THE UNIVERSITY OF SYDNEY

Liquid Metals Enable the Next Generation of Ultrathin Transparent Conductive Materials

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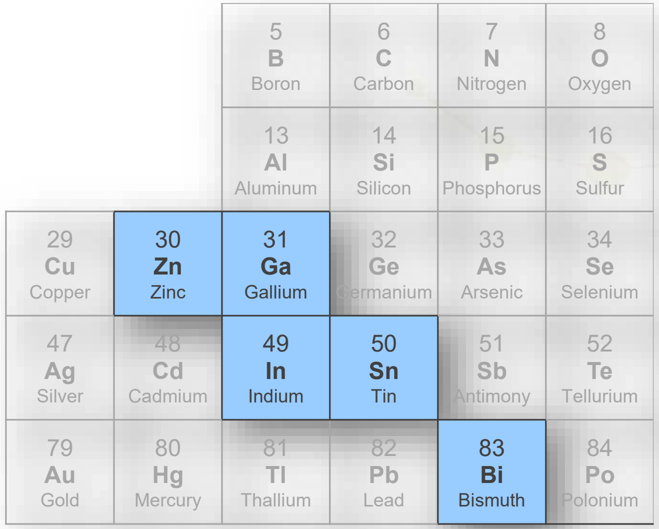
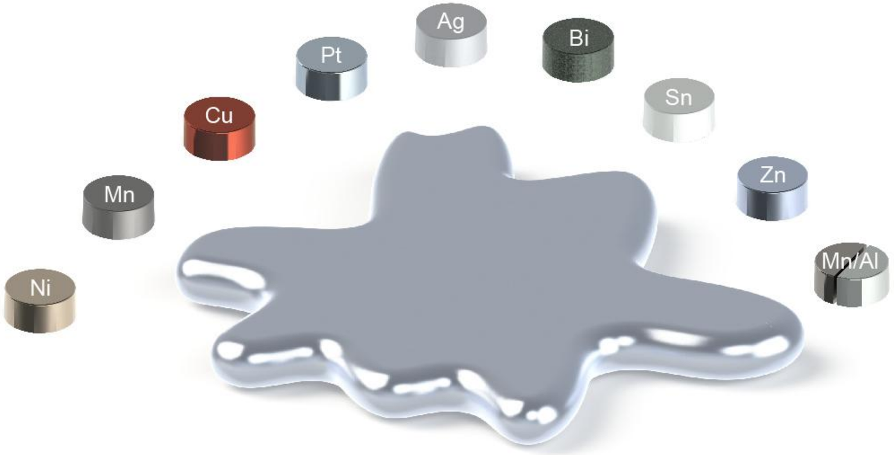
What are Liquid Metals (LM) ?

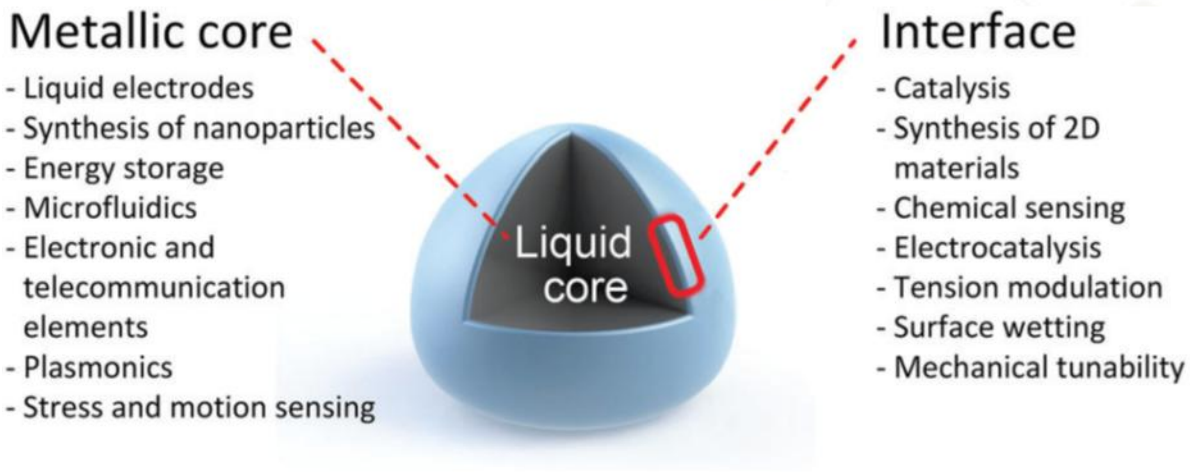
Liquid Metals (LM):

- Post transition elements
  Ga, In, Tl, Sn, Pb, Al, Bi

- Zinc group (group 12) elements
  Zn, Cd and Hg

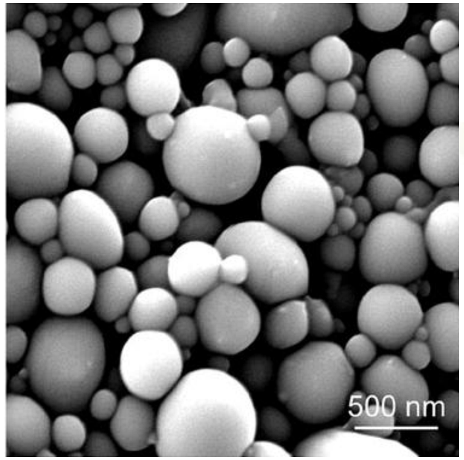




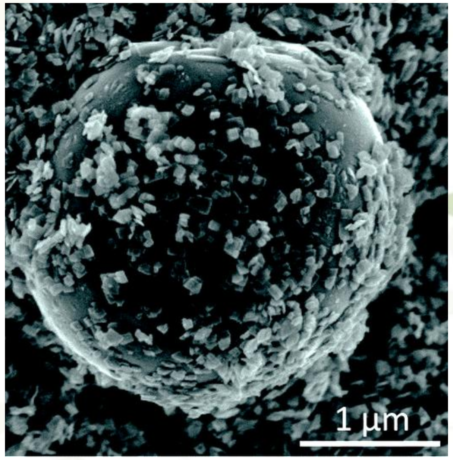


Synthesis and functionalisation of LM nanoparticles

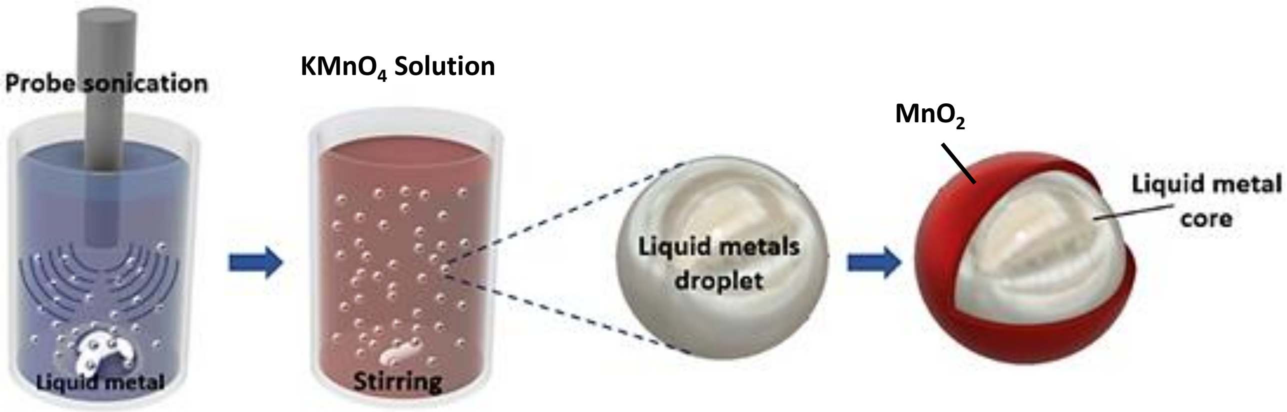
Physical functionalisation

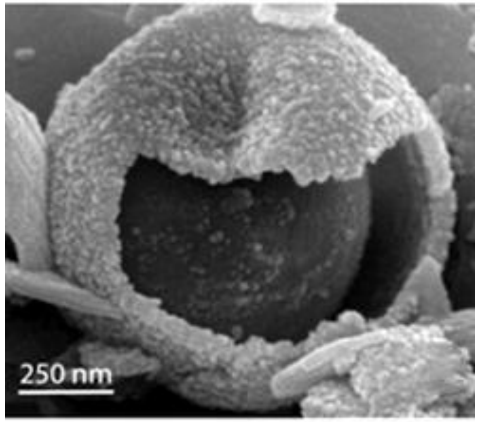


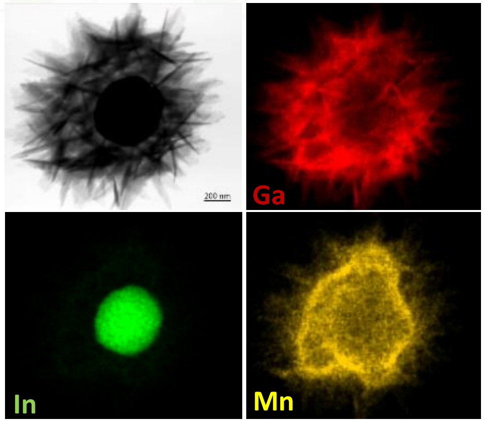
WO_3 flakes



Chemical functionalisation







Han J. *et al.,* Liquid metals for tuning gas sensitive layers, *Journal of Materials Chemistry C* 2019,7, 6375-6382.
Ghasemian M.B. *et al.,* Coating of gallium-based liquid metal particles with molybdenum oxide and oxysulfide for electronic band structure modulation, Nanoscale, 2023, 15, 5891-5898.
Ghasemian M.B. *et al.,* Self-Limiting Galvanic Growth of MnO_2 Monolayers on a Liquid Metal—Applied to Photocatalysis, *Advanced Functional Materials* 2019,29, 1901649.

Two-dimensional (2D) materials

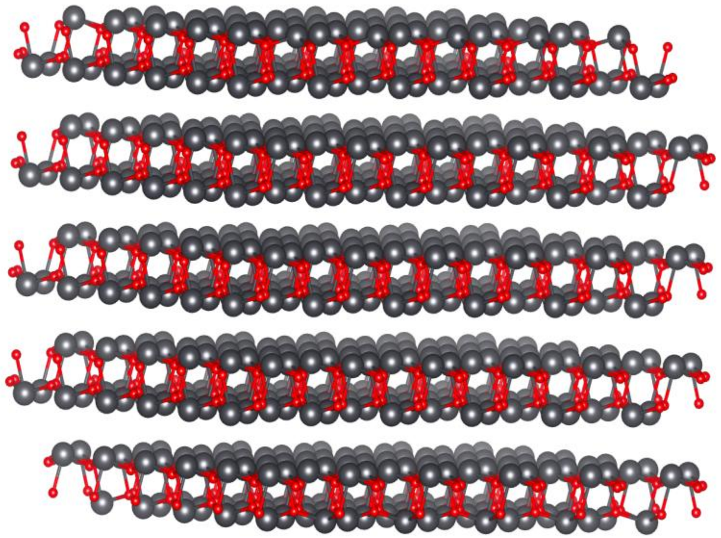
- Two-dimensional (2D) materials are planar structures with nanometer thicknesses
- Electronic band structure of 2D materials usually changes with composition and thickness variation

Preparation methods of 2D materials:

1. Exfoliation:
- Mechanical cleavage
- Chemical exfoliation
- Ion intercalation
- Surfactant assisted ultrasonication

2. Deposition:
- Chemical vapour deposition (CVD)
- Molecular beam epitaxy (MBE)
- Pulsed laser deposition (PLD)

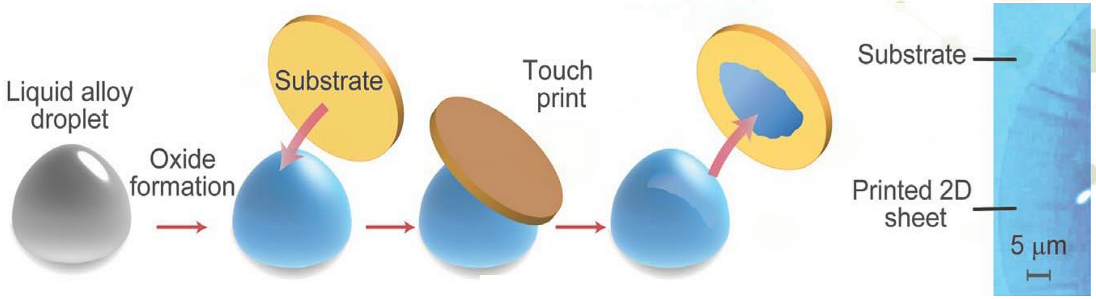
3. Liquid metal-based printing



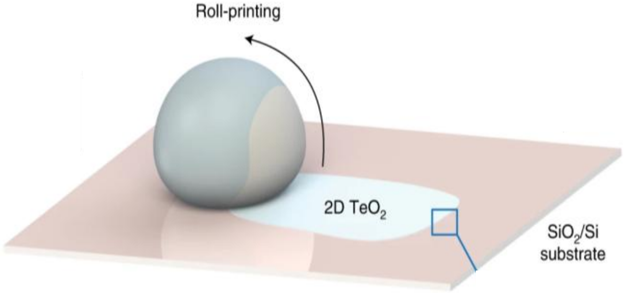
Synthesis of 2D and ultrathin materials by LM printing

Liquid metal printing principal:

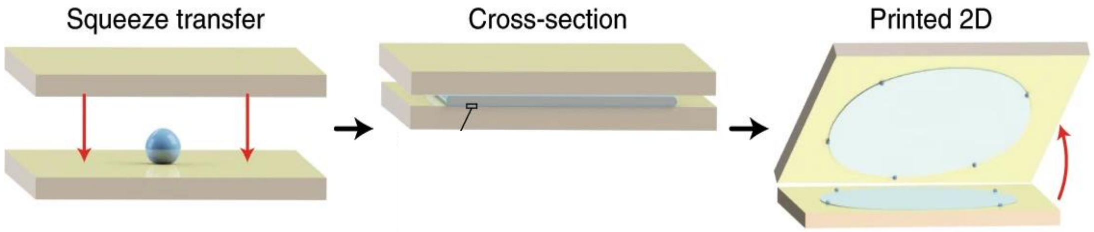
- An atomically thin layer of oxide grows on the surface of liquid metals
- There is no covalent bond between liquid metal and its surface oxide
- There are strong van der Waals interactions between surface oxide and the transfer substrate



Touch print



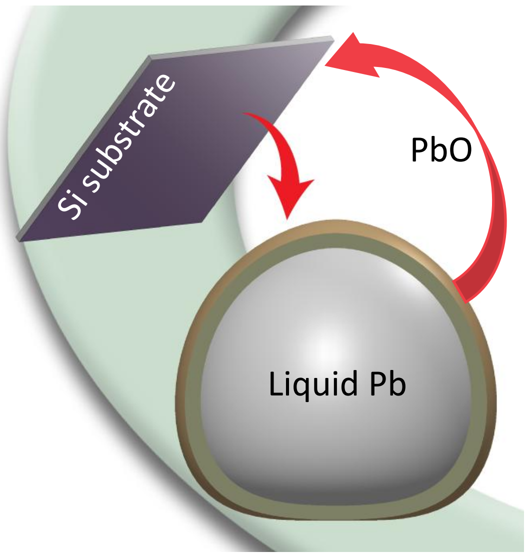
Roll print



Squeeze print

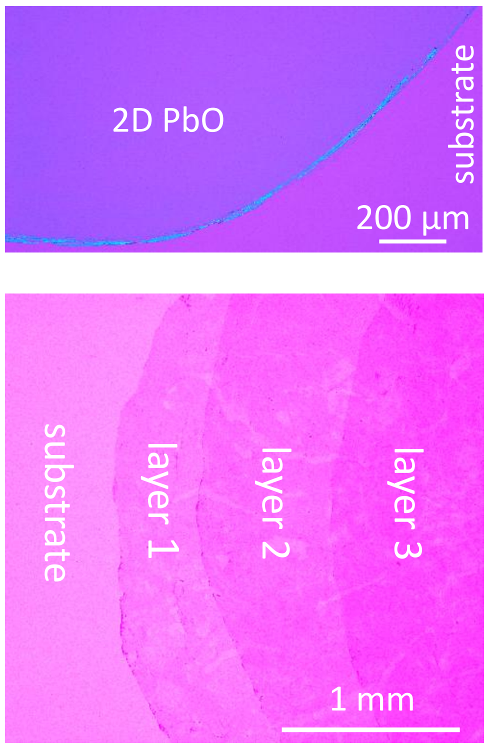
Zavabeti A., *et al*., A liquid metal reaction environment for the room-temperature synthesis of atomically thin metal oxides. *Science,* 2017, 358, 332-335.
Datta R. S., *et al.*, Flexible two-dimensional indium tin oxide fabricated using a liquid metal printing technique. *Nature Electronics,* 2020, 3, 51-58.

Environmentally friendly PbO monolayers by LM

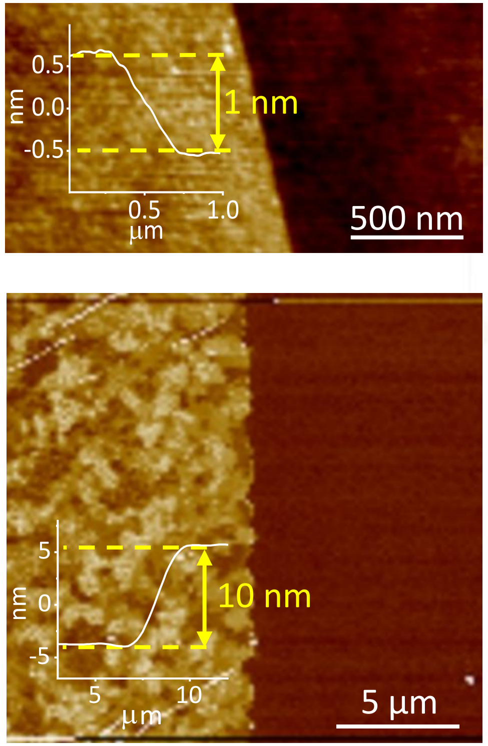


Harvesting PbO sheets with different thicknesses from the surface of liquid Pb through the touch-printing process

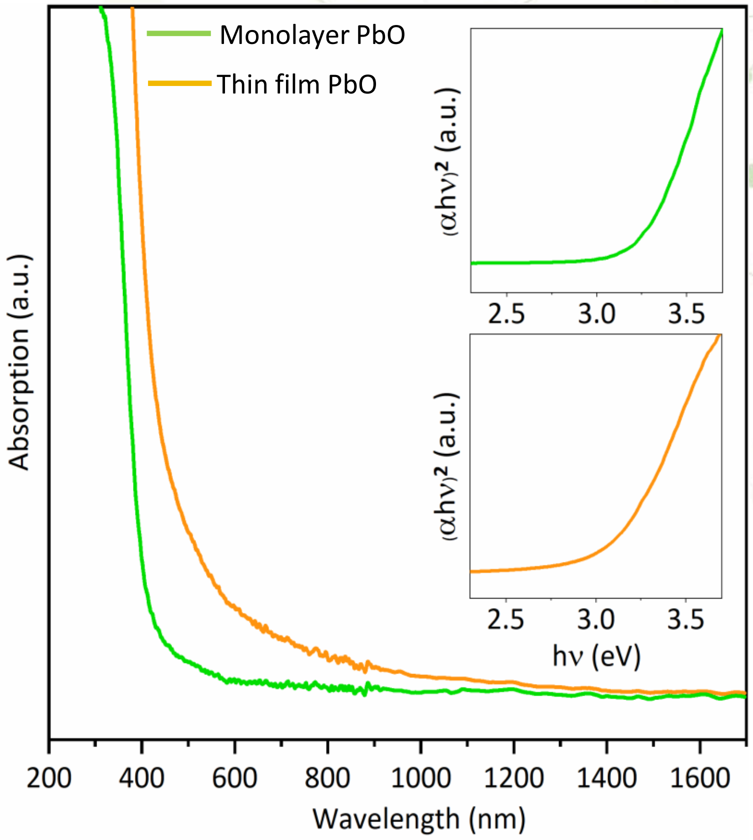
Optical images



AFM images



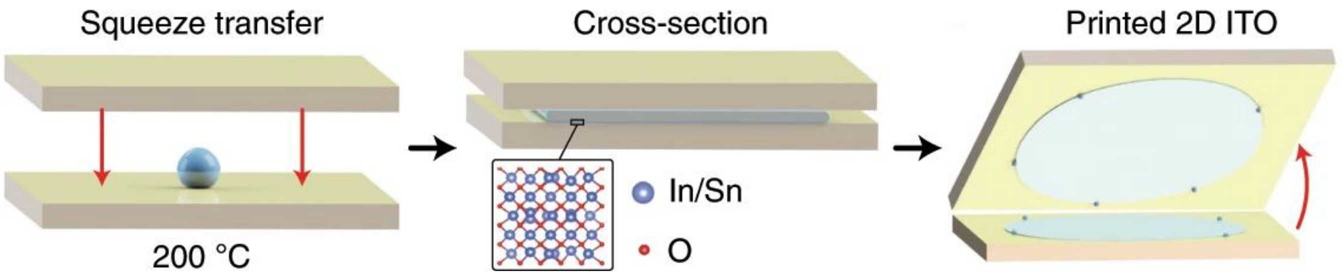
UV- Vis and Tauc plots for band gap measurements

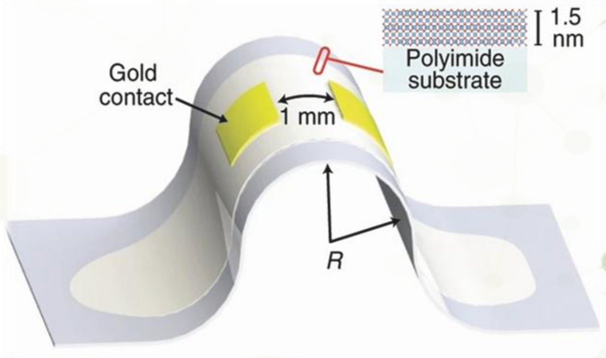


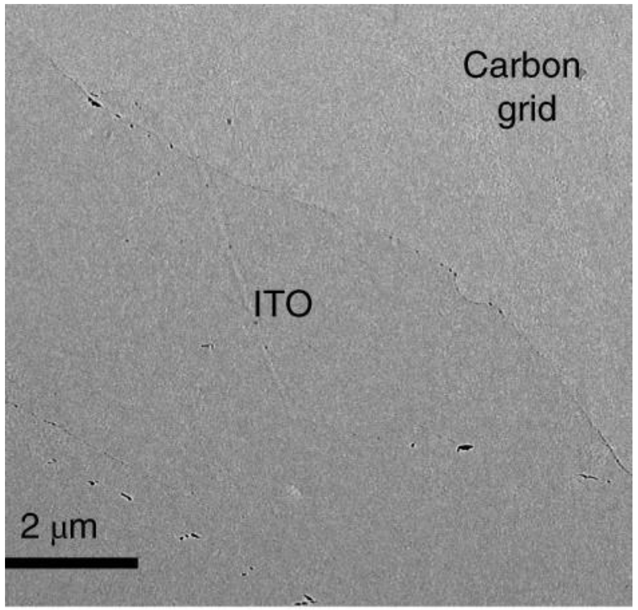
- PbO monolayers showed a piezoelectric coefficient of ~30 pm/V
- 10^4 times less Pb than commercial PZT thin films

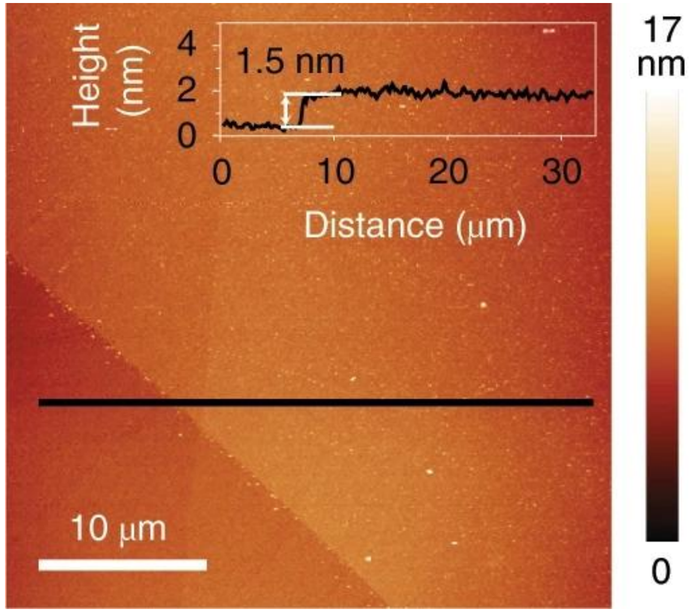
Ghasemian, M. B., *et al.,* Ultra-thin lead oxide piezoelectric layers for reduced environmental contamination using a liquid metal-based process. *Journal of Materials Chemistry A,* 2020, 8, 19434-19443.

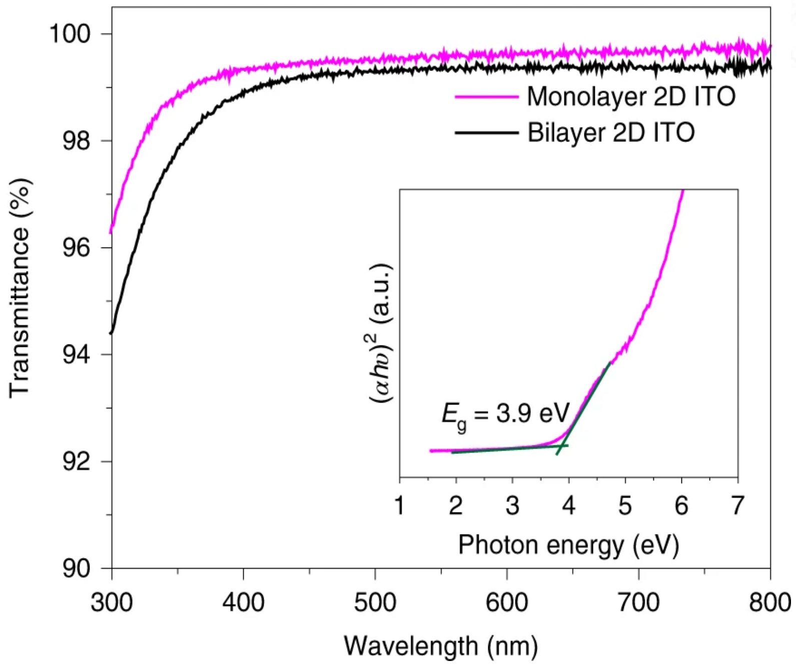
Liquid metal-based ultrathin transparent ITO





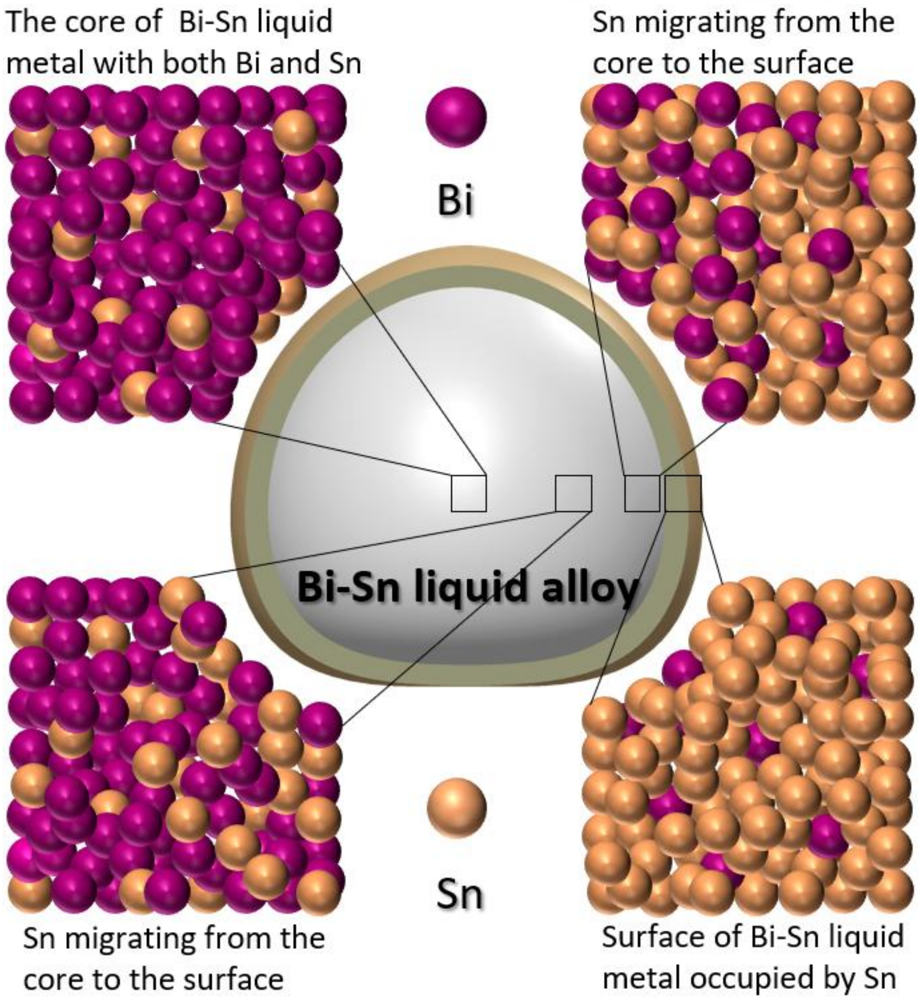


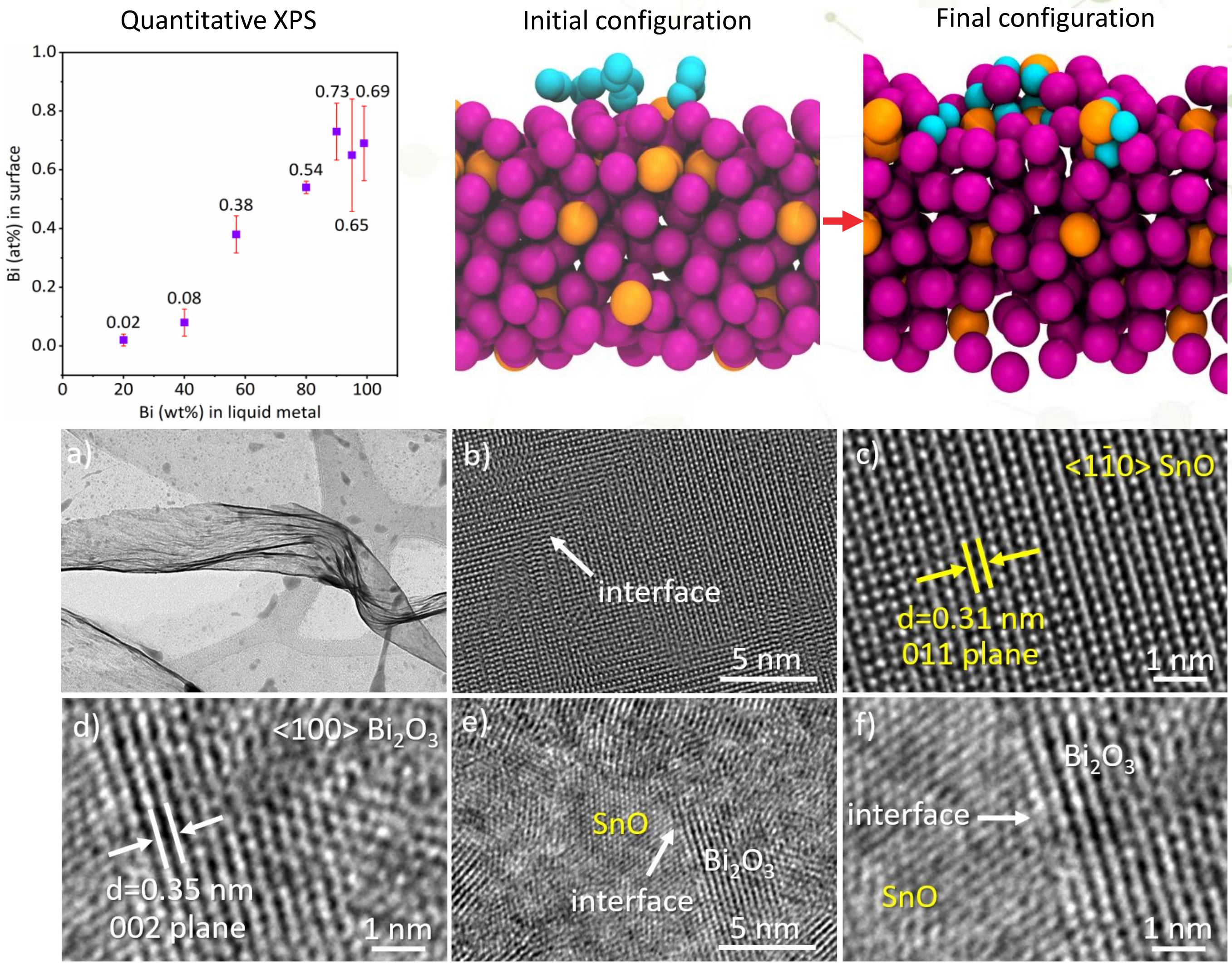




Datta R. S., *et al.*, Flexible two-dimensional indium tin oxide fabricated using a liquid metal printing technique. *Nature Electronics,* 2020, 3, 51-58.

Liquid metals as a doping strategy

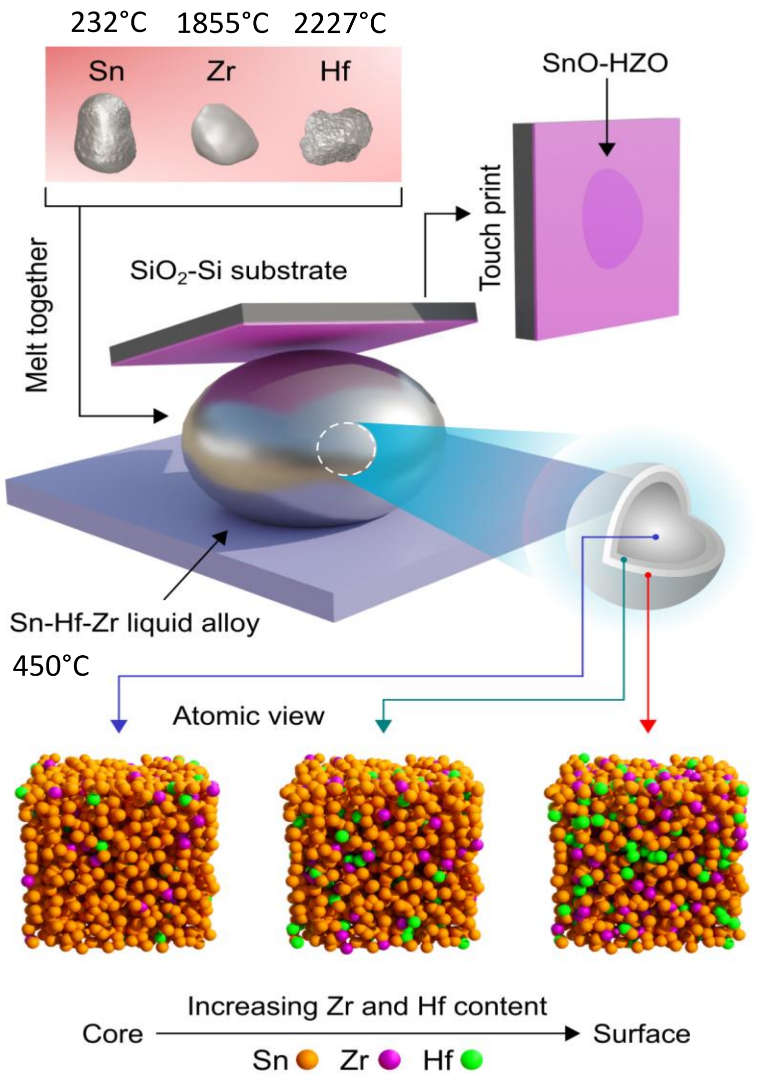


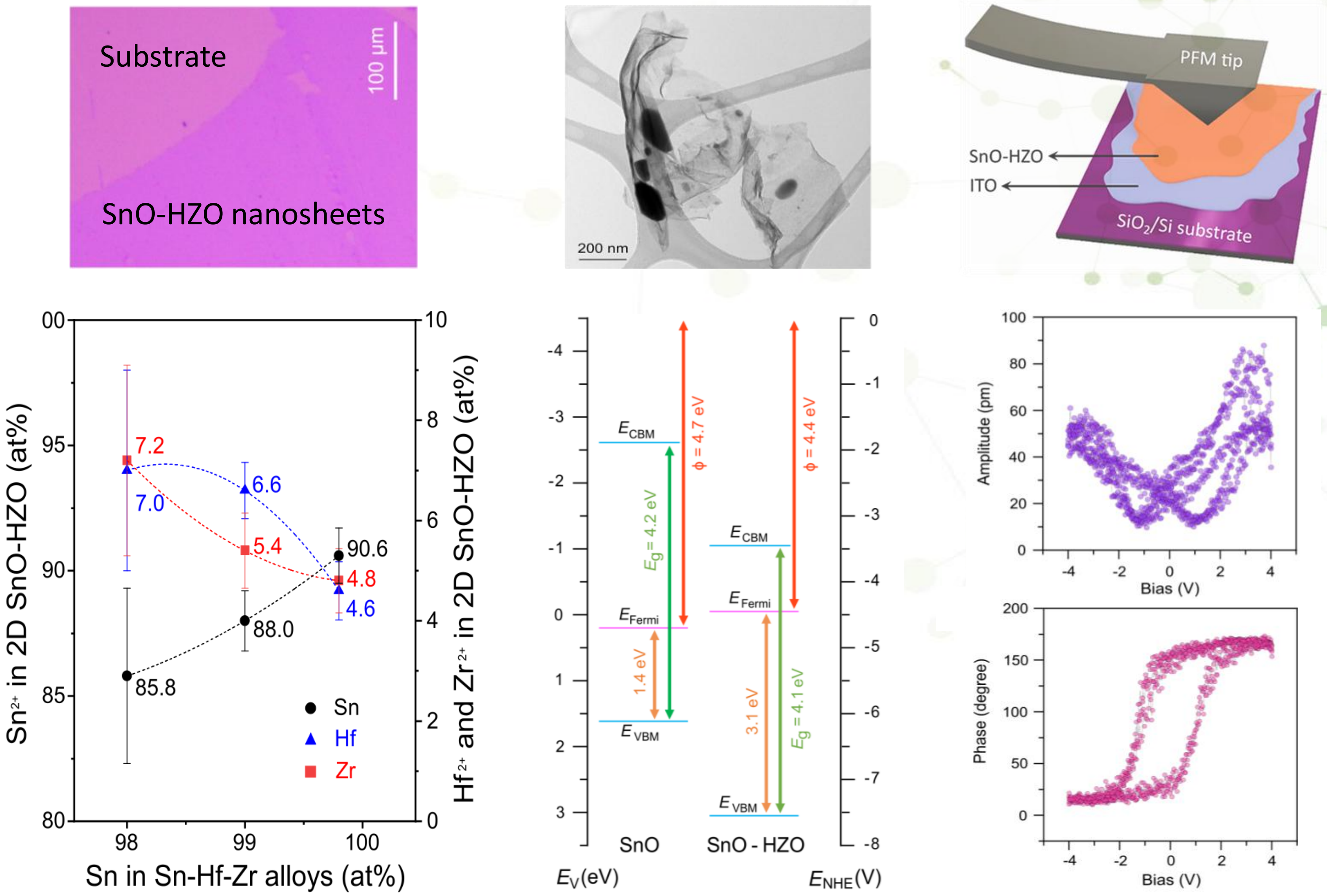


Bi_2O_3 ΔG_f = -574 kJ/mol SnO_2 ΔG_f = -578 kJ/mol

Ghasemian, M. B., *et al.,* Doping Process of 2D Materials Based on the Selective Migration of Dopants to the Interface of Liquid Metals. *Advanced Materials,* 2021, 33, 2104793.

2D materials from high-melting-point metals





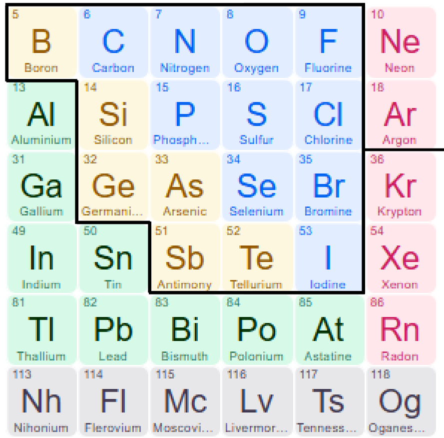
SnO_2 ΔG_f = -578 kJ/mol

HfO_2 ΔG_f = -1145 kJ/mol

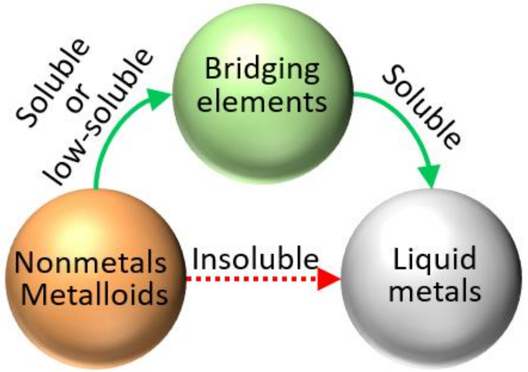
ZrO_2 ΔG_f = -1100 kJ/mol

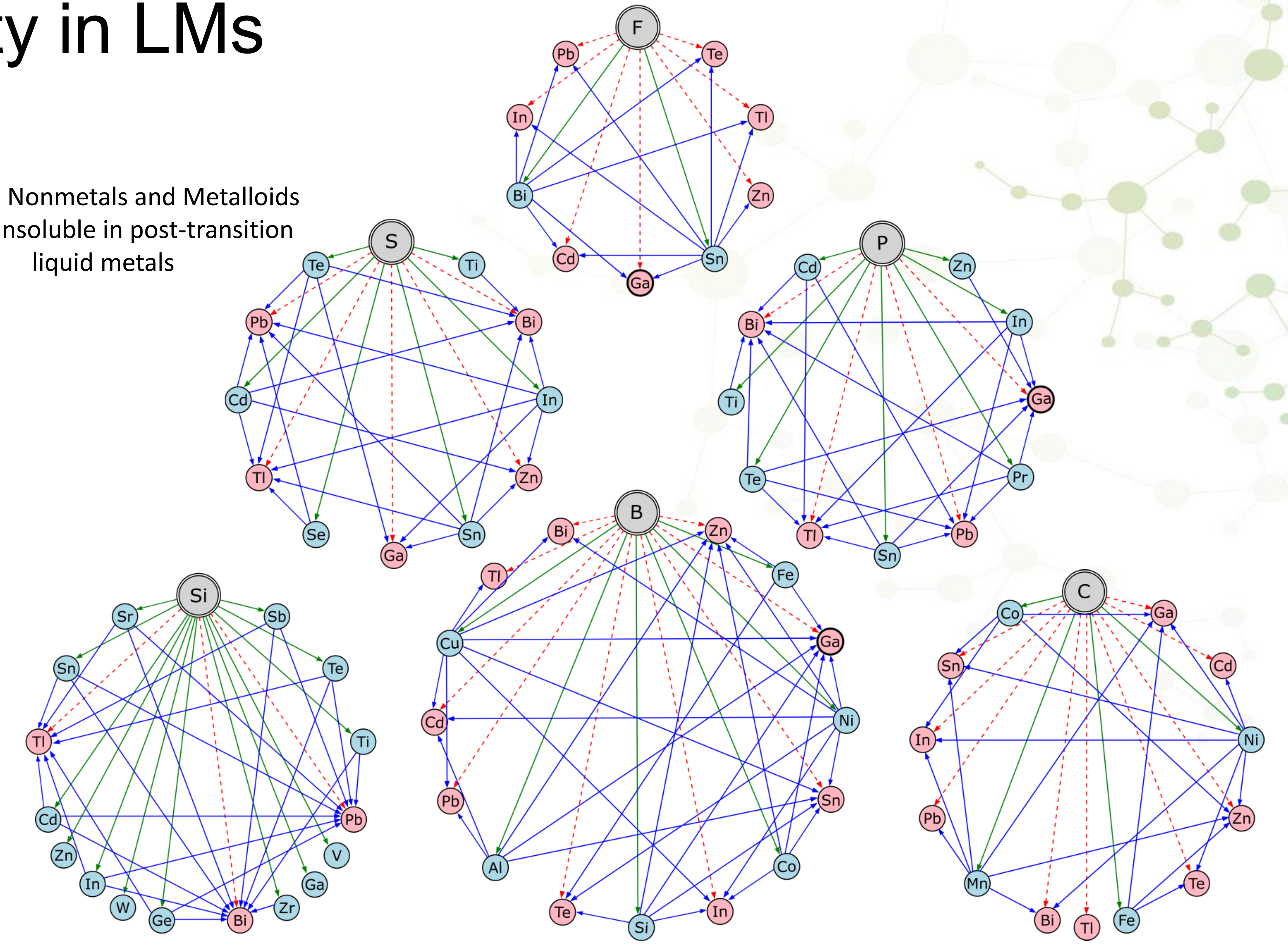
Ghasemian, M. B., *et al.,* Liquid Metal Doping Induced Asymmetry in Two-Dimensional Metal Oxides. *Small,* 2024, 2309924.

Bridge solubility in LMs



Reactive Nonmetals and Metalloids
Mostly insoluble in post-transition liquid metals

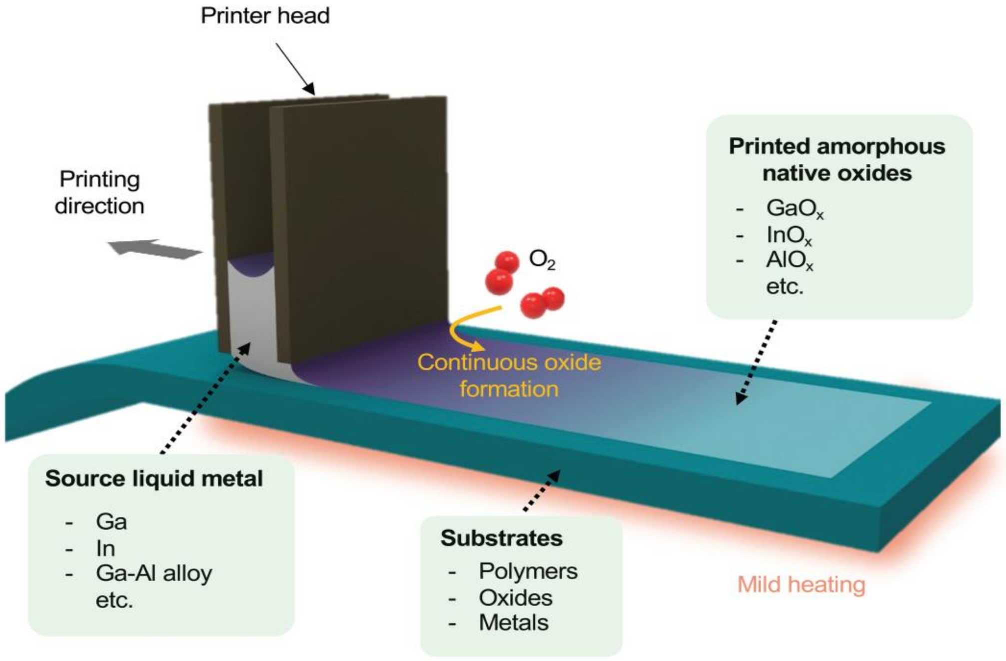


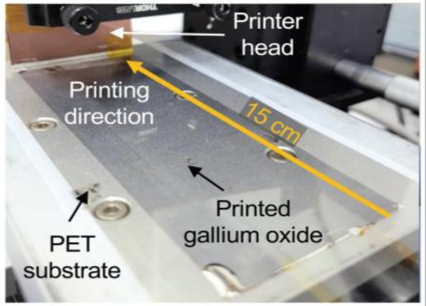


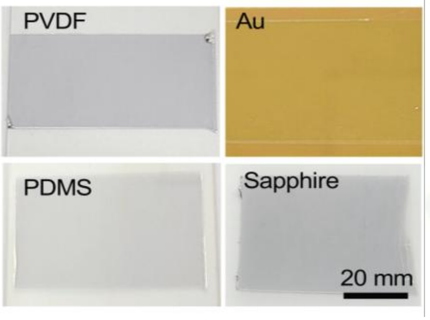
An element with natural solubility in both liquid metals and nonmetals/metalloids, acts as a bridge or carrier between the two insoluble phases.
Solubility criteria: least 10 at% at below 1500 °C.

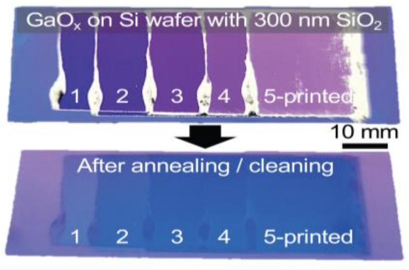
Ghasemian, M. B., *et al.*, Bridge Doping Unlocks Hidden Pathways in Liquid Metal Chemistry. *Accounts of Materials Research, 2025.*

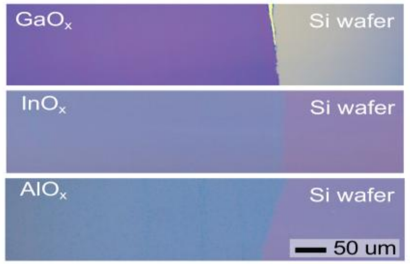
Large Scale Production of 2D Materials by LM

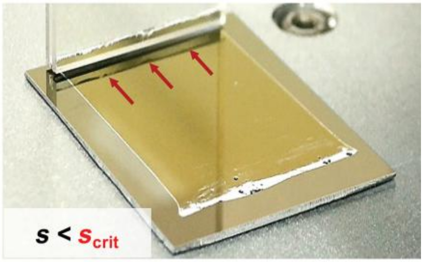










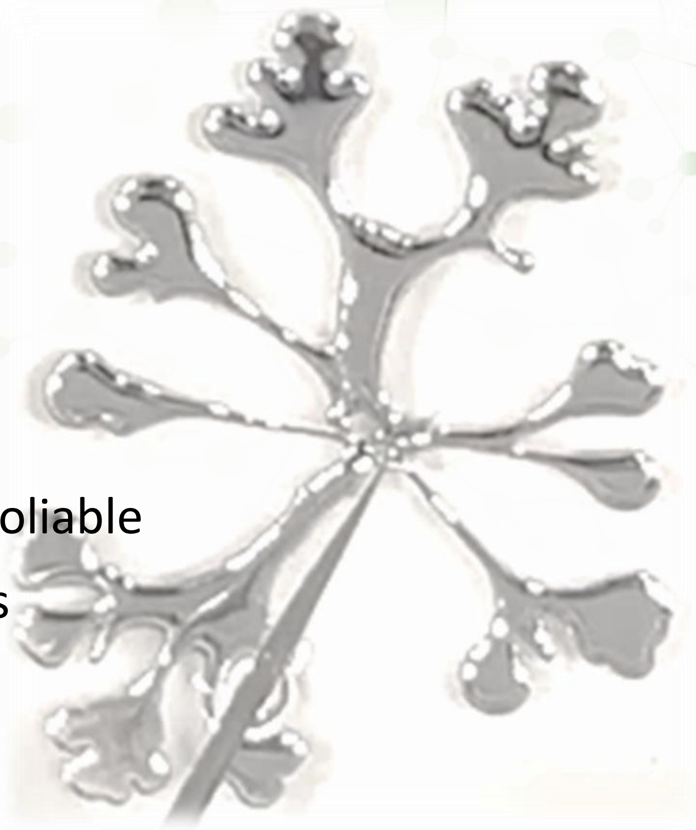


Kong M., *et al*., Ambient printing of native oxides for ultrathin transparent flexible circuit boards. *Science,* 2024, 385, 731-737.

Summary

Advantages of the liquid metal process for the synthesis of nanoparticles and doping of 2D materials:

- Low or moderate working temperature
- Simultaneous functionalization
- Vacuum free
- Large smooth atomically thin sheets
- Thickness control
- Access to single atomic layers that are not intrinsically layered and exfoliable
- Introducing dopants at desired concentrations and avoiding impurities
- No need for extremely clean environments (cleanrooms)
- No need for sophisticated and costly instruments and processes
- Adoptability with low temperature roll to roll processes



Thank You