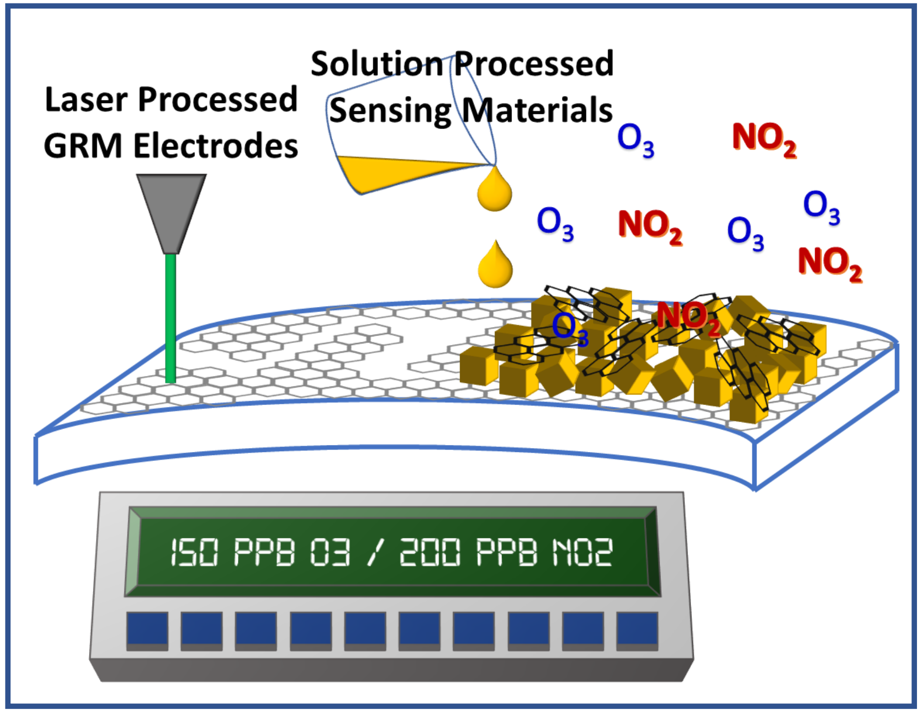
Solution-Processed Perovskite/Graphene Nanocomposites for Self-Powered Gas Sensors (PeroGas)

(JTC-2019-016, FLAG-ERA Joint Transnational Call (JTC) 2019)

Main area: Sensors from Graphene related materials (GRMs) and their heterostructures
Duration: 36 months
Total project funding: € 657.725



Consortium:
Istituto Italiano di Tecnologia –Italy –(coordinating)

Foundation for Research and Technology - Hellas – Greece – Funded by: GSRI

Bar-Ilan University – Israel – Funded by: InnovationAuth

Main Objectives:

- Development of sensors based on GRMs and halide perovskites, targeting mainly gaseous air pollutants (CO_2, CO, O_3, NO_x and SO_x), adaptable to smart/portable devices, which can be used to monitor the quality of breathing air in homes and cities (**with fast response, high selectivity & high sensitivity**).

- PeroGaS will generate know-how and technological solutions that will be useful also for other applications (solar cells, light emitting devices, and flexible electronics).

Main points of strengths of the PeroGaS project:

Development of a sensing composite material consisting of metal halide perovskite crystals conjugated to reduced graphene oxide (rGO)

This sensing material will be deposited directly onto rGO laser-fabricated interdigitated electrodes

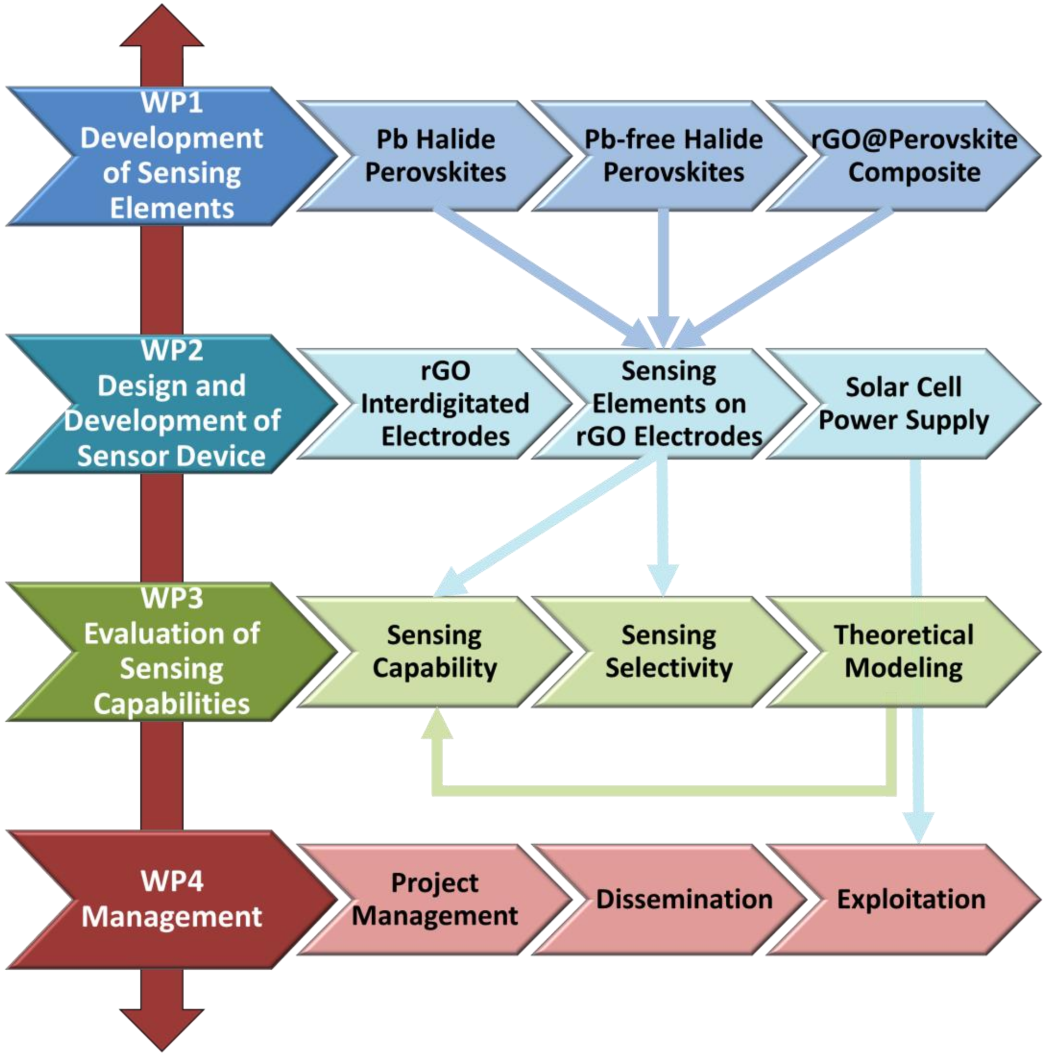
We will develop lead-free perovskites to mitigate toxicity issues

The electrodes will be environmentally sustainable, as they will be based on rGO rather than indium tin oxide (ITO) or noble metals. rGO will provide both thermal stability and enhanced conductivity

The sensing elements are solution processable, compatible with printed electronics concepts, and printable onto flexible substrates

We address gas selectivity by using Continuous Wave Stimulated Raman Scattering. This technique can quantify and differentiate the contributions of the various adsorbed gases to the generated electrical signal.

Workpackages



PARTNERS AND THEIR ROLE

ISTITUTO ITALIANO DI TECNOLOGIA

- <u>**Coordinating**</u>
- **Synthesis of perovskite nanocrystals**
- **Development of surface treatments**
- **Development of deposition treatments**

FORTH
FOUNDATION FOR RESEARCH AND TECHNOLOGY - HELLAS

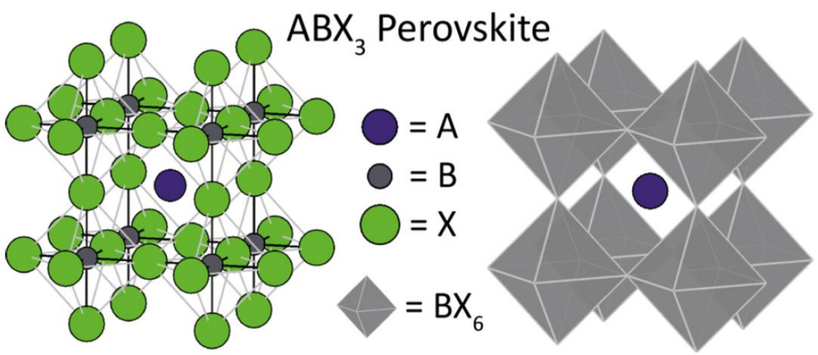
- **Synthesis of perovskite microcrystals**
- **Fabrication of perovskite@rGO conjugates**
- **Testing of gas sensing capability**
- **Preparation of rGO electrodes and solar cell power supply**

Bar-Ilan University
אוניברסיטת בר אילן

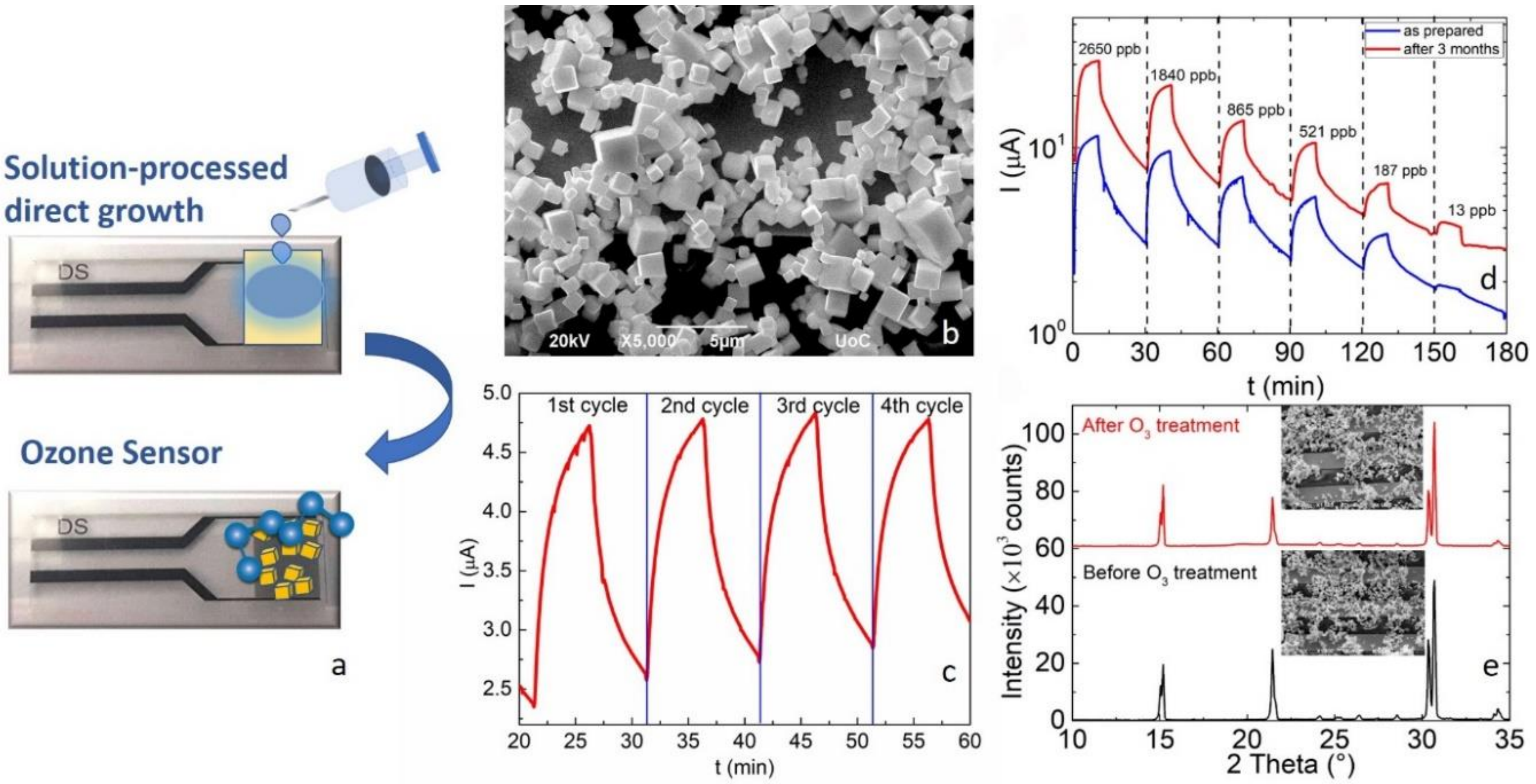
- **Testing of gas sensing selectivity**
- **Stimulated Raman Spectroscopy**

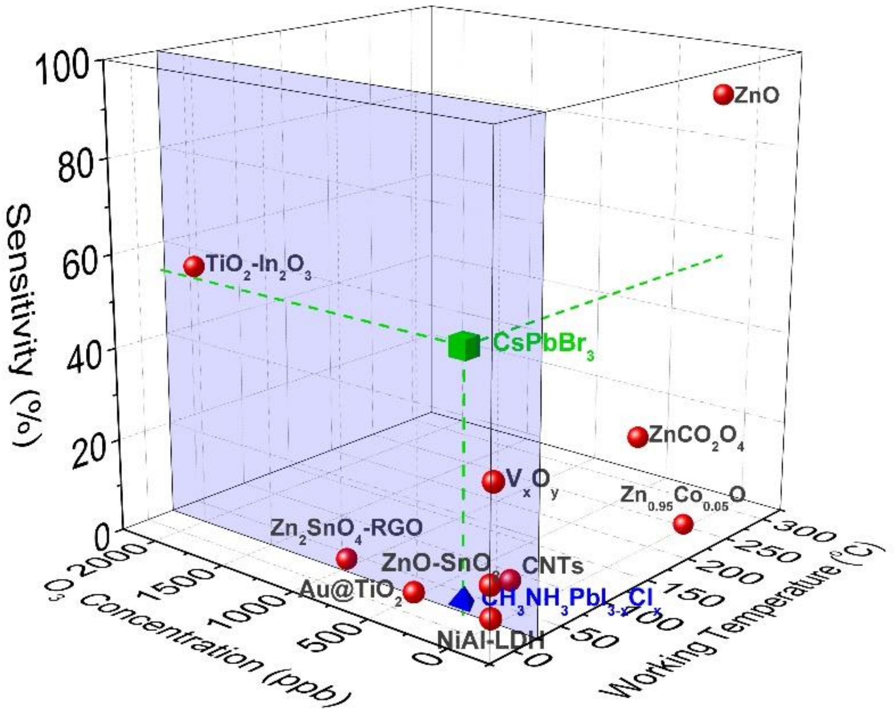
Why using halide perovskite-based materials?

High charge mobility, therefore, an electrical readout can easily be obtained as a result of variations in the environmental gas concentration. Also, these materials can be easily produced by solution-based processes.

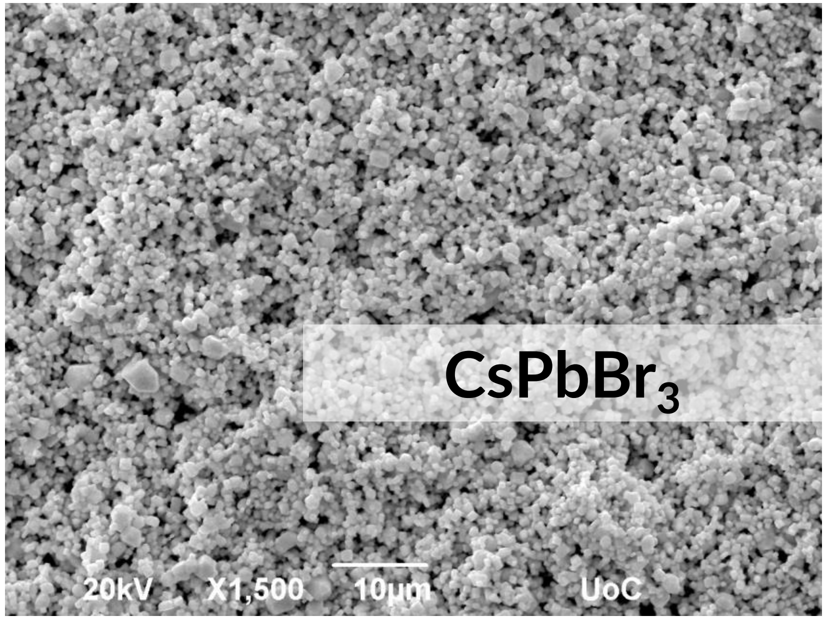


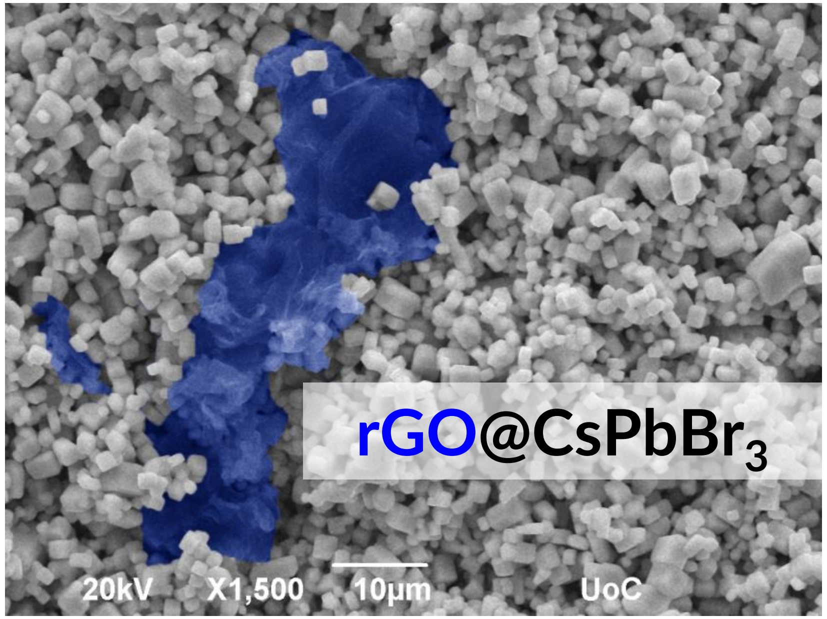
Preliminary data on ozone sensing (beginning of the project) – FORTH: detection limit of 187 ppb

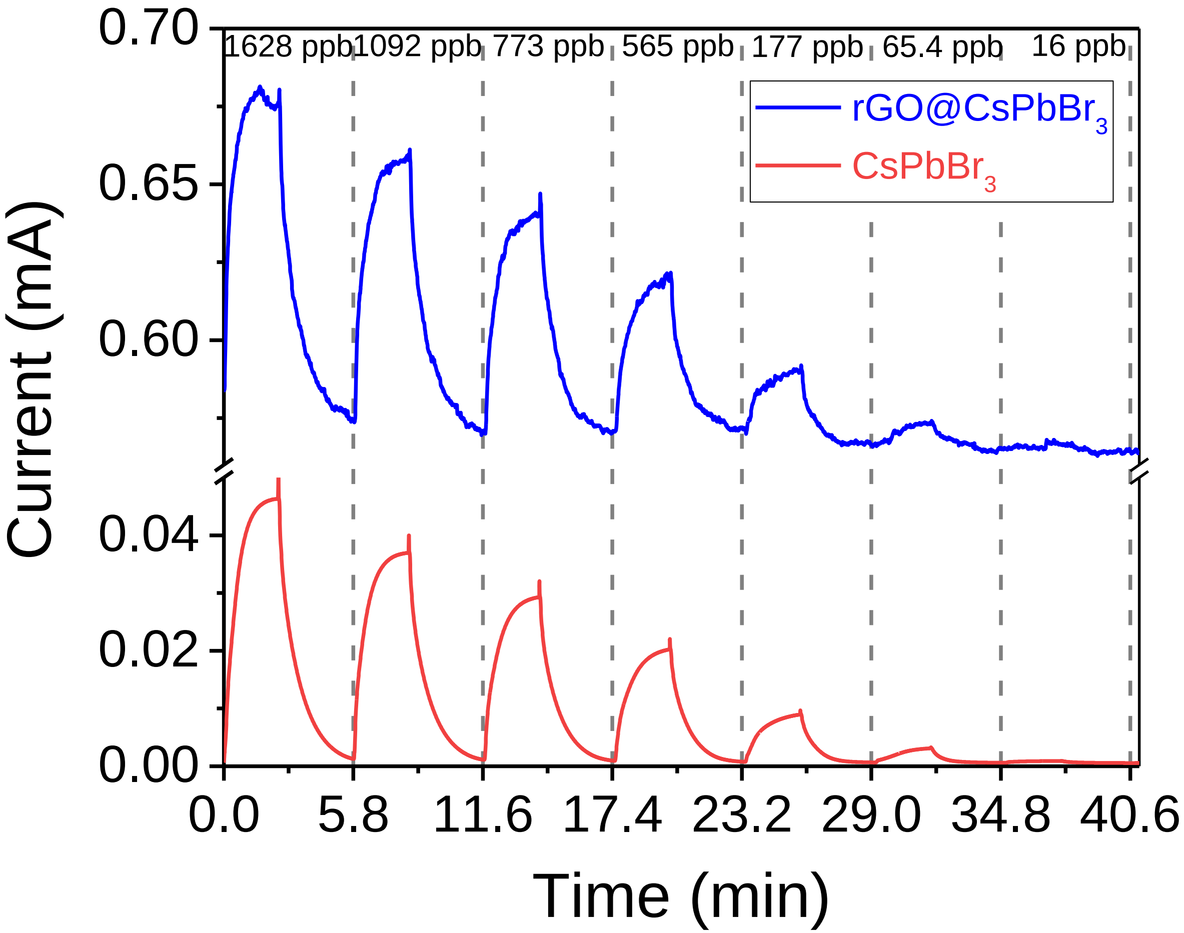




Pb Halide Perovskite μCs





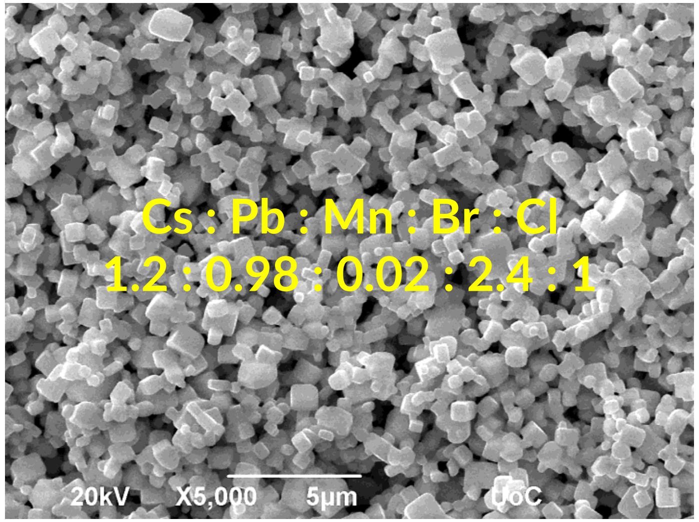


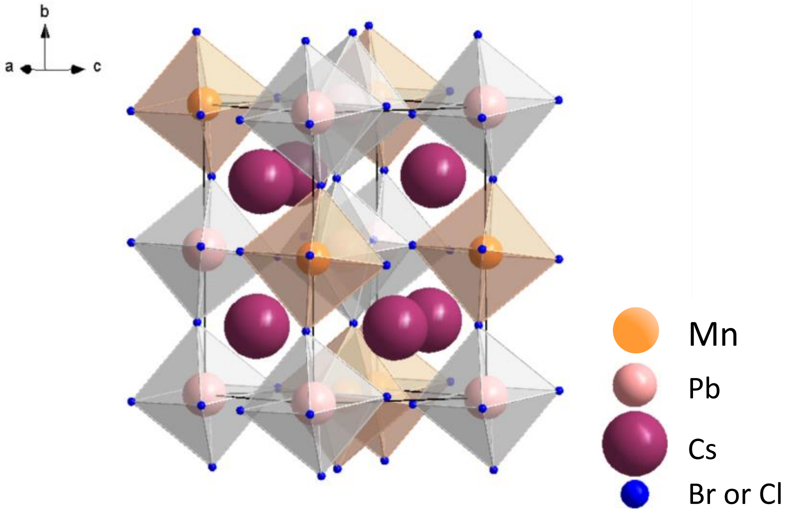
Depositing rGO flakes during the fabrication of $CsPbBr_3$ microcrystals:
the current response in one order of magnitude higher than with the "bare" microcrystals (but no influence on sensitivity)

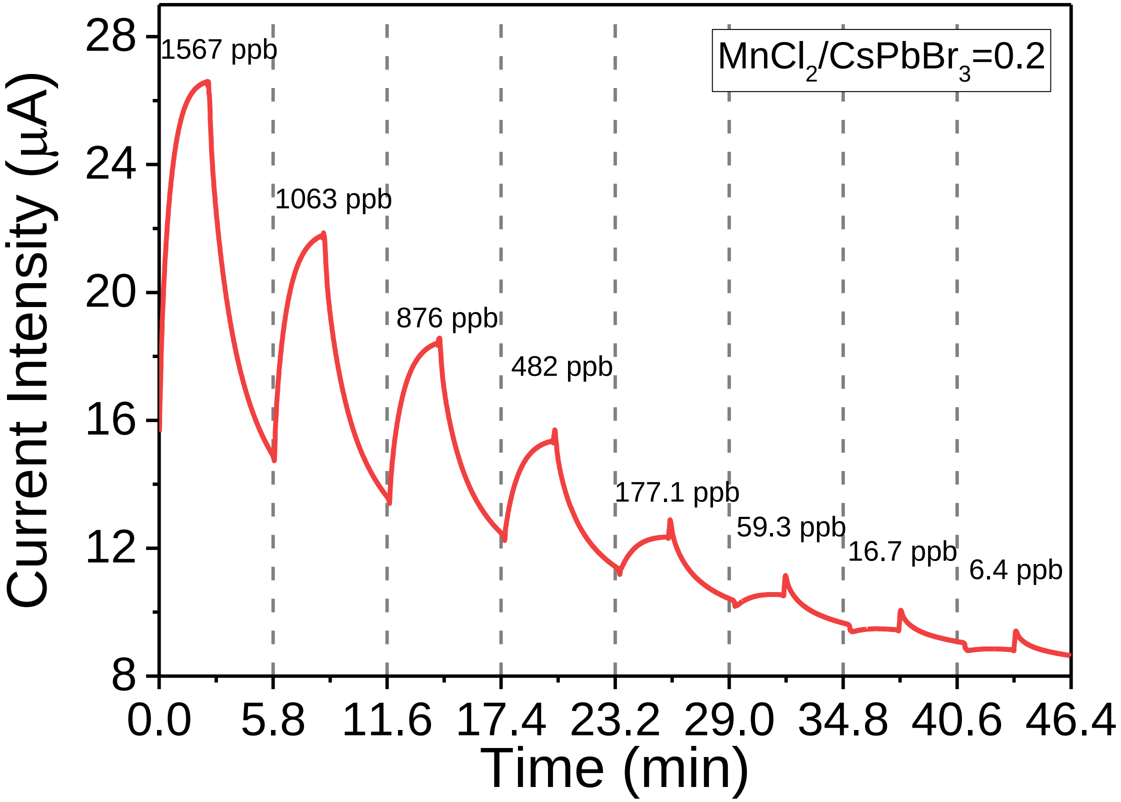
(Unpublished results)

Mn doped $CsPbBr_{1-x}Cl_x$ microcrystals

Mn dopped $CsPbBr_{1-x}Cl_x$





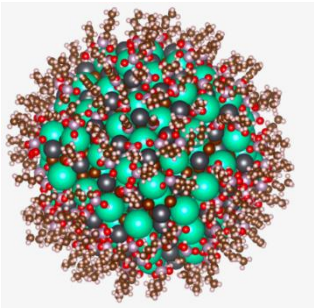


Ligand-free Mn doped $CsPbBr_{3-x}Cl_x$ microcrystals capable to detect O_3

Sensing capability lower than $CsPbBr_3$ microcrystals

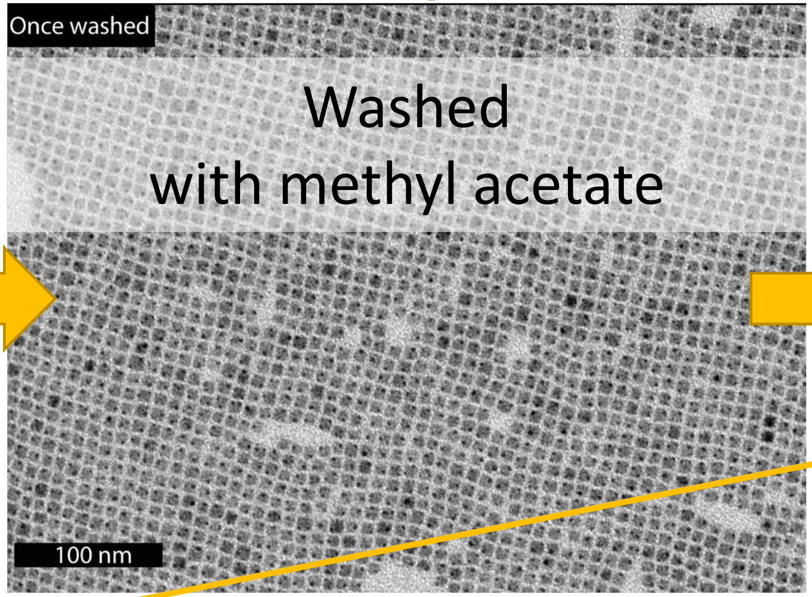
(Unpublished results)

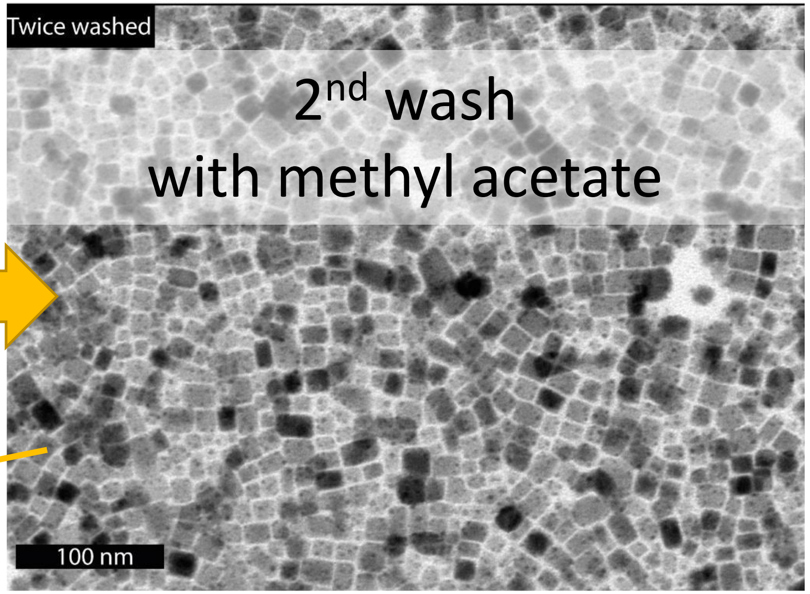
Sensors based on $CsPbBr_3$ Halide Perovskite NCs

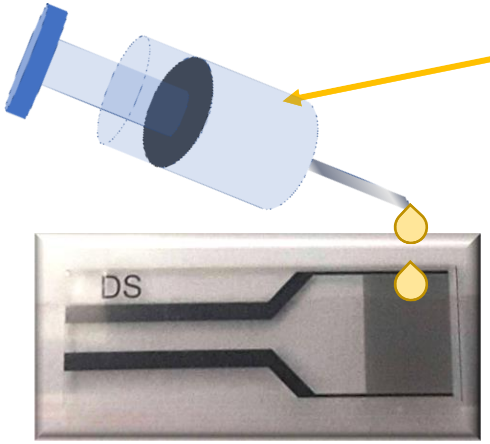


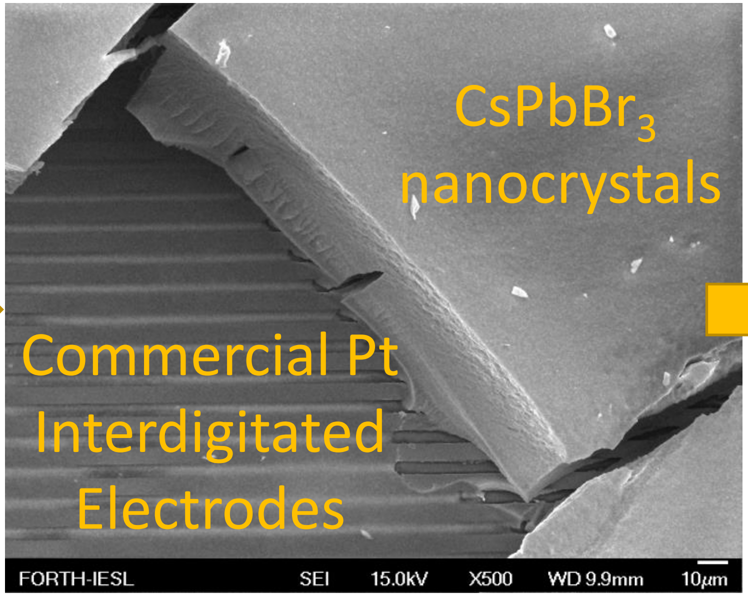
$CsPbBr_3$ nanocrystals in Octadecene

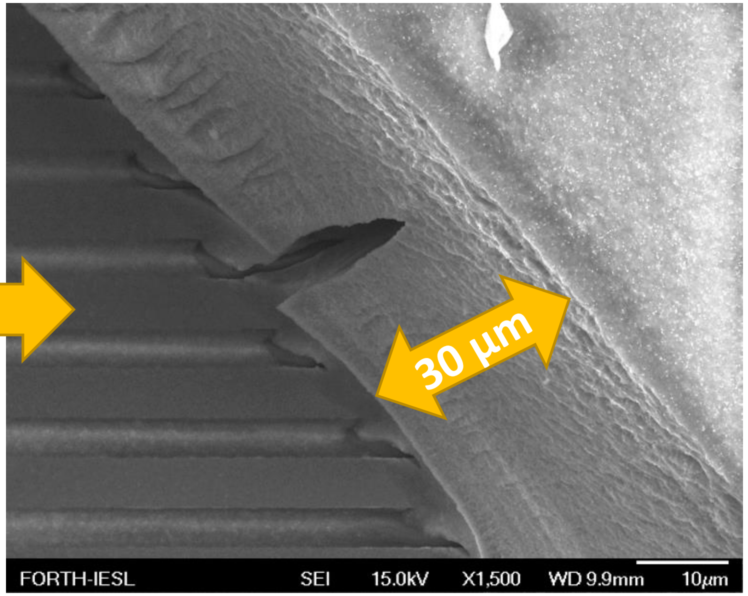
M. Imran et al., Nano Lett. 2018, 18, 12, 7822





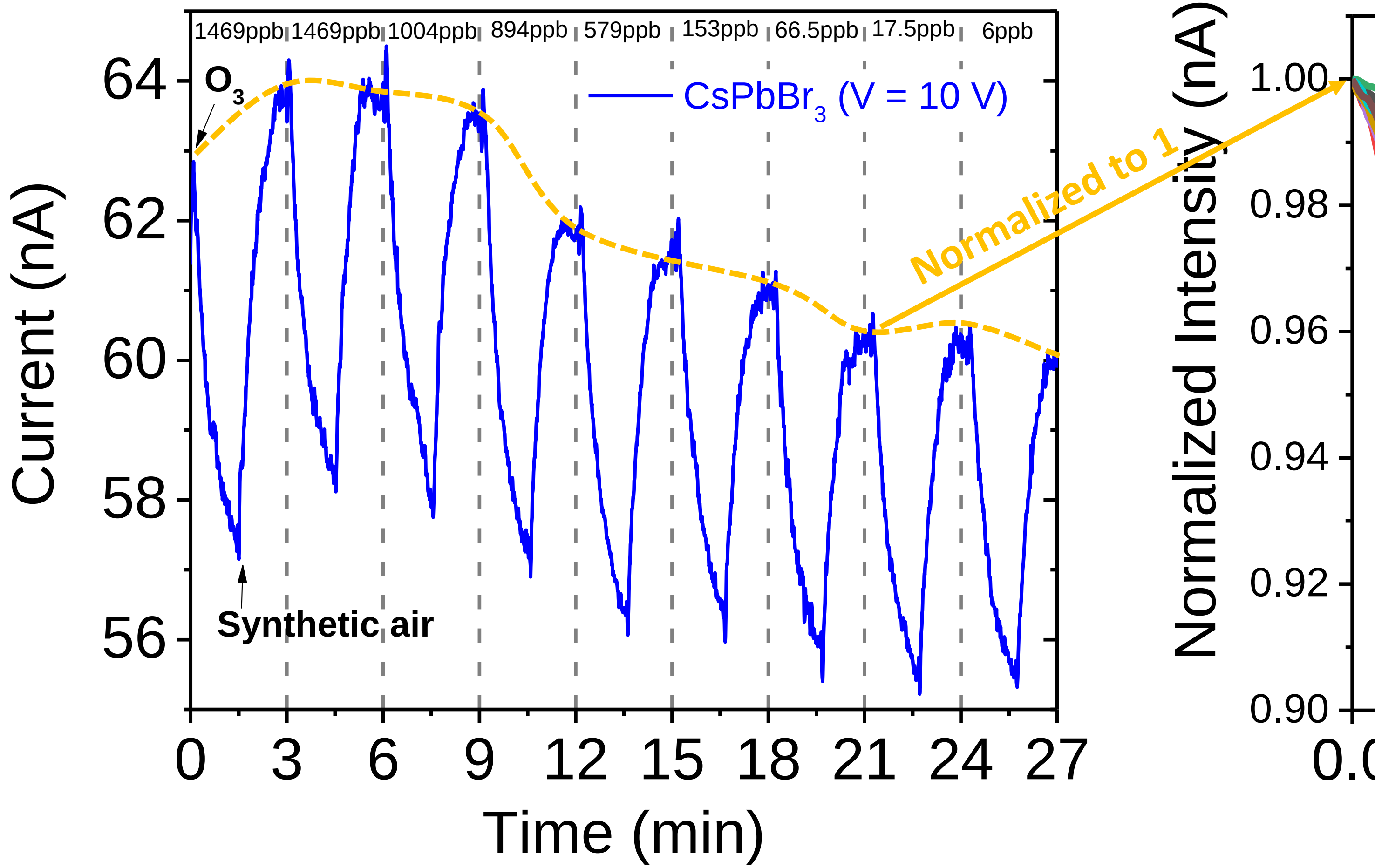


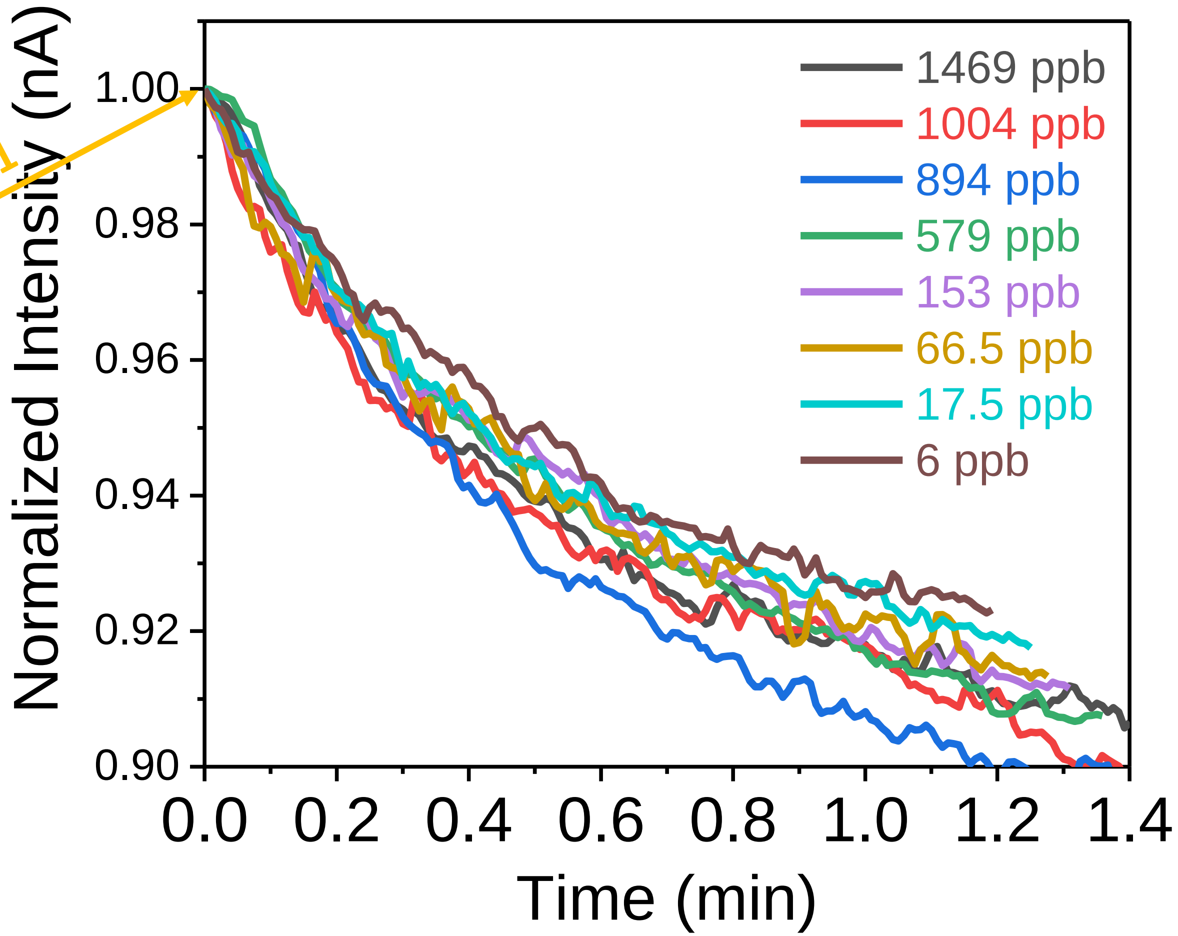




IIT and FORTH: Research highlights during the 2nd year of PeroGaS

The NC films interact with O_3 but not with the desired sensing behavior



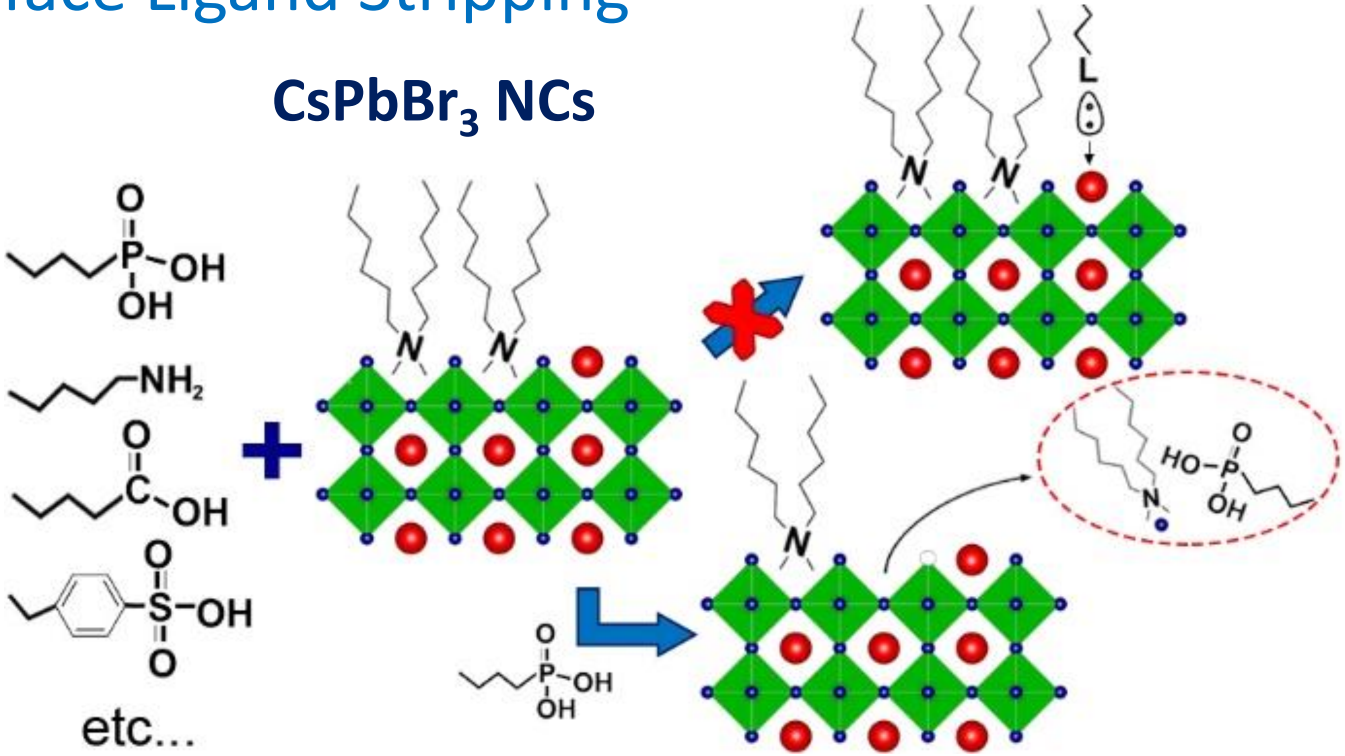


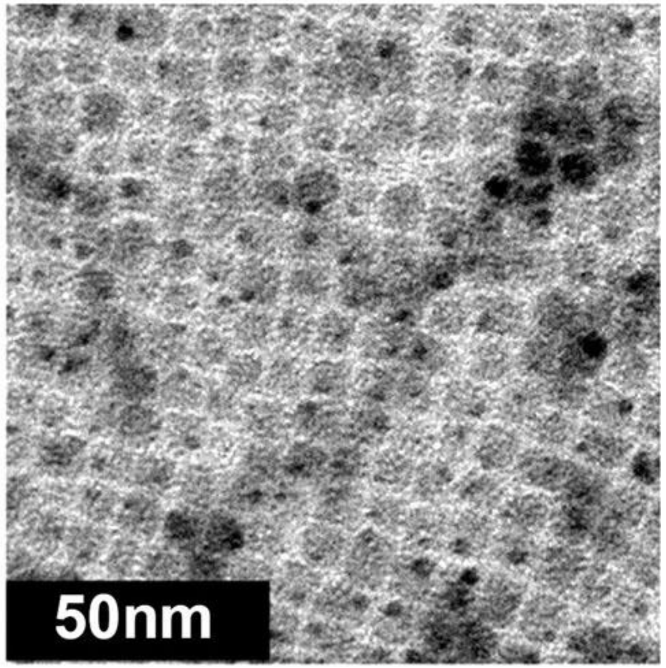
Too low conductivity (10 V resulted only few nA)
Not fully recovery after O_3 exposure

Too noisy exponential curves
Not capable to distinguish different O_3 concentrations

Pb Halide Perovskite NCs

Surface Ligand Stripping



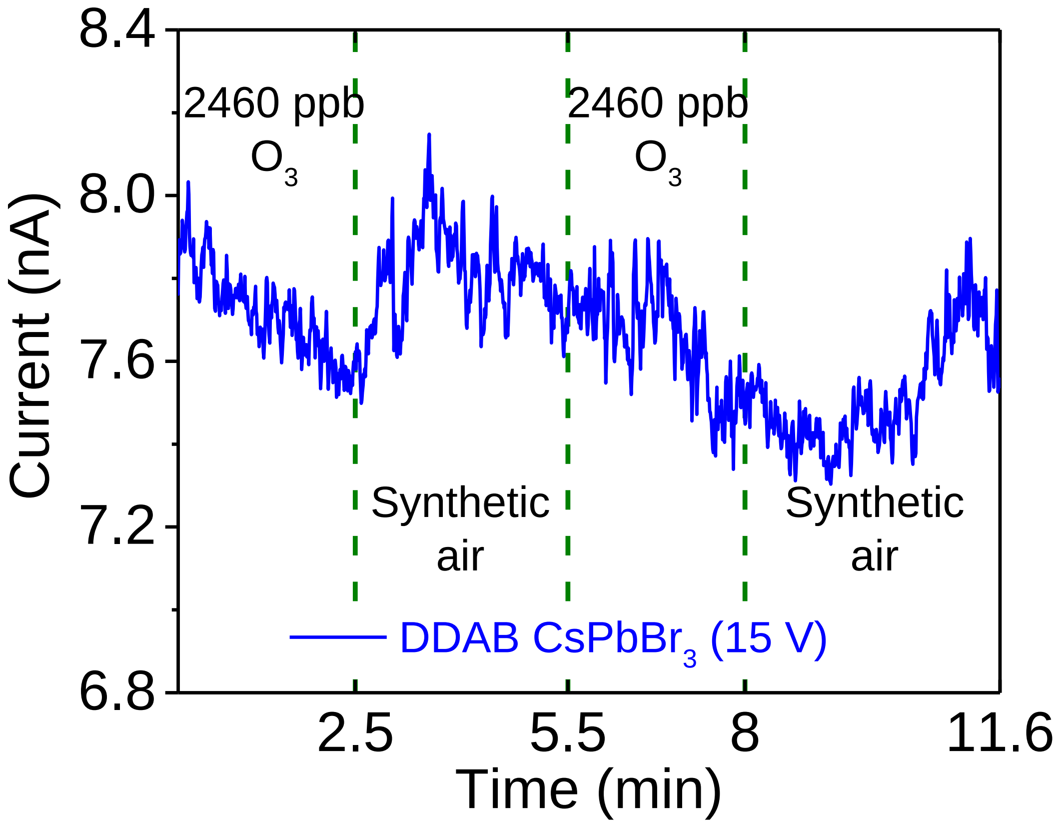


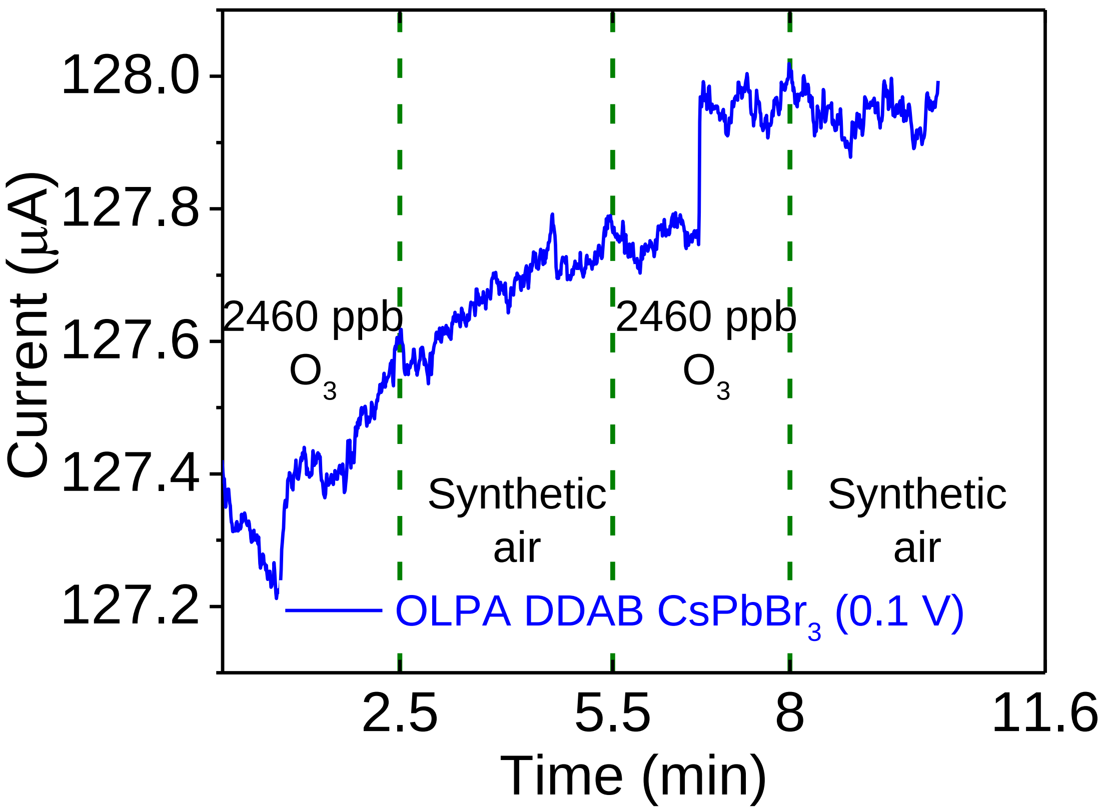
Removal of up to 40% of DDA(Br)

Unfortunately, the ligand stripping was not sufficient to prepare NC films of sufficient conductivity for sensing applications

Zaccaria, F., […] De Trizio L.*, Manna, L.*, *ACS Nano* **2022**, 16, 1, 1444–1455

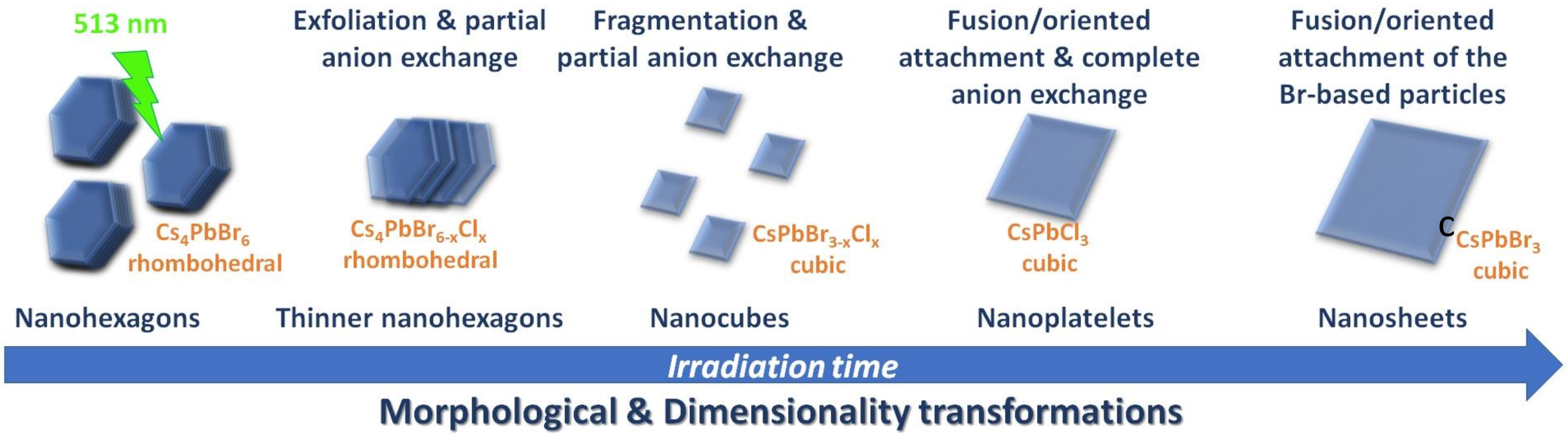
Pb Halide Perovskite NCs

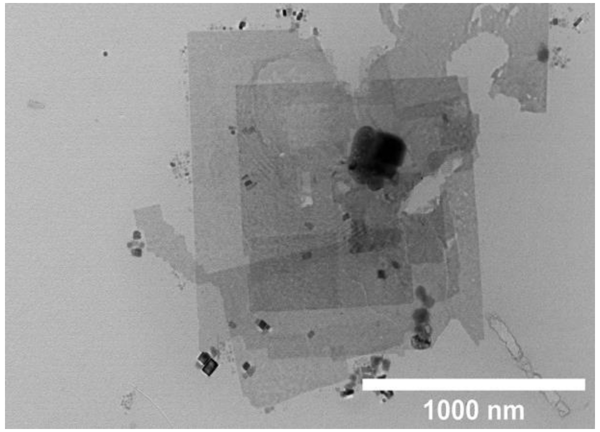




Partial ligand stripping did not favor O_3 sensing capability

Laser-induced changes of $Cs_4PbBr_6/CsPbBr_3$ nanohexagons dispersed in dichlorobenzene, under different irradiation times.





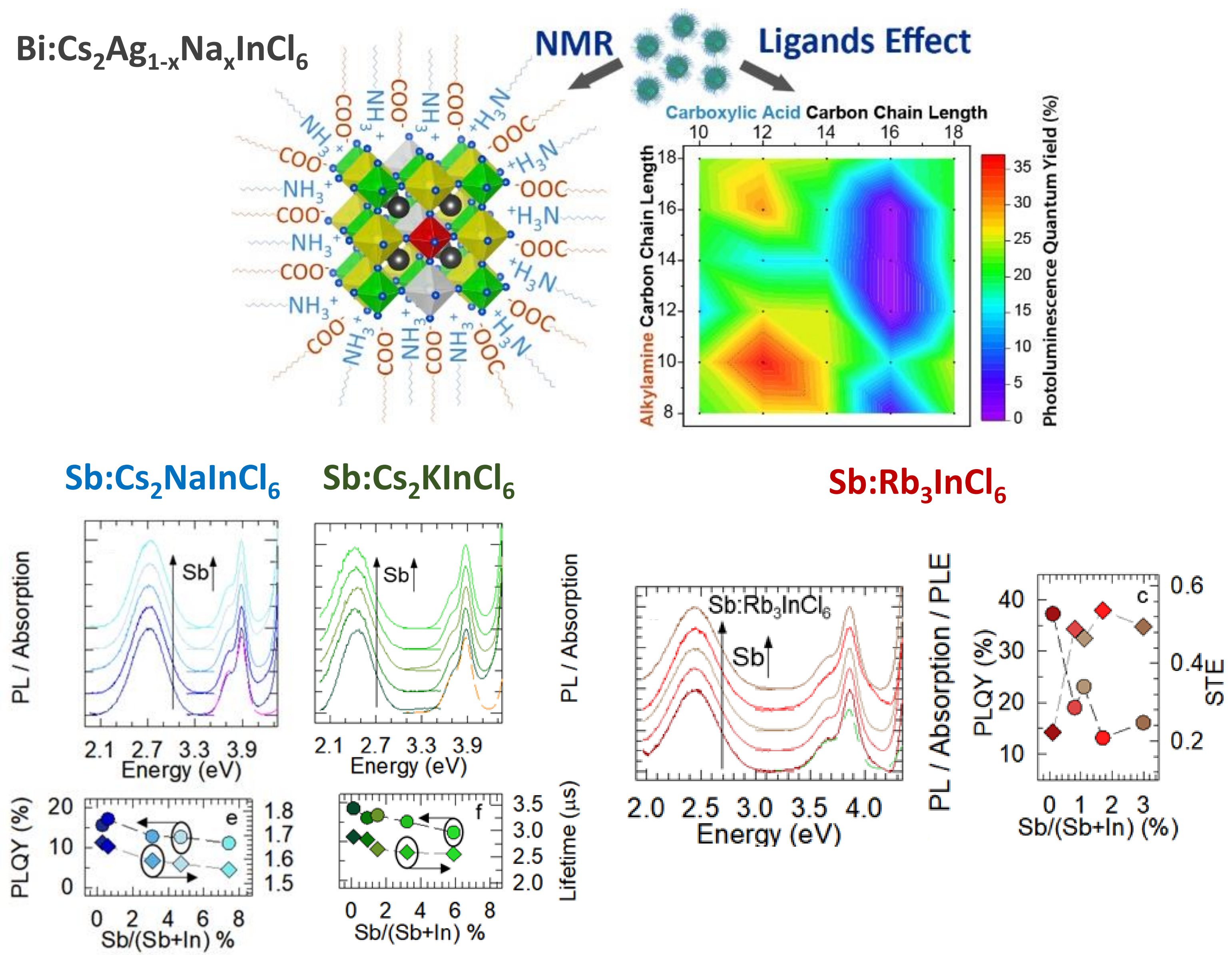
A room temperature rapid method to modify and tune nanocrystals features

Perspective: A room temperature rapid method to modify and tune nanocrystals features, suitable for gas sensing applications

A. Kostopoulou et al., Nanomaterials 2022, 12, 4, 700

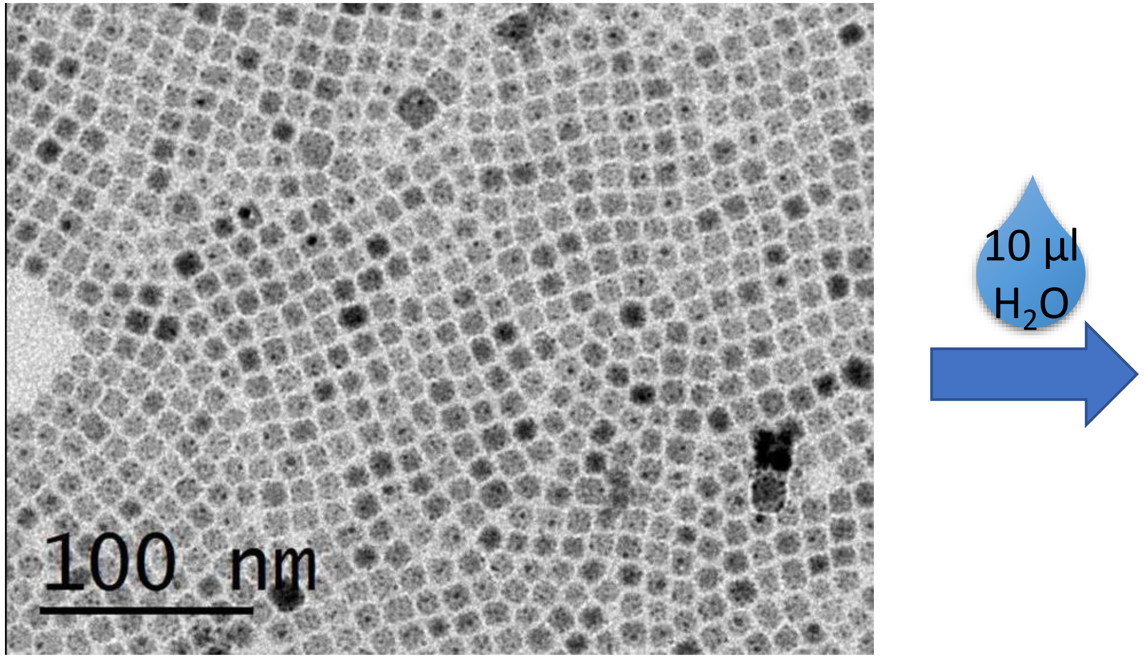
IIT: Research highlights during the 1st – 2nd year of PeroGaS

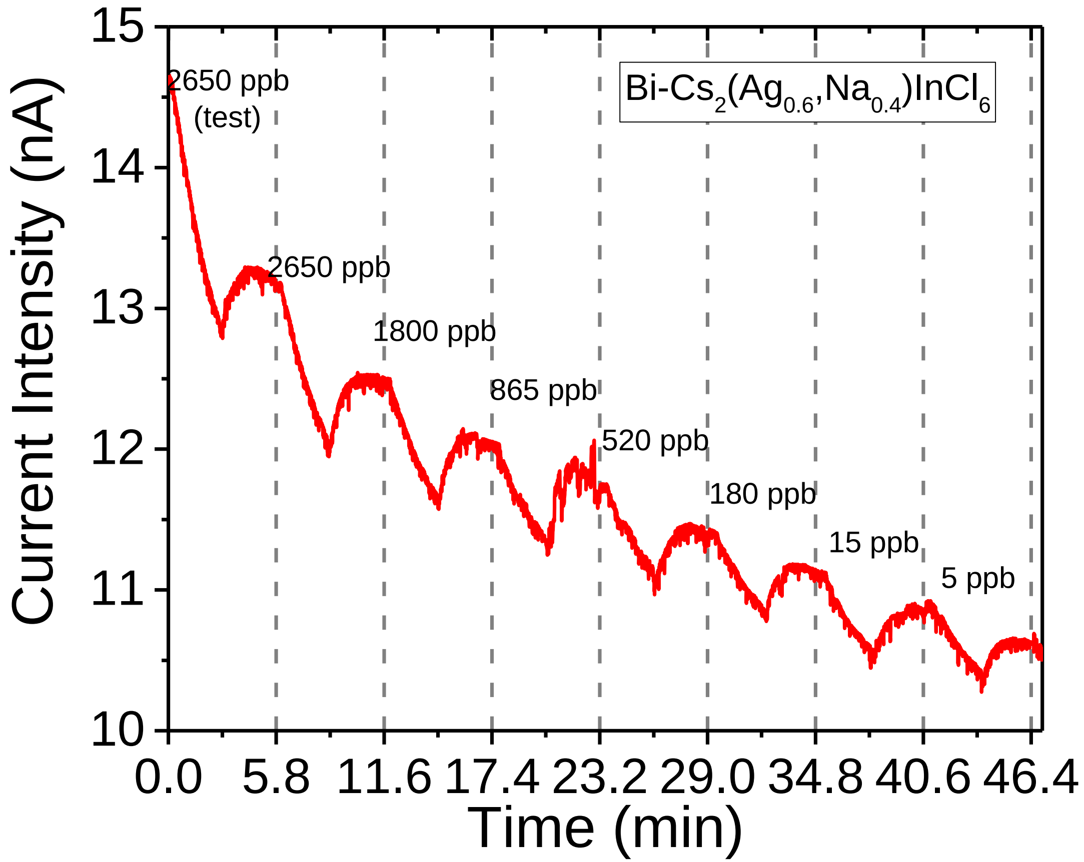
Synthesis of Pb-free metal halide nanocrystals



Pb-free Halide Perovskite NCs

$Bi\text{-}Cs_2(Ag_{0.6}Na_{0.4})InCl_6$

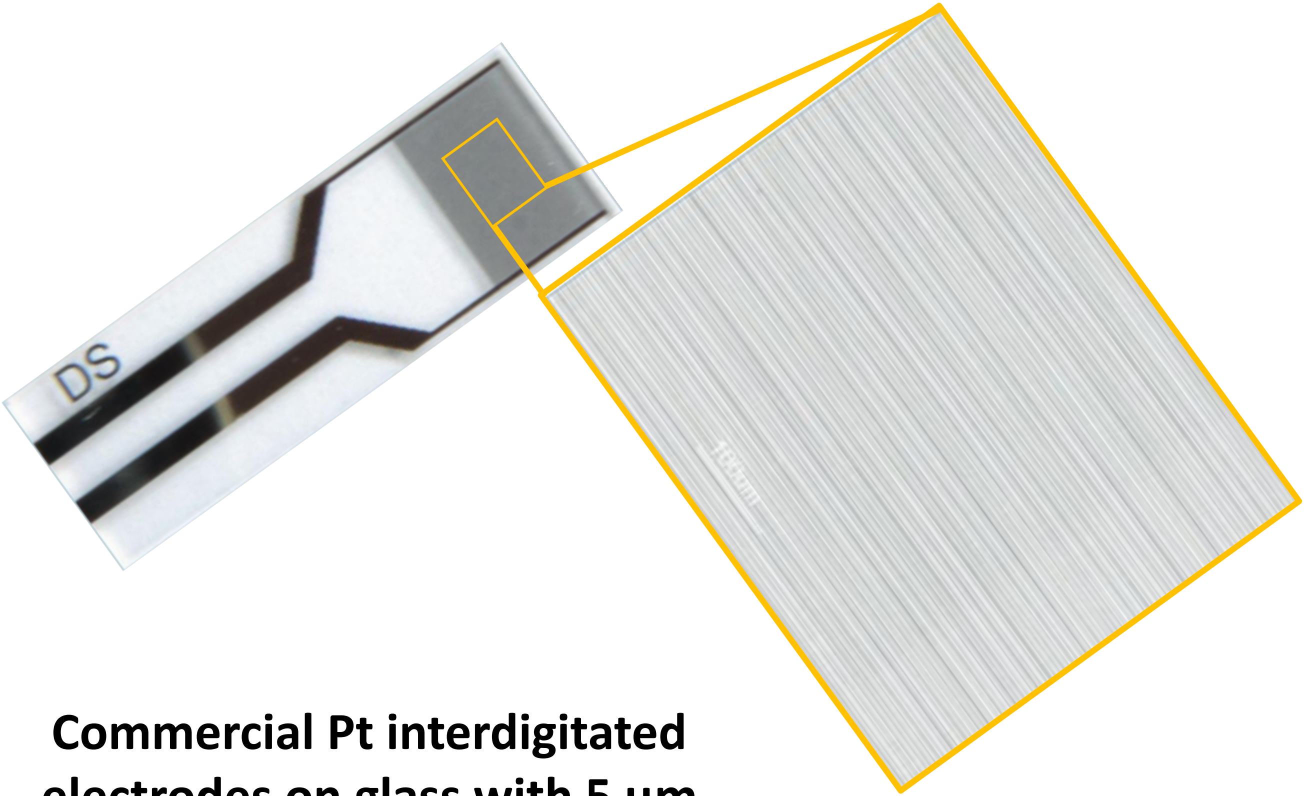




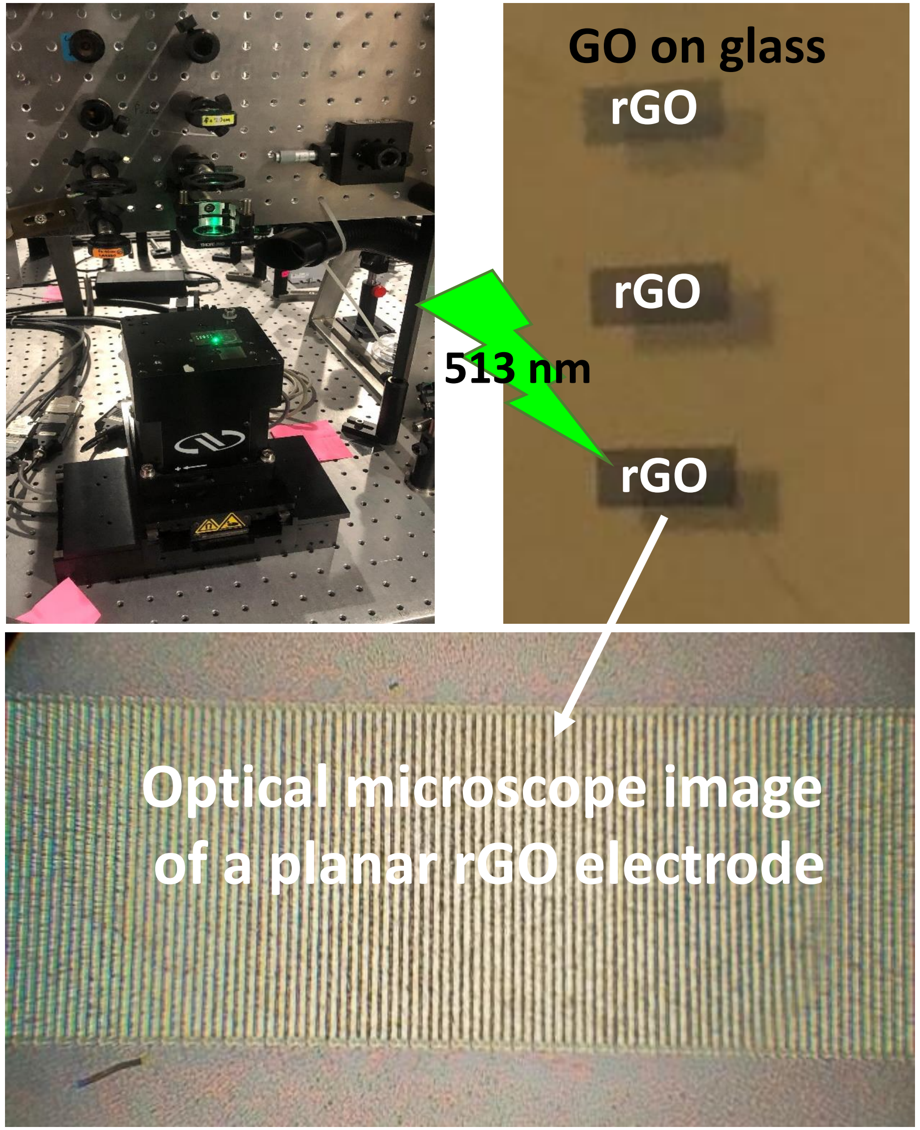
(preliminary results)

FORTH: Research highlights during the 2nd year of PeroGaS

PeroGaS project envisages to replace noble metal electrodes with graphene-based ones.



Commercial Pt interdigitated electrodes on glass with 5 µm bands and gaps



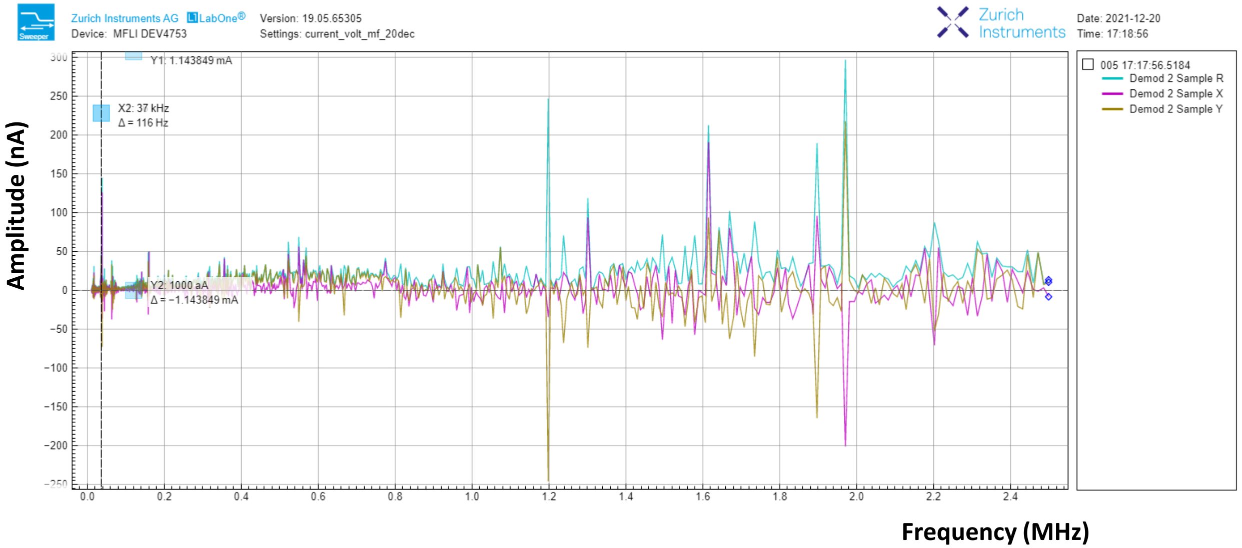
Lowest resistance to date 2 kΩ

Spray GO dispersion on a chosen substrate → Let to dry → Irradiate areas with a fs laser at 513 nm → GO reduced to rGO

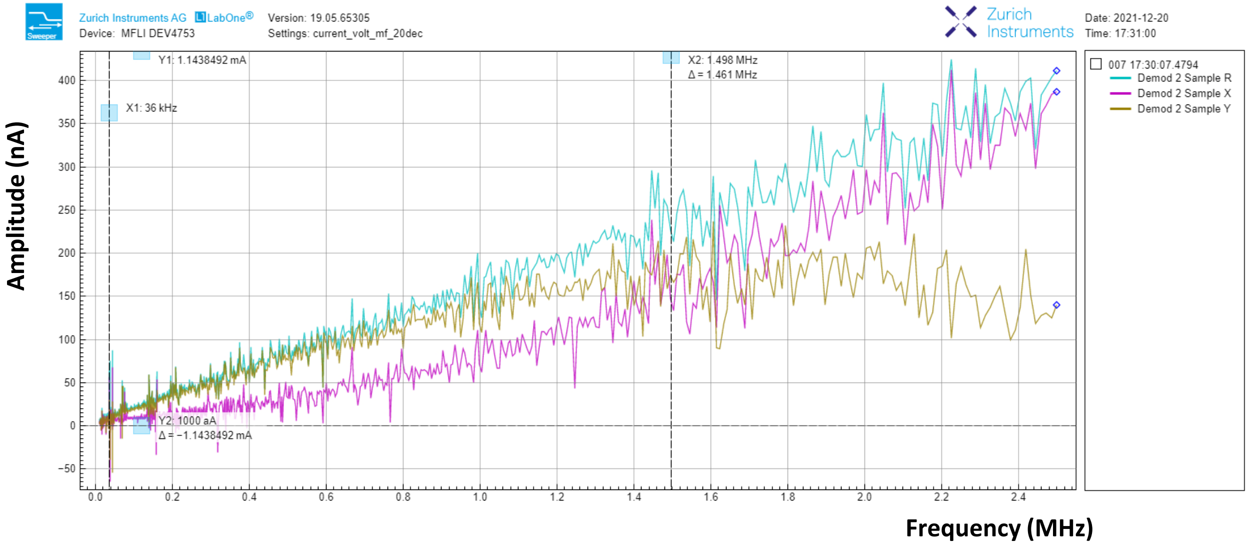
BIU and FORTH: Research highlights during the 2nd year of PeroGaS

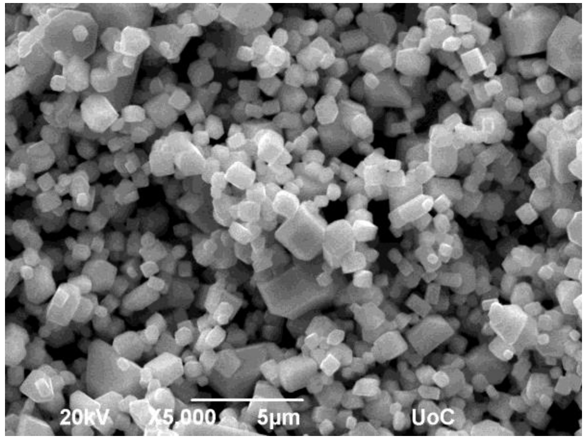
Incorporating Lock-in amplifier on O_3 gas sensing (preliminary results)

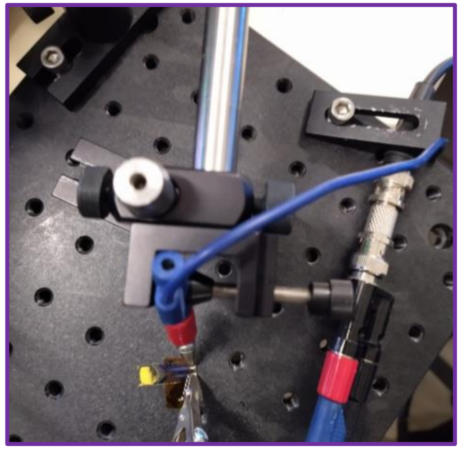
$CsPbBr_3$ microcrystals before ozone exposure



$CsPbBr_3$ microcrystals during ozone exposure





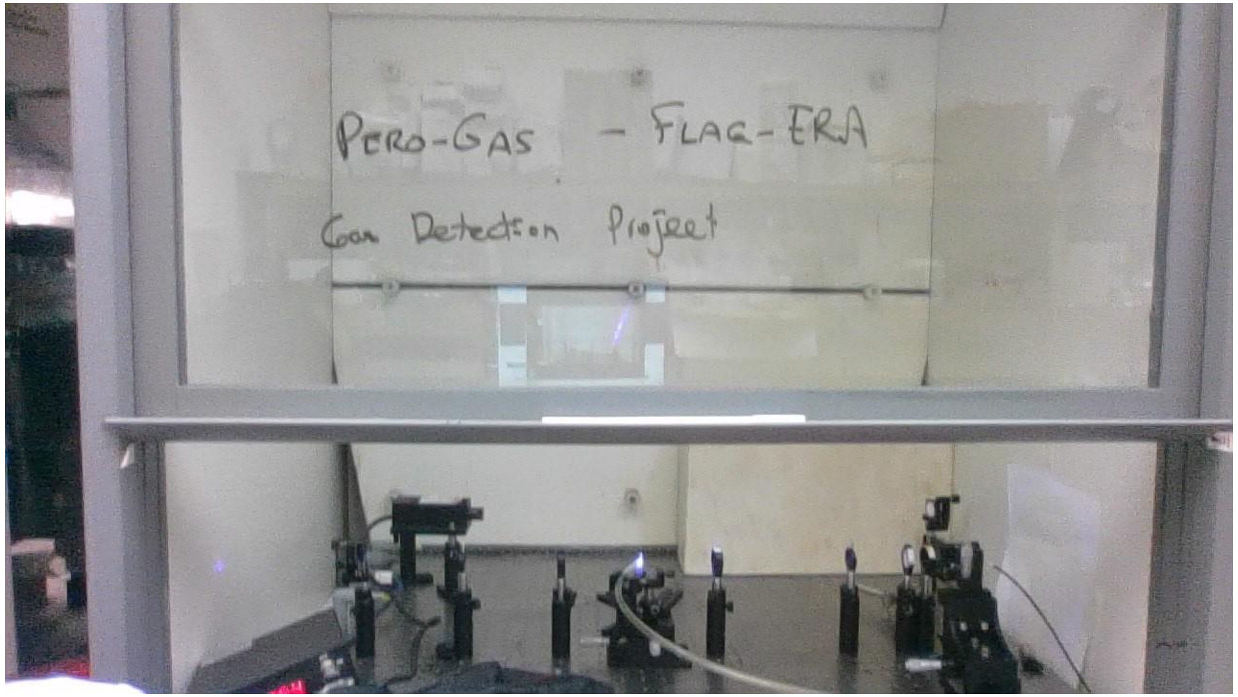


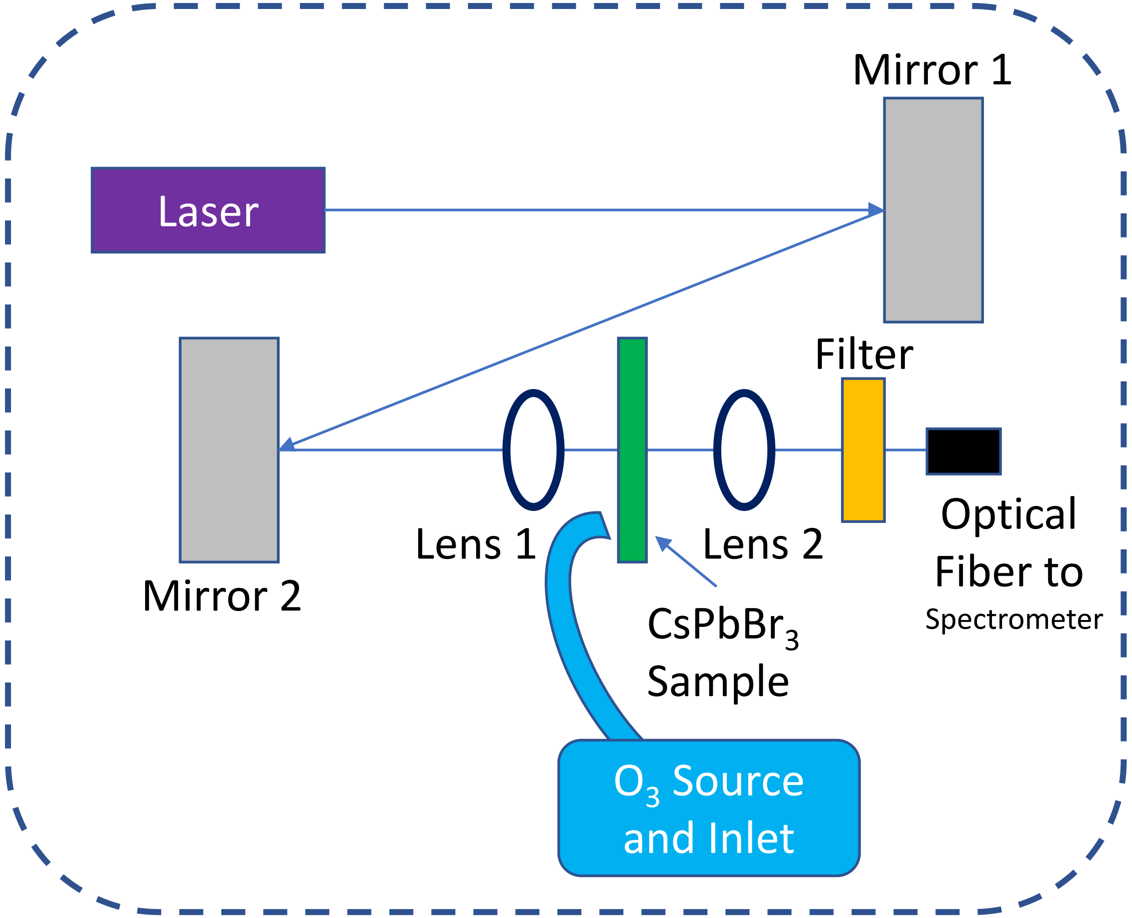
- Large increase in capacitive current detected at high modulation frequency (i.e. driving the IDE with AC voltage at high frequency)
- Faster Detection Response
- Smaller Applied Voltage (~10 uV)

BIU and FORTH: Research highlights during the 2nd year of PeroGaS

In-situ O_3 Exposure and Spectroscopic Gas Detection (preliminary results)

Chemical Hood containing Setup





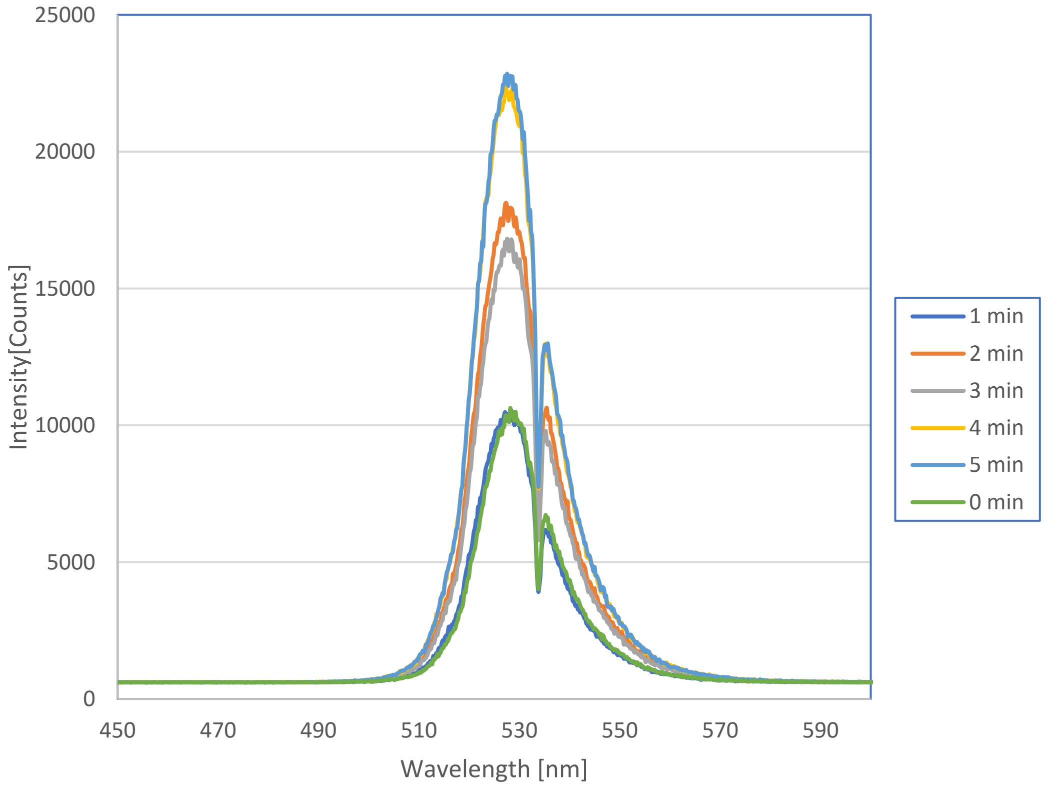
- Current setup involves Fluorescence and in-situ Ozone Source
- Next Setup will contain in-situ absorption
- Then Raman, and Quantum Yield

BIU and FORTH: Research highlights during the 2nd year of PeroGaS

In-situ O_3 Exposure and Spectroscopic Gas Detection (preliminary results)

Optical Excitation of $CsPbBr_3$ with 405 nm laser

PL after "X" minutes of continuous O_3 exposure



- PL intensity increases upon O3 exposure!
- From 10000 counts to 22,0000 counts after 5 minutes!
- See similar behavior with 405 nm and 532 nm excitations

Will repeat with different filtering…

PeroGaS research activities that expected to follow

WP1: Development of Sensing Elements

- Establishment of a methodology to treat ligand capped nanocrystals
  - Nanocrystals need to be become capable of detecting air pollutant gases
- Pb-free perovskite-based sensing element
  - Quickly identify the best candidates
- Conjugate Pb-free perovskite micro/nanocrystals with rGO
  - These should be capable to detect air pollutant gases similarly to the Pb-based materials

WP2: Design and Development of the Sensor Device

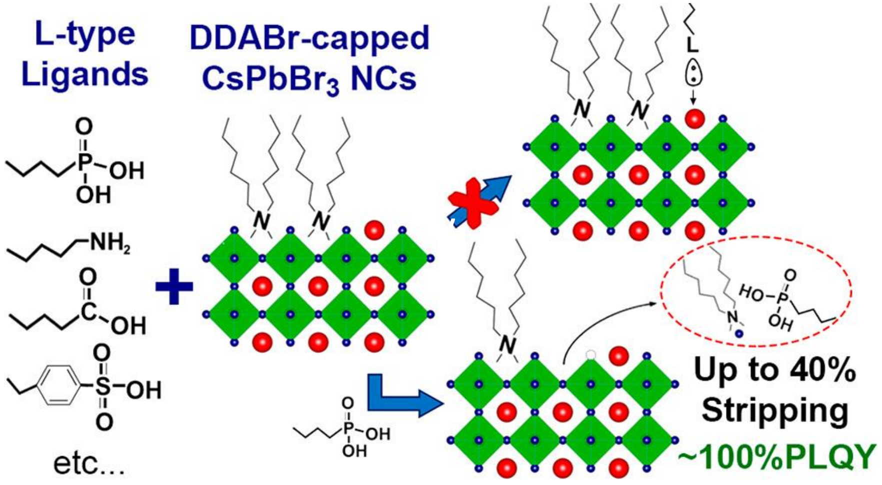
- Fabrication of rGO interdigitated electrodes
  - Optimize laser-based fabrication procedures
- Power supply with a solar cell
  - Design, fabricate and test a suitable all-inorganic or organic solar cell

WP3: Evaluation of Sensing Abilities

- Incorporating Stimulating Raman Scattering technique to detect air pollutant gases
  - Identifying gases on a mixture of air pollutants
- Theoretical modeling
  - Study the impact of rGO component on the gas sensing mechanism

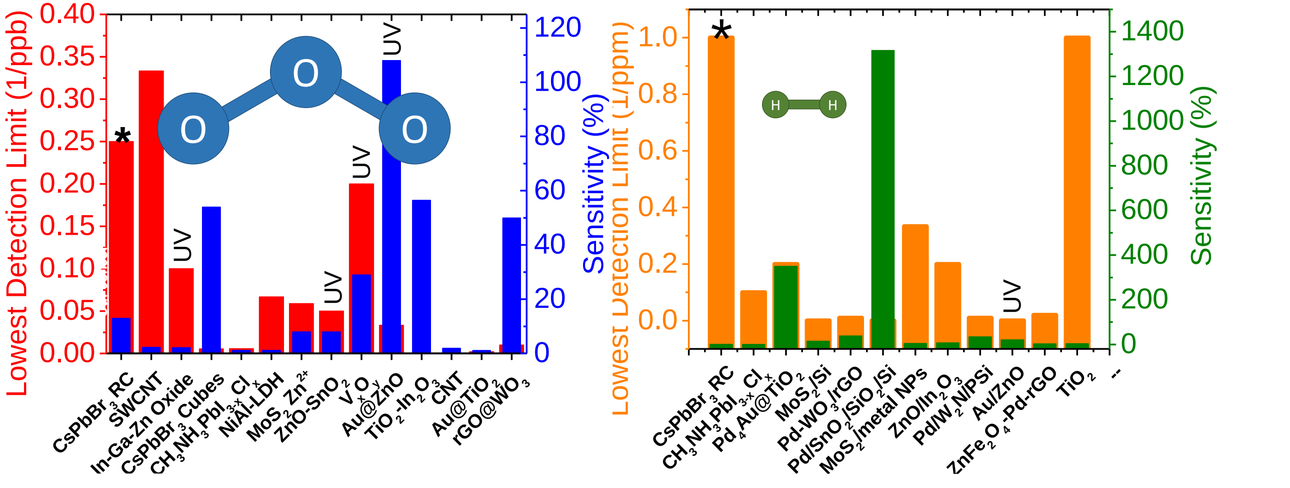
Publications during the 2nd year of PeroGaS

The Reactivity of $CsPbBr_3$ Nanocrystals toward Acid/Base Ligands



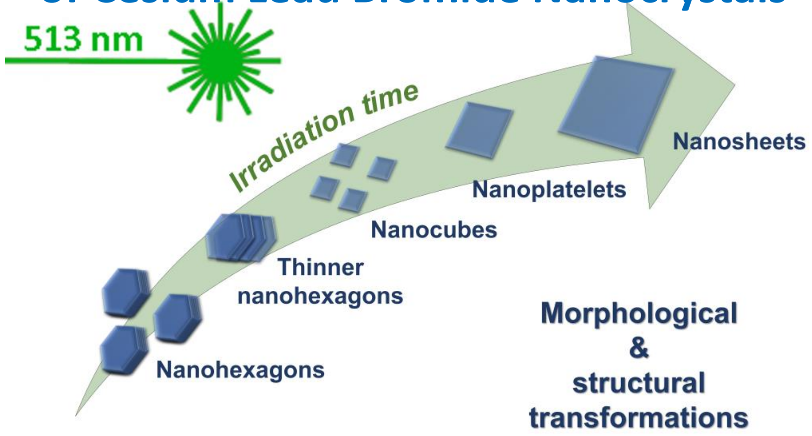
F. Zaccaria et al., ACS Nano 2022, 16, 1, 1444-1455 **(IIT)**

Highly sensitive ozone and hydrogen sensors based on perovskite microcrystals directly grown on electrodes



A. Argyrou et al., Journal of Materiomics 2022, 8, 2, 446-453 **(FORTH)**

Laser-Induced Morphological and Structural Changes of Cesium Lead Bromide Nanocrystals



A. Kostopoulou et al., Nanomaterials 2022, 12, 4, 700 **(FORTH, IIT)**

Dissemination and communication actions during the 2nd year of PeroGaS

(IIT)

1. L. Manna, "Halide Perovskite Nanocrystals: Synthesis, the Role of the Surface, Heterostructures", COPAC symposium on Parallel Computing Quantum Devices, March 23 2021
2. L. Manna, "Metal Chalcohalide Nanocrystals and Their Heterostructures with Halide Perovskite Nanocrystals", MRS Virtual Spring Meeting, April 22 2021
3. L. Manna, "Metamorphoses in Cesium Lead Halide Nanocrystals", ACS Journal Club symposium on "Transformative Inorganic Nanocrystals", July 27th 2021
4. L. Manna, "Halide Perovskite Nanocrystals: Synthesis and Optical Properties", 107° Congresso Nazionale della Società Italiana di Fisica, September 13th 2021
5. L. Manna, "Nanocrystal Heterostructures Involving Halide Perovskites and other Materials", MRS Virtual Fall Meeting 2021, December 7th 2021
6. L. Manna, "Accelerated discovery of nanocrystal materials", AL4QD workshop "Designing Nanomaterials of the Future", December 14th 2021

(FORTH)

1. A. Kostopoulou, K. Brintakis, K. Savva, N. Livakas, E. Stratakis, "Laser-assisted processes on metal halide nanocrystals: Shape/dimensionality transformations and conjugation with 2D materials", Internet NanoGe Conference on Nanocrystals 28/6 – 2/7 2021
2. K. Brintakis, A. Argyrou, A. Kostopoulou, E. Stratakis, "$CsPbBr_3$ perovskite microcrystals and their capability to detect ultra-low ozone and hydrogen concentrations", AIP Horizons – Energy Storage and Conversion 4-6 August 2021
3. A. Kostopoulou, K. Brintakis, K. Savva, E. Stratakis, "Laser-assisted processes on metal halide nanocrystals: Shape/dimensionality transformations and conjugation with 2D materials", E-MRS 2021 Fall Meeting 20-23 September
4. A. Argyrou, K. Brintakis, A. Kostopoulou, E. Gagaoudakis, E. Stratakis, "Highly sensitive ozone and hydrogen sensors based on perovskite microcrystals directly grown on electrodes", Panhellenic Solid State Physics Conference 26-29 September 2021
5. K. Brintakis, A. Argyrou, A. Kostopoulou, E. Stratakis, "$CsPbBr_3$ perovskite microcrystals and their capability to detect ultra-low ozone and hydrogen concentrations", NanoGe Fall Online Meeting 18-22 October 2021

Responsible research and innovation (RRI) actions

Open Science: our articles are open access, also datasets are uploaded on public repositories

Interactions with the Graphene Flagship:

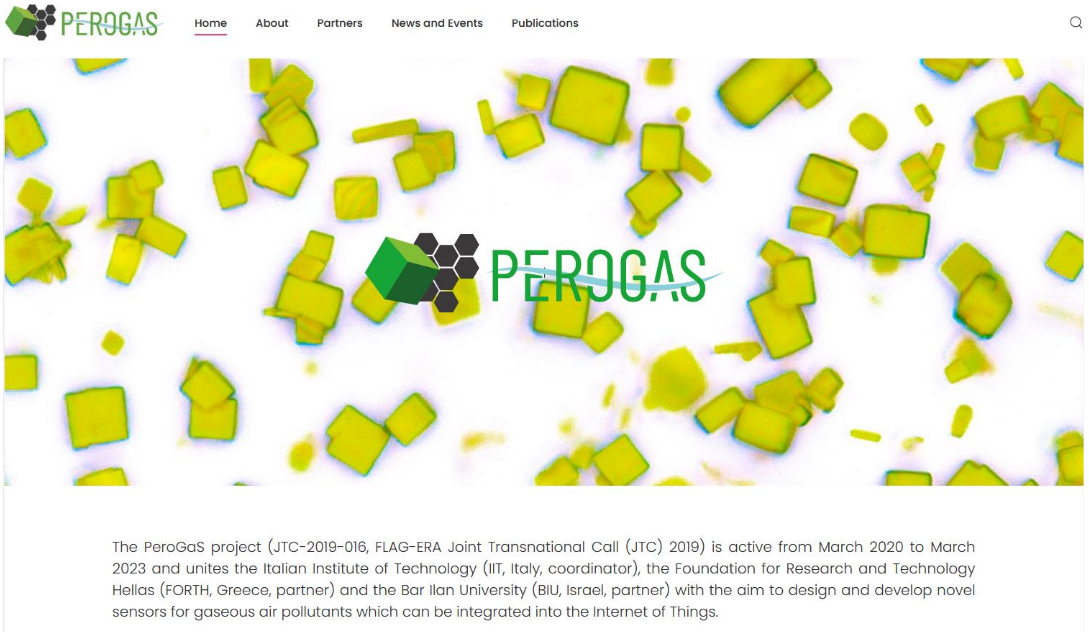
We have been having discussions and a meeting with Dr. Camilla Coletti, Deputy di WP10 (Wafer Scale Integration) on collaborations:

- rGO deposition
- Interfacing of perovskites with rGO

Further discussions and start of a collaboration are foreseen in the 3rd year

PeroGaS website and twitter account

https://perogas.eu/



https://twitter.com/PEROGAS_FLAGERA