UNIVERSITY OF OXFORD

Hoye Group

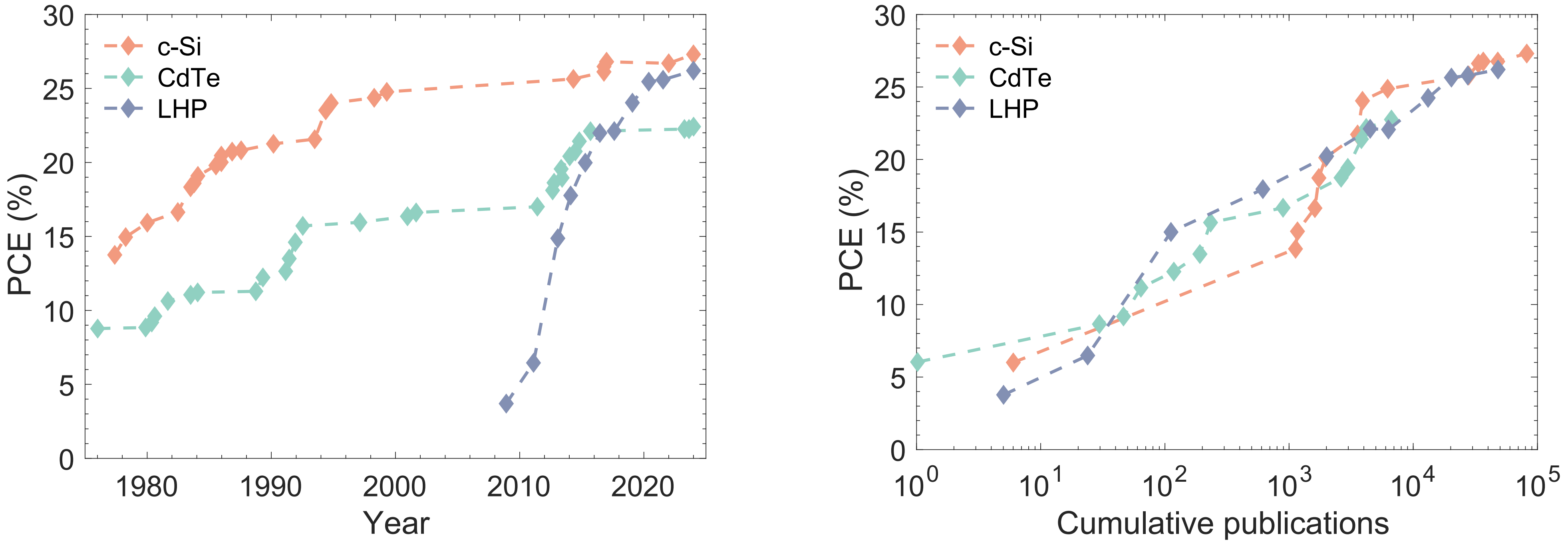
Chemistry of Sustainable Materials

ns^2 semiconductors: Discovery, AI and Photoelectrochemical Applications

Prof. Robert Hoye

Inorganic Chemistry Laboratory, University of Oxford

Rapid technological learning rate of LHP photovoltaics



Mosquera-Lois, Huang, Lohan, Ye, Walsh,* Hoye,* *Nat. Rev. Chem.* **9**, 287 (2025)

Outline of talk

1. Materials discovery
2. Turning CO_2 into useful chemicals
3. AI to accelerate materials optimisation

Defect tolerance

Section 1

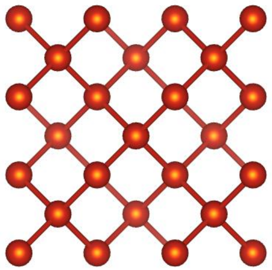
Our proposed definition of defect tolerance

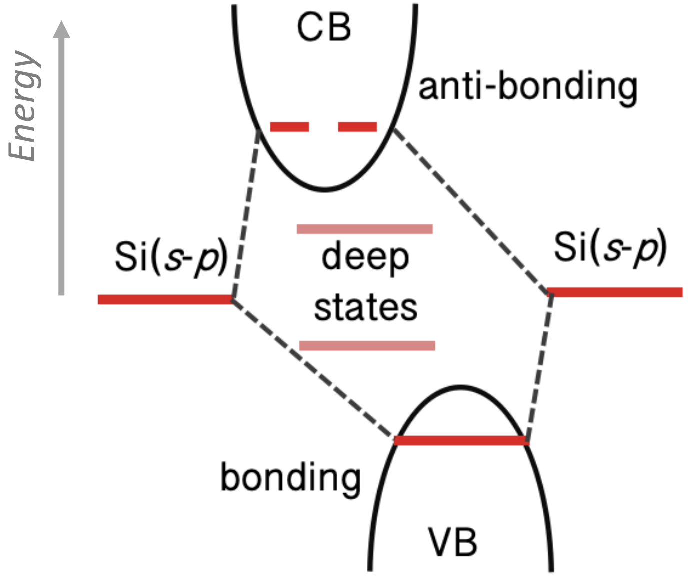
"the effect, where a semiconductor, which readily forms free carriers, does not experience a substantial increase in its non-radiative recombination rate or reduction in charge-carrier mobilities when defects are present in high concentrations"

Mosquera-Lois, Huang, Lohan, Ye, Walsh,* Hoye,* *Nat. Rev. Chem.* **9**, 287 (2025)

Inferring Defect Tolerance from Electronic Structure

Silicon (defect-sensitive)

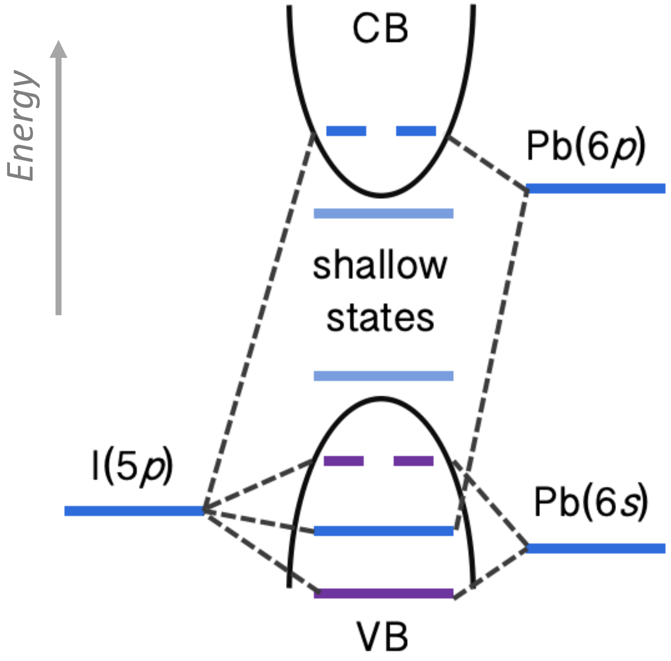


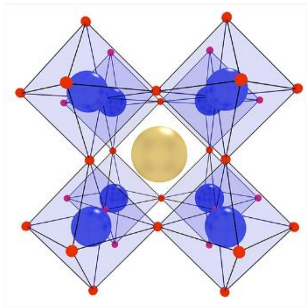


Defect density:
10^8 cm^{-3}

PV efficiency:
23.3%

Lead-halide perovskite (defect-tolerant)



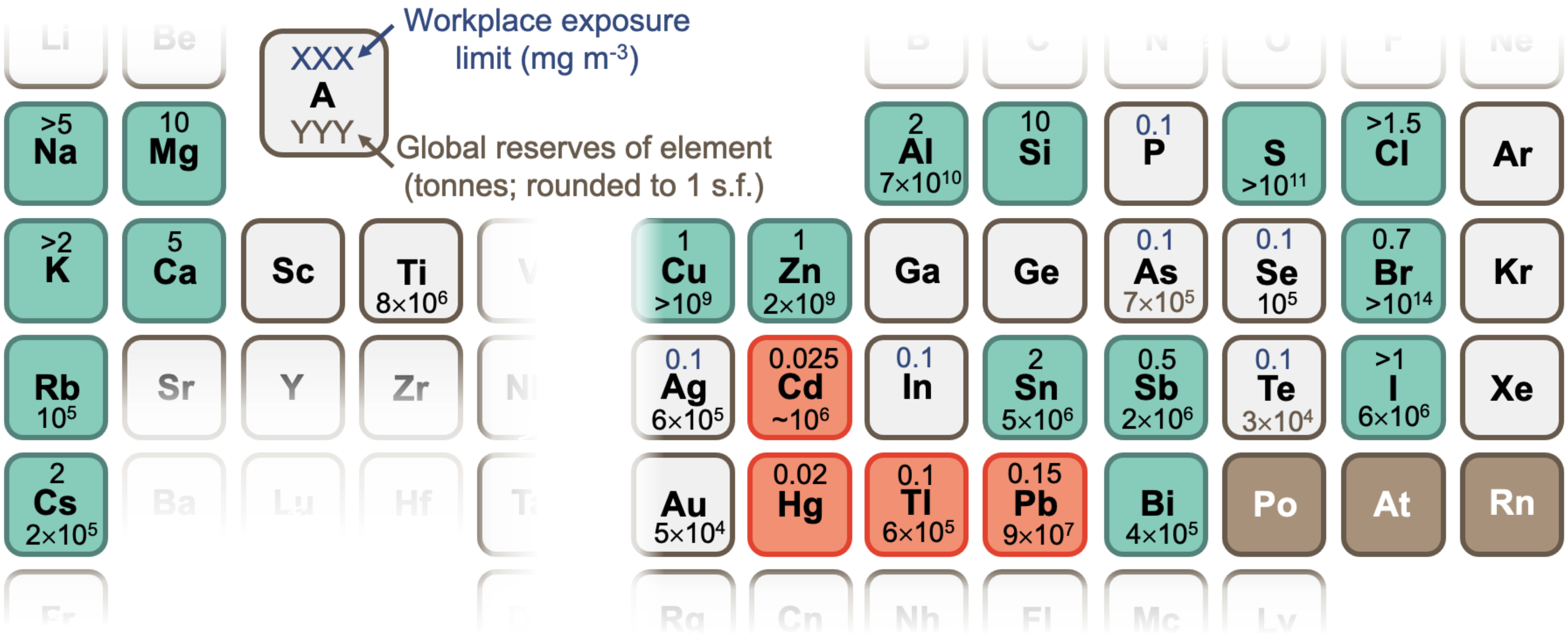


Defect density:
10^{15}–10^{16} cm^{-3}

PV efficiency:
28.0%

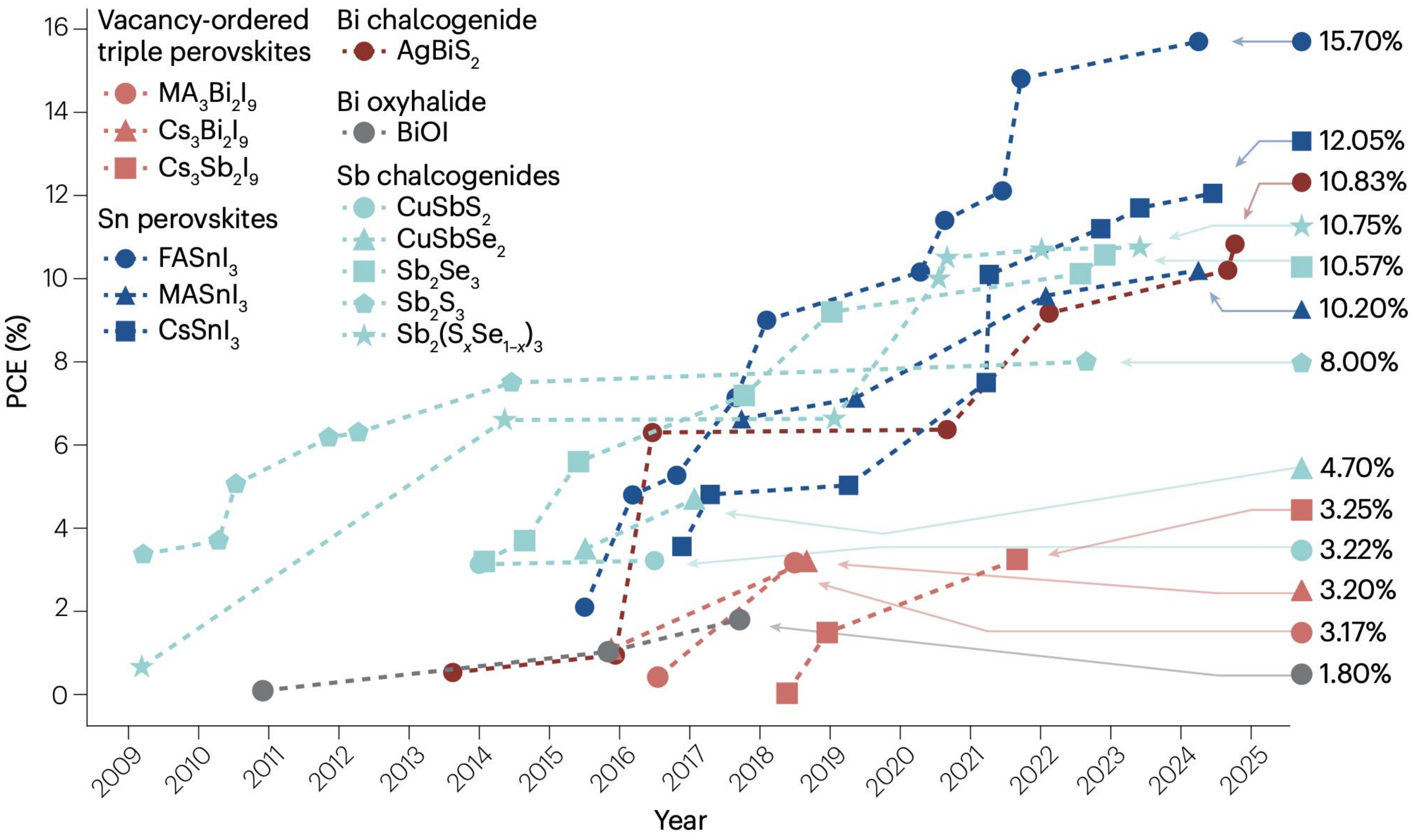
Brandt, Stevanović, Ginley, Buonassisi, *MRS Commun.*, **5**, 265 (2015)

Bismuth – A Green Element in Poisoner's Corridor



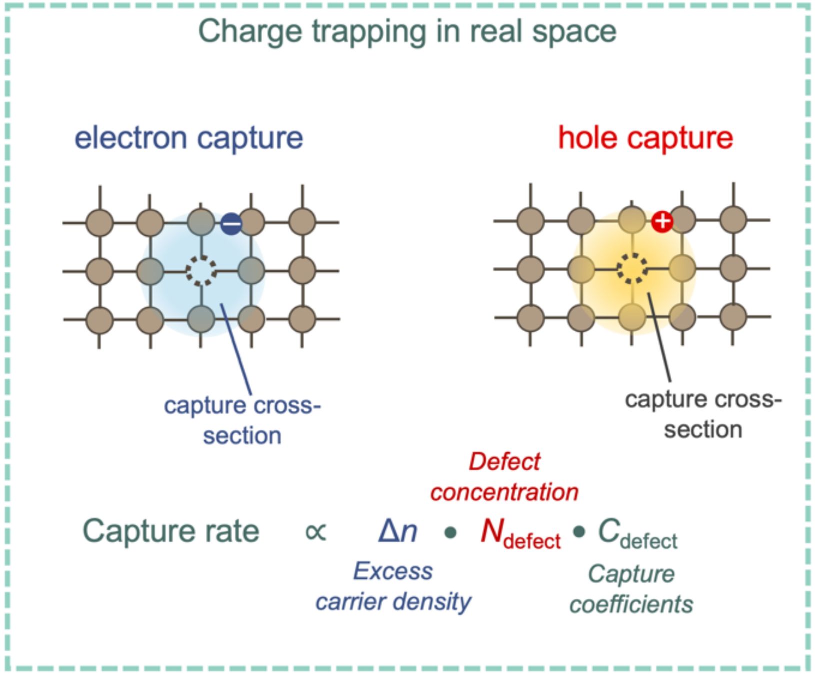
Hoye, *et al.*, *Adv. Energy Mater.*, **12**, 2100499 (2021)

Slower development of Pb-free alternatives



Mosquera-Lois, Huang, Lohan, Ye, Walsh,* Hoye,* *Nat. Rev. Chem.* **9**, 287 (2025)

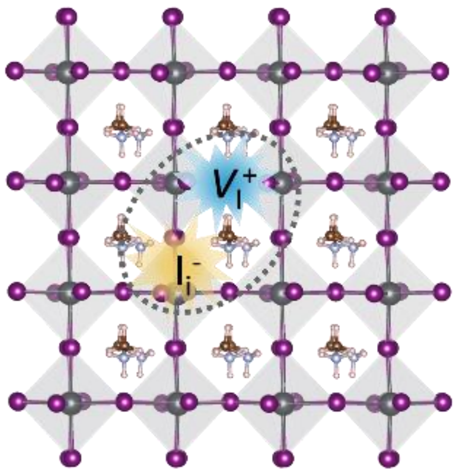
Manifestations of defect tolerance



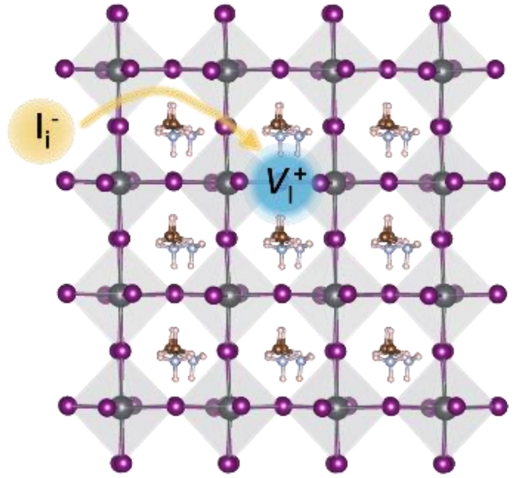
1. Low C_{defect}

- Shallow traps
- Low capture cross-sections

2. Defect complexes

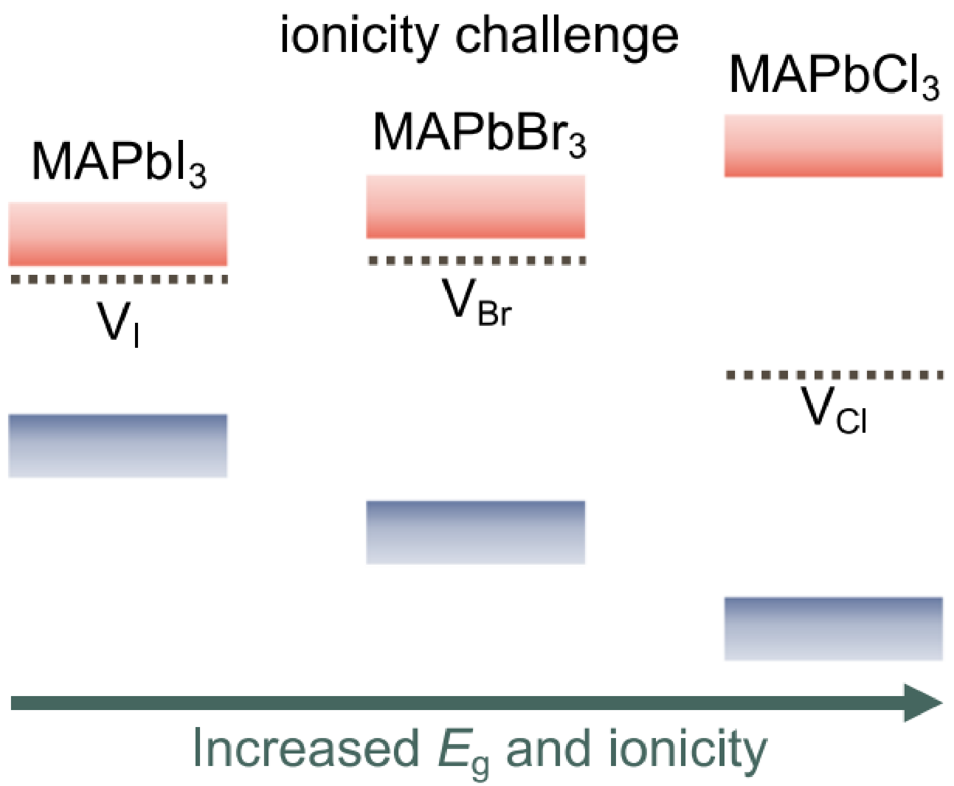


3. Self-healing



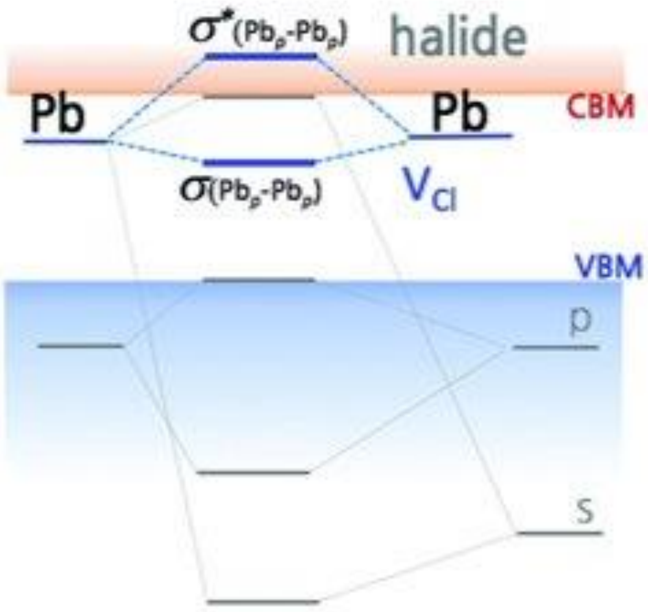
Mosquera-Lois, Huang, Lohan, Ye, Walsh,* Hoye,* *Nat. Rev. Chem.* **9**, 287 (2025)

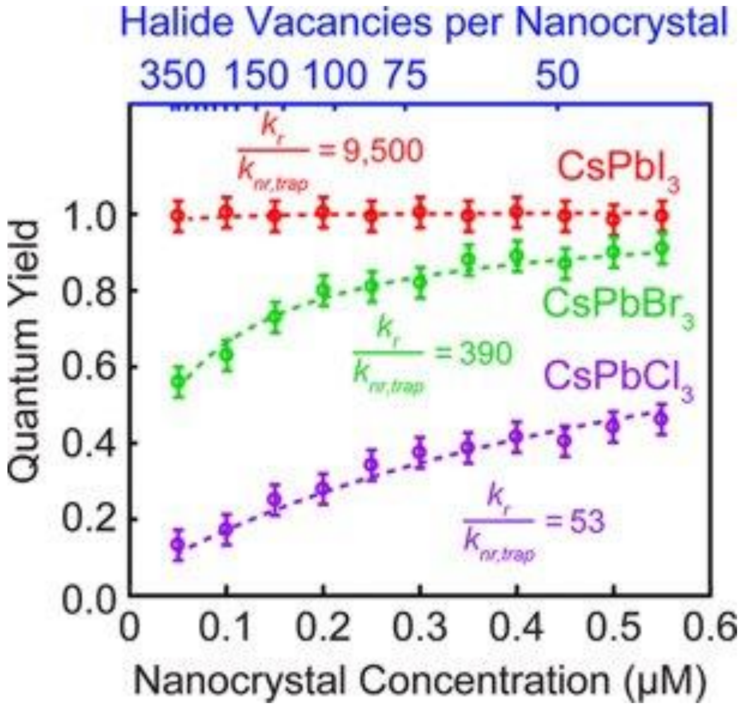
Dangling bond hybridization needs to be accounted for

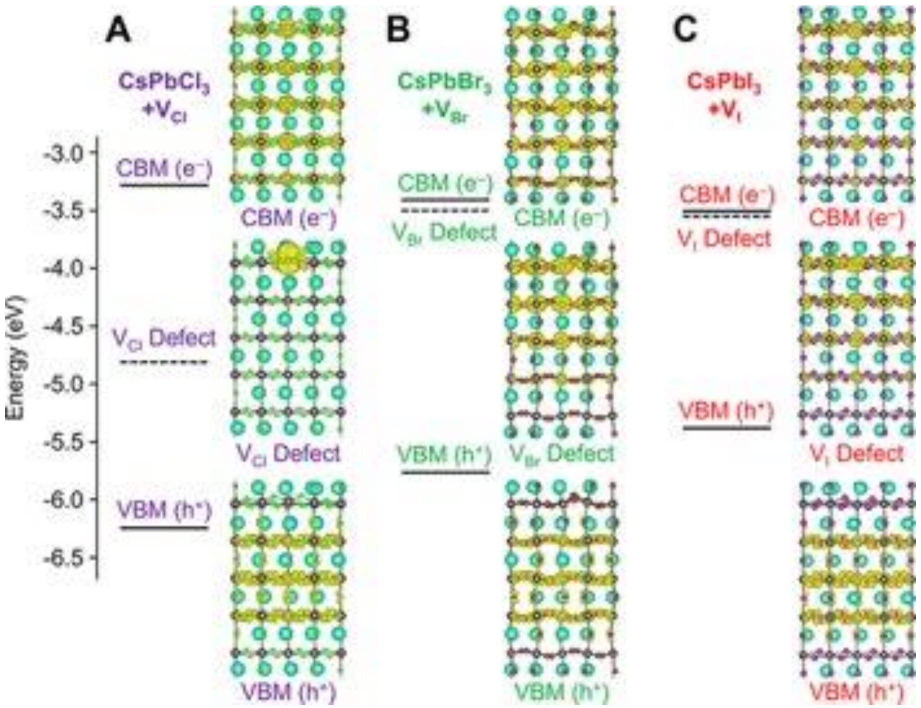


Ganose, Scanlon, Walsh, Hoye,* *Nat. Commun.*, **13**, 4715 (2022)

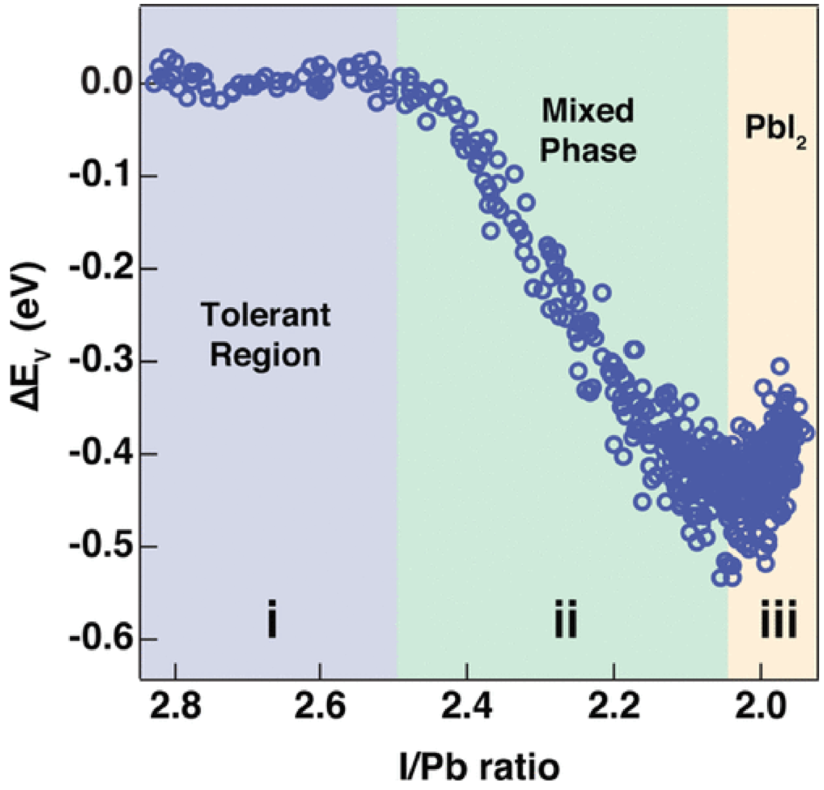
Dangling bond hybridization needs to be accounted for

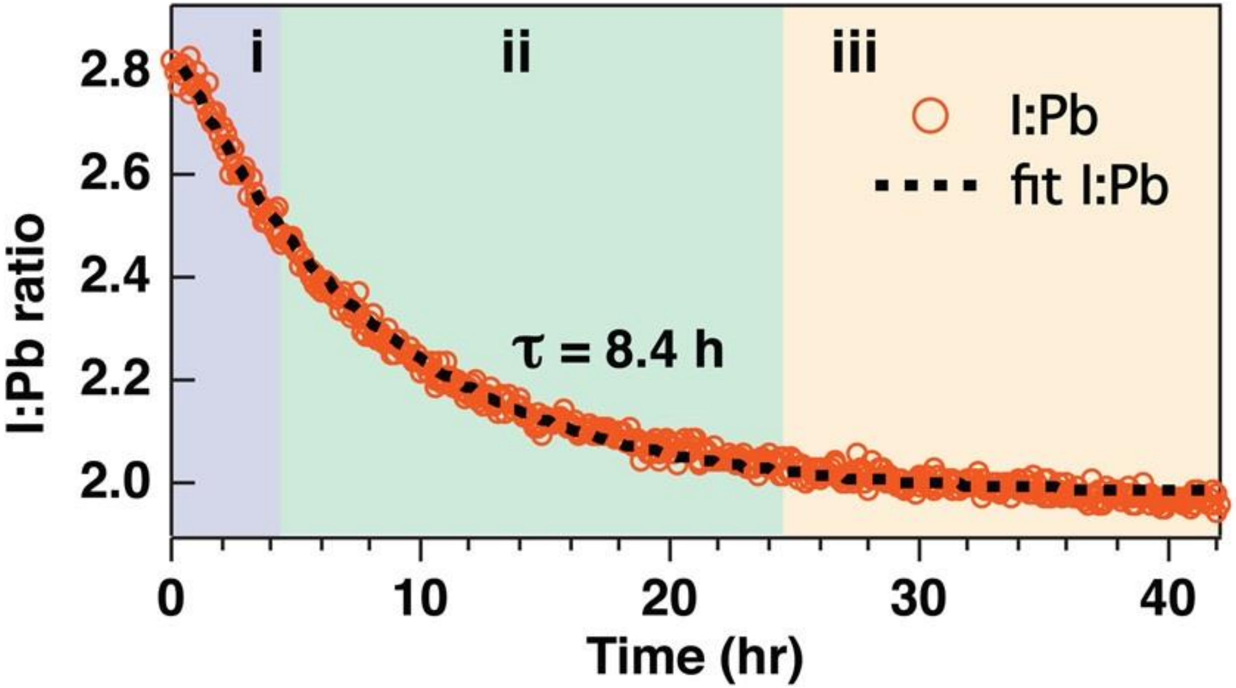






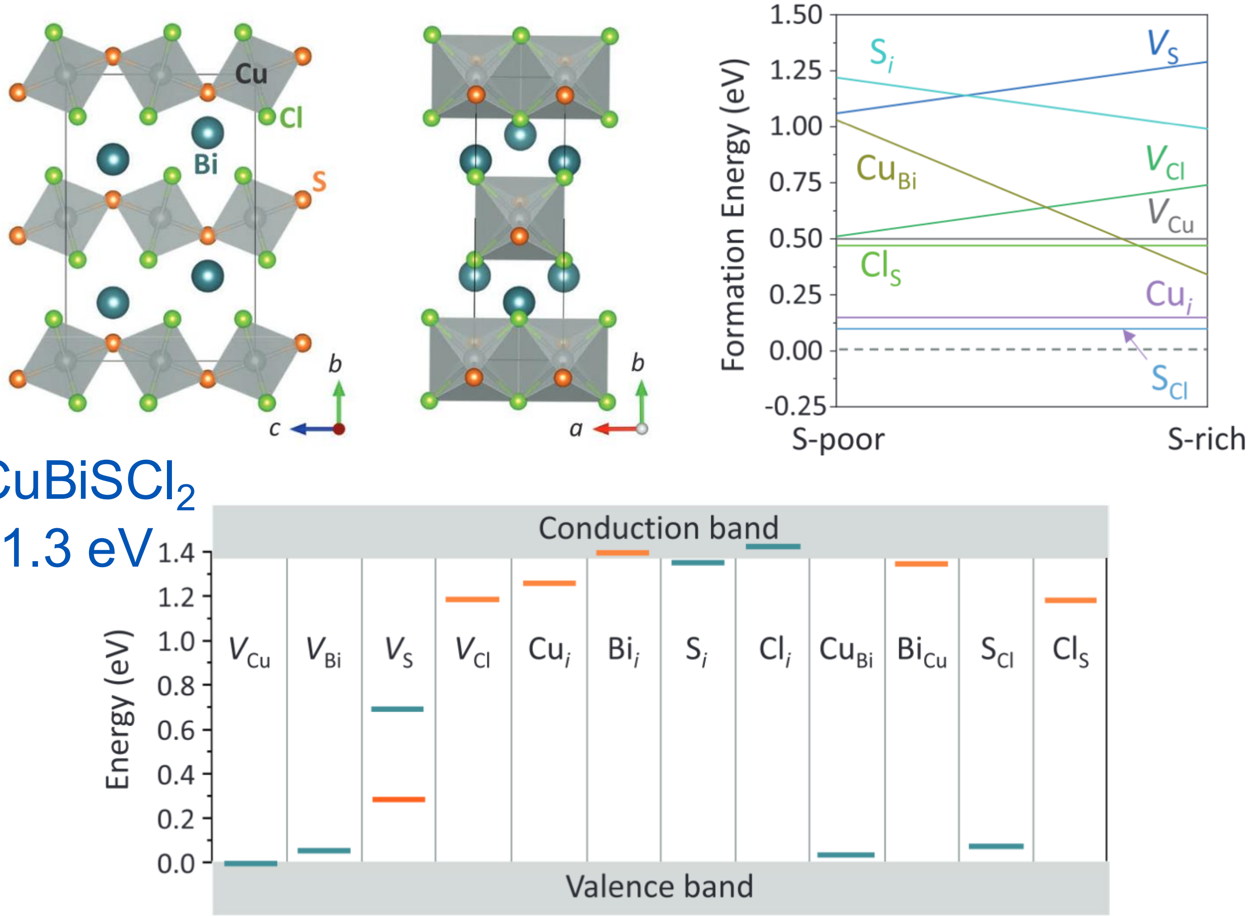
Experimental evidence for defect tolerance





Steier, *et al.*, *ACS Energy Lett.*, **1**, 360 (2016)

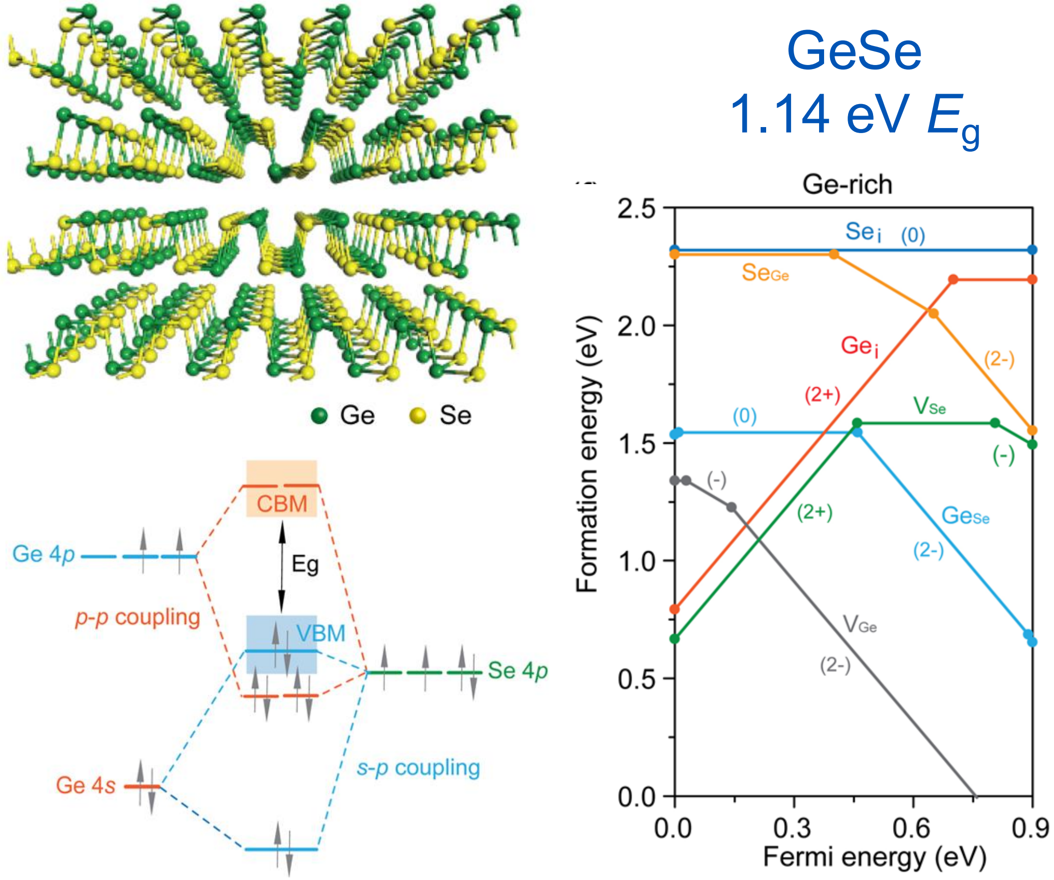
Other examples of materials suggested to be defect tolerant



$CuBiSCl_2$
1.3 eV

Adv. Funct. Mater., **32**, 2112682 (2022)

GeSe
1.14 eV E_g

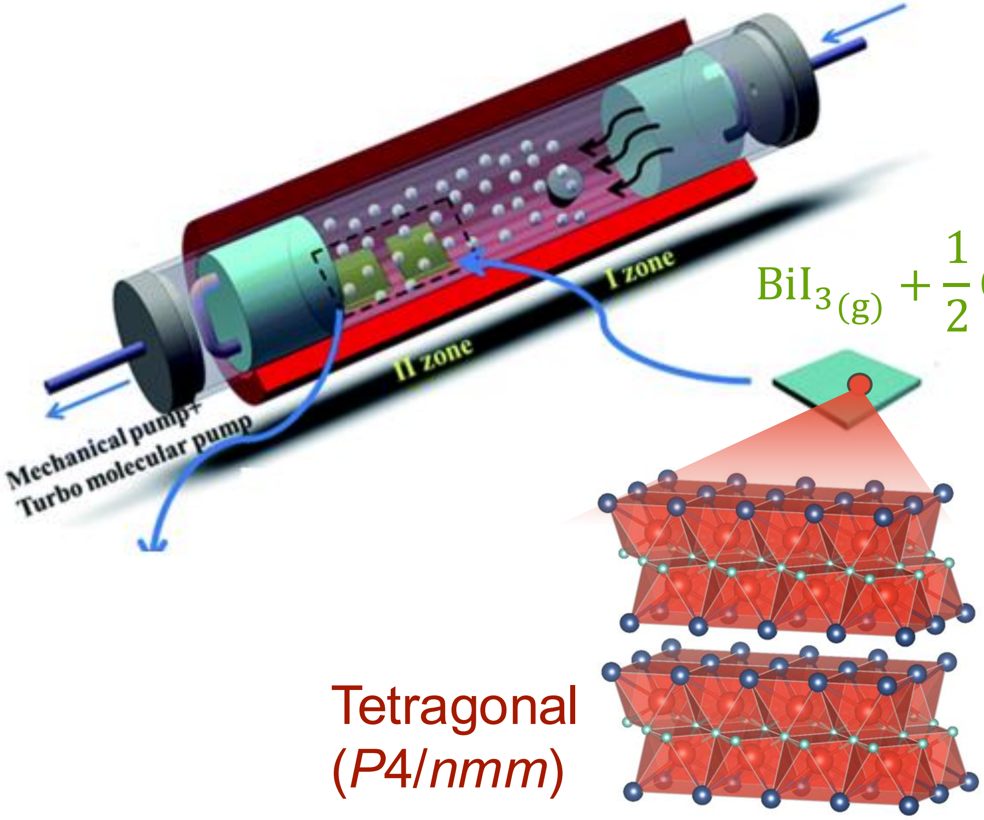


Nat. Commun., **12**, 670 (2021)

Solar fuels

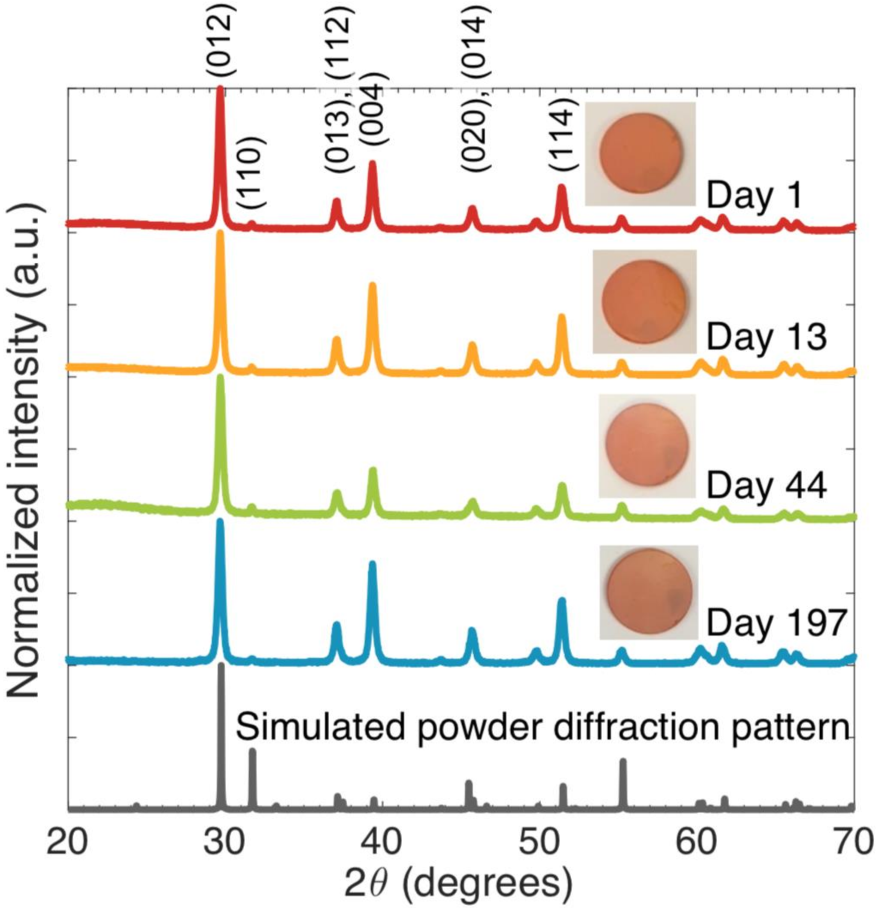
Section 2

Example material: BiOI – stable ns^2 compound



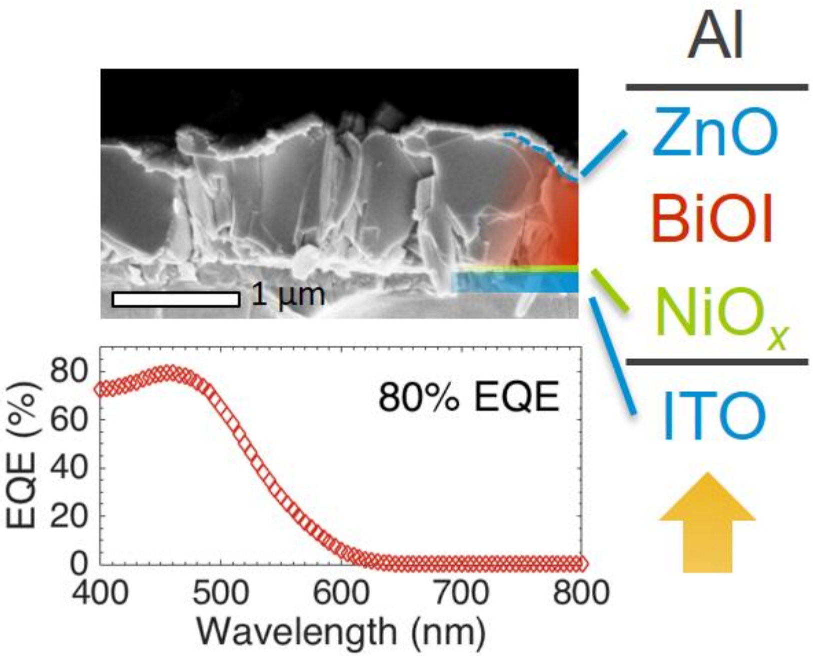
$$BiI_{3\,(g)} + \frac{1}{2} O_{2\,(g)} \rightleftharpoons BiOI_{(s)} + I_{2\,(g)}$$

Tetragonal
($P4/nmm$)



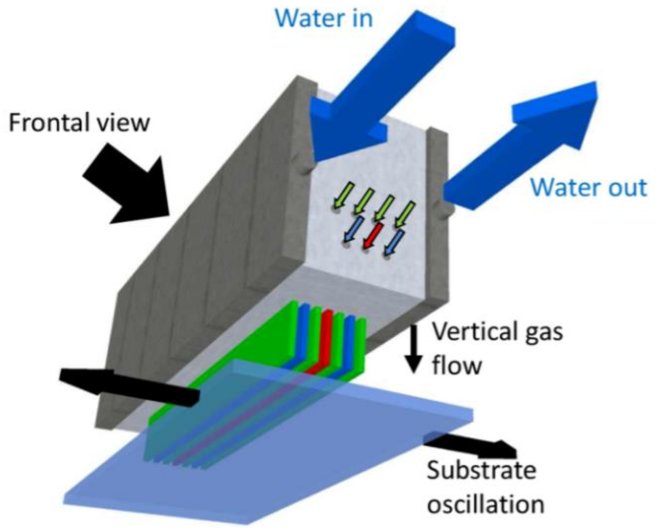
Hoye, *et al.*, *Adv. Mater.*, **29**, 1702176 (2017)

All-inorganic device structure that achieved EQE up to 80%

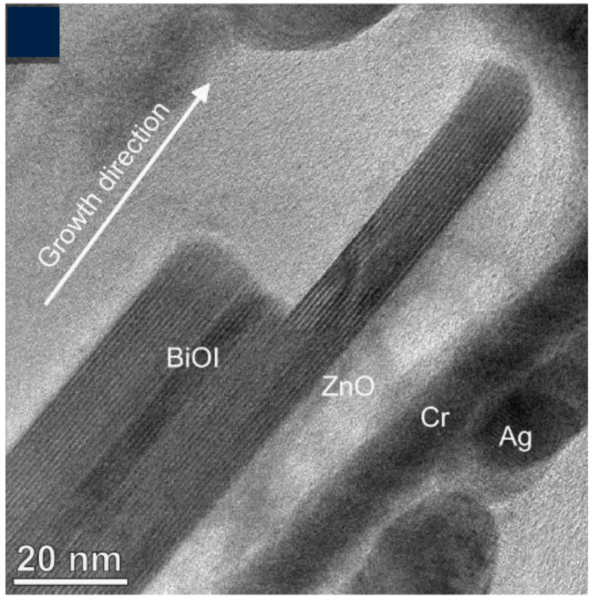


Band gap: 1.9 eV (650 nm)

Hoye, *et al.*, *Adv. Mater.*, **29**, 1702176 (2017)

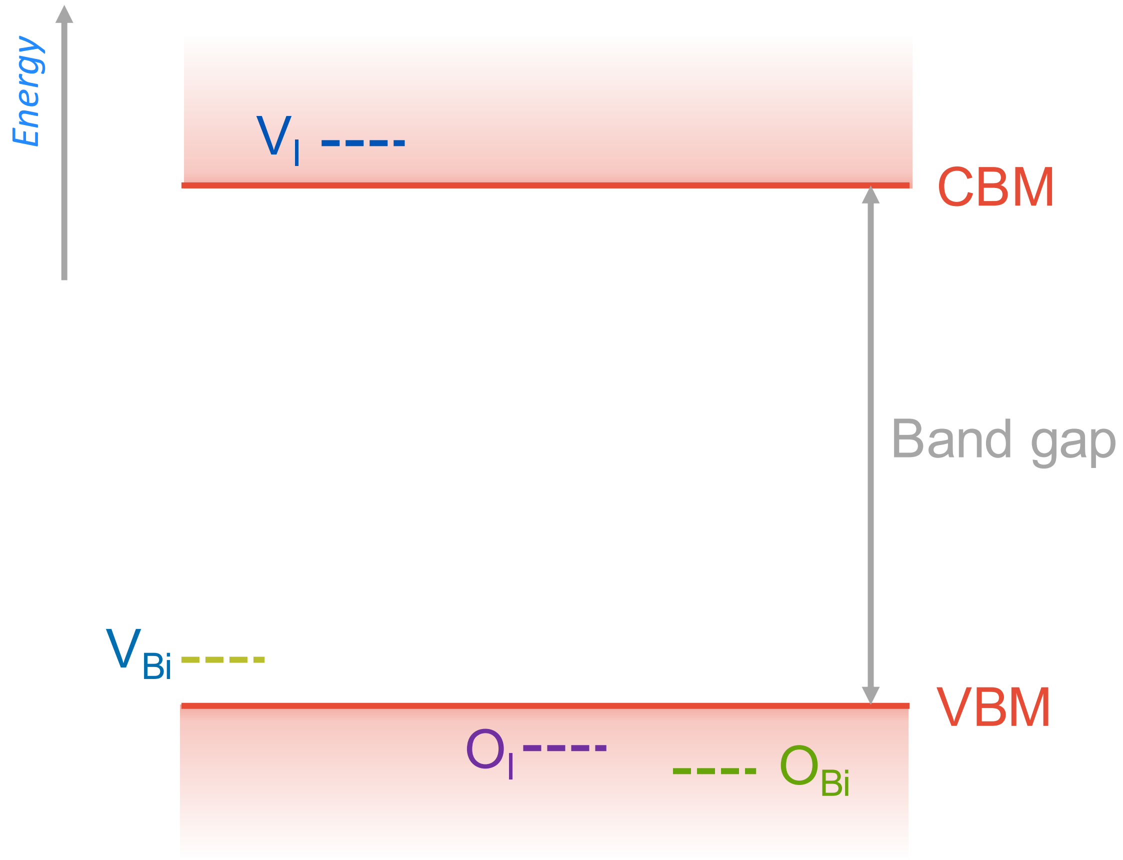


Hoye, *et al.*, *ACS Appl. Mater. Interfaces.*, **2015**, *7*, 10684



Andrei, Jagt ..., MacManus-Driscoll,* Hoye,* Reisner,* *Nat. Mater.*, **21**, 864 (2022)

BiOI tolerant to vacancy and anti-site defects

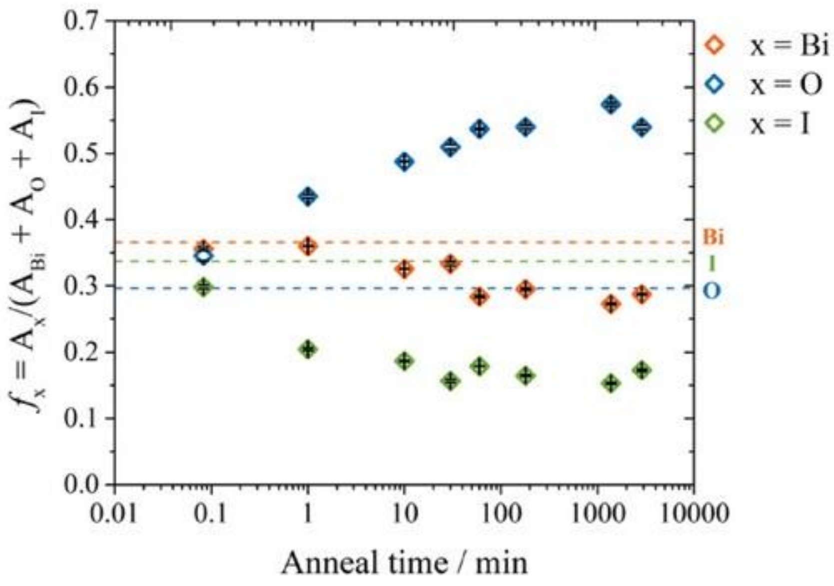


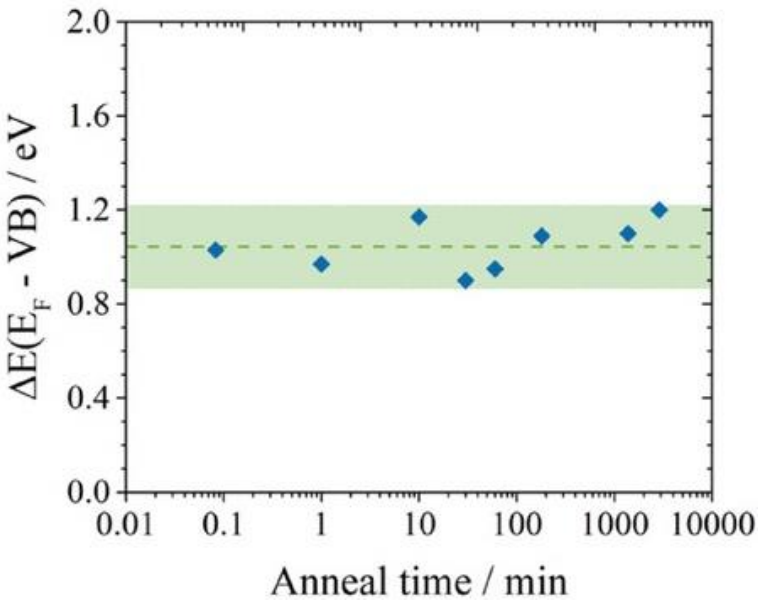
All trap levels resonant in bands or shallow

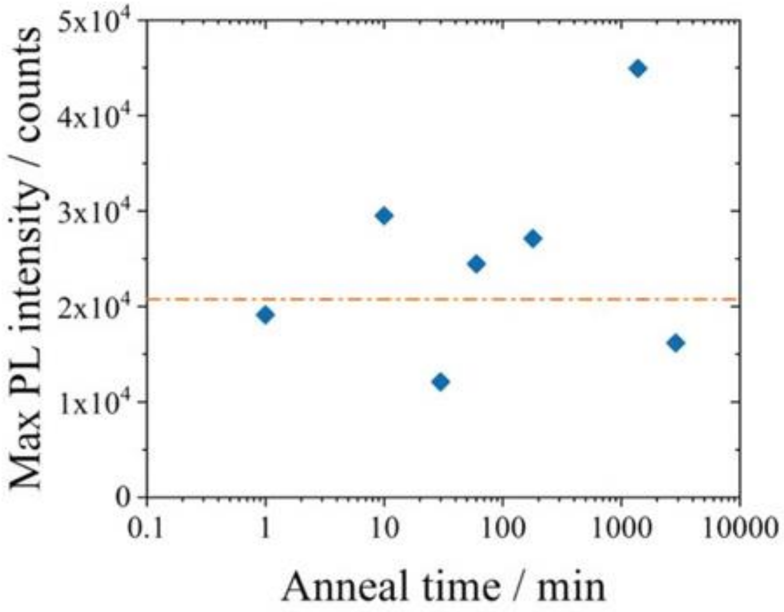
Collaborator: Prof. Vladan Stevanović (NREL)

Hoye, *et al.*, *Adv. Mater.*, **29**, 1702176 (2017)

BiOI tolerant to vacancy and anti-site defects

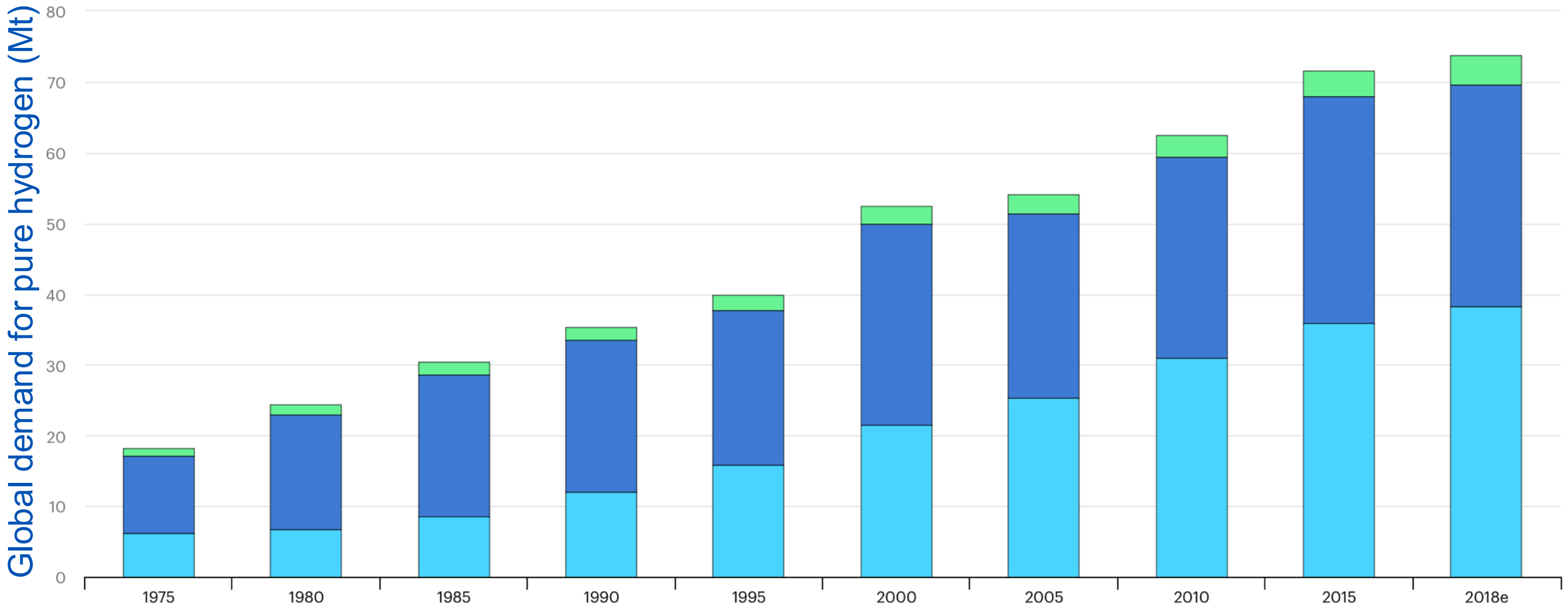






Huq, …, Hoye,* *Adv. Funct. Mater.*, **30**, 1909983 (2020)

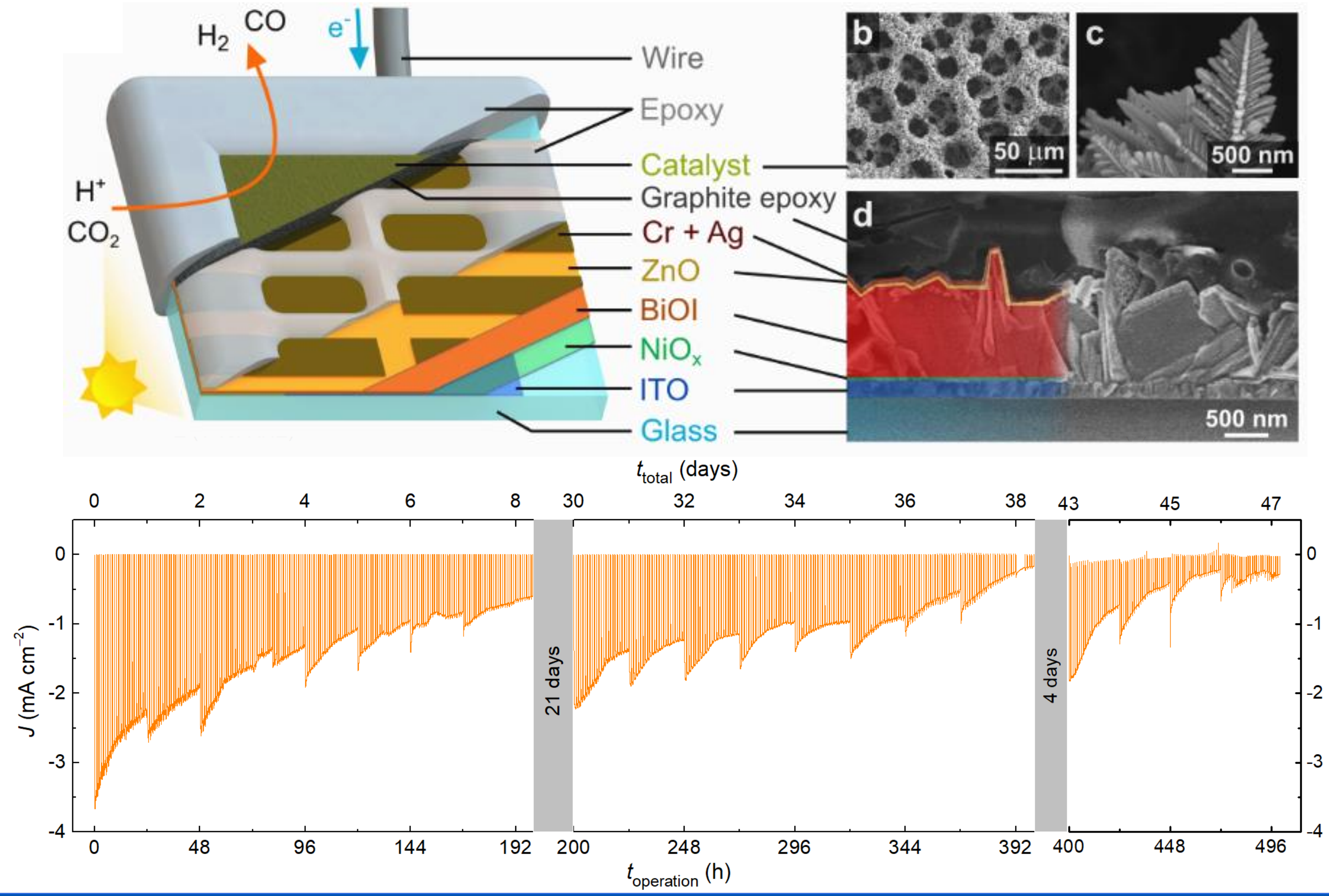
Green solar fuels to decarbonize chemicals industry



- Majority of H_2 sources from natural gas and coal
- H_2 production accounts for 830m tonnes CO_2eq

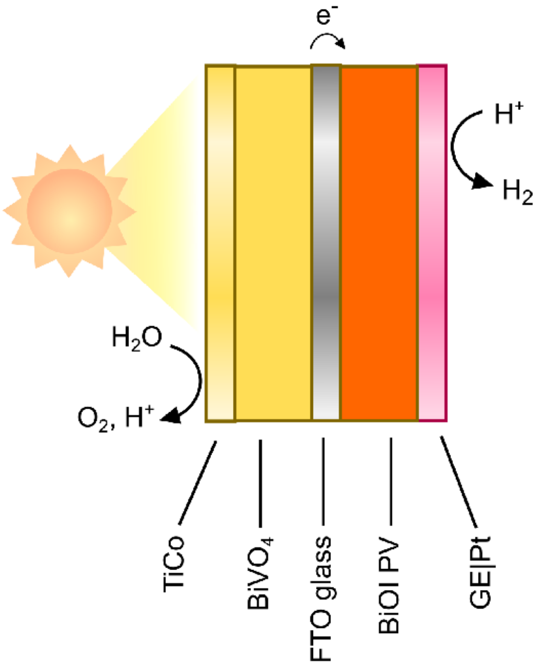
International Energy Agency, *The Future of Hydrogen* (2019)

Stable BiOI photocathodes

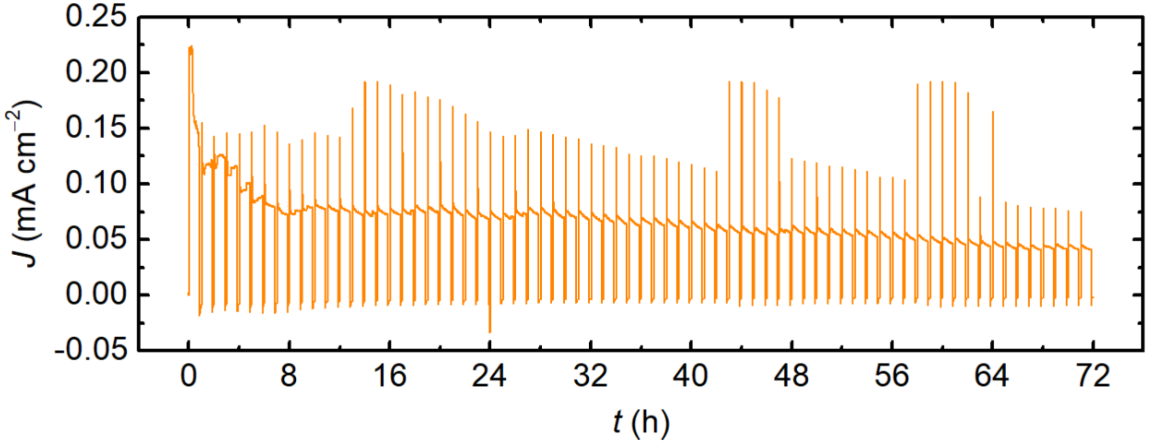


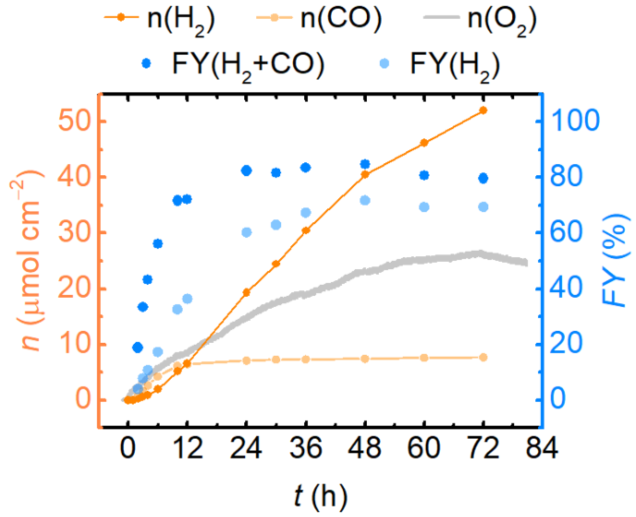
Andrei, Jagt ..., MacManus-Driscoll,* Hoye,* Reisner,* *Nat. Mater.*, **21**, 864 (2022)

Oxide artificial leaves for water and CO_2 splitting



0 V applied bias

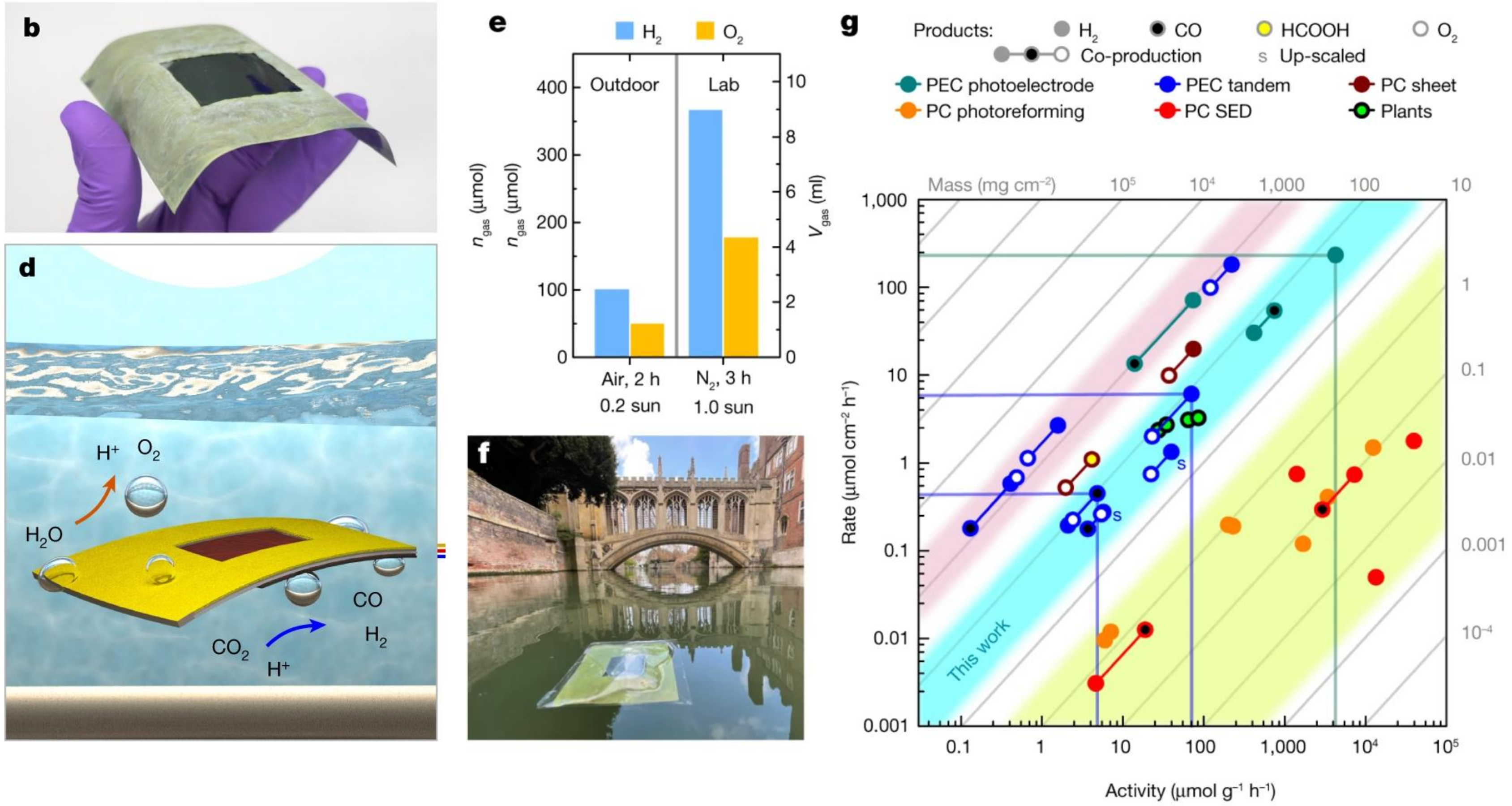




H_2 + CO Faradaic Yield ~85%

Andrei, Jagt ..., MacManus-Driscoll,* Hoye,* Reisner,* *Nat. Mater.*, **21**, 864 (2022)

Graphite epoxy encapsulation broadly applicable

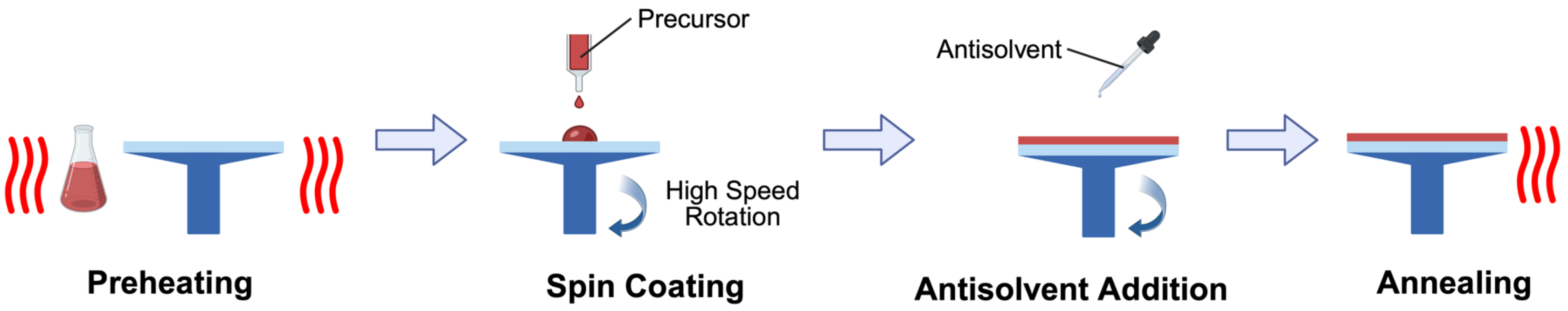


Andrei, ...Hoye, … Reisner,* *Nature*, **608**, 518 (2022)

AI to Accelerate Optimisation

Section 3

Morphology optimisation necessary but time-consuming

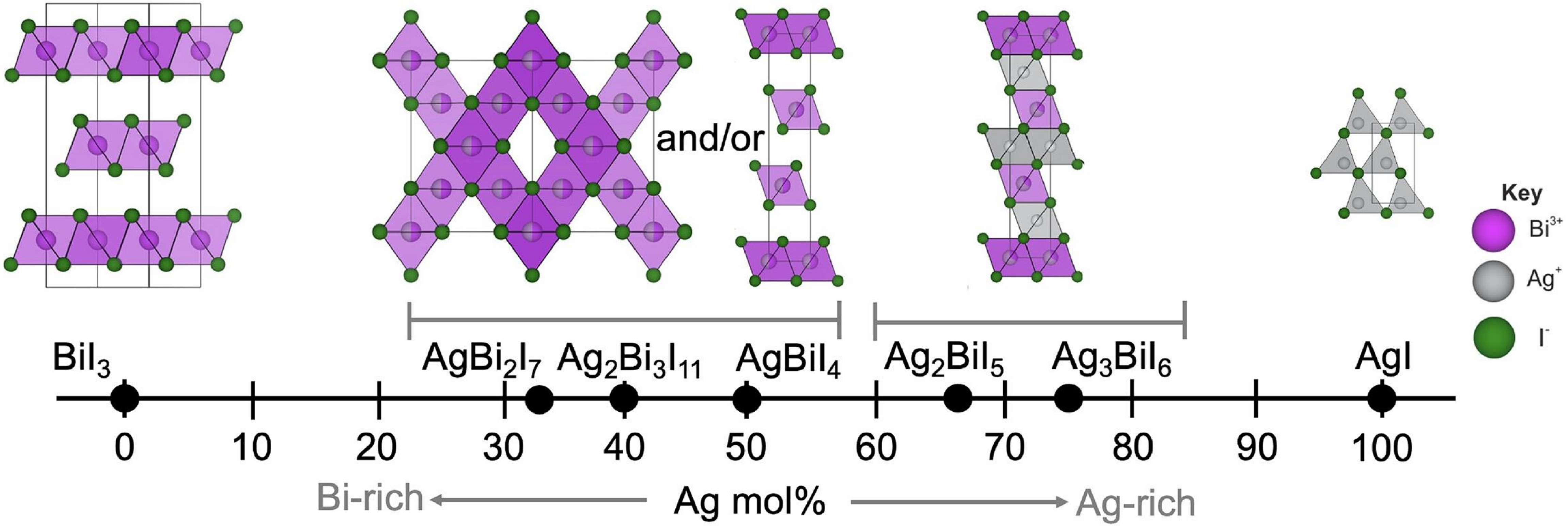


Example: parameters optimised in spin coating:

- Pre-heat/post-heat temperature and duration
- Spin coating speed
- Antisolvent addition
- >1700 different combinations of parameters
- 87 weeks continuous effort required to explore parameter space for one material

Nadishwara, ..., Hoye,* Sun,* *npj Comp. Mater.*, **11**, 210 (2025)

Focus materials: $AgBiI_4$, Ag_2BiI_5 and Ag_3BiI_6



Zhu,* …, Hoye,* *Int. Mater. Rev.*, **11**, 210 (2025)

Key Challenges

- Analysing SEM images time consuming (25 min per micrograph)

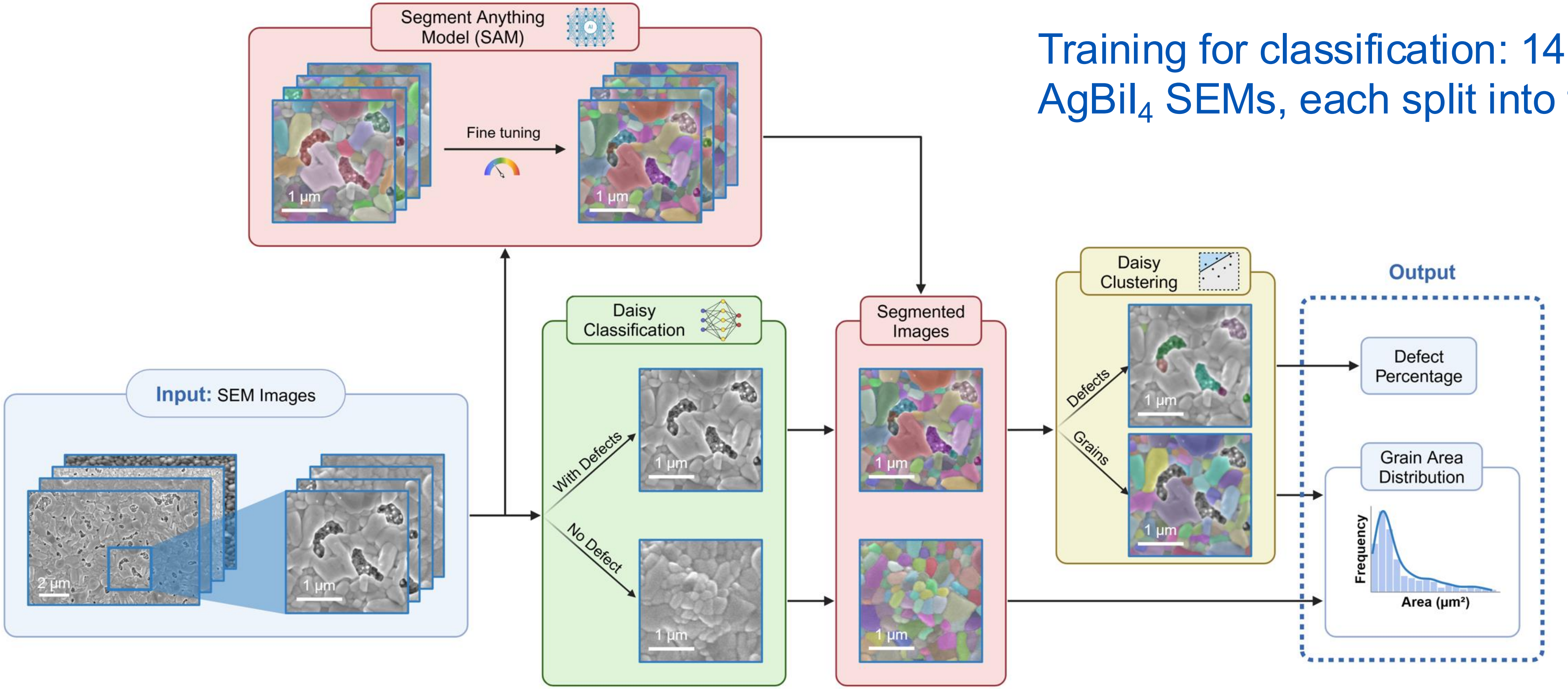
  Daisy Image Interpreter

- Need to more efficiently and rigorously move through parameter space

  Daisy Synthesis Planner

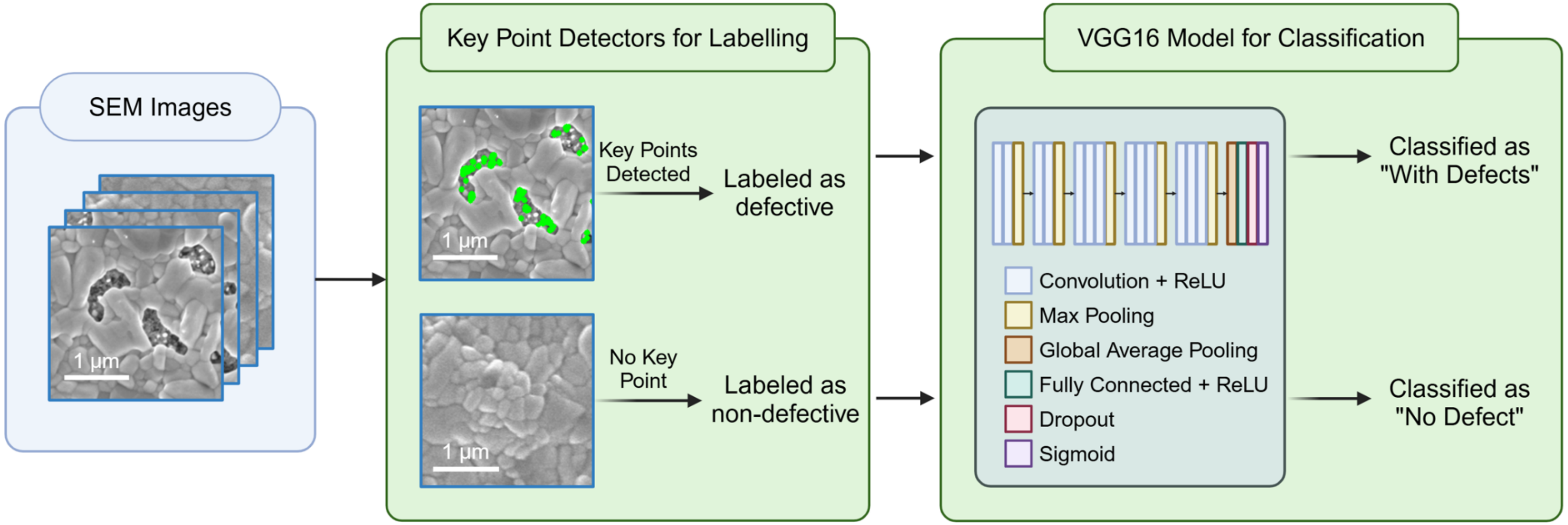
Daisy Image Interpreter

Training for classification: 141 $AgBiI_4$ SEMs, each split into four



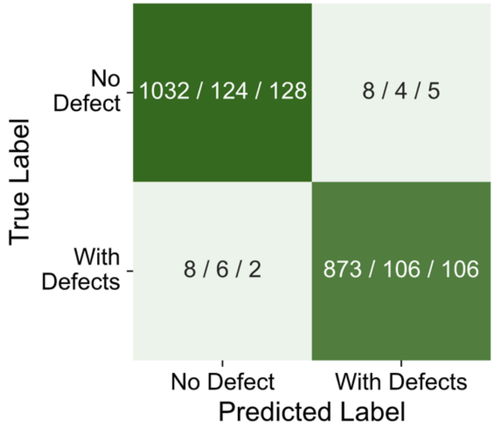
Nadishwara, ..., Hoye,* Sun,* *npj Comp. Mater.*, **11**, 210 (2025)

Daisy Image Interpreter: Classification Model



Number of image patches on

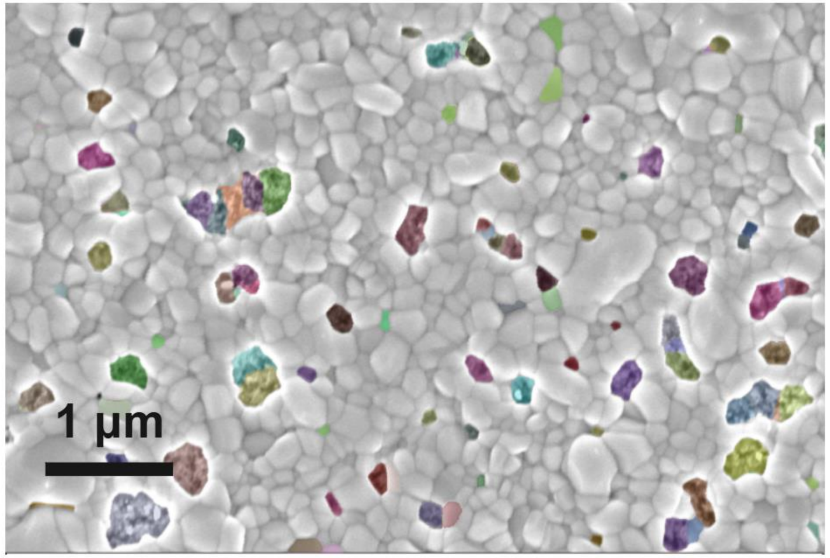
Training set / validation set / test set

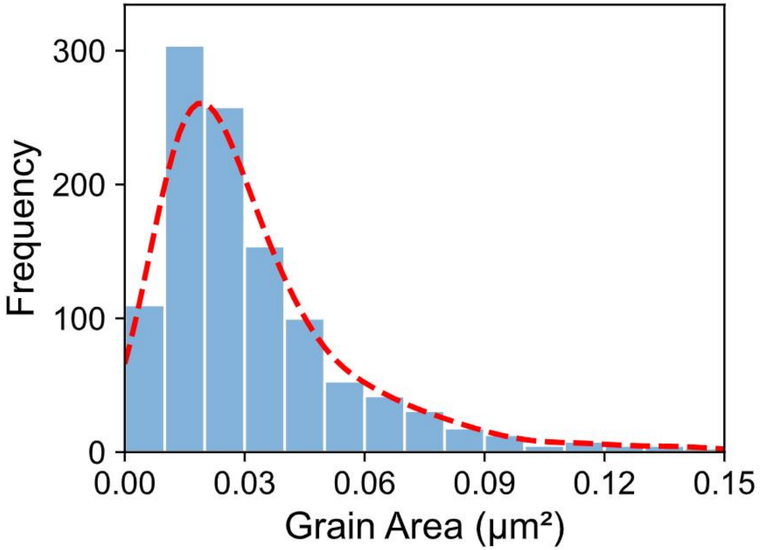


97% accuracy

Nadishwara, ..., Hoye,* Sun,* *npj Comp. Mater.*, **11**, 210 (2025)

Example result from Daisy Image Interpreter





Human: 25 min

Daisy: 38 s

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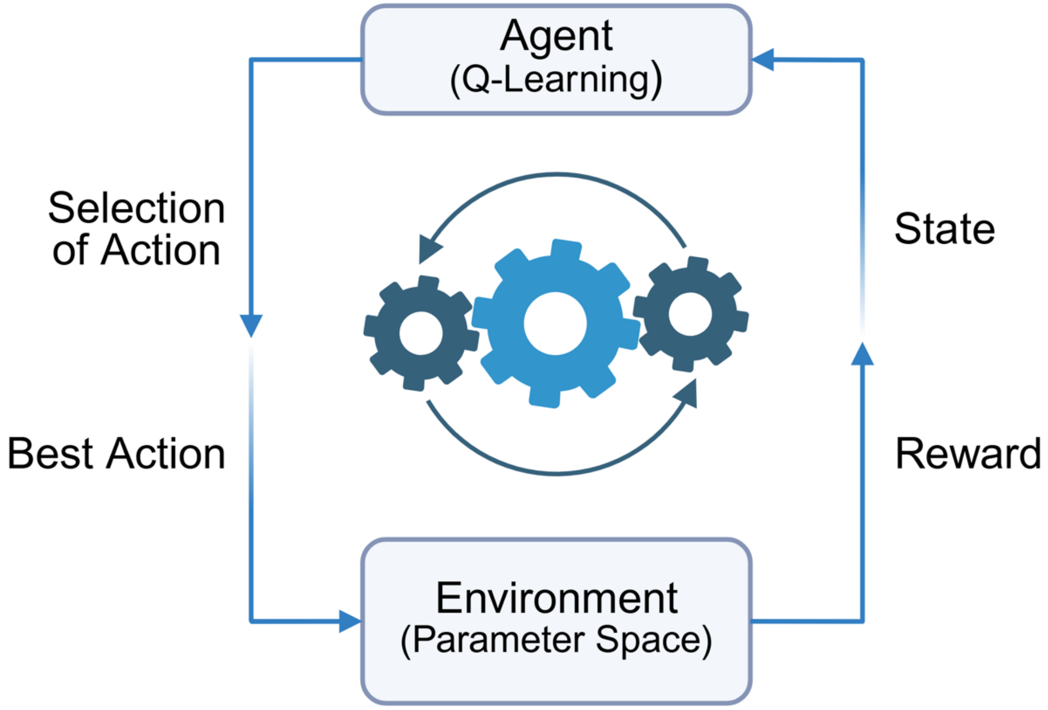
Daisy Synthesis Planner: Reinforcement Learning (RL)



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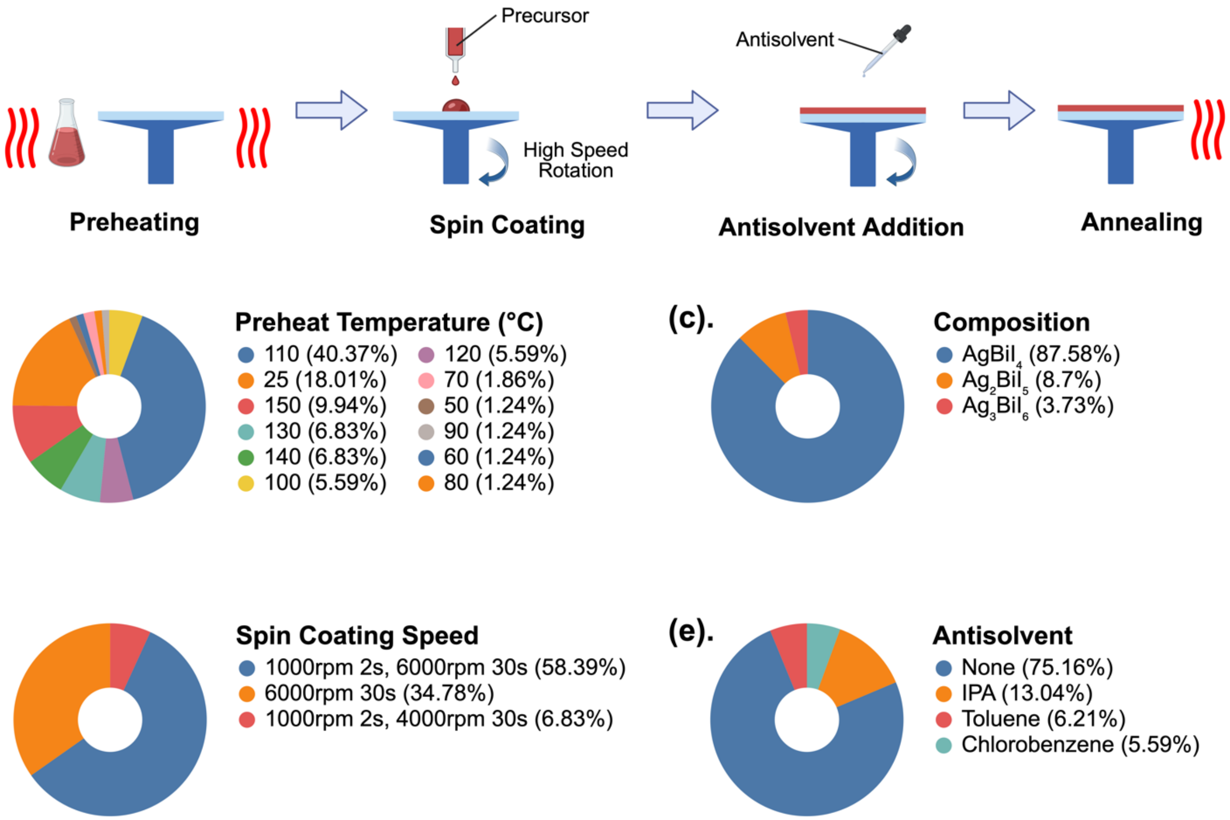
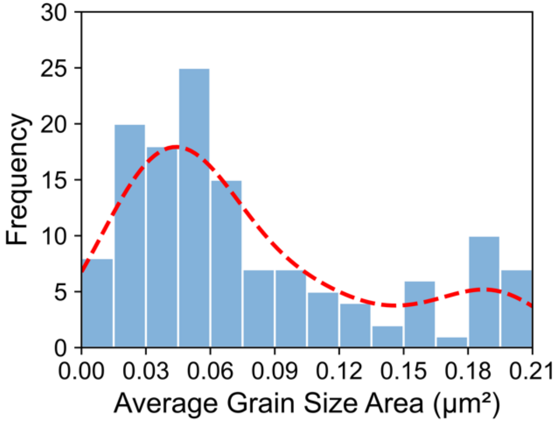
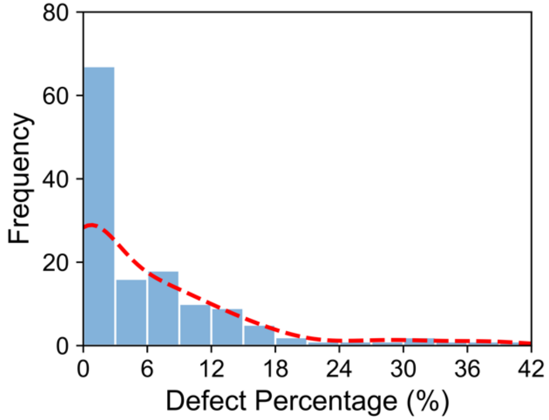
Data input: 161 SEM images of $AgBiI_4$, Ag_2BiI_5 and Ag_3BiI_6







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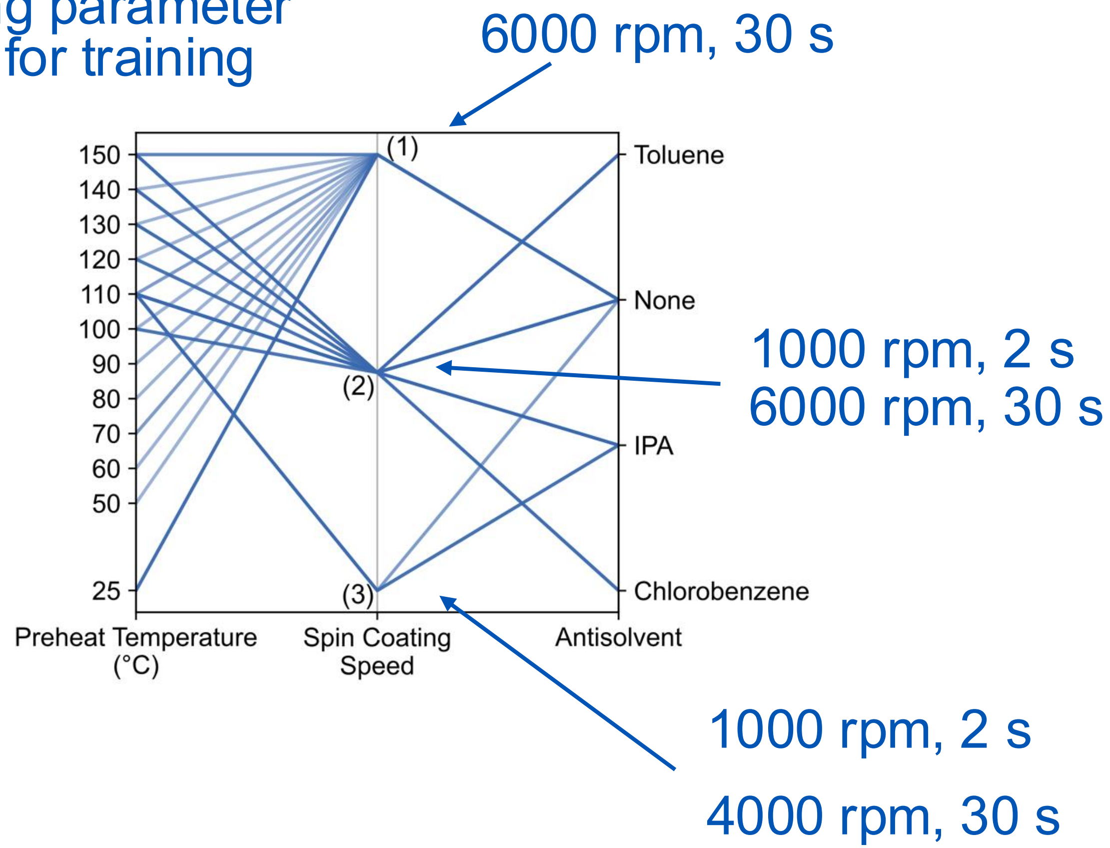
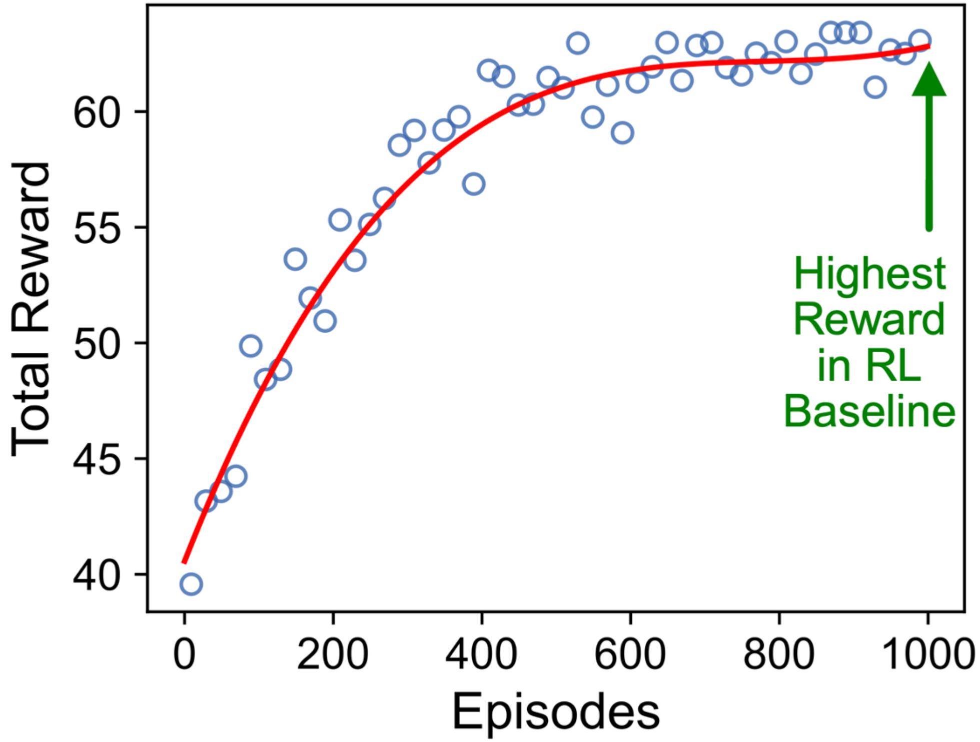
Training of Daisy Synthesis Planner: Focus on $AgBiI_4$

Existing parameter space for training





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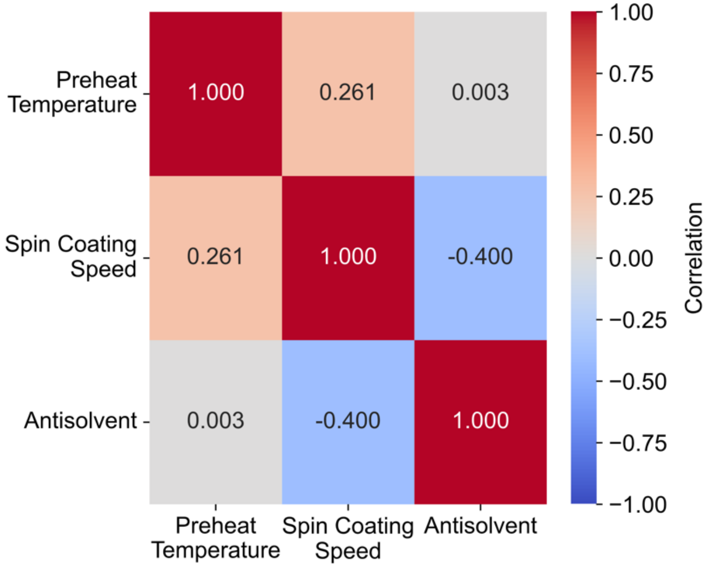
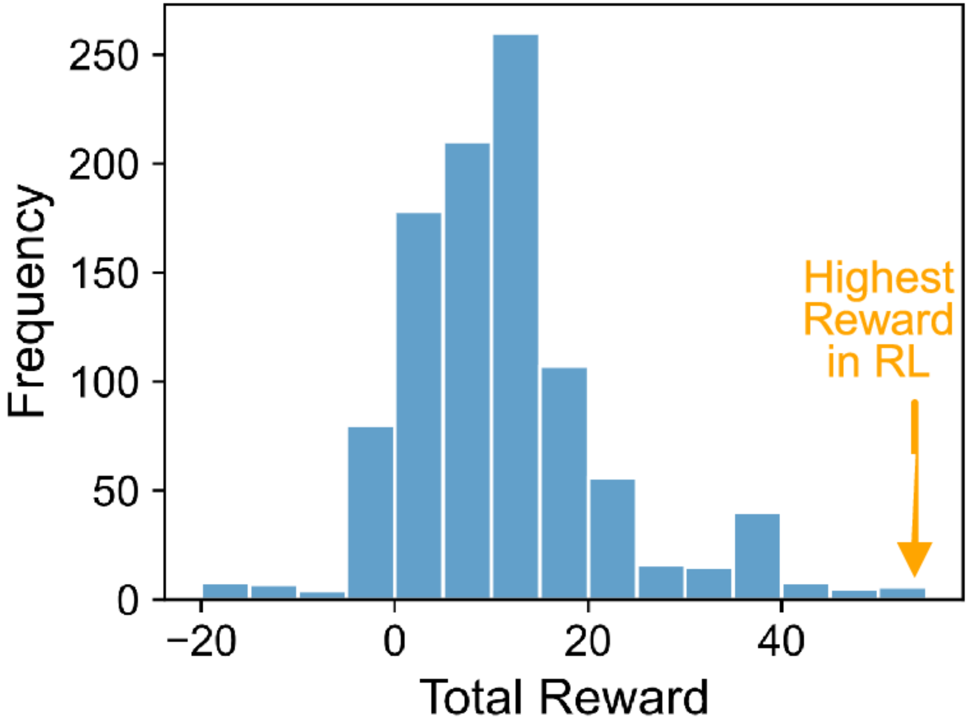
Exploratory RL: Vary each parameter step-by-step

Minimal interdependence of processing conditions





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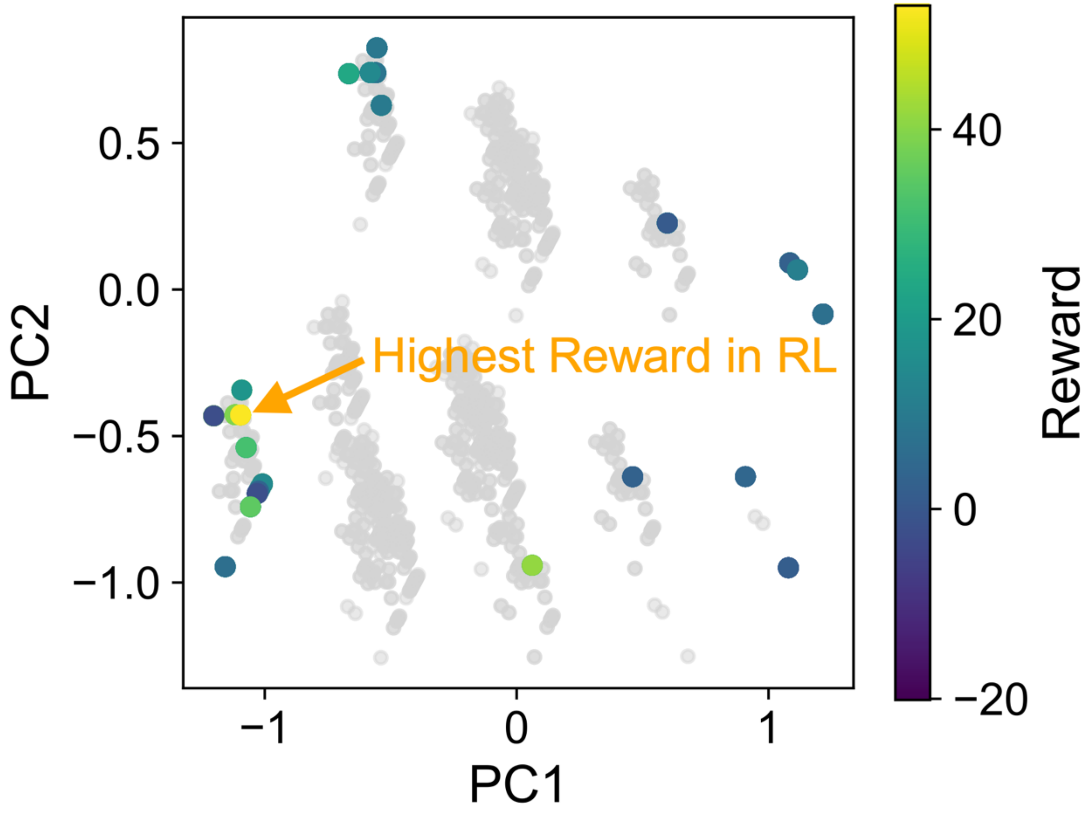
Subset of entire parameter space sampled – $AgBiI_4$



Grey: 1728 unique combination of processing parameters

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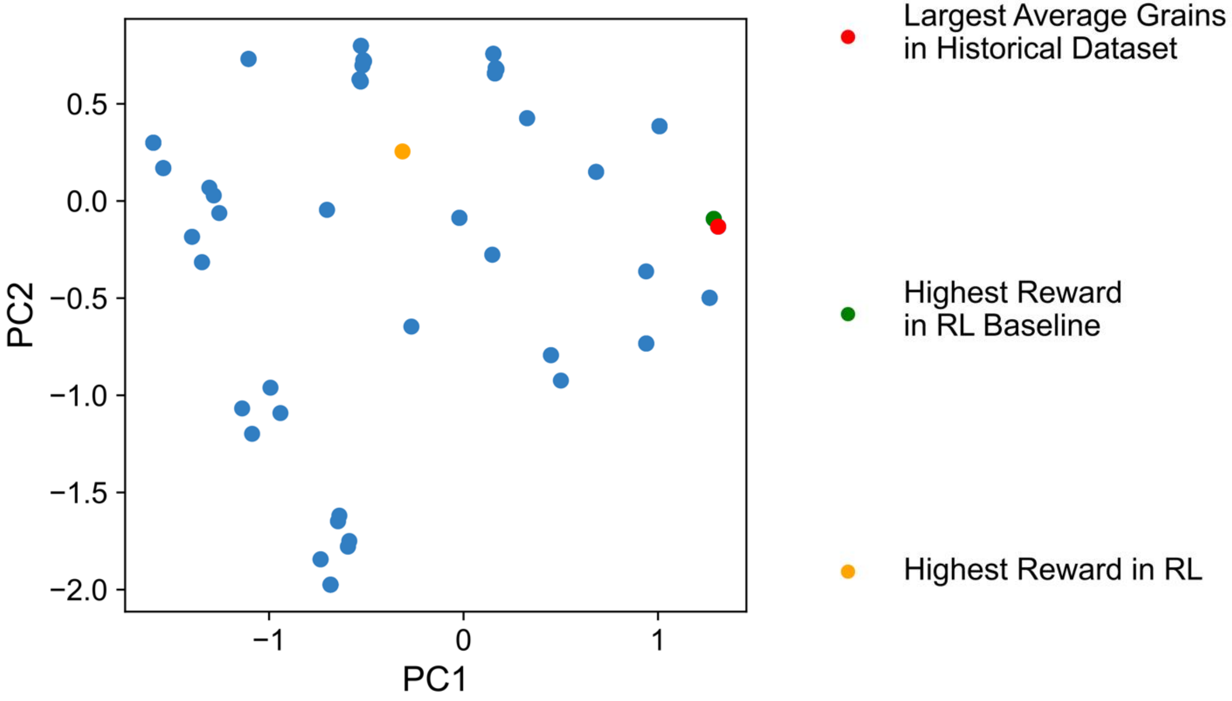
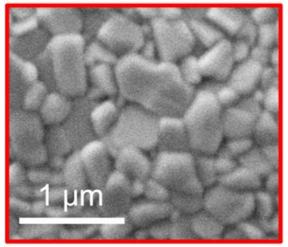
Verification of Optimal Solution: PCA for full parameter space

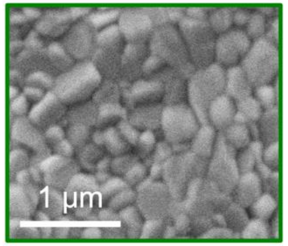




Preheat: 110 ºC

1000 rpm, 2 s

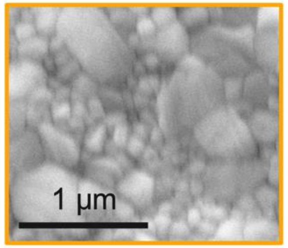
6000 rpm, 30 s with toluene a/s



Preheat: 110 ºC

1000 rpm, 2 s

6000 rpm, 30 s with chlorobenzene a/s



Preheat: 140 ºC

6000 rpm, 30 s

No antisolvent

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Key takeaways

- Defect tolerance offers opportunity for efficient performance to be achieved with cost-effective, low-CO_2eq synthesis methods
- BiOI made in stable light harvester for solar fuels through graphite epoxy encapsulation
- Daisy Image Interpreter analyses SEM images >120× faster than human, 97% accurate
- Daisy Synthesis Planner uses reinforcement learning agent to identify optimal parameter space

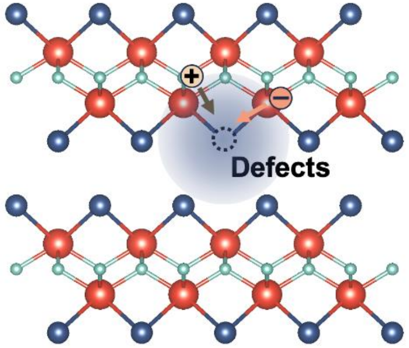
Acknowledgements – People and funders

- Dr. Irea Mosquera-Lois, Prof. Aron Walsh
- Dr. Rob Jagt, Dr. Tahmida Huq, Prof. Judith Driscoll (Cambridge)
- Prof. Virgil Andrei (NTU)
- Prof. Erwin Reisner (Cambridge)
- Dr. Ivy Liu, Dr. Huimin Zhu, Xiaoyu Guo (Oxford)
- Prof. Shijing Sun (Cambridge), KS Nadishwara, Dr. Shuan Cheng (UW)

erc
Royal Academy of Engineering
St John's College Oxford
NSF
UKRI UK Research and Innovation
UKRI Engineering and Physical Sciences Research Council
University of Oxford John Fell Fund
First Solar
The Royal Society
UKIERI UK-India Education and Research Initiative
Henry Royce Institute

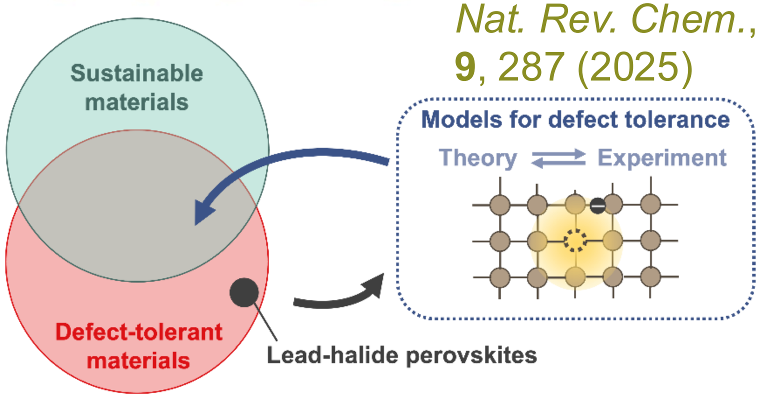
Group website: hoyegroup.site.ox.ac.uk

Reviews and perspectives from us



Ganose, Scanlon, Walsh, Hoye,*
Nat. Commun., **13**, 4715 (2022)

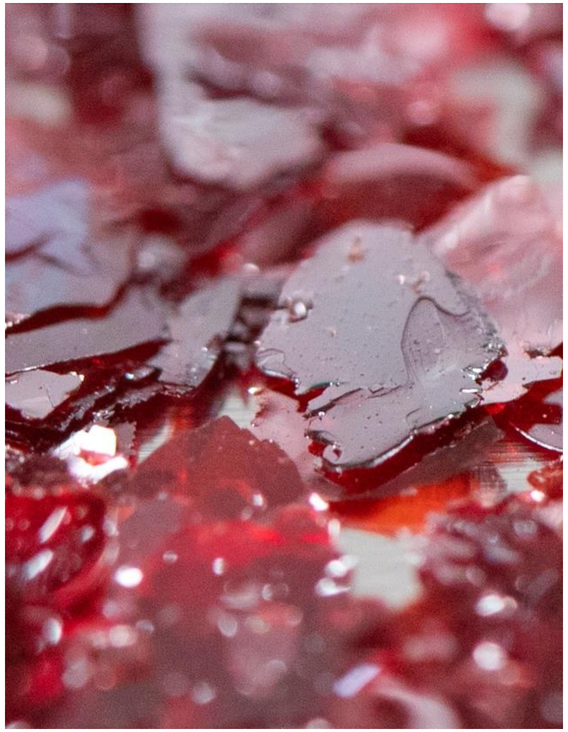
Nat. Rev. Chem.,
9, 287 (2025)



Other groups:

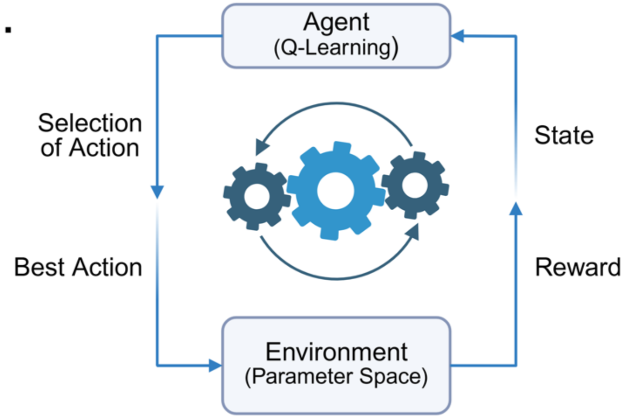
Cahen, Kronik, Hodes, *ACS Energy Lett.*, **6**, 4108 (2021)
Heiss and co-workers, *Nat. Rev. Mater.*, **10**, 311 (2025)

BiOI Solar Fuels



Andrei, Jagt, …, Hoye,* Reisner,*
Nat. Mater., **21**, 864 (2022)

AI to accelerate materials optimisation



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