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QUILL

Liquid coordination complexes (LCCs) for the synthesis of semiconductor nanoparticles

Beth Murray

Supervisors: Prof. Gosia Małgorzata Swadźba-Kwaśny and Prof. John D. Holbrey

QUILL Meeting, 26th March 2024

Abbreviations

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- LCCs – liquid coordination complexes
- TEM – transmission electron microscopy
- $P_{888}Se$ – trioctylphosphine selenide
- $P_{888}O$ – trioctylphosphine oxide

Presentation overview

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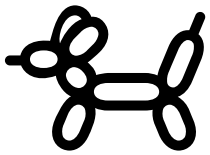
Introduction

Methodology: *In operando* synthesis

Results & discussion: TEM nanoparticle synthesis



Conclusions

Introduction

Liquid coordination complexes (LCCs)

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Angewandte Communications

DOI: 10.1002/anie.201306267

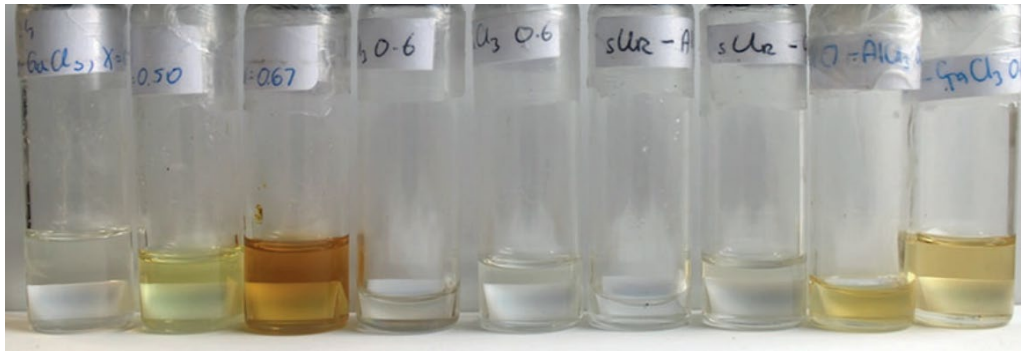
Liquid Coordination Complexes

Liquid Coordination Complexes Formed by the Heterolytic Cleavage of Metal Halides**

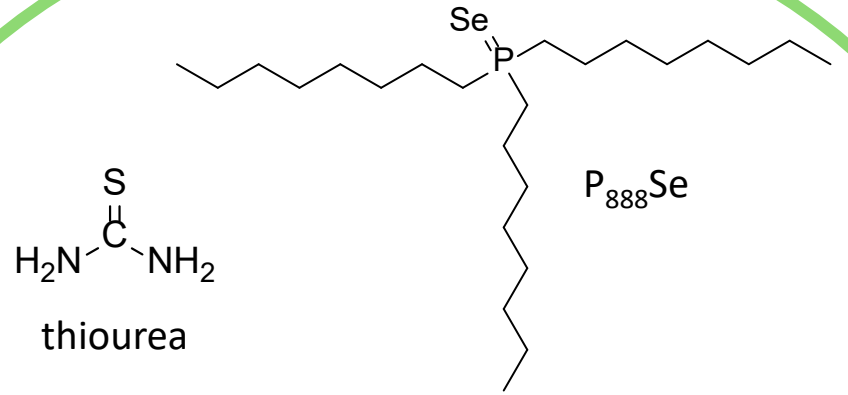
*Fergal Coleman, Geetha Srinivasan, and Małgorzata Swadźba-Kwaśny**

$AlCl_3 + L \xrightarrow{\chi_{AlCl_3} = 0.50 \text{ to } 0.60}$ mobile liquids

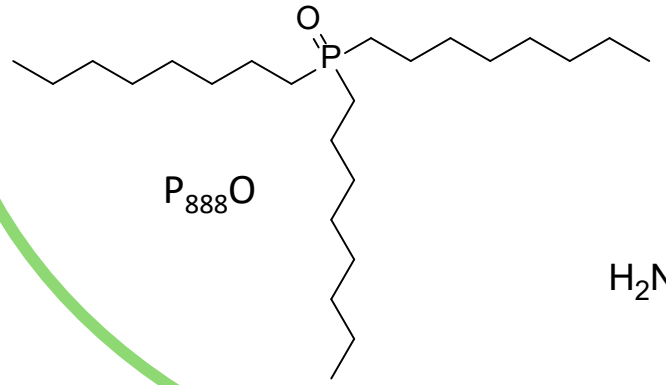
$GaCl_3 + L \xrightarrow{\chi_{GaCl_3} = 0.60 \text{ to } 0.75}$ mobile liquids

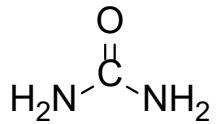


Donors



thiourea





urea

Angew. Chem., Int. Ed., 2013, **52**, 12584

Comparison of liquid coordination complexes and ionic liquids

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χ_{MCl_3}	LCCs	ILs
	$2MCl_3 + 2L$	MCl_3 + [cation]Cl
	↓	↓
0.50	$[MCl_2L_2][MCl_4] \rightleftharpoons 2[MCl_3L]$	[cation][MCl_4]
	↓ + MCl_3	
0.60	$[MCl_2L_2][M_2Cl_7] \rightleftharpoons [MCl_3L] + [M_2Cl_6L]$	+ MCl_3
	↓ + MCl_3	
0.67	$[MCl_2L_2][M_3Cl_{10}] \rightleftharpoons 2[M_2Cl_6L]$	[cation][M_2Cl_7]

Angew. Chem., Int. Ed., 2013, **52**, 12584

Dalton Trans, 2017, **99**, 2071.

Dr James Hogg

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Cite this: *Green Chem.*, 2015, **17**, 1831

Liquid coordination complexes: a new class of Lewis acids as safer alternatives to BF_3 in synthesis of polyalphaolefins

James M. Hogg, Fergal Coleman, Albert Ferrer-Ugalde, Martin P. Atkins and Małgorzata Swadźba-Kwaśny*

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Cite this: *Green Chem.*, 2015, **17**, 4255

Friedel–Crafts alkylation catalysed by $GaCl_3$-based liquid coordination complexes

Karolina Matuszek,[a] Anna Chrobok,*[a] James M. Hogg,[b] Fergal Coleman[b] and Małgorzata Swadźba-Kwaśny*[b]

Dr Karolina Matuszek

Semiconductors and nanoparticles

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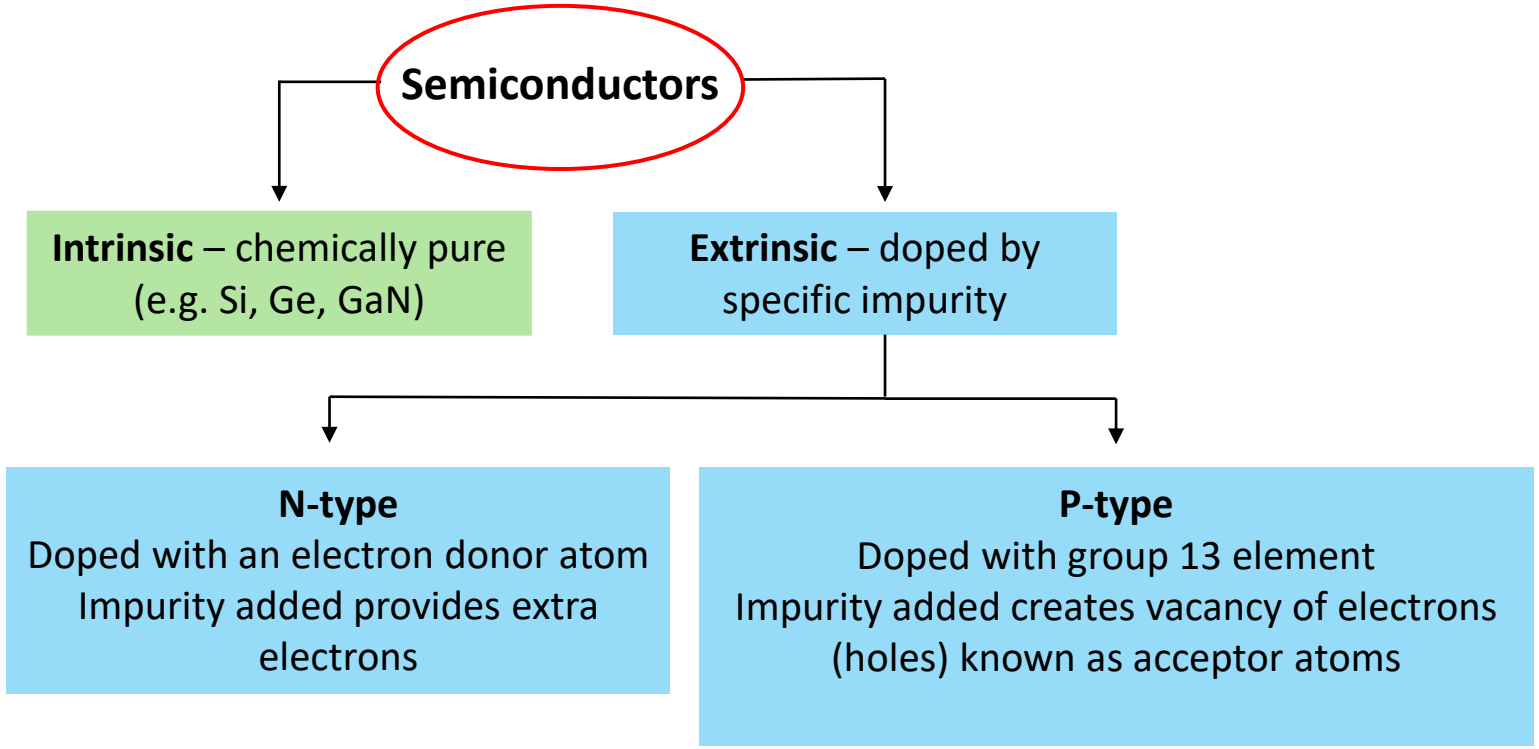

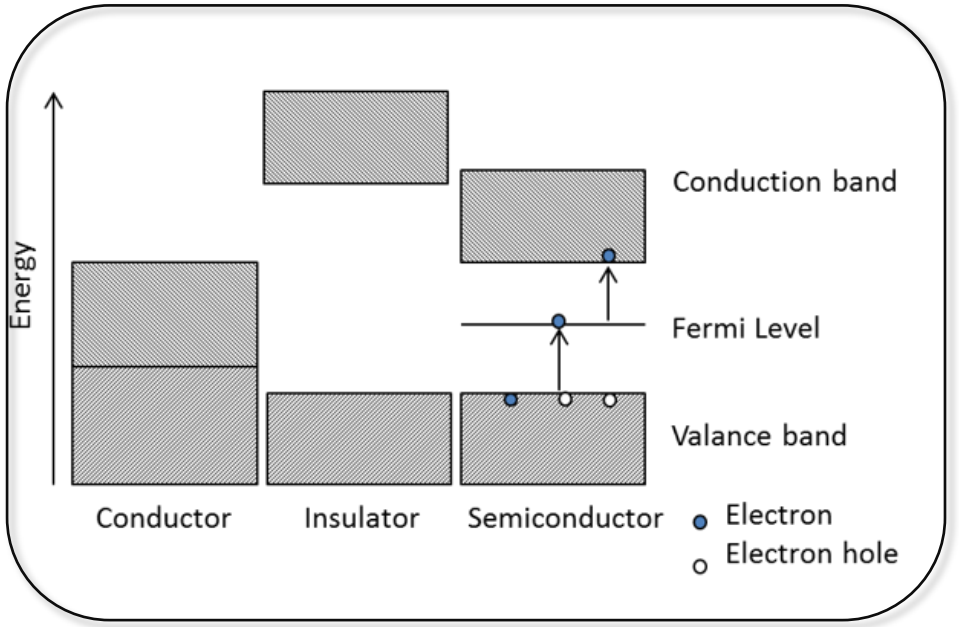

Conduct electrical current only when influenced by external stimuli (e.g. light or heat)

What is the need for nanostructure semiconductors?

Shriver and Atkins' Inorganic Chemistry, Fifth Edition, Oxford University Press, Oxford, 2010
Mater. Sci. Eng. B, 2021, **272**, 115363

Semiconductors for solar energy storage

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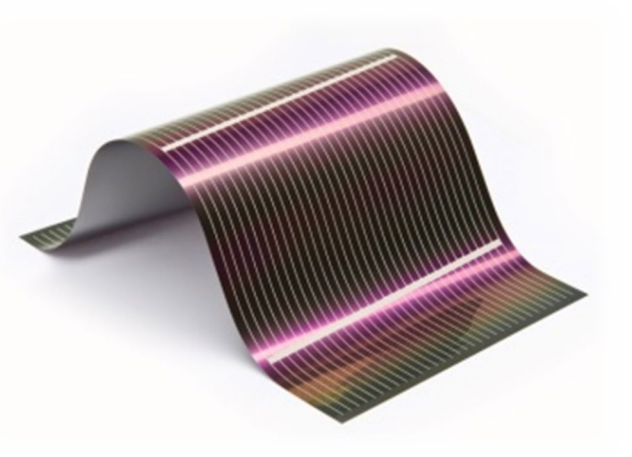
Si solar cells – rigid, heavy and brittle



Nanoparticles as thin film solar cells

Previous work

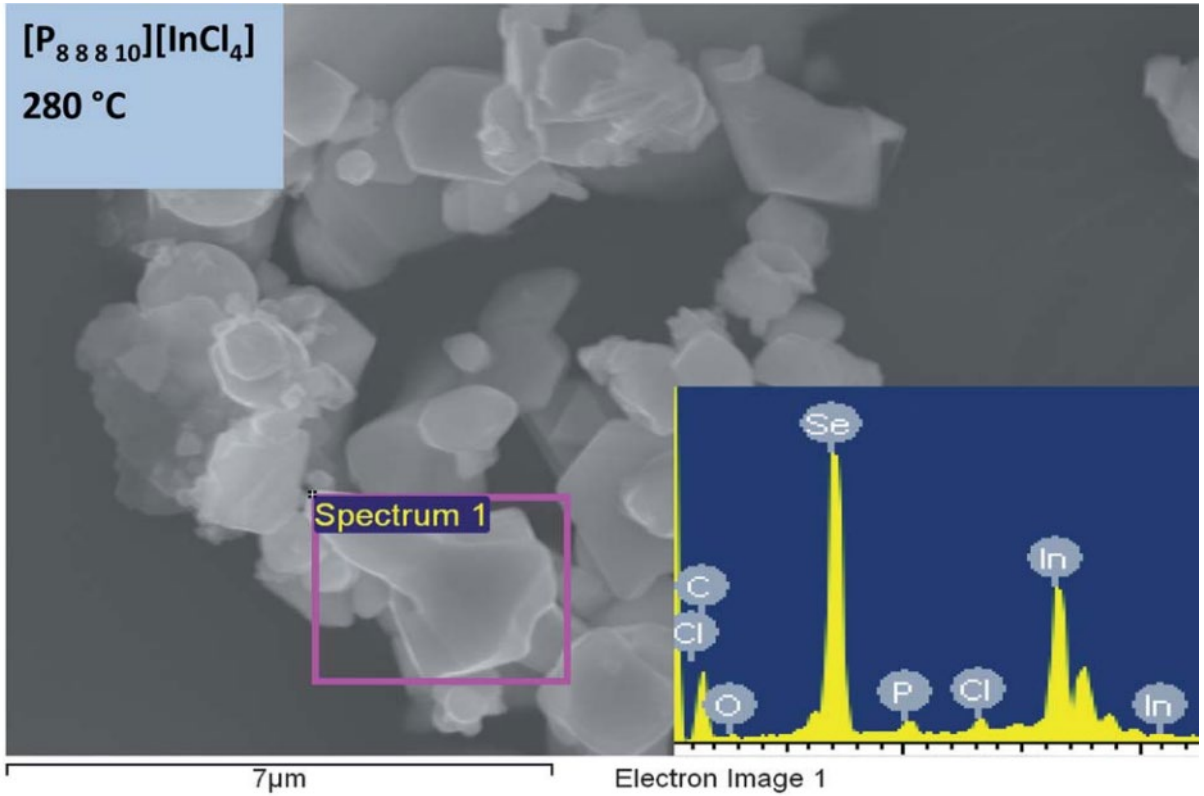
Synthesis of In_2Se_3 from ILs/LCCs

IL system
- In source: $[P_{8\,8\,8\,10}][InCl_4]$
- Se source: Ph_2Se_2
- Reaction temperature: up to 240 °C

LCC system 1
- In and Se source: $P_{888}Se\text{-}InCl_3$ $\chi_{InCl_3} = 0.25$
- Reaction temperature: 250 °C

LCC system 2
- In and Se source: $P_{888}Se\text{-}InCl_3$ $\chi_{InCl_3} = 0.50$
- Reaction temperature: 250 °C

Microwave synthesis



J. Mater. Chem. A, 2014, **2**, 2616

In operando TEM synthesis of In_2Se_3 from LCCs

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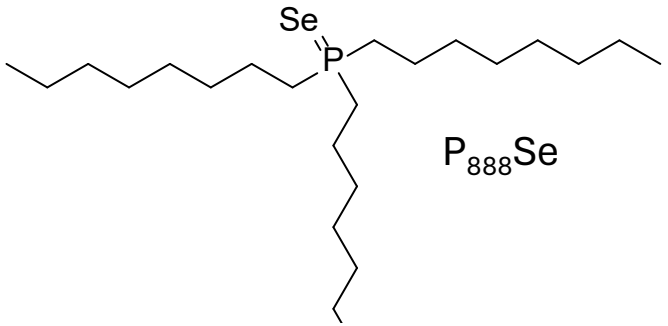
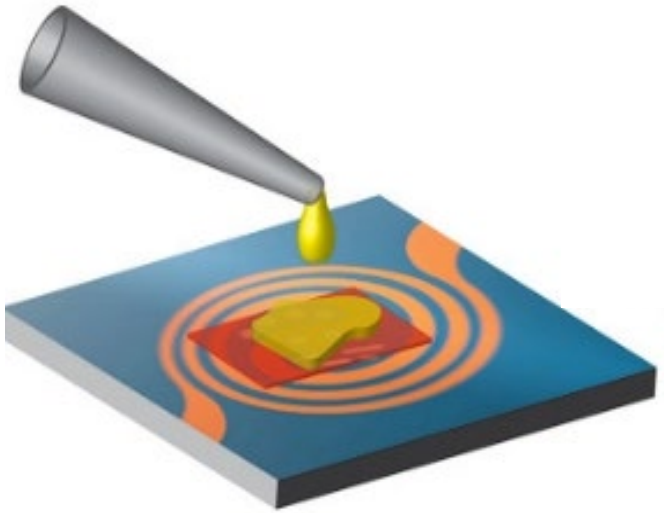
TEM: Transmission electron spectroscopy

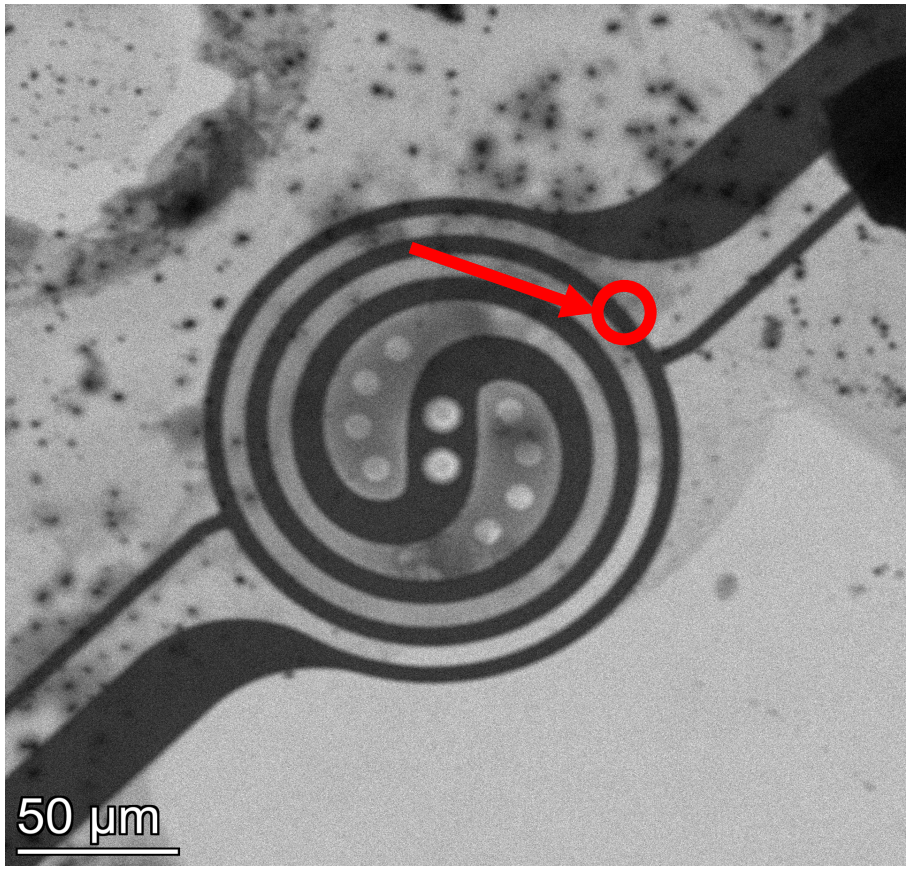
Experimental set-up

- In and Se source: $P_{888}Se$-$InCl_3$ $\chi_{InCl_3} = 0.50$
- LCC diluted with dichloromethane
- Electron dose ~ 30 $e^-/ Å^2s$
- Heating – 2 °C/s until 260 °C



Dr Miryam Arredondo-Arechavala
School of Mathematics and Physics





In operando TEM synthesis of In_2Se_3 from LCCs

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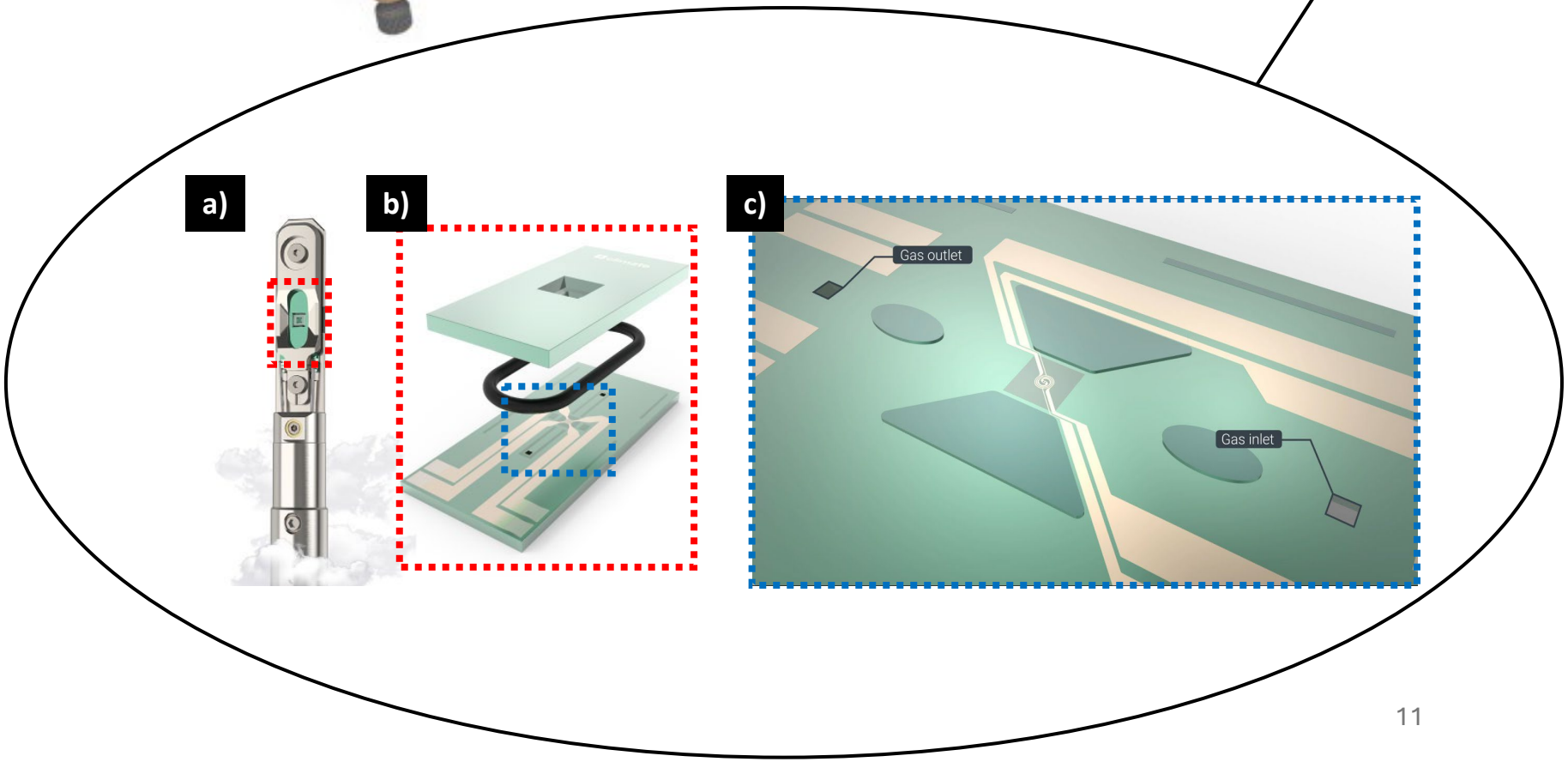
DENS solutions



Results and discussion

In operando TEM synthesis of Indium(III) selenide from LCCs

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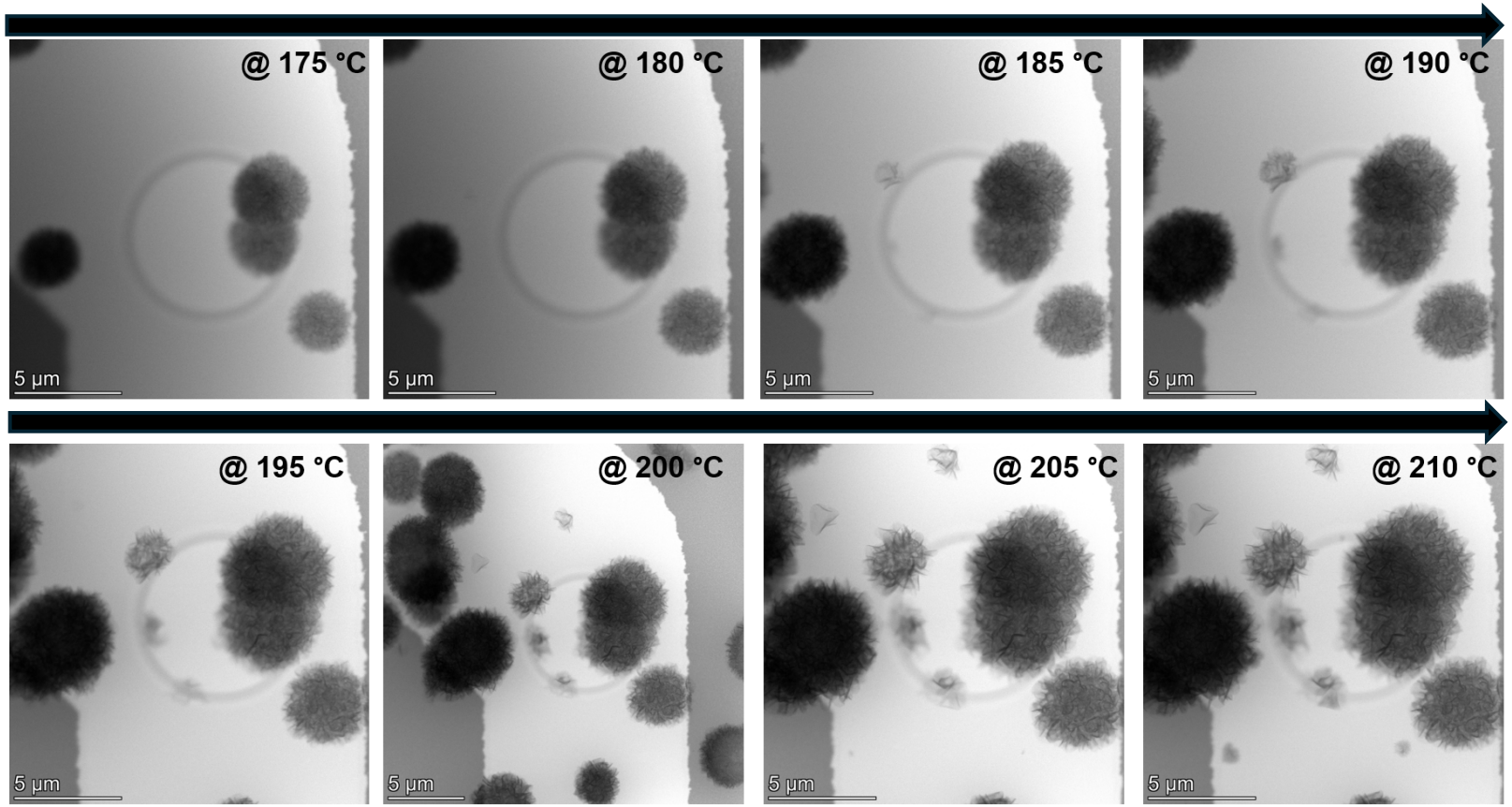
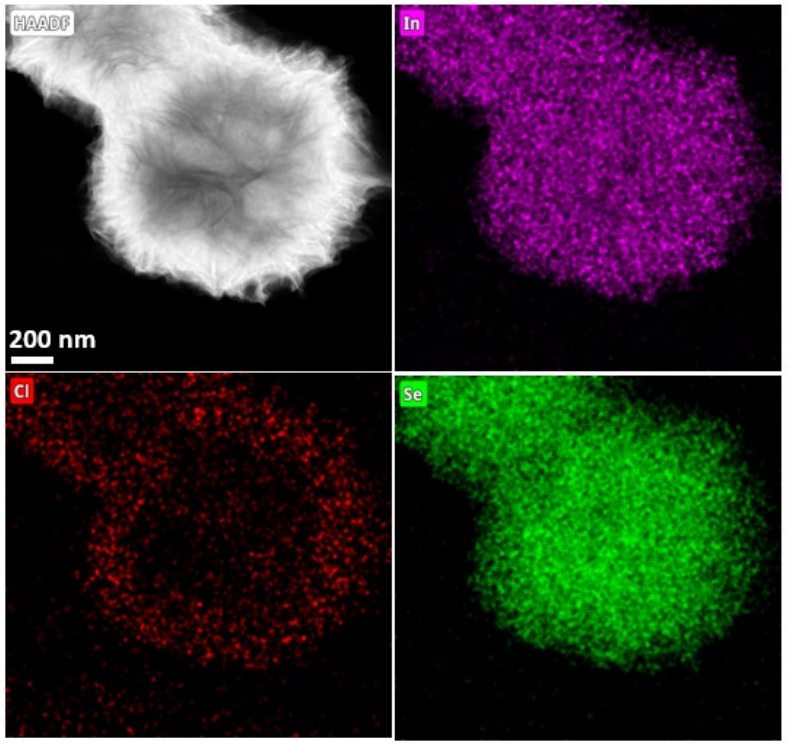
$P_{888}Se\text{-}InCl_3$ (χ_{InCl_3} = 0.50)

In_2Se_3 nanoparticle formation

Heating: 2 °C/s





Unique nanostructures – 'dandelion' morphology

EDX analysis confirms structures are primarily comprised of In and Se

TopSe-$InCl_3$

Heating 245 - 250°C

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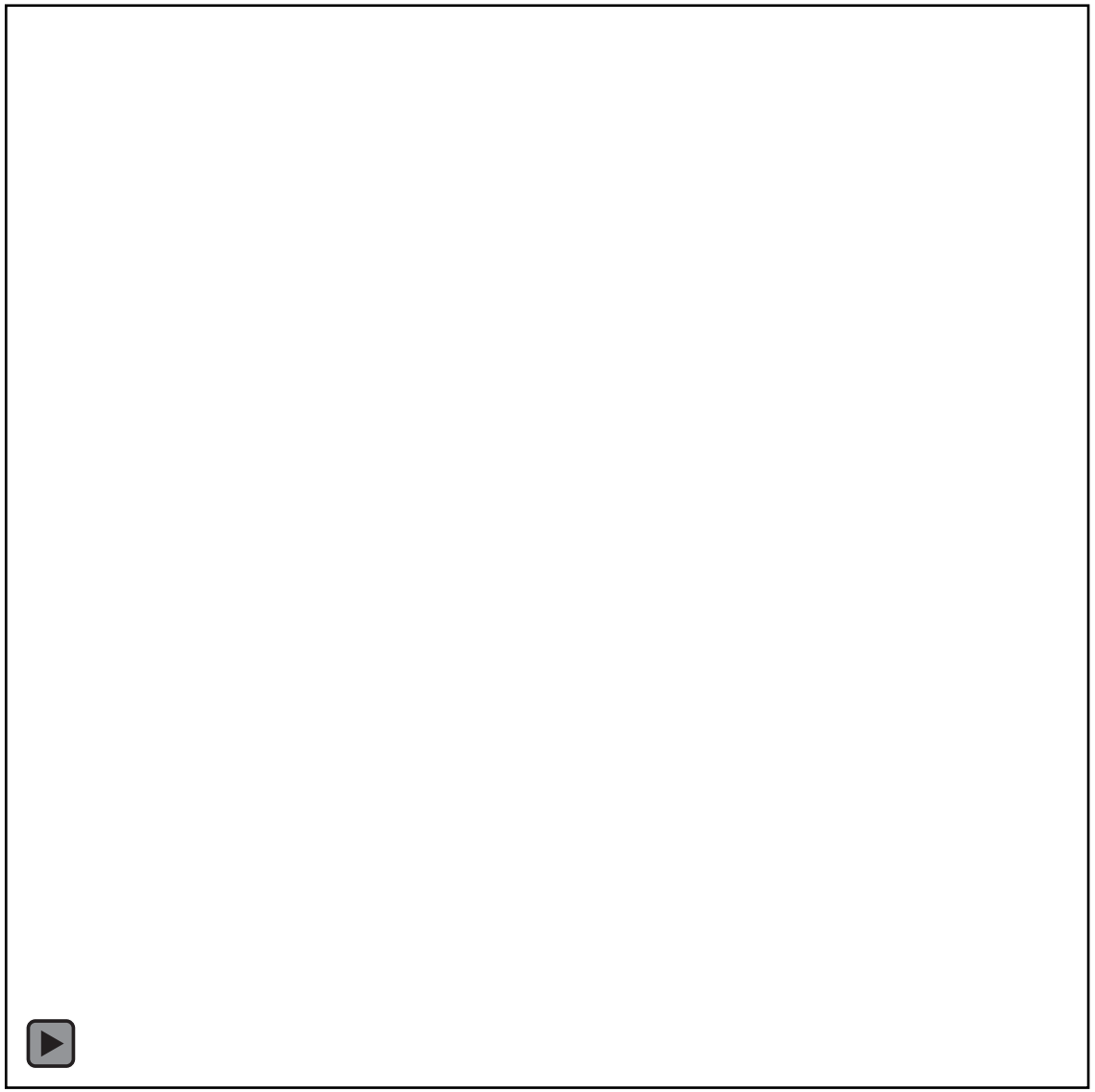
Ostwald ripening

- Droplets flatten when heated – look like they disappear
- Droplets grow when further heated
- Nanoparticles then form very quickly



Kinetic study of In_2Se_3 nanoparticles

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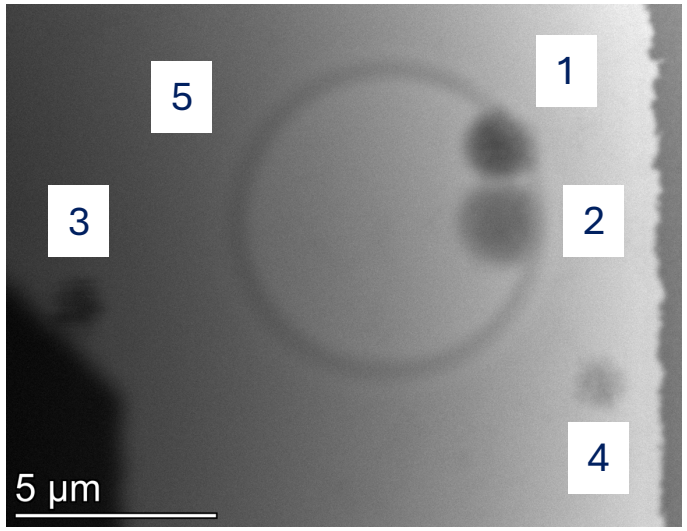
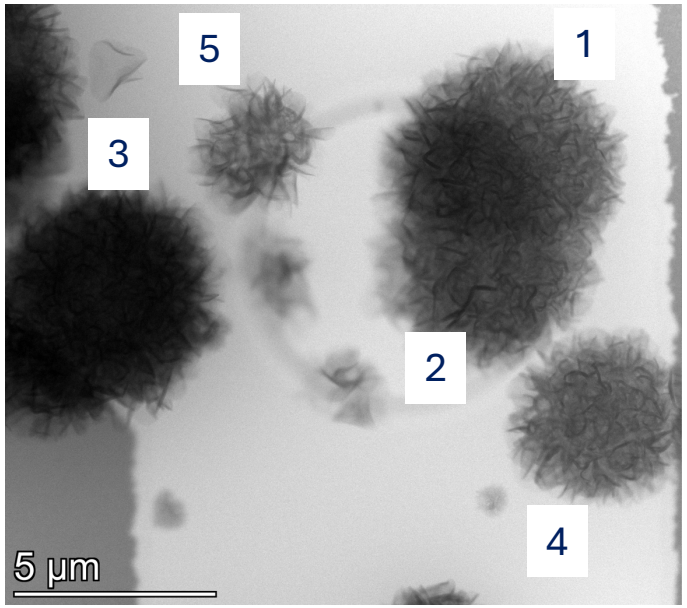
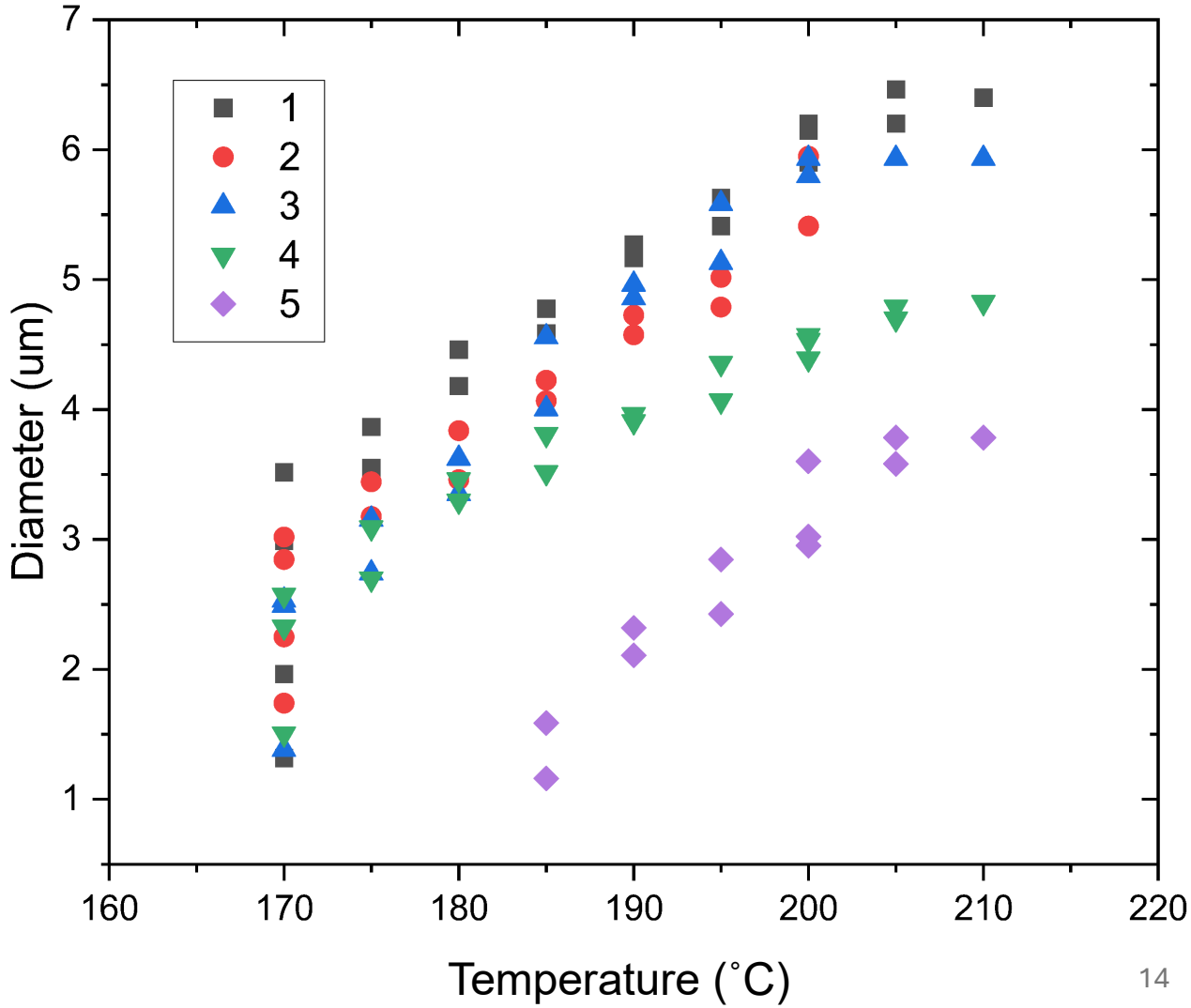
@ 170 °C



@ 210 °C



Growth as a function of temperature



Conclusions

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- *In operando* TEM synthesis to provide insights into the dynamics for indium(III) selenide nanoparticle formation from LCCs
- Smaller droplets coalesce quicker
- 'Dandelion-like' morphology observed
- Submitting for publication in Journal of Materials Chemistry A

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