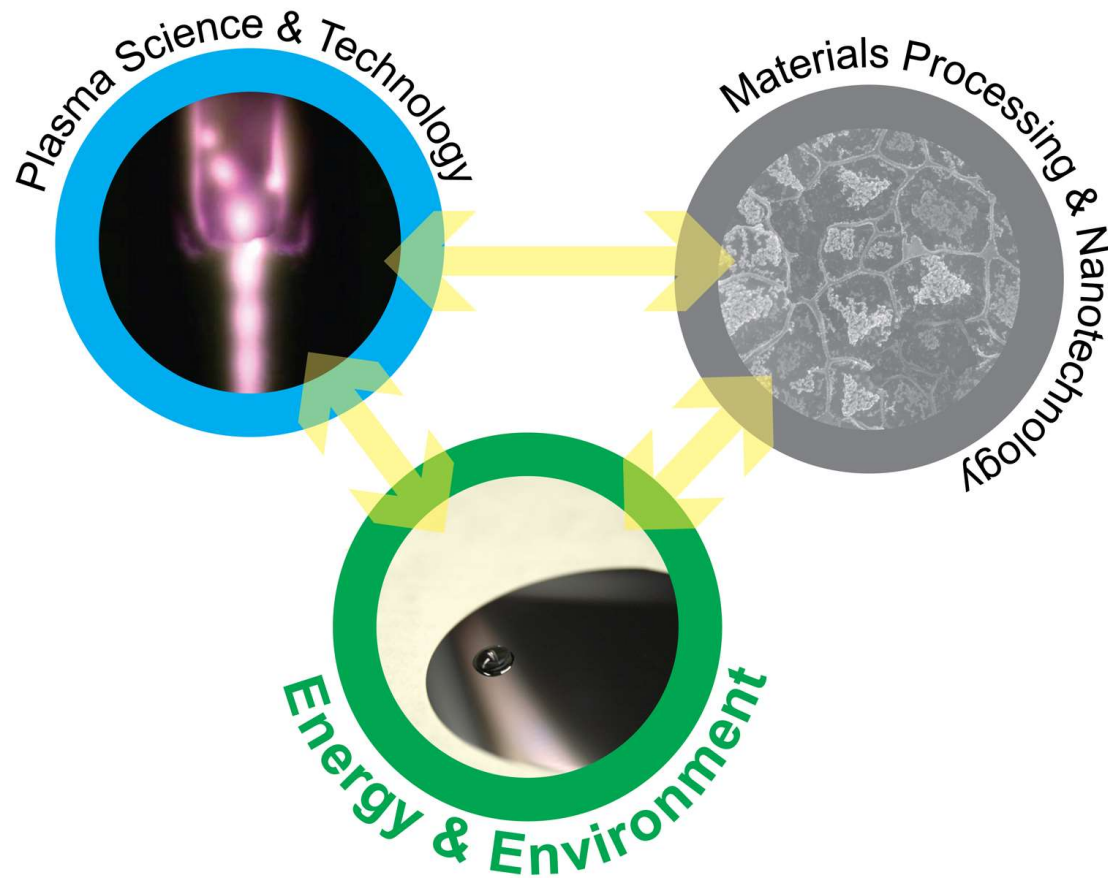


# *Atmospheric pressure plasmas: from materials discovery to device manufacturing*



***Prof Davide Mariotti***

*Plasma Science &  
Nanoscale Engineering Group*

*[www.plasmamate.org](http://www.plasmamate.org)*

# Prof Mariotti

Plasma Science & Nanoscale Engineering Group  
([www.plasmamate.org](http://www.plasmamate.org))

## PostDocs

- Dr Dilli Padmanaban
- Dr Natalie Tarasenko (Newtown Fellow)
- Dr Ali Khatibi
- Dr Ankur Kambley

# EPSRC

Pioneering research  
and skills



THE  
ROYAL  
SOCIETY



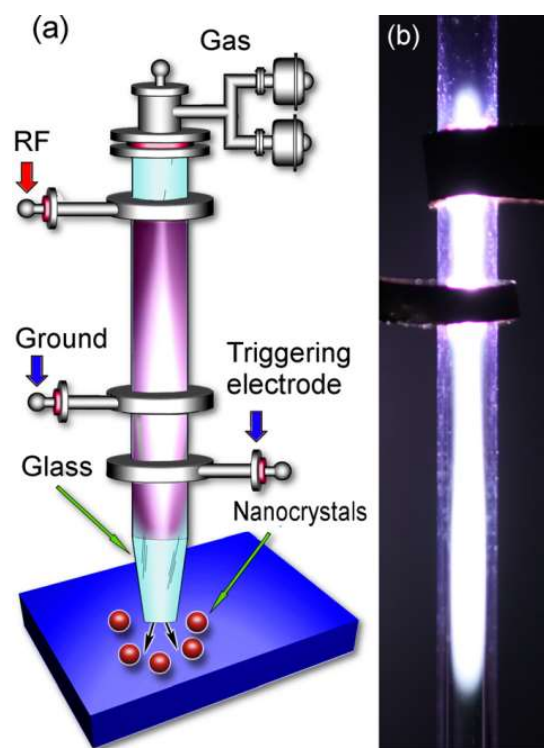
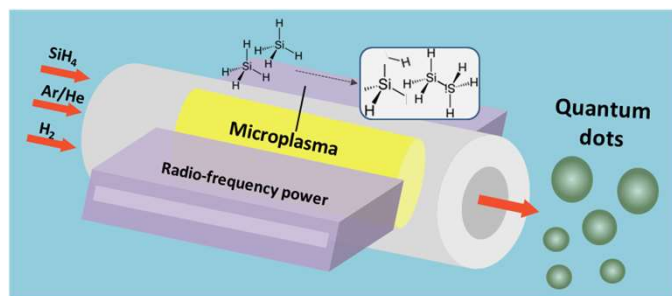
# Acknowledgements



## CURRENT FUNDING

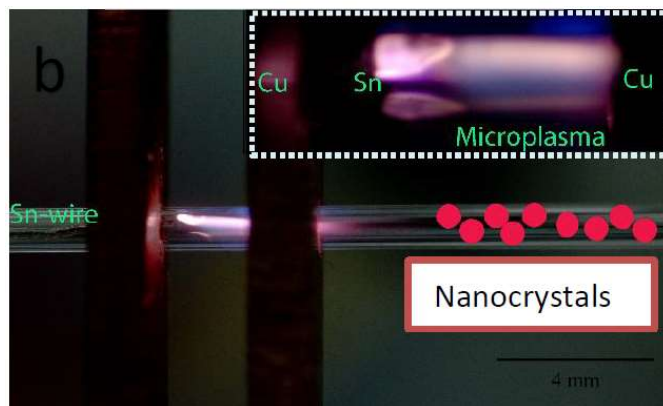
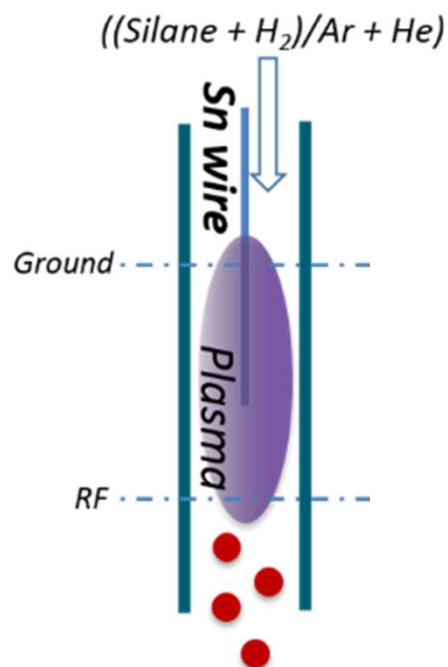
- **EPSRC** (EP/V055232/1) “*Plasma Microreactors: a Manufacturing Platform for Nanoscale Metal Oxides*”
- **EPSRC** (EP/T016000/1) “*An ocean microlab for autonomous dissolved inorganic carbon depth profile measurement*”
- **Department for Economy & National Science Foundation** (US1146) “*Strained Engineered Germanium Quantum-Well Laser on GaAs and Si for Optical Coherence Tomography*”
- **Royal Society** Newton International Fellowship (NIF\R1\221880) & *International Exchanges* (IES\R2\212049)

## Gas-phase precursors



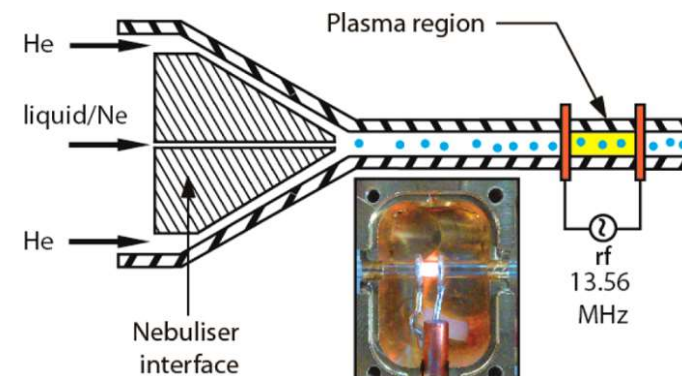
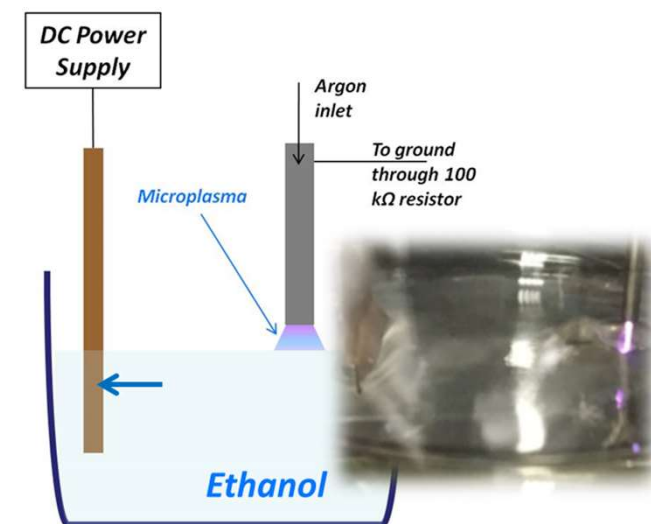
*Adv Mater* 27 (2015) 8011  
*Plasma Proc Polym* 17 (2020) 1900243  
*J Phys Chem Lett* 11 (2020) 1721  
*Faraday Discuss* 222 (2020) 390

## Solid precursors



*Nature Comm* 10 (2019) 817  
*Nanoscale Adv* 3 (2021) 781  
*Nanotechnology* 31 (2020) 215707

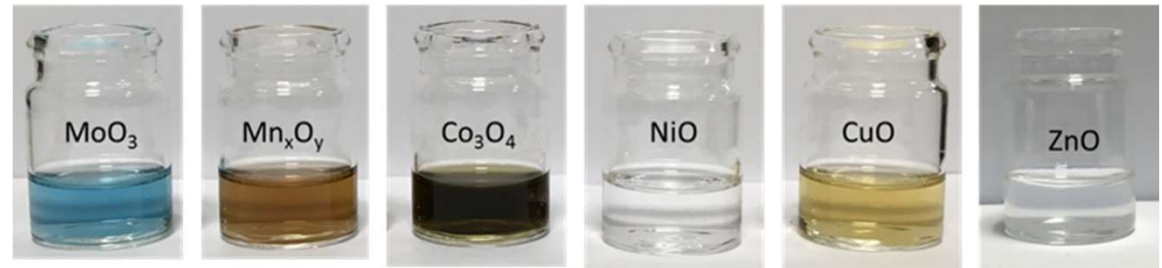
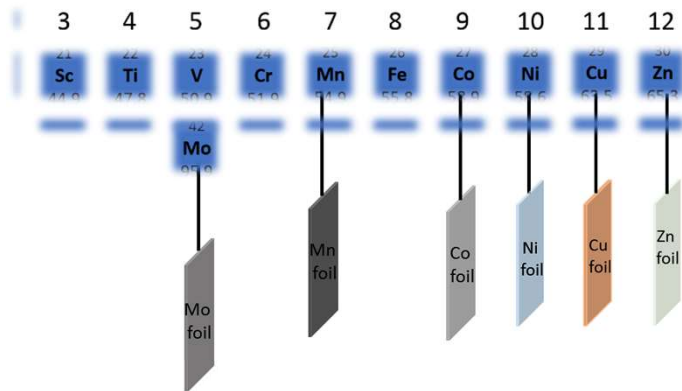
## Liquid precursors



*Adv Funct Mater* 23 (2013) 6051  
*Adv Funct Mater* 27 (2017) 1701898  
*Green Chem* 20 (2018) 2101  
*Green Chem* 23 (2021) 3983  
*Carbon* 183 (2021) 1  
*Solar Energy* 203 (2020) 37

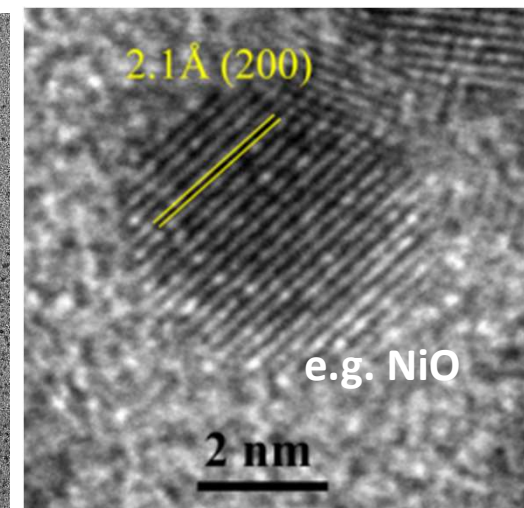
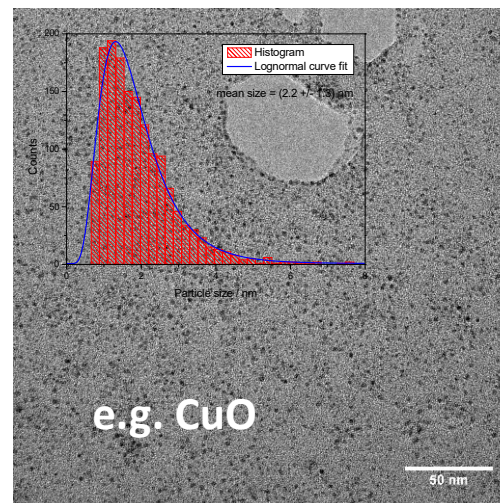
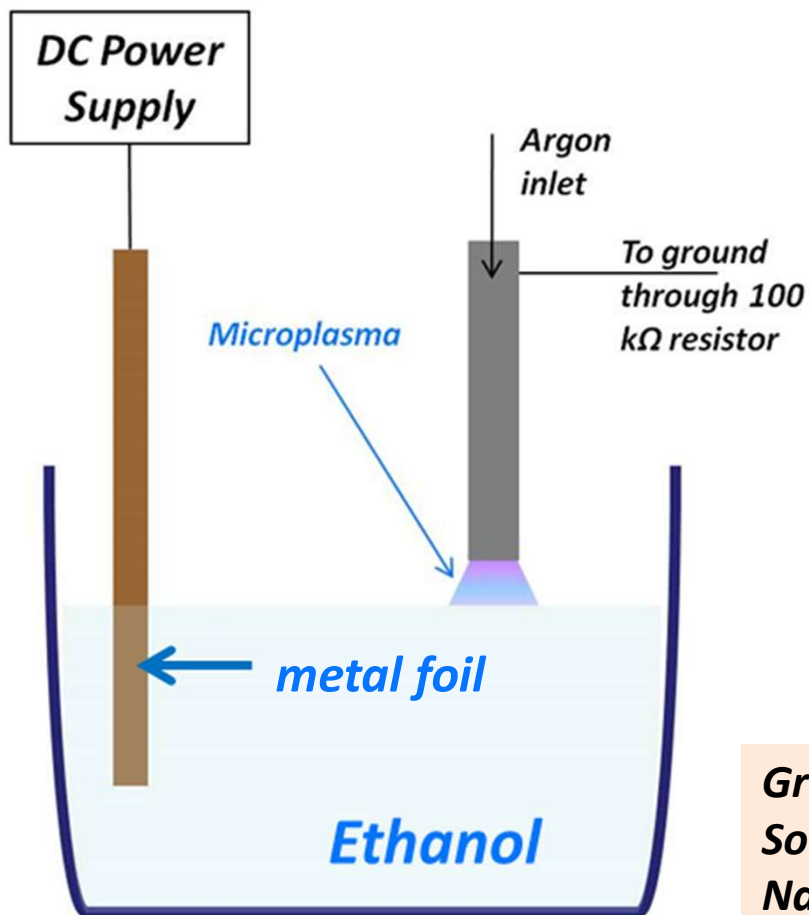
# Solid precursor: a generalized method for metal oxides (plasma-liquid)

## 3d transition metals



## Synthesis conditions

- 0.5 mA constant with 2-3 kV
- Cu foil: 1 mm thick & immersed by 5 mm
- Ni tube 0.7 mm ID and 1 mm OD



*Green Chem* 23, 2021, 3983  
*Solar Energy* 203, 2020, 37  
*Nanomaterials* 2023, 13, 12

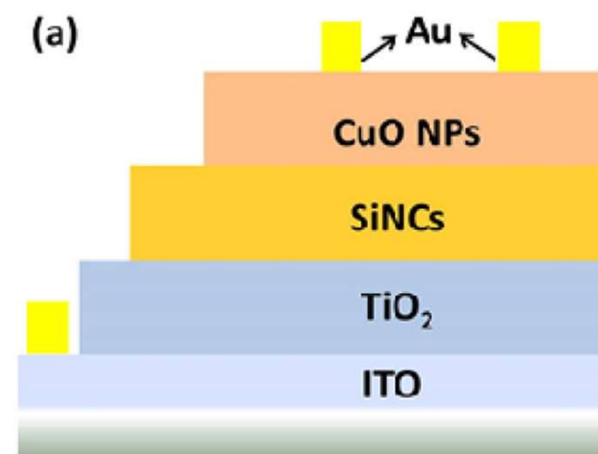
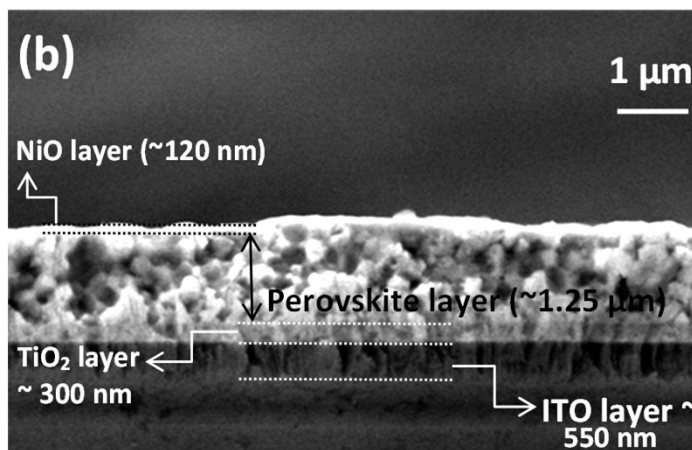
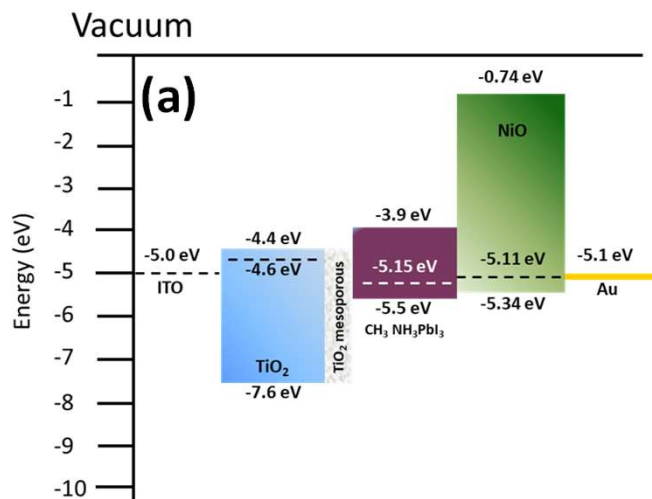
*Nano Energy* 108, 2023, 108112  
*Nanoscale Advances* 3, 2021, 781  
*Nanoscale Advances* 1, 2019, 4915



# Application of metal oxide QDs to solar energy conversion

## NiO QDs for Perovskite solar cells

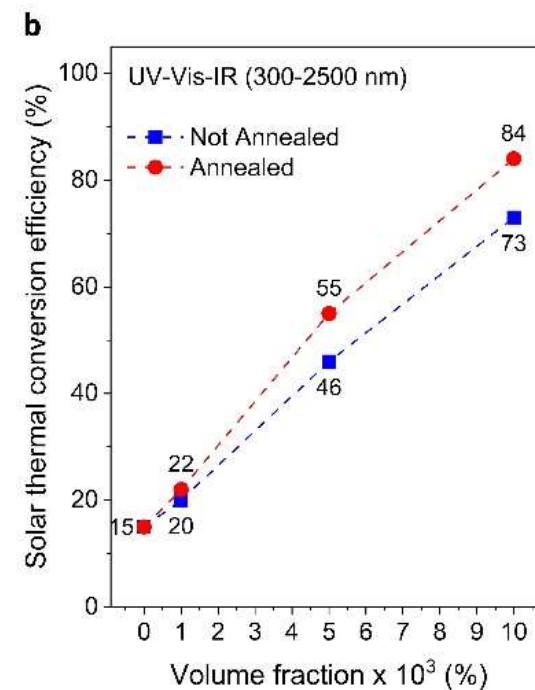
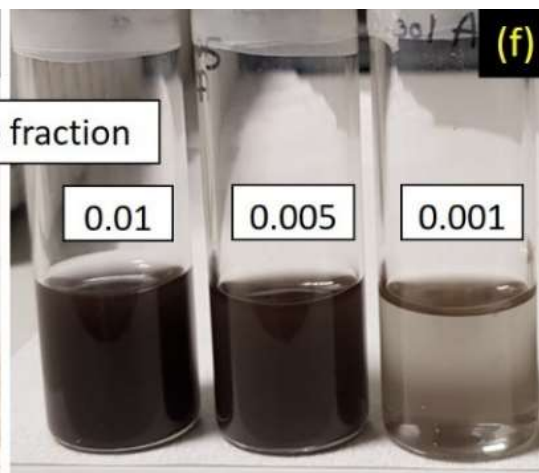
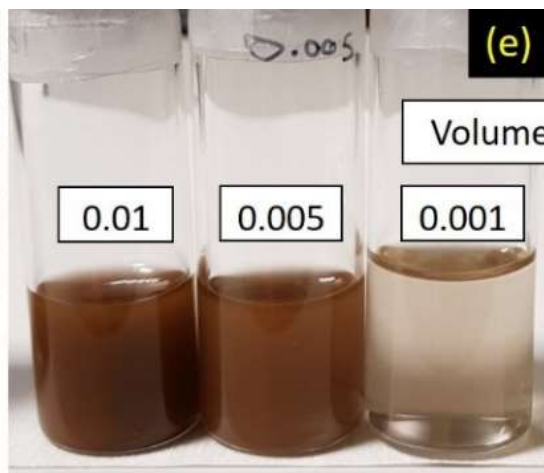
## CuO QDs for Si NC solar cells



*Nanoscale Advances* 1, 2019, 4915

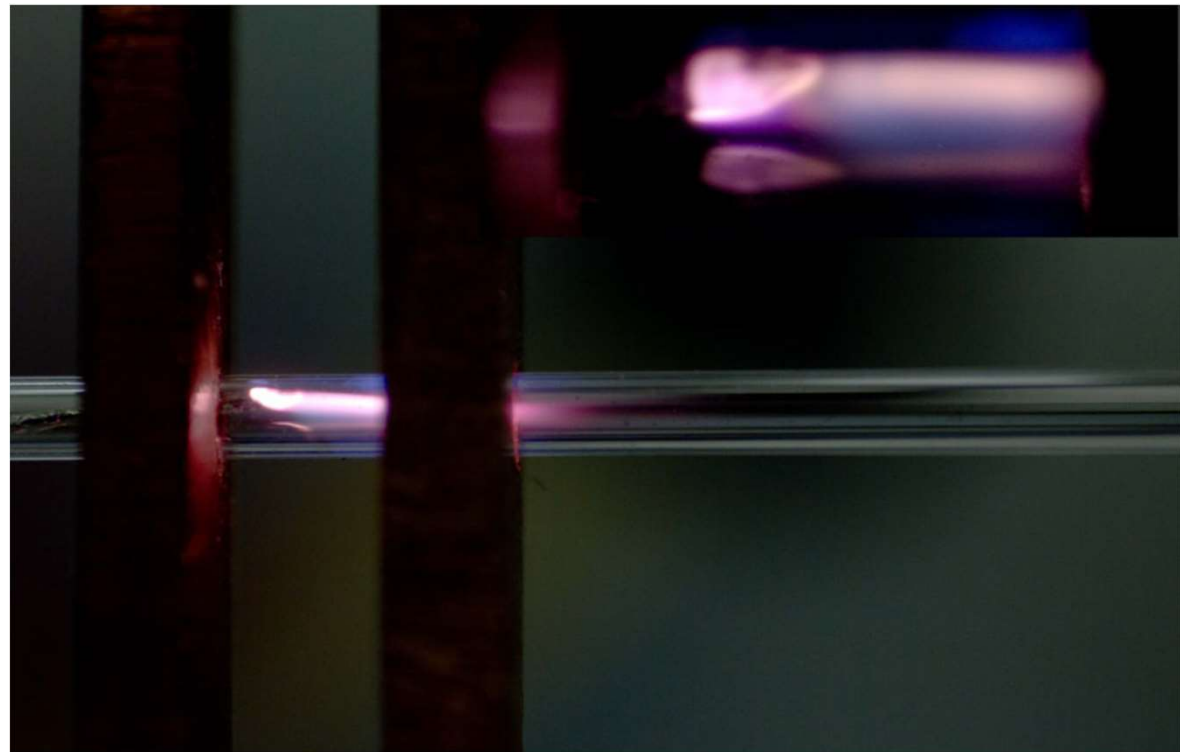
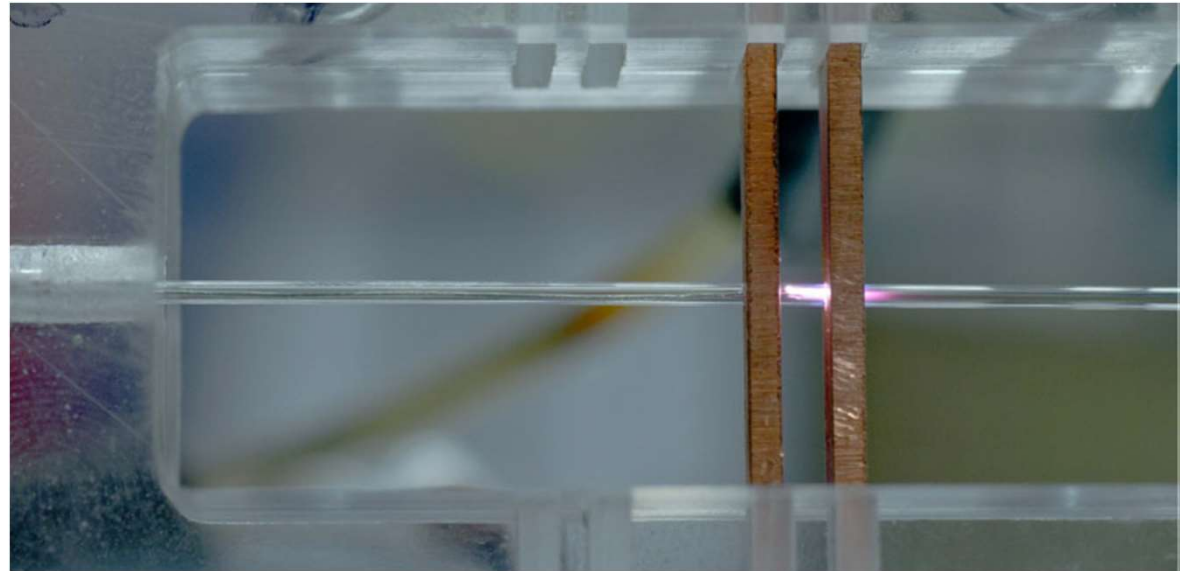
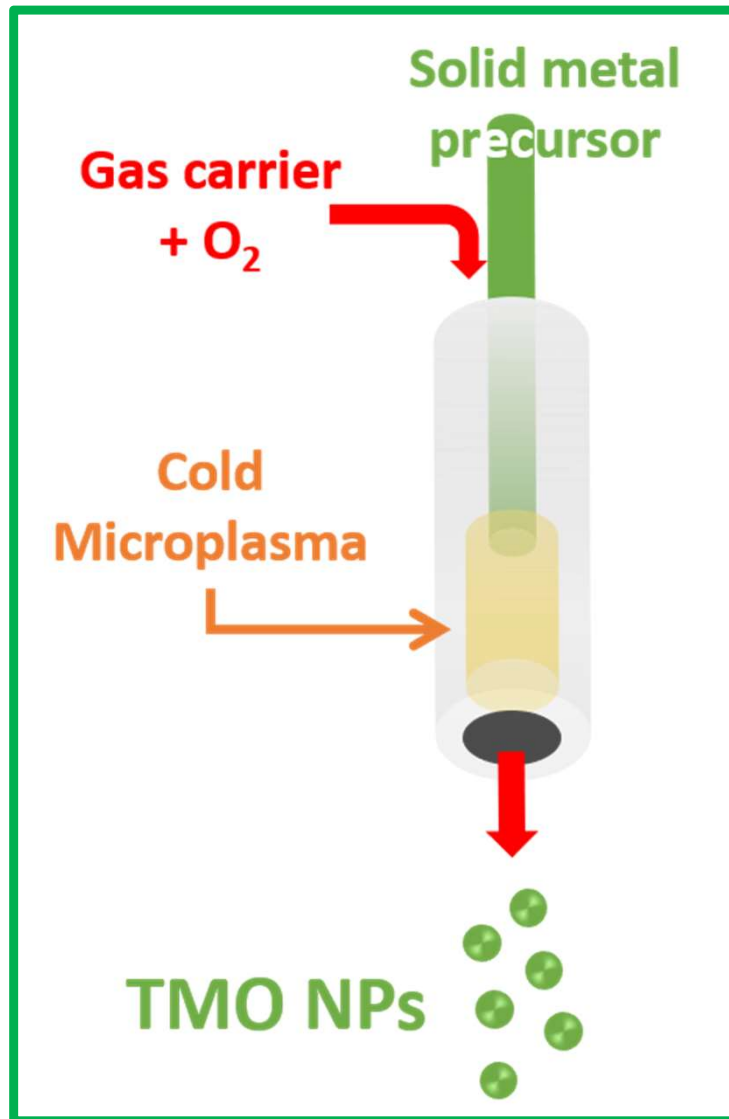
*Plasma Process Polymers* 14, 2017, 1600224

## CuO NPs nanofluids for solar-thermal energy conversion



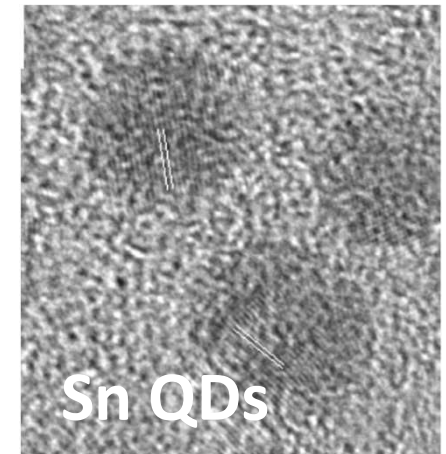
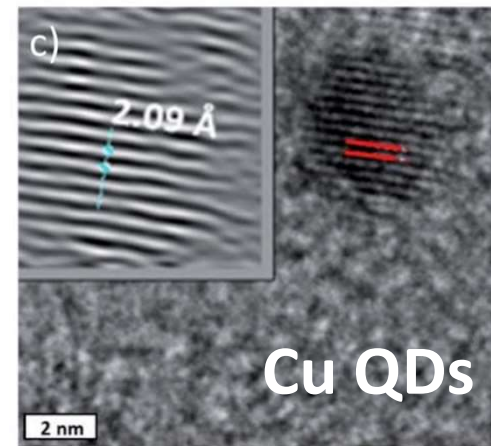
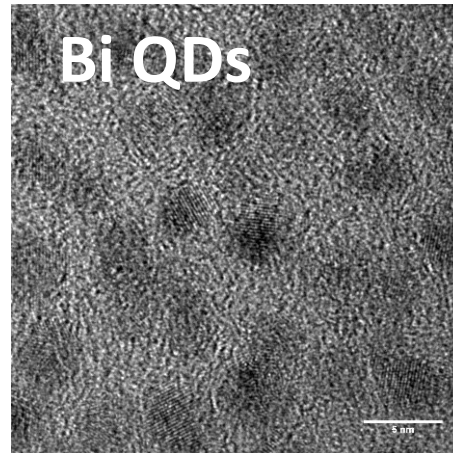
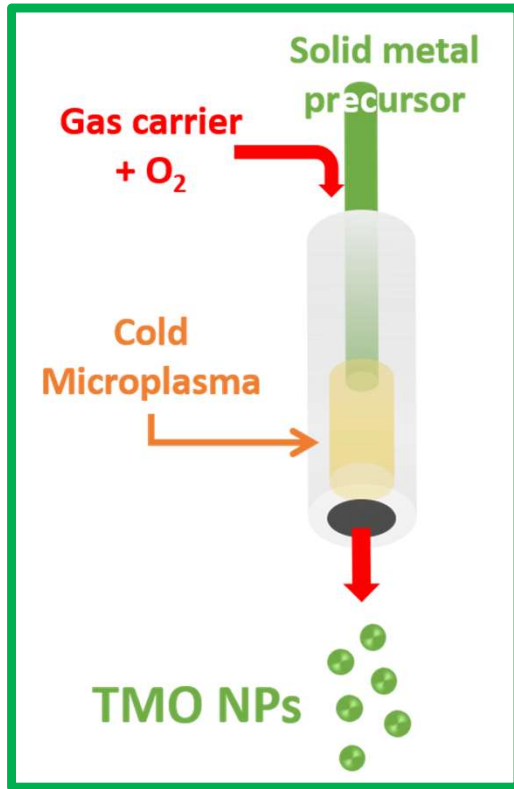
*Nano Energy* 108, 2023, 108112

# A basic configuration for simple precursors delivery (gas phase)



# A versatile configuration for simple precursors delivery

## No Oxygen, w/o Hydrogen



*Small Methods* 2023, 2300710

*Nanoscale Adv* 3, 2021, 781

*Nature Comm* 10, 2019, 817

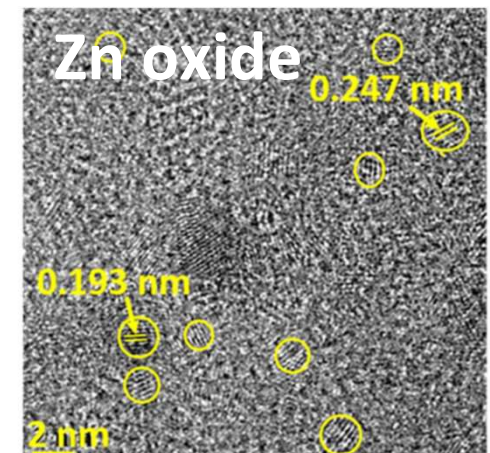
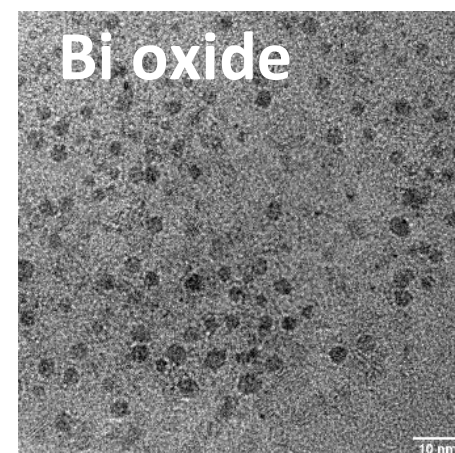
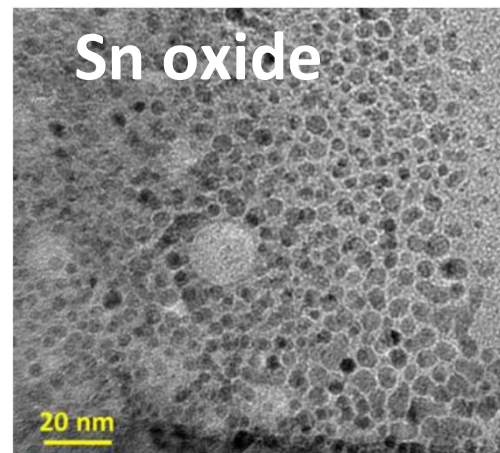
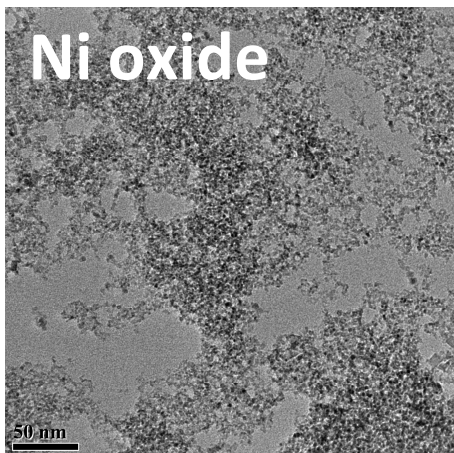
*Nanotechnology* 31, 2020, 215707

*Plasma Process & Polym* 14, 2017, 1700052

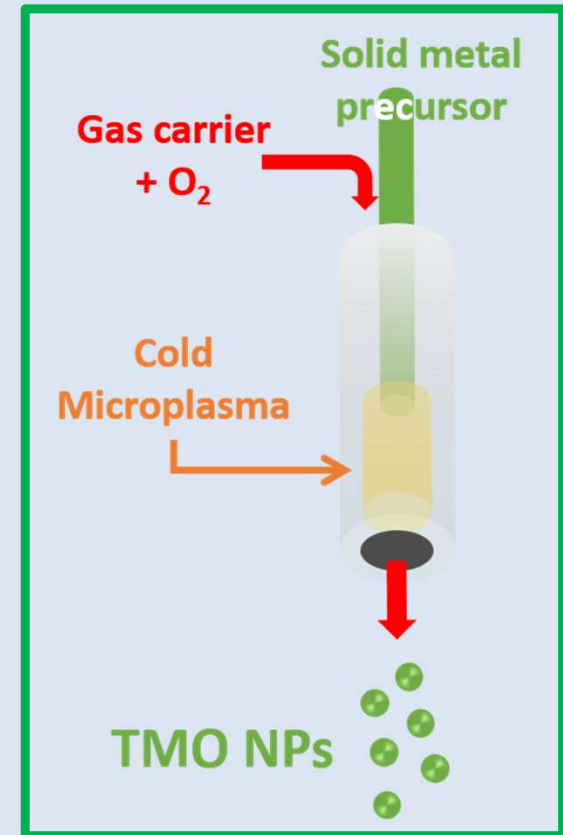
*J Phys D: Appl Phys* 42, 2009, 092002

... also W, Mo, Sb etc.

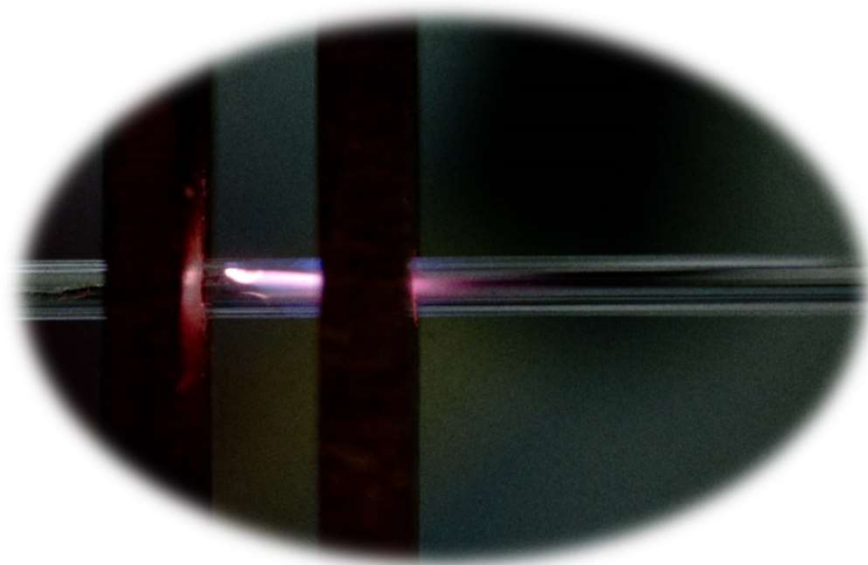
## With oxygen



- “Cluster doping”
- Plasma-wire mechanisms
- Nanomanufacturing



- Exsolution

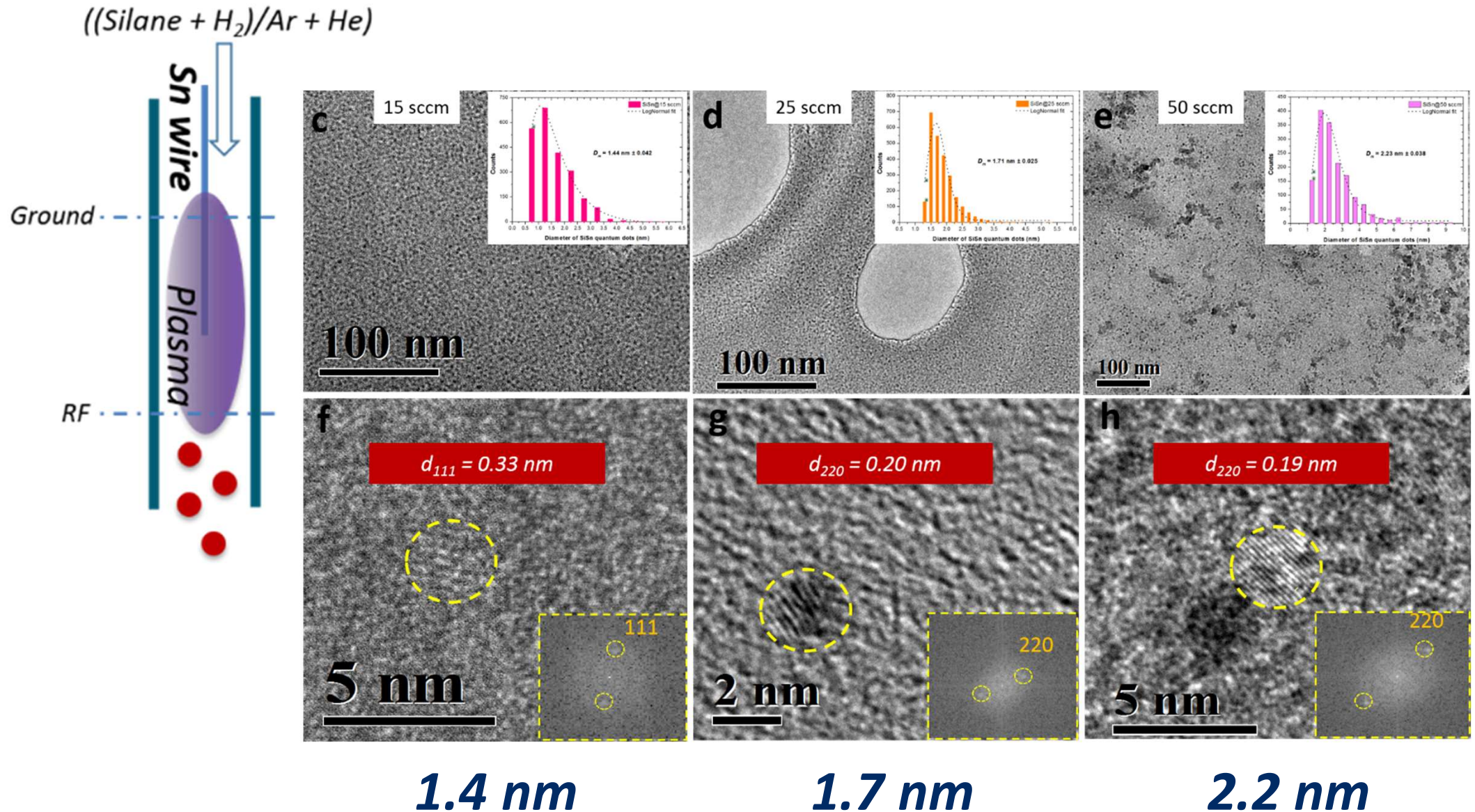


***Cluster doping***

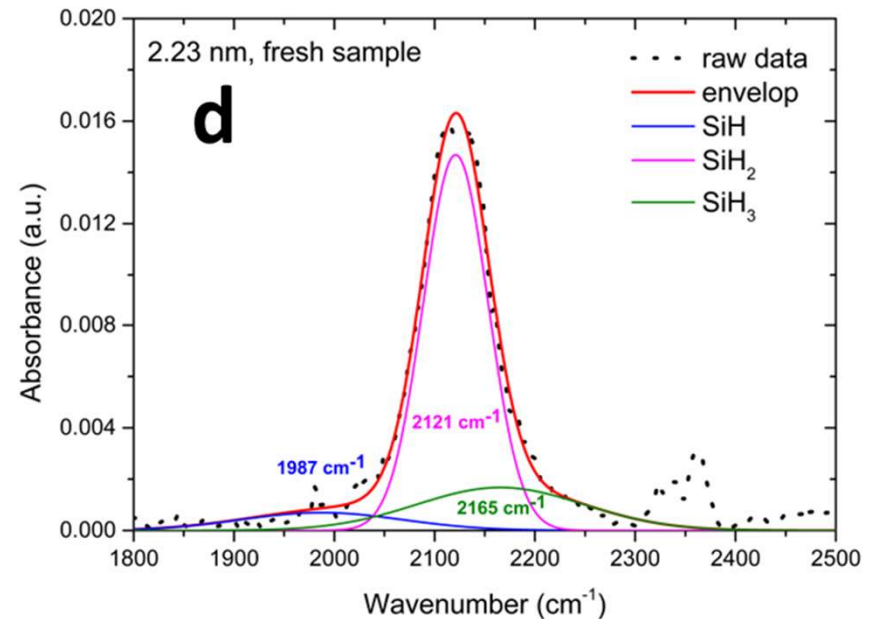
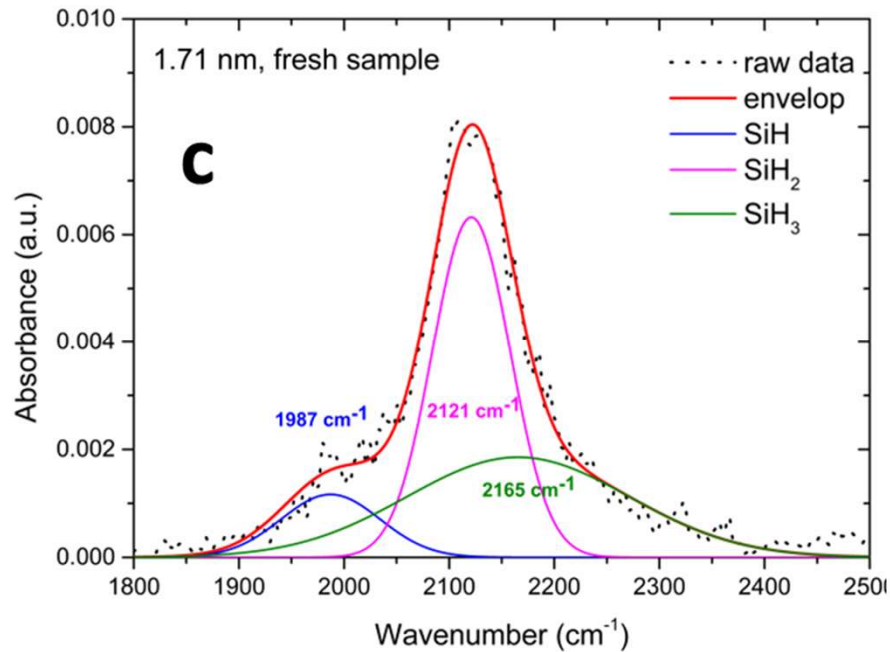
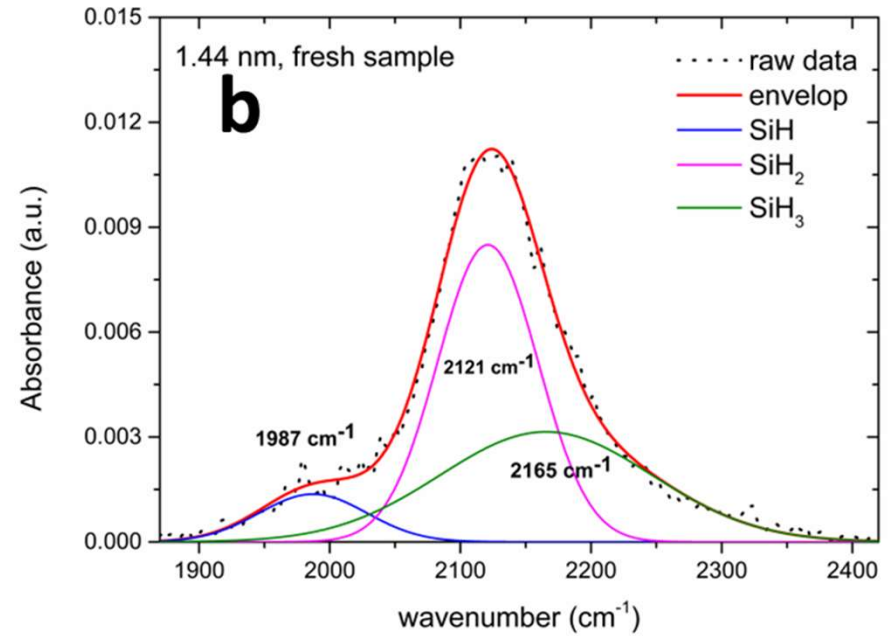
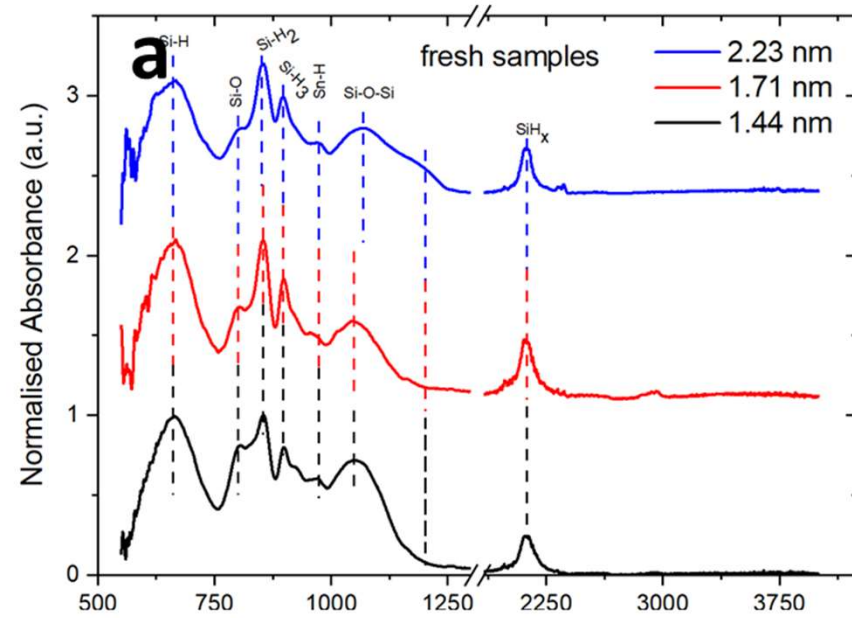
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# Silicon-tin nanocrystals from solid-gaseous precursors

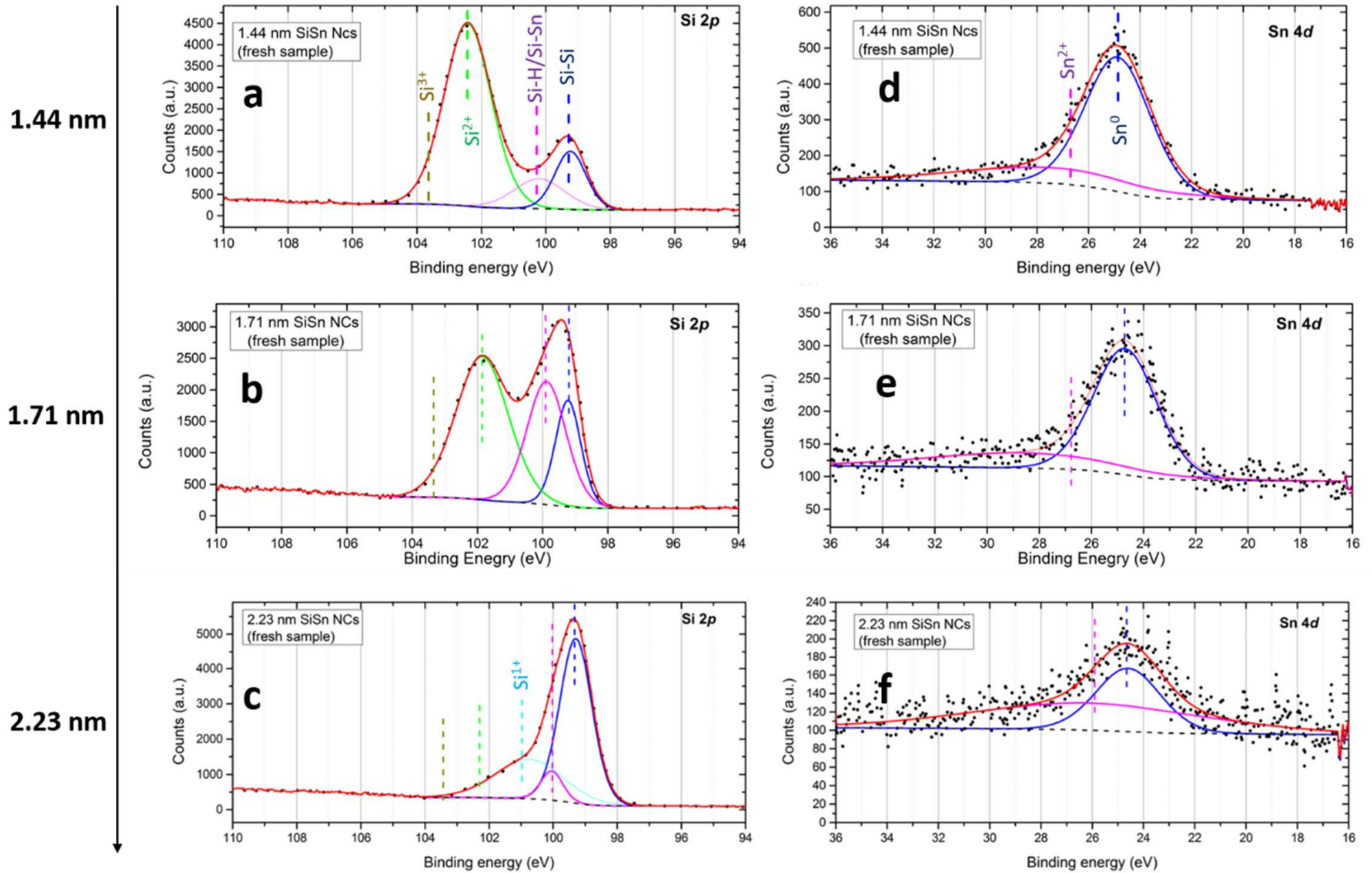
Copper electrodes separated by 2 mm spacing. Quartz capillary (diameter of 0.7 mm). A wire of tin (Sn, diameter of 0.25 mm). Helium background. RF power of 40 W at 13.56 MHz. Silane in Ar of 15 sccm, 25 sccm and 50 sccm.



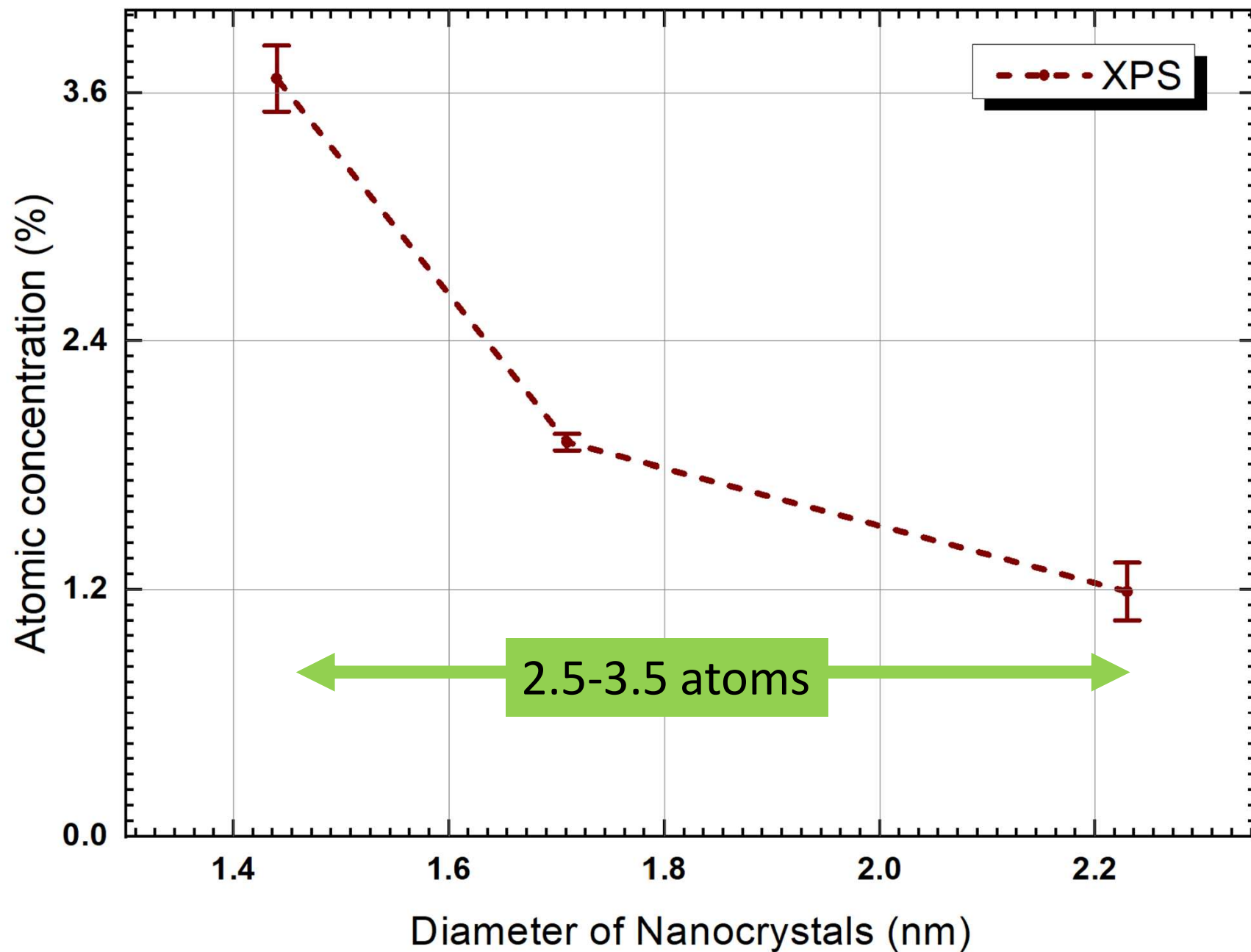
# Silicon-tin nanocrystals from solid-gaseous precursors



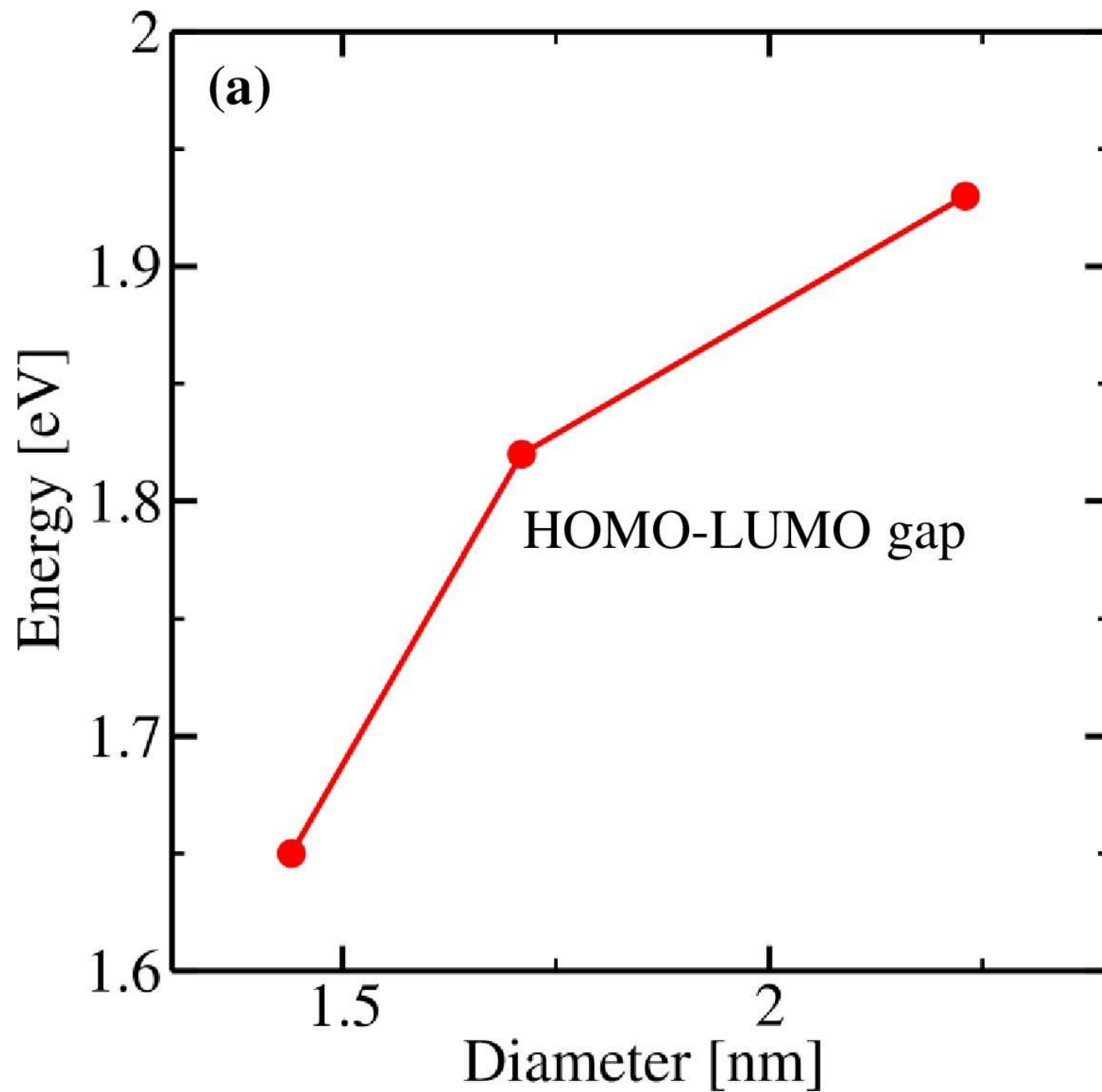
# Silicon-tin nanocrystals from solid-gaseous precursors



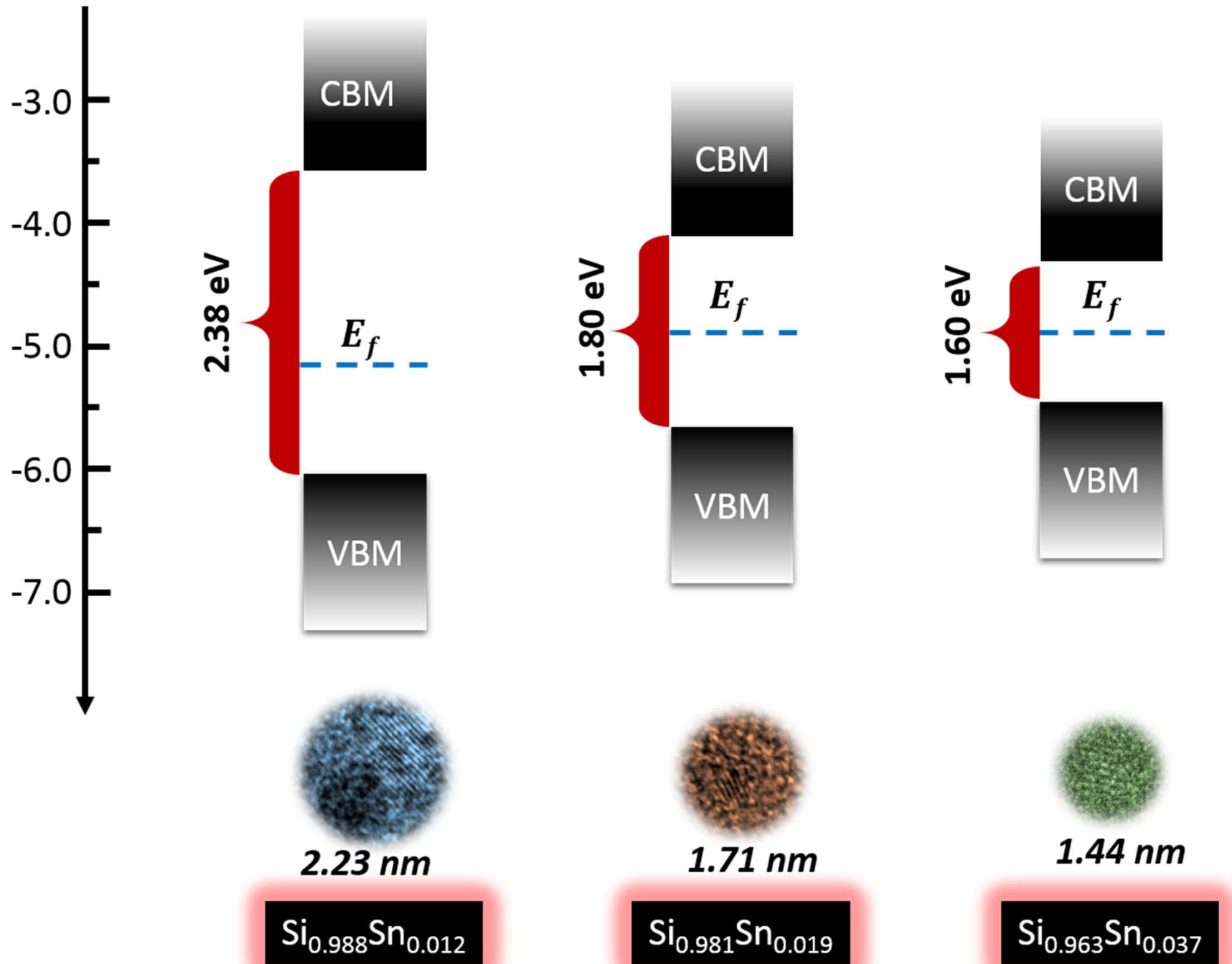
# Silicon-tin nanocrystals from solid-gaseous precursors

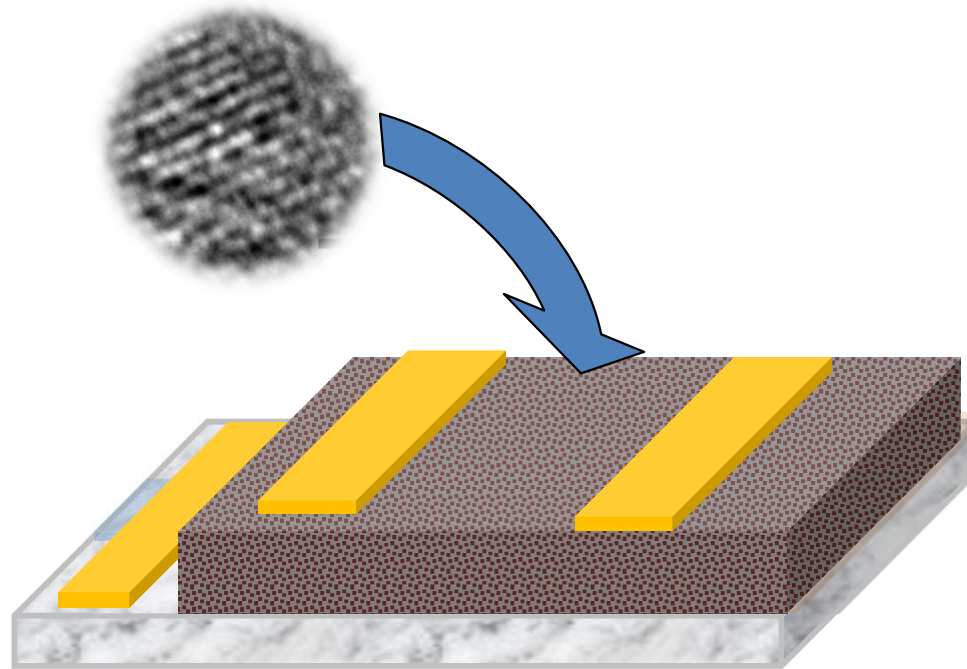


## *Anomalous band energy behaviour*



# Anomalous band energy behaviour

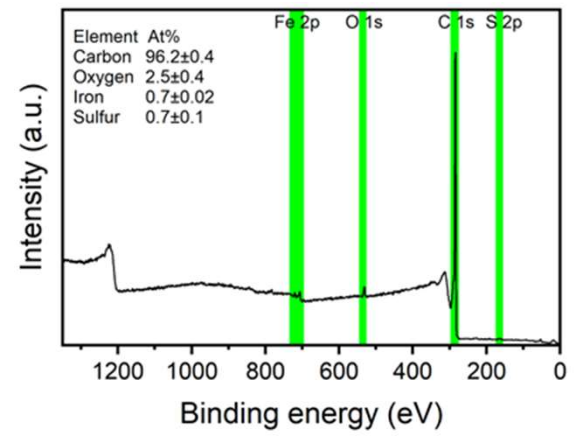
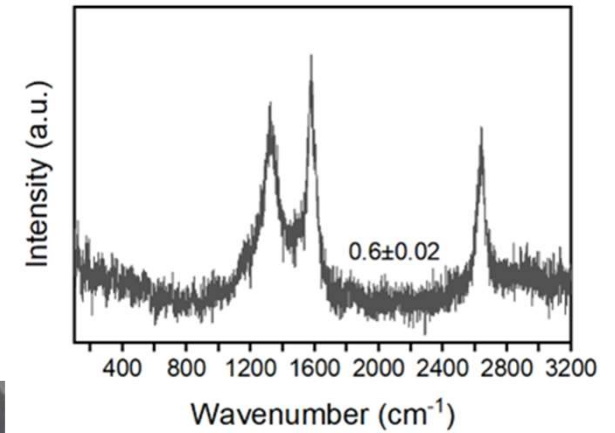
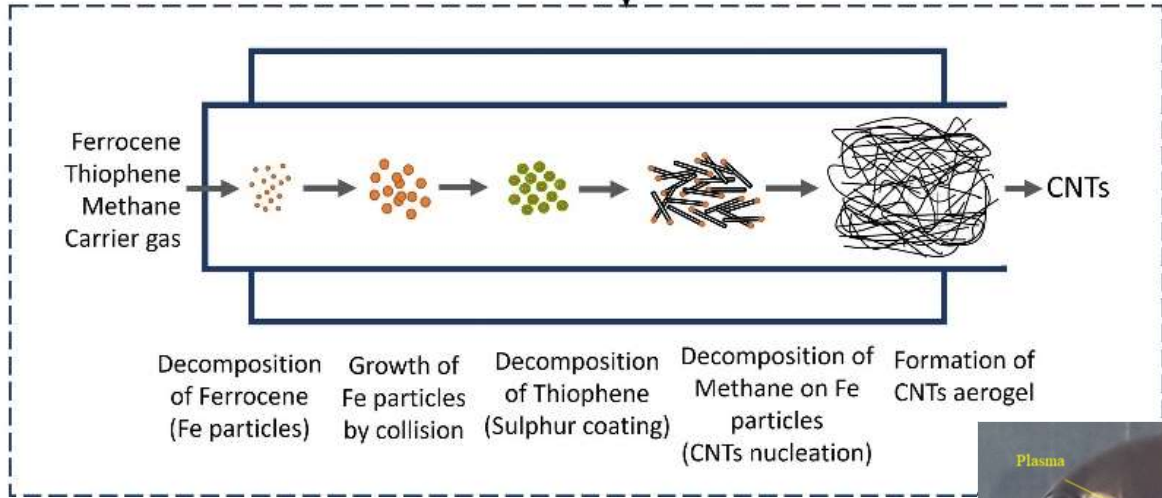
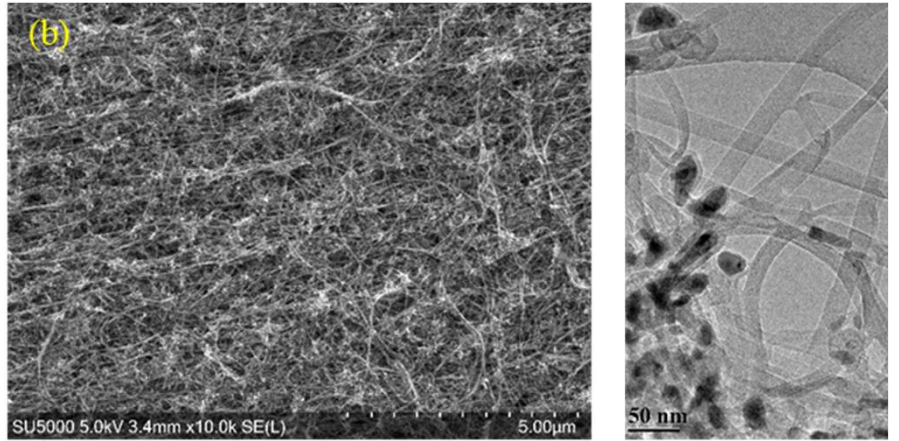
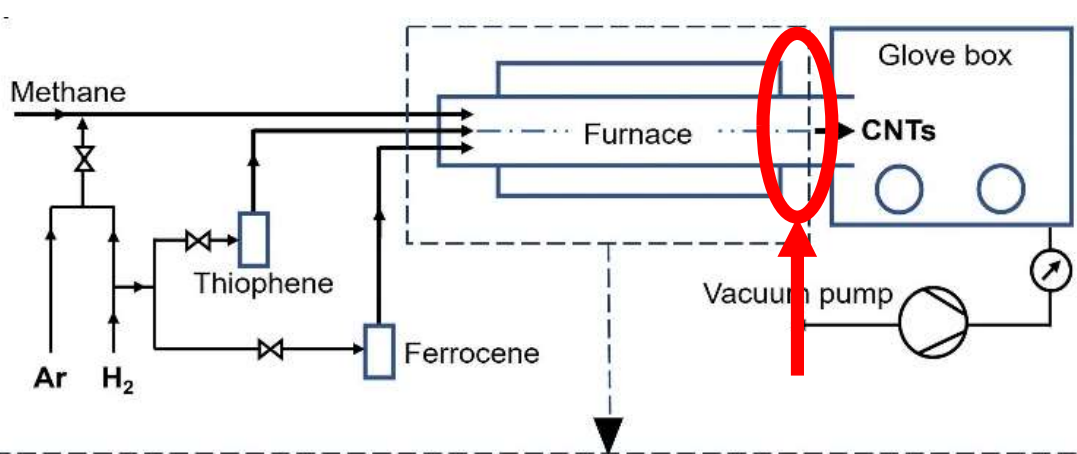




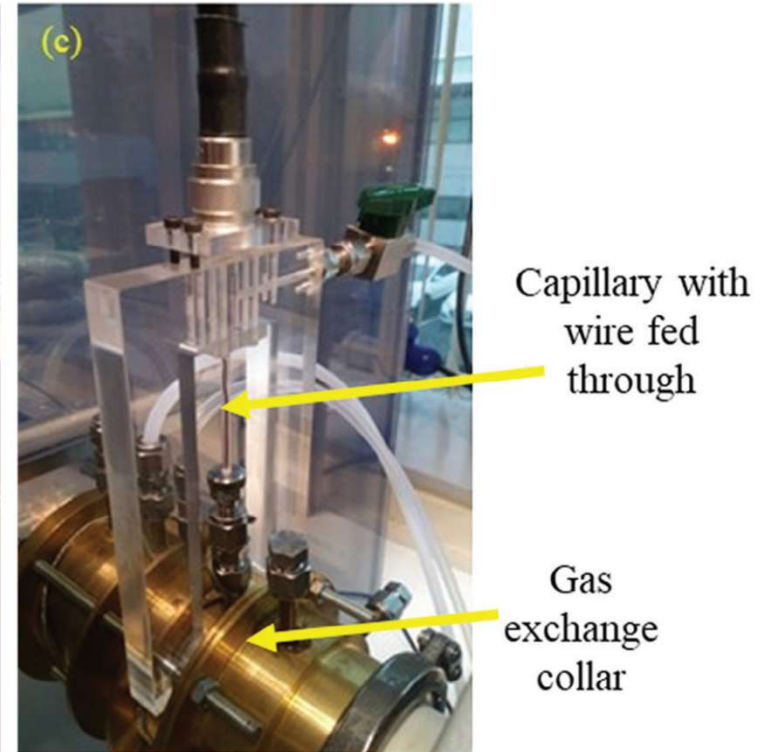
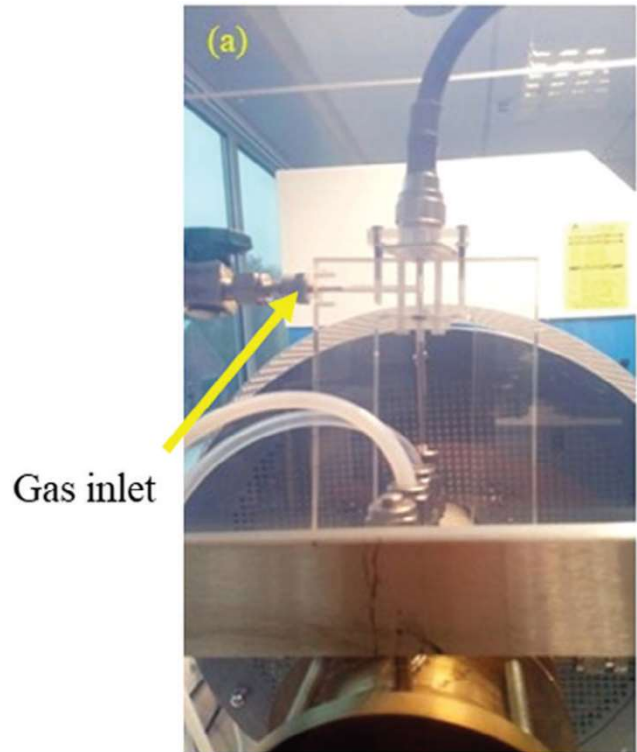
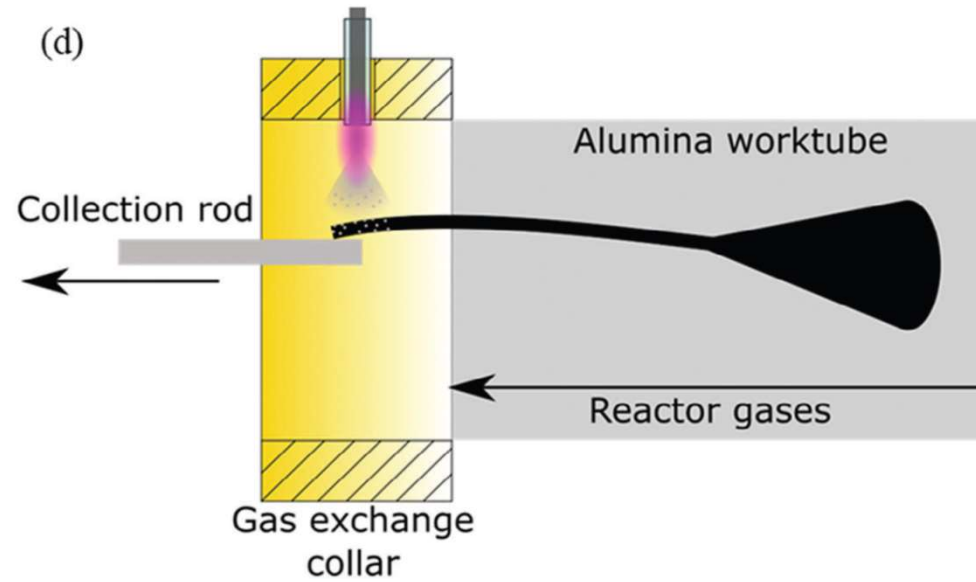
***... towards nanomanufacturing I***

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# Synthesis of macroscopic CNT ribbons

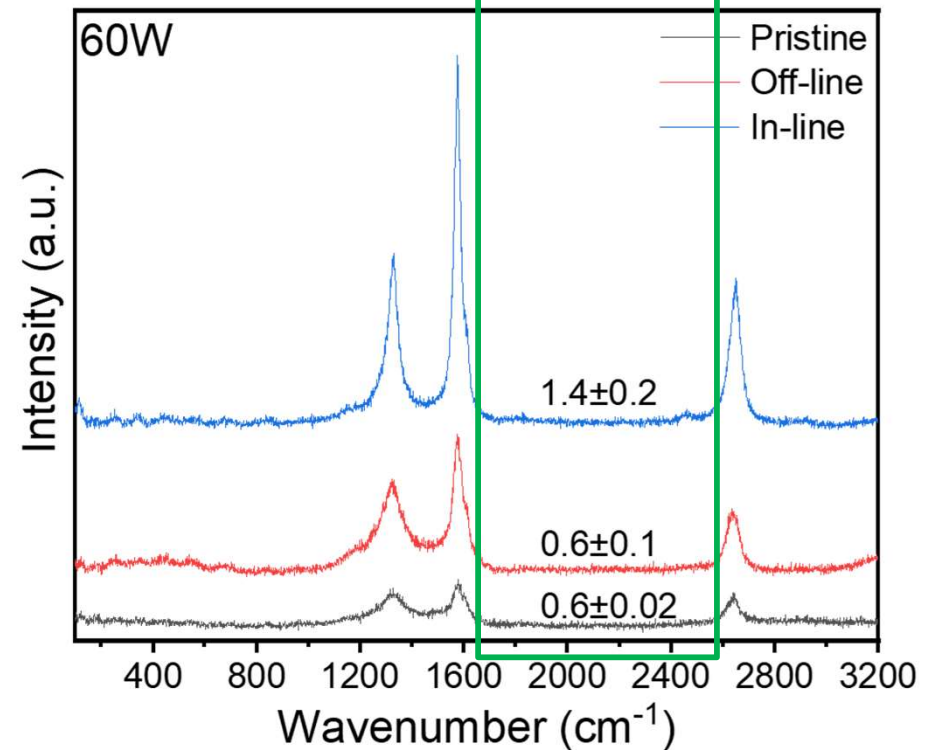
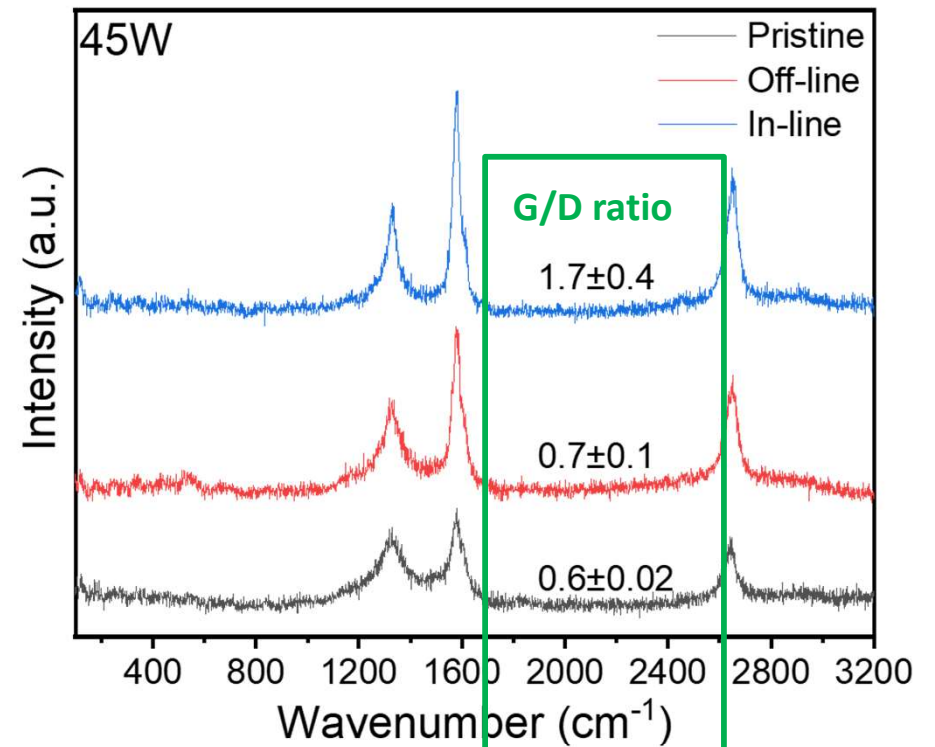
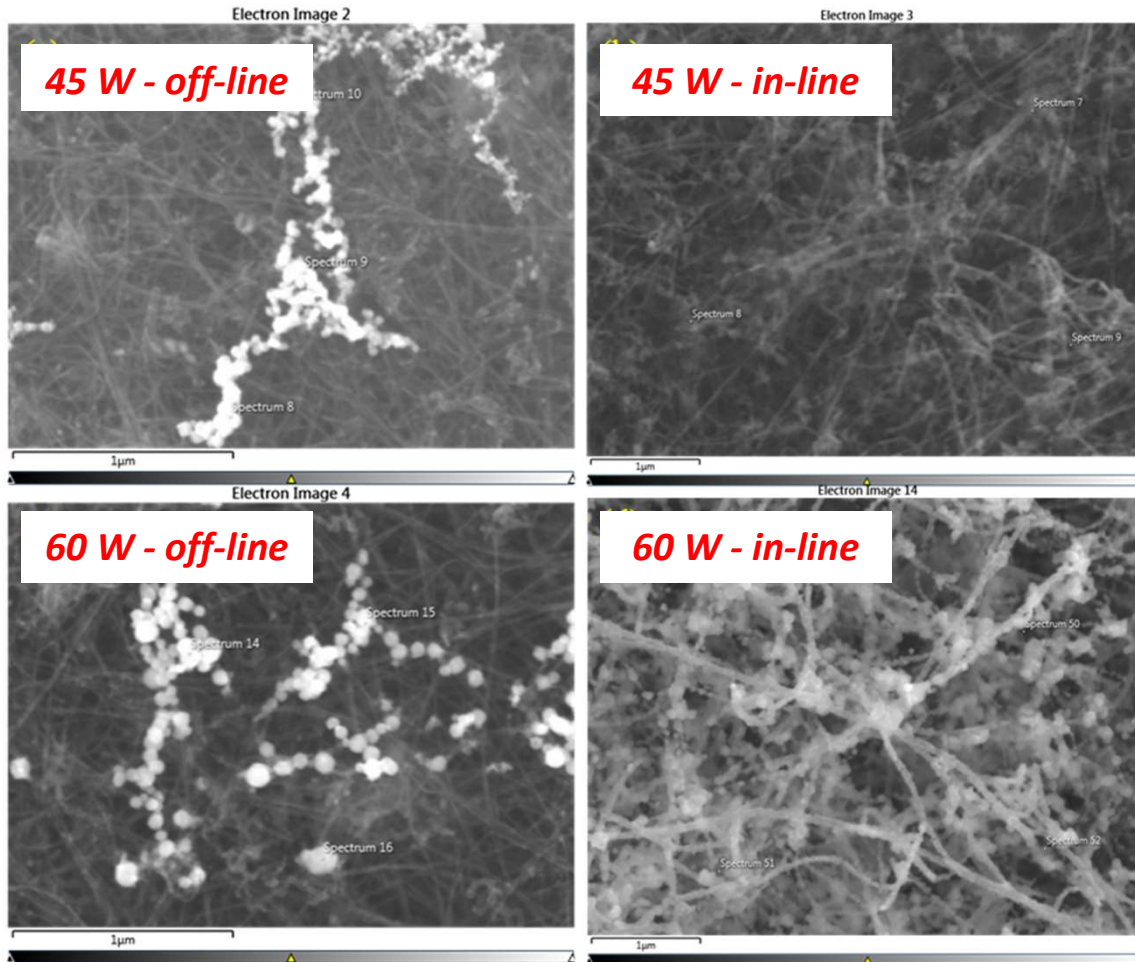


# Zn-based NP/CNT composites

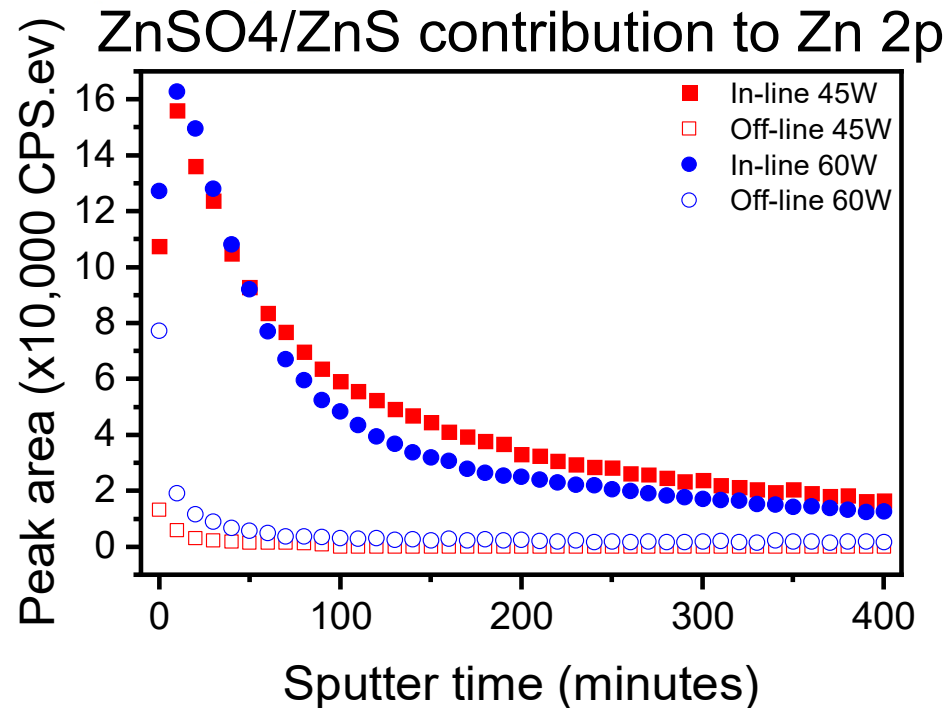
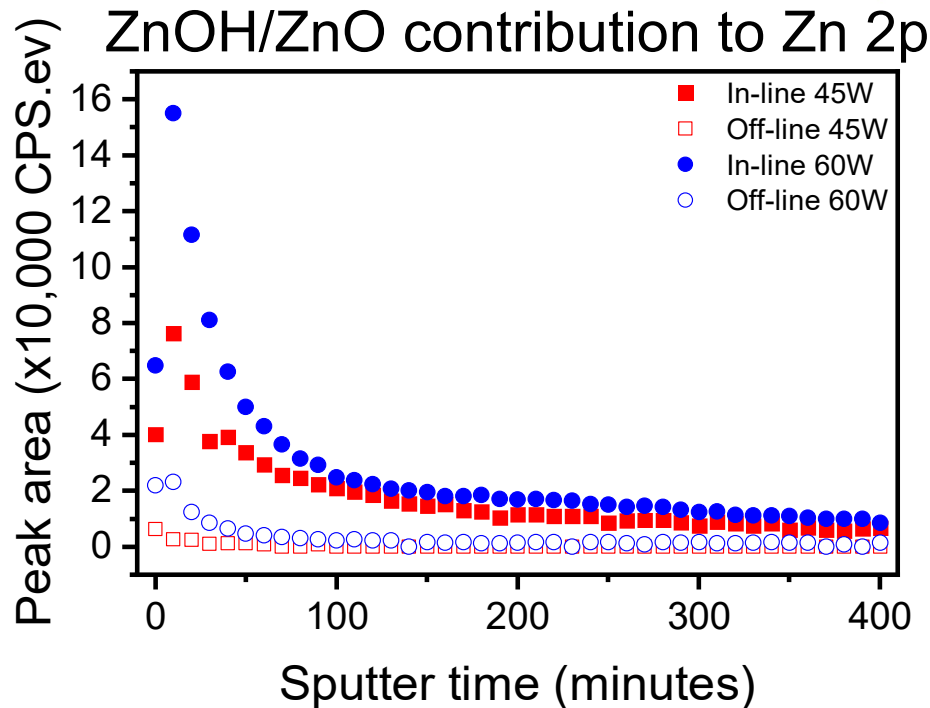
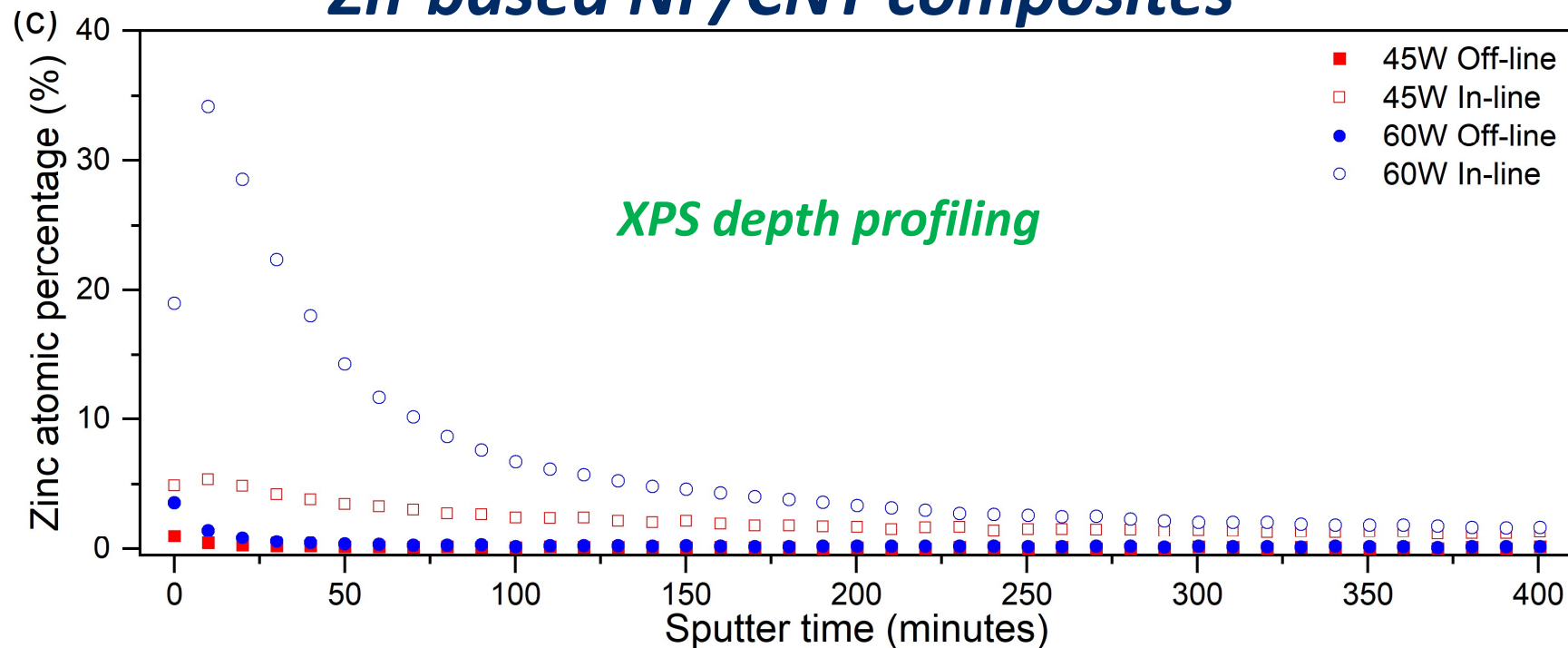


# Zn-based NP/CNT composites

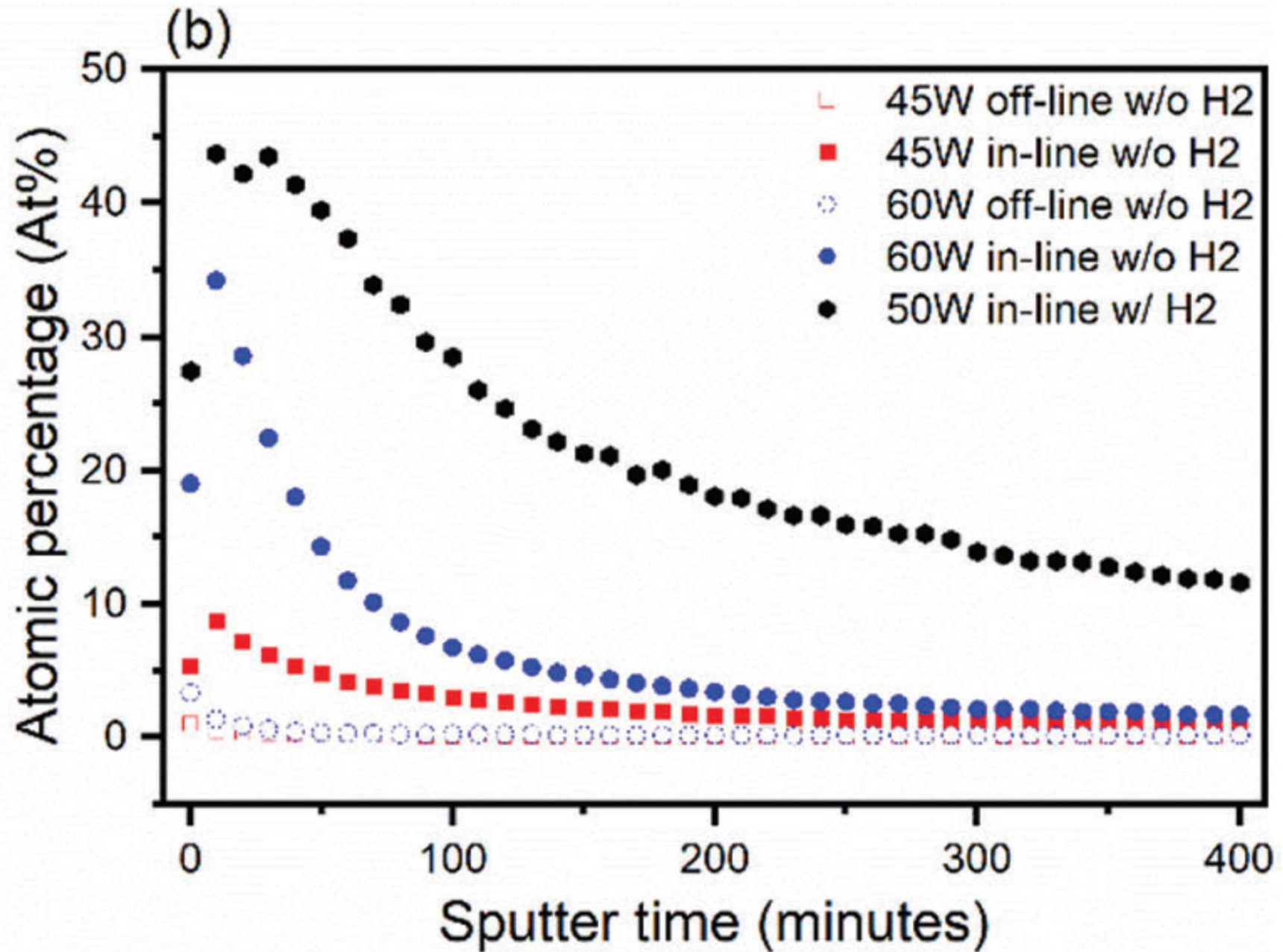
*We compare the in-line process with NP deposition post synthesis (off-line)*

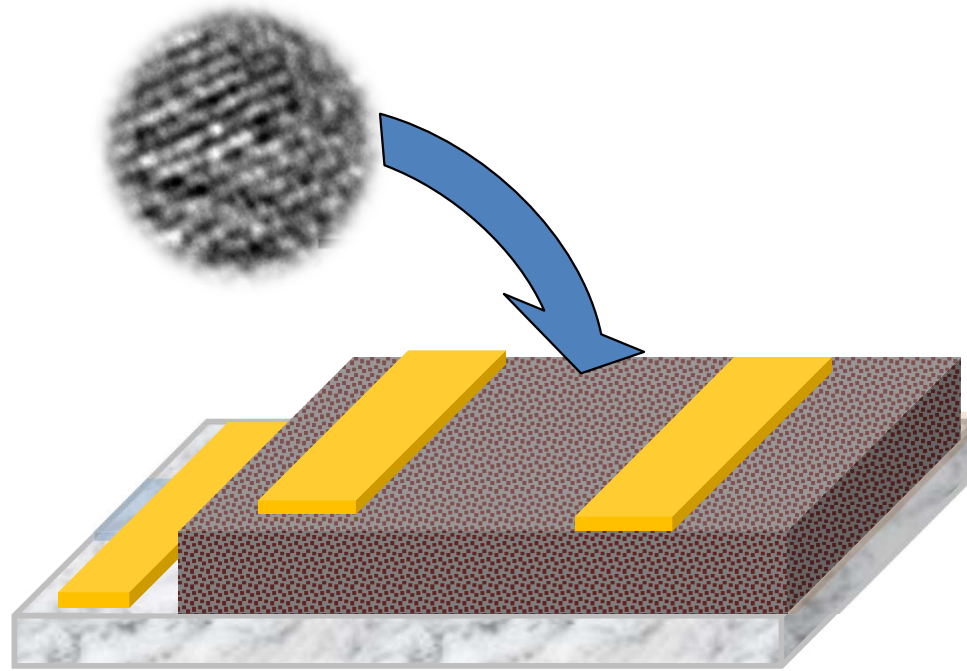


# Zn-based NP/CNT composites



# Zn-based NP/CNT composites

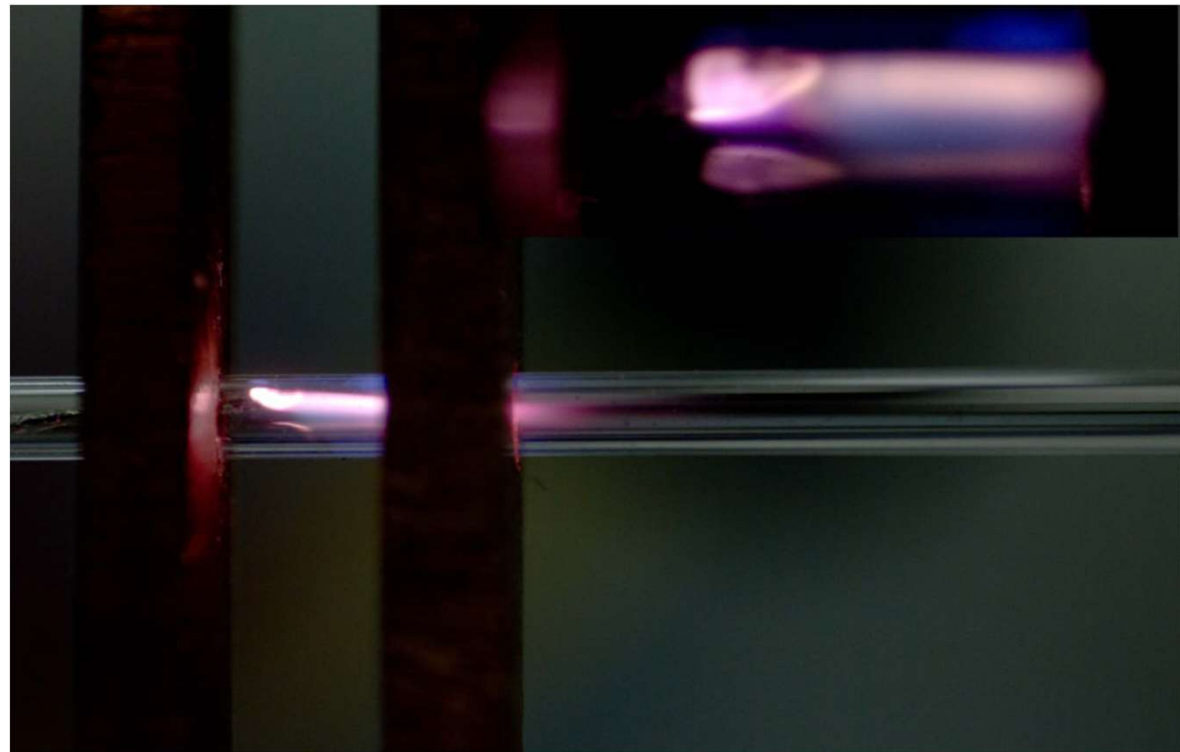
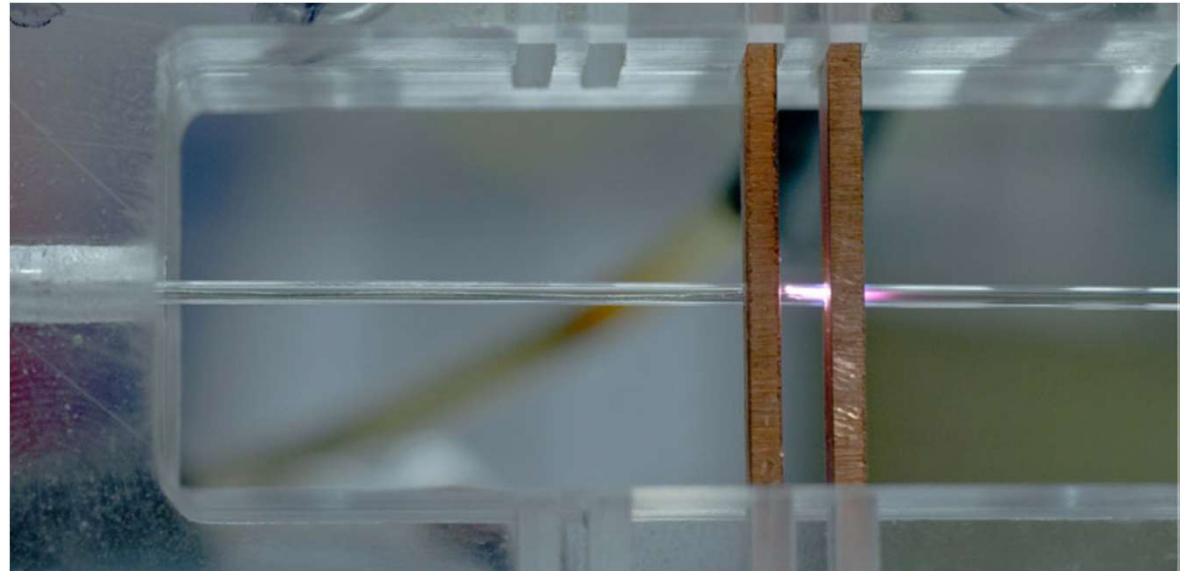
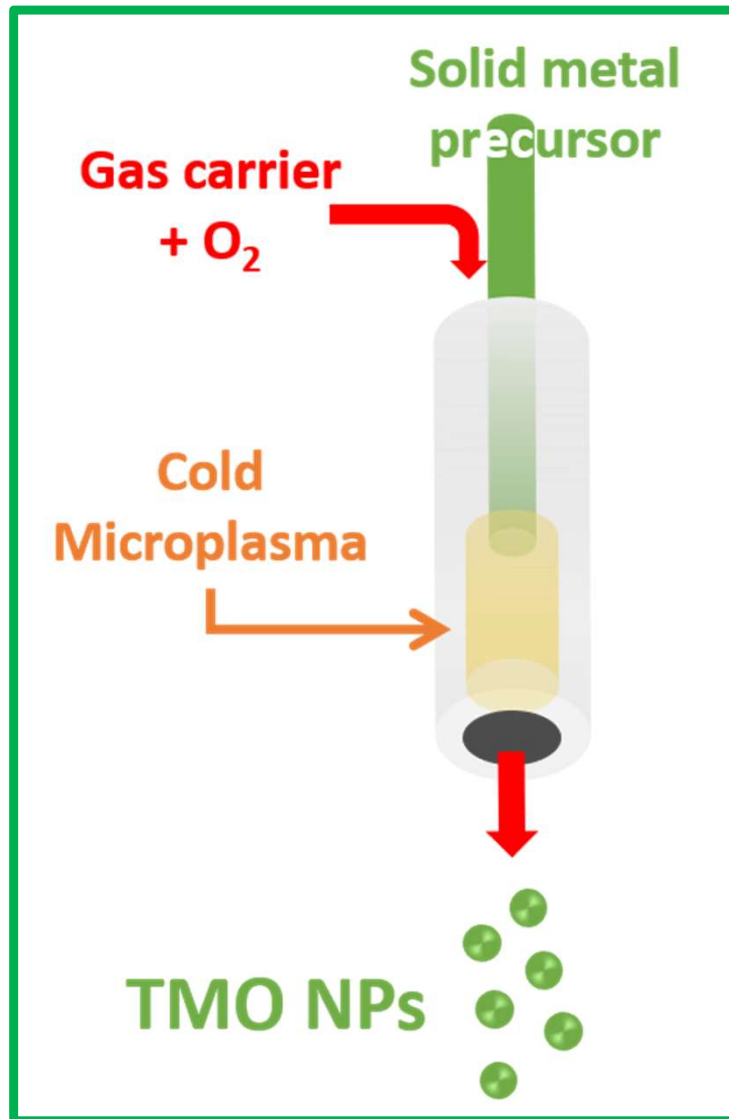




***... towards nanomanufacturing II***

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# A basic configuration for simple precursors delivery



# Atmospheric pressure plasmas with solid precursors offer versatile fabrication methodologies

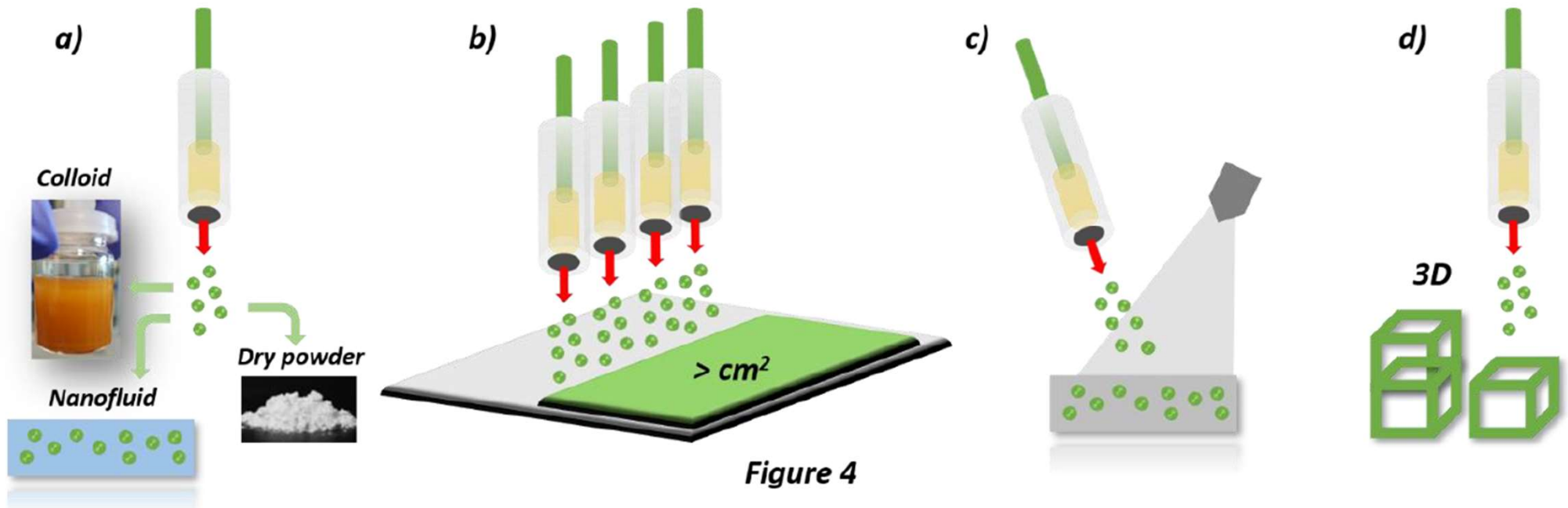
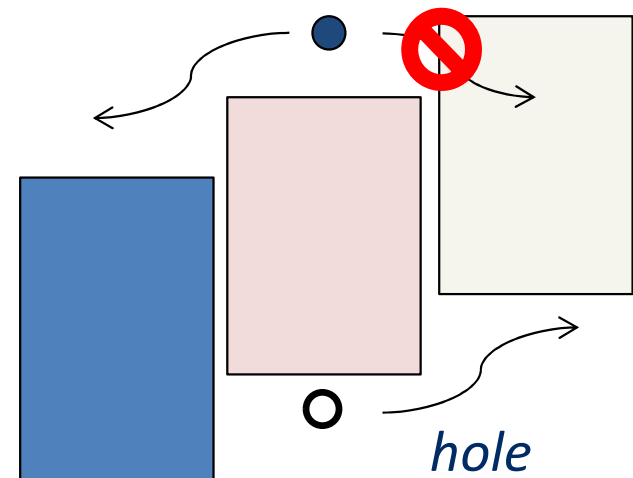
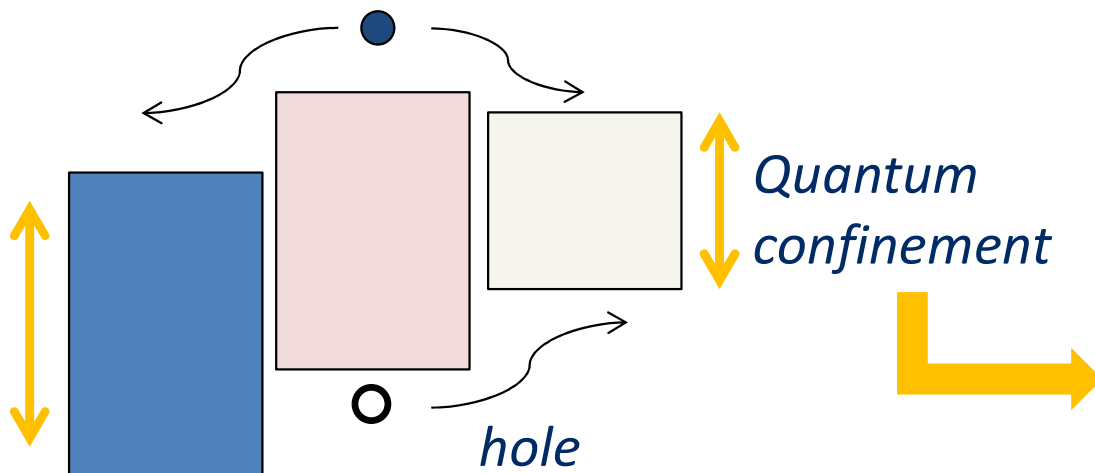
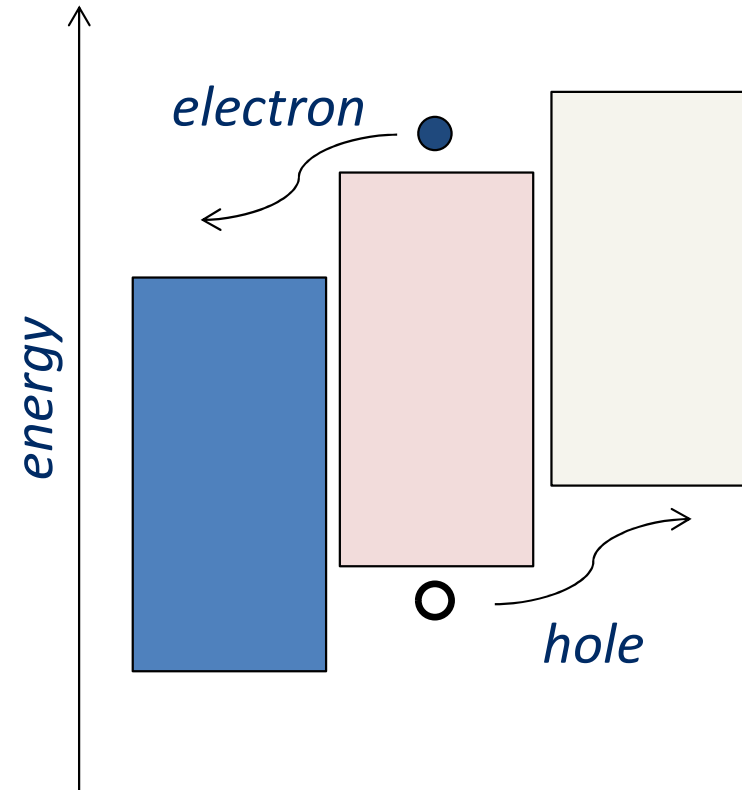
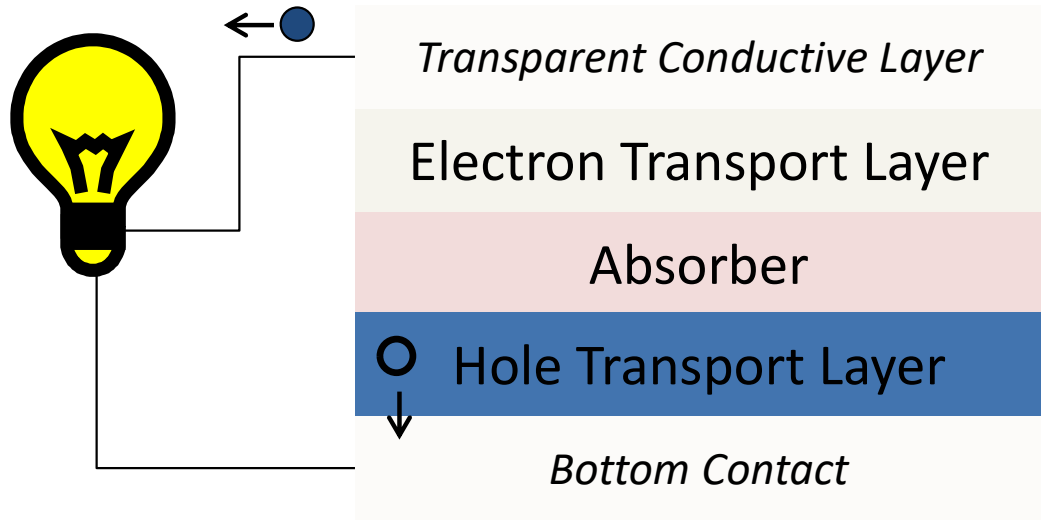
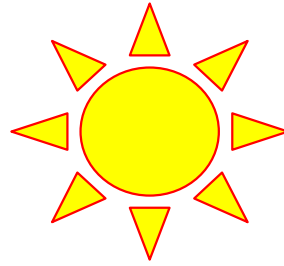


Figure 4

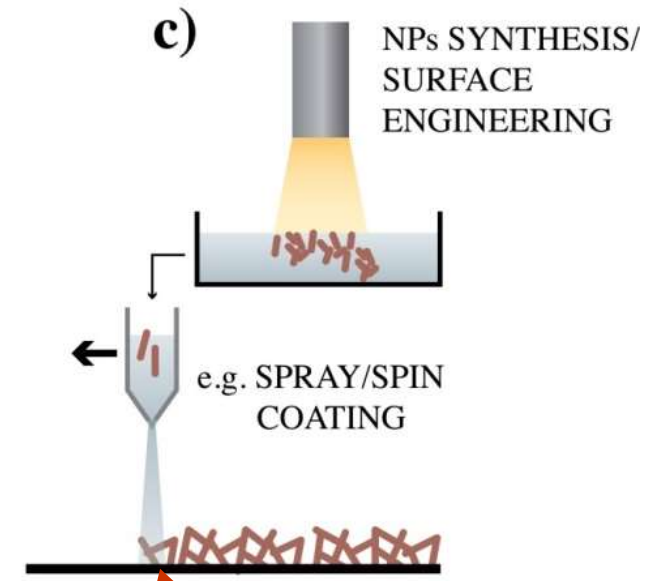
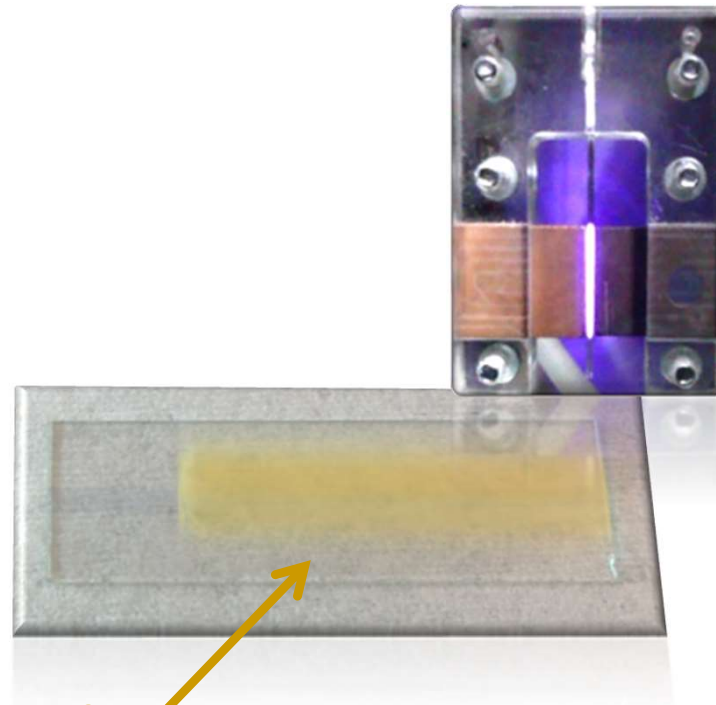
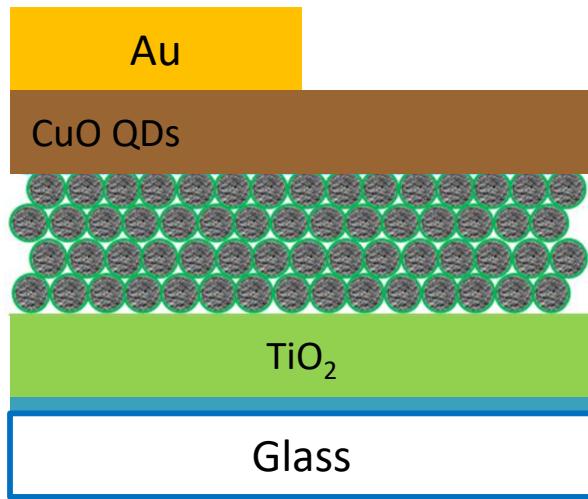
(i) highly versatile and (ii) 'lean & green' process capable of delivering materials with precise (iii) nanoscale to sub-nanoscale morphology, (iv) a tuneable non-stoichiometric chemical composition and (v) chemical specificity leading to high yield and high throughput

# Opportunities offered by metal oxides quantum dots (QDs)

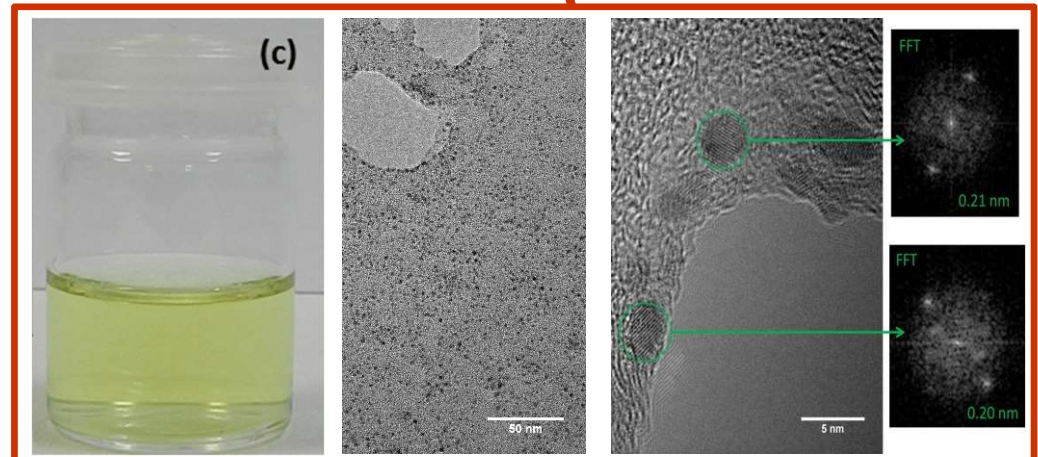
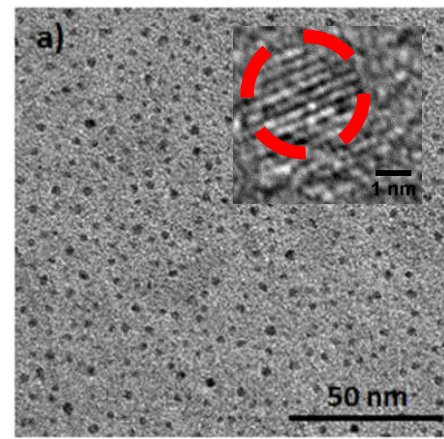
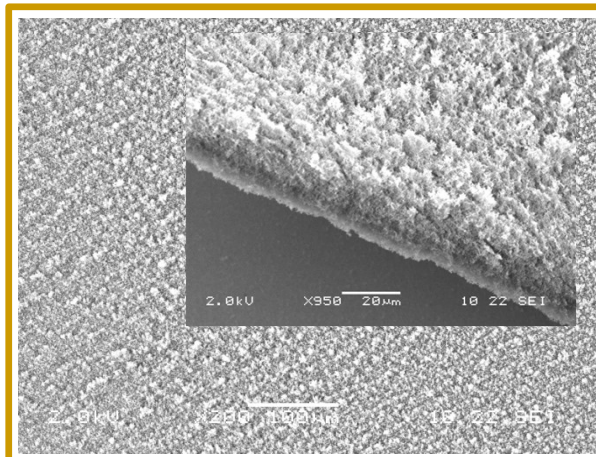
- All next generation solar cells (e.g. organic, perovskites, and quantum dot)



# Materials and process integration in device fabrication



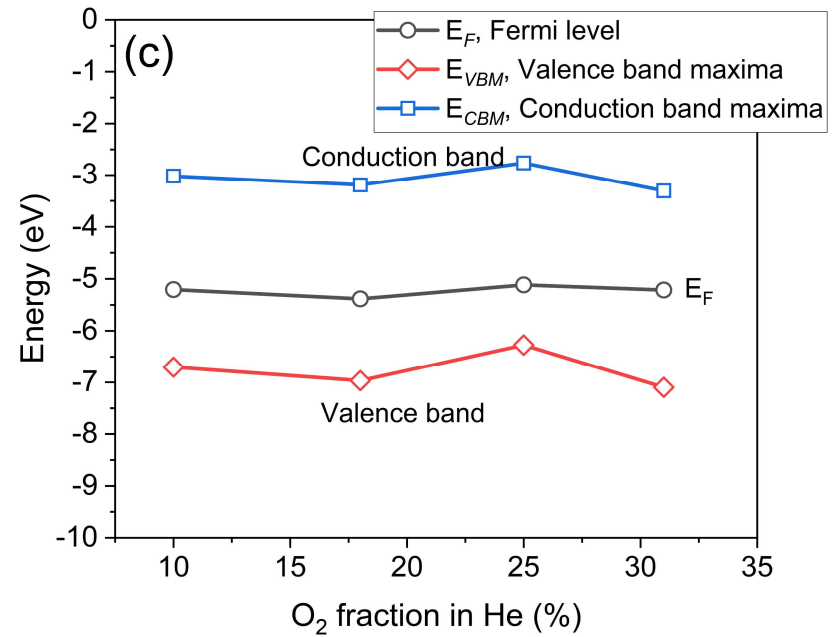
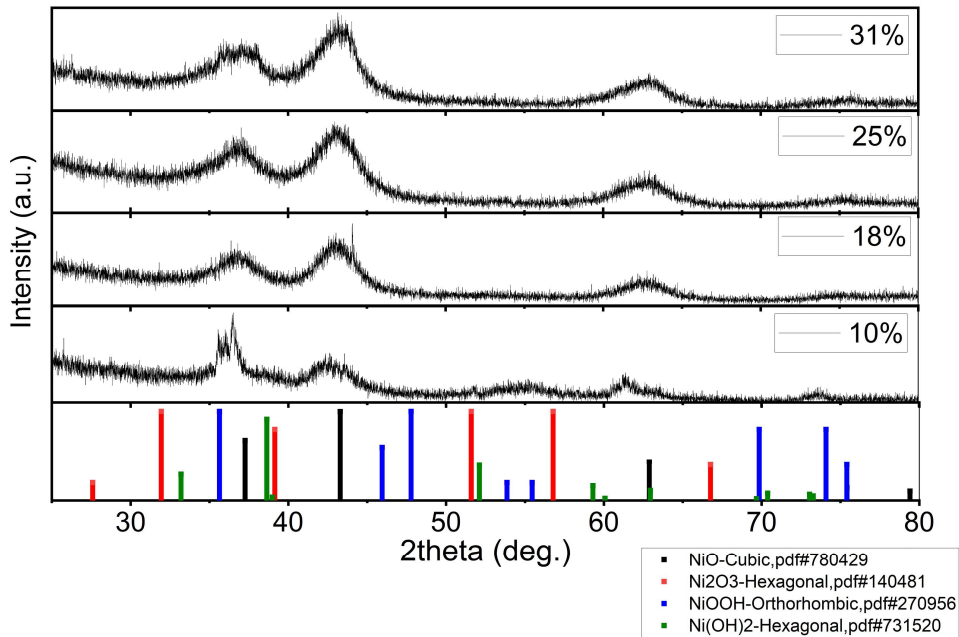
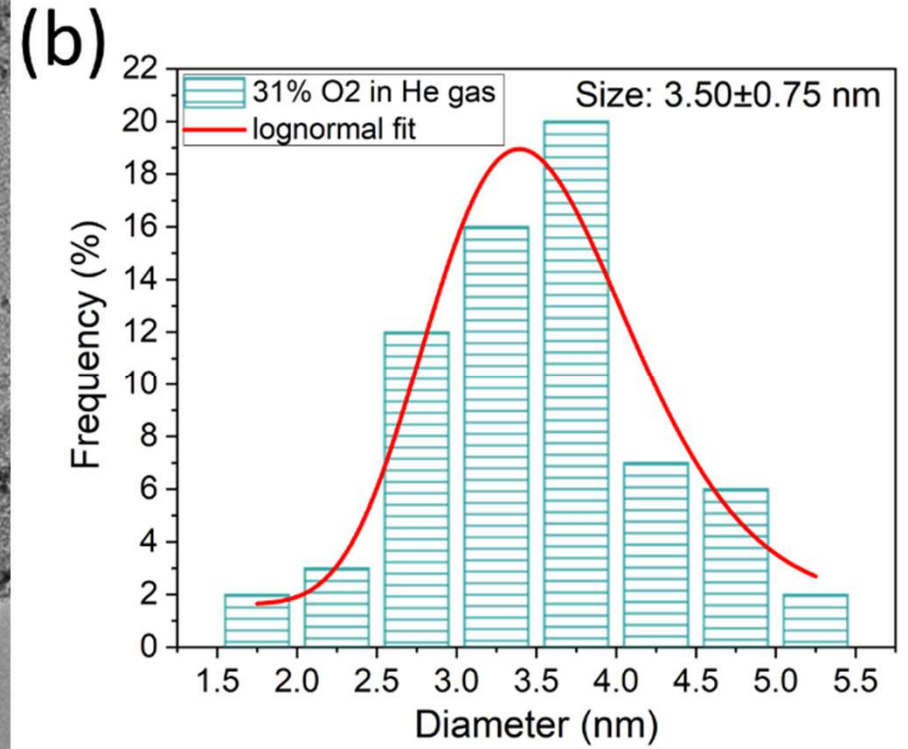
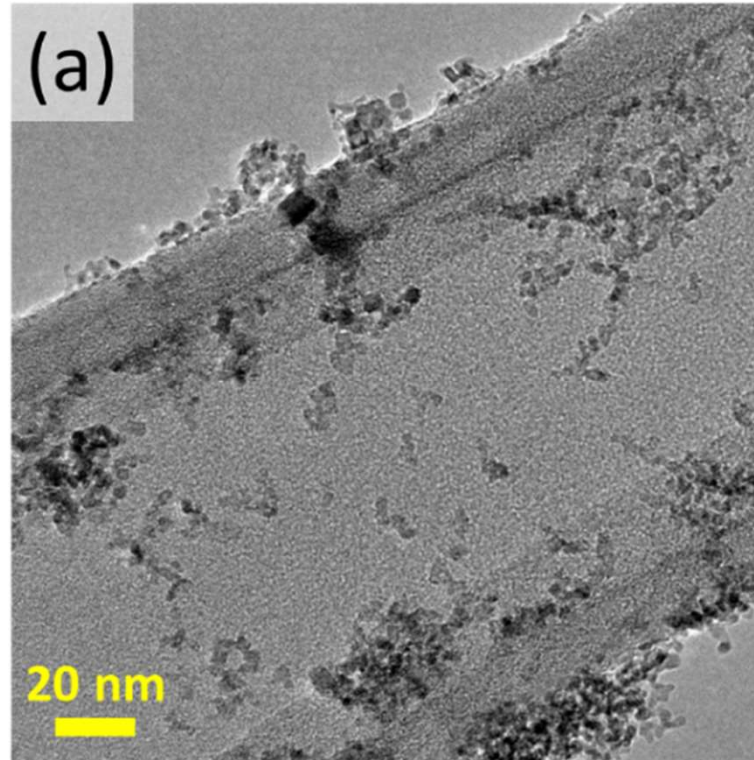
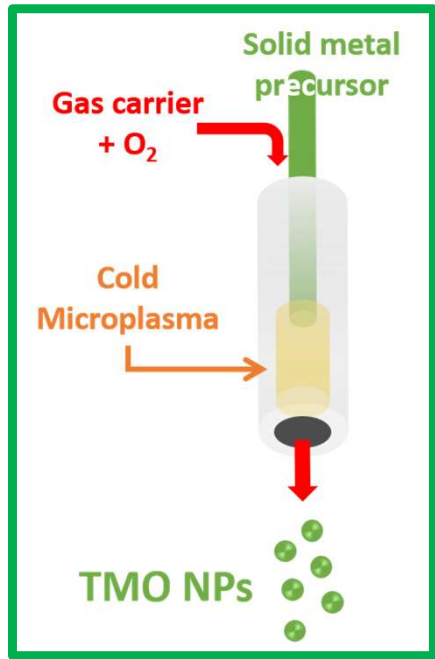
CuO quantum dots



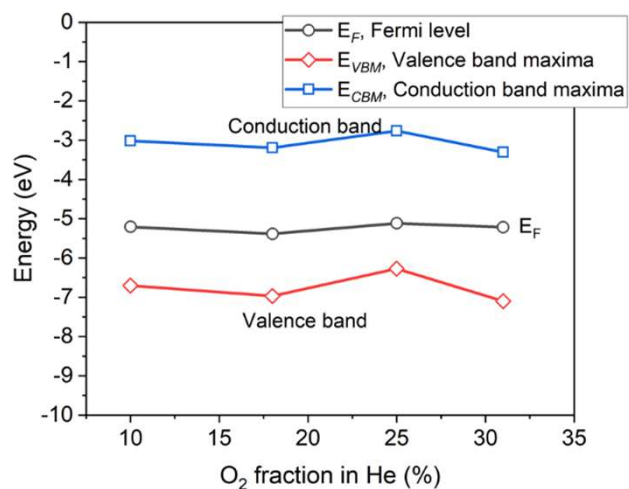
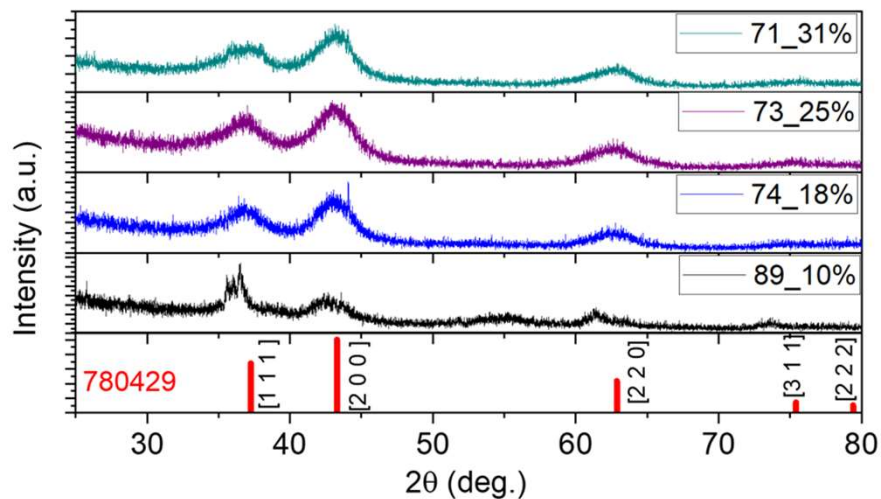
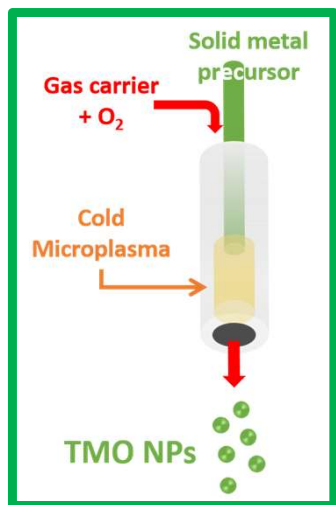
*J Phys D Appl Phys* 43 (2010) 415402  
*Appl Phys Lett* 104 (2014) 163103

*J Phys D: Appl Phys* 48 (2015) 314002  
*Nanoscale* 8 (2016) 6623

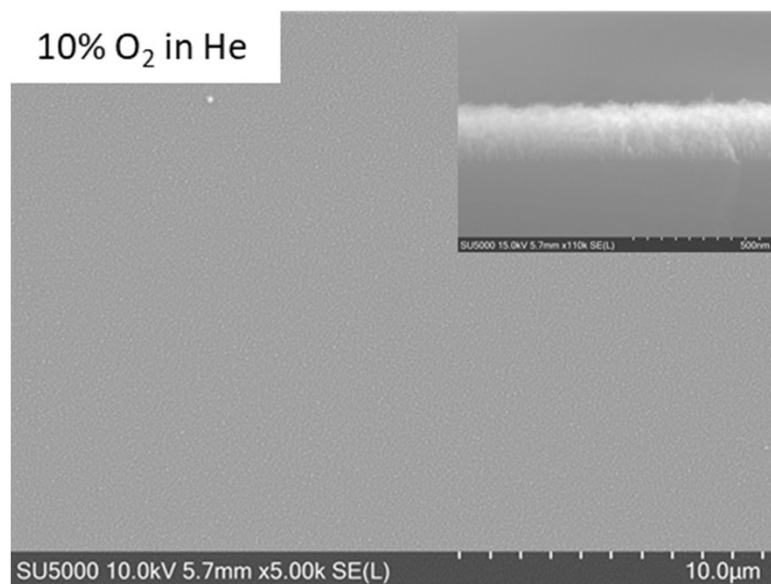
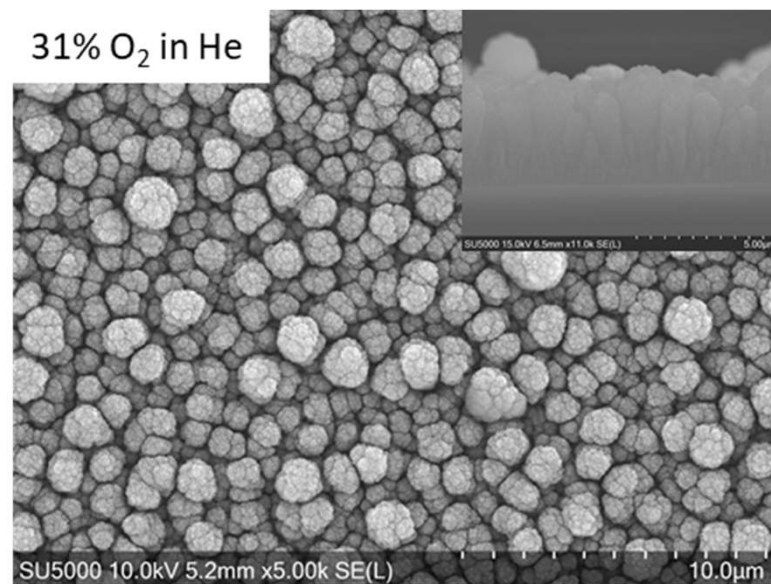
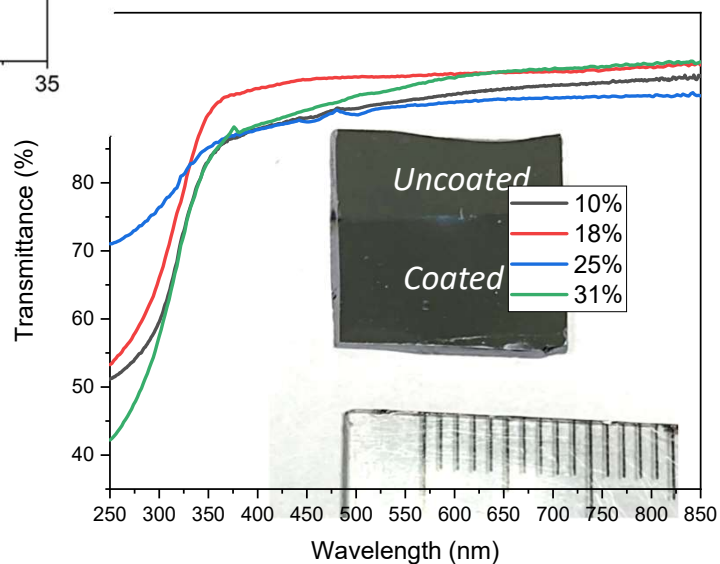
# NiO NP films



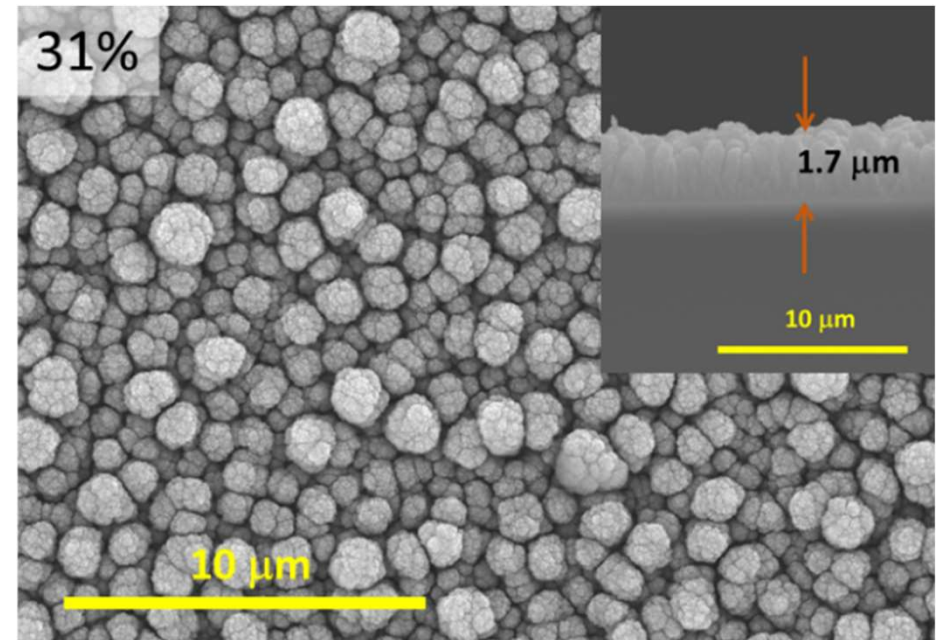
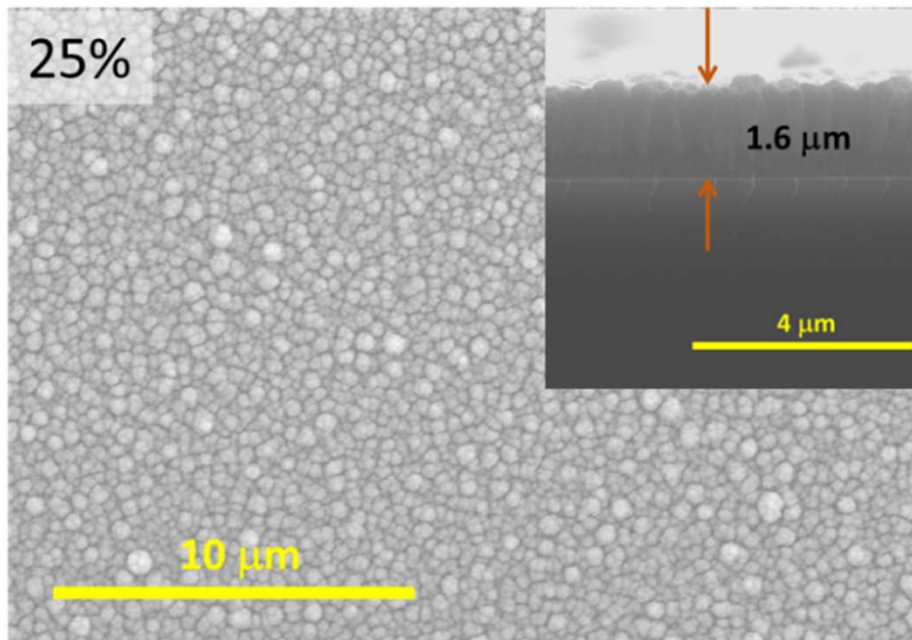
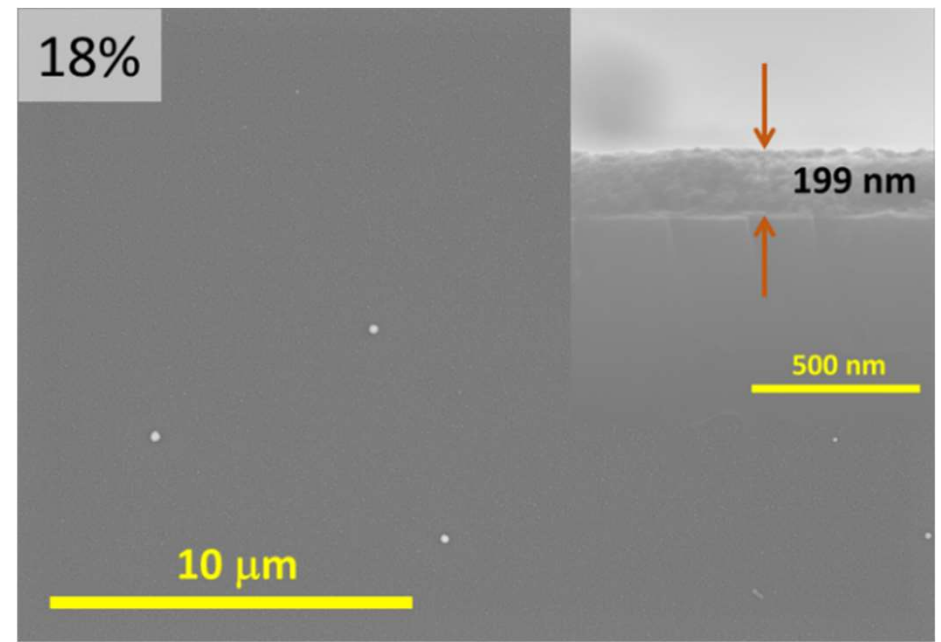
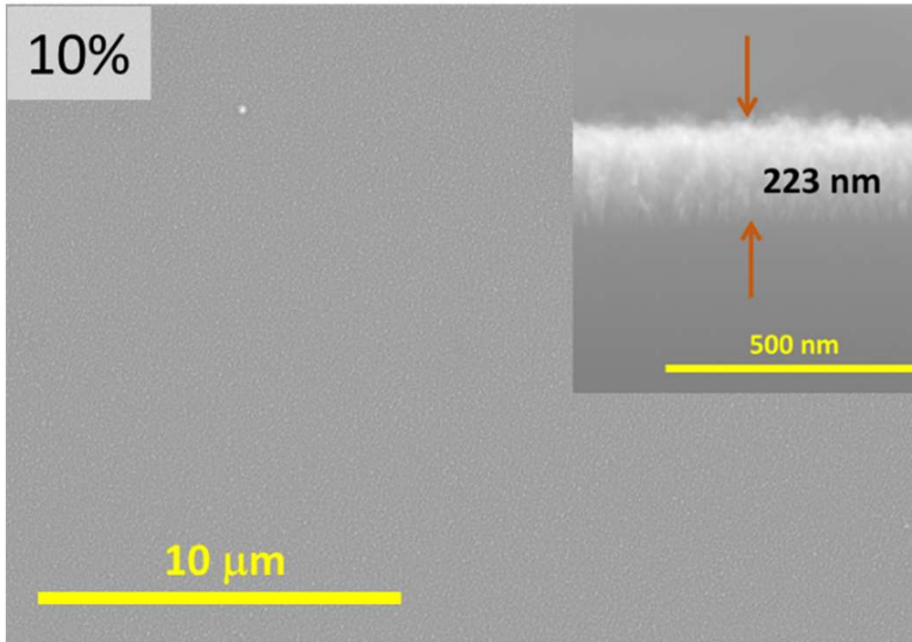
# Direct deposition of NiO NPs as transport layer for solar cells



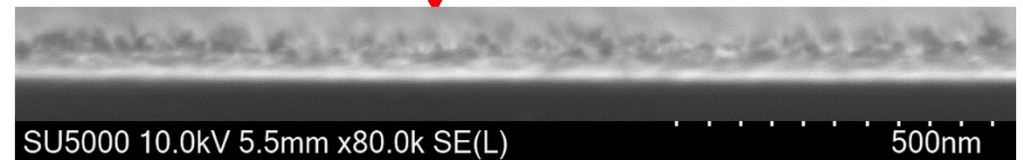
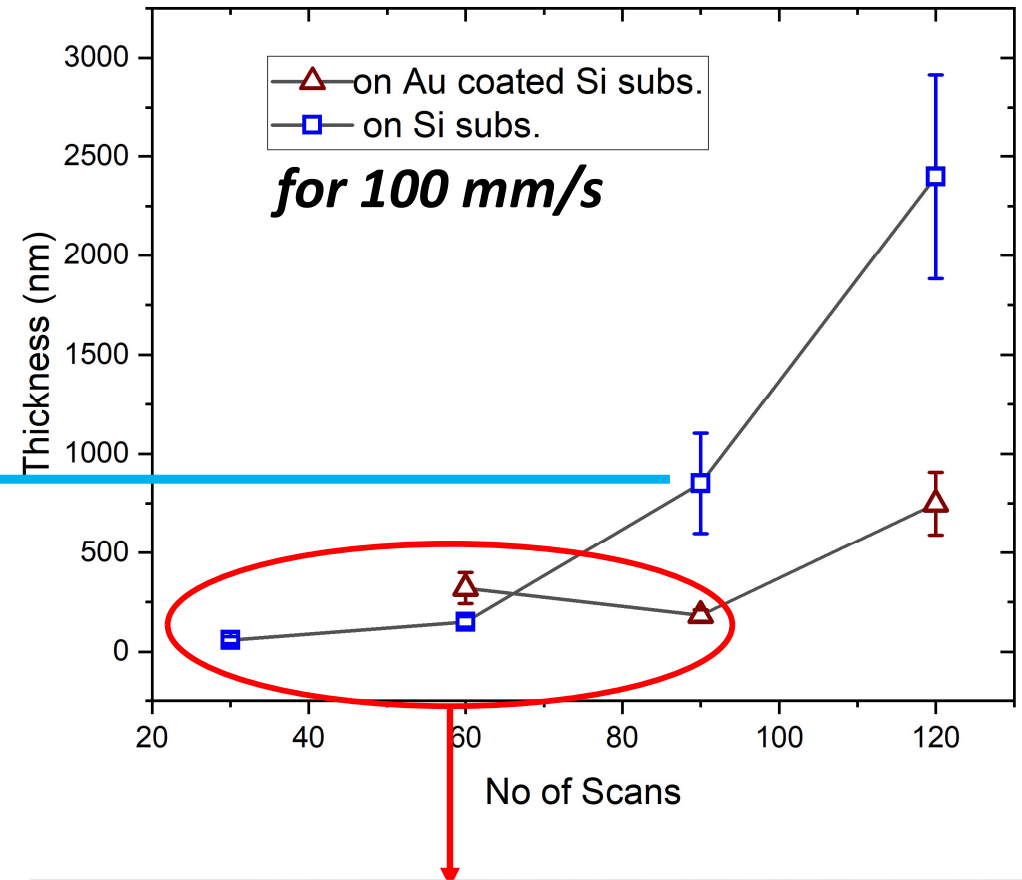
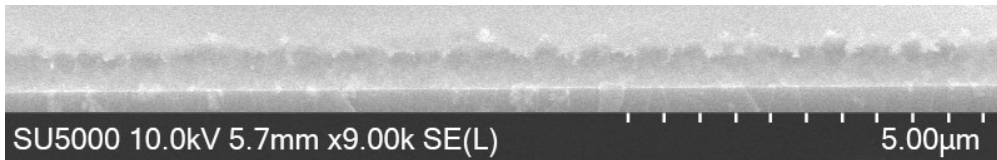
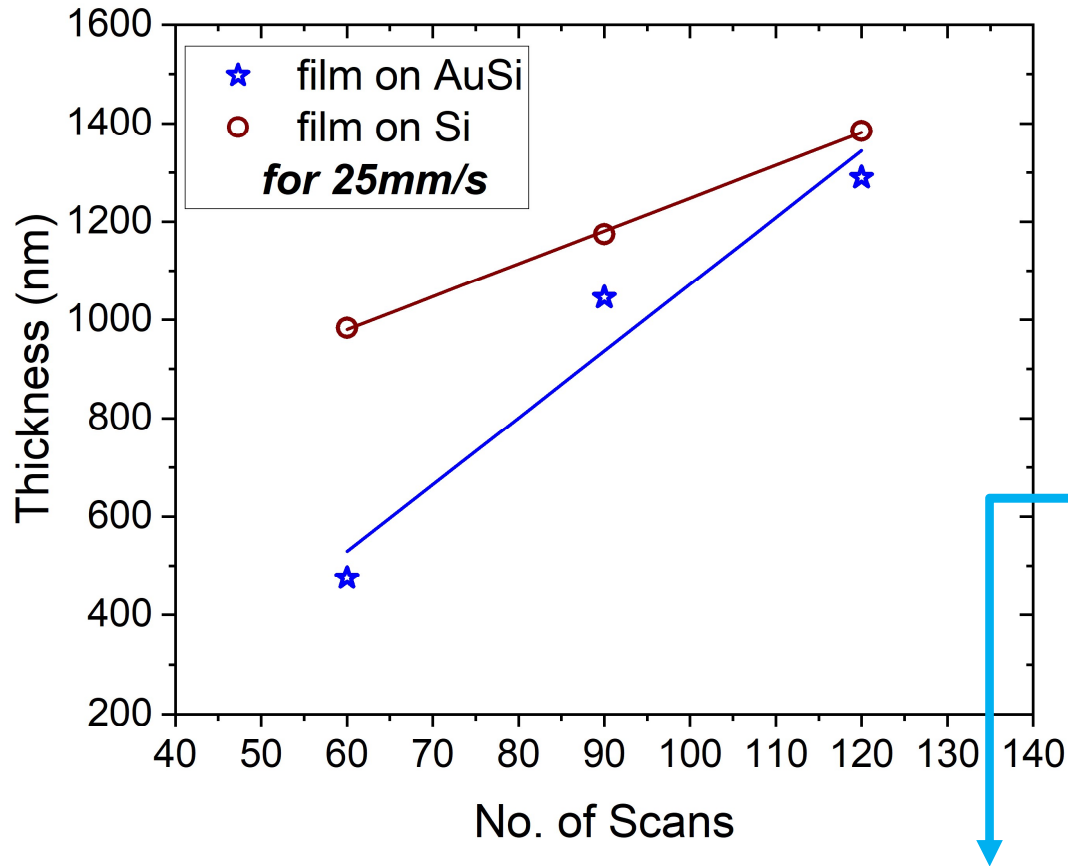
Oxygen  
10-31%



# NiO NP films



# NiO NP and film deposition

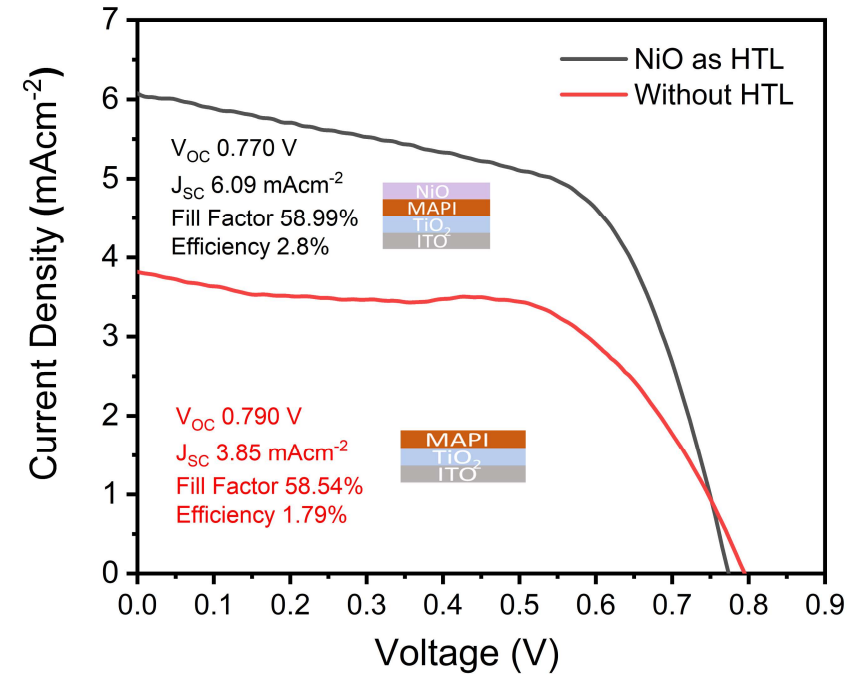
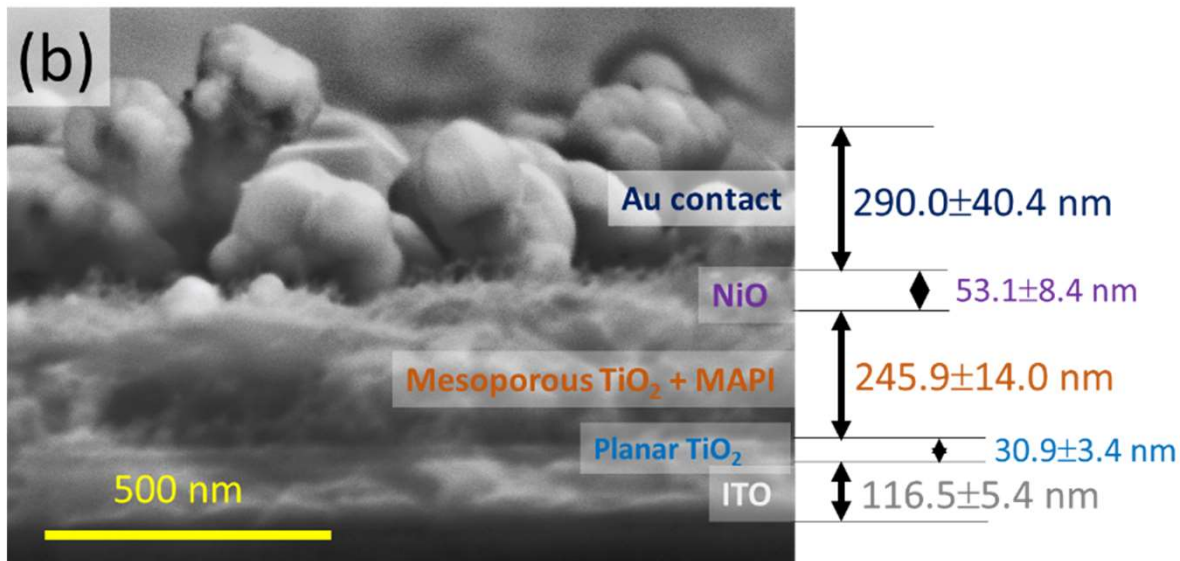


- current 750 nm thick:  $1.2 \times 10^{-2} \text{ m}^2 \text{ h}^{-1}$
- $\sim 7.5 \text{ nm}$  thick:  $1.2 \text{ m}^2 \text{ h}^{-1}$
- with 10x array:  $12 \text{ m}^2 \text{ min}^{-1}$  or  $12 \text{ m}^2 \text{ h}^{-1}$

Work in progress:

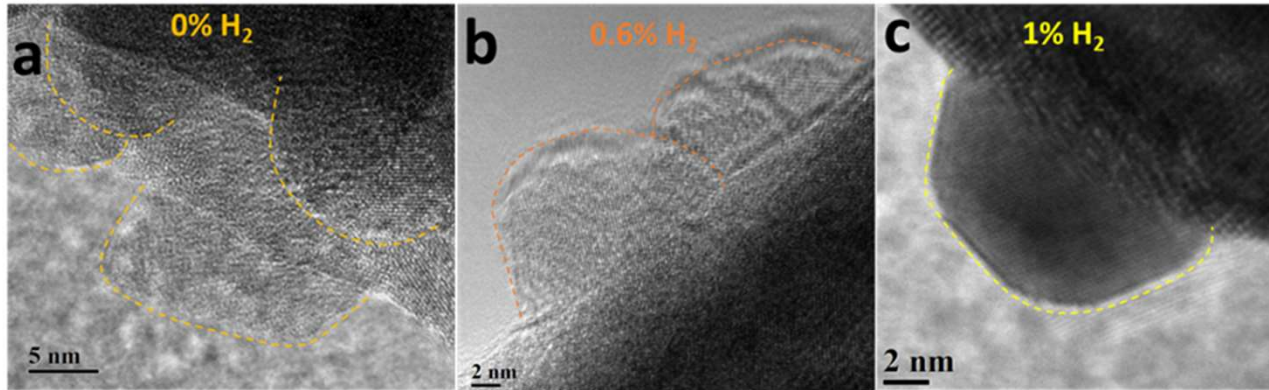
- Achieve required deposition speed
- Minimize roughness
- Assess and reduce porosity

# NiO QDs films



## FUTURE WORK

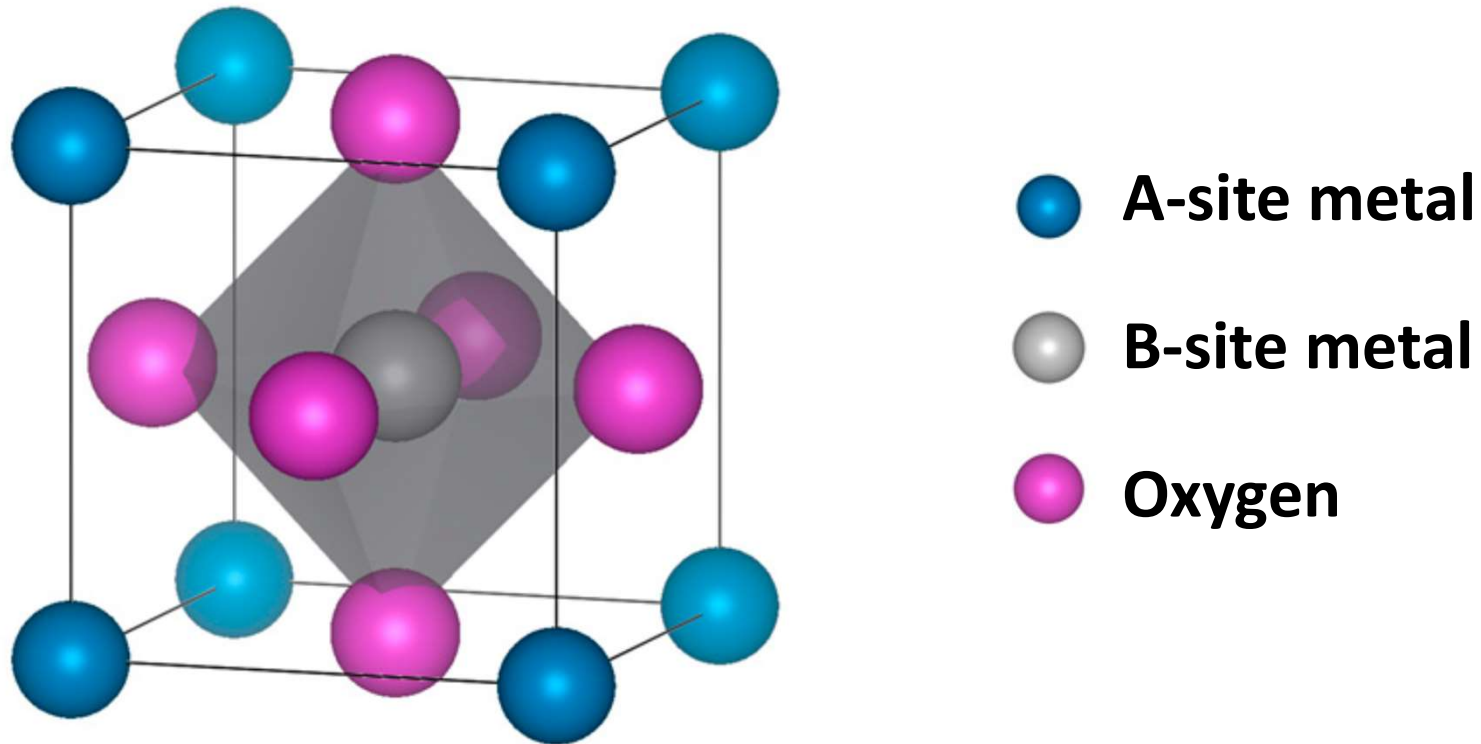
- Our target is ~10 nm thick film
- Reduce porosity and roughness
- Accurate evaluation of deposition parameters (e.g. speed, thickness, uniformity)



## *Exsolution from perovskite oxides*

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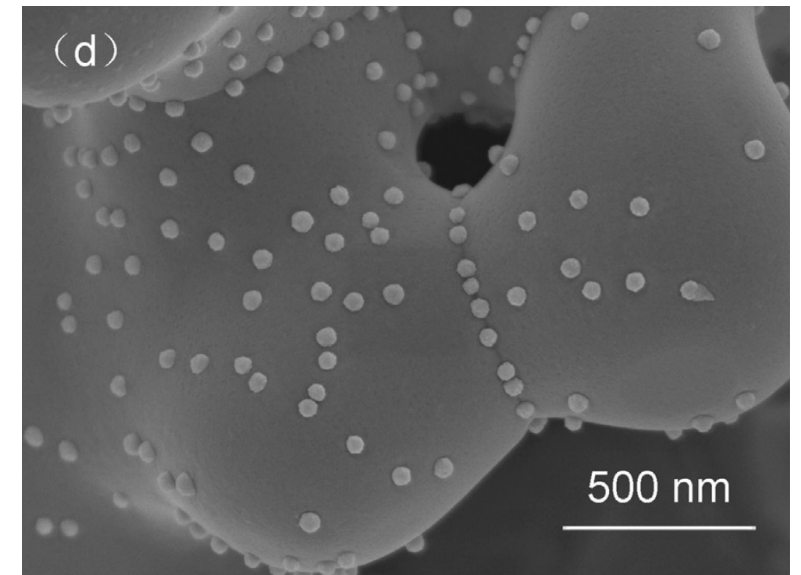
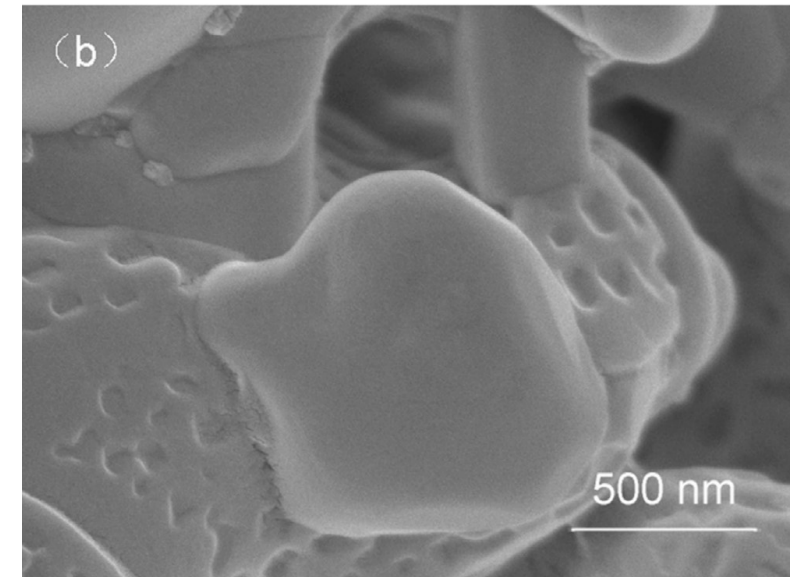
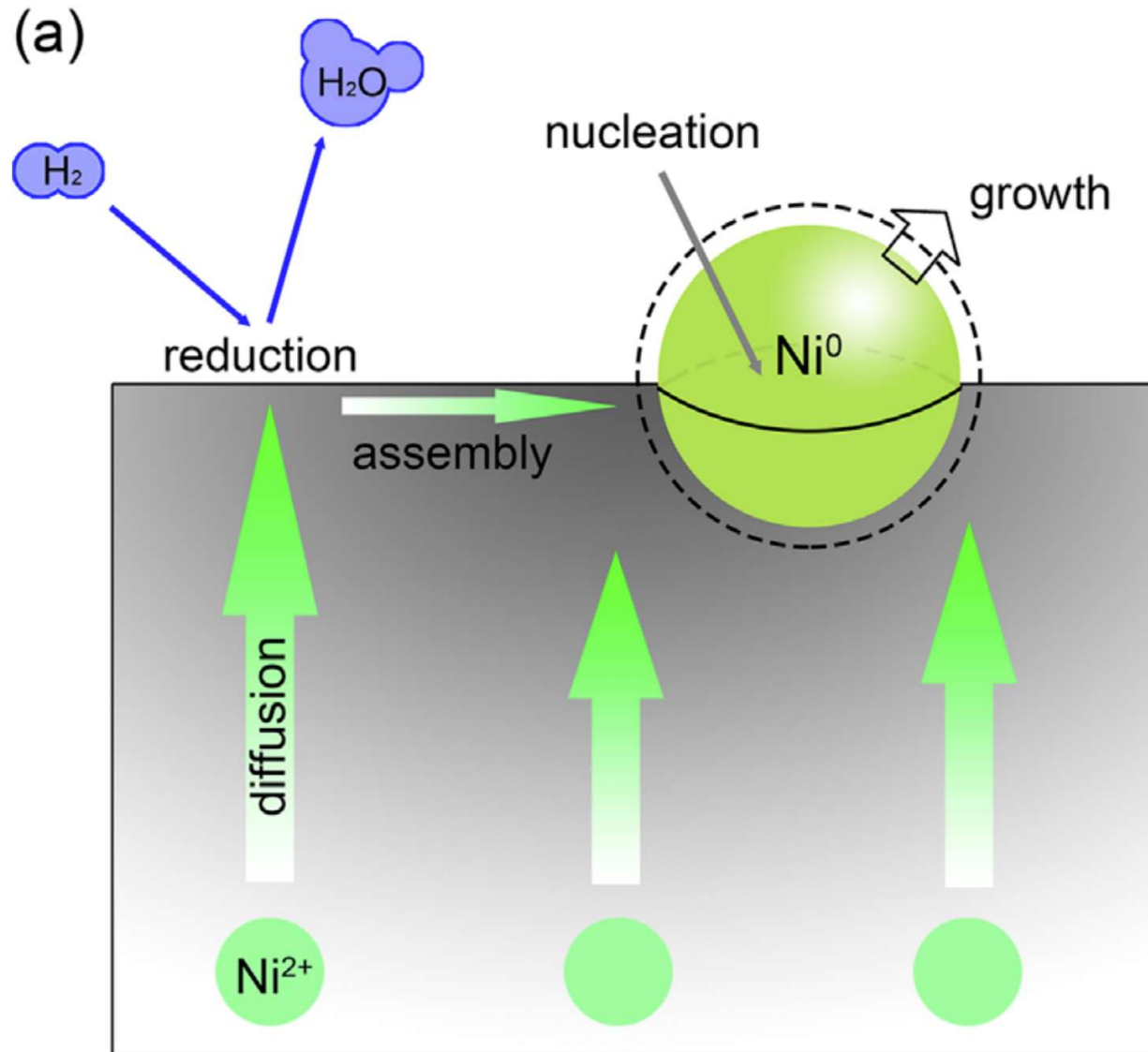
# *Perovskite oxides*



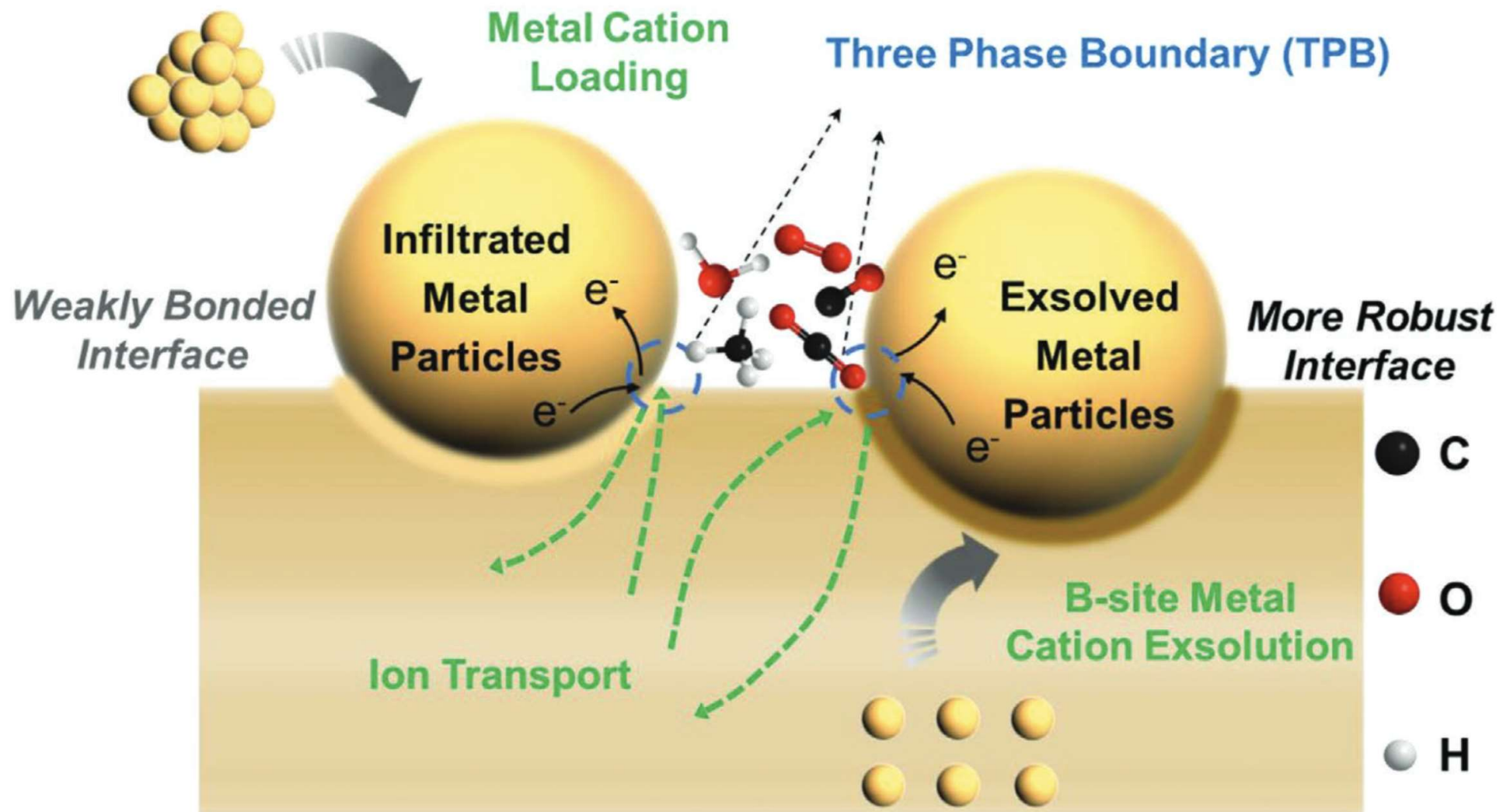
Many combinations are possible where doping and deficiency can play an important role



# Thermal exsolution by reducing atmosphere of perovskite oxides



# Thermal exsolution by reducing atmosphere of perovskite oxides

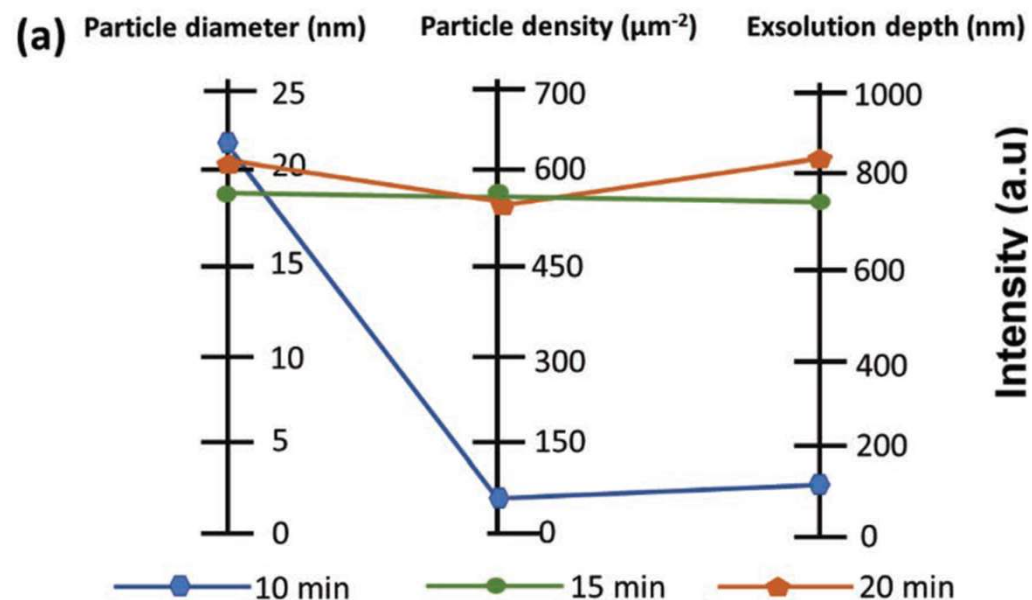
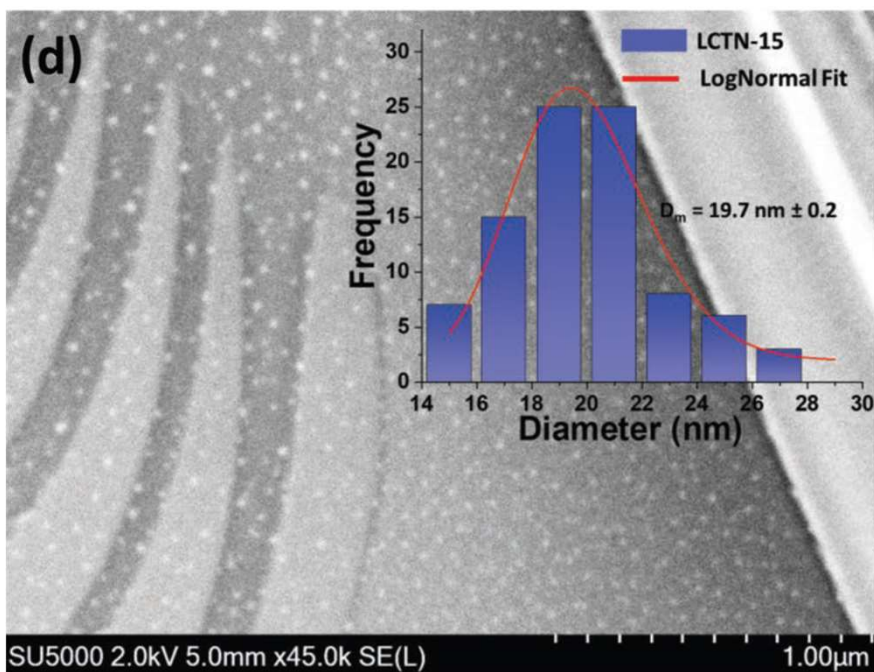


Very high temperatures!!!

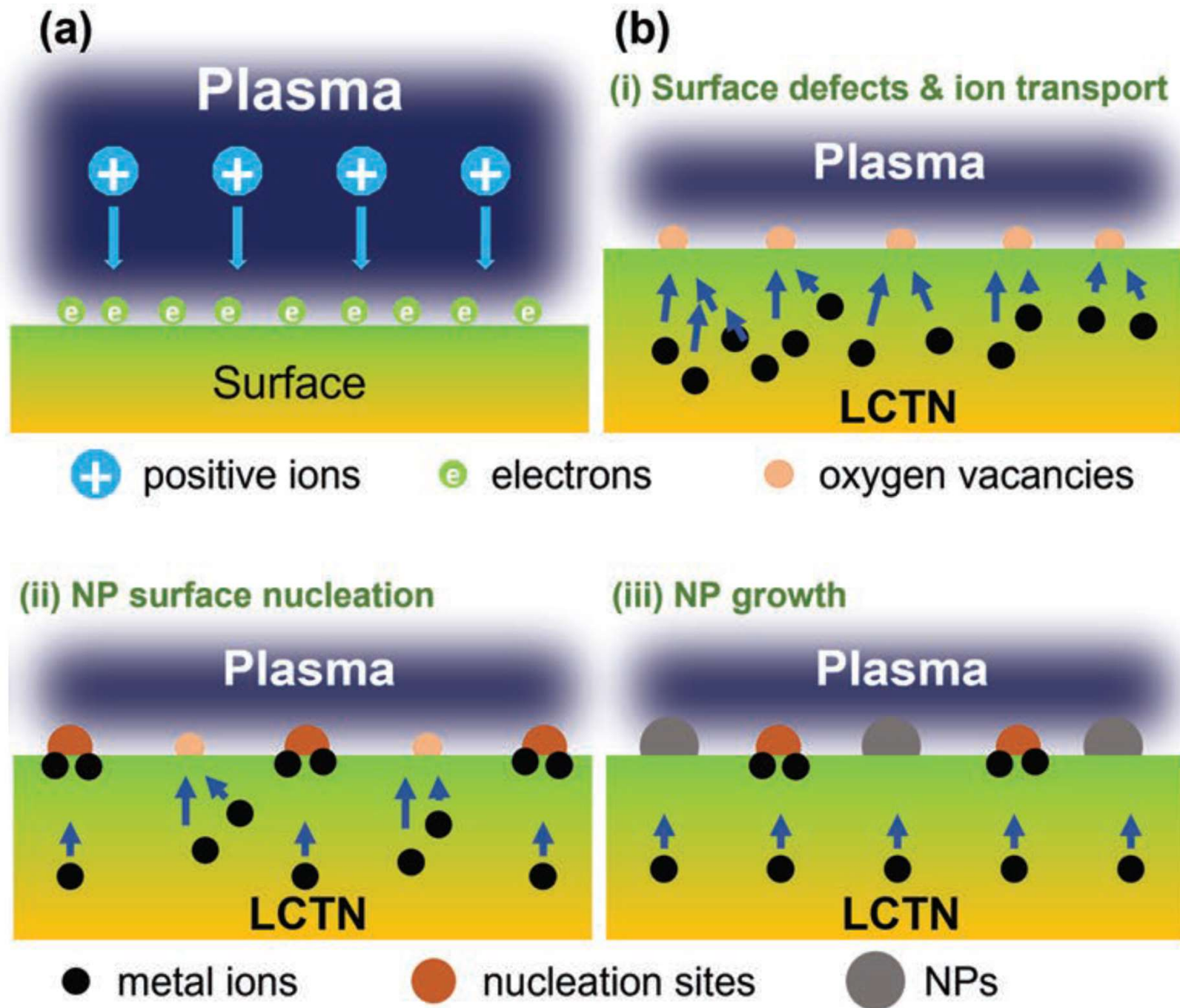
Small 2021, 17, 2005383

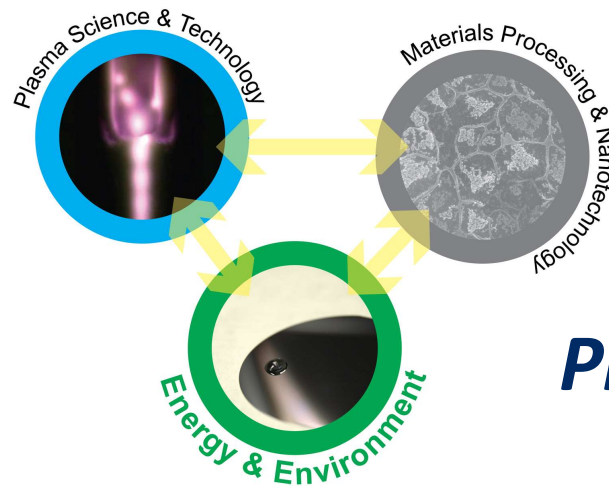
# Rapid Plasma Exsolution from an A-site Deficient Perovskite Oxide at Room Temperature

Hessan Khalid,\* Atta ul Haq, Bruno Alessi, Ji Wu, Cristian D. Savaniu, Kalliopi Kousi, Ian S. Metcalfe, Stephen C. Parker, John T. S. Irvine, Paul Maguire, Evangelos I. Papaioannou, and Davide Mariotti\*



# Mechanisms of plasma exsolution





***Prof Davide Mariotti***

*([www.plasmamate.org](http://www.plasmamate.org))*

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