original}$ [nm]	$\rho_{averaged}$ [nm]	$\rho_{averaged/filtered}$ [nm]
OCT	$\langle\Delta\phi\rangle_{OCT} = 0.010 \pm 0.002$	0	49.3 ± 1.0	41.8 ± 1.0	24.5 ± 1.0
PS350_thin	$\langle\Delta\phi\rangle_{thin}^{PS350} = 0.030 \pm 0.002$	0.307 ± 0.010	42.2 ± 1.0	36.8 ± 1.0	26.0 ± 1.0
PS350	$\langle\Delta\phi\rangle_{free}^{PS350} = 0.020 \pm 0.002$	24 ± 4	52.5 ± 1.0	39.4 ± 1.0	32.5 ± 1.0
PS190	$\langle\Delta\phi\rangle_{free}^{PS190} = 0.0275 \pm 0.002$	24 ± 4	41.9 ± 1.0	37.4 ± 1.0	26.2 ± 1.0

Table 1. Mean phase retardation (<Δϕ>) and polymer thickness (t_{PS}).

Averaging/deblurring/denoising allowed improving image contrast and reducing noise level in the background between octapod nanostructures. This consented to visualize the sample structures at a resolution close to the **nominal one (27 nm).**

✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167

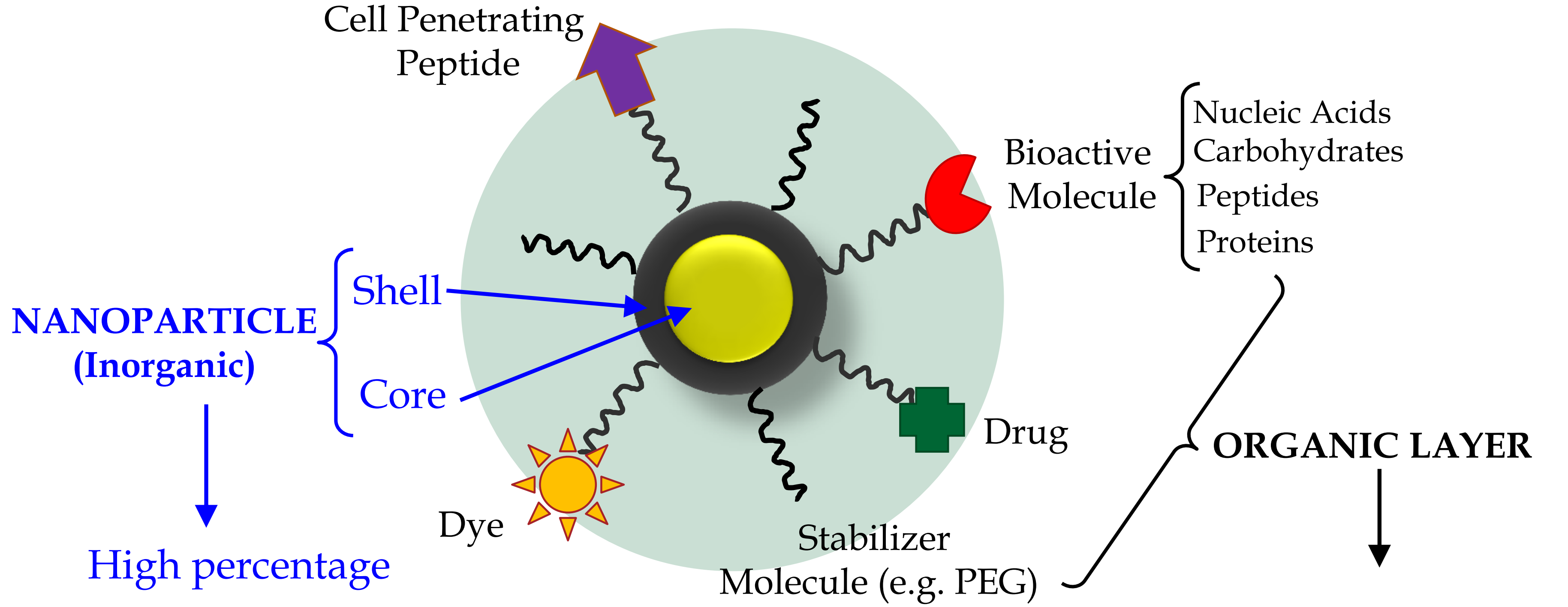
CNR | Istituto di Cristallografia

Conclusions

- Colloidal nanomaterials have been used for major technological advances.
- Examples of diffraction/imaging studies have been shown on
  - Nanomaterials in solutions >> SAXS/WAXS
  - Nanomaterials in powders, solid state >> WAXS/XRD
  - Nanomaterials assembled onto surfaces >> GISAXS – GIWAXS
  - Nanomaterials diluted in thick polymers >> Ptychography/CDI
  - Single Nanomaterials >> EDI

✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167
CNR | Istituto di Cristallografia

Nanocrystals for medicine: multiple functions within one system possible



High percentage

of atoms in its surface

(Size & Shape)

Special Physical Properties

- Superparamagnetism
- Optical Properties (LSPR, Fluorescence)
- …

B. Pelaz, *et al*. ACS Nano **2017**, 11,2313–2381

cinzia.giannini@ic.cnr.it
+39 080 5929167

IC CNR Istituto di Cristallografia

xmi l@b

Nanostructured particles

Table 1

List of nanostructured particles associated with the human body.

Nanostructure	Size	Ref.
glucose	1 nm	[244]
DNA	2.2–2.6 nm	[245]
average size of protein (rubisco monomer)	3–6 nm	[246]
haemoglobin	6.5 nm	[244]
micelle	13 nm	[244]
ribosomes	25 nm	[247]
enzymes and antibodies	2–200 nm	[248]

BEILSTEIN JOURNAL OF NANOTECHNOLOGY

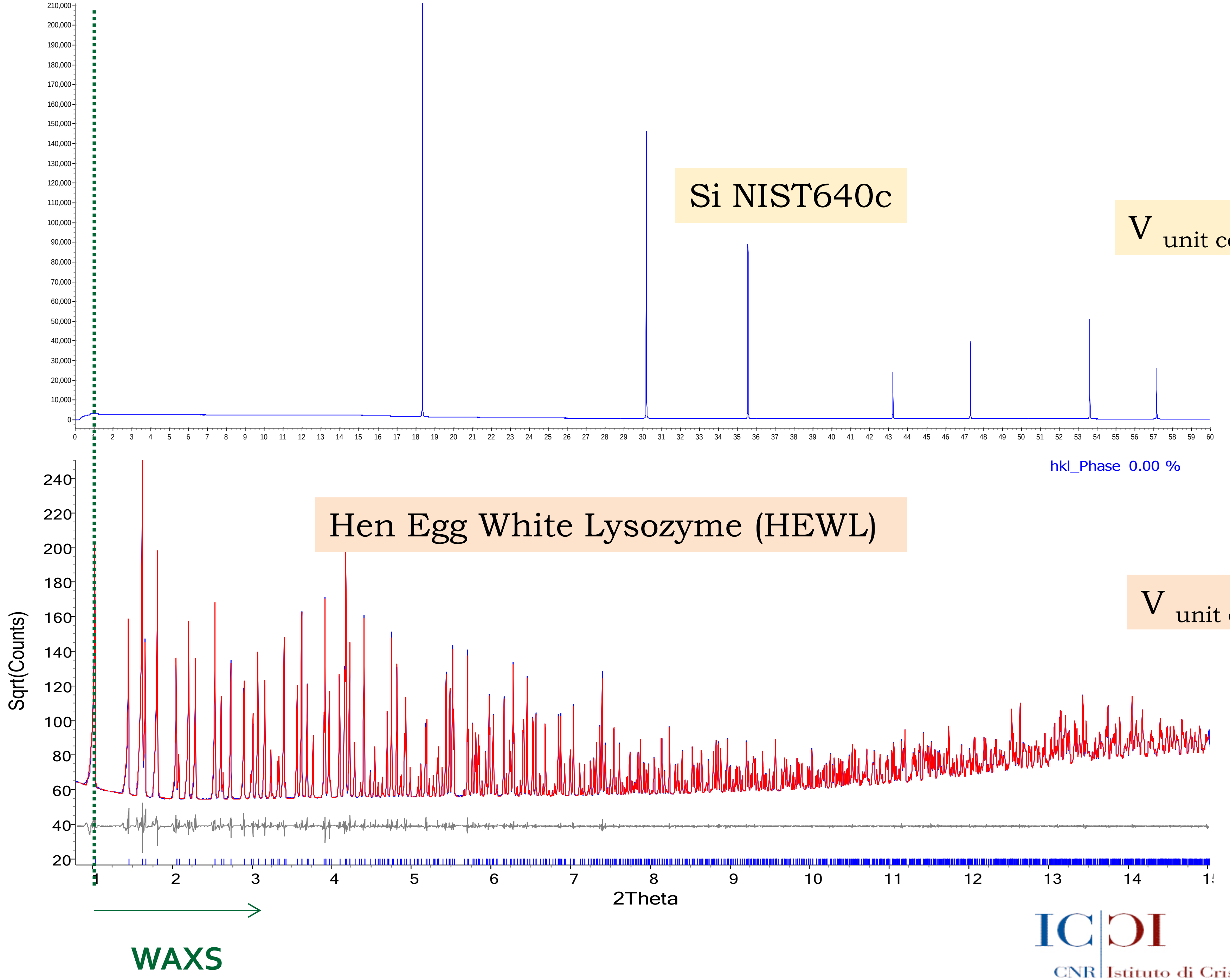
Beilstein J Nanotechnol. 2018; 9: 1050–1074. PMCID: PMC5905289
Published online 2018 Apr 3. doi: 10.3762/bjnano.9.98 PMID: 29719757

Review on nanoparticles and nanostructured materials: history, sources, toxicity and regulations

Jaison Jeevanandam,[1] Ahmed Barhoum,[2,3] Yen S Chan,[1] Alain Dufresne,[4] and Michael K Danquah[1]

cinzia.giannini@ic.cnr.it
+39 080 5929167

CNR Istituto di Cristallografia



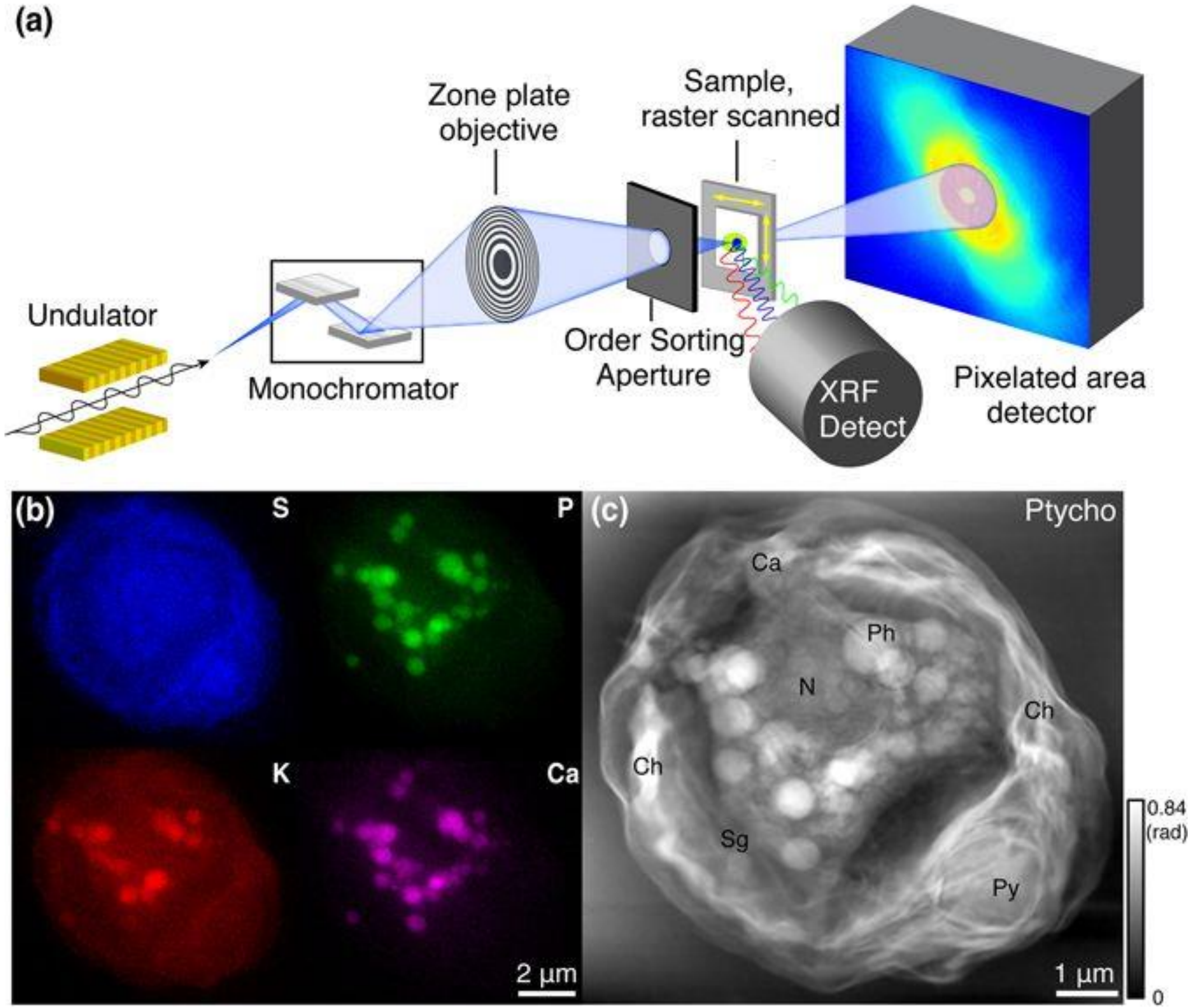
V $_{unit\ cell}$= 160 Å

V $_{unit\ cell}$= 240’217 Å

✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167

Bio-Ptychography

Scientific Reports **7**, Article number: 445 (2017)

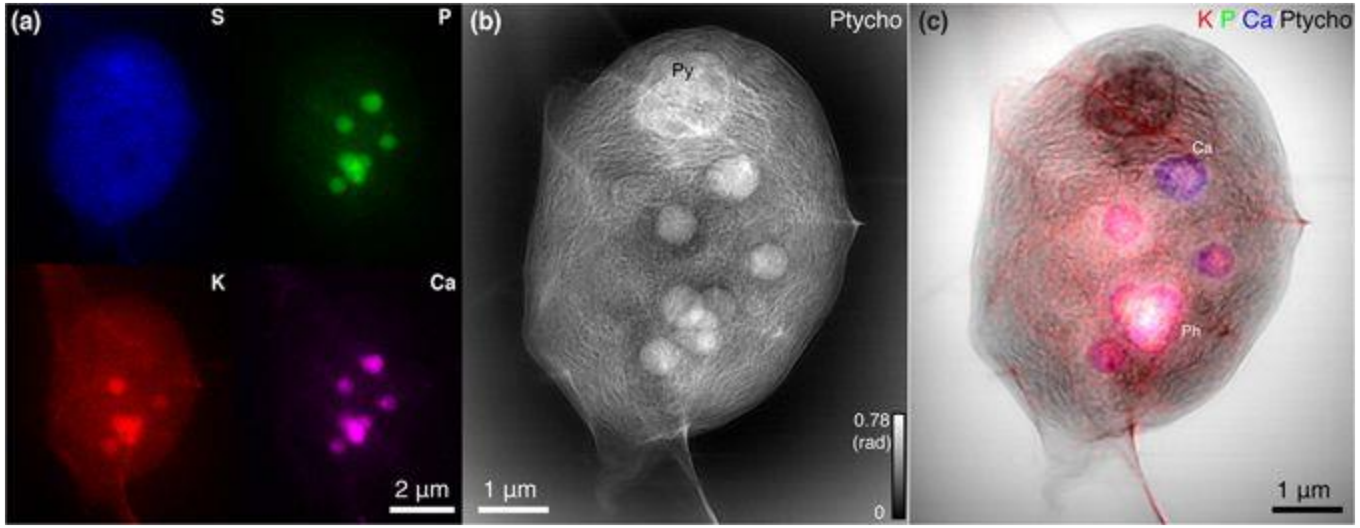


Combined x-ray fluorescence and ptychographic imaging of a frozen hydrated *Chlamydomonoas reinhardtii* alga: single cup-shaped chloroplast (Ch), as well as a number of other organelles: pyrenoid (Py), nucleus (N), starch granule (Sg), and polyphosphate bodies (Ph).

✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167
CNR | Istituto di Cristallografia

Bio-Ptychography

Scientific Reports **7**, Article number: 445 (2017)



Fluorescence and ptychographic x-ray images of a second unsectioned frozen-hydrated *Chlamydomonas* alga:

The 5.2 keV x-ray ptychographic phase contrast image (**b**) shows unlabeled subcellular structures, including a big pyrenoid (Py).

Because the fluorescence and ptychographic image data are recorded simultaneously, the various images are in perfect registry.

✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167
IC CNR Istituto di Cristallografia
xmi l@b

Perspectives ?

- Use of IV generation synchrotron sources with higher brilliance and coherence are extremely important
- Multiple techniques beamlines are extremely important
- to address the problem of incoherent assembly of nanocrystals in cells, in tissues, in soft matter

✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167

IC CNR Istituto di Cristallografia

xmi l@b

Acknowledgements for coherent related work

- **CNR Bari/Lecce (Italy)**
- L. De Caro, E. Carlino, D. Siliqi, D. Altamura

- **IIT Genova (Italy)**

L. Manna, D. Baranov, S. Toso, M. Arciniegas, M. Prato

- **Nanotec Lecce (Italy)**

D. P. Cozzoli

- **ESRF Grenoble (France)**

F. Zontone, Y. Yuskin

- **SLS (Switzerland)**
- A. Diaz, A. Menzel

✉ cinzia.giannini@ic.cnr.it
✆ +39 080 5929167

IC CI
CNR | Istituto di Cristallografia

xmi l@b