ESRF - EBS Workshop Series

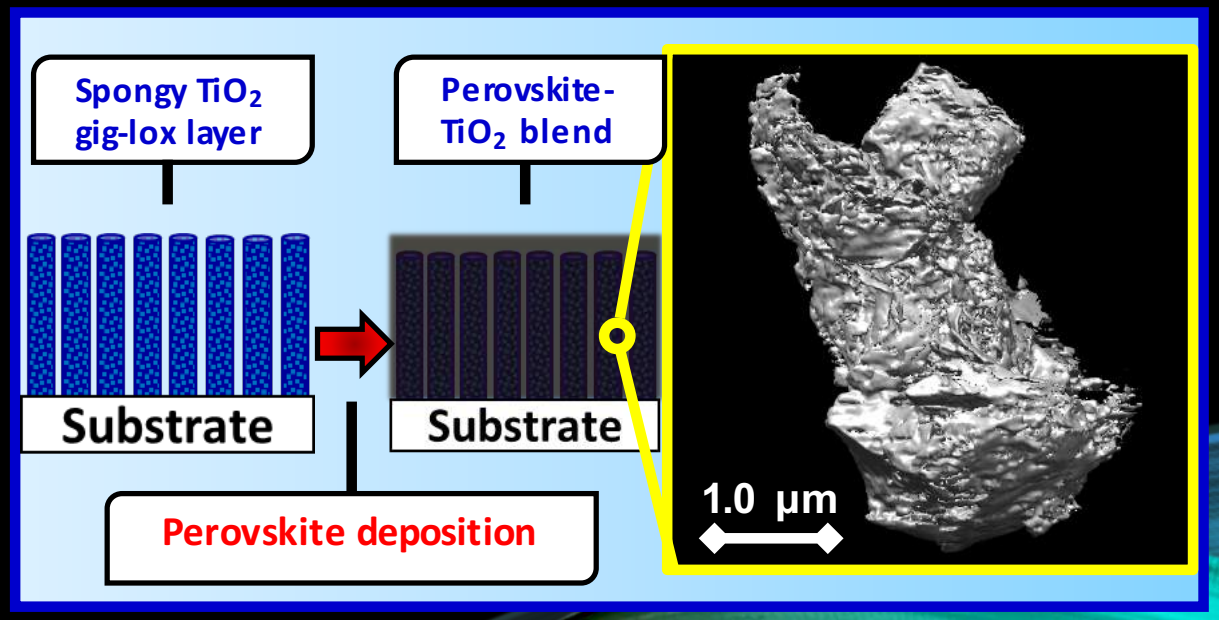
ESRF-EBS
Extremely Brilliant Source

Workshop on
Coherence at ESRF-EBS

ESRF - Grenoble - France
9 - 13 September 2019

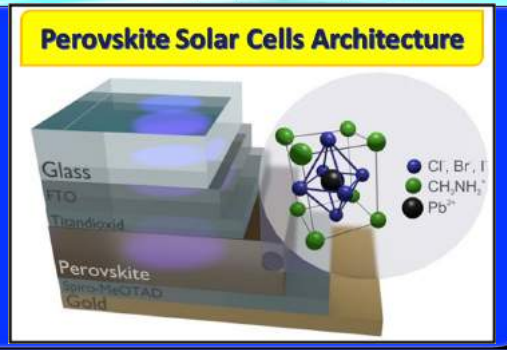
Structural characterization of TiO_2 gig-lox sponges by Coherent X-ray Diffraction Imaging

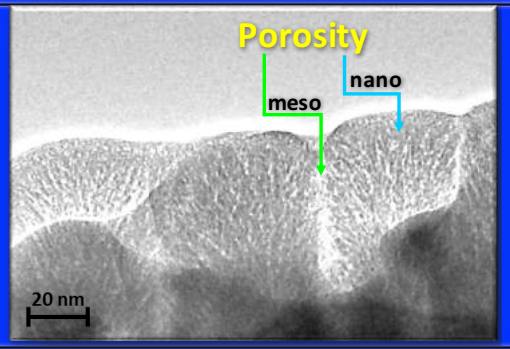
Salvatore Sanzaro, Federico Zontone, David Grosso, Thomas Bottein, Fortunato Neri, Emanuele Smecca, Giovanni Mannino, Corrado Bongiorno, Corrado Spinella, Antonino La Magna and Alessandra Alberti



Outline

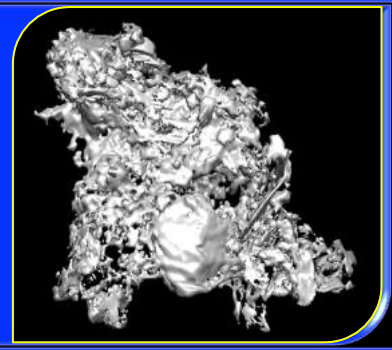
Perovskite Solar Cells (PSC)

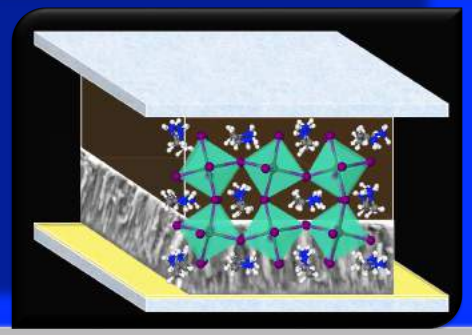




New sputtering method: spongy TiO_2 layer

Bimodal porosity characterization by 3D-CXDI

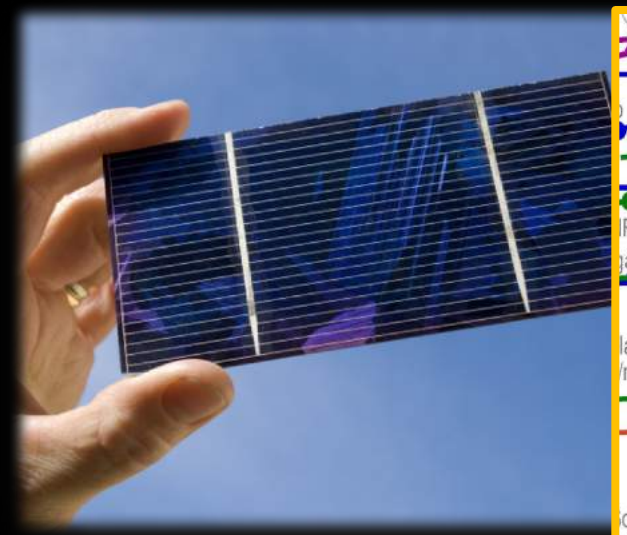


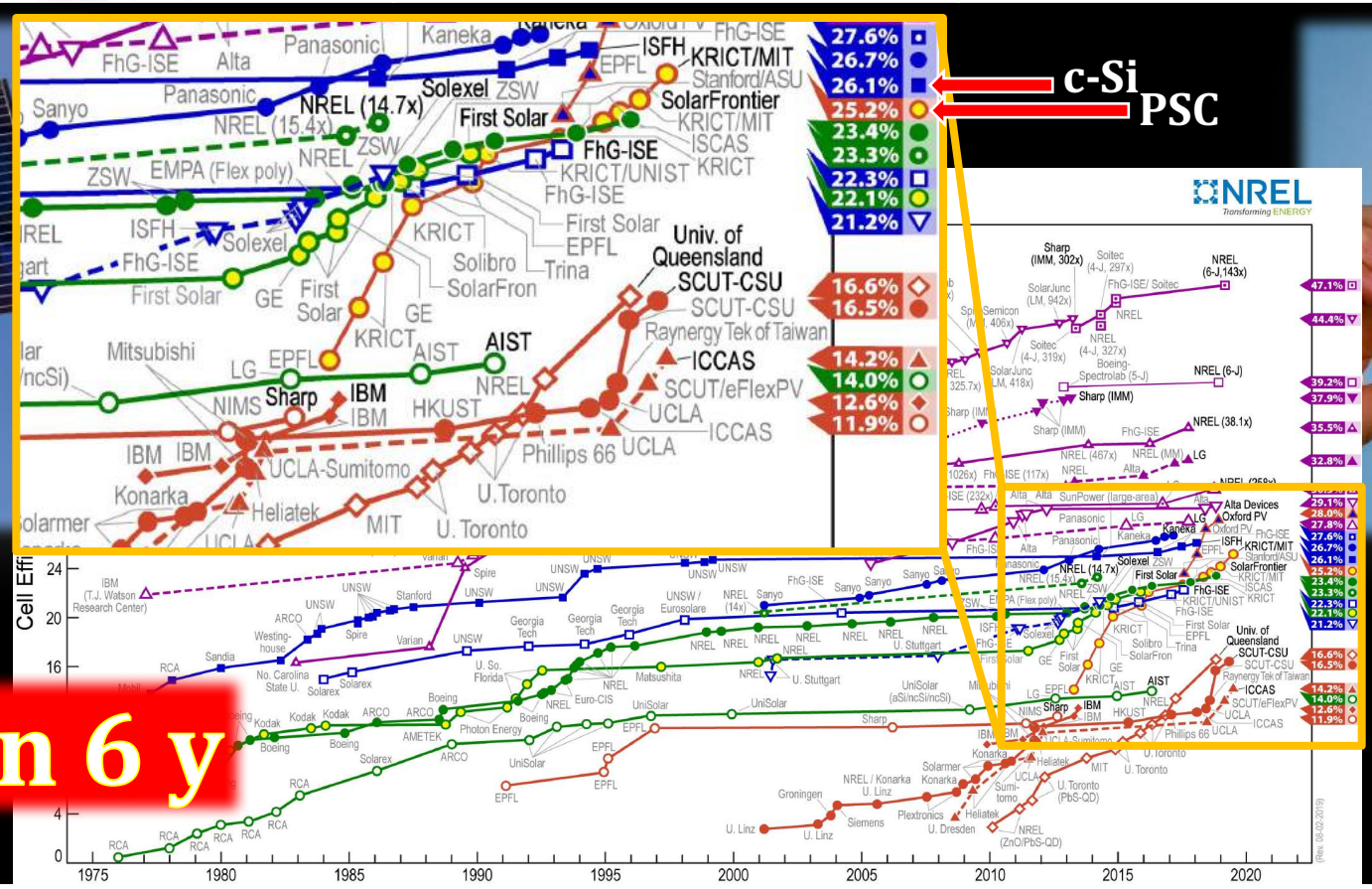


TiO_2 gig-lox layer in PSC Architectures

Crystalline Si cells vs. PSC

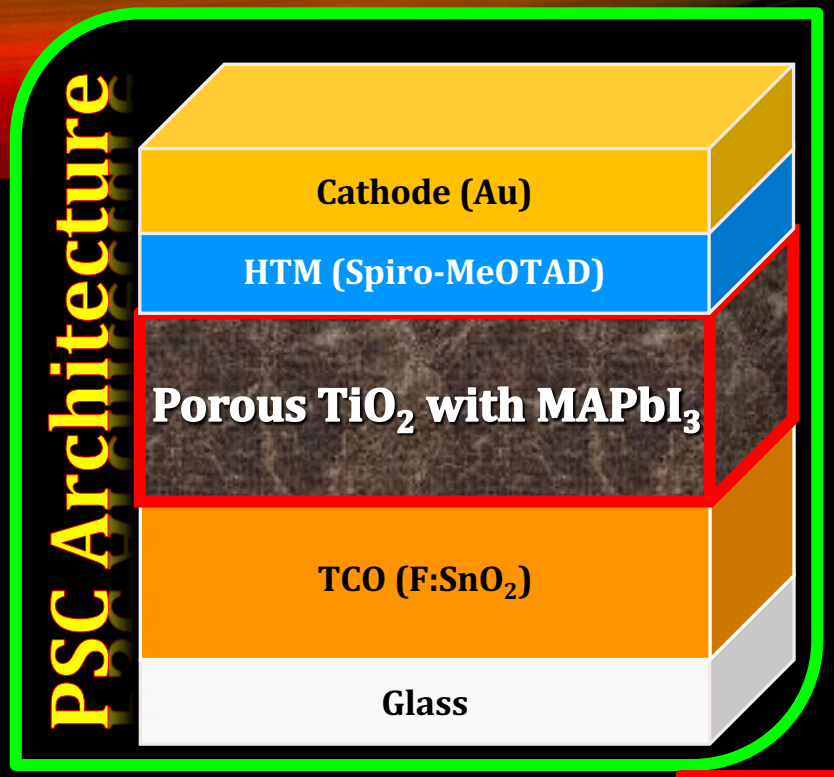
Parameters	c-Si	PSC
Gap Type	indirect	direct
Bandgap E_g	IR-UV	Visible-UV
Adsorption depth (μm)	~1.0-1000	~0.02-0.2
η_{max} (%)	26.1	25.2





+11% in 6 y

Perovskite Solar Cells (PSC)



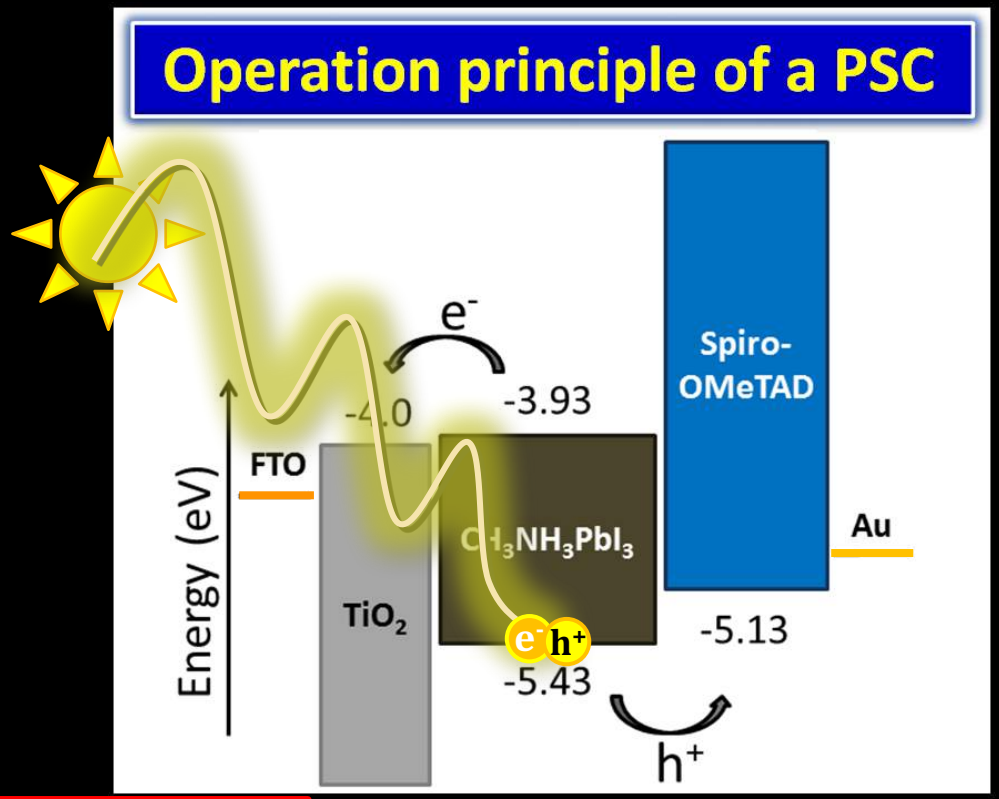
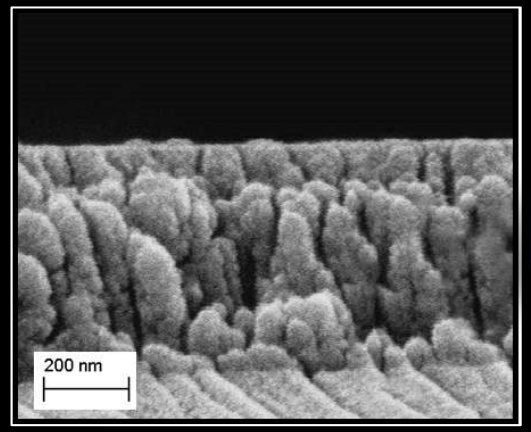
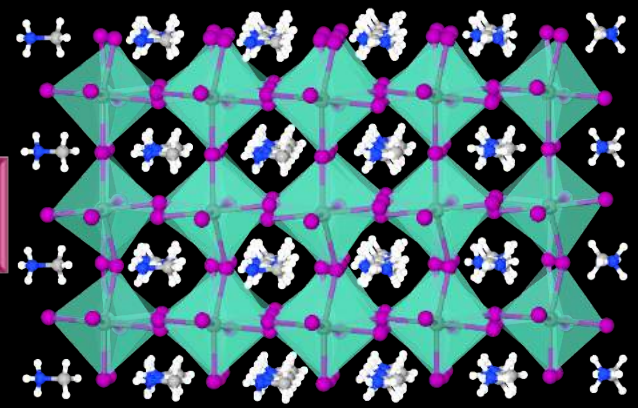


Photo-active Blend:

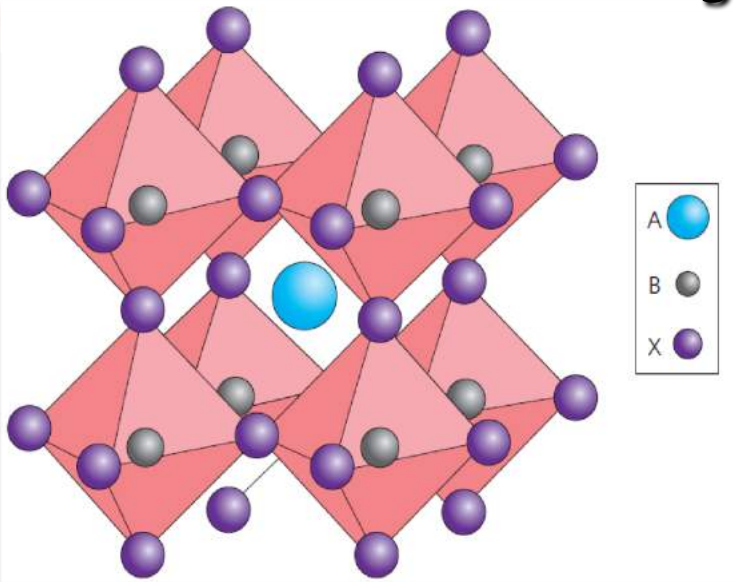


porous TiO_2 + $MAPbI_3$



Perovskite layer

Perovskites = ABX_3

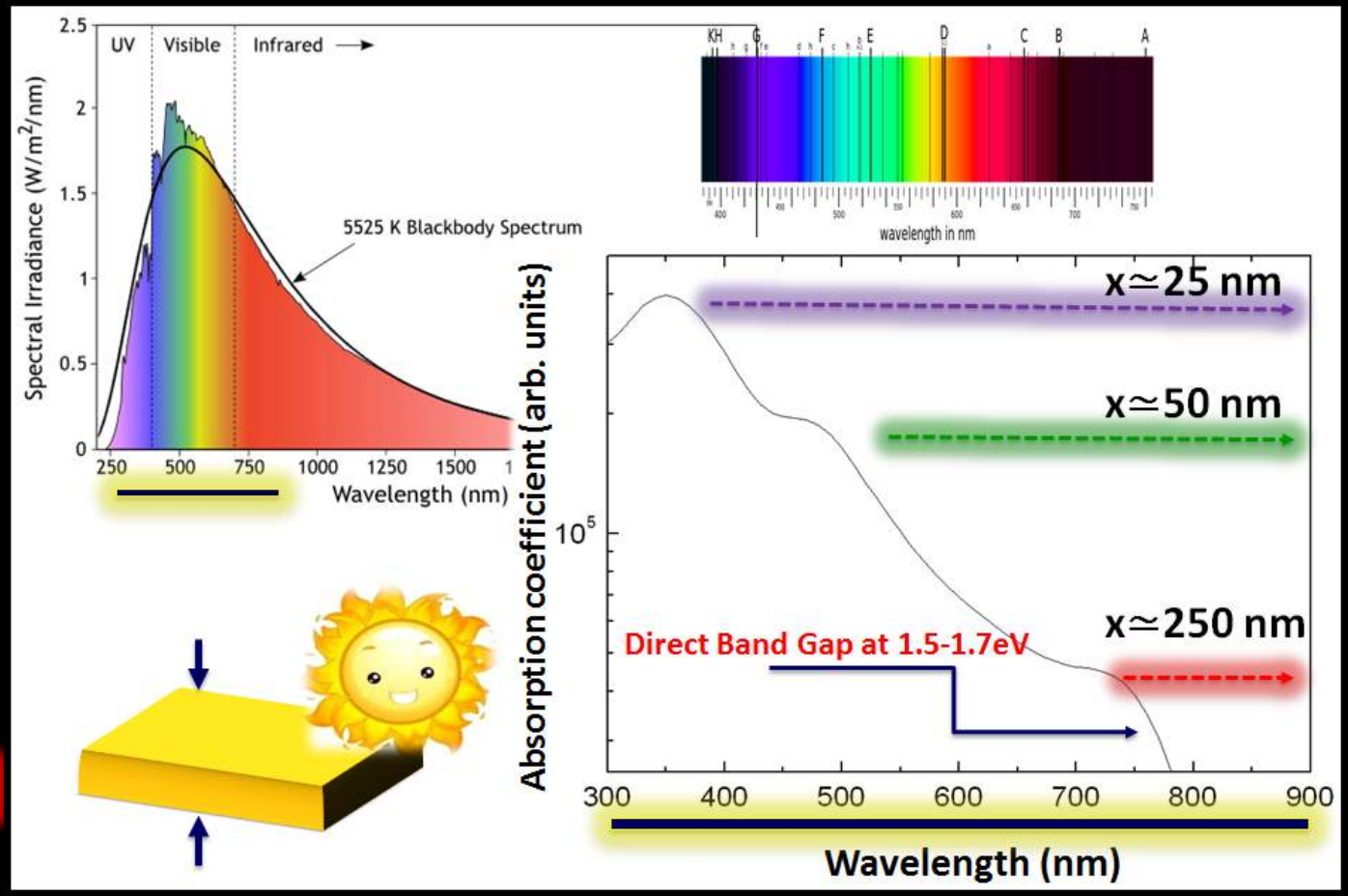


Hybrid perovskites

Inorganic cage + Organic cations

A = Big Cation	Pb^{2+}
B = Small Cation	$CH_3NH_3^+$
X = Anion	I^-

$CH_3NH_3PbI_3$ = $MAPbI_3$

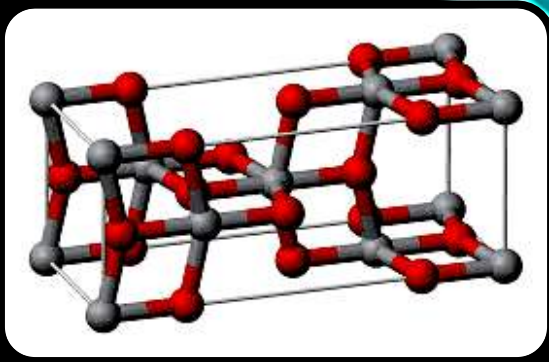


Miyasaka, T., *Chem. Lett.* 2015, *44*, 720.
Miyasaka, T. et al., *Chem. Rev.* 2019, *119*, 3036.

Why should TiO_2 be porous?

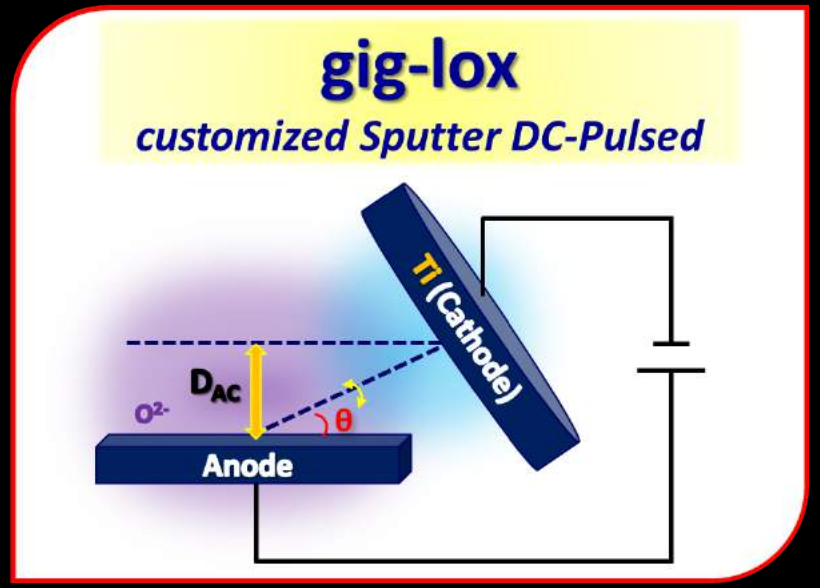
TiO_2 based blending materials have raised great interest in many technological areas, *e.g.* in photovoltaics, photocatalysis, biomedical devices, lithium-ion batteries…

In photovoltaics, the key parameter for the best efficiency in hybrid solar cells is porosity

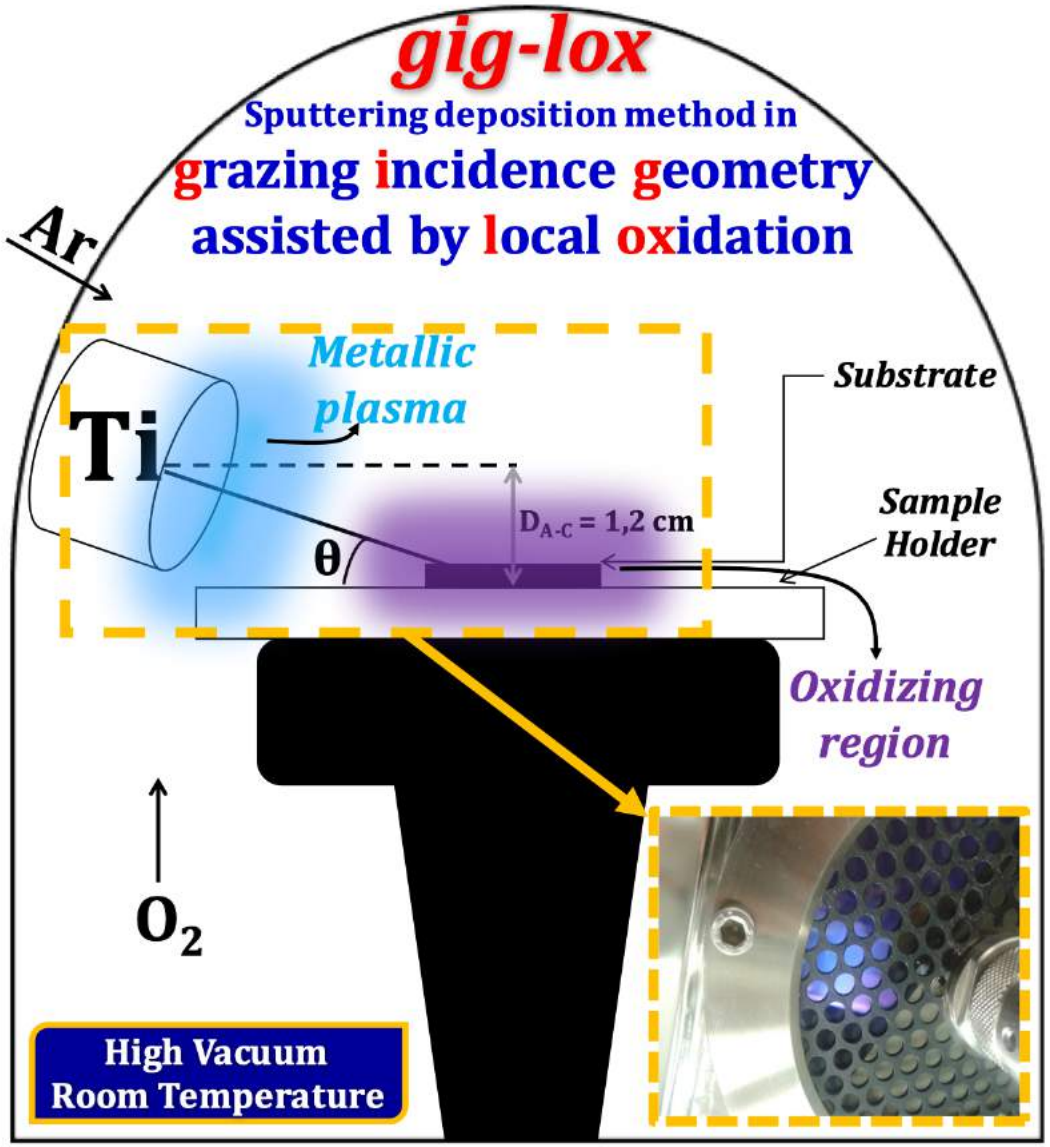


Customized Magnetron Sputter DC-pulsed equipment

Located at CNR-IMM HQ inside the STMicroelectronics Lab. in Catania, Italy



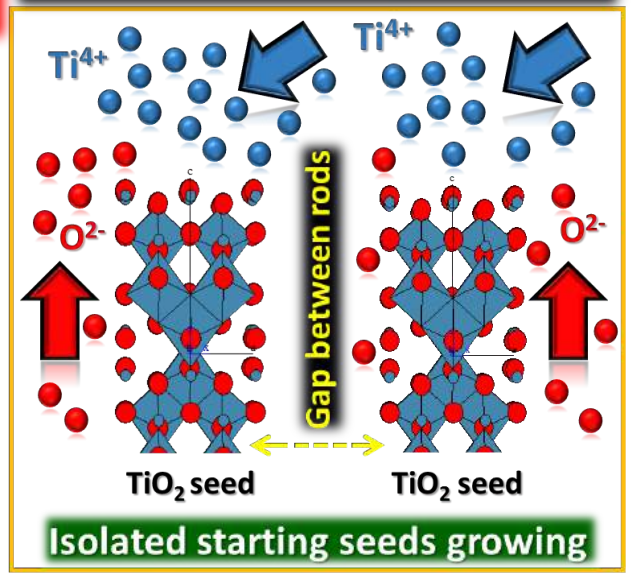
New sputtering method: spongy TiO_2 gig-lox



Sanzaro et al., Sci. Rep., 2016, 6, 39509
Sanzaro et al., J. Mat. Chem. A, 2017, 5, 2559

Pore-size 10-100 nm

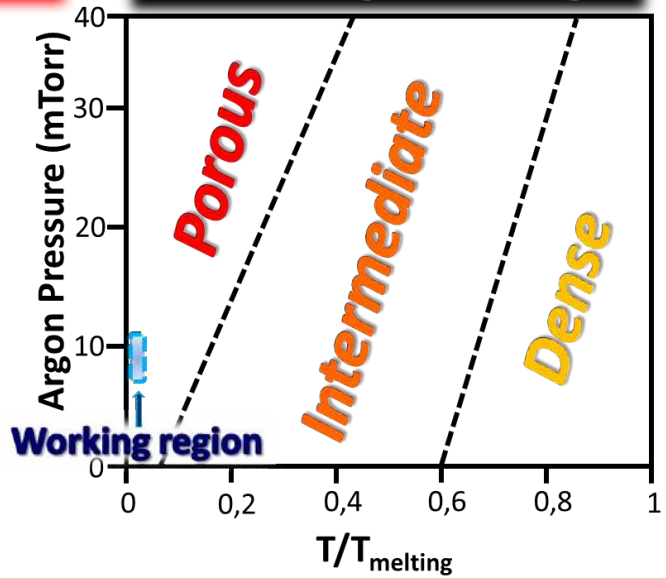
Meso-porosity



+

Pore-size 1-10 nm

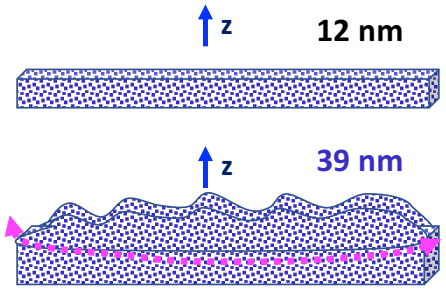
Nano-porosity

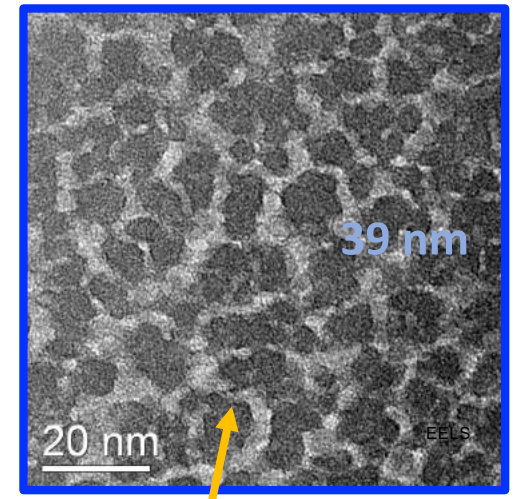


Controlling porosity in spongy TiO_2 gig-lox

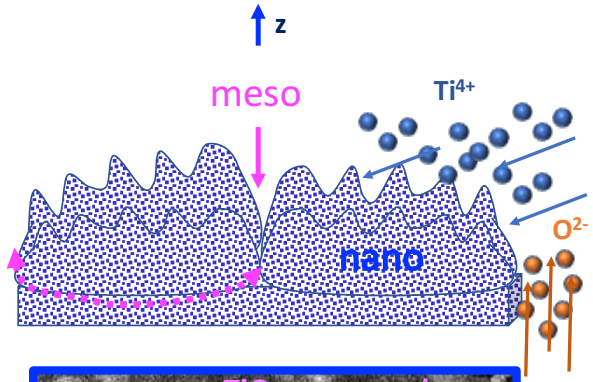
TiO_2 gig-lox TEM plan view

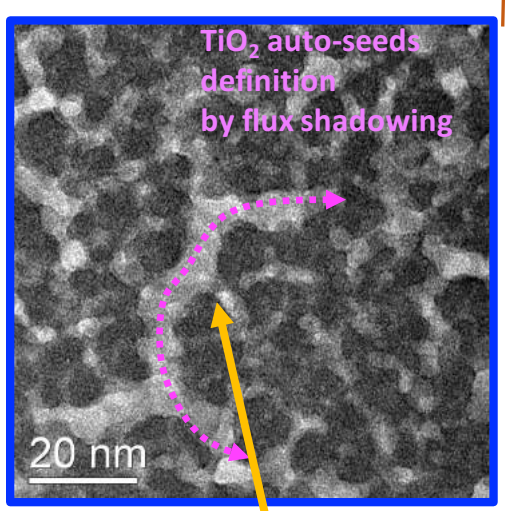
Nano-porosity

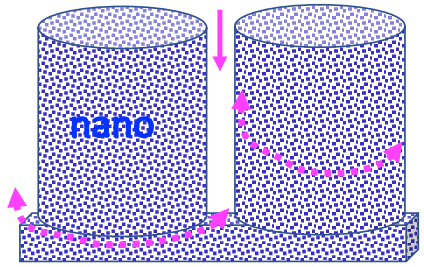


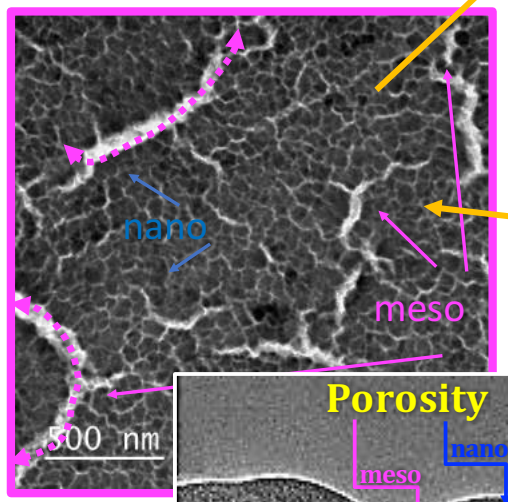


Meso-porosity





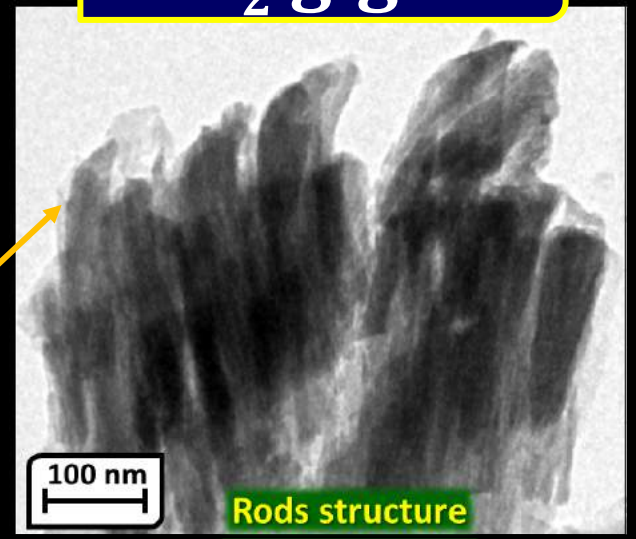




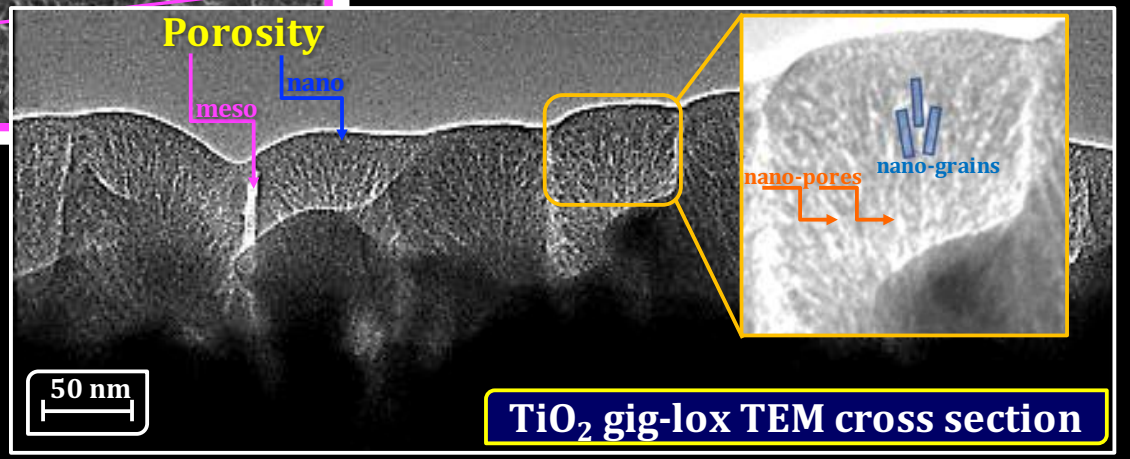
Initial growth, the layer containing auto-seeds

Thicker layer with meso-pores starting to be defined

TiO_2 gig-lox



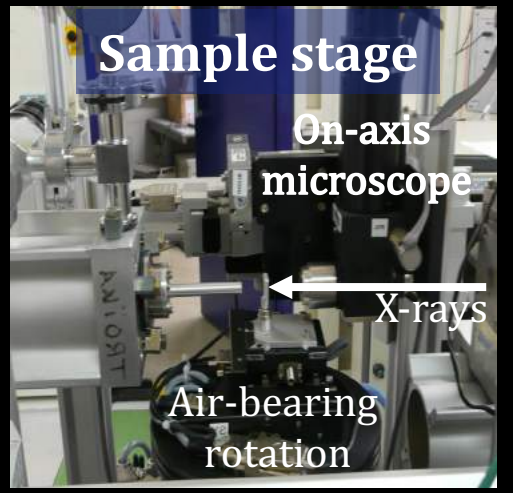
Final layer (400 nm) with meso- and nano-porosity defined on a large scale

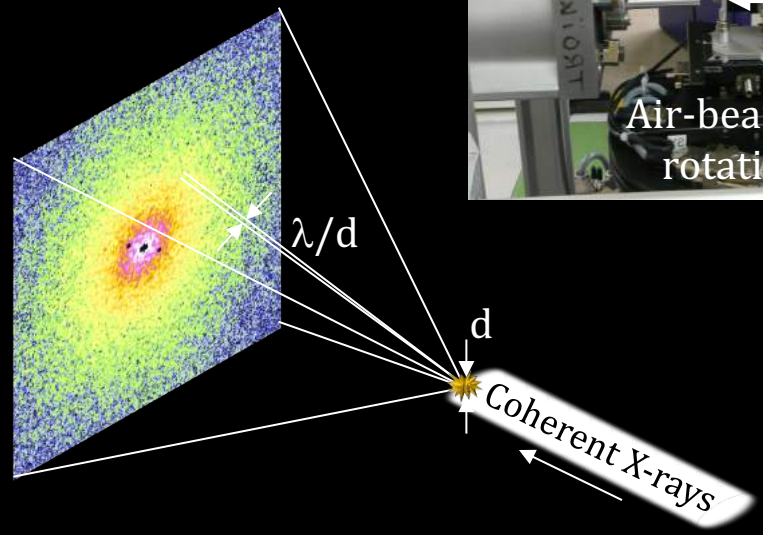


TiO_2 gig-lox TEM cross section

CXDI: why and how?

We are interested in CXDI because is a non-destructive technique to image samples in 3D at high resolution





- ω goniometer with samples on Si_3N_4 membranes
- Sample alignment assisted by an on-axis microscope
- Maxipix2x2 detector (516x516, 55mm pixel size)

Chushkin, Zontone et al., J. Synchrotron Rad., 2014, 21, 594.

We used the ID10 setup at 8.1 keV in SAXS geometry with 3.3 m as sample-to-detector distance (oversampling ~3)

CXDI: why and how?

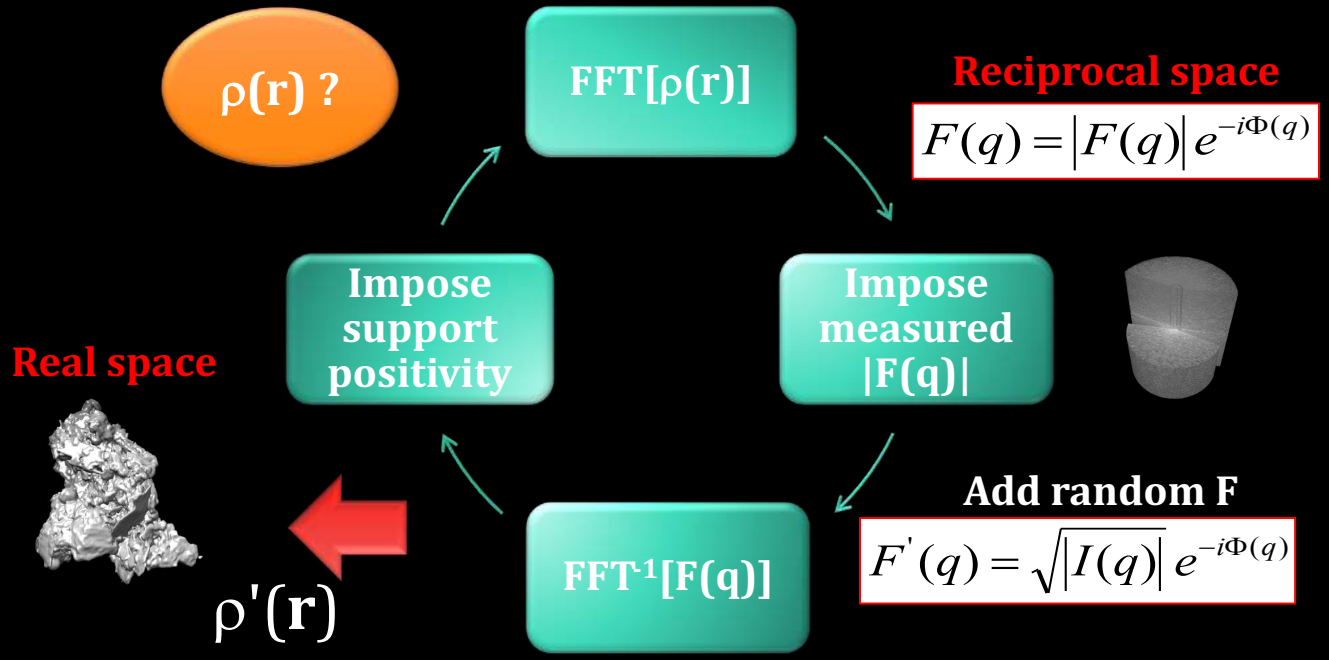
CUDA Python in-house software (by Yuriy Chushkin)

Pre processing

Raw data:

- ❑ Background subtraction
- ❑ Projection into the Fourier 3D matrix

Iterative phase retrieval algorithm



- ❑ hybrid input-output and error-reduction algorithms
- ❑ Shrink-wrap algorithm for sample support

Finup J.R., Appl. Opt. 21 (1982) 2758

Marchesini et al, Phys. Rev. B 68, 140101 (2003)

Post processing

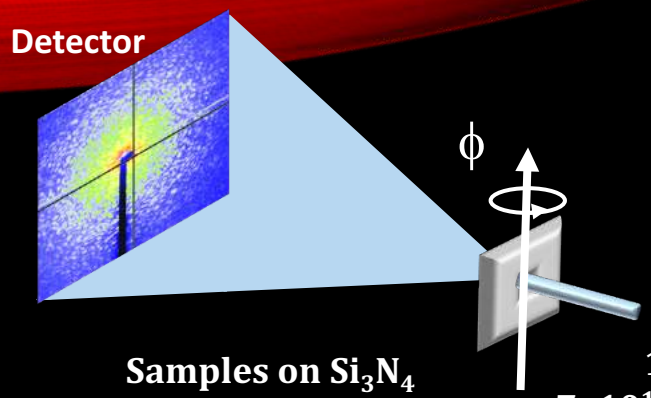
Final reconstructions:

- ❑ Aligned with sub-pixel precision
- ❑ Final averaging

Guizar-Sicairos et al, Opt. Lett. 33(2008)156

3D-CXDI at ID10

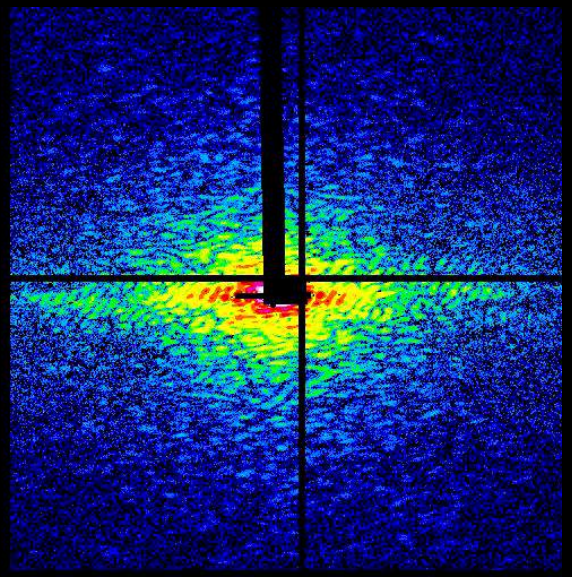
From data collection…



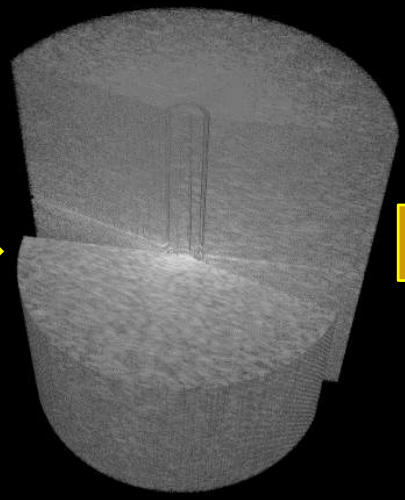
Samples on Si_3N_4 membranes

10μm beam
$7x10^{10}$ ph/s at 8.1 keV

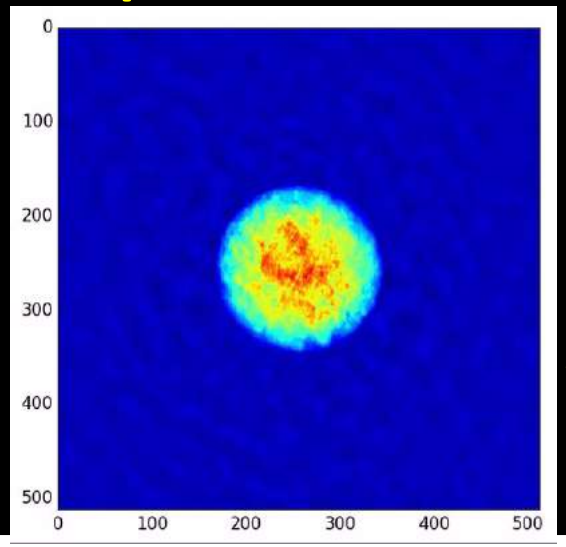
ϕ scan: -84°,+78°, 0.25° step



512x512x512 Fourier (q_x,q_y,q_z) grid

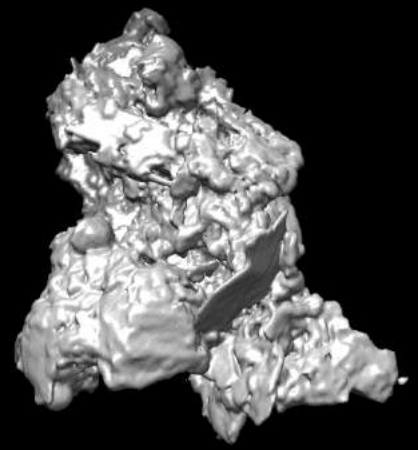


… to sample reconstruction

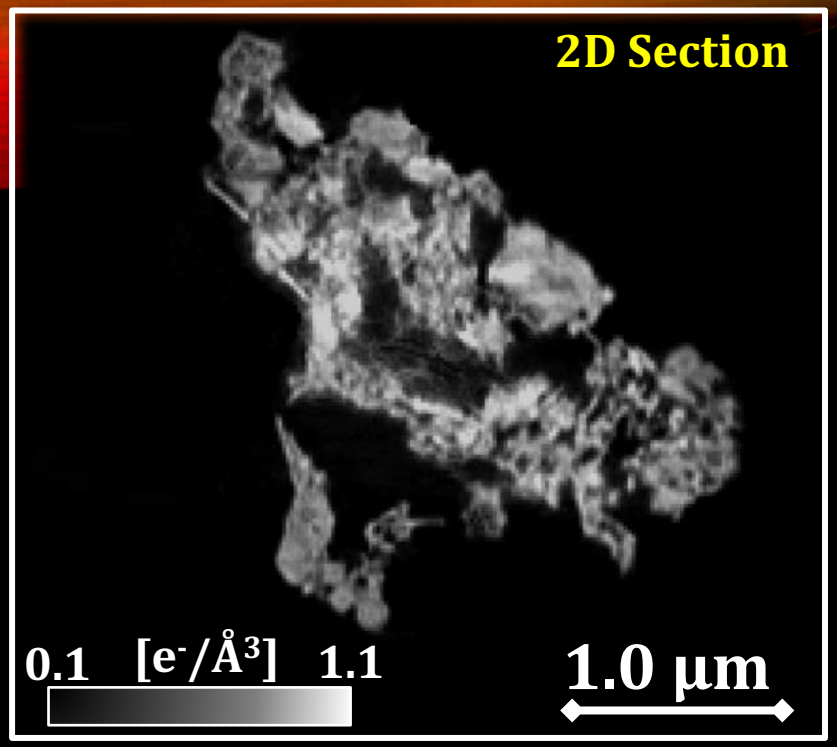


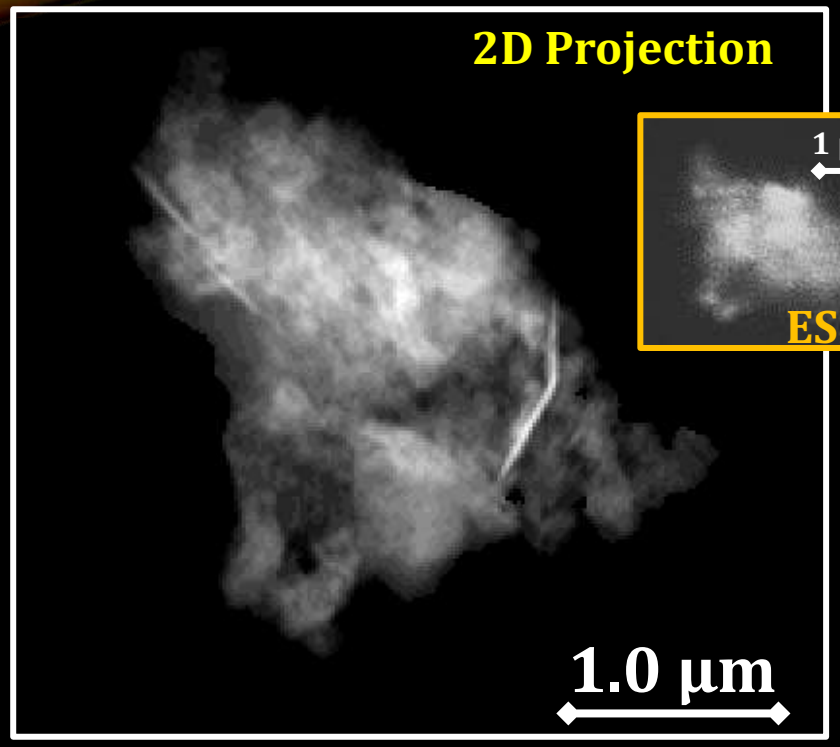
The Fourier volume has been normalized to absolute units for the quantitative determination of the electron density in $e^-/Å^3$

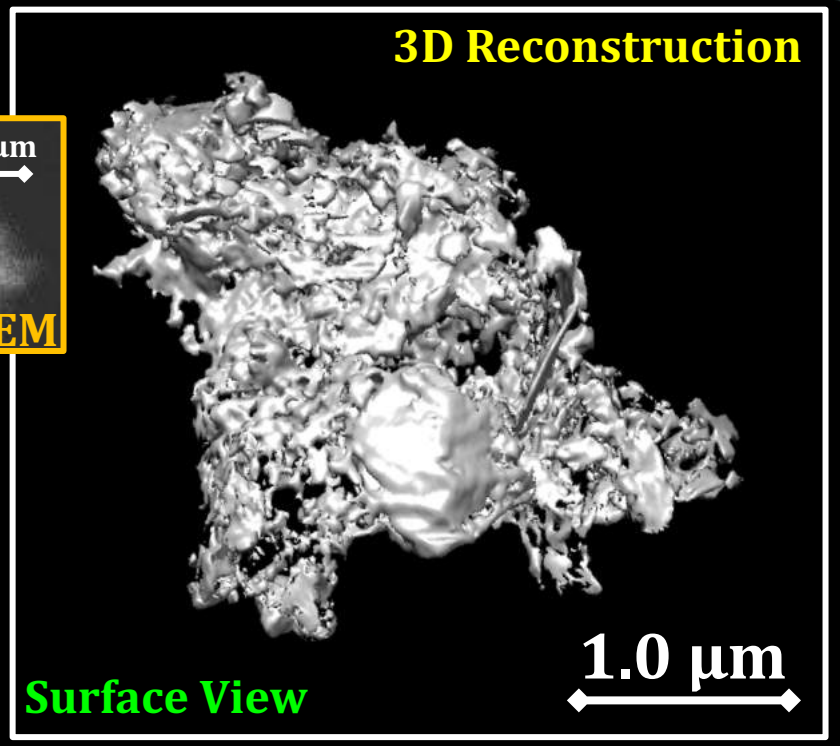
Chushkin, Zontone et al., J. Appl. Cryst. 52, 2019, 571



Meso-porosity (10-100 nm) in spongy TiO_2 gig-lox layer

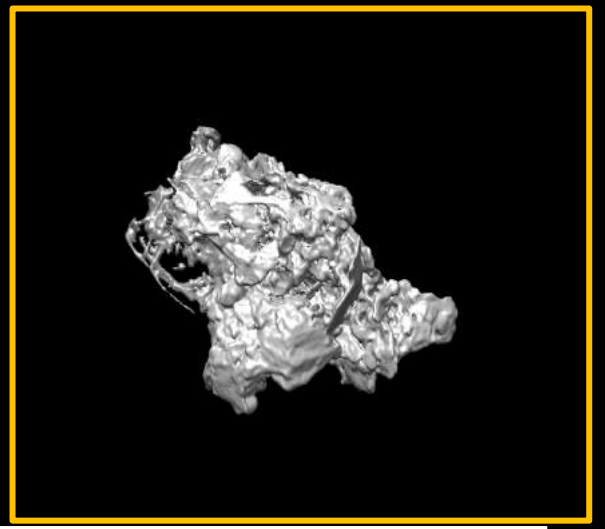






3D-CXDI on a TiO_2 fragment: highly "chaotic" morphology with pores having a large distribution in size (inherent to the gig-lox deposition method)

Sampling: 17.8 nm/vx

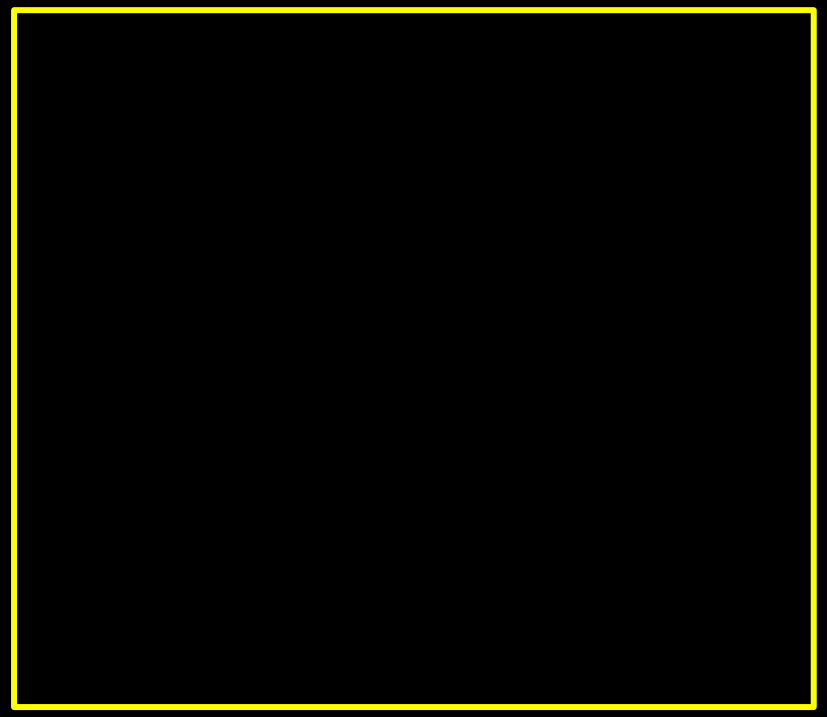


Surface-to-Volume ratio = 0.06 nm^{-1} (by CHIMERA software)
CXDI matches a rod structure (S/V = 2/r) with radius r ~ 33nm as seen by TEM

Nano-porosity (1-10 nm) in spongy TiO_2 gig-lox layer

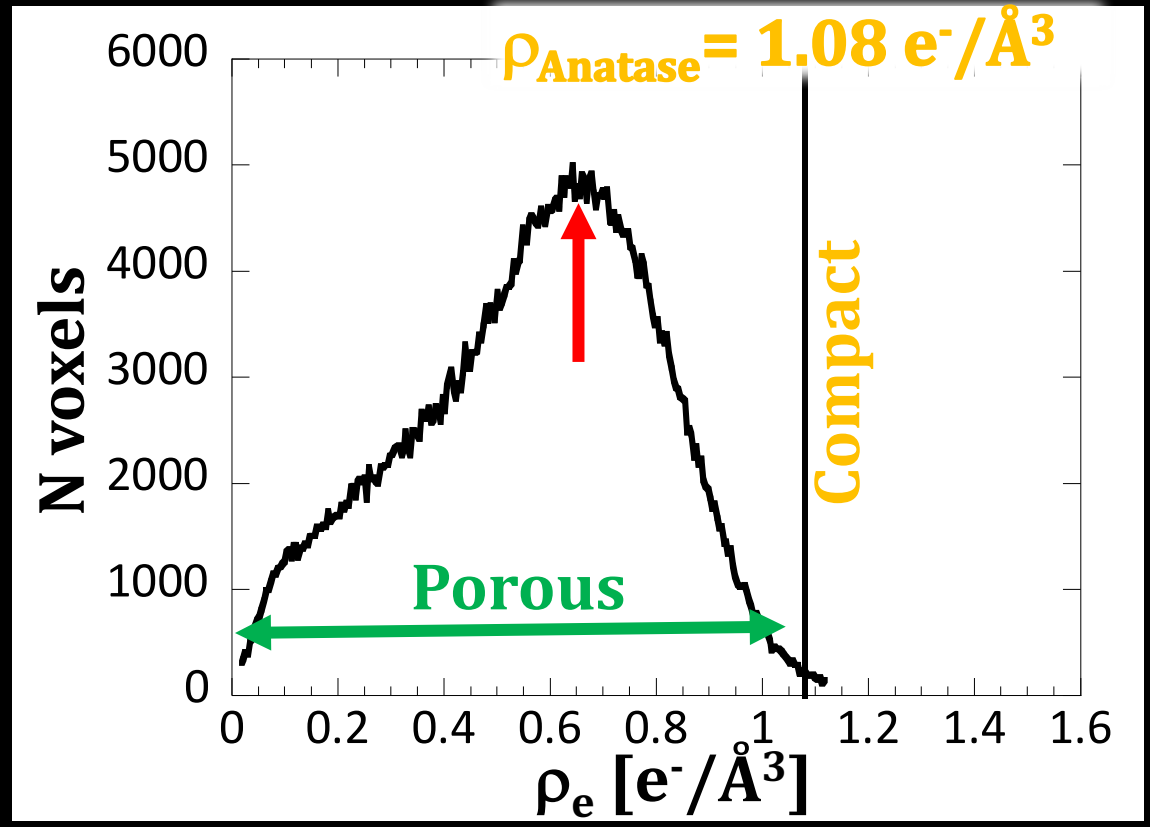
Quantitative 3D-CXDI has been applied to determine the nano-porosity

The segmented matrix



Sampling: 17.8 nm/vx

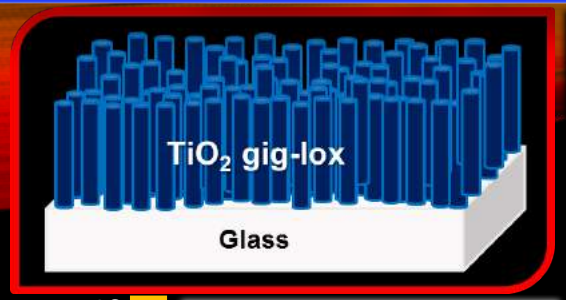
By "Trainable Weka Segmentation" under Fiji software



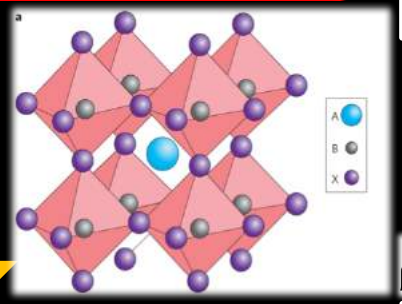
$$P(\%) = \left[1 - \left(\frac{\rho_{Matrix}}{\rho_{Anatase}}\right)\right] \times 100$$

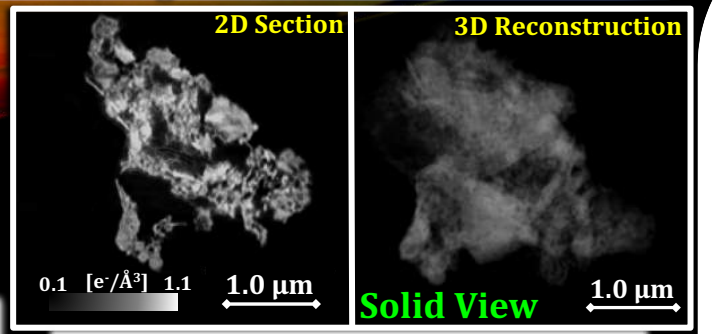
$\rho_{Matrix} \sim 0.63\ e^-/Å^3$ => P ~ 42% (as seen by EEP)

Effect of $MAPbI_3$ loading



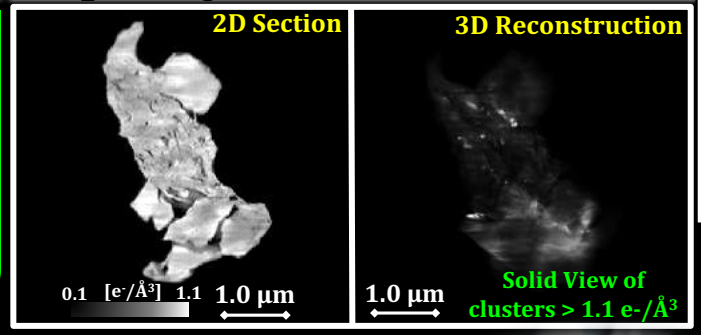
$MAPbI_3$

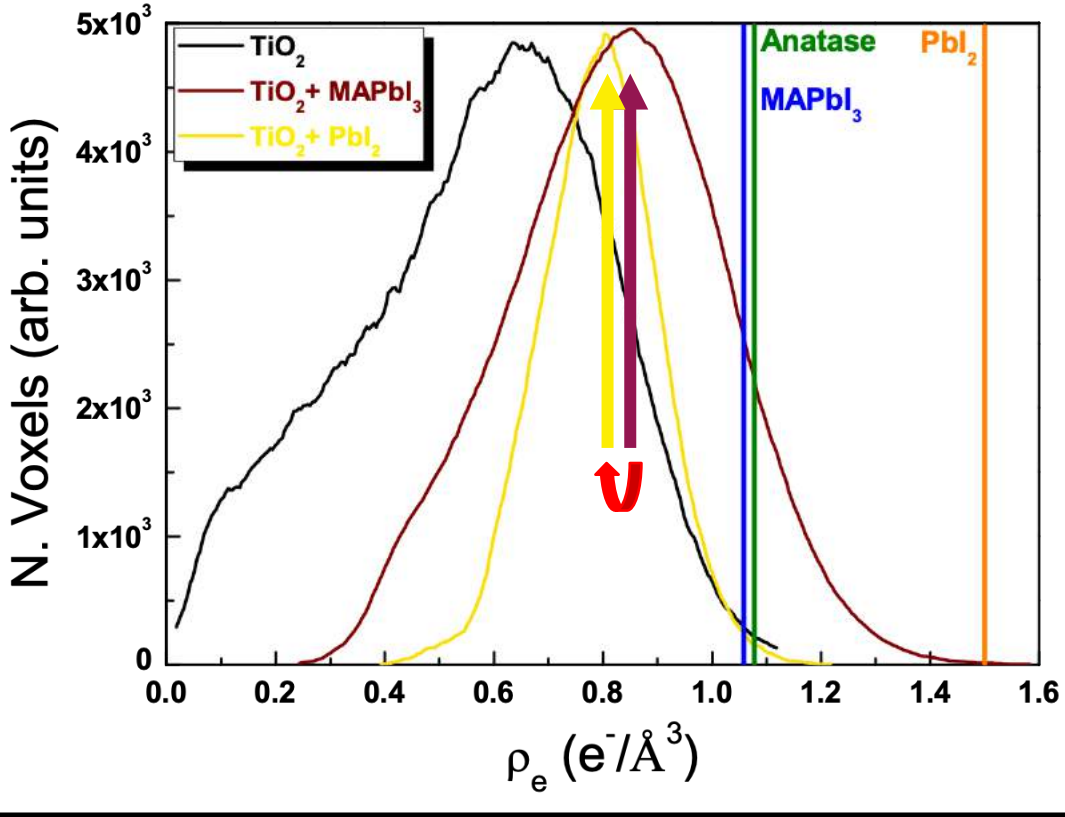




$\rho_{TiO_2} \sim 0.63\ e^-/Å^3 \Rightarrow P \sim 42\%$

$\rho_{TiO_2+MAPbI_3} \sim 0.88\ e^-/Å^3 \Rightarrow P \sim 18\%$



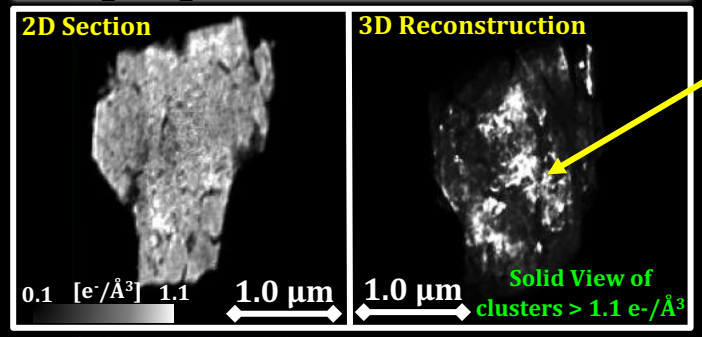


$TiO_2 + MAPbI_3$

Degradation

$TiO_2 + PbI_2$

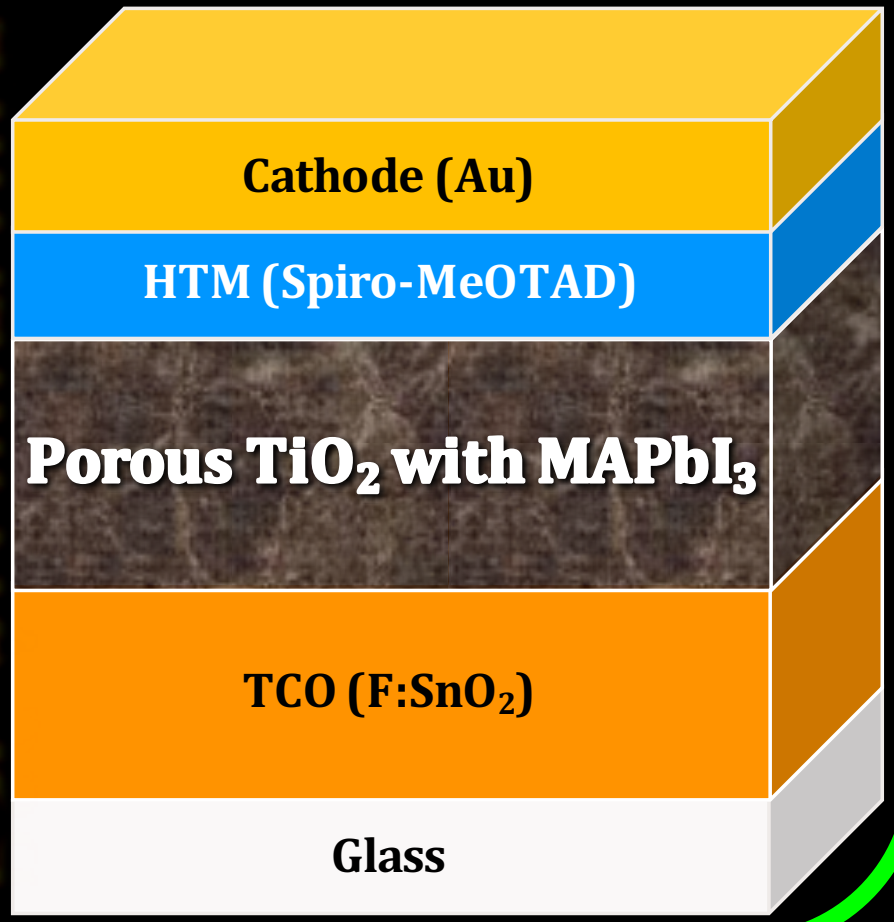
$\rho_{TiO_2+PbI_2} \sim 0.80\ e^-/Å^3 \Rightarrow P \sim 26\%$

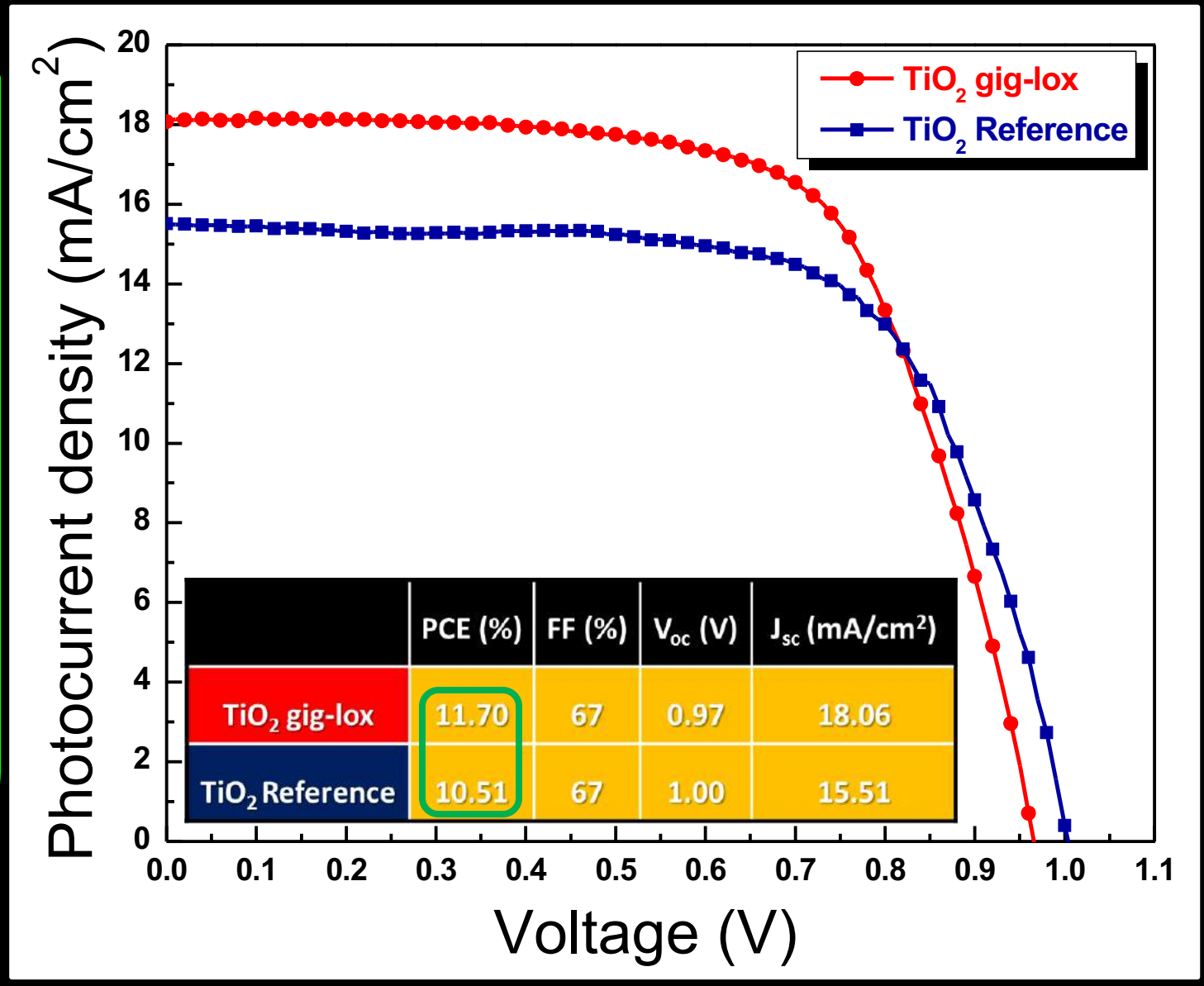


PbI_2 (as seen by STEM)

TiO_2 gig-lox integrated in a PSC architecture

PSC Architecture





	PCE (%)	FF (%)	V_{oc} (V)	J_{sc} (mA/cm²)
TiO_2 gig-lox	11.70	67	0.97	18.06
TiO_2 Reference	10.51	67	1.00	15.51

Conclusions

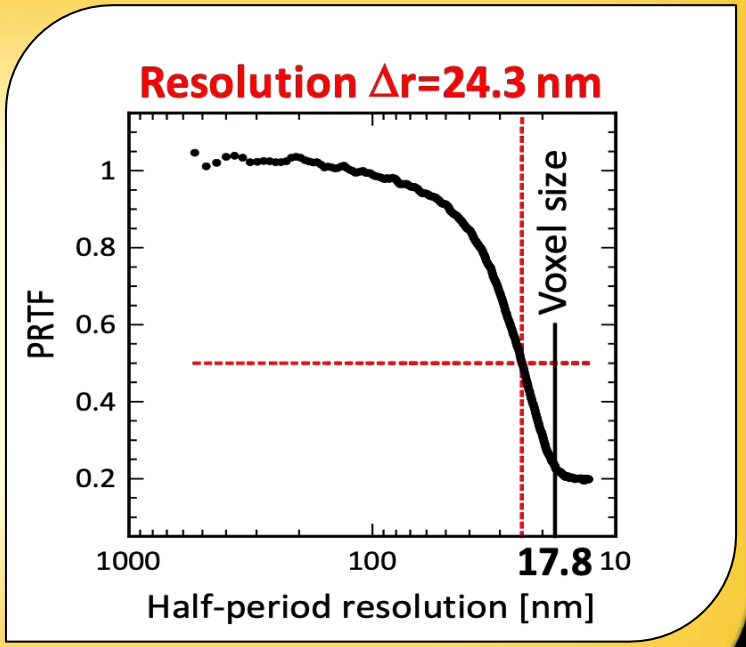
- New deposition sputtering method (gig-lox) to obtain spongy TiO_2 layers
- Multi porosity (meso-, nano-scale) of the TiO_2 layers

Sanzaro, Zontone et al., Nanomaterials (2019, 9, 1300)

- We applied successfully 3D-CXDI to study how an hybrid perovskites infiltrates a gig-lox TiO_2 sponge and successively degrades in air in a quantitative way
- The extracted information (porosity, PbI_2 degradation) nicely complement our laboratory measurements

Our wishes list at EBS

- Higher resolution (better than 10 nm) close to electron microscopy, *e.g.* to see the nano-porosity
- Faster scanning time into minutes, *e.g.* to follow phase transitions vs. Temperature in perovskite materials and transformations in perovskite covered with Si NPs…
- Larger Field of View for larger samples for more "averaged" information (10-20 μm)



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